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Innovative SANEX process for trivalent actinides separation from PUREX raffinate

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1. Abstract

Recycling of nuclear spent fuel and reduction of its radiotoxicity by separation of long-lived radionuclides would definitely help to close the nuclear fuel cycle ensuring sustainability of the nuclear energy. Partitioning of the main radiotoxicity contributors followed by their conversion into short-lived radioisotopes is known as partitioning and transmutation strategy. To ensure efficient transmutation of the separated elements (minor actinides) the content of lanthanides in the irradiation targets has to be minimised. This objective can be attained by solvent extraction using highly selective ligands that are able to separate these two groups of elements from each other.

The objective of this study was to develop a novel process allowing co-separation of minor actinides and lanthanides from a high active acidic feed solution with subsequent actinide recovery using just one cycle, so-called innovative SANEX process. The conditions of each step of the process were optimised to ensure high actinide separation efficiency. Additionally, screening tests of several novel lipophilic and hydrophilic ligands provided by University of Twente were performed. These tests were aiming in better understanding the influence of the extractant structural modifications onto An(III)/Ln(III) selectivity and complexation properties.

Optimal conditions for minor actinides separation were found and a flow-sheet of a new innovative SANEX process was proposed. Tests using a single centrifugal contactor confirmed high Eu(III)/Am(III) separation factor of 15 while the lowest $SF_{Ln/Am}$ obtained was 6,5 (for neodymium). In addition, a new masking agent for zirconium was found as a substitution for oxalic acid. This new masking agent (CDTA) was also able to mask

palladium without any negative influence on An(III)/Ln(III). Additional tests showed no influence of CDTA on plutonium present in the feed solution unlike oxalic acid which causes Pu precipitation. Therefore, CDTA was proposed as a Zr masking agent in GANEX process where high content of Pu is expected. In this so called GANEX (Group Actinide Extraction) process all actinides are separated as a group from the lanthanides and fission products.

Within the new ligands delivered by University of Twente four water-soluble and four lipophilic ones showed good An(III)/Ln(III) complexation thus they deserve further studies with possible implementation in already existing or new processes.

Zusammenfassung

Die Rezyklierung von gebrauchtem Kernbrennstoff und die Reduktion seiner Radiotoxizität durch die Abtrennung von langlebigen Radionukliden werden sicherlich helfen, den nuklearen Brennstoffkreislauf zu schließen und so die Nachhaltigkeit der nuklearen Energieerzeugung sicherzustellen. Die Abtrennung (engl. Partitioning) der hauptsächlich zur Radiotoxizität beitragenden Bestandteile und ihre anschließende Umwandlung in kurzlebige Radioisotope (Transmutation) ist als „Partitioning and Transmutation“ Strategie bekannt. Um eine effiziente Transmutation der abgetrennten Elemente (minore Actinide) zu ermöglichen, muss der Inhalt an Lanthaniden in den Bestrahlungstargets minimisiert werden. Dieses Ziel kann durch Flüssig-Flüssig-Extraktion erreicht werden, wobei hochselektive Liganden verwendet werden, um die beiden Elementgruppen voneinander zu trennen.

Das Ziel dieser Arbeit war die Entwicklung eines neuen Prozesses, der die Co-Abtrennung von minoren Actiniden und Lanthaniden aus einer hochradioaktiven, säurehaltigen Ausgangslösung mit anschließender Rückgewinnung der Actiniden in einem einzigen Abtrennprozess, der sogenannte „innovative-SANEX Prozess“, ermöglicht. Die Bedingungen für jede Stufe des Prozesses wurden optimiert, um eine hohe Effizienz der Actinidenabtrennung zu erreichen. Zusätzlich wurden verschiedene neue lipophile und hydrophile Liganden, die von der Universität Twente bereitgestellt wurden, in Screening Tests untersucht. Das Ziel dieser Tests war es, den Einfluss von strukturellen Modifikationen an den Extraktionsmitteln auf die An(III)/Ln(III) Selektivität und ihre Komplexierungseigenschaften, besser zu verstehen.

Es wurden optimierte Bedingungen für einen Abtrennprozess von minoren Actiniden gefunden, und ein Flussschema für einen „innovative-SANEX Prozess“ wurde vorgeschlagen. Versuche mit einer einzelnen Zentrifugal-Kontaktor-Stufe bestätigten einen hohen Eu(III)/Am(III) Abtrennfaktor von 15, mit dem niedrigsten Ln/Am Abtrennfaktor von 6,5 für Neodym. Zusätzlich wurde ein neues Maskierungsmittel für Zirkonium, als Ersatz für Oxalsäure, gefunden. Mit diesem neuen Maskierungsmittel (CDTA) konnte auch Palladium maskiert werden, ohne einen negativen Einfluss auf die An(III)/Ln(III) Abtrennung. Weitere Versuche zeigten, dass CDTA auch keinen negativen Einfluss auf das in der Ausgangslösung enthaltene Plutonium hat, anders als Oxalsäure, das mit Plutonium ausgefällt wird. Deshalb wurde CDTA als Zirkonium-Maskierungsmittel in einem GANEX-Prozess vorgeschlagen, in dem hohe Plutoniumgehalte erwartet werden. In diesem sogenannten GANEX-Prozess (Group Actinide Extraktion) sollen alle Actiniden als Gruppe von den Lanthaniden und anderen Spaltprodukten abgetrennt werden.

Unter den neuen Liganden, die von der Universität Twente bereitgestellt wurden, zeigten vier wasserlösliche und vier lipophile Liganden gute An(III)/Ln(III) Komplexierungseigenschaften, so dass weitergehend untersucht werden sollte, ob diese Liganden möglicherweise in neuen oder bereits entwickelten Prozessen eingesetzt werden können.

I dedicate this work to my parents for all their support

2. Introduction

In the 1940s the total world population has started its fast increase, which is estimated to be the biggest increase in human history. The reason of this fast growth was due to lessening of the mortality rate in many countries, medical advances and massive increase in agricultural productivity attributed to the 'Green Revolution'[1] – an increased agricultural production resulted from research, development and technology transfer initiatives. During the last 10 years the world population has increased by more than 12%. At the same time the world primary energy consumption has seen an increase of 20% with leading Asia where 4.8 times higher increase was observed compared to Europe. However, the world electricity consumption has increased by 31.5% again led by Asia which increased its consumption by 60%.[2]

According to the reference scenario of International Energy Agency (IEA), the world demand for primary energy will increase by 50% between 2007 and 2030 and its electricity consumption will nearly double.[3]

Electricity is of paramount importance for economic development with the best example of China and India which are the leading countries in energy consumption 'per capita'. Nevertheless, the consumption of fossile fuels, which are the primary sources of electricity at present, has to be reduced to preserve the environment and irreplaceable resources for future generations. The IEA projects, that even with continuous subsidy and research support, new renewable sources of energy can provide only around 6% of world electricity by 2030.[4] The main challenge is not to choose between fossil, nuclear or renewable sources but to make sure that all sources and energy-saving means are used efficiently taking into account their environmental, social and economic characteristics.

The nuclear energy based on the fission of uranium contributes to diversity and security of energy supply. It is considered to have a very small '*carbon foot-print*' with 2.5 – 5.7 grams of carbon emission per kWh of electricity generated compared to 100 – 350 g CO_2/kWh for fossil fuel chains and 2.5 – 75 g CO_2/kWh for various renewable energy chains.[5] Moreover, uranium has no significant use other than energy source. The nuclear power plants operating now already achieve higher efficiency than reactors of previous generations by higher burn-ups of the fuel. In the longer term, advanced systems such as fast neutron systems, which are under development, will offer more drastic improvements through recycling of fissile materials. The reduction of waste volume and radiotoxicity are expected to be obtained with the development of Generation IV nuclear systems, which would allow closing the fuel cycle.

The status of the nuclear industry at the beginning of 2011 reported 442 nuclear reactors in operation and 65 under construction. Countries such as Czech Republic, Finland, Japan and Korea were planning to build new reactors within the next 20 years. Germany and Spain prolonged the operational life-time of their existing nuclear reactors.[6] With the recently active environmental movements and an increase on energy consumption the nuclear industry seemed to be heading towards its *Renaissance*. The recent incident in Fukushima nuclear power plant on 11th of March 2011, resulted from the enormous earthquake followed in consequence by tsunami, has significantly influenced the world perspective on nuclear energy. In response Germany temporarily shut down the country's seven oldest nuclear power plants. Switzerland has suspended its plans to build and replace ageing plants to reassess safety standards at existing ones. The United Kingdom has ordered an official investigation into nuclear power while the European Energy Council decided to develop a 'stress test for nuclear power plants' throughout the European Union. However, countries like Finland, Poland, Lithuania, Slovakia, the Czech Republic, Bulgaria, Romania and Turkey still intend to build new nuclear power plants.[7]

2.1. Nuclear fuel cycle

At the present time, the most common type of operating nuclear reactors are thermal reactors which include Light Water Reactors (LWR): pressurised water reactors (PWR) and boiling water reactors (BWR). Thermal type means that the fission is inducted by low energy, thermal moderated neutrons. The fresh fuel in thermal reactors consists of uranium dioxide containing 96.5% ^{238}U as a major component, and ~ 3.5% of the fissionable ^{235}U. In an operating reactor ^{235}U fissions by collision with a thermal neutron and splits into two different fission products (FP) of which the residual masses are lower than the parental nuclide. This mass difference (called binding energy) is converted into released energy of about 200MeV per every atom that fissions. In comparison the burning of fossil fuel is based only on the breaking of chemical bonds resulting in just 4eV per CO_2 released. Besides the fission of ^{235}U, other competing processes contribute into the final composition of the spent nuclear fuel, such as neutron capture(s) and radioactive decay of the fuel original and arising nuclides (Figure 1). The example of the spent fuel composition is shown in Table 1.

Table 1. Typical components of spent nuclear fuel coming from light water reactor (LWR-PWR, burn rate of ~33GWd/tone).

Contribution (%)	Component	Disposition
95.6	Uranium	Recycled or disposed as low-level waste
3	Stable or short lived fission products	Non problematic disposal
0.3	Major fission products	Caesium and strontium as main near-term heat sources – vitrification with the rest of FP
0.1	Long-lived fission products	Mainly iodine and technetium – storage or removal and transmutation
0.9	Plutonium	Prospective separation and burning as fuel (MOX)
0.1	Long-lived minor actinides	Prospective separation and fission with fast neutrons

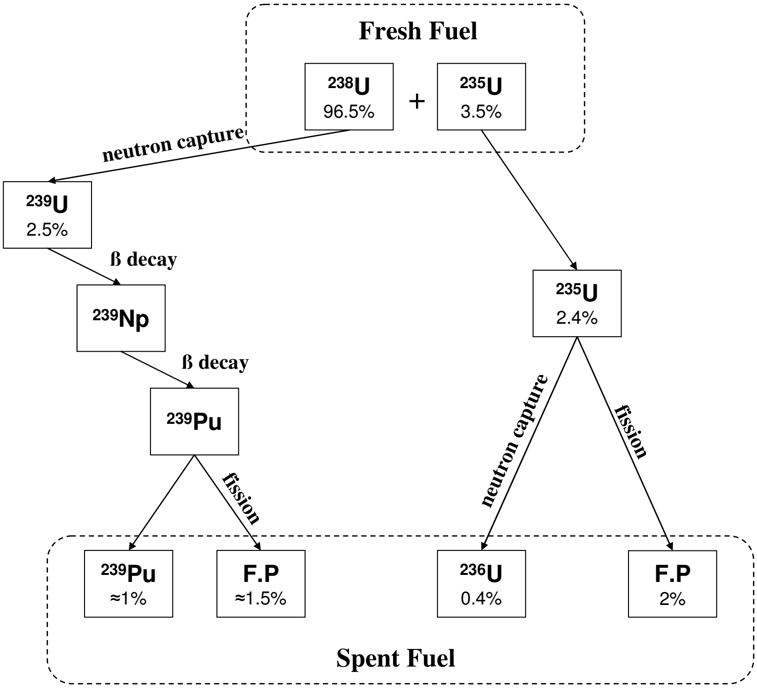

Figure 1. The reactions involved in spent fuel generation from fresh enriched uranium fuel (LWR- PWR, burn rate of ~33GWd/tone) with a percentage of adequate components regarding the total mass of the fresh fuel.

The nuclear spent fuel removed from the nuclear reactor can be managed in two different scenarios. The first concept called *once through* considers the storage of the spent fuel without any recycling. In this concept the fuel has to be ‘cooled down’ in an interim storage for about 30 – 40 years before being placed in the final deep repository. The spent fuel must be safely isolated from the environment for more than 200,000 years until the radiotoxicity of a natural uranium ore is reached. This strategy places the largest demand on capacity of repository and the biggest proliferation concerns since after 50 -100 years the decayed fission products (mainly alpha radionuclides left) allow access and retrieval of plutonium. The only advantage is that in the near-term dangerous and uneconomical handling and reprocessing of spent fuel is avoided. Currently, this concept is practiced in the United States, Sweden, Finland, Germany, Spain, Canada and South Korea.

The second concept considers reprocessing of the spent fuel to recover uranium and plutonium which can be used to fabricate new fuel, so-called mixed oxide fuel (MOX). The recovery of Pu and U is done in the PUREX process (**P**lutonium **U**ranium **R**ecovery by **Ex**traction) which is currently used in La Hague (France), Sellafield (United Kingdom), Mayak (Russia) and Rokkasho (Japan). The waste coming from the PUREX process, High Level Liquid Waste (HLLW), is solidified by vitrification and stored for a long time (similar as in the once through concept).

2.2. Radiotoxicity and time required for the waste storage

The contribution of individual components on the total radiotoxicity[a] of spent nuclear fuel and its evolution in time is shown in Figure 2. During the first 300 years after removal of nuclear fuel from a reactor, the main contributors to the total radiotoxicity and thermal burden of High Level Waste (HLW) are short-lived radionuclides such as ^{90}Sr and ^{137}Cs. Between 300 – 500 years the majority of short-lived fission products is decayed and the predominant radiotoxicity is due to the decay of actinides and to some extent long-lived fission products (e.g. ^{99}Tc, ^{129}I, ^{79}Se, ^{93}Zr, ^{135}Cs, ^{126}Sn). After more than 200,000 years, the radiotoxicity of spent fuel (without re-processing) reaches the level of uranium-ore, which is regarded as nonhazardous to the environment. The separation of U and Pu from the spent fuel reduces this time to 10,000 years which is still significantly long considering the assurance of safety in deep geological repositories. However, the removal of minor actinides (MA) and their transmutation reduces it further to 300 – 500 years.

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[a] Measure of how nocuous a radionuclide is to health. The type and energy of rays, absorption in the organism, residence time in the body, etc. influence the degree of radiotoxicity of a radionuclide.

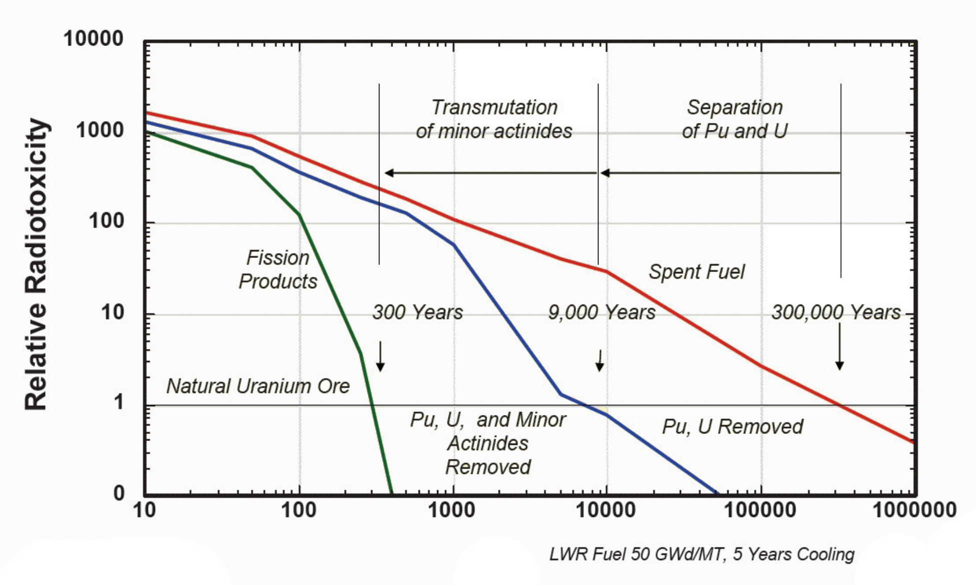


Figure 2. Evolution of spent nuclear fuel radiotoxicity in time and the main contributors.[8]

2.3. Partitioning and Transmutation

In a nuclear spent fuel plutonium and MA are the main long-term contributors to its total radiotoxicity. Their removal by different chemical processes (partitioning) significantly reduces the burden on a geological disposal. The separated MA can be transformed in dedicated reactors into short-lived or stable isotopes by neutron capture imposing their nuclear fission (transmutation). This concept called Advanced Fuel Cycle (AFC) considers further reprocessing of the HLLW by removal and destruction of the minor actinides and the long-lived fission products through partitioning and transmutation (P&T). This includes new fuel cycle concepts with minimum waste release combined with proliferation resistance. One of the new concepts in AFC is the use of naturally abundant isotope of thorium, ^{232}Th, which after transformation into ^{233}U (by neutron capture and two β^- decays) can be used as a fuel.

2.4. Fast Reactors

Since only the fissile ^{235}U isotope content in fresh LWR-type fuel can produce energy when undergoing fission, the initial motivation for fast reactors (FR) was to breed ^{239}Pu from ^{238}U to maximise the uranium fuel utilisation, especially considering the abundance of ^{235}U in natural uranium ore (≈ 0.72%). The fissile ^{239}Pu isotope is also generated in LWR-type reactors during the reactor cycle (Figure 1) and its partial fission is responsible for about 40% of the total energy gained in this type of reactors.[9] In order to exploit more energy, Pu could be produced in fast breeder reactor (FBR) by neutron capture on uranium content in a 'blanket' around the core. It is estimated that about 70% of ^{238}U can be converted into ^{239}Pu using fast neutron spectrum. Typical FR-type fuel consists of either highly enriched ^{235}U or a mixture of ^{239}Pu and ^{238}U, although the Pu loading has to be at least 20 – 30% due to its rather low fast neutron absorption cross-section. This concept of breeding Pu was developed during the time when the thermal reactors were used for commercial production of power, as in the 1980s a major crisis was expected concerning shortage of uranium. However, the crisis did not materialise hence the need for fast reactors to breed plutonium was neither compelling nor economical.

The P&T strategy anew brought an interest in fast reactor technology. The MA transmutation is not as efficient using thermal neutrons compared to fast neutron spectrum, therefore fast neutron devices are much preferred for the conversion of plutonium and the complete destruction of all of the minor actinides.

The most considered device for fast neutron spectrum production is a fast reactor configured to operate as actinide 'incinerator' instead of 'breeder' and the accelerator-driven system (ADS). The FR technology is relatively mature, after the experience gained with Pu breeders, whereas ADS is a new concept. ADS consists of a high power proton accelerator to produce a high energy proton beam which releases neutrons when colliding with a subcritical target. The released neutrons induce the fission of the actinides and transmute the fission products contained in a solid form. Additionally, a chemical processing plant supports the ADS fuel cycle system.

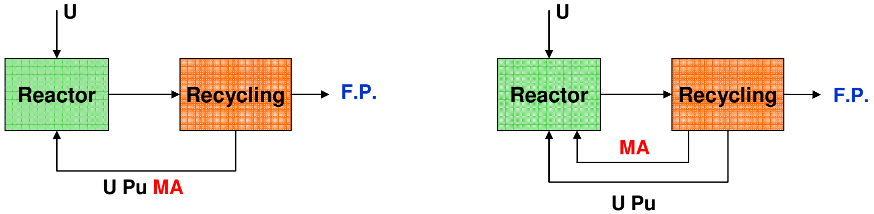
The advantage of ADS compared to other technologies, where the reactor operates in critical mode, is its subcriticality. When the proton beam is off in ADS, no neutrons are produced to sustain the nuclear reaction.

The waste transmutation programs are under development in the countries leading in nuclear technology: France, Japan, USA as well as by the European Organisation for Nuclear Research (CERN, formally Conseil Européen pour la Recherche Nucléaire).

2.5. Nuclear fuel cycle strategies including P&T

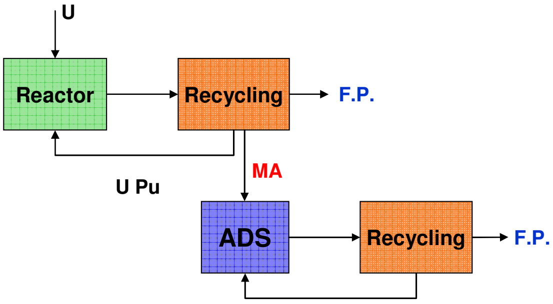
Various concepts are under development for MA recycling, however there are three main recycling strategies which are taken under consideration (Figure 3). In the heterogenous recycling U and Pu are separated first, followed by separation of MA. The recovered U and Pu are re-directed to the reactor as a new fuel (MOX) with MA as separate targets (blankets) for transmutation. However, this concept increases the proliferation risk due to the separation of Pu from MA. The homogenous recycling avoids this risk because the MA are separated together with U and Pu from HLW. The new fabricated fuel (recovered U, Pu and MA) has a homogenous core and is characterised by a low MA content (1 – 2 %). Both heterogeneous and homogenous recycling is dedicated only to generation IV reactors (GEN IV).

The radiotoxicity of the recovered MA (Np, Am and Cm) can be significantly reduced by their transmutation into short-lived or stable nuclides in ADS or in a fast reactor. In this strategy called *double-strata* the MA are transmuted separately in dedicated ‘burners’ where Pu and MA content is ~50%. After transmutation and dissolution of the targets, the arising



Homogenous recycling

Heterogenous recycling



Recycling in Accelerator Driven System (double strata)

Figure 3. Different HLW recycling strategies (ADS – Accelerator Driven System).

fission products can be separated for further disposal and the recovered Pu and MA is again re-directed to ADS system (see Figure 3) as fuel.

Currently, there is no technology which can selectively transmute minor actinides to a meaningful degree for waste management as long as they are contained in reprocessed spent nuclear fuel. Prior to the transmutation the elements possessing large neutron absorption cross-section (e.g. lanthanides) must be removed as their presence would significantly decrease the transmutation yield.

All the processes for MA separation can be organised in just two categories: dry and wet processes. Dry processes (*pyro-processes*) are based on chemical operations at high temperature to extract or separate metals from different sources. This method allows recovering the radioactive elements of interest directly in the halogenide form. The metallic fuel can be easily used in fast reactors. Moreover, in pyro-processes due to higher radiation stabilities of non-aqueous reagents a short-cooled and high burn-up fuel can be recycled. Wet or aqueous processes (*hydro-processes*) are mainly employed for oxide type fuels. They involve liquid-liquid extraction (*solvent extraction*) which has an advantage of easy implementation at industrial scale as a continuous process. Hydrometallurgical processes rely on the dissolution of spent nuclear fuel in an acidic solution (usually nitric acid) followed by extraction of metals of interests.

2.6. Fundamentals of solvent extraction

Liquid-liquid extraction is a method relied on selective extraction of species from one solvent into another immiscible solvent enabling the separation of various elements previously mixed together (Figure 4). Organic and aqueous liquid solvents are used, and the separation of phases is based on a difference of their density. The organic solvent is generally composed of a mixture of organic diluents with one or several extracting ligands to facilitate the extraction. As for nuclear applications, preferred diluents are aliphatic hydrocarbons (e.g. odourless kerosene, n-dodecane) due to their good hydraulics, low aqueous solubility and resistance to radiation degradation.[10-11]

In order to increase the diffusion of the species from the bulk to the interface, the organic and aqueous phase are mixed together which increases the exchange surface area (small droplets). The mixing is achieved usually by means of mixer-settlers, annular centrifugal contactors or

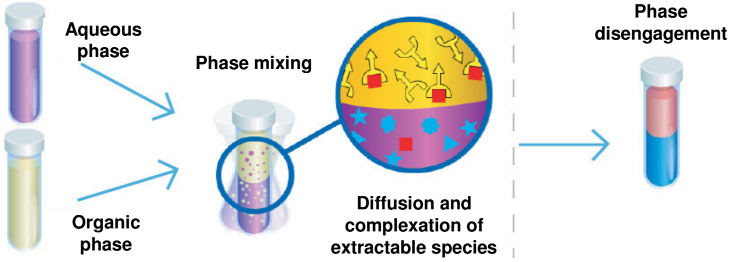


Figure 4. Concept of solvent extraction

pulsed columns.[12] After the chemical equilibrium is achieved the phases are separated from each other either by gravity or centrifugal forces.

Extraction mechanisms

The extraction of a given metal cation M^{n+} into an organic solvent can proceed through three different mechanisms:

- *Solvate extraction* takes place when a neutral extracting agent (L) co-extracts the metal cation (M^{3+}) together with the anion(s) (A^-) to compensate the positive charge of extracted metal, forming a neutral complex in the organic phase. In case of trivalent actinides or lanthanides the reaction equation is as follows:

$$M^{3+} + 3A^- + \overline{nL} \xleftrightarrow{K_{ex}} \overline{MA_3L_n} \qquad \text{Eq 1}$$

  The bar over the species denotes that they are present in an organic phase and K_{ex} is the stability constant of the described extraction reaction.

- *Anion exchange* occurs when a positively charged extractant forms neutral complex with a negatively charged ion pair metal-anion (usually formed in an aqueous feed).

$$\overline{L_3N} + X^- + H^+ \xleftrightarrow{K_{ex}} \overline{L_3NH^+, X^-} \qquad \text{Eq 2}$$

  where X^- – transferable as anionic metallic complex $(MA_n)^{m-}$

- *Cation exchange* occurs when the metal cation is complexed by the acidic extractant (HL) with a release of a proton(s).

$$M^{3+} + n(HL)_2 \xleftrightarrow{K_{ex}} \overline{ML_3(HL)_{2n-3}} + 3H^+ \qquad \text{Eq 3}$$

Solvent extraction has become the reference technique for spent nuclear fuel reprocessing at industrial scale for following reasons:[10-11]

- The flexibility in the formulation of the chemical systems for separation

- The desired separation and purification are easily obtained by implementation of extraction, scrubbing and stripping steps
- The continuity of the process in case of all-liquids operations
- Low criticality risk as the safety geometric requirements can be easily implemented
- Low energy input for running hydrometallurgical processes (room temperature, normal pressure)

However, solvent extraction methods allow to separate plutonium from the spent nuclear fuel cycle which is a major issue concerning proliferation. In addition, use of flammable liquids and disposal of spent solvents has to be also taken into account, while developing a new partitioning process based on this technique.

2.7. Separation of trivalent actinides from trivalent lanthanides

As mentioned previously prior to transmutation of MA the radionuclides possessing a large neutron absorption cross-section, such as lanthanides, must be removed from the MA. The separation of transplutonium actinides (5*f* elements) from lanthanides (4*f* elements) is not an easy task due to the similarities between them[13-17]. Both element groups are in trivalent oxidation state in acidic aqueous solutions. The cation radii decrease along the series with increasing the atomic number resulting in similar cation radii for certain An(III) and Ln(III). In the first coordination sphere, hydratation number starts from 9 at the beginning of the series and ending with 8 at the end of the series. They also possess hard electron-acceptor properties according to Pearson's theory of hard and soft acids[18] thus electrostatic interactions with oxygen-bearing ligands such as –C=O or –P=O groups are in favour. However, it is assumed that the slightly greater spatial extension of the 5*f* orbitals is responsible for the existence of some degree of covalence in bonding interactions between An(III) and soft bases (S or N bearing ligands)[19-22]. This feature is a key which opens possibilities to separate An(III) from Ln(III) thus for successful feasibility of the P&T strategy.

The requirements for a novel solvent extraction process for An(III) separation are:[10-11]

- assurance of high An(III) recovery yields
- assurance of high An(III) decontamination factors (DFs) towards other elements present in the feed stream (especially those possessing large neutron cross-section).
- minimisation of changes in highly active feed composition in order to avoid precipitation which would decrease the An(III) recovery yield
- minimisation of secondary waste creation
- assurance of fast mass transfer to shorten the process time and allow the use of small volume contactors

2.8. State of art in the minor actinide partitioning

The countries concerned with the reprocessing of spent nuclear fuel for decades were dissolving the fuel in nitric acid generating the Highly Active Waste (HAW). This liquid waste is undergoing the PUREX process and thereafter is currently stored as a liquid in tanks or has been vitrified or cemented. The PUREX process[23-26] aiming in uranium and plutonium partitioning can be modified in order to additionally separate neptunium from dissolved spent nuclear fuel.[27-28] Therefore, the main contributors to the radiotoxicity of HAW are minor actinides: americium and curium. Due to the complexity of the initial HAW still containing about 1/3 of the periodical table, it was easier to design several different processes to achieve MA separation in a few subsequent steps. Furthermore, in earlier times of MA partitioning concept, there was no need to separate MA from lanthanides as the main objective was to make the residual waste free from alpha radionuclides for shallow land disposal. Consequently, most of the developed processes were designed to extract these two groups of elements without separating them from each other. The advanced fuel cycle however, brought a need to additionally separate lanthanides from MA to achieve an efficient transmutation of the latter ones.

The main drawback of having a process for MA separation consisting of several cycles (*multi-cycle process*) is the generation of large amount of secondary waste. Additionally, the complexity of such expanded process makes it economically less favourable (synthesis of several extractants and their clean-up cycles etc). The way to avoid most of these problems is to design a process, where in one cycle using just one extractant (or mixture of two extractants) the selective separation of MA with high yield could be obtained. The processes based on this idea are called *one-cycle* processes (Figure 5).

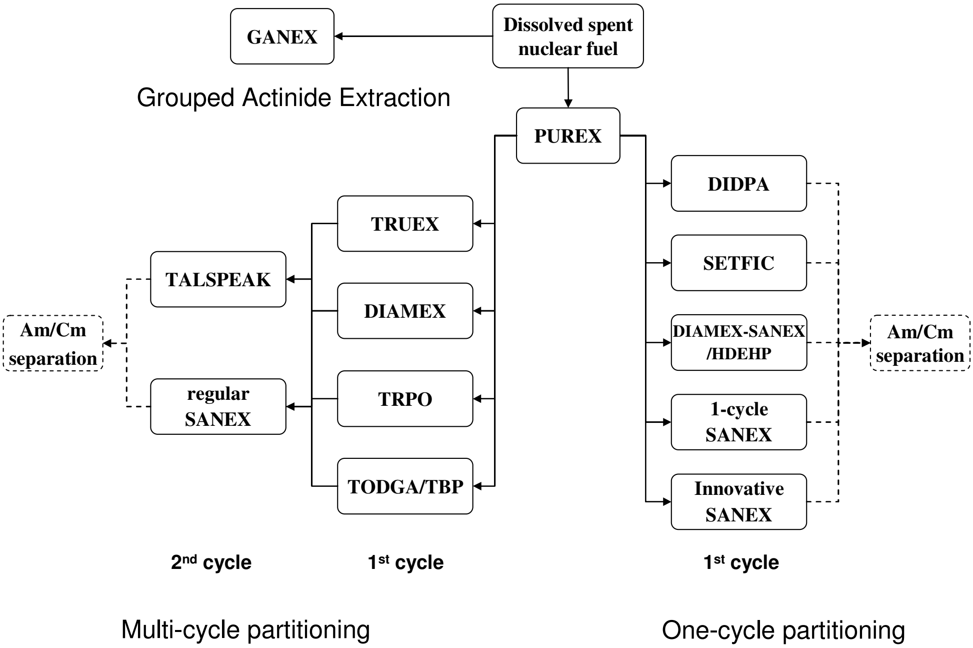


Figure 5. Some of the developed processes and new concepts to achieve MA separation from spent nuclear fuel.

2.9. Multi-cycle processes

The separation of MA using multi-cycle processes is achieved usually within two separate cycles. In the first cycle the minor actinides are co-extracted together with lanthanides (utilising their similar chemical and physical properties) to be thereafter separated from each other in the second cycle. The separation of trivalent americium from curium after the second cycle is optional and could be performed using e.g. LUCA process.[29-30]

Minor actinides + lanthanides co-extraction (1st cycle)

TRUEX process[31-32] (**Tr**ans**u**ranium **Ex**traction) developed by American researchers allows to co-extract An(III) together with Ln(III) (also tetra- and hexavalent elements) from HAW (e.g. PUREX raffinate). The mentioned two groups of elements are extracted by a neutral extractant n-Octyl-phenyl-N,N'-di(iso)butyl-carbamoyl-methyl phosphine oxide (CMPO) mixed with tributylphosphate (TBP) from acidic media, while fission products (F.P.) stay in the aqueous feed. Subsequently, the An(III) are stripped together with Ln(III) using low concentrated nitric acid. The process is characterised by high extractability of the mentioned elements. However, the presence of phosphorus in the extractant structure makes it not fully incinerable (does not follow the CHON principle – **C**arbon, **H**ydrogen, **O**xygen, **N**itrogen).

In the 1980s the Commissariat à l'Énergie Atomique (CEA) proposed the use of diamide extractant N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide (DMDBTDMA) for separation of An(III) + Ln(III) from PUREX raffinate in a process called DIAMEX (**Diam**ide **Ex**traction).[33] The trivalent actinides and lanthanides are extracted from an acidic feed solution coming from PUREX process. Subsequently, the An(III) and Ln(III) are stripped into the aqueous phase using diluted nitric acid. Since 1999 the reference molecule for DIAMEX process has become N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA)[34-35] enhancing the extractive properties toward trivalent elements and shortens the degradation compounds formed by acidic hydrolysis and radiolysis.[36] The main drawback is the partial co-extraction of Pd and Ru with MA.

The Chinese researchers developed in the 1990s a process called TRPO[37-41] where a mixture of trialkylphosphine oxides is used to co-extract An(III) + Ln(III) from a solution of acidity < 1 mol/L HNO_3. The following stripping of the extracted elements is achieved using 5.5 mol/L HNO_3. The main drawback of this process is the necessity of diluting the feed (HLLW) in order to reduce its acidity and the use of high concentrated HNO_3 to strip An(III)/Ln(III) which complicates the possible subsequent An(III)/Ln(III) partitioning step.

Recently, a new process for recovery of trivalent actinides from PUREX type raffinate was developed in Germany utilizing a novel Japanese extractant N,N,N',N'-tetraoctyl-3-

oxapentanediamide (TODGA).[42-44] A very efficient extraction of An(III) and Ln(III) from acidic medium is performed in a first step, followed by their stripping using diluted nitric acid.[45] The organic solvent capacity was later improved by the addition of TBP,[46-48] an organic phase modifier, thus the process is called TODGA/TBP.[47-48]

Selective minor actinides extraction (2nd cycle)

The two processes described below aim in selective trivalent actinide separation (Am, Cm) from raffinate resulted from one of the 1st cycle processes (e.g. DIAMEX).

In the late 1960s at the Oak Ridge National Laboratory (USA) a process for partitioning of An(III) was developed. This TALSPEAK (**T**rivalent **A**ctinide-**L**anthanide **S**eparation by **P**hosphorus reagent **E**xtraction from **A**queous **K**omplexes) process[49-50] rely on the partition of Ln(III) and An(III) between an acidic organophosphorus extractant di(2-ethylhexyl)-phosphoric acid (HDEHP) and an aqueous phase buffered with a carboxylic acid and containing a polyaminocarboxylic acid complexant. Under these conditions Ln(III) are extracted while An(III) stay in the aqueous phase complexed by polyaminocarboxylic acid. As main drawbacks of this process the necessity to adjust pH of the feed solution, a limited solvent loading of metal ions and difficult solvent clean-up has to be mentioned.

In 1995 a new process called CYANEX 301 utilising dialkyldithiophosphinic acid was proposed for An(III)/Ln(III) separation by Chinese researchers.[51] At high initial pH (3 – 5) of the feed solution the sulphur-containing ligand extracts An(III) more efficiently compared to Ln(III) with a very high separation factor. The feed pH adjustment together with a complicated solvent clean-up are the weak points of this process. A few years later Modolo and Odoj[52-53] developed a process where a synergistic effect of aromatic dithiophosphinic acid and trioctylphosphine oxide (TOPO) allowed to achieve good separation of An(III) from Ln(III) at higher acidities of the feed solution (up to 1.5 mol/L) compared to the Chinese

CYANEX 301 process. The main disadvantage of this process, and also for the Chinese CYANEX 301, is the presence of phosphorus and sulphur in the extractant structure (CHON principle not followed).

One of the newest European concepts called regular SANEX (**S**eparation of **A**cti**n**ide elements by **Ex**traction) utilises an extractant of very high selectivity for An(III) compared to Ln(III). The An(III) are selectively extracted from a DIAMEX-type raffinate separating them from Ln(III). Recently, a process based on this concept was developed utilising CyMe$_4$-BTBP as an extractant.[54]

Optionally, for transmutation purposes it is also useful to separate Am from Cm which facilitates co-conversion of MAn into transmutation targets. This separation, which is considered to be the most challenging type of separation process due to very similar properties of Am and Cm, was achieved in LUCA process[29-30] with relatively high separation factor.

