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Aqueous Partitioning of Minor Actinides by Different Processes

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*Actinide partitioning is a proposed strategy for effective mitigation of the long-term hazards associated with high-level waste (HLW). Octyl-(phenyl)–*N,N*-diisobutyl carbamoyl methyl phosphine oxide (CMPO) and diphenyl–*N,N*-diisobutyl carbamoyl methyl phosphine oxide (DϕCMPO) are amongst the promising extractants extensively studied since the 1980s for actinide partitioning from wastes of different origin. During the last two decades, substituted malonamide extractants such as* N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA) and* N,N'*-dimethyl-*N,N'*-dioctyl hexylethoxy malonamide (DMDOHEMA) have emerged as viable green alternatives to phosphine oxides. During the last decade, diglycolamide-based extractants such as* N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) and* N,N,N′,N′*-tetra-2-ethylhexyl diglycolamide (TEHDGA) have received considerable attention due to overwhelmingly favourable extraction and stripping efficiencies of minor actinides from different types of transuranium (TRU) wastes. The focus of the present review is to carry out comparative evaluation of the key physical and chemical properties of these extractants for hydrometallurgical applications. Merits of flow sheets proposed for the separation and recovery of minor actinides from high-level wastes have also been discussed.*

KEYWORDS Actinide partitioning, waste management, separation, solvent extraction

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INTRODUCTION

The long-lived radionuclides present in the High-Level Waste (HLW) generated after reprocessing of spent nuclear fuels are of major environmental concern. The HLW generally contains un-extracted U, Pu and the bulk of minor actinides (MA) such as Am, Np, Cm. The long-term radiation hazards of HLW is due to the minor actinides and a host of long-lived fission products such as ^{99}Tc, ^{107}Pd, ^{93}Zr, ^{129}I, ^{135}Cs, ^{137}Cs and ^{90}Sr. At present, the most accepted conceptual approach for the management of HLW is to vitrify it in a suitable matrix, followed by disposal in deep geological repositories (1). Since the half-lives of the minor actinides concerned, range between a few hundred to millions of years, the surveillance of vitrified mass for such a long period is debatable from economical as well as environmental safety considerations. On the other hand, the vitrified mass of HLW will have to withstand the heat and radiation damages caused by the decay of beta/gamma emitting fission products, such as ^{137}Cs and ^{90}Sr for about 200 years. Consequently, it may cause the risk for the migration of long-lived alpha emitting minor actinides from repository to the aquatic environment. The residual activity level of 4000 Bq per gram (in terms of alpha activity) is considered benign enough to be treated as Low Level Waste (LLW), which can be disposed of in sub-surface repositories (1,2). Thus, the removal of major and minor actinides from the waste reduces its radiotoxicity to that of uranium ore after a few hundred years (Fig. 1).

The Partitioning & Transmutation (P&T) process envisages the quantitative removal of minor actinides from radioactive waste and their subsequent burning in high flux reactors / accelerators in suitable chemical forms (3–5). Exercise of P&T option seeks to convert all long-lived nuclides into short-lived (or stable) species. This process apart from generation of energy alleviates the need for the long-term surveillance of geological repositories. Although the cost of P&T exceeds the cost of energy gained from actinide incineration, the added safety margin for the repository could justify the additional expenditure. After removing the minor actinides along with the long-lived fission products, the residual waste can be vitrified and buried in sub-surface repositories at a much reduced risk and cost. The successful application of this approach to radioactive waste management could substantially reduce the requirement for geological repository capacity.

The well known tri-*n*-butyl phosphate (TBP), which is used in reprocessing of the spent nuclear fuel is not suitable for extracting minor actinides from HLW. Towards this end, several organophosphorous as well as amide-based extractants have been developed in different countries and evaluated for the recovery of actinides and lanthanides from HLW (Table 1) (6–10). The focus has been principally on octyl-(phenyl)–*N,N*-diisobutyl carbamoyl methyl phosphine oxide (CMPO), *N,N*'-dimethyl-*N,N*'-dibutyl tetradecyl malonamide (DMDBTDMA), *N,N*'-dimethyl-*N,N*'-dioctyl

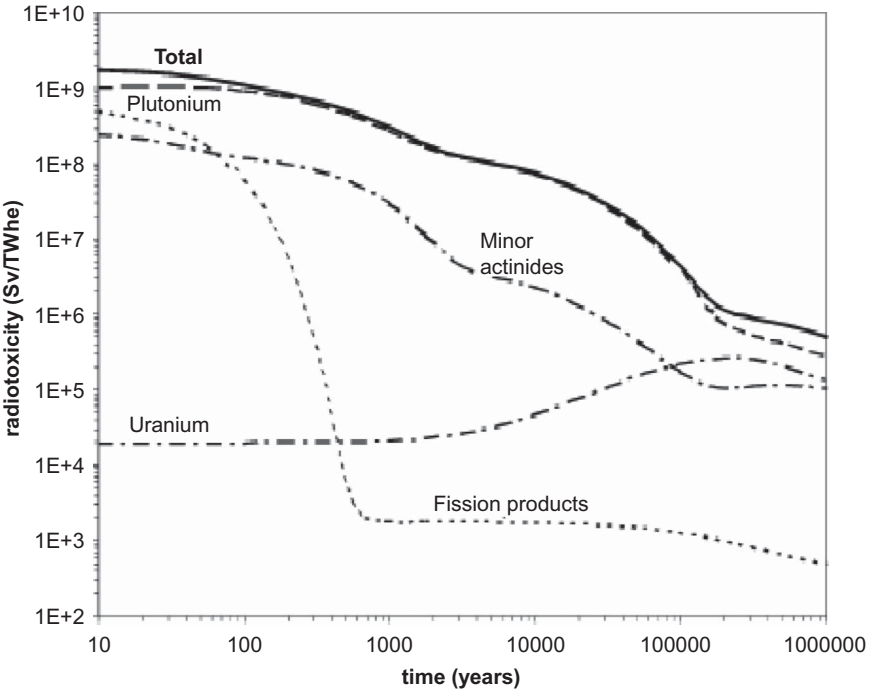

FIGURE 1 Partitioning of minor actinides: impact on waste management. Reproduce with permission from Ref (59).

hexylethoxy malonamide (DMDOHEMA), *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA). The primary objective of this review is to qualitatively (or semi-quantitatively) compare the performance of the above proposed extractants for actinide partitioning. We have chosen not to discuss the fundamental chemistry of extraction reactions or extractant development. Instead, the emphasis has been made on the status of process development with these extractants.

ACTINIDE PARTITIONING WITH CMPO

In the early 1960s, Siddall (11,12) synthesized a few bidentate carbamoyl phosphonate compounds (Fig. 2a) and demonstrated their ability for the extraction of trivalent Am, Ce and Pm from moderately acidic solutions. The bifunctional nature of these extractants reduces the competition between HNO_3 and the target metal ion for the primary functional group (P = O) of the ligand. Schulz et al. (13) made a significant contribution by synthesizing several new compounds of this class and utilizing them for the extraction of actinides and lanthanides. Thereafter, several groups in the United States and other countries have synthesized numerous derivatives of

TABLE 1 Various Extractants Investigated for the Separation of Minor Actinides from High-Level Waste Solutions; Diluent: Dodecane / Normal Paraffinic Hydrocarbon (NPH)

Extractant	(HNO_3) M for $D_{Am} > 3$	(HNO_3) M for $D_{Am} < 0.1$	Remarks	Country of origin	Principal Investigator(s)	Year
Tetra octyl-3-oxapentane diamide (TOOPDA), 0.1 M	>0.5	<0.3	U(VI) extraction poor; moderate neutral extractant An(III)>An(IV)>An(VI)>An(V)	Japan[b]	Y. Sasaki, S. Tachimori	1996
CMPO, 0.2 M	>0.3	<0.02	Synthesis difficult; radiolytic products interfere; strong neutral extractant; well investigated	USA[b]	E.P. Horwitz,	1981
DHDECMP, 0.75M	>2	<0.15	Difficult to purify; moderate neutral extractant;	USA	E.P. Horwitz,	1981
Di-phenyl-di-butyl-derivative of CMPO[a]	>0.3	<0.02	Synthesis difficult; radiolytic products interfere; strong neutral extractant	Russia	B.F. Myasoedov	1993
DMDBTDMA, 1 M	>2	<0.5	Synthesis easy; radiolytic products innocuous; moderate neutral extractant; completely incinerable	France[b]	C. Madic	1994
DMDOHEMA, 1 M	>2	<0.5	Moderate neutral extractant; completely incinerable	France[b]	C. Madic	2000
Trialkyl phosphine oxide (TRPO); 30 vol %	<2	>5	Commercially available, high radiolytic stability; strong neutral extractant	China[b]	Zhu Yongjun	1992
Diisodecyl phosphoric acid (DIDPA); 0.5 M	<0.5	>4	Acidic extractant; slow kinetics	Japan	Y. Morita	1995

[a]Diluent: Flouropol-732; [b]A significant amount of work has also been carried out in India.

