Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA

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Abstract

Over the last decade there has been much interest in the applications of diglycolamide (DGA) ligands for the extraction of the trivalent lanthanide and actinide ions from PUREX high active raffinates or dissolved spent nuclear fuel. Of the DGAs, the N,N,N',N'-tetraoctyldiglycolamide (TODGA) is the best known and most widely studied. A number of new actinide separation processes have been proposed based on extraction with TODGA. This review covers TODGA based processes and extraction data, specifically focusing on how phase modifiers have been used to increase metal loading and thus enhance the operating process envelopes. Effects of third phase formation and the organic phase speciation are reviewed in this context. Relevant aspects of the extraction chemistry of important solvents (TODGA-modifier-diluent combinations) are described and their performances demonstrated by a consideration of the published flowsheet tests. It is seen that modifiers are successfully enabling the use of TODGA in actinide separation processes but to date the identification and testing of suitable modifiers has been rather empirical. There is a growing understanding of the fundamental chemistry occurring in the organic phase and how that affects extractant speciation and metal loading capacity but studies are still needed if TODGA-based flowsheets are to become an industrially deployable option for minor actinide (MA) recovery processes.

Keywords

TODGA; modifier; third phase; diglycolamide; DGA; extraction; review

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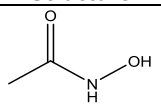
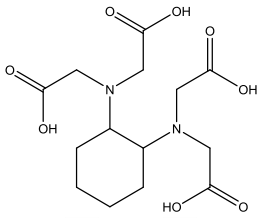
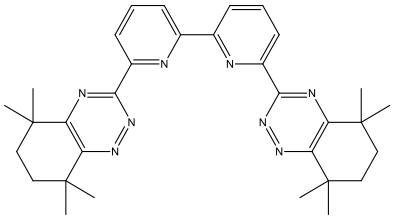
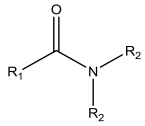
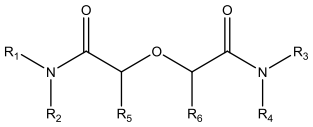
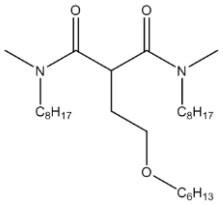
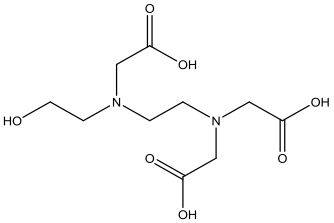
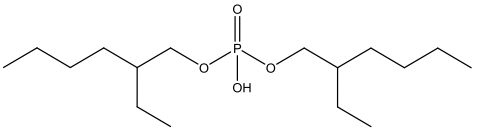
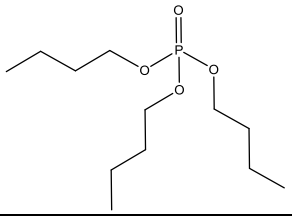
LIST OF ABBREVIATIONS AND MOLECULES

AHA	Acetohydroxamic Acid
An	Actinide(s)
BWR	Boiling Water Reactor
CDTA	Cyclohexyl-1,2-diamine-N,N,N′,N′-tetraacetate
D	Distribution ratio, the ratio of $[M]_{org}$ against $[M]_{aq}$
D2EHAA	di(2-ethylhexyl)acetamide
DGA	Diglycolamide
DHOA	N,N-dihexyloctanamide
DLS	Dynamic Light Scattering
DMDODGA	N,N′-dimethyl-N,N′-dioctyl-DGA
DMDOHEMA	N,N′-dimethyl-N,N′-dioctyl-hexyl-ethoxy-malonamide
EDTA	Ethylenediamine-N,N,N′,N′-tetraacetate
FHA	Formohydroxamic Acid
GANEX	Grouped ActiNide EXtraction
GDF	Geological Disposal Facility
Gy	Gray (unit of radiation dose)
HAR	Highly Active Raffinate
HDEHP	Di(2-ethylhexyl)phosphoric acid
HEDTA	N-hydroxy-ethylenediamine-N,N′,N′-triacetate
HLW	High Level Waste
HAF	Highly Active Feed
HWR	Heavy Water Reactor
IFT	Interfacial Tension
Ln	Lanthanide
LOC	Limiting Organic Concentration
MA	Minor Actinide
MOX	Mixed Oxide
MWd	Megawatt days
NPH	Normal Paraffinic Hydrocarbons
PHWR	Pressurised Heavy Water Reactor
PUREX	Plutonium URanium EXtraction
SANEX	Selective ActiNide EXtraction
SO_3-Ph-BTP	2,6-Bis(5,6-di(3-sulfophenyl)-1,2,4-Triazin-3-yl)Pyridine
SHLW	Simulated High Level Waste
T2EHDGA	N,N,N′,N′-tetra-2-ethylhexyl-DGA
TALSPEAK	Trivalent Actinide-Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TBP	Tributylphosphate
TDDGA	N,N,N′,N′-tetradecyl-DGA
THDGA	N,N,N′,N′-tetrahexyl-DGA
t_{HM}	Tonne Heavy Metal
TODGA	N,N,N′,N′-tetraoctylDGA
Me_2-TODGA	TODGA with two methyl groups either side of etheric O
Me-TODGA	TODGA with one methyl group next to etheric O
P&T	Partitioning and Transmutation
TPeDGA	N,N,N′,N′-tetrapentyl-DGA
TPH	Hydrogenated Tetrapropylene
TRLFS	Time Resolved Laser Fluorescence Spectroscopy

Abbreviation	Structure
AHA	
CDTA	
$CyMe_4$-BTBP	
D2EHAA (R_1 = methyl, R_2 = 2-ethylhexyl) DHOA (R_1 = octyl, R_2 = hexyl)	
Depiction of DGA backbone. Where R groups can vary as alkyl or H.	
DMDOHEMA	
HEDTA	
HDEHP	
TBP	

1 Introduction

1.1 Minor actinide separations in future nuclear fuel cycles

One of the major problems nuclear power faces is the issue of what to do with the fuel once it has been used in the reactor. Interim storage followed by disposal in a geological disposal facility (GDF) is presently the preferred option in many countries. However, used nuclear fuels from the current generation of thermal reactors contain ~96 % of the initial U inventory, ~3 % fission products (FPs) and ~1 % Pu and MA.[1] Recovery and re-use of the U and Pu increases the longevity of U based nuclear fuel cycles dramatically, particularly in fuel cycle scenarios with multiple recycling of U and Pu in next generation fast reactors. Currently, once the U and Pu are removed from used (or spent) nuclear fuel by reprocessing, the remaining waste is then isolated and packaged for disposal in a repository, where it will need to remain isolated from the biosphere for >100,000 years.[2]

It is the Pu and MA inventory of the used fuel that is the cause of the long-lived heat and radiotoxic loading of nuclear waste after ~1000 years. If these elements could be isolated then they could be transmuted - the process of placing them in a fast neutron flux or accelerator driven system to initiate fission, creating isotopes of shorter half-life.[3] This could be simply as a means of disposal or through inclusion in next generation fuel cycles as fuel. This 'partitioning and transmutation' (P&T) scenario thus offers the potential to substantially reduce the heat loading, and hence footprint, of the GDF as well as the time taken for the radiotoxicity to decrease to 'natural' levels. Reductions in the inventory and longevity of the high level waste (HLW) as well as the size of the GDF (or number of GDFs) required can also have positive effects on public acceptance of nuclear energy and radioactive waste disposal.[4,5] However, whilst separations of U and Pu are well established at the industrial scale, in order to implement any P&T strategy the MA must also be separated from the HLW. In the case of the trivalent MA ions, separation from the chemically similar lanthanide (Ln) ions is very challenging but necessary due to the high neutron capture cross-sections of some of the Ln, which would dramatically reduce the efficiency of the transmutation process, create more activation products and lead to mal-operation concerns in the reactor.

Current reprocessing strategies utilise the PUREX (Plutonium and URanium EXtraction) process to recover only U and Pu from the fuel, after dissolution in nitric acid solution (with modification, Np can also be recovered but not the trivalent actinide ions). Therefore, methodologies for isolation of the MA from the PUREX raffinate solution have received much attention in recent years. There have been many processes developed to achieve MA recovery either from the PUREX HLW stream or together with U/Pu in a group separation. Post-PUREX reprocessing, the MA can be isolated in a two-step separation process as with the DIAMEX-SANEX and TRUEX-TALSPEAK processes or in a single cycle process such as in the 1-cycle SANEX, innovative-SANEX and EXAm processes.[6,7,8,9,10]

So, as tri-butyl phosphate (TBP), the extractant used in the PUREX process, is not capable of extracting the trivalent MA ions, alternative molecules are required for putative MA separation processes. Over the last few decades a range of candidate molecules have been developed based around oxygen and nitrogen donor atoms. A number of these molecules such as CMPO

(octyl(phenyl)-N,N-di*iso*butylcarbamoylmethylphosphine oxide) and HDEHP (hydroxy-di-2-ethylhexylphosphate) have been used in processes such as TRUEX or TALSPEAK to separate the MA ions from acidic aqueous waste streams.[11] In recent years there has been a further trend towards molecules that fulfil the CHON principle, whereby the molecules contain only carbon, hydrogen, oxygen and nitrogen atoms. This principle is beneficial as it enables incineration of waste without the generation of secondary waste streams.[12] This has led towards the applications of malonamide-based molecules that co-extract An and Ln ions. More recently, the focus has been to simplify the recovery of trivalent An from PUREX raffinate to a single-cycle solvent extraction system with a minimum number of stages. This approach to ligand design and process development has led to much interest in the class of ligands called the DiGlycolAmides (DGAs). These molecules show significant promise for use in MA separation processes. The fundamental chemistry of the DGAs has recently been reviewed by Ansari *et al*.[13] However, as it will be seen below, the DGAs are susceptible to third phase formation as their metal loading capacities tend to be low. To utilise DGAs in practical solvent extraction processes, therefore, phase modifiers are usually introduced into the solvent composition. This is not an ideal situation as it complicates the process chemistry and solvent management. This two-part review now covers the role that modifiers play in various DGA based solvent extraction processes that have been proposed for actinide (An) separations as well as the potential for the removal of modifiers by alterations to the extractant molecule design. The consequences of adding/removing modifiers to the DGA-based solvent and changing the DGA molecule itself to increase loading capacity on other critical solvent properties are also considered in view of the goal of developing an industrially deployable MA separation process.

DGAs are currently being developed as extractants for the partitioning of the MA and Ln from the Highly Active Raffinate (HAR) generated by the PUREX process or aqueous raffinate from the first cycle of the GANEX process (GANEX-1: Grouped ActiNide EXtraction 1st cycle). The DGA (3-oxapentane-1,5-diamides) backbone was originally developed for the extraction of Sr.[14] Further work led to the DGA motif being used for the extraction of a range of di- and trivalent metal ions, demonstrating very high distribution ratios (D) (the amount of a metal partitioned into the organic phase *cf*. metal remaining in the aqueous phase) for the trivalent Ln ($D_{Ln(III)}$).[15] Continued research led to the identification of the DGA molecules as particularly useful for the extraction of the An ions.[16,17,18] The inclusion of the additional etheric oxygen atom into the diamide molecule increases the extraction efficiency of the ligands with respect to the trivalent ions compared to the malonamides. A wide range of DGA molecules have been developed and tested for their solvent extraction abilities with Ln and An ions; key examples are listed in Table 1 with the DGA backbone depicted in Figure 1. Of those listed, the best known and most studied is the tetra-octyl version, TODGA. This ligand has been used as the benchmark for development of the DGA molecule class due to its excellent properties for application in An separation processes. Consequently, a number of solvent extraction based processes are now under development based on the use of DGA molecules for MA separations.[19] However, the hard oxygen donor atoms of the DGAs lack the ability to discern between the 4f and 5f trivalent metal groups and so both are extracted concurrently. Once the MA and Ln have been isolated together they can then be separated through use of other An/Ln discriminating aqueous or organic phase molecules.[7,20]

Figure 1 and Table 1 near here

There are subtle differences between all of the processes surveyed in Section 2. However, in general (except the EXAm process) the lipophilic DGA molecule is used to extract the trivalent MA and Ln from an acidic aqueous raffinate into an organic phase, which in some instances contains a modifier or co-extractant.

1.2 Role of modifiers in solvent extraction processes

Modifiers have been defined by IUPAC as, "A substance added to a solvent to improve its properties, e.g. by increasing the solubility of an extractant, changing interfacial parameters or reducing adsorption losses."[21] In nuclear fuel reprocessing these additional (modifier) molecules are usually required to increase the metal loading capacity of the DGA-based solvent for metal ions before third phase formation occurs. However, this is at the expense of an increased complexity of the organic phase (acid extraction, speciation etc.) and hence introduces new problems in terms of solvent clean up and regeneration. They also make it more difficult to accurately model and control processes. The third phase is a separate organic phase that contains an increased concentration of extractant and metal ions, with the concomitant formation of separate acid and diluent rich phases. Third phase formation must be avoided due to its unpredictable physical properties and enhanced concentration of metal ions, which may in turn lead to problems such as criticality hazards when reprocessing used fuel.[22] Additionally, formation of a third phase presents issues with the equipment as it is designed for extraction using two phases, not three. The precise role of modifiers in altering third phase formation characteristics of the organic phase is not known. It has, however, been described as being due to increasing diluent polarity and/or disruption of the extended polymer/oligomer-like chains that form the heavy organic phase.[23]

The relative metal loading capacity of DGA ligands such as TODGA in organic phases and the consequent need for modifiers will be discussed in detail later in this review.

1.3 Solvent requirements

A good extractant molecule for An extraction must meet certain requirements. Whilst these are generally well known, the impacts of introducing modifiers on these other, equally critical, extractant properties must be considered during the course of this review; the basic list is;

- adhere to the CHON principle (contain only carbon, hydrogen, oxygen and nitrogen), minimizing secondary waste generation,
- be resistant to radiolysis and hydrolysis,
- be soluble enough in the diluent to minimize the volume of organic phase needed,
- present a good affinity for An,
- present high selectivity for An versus mineral acid and other metal cations (FP) in the feed,
- avoid third phase formation or have a large margin before formation based on expected aqueous phase compositions,
- present an extraction reversibility for An,
- kinetics of the mass transfer should be fast, both for extraction and stripping.

These characteristics should be borne in mind whilst designing a new process; fulfilling these requirements, as well as others described below, is the main research goal when designing new extractants and ligands for next generation reprocessing and MA partitioning. As well as the extractant and phase modifier, the diluent can also play an important role in the development of a practical process suitable for industrialisation and so this review will frequently refer to the overall solvent formulation.

1.4 Aims and scope of review

The aim of this review is to provide a good understanding of the current state of knowledge regarding the application of DGA extractants in MA separation processes, focusing especially on the use of modifiers. Phase modifiers have typically been introduced through a trial and error process (albeit guided by experience) in order to improve the characteristics (loading capacity and/or hydrodynamic properties) of DGA containing organic phases. However, this creates more complex process flowsheets and operations, and increasingly complex requirements for used solvent management. This has led to the question as to whether it is possible to either reduce or remove the modifier content through improved extractant design and/or better understanding of how the modifiers affect the process. This would have significant potential for simplifying the separations processes and enhance the prospect for industrialisation of DGA based processes. However, the choice of extractant is also highly dependent on various other chemical and physical properties that affect the solvent extraction process, including radio/hydrolytic stability; distribution ratios for both extraction and stripping; kinetics of mass transfer; hydrodynamic properties such as viscosity, density and phase disengagement; affinity for fission products; diluent, etc.

Part 1 of this review will cover the use of TODGA (including modifiers), as this is the most well studied of the DGAs whilst the subsequent part, will cover alternative DGA molecules (including use and avoidance of modifiers). Both reviews will cover relevant basic and process chemistry as well as the development and testing of solvent extraction flowsheets.

It should be noted that the review is not a comprehensive account of DGA based separation processes but rather is directed towards an improved understanding of the factors that will enable rational decisions to be made with respect to modifier (co-extractant) choice for specific applications as well as developments that could lead to the overall simplification of the separation process by elimination of modifiers.

1.5 DGA based processes

The DGA ligands have been developed to the point where flowsheets of processes for MA(+Ln) separations have been designed and tested, in some instances on genuine dissolved fuel solutions (obtained from nuclear fuel irradiated in a reactor). The majority of the successful tests have used TODGA as the extractant although the concept and configuration has varied widely; with selective extraction or stripping and contactor type, aqueous phase composition, modifiers etc. all being altered to fulfil certain needs. The main processes developed to date and their key features are summarised in Table 2. Briefly these key processes are:

DIAMEX-type - the MA and Ln are co-extracted from the PUREX raffinate before selective separation of the MA from Ln in a downstream SANEX-type process.