2.10. One-cycle processes

Development of a process classified as one-cycle process is more challenging compared to multi-cycle processes. The extractant has to possess high loading capacity to co-extract An(III) together with more abundant Ln(III). Moreover, it should additionally have at least slightly higher affinity towards one of the element groups, Ln(III) or An(III) thus the separation could be enhanced using a hydrophilic complexant of high selectivity.

In the 1970s at Japan Atomic Energy Research Institute (JAERI, today JAEA – Japan Atomic Energy Agency) a process for transuranium (TRU) elements separation was proposed.[55-58] The TRU elements and Ln(III) are co-extracted from feed of low acid concentration by di-isodecyl phosphoric acid (DIDPA) mixed with TBP. Subsequently, Am and Cm are stripped by means of hydrophilic complexant followed by Ln(III) stripping using concentrated nitric acid. The last step allows removal of Np and Pu from the organic solvent.

Another Japanese process for An(III) recovery called SETFIC (**S**olvent **E**xtraction for **T**rivalent **f**-elements **I**ntragroup Separation in CMPO-**C**omplexant **S**ystem)[59-61] allows co-extraction of An(III) + Ln(III) from an acidic medium followed by An(III) stripping using hydrophilic complexant (the same as for DIDPA process). Ln(III) are stripped in the last step using diluted nitric acid. The utilised extractant is CMPO, the same as for TRUEX process.

A mixture of two different extractants utilised in one-cycle process was proposed by French researchers. The DIAMEX-SANEX/HDEHP process[36] relies on co-extraction of An(III) + Ln(III) by mixture DMDOHEMA/HDEHP from a PUREX-type raffinate. Applying salting out agent and hydrophilic complexant, An(III) are selectively stripped leaving Ln(III) in the organic solvent until the following step where they are recovered by acidity adjustment.

2.11. New European concepts under development

Within the Framework of a new European project ACSEPT (**Ac**tinide **Se**paration by **P**artitioning and **T**ransmutation)[62] three new concepts for MAn partitioning are under development. Two one-cycle processes: 1-cycle SANEX and innovative SANEX allow selective An(III) separation from PUREX-type raffinate. The first one utilises highly selective extractant to separate An(III) from F.P. by extraction. Recently proposed 1-cycle SANEX process used $CyMe_4$-BTBP/TODGA mixture as an extractant.[63] In innovative SANEX an extractant such as malonamide or diglycolamide is used to co-extract An(III) and Ln(III) followed by selective An(III) stripping using hydrophilic complexant in buffered solution. An example of this process based on TODGA was proposed by the French CEA.[64]

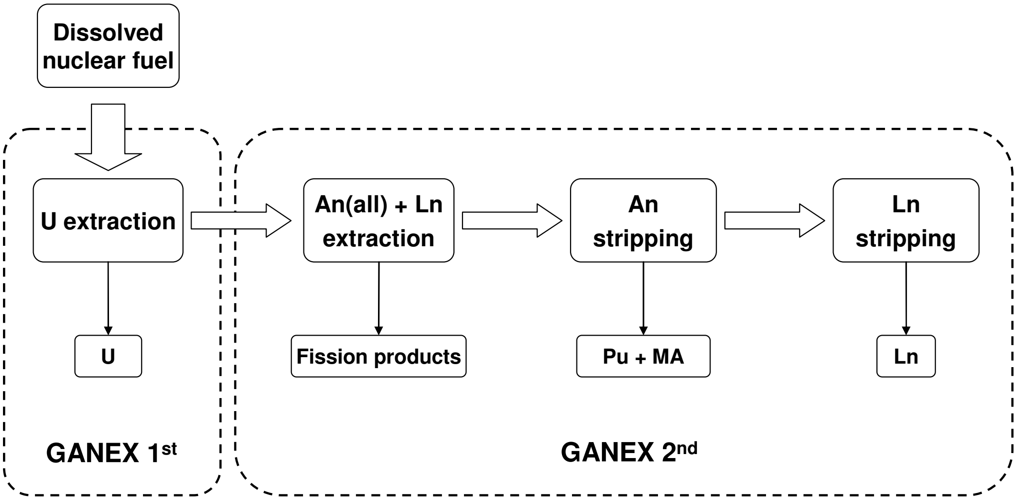


Figure 6. Group actinide separation in GANEX concept.

The third concept arose from the idea to transmute MA in fast reactors together with U and Pu thus Am and Cm could stay in the U/Pu stream hence proliferation issues would be avoided. GANEX (**G**rouped **A**cti**n**ide **Ex**traction) concept shown in Figure 6 consists of two cycles: first for separation the main bulk of uranium and second where TRU elements are separated from fission products (including lanthanides).

2.12. Scope of the work

The separation of minor actinides from trivalent lanthanides is a very challenging task. The world-wide research is focused on the improvement of already existing processes but also on new concepts which would simplify the Actinides partitioning into one robust and well-controlled process.

This work is devoted to the development of a new innovative process aiming in minor actinides recovery from Highly Active Waste solution in one cycle by liquid-liquid extraction. The objectives of the present work are:

1) To investigate the influence of a buffer, complexing agents and pH on trivalent actinide stripping in reverse-TALSPEAK process.
2) The utilisation of the optimised actinide stripping solution in DIAMEX-SANEX process based on TODGA/HDEHP solvent.
3) Determination of the optimal conditions for trivalent actinides extraction and selective stripping in innovative-SANEX process.
4) Substitution of oxalic acid for a novel zirconium masking agent.
5) Single centrifugal contactor test of the innovative-SANEX process with optimised conditions. The results of this test are necessary to design a flow-sheet for a battery of centrifugal contactors in order to test the process on a lab-scale.
6) Screening tests of novel lipophilic ligands that could be used in innovative SANEX process for An(III)/Ln(III) co-extraction and novel hydrophilic ligands that could improve the separation factors of Ln(III)/An(III) by selective complexation of An(III) in the aqueous phase.

3. Experimental Part

3.1. Procedures

3.1.1. Determination of distribution ratios and separation factors

The batch extraction experiments were performed in 2 mL glass vials. The aqueous phase was spiked with 10 µL of radiotracer (^{241}Am, ^{152}Eu, ^{244}Cm, ^{242}Cf) and contacted with 500 µL of organic phase. The mixture was shaken by an orbital shaker (IKA Vibrax Orbital Shaker Model VXR, 2200rpm) for an appropriate time until the equilibrium was reached. Separation of the phases by centrifugation was followed by sampling of 200 µL of each phase for analysis.

The radioisotopes ^{241}Am and ^{152}Eu were directly analysed using high-purity germanium spectrometer system (EG&G Ortec, Munich, Germany; equipped with the Gamma Vision software) without any additional sample preparation. The γ-lines at 59.5 keV and 121.8 keV were examined for intensity of ^{241}Am and ^{152}Eu, respectively.

The alpha nuclides ^{241}Am, ^{244}Cm and ^{252}Cf were analysed by means of alpha-spectrometry (Alpha Spectrometer Octête^{TM} PC obtained from EG&G Ortec, Munich, Germany). The aqueous samples were prepared by spreading 10 µL of the aqueous phase on stainless steel plates in order to obtain a very thin and even layer. In case of organic samples 10 µL of the organic phase was first mixed with a solution of cellulose lacquer/acetone (dilution 1:100) and then applied on a stainless steel plate. The samples were allowed to air-dry to remove the acetone followed by cellulose lacquer removal by using a lab burner blowtorch. This procedure allowed obtaining very thin layers from the organic samples with practically no organic residues that could lower the alpha measurement efficiency.

Other non-radioactive elements were analysed using ICP-MS system (Elan 6100 DRC obtained from Perkin Elmer Sciex, Roggau-Jügesheim, Germany) to determinate the concentration of each element in the organic and aqueous phase. The aqueous phases were diluted with ultrapure water (18Ω•cm^{-1}) to an appropriate concentration and measured directly. The organic phases were diluted with ultrapure water and 0.1 % Triton-X solution was added in order to disperse the organic phase in the sample homogenously.

Distribution ratios of the metals (D_M) were calculated using the following equation:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \qquad \text{Eq 4}$$

$[M]_{org}$ – concentration of the metal M in the organic phase

$[M]_{aq}$ – concentration of the metal M in the aqueous phase

Separation factors were calculated by means of equation:

$$SF_{M1/M2} = \frac{D_{M1}}{D_{M2}} \qquad \text{Eq 5}$$

D_{M1}, D_{M2} – distribution ratios of metal M1 and M2

The mass balances of the measurements were 100 ± 3% for gamma and 100 ± 5% for alpha and ICP-MS measurements. Distribution ratios between 0.01 and 100 exhibit a maximum error of ±5%. The maximum and minimum distribution ratios arising from the detection limits in the aqueous and organic phases were 1000 and 0.001, respectively.

3.1.2. High Active Raffinate solutions

The composition of the synthetic High Active Raffinate (HAR) solution from the PUREX process used in the batch tests is shown in Table 2. It was prepared by a specific dissolving strategy, mainly based on the use of metal nitrate salts. It corresponds to a PUREX raffinate with a volume of 5000L/t UOx fuel with initial ^{235}U enrichment of 3.5%, thermal burn-up of 33000 MWd/tHM and 3 years cooling.[65]

During each experiment using HAR simulate solution its composition was measured together with the samples because a small precipitation in the stock bottle indicated possible metal concentration changes. Therefore, the metal concentrations in the Table 2 correspond to the concentrations obtained by ICP-MS measurements just after the preparation of the main stock solution.

The second type of a HAR simulate solution used in this work was prepared in the Institute of Transuranium Elements in Karlsruhe (ITU) and its composition is shown in the Table 3. This solution was used only in the single centrifuge contactor tests. The main difference between these two HAR solutions is that the FZJ one additionally contains the corrosion products Fe, Cr, Ni and Cu, the fission product Sn and a large amount of Na (1.6 g/L) simulating solvent clean-up from acidic impurities.[65-67].

Table 2. The composition of the HAR simulate solution prepared at FZJ (HAR-FZJ).

Element	[mg/L]	Element	[mg/L]
Ag	12	Ni	40
Al	2	Pd	168
Ba	264	Pr	223
Cd	17	Rb	66
Ce	567	Rh	73
Cr	93	Ru	356
Cs	542	Sb	4.6
Cu	19	Se	10
Eu	34	Sm	149
Fe	1900	Sn	11
Gd	35	Sr	180
La	239	Te	165
Mo	678	Y	90
Na	1600	Zr	1071
Nd	718		
HNO_3	3.1 mol/L		

Table 3. The composition of the HAR simulate solution prepared at ITU (HAR-ITU).

Element	[mg/L]	Element	[mg/L]
Ag	8	Pd	265
Ba	526	Pr	301
Cd	29	Rb	63
Ce	620	Rh	48
Cs	668	Ru	225
Eu	33	Sb	9
Gd	101	Sm	203
La	337	Sr	162
Mo	448	Te	127
Nd	1081	Y	83
Ni	40	Zr	413
HNO_3	4.6 mol/L		

3.1.3. DIAMEX raffinate solution

In order to study the stripping of actinides from a loaded organic phase a solution containing trivalent lanthanides in 0.5mol/L HNO_3 was used (Table 4). This corresponds to an An/Ln loading of the HAR after the DIAMEX process.

Table 4. An(III)/Ln(III) product solution generated after DIAMEX.

Element	[mg/L]	Element	[mg/L]
Y	213	Gd	146
La	753	Nd	2423
Pr	655	Ce	1453
Eu	89	Sm	469
HNO_3	0.5 mol/L		

3.1.4. Determination of the nitric acid extraction into the organic phase

The nitric acid extraction into the organic solvents was studied in batch tests. The desired organic solvent (500 µL) was contacted with the aqueous phase (500 µL) consisting of variable nitric acid concentration solutions in 2 mL glass vials and shaken by an orbital shaker for 15 minutes. Separation of the phases by centrifugation was followed by sampling of 400µL of each phase. The acidity of the aqueous phase was directly measured by titration with 0.01 or 0.1 mol/L NaOH (Metrohm 798 MPT Titrino). The nitric acid of the organic phase (400 µL) was backextracted with an aqueous phase of 1200 µL of ultrapure water followed by centrifugation and sampling. The concentration of the re-extracted nitric acid was determined by titration similar as for the aqueous sample.

3.1.5. Determination of the limiting organic concentration

The limiting organic concentration (LOC) is defined as the maximal concentration of the metal in the organic phase without formation of a third phase (splitting of the organic phase into a lighter and a heavier organic layer). For the processes where trivalent actinides are co-extracted together with trivalent lanthanides the reference metal is neodymium due to its major content in High Level Liquid Waste (HLLW) considering the lanthanide group members.

The loading of the organic solvent with neodymium was performed in batch tests similar as for the determination of the D-values described above except the radiotracers which were substituted by the stable isotope Nd. The concentration of the metal in the organic and aqueous phase was measured by ICP-MS. The presence of the third phase was determined visually and by the mass balance calculations.

3.1.6. Screening tests of the new compounds delivered by University of Twente

The University of Twente provided two types of novel ligands: lipophilic and hydrophilic. The lipophilic ligands were designed to act as selective trivalent actinides extractants. The hydrophilic ligands were designed to complex preferably the trivalent actinides in aqueous solutions.

The new lipophilic compounds were screened in batch tests. The compound was dissolved in hydrogenated tetrapropene (TPH) to the standard concentration 0.1mol/L. If the compound solubility in this type of solvent was poor, small amounts of 1-octanol were added until complete dissolution. The 1-octanol alone was used for compounds with the lowest solubility in non-polar diluents. Diluted nitric acid of different concentrations ranged from 0.01 to 4 mol/L served as an aqueous phase after being spiked with 10µL of radiotracer (^{241}Am, ^{152}Eu, approx. 25 kBq/mL). The same aliquots (500µL) of organic and aqueous phase were contacted for an appropriate time (15 or 60 minutes) at 22°C±1° using an orbital shaker. The centrifugation, sampling and measurement using gamma spectrometer were performed exactly as described in subchapter 3.1.1.

The new hydrophilic compounds were also screened in batch tests, although the strategy differed from the one used for the organic compounds. All the aqueous solutions were prepared by dissolution of weighted amounts of the ligand in ultrapure water (resistivity 18MΩ·cm^{-1}) containing 0.5 mol/L NH_4NO_3 (salting-out agent). The initial pH_{ini} of the aqueous phase was adjusted using ammonia or diluted nitric acid. The organic solvent consisted of 0.2 mol/L TODGA + 5 vol.% 1-octanol dissolved in TPH. TODGA was chosen as an extractant for these screening tests due to its high affinity to trivalent actinides and lanthanides and the An/Ln separation factor it exhibits at medium acidity (~1 mol/L HNO_3). The organic phase was not pre-loaded with ^{241}Am and ^{152}Eu followed by stripping because TODGA extracts significant amounts of HNO_3 which would prevent obtaining reasonable results at $pH_{eq}>1$ without using a buffer. Instead each of the aqueous phases (500µL) were spiked with 10µl of radiotracer (^{241}Am, ^{152}Eu, approx. 25kBq/mL) and contacted with the organic solvent (500µL) by shaking for 60 minutes at 22°C±1° using an orbital shaker. After phase separation by centrifugation, 200 µL aliquots of each phase were withdrawn for radio analysis. The kinetics of the extraction experiments were performed similarly as described above except the phases contact time (mixing time). The acidities of the initial and final aqueous solutions were determined using a pH meter 691, Metrohm, 3 mol/L KCl.

3.1.7. The determination of stability constants of Zr complexes with CDTA and EDTA.

The stability constants of complexes Zr-CDTA and Zr-EDTA were determined by potentiometric titration. By this method the concentrations of the free hydrogen ions H^+, coming from dissociation of the ligand CDTA or EDTA, were measured with a combined glass electrode (Mettler Toledo) connected to an automatic titrator (Titro processor Methrom 636) at 25 °C. The electrode parameters were derived from the titration of a strong acid (HNO_3) with a strong base using a computer software GLEE.[68]

The procedure of pH-metric titration consisted of the following steps:

- Titrations of an acidic ligand solution (C_L c.a. 10^{-3} mol/L) in the presence of a supporting-electrolyte (10^{-1} mol/L $NaNO_3$ or Et_4NNO_3) with a base (NaOH or Et_4NOH) in order to determine ligand protonation constants. The base solution was previously standardised using a solution of potassium hydrogenphthalate. Due to solubility problems, the ligands were first partly deprotonated by adding two equivalents of the base (except EDTA as it was mostly used as the salt Na_2EDTA).
- Titration of the same ligand solution with the base in the presence of zirconium. Concentration of the ligand and the metal were equal. The extent of complexation was shown by the drop of pH with respect to the titration curve of the ligand in the absence of metal. Attempts to obtain $Zr(NO_3)_4$ solution were made, although this salt was very poorly soluble in water and a white powder was still visible at the concentration 1.25×10^{-2} mol/L.

Therefore, $ZrO(NO_3)_2$ stock solution of concentration 2.5×10^{-2} mol/L was prepared in distilled water and standardised with EDTA in the presence of thorium nitrate $Th(NO_3)_4$.

- The experimental data (potentials in mV or directly pH values) were treated by a computer software Hyperquad.[69] The protonation constants of the two ligands were set as constants, as well as the formation constants β_n^* of the hydroxo complexes of the metal, corresponding to the equilibrium:

  $ZrO^{2+} + n\,H_2O \leftrightarrow ZrO(OH)_n^{(2-n)+} + nH^+$.

  The formation constants β_n^* values were obtained by titration of a solution of $ZrO(NO_3)_2$ with NaOH or Et_4NOH.

3.2. Chemicals and reagents

- Nitrilotriacetic acid trisodium salt, (≥ 98% pure), Sigma Aldrich
- Ethylenediaminetetraacetic acid tetrasodium salt hydrate, (98% pure), Alfa Aesar (not sodium salt)
- N-(Hydroxyethyl)ethylenediaminetriacetic acid, (99% pure), Acros Organics
- Diethylenetriaminepentaacetic acid, (>98% pure), Alfa Aesar
- Diethylenetriamine-pentaacetic acid Pentasodium salt Solution, (purum grade), ~40% in water, Fluka
- Trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid Monohydrate, (≥ 98.0% pure), Fluka
- Triethylenetetramine-N,N,N',N'',N''',N'''- hexaacetic acid, purum >98%, Fluka
- Bromohexanoic acid, 97%, Aldrich
- Ammonia solution, ≥ 25%, p.a., Roth
- Ammonium nitrate, (≥95% pure), Merck
- Sodium nitrate, (pro analysis), Merck

- Citric acid, (≥99% pure), Merck
- Glycolic acid, (≥99.5% pure), Merck
- Lactic acid, (~90% pure), Merck
- DL-Malic acid, (≥99.5% pure), Merck
- Diglycolic acid, (≥97.0% pure), Fluka
- Oxalic acid, (99.5% pure), Merck
- Glycine, (99% pure), Alfa Aesar
- Bis(2-ethylhexyl) phosphate, (97% pure), Sigma Aldrich
- Nitric acid 69%, Merck
- Nitric acid 65% Suprapur, Merck, for ICP-M
- Diethyl ether, GR for analysis, Merck
- Copper (II) sulphate pentahydrate, GR for analysis, Merck
- Hydrogen peroxide 30%, extra pure, Merck
- 1-octanol, for synthesis, Merck
- Hydrochloric acid 32%, for analysis, Merck
- Sodium hydroxide, GR for analysis, Merck
- Tributyl phosphate, Aldrich Chemical company, purity 99%
- Hydrogenated tetrapropylene (TPH)
- N,N,N’,N’-tetraoctyl-3-oxapentanediamide (TODGA) – self synthesised and purified
- Radiotracers ^{241}Am, ^{244}Cm, ^{252}Cf, ^{152}Eu, Isotopendienst M. Blaseg GmbH, Waldburg, Germany

3.3. Apparatus

- High-purity germanium spectrometer system, EG&G Ortec, Munich, Germany; equipped with the Gamma Vision software
- Alpha spectrometer, Octête^{TM} PC EG&G Ortec, Munich, Germany

- ICP-MS system, Elan 6100 DRC from Perkin Elmer Sciex, Roggau-Jügesheim, Germany
- A pH meter, 691 Metrohm, using 3 mol/L KCl, pH capacity between 0 and 14
- A self-constructed orbital shaker, IKA Vibrax Model VXR, 2200rpm with a thermostated aluminium block for 6 samples
- Orbital shaker Heidolph REAX 2000; 2400 rpm
- A titrator, A 798 MPT Titrino, Metrohm
- A glass electrode (Mettler Toledo) connected to an automatic titrator Titro processor Methrom 636, computer software GLEE and HYPERQUAD
- Syringe pumps “Genie"
- Batteries of centrifugal contactors – designed and fabricated at INET, Tsinghua University, Beijing, China. (the rotor diameter : 10 mm, the hold-up volume : 3–4 mL of a single stage)
- A single centrifugal contactor made out of plexiglass – the rotor diameter : 10 mm, the hold-up volume : 3–4 mL of a single stage
- Vacuum system B-172 and Rotavapor R-114, Buchi, Switzerland

4. Results and Discussion

The *Results and Discussion* chapter is divided into six parts. Each of the parts starts with an introduction to the subject described in it, followed by the presentation and discussion of the results.

The first part called ***Reversed TALSPEAK*** describes the optimisation of the formulation of the stripping solution for selective An(III) stripping in the reversed-TALSPEAK process. Different buffers and complexing agents were tested at various pH of the stripping solution. The main focus was placed on the influence of tetraminohexaacetic acid (TTHA) on the Ln(III)/An(III) separation factors compared to other well-known aminopolycarboxylic acids such as DTPA, EDTA.

In the second part (***DIAMEX-SANEX***) the optimised An-stripping solution was applied in DIAMEX-SANEX process where the solvent consisted of two extractants: HDEHP and TODGA.

The third part, the main part of this work, ***Innovative-SANEX***, describes the development of a novel process based on TODGA extractant for trivalent actinides separation from PUREX raffinate in just one cycle. Two different formulas of the organic solvent were tested (containing either TBP or 1-octanol). The optimal conditions for the An/Ln co-extraction and An-stripping step were found.

The search for an oxalic acid substitution (Zr masking agent) resulted in successful utilisation of CDTA and is described in the forth part called ***New masking agent***. This aminopolycarboxylic acid efficiently complexes Zr and Pd, the elements that are considered as problematic in processes where TODGA is used as an extractant (their undesirable co-extraction with An(III)/Ln(III)).

Each step of the optimised innovative-SANEX process was tested using a single centrifugal contactor (fifth part: ***Single centrifugal contactor test***). The results of those tests were used to design a flow-sheet for a battery of centrifugal contactors and are reported in part five.

The final part of this work describes the results of the screening tests of novel ligands which were synthesised and provided by the University of Twente. The aim of the screening tests was to find novel lipophilic extractants with high affinity towards trivalent lanthanides and actinides with possible discrimination between these two element groups. The screening also covered water-soluble ligands since new hydrophilic complexants with high selectivity for An(III) were desirable to enhance An-stripping in the innovative-SANEX process.

4.1. Reversed TALSPEAK

In the late 1950s the extraction of the trivalent lanthanides, yttrium and tri- and tetravalent actinides by di(2-ethylhexyl)phosphoric acid (HDEHP) was reported.[70-71] HDEHP is a liquid cation exchanger (Figure 7) which usually forms tris complexes with trivalent lanthanides and trivalent actinides releasing at the same time three H^+ for each trivalent metal complexed. Consequently, the extraction of these metals is most effective from low acidic solutions as it is shown in Figure 8. The distribution ratios of about 100 at acidity $<10^{-2}$ mol/L indicate very efficient extraction of Am and Eu. Further increase of the aqueous phase acidity caused drop of the D-values and at 1 mol/L HNO_3 and higher most of the metals stay in the aqueous phase ($D_M < 1$).

The cation exchange mechanism can change into a solvating mechanism if the nitrate concentration increases, although mainly for tetra and hexavalent actinides.[72] In that case nitrate ions serve as a salting-out agent.

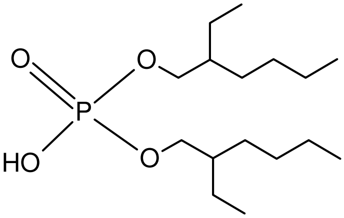


Figure 7. The chemical structure of di(2-ethylhexyl)phosphoric acid (HDEHP).

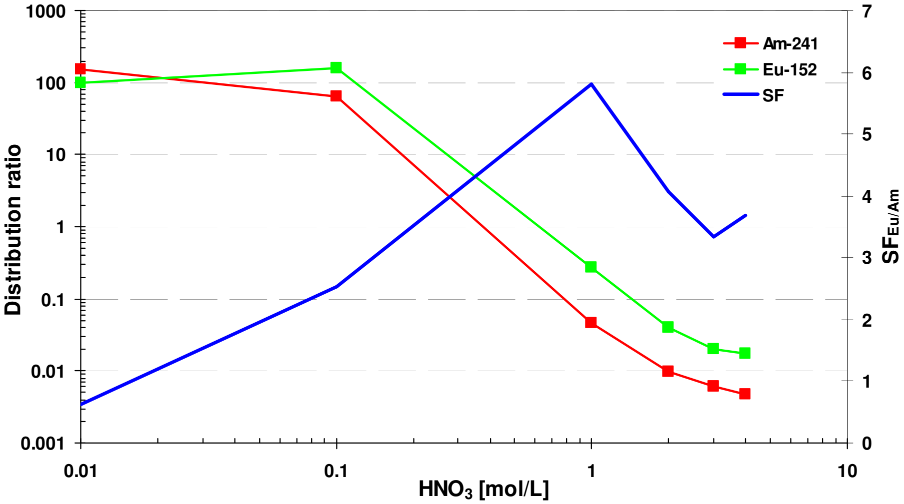


Figure 8. The extraction of ^{241}Am and ^{152}Eu as a function of nitric acid concentration.

Organic phase:	0.5 mol/L HDEHP in TPH (extractant purity: 92%)
Aqueous phase:	variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

Peppard et al. reported that HDEHP undergoes dimerisation in inert solvents through hydrogen bonding.[73] Therefore the extraction equilibrium shown in equation Eq 6 is the most probable formulation.

$$M^{3+} + \overline{3(HA)_2} \longleftrightarrow \overline{M(AHA)_3} + 3H^+ \qquad \text{Eq 6}$$

where: HA – monomeric HDEHP

AHA – hydrogen-bonded dimmer of HDEHP

In 1964 Kappelmann and Weaver published their work on a new process for the separation of trivalent actinides from trivalent lanthanides using HDEHP,[49] called TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes). They pointed out that HDEHP alone does not distinguish between trivalent lanthanides and actinides extracting these two element groups with comparable effectiveness.

Moreover, due to the significant differences in the distribution ratios of the individual members of the lanthanide series, overlapping with the distribution ratios of trivalent actinides takes place e.g. americium is extracted to the same degree as cerium and praseodymium. However, by altering the composition of the aqueous phase the separation between these two groups of elements became possible. The altering considered the substitution of the mineral acid for a carboxylic acid (lactic acid) and the introduction of a polyaminocarboxylic acid (diethylenetriaminepentaacetic acid, DTPA). The mechanism of the extraction reaction (Eq 6) results in the high sensitivity of the metal extraction to changes in $[H^+]$. By a strong buffering agent such as lactic acid this was performed. Besides the pH stabilisation role, lactic acid possesses additional properties which enhance the TALSPEAK performance:

- speeds up the extraction kinetics[72]
- increases solubility of the polyaminocarboxylic acid[72]
- facilitates the phase disengagement
- increases the Ln/Am separation factor[50]
- its lanthanide salts are highly soluble[50]

The deprotonated form of polyaminocarboxylic acid DTPA forms complexes with An(III) and Ln(III) in the aqueous phase. However, due to the differences in the electronic structure of actinides and lanthanides i.e. slightly greater spatial extension of the 5f– than the 4f–electron shell, trivalent actinides bind more strongly to donor atoms softer than oxygen (nitrogen, sulphur) compared to trivalent lanthanides. DTPA has three nitrogen atoms in its structure (Figure 9) which enhance the Ln/An separation.

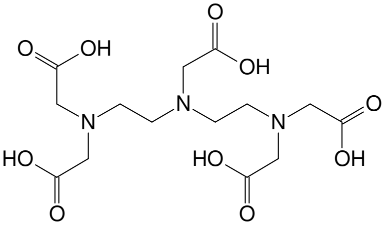


Figure 9. The chemical structure of diethylenetriaminepentaacetic acid (DTPA).

The polyaminocarboxylic acids require higher pH as only the de-protonated forms are able to complex trivalent metals. It has been reported that DTPA forms two kinds of complexes with trivalent lanthanides and actinides:[74]

$$M^{3+} + X^{5-} \longleftrightarrow MX^{2-} \qquad \text{Eq 7}$$

$$M^{3+} + X^{5-} + H^{+} \longleftrightarrow MXH^{-} \qquad \text{Eq 8}$$

where: X – deprotonated DTPA

TALSPEAK process in its original mode assumes predominant extraction of Ln(III) while most of An(III) are complexed in the aqueous phase by DTPA. The reversed mode of this process called reversed-TALSPEAK applies selective stripping of trivalent actinides from a loaded organic phase (HDEHP) with DTPA. Therefore, in the preliminary step Ln(III) together with An(III) are extracted into the organic phase and then the stripping solution containing DTPA is applied. An attempt to develop a process containing reversed-TALSPEAK stripping was made resulting in the so called CTH-process [75] (Chalmers Tekniska Högskola) (Figure 10). In the first step of CTH process highly acidic HAW solution is contacted with organic solvent containing HDEHP since light actinides (U, Np, Pu) are well extracted at this condition. Further the acidity of the resulting aqueous solution containing the heavy actinides (Am and Cm), trivalent lanthanides and fission products is reduced using TBP (extraction of HNO_3). Once again the aqueous solution is contacted with a solvent containing

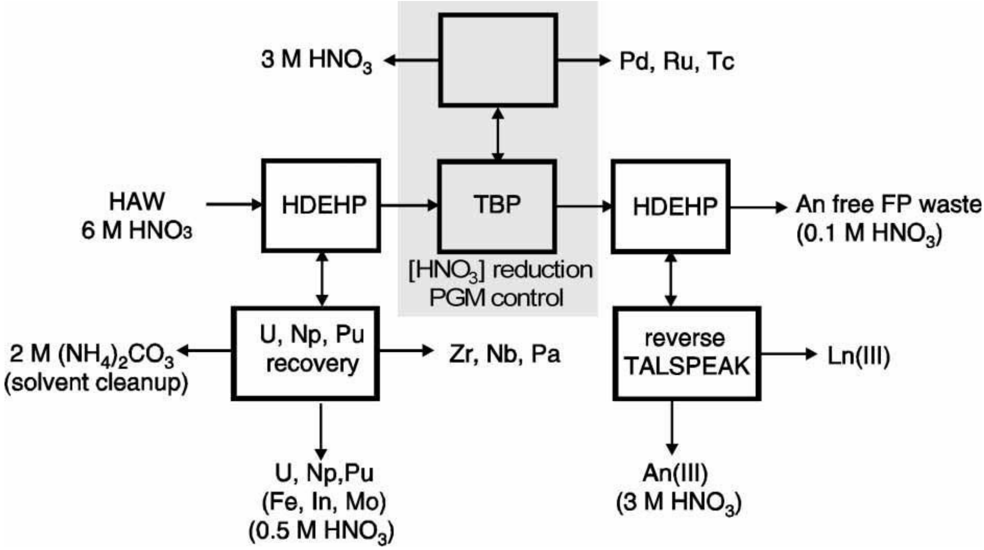


Figure 10. General outline of the CTH process (Figure copied from Nilsson et al[76]).

HDEHP thus the trivalent actinides and lanthanides are extracted leaving the fission products in the aqueous solution. The last step consists of reversed-TAKSPEAK, where An(III) are selectively stripped by the fresh aqueous solution containing DTPA.

The reversed-TALSPEAK stripping was a basis for the selective stripping of An(III) in the innovative SANEX process described further in this thesis.

4.1.1. The influence of the purity of the extractant on An(III) separation

The purity of the HDEHP used in the TALSPEAK process is a key issue. The main impurity which can be found together with HDEHP is mono(2-ethylhexy1)phosphoric acid (Figure 11). In the commercially available HDEHP normally it is present in minor amounts (3%). In more significant amounts it can appear as a degradation product of disubstituted phosphoric acid upon radiolysis.[77-78] In moderate amounts it increases the distribution ratios of trivalent metals while decreasing the separation factor of lanthanides over actinides, which makes stripping more problematic. However, its presence in high concentration decreases the distribution ratios.[77, 79]

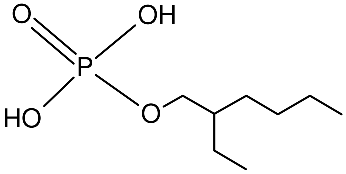


Figure 11. The chemical structure of mono(2-ethylhexy1)phosphoric acid (H_2MEHP).

The same effect has been observed in the present work when the purchased extractant of purity 48% HDEHP (52% of H_2MEHP) was used (Figure 12). The distribution ratios of Am and Eu were in a range of 10^2 - 10^3 (green lines) with an Eu/Am separation factor around 2 (blue dotted line). After purification of the extractant using the method described by Partridge[80] a purity of 99.9 % was confirmed by titration of the extractant (acidic impurities including H_2MEHP) and ^1H and ^{13}C NMR. The distribution ratio of Eu (red line, full dots) did not change significantly in comparison to D_{Eu} of the unpurified ligand. However, the D_{Am} (red line, blank dots) decreased drastically giving high $SF_{Eu/Am}$ up to 50 (blue line).

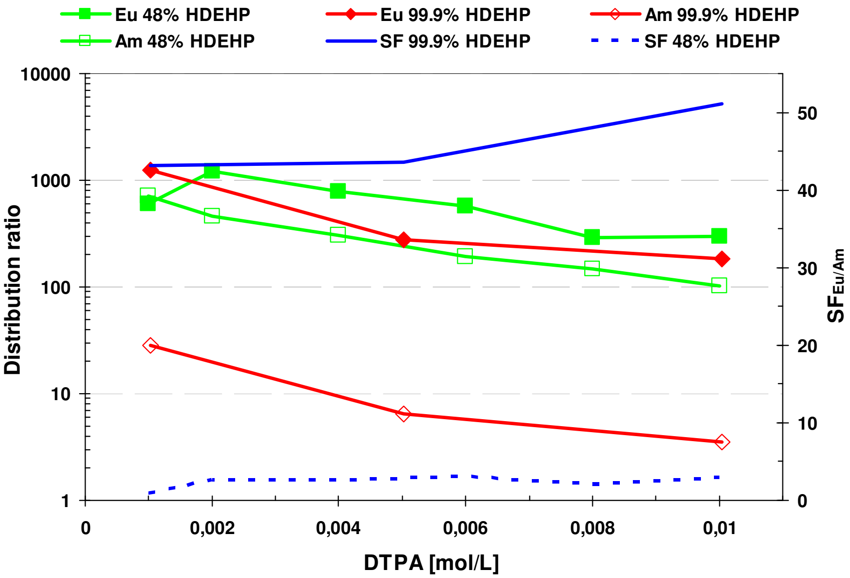


Figure 12. The extraction of ^{241}Am and ^{152}Eu as a function of DTPA concentration.

Organic phase: 0.5 mol/L HDEHP (48% and 99.9 % purity) in TPH

Aqueous phase: variable concentration of DTPA, 1 mol/L lactic acid, pH_{ini}=3, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.1.2. The influence of pH on the extraction of actinides(III) and lanthanides(III).

The effect of pH change on the TALSPEAK performance has been studied by several research groups.[50, 81-82] They stated that the distribution ratios of An(III) and Ln(III) are increasing with decreasing initial pH of the stripping solution. Since the extraction of the trivalent metals by HDEHP is less favourable at lower pH (see Eq 6), the increase of An(III) and Ln(III) distribution ratios at lower pH indicates poor metal complexation by DTPA or lactate in the aqueous phase. This results in better An(III)/Ln(III) extraction by HDEHP (higher D-values) at low pH_{ini}.

This effect has been confirmed in the pH_{ini} range of 2 – 4.5 for An(III) and Ln(III) using purified HDEHP dissolved in tert-butylbenzene (TBB). ^{241}Am and ^{152}Eu were better complexed by DTPA in the aqueous phase at higher pH_{ini} resulting in a decrease of extraction efficiency (lower D-values) (Figure 13). Californium was the most extracted transplutonium element, which is typical for TALSPEAK conditions.[50] The extractability order is Cm < Am < Cf where curium is nearly similar extractable as americium. The separation factors for trivalent lanthanides over americium are shown in Table 5.