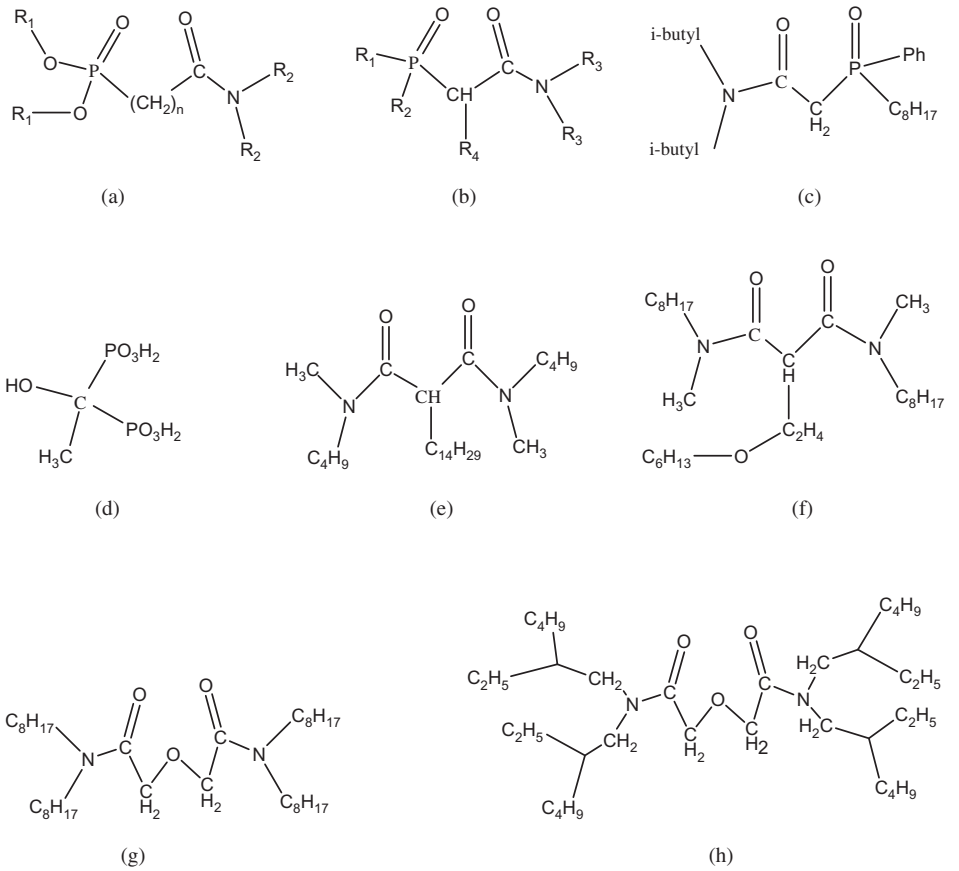

FIGURE 2 Structural formulae of the proposed extractants for actinide partitioning; (a) carbamoyl alkyl phosphonate, (b) carbamoyl methylene phosphine oxide, (c) CMPO, (d) 1-hydroxyethane-1,1-diphosphonic acid, (e) DMDBTDMA, (f) DMDOHEMA, (g) TODGA, and (h) TEHDGA.

CH_2-bridged (Carbamoyl Methyl Phosphonates) and unbridged (Carbamoyl Phosphonates) extractants and studied the extraction behaviour of hexa-, tetra- and trivalent actinides and a few lanthanides using the extractant alone or in combination with TBP in various diluents (14–16).

Navratil et al. (17) conducted a preliminary study for the separation of actinides from synthetic nuclear waste solutions using carbamoyl methyl phosphonate (CMP). The synthetic solution was a mixture of Na_2CO_3, Na_3PO_4, NaCl, Na_2SO_4, and the actinides, Pu, Am and U. This solution was first contacted with 30% TBP/dodecane to removed >99.99% of U and most of the Pu. The aqueous raffinate was then contacted with 20–30% CMP/CCl_4 which removed >99.9% of Am and all residual Pu and other actinides. Rapko et al. (18) found that 0.75 M CMP formed a third phase when contacted with 2 M HNO_3, even in the presence of 1 M TBP. Addition of about 2 M NO_3^-

was necessary to avoid third-phase formation and to attain reasonably good D_{Am} values (~5). Radiolytic and hydrolytic degradation products as well as acidic impurities in CMP inhibit stripping of Pu and U. The increased volume of wastes resulting from the presence of salting out agent is another drawback of this class of reagents.

To overcome these limitations of the CMP-class of extractants, a modified class of extractants containing more basic phosphine oxide functional group were synthesized (Fig. 2b). A series of carbamoyl methyl phosphine oxides with different substituents were synthesized and extraction behaviour of trivalent actinides, lanthanides and a few other metal ions was studied (19–21). Their extraction properties and phase compatibility varied significantly with the nature of the alkyl substituents. Amongst these extractants, CMPO (Fig. 2c) was found to possess the best combination of properties for actinide extraction in a PUREX-compatible diluent system. Numerous investigations have been carried out to demonstrate quantitative extraction of Am(III) by CMPO from HNO_3 or from HCl solutions into diluents like diethyl benzene, CCl_4, tetrachloroethylene (C_2Cl_4), and paraffinic hydrocarbons (21–24). Extraction studies on Eu(III) from HNO_3 or HCl medium, with either CMPO alone or a mixture of CMPO and TBP in mesitylene or dodecane have also been reported (25). A mixture of CMPO and TBP in *n*-dodecane has been used to extract actinides (Np, Am, Pu, U), fission products (Pm, Zr, Ru, Pd) and Fe from HNO_3 medium (26–29). Acronym for the process developed at Argonne National Laboratory, USA based on CMPO is TRUEX (Trans Uranium EXtraction). The TRUEX extractant is 0.2M CMPO + 1.2M TBP in paraffinic hydrocarbon (*n*-dodecane). TBP contributes to favourable D_{Am}, better phase compatibility, and reduces hydrolytic and radiolytic degradation of CMPO in the presence of moderate nitric acid concentration. The basic extraction data of various metal ions relevant from actinide partitioning point of view by TRUEX solvent is shown in Table 2. High distribution ratio (D) values of tri-, tetra-, and hexavalent actinides from solutions of moderate acid concentration and good selectivity over most fission products is the key feature of this extractant which makes it a suitable candidate for actinide partitioning from HLW. From process perspective, near constancy in the D values of Pu(IV), U(VI) and Am(III) between 1 and 6 M HNO_3 is advantageous as it allows efficient extraction of actinides from wastes without feed acidity adjustment.

Demonstration of the TRUEX Process

The TRUEX (Trans Uranium Extraction) solvent containing CMPO has undergone many modifications after its first use way back in 1985 (30). At Los Alamos National Laboratory (LANL) substantial amounts of solid waste containing moderate concentrations of Pu and Am were directly dissolved in HCl and the resulting feed was used for the separation of actinides using

TABLE 2 Distribution Behaviour of Various Metal Ions by TRUEX Solvent

	Distribution ratio of the metal ions						
HNO_3;M	U(VI)	Pu(IV)	Am(III)	Zr(IV)	Ru(III)	Fe(III)	Pd(II)
0.01	–	–	0.01	–	0.15	0.002	0.31
0.2	83	122	1.9	–	0.26	0.008	0.23
0.58	110	987	7.4	–	0.28	0.022	0.18
1	152	1835	14.3	0.71	0.26	0.045	0.10
2	–	–	20.8	0.82	0.21	0.15	0.04
3	274	3250	21.7	0.79	0.20	0.33	0.02
4.5	–	3272	22.8	0.93	0.13	1.10	0.01
6	283	–	23.7	1.82	0.09	8.72	0.004

Organic phase: 0.2 M CMPO + 1.2 M TBP in *n*-dodecane; Temperature: 25°C.

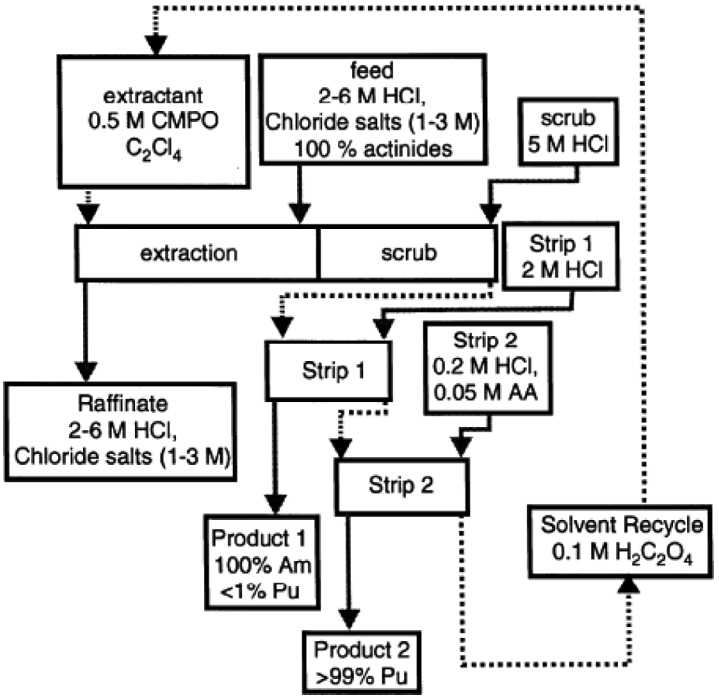

FIGURE 3 TRUEX Flow sheet for removal of actinides from chloride solutions; AA = ascorbic acid. Solid lines represent aqueous streams. Dotted line represents organic streams (7). Reproduced with permission of Taylor & Francis.

0.5 M CMPO in C_2Cl_4. A flow-sheet for the generic TRUEX process for the removal of actinides from aqueous chloride solutions is given in Figure 3. Demonstration runs with the flow sheet discussed previously achieved an alpha decontamination factor > 100 (30).

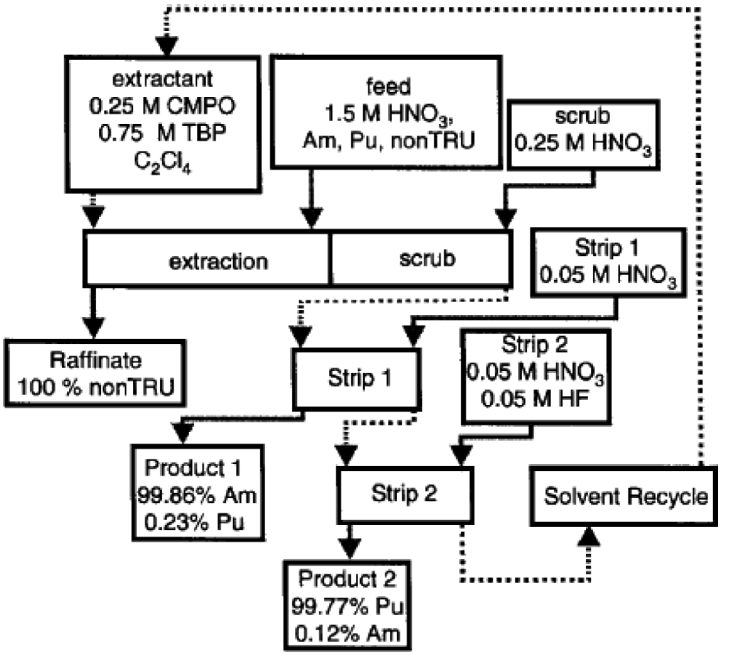

FIGURE 4 TRUEX Flow sheet for removal of Am and Pu from Plutonium Finishing Plant (PFP) wastes. Solid lines represent aqueous streams. Dotted line represents organic streams (7). Reproduced with permission of Taylor & Francis.