SANEX-type – MA are selectively extracted from DIAMEX or PUREX raffinate directly. Two variations are the 1-cycle SANEX where TODGA is the phase modifier and $CyMe_4$-BTBP is the An selective extractant and the innovative-SANEX process where MA and Ln are co-extracted by TODGA before the MA are selectively backwashed into an acidic aqueous phase using a hydrophilic complexing agent.

ALSEP – an American variation of the SANEX methodology that uses T2EHDGA instead of TODGA.

GANEX-type – all Ln and transuranic An are co-extracted before the An are selectively stripped.

AMPPEX – a specific radioisotope separation process to enable the recovery of ^{241}Am from unirradiated and aged Pu dioxide powders.

Table 2 near here.

The processes will be discussed in later sections, where relevant, to illustrate how the individual flowsheets have been developed. However, specific challenges remain in the development of these processes before full-scale deployment could be considered for any of these options. Specifically, further development towards the elimination of modifiers without risks of third phase formation will significantly enhance their implementation potential.

2 TODGA

A thorough review of the extraction chemistry of TODGA has been performed by Ansari *et al.*[13] A further review of the effect of the alkyl substituent on the amidic N atoms has also been completed by Sasaki *et al.*[24] Readers are referred to these articles for in-depth reviews of the basic DGA chemistry. Nevertheless, essential elements of the extraction chemistry have also been covered here to aid understanding of how the structure of the DGA molecule affects metal loading capacity and how changes to substituents can improve the third phase and extraction properties. The initial focus will be TODGA as the most widely studied and reference DGA molecule.

2.1 Extraction chemistry[†]

One of the first examples of DGA based extractants for the 4*f*-block (Ln) elements was reported by Stephan *et al.*[15] Using N,N'-dimethyl-N,N'-dioctyldigylcolamide (DMDODGA) they studied a range of metal ions and their distribution ratios, in extraction from HNO_3 buffer at pH = 5.2. The highest distribution ratios were observed with Yb and La with Sr and Ca being the next most extracted elements. The lack of study of pH dependence of the distribution ratio means that the true potential of the DGA molecules for the extraction of Ln (and An) is not realised in these early reports. Further work by Guoxin *et al.* studied the acid extraction properties and the Ln extraction dependence on acid concentration and temperature, filling in some of the gaps.[25] TODGA was developed by Sasaki *et al.* in Japan.[18] The amidic octyl chains increase the solubility in hydrocarbon diluents, which are commonly employed as the organic diluents in biphasic nuclear waste separations. The group synthesised multiple DGA molecules and found that the longer the amidic alkyl chain the lower the Am^{3+} and Eu^{3+} distribution ratios but the greater the solubility in organic diluents. They also found that the distribution ratios increased with increasing HNO_3 concentration for all An in all oxidation states up to a value of 6 M HNO_3 (the highest they measured). Slope analysis of the extraction data demonstrated that the M:L stoichiometry of complexation was between 1:3 and 1:4 for Th^{4+}, UO_2^{2+}, Pu^{4+}, Am^{3+} and Cm^{3+}. Due to the size of the DGAs (and the shape of UO_2^{2+}) it is unlikely that these are all inner sphere processes and more likely a combined inner and outer sphere association with micelle formation operates (see Section 2.2).[26] Distribution ratios were greater for the heavier Ln and An, with the Ln being more readily extracted than the An in *n*-dodecane (see Table S7).

Zhu *et al.* performed a thorough study of a large portion of the periodic table determining distribution ratios with TODGA in *n*-dodecane.[27] Their study presents some key findings with respect to understanding the behaviour of a wide range of elements in solvent extraction processes with TODGA from nitric acid. From Figure 2, it is possible to separate the elements and oxidation states into four groups based on the magnitude of their distribution ratios: high (>10), intermediate (1-10), low (0.01-1) and inextractable cations, which were (ignoring oxonium ions): Figure 2 near here.

High: Ca^{2+}, Sc^{3+}, Y^{3+}, Zr^{4+}, In^{3+}, Ln^{3+}, Hf^{4+}, W^{6+}, Au^{3+}, Hg^{2+}, Bi^{3+}, Th^{4+}, U^{6+} and Pu^{4+}.

[†] Tables of distribution ratios are summarised in the electronically available Supplementary Information (section 2)

Intermediate: Cr^{6+}, Sr^{2+}, Tc^{7+}, Pd^{2+}, Sb^{3+}, Re^{7+}, Os^{8+}, Ir^{3+} and Pb^{2+}.

Low: Mo^{6+}, Ru^{3+}, Cd^{2+}, Sn^{4+}, Ba^{2+}, Pt^{4+} and Np^{5+}.

Inextractable: Be^{2+}, B^{3+}, Mg^{2+}, Al^{3+}, Si^{4+}, Ti^{4+}, V^{5+}, Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, Ge^{4+}, As^{3+}, Se^{4+}, Nb^{5+}, Rh^{3+}, Ag^{+}, Te^{4+}, Ta^{5+} and Tl^{+}.

It is noted that the valence and radius of an ion seems to affect the magnitude of the distribution ratio as shown in Table 3. The oxonium ions are hexa and heptavalent metal ions; $Cr_2O_7^{2-}$, MoO_4^{2-}, TcO_4^{-}, WO_4^{2-}, ReO_4^{-} and UO_2^{2+}. The anions are both extracted through coordination and co-extracted through charge balancing in processes and therefore their distribution ratios decrease with increasing HNO_3 concentration due to both competition and the large steric hindrance they experience during complexation compared with the smaller NO_3^{-} ion.

Table 3 near here.

2.2 Coordination chemistry and organic phase speciation

Mowafy and Aly investigated the post-separation speciation of Sr^{2+}, Eu^{3+} and Am^{3+} with TODGA in both benzene and *n*-dodecane solution.[28] Through measurement of distribution ratios with varying TODGA concentrations they proposed that speciation is dominated by $Sr(TODGA)_3(NO_3)_2$, $Eu(TODGA)_4(NO_3)_3$ and $Am(TODGA)_4(NO_3)_3$ from 1 M HNO_3 with the stoichiometry decreasing as the HNO_3 concentration increases. This result is supported by Arisaka and Kimura who investigated the speciation of Eu^{3+} in *n*-dodecane organic phases post-extraction by various concentrations of TODGA from multiple HNO_3 concentrations using TRLFS.[29] The results clearly showed that in the organic phase the coordination sphere of Eu^{3+} does not contain any H_2O and is, therefore, dominated by TODGA or NO_3^{-} after extraction from all HNO_3 concentrations. In contrast to this work, Tachimori *et al.*[30] assign complexation of the TODGA-Nd complexes as being both an inner and outer sphere process in *n*-dodecane. Suggesting that there are two TODGA and some water molecules in the inner sphere and one TODGA and further water molecules in the outer sphere.[31] Pathak *et al.* performed a detailed Dynamic Light Scattering (DLS) study of aggregation in the organic phase post-extraction and demonstrated the micellar organisation and its importance for the extraction of Am and Eu.[26] Using $HClO_4$, HNO_3 and HCl they demonstrated that the rate of americium extraction is in the order: $HClO_4$>HNO_3>HCl. This is counter intuitive unless consideration is made toward outer sphere organisation and subsequent micellar formation, where ClO_4^{-} can interact and form micelles much more readily (will be discussed in more detail in the second part of this review). The authors demonstrate that in order to obtain maximum extraction a 2 nm aggregate must form and increasing the size further does not further increase extraction (Figure 3). To generalize, these studies suggest that, where more than 2-3 TODGA molecules are apparently involved in the extracted complex, it is, in fact, participation in micellar organisation. Likewise, the branched/long chain DGAs display a 1:3 (M:L) stoichiometry and a lower propensity for third phase formation. It is, therefore, likely that there is correlation between the ability to resist micellar aggregation in the organic phase and a reduced tendency to form a heavy organic (third) phase.

Figure 3 near here.

Pathak *et al.* further investigated the speciation of TODGA-Eu systems using TRLFS.[32] Using ethanol/water solvent mixtures they obtained conditional stability constants (log $ß_n$) for 1:1, 1:2

and 1:3 M:L complexes of 6.1±0.5, 10.8±0.7 and 14.3±0.6, respectively. Importantly, they demonstrated that the post-extraction speciation from *n*-dodecane was a 1:3 (Eu:TODGA) species ([M]:[L] = 1:100), with no higher order inner sphere complexes observed. It is important to note that the methodology of analysis of the data using the decay lifetimes and ratio of intensity of transition only analyses inner sphere effects so would not observe micellar processes. This gives further evidence that outer sphere interactions of DGA molecules are present where more than 3 DGA molecules have been shown to affect extractions (greater than 1:3, M:L extraction stoichiometry) and that these interactions affect third phase formation. Further studies on the speciation of TODGA and the methyl substituted variants Me-TODGA and Me_2-TODGA using slope analysis confirmed this assignment.[33] TRLFS lifetime analysis also showed a lack of OH oscillators further confirming the 1:3 (M:L) assignment but titration data analysis revealed complexation constants for Cm and Eu for 1:3 and 1:1 M:L species for all the DGA extractants but 1:2 M:L are not observed through any technique. Gujar *et al.* used slope analysis to understand the speciation post extraction of Np^{4+} and Pu^{4+} with a range of DGA ligands, TPeDGA (N,N,N',N'-tetrapentyldiglycolamide), THDGA, TODGA and TDDGA from 3 M HNO_3.[34] This gave slopes of ~2, implying a 1:2 M:L complex, with Np values being slightly lower than Pu, possibly implying some 1:1 contribution, assigned as potentially being due to the presence of the linear cations, NpO_2^+ or NpO_2^{2+}. Sasaki, however, found 1:3 complex formation with Pu^{4+}/TODGA, this may be due to the use of lower HNO_3 concentration (1 M) altering the coordination sphere post extraction.[18] Likewise, Carrott *et al.* found 1:2 (M:L) by slope analysis for Np^{4+}, decreasing slightly with acidity increase from 0.5 to 3 M and 1:2, decreasing to 1:~1 (M:L) for NpO_2^{2+} as acidity increased from 0.5 to 4 M.[35] K_{ex} values of the extraction generally increase with the alkyl chain length and the values for Pu^{4+} are generally larger than for Np^{4+} for all except TDDGA. The claims of mixed NpO_2^+ speciation have been verified by Tian *et al.* who studied complexation by absorption spectroscopy with a variety of DGA based ligands.[36] Both 1:1 and 1:2 M:L complexes were formed on addition of the extractants to $NpO_2(ClO_4)$ and shifts in the absorption spectra were shown for the 1:1 complex whilst the 1:2 complex displayed very little/no absorption (Figure 4). This is due to the highly symmetrical nature of the complex creating a centre of inversion and so La Porte's selection rules forbid the *f-f* excitation and accompanying absorption.

Figure 4 near here.

Yaita *et al.* discuss the differences observed by the many groups with respect to the stoichiometry of extracted complexes.[37] Similar to Pathak *et al.* they suggest that the many differences stem from the concept of the difference between inner and outer sphere coordination. Different measurement methods, aimed at bulk or local coordination, would determine the values differently. However, an appreciation for the formation of micelles containing the extracted metal ion, NO_3^- and a hyperstoichiometric number of DGA molecules can account for all the observations in terms of large dependence on HNO_3 and DGA concentration for the distribution ratios. This is further studied and discussed by Jensen *et al.* and discussed later in this paper.[38]

2.2.1 Comments

There are some clear trends on the speciation of TODGA and yet there is also some disagreement between groups. For the trivalent ions, most show that the inner coordination sphere is completed by non-OH oscillators (not H_2O); therefore, implying the inner coordination sphere is completed by $(TODGA)_x(NO_3)_y$, where x+y=3 and x=2 or 3. 1:1 species have been

spectroscopically observed albeit in non-process alcoholic diluents. Where it is suggested that water or more NO_3^- or TODGA molecules are playing a part in coordination it seems that this may be an outer sphere process. Np^{4+} and Pu^{4+} complexes have been assigned as 1:2 M:L complexes albeit with some interference from the linear oxo-cations preventing definitive assignment.

2.3 Loading and third phase formation

Gujar *et al.* studied the inhibition of third phase formation with TODGA (0.1 M) using DHOA (N,N-dihexyloctanamide), TBP, *n*-octanol or *iso*-octanol (0.5 M) in *n*-dodecane in contact with 3 M HNO_3.[39] Under no circumstances, with modifier, was third phase formation observed even when in contact with an aqueous phase containing 0.35 M Nd (where the maximum, stoichiometric, organic concentration was reached). This was observed with both fresh solvent and solvent irradiated up to 1000 kGy at a dose rate of 5.3 $kGyhr^{-1}$.

Third phase formation in TODGA/HNO_3/TPH systems has been studied visually and by determination of D_{HNO_3} values, Modolo *et al.* compared results directly to *n*-dodecane systems.[40] Visually, third phase was only noted with TPH when $[HNO_3]$>4 M and $[TODGA]_{ini}$<0.4 M or $[HNO_3]$ = 5-6 M and $[TODGA]_{ini}$<0.6 M. This (relative to *n*-dodecane) low propensity to form a third phase is proposed to be due to the increased branching in TPH *cf. n*-dodecane; with *n*-dodecane the D_{HNO_3} values are slightly higher at higher [TODGA]. Nd loading experiments for the organic phase demonstrated that with the addition of TBP (0.5 M TBP with 0.1 M TODGA in TPH) no third phase was observed and the theoretical maximum loading of Nd was possible (~0.033 M, assuming 1:3 M:L stoichiometry). When no TBP (in TPH) was present, the third phase was formed with a greater Nd concentration than with *n*-dodecane (0.011 cf. 0.0081 M). Other teams have also demonstrated that the TODGA/TPH system extracts less HNO_3 into the organic phase than the equivalent TBP or DHOA containing phase (Table 4).[41] Further, they have demonstrated that 1:3 M:L stoichiometric loading could be achieved without third phase formation by contacting an organic phase of 0.1 M TODGA, 5 v/v % 1-octanol in TPH with 5 M HNO_3 containing >0.037 M Nd. This also implies a near quantitative extraction of Nd from the aqueous phase.

Table 4 near here.

Tachimori *et al.* reported the formation of third phase in extractions using TODGA and various diluents with and without DHOA added as a phase modifier.[30] Initial investigations focussed on third phase formation during the mixing of aqueous phases containing varying initial Nd concentrations and a variety of HNO_3 concentrations with 0.1 M TODGA in *n*-dodecane.. The authors defined the third phase as the point at which the organic phase Nd concentration deviated from linearity compared with $[Nd]_{ini}$. This demonstrated that the greater the HNO_3 concentration the lower the possible loading of the organic phase (Table 5). It is clear that these values are lower than the theoretical maximum of 0.033 M (for a 1:3, M:L complex). Increased temperatures allow for a greater extent of loading of the organic phase up to a certain point and the anion has a definite effect on the loading. When it is ClO_4^-, the distribution ratios are much greater at lower TODGA concentrations as ClO_4^- has a synergistic effect on extraction due to decreased hydration compared with NO_3^-, but also increases the ease of third phase formation (lower LOC) presumably by a similar coordination mechanism that allows increased distribution ratios (assumed hydrogen bonding between complexes and water molecules in the organic phase, despite the non-complexing

nature of ClO_4^-). Systematic study of the diluent chain length (C_{11}, C_{12}, C_{14}) showed a decrease of LOC (from 1 M HNO_3) as the chain length increased. With the addition of 0.5 or 1 M DHOA to the system, no third phase was observed in the (0.1-0.2 M) TODGA/*n*-dodecane/(0.5-1 M) DHOA system. The authors suggest that third phase formation occurs through inner and outer sphere coordination of the TODGA molecules to anions and water molecules. In essence, this is in agreement with the assignment by other groups of the third phase as being a result of micellization.

Table 5 near here

2.3.1 Comments

These studies agree well with the previous coordination and stoichiometry measurements of other authors. They provide compelling evidence that third phase formation is an inner/outer sphere process and that it can be limited by the addition of modifiers. This would presumably occur by disrupting the tendency for outer sphere coordination and extractant organization in the organic phase. Additionally, it is clear that a definitive method of quantifying the onset of third phase formation should be adopted to allow for much greater ease of comparing results. It seems that the point at which the organic phase concentration deviates from linearity, assuming this is significantly lower than the expected saturation point, is a good measure as it is easily quantified. It also shows that there is a change in speciation that is likely the result of the onset of the formation of another, i.e. the third, phase.