Table 5. The separation factors of Ln(III)/Am(III) for different initial pH of the aqueous phase

pH	2.0	2.5	3.0	3.5	4.0	4.5
	$SF_{Ln/Am}$					
Y	18049	10896	27771	29604	15877	19229
La	60	235	390	415	336	286
Ce	72	130	150	141	125	116
Pr	44	54	54	53	48	46
Nd	26	28	27	27	25	26
Sm	44	42	39	42	42	40
Eu	67	63	61	65	63	44
Gd	116	106	101	106	103	55
Tb	418	355	346	357	278	61
Dy	907	796	788	776	560	84
Ho	2641	1863	1994	1938	1479	155
Er	3564	3028	3510	3206	2801	424
Tm	23338	11524	23615	21513	15379	3223
Yb	8535	6280	9482	9894	7875	4803
Lu	22310	11215	23383	23363	15095	4990

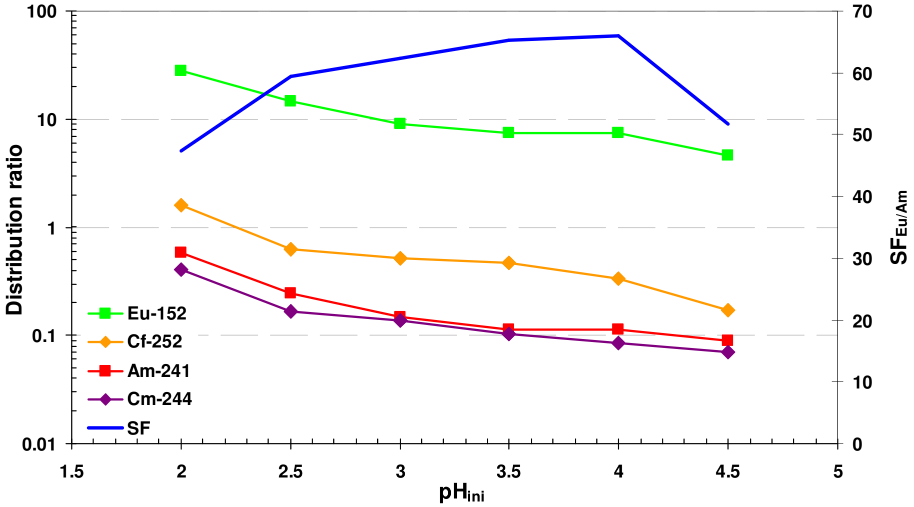


Figure 13. The extraction of ^{241}Am, ^{152}Eu, ^{244}Cm and ^{252}Cf as a function of initial pH of the aqueous phase.

Organic phase: 0.5 mol/L HDEHP (99 % purity) in tetr-butylbenzene (TBB)

Aqueous phase: variable pH$_{ini}$, 0.01 mol/L DTPA, 1 mol/L lactic acid, 5x10^{-4} mol/L Ln, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, ^{252}Cf; mixing time: 15min.

A similar behaviour was observed on the extraction of lanthanides (Figure 14 and Figure 15). The lighter ones formed stronger complexes with DTPA in the aqueous phase. They are less extractable than the heavier ones. The distribution ratios of all the light lanthanides decreased with increasing pH$_{ini}$ of the stripping solution. Only lanthanum showed different behaviour by increased extraction at pH$_{ini}$ 2.0 - 2.5 with maximum at pH$_{ini}$ = 2.5. However, further decrease of the proton concentration in the aqueous phase resulted in decreased distribution ratios similar as for the rest of light lanthanides. Weaver and Kappelmann[50] observed the same trend with La, Eu, Sm and Nd. In their studies neodymium was also the least extractable metal within all the lanthanides.

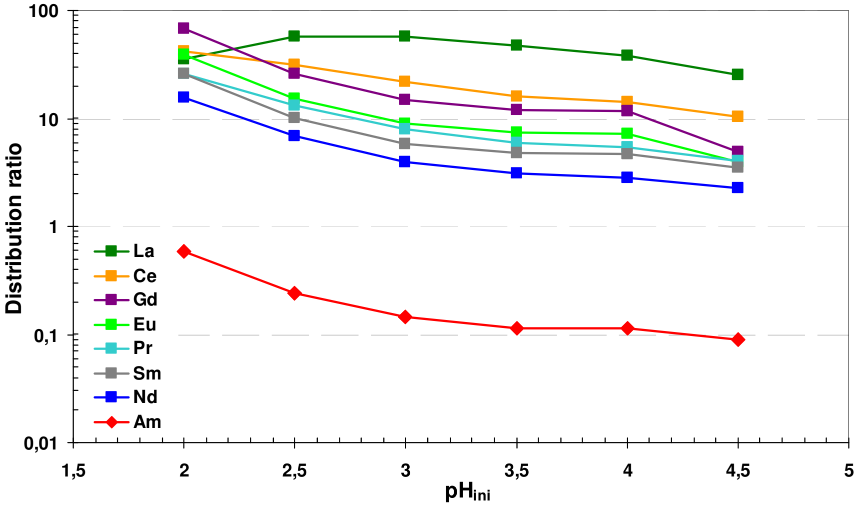


Figure 14. The extraction of light lanthanides as a function of initial pH of the aqueous phase. Conditions: see Figure 13.

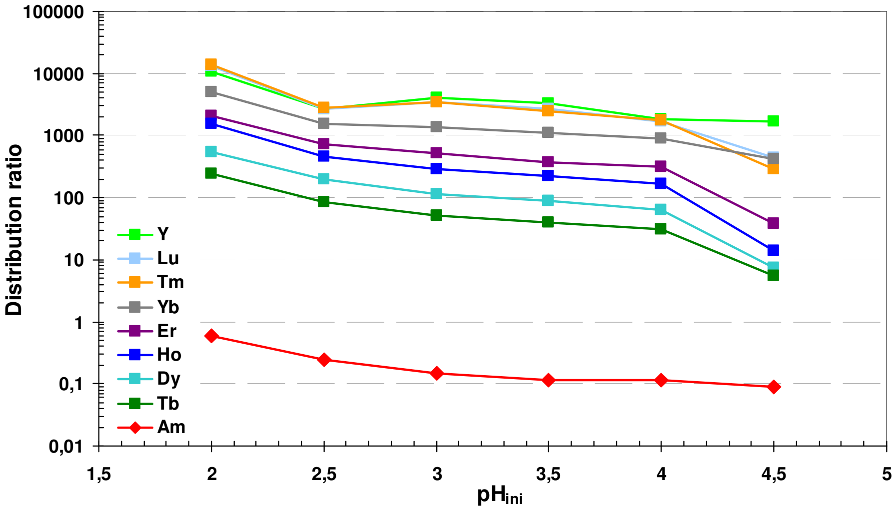
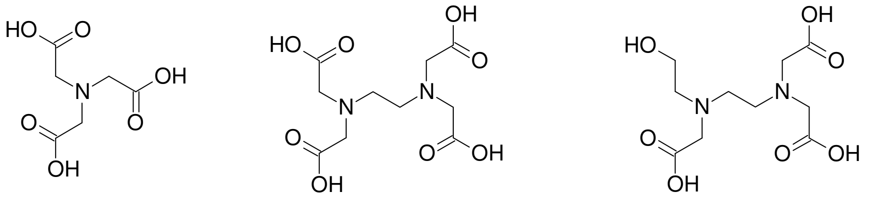


Figure 15. The extraction of heavy lanthanides and yttrium as a function of initial pH of the aqueous phase

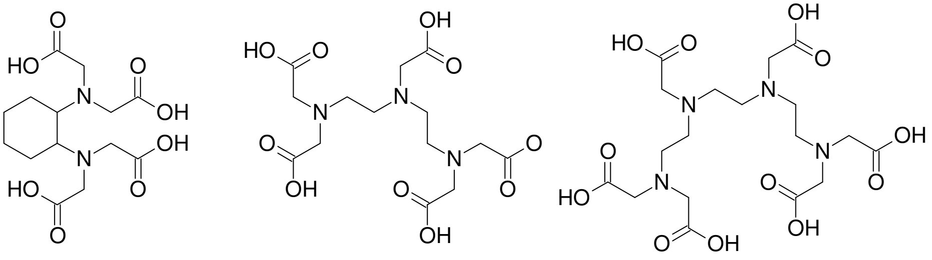
Conditions: see Figure 13.

4.1.3. The influence of different polyaminocarboxylic acids on An(III) and Ln(III) extraction.

Kappelmann and Weaver[49] tested several hydrophilic complexing agents (Figure 16) to determinate their complexing properties with trivalent actinides and lanthanides. Among 6 tested agents only DTPA showed efficient complexation of Am and Cm resulting in good Ln/An separation. The polyaminocarboxylic acid containing one additional amino and carboxylate group in its structure compared to DTPA, namely TTHA, was tested by them only up to a concentration of 0.024 mol/L due to the lack of the complexant. Therefore, in the current thesis the influence of TTHA on Ln/An separation factor was tested also at higher complexant concentrations.



Nitrilotriacetic acid (NTA) Ethylenediamine-tetraacetic acid (EDTA) Hydroxyethylethylenediamin-tetraacetic acid (HEDTA)



1,2-Diaminocyclohexane-tetraacetic acid (CDTA) Diethylenetriamine-pentaacetic acid (DTPA) Triethylenetetraamine-hexaacetic acid (TTHA)

Figure 16. The chemical structures of the tested polyaminocarboxylic acids.

The complex stability constants of DTPA with lanthanides reported by Moeller et al.[74] are lower than for TTHA[83] (Table 6). Therefore, it can be assumed that the separation factor

Ln(III)/An(III) in the TALSPEAK process can be enhanced by the substitution of DTPA by TTHA.

Table 6. Logarithmic stability constants for Ln(III) complexes with polyaminocarboxylic acid ligands ($\log K_{ML}$)[84]

	DTPA	TTHA
La^{3+}	19.48	23.4
Ce^{3+}	20.5	-
Pr^{3+}	21.07	23.7
Nd^{3+}	21.6	23.8
Sm^{3+}	22.34	23.7
Eu^{3+}	22.39	23.5
Gd^{3+}	22.46	23.5
Tb^{3+}	22.71	23.6
Dy^{3+}	22.82	23.7
Ho^{3+}	22.78	23.6
Er^{3+}	22.74	23.2
Tm^{3+}	22.72	23.2
Yb^{3+}	22.62	23.0
Lu^{3+}	22.44	23.0

Both polyaminocarboxylic acids have been applied under TALSPEAK conditions with the initial pH of the aqueous phase adjusted to 3 which is typical for this process.

Using the pentaacetic acid (DTPA) the separation factor of ^{152}Eu over ^{241}Am increased from 43 to 64 with increasing the ligand concentration (Figure 17). Unfortunately, the hexaacetic acid (TTHA) could not be dissolved as easily as DTPA due to its acidic form (DTPA was used as a pentasodium salt which is easily soluble in water). Therefore, the highest TTHA concentration obtained was 0.015 mol/L which gave a $SF_{Eu/Am}$ of 25. However, the maximal separation factor of 51 was obtained at lower TTHA concentration, namely 0.01 mol/L.

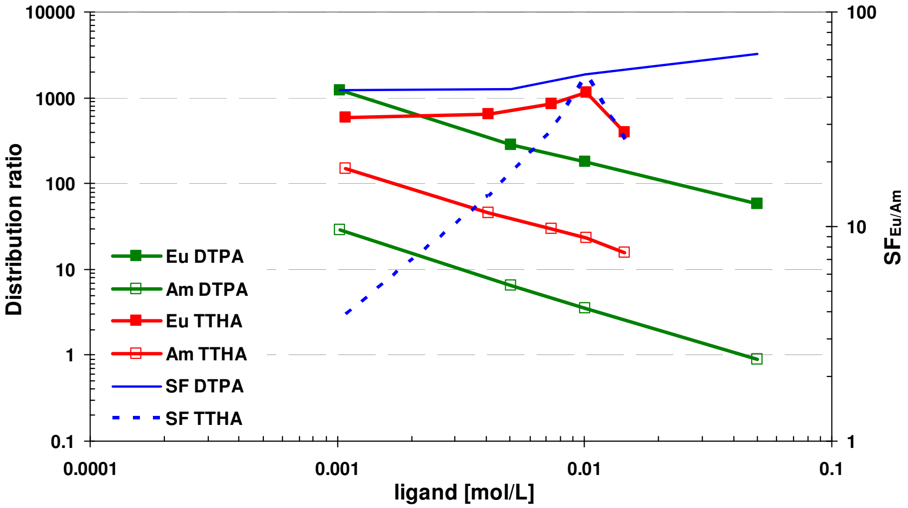


Figure 17. The extraction of ^{241}Am and ^{152}Eu as a function of the ligand concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: pH_{ini}=3, variable ligand conc., 1 mol/L lactic acid, 5x10^{-4} mol/L Ln, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

Due to the solubility problems with TTHA the initial pH of the aqueous phase was increased to pH_{ini} = 4 at which TTHA can be dissolved up to 0.2 mol/L. Therefore, the rest of the hydrophilic complexing agents were also tested at pH_{ini} = 4 (see Figure 18 – 25). Additionally, in the following studies the aromatic diluent diisopropylbenzene, typical for TALSPEAK process, was replaced with TPH (hydrogenated tetrapropene).TPH is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Some chemicals that may be found in TPH are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals.[85] TPH is commonly used as a diluent in AREVA's reprocessing plants.

4.1.3.1 NTA

Nitrilotriacetic acid (NTA) (see Figure 16) contains only one nitrogen atom in its structure and three acetic acid groups, therefore its complexes with An(III) and Ln(III) are expected to be the weakest among the tested polyaminocarboxylic acids. Figure 18 shows the decrease of the distribution ratios of Am, Eu, Cm and increase of separation factor of Eu/Am with increasing NTA concentration. The distribution ratios for ^{244}Cm were nearly the same as for ^{241}Am, therefore the separation of these two radionuclides from each other was not possible.

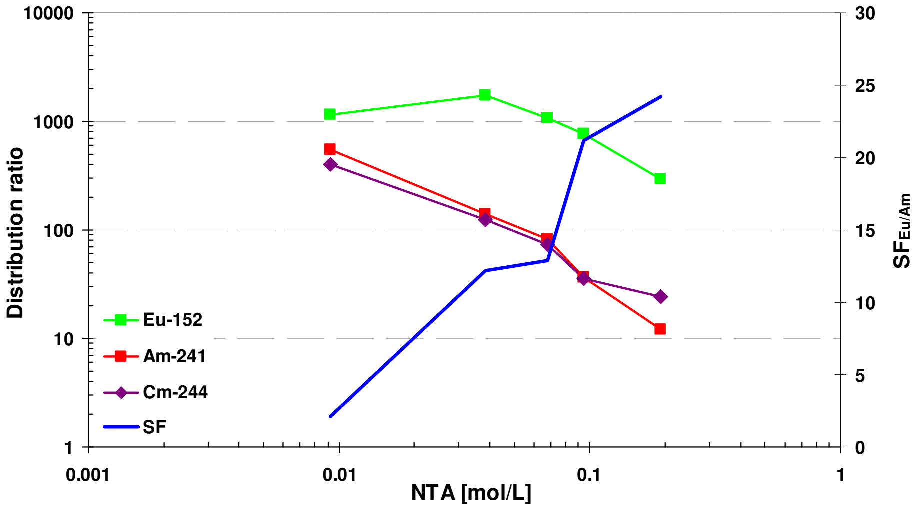


Figure 18. The extraction of ^{241}Am, ^{152}Eu and ^{244}Cm as a function of NTA concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, variable concentration of NTA, 10^{-4} mol/L Ln, pH_{ini}=4, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, mixing time: 15min.

4.1.3.2 EDTA

Ethylenediaminetetraacetic acid (EDTA) was not tested because precipitation appeared at pH=3.5 while preparing aqueous solutions of ≥ 0.04 mol/L EDTA. The available ligand was in an acidic form which is very poorly soluble in water.

Kappelmann and Weaver[49] tested EDTA for the complexation of Am and Ln(III) in the aqueous phase. They used the disodium salt of EDTA, which is more easily soluble in water than its acidic form, obtaining $SF_{Eu/Am} = 65$ (0.01 mol/L EDTA, glycolic acid). They stated that the extraction data indicates strong complexation of EDTA with Am preferentially, however the ligand solubility was too low for useful application.

4.1.3.3 HEDTA

The N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) has a similar structure to EDTA, but one of the carboxylic acid groups is substituted by an alcohol function which makes this complexant better soluble in water compared to EDTA. The distribution ratios of ^{241}Am, ^{152}Eu, ^{244}Cm and ^{252}Cf decreased with increasing concentration of the complexing agent (Figure 19). Curium was extracted with the D-values nearly the same as for Am. Californium gave 5-8 times higher D-values than Am as it is the most extractable member of the actinide group. The partitioning of Eu and Cf from Am is more efficient when HEDTA concentration increases (Table 7). The separation factor of Cm over Am is practically constant with increasing the complexant concentration which is caused by their very similar chemical properties.

Table 7. Influence of HEDTA concentration on the separation of Eu, Cm and Cf from Am

HEDTA [mol/L]	0	0.01	0.04	0.06	0.09	0.18
	$SF_{X/Am}$					
^{152}Eu	2.07	23	41	41	52	70
^{244}Cm	1.05	1.25	1.03	1.15	1.02	1.15
^{252}Cf	2.34	5.45	7.63	9.73	8.83	10.1

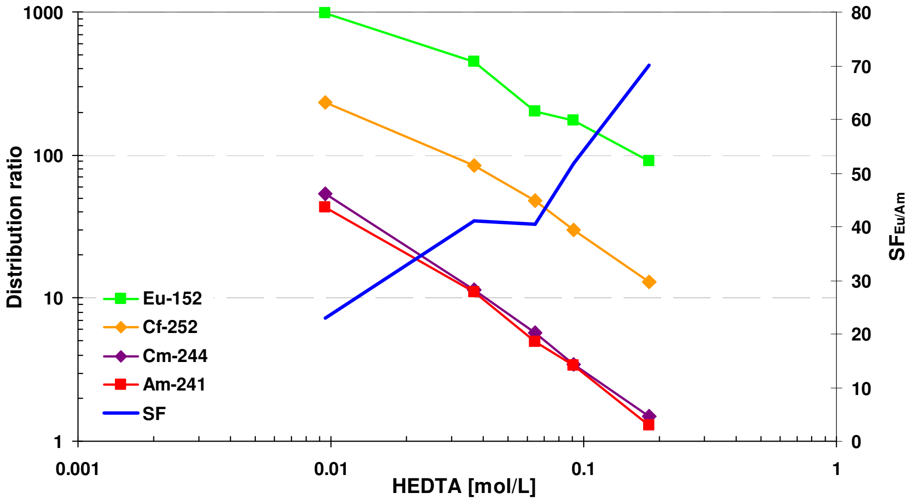


Figure 19. The extraction of ^{241}Am, ^{152}Eu, ^{244}Cm and ^{252}Cf as a function of HEDTA concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, variable concentration of HEDTA, 10^{-4} mol/L Ln, pH_{ini}=4, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, ^{252}Cf, mixing time: 15min.

4.1.3.4 CDTA

Cyclohexanediaminetetraacetic acid (CDTA) was not tested by Weaver et al.[49] due to an extensive precipitation which occurred during the attempt to obtain 0.1 mol/L CDTA solution. Therefore, for these studies same solutions of lower concentration of this complexing agent were prepared with the maximum of 0.025 mol/L CDTA.

The extraction of ^{241}Am, ^{152}Eu and ^{241}Cm decreased with increasing complexant concentration (Figure 20). A very interesting behaviour was shown by curium. Within the hydrophilic complexing agents studied (Figure 16) only CDTA complexed Am and Cm differently. Separation factors of Eu and Cm over Am are shown in Table 8. It seems that the CDTA complexes with Cm were more stable than those with Am. It is very difficult to directly point out the explanation of this effect. HDEHP extracts Cm better than Am, although

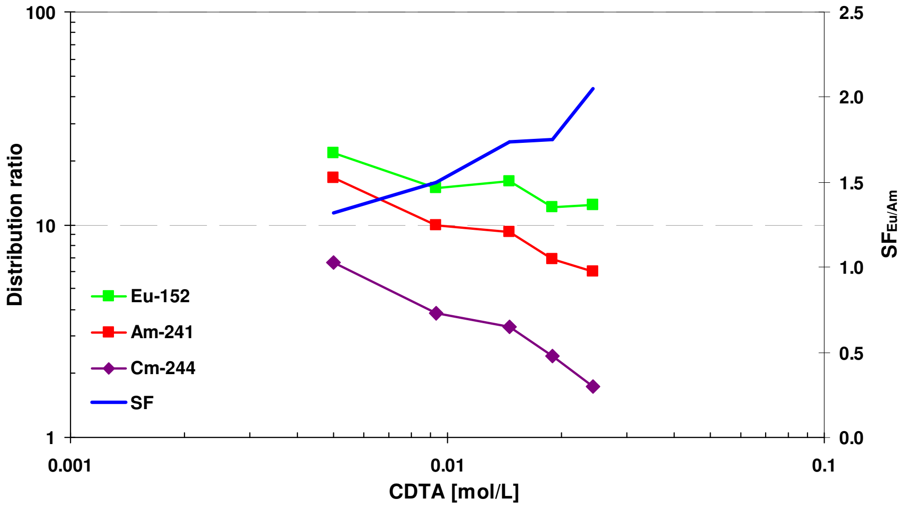


Figure 20. The extraction of ^{241}Am, ^{152}Eu and ^{244}Cm as a function of CDTA concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, variable concentration of CDTA, 10^{-4} mol/L Ln, pH_{ini}=4, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, mixing time: 15min.

the difference is not large (K_{ex}=0.020 and 0.035 for Am and Cm, respectively)[86]. In the aqueous phase the trivalent metals form complexes with lactic acid and with the polyaminocarboxylic acid. Only minimal difference in constant stabilities is between lactate complexes of Cm and Am (logß=6.00 and 5.76, respectively)[87] although they are relatively weak in comparison to complexes of these metals with poylaminocarboxylic acids. CDTA forms more stable complexes with Cm than Am (logß=18.35 and 18.21, respectively).[86] It could be assumed though the major influence on the extraction of Am and Cm in TALSPEAK system has the polyaminocarboxylic acid.

Table 8. Influence of CDTA concentration on $SF_{Eu/Am}$ and $SF_{Am/Cm}$

CDTA [mol/L]	0	0.005	0.009	0.015	0.019	0.024
$SF_{Eu/Am}$	1.28	1.32	1.50	1.74	1.75	2.05
$SF_{Am/Cm}$	0.61	2.51	2.60	2.79	2.86	3.50

4.1.3.5 DTPA

Diethylenetriaminepentaacetic acid (DTPA), the reference complexing agent for TALPEAK process forms 1:1 complexes with An(III) and Ln(III).[76] In the Figure 21 the slopes for ^{241}Am and ^{152}Eu are -0.91 and -0.93, respectively, which suggest that 1:1 complexes were formed. The distribution ratios of ^{244}Cm and ^{252}Cf express slopes similar to Am and Eu apart from the values at [DTPA] > 0.05 mol/L, where an increase of D-values is observed. This was a result of self-absorption of the alpha radiation of ^{244}Cm and ^{252}Cf in the sample of an aqueous phase, where significant amounts of sodium salt were present (Na_5DTPA). When a very low concentration of these metals was present in the aqueous phase (high D-values) the measured alpha activities were underestimated.

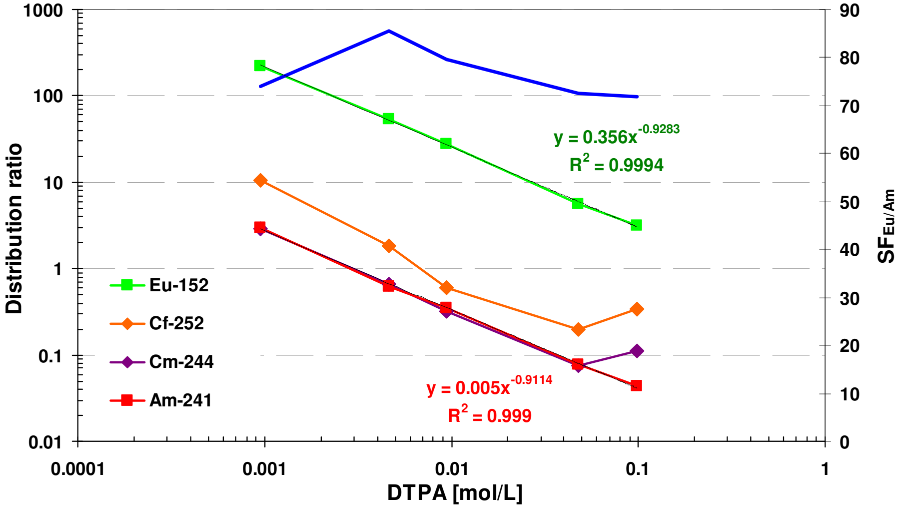


Figure 21. The extraction of ^{241}Am, ^{152}Eu, ^{244}Cm and ^{252}Cf as a function of DTPA concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, variable concentration of DTPA, 10^{-4} mol/L Ln, pH=4, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, ^{252}Cf, mixing time: 15min.

Trustable results of lanthanide concentration were obtained using ICP-MS (Figure 22 and Figure 23). Only the values at 0.001 mol/L of DTPA were omitted due to the very low concentration of the metals in the aqueous samples (below detection limit). The strongest DTPA complexes were formed with lanthanides beginning from praseodymium to holmium. The rest of the lanthanide group members were better extracted with the highest distribution ratio for ytterbium and lutetium. Yttrium was extracted quantitatively even at DTPA concentration of 0.1 mol/L, thus there was no complexation of this element in the aqueous phase. The separation factor of Cm and Cf over Am are shown in Table 9. Similarly as in case of HEDTA the separation factor of Cm over Am was constant with minor fluctuations and equalled 1. This means that the separation of Cm from Am by introducing DTPA into the aqueous phase still would not be possible. An increased separation of Cm and Cf from Am was observed for the highest DTPA concentration used (0.098 mol/L, Table 9 column 7). However, as it was mentioned above this deviation results from the absorption of the alpha radiation in the measured sample due to significant concentration of sodium salts in the sample.

Table 9. Influence of DTPA concentration on $SF_{Cm/Am}$ and $SF_{Cf/Am}$

DTPA [mol/L]	0	0.001	0.005	0.009	0.048	0.098
$SF_{Cm/Am}$	0.60	0.97	1.04	0.90	0.95	2.55
$SF_{Cf/Am}$	0.97	3.55	2.91	1.69	2.57	7.82

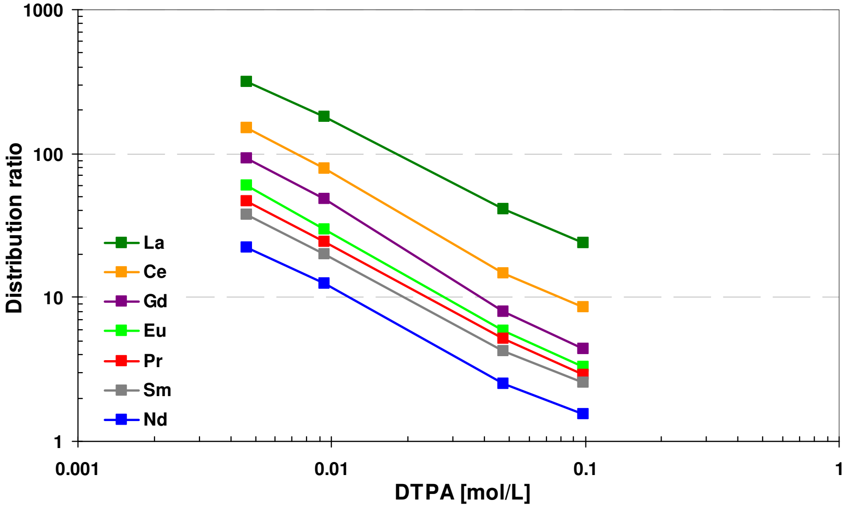


Figure 22. The extraction of light lanthanides as a function of DTPA concentration. Conditions: see Figure 21.

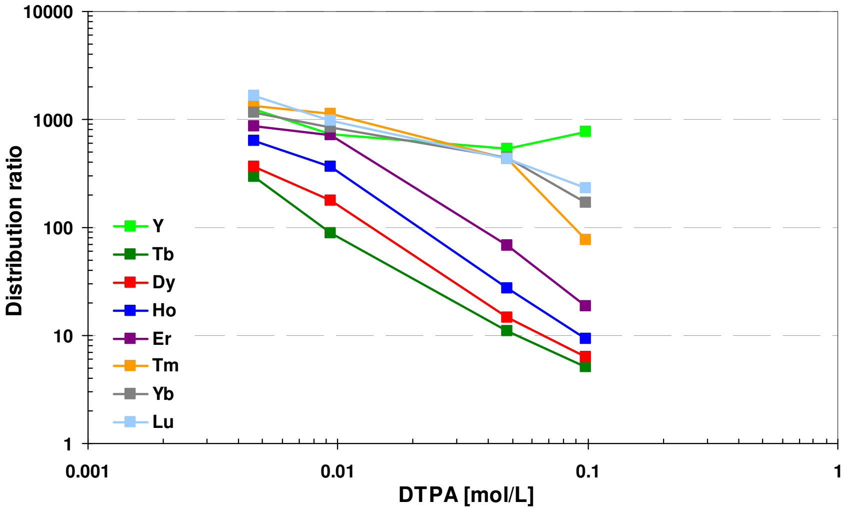


Figure 23. The extraction of heavy lanthanides and yttrium as a function of DTPA concentration.

Conditions: see Figure 21.

4.1.3.6 TTHA

As it was mentioned previously this compound possesses the largest number of the donor atoms and thus should be the most sterically demanding within all ligands tested.

The extractability of Eu, Am and Cm was decreasing with increasing the ligand concentration (Figure 24). Curium was slightly better extracted than Am. The separation factor of europium over americium was very high comparing to the one obtained with DTPA. At the ligand concentration of 0.01 mol/L the $SF_{Eu/Am}$ equalled 272 and increased up to 409 for 0.18 mol/L of the ligand.

The light lanthanides were complexed in the aqueous phase by TTHA which is assumed from the decrease of their distribution ratio during increasing the ligand concentration (Figure 25). The complexes of the ligand with the heavy lanthanides were relatively weaker compared to the light ones. Low concentration of the heavy Ln in the aqueous phase after extraction resulted in a significant error in the ICP-MS measurements. Thus their distribution ratios could only be estimated as > 200.

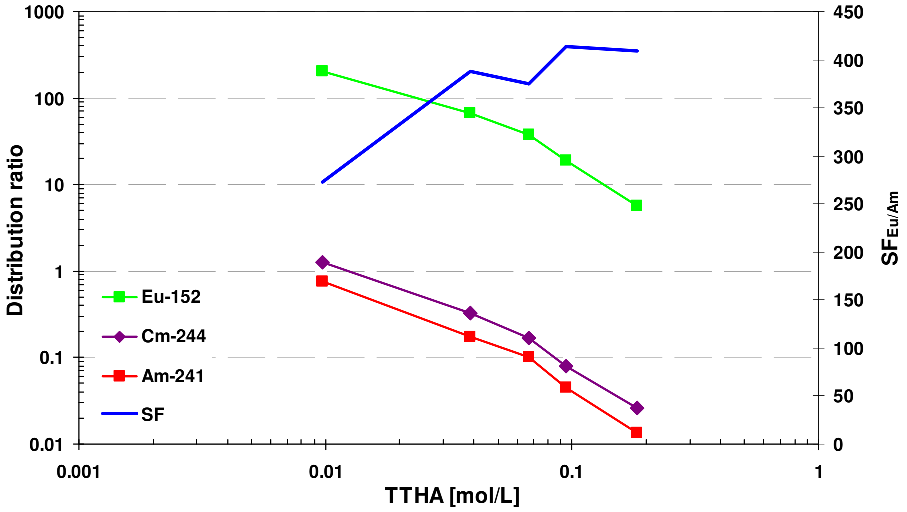


Figure 24. The extraction of ^{241}Am, ^{152}Eu, ^{244}Cm as a function of TTHA concentration.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, variable concentration of TTHA, 10^{-4} mol/L Ln, pH$_{ini}$=4, tracers: ^{241}Am, ^{152}Eu, ^{244}Cm, mixing time: 15min.

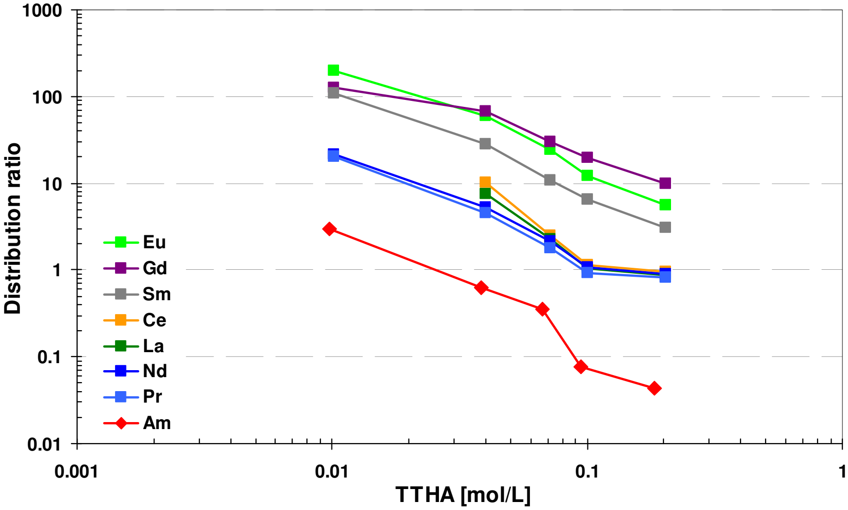


Figure 25. The extraction of light lanthanides as a function of TTHA concentration. Conditions: see Figure 24.

4.1.4. The performance of DTPA and TTHA in the reversed-TALSPEAK

The triethylenetetraamine-hexaacetic acid (TTHA) forms stronger complexes with trivalent lanthanides and actinides compared to its better known derivative DTPA. The former exhibits higher affinity towards lighter lanthanides while the latter forms more stable complexes with the heavier Ln (Table 6).

At the TALSPEAK conditions lanthanum and heavier lanthanides from erbium to lutetium are better extractable than the metals from the middle of the lanthanide series with neodymium being the least extractable (Figure 26, green line). This is a typical behaviour in TALSPEAK which was also reported by other researchers.[50]

When DTPA was replaced with TTHA the extraction pattern of lanthanides changed significantly (Figure 26, blue line). The light lanthanides from lanthanum to neodymium were poorly extracted although their distribution ratios did not differ much from each other. A steep rise of the distribution ratio curve was observed for the lanthanides heavier than neodymium.

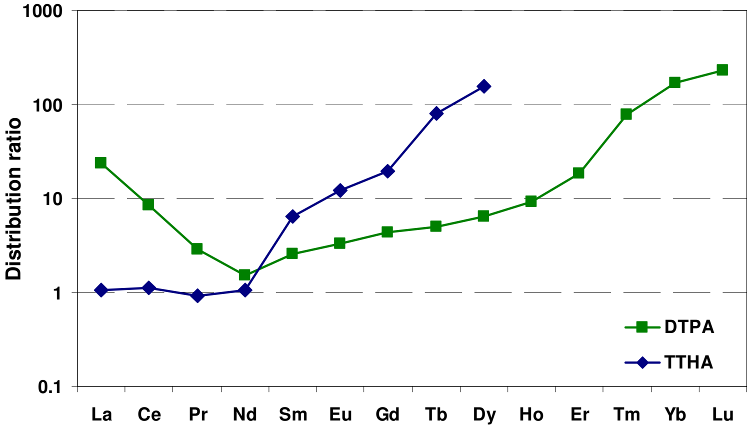


Figure 26. The extraction profile of lanthanides depending on the ligand used.

Organic phase: 0.5 mol/L HDEHP (99.9 % purity) in TPH

Aqueous phase: 1 mol/L lactic acid, 0.1 mol/L of ligand, 10^{-4} mol/L Ln, pH_{ini}=4, mixing time: 15min.

For the heavy ones from holmium to lutetium the distribution ratios were well above 200 (not shown on the graph).

Since in the nuclear spent fuel the dominant lanthanides are the light ones,[88] TTHA seems to be a better choice than DTPA to perform selective actinide separation.

The separation factors of trivalent lanthanides over americium are shown in Table 10. Lanthanum, cerium, praseodymium and neodymium are weaker complexed by DTPA compared to TTHA that results in their better separation from americium. However, the rest of lanthanides were more efficiently separated with TTHA.

The main disadvantage of using these hydrophilic complexing agents is the necessity to work at elevated pH (up to 4) to obtain sufficient separation factors. Additionally, the concentration of the complexing agent has to be high enough to obtain suitable distribution ratios for americium stripping (D_{Am} « 1 and D_{Ln} > 1) at this elevated pH of the stripping solution.

Table 10. The comparison of the separation of Cm, Cf and lanthanides from Am for DTPA and TTHA (conditions: see Figure 21 and Figure 24).