The first successful demonstration of TRUEX process on genuine waste was reported with Plutonium Finishing Plant (PFP) waste from Hanford (31). The aqueous waste contained 0.09 M HF, 0.2 M U, 10^{-5} to 10^{-4} M Pu, 10^{-6} to 10^{-5} M Am, less than 6×10^{-4} M Be, Cr, Ni, Zn, Pb at 3 M $NO_3^-{}_{total}$ (HNO_3 / $Al(NO_3)_3$). The TRUEX solvent employed was 0.25 M CMPO + 0.75 M TBP in C_2Cl_4. A flow-sheet for the removal of Am and Pu from PFP waste is given in Figure 4. Countercurrent runs were carried out with 10 liters of the clarified waste resulted in the alpha activity of the aqueous raffinate 1–2 nCi/g, and a TRU decontamination factors (DF) of 10^4 (31). Chamberlain et al. (32) followed TRUEX process with a modified flow sheet for phosphate /oxalate feed as shown in Figure 5. Four major improvements made in the modified flow sheet were: (i) Use of *n*-dodecane instead of the chlorinated solvent, (ii) aluminium nitrate scrub was given to strip oxalic acid from the solvent; (iii) ammonium nitrate was incorporated in the flow-sheet as it is a very good strippant of Pu, and (iv) An online alumina column to improve solvent quality during each process run. A large scale demonstration with a 20 stage centrifugal contactor using the preceding flow sheet achieved an alpha decontamination factor up to 6.5×10^4 (32).

The complexant concentrate (CC) waste generated at the Hanford site is alkaline and contains apart from TRU elements, high concentrations of

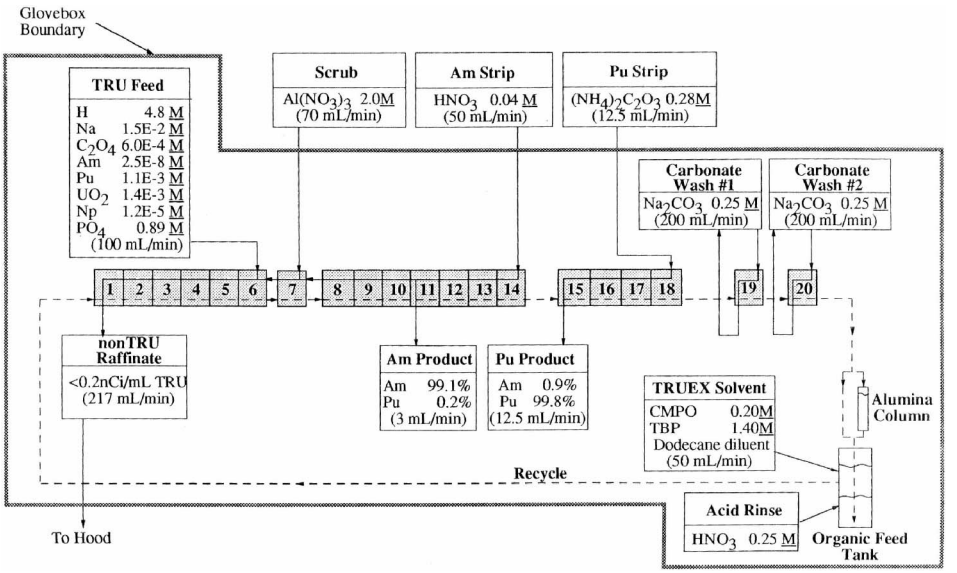

FIGURE 5 Improved TRUEX Flow sheet. Solid lines represent aqueous streams. Dotted line represents organic streams (32). Reproduced with permission of Taylor & Francis.

Na^+, NO_3^-, NO_2^-, CO_3^{2-}, Al^{3+}, EDTA (ethylene diamine tetraacetic acid), HEDTA (*N*-(2-hydroxyethyl)-ethylenediamine triacetic acid), citric acid and their radiolytic and hydrolytic degradation products along with moderate concentrations of Cs-137 and Sr-90. After acidification, bench-scale batch extraction tests with actual CC waste were performed. The DF_{TRU} was found to be of the order of 100 (30). The TRU concentration in the effluent was 1 nCi/g. Neutralized Cladding Removal Waste (NCRW) consisted of solids (principally $ZrO_2.xH_2O$) generated while treating zircalloy-clad fuels. It contained moderate amounts of TRU elements. A preliminary test with actual NCRW dissolved in HNO_3 or HNO_3-HF solutions using the TRUEX solvent has shown satisfactory uptake of the actinides (30). At the Pacific Northwest National Laboratory (PNNL), highly encouraging results have been reported for actinide removal by TRUEX treatment of NCRW sludge and of PFP sludge (33,34).

The most extensive pilot-scale testing of the TRUEX process has been done at the Idaho National Engineering and Environmental Laboratory (INEEL). Several TRUEX demonstration runs have been made on Sodium Bearing Wastes, a secondary acidic HLW (35). An optimized TRUEX flow-sheet was tested in shielded hot cells at the Remote Analytical Laboratory using a 20-stage bank of 2 cm centrifugal contactors. Stripping of the actinides from the loaded process solvent was accomplished with >99% efficiency (99.84% for Am, 99.97% for Pu, 99.80% for U) using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) as the stripping agent

(Fig. 2d). A second demonstration using a dissolved zirconium calcine feed recovered 99.2% of Am (36). The HEDPA strip in this case was less efficient due to problems created by precipitation of zirconium phosphate. Presumably, the phosphate is present as an impurity in the HEDPA solution.

The evaluation studies on TRUEX solvent were mainly reported from USA laboratories and only limited reports are available from European countries. Under R&D programme on the management and disposal of radioactive wastes, the Fuel Cycle Department, ENEA, Italy, has reported that the mixture of TBP and CMPO in chlorinated or aliphatic hydrocarbons achieved a very high DF for actinides (37,38). Batch and counter-current extraction experiments performed with simulated HLW of the EUREX reprocessing plant and with analytical wastes from control laboratories suggested excellent DF values for actinides without requiring any salting agents (37,38). At Karlsruhe, Germany, actinide partitioning was demonstrated with the reprocessing raffinate of light water reactor (LWR) fuels using TRUEX solvent (39). A mixture of 0.2 M CMPO and 1.4 M TBP was used as the extractant where Am(III) and Cm(III) could be quantitatively extracted in 5 stages at organic to aqueous phase ratio of 2. Stripping was carried out with three strippant, viz. 0.05 M HNO_3 for Am and Cm, 0.05 M HNO_3 + 0.05 M HF for Np and Pu, and 5% Na_2CO_3 for U. The results showed that Am and Cm were accumulated in the organic phase and only low amounts of these elements were recovered in the stripping solution.

Russians developed a TRU extraction process based on a somewhat simpler derivative of CMPO (diphenyl-N,N-di-*n*-butyl CMPO) employing a Fluoroether diluent (Fluoropol-732) (40,41). This process behaves similar to the TRUEX process in terms of its efficiency for actinide extraction, shows little tendency toward third-phase formation, and avoids the interferences caused by degradation of TBP. It was tested in centrifugal contactors and was found to recover actinides with >99.5% efficiency (40). Possible limitations of the proposed process include corrosive products of diluent degradation (e.g., HF), difficult back extraction due to the requirement of very low acidity, and possibly complex solvent cleanup for the recycling of the extractant (41).

Application of diphenyl-N,N-di-*n*-butyl CMPO at KRI, Russia and INEEL, USA led to the development of Universal Solvent Extraction (UNEX) Process. The aim was to extract alpha and beta emitters (Actinides, Cs and Sr) together using a mixture of solvents, viz. CMPO for actinides, CCD for Cs and PEG-400 for Sr. UNEX solvent comprises of 0.08 M CCD + 0.5% (v/v) PEG-400 + 0.02 M Ph_2Bu_2-CMPO in FS-13 solvent. A flow-sheet with UNEX solvent has been developed for the treatment of actual acidic waste from INEEL waste tank (42). It was found that 99.4% Cs, 99.9% Sr and 99.9% actinides could be removed along with < 0.14% Tc. As mentioned earlier,

the limitation of the process includes corrosive degradation product (HF) of the solvent, difficulty in the back-extraction of Am with dilute acid solution, and complex solvent cleanup.

At Japan's Power Reactor and Nuclear Fuel Development Corporation (PNC), batch and counter–current runs with real high–active raffinate from FBR spent fuel reprocessing have been carried out without adjusting acidity using 0.2 M CMPO + 1.2 M TBP in *n*-dodecane (43). The mixer-settler employed in this study had 19 stages for extraction-scrubbing and 16 stages for stripping. The rare earths were extracted along with the actinides and a part of ruthenium. The DF for actinides was greater than 1000. Oxalic acid was added in the feed and scrubbing solutions to improve decontamination of Ru, Zr and Mo. In another communication (44) from the same lab, the feed acidity was increased to about 5 M to increase Ru decontamination in the actinide fraction. The improved flow-sheet (Fig. 6) used salt-free reagents like hydrazine oxalate, hydrazine carbonate and tetramethyl ammonium hydroxide for stripping and cleanup steps so that the final raffinate obtained was inactive and salt-free.