2.4 TODGA and phase modifiers[‡]

2.4.1 DHOA and other amides

2.4.1.1 Extraction chemistry

Studies on the combined effects of acid, phase modifier and diluent on the extraction performance of TODGA are necessary. Variation of diluent indicates that *n*-dodecane is not optimal in terms of distribution ratios but its known hydrocarbon composition is often advantageous, particularly in systematic studies of the effect of phase modifier.[42] Examination of different N-substituted amides as phase modifiers gave the highest distribution ratios with di(2-ethylhexyl)acetamide (D2EHAA) from 1 M HNO_3. However, with 3 M HNO_3, DHOA allowed for larger Nd loading of the organic phase and higher distribution ratios. DHOA precluded third phase formation and increased Nd loading to stoichiometric levels (0.035 M at 1:3, M:L). Increasing $[Nd]_{ini}$ from 0.04 to 0.1 M suppresses D_{Nd} from 3.0 to 0.56, respectively (at 3 M HNO_3), due to organic saturation. In $[HNO_3]$>2 M, no significant change in distribution ratios was observed for Am. Fast equilibrium between phases was reached within 1 minute for TODGA extractions with and without the addition of DHOA. The extractions of Am^{3+}, UO_2^{2+}, Pu^{4+}, Fe^{3+}, Eu^{3+}, Sr^{2+} and Cs^+ from both idealised and SHLW (Simulated High Level Waste) solutions using TODGA/DHOA in *n*-dodecane (0.1 and 0.5 M, respectively) have also been compared. In both cases the distribution ratios of Eu^{3+}, Am^{3+}, Pu^{4+} and UO_2^{2+} increased steadily until ~2 M HNO_3 when they reached a

[‡] HAR/GANEX-1 product compositions and solvent dose rates used in testing TODGA-based processes are given in the electronically available Supplementary Information section 1. Data from flowsheet tests are given in the electronically available Supplementary Information section 3.

plateau (saturation as the authors describe although in reality this might reflect detection limits). Fe^{3+} and Cs^{+} were effectively not extracted under either conditions and Sr^{2+} extraction was suppressed by the addition of DHOA (from D_{Sr} = 4.0 to 0.9 at 3 M HNO_3). In all cases the distribution ratios were lower from SHLW than the pure tracer experiments; this effect being assigned to the co-extraction of other metals. The plots for pure tracer and SHLW extractions are presented in Figure 5. Similar TODGA/DHOA studies have been conducted initially using 1-octanol as the diluent.[30] It became apparent that organic loading surpassed the known 1:3 M:L ratio expected of Ln-TODGA complexes (tending toward 1:2, M:L). Therefore, examinations of Nd loading with DHOA were then performed in 0.1 M TODGA/*n*-dodecane. The initial organic loading (0.1 M TODGA, 0.5 M DHOA in *n*-dodecane) was quantitative until ~0.025 M Nd then the efficiency decreased, tending toward a maximum at ~0.033 M Nd, as expected for a 1:3 M:L complex (Figure 6) and no third phase was observed. It is clear from Figure 6 that increasing DHOA concentration suppresses Nd organic phase loading and the distribution ratios of both Nd and Am slightly. However, it is also clear that the increased $[Nd]_{ini}$ does not out compete the extraction of Am alongside the Nd as the low distribution ratios are due to organic phase saturation (distribution ratio of Am is always larger than Nd, regardless of $[Nd]_{ini}$). Furthermore, when TODGA = 0.2 M and DHOA = 1 M the organic phase can be loaded to the stoichiometric limit (0.066 M) without third phase formation. Examination of the D_{Am} with respect to HNO_3 and DHOA concentration was also investigated. At low HNO_3 concentrations (<3 M) the D_{Am} value decreases slightly with increased DHOA concentration. However, at a HNO_3 concentration of ~3 M the values are similar (essentially, D_{Am} is independent of DHOA concentration) and, importantly, sufficiently large enough for potential process implementation (>100). Other groups have shown that a DHOA concentration of 1 M was necessary to prevent third phase formation in extractions with Zr and Nd and that DHOA synergistically increased the extraction of Zr.[43,44] For Ca, 0.5-1 M DHOA was found to be sufficient to prevent third phase formation; however, organic phase loading by Ca and Zr is undesirable in a process as these would then need scrubbing prior to back extraction of Ln/An. The authors do note that Ca and Nd loading of the organic phase decreases with increased HNO_3 concentration due to HNO_3 extraction and, therefore, a decreased activity of TODGA. This is different for Zr where the LOC increases up to 3 M HNO_3 and then decreases. The authors suggest this is due to the formation of ZrO^{2+} and hydroxide species in low HNO_3 concentrations which reduces the extractability of Zr.

Figure 5 near here.

Figure 6 near here.

2.4.1.2 Flowsheet tests

Further studies were made by Ansari *et al.* with DHOA as phase modifier to compare to the use of TBP and when using real counter-current conditions.[45] Initial Nd loading experiments showed that when contacting an organic phase containing TODGA and phase modifier in NPH (Normal Paraffinic Hydrocarbons – straight chain alkanes of unspecified length) the greatest Nd loading is possible with DHOA followed by TBP and 1-decanol when $[Nd]_{eq}$<0.069 M. However, when $[Nd]_{aq}$>0.069 M, the greatest organic loading is achieved with TBP as phase modifier (Figure 7). It was concluded that as HLW solutions are expected to have a metal content of ~0.003-0.055 M, DHOA is the most suitable modifier. Initial experiments used an aqueous phase with 0.026 M Nd, representative of the total Ln inventory of HLW from a Fast Breeder Reactor fuel. It was found

that in the stripping of the organic phase using 0.01 M HNO_3, poor phase disengagement occurred (emulsion). As a result, the strip solution was altered to 0.2 M HNO_3 as this was above the point at which the measured Interfacial Tension (IFT) values between the two phases plateaued (0.1 M HNO_3), thereby allowing rapid phase disengagement. A multi-stage mixer-settler experiment with 0.1 M TODGA/0.5 M DHOA/NPH was performed as detailed in Figure 8. Extraction and stripping are performed in four and five stages, respectively, and are quantitative (below the limit of detection of the measurement method). HNO_3 extraction is observed but it is also stripped quantitatively. Interestingly, the stripping section was used to concentrate the raffinate by using O/A = 1.5 (Figure 8) without sacrificing recovery of Nd. Performing the extraction on the simulant HAR (detailed in Table S2) gave very promising results with complete recovery of the Ln in the strip solution and routing of other elements with the aqueous waste. Similar results were achieved after the organic phase received a dose of 100 kGy. However, post-irradiation the strip solution also contained 15-20 % of the simulant HAR Mo and Cr content (not observed in fresh solvent). The authors compared this system to one containing TBP (instead of DHOA), noting the increased extraction of HNO_3 with TBP and the resultant increased number of stripping stages due to increased distribution ratios as a result of $[HNO_3]_{org}$.[46] They also identify that increased TODGA concentration increased the extraction of HNO_3. However, increased concentrations of TODGA may be necessary for higher burn-up fuels containing greater amounts of Ln/An.

Figure 7 near here.

Figure 8 near here.

Baker *et al.* have used a solvent system containing TODGA and DHOA to recover ^{241}Am from aged Pu powders.[47] This system was designed for a rather specific application where the Am is recovered from a Ag/Am solution in near quantitative yield. A full flowsheet has been run and a plant designed for high throughput Am recovery. It is run with a high HNO_3 concentration extract section followed by a low HNO_3 strip.

2.4.2 TBP

2.4.2.1 Extraction chemistry

Early centrifugal contactor studies by Modolo *et al.* using TODGA/TPH necessitated the addition of oxalic acid (0.4 M) to suppress third phase formation and decrease D_{Zr} values compared with TODGA alone.[40] This led to precipitation of Ln/An oxalates in the stripping process, a very undesirable facet of a potential process. As a result, TBP was added as a phase modifier. The effects that variation of TBP and oxalic acid concentration had on the distribution ratios of TODGA (containing HEDTA – for D_{Pd} supression) in TPH from a 3 M aqueous phase of simulated HAR with composition as detailed in Table S3 were studied. In batch experiments containing only TODGA (0.2 M) in TPH and HEDTA (0.05 M), and varying concentrations of oxalic acid (from 0.15 to 0.4 M) in a synthetic HAR, high distribution ratios were observed for Ln and An (>200 and >30/>90 for La/Ce, respectively, all of which increase with increasing oxalic acid concentration). No third phase was observed even at low oxalic acid concentrations (<0.3 M), contrary to previous observations when used without a modifier. D_{Zr} decreases with increasing oxalic acid concentration (0.68 to 0.042,) whilst D_{Mo} increases slightly (0.081 to 0.14) with oxalic acid concentrations of 0.15 to 0.4 M, respectively. Pd extraction is suppressed by the addition of HEDTA whilst Sr appears to be

co-extracted with the distribution ratio increasing from 1 to 2 with increasing oxalic acid concentration. The authors note that an oxalic acid concentration of 0.3 M should be sufficient to adequately suppress Zr extraction in processes (D<0.1). Addition of TBP to the organic phase allows lower concentrations of oxalic acid to be used to obtain acceptable distribution ratios for Zr and Mo, with the distribution ratios being increased slightly for Zr and Sr when lower concentrations of TBP are used (0.25 vs. 0.5 M). However, it is noted by the authors that, with TBP addition, an oxalic acid concentration of 0.15 M is sufficient for process development ($D_{Ln/An(III)}$ >200 and most D_{FP} <0.03, Table S8). Plots of the dependence of distribution ratios on the variation of HNO_3 concentration for some An and FPs are presented in Figure 9. All An except UO_2^{2+} are extracted with high distribution ratios, UO_2^{2+} distribution ratios are low but still >10 at HNO_3 concentrations >2 M. The D_{Zr} values rise with increasing HNO_3 concentration but are suppressed with the addition of 0.2 M oxalic acid and, as can be seen from the results in Table S9 (bottom), addition of HEDTA effectively suppresses Pd extraction.

Figure 9 near here.

Further studies on the extraction behaviour of TBP/TODGA have been performed using odourless kerosene (OK) as the diluent.[48] The authors show that the extraction of Am and Eu is performed by the TODGA not TBP and that it proceeds even in the presence of U at 0.21 M. Np extraction by 30 v/v % TBP and TODGA 0.1-0.4 M in OK is favourable with D_{Np}>5 when [HNO_3]>2 M. This is interesting as it does not require any oxidation state control and the usually inextractable (by TBP alone) NpO_2^+ is extracted by this composition. Similarly, when the U concentration is increased from 0.021 to 0.21 M D_{Np} increases from 3 to 10. The authors also studied technetium (Tc) behaviour with the solvent system as it is known to be co-extracted as a counter ion in extraction processes. It was observed that TODGA increases D_{Tc} compared with TBP alone; therefore, it must be forming Tc/TODGA complexes. Increasing the concentration of HNO_3 decreases D_{Tc} to <1 when HNO_3 concentration is >3 M (Figure 10). This implies that a high HNO_3 concentration scrub should be capable of removing the co-extracted Tc during a process. The authors also demonstrated the strong preference TODGA displays for Pu^{3+} over Pu^{4+} (using ascorbic acid as the reductant), thereby increasing D_{Pu} by an order of magnitude, as observed elsewhere.[27,42] The authors also probed the effect of U in the extraction, in a scenario that would route some U with the remaining An to alleviate Pu proliferation concerns by not creating a pure Pu waste form. They demonstrated competition between TBP and TODGA for binding U in the organic phase.

Figure 10 near here.

2.4.2.2 Flowsheet tests

Building on batch test work, Modolo *et al.* developed flowsheets for use on the HAR simulant detailed in Table S3, Supplementary Information.[40] With an aqueous phase consisting of 4.4 M HNO_3, 0.2 M oxalic acid and 0.05 M HEDTA and organic phase with 0.2 M TODGA, 0.5 M TBP in TPH they performed two experiments. The second one used the optimised acidities and flow rates deduced from the first test; the flowsheet is presented in Figure 11. Recoveries following the flowsheet tests were >99.9 % of An and Ln in the product stream with most of the U (~1.5 % U was routed with the raffinate). Ru presented an issue with ~10 % being co-extracted with the An and Ln and ~7.5 % remaining in the solvent after back-extraction. The final An and Ln fraction

contained 0.03 % Sr, 0.12 % Zr and 1.5 % Ru (of the initial content). All the mass balances and routings of the elements are presented in Table S9. It can be seen that with a fresh solvent (radionuclides were added one day prior to experiment) and the addition of oxalic acid coupled with the high number of strip stages and optimised acidities, the extraction of Zr and Mo can be successfully suppressed in contrast to trials by Ansari *et al.* using DHOA as a modifier (see Section 2.4.1.2). Additional development work has been performed, leading to the production and validation of a model using the PAREX code.[49] The feed was 3-4 M HNO_3 and a scrub of HEDTA and oxalic acid was used to control the problematic fission products. Cold tests and subsequent spiked testing validated the model and led to genuine hot tests. as published by Magnusson *et al.*[50] Using an organic phase of TODGA (0.2 M) with TBP (0.5 M) as phase modifier a 32 stage centrifugal contactor extraction was performed on an aqueous phase of 4.4 M HNO_3, 0.2 M oxalic acid and 0.05 M HEDTA. The results of the experiment are very promising (Table S12) with the only identified issue being organic entrained HNO_3 (solved with increased scrub stages) and Ru retention in the organic phase post-scrub. Note, however, that this is a single use test of the organic phase so little solvent degradation is observed, thus the potential for further elemental retention by degradation products is not apparent. The authors also note that a 3.5 fold increase in aqueous waste volume compared to the initial feed occurs due to low HNO_3 concentration scrubbing that is required to decrease acidity and the content of co-extracted elements.

Figure 11 near here.

2.4.3 Octanol and other alcohols

2.4.3.1 Extraction chemistry

The chemistry of the organic phase has been further developed by the addition of 5 % *iso*-decanol in *n*-dodecane,[51] using a relatively low concentration of TODGA (0.05 M), which is justified by the lower concentration of extractable metal ions in Pressurised Heavy Water Reactor (PHWR) waste (<2 gL^{-1}). The use of *iso*-decanol prevented the formation of a third phase even when in contact with a 3 M HNO_3 aqueous phase of 0.35 M Nd and allowed maximum loading of the organic phase, leading to an organic phase of 0.016 M Nd^{3+} (implying stoichiometric loading of a 1:3 M:L species). Gujar *et al.* measured distribution ratios for Np(IV) and Pu(IV) for a range of DGA molecules, TPeDGA, THDGA, TODGA and TDDGA in *n*-dodecane containing 30 v/v% *iso*-decanol.[34] Using 0.1 M of each DGA the authors measured distribution ratios between 0.5 and 6 M HNO_3. Once the HNO_3 concentration was >1 M, TODGA displayed a greater preference for Np than Pu. For Pu, TODGA distribution ratios were greatest between 2-3 M HNO_3. Np extraction in all cases exhibited a sharp increase in distribution ratio to 3 M HNO_3 and then increased slowly to 6 M HNO_3, whereas for Pu the increase in D_{Pu} was gradual throughout the increase in HNO_3 concentration.

Work using 5 v/v.% 1-octanol as the modifier with 0.2 M TODGA in TPH has provided distribution ratios for almost the entire Ln series and Am and Cm.[52] The results show a strong HNO_3 concentration dependence of the distribution ratios and the increased extractability of the heavier Ln compared with the lighter Ln (Figure 12). It is also clear that there is a slight preference for Cm over Am over the entire HNO_3 concentration range.

Figure 12 near here.

2.4.3.2 Flowsheet tests

Figure 13 shows the flowsheet used and Table S11 shows the elements recovered from the processing of simulated PHWR wastes using TODGA/*iso*-decanol/*n*-dodecane organic phases by Gujar *et al*.[51] The results obtained show promise for processing of BWR (Boiling Water Reactor) fuels. Extraction of Fe and Zr is suppressed with the use of oxalic acid/HEDTA and the extracted Mo and Ru ions are effectively scrubbed in the scrubbing stages leaving a pure Ln/An and Y product stream containing the Ln: La, Ce, Pr, Nd and Sm (see Table S11 for data on some Ln, An and important FPs).

Figure 13 near here.

The *i*-SANEX process has been demonstrated with full scale centrifugal contactor counter current extraction experiments. The process demonstration used an organic phase consisting of 0.2 M TODGA with 5 v/v% 1-octanol in TPH and an aqueous phase similar in composition to that described in Table S1, with 0.05 M CDTA instead of oxalic acid.[53,54] The full process included: a Ln/An extraction step using TODGA; HNO_3, Mo and Sr scrubbing using oxalic acid and CDTA; selective An stripping using the hydrophilic ligand SO_3-Ph-BTP (tetra(sulphophenyl)-substituted-bis-triazinylpyridine) and a final Ln strip using an aqueous citric acid buffer solution at pH 4, as shown in Figure 14. Mo, Zr and Pd were efficiently held in the initial aqueous phase using CDTA but the scrub sections proved less efficient for the back-extraction with distribution ratios >1 (Table S13). However, the initial addition of CDTA to the feed made this much less of an issue due to the low initial amounts in the organic phase requiring scrubbing. Sr scrubbing was proven to be highly efficient with the low HNO_3 concentration in the 2nd scrub bank, back extracting almost all the co-extracted Sr. The issue of Ru retention in the organic phase was once again highlighted as being a fundamental issue for DGA based extraction processes. The final An stripping stage using a fresh organic TODGA solution and an aqueous phase of SO_3-Ph-BTP in HNO_3 recovered near quantitative amounts of Am and Cm with slight retention of Ru and Sr. Final Ln stripping by citrate was highly efficient for the heavier Ln and displayed the lowest efficiency with La where 0.4 % remained in the organic phase. Ru, however, was again not stripped from the organic phase with either SO_3-Ph-BTP or citrate, with 14.7 % remaining in the organic phase (Table S13).