	DTPA = 0.048 mol/L	TTHA = 0.07 mol/L
	$SF_{X/Am}$	$SF_{X/Am}$
Cm	0.95	1.64
Cf	2.57	-
Y	> 1000	> 1000
La	529	22
Ce	187	24
Pr	66	18
Nd	32	21
Sm	55	107
Eu	75	374
Gd	102	291
Tb	140	> 1000
Dy	188	> 1000
Ho	352	> 1000
Er	866	> 1000
Tm	> 1000	> 1000
Yb	> 1000	> 1000
Lu	> 1000	> 1000

Summarising, the most efficient polyaminocarboxylic acids in the reversed-TALSPEAK process under applied conditions were DTPA and TTHA with high separation factors $SF_{Ln/An}$ (see Table 10). Complexants NTA and HEDTA gave reasonably high $SF_{Ln/An}$, although is was not possible to strip most of An(III) into the aqueous phase ($D_{An(III)} > 1$) even at high complexant concentration (0.2 mol/L). EDTA due to its poor solubility in solution at pH > 3.5 was not tested in this work. CDTA similarly as in case of NTA and HEDTA did not stripped An(III) efficiently ($D_{Am(III)} > 1$). However, CDTA was the only one within all tested polyaminocarboxylic acids that gave reasonably high separation between Am and Cm ($SF_{Am/Cm} = 3.5$).

4.2. DIAMEX-SANEX

The TALSPEAK process developed for the separation of trivalent actinides from lanthanides requires a low feed acidity (pH ≈ 2) for the metals extraction. The feed pH adjustment can be avoided when an acidic extractant, such as HDEHP (see Figure 7), is used along with a neutral extractant (e.g. CMPO, DMDOHEMA) resulting in a process that combines DIAMEX and TALSPEAK process. This new concept called DIAMEX-SANEX is shown in Figure 27. The neutral ligand extracts the trivalent actinides and lanthanides from an acidic solution. The exact extracting conditions depend on the extractant used, for instance in the comparative experiment CMPO required feed of acidity over 1 mol/L HNO_3 while DMDOHEMA of more than 3 mol/L HNO_3 (Figure 28). The second extractant, HDEHP, is the active constituent of the extractant mixture in the stripping step of the process under decreased acidity. It complexes trivalent lanthanides in the organic phase while trivalent actinides are selectively stripped into the aqueous phase by means of a buffered solution containing a hydrophilic complexing agent (e.g. HEDTA, DTPA), which is similar to reversed-TALSPEAK.

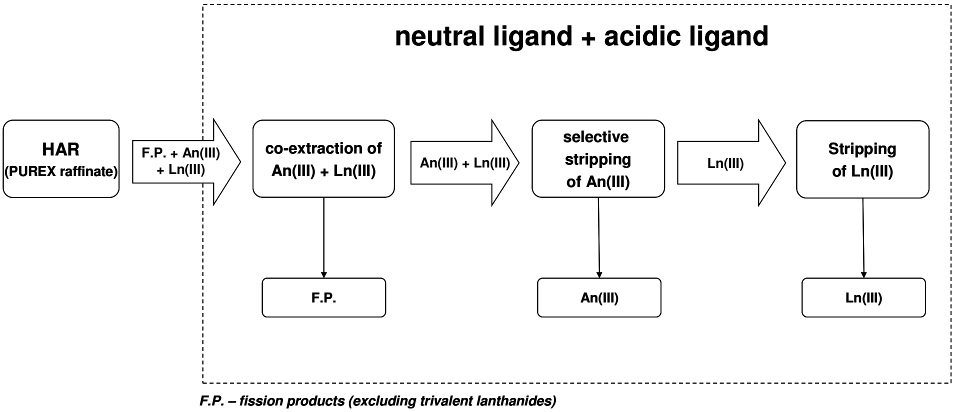


Figure 27. The concept of the process based on a mixture of neutral and acidic ligand.

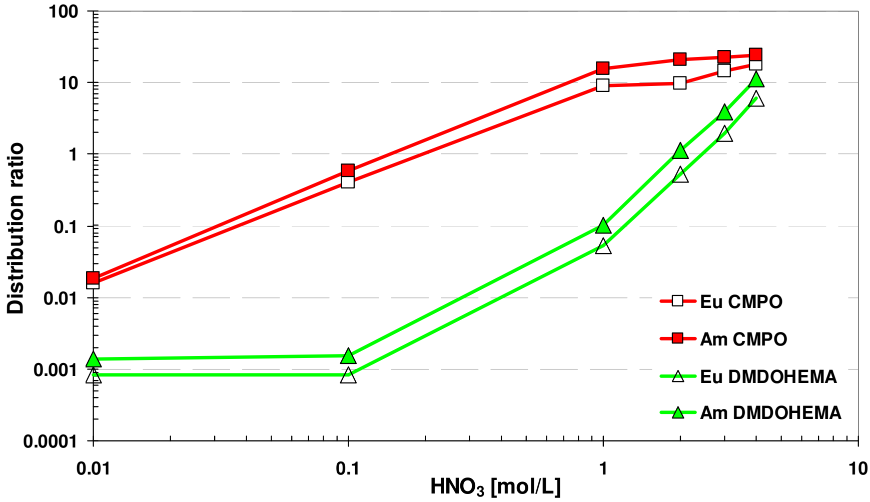


Figure 28. The extraction of ^{241}Am and ^{152}Eu as a function of nitric acid concentration.

Organic phase: 0.2 mol/L CMPO + 1.4 mol/L TBP in n-dodecane (squares) or 0.65 mol/L DMDOHEMA in TPH (triangles)

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

This concept of using a mixture of two extractants was studied in India[89] and France.[90-91] The process proposed by Indian researchers implemented mixed organic solvent consisting of CMPO and HDEHP. In the French PALADIN process the malonamide extractant DMDOHEMA is used instead of CMPO due to its complete incinerability thus avoiding generation of secondary solid waste (CHON principle). Also the radiochemical degradation products of DMDOHEMA do not interfere with the separation process.[92-93] The problems of co-extraction of some of the fission products from HLLW (Fe, Mo, Zr, Pd) resulted in a complex process flow-sheet with extended stripping parts for these metals. This resulted in the generation of large volumes of effluents thus a modification of the PALADIN process was proposed.[94] The modification was based on the extraction of Ln(III) and An(III) with DMDOHEMA and further addition of the acidic extractant just before the actinide(III) selective stripping. After stripping of Ln most of the neutral extractant was separated and returned to the front part of the process (extraction).

In 2007 another modification of the PALADIN process was proposed[91] i.e. HDEHP was substituted by its more hydrophilic derivative di-n-hexylphosphoric acid (HDHP, Figure 29). HDHP is sufficiently hydrophobic for use in solvent extraction as an organic ligand. At the same time its increased hydrophilicity (compared to HDEHP) enhanced the separation of the acidic extractant from DMDOHEMA.

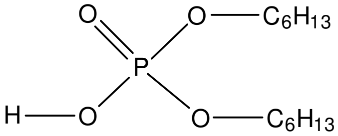


Figure 29. Chemical structure of HDHP

In the present thesis the neutral extractant was represented by N,N,N',N'-tetraoctyl diglycolamide (TODGA, Figure 30), an extractant possessing very high affinity for trivalent lanthanides and actinides with only a small discrimination between Eu and Am at lower nitric acid concentrations. TODGA extracts metals by a solvating mechanism i.e. a metal is extracted together with an anion (NO_3^-) to compensate the extracted metal charge:

$$M^{n+} + \overline{aTODGA} + nNO_3^- \longleftrightarrow \overline{M(NO_3)_n(TODGA)_a} \qquad \text{Eq 9}$$

where: M^{n+} - metal to be extracted; the bars over the species denote their presence in the organic phase

The extractant TODGA is described in more details in chapter 4.3 Innovative SANEX (page 83).

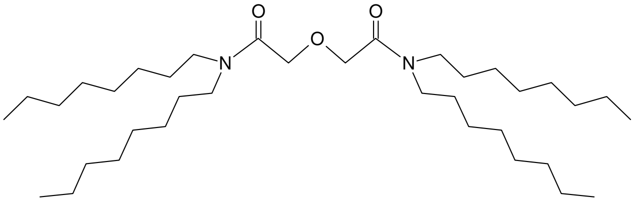


Figure 30. Chemical structure of TODGA.

4.2.1. Nitric acid concentration dependency on An(III) + Ln(III) extraction

As it is shown in Figure 31, TODGA co-extracts Eu and Am from nitric acid solutions at concentrations above 1 mol/L (triangles) nearly quantitatively. At lower acidity the metals

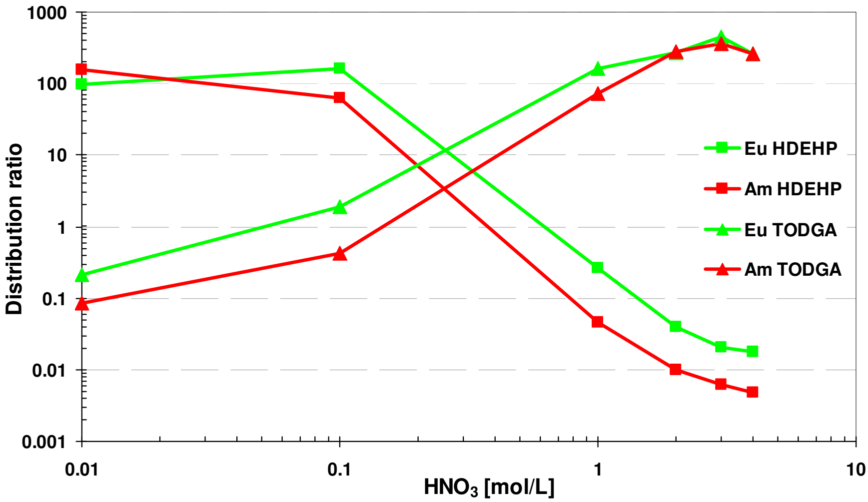


Figure 31. The extraction of ^{241}Am and ^{152}Eu as a function of nitric acid concentration.

Organic phase: 0.5 mol/L HDEHP in TPH (squares) or 0.2 mol/L TODGA in TPH (triangles)

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

stay predominantly in the aqueous phase. However, the acidic extractant HDEHP can extract these metals from an aqueous solution of $pH_{ini} > 1$. By adjusting the acidity of the aqueous phase it is possible to switch the extraction from one ligand onto another.

When the two extractants were mixed together and used for extraction of Am and Eu from variable concentration of nitric acid no decrease of distribution ratios of the two radionuclides was observed (Figure 32). This suggested good extraction of An(III) and Ln(III) (first step of the process) but also indicated possible difficulties in Ln stripping after removing the An from the loaded organic phase (last step). The An(III) could be stripped into the aqueous phase by complexation with a polyaminocarboxylic acid, such as DTPA. Thus the main focus was on Ln(III) stripping.

In order to remove trivalent lanthanides and actinides from the loaded organic phase consisting of just HDEHP, simple pH decrease of the aqueous solution results in their

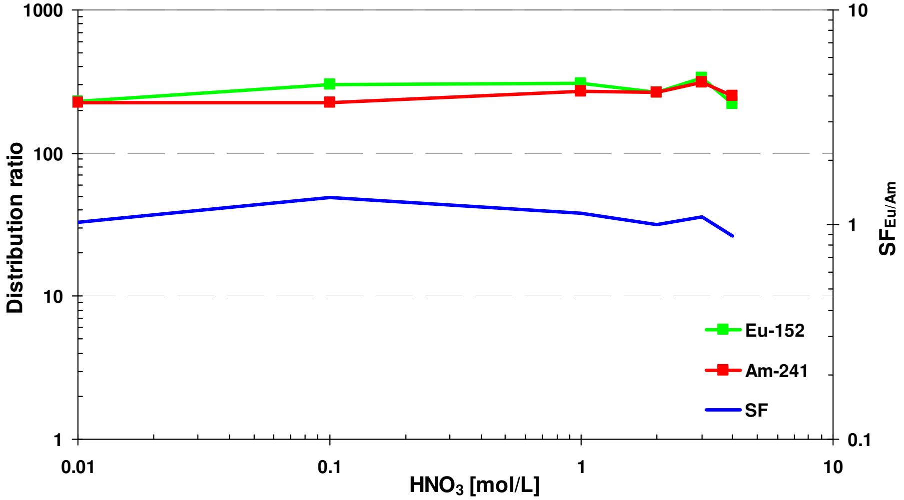


Figure 32. The extraction of ^{241}Am and ^{152}Eu as a function of nitric acid concentration.

Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

stripping from the organic phase. In case of a solvent consisting of TODGA these trivalent metals can be stripped off by decreasing the nitrate ion concentration in the aqueous phase. In case of a mixture of the two extractants, as it is the case in DIAMEX-SANEX process, the decrease of pH by using moderately concentrated nitric acid would result in an increase of the nitrates concentration thus higher extraction of the metals by TODGA. Therefore, the addition of a Ln complexing agent into the aqueous phase, instead of just nitric acid concentration adjustment, was considered.

4.2.2. Co-extraction of Ln(III)/An(III) from HAR

Experiments with High Active Raffinate simulate solution (HAR-FZJ) were performed to see whether HDEHP had any influence on the Ln/An extraction by TODGA from highly concentrated nitric acid solution (≥ 3 mol/L HNO_3) and if non-lanthanide fission products could possibly be extracted.

As it is shown in Table 11 the extraction of ^{241}Am and Ln was very efficient with distribution ratios over 100. As expected zirconium was also well extracted (D_{Zr} = 29), as TODGA extracts this element in significant extent,[95] its extraction can be suppressed by the use of oxalic acid.[33, 35] Strontium with a D-value of 1.18 also partly ended up in the organic phase, although it can possibly be removed in the scrubbing step with low concentrated nitric acid (0.5 mol/L HNO_3).[47, 95]

Table 11. The distribution ratios of HAR elements extracted by a mixture of TODGA/HDEHP from 3 mol/L HNO_3.

Element	D-value	Element	D-value
^{241}Am, ^{152}Eu	>200	Gd	>100
Y	>100	Zr	29
La	98	Sr	1.18
Ce	>100	Cu	0.140
Pr	>100	Cd	0.132
Nd	>100	Sb	0.071
Sm	>100	Cr	<0.01
Eu	>100	Ba	<0.01

Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH

Aqueous phase: HAR elements in 3 mol/L HNO_3, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.2.3. Selective stripping of An(III)

The formula of the actinide stripping solution was adopted from the reversed-TALSPEAK process development presented in chapter 4.1 Reversed TALSPEAK. The solution was buffered using lactic acid and the initial pH was adjusted to 4. The separation of Am from Eu was driven by an hydrophilic complexant (polyaminocarboxylic acid). Europium nitrate of a concentration of 0.01 mol/L was used to simulate the loading effect of the organic phase with lanthanides. The two complexants DTPA and TTHA, which gave the highest Ln/An separation factor in the screening test of the TALSPEAK process (described in the previous chapter), were employed.

Similar as in the TALSPEAK screening test the separation factors of Eu over Am were much higher using TTHA compared to DTPA (Figure 33).

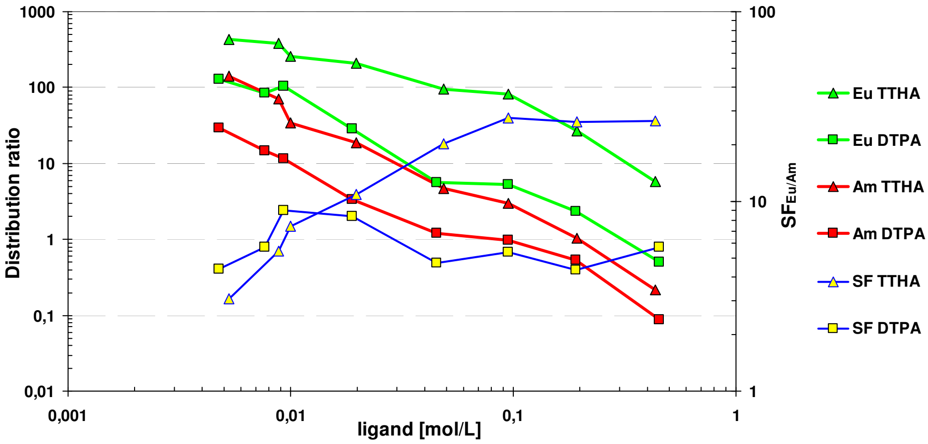


Figure 33. The extraction of ^{241}Am and ^{152}Eu as a function of ligand concentration.

Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH

Aqueous phase: variable ligand concentration, 0.01 mol/L of europium, 1 mol/L lactic acid, pH_{ini}=4, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min

While increasing the concentration of the complexing agents the D_{Am} and D_{Eu} were decreasing (Figure 33). The separation factor of Eu over Am ($SF_{Eu/Am}$) increased with increasing ligand concentration, although a plateau was reached at about 0.01 mol/L for DTPA and 0.1 mol/L TTHA. A further increase of the ligand concentration in the aqueous phase had influence only on the Am and Eu distribution ratios.

At the DTPA concentration of 0.2 mol/L the distribution ratio of Am was below 1 therefore >50% of this element was stripped into the aqueous phase while Eu stayed in the organic phase. A further increase of the complexing agent concentration resulted in the complexation of both radioelements in the aqueous phase preventing their extraction by HDEHP. The Eu/Am separation factor did not exceed 8 even at [DTPA]=0.5 mol/L.

TTHA gave higher Eu/Am separation factor than DTPA similarly as in the complexant screening test in the TALSPEAK process (previous chapter), although a high concentration was required to separate Am from Eu. The concentration of TTHA > 0.2 mol/L was sufficient to selectively complex more than 50 % of Am in the aqueous phase with a Eu/Am separation factor of 26.

In the PALADIN process[90] an americium distribution ratio around 0.1 was obtained with just 0.005 mol/L DTPA, whereas in this work at the same ligand concentration the americium distribution ratio was about 30 (Figure 33). The explanation for the poorer stripping performance is probably the use of much stronger neutral extractant (TODGA) compared to less efficient An(III)/Ln(III) extractant DMDBTDMA used in PALADIN process. Additionally, in this work 0.01 mol/L $Eu(NO_3)_3$ was used to simulate the loading of the solvent with high amounts of lanthanides while in the PALADIN process tracers of ^{241}Am and ^{152}Eu were used (thus no nitrates present in the aqueous phase). This would mean that a total nitrate ion concentration of 0.03 mol/L was present in the stripping solution (resulting from Eu salt dissolution) hence an increased influence of TODGA on the metal extraction at pH=4 could be expected. This effect together with metal extraction by HDEHP resulted in non-efficient Am(III)-stripping. In the full process even higher D-values could be expected as 0.2 mol/L TODGA extracts about 0.2 mol/L of nitric acid from its initial concentration of 3 mol/L (typical acidity of the HLLW solution) thus 1:1 complex TODGA:HNO_3 is formed. This will be back extracted to the aqueous phase in the stripping step, causing an increase in the total nitrate concentration. For this reason the experiments with HAR surrogate were carried out using the stronger complexant of the two tested, namely TTHA, for selective An(III) stripping.

Experiments of loading the solvent with HAR-FZJ simulate solution followed by selective stripping of Am were performed. The results (Table 12) show nearly quantitative extraction of americium and trivalent lanthanides with distribution ratios over 200. Only lanthanum was extracted in lesser extent with D_{La}=87.1.

Table 12. The distribution ratios of HAR elements extracted and stripped from a mixture of TODGA + HDEHP solvent

Element	Distribution ratio	Distribution ratio	$SF_{Ln/Am}$	Distribution ratio	$SF_{Ln/Am}$
	Extraction	Stripping A		Stripping B	
^{241}Am	> 200	5.12	-	0.56	-
^{152}Eu	> 200	81.3	16	11.5	21
La	87.1	199	39	25.2	45
Ce	> 200	114	22	13.7	25
Pr	> 200	87.3	17	10.3	19
Nd	> 200	75.3	15	9.46	17
Sm	> 200	71.9	14	10.87	20
Eu	> 200	83.4	16	12.06	22
Gd	> 200	94.1	18	12.37	22
Y	233	184	36	157	282
Zr	37.0	11.6	2,3	9.58	17
Sr	1.19	39.9	7,8	37.5	68
Ba	0.76	4.84	0,95	2.95	5.3
Sb	0.14	1.08	0,21	1.31	2.4
Cd	0.13	0.13	0,03	0.16	0.3

Extraction

Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH

Aqueous phase: HAR-FZJ simulate solution in 3 mol/L HNO_3, tracers: ^{241}Am, ^{152}Eu, mixing time: 15min

Stripping A and B

Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH (loaded in the extraction step)

Aqueous phase: 1 mol/L lactic acid, pH_{ini}=4, TTHA 0.17 mol/L (Stripping A) or 0.43 mol/L (Stripping B), mixing time: 15min.

Yttrium followed the lanthanides into the organic phase also with very high distribution ratios. Relatively good extraction of zirconium was observed when no masking agent for this metal was used and an extraction of about 50 % of strontium (D_{Sr}=1.19). The extraction results are in good agreement with the results obtained for similar processes where TODGA was used as a single extractant.[95] Only the extraction of zirconium (D_{Zr}=37) was lower than the one reported by Modolo et al. In his studies the distribution ratio of zirconium reached 100 at 1 mol/L HNO_3 and did not change significantly with increasing acidity of the aqueous phase up to 3 mol/L HNO_3. The reason of the lower zirconium extraction was not studied here, although it could be the influence of the second extractant used, namely HDEHP.

The selective stripping of the trivalent actinides (here represented by ^{241}Am) was performed using the loaded organic solvent from the extraction step (described above) with HAR elements. TTHA was used for the selective stripping of Am into the aqueous phase at two different concentrations: 0.17 and 0.43 mol/L. The stripping solution was buffered with lactic acid (1 mol/L) to minimise pH changes. The results of the stripping experiments are shown in Table 12. The stripping solution A with a TTHA concentration of 0.17 mol/L appeared to be not sufficient for efficient Am stripping. The distribution ratios of ^{241}Am and ^{152}Eu were higher than the ones obtained in the previous experiment (Figure 33, D_{Am}=1 and D_{Eu}=27) where the loading step was omitted. This can be due to a change of the pH_{aq} at equilibrium. While actinide stripping is performed the HDEHP forms mostly complexes with trivalent Ln in the organic phase and at the same time releasing protons into the aqueous phase according to Eq 6 (4.1 Reversed TALSPEAK, page 46). The lactic acid buffers the stripping solution to minimise the pH change as in the TALSPEAK process. The additional extractant TODGA extracts part of the nitric acid during the metal extraction from highly acidic solutions (the extraction step) which increases the acidity of the actinide stripping solution as the extracted acid is also stripped into the aqueous phase (described in more details in the following chapter).

The stripping solution B with a higher concentration of TTHA (0.43 mol/L) re-extracted the ^{241}Am from the loaded organic phase more efficiently compared to stripping solution A, and most of Am(III) was back-extracted to the aqueous phase. At the same time trivalent lanthanides and yttrium were kept mainly in the organic phase with the lowest Ln/Am separation factor of 17 for neodymium (Table 12, column 6). Most of the extracted strontium and zirconium followed the lanthanides through the An-stripping step.

4.2.4. Stripping of Ln(III)

As described previously the stripping of trivalent lanthanides from the loaded organic solvent after the actinide stripping cannot be performed using diluted nitric acid. However, it was reported that TODGA extracts Am from hydrochloric acid concentration higher than 5 mol/L (Figure 34). Similar behaviour of trivalent lanthanides was expected. Therefore the extraction studies of ^{241}Am and ^{152}Eu were carried out from a HCl concentration range of 0.1 to 5 mol/L. The results of this experiment are shown in Figure 35. The distribution ratios of Am and Eu decreased with increasing HCl concentration up to 2.0 mol/L HCl where the minimal D-values were obtained, namely 1.1 and 3.2 for Am and Eu, respectively. However, they were still above 1. Thus an efficient removal of Ln(III) from the organic phase would probably not be possible. A further increase of the hydrochloric acid concentration rapidly increased the extraction of the radionuclides.

In conclusion, the organic solvent consisting of a mixture of HDEHP and TODGA appeared to be not suitable for An(III) partitioning. The separation of Am from Ln(III) is possible using the hydrophilic complexing agent TTHA which forms much stronger An and Ln complexes compared to DTPA. However, the stripping agent (hydrophilic complexant) has to be applied at significantly high concentration of 0.43 mol/L. Another problem appears after selective stripping of An(III) where the organic solvent is still highly loaded with trivalent lanthanides. Their stripping with HCl is not efficient. Moreover in the reprocessing of the spent nuclear fuel nitric acid is the predominant medium (spent fuel dissolved in nitric acid for Pu and U recovery in PUREX process).

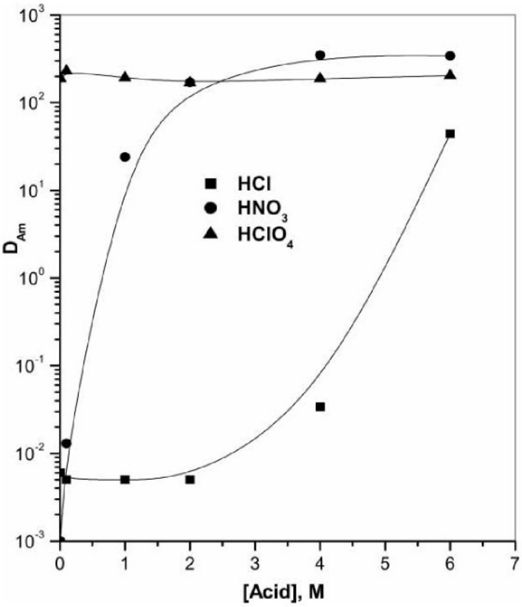


Figure 34. The extraction of Am as a function of concentration of different acids. The figure and conditions taken from Ansari et al.[96]

Organic phase: 0.1 mol/L TODGA in n-dodecane

Aqueous phase: variable concentration of HCl, HNO_3 and $HClO_4$, tracer: ^{241}Am; mixing time: 45min

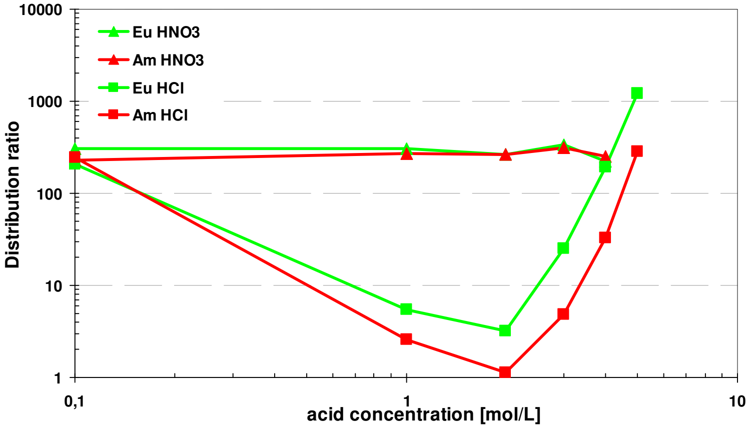


Figure 35. The extraction of ^{241}Am and ^{152}Eu as a function of acid concentration.

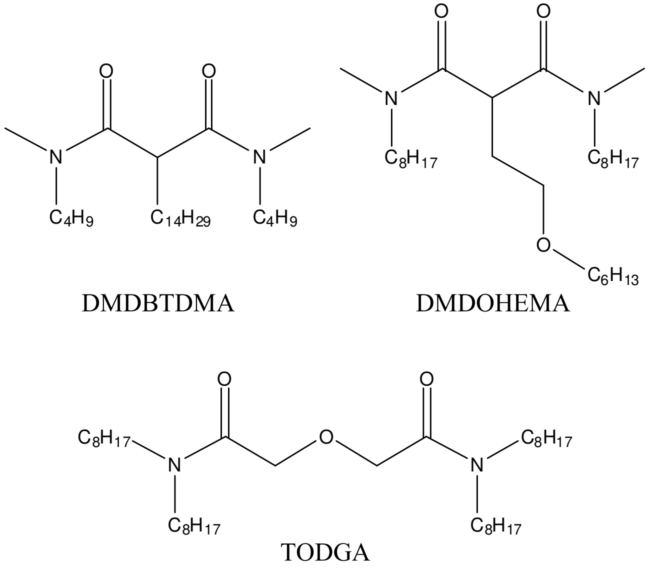
Organic phase: 0.5 mol/L HDEHP + 0.2 mol/L TODGA in TPH

Aqueous phase: variable concentration of acid, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min

4.3. Innovative SANEX

The DIAMEX process developed by French researchers in 1994 implemented the use of N,N'dimethyl-N,N'dibutyl-tetradecyl-malonamide (DMDBTDMA, Figure 36) for co-extraction of trivalent actinides together with trivalent lanthanides from the PUREX waste stream.[35, 97] DMDBTDMA was not sufficiently robust against hydrolysis and radiolysis, therefore a new DIAMEX reference molecule was selected, N,N'-dimethyl-N,N'-dioctyl-hexylethoxy-malonamide (DMDOHEMA, Figure 36).[98-99]

In 2001 Sasaki et al.[44] synthesised six diglycolamides with different length of the alkyl chains and tested their extraction properties for actinides and lanthanides from various concentrations of nitric acid. One of these organic ligands N,N,N',N'-tetraoctyl diglycolamide (TODGA, Figure 36) showed high distribution ratios for An and Ln from highly concentrated nitric acid combined with a very good solubility in n-dodecane.


DMDBTDMA

DMDOHEMA

TODGA

Figure 36. Chemical structures of DMDBTDMA, DMDOHEMA and TODGA

TODGA possesses higher affinity to An(III) and Ln(III) than the French DMDOHEMA. The extraction of these two groups of elements is efficient even from high concentrations of nitric acid. A comparative experiment showed that the efficient metal extraction by TODGA is possible from an acidic solution of 1mol/L HNO_3 or higher while for DMDOHEMA the nitric acid concentration must have been higher than 2mol/L (Figure 37). The different concentrations of the two extractants in that experiment resulted from the original solvent formula of the DIAMEX (DMDOHEMA) and TODGA/TBP processes. DMDOHEMA possesses higher affinity to Am than Eu while the extraction order of these elements by TODGA is exactly opposite ($D_{Eu} > D_{Am}$). Moreover, TODGA exhibits some separation factor of Ln(III) over Am(III) ($SF_{Eu/Am}$=4.4 at 0.1mol/L HNO_3) that can be enhanced by use of hydrophilic complexing agents.

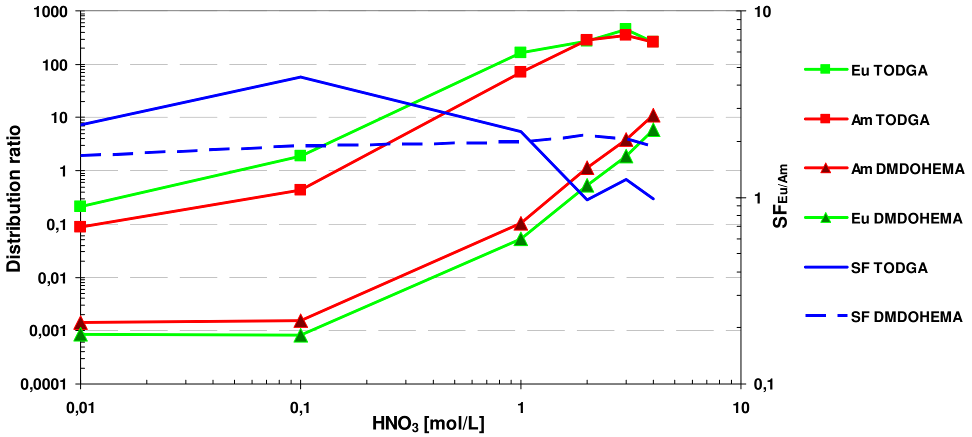


Figure 37. The separation of ^{241}Am and ^{152}Eu with TODGA and DMDOHEMA as a function of the nitric acid concentration.

Organic phase: 0.2 mol/L TODGA in TPH (squares) or 0.65 mol/L DMDOHEMA in TPH (triangles)

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu;
mixing time: 15min.

The number of TODGA molecules involved in the extraction reaction depends on the polarity of the solvent. Extracted species with poor lipophilicity containing just 2 molecules of TODGA can be stable in polar diluents (1-octanol and 1,2-dichloroethane), whereas the highly lipophilic ones require 3 or 4 TODGA molecules to remain stable in non polar diluents (e.g. chloroform, toluene and 1-dodecane).[100]

Assuming that TODGA dissolved in a non-polar diluent, such as n-dodecane, forms 1:3 complexes of metal:ligand, the maximal concentration of extracted metal in the organic phase should be three times lower than the TODGA concentration (one metal cation extracted by three TODGA molecules - Eq 10).

$$M^{n+} + \overline{3TODGA} + nNO_3^- \longleftrightarrow \overline{M(NO_3)_n(TODGA)_3} \qquad \text{Eq 10}$$

However, it was found that the actual maximal concentration of a metal in the organic phase is significantly lower.[101] The poor loading capacity of TODGA can result in a splitting of the organic phase into a heavier and a lighter part when it is loaded with high amounts of extracted metals.[101] This effect is called “third phase formation” and appears when the limiting organic concentration (LOC) of the organic solvent is exceeded. In order to increase the LOC of a solvent an organic phase modifier such as DHOA[101] or TBP[95] can be added. The addition of TBP to the TODGA/TPH solvent does not change significantly the distribution ratios of Am(III) and Eu(III) compared to the extraction without a modifier as shown in Figure 38.

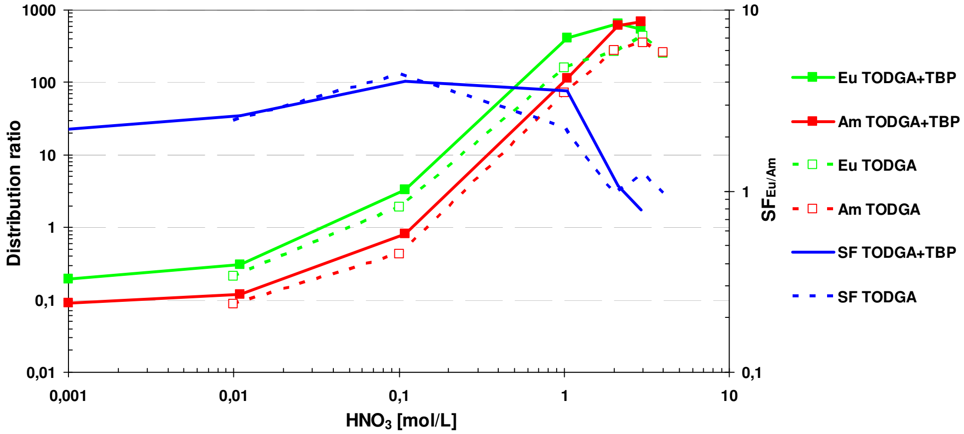


Figure 38. Extraction of ^{241}Am and ^{152}Eu as a function of the nitric acid concentration.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH or 0.2 mol/L TODGA in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu;
mixing time: 15min.

4.3.1. Solvent based on TODGA + TBP

In 2007 Modolo et al.[47, 95] developed a process for An(III) partitioning based on TODGA/TBP dissolved in TPH. The process consisted of an An(III) / Ln(III) co-extraction by TODGA, thus separating those two groups of elements from the fission products, followed by an An(III) / Ln(III) co-stripping using diluted nitric acid.

Since TODGA exhibits a slightly higher affinity to Ln(III) in comparison to An(III) at low nitric acid concentrations, a one-cycle separation process is proposed in this work enhancing this difference by using a hydrophilic ligand such as DTPA in order to selectively strip the trivalent actinides into the aqueous phase, leaving the lanthanides in the organic phase.

This new process (illustrated in Figure 39) called innovative-SANEX, which is the main topic in the present work, consists of three major steps. The first one is the co-extraction of trivalent lanthanides and actinides by TODGA from highly acidic HAR solution, e.g. PUREX

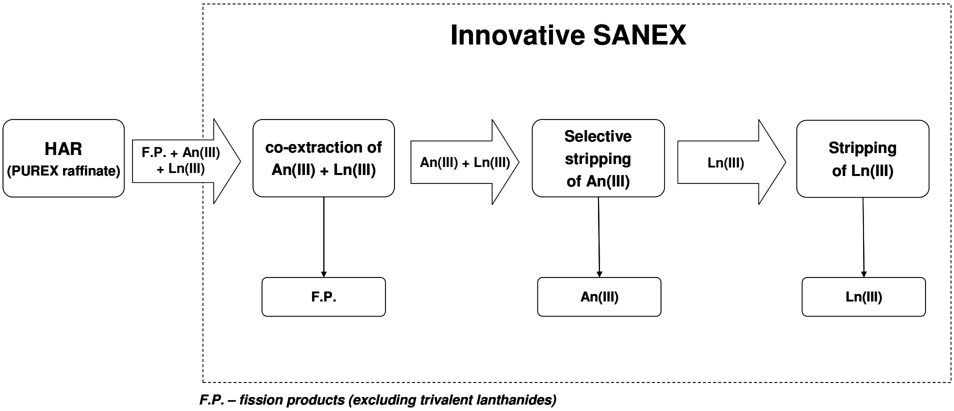


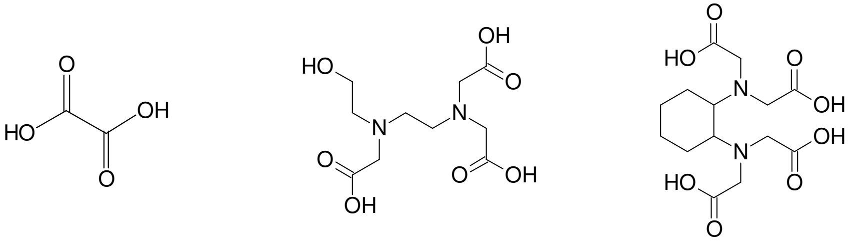
Figure 39. The concept of an innovative SANEX process.

raffinate. In the second step the actinides are selectively stripped by low acidic solution containing a hydrophilic ligand selective for An, similar as in reversed-TALSPEAK. The lanthanides from the loaded organic phase are stripped in the last step using a low concentrated nitric acid solution.