At the Bhabha Atomic Research Centre in India, basic solvent extraction data was generated for the extraction of actinides and few fission / corrosion products and structural elements using TRUEX solvent (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) (29,45–48). Subsequent studies examined the extraction and separation of actinides from sulphate-bearing waste (SBW) at low acidity of about 0.3 M, simulated HLW originating from pressurized heavy water reactor (PHWR) and from fast breeder reactor (FBR) at 3 M HNO_3, and High Active Waste (HAW) solutions generated from the reprocessing of research reactor fuels at this Centre. The HAW was contacted twice with fresh 0.2 M CMPO + 1.2 M TBP solution in *n*-dodecane in 1:1 ratio. After two contacts, 99.8% of the alpha activity was found in the organic phase. The rare earths Ce, Pm, Eu etc. followed the Am(III) stream, while Ru was partially extracted, and Cs and Sr were not extracted at all (29). In case of HLW, one contact with 30% TBP/dodecane was given to deplete the U content. Subsequently, four contacts were made with the solvent, 0.2 M CMPO + 1.4 M TBP in *n*-dodecane. The raffinate was found to contain about 0.06% of the total alpha activity (29). With SBHLW, two contacts were made with 30% TBP followed by four contacts with 0.2 M CMPO + 1.2 M TBP in dodecane. Even at the low acidity of 0.3 M and 0.16 M SO_4^{2-}, about 99.6% of the total alpha activity could be removed from HLW solutions (49).

Mixer-settler experiments employing a 6-stage unit with synthetic sulphate bearing and PHWR-HLW have been reported (50–52). The flow sheet followed at BARC is shown in Figure 7. The flow sheet was tested with actual HAW solutions generated from the reprocessing of research reactor fuels. In the first step, U, Pu and Np were removed with 30% TBP. The extracted Pu

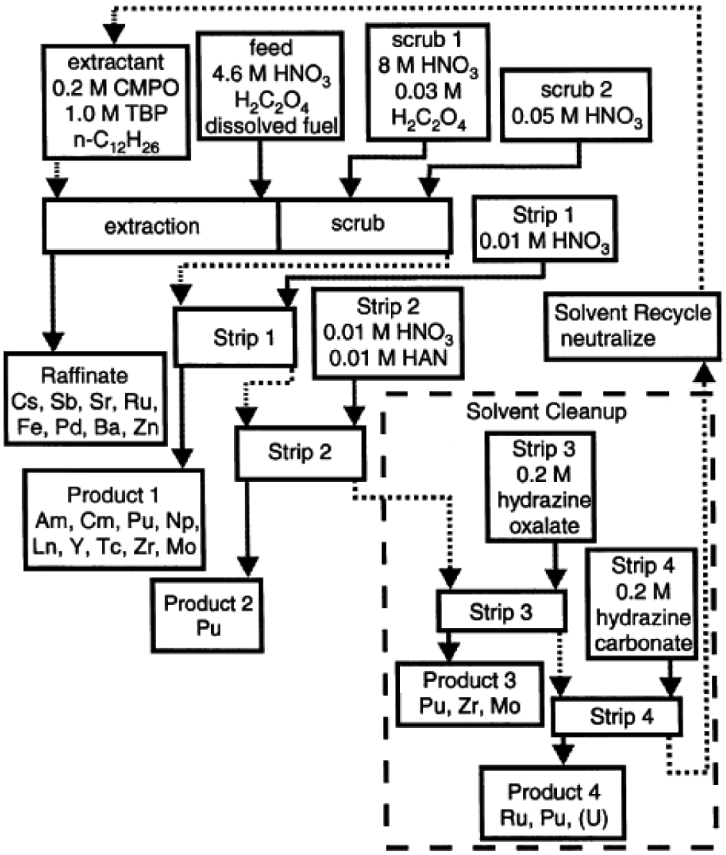

FIGURE 6 TRUEX Flow sheet for actinide partitioning from dissolved fuel as proposed by PNC. HAN: hydroxyl ammonium nitrate. Solid lines represent aqueous streams. Dotted line represents organic streams (7). Reproduced with permission of Taylor & Francis.

and Np were subsequently stripped with H_2O_2 and ascorbic acid followed by U stripping by dilute nitric acid. The raffinate of the first stage containing residual U, Np, Pu and the trivalent actinides and lanthanides (at ~3 M HNO_3) was the feed for a subsequent mixer-settler experiment using 0.2 M CMPO + 1.2 M TBP in dodecane. In all the cases, the HAW raffinate leaving the extraction section showed alpha activity near the background level. Final analysis indicated that nearly 99.7% of the rare earths are extracted along with the actinides and ~30% Ru.

TRUEX process with Simulated HLW was demonstrated recently with 0.25 M CMPO + 1.2 M TBP in *n*-dodecane (53). A stripping composition of 1.5 M NaOH + 1.5 M Formic acid + 0.05 M DTPA gave total stripping of the extracted metal ions such as La and Ce. Results demonstrated successful recovery of lanthanides (La and Ce) with reduced secondary waste volumes as scrub cycle was avoided in the process.

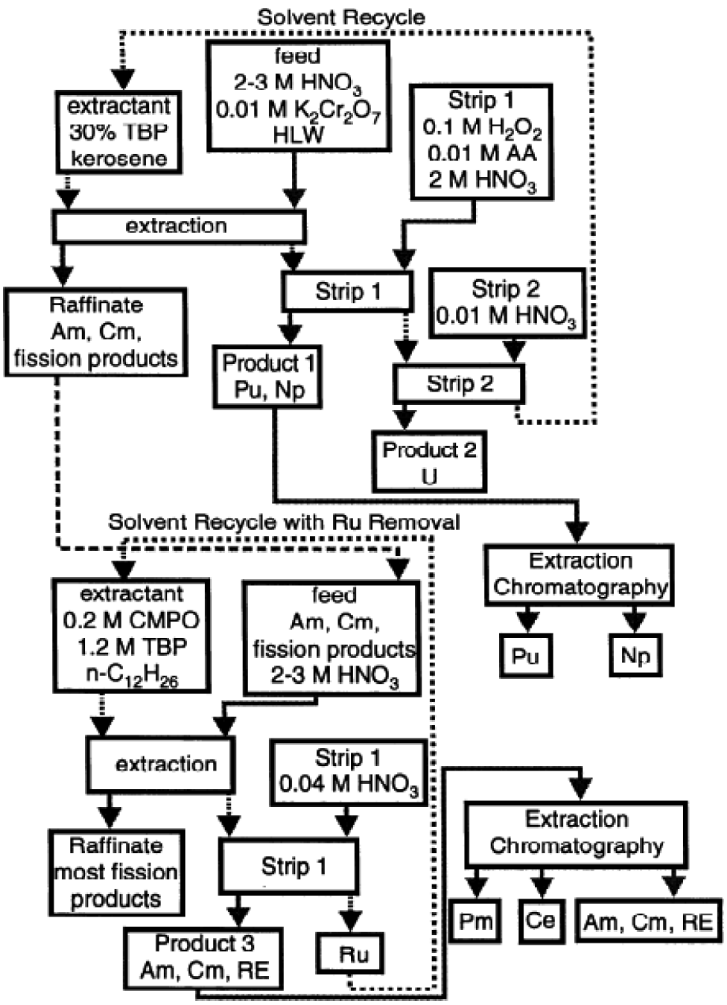

FIGURE 7 PUREX-TRUEX Flow sheet for actinide partitioning from dissolved fuel as proposed at BARC. AA is ascorbic acid. Solid lines represent aqueous streams. Dotted line represents organic streams (7). Reproduced with permission of Taylor & Francis.

Degradation, Cleanup and Reusability of TRUEX Solvent

The hydrolytic and radiolytic degradation of CMPO was studied in CCl_4 and decalin (decahydronaphthalene) (54), C_2Cl_4 or in a mixture of TBP and C_2Cl_4 (55). Hydrolytic and radiolytic degradation of the TRUEX process solvent (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) was investigated in the presence of 5 M HNO_3 (56,57) and under dynamic conditions in contact with 3 M HNO_3 or synthetic PHWR-HLW (58). The G-values (molecules/100 ev deposited) for the disappearance of CMPO in CMPO-TBP mixture were reported to be 1.2±0.3 in *n*-dodecane, 4.5±0.3 in TCE and 16.4±1.7 in CCl_4 (55,56), indicating the more reactive conditions created upon radiolysis

TABLE 3 Distribution Ratio of Am (D_{Am}) with TRUEX Solvent After Irradiation with Gamma Irradiator in Contact with Nitric Acid; Extractant: 0.2 M CMPO + 1.2 M TBP / *n*-Dodecane

	D_{Am} Ref (57)			D_{Am} Ref (58)	
	Static irradiation in contact with 5 M HNO_3			Dynamic irradiation in contact with 3 M HNO_3	
Dose (kGy)	pH 2.0	0.04 M	Dose (kGy)	pH 2.0	0.04 M
0	0.011	0.13	0	0.016	–
70	0.87	0.72	~50	0.55	0.23
130	0.91	0.61	~110	2.7	0.38
200	1.33	0.59	~210	16.4	0.81
280	1.42	0.58	~260	32.7	1.21

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

of chlorinated diluents. Hydrolysis generates only acidic compounds while radiolysis produces both acidic and neutral compounds. The degradation products reported are methyl octylphenyl phosphine oxide, octyl(phenyl)-N-monoisobutyl carbamoyl methyl phosphine oxide, dibutyl phosphoric acid, octyl(phenyl) phosphinic acid, octyl(phenyl) phosphinyl acetic acid (57), and methyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphinic acid and phenyl(diisobutyl) carbamoyl nitromethyl phosphine oxide (58). The presence of the acidic extractants as degradation products increases D_{Am} under stripping conditions. Such impurities must be completely removed from the used TRUEX solvent prior to the recycling of the extractant. Table 3 gives the D_{Am} with an irradiated CMPO mixture under static conditions in contact with 5 M HNO_3 (57) and under dynamic conditions in contact with 3 M HNO_3 (58). The D-values at pH 2.0 are quite high and increase with absorbed dose. Up to an absorbed dose of ~200 kGy, primary cleanup with 0.25M Na_2CO_3 will remove most of the acidic impurities. Although the D_{Am} at pH 2.0 may not match the reference condition, the D_{Am} value at 0.04M HNO_3 is low enough to allow counter-current stripping of Am. However, at high radiation doses a secondary clean-up with macroporous anion exchange resin (57) or with basic alumina (58) is necessary.