Figure 14 near here.

2.4.4 DMDOHEMA

DMDOHEMA can extract the trivalent An and Ln and other metal ions and is used as the extractant for the DIAMEX-SANEX process.[55] However, in the context of TODGA-based extractions, its primary function is to increase the loading capacity and available operating window of the solvent, acting as a phase modifier as well as a co-extractant. Given the practical application of DMDOHEMA in DGA based processes, that is to increase loading capacity, it is necessary to discuss its applications here. More information on the basic extraction chemistry of DMDOHEMA is available elsewhere.[56,57,58]

2.4.4.1 Extraction chemistry

Brown *et al.* have performed a study on the ability of a variety of DGA solvents to extract aqueous phases of relatively high Pu loadings.[59] The need to understand the behaviour of biphasic systems such as these is that, during homogeneous An recycling scenarios, dissolved used fuels

659 from fast reactor fuel cycles will have much higher Pu contents than thermal reactor fuels. In
660 Europe, it is currently envisaged that GANEX processes would be suitable options for this fuel cycle
661 scenario. The GANEX process requires a CHON solvent capable of extracting An from Np to Cm in
662 oxidation states from III-VI; DGA ligands are thus promising ligands for this application. This range
663 of oxidation states brings additional issues and concerns particularly regarding the loading capacity
664 of the organic phase. Initial experiments utilised Th as an analogue of Pu, with an organic phase
665 containing TODGA, TBP and 1-octanol in various ratios (Table 6). Without the addition of 1-octanol
666 or TBP as phase modifiers, solvent loading is very low. However, alongside the increased loading
667 there is a concomitant decrease in D_{Eu} and D_{Am} due to competition for organic phase solvation.
668 Upon moving to Pu from Th, very different behaviour was observed with the precipitation of a
669 brown solid (only redissolved by AHA, acetohydroxamic acid) upon extraction from HNO_3 solution;
670 this is instead of a traditional third phase. The solid was shown to be a Pu-TODGA compound, likely
671 to be similar in composition to that crystallographically identified by Reilly *et al.* for the tetramethyl
672 analogue – $[Pu(TMDGA)_3][NO_3]_4.EtOH$.[60] As can be seen in Table 7, increased concentration of
673 TBP and 1-octanol could not prevent the formation of the solid (at best it could allow loading up to
674 around 0.053 M). Due to the issues surrounding the observed precipitate, the organic phase
675 modifier was varied, using other molecules already used in alternative processes, HDEHP,
676 DMDOHEMA and DHOA. As well as varying the modifier, the DGA was altered to the dodecyl
677 version (TDdDGA, TetraDodecylDGA), which had shown no third phase formation in contact with
678 high Nd concentration solutions (Table 8, top). Consequently, it was shown that HDEHP provides
679 the highest loading but does not allow easy back extraction of the Pu. However, the malonamide,
680 DMDOHEMA, provided the optimal modification in terms of organic phase loading and stripping
681 ability for both DGAs. The use of TDdDGA improved organic phase loading but caused the solvent
682 to become very viscous – an undesirable property. Further optimisation of the solvent composition
683 (Table 8, bottom) led to 0.2 M TODGA and 0.5 M DMDOHEMA being selected as the most suitable
684 organic phase composition for further development. Further work gave the best strip solution for
685 Pu^{4+} as 0.1 M HNO_3 with 0.5 M AHA with D_{Pu}~0.14; however, this was found to be very acid
686 dependent. Aqueous phases containing AHA and/or SO_3-Ph-BTP can be used to selectively or
687 concurrently strip Np/Pu and Am/Cm.[61]

688 Table 6 near here.

689 Table 7 near here

690 Table 8 top+bottom near here

691 Further work on the 0.2 M TODGA and 0.5 M DMDOHEMA system used the diluent
692 Exxsol-D80, similar in composition to OK.[62] Distribution ratio measurements were undertaken for
693 most of the Ln series and Am and Pu from a range of HNO_3 concentrations (Figure 15). The solvent
694 composition behaved very similarly to one containing TODGA alone with an improved operating
695 envelope before third phase formation characteristics when in contact with high Pu concentrations.
696 The behaviour of the solvent system with a variety of fission products that have been shown to be
697 co-extracted with the An and Ln was also studied; with Zr and Pd being a key focus[54]. With the
698 addition of CDTA to the aqueous phase prior to extraction, Zr and Pd extraction can be suppressed
699 even in the presence of macro concentrations of Pu (Table S13). Similar to the results published by
700 Wilden *et al.*, CDTA shows promise for the masking of the problematic FPs during separations using
701 TODGA, with D_{Zr} and D_{Pd} decreasing by orders of magnitude whilst D_{Pu} remains sufficiently large for

extractions to proceed.[53,54]Studies on the extraction of Np in various oxidation states by TODGA, DMDOHEMA and the proposed GANEX solvent containing TODGA and DMDOHEMA have also been reported.[35] It is well known that Np displays a complex chemistry in nitric acid with at least three inter-convertible oxidation states (IV,V,VI) each with a varying affinity for organic phases; therefore, specific data on Np behaviour in the GANEX system was considered essential. The authors obtained D_{Np} values for Np^{4+}, NpO_2^+ and NpO_2^{2+}. Initial studies into the stoichiometry of extracted species (from Odourless Kerosene) showed variation to be dependent on oxidation state, extractant and aqueous phase HNO_3 concentration (Table 9). Where the stoichiometry is >2 for TODGA/NpO_2^{2+} it is assumed this is due to outer sphere effects or lower denticity of coordination of TODGA. It was shown that the individual extractants can work independently and, synergistically, in the order Np^{4+}>NpO_2^{2+}>>NpO_2^+ (Figure 16). They demonstrated that through addition of 0.5 M AHA (or formohydroxamic acid, FHA) with HNO_3 concentrations <0.3 M to the aqueous strip phase, D_{Np}<0.1 was achieved, which will allow stripping of Np in processes. In the organic phase, NpO_2^+ rapidly disproportionates into Np^{4+} and NpO_2^{2+} and, therefore, becomes more extractable. Even with attempts to stabilise the NpO_2^{2+} to NpO_2^+ reduction using hydroquinone, disproportionation was extremely rapid when extracted from HNO_3 concentrations >3 M. The results suggest that NpO_2^+ stability with respect to disproportionation follows the pattern; 0.2 M TODGA/OK < 0.2 M TODGA/0.5 M DMDOHEMA/OK < 0.5 M DMDOHEMA/OK. Further work is acknowledged to ensure that complete recovery of the full An inventory can be achieved using conditions that are amenable to Np recovery. However, the potential for Np recycle in low HNO_3 concentration scrub sections (required for Fe and Sr scrubbing) remains a distinct possibility and so a detailed kinetic analysis of Np(V) disproportionation and oxidation in the GANEX system is needed for developing a quantitative model of its behaviour.

Figure 15 near here.

Table 9 near here.

Figure 16 near here.

Further work by Carrott *et al.* continued to investigate the behaviour of the EURO-GANEX solvent formulation of 0.2 M TODGA/0.5 M DMDOHEMA in Exxsol D80 with regard to Pu, Am and some of the problematic (with DGAs) fission products.[63] The main issues highlighted were with Fe, Sr, Pd, Ru, Tc, Mo and Zr; there is also the issue of the behaviour of the solvent system when loaded/in contact with a HAR containing the whole range of potential metal ions, similar to that given in Table S3. Concern about the behaviour of Sr in processes using TODGA has been expressed by multiple groups but Carrott and co-workers demonstrated that performing the extraction at >5 M HNO_3, followed by a 0.5 M HNO_3 scrub to remove excess acid from the solvent is sufficient to prevent Sr breakthrough to the organic product.. Fe, however, is not as easily managed, demonstrating a sharp increase in distribution ratio at >1 M HNO_3 and third phase formation once Fe concentration is >0.23 M, see Figure 17. This can be partially mitigated through the addition of CDTA but it will still create issues. Therefore, it is proposed that the extract section is decreased to <3 M HNO_3. However, this may then cause difficulties with regard to Np behaviour as discussed previously.[35] The authors measured batch distribution ratios for a whole range of metal ions under conditions found at various points in proposed flowsheets and these are reported in Table 10. As can be seen the An and Ln are efficiently extracted and remain in the organic phase under scrubbing conditions. The Sr may present an issue in initial extraction but can be scrubbed

(D<0.5) using low HNO_3 concentration conditions. Likewise, Zr and Pd are held back in the HAF (Highly Active Feed) through use of CDTA. Se, Mo and Ru also present issues with sufficiently large distribution ratios in the extract and scrub experiments. Further batch tests investigating the effect of increasing the CDTA concentration showed that this is not sufficient to preclude extraction and so it is likely that these would be extracted and could not be scrubbed in the process. It is, therefore, likely that the solvent would become contaminated by Ru and possibly Se and Mo and that a separate process of the clean-up of used solvent will be required in a continuous process using recycled solvent.

Figure 17 near here

Table 10 near here.

It is clear that the substantial addition of DMDOHEMA as a phase modifier / co-extractant to the TODGA/kerosene solvent, to manage the Pu loading challenge, has added significant complexity in the GANEX system. This specific example nicely reinforces the need to look at all aspects of solvent behaviour that can affect process performance in an integrated fashion.

2.4.4.2 Flowsheet testing

Centrifugal contactor extractions on simulated high burn-up, high Pu content fuel, simulating the GANEX-1 product (Pu loading 0.041 M), including a final An/Ln separations step, have been undertaken (the so-called 'EURO-GANEX' process).[64] There are some important differences between the experimental conditions here and other flowsheet tests, mainly in the addition of 0.05 M CDTA to the HAR to successfully prevent Zr and Pd extraction.[54] The experimental design is presented in Figure 18 and will be discussed briefly. The high active feed, *i.e.* GANEX-1 product, is contacted with 0.2 M TODGA/0.5 M DMDOHEMA in Exxsol D80 to isolate the Ln and An. This is then scrubbed using 0.5 M HNO_3 to remove co-extracted Sr and Fe, these high and low concentration HNO_3 stages cause accumulation across the contactors (as the change in distribution ratios between the high and low HNO_3 concentration conditions allows extraction and back extraction in one battery). The An were then stripped using SO_3-Ph-BTP and 0.054 M AHA and a follow up stage with decreased concentration of SO_3-Ph-BTP (0.018 M). The Ln were finally recovered from the organic phase using a glycolate strip solution. Whilst the flowsheet test was generally successful, there was incomplete extraction of Np in the first extract scrub contactor; this was addressed in a later flowsheet test discussed below.[65] The subsequent resolution to this problem is believed to be due to the formation of nitrous acid from radiolytic degradation of HNO_3, thereby catalysing the oxidation of Np(V) and so increasing the concentration of Np in extractable oxidation states, as has been observed in the PUREX process.[66] There is also some contamination of the An product with Eu (a model Ln), a failing that again was solved in subsequent work.[65]

Figure 18 near here.

A hot test to demonstrate the EURO-GANEX process flowsheet was performed and results have been partially published by Malmbeck *et al*.[65] Following dissolution of a legacy fast reactor fuel, uranium extraction in the GANEX first cycle was implemented. Post uranium removal, CDTA was added to the GANEX-1 product stream to act as a Zr and Pd hold back reagent, the Pu concentration was altered to 0.041 M and the HNO_3 concentration increased to 5.9 M to enhance disproportionation of NpO_2^+. Using an organic phase comprised of 0.2 M TODGA and 0.5 M DMDOHEMA in Exxsol-D80, recovery of An and Ln was very good. Following co-extraction,

separation and recovery of the An from the Ln was done by selective stripping using SO_3-Ph-BTP+AHA (Figure 19). Further development of the process is envisaged to include development of CHON aqueous phase selective An complexants (instead of SO_3-Ph-BTP).

Figure 19 near here.

A modification to the EURO-GANEX flowsheet was subsequently reported by Carrott *et al.* This was termed the TRU-SANEX process and aimed at heterogeneous recycle of An.[67] The extraction-scrub section of this flowsheet was essentially the same as EURO-GANEX but then separately stripped Np+Pu followed by Am+Cm and finally Ln. The results show similar findings to those discussed above with slight variation. A high concentration of HNO_3 (5.9 M) improved the extent of disproportionation/oxidation of the inextractable Np(V) and the number of low acidity scrub stages was reduced to limit Np backwashing. This led to ~6-9 % of the Np being lost to the aqueous raffinate but it is envisaged that in a hot test using genuine fuel this would be avoided, similar to the reports of Malmbeck *et al.* through (radiolytically generated) HNO_2-induced Np(V) oxidation.[65] Cs and Sr were scrubbed as in the EURO-GANEX process, with Sr being slightly recycled between high and low acid sections of the flowsheet. Mo and Ru were shown to be issues, being routed with the solvent (~100 % of Mo and 50 % Ru) and attempts at stripping failing, implying either contamination of the solvent or routing with the Np+Pu product – an issue which still must be resolved. Pd also proved problematic despite the use of CDTA in the aqueous feed, this is postulated as being due to precipitation of PdO. The stripping of the loaded organic was achieved through two separate stages, one containing AHA in HNO_3 and the other SO_3-Ph-BTP in HNO_3, yielding separate Np+Pu and Am+Cm product streams.

2.4.5 Comments

Addition of modifiers to TODGA based organic phases can sufficiently increase the operating window to allow for macro loading of the organic phase without third phase formation. Modifier (or in some cases co-extractant) choice can vary the potential application of the solvent formulation with several examples provided. These include the use of:

- DMDOHEMA for high burn-up, high Pu (and other metal) content spent fuel liquors – EURO-GANEX.
- Alcohols for the *i*-SANEX-type processes, which operates post U(/Pu/Np) removal.
- TBP, which works well but does not adhere to the CHON principle.
- Or other amides, which work but have not been as extensively tested as the others and have, in part, been superseded.

All of the processes performed satisfactorily, particularly with respect to the An (and Ln) solvent loading, but have residual issues with the extraction of FP (Sr, Tc, Fe, Mo and Ru); some of which have been overcome (Sr, Fe and Tc) through low/high concentration acid scrubbing whilst some remain outstanding (Mo and Ru). None of the reports thus far have dealt with issues related to multiple reuse of the TODGA solvents such as potential build-up of the unwanted species or degradation products and the configuration of a solvent clean-up process.

3 Conclusions

DGAs have been clearly demonstrated to be a promising class of molecules for extracting trivalent actinides and lanthanides from nitric acid. The most well-known and studied example is TODGA but this has known problems with third phase formation and fission product co-extraction. A number of TODGA-based solvent extraction processes for the recovery of minor actinides have been devised and successfully tested with simulant feeds and in some cases with irradiated nuclear fuel solutions.

The modifiers that have been tested with TODGA are DHOA, TBP, 1-octanol, *iso*-decanol, *n*-decanol and DMDOHEMA. Each have their own advantages and disadvantages. With DHOA >1 M third phase formation is suppressed but acid extraction is increased considerably and metal loading is also suppressed. TBP has been shown to work on genuine fuel raffinate without third phase formation but is not CHON and speciation in the organic phase is unknown. Octanol extracts relatively little acid and allows stoichiometric loading in most instances (>5 % v/v) and has also been demonstrated in counter-current flowsheet tests. DMDOHEMA has been shown to allow contact of TODGA solutions with aqueous phases of high tetravalent actinide (Th/Pu^{4+}) concentrations, which none of the other modifiers were capable of. Modifier choice would likely be dependent on the nature of aqueous phase composition but DMDOHEMA and (1/*iso*)-alcohols would appear to demonstrate the best characteristics for most circumstances.

Post extraction organic phase speciation with An^{3+} has largely been shown to be 1:3 (M:L). Where measurements have found it to be 1:4 or higher this is likely to be due to outer sphere organisation of the DGAs in micellar type structures. The micellization of the extractant in the organic phase leads to third phase formation and modifiers are thus important in disrupting this tendency. The hydrodynamic properties of DGA-containing organic phases pre- and post-irradiation have been shown to be generally acceptable for processes with and without phase modifiers although increased viscosities of highly loaded organic phases containing TDdDGA have been noted.