4.3.1.1. Co-extraction of Ln(III) + An(III) from HAR solution

In the first step of the innovative SANEX process trivalent lanthanides are co-extracted together with trivalent actinides from a highly acidic solution containing the minor actinides, fission products (including lanthanides) and corrosion products (e.g. PUREX raffinate). Unfortunately, some of the fission products, such as Zr, Pd, Sr, Ru and Mo, are also co-extracted by TODGA.[95] The extraction of Zr and Pd can be suppressed by their complexation in the aqueous phase with oxalic acid and HEDTA, respectively. These two masking agents were successfully used in the former processes for An partitioning.[35, 47]

In this work CDTA was proposed as substitute for oxalic acid and HEDTA (Figure 40) since this complexing agent showed very promising results in Zr and Pd complexation from HAR solution (D_{Zr}<0.01 and D_{Pd}<0.07; for details see chapter 4.4 New masking agent, page 123).



Oxalic acid

Hydroxyethylethylenediamintetraacetic acid (HEDTA)

1,2-Diaminocyclohexanetetraacetic acid (CDTA)

Figure 40. The chemical structures of oxalic acid, HEDTA and CDTA.

The influence of the masking agents CDTA and HEDTA on the metal extraction by TODGA was determined. Three separate extraction experiments were carried out: a) without masking agent (complexant), b) with the addition of CDTA or c) with the addition of HEDTA. The results of these experiments are shown in Table 13.

The two masking agents used had no influence on the good extraction of ^{241}Am, the light Ln(III) and Y. Zirconium and palladium were also extracted when no masking agent was used. When CDTA was added to the feed solution before contacting the two phases, its complexation with zirconium and palladium suppressed the extraction of these two metals into the organic phase. The second masking agent tested, HEDTA, complexed only Pd thus the extraction of Zr was still high. The extraction of strontium is not directly affected by the use of the masking agents as they do not complex this metal. The increased D_{Sr} in the experiment with CDTA results from the suppression of the zirconium extraction. The high concentration of Zirconium in the HAR solution (1071 mg/L) occupies a high amount of TODGA molecules thus lowering the free TODGA concentration. With the addition of a complexant and the suppression of the zirconium extraction, a higher amount of free TODGA is available for the Sr extraction. Therefore, the Sr distribution ratio increases when a Zr-masking agent is applied.

Partly co-extracted strontium and molybdenum can be removed from the organic phase by two additional scrubbing steps with different concentrations of nitric acid similar as in the TODGA/TBP process developed in Jülich.[47] The extraction of strontium decreases with decreasing nitric acid concentration ($D_{Sr}<1$ for $HNO_3<1mol/L$) while the extraction of molybdenum decreases with increasing nitric acid concentration ($D_{Mo}<0.1$ for $HNO_3>1mol/L$).

Table 13. Distribution ratios of HAR elements and the influence of complexants

Element	Without complexant	CDTA	HEDTA
	Distribution ratio D		
^{241}Am, ^{152}Eu	>100	>100	>100
Y, La, Ce, Pr, Nd, Sm, Eu, Gd	>100	>100	>100
Zr	>100	0.01	32.8
Pd	9.31	0.07	0.07
Sr	1.50	3.31	1.54
Ag	0.69	0.01	0.59
Ru	0.34	0.32	0.23
Mo	0.26	0.19	0.23
Cd	0.14	0.08	0.14
Ba	0.13	0.03	0.01
Rb	0.10	0.14	0.09
Ni	0.05	0.01	0.08
Cu	0.03	0.03	<0.01
Cr, Fe, Sn, Sb	<0.1	<0.1	<0.1
Cs, Rh, Te	<0.01	<0.01	<0.01
Al, Se, Na	n.d.	n.d.	n.d.

n.d.: not determined

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: 3.1 mol/L HNO_3, solution of HAR-FZJ, 0.05 mol/L CDTA or HEDTA, tracers: ^{241}Am, ^{152}Eu, mixing time: 15 min.; T = 22°C ± 1°

4.3.1.2. Selective stripping of trivalent Actinides

As was mentioned earlier the separation of trivalent actinides from lanthanides is increased by adding polyaminocarboxylic acid to the stripping solution with reduced acidity as compared to TALSPEAK conditions (4.1 Reversed TALSPEAK, page 45) i.e. pH > 1.5.

In the extraction step of the proposed innovative-SANEX process (Ln(III)+An(III) co-extraction), also nitric acid is partly extracted by TBP and TODGA. From HAR solution of an initial acid concentration of 3 mol/L HNO_3 about 0.42 mol/L of the nitric acid are extracted into the organic phase by the TODGA/TBP mixture.[102] Before stripping the actinides several scrubbing sections are necessary to back-wash co-extracted metals and to reduce the nitric acid concentration in the organic phase. In the proposed process the organic phase loaded with An + Ln is washed with 0.5 mol/L HNO_3 to reduce the concentration of the co-extracted HNO_3 from 0.42 mol/L down to 0.041 mol/L. The acid left in the solvent after the acid scrubbing is further back-extracted into the aqueous phase during the An-stripping step, thereby decreasing again the pH of the stripping solution. However, the polyaminocarboxylic acid responsible for the complexation of An(III) in the aqueous phase requires higher pH-values (pH=2-3). As shown in the chapter "*Reversed-TALSPEAK*" polyaminocarboxylic acids are only able to complex the trivalent actinides in their fully deprotonated form. Therefore, any variations of the stripping solution acidity have a significant impact on the Ln/An separation. By decreasing the pH of the stripping solution the $SF_{Ln/An}$ decreases as there is less deprotonated polyaminocarboxylic acid available to complex the trivalent actinides. One measure to cope this problem is to buffer the stripping solution with a suitable buffer minimising its pH change. Therefore, screening tests of different buffers and complexing agents were carried out.

In all experiments for the selective actinide stripping the organic solvent was first contacted with a solution of Ln(III) at 0.5 mol/L HNO_3 in order to load the organic phase with Ln. The concentration of Ln(III) in this solution was 2.5 times higher compared to their concentration in the HAR solution (Table 4). This higher concentration of lanthanides is expected after the first step of the process, i.e. co-extraction of Ln+An and their scrubbing. This increased Ln concentration is due to the difference in the flow-rate of the organic and the aqueous phase when using a battery of centrifugal contactors. The factor 2.5 was based on the results obtained by Modolo et al. in TODGA/TBP counter-current test.[47] The trivalent actinides were represented only by ^{241}Am in trace amounts. The low acidity of 0.5 mol/L HNO_3 of this solution simulates the scrubbing step required for the removal of nitric acid and strontium from the loaded organic solvent as in the similar TODGA/TBP process.[47] The organic solvent after pre-loading with trivalent lanthanides was further used in the An-stripping step. The approximate concentration of trivalent lanthanides after the pre-loading step is shown in Table 14.

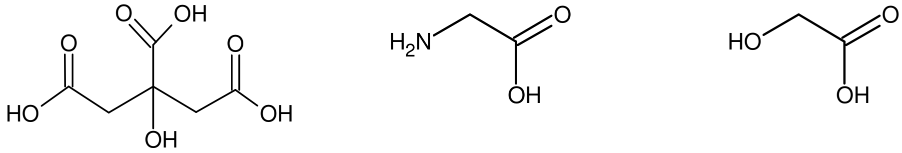
Table 14. The concentration of trivalent lanthanides in the organic phase after the pre-loading step.

Element	[mg/L]	Element	[mg/L]
Y	230	Gd	110
La	430	Nd	1700
Pr	670	Ce	890
Eu	80	Sm	400

4.3.1.2.1 Screening of buffers and complexing agents

A screening test with 5 buffers (Figure 41) together with the two complexing agents HEDTA and DTPA (see structures in Figure 16), was performed to identify the most efficient composition of the An-stripping solution. The main requirements for the stripping solution were a minimal change of the pH (the difference of the initial pH and after the equilibrium was reached) and a high separation factor of ^{152}Eu over ^{241}Am.

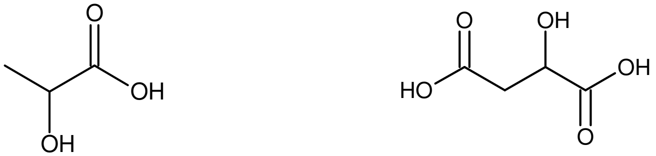
The pre-loaded organic solvent was contacted with stripping solutions composed of different buffers and complexing agents. Sodium nitrate was added to the stripping solutions to increase the distribution ratios so that Eu would be kept in the organic phase while Am is stripped into the aqueous phase (see Eq 9).



Citric acid $pK_{a1} = 3.1$ $pK_{a2} = 4.8$ $pK_{a3} = 6.4$

Glycine $pK_a = 2.3$ $pK_N = 9.8$

Glycolic acid $pK_a = 3.8$



Lactic acid $pK_a = 3.9$

Malic acid $pK_{a1} = 3.5$ $pK_{a2} = 5.1$

Figure 41. Chemical structures and corresponding pK_a values of carboxylic acids used to buffer the An-stripping solution.

The results of the screening tests are shown in the Figure 42 – 44.

The variations of metal D-values for DTPA or HEDTA result from the different acidity of the stripping solution at equilibrium. When no buffer was used, a significant pH change was expected. This caused an increase of the stripping solution acidity while decreasing the concentration of the deprotonated complexant. Therefore, less complexant was available to complex Am resulting in the highest D-values compared to samples where a buffer was used (Figure 42).

The highest Eu/Am separation factors were obtained with DTPA + malic acid or DTPA + citric acid (13.1 and 12.5, respectively) (Figure 43). Also lactic acid gave a high separation

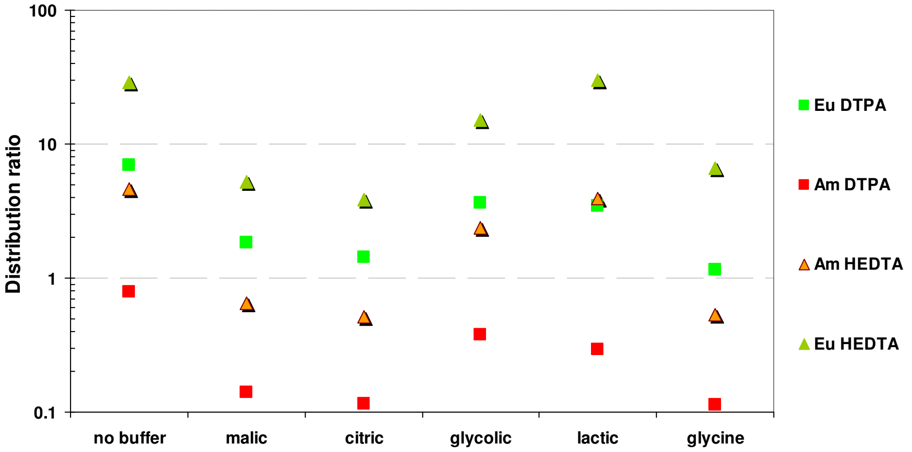


Figure 42. Screening of buffers and complexing agents for the selective stripping of Am.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L buffer, 0.05 mol/L DTPA or HEDTA, 1 mol/L $NaNO_3$, $pH_{ini}=2$, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

factor of 11.8. However, considering the pH change lactic acid did not buffer the aqueous phase effectively (ΔpH=0.47 for DTPA) while citric acid and glycine showed the best buffering properties (ΔpH=0.23 and 0.18 for DTPA, respectively) (Figure 44). Glycine has the lowest pK_a value (acid dissociation constant) of all tested buffers (Figure 41) which is close to the initial pH-value of the stripping solution at which the test was performed. That means at pH = 2 glycine had the highest number of molecules in the basic form (deprotonated) compared to the rest of the tested buffers. Therefore, it can neutralize more H^+ coming from the back-extracted nitric acid. The biggest difference between the pK_{a1} (the first acid dissociation constant – deprotonation of the first H^+) value of the tested buffers and the initial pH of the stripping solution ($pH_{ini}=2$) is for lactic (ΔpH=1.9) and glycolic acid (ΔpH=1.8) resulting in the largest pH change (Figure 44).

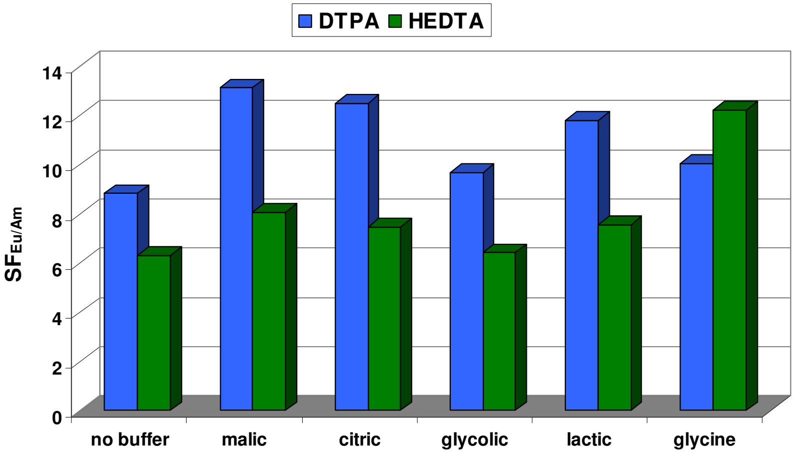


Figure 43. Influence of buffers and complexants on the Eu/Am separation factors (experimental conditions shown in Figure 42).

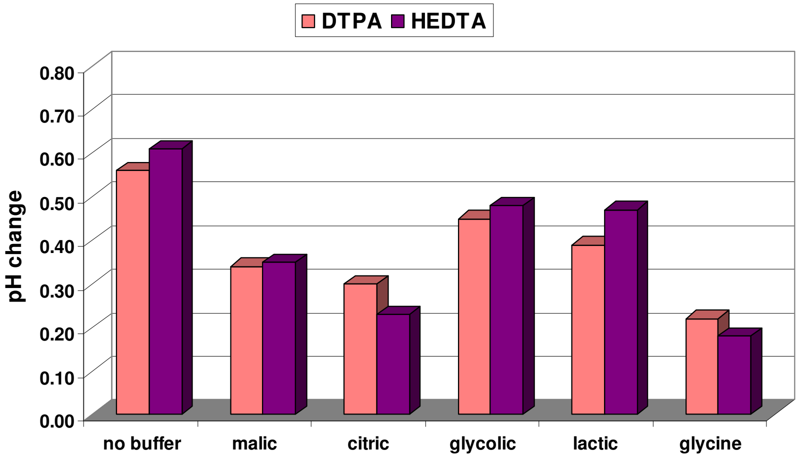


Figure 44. Influence of buffers and complexants on the pH change (experimental conditions shown in Figure 42).

The Figure 45 shows the relation between pK$_{a1}$ of the tested buffers and pH changes obtained. As expected the buffer with the closest pK$_{a1}$ value to the initial pH of the stripping solution is glycine and it most efficiently prevented pH change compared to the rest of the tested buffers.

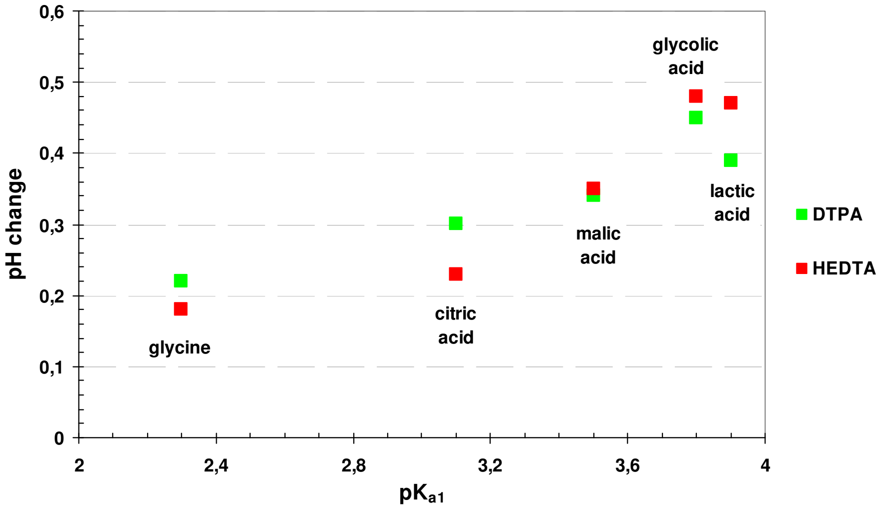


Figure 45. pH change of the An-stripping solution as a function of pK_{a1} of the used buffers (experimental conditions shown in Figure 42).

With an increase in pK_{a1} value the observed pH change was also increasing. The only deviation from this pattern was observed for glycolic acid where the pH change seemed to be somewhat high.

Malic acid gave a slightly higher pH change than citric acid (for DTPA), although the obtained Eu/Am separation factor was the highest one within all tested buffers. Therefore, further optimisation studies were focused only on glycine and malic acid.

From Figure 43 and Figure 44 one might deduce that the combination of HEDTA and glycine would give high Ln/Am separation factor with very good pH stabilisation. However, Figure 43 shows only the Eu/Am separation factor. If we compare the separation factors of all tested lanthanides ($SF_{Ln/Am}$) it becomes clear than the performance of a buffer cannot be judged based only on $SF_{Eu/Am}$. The Eu/Am separation factor using HEDTA was the highest within the light lanthanides ($SF_{Eu/Am}$=12.2, Figure 46). The lowest separation factor was obtained for

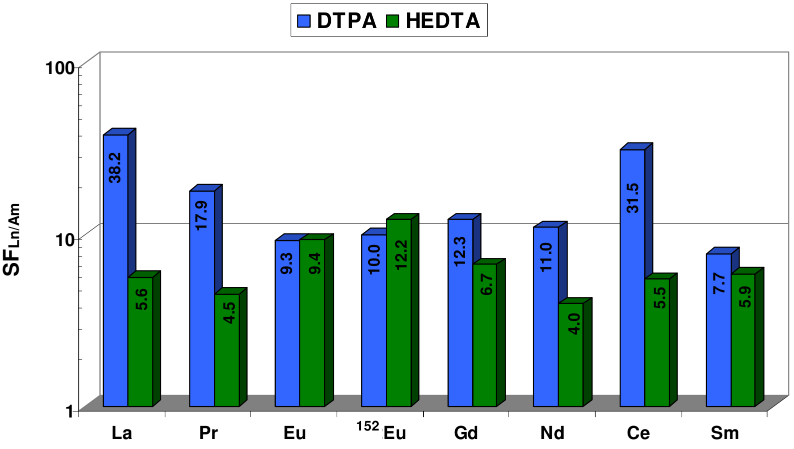


Figure 46. Separation factors of the light lanthanides from americium for DTPA and HEDTA with glycine (experimental conditions shown in Figure 42).

praseodymium (4.5) and neodymium (4.0). In comparison DTPA appeared to be more efficient for the separation of the light lanthanides from americium. The lowest separation factor was obtained for samarium (7.7) and europium (10) whereas lanthanum (38.2) and cerium (31.5) were exceptionally well separated from the actinide (Figure 46).

Within all systems studied here, the combination of DTPA and malic acid or glycine gave high Ln/Am separation factors and good pH stability that were required for efficient americium stripping.

4.3.1.2.2 The influence of the DTPA concentration

In order to find the optimal DTPA concentration several extractions were performed with variable concentration of the complexing agent for the two chosen buffers (glycine, malic acid).

With an increasing DTPA concentration the distribution ratio of most Ln and Am decreased (Figure 47 and Figure 48). The extraction of some lanthanides such as La and Ce (for malic acid and glycine) or Nd and Pr (only for malic) was not influenced by changing the DTPA

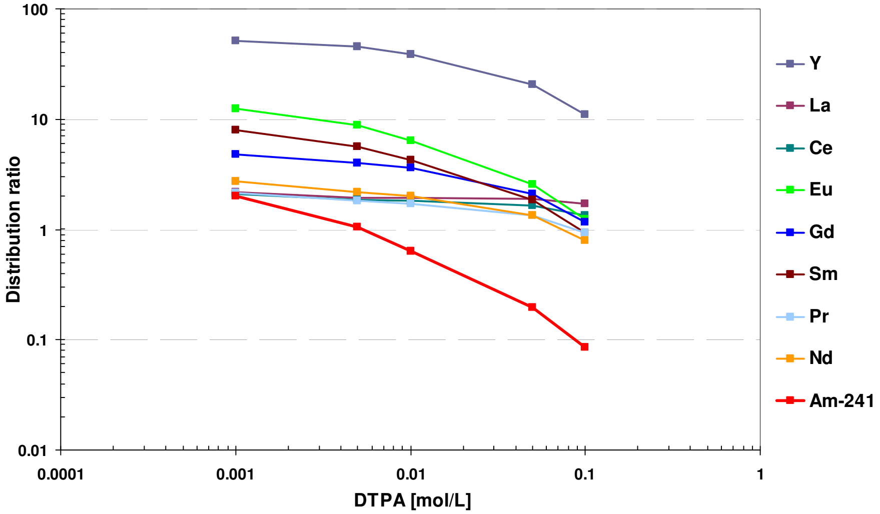


Figure 47. Americium and light lanthanides distribution ratios as a function of the DTPA concentration (malic acid).

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L malic acid, variable DTPA conc., 1 mol/L $NaNO_3$, pH_{ini}=2, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

concentration. It probably results from the larger ionic radius of these lanthanides (decreasing ionic radius with increasing atomic number in the lanthanide series) that impedes them from being complexed by DTPA. La and Ce form the weakest complexes with DTPA within the lanthanide group (lowest stability constants - see Table 6).

The pH of the stripping solution was stabilised much better by glycine compared to malic acid thus a lower DTPA concentration was required to obtain good separation factors of Ln from Am (more deprotonated DTPA available in case of glycine to complex Am). Just 0.005 mol/L DTPA was sufficient to obtain reasonable Ln/Am separation factors with the lowest one corresponding to 7.7 for Sm (the least extracted lanthanide, Figure 48), while 10 times more DTPA was necessary in the case of malic acid to obtain a comparable result ($SF_{Nd/Am}$=6.9, Figure 47).

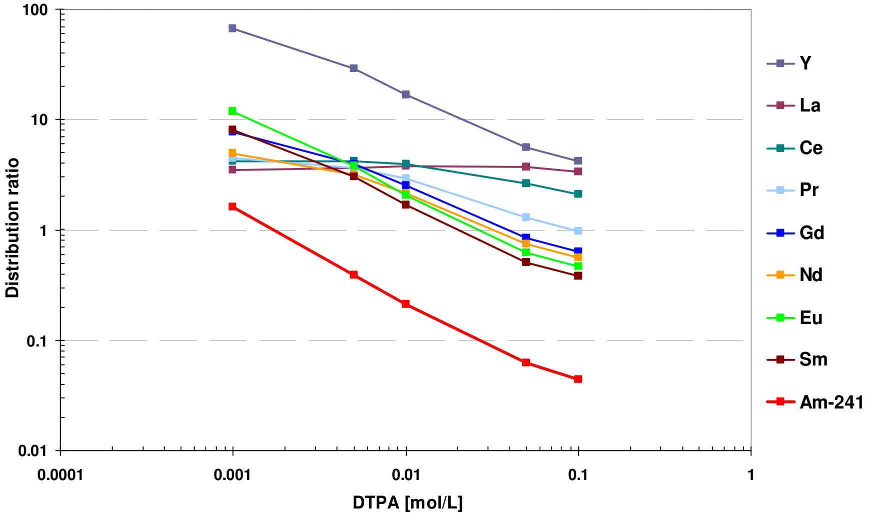


Figure 48. Americium and light lanthanides distribution ratios as a function of the DTPA concentration (glycine).

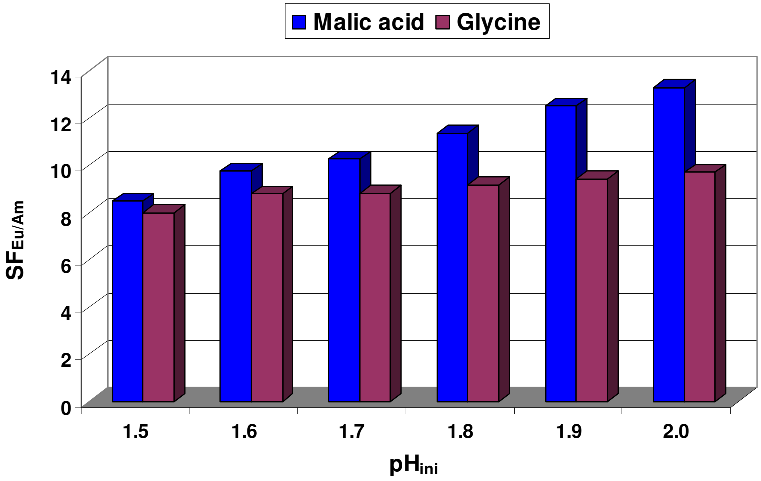
Organic phase:	0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)
Aqueous phase:	1 mol/L gylcine, variable DTPA conc., 1 mol/L $NaNO_3$, pH_{ini}=2, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.3.1.2.3 The influence of the initial pH

In order to find the optimal pH_{ini} at which the An-stripping is most efficient, stripping solutions consisting of 0.05mol/L DTPA and 1mol/L glycine or malic acid at variable initial pH were used to strip Am from the organic phase loaded with light lanthanides (La - Gd) and tracers of americium.

In case of glycine the Eu/Am separation factor increased slightly from 8.0 to 9.7 with increasing the initial pH (Figure 49a). Much higher increase of the $SF_{Eu/Am}$ was observed for malic acid where the maximal value of 13.3 was reached at pH_{ini} = 2.0. Nevertheless, glycine buffered the solution much more effectively than malic acid since smaller pH changes were observed in the case of the former one (Figure 49b).

a)



b)

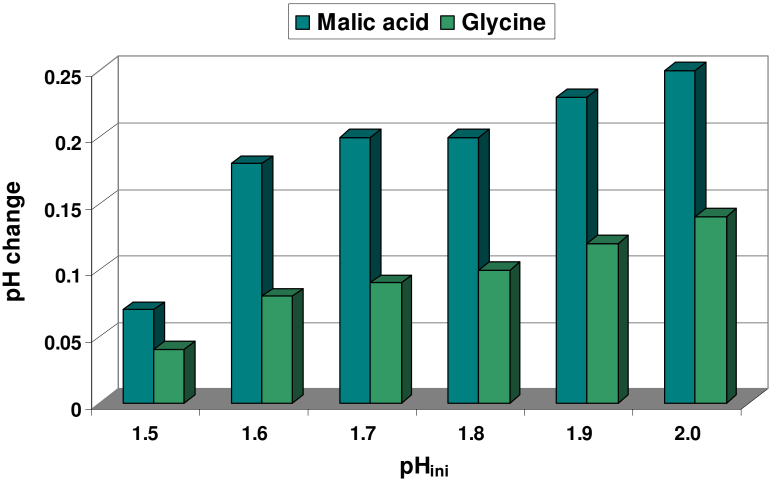


Figure 49. Eu/Am separation factors (a) and pH_{ini} changes (b) as a function of the initial pH of the stripping solution for different buffers.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L glycine or malic acid, 0.05 mol/L DTPA, 1 mol/L $NaNO_3$, variable pHini, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

Although a good separation of Eu from Am was obtained using malic acid, the rest of the lanthanides, especially the lighter ones (La – Gd), were not adequately separated at low initial pH (1.5 – 1.7) (Figure 50a). Glycine as a buffer (better pH stabilization compared to malic acid) showed a good separation of Am from the light Ln even at pH_{ini} = 1.5 (Figure 50b).

In the case of malic acid the effective separation of Am from the lanthanides was obtained at initial pH-values between 1.8 – 1.9 (Table 15). At the highest tested pH_{ini} (2.0) the distribution ratios of the Ln were still above 1 (>50% extracted), although the SFs were rather low. This might cause a significant contribution of Ln in the An product.

Using glycine as a buffer reasonably high separation factors were obtained at initial pH in the range of 1.7 – 1.8 (Table 15). At initial pH=2 the distribution ratios of Sm and Eu were below 1 that resulted in their stripping together with Am. The results obtained using glycine are much more promising compared to malic acid, as a lower initial pH of the stripping solution leads to smaller pH changes caused by the acid back-extracted from the loaded solvent.

Table 15. The separation factors of lanthanides over americium for malic acid and glycine (conditions shown in Figure 50a and b).

		Y	**Eu**	**Gd**	**Sm**	**La**	**Ce**	**Pr**	**Nd**
Buffer	**pH_{ini}**	**$SF_{Ln/Am}$**							
Malic acid	**1.8**	83	4.2	3.9	12	7.5	4.5	4.2	8.2
	1.9	100	6.1	5.2	13	9.4	5.7	5.8	9.2
	2.0	107	9.3	6.7	13	11	6.7	8.2	9.6
Glycine	**1.7**	77	11	10	9.4	10	8.4	12	7.7
	1.8	78	16	13	9.6	11	9.6	17	7.8
	1.9	94	35	19	11	14	12	31	8.8

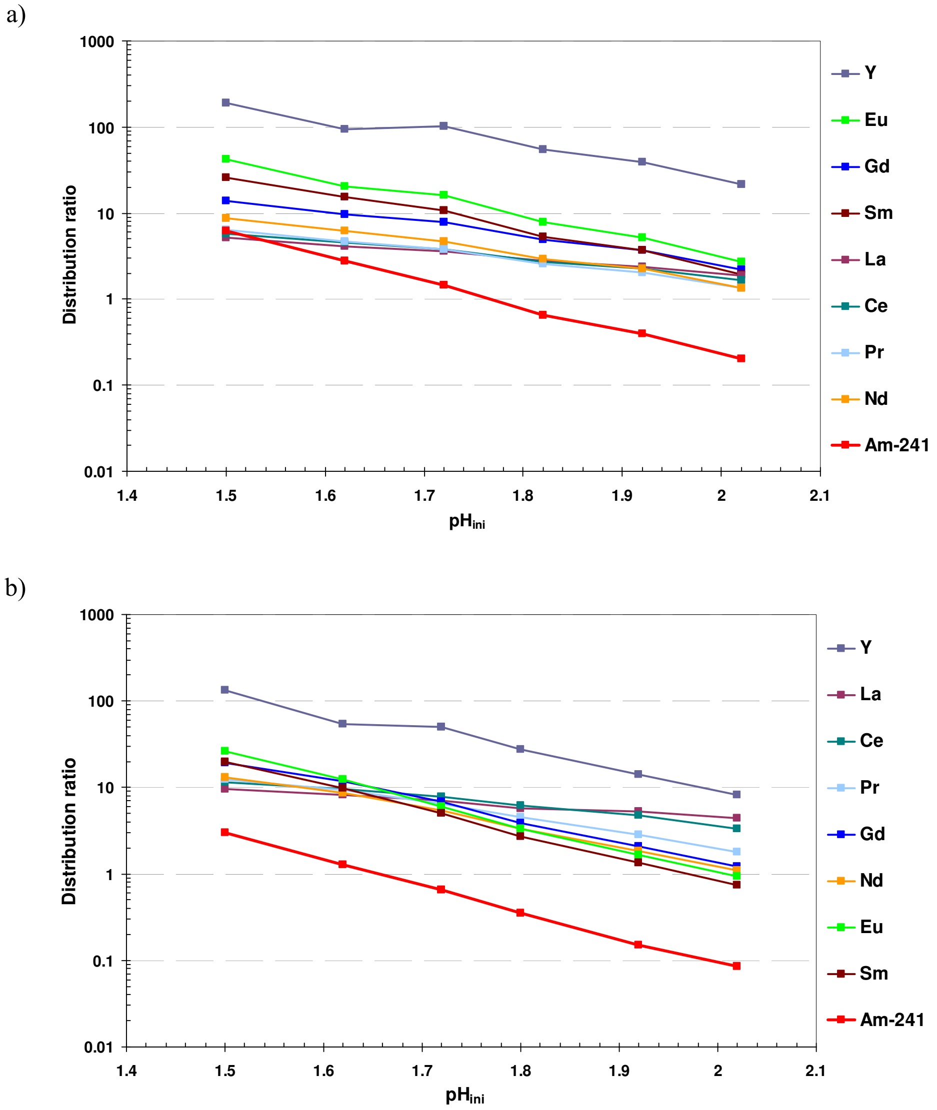


Figure 50. Am and light lanthanides distribution ratios as a function of the initial pH of the stripping solution using malic acid (a) or glycine (b).

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L malic acid or glycine, 0.05 mol/L DTPA, 1 mol/L $NaNO_3$, variable pH_{ini}, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.3.1.2.4 The influence of the nitrate ion concentration

The extractant TODGA requires anions during the extraction of metal cations to compensate the positive charge of the metal (only neutrally charged complexes can exist in molecular solvents) (see Eq 9, page 72). In the extraction step of the innovative SANEX process nitrates from dissociated nitric acid (highly acidic HAR solution) participate in a formation of a neutral complex [M(III)-TODGA$_n$-(NO$_3$)$_3$]. However, the concentration of nitrate ions in the An-stripping step is not sufficient to keep the lanthanides in the organic phase while actinides are being stripped into the aqueous phase. Therefore, additional nitrates have to be introduced into the stripping solution e.g. in the form of $NaNO_3$.

The influence of the nitrate concentration on the Eu and Am distribution ratio was studied. When the actinide stripping solution did not contain any additional nitrate ions (no $NaNO_3$ added), the distribution ratios of Eu and Am were below 1 (D_{Eu}=0.51 and D_{Am}=0.05). Therefore both elements were predominant in the aqueous phase. Thus no separation between them was possible as can be seen in Figure 51. By addition of nitrate ions to the stripping solution D_{Ln} and D_{Am} were shifted up, i.e. TODGA was able to complex more of the trivalent metals of interest. It was found that at least 1 mol/L NO_3^- is sufficient to selectively strip Am into the aqueous phase separating it from the trivalent lanthanides which were kept mostly in the organic phase due to the salting-out effect (increased solubility of ligand-metal complexes in the organic solvent with increasing salt ions concentration in the aqueous phase). A further increase of the nitrate ions concentration did not change significantly the distribution ratios of Am and Eu (Figure 51). The sodium nitrate concentration of 1mol/L is sufficient to keep the distribution ratios of Ln(III) constant if the nitrate concentration changes. One could point out that by adjusting the nitrate concentration the distribution ratios of An(III) and Ln(III) could be controlled in order to obtain the most efficient An(III) stripping. However, this would be a disadvantage since the An-stripping is already very sensitive for any pH changes and an

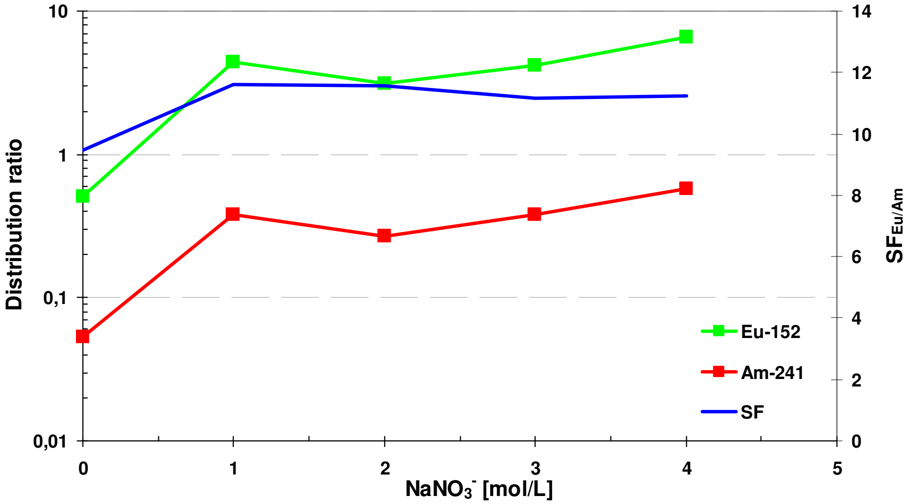


Figure 51. Distribution ratios of ^{152}Eu and ^{241}Am as a function of the sodium nitrate concentration in the stripping solution.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L lactic acid, 0.05 mol/L DTPA, variable $NaNO_3$ conc., pH_{ini}=2, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

additional factor that has to be controlled would result in a very complex and unstable process.

Based on the obtained results it was decided that the most optimal composition of the actinide stripping solution within the tested conditions are shown in Table 16.