ACTINIDE PARTITIONING WITH MALONAMIDES

The major drawbacks of the phosphorus based extractants include generation of large volumes of secondary waste as solid residue after incineration of the spent solvent. Malonamide based extractants have been reported to be a viable green alternative (59,60). These extractants are completely incinerable, which implies that the amount of solid secondary waste generated in nuclear waste treatment could be significantly reduced.

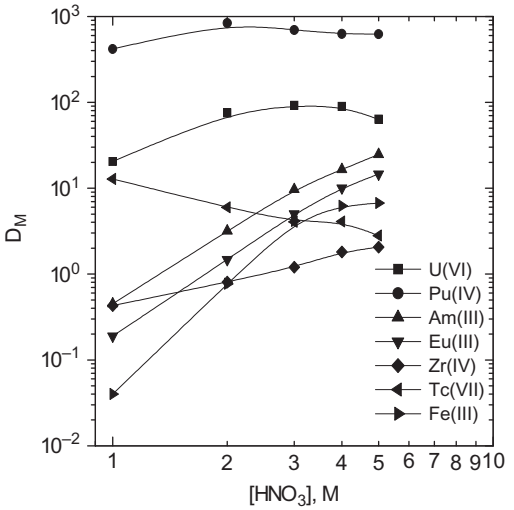

FIGURE 8 Distribution behaviour of various metal ions by DIAMEX solvent; Organic phase: 1 M DMDBTDMA in *n*-dodecane; Temperature: 25°C.

Amongst several malonamides studied, N,N'-dimethyl-N,N'-dibutyl tetradecyl malonamide (DMDBTDMA, Fig. 2e) and N,N'-dimethyl-N,N'-dioctyl hexylethoxy malonamide (DMDOHEMA, Fig. 2f) were found to be promising for actinide partitioning in the so called DIAMEX (Diamide Extraction) Process (59–68). Extensive studies have been carried out during last two decades on this class of extractants under the programme commonly referred to as "EUROPART" (59,60). Initially, DMDBTDMA was proposed as the reference molecule for DIAMEX process. Basic solvent extraction studies data of various metal ions by this DIAMEX solvent, which are important from actinide partitioning point of view is shown in Figure 8. The relative extractability of the actinides followed the order Pu(IV) > U(VI) > Am(III), while fission product ions such as Eu^{3+}, Zr^{4+}, TcO_4^- and Fe^{3+} are also extracted significantly in the acidity range of 3–4 M HNO_3.

Demonstration of the DIAMEX Process with DMDBTDMA

DIAMEX process with genuine radioactive waste has been demonstrated at ITU, Karlsruhe, Germany using centrifugal extractor battery (64,65). The flow sheet used is shown in Figure 9A. The flow sheet was demonstrated with genuine HLW, which was obtained after the reprocessing of commercial UO_2 fuel of 45 GWd/Te of burn-up (65). It was found that 6 extraction stages were sufficient to achieve feed decontamination factors between 100 and 230 for lanthanides and above 300 for minor actinides. Co-extraction of molybdenum and zirconium was prevented by a scrubbing cycle using oxalic acid.

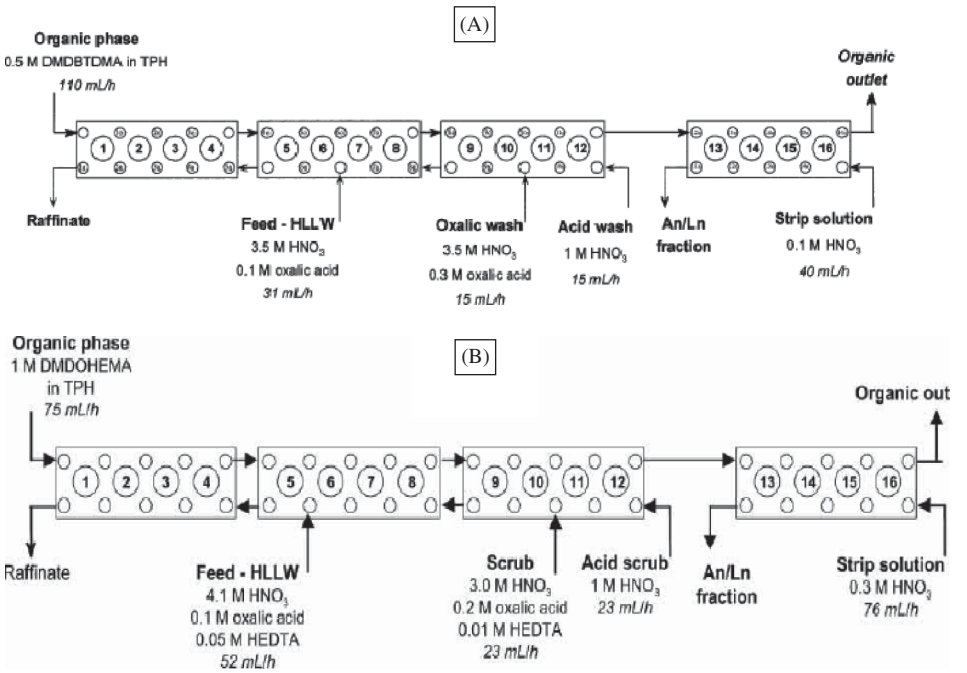

FIGURE 9 (A) Flow sheet tested with DIAMEX solvent at ITU, Karlsruhe; Reproduced with permission from Ref (65); (B) Flow sheet tested with DMDOHEMA at ITU, Karlsruhe, Germany (68). Reproduced with permission of Taylor & Francis.

Salient feature of this process was that the back extraction proved to be very efficient, yielding more than 99.9% recovery of both the lanthanides and the actinides in 4 stages. Authors reported the need for process optimization to prevent co-extraction of technetium, ruthenium, palladium and neptunium, which are accumulated in the back-extraction section (65).

Demonstration of the DIAMEX Process with DMDOHEMA

Recently, DMDOHEMA has been selected as the new reference molecule for the DIAMEX process (in place of DMDBTDMA), because: (i) introduction of hexyl ethoxy group on the central alkyl chain slightly enhances the affinity for trivalent actinides and lanthanides, (ii) presence of bulky alkyl group on the amido group increases the lipophilicity and, therefore, limit the third phase phenomena, and (iii) shortening of the length of the alkyl chain at centre carbon atom shortens the chain length of the degradation products and, therefore, facilitates their elimination by alkaline scrubbing (66). A hot demonstration of the DIAMEX process using this new reference molecule (DMDOHEMA) with a genuine high-level PUREX raffinate as the

feed was reported at ITU, Karlsruhe (67). The genuine HLW feed was produced by small scale PUREX reprocessing of dissolved commercial PWR MOX fuel (30 GWd/tM), while the continuous counter-current experiments were carried out in a 16-stage centrifugal extractor battery installed in a hot cell. It was demonstrated that 5 extraction stages were sufficient to achieve feed decontamination factors above 2200 and 320 for Am and Cm, respectively. Co-extraction of Mo and Zr, as well as that of Pd, was efficiently prevented using oxalic acid and HEDTA scrubbing, respectively. However, Tc, Y, and to some extent Ru, were co-extracted. The back-extraction of Am and Cm proved to be very efficient, yielding more than 99.9% recovery in 4 stages.

Another hot test at ITU with DMDOHEMA as the extractant was demonstrated with a High Active Concentrate (HAC), which was obtained after concentration and denitration of high active raffinate with a concentration factor of 10 with feed acidity of ~4 M HNO_3 (68). During concentration and denitration, a precipitate of Sr, Zr, Mo, Sn and Ba was formed, however, minor actinide precipitation was not significant (<0.001%). The removal of Zr (85%) and Mo (90%) in the precipitate contributed significantly to simplify the subsequent DIAMEX process, where oxalic acid was added to prevent co-extraction of these elements. The flow-sheet shown in Figure 9B, was used for spiked DIAMEX-HAC test, which demonstrated that this process could treat a feed solution containing high concentrations of fission products. The extraction performance goals were achieved, where actinide(III) and lanthanide(III) extraction and stripping were quantitative. Back extraction of Zr and Pd was very good employing oxalic acid and HEDTA scrubs, respectively. Molybdenum was distributed to the actinide(III) / lanthanide(III) product (4.4%) and to the spent solvent (3%).

Stability of Malonamide Extractants

Berthon et al. (69) have reported the radiolytic and hydrolytic stability of malonamides using potentiometric titrations and gas chromatography techniques. The radiolytic stability studies show that the concentration of the malonamide extractants decreased strongly with the irradiation dose. The disappearance rate of the extractants was estimated to be 0.32 $mol.L^{-1}.(MGy)^{-1}$ for DMDOHEMA and 0.46 $mol.L^{-1}.(MGy)^{-1}$ for DMDBTDMA in the presence of 4 mol/L aqueous nitric acid. However, effect of HNO_3 on the radiolytic stability of malonamides was not significant. Malonamide extractants degrade by hydrolysis or radiolysis, mainly to the amide-acid and a secondary amine ($R'CH_3NH$, R'=alkyl group at amide nitrogen). The aqueous solubility of secondary amine formed depends upon the chain length of the R' group. If the R' alkyl group of the malonamides is long enough, it remains soluble in the organic phase. However, if this R'

group is short (for example, the butyl group), the amine species formed during degradation is soluble in the aqueous phase. The extracting properties of actinides(III) and lanthanides(III) by irradiated malonamide extractants suggested that the degradation of the solvent leads to a decrease in the distribution ratios of trivalent actinides and lanthanides which was ascribed to decrease in the malonamide concentration. Acidic and basic solvent washings were found to be promising approach for removal of degradation products of malonamides.