The different methodologies of measurement of third phase formation and use of *n*-dodecane for testing mean that further testing must be performed in industrially applicable diluents such as Exxsol-D80 or TPH, as are currently used. This is due to the high dependence of third phase formation on the diluent due to micellar formation and aggregation. Exxsol-D80, for instance, is partially branched with (very low levels of) aromatic hydrocarbons that will affect the characteristics in processes.

In summary, modifiers are successfully enabling the use of TODGA in actinide separation processes but to date the identification and testing of suitable modifiers has been rather empirical. There is a growing understanding of the fundamental chemistry occurring in the organic phase and how that affects extractant speciation and metal loading capacity but more studies are needed if TODGA-based flowsheets are to become an industrially deployable option for MA recovery processes.

Extraction of FPs by TODGA is an undesirable feature and some key elements that have been shown to present issues are Zr, Pd, Sr, Ru, Mo and Tc. Zr and Pd hold back in the aqueous phase has been successfully demonstrated by several groups through conditioning of aqueous feeds with CDTA and Sr can be scrubbed by lower HNO_3 concentrations. Ru and Mo have proven difficult to

control in all circumstances with high HNO_3 concentration scrubbing appearing to be the only method that has any effect on the distribution ratios. Post-irradiation, the behaviour of these elements is even more unpredictable, an issue that needs further investigation before DGA based processes can be implemented in next generation reprocessing. Likewise, the behaviour of Tc and other anionic elements is poorly understood as they are co-extracted with cations but can be controlled by high HNO_3 concentration (and, therefore, NO_3^-) scrub stages.

The second part of this review will focus on alternative DGA based extractants and their associated separation processes, retaining the major focus on modifiers and whether these can be eliminated by improved design of the DGA ligand in the organic phase. The review will consider the degradation processes, extractant design and other factors that can affect solvent choice and process development.

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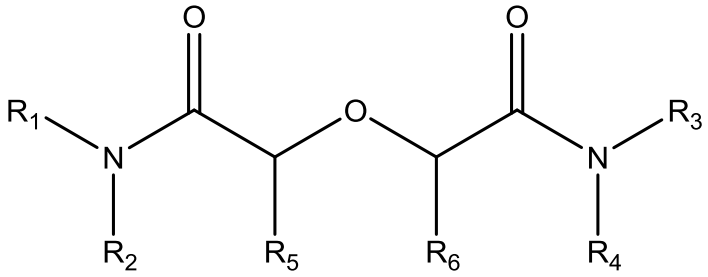

Figure 1: Depiction of DGA backbone. Where R groups can vary as alkyl or H (see Table 1).

Name	R_1	R_2	R_3	R_4	R_5	R_6
TODGA	C_8H_{17} (oct)				H	
THDGA	C_6H_{13} (hexyl)				H	
Me-TODGA	C_8H_{17} (oct)				H	Me
Me_2-TODGA	C_8H_{17} (oct)				Me	
TDDGA	$C_{10}H_{21}$ (decyl)				H	
TDdDGA	$C_{12}H_{25}$ (dodecyl)				H	
T2EHDGA	C_8H_{17} (2-ethylhexyl)				H	

Table 1: Identity of R groups for modified DGA extractants.

Process	EURO-GANEX	1-cycle SANEX	innovative-SANEX	ALSEP	TODGA-TBP
DGA	TODGA	TODGA	TODGA (multiple)	TODGA/ T2EHDGA	TODGA
Modifier (or Co-Extractant)	DMDOHEMA	$CyMe_4$-BTBP	SO_3-Ph-BTP	HDEHP/ HEH(HEP	TBP
CHON	Yes	Yes	No	No	No
Can be used on raffinate?	Yes	Yes	Yes	Yes?	Yes
Depends on other process?	UREX/U extraction	Advanced PUREX (Np control)	Advanced PUREX (Np control)	Likely, PUREX or other	Advanced PUREX (Np control)
Known distribution ratios	Yes	Yes	Yes	Yes	Yes
References	[64]	[68]	[9]	[69]	Section 2.4.2

Table 2: Selected data for processes which have been developed using DGA-based extractants.

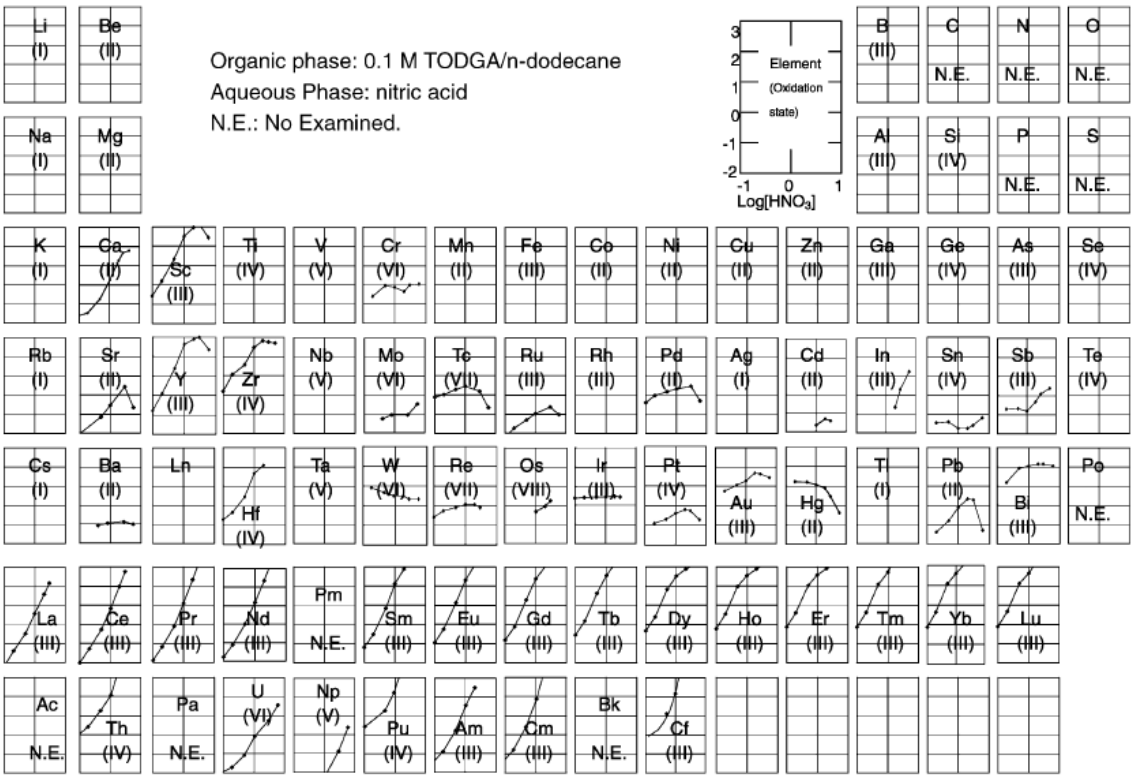

Figure 2: Plots of distribution ratios for all the metals studies by Zhu *et al.* [27] Extracted into an organic phase containing 0.1 M TODGA in *n*-dodecane.§

Property	Valence/Form			
	Divalent	Trivalent	Tetravalent	Oxonium
High and Intermediate Extractable radii (pm)	86-119	70-113 (highest 87-113)	83-105	
Inextractable radii (pm)	<75		<70 Except Pt^{4+} ~63	
Stoichiometry (M:L)	1:2	1:3/1:4 Ru^{3+} forms nitrosyl complexes too	1:3 Pt and Sn different	~1:2
Notes	Max D_{Ca}	Likely outer sphere coordination - see later. Later Ln higher D than early.		Most likely anions extracted as charge balancing – decrease D with $[HNO_3]$

Table 3: Key data of ionic radii and stoichiometry which allow/preclude extraction of various ions as reported by Zhu *et al.*[27]

§ Reprinted from Analytica Chimica Acta, 527/2, Z.-X. Zhu, Y. Sasaki, H. Suzuki, S. Suzuki and T. Kimura, Cumulative study on solvent extraction of elements by N,N,N′,N′-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into n-dodecane, 163, Copyright 2004, with permission from Elsevier.

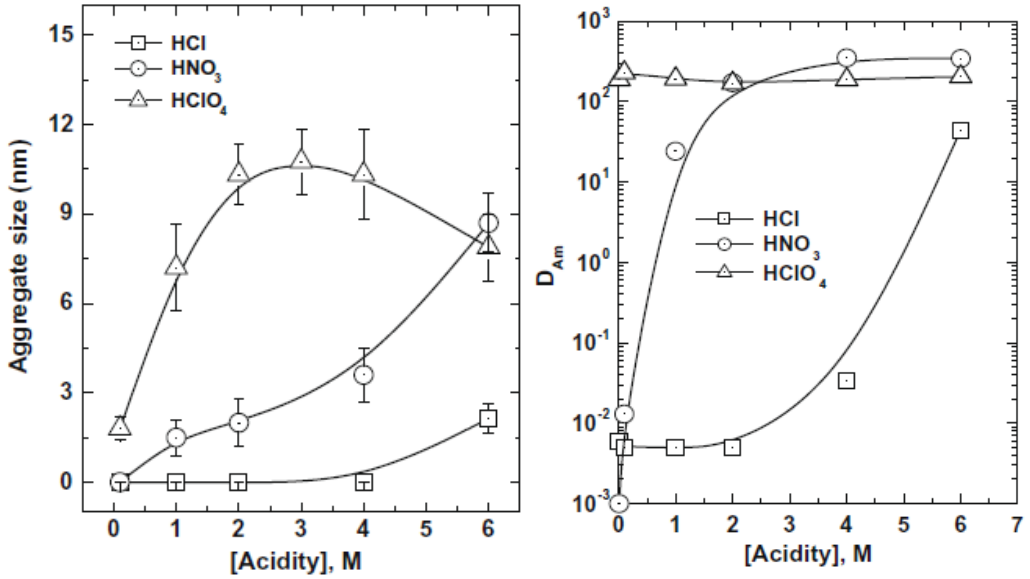

Figure 3: [acid] plotted against D_{Am} and aggregate size to demonstrate the optimum aggregate size for extraction by TODGA in *n*-dodecane.[26]**

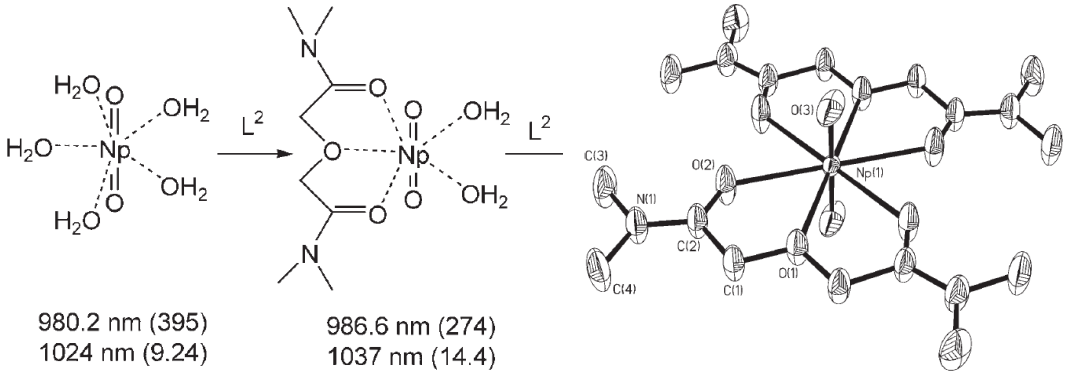

Figure 4: Scheme of the complexation of NpO_2^+ by TMDGA.[36] Displayed are the absorption parameters measured by Tian *et al.* and the final non-absorbing complex as measured through single crystal x-ray diffraction.

** Reprinted from Journal of Colloid and Interface Science, 342/1, P.N. Pathak, S.A. Ansari, S. Kumar, B.S. Tumar and V.K. Manchanda Dynamic light scattering study on the aggregation behaviour of *N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) and its correlation with the extraction behaviour of metal ions, 114, Copyright 2010, with permission from Elsevier.

Modifier	0.5 M $[HNO_3]_{aq,ini}$	3.0 M $[HNO_3]_{aq,ini}$
	$[HNO_3]_{org,eq}$ (M)	
5 v/v % 1-octanol	0.013	0.22
0.5 M TBP	0.041	0.42[40]
1 M DHOA[30]	0.05	0.69

Table 4: Extraction of HNO_3 into organic phases of 0.2 M TODGA in TPH (this work) or *n*-dodecane (referenced values) from HNO_3 aqueous phases.[

[acid]	LOC (M)		
	15 °C	25 °C	35 °C
1 M HNO_3	0.013	0.014	
2 M HNO_3	0.010	0.014	0.012
3 M HNO_3	0.0052	0.0081	0.0083
1 M $HClO_4$		0.0068	
2 M $HClO_4$		0.0023	
3 M $HClO_4$		0.0019	

Table 5: Table of maximum organic phase [Nd] before a third phase is formed against aqueous phase [acid] at different temperatures, as measured by Tachimori *et al.* LOC = Limiting Organic Concentration – the maximum organic phase concentration before a third phase is formed. Organic phase = 0.1 M TODGA in *n*-dodecane.[30]

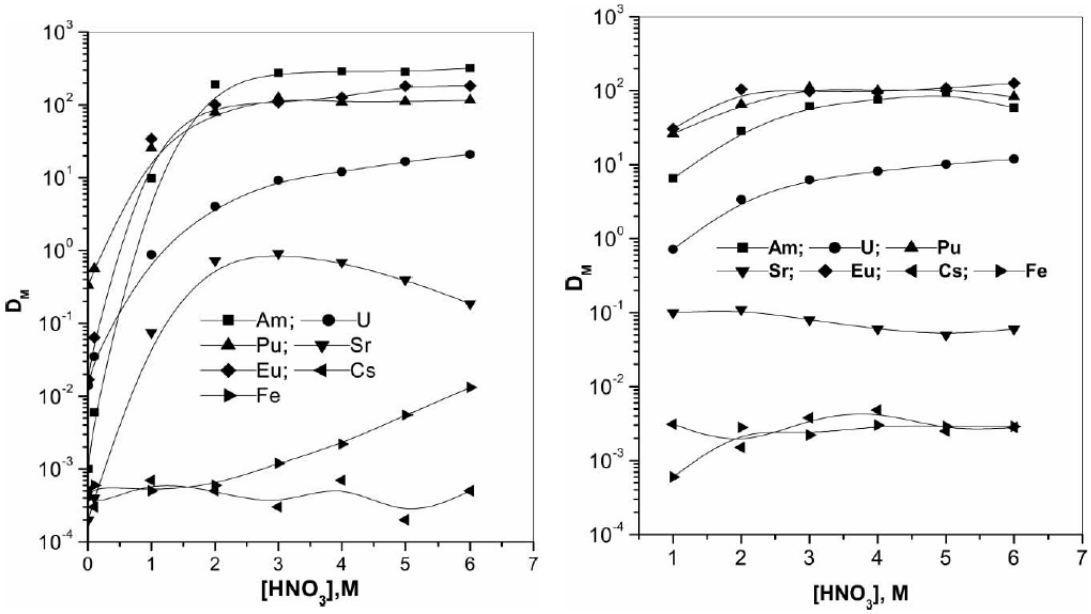

Figure 5: Results of the extractions of metal ions by Ansari *et al.* Organic phase = 0.1 M TODGA + 0.5 M DHOA. Pure tracer experiment (left) and SHLW extraction (right).[42]††

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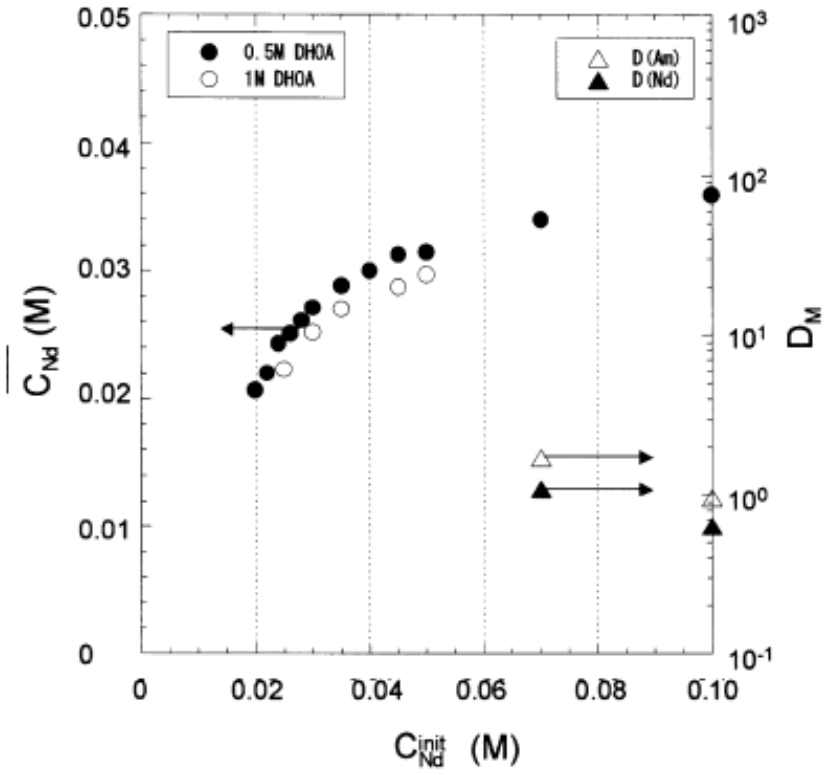