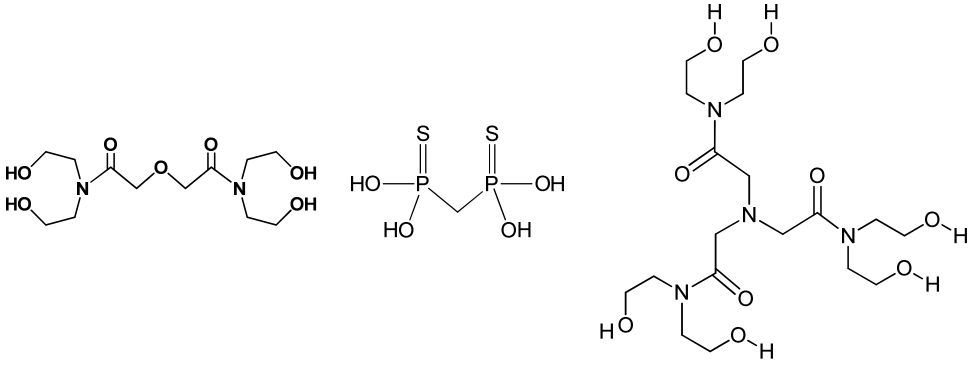
Table 16. The optimal composition of the actinide stripping solution.

Complexing agent	DTPA	0.05 mol/L
Buffer	Glycine	1 mol/L
Addition of salt	$NaNO_3$	1 mol/L
Initial pH	1.7 – 1.8	

4.3.1.3. Stripping of trivalent Lanthanides

The last step of the proposed innovative SANEX process, i.e. the stripping of the trivalent lanthanides, was not tested in this work. Nevertheless, this step is not considered to be complicated. In the TODGA/TBP process[47] the lanthanides were completely removed from the organic phase using 0.01 mol/L HNO_3. In the innovative-SANEX process diluted nitric acid can also be used to back-extract Ln from the organic phase. The drawback of this method is the slow back-extraction kinetics which require the use of a higher number of stages (centrifugal contactors) in order to achieve a good clean-up of the spent solvent.

The problem of slow kinetics can be overcome by the use of complexants for trivalent lanthanides. As a result of the screening tests of new water-soluble ligands provided by the University of TWENTE, three ligands were found to possess very good complexing properties towards Am and Eu (Figure 52). Despite the lack of selectivity between Eu/Am, these new ligands are still very desirable for a lanthanide stripping as at the last step there are no actinides in the organic phase (see chapter 4.6.2 Water-soluble ligands, page 185).



2,2'-oxybis(N,N-bis(2-hydroxyethyl)acetamide)
(TWE-18)
$D_{Eu,Am} < 0.04$
$pH_{ini}=3$

methylenediphosphonothioic O,O-acid
(TWE-32)
$D_{Eu,Am} < 0.007$
$pH_{ini}=4$

2,2',2''-nitrilotris(N,N-bis(2-hydroxyethyl)acetamide)
(TWE-A6)
$D_{Eu,Am} < 0.01$
$pH_{ini}=4$

Figure 52. Novel water-soluble ligands for Ln(III) stripping.

4.3.2. Solvent based on TODGA + 1-octanol

The innovative-SANEX process based on TODGA + TBP was shown to be very sensitive towards pH changes during the actinides(III) stripping. The initial pH of the actinide stripping solution is influenced by the back-extracted nitric acid hence minimising the An(III)/Ln(III) separation yield. This major draw-back was also found by a French group,[64] which also studied this process using TODGA + TBP as an organic solvent although with different An(III) stripping solution compounds.

The introduction of a scrubbing step with 0.5 mol/L HNO_3 can significantly reduce the content of nitric acid in the loaded organic solvent coming from the extraction step.[95] A lower acidity of this scrubbing solution could remove even more of the extracted acid from the organic phase. However, the Ln and An distribution ratios would also be lowered and a significant amount of these metals would be re-directed towards the extraction step. Additionally, possible accumulation of some elements in some stages could appear due to their low distribution ratios and cause third phase formation (overloaded organic solvent).

One of the solutions to this problem is to minimise the amount of the nitric acid extracted in the extraction step (Ln+An co-extraction). Geist and Modolo[102] found that the organic phase modifier TBP can be replaced by 1-octanol which extracts much less nitric acid than TBP. Moreover, it increases the metal loading capacity of the solvent compared to TBP (higher concentration of metals can be loaded into the organic solvent) and fulfil the CHON principle (complete incineration). The most optimal organic solvent formulation found was 5 volume percent of 1-octanol dissolved in TPH. Therefore, the new organic solvent studied here consisted of 0.2 mol/L TODGA and 5vol.% 1-octanol in TPH. Due to this major change of the process conditions the extraction of the An(III) and Ln(III), the scrubbing of the extracted acid and the formula of the actinide stripping solution had to be reinvestigated.

4.3.2.1. *Nitric acid concentration dependency*

The profile of the Eu and Am extraction by TODGA/octanol from solutions of different nitric acid concentration (Figure 53) is very similar to the one obtained with TODGA/TBP.

The substitution of TBP with 1-octanol resulted in higher distribution ratios for Am(III) and Eu(III), although the difference is more satisfactory at lower concentration of nitric acid. The same effect was observed by Geist et al.[102]

The mechanism of the nitric acid extraction was studied in more details to find the main constituent responsible for the acid extraction.

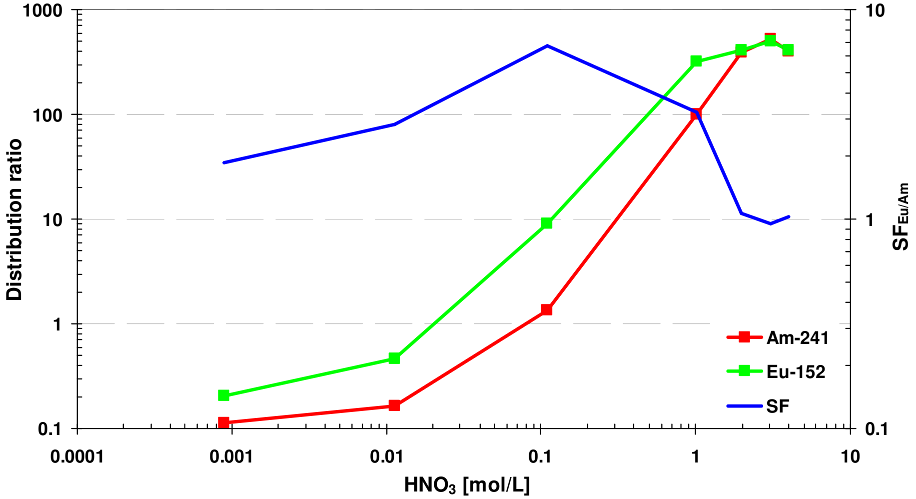


Figure 53. The extraction of ^{241}Am and ^{152}Eu as a function of nitric acid concentration

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu;
mixing time: 15min.

4.3.2.2. Nitric acid extraction

Table 17 summarises the results of nitric acid extraction with TODGA in TPH and the influence of the organic phase modifier. It can be seen that much less nitric acid is extracted by a solvent consisting of TODGA + octanol as compared to TODGA + TBP.

Table 17. Influence of the organic phase modifier on nitric acid extraction by TODGA in THP[102]

Modifier	$[HNO_3]_{aq,ini}$ = 0.5 mol/L	$[HNO_3]_{aq,ini}$ = 3 mol/L
	$[HNO_3]_{org,eq}$	
5 vol.% 1-octanol	0.013 mol/L	0.22 mol/L
0.5 mol/L TBP	0.041 mol/L	0.42 mol/L

The nitric acid extraction equilibrium can be expressed as follows:

$$H^+_{aq} + NO^-_{3,aq} + nL_{org} \xleftrightarrow{K_H} HNO_3 \times nL_{org} \qquad \text{Eq 11}$$

where L corresponds to a TODGA molecule. The amount of the extracted nitric acid expressed as $[HNO_3]_{org,eq}$ increases with increasing concentration of TODGA and initial nitric acid concentration (Figure 54). The results obtained in this work are in a good agreement with those obtained by Geist et al.[102]

The extraction constant (K_H) is defined as:

$$K_H = \frac{[HNO_3 \times nL]_{org}}{[H^+]_{aq}[NO_3^-]_{aq}[L]^n_{org,free}} \qquad \text{Eq 12}$$

By taking the logarithm on both sides of the Eq 12 and rearranging we obtain:

$$\log[H^+]_{org} - 2\log[H^+]_{aq} = \log K_H + n\log[L]_{org,free} \qquad \text{Eq 13}$$

with $[H^+]_{org} = [HNO_3 \text{ x } nL]_{org}$ and $[H^+]_{aq} = [NO_3^-]_{aq}$

$[H^+]_{aq}$ was calculated using the experimental value (here expressed as T) obtained from potentiometric titration of the aqueous phase in equilibrium, and dissociation constant of HNO_3, $K_a = 23.5$.[103]

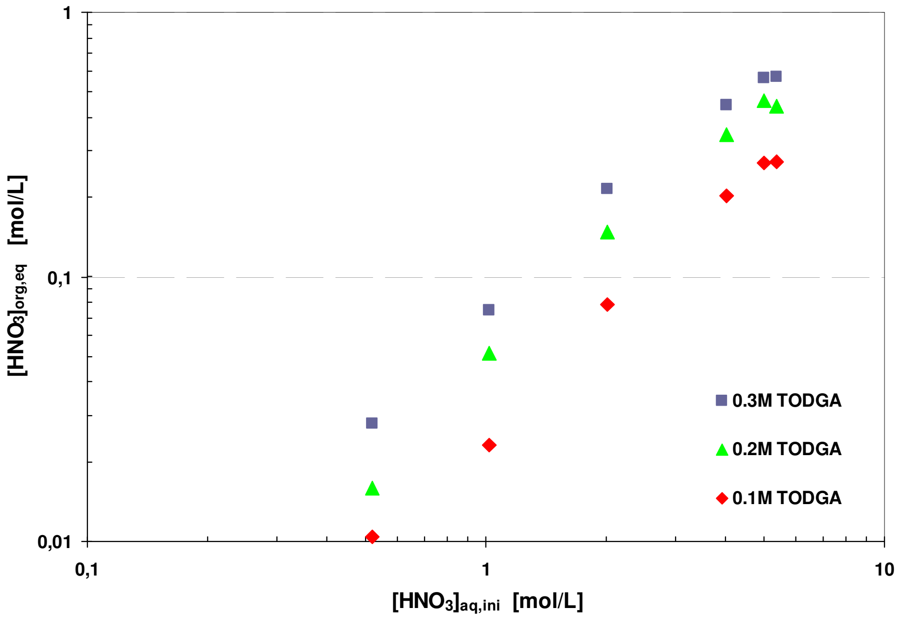


Figure 54. The extraction of nitric acid as a function of the TODGA and initial nitric acid concentration.

Organic phase: variable TODGA concentration + 5 vol.% 1-octanol in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu;
mixing time: 15min.

K_a is defined as:

$$K_a = \frac{[H^+]_{aq}[NO_3^-]_{aq}}{[HNO_3]_{aq}} = \frac{[H^+]_{aq}^2}{T-[H^+]_{aq}} \qquad \text{Eq 14}$$

with $[H^+]_{aq} = [NO_3^-]_{aq}$, $T = ([H^+]_{aq} + [HNO_3]_{aq})$

Rearranging equation Eq 14 gives:

$$[H^+]_{aq}^2 + K_a[H^+]_{aq} - K_a \times T = 0 \qquad \text{Eq 15}$$

Eq 13 is a linear equation and a plot of $\{log[H^+]_{org} - 2log[H^+]_{aq}$ against $log[L]_{org,free}$ should give a straight line with the slope n corresponding to the number of TODGA molecules involved in the formation of the TODGA x HNO_3 adduct and the intercept $logK_H$ is corresponding to the basicity of the ligand. The formation of 1:1 complexes between HNO_3 and TODGA was assumed by Ansari et al.[96] in order to calculate the basicity of the extractant. This assumption is required to predict the concentration of $TODGA_{org,free}$. Thus the following equation is used:

$$[L]_{org,free} = [L]_{ini} - [HNO_3]_{org,eq} \qquad \text{Eq 16}$$

Even though the slopes deviate slightly from 1 (Figure 55), the obtained results confirm that 1:1 complexes are formed. Nevertheless, this effect can only be observed at low initial nitric acid concentrations. From the results in Table 18 it is clear that more than one molecule of HNO_3 is bound to one TODGA molecule at higher initial nitric acid ($[HNO_3]_{org}$ > $[TODGA]_{ini}$ at 4 and 5 mol/L $HNO_{3,ini}$).

Table 18. Nitric acid extraction by TODGA/1-octanol.

$[TODGA]_{ini}$ (mol/L)	$[HNO_3]_{org}$ (mol/L)	$[H^+]_{ini}$ (mol/L)
0.2	0.02	0.5
0.2	0.05	1.0
0.2	0.15	2.0
0.2	0.34	4.0
0.2	0.46	5.0

Organic phase: 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH

Aqueous phase: variable concentration of nitric acid, mixing time: 15min.

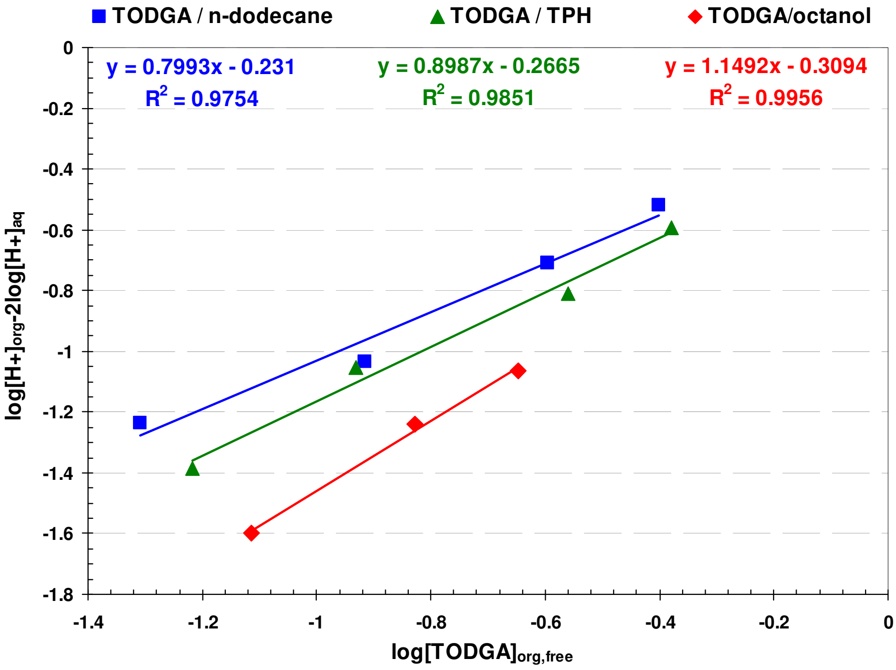


Figure 55. Plots of $log[H^{+}]_{org} - 2log[H^{+}]_{aq}$ vs. $log[TODGA]_{org,free}$ (the results of TODGA/THP and TODGA/n-dodecane were taken from Modolo et al.[95]).

Organic phase: variable TODGA concentration (+ 5 vol.% 1-octanol) in TPH or n-dodecane

Aqueous phase: 1 mol/L HNO_3, mixing time: 15min.

In Table 19 the extraction coefficient K_H obtained for the TODGA/1-octanol system is compared to the results obtained by other researchers who also used TODGA but in different diluents. It seems that the co-extraction of nitric acid is mainly controlled by the TODGA concentration and not by the diluent since the range of order of K_H is independent of the system used.

Table 19. Comparison of extraction coefficients K_H for TODGA systems.

system	K_H
n-dodecane (Arisaka)[104]	0.38
n-dodecane (Modolo)[95]	0.59
TPH (Modolo)[95]	0.54
TPH/1-octanol [This work]	0.49

4.3.2.3. The extraction of HAR elements

In order to determinate the co-extraction efficiency for Ln(III) + An(III) and possibly some of the non-lanthanide fission products, extraction experiments with a HAR-FZJ simulate solution were performed. Very often in a counter-current process the scrubbing solution(s) of lower acidity are mixed with the HAR feed at the feed inlet stage changing the final feed acidity.

The results of the metal extraction from HAR solutions of different (1 – 4 mol/L HNO_3) acidity would help to design a future process flow-sheet.

The composition of the used solutions is shown in the Table 20. Lower concentration of Mo and Zr in the HAR solution at 1.21 mol/L HNO_3 is caused by their partial precipitation at this acidity. The co-extraction of Zr and Pd was suppressed using 0.05 mol/L CDTA (0.025 mol/L in case of 1 mol/L HNO_3) (more details in chapter 4.4 New masking agent, page 123).

Table 20. The composition of the High Active Raffinate simulate solutions.

HNO_3 [mol/L]	1.21	2.26	3.17	4.38
Element	[mg/L]	[mg/L]	[mg/L]	[mg/L]
^{152}Eu, ^{241}Am	tracer	tracer	tracer	tracer
Ag	24.2	17.4	14.5	18.1
Ba	371	357	336	342
Cd	21.8	21.7	24.8	25.0
Ce	687	699	685	682
Cr	116	121	114	116
Cs	637	637	637	630
Cu	24.4	25.0	23.8	27.2
Eu	46.8	46.5	43.3	45.4
Gd	69.4	68.8	67.1	65.0
La	299	297	292	294
Mo	118	805	809	794
Nd	889	922	882	893
Ni	60.7	53.7	55.7	52.3
Pd	126	241	124	236
Pr	278	277	274	277
Rb	82.5	76.1	79.4	80.2
Rh	101	100	100	98.0
Ru	455	456	453	446
Sb	14.2	7.39	5.74	5.06
Sm	192	192	185	187
Sr	205	202	198	200
Te	82.5	134	132	130
Y	110	102	102	100
Zr	596	1019	964	1009

The extraction results are shown in Table 21. The trivalent lanthanides and americium were quantitatively extracted at all 1, 2, 3 and 4 mol/L HNO_3 concentrations. Strontium was well extracted with $D_{Sr} \approx 2$ at $HNO_3 > 2$ mol/L, however, this element can be easily removed from the loaded organic phase by introducing a scrubbing step with 0.5 mol/L HNO_3 (described further). The distribution ratios of molybdenum ($D_{Mo} \approx 0.2 - 0.4$) do not seem to be a significant problem, although considering the high amount of this element in the HAR solution (Table 20) an additional scrubbing step for its removal will be required. Palladium and zirconium were complexed by CDTA directly in the feed solution thus only small amounts of these metals were extracted. The extraction of the rest of the fission and corrosion products was negligible and should not have a significant influence on the actinide product purity in the final process.

At 1 mol/L HNO_3 the distribution ratios for Ln(III) were lower than 100 but still high enough for the process development. However, an emulsion between the organic and aqueous phase was observed after the equilibrium was reached. The metal distribution ratios of this sample were calculated from the concentrations (or gamma activities in case of ^{152}Eu and ^{241}Am) of the elements in the top organic layer (above the emulsion) and the clear aqueous phase. To make sure that the emulsion was not caused by the use of CDTA, two more samples without this masking agent were prepared, namely 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH and 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH. In both additional samples an emulsion appeared at 1 mol/L. Therefore, it can be assumed that the formation of the emulsion with HAR solution at 1 mol/L HNO_3 is not caused by the masking agent CDTA. Nevertheless, in the process the nitric acid concentration at the feed inlet stage must be kept above 1 mol/L to avoid emulsion formation.

Table 21. Extraction of metals from HAR simulate solutions of different acidity (n.d. – not determined).

HNO_3 [mol/L]	1.21	2.26	3.17	4.38
Element		Distribution ratios		
^{241}Am	168	> 200	> 200	> 200
^{152}Eu,	> 200	> 200	> 200	> 200
Y	56.5	98.9	> 200	> 200
La	15.4	77.5	144	177
Ce	31.5	> 200	> 200	> 200
Pr	55.4	> 200	> 200	> 200
Nd	136	> 200	> 200	> 200
Sm	97.4	> 200	> 200	> 200
Gd	28.5	61.8	> 200	188
Sr	0.47	2.00	2.50	1.67
Mo	0.37	0.22	0.29	0.39
Cr	0.32	0.25	0.29	0.23
Ru	0.08	0.15	0.22	0.25
Pd	0.39	0.04	0.09	0.04
Cd	0.02	0.08	0.12	0.13
Ni	0.02	0.04	0.06	0.07
Ba	0.07	0.10	0.09	0.05
Rb	0.03	0.02	0.03	0.02
Cu	< 0.01	< 0.01	< 0.01	< 0.01
Te	0.046	0.009	0.003	0.004
Zr	0.005	0.002	0.004	0.007
Rh	0.003	<0.001	<0.001	<0.001
Cs	0.001	<0.001	<0.001	<0.001
Ag, Sb	n.d.	n.d.	n.d.	n.d.

Organic phase: 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH

Aqueous phase: HAR simulate solution of variable nitric acid conc., 0.05 mol/L CDTA, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.3.2.4. The extraction of Strontium

The masking agent CDTA does not prevent the extraction of Sr by TODGA, although the extraction of this metal can be controlled by varying the HNO_3 concentration (see distribution ratios of Sr in Table 21). Hence the influence of the nitric acid concentration on the strontium extraction was investigated and the results are shown in Figure 56.

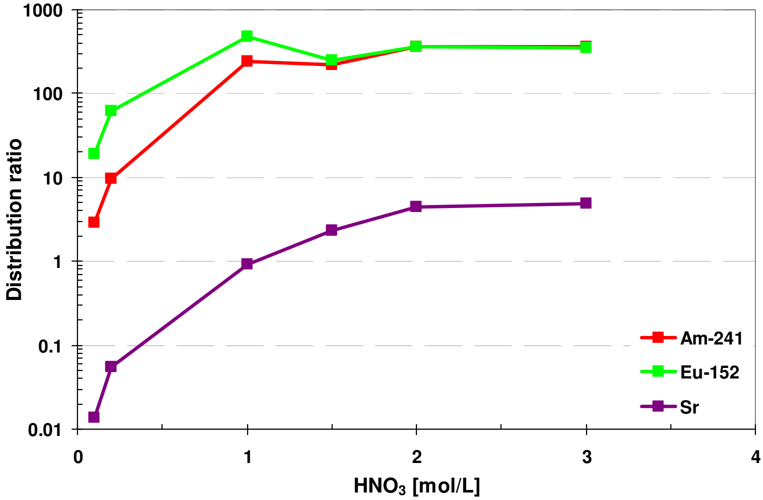


Figure 56. Distribution ratios of ^{241}Am and ^{152}Eu as a function of the nitric acid concentration.

Organic phase: 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH

Aqueous phase: 10^{-4} mol/L strontium solution of variable nitric acid conc., tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

At nitric acid concentrations higher than 1 mol/L most of strontium was extracted into the organic phase. The maximum distribution ratio reached 4.8 at 3 mol/L HNO_3 although from 2mol/L HNO_3 a plateau of the extraction profile could be observed. Strontium can be scrubbed from the organic phase by contacting the loaded organic phase coming from the extraction step of the process with nitric acid of low concentration. The scrubbing step responsible for decreasing the amount of the extracted acid in the organic phase using 0.5 mol/L HNO_3 can also be used for the stripping of strontium before the next step – the An(III)-stripping. The distribution ratios of ^{152}Eu and ^{241}Am at 0.5 mol/L HNO_3 are still high enough (both D-values above 30) thus both elements should stay in the organic phase while Sr is back-extracted.

4.3.2.5. Selective stripping of trivalent actinides

The stripping of An(III) step is the most crucial one within the innovative-SANEX process. Hérès et al. [64] suggested that the separation factors of Ln over An should not be lower than 6 to provide efficient separation in the continuous process. The requirements of the trivalent actinide stripping solution (complexing agent, buffer, nitrates and carefully tuned initial pH) had to be studied similarly as for i-SANEX process based on the TODGA/TBP solvent described above (see chapter *Solvent based on TODGA + TBP*).

4.3.2.5.1. Screening of buffers and complexing agents

The same set of complexing agents (DTPA, HEDTA) and buffers (malic, citric, glycolic, lactic acid and glycine) as for TODGA/TBP were screened. The results are shown in Figure 57. All tested buffers gave high $SF_{Eu/Am}$ when combined with DTPA. In case of HEDTA only the combination with glycine resulted in a high separation factor. Considering the pH stabilization properties citric acid and glycine were the most efficient in minimizing pH changes when used together with DTPA.

Lactic acid + DTPA gave higher separation Eu/Am than glycine + DTPA, although the pH stabilisation was better with glycine. The lower separation factor can be compensated by increasing the number of stages for the actinide stripping step. More important was to keep the pH change as low as possible. Moreover, lactic acid and citric acid are hard to destroy in the actinide co-conversion step, which will follow the partitioning process.[105] Therefore, similar as for the TODGA/TBP based process, glycine and DTPA appeared to be the best choice for the actinide stripping solution composition.

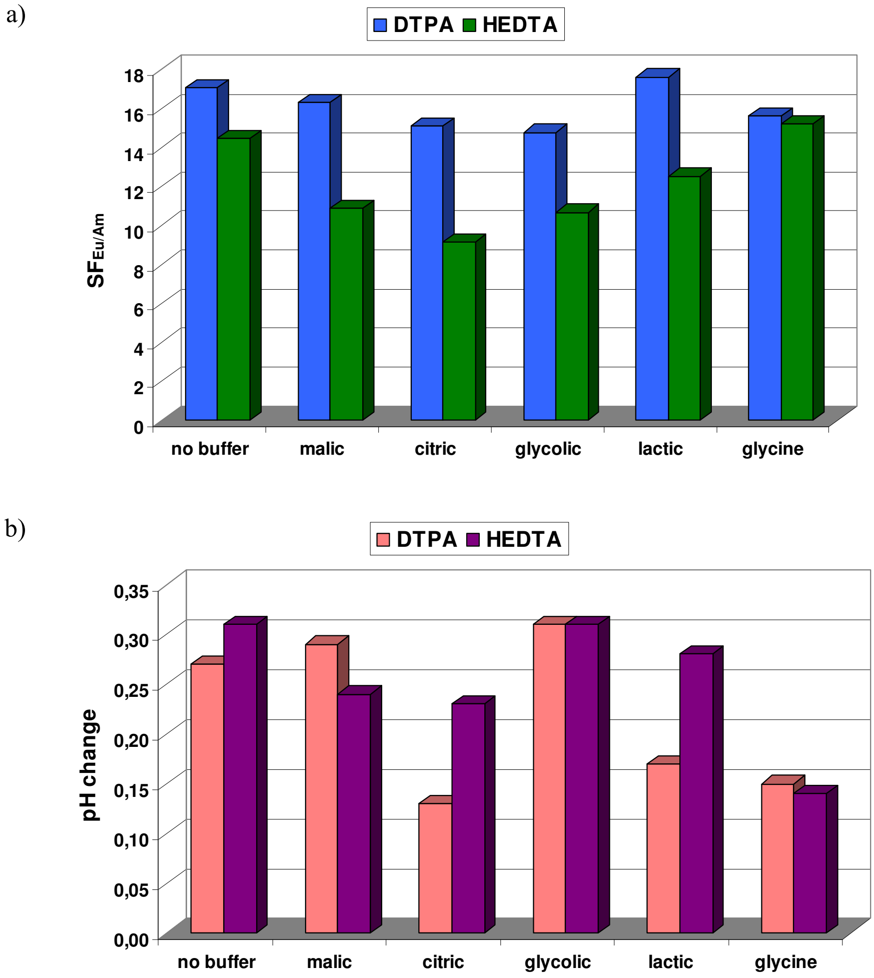


Figure 57. Influence of buffers and complexants on the Eu/Am separation factors (a) and pH change (b).

Organic phase:	0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)
Aqueous phase:	1 mol/L buffer, 0.05 mol/L DTPA or HEDTA, 1 mol/L $NaNO_3$, pH_{ini}=2, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

The extraction of all the process relevant lanthanides (La – Gd) had to be also investigated in more details as the complexation of each Ln(III) with DTPA/HEDTA is different. TODGA extracts each Ln element with a different strength and the affinity is more pronounced at low nitric acid concentrations.

The good Eu/Am separation factor of 17 obtained with HEDTA + glycine during the screening tests of different buffers appears to be the highest within the lanthanide series (Table 22). The rest of Ln were not as good extracted as Eu, moreover some of them (La, Ce and Pr) were poorly separated from Am ($SF_{Ln/Am}$< 2.7). Furthermore, the separation of Am from the Ln was possible only with solutions of initial $pH_{ini} \geq 2.0$ (Figure 58). Higher initial pH (> 2) of the stripping solution is not desired as the influence of the back-extracted acid on pH_{ini} is more pronounced.

Table 22. Influence of the complexant on the Ln/Am separation factor.

Complexant	HEDTA	DTPA
	$SF_{Ln/Am}$	
La	2.3	23
Pr	2.7	11
Eu	16.8	16
Gd	6.1	15
Nd	3.5	10
Ce	2.6	18
Sm	9.5	12

Organic phase:	0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)
Aqueous phase:	1 mol/L glycine, 0.05 mol/L complexant, 1 mol/L $NaNO_3$, pH_{ini}=2, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

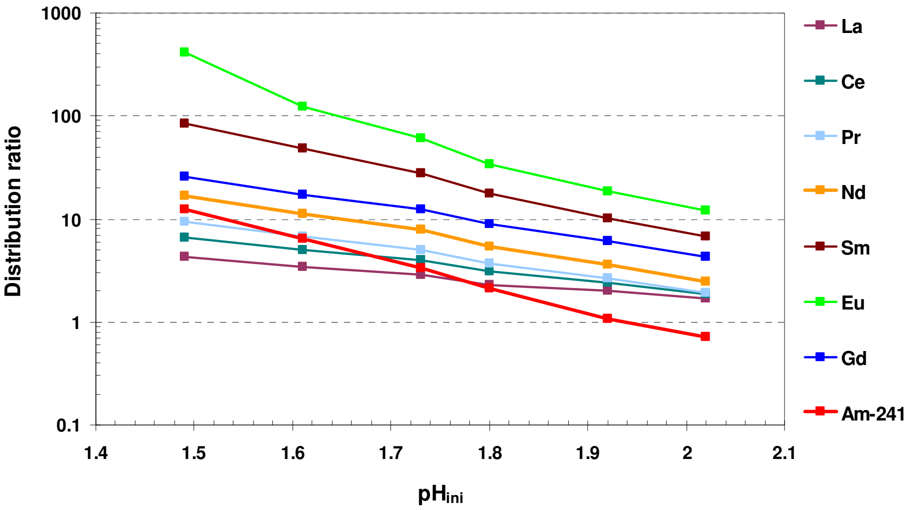


Figure 58. Am(III) and Ln(III) distribution ratios as a function of the initial pH.

Organic phase: 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: 1 mol/L glycine, 0.05 mol/L HEDTA, 1 mol/L $NaNO_3$, variable pH_{ini}, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

4.3.2.5.2. The influence of the initial pH

The influence of the initial pH of the stripping solution on Ln/Am separation was studied to optimise the distribution of Am(III) and Ln(III) between the two phases – organic and aqueous. Based on the results of the buffer and complexant screening tests, glycine and malic acid in combination with DTPA were tested.

The distribution ratios of the Ln decreased slowly with increasing the initial pH of the stripping solution for both buffers (Figure 59). In case of malic acid (Figure 59a) the Ln distribution ratios were significantly low which in a continuous process would result in contamination of the An-product with some of the lanthanides. When glycine was tested (Figure 59b) the best conditions for the separation were found at pH_{ini} between 1.7 and 1.8 because the D_{Ln} were reasonably high while the corresponding D_{Am} was lower than 1.

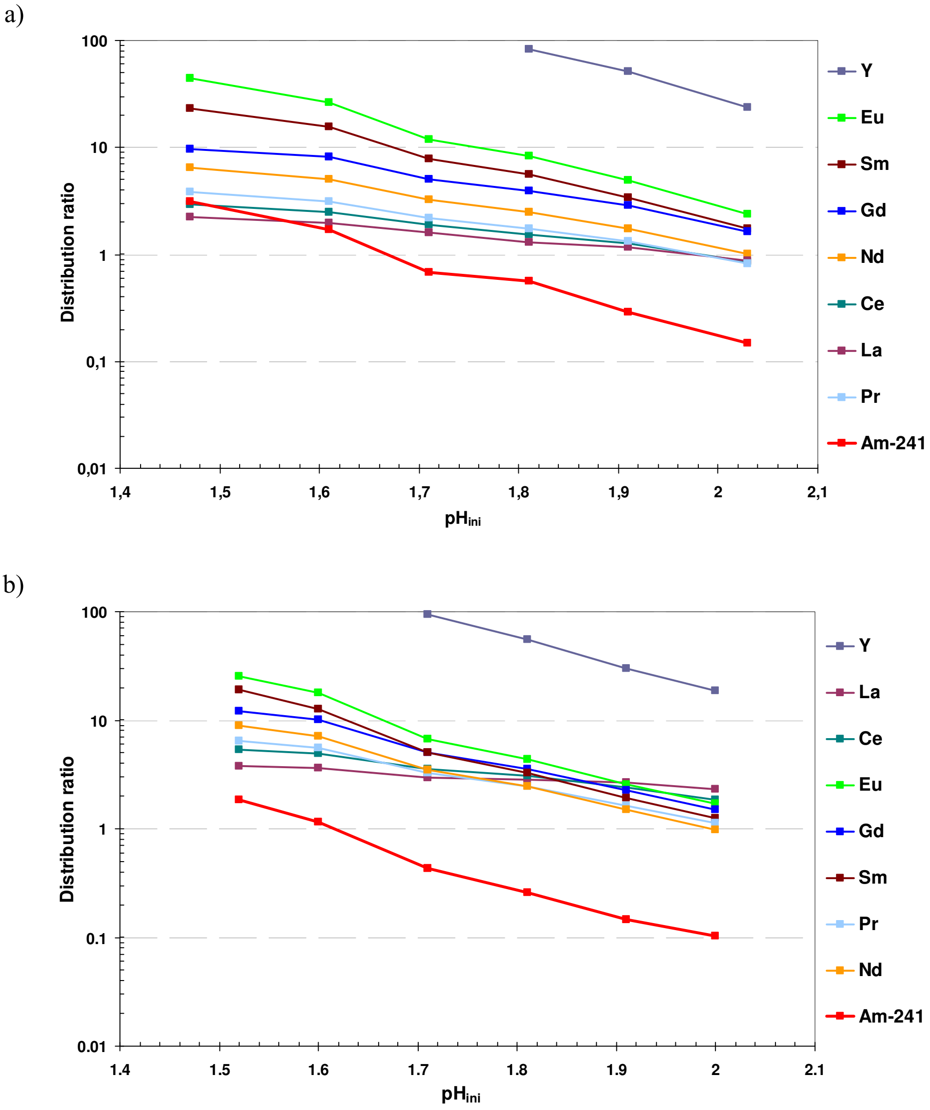


Figure 59. Am(III) and Ln(III) distribution ratios as a function of the initial pH using malic acid (a) and glycine (b).

Organic phase: 0.2 mol/L TODGA + 5 vol.% 1-octanol in TPH (pre-loaded with Ln solution of 0.5 mol/L HNO_3)

Aqueous phase: a) 1 mol/L malic acid or b) 1 mol/L glycine; 0.05 mol/L DTPA, 1 mol/L $NaNO_3$, variable pH_{ini}, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.

The Ln/Am separation factors were much higher for glycine compared to malic acid (Table 23). It resulted from its better stabilisation of the stripping solution pH (Figure 60), which provided more deprotonated DTPA molecules to complex Am (increased $SF_{Ln/Am}$). The least extractable element within the lanthanide series, neodymium, was separated with a $SF_{Nd/AM}$=9.4 at pH_{ini}=1.8 (Table 23, column 4).

a)

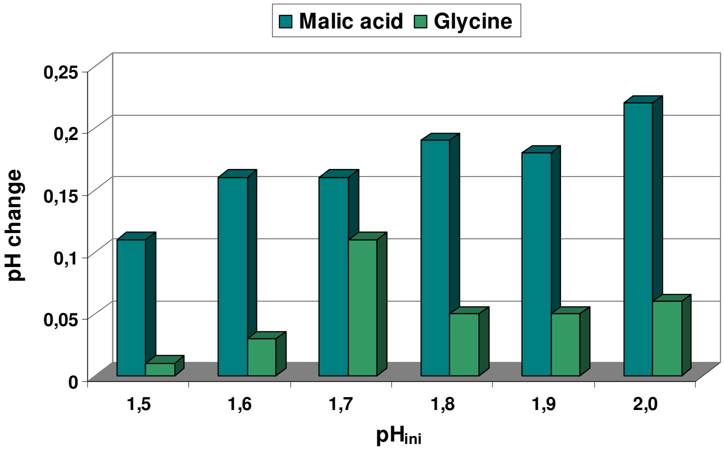


Figure 60. Influence of glycine and malic acid on the pH change of the stripping solution. Conditions: see Figure 59.

Table 23. Influence of the complexant on the Ln/Am separation factor

	Malic acid	Glycine	
pH_{ini}	***1.7***	***1.7***	***1.8***
La	2.3	6.8	11.0
Pr	3.2	7.5	9.5
Eu	17.5	15.5	16.9
Gd	7.4	11.5	13.7
Nd	4.7	7.9	9.4
Ce	2.8	8.1	12.0
Sm	11.4	11.6	12.7

The combination of DTPA and glycine similar to the use of TODGA/TBP solvent appeared to be the most efficient choice.

The final composition of the actinide stripping solution based on these batch tests is shown in Table 24.

Table 24. The optimal composition of the actinide stripping solution.