ACTINIDE PARTITIONING WITH DIGLYCOLAMIDES

Due to the relatively weak affinity of the carbonyl groups of malonamide for the actinide / lanthanide ions, the DIAMEX process requires high concentration of the extractant (0.5–1 M) solvent for actinide partitioning, which is responsible for the co-extraction of many unwanted fission products. During the last few years, diglycolamides (DGA), developed at JAERI have caught the attention of radiochemists all around particularly in the countries like Japan, Germany and India. DGA based extractants are capable of extracting trivalent actinides from moderately acidic feeds (3–4 M HNO_3), such as the HLW. Sasaki et al. (70) synthesized a series of diglycolamides (Fig. 2g) having same central frame with different alkyl chains (ranging from *n*-propyl to *n*-dodecyl) attached to the amidic nitrogen atoms. Various properties of the synthesized diglycolamide derivatives are listed in Table 4. It was found that the diglycolamide derivatives with smaller alkyl chain (propyl and butyl) were soluble in water due to the presence of three polar oxygen atoms and lower alkyl chains. These derivatives of diglycolamide were used for aqueous complexation of the metal ions (71,72). Although the higher homologues of diglycolamide were practically insoluble in water and freely soluble in paraffinic solvents, the distribution ratio values for Am(III) were found to decrease due to steric hindrance during complexation of the bulky molecules. Among different derivatives synthesized, tetraoctyl diglycolamide (TODGA, Fig. 2g) was found to be the most promising with reference to its free solubility in *n*-dodecane and significantly high distribution coefficient values for trivalent actinides. Recently, Mowafy et al. (73) synthesized a series of diglycolamides with different alkyl groups and reported similar results to those published by Sasaki et al. (70). Recently, few studies with the branched analog of TODGA, namely N,N,N′,N′-tetra-2-ethylhexyl diglycolamide (TEHDGA, Fig. 2h) have been reported (53,74–76).

Extensive solvent extraction studies with TODGA have been pursued at JAERI (Japan), BARC (India) and ITU-Karlsruhe (Germany) (77–82). In view of third-phase formation, a mixture of 0.1 M TODGA + 0.5 M DHOA was proposed a suitable solvent for actinide partitioning. DHOA was selected

TABLE 4 Properties of Tetra-*n*-Propyl, *n*-Butyl, *n*-Amyl, *n*-Hexyl, *2*-Ethylhexyl, *n*-Octyl, *n*-Decyl and *n*-Dodecyl Diglycolamide

Diglycolamide (DGA)	Solubility in water (mM)	Solubility in *n*-dodecane	D_{Am} by 0.1M DGA in *n*-dodecane (1 M HNO_3)
TPDGA	57.0	Very poor	—
TBDGA	2.3	poor	—
TADGA	0.27	Soluble	100
THDGA	0.11	Soluble	40
TODGA	0.04	Freely soluble	30
TEHDGA	0.04	Freely soluble	0.5
TDDGA	0.04	Freely soluble	18
TDDDGA	0.04	Freely soluble	11

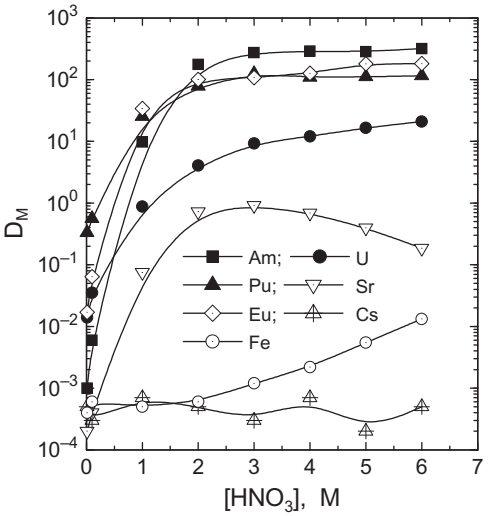

FIGURE 10 Distribution behaviour of various metal ions by TODGA solvent; Organic phase: 0.1M TODGA + 0.5M DHOA in *n*-dodecane (78). Reproduced with permission of Taylor & Francis.

as the phase modifier due to its CHON constituents as well as satisfactory LOC values for Nd (77,78). At ITU- Karlsruhe, however, a mixture of 0.2 M TODGA + 0.5 M TBP has been used for actinide partitioning test runs (80–82). Basic extraction data for some of the important metal ions with TODGA solvent (0.1 M TODGA + 0.5 M DHOA) have been shown in Figure 10.

Demonstration of the TODGA Processes

The major focus of the work carried out at JAERI, Japan has been the development of ARTIST (Amide-based Radio-Resources Treatment with Interim Storage of Trans Uranics) process using amide-based extractants.

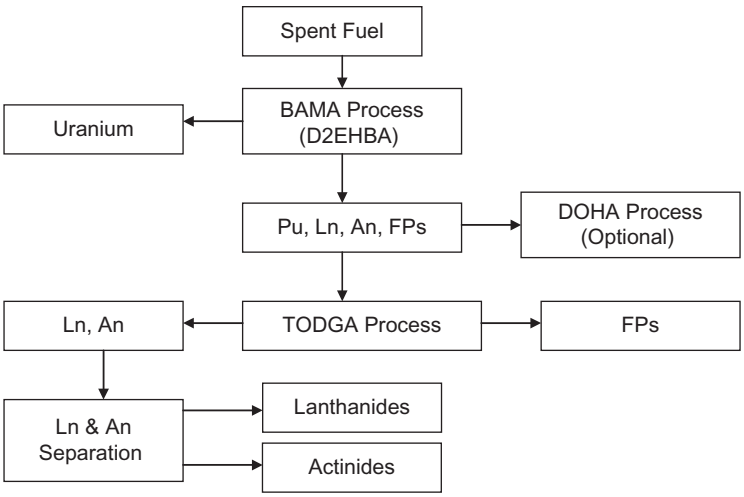

FIGURE 11 Concept of ARTIST Process.

The process consists of mainly two steps: (i) exclusive isolation of uranium using branched alkyl monoamides (BAMA), and (ii) total recovery of TRU using TODGA. The concept of ARTIST Process is shown in Figure 11. After recovery of uranium, an optional stage is the recovery of Pu, which can be achieved using mono amides like N,N-dioctyl hexanamide (DOHA).

Authors have carried out extensive counter current extraction studies with TODGA using a 16-stage mixer-settler battery (79). Figure 12 shows the profile of Nd concentration in the organic phase as well as in the aqueous phase at steady state for different stages of the mixer-settler units. Quantitative extraction and stripping of Nd was achieved in 5 stages each. The product could be concentrated ~2 times by reducing the strippant flow rate. The organic phase could be recycled without any significant change in the extraction profile. Mixer-settler runs with PHWR-SHLW demonstrated that the lanthanides were quantitatively extracted in 4 stages, while stripping was quantitative in equal number of stages. Elements such as Fe, Ni, Mn and Sr were practically not extracted from SHLW. Mixer-settler PHWR-SHLW runs with irradiated solvent (100 kGy) did not show any change in the extraction properties.

Development of the TODGA based process for actinide partitioning was also pursued at ITU-Karlsruhe, Germany, where 0.2 M TODGA + 0.5 M TBP (as phase modifier) was employed as the extractant in mixer-settler runs (81,82). The results showed that An(III) and Ln(III) were quantitatively extracted (>99.99%) with very high decontamination factor ($>10^3$ – 10^4). However, the stripping of lanthanides was not quantitative in 4 stages (81). Subsequently, 16-stage stripping was used for the quantitative recovery of the product. The main features of ITU-Karlsruhe work are: (i) trivalent

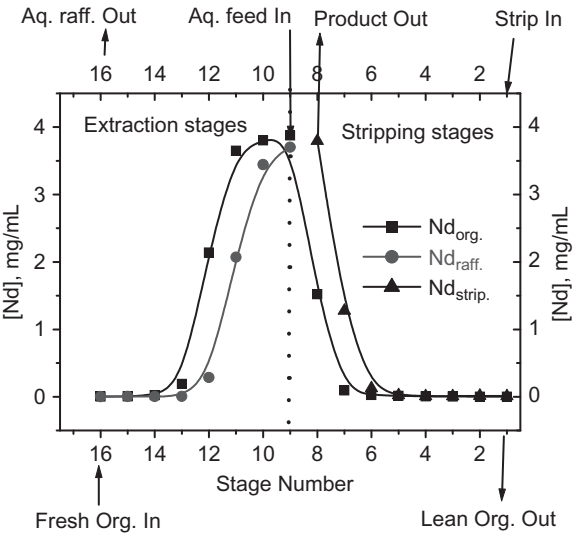

FIGURE 12 Mixer-settler run carried out at BARC with TODGA; Extraction stages 8–16; Stripping stages 1–8.

lanthanides and actinides were not found in the raffinate, (ii) only 0.25 % U was found in the raffinate, (iii) The quantitative back extraction of lanthanides and actinides was achieved in 12 stages, (iv) after stripping, the spent solvent was free from any metal ions, except Ru (~7.5%), and (v) the actinide / lanthanide product contained only 0.03% Sr, 0.12% Zr and 1.5% Ru. It should be noted that the work carried out at BARC employed 0.1 M TODGA + 0.5 M DHOA as the solvent, while the work carried out at ITU-Karlsruhe employed 0.2 M TODGA+ 0.5 M TBP as the solvent. Use of TBP as phase modifier and higher concentration of TODGA (0.2 M) enhances the extraction of acid in the organic phase, which adversely affects the stripping of metal ions. A mixture of 0.1 M TODGA + 0.5 M DHOA, thus, appears to be advantageous including reduction of ligand inventory and low secondary waste.

Recently, the TODGA process was demonstrated with genuine PUREX raffinate at ITU, Karlsruhe (82). The flow-sheet used is shown in Figure 13. Efficient extraction of lanthanide(III) and actinide(III) (>99.9%) was reported with DF value $>10^4$. Out of fission products, only Y and small fraction of Ru (~3%) was found in the product. The product acidity was 0.13 M HNO_3, which was recommended for the subsequent lanthanide/actinide separation with little feed adjustment. A comparison of hot tests of DMDBTDMA, DMDOHEMA, and TODGA processes demonstrated at ITU, Karlsruhe, Germany is shown in Table 5.