Figure 6: Graph of $[Nd]_{ini}$ against $[Nd]_o$ at equilibrium from an aqueous phase of 3 M HNO_3 and an organic phase of 0.1 M TODGA and DHOA in *n*-dodecane. Increased [DHOA] suppresses Nd loading/extraction.[30]††

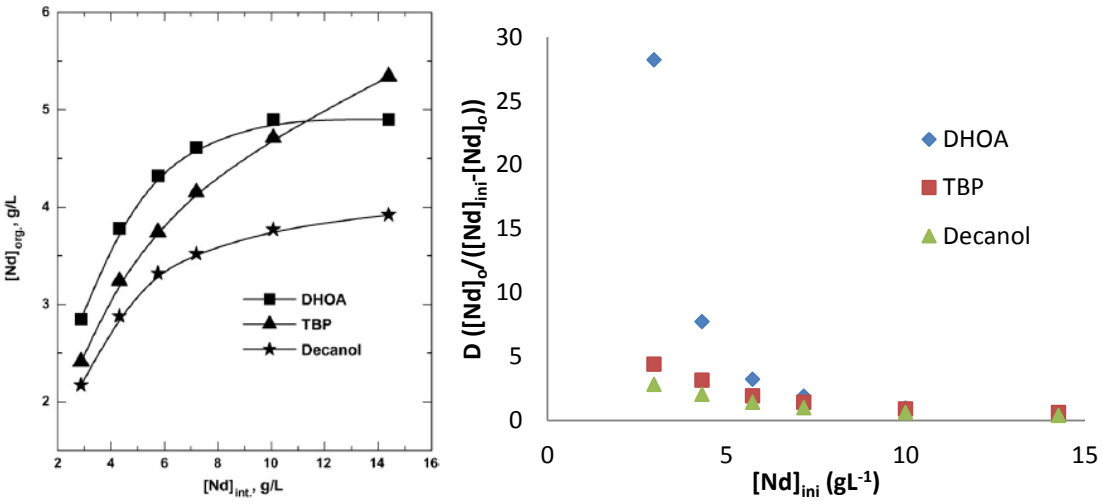

Figure 7: Data for initial aqueous phase [Nd] (3 M HNO_3) against $[Nd]_{org}$ loading (left) and the distribution ratios as calculated through mass balance (right) for 0.1 M TODGA, 0.5 M phase modifier extractions.[45]‡‡

‡‡ Reprinted from Separation and Purification Technology, 66/1, S.A. Ansari, D.R. Prabhu, R.B. Gujar, A.S. Kanekar, B. Rajeswari, M.J. Kulkarni, M.S. Murali, Y. Babu, V. Natarajan, S. Rajeswari, A. Suresh, R. Manivannan, M.P. Antony, T.G. Srinivasan and V.K. Manchanda, Counter-current extraction of uranium and

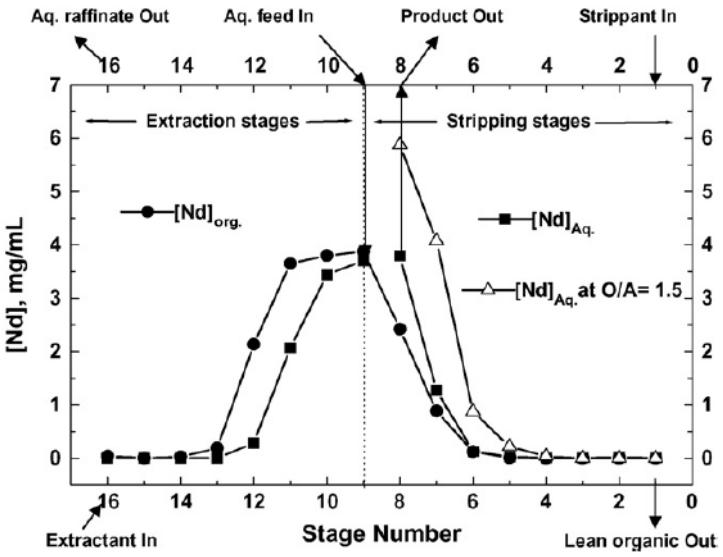

Figure 8: [Nd] at various stages in the multi-stage mixer-settler study undertaken by Ansari *et al.*[45] Extractant = 0.1 M TODGA/0.5 M DHOA/NPH, aq. Feed = 0.026 M Nd.3.5 M HNO_3, strippant = 0.2 M HNO_3. Extraction and stripping are achieved after four stages each.§§

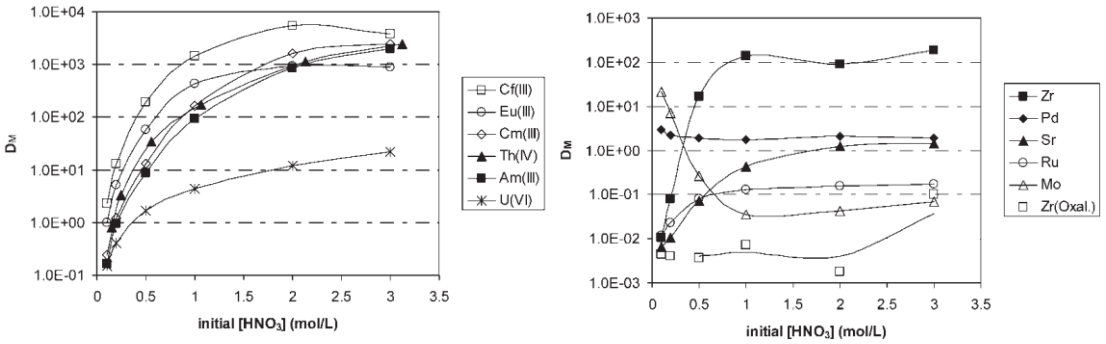

Figure 9: Plots of D against [HNO_3] for various An and FPs. Eu, Am, Cm, Cf at tracer level, U(VI), Th(IV), Zr, Pd, Sr, Ru and Mo at 0.01 M, Zr(oxal.) contains [oxalic acid] = 0.2 M.[40] Organic phase contains TODGA = 0.2 M, TBP = 0.5 M in TPH (not pre-equilibrated with HNO_3).***

lanthanides from simulated high-level waste using N,N,N',N'-tetraoctyl diglycolamide,118, Copyright 2009, with permission from Elsevier.

§§ Reprinted from Separation and Purification Technology, 66/1, S.A. Ansari, D.R. Prabhu, R.B. Gujar, A.S. Kanekar, B. Rajeswari, M.J. Kulkarni, M.S. Murali, Y. Babu, V. Natarajan, S. Rajeswari, A. Suresh, R. Manivannan, M.P. Antony, T.G. Srinivasan and V.K. Manchanda, Counter-current extraction of uranium and lanthanides from simulated high-level waste using N,N,N',N'-tetraoctyl diglycolamide,118, Copyright 2009, with permission from Elsevier.

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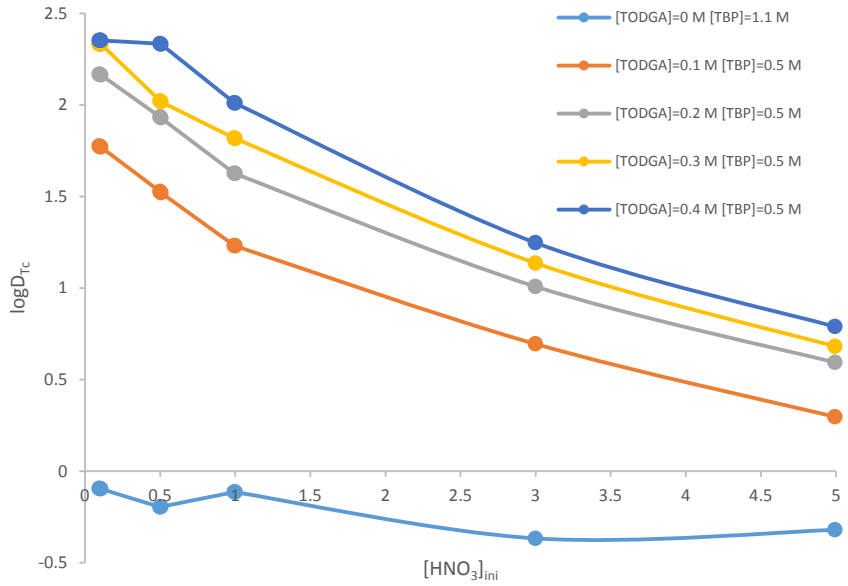

Figure 10: distribution ratio for Tc with respect to varying HNO_3 concentration as reported by Brown *et al.*[48]

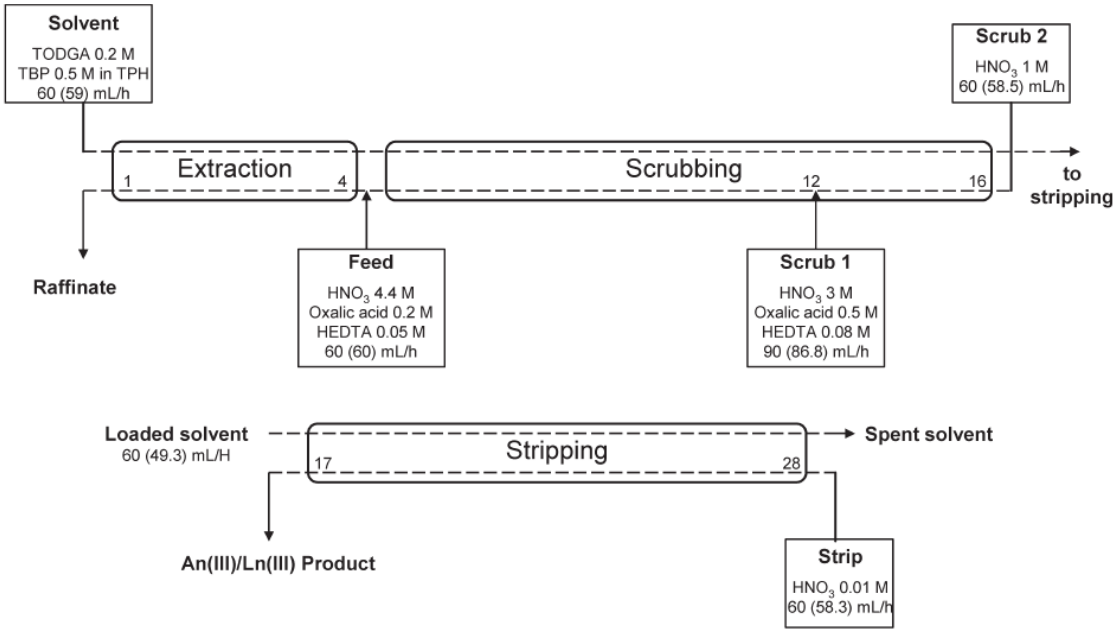

Figure 11: Flowsheet developed by Modolo *et al.* for the use of TBP and TODGA in an organic phase to isolate the Ln and An.[40]†††

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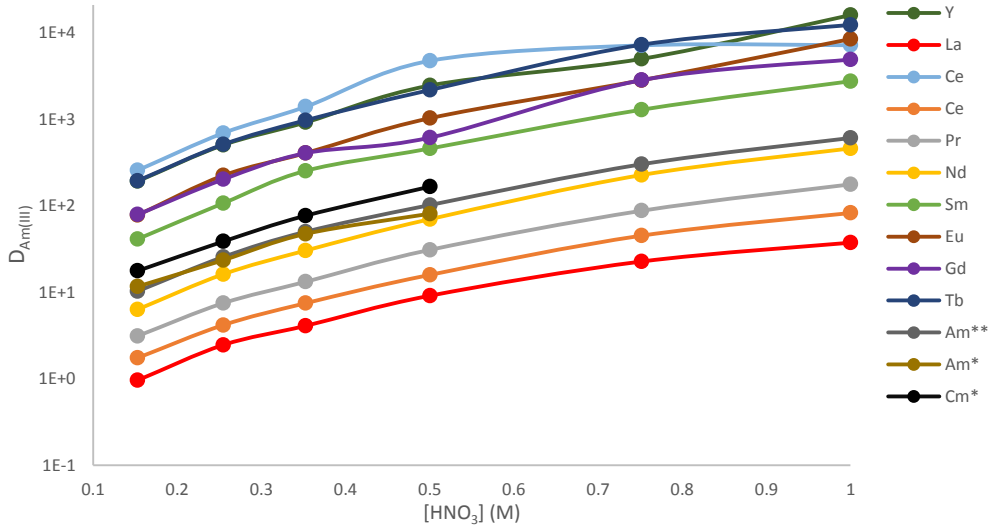

Figure 12: distribution ratios as measured by Geist *et al.* from an aqueous phase of varying [HNO_3], organic phase consists of 0.2 M TODGA/5 % 1-octanol in TPH.[52] [Am] and [Cm] = 1 $kBqmL^{-1}$ and [Y] and [Ln] = 20 mgL^{-1}. * = α spectroscopy; ** = γ spectroscopy.‡‡‡

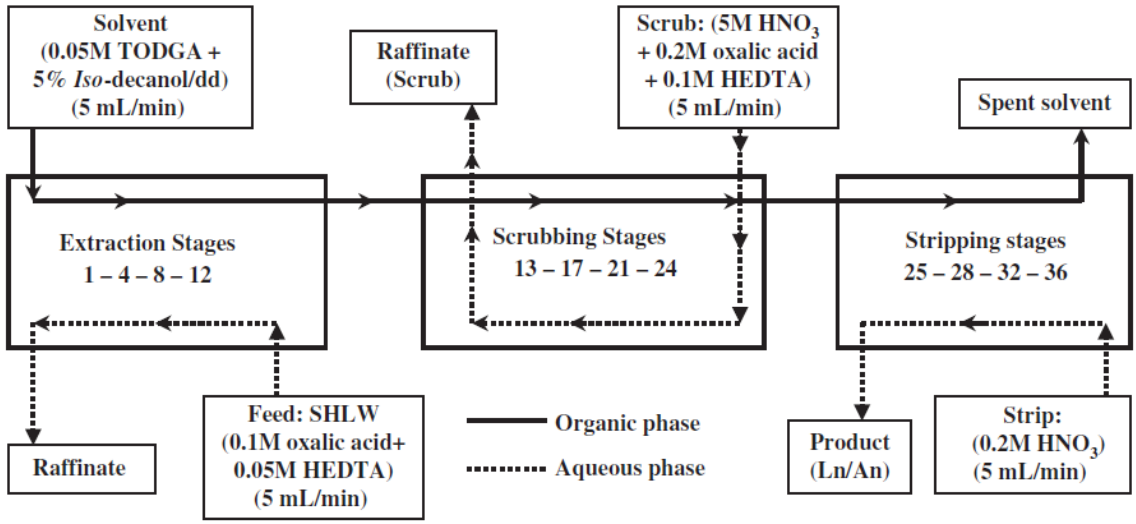

Figure 13: Flowsheet of experimental setup of counter-current mixer-settler setup used by Gujar *et al.*[51]§§§

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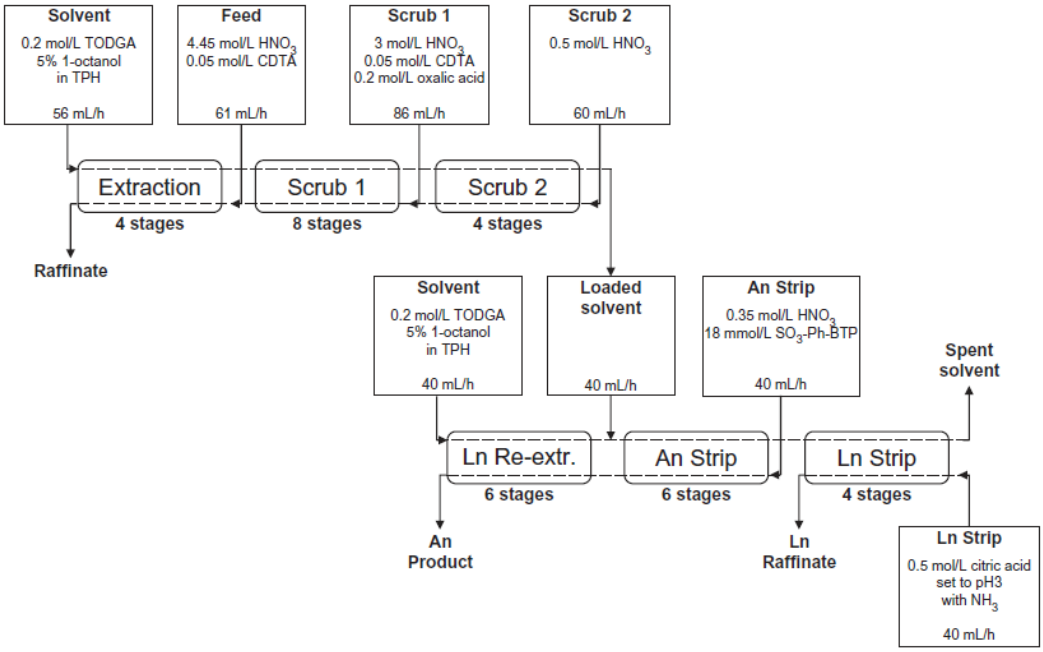