Complexing agent	DTPA	0.05 mol/L
Buffer	Glycine	1 mol/L
Addition of salt	$NaNO_3$	1 mol/L
Initial pH	1.7 – 1.8	

4.4. New masking agent

One of the main aims for the development of a new innovative SANEX process for An(III) partitioning using TODGA-based extractants was to find a substitution for oxalic acid to prevent zirconium and molybdenum extraction by TODGA. Oxalic acid was successfully used in processes like the French DIAMEX or the German TODGA/TBP process as an efficient zirconium and molybdenum masking agent. However, oxalic acid exhibits some major drawbacks such as its partial extraction into the organic solvent and possible precipitation of lanthanide oxalates which may occur at higher oxalic acid concentration.[46] Moreover, in the new concept studied in Europe, called GANEX process, all transuranium elements are co-extracted together with the lanthanides followed by a selective An/Ln separation. As plutonium precipitates in the presence of oxalic acid thus this dicarboxylic acid should not be used as a masking agent in GANEX process. Therefore, the substitution of oxalic acid by another masking agent was studied not only in view of the innovative SANEX, but also generally for processes where significant concentrations of Pu had to be handled.

The first approach was to study the extraction of zirconium into TODGA-based solvents in the presence of different polyaminocarboxylic acids such as DTPA, EDTA, HEDTA and CDTA. These preliminary experiments showed that CDTA and EDTA were able to prevent the extraction of zirconium but also of palladium. CDTA showed much stronger complexation of Zr compared to EDTA.[106]

In further experiments trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA) (Figure 61) was studied in more details for the complexation of Zr and Pd.

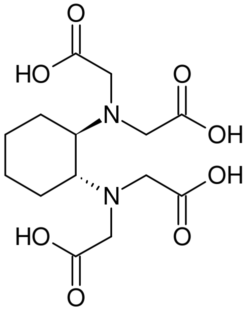


Figure 61. Chemical structure of trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA).

CDTA is a well-known commercially available complexant used in complexometric titration of different metals e.g. calcium, magnesium[107] or copper.[108] However, its complexing properties were utilised mainly at higher pH, where the deprotonation of the ligand appears.[109-110] The lack of the thermodynamic data and the complexation models on the complexation of metals by CDTA at moderate and high nitric acid concentration required closer look at its behaviour at the mentioned conditions.

4.4.1. The influence of CDTA on the extraction of HAR elements

The extraction experiments were carried out using HAR simulate solution (HAR-FZJ) in order to study the influence of CDTA on the metal extraction by three different organic solvents: TODGA/TBP, TODGA/1-octanol and DMDOHEMA. TODGA was chosen as a good candidate for the innovative SANEX process while DMDOHEMA is the reference extractant for the already existing DIAMEX process. TPH was used as a diluent. Additionally the behaviour of ^{239}Pu in presence of CDTA was studied. If CDTA does not have any negative influence on plutonium extraction, this masking agent could be successfully used in processes such as GANEX, where up to 50g/L of plutonium are present.

The composition of the HAR simulate solution used in the experiments and the corresponding distribution ratios of the metals are shown in Table 25. The results from the extraction experiments using trace amounts of ^{239}Pu are also included into this table. The experiments with ^{239}Pu have been conducted separately but under the same experimental conditions using identical aqueous and organic phase compositions. As expected ^{241}Am, the trivalent lanthanides, yttrium and ^{239}Pu were quantitatively extracted by TODGA/TBP. The oxidation state of plutonium in the extraction experiments was not adjusted. Similar distribution ratios for the above mentioned elements (excluding ^{239}Pu) were obtained with TODGA/1-octanol as a solvent. Furthermore, Table 25 shows the distribution ratios of the inactive elements contained in different concentrations in the HAR solution. Without the addition of CDTA zirconium was extracted nearly quantitatively (D_{Zr} > 100) and palladium was also well extracted with a distribution ratio of 9.31 and 4.75 for TODGA/TBP and TODGA/1-octanol, respectively.

The use of CDTA showed the same complexation behaviour as HEDTA concerning Pd,[35, 95, 98] but furthermore it also complexes Zr, an element which is not complexed by HEDTA. The distribution ratios of Zr in the experiments using CDTA equalled 0.01 (TODGA/TBP). CDTA also seems to have some small influence on Ag and Mo distribution ratios, although molybdenum suppression is more pronounced in the case of DMDOHEMA. Similar to the TODGA/1-octanol-system the use of CDTA resulted in a distribution ratio of Zr below 0.01 and Pd of 0.05. Also for this solvent a small influence of CDTA on the Mo extraction was observed as D_{Mo} decreased from 7.71 to 2.07 after using CDTA (Table 25, column 6).

The extraction behaviour of Ru and Sr for TODGA-based solvents was not directly influenced by the use of the masking agent even though the extraction of strontium by TODGA was greater when CDTA was used. The same strontium behaviour was observed by Modolo et al.[95] and is caused by the higher concentration of free TODGA molecules available for metal complexation, such as Sr, when the masking agent is used. When no CDTA was present in the aqueous phase about 1060 mg of Zr (99% of the total content) and 152 mg of Pd (90% of the total content) were extracted by TODGA/TBP. By using CDTA only 10.6 mg of Zr (0.99%) and 11 mg of Pd (6.5%) were extracted into the organic phase.

The French DIAMEX-extractant DMDOHEMA is not as strong Ln(III) and An(III) extractant as TODGA . When no complexing agent is used the distribution ratios of ^{241}Am and the Ln(III) are below 3 (Table 25, column 7) and they are in a good agreement with the literature.[99] DMDOHEMA extracted Zr quantitatively with D_{Zr}=104, Pd was less extractable with D_{Pd}=3.7. The use of CDTA suppressed the extraction of both metals resulting in distribution ratios of 0.01 and 0.03 for Zr and Pd, respectively. Similarly as for the TODGA-based solvents CDTA reduced the extraction of Mo from distribution ratios of 7.7 to 2.1. Strontium was not extracted by the DMDOHEMA, although small amounts of Ru followed the extraction of An(III) and Ln(III) (similar as for TODGA solvents). Due to the suppressed extraction of some of the fission products by CDTA the distribution ratios of ^{241}Am and the Ln(III) increased slightly. This is caused by the same effect as for the strontium extraction by TODGA-based solvents.

CDTA proved to be a good masking agent for palladium and zirconium present in the HAR simulate solution of acidity 3.1 mol/L HNO_3. Nevertheless, the masking properties of CDTA with Zr and Pd at different concentration of nitric acid had to be studied more intensively.

Table 25. Composition of the synthetic HAR-FZJ solution and distribution ratio D for the extraction with different solvents, without complexant and with 0.05 mol/L CDTA.

		TODGA/TBP		TODGA/Octanol		DMDOHEMA	
Element	Conc. [mg/L]	Without complexant	CDTA	Without complexant	CDTA	Without complexant	CDTA
		Distribution ratio D		Distribution ratio D		Distribution ratio D	
^{241}Am	traces	>100	>100	>100	>100	2.10	2.65
^{239}Pu	traces	>100	>100	n.d.	n.d.	n.d.	n.d.
Y	90	>100	>100	>100	>100	0.32	0.40
La	239	>100	>100	88	>100	1.69	2.13
Ce	567	>100	>100	>100	>100	2.06	2.62
Pr	223	>100	>100	>100	>100	2.04	2.52
Nd	718	>100	>100	>100	>100	1.77	2.16
Sm	149	>100	>100	>100	>100	1.36	1.67
Eu	34	>100	>100	>100	70	1.14	1.39
^{152}Eu	traces	>100	>100	>100	>100	1.04	1.27
Gd	51	>100	>100	>100	>100	1.32	1.84
Ni	40	0.05	0.01	<0.01	<0.01	<0.01	<0.01
Cu	19	0.03	0.03	<0.01	<0.01	0.04	0.08
Zr	1071	>100	0.01	>100	<0.01	104	0.01
Mo	678	0.26	0.19	0.24	0.19	7.71	2.07
Pd	168	9.31	0.07	4.75	0.05	3.69	0.03
Ag	12	0.69	0.01	n.d.	n.d.	n.d.	n.d.
Cd	15	0.14	0.08	0.07	0.11	0.19	0.08
Cr	93	<0.1	<0.1	<0.1	0.11	0.01	0.01
Sn	11	<0.1	<0.1	<0.1	<0.1	0.04	0.03
Sb	4.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rb	63	0.10	0.14	<0.01	<0.01	0.09	0.09
Ru	356	0.34	0.32	0.21	0.13	0.27	0.28
Rh	73	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Te	165	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	177	1.50	3.31	1.23	3.14	<0.01	<0.01
Ba	259	0.13	0.03	<0.01	<0.01	<0.01	<0.01
Cs	542	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al	2	n.d.	n.d.	n.d	n.d	n.d	n.d
Fe	1900	<0.1	<0.1	n.d	n.d	n.d	n.d
Se	10	n.d.	n.d.	0.05	n.d	n.d	n.d
Na	1600	n.d.	n.d.	n.d.	n.d	n.d	n.d
HNO_3	3.1 mol/L						

n.d. – not determined

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH, 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH or 0.6 mol/L DMDOHEMA in TPH.

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), (0.05 mol/L CDTA), tracers: ^{241}Am, ^{152}Eu, ^{239}Pu; mixing time: 15min; T = 22°C ± 1°

4.4.2. Influence of the nitric acid concentration on the Pd, Zr, ^{241}Am and ^{152}Eu extraction.

The results of the complexation of Pd and Zr by CDTA depending on the nitric acid concentration show whether this masking agent can be used in scrubbing steps often having different acidity than variations in the feed solution. Each of the aqueous solutions used in this experiment were saturated with CDTA, therefore its precise concentration cannot be stated.

The extraction of ^{241}Am and ^{152}Eu as representatives for trivalent actinides and lanthanides is shown in Figure 62. At nitric acid concentration ranges from 1 to 3 mol/L the distribution ratios of used radionuclides were very high even in the presence of CDTA. At nitric acid concentration below 1 mol/L a decrease of the Am and Eu distribution ratios was observed independently of a presence of CDTA. This was caused by a lower extraction of trivalent

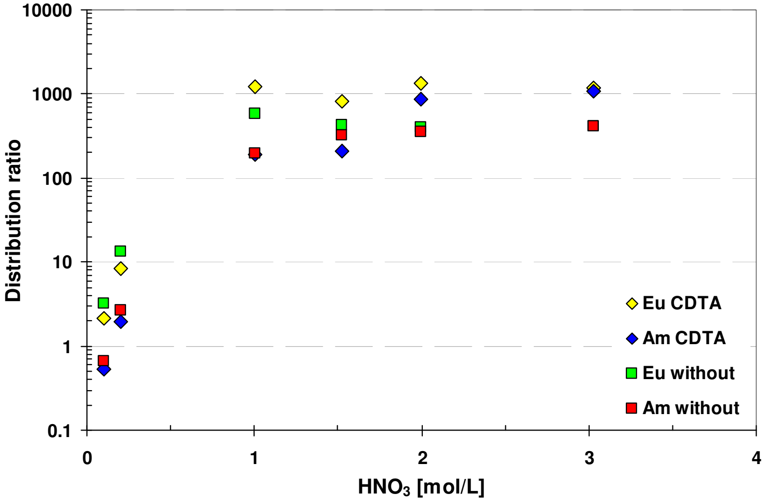


Figure 62. Distribution ratios of ^{241}Am and ^{152}Eu as a function of the nitric acid concentration in a presence and absence of CDTA.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: CDTA, variable HNO_3 concentration, tracers: ^{241}Am, ^{152}Eu;
mixing time: 15min.; T = 22°C ± 1°

lanthanides and actinides by TODGA at low nitric acid concentrations, which is typical for this extractant.

Figure 63 shows the Pd and Zr distribution ratios against the nitric acid concentration with and without addition of the complexant. TODGA/TBP extracted Pd in the whole nitric acid region with only a small decrease of D-values from D_{Pd} = 3.4 at 0.1 mol/L HNO_3 to D_{Pd} = 1.7 at 3 mol/L HNO_3 when CDTA was not used. These results are similar to those reported by other researchers.[95] After the addition of CDTA to the HAR solution the Pd extraction decreased down to D_{Pd}=0.06 and remained on this level through the whole acidity rage tested with only minor fluctuations.

The distribution ratios of Zr without the complexant increased with increasing nitric acid concentration and reached a maximum value of 5 at 1.5 mol/L HNO_3, then remained constant up to 3 mol/L HNO_3. The distribution ratios in the presence of CDTA were not affected by

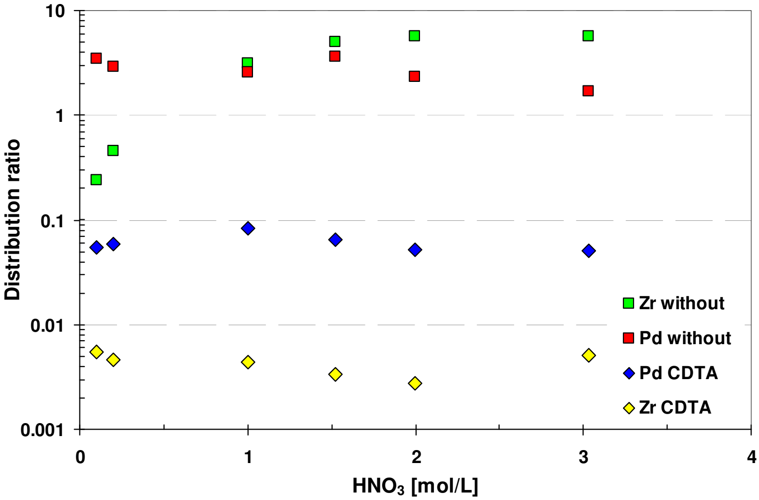


Figure 63. Distribution ratios of Zr and Pd as a function of the nitric acid concentration in a presence and absence of CDTA.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: 10^{-4} mol/L Zr and Pd, CDTA, variable HNO_3 concentration; mixing time: 15min.; T = 22°C ± 1°

the nitric acid concentration and the zirconium extraction was suppressed well over the whole acidity range. Compared to the results shown in Table 25 (column 3) the distribution ratios in the Figure 63 are slightly lower. In the experiment shown in the Table 25 High Active Raffinate simulate solution was used. The concentration of Zr in that solution was 1081 mg/L whereas in the experiment with varying HNO_3 concentration (Figure 63) the Zr concentration was only 9.1 mg/L Zr (10^{-4} mol/L). The complexation of Zr by CDTA is more efficient in the case of a lower concentration of this metal (less metal to be complexed), which results in lower D_{Zr}. The result for zirconium in the Table 25 is in good agreement with the results obtained by Modolo et al.[95]

4.4.3. Influence of the CDTA concentration on the ^{241}Am and ^{152}Eu extraction

Further studies were focused on investigating the influence of the CDTA concentration on the extraction of fission products, trivalent actinides and trivalent lanthanides. Again three different solvents were tested, namely TODGA/TBP in TPH, TODGA/1-octanol in TPH and DHDOHEMA in TPH. The results of these studies are shown in Figure 64 and Figure 65.

The extraction of ^{241}Am and ^{152}Eu and the trivalent lanthanides was not negatively affected by CDTA even at concentrations up to 0.10 mol/L of the complexing agent (Figure 64). The lanthanides were extracted with distribution ratios over 100 for TODGA-based solvents and around 2.5 for DMDOHEMA in the whole range of CDTA concentration.

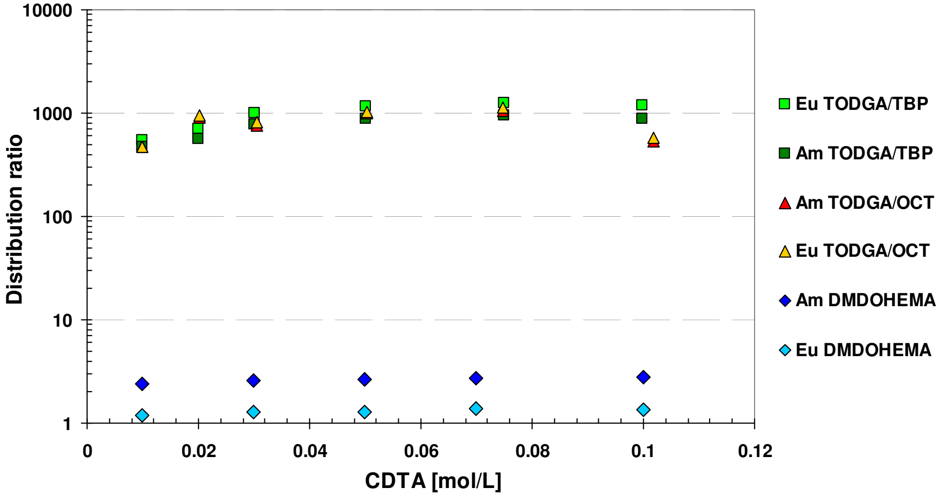


Figure 64. Distribution ratios of ^{241}Am and ^{152}Eu as a function of the CDTA concentration for three different organic solvents.

Organic phase:	0.2 mol/L TODGA + 0.5 mol/L TBP in TPH, 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH or 0.6 mol/L DMDOHEMA in TPH
Aqueous phase:	HAR elements in 3.1 mol/L HNO_3 (HAW-FZJ), variable CDTA concentration, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.; T = 22°C ± 1°

The addition of CDTA to the aqueous phase suppressed the extraction of Pd and Zr by all three studied organic solvents (Figure 65). For TODGA-based solvents only 0.02 mol/L of CDTA was needed to decrease zirconium distribution ratio drastically from about 100 to below 0.01. In the case of DMDOHEMA more masking agent was necessary, namely 0.03 mol/L, to reduce the zirconium extraction to the same extent as for TODGA solvents (<0.01). The reason for this could be the higher concentration of DHDOHEMA (0.6 mol/L) in comparison to TODGA (0.2 mol/L).

The suppression of palladium extraction was not as good as for zirconium; however palladium is present in smaller amount in the HAR solution than Zr. The Pd distribution ratios decreased with increasing masking agent concentration (Figure 65) and a plateau was

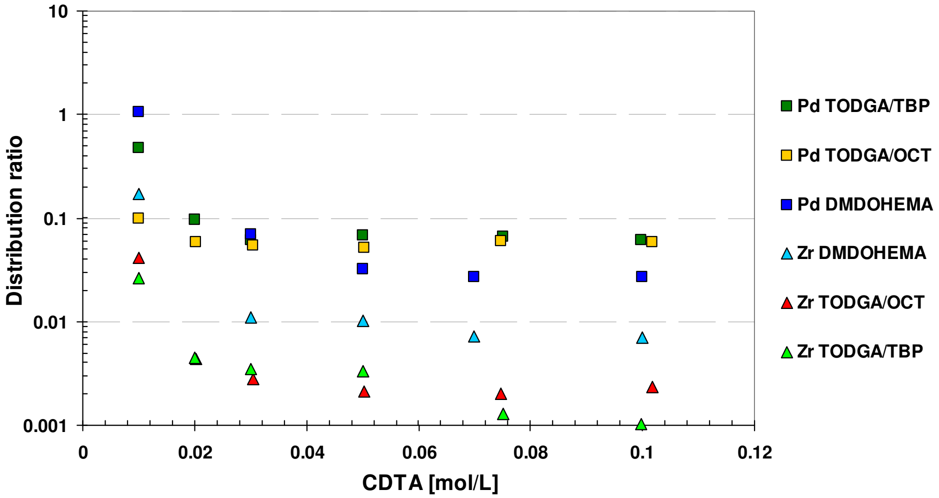


Figure 65. Distribution ratios of Zr and Pd as a function of the CDTA concentration for three different organic solvents.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH, 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH or 0.6 mol/L DMDOHEMA in TPH

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), variable CDTA concentration, tracers: ^{241}Am, ^{152}Eu; mixing time: 15min.; T = 22°C ± 1°

observed at concentration > 0.03 mol/L (TODGA solvents) and >0.05 mol/L of CDTA (DMDOHEMA).

Summarising, 0.05 mol/L of the masking agent was the optimal concentration needed to keep more that 99% Zr and >90% Pd in the aqueous phase.

4.4.4. The influence of the Zr concentration on its complexation by CDTA

The concentration of zirconium in different HAR solutions can vary, although it is usually present in large amounts due to a partial dissolution of Zircaloy (zirconium alloy) used as cladding material of fuel rods in nuclear reactors. A good masking agent should be able to handle high concentrations of the masked metal without causing any precipitation. Therefore, solutions of different concentrations of zirconium in 1 and 3 mol/L HNO_3 were contacted with the TODGA/TBP solvent. CDTA was present in the aqueous phase in two different concentrations, 0.025 and 0.05 mol/L as the solubility of CDTA is limited but increases with the acidity. In 1 mol/L of nitric acid it was possible to fully dissolve 0.025 mol/L CDTA, while the solution with 0.05 mol/L of CDTA still contained undissolved complexant and could not be used in the experiment. This problem was not observed in 3 mol/L of nitric acid and a solution with 0.05 mol/L CDTA was easily obtained. The distribution ratios calculated from the obtained results are shown in Table 26.

Zirconium was nearly quantitatively complexed in the aqueous phase and its distribution ratios did not exceed 0.005, even at the highest concentration tested (1099 mg/L = 0.012 mol/L). This result was very promising as in this case 99.5 % of the metal was complexed in the aqueous phase and only 0.5 % was extracted by the TODGA/TBP solvent.

The second tested solution with lower concentration of CDTA in 1 mol/L HNO_3 gave a maximum Zr distribution ratio D_{Zr} of 0.011 at the highest Zr concentration tested (Table 26– last column). Both experiments showed a slight increase in the Zr distribution ratios with increasing Zr concentration.

Table 26. The extraction of Zr by a TODGA/TBP mixture in a presence of CDTA in the aqueous phase.

	Distribution ratios of Zr					
Zr [mol/L]	0.0004	0.001	0.0015	0.003	0.006	0.012
1 M HNO_3 0.025 mol/L CDTA	< 0.001	< 0.001	< 0.001	0.002	0.004	0.011
3 M HNO_3 0.050 mol/L CDTA	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.005

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: variable Zr concentration in: 1 mol/L HNO_3 + 0.025 mol/L CDTA or 3 mol/L HNO_3 + 0.050 mol/L CDTA, mixing time: 15 min.; T = 22°C ± 1°

4.4.5. The influence of CDTA on the extraction kinetics

In order to study the stability of the Zr- and Pd-CDTA complexes an experiment with variable mixing time was carried out and the results are shown in the Figure 66 and Figure 67.

The complexation of Zr and Pd by CDTA must have been reasonably fast since just after dissolving CDTA in a HAR solution and contacting it with the organic solvent for 1 minute (mixing time) the extraction of the two metals was minimised (Figure 66). The palladium complexes with the masking agent were stable for at least 10 minutes of the mixing time. The CDTA-Zr complexes were less stable. A slow increase of the distribution ratio with the mixing time was observed (Figure 66, yellow triangles). This suggests a very slow de-complexation of Zr-CDTA complex and immediate extraction of the released Zr by TODGA which forms a Zr-TODGA complex in the organic phase. This should not be a major problem for the process application because the phase contact time in a centrifugal contactor is much

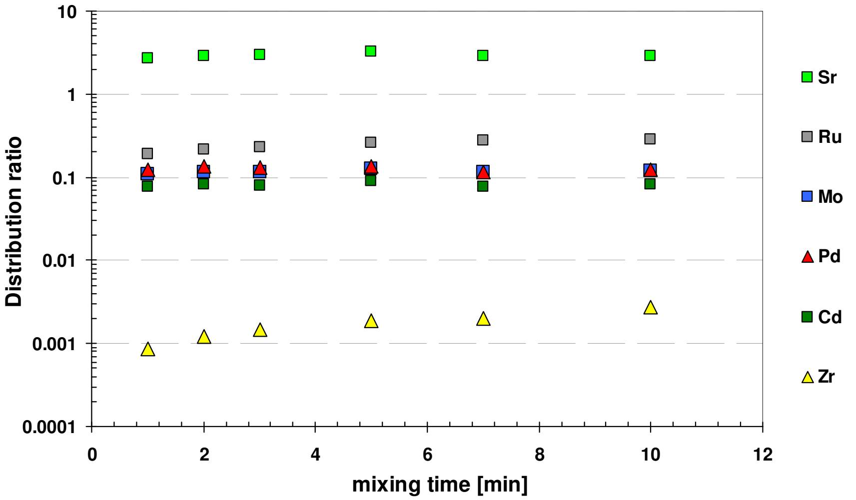


Figure 66. Distribution ratios of Sr, Ru, Mo, Pd, Cd and Zr as a function of the mixing time.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), 0.05 mol/L CDTA, tracers: ^{241}Am, ^{152}Eu; variable mixing time; T = 22°C ± 1°

shorter than 10 minutes. The rest of the metals were not affected by the masking agent within the tested time range.

The extraction of ^{241}Am, ^{152}Eu and some of the trivalent lanthanides was not affected by the use of the masking agent (Figure 67).

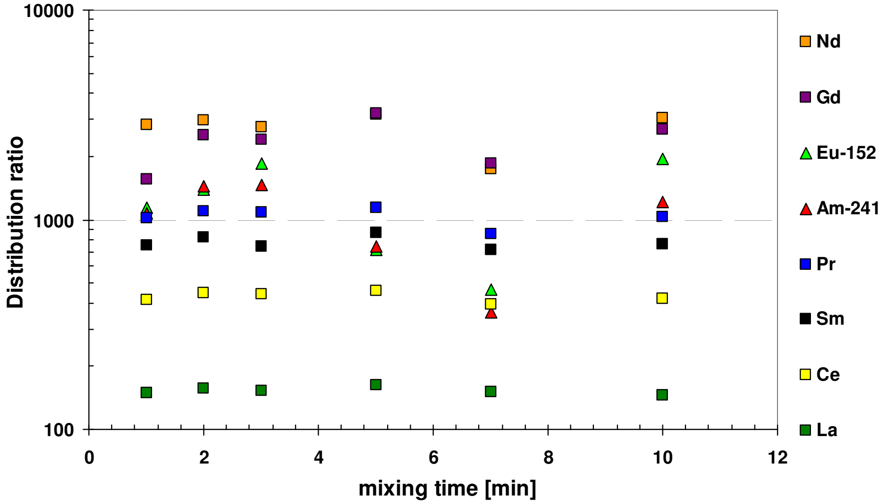


Figure 67. Distribution ratios of ^{241}Am, ^{152}Eu and some of the Ln(III) as a function of the mixing time.

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), 0.05 mol/L CDTA, tracers: ^{241}Am, ^{152}Eu; variable mixing time; T = 22°C ± 1°

4.4.6. The influence of CDTA on Zr and Pd extraction after extended phase contact time

The increase of the distribution ratio of Zr with the mixing time suggested a slow extraction of this metal despite the presence of CDTA (Figure 66). An additional experiment was performed with the same composition of organic and aqueous phase as in the extraction kinetics studies described above but the phase contact time was extended to 144 hours (6 days). The organic and the aqueous phases were mixed for 30 minutes every 24 hours and the sampling of the phases for measurements was done on the 6th day of the experiment. The distribution ratios of the HAR elements of this experiment are shown in Table 27.

The distribution ratio of Zr after 6 days phase contact time increased from 0.01 to 0.13. The D-values of some of the Ln(III) decreased slightly. However, they were still very high. Also ruthenium was slowly extracted into the organic phase since its D_{Zr} increased from 0.32 (15 min) up to 1.63 after 6 days contact time. Palladium distribution ratio of 0.35 (column 4) was significantly higher compared to 0.01 after 15 min mixing time (column 3). However, the mass balance of this metal indicated a loss of about 25% which could be caused by precipitation.

The slow increase of the Zr distribution ratio with the mixing time required some additional experiments with an extended phase contact time. Two experiments were conducted. In the first experiment (extraction), 5 mL of 0.2 mol/L TODGA in TPH were contacted with 5 mL of a Zr solution (35 mg/L Zr) containing 3 mol/L HNO_3 and 0.05 mol/L CDTA. The phases were continuously stirred for 16 days and aliquots of both phases were taken daily for analysis. In the second experiment (scrubbing), 5 mL of 0.2 mol/L TODGA in TPH were pre-loaded with Zr by extraction from a Zr solution (35 mg/L Zr) at 3 mol/L HNO_3. Then, the pre-loaded org. phase was contacted with a fresh aqueous phase at 3 mol/L HNO_3 containing

0.05 mol/L CDTA. The phases were also continuously stirred for 16 days and aliquots of both phases were taken daily for analysis.

The results showed a very slow increase in the distribution ratios of Zr with the equilibrium value being reached after approx. 14 days. The results from the scrubbing experiment showed that after the extraction of Zr into TODGA it is not possible to scrub it back to the aqueous phase with CDTA. Even after 16 days a distribution ratio >100 was measured.

This illustrated that the extraction kinetics for Zr extraction in the presence of CDTA is very slow. It is assumed that the Zr-TODGA complex is thermodynamically more stable, but the decomplexation of the Zr-CDTA complex is very slow. Since in a technical process, the residence time in the contactor is short, CDTA can be used as a masking agent, although the distribution ratios of Zr are not in equilibrium and thus underestimated. Hence, it is quite difficult to elaborate a thermodynamic model for flow-sheet calculations. In extraction experiments without the addition of CDTA it was shown that the equilibrium distribution ratio (D_{Zr}>100) was reached after a few minutes.

Table 27. The distribution ratios of HAR elements after 6 days phase contact in a presence of CDTA.

Element	Without complexant	CDTA 15 min phase contact	CDTA 6 days phase contact
	Distribution ratio D		
Ce, Pr, Nd, Sm	>100	>100	>100
Y	>100	>100	76.7
La	>100	>100	87.3
Gd	>100	>100	43.0
Eu	>100	>100	38.3
Zr	>100	0.01	0.13
Pd	9.31	0.07	0.35*
Sr	1.50	3.31	1.49
Ru	0.34	0.32	1.63
Mo	0.26	0.19	0.18
Rb	0.10	0.14	0.07
Ag	0.69	0.01	n.d.
Cd	0.14	0.08	0.08
Ba	0.13	0.03	0.01
Ni	0.05	0.01	<0.01
Cu	0.03	0.03	0.02
Cr, Sn	<0.1	<0.1	<0.1
Sb, Fe	<0.1	<0.1	n.d.
Te	<0.01	<0.01	0.015
Rh, Cs	<0.01	<0.01	<0.01
Al, Se, Na	n.d.	n.d.	n.d.

n.d. – not determined

* the mass balance equalled -26%

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), 0.05 mol/L CDTA, mixing time: 15min. and 144 hours (6 days)

4.4.7. Distribution ratios of HAR elements in the extraction and scrubbing steps

The masking agent added to the feed solution in the continuous process suppresses the extraction of undesired metals by the organic solvent. If the suppression is not very efficient it is possible to further decrease their extraction by adding the same masking agent into the scrubbing solution. The undesired metals co-extracted together with An(III)/Ln(III) in the extraction section of the process can be back-extracted to the aqueous phase in the additional scrubbing stages. In order to test the performance of CDTA in the scrubbing solution an extraction experiment was conducted without addition CDTA into the aqueous phase. The organic solvent was thereby loaded with the co-extracted HAR including Pd and Zr. Further, the loaded solvent was split into six parts and each part was contacted with a freshly prepared aqueous phase containing different concentrations of nitric acid and 0.025 or 0.05 mol/L CDTA. The results of this experiment are shown in Table 28. Zirconium was extracted by TODGA in the extraction step with a distribution ratio of 45 (column 2) but stayed in the organic phase during scrubbing with $D_{Zr} > 100$ (columns 3 – 8). Palladium was just partly removed from the loaded organic phase. More than 50% ($D_{Pd} > 1$) of the metal was not stripped regardless of the nitric acid and CDTA concentration of the stripping solution. Only at 3.0 mol/L HNO_3 (5 column) the D_{Pd} was above 1 (D_{Zr}=0.9). The low distribution ratios of lanthanum in the scrubbing step (columns 6 – 8) were mostly caused by the decrease of the nitric acid concentration of the scrubbing solution. The lower the concentration the weaker the La extraction by TODGA.

Summarising from the experimental results: CDTA can sufficiently prevent the extraction of palladium and zirconium if it is added directly to the feed solution resulting in Zr distribution ratios low enough for process applications. As the distribution ratio of Pd ($D_{Pd} < 0.07$, Table 25) was higher than this of Zr, the possibility of using an additional Pd masking agent namely HEDTA in the scrubbing step was tested.

Table 28. The extraction of HAR elements by the TODGA/TBP solvent followed by scrubbing steps with different nitric acid concentrations containing CDTA.

Element	Distribution ratio						
CDTA [M]	-	0.05	0.05	0.05	0.05	0.025	0.025
HNO_3 [M]	3.1	5.0	4.0	3.0	2.0	2.0	1.5
extraction		scrubbing					
^{241}Am, ^{152}Eu	>100	>100	>100	>100	>100	>100	>100
Y, Sm, Eu, Gd	>100	>100	>100	>100	>100	>100	>100
Nd	76	>100	>100	>100	>100	>100	>100
Pr	54	>100	>100	>100	>100	>100	>100
Ce	41	>100	>100	>100	>100	>100	69
La	27	147	88	119	17	17	27
Zr	45	>100	>100	>100	>100	>100	>100
Pd	4.00	1.3	2.1	0.9	4.2	6.0	-
Cd	0.137	1.74	1.17	2.04	1.49	1.67	3.25
Mo	0.223	0.48	0.42	0.56	0.41	0.43	0.72
Ru	0.306	2.1	4.8	1.2	15.5	14.9	-
Sr	0.88	0.33	0.72	0.16	1.15	1.15	0.94
Rb	0.072	D-values cannot be calculated due to low concentration of the metals in the samples after extraction step					
Cu	0.024						
Sb	0.020						
Ba	0.019						
Cr	0.010						
Cs, Ni, Sn, Rh, Te	<0.01						

Extraction step

Organic phase: 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH

Aqueous phase: HAR elements in 3.1 mol/L HNO_3 (HAR-FZJ), tracers: ^{241}Am, ^{152}Eu; mixing time: 15 min.; T = 22°C ± 1°

Scrubbing step

Organic phase: the solvent loaded the extraction step

Aqueous phase: variable HNO_3 concentration, 0.05 mol/L or 0.025mol/L CDTA; mixing time: 15 min.; T = 22°C ± 1°

4.4.8. The extraction of Pd and Zr in the presence of CDTA and HEDTA

An organic solvent consisting of 0.2 mol/L TODGA + 5 vol.-% 1-octanol was contacted with the HAR simulate solution (HAR-FZJ) containing 0.05 mol/L of CDTA and variable concentration of HEDTA. The results of this experiment are shown in the Figure 68.

Without addition of HEDTA the extraction of Zr and Pd was prevented by their complexation with CDTA in the aqueous phase (no HEDTA added, Figure 68). Surprisingly with increasing concentration of HEDTA in the aqueous phase the distribution ratios of Zr were increasing. At the highest HEDTA concentration tested (0.1 mol/L) D_{Zr} reached a value of 0.16 (almost 50 times higher comparing to D_{Zr} without addition of HEDTA). The addition of HEDTA into the feed did not further decrease the extraction of palladium.

The distribution ratios of ^{241}Am, ^{152}Eu, the light trivalent lanthanides (La – Gd) and Y were above 100 and no influence of HEDTA on their extraction was observed. The extraction of the rest of fission products was also not affected by the presence of HEDTA.

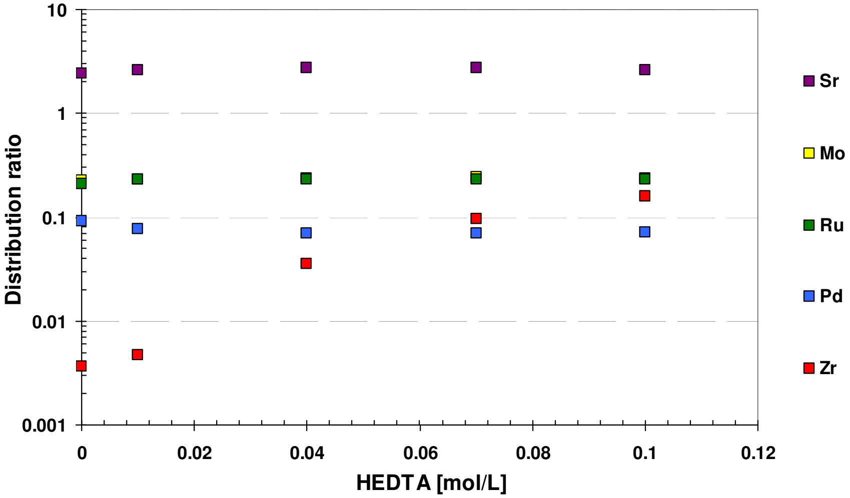


Figure 68. Distribution ratios of Zr, Pd, Mo, Ru and Sr as a function of the HEDTA concentration.