It should be noted that, ITU has recently proposed 0.2 M TODGA + 5% 1-octanol as extractant due to following reasons; (i) the presence of

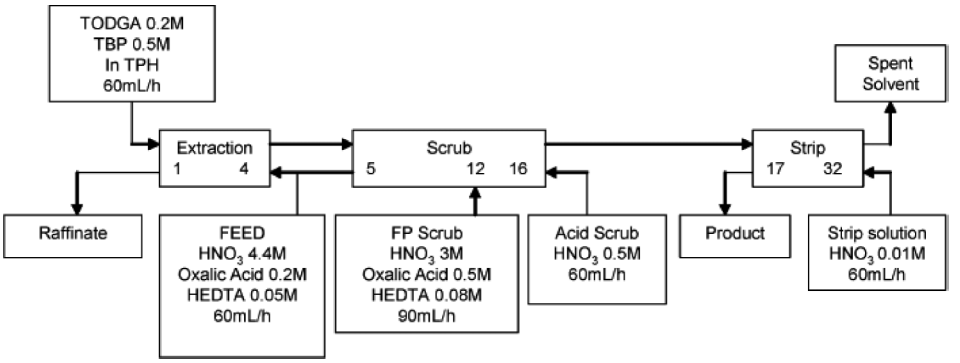

FIGURE 13 Flow sheet tested with TODGA at ITU, Karlsruhe, Germany (82). Reproduced with permission of Taylor & Francis.

TABLE 5 Comparison of Results Between Two DIAMEX and TODGA Processes Demonstrated at ITU, Germany

Solvent	0.5 M DMDBTDMA	0.65 M DMDOHEMA	0.2 M TODGA
Feed	Irradiated UO_2, (HNO_3) = 3.5 M, (Oxalic acid) = 0.1 M	Irradiated MOX, (HNO_3) = 4 M, (Oxalic acid) = 0.1 M, (HEDTA) = 0.01 M	Irradiated UO_2, (HNO_3) = 4.4 M, (Oxalic acid) = 0.2 M, (HEDTA) = 0.05 M
Product	>99.9% An	>99.96% An	>99.99% An
	>99.9% Ln	>99.8% Ln	>99.9% Ln
	94% Pd	<0.04% Pd	<0.01% Pd
	16%Ru	3% Ru	~ 1% Ru
	51% Tc	62% Tc	
Raffinate	<0.01% An	<0.04% An	>0.01% An
	<0.01% Ln	<0.2% Ln	>0.1% Ln
	99.9% Zr	99.7% Zr	99.9% Zr
	99.9% Mo	99.8% Mo	99.9% Mo
	84% Ru	96% Ru	~ 82% Ru
	<0.01% Pd	>99.9% Pd	>99.99% Pd

Results are expressed as recoveries in the outgoing fractions; Ref. (82). Reprinted with permission of Taylor & Francis.

a non-CHON compound (TBP), and (ii) the pronounced co-extraction of nitric acid (e.g., 0.2 M TODGA + 0.5 M TBP in TPH extracts approx. 0.6 M HNO_3 from 4 M HNO_3). In the presence of 1-decanol, the amount of HNO_3 extraction was reduced to ~ 50 % as compared to that of 0.2 M TODGA + 0.5 M TBP in TPH.

Stability of TODGA

It is essential to understand the radiation as well as hydrolytic stability of the extractant involved for its application for processing radioactive waste solutions. Sugo et al. (83) reported good hydrolytic stability of TODGA as

they found no degradation product when 0.1 M TODGA in *n*-dodecane was contacted with 3 M HNO_3 for 4 weeks when analyzed by GC-MS technique. Similar hydrolytic stability has been shown for 0.2 M TODGA + 0.5 M TBP in TPH when kept in contact with 3 M HNO_3 for 60 days (80). The radiation stability of TODGA has been studied and the G-value (number of molecules decreased after absorption of 100 eV of energy) was found to be 8.5±0.6 molecules/eV (83). It was found that the radiation stability of TODGA could be increased with the addition of benzene as well as DHOA. The main degradation products of TODGA are dioctylamine, dioctyl acetamide, dioctyl glycolamide and dioctyl formamide. Authors have reported excellent radiation stability of TODGA solvent (0.1 M TODGA+ 0.5 M DHOA in *n*-dodecane) up to 500 kGy dose when the solvent was irradiated in contact with SHLW with ^{60}Co source (79). Modolo et al. (80) and Mincher et al. (84) have also reported excellent radiolytic stability of 0.2 M TODGA + 0.5 M TBP in TPH up to 600 kGy even when the extractant was irradiated in contact with 3M HNO_3. Alpha radiolysis of TODGA in *n*-dodecane was also investigated by irradiation with helium ion beam (85). It was postulated that the charge transfer reaction from the radical cations of *n*-dodecane to the TODGA molecules is more with low LET (linear energy transfer) radiations such as gamma rays. In contrast, irradiation with high LET radiations such as alpha particles, activated species were formed locally at a high density in the track where recombination is predominant. As a result, the degradation of TODGA by alpha particles is lower as compared to that with gamma radiation. Diglycolamide derivatives containing aromatic functional groups exhibited higher radiation stability, possibly due to interamolecular energy transfer to the benzene ring (86). The radiation dose during actinide partitioning from actual HLW can be estimated with the knowledge of (a) the burn-up and cooling of spent fuel, (b) volume reduction from PUREX raffinate to HLW, (c) concentrations, and energies of the beta/gamma emitters, and (d) the contact time during each cycle of actinide partitioning. Typically, the radiation dose in HLW solutions emanating from Pressurized Heavy Water Reactor (PHWR; burn up ~7000 MWD/Te) and Pressurized Water Reactor (PWR; burn up ~33000 MWD/Te) with 3 years' cooling are expected to be ~20 kGy and ~100 kGy. The radiolytic damage to the TODGA solvent system appears not to influence its performance in either extraction or stripping cycle under these conditions.

Actinide Partitioning with TEHDGA

Actinide partitioning studies with other diglycolamide extractants are limited and only few studies with TEHDGA have been reported (53,74–76). Manohar et al. (53) carried out mixer-settler runs using 0.2 M TEHDGA + 30% isodecanol for extraction of lanthanides and actinides from simulated HLW. The results of the counter-current extraction studies with SHLW are summarized

TABLE 6 Results of Mixer-Settler Experiment Carried out at BARC with SHLW Using TEHDGA

Element	Feed (ppm)	Raffinate (ppm)	Product (ppm)	% Recovery	Material balance (%)
La	304	9	596	98.0	101
Ce	186	0.3	305	82.0	82.1
Ru	24	23	2	4.2	100
Mo	154	123	47	15.3	95.1
Sr	67	65	5	3.7	100.7

Extractant: 0.2 M TEHDGA + 30% *iso*-decanol/*n*-dodecane; Strippant: 0.01 M HNO_3; Ref (53).

in Table 6. Deepika et al. (75) studied the effect of phase modifiers along with 0.2 M TEHDGA and found DHOA more promising than *iso*-decanol and 1-decanol. However, 0.2 M TEHDGA + 1 M DHOA / *n*-dodecane formed third phase at 7.8 M HNO_3, whereas, no third phase was observed even with 15.7 M HNO_3 when 1 M 1-decanol or 1 M *iso*-decanol were used as the phase modifiers. The acid extraction was also larger in the presence of DHOA as compared to decanol. The extraction studies with 0.2 M TEHDGA + 1 M DHOA suggested that Am(III) is efficiently extracted under HLW condition, whereas elements like Ni, Fe, Mn, Mo, Ru and Cs were not extracted.

Recently, Gujar et al. (76) compared the extraction behaviour of actinides, lanthanides, fission products and structural elements with TODGA and TEHDGA as the extractants. They carried out systematic investigation and reported that TODGA displayed higher extraction of actinides / lanthanides even with lower concentration of ligand (0.1 M) as compared to TEHDGA (0.2 M). An attempt was also made to evaluate the extraction behaviour of actinides / lanthanides from HLW using 0.1 M TEHDGA + 5% (v/v) *iso*-decanol (87). Use of lower concentration of extractant and phase modifier was guided by the limited concentration of extractable metal ions in the HLW, ease of stripping and economic use of the ligand as compared to earlier proposed composition of TEHDGA (0.2 M TEHDGA + 30% *iso*-decanol) (53). Batch extraction data for various metal ions from PHWR-SHLW with 0.1 M TEHDGA + 5% (v/v) *iso*-decanol (Table 7) suggested good decontamination factor (D.F.) of Am(III) with respect to other metal ions, viz. Fe, Cs, Pd and Sr. Countercurrent mixer settler studies for actinide partitioning were carried out using 0.1 M TEHDGA + 5% isodecanol as the extractant (88). The feed solution was Simulated High-level Waste of Pressurized Heavy Water Reactor origin (PHWR-SHLW) spiked with ^{241}Am, ^{152,154}Eu, ^{137}Cs, ^{85,89}Sr, ^{59}Fe, ^{106}Ru, ^{109}Pd, ^{95}Zr and ^{99}Mo tracers. More than 99.9% of the trivalent actinides and lanthanides were extracted in four stages, and the D.F. values were $>10^3$ for most fission products. The co-extraction of Zr and Pd was prevented by the addition of oxalic acid and HEDTA into the feed solution, respectively. However, ~20% Ru and 10% Mo were extracted in to the organic phase, which was successfully scrubbed using a

TABLE 7 Distribution Ratio of Different Metal Ions Under Extraction and Stripping Conditions by TEHDGA

	Distribution ratio of metal ions		
Metal Ions	0.01 M HNO_3	3 M HNO_3	PHWR-SHLW
Am	<0.002	29.3 ± 2.6	13.9 ± 1.9
Pu	–	55.7 ± 3.5	35.6 ± 2.6
U	<0.002	1.43 ± 0.3	1.08 ± 0.5
Eu	<0.002	95.4 ± 5.8	45.8 ± 3.0
Sr	<0.002	0.16 ± 0.02	0.07 ± 0.02
Cs	<0.001	<0.001	<0.001
Tc	27.4 ± 2.0	0.38 ± 0.05	0.34 ± 0.04
Pd	<0.002	0.05 ± 0.02	0.02 ± 0.01
Fe	<0.001	<0.001	<0.001
Mo	7.0 ± 1.5	0.42 ± 0.05	0.31 ± 0.05

Organic phase: 0.1 M TEHDGA + 5% *iso*-decanol / *n*-dodecane; Temperature: 25°C; Ref (87). Reprinted with permission of Taylor & Francis.

mixture of 0.2 M oxalic acid and 0.1 M HEDTA in 5 M HNO_3. Finally, the extracted actinides and lanthanides were quantitatively stripped with 0.2 M HNO_3. Raffinate of the extraction cycle was found to be free from any alpha activity.