Figure 14: Flowsheet designed and tested by Wilden *et al.* for the *i*-SANEX process.[53]**

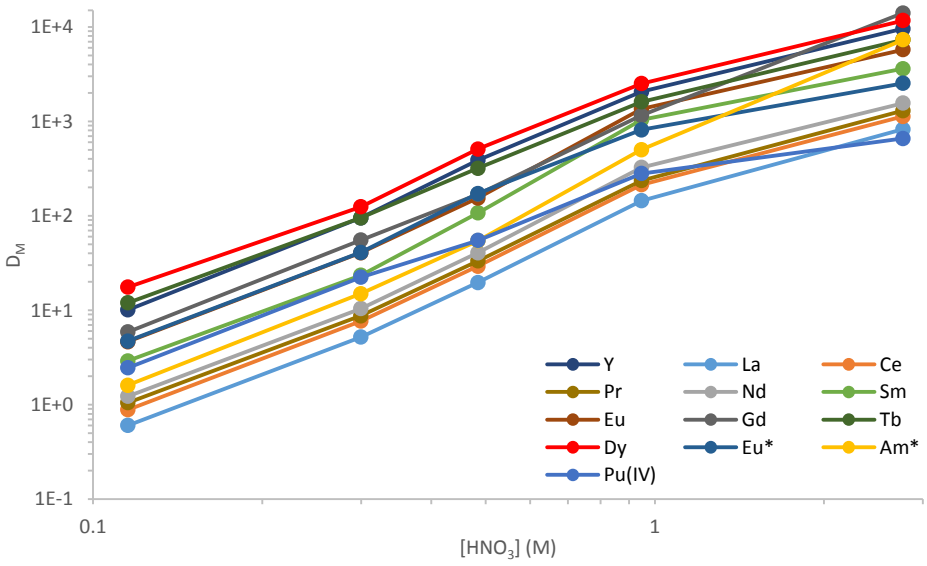

Figure 15: distribution ratios measured by Bell *et al.* for an aqueous phase of 0.2 M TODGA and 0.5 M DMDOHEMA in Exxsol-D80 from a range of HNO_3 concentrations.[62] [Ln] = 0.1 mM, [Pu] = 1 µM and [Am]/[Eu] = 1 $kBqmL^{-1}$ each and temperature = 293 K. *=γ spectroscopy.

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$[HNO_3]$ (M)	[TODGA] (M)	[1-octanol] (vol.%)	[TBP] (M)	Limiting $[Th]_{ini}$ (gL^{-1})
5	0.2	0	0	5.5
3, 4 and 5	0.2	5	0	40
3, 4 and 5	0.2	5	0.5	-

Table 6: Organic and aqueous phase compositions examined and the observed Limiting Organic Concentration (LOC) of Th. - = no third phase observed.[59]

$[HNO_3]_{ini}$ (M)	[TODGA] (M)	[TBP] (M)	[1-octanol] (%)	Limiting $[Pu]_{ini}$ (gL^{-1})
0.5	0.2	0.5	0	4
1	0.2	0.5	0	3
2	0.2	0.5	0	4
3	0.2	0.5	0	3
4	0.2	0.5	0	5
5	0.2	0.5	0	5
5	0.1	1.1	0	<3
5	0.2	1.1	0	5
5	0.4	1.1	0	12
5	0.2	0	5	5
3	0.2	0	100*	13
3	0.2	0.5	5	6
3	0.2	0.5	100*	11

Table 7: Organic and aqueous phase compositions examined and the observed LOC of Pu for the mixture.[59] * 1-octanol diluent.

Solvent composition (in OK)		Limiting $[Pu]_{ini}$ (gL^{-1})
[Extractant] (M)	[Modifier] (M)	
TODGA (0.2)	HDEHP (0.5)	52
TODGA (0.2)	DMDOHEMA (0.5)	35
TODGA (0.2)	DHOA (0.5)	<5
TDdDGA (0.2)		<5
TDdDGA (0.2)	TBP (1.1)	5
TDdDGA (0.2)	DMDOHEMA (0.5)	>60
	DMDOHEMA (0.5)	10

$[HNO_3]_{ini}$ (M)	[TODGA] (M)	[DMDOHEMA] (M)	Limiting $[Pu]_{ini}$ (gL^{-1})	D_{Pu} (stripping)#
3	0.2	0.5	40	2.55
3	0.2	0.1	<10*	NM
3	0.2	0.25	20*	1.21
3	0.2	1	>50	15.5
3	0.1	0.5	30	0.57
3	0.3	0.5	50	14.9
3	0.4	0.5	>50	29.1
2	0.2	0.5	45	1.3
4	0.2	0.5	25	6.6
4.5	0.2	0.5	30	NM

Table 8: Phase compositions investigated for Pu loading of the organic phase from HNO_3 solution.[59] Top, aqueous phase = 3 M HNO_3. Bottom, strip solution = 0.2 M HNO_3 + 0.5 M AHA. * = precipitation noted on loading. # = 10 gL^{-1} content. NM = Not Measured.

Ox. State	$[HNO_3]_{aq,eqm}$	Extractant	Solv. Number (±2σ)
Np^{4+}	0.5	TODGA	1.8±0.0
	1		2.0±0.1
	3#		2.22±0.15
NpO_2^{2+}	0.5		2.4±0.3
	1		2.4±0.5
	2		1.8±0.1
	3#		1.38±0.08
	4		1.1±0.1
Np^{4+}	0.5	DMDOHEMA	2.3±0.5
	1		4.1±0.5
NpO_2^{2+}	0.5		2.9±0.3
	1		2.9±0.2
	2		2.6±0.1
	4		1.6±0.1

Table 9: Speciation data for organic phase Np, extracted from OK.[35] # = data taken from Ansari *et al.*[70]

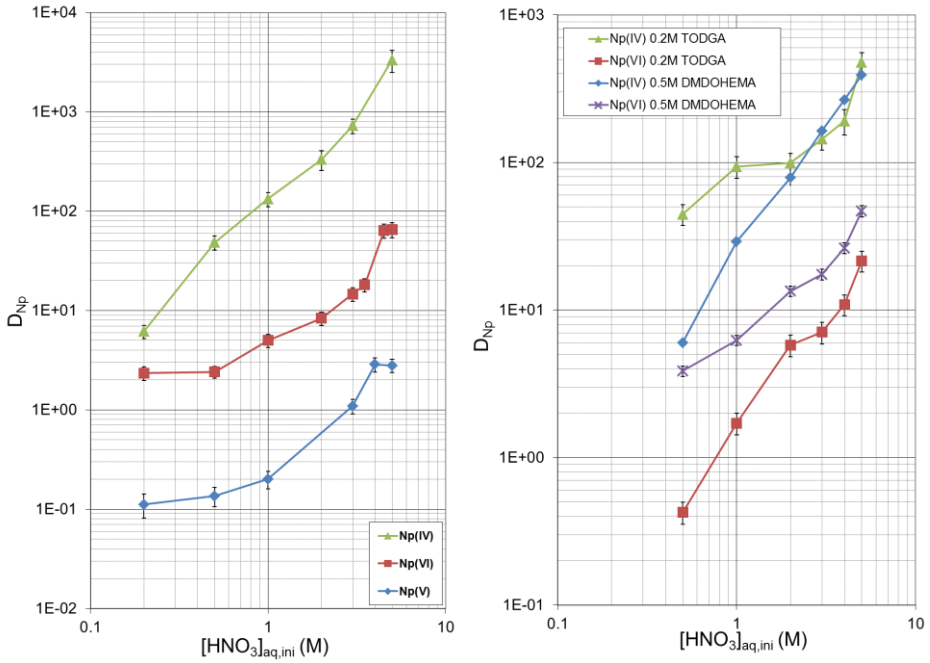

Figure 16: D_{Np} values as measured by Carrott *et al.* post-extraction from varying $[HNO_3]$ into organic phases containing TODGA or DMDOHEMA (right) or TODGA (0.2 M) and DMDOHEMA (0.5 M) (left), all in OK.[35]††††

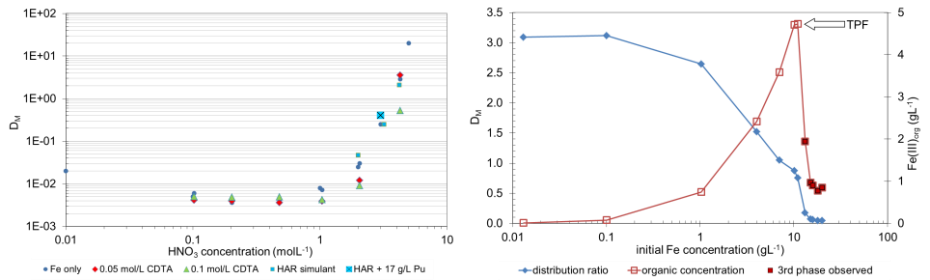

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Figure 17: distribution ratios for Fe for the EURO-GANEX solvent formulation of 0.2 M TODGA and 0.5 M DMDOHEMA in Exxsol-D80 with respect to HNO_3 (left) and Fe (right) concentration, as reported by Carrott *et al.*[63] Aqueous phase compositions are as denoted on chart (left) or 4.1 M HNO_3 (right) where TPF = Third Phase Formation.

Element*	Extraction	Scrubbing
	[HNO_3] (M)	
	3.2	0.5
Y	>100	>100
Ce	>100	61
Pr	>100	71
Nd	>100	87
Sm	>100	>100
La	>100	40
Eu	68	>100
Gd	>100	>100
Mo	1.7	0.43
Sr	2.0	0.43
Pd	0.22	31
Se	0.18	94
Cd	0.16	0.21
Ru	0.41	8.9
Ba	0.14	0.058
^{152}Eu	>100	>100
^{241}Am	>100	>100
^{239}Pu	>100	>100

Table 10: D data reported by Carrott *et al.* for batch extractions with the EURO-GANEX solvent of 0.2 M TODGA and 0.5 M DMDOHEMA in Exxsol-D80.[35] Aqueous phases were: extraction, HAR (Table S3) with 0.05 M CDTA; stripping, 0.04 M SO_3-Ph-BTP and 1 M AHA. Mixed for 15 mins at 22±1 °C.

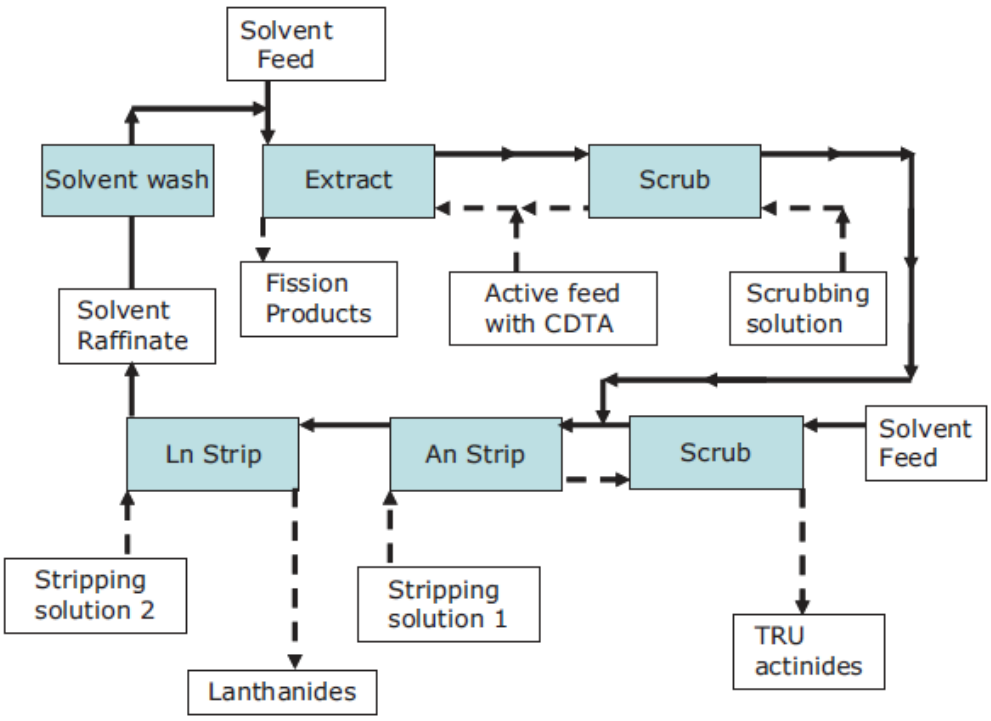

Figure 18: Diagrammatic depiction of the experimental design undertaken by Carrott *et al.*[64]‡‡‡‡

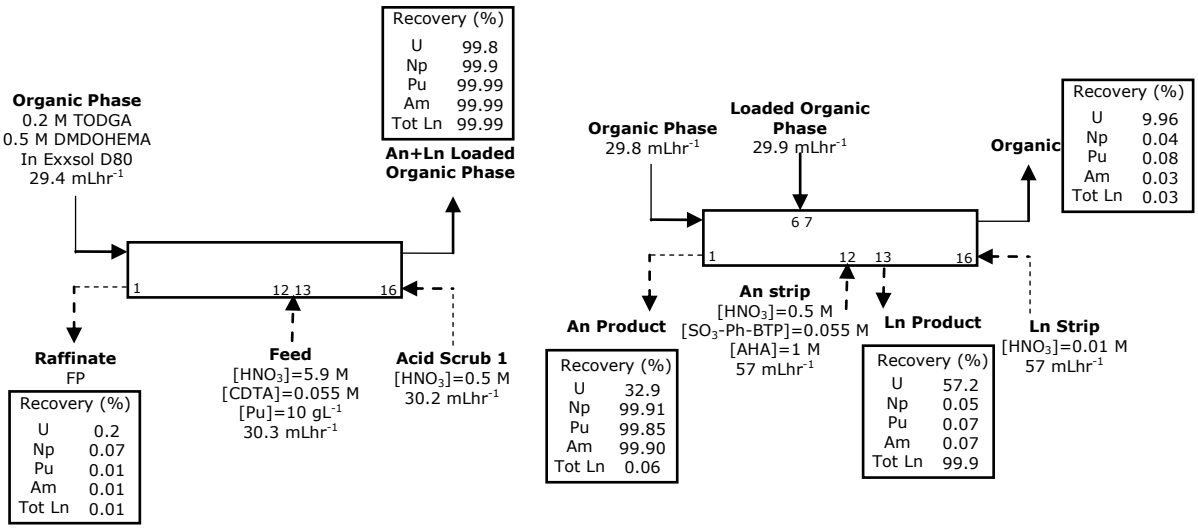

Figure 19: Flow sheets of the extraction (left) and scrub sections of the centrifugal contactor experiments performed by Malmbeck *et al.*[65]

Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA

Supplementary Information

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Section 1: HAR/GANEX-1 product compositions and solvent dose rates

Compositions of HAR/GANEX-1 product vary by fuel, reactor type and burn-up. Magnusson performed calculations in this regard for a range of scenarios of fuel type, burn up and cooling period, these can be found in reference [71]. Table S1 lists the composition detailed for a HAR of 5000 $L.t^{-1}$ UO_2 with an initial enrichment to 3.5 % ^{235}U and a thermal burn-up of 33 $GWd.t_{HM}^{-1}$ after 3 years of cooling. The high Na and Fe content were added to account for the U and Pu conditioning/purification steps.

Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]
^{241}Am	5.2 $MBqL^{-1}$	Ag	0.009	Pd	0.102
^{244}Cm	5.2 $MBqL^{-1}$	Al	0.002	Rb	0.067
^{152}Eu	9.3 $MBqL^{-1}$	Ba	0.247	Rh	0.077
Y	0.078	Cd	0.019	Ru	0.368
La	0.209	Cr	0.080	Sb	0.004
Ce	0.480	Cs	0.449	Se	0.024
Pr	0.195	Cu	0.020	Sn	0.011
Nd	0.716	Fe	1.979	Sr	0.156
Sm	0.146	Mo	0.642	Te	0.109
Eu	0.040	Na	2	Zr	0.698
Gd	0.046	Ni	0.041		
HNO_3	3.1 M				
Oxalic acid	0.3 M *				

Table S1: Typical HAR composition as detailed in reference [68]. * added to improve extractions.

Table S2 lists the composition detailed for a PHWR of ~6500 $MWd.t^{-1}$ as reported by Gujar *et al.* The dissolution represents ~800 L solution per tonne of used fuel.[51] The authors further report that the expected total concentration of trivalent An and Ln in PHWR is likely to be <4 gL^{-1} and fast reactor is likely to be 5-6 gL^{-1}. [72]

Element	Conc.	Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]
^{241}Am	0.17 $MBqL^{-1}$	Na	5.50	Pd	0.03
^{152}Eu	0.18 $MBqL^{-1}$	K	0.22	Mo	0.14
^{59}Fe	0.17 $MBqL^{-1}$	Cr	0.12	Ba	0.06
$^{85,89}Sr$	0.17 $MBqL^{-1}$	Mn	0.43	Y	0.06
^{95}Zr	0.04 $MBqL^{-1}$	Fe	0.72	La	0.18
^{99}Mo	0.17 $MBqL^{-1}$	Sr	0.03	Ce	0.06
^{106}Ru	0.05 $MBqL^{-1}$	Cs	0.22	Pr	0.09
^{109}Pd	0.05 $MBqL^{-1}$	Zr	0.09	Nd	0.12
^{137}Cs	0.15 $MBqL^{-1}$	Ru	0.04	Sm	0.09
HNO_3	3 M				
Oxalic acid	0.1 M *				

Table S2: Typical HAR composition as detailed in reference 51. * added to improve extractions.

Modolo *et al.* report a HAR composition for a PUREX raffinate of volume 5000 $L.t^{-1}$ UO_x fuel (Table S3). The initial enrichment (^{235}U) was 3.5 % with a burn-up of 33 $GWd.t_{HM}^{-1}$ after 3 years of cooling. Additionally they spiked the feed with ^{241}Am, ^{244} Cm, ^{252}Cf and ^{152}Eu for extraction experiments.[40]

Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]
Ag	0.0126	Fe	1.9	Pr	0.219
Al	0.002	Gd	0.035	Rh	0.080
Ba	0.264	La	0.218	Ru	0.388
Cd	0.017	Mo	0.672	Sb	0.0044
Ce	0.518	Te	0.481	Se	0.009
Cr	0.091	Na	2.034	Sm	0.146
Cu	0.019	Nd	0.718	Sn	0.011
Cs	0.556	Ni	0.047	Sr	0.167
Y	0.102	Pd	0.123	Zr	1.165
Eu	0.033	Rb	0.065	HNO_3	3.2 M

Table S3: HAR composition as detailed by Modolo *et al.*[40]

An alternative composition used by Modolo *et al.* as a PUREX raffinate is shown in Table S4.[40] The main difference here is the inclusion of Cs as a radiotracer and the removal of some of the elements which were previously included and the inclusion of some U.

Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]	Element	Conc.
Ag	0.002	Pd	0.291	Zr	0.675 gL^{-1}
Ba	0.452	Pr	0.246	^{252}Cf	2.8 $MBqL^{-1}$
Cd	0.026	Rb	0.069	^{241}Am	5.1 $MBqL^{-1}$
Ce	0.49	Rh	0.040	^{244}Cm	5.4 $MBqL^{-1}$
Cs	0.567	Ru	0.201	^{152}Eu	5.2 $MBqL^{-1}$
Eu	0.029	Sm	0.166	^{134}Cs	2.2 $MBqL^{-1}$
Gd	0.087	Sr	0.143		
La	0.264	Te	0.397	Oxalic acid	0.2 M *
Mo	0.415	U	0.089	HEDTA	0.05 M *
Nd	0.905	Y	0.076	HNO_3	4.4 M

Table S4: HAR composition used by Modolo *et al.* in centrifugal counter tests for TBP/TODGA extraction tests.[68] * added to improve extractions.

A different composition was used by Ansari *et al.*; however, there was no justification provided for the values chosen based on any specific reactor or burn-up only that it was post-PUREX style processing so contained no U.[42]

Ravi *et al.* provided a waste composition resulting from a fast reactor fuel of initial composition $(U_{0.71}Pu_{0.29})O_2$ with a burn-up of 129 $GWd.t^{-1}$ and a cooling period of one year (Table S5).[73] Sodium nitrite was added to 0.2 mL of the solution to condition the Pu to Pu^{4+} and was then contacted 3 times with 30 % v/v TBP in *n*-dodecane to remove the U and Pu.

Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]
Ag	0.13	Mo	1.09	Sb	0.02
Ba	0.41	Na	3.00	Se	0.01
Cd	0.04	Nd	1.13	Sm	0.05
Ce	0.69	Ni	0.10	Sr	0.14
Cr	0.10	Pd	0.60	Tb	0.01
Cs	1.12	Pm	0.05	Tc	0.26
Dy	0.01	Pr	0.34	Te	0.16
Eu	0.31	Rb	0.06	U	2.64
Fe	0.50	Rh	0.26	Y	0.08
Gd	0.07	Ru	0.81	Zr	0.89
La	0.48	Sb	0.01	[HNO_3]	4 M

Table S5: Composition of HLLW post dissolution of test fast reactor.

Gujar *et al.* also report the expected dose rate of LWR fuel as 0.03-0.2 $kGy.hr^{-1}$ for U fuel and 0.4-0.8 $kGy.hr^{-1}$ for MOX fuel.[39]

Nayak *et al.* published the composition of a dissolved fast reactor fuel with a burnup of 80000 $MWd.t^{-1}$ and two years of cooling (Table S6).[74]

Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]	Element	Conc. [gL^{-1}]
Ag	0.109	Na	3.000	Sn*	0.163
Ba	0.414	Nd	1.125	Sr	0.147
Cd	0.038	Ni	0.100	Tb*	0.011
Ce	0.684	Pd	0.600	Tc*	0.262
Cr	0.101	Pm*	0.053	Te	0.163
Cs	1.125	Pr	0.339	Y	0.074
Dy	0.006	Rb	0.055	Zr	0.822
Eu	0.032	Rh	0.262	$^{(152+154)}$Eu	tracer
Fe	0.500	Ru	0.813	^{241}Am	0.218
Gd	0.065	Sb*	0.007		
La	0.342	Se*	0.002		
Mo	1.092	Sm	0.306	[HNO_3]	~3 M

Table S6: Composition of HLLW from a fast reactor with a burnup of 80000 $MWd.t^{-1}$ and two years of cooling as published by Nayak *et al.*[74] * Sb, Se and Sn were not added to the solution due to very low solubilities. La was added in place of Tb and Pm and Tc was not included.

Section 2: Tables of batch distribution data

Extractant		TODGA		
[Extractant]		0.1 M		
Diluent		1-octanol	*n*-dodecane	*n*-hexane
$[HNO_3]$			1 M	
Modifier			N/A	
D	La^{3+}	>500	5.3	>500
	Eu^{3+}		265	
	Lu^{3+}		631	
	Th^{4+}		147	
	UO_2^{2+}		0.8	
	NpO_2^{+}		0.0056	
	Am^{3+}	81	30	33
	Cm^{3+}		78	
	Cf^{3+}		156	

Table S7: Distribution ratio data produced by Sasaki *et al.* in ref. [18].

Element	Distribution ratios (D) for $[H_2C_2O_4]$ (M)					
	0.15	0.2	0.25	0.3	0.35	0.4
Am, Cm	>200	>200	>200	>200	>200	>200
Cf	>1000	>1000	>1000	>1000	>1000	>1000
Eu, Gd, Nd, Pr, Sm	>200	>200	>200	>200	>200	>200
Y	>1000	>1000	>1000	>1000	>1000	>1000
La	32	31	44	43	43	51
Ce	98	108	170	164	164	197
Mo	0.081	0.071	0.087	0.11	0.12	0.14
Pd	0.16	0.091	0.048	0.055	0.046	0.038
Sr	1.1	0.84	1.5	1.6	1.8	1.9
Zr	0.68	0.26	0.10	0.097	0.056	0.042
Ru	0.17	0.22	0.20	0.19	0.16	0.18
Ag	0.62	0.28	0.12	0.11	0.066	0.056
Cd	0.039	0.039	0.050	0.052	0.059	0.062
Ba, Cr, Cs, Cu, Fe, Na, Ni, Rb, Rh, Sb, Se, Sn, Te	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Concentration (M)								
$[H_2C_2O_4]$	0.05	0.05	0.10	0.10	0.15	0.15	0.20	0.20
[TBP]	0.50	0.25	0.50	0.25	0.50	0.25	0.50	0.25
[HEDTA]	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Element	Distribution ratios							
Am, Cm, Cf	>200	>200	>200	>200	>200	>200	>200	>200
Ln^{3+}	>200	>200	>200	>200	>200	>200	>200	>200
Mo	0.06	0.08	0.05	0.06	0.04	0.05	0.04	0.05
Pd	0.30	0.36	0.16	0.18	0.07	0.07	0.03	0.04
Ru	0.23	0.22	0.22	0.19	0.25	0.20	0.25	0.21
Sr	0.40	0.59	0.54	0.73	0.44	0.77	0.42	0.64
Zr	5.9	5.8	0.82	1.1	0.18	0.19	0.06	0.09
Rest FPs	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03

Table S8: Distribution ratio data for selected elements from batch experiments as reported by Modolo *et al.* Aqueous phase = 3.2 M HNO_3, 0.05 M HEDTA and varying [oxalic acid].[40] Organic phase = 0.2 M TODGA in TPH (top) and 0.2 M TODGA and varying [TBP] (bottom).

Element	% in Raffinate	% in An/Ln product	% in solvent (stage 16)	% in solvent (stage 28)	Balance	$DF_{feed/raff.}$
Rb	99	D.L.	D.L.	D.L.	99	1.01
Cs	101	D.L.	D.L.	D.L.	101	0.99
Sr	104	D.L.	0.03	D.L.	104	0.96
Ba	100	D.L.	D.L.	D.L.	100	1.00
Zr	116	0.1	0.3	0.017	116	0.86
Mo	102	D.L.	D.L.	D.L.	102	0.98
Ru	90	1.8	11	7.5	99	1.12
Rh	100	D.L.	D.L.	D.L.	100	1.00
Pd	96	0.12	0.7	0.5	96	1.05
Ag	103	D.L.	D.L.	D.L.	103	0.97

Element	% in Raffinate	% in An/Ln product	% in solvent (stage 16)	% in solvent (stage 28)	Balance	$DF_{feed/raff.}$
Cd	100	D.L.	D.L.	D.L.	100	1.00
Te	106	D.L.	D.L.	D.L.	106	0.94
Y	0.025	89	102	0.016	89	4042
La	0.010	98	99	0.0015	98	>10000
Ce	0.01	99.44	99.9	0.02	99	7336
Pr	D.L.	101	100	0.0014	101	>10000
Nd	0.002	102	101	0.0018	102	>10000
Sm	0.1	108	101	0.004	108	699
Eu	0.6	109	101	0.009	109	175
Gd	D.L.	107	101	0.006	107	>10000
U	1.5	94	99	1.1	96	69
^{241}Am (γ)	D.L.	116	109	D.L.	116	>10000
^{152}Eu (γ)	D.L.	105	109	D.L.	105	>10000
^{134}cs (γ)	105	D.L.	D.L.	D.L.	105	0.95
^{244}Cm (α)	D.L.	122	116	D.L.	122	>10000
^{252}Cf (α)	D.L.	83	116	D.L.	83	>10000
^{241}Am (α)	D.L.	121	121	D.L.	121	>10000

Table S9: Data from the extractions from simulant HAR recorded by Modolo *et al.*[40] Balance is the mass balance of all streams and D.L. = below Detection Limit.

	distribution ratio; [CDTA] (M)		
element	0.01	0.05	0.1
^{241}Am(III)	65	42	40
^{239}Pu(IV)	60	35	32
Zr(IV)	7.7	1.2	0.2
Pd(II)	0.5	0.05	0.02

Table S10: Distribution ratios for the EURO-GANEX solvent composition of 0.2 M DMDOHEMA, 0.5 M TODGA in Exxsol-D80 as measured by Bell *et al.*[62] Aqueous phase comprised of 3 M HNO_3, [Pu] = 0.071 M, [Am] = 0.42 mM, HAR elements and CDTA.

Section 3: Tables of flowsheet test data

Element	Feed (counts/5 min)	Recoveries (% Feed)		% Material Balance	DF w.r.t. ^{241}Am
		Product	Raffinate		
^{241}Am	7511±350	>99.9	<0.01	102.9	-
^{152}Eu	7450±325	>99.9	<0.01	101.3	0.98±0.09
^{85,89}Sr	6226±250	<0.01	>99.9	97.4	2990±235
^{59}Fe	6025±275	<0.01	>99.9	99.7	1997±135
^{137}Cs	3940±285	<0.01	>99.9	103.1	3918±380
^{106}Ru	1415±85	<0.01	>99.9	96.1	1407±150
^{99}Mo	6530±450	<0.01	>99.9	94.8	3250±375
^{109}Pd	2385±215	<0.01	>99.9	103.1	1185±225
^{95}Zr	1780±125	<0.01	>99.9	95.8	1150±125

Table S11: γ counted recovery rates of selected elements from mixer-settler studies performed by Gujar *et al.*[51]

Element	Feed (ppm)	Recoveries (% Feed)			DF Extraction
		Raffinate	An/Ln	Org-out	
Rb	51	>99.9	<0.1	-	1.0
Sr	113	>99.9	<0.1	-	1.0
Y	72	<0.1	>99.9	-	1600
Zr	538	>99.9	<0.1	-	1.0
Mo	342	>99.9	<0.1	-	1.0
Ru	153	~82	~1	~17	1.2
Rh	28	>99.9	<0.1	-	1.0
Ag	4	>99.9	<0.1	-	1.0
Pd	172	>99.9	<0.1	-	1.0
Te	85	>99.9	<0.1	-	1.0
Cs	415	>99.9	<0.1	-	1.0
Ba	407	>99.9	<0.1	-	1.0
La	224	<0.1	>99.9	-	>1000
Ce	410	<0.1	>99.9	-	5400
Pr	202	<0.1	>99.9	-	12000
Nd	720	<0.1	>99.9	-	15000
Sm	124	<0.1	>99.9	-	1600
Eu	22	<0.1	>99.9	-	>1000
Am	110	<0.01	>99.99	-	41000
Cm	42	<0.01	>99.99	-	40000

Table S12: Selected results of the hot test as published by Magnusson *et al.*[50]

Element	% in Raffinate	% in loaded solvent	% in An product	% in Ln product	% in spent solvent	$DF_{feed/raff.}$
^{241}Am	<0.1	99.9	99.9	0.1	<0.1	2600
^{244}Cm	0.1	99.9	99.7	0.1	0.1	750
^{152}Eu	0.1	99.9	0.1	99.8	0.1	1100
La	<0.1	99.9	0.1	99.5	0.4	23000
Ce	<0.1	99.9	D.L.	99.7	0.3	570000
Pr	<0.1	99.9	D.L.	99.7	0.36	220000
Nd	<0.1	99.9	D.L.	99.8	0.2	39000
Sm	<0.1	99.9	D.L.	99.9	0.1	3400
Eu	0.3	99.7	D.L.	99.7	0.1	380
Gd	<0.1	99.9	D.L.	99.9	0.1	49000
Y	<0.1	99.9	D.L.	99.9	D.L.	47000
Ru	84.0	16.0	0.4	0.9	14.7	1.2
Pd	97.2	2.8	0.0	2.8	<0.1	1.0
Zr	99.9	0.1	0.1	<0.1	<0.1	1.0
Mo	99.9	0.1	0.1	<0.1	<0.1	1.0
Sr	99.7	0.3	0.3	<0.1	D.L.	1.0
Rh	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Rb	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Ba	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Cs	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Te	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Cd	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Sn	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Sb	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Ag*	52.1*	D.L.	D.L.	D.L.	D.L.	1.0

Element	% in Raffinate	% in loaded solvent	% in An product	% in Ln product	% in spent solvent	$DF_{feed/raff.}$
Cu	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Ni	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Cr	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Fe	99.9	D.L.	D.L.	D.L.	D.L.	1.0
Na	99.9	D.L.	D.L.	D.L.	D.L.	1.0

Table S13: Data from the extractions from simulant HAR recorded by Wilden *et al.*[53] Balance is the mass balance of all streams. D.L. = below Detection Limit. * = poor mass balance but belief is that it was not extracted at all.

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