CONCLUSIONS AND PERSPECTIVES

A brief comparison of the different extractants proposed for actinide partitioning is summarized in Table 8. The main drawbacks of the TRUEX process are; (a) the poor back extraction of Am(III) and Cm(III) with dilute nitric acid, and (b) interference due to solvent degradation products. At the same time, high distribution ratio of tri-, tetra- and hexavalent actinides from moderate acidic solutions and good selectivity over fission products is the key feature of TRUEX solvent. Malonamides have been found promising over the phosphorus-based extractants because of improved back extraction properties for Am(III) / Cm(III). It is due to the gradual increase in distribution ratio of Am(III) with acidity in the range 0.01 M to 2 M HNO_3, and due to innocuous nature of their radiolytic and hydrolytic products (mainly carboxylic acids and amines) that can be easily washed out. Though the completely incinerable DMDBTDMA and DMDOHEMA were reported to be promising candidates, they showed moderate extraction for Am(III) / Cm(III) from HLW at acidity $\leq$ 3 M HNO_3.

The more recently developed diglycolamide based extractants have been identified as amongst the most promising extractants for the partitioning of trivalent actinides and lanthanides from HLW solutions. Amongst diglycolamides, N,N,N′,N′-tetraoctyl diglycolamide (TODGA) has been

TABLE 8 A Brief Summary of the Properties of Various Extractants Proposed for Actinide Partitioning

	Extractants				
Parameters	CMPO	DMDBTDMA	DMDOHEMA	TODGA	TEHDGA
Concentration proposed	0.2 M	0.5 - 1 M	0.65 M	0.05 - 0.2 M	0.1- 0.2 M
Phase modifier used	1.2 M TBP	NIL	NIL	0.5 M DHOA/TBP, 5% isodecanol	5% – 30% isodecanol
DAm at 3 M HNO_3	25	11	10	>300	100
DAm at 0.01 M HNO_3	10^{-2}	10^{-3}	10^{-3}	10^{-3}	10^{-3}
Scrub recommended	0.3M HNO_3	3.5M HNO_3 + 0.3M O.A.	3M HNO_3 + 0.2M O.A. + 0.01M HEDTA	3–5M HNO_3 + 0.2M O.A. + 0.1M HEDTA	3–5M HNO_3 + 0.2M O.A. + 0.1M HEDTA
Strippant recommended	buffer solution	dilute acid	dilute acid	dilute acid	dilute acid
Extraction of Zr	Moderate	Moderate	Extracted[a]	Extracted[a]	Extracted[a]
Extraction of Fe	Moderate	Moderate	Moderate	No extraction	No extraction
Extraction of Sr	No extraction	No extraction	No extraction	Low	Low
Extraction of Tc	Moderate	Moderate	Moderate	Moderate	Moderate
Extraction of Mo	Moderate	–	–	Low	Low

[a]extraction suppressed in the presence of oxalic acid; Low: D = <0.5; Moderate: D = 0.5 - 10; Extracted: D = >10; O.A.: oxalic acid.

extensively evaluated and shown excellent properties for the partitioning of actinides from HLW solution. Distribution ratio data of various metal ions with different proposed extractants for actinide partitioning have been summarized in Table 9.

ABBREVIATIONS

ARTIST	Amide-based Radio-Resources Treatment with Interim Storage of Trans Uranics
BAMA	Branched Alkyl Monoamides
BARC	Bhabha Atomic Research Centre
CCD	Chlorinated Cobalt Dicarbolide
CMP	Carbamoyl Methyl Phosphonate
CMPO	octyl-(phenyl)–*N,N*-diisobutyl carbamoyl methyl phosphine oxide
D	Distribution ratio
DϕCMPO	diphenyl–*N,N*-diisobutyl carbamoyl methyl phosphine oxide
DF	Decontamination Factor

TABLE 9 Distribution data of different metal ions with proposed extractants for actinide partitioning under varying experimental conditions; Temperature: 298 K

S.N.	Extractants	(HNO_3), M	U(VI)	Pu(IV)	Am(III)	Eu(III)	Zr(IV)	Fe(III)	Ref.
1	0.2 M CMPO +	0.01	–	–	0.01	0.01	–	$\sim10^{-3}$	(29)
2	1.2 M TBP	0.2	83	122	1.9	1.8	–	$\sim10^{-2}$	
3		0.5	110	987	7.4	6.2	–	0.022	
4		1	152	1835	14.3	8.5	0.7	0.045	
5		2	200	–	20.8	11.2	0.8	0.15	
6		3	274	3250	21.7	13.0	0.8	0.33	
7		4	250	3300	23.9	13.0	0.9	1.10	
8		6	283	–	23.7	21.5	1.8	8.72	
9	1 M DMDBTDMA	0.01	–	–	0.002	–	–	–	(61)
10		0.2	–	–	0.003	–	–	–	
11		0.5	–	–	0.07	–	–	–	
12		1	20.5	415	0.45	0.19	0.43	0.04	
13		2	75.6	835	3.2	1.5	0.81	0.8	
14		3	92.0	695	11.2	5.0	1.2	4.1	
15		4	89.9	625	16.5	10.1	1.8	6.2	
16		5	63.5	623	22.7	14.6	2.1	6.7	
17	1 M DMDOHEMA	1	100	10	0.9	0.6	9.5	0.03	(3)
18		2	230	80	3.5	4.0[a]	–	–	
19		3	600	400	9.0	10.0[a]	–	–	
20		4	800	600	15	15.0[a]	–	–	
21		6	700	500	95	12.0	80	90	
22	0.1 M TODGA +	0.01	$\sim10^{-3}$	–	$\sim10^{-3}$	$\sim10^{-3}$	0.01	$\sim10^{-3}$	(78)
23	0.5 M DHOA	0.1	0.03	0.5	0.006	0.06	–	$\sim10^{-3}$	
24		1	0.90	25.4	9.8	34.1	–	$\sim10^{-3}$	
25		2	4.1	78.9	175	100	–	$\sim10^{-3}$	
26		3	9.2	125	275	210	~300	$\sim10^{-3}$	
27		4	12.1	110	290	230	–	$\sim10^{-3}$	
28		6	20.9	115	320	280	–	$\sim10^{-3}$	
29	0.2M TODGA + 0.5M	0.1	0.1	–	0.1	1.0	0.01	–	(80)
30	TBP	0.5	1.5	–	9.5	70	15	–	
31		1	5.0	–	100	500	150	–	
32		2	10.5	–	1000	1000	100	–	
33		3	22	–	2000	1000	150	–	
34	0.05 M TODGA +	0.01	–	–	$\sim10^{-3}$	$\sim10^{-3}$	–	$\sim10^{-3}$	
35	5% iso-decanol	3	0.62	110	210	250	–	$\sim10^{-3}$	
36	0.1 M TEHDGA +	0.01	0.001	–	0.001	0.001	–	$\sim10^{-3}$	(87)
37	5% iso-decanol	3	1.43	55.7	29.3	95.4	–	$\sim10^{-3}$	
38	0.2 M TEHDGA +	0.01	–	–	0.001	–	–	$\sim10^{-3}$	(76)
39	5% iso-decanol	3	–	–	85	–	–	$\sim10^{-3}$	

[a]D_{Eu} data for 1M DMDOHEMA refers to Sm(III).

DGA	Diglycolamide
DHOA	N,N-dihexyl octanamide
DIAMEX	Diamide Extraction
DMDBTDMA	N,N'-dimethyl-N,N'-dibutyl tetradecyl malonamide
DMDOHEMA	N,N'-dimethyl-N,N'-dioctyl hexylethoxy malonamide
DTPA	Diethylene triamine penta acetic acid
EDTA	Ethylene diamine tetra acetic acid

FBR	Fast Breeder Reactor
GWd/Te	Gigawatt day per tonne
HAC	High Active Concentrate
HAW	High Active Waste
HEDPA	1-hydroxyethane-1,1-diphosphonic acid
HEDTA	*N*-(2-hydroxyethyl)-ethylenediamine triacetic acid
HLW	High-Level Waste
ITU	Institute for Trans Uranium Elements
JAERI	Japan Atomic Energy Research Institute
LET	Linear Energy Transfer
LLW	Low Level Liquid Waste
LOC	Limiting Organic Concentration
MA	Minor Actinide
MOX Fuel	Mixed Oxide Fuel
MWd/Te	Megawatt day per tonne
NCRW	Neutralized cladding removal waste
PEG	Polyethylene glycol
PFP	Plutonium Finishing Plant
PHWR	Pressurized Heavy Water Reactor
PUREX	Plutonium uranium reduction extraction
PWR	Pressurized water reactor
SBW	Sulphate Bearing Waste
SHLW	Simulated High-Level Waste
TBP	Tri-*n*-butyl phosphate
TEHDGA	N,N,N',N'-tetra-2-ethylhexyl diglycolamide
TODGA	N,N,N',N'-tetraoctyl diglycolamide
TRU	Trans uranium
TRUEX	Trans Uranium Extraction
UNEX	Universal Solvent Extraction

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