Organic phase:	0.2 mol/L TODGA + 5vol.% 1-octanol in TPH
Aqueous phase:	HAR elements in 3.1 mol/L HNO3 (HAR-FZJ), 0.05 mol/L CDTA, variable HEDTA concentration, tracers: ^{241}Am, ^{152}Eu; variable mixing time; T = 22°C ± 1°

The application of the additional palladium scrubbing step using HEDTA would therefore be possible but only if the aqueous phase after the scrubbing section was not mixed with the feed entering the extraction section. Thus CDTA could not be mixed with HEDTA (Figure 69). The major part of Pd (≈ 93% ⇔ D_{Zr} = 0.07; Table 25 column 4) would be kept in the aqueous phase using CDTA and end up in the raffinate. The remaining 7% of Pd would be scrubbed using HEDTA assuming quantitative Pd scrubbing.

A possible process flow-sheet shown in Figure 69 may also be risky as some of the An(III) and Ln(III) can end up in the Pd scrub raffinate. The distribution ratios of these metals are very high in the first stage of the scrubbing section. Although even if only 1% is back-extracted into aqueous phase it will be found in the Pd scrub raffinate.

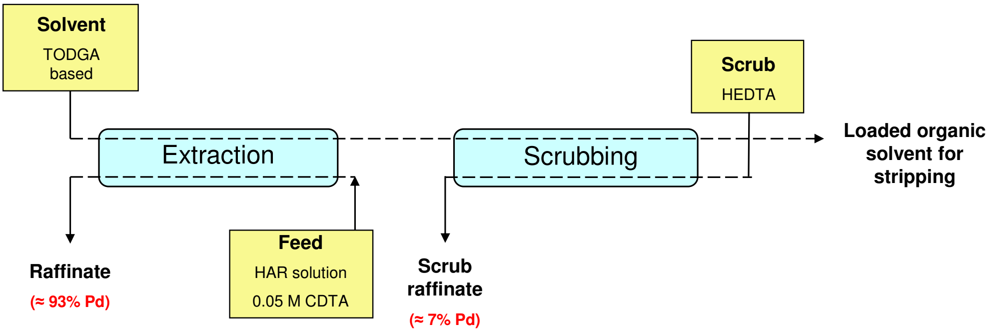


Figure 69. The example of a process flow-sheet with additional Pd scrub section.

It can be concluded that CDTA is a promising substitute for oxalic acid and possibly HEDTA if some modifications of the process flow-sheet are taken into account. This new masking agent was chosen for a spiked test using centrifugal contactors in counter-current mode thus its performance could be compared with the oxalic acid/HEDTA from the TODGA/TBP process developed in Germany.[47-48]

4.4.9. Determination of the stability constants of complexes Zr with CDTA and EDTA

The stability constants of the complexes formed between metal and ligand (or hydrophilic complexant) are crucial because they allow simulation studies of the metal behaviour in the aqueous or organic phase. Based on these stabilities it can be predicted which metal from a solution of several different metals will be preferably extracted (in case of an organic ligand) or better complexed in the aqueous phase (hydrophilic complexant). From Table 6 containing stability constants for complexes Ln(III)-ligand (DTPA or TTHA) it can be seen that stronger complexes are formed between Ln(III) and TTHA (higher $\log K_{ML}$) than with DTPA.

The stability constants of metal-ligand complexes were determined using pH metric titration. The method is based on the competition between the proton and the metal ion for the complexation with the studied ligand. This method can be used when the ligand possesses acid-base properties i.e. when its complexation properties depend on the pH.

CDTA is bearing four carboxylic groups that can de-protonate by losing their protons H^+. Its deprotonation in four steps is shown in the Eq 17 - Eq 20:

$$H_4L \xleftrightarrow{K_1} H_3L^- + H^+ \qquad \text{Eq 17}$$

$$H_3L^- \xleftrightarrow{K_2} H_2L^{2-} + H^+ \qquad \text{Eq 18}$$

$$H_2L^{2-} \xleftrightarrow{K_3} HL^{3-} + H^+ \qquad \text{Eq 19}$$

$$HL^{3-} \xleftrightarrow{K_4} L^{4-} + H^+ \qquad \text{Eq 20}$$

where L is the fully deprotonated CDTA

The fully deprotonated form of CDTA (CDTA^{4-}) is able to complex a metal cation. The stepwise complex formation for CDTA (L) and a given metal M^{2+} can be written as follows:

$$M^{2+} + L^{4-} \xleftrightarrow{K_5} ML^{2-} \qquad \text{Eq 21}$$

$$ML^{2-} + H^{+} \xleftrightarrow{K_6} MLH^{-} \qquad \text{Eq 22}$$

$$MLH^{-} + H^{+} \xleftrightarrow{K_7} MLH_2 \qquad \text{Eq 23}$$

where K$_5$, K$_6$ and K$_7$ can be written as:

$$K_5 = \frac{[ML^{2-}]}{[M^{2+}][L^{4-}]} \qquad \text{Eq 24}$$

$$K_6 = \frac{[MLH^{-}]}{[ML^{2-}][H^{+}]} \qquad \text{Eq 25}$$

$$K_7 = \frac{[MLH_2]}{[MLH^{-}][H^{+}]} \qquad \text{Eq 26}$$

The cumulative stability constant of a complex can be always expressed as a product of stepwise constant:

$$\beta_{111} = K_5 \cdot K_6 = \frac{[MLH^{-}]}{[M^{2+}][L^{4-}][H^{+}]} \qquad \text{Eq 27}$$

The subscript 111 in Eq 27 express that the formed complex contains one metal atom, one acidic ligand (CDTA) and one proton.

The cumulative stability constant of a complex [MLH$_2$] can be expressed as:

$$\beta_{112} = K_5 \cdot K_6 \cdot K_7 = \frac{[MLH_2]}{[M^{2+}][L^{4-}][H^{+}]^2} \qquad \text{Eq 28}$$

The subscript 112 in Eq 28 express that one metal atom, one acidic ligand and two protons form the complex.

The studied metal cation undergoes hydrolysis at higher pH and this reaction can be described as follows:

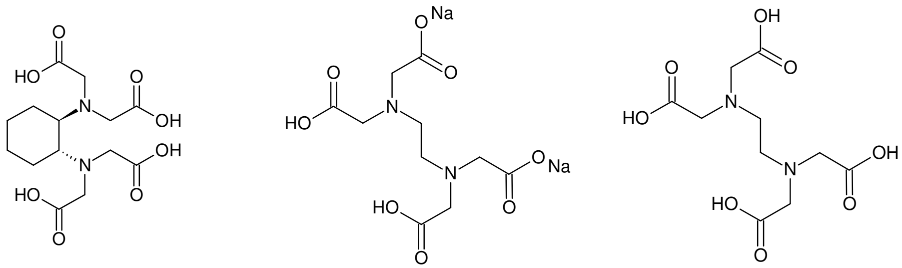
$$M^{2+} + OH^{-} \xleftrightarrow{K_8} MOH^{+} \qquad \text{Eq 29}$$

$$MOH^{+} + OH^{-} \xleftrightarrow{K_9} M(OH)_2 \qquad \text{Eq 30}$$

The studied ligands (Figure 70) contain in their structures four acetic groups. In case of Na_2EDTA two de-protonating H^+ were substituted by Na atoms which increased significantly the solubility of the ligand in water.

At first two metals, namely Pd and Zr, were planned to be studied. However, when palladium was added to the solution containing the dissolved ligand, the metal precipitated immediately. Commonly $PdCl_2$ is used in this type of studies, however in this work only nitrate ions could be present in the studied solution, therefore only zirconium was used in further studies.

Figure 70. Chemical structures of the studied compounds.



Trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA)

Ethylenediamine-tetraacetic acid disodium salt dehydrate (Na_2EDTA)

Ethylenediamine-tetraacetic acid (EDTA)

Both ligands were tested at constant ionic strength of 0.1 mol/L using sodium nitrate ($NaNO_3$) or tetraethylammonium nitrate (Et_4NNO_3). The latter one was used additionally to see if sodium had any influence on the stability constants since this metal could also be complexed by the studied ligand.

4.4.9.1. EDTA

The titration results of EDTA without the presence of a metal (Figure 71a) and the comparison with the fitted model indicates three protonated species: LH^{3-}, LH_2^{2-} and LH_3^{-} (where ligand is represented by L). The model (dotted red line) fits very well into the experimental results (blue diamonds). The corresponding protonation constants are shown in the Table 29.

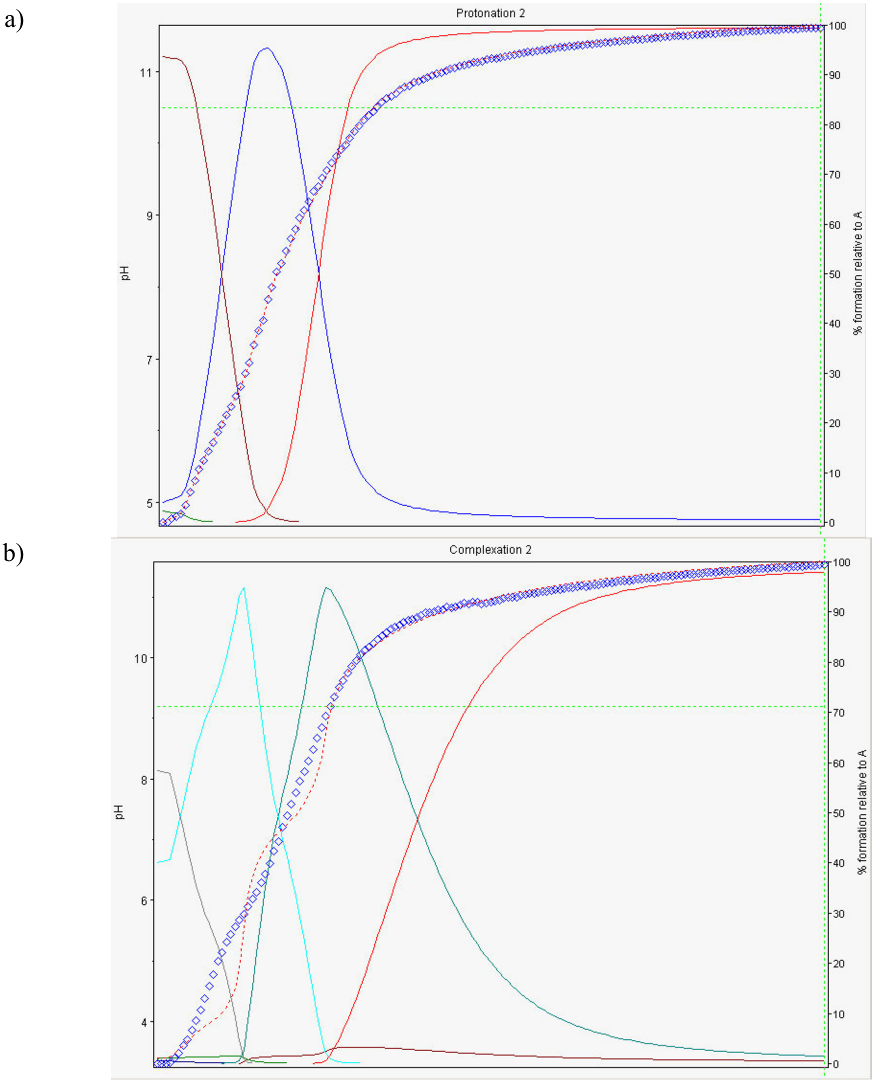


Figure 71. Titration curve of EDTA a) alone and b) in a presence of 1:1 EDTA:$ZrO(NO_3)_2$ mixture (red dotted line – calculated fitting curve; blue points – experimental points curve).

The protonation constants of EDTA calculated based on model shown in Figure 71a were included in the complexation model of Zr with EDTA. This complexation model does not fit exactly into the experimental results (Figure 71b) – the model line (dotted red line) deviates from the experimental results (blue diamonds). It is probably a result of missing additional species that existed in the solution during its titration. These missing species could be related to additional Zr complexes and would have an influence on pH change during titration (the shape of the model line would be slightly different).

The stability constants obtained for Na_2EDTA (Table 29, column 2 and 3) are comparable with the literature values (column 5 and 6). The first and second stability constant for EDTA (column 4) are deviated from the literature values, however these experimental values are less precise compared to Na_2EDTA since EDTA has very poor solubility in water and it was impossible to obtain a solution with dissolved ligand at desired concentration.

Table 29. Logarithms of the protonation constants of EDTA - Comparison with literature data

Equilibria	I=0.1($NaNO_3$) Na_2EDTA	I=0.1(Et_4NNO_3) Na_2EDTA	I=0.1($NaNO_3$) EDTA	I=0.1($NaNO_3$) (T=21.7 °C)[103]	I=0.1(KNO_3) (T=25 °C)[103]
1	2	3	4	5	6
$4H^+ + L^{4-} \leftrightarrow HL^{3-}$	9.34	9.90	11.17	10.23	10.27
$HL^{3-} + H^+ \leftrightarrow H_2L^{2-}$	6.07	5.98	8.59	6.16	6.16
$H_2L^{2-} + H^+ \leftrightarrow H_3L^-$	3.07	3.62	3.22	2.67	2.67
$H_3L^- + H^+ \leftrightarrow H_4L$	-	-	-	1.99	2.0

Three different complexes of Zr with EDTA were found (Table 30): $[ZrO\text{-}EDTA]^{2-}$, $[ZrO\text{-}EDTAH^-]$ and $[ZrO\text{-}EDTAH_2]$. The obtained stability constants are comparable to those in the literature (Table 33, column 2). Since Zr hydrolyses at higher pH the constant stabilities for these complexes were also determined (Table 30, column 5).

Table 30. Logarithms of the stability constants (log β_{11n}) of ZrO^{2+} complexes with EDTA

Counter-ion	$ZrOL^{2-}$	$ZrOLH^{-}$	$ZrOLH_2$	$ZrOL(OH)^{3-}$
1	2	3	4	5
Na^+ *	20.95	28.04	31.61	-7.25
Et_4N^+ *	24.07	31.18	34.93	-1.61
Et_4N^+	9.42	31.41	37.44	-6.67

* Titration of Na_2EDTA

4.4.9.2. CDTA

The second studied complexant CDTA gave a similar protonation profile as EDTA. It was expected since both complexants have very similar structures and both contain the same number of carboxylic groups that they can protonate/de-protonate depending on pH. The only difference could be the stability constants. CDTA is expected to form more stable complexes due to its cyclic ring which makes it less flexible compared to EDTA. The spatial structure of CDTA favours the complexation of metals since it does not have to rotate to a position suitable for complexation as in the case of EDTA. The de-protonation of CDTA (titration experiment in absence of the metal) is shown in Figure 72a and its complexation with Zr in Figure 72b.

The obtained protonation constants of CDTA (Table 31, column 2 and 3) are comparable with the literature data (column 4, 5 and 6) besides the first constant found (9.70) when $NaNO_3$ was used as a medium.

Table 31. Logarithms of the protonation constants of CDTA - Comparison with literature data

Equilibria	I =0.1($NaNO_3$)	I =0.1(Et_4NO_3)	T= 25 °C I = 0.1[111]	T= 20 °C I = 0.1[111]	T = 20 °C I = 0.1(KCl)[112]
$H^+ + L^{4-} \leftrightarrow HL^{3-}$	9.70	11.74	12.3	12.4	11.70
$HL^{3-} + H^+ \leftrightarrow H_2L^{2-}$	6.10	6.32	6.12	6.15	6.12
$H_2L^{2-} + H^+ \leftrightarrow H_3L^-$	3.87	4.50	-	3.53	3.52
$H_3L^- + H^+ \leftrightarrow H_4L$	-	-	-	2.42	2.43

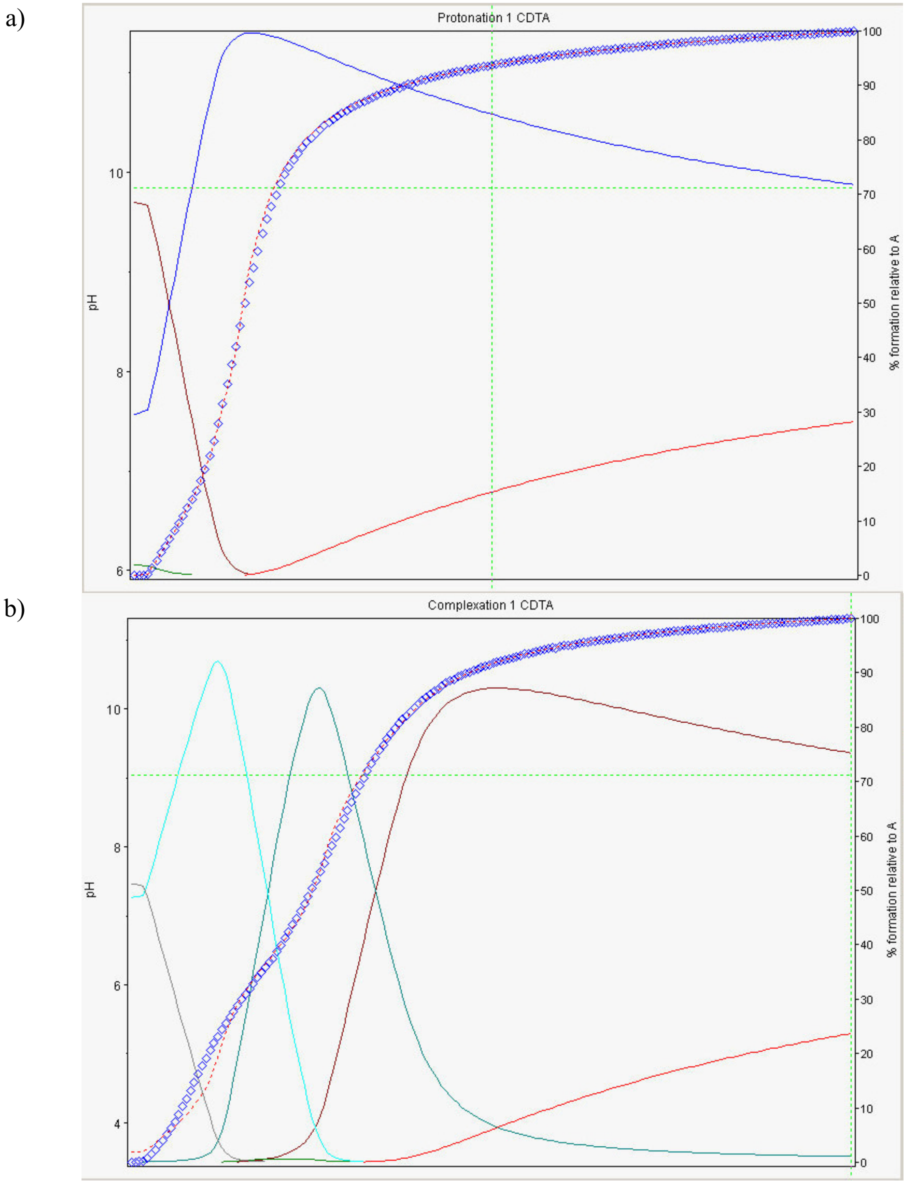


Figure 72. Titration curve of CDTA a) alone and b) in a presence of 1:1 CDTA:$ZrO(NO_3)_2$ mixture (red dotted line – calculated fitting curve; blue points – experimental points curve).

The stability constants for complexes of Zr with CDTA are shown in Table 32. Similarly as in the case of EDTA, three different complexes were found: [ZrO-CDTA^{2-}], [ZrO-CDTAH^{-}] and [ZrO-CDTAH$_2$]. The values are much higher when Et_4NNO_3 was used as a medium. As it was mentioned before Na can possibly compete with Zr to be complexed by CDTA thus the stability constants of Zr-CDTA in NaOH medium are expected to be lower compared to Et_4NNO_3.

Table 32. Logarithms of the stability constants (log β_{11n}) of zirconyl complexes with CDTA

Counter-ion	$ZrOL^{2-}$	$ZrOLH^{-}$	$ZrOLH_2$	$ZrOL(OH)^{3-}$
Na^+	18.39	24.52	27.82	9.45
Et_4N^+	23.83	30.22	33.52	-3.63

Table 33. Stability constants of complexes CDTA-Zr and EDTA-Zr (literature)

	EDTA-Zr	CDTA-Zr
Liquid ion exch.[113]	27.91	29.88
Ion exch. resin[114]	28.0	-
Sorption on silica gel[115]	28.5	-
Spectrophotom.[116]	29.9	-
Glass el.[117]	19.40	-
Polarography[118]	18.0	21.9
Potentiom.[119]	-	20.68

The potentiometric titration studies on CDTA confirmed its very strong complexation of Zr and the obtained results were comparable with the literature. However, due to precipitation the other element of interests (Pd) could not be studied using this method. Additional experiments should be performed at high nitric acid concentration (3 – 4 mol/L) to determinate the form and behaviour of Zr, Pd and CDTA at those conditions. Unfortunately, potentiometric titration can not be used at high acidic conditions. Probably a better technique would be microcalorimetry which is not available in the laboratory of IEK-6.

4.5. Single centrifugal contactor test

A battery of miniature centrifugal contactors in counter-current mode (Figure 73) is commonly used at Forschungszentrum Jülich (in the laboratory of IEK-6) to confirm the applicability of liquid-liquid processes for the partitioning of nuclear spent fuel. In order to perform this type of test, a designed flow-sheet is necessary to estimate how many stages (centrifugal contactors) will be necessary for each of the steps (extraction, scrubbing, stripping) in the process tested.

The flow-sheet is prepared using computer calculation models, where thermodynamic data including the efficiency of the apparatus, kinetics of the extraction system, change of the flow-rates of the fluxes are applied. These kinds of data can be obtained by performing a single centrifugal contactor test (Figure 74). Using one centrifugal contactor the efficiency of one stage of each of the steps in the process can be obtained. Each step is tested separately and the order of tested steps is the same as foreseen in the process. In case of the proposed i-SANEX process, first the extraction step is studied, followed by the selective actinide

Figure 73. Battery of miniature centrifugal contactors for performing tests in counter-current mode.

stripping and subsequently the lanthanide stripping. The loaded organic phase from one step is used as the organic phase in the subsequent step e.g. the organic solvent loaded with metals in the extraction step is used as the organic phase in the An-stripping step. The optimal conditions to be used for each step in a single centrifugal contactor test were developed during the batch tests described in previous chapter (*Solvent based on TODGA + 1-octanol*).

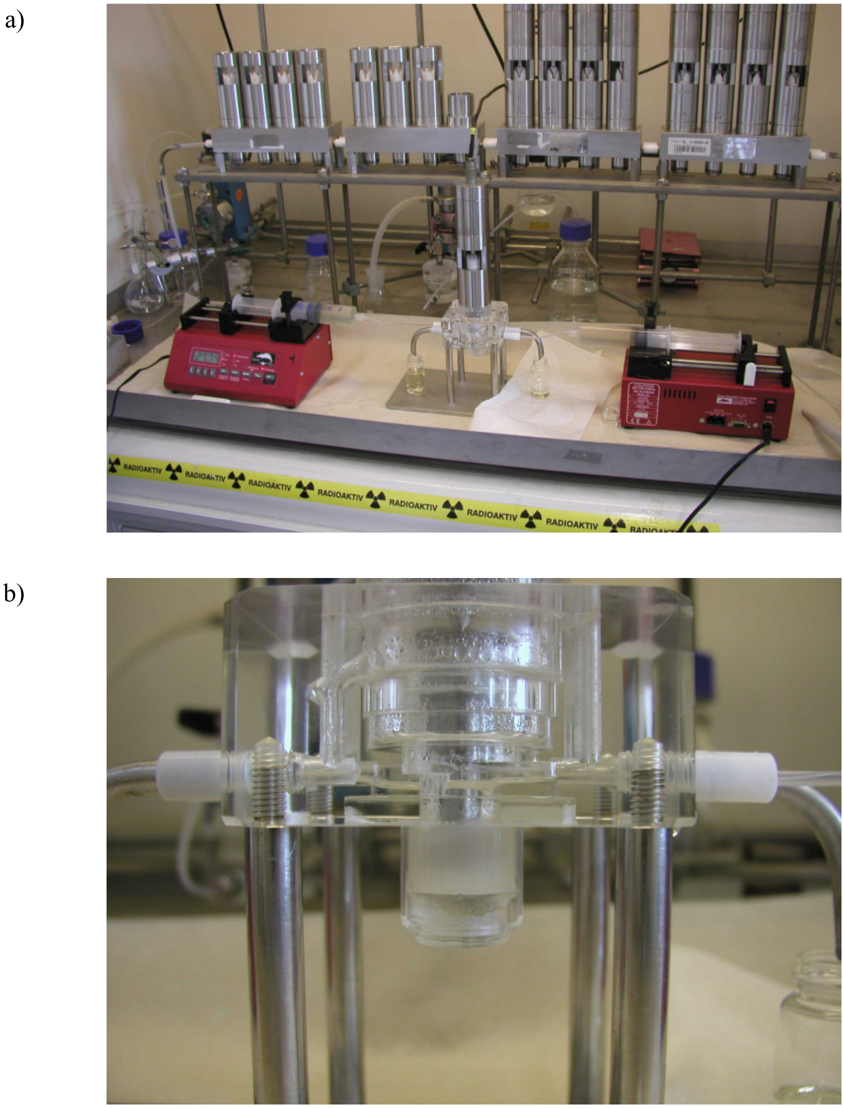


Figure 74. Experimental setup of the single centrifugal contactor tests. a) syringe pumps with a contactor in the middle, b) mixing chamber of the contactor.

The composition of the organic solvent, scrubbing and stripping solutions and the choice of the masking agent were based on the results obtained in the batch tests described in chapter 4.3 Innovative SANEX, pages 83.

The draft of a flow-sheet for an innovative-SANEX process (Figure 75) was based on the published TODGA/TBP process for partitioning of trivalent actinides.[47-48, 95] The main change in the structure of the flow-sheet was the splitting of the An+Ln stripping step into two separate steps, namely selective actinide stripping and lanthanide stripping.

Three separate tests were performed simulating the conditions in the extraction, scrubbing and An-stripping step (arrows marked in Figure 75).

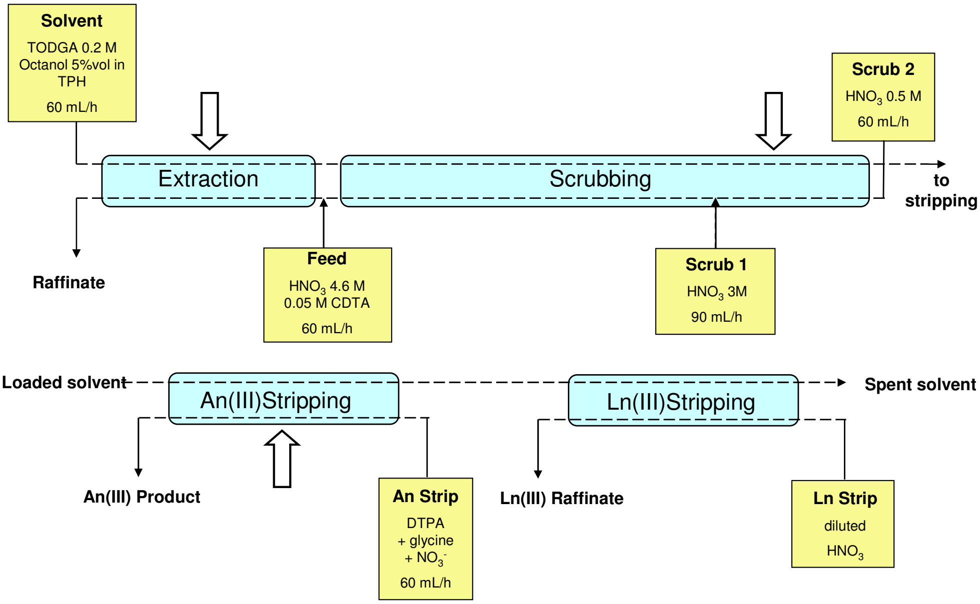


Figure 75. The proposed flow-sheet of the innovative-SANEX process for An(III) partitioning.

4.5.1. The extraction step

The organic phase (60 mL) consisted of 0.2 mol/L TODGA + 5vol.% 1-octanol dissolved in TPH. The aqueous phase contained 60 mL of the Feed solution (HAR-ITU, Table 3), 90 mL of Scrub 1 solution (3.0 mol/L HNO_3) and 60 mL of Scrub 2 solution (0.5 mol/L HNO_3) (Figure 76). The flow-rates were adjusted to 60 mL/h and 210 mL/h for the organic and the aqueous phase, respectively, using syringe pumps. The accuracy of the syringe pumps was tested before. As it is shown in Figure 75 the feed introduced into the extraction step has an acidity of 4.6 mol/L HNO_3 in which 0.05 mol/L CDTA are dissolved. Nevertheless, to simulate the conditions in the extraction step of an entire multi-centrifugal contactor test, the dilution of the feed by the Scrub 1 and Scrub 2 solutions has to be taken into account. Therefore, the dilution of the feed was done by adding the appropriate volumes of the two Scrub solutions which resulted in a final acidity of 2.8 mol/L HNO_3 and 3.5 times lower concentration of the metals compared to HAR-ITU.

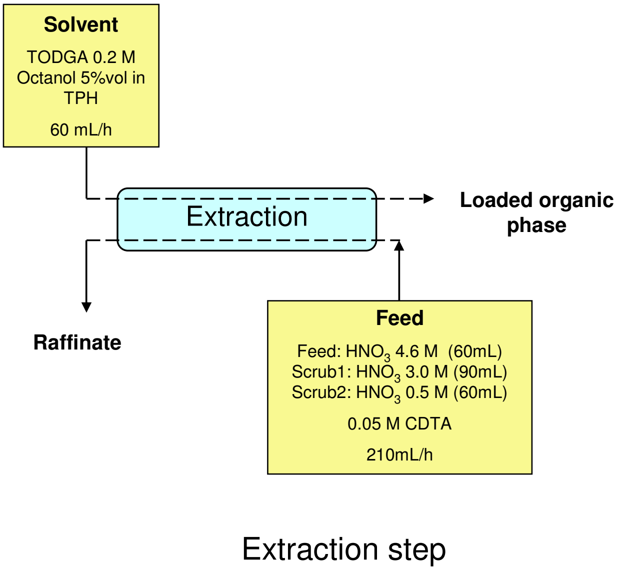


Figure 76. The composition and flow-rates of the organic and aqueous phases in the test simulating the extraction step.

In this step the feed was not spiked with radiotracers (^{241}Am, ^{152}Eu) since significant volume of the radiotracer solution would have to be used. Instead, the radiotracers were added to the scrubbing solution (described further) as its volume was 3.5 lower compared to the feed in the extraction step. Due to the expected high distribution ratios of An(III) and Ln(III) at [HNO_3]=2.8 mol/L the quantitative extraction of these metals was assumed. The test was running for 60 minutes and no hydrodynamic problems were encountered. The samples of both phases from the outlets of the contactor were collected in variable time intervals in order to determinate whether the steady state was reached. After 60 minutes the centrifugal contactor was stopped and the mixed residual phases from the contactor chamber were collected in a glass tube and mixed for another 15 minutes, followed by centrifugation and phase separation. The concentration of the elements in each phase was measured and compared with the metal concentrations of the last collected organic and aqueous sample during the test run (57th minute – Table 34) in order to determinate whether the equilibrium state was achieved. Using these metal concentrations the corresponding distribution ratios were calculated and are shown in Table 34.

Very high distribution ratios of the Ln(III) and Y in the extraction step indicate their quantitative extraction. Strontium was partly extracted with distribution ratios around 2.7. Molybdenum and ruthenium were partly co-extracted (D_{Mo}=0.42 and D_{Ru}=0.15). However, their distribution ratios were relatively small in comparison to Sr (D_{Sr}=2.81). Nevertheless, in the multi-stage centrifugal contactor test the two scrubbing sections (Scrub 1 and 2) would consist of several separate stages thus the scrubbing of Mo and Sr would be much more efficient. In systems based on TODGA as a main extractant, ruthenium is known for its partial extraction into the organic phase, where it stays through the whole process and ends up in the spent solvent.[47-48] Zirconium was quantitatively complexed by CDTA and stayed in the aqueous phase similarly to the major part of palladium of which only about 4% (D_{Pd}≈0.042) was co-extracted into the organic phase. The rest of the fission products were not substantially extracted, therefore their concentrations in the organic phase were below the detection limits of the ICP-MS equipment.

Table 34. The HAR elements distribution ratios in the extraction step of the single centrifugal contactor test.

Time	10 min	17 min	35 min	45 min	50 min	57 min	Eq
	Distribution ratios						
Y, Ce, Pr, Sm, Eu, Gd	> 200	> 200	> 200	> 200	> 200	> 200	> 200
La	> 200	177	114	> 200	199	> 200	> 200
Nd	> 200	> 200	> 200	> 200	> 200	101	174
Sr	2.77	2.62	2.42	2.73	2.81	2.81	2.51
Mo	0.44	0.39	0.38	0.42	0.42	0.42	0.41
Ru	0.14	0.13	0.15	0.16	0.15	0.15	0.28
Pd	0.037	0.042	0.044	0.043	0.043	0.042	0.029
Sb	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cd, Rb, Rh	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Te	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Ba, Cs, Zr	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

The distribution ratios of Sr, Mo, Ru and Pd were used to determine the achievement of the steady state in the extraction step (Figure 77). Very steady D-values indicated the achievement of the steady state. The dotted coloured lines in Figure 77 show the distribution ratios of the metals in equilibrium (values taken from last column in Table 34). The extraction of strontium and molybdenum reached equilibrium in the steady-state conditions of the single centrifugal contactor test (dotted lines in Figure 77). The extraction efficiency of ruthenium in the single centrifugal contactor for a given mixing speed and flow-rate was lower than 100% as the equilibrium value was not reached. This effect was also observed when the organic solvent based on TODGA was contacted with the HAR solution for 6 days (see 4.4 New masking agent, page 136). In that experiment the distribution ratio of Ru after 15 minutes phase contact time equalled 0.32 mol/L and increased up to 1.63 after extending the phase

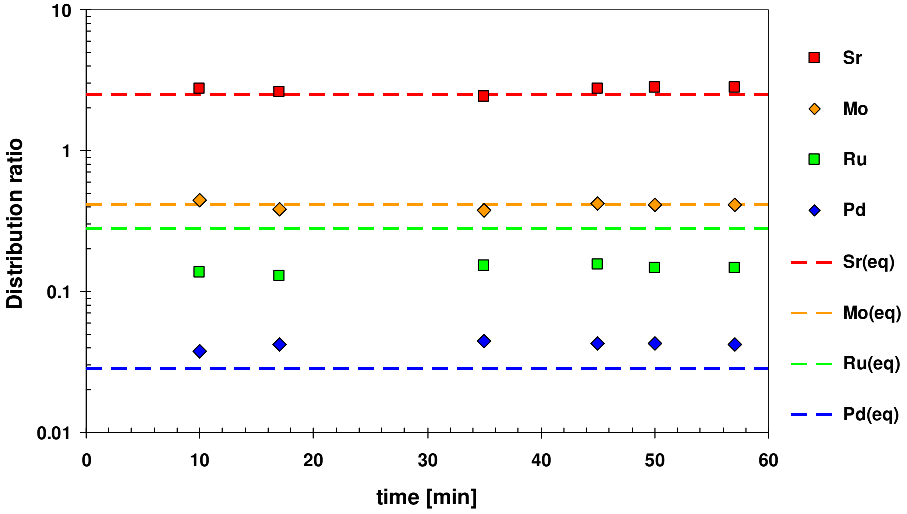


Figure 77. The distribution ratio profiles of some of the fission products in the extraction step.

contact time to 6 days. It indicated a very slow extraction of this metal independently on the masking agent used (CDTA).

The Palladium behaviour is difficult to explain as the results in the Figure 77 indicate its extraction efficiency to be higher than 100% (the equilibrium result).

4.5.2. The scrubbing step

In this single centrifugal contactor test only the second scrubbing step with 0.5 mol/L HNO_3 was tested. The first high acid scrubbing step (3 mol/L HNO_3) is introduced to remove co-extracted molybdenum from the organic phase. This step should not have a major influence on the An(III) and Ln(III) present in the loaded organic phase as in this step the aqueous phase contains acidity which is about 2.0 mol/L HNO_3 (Scrub 1 mixed with Scrub 2) and the corresponding metal D-values at this acidity are mostly over 200 (see Table 21, column 3 on page 114). Therefore, the introduction of this step in the full contactor battery test would result mainly in lower D_{Mo} compared to the obtained results.

The loaded organic solvent collected in the previous step (extraction) was used in the scrubbing step. Low concentrated nitric acid (0.5 mol/L HNO_3) spiked with radiotracers ^{152}Eu and ^{241}Am was used as the aqueous phase. The flow-rates were adjusted to 60 mL/h for both phases (Figure 78). Similarly as in the extraction test, samples of the aqueous and organic phases were collected in variable time intervals. The residual mixed phases from the contactor were collected after the run and treated in the same way as in the extraction step to obtain the metal distribution ratios in equilibrium.

The distribution ratios of the metals in the scrubbing step are shown in Table 35. More than 80% of the co-extracted strontium (D_{Sr}=0.24) was scrubbed from the organic solvent by the Scrub 2 solution. Ruthenium and palladium stayed mostly in the organic phase (D_{Ru}=5 and D_{Pd}=30) together with the trivalent lanthanides, yttrium and americium. The precise determination of Sm, Eu (stable isotope ^{153}Eu) and Gd concentrations was not possible due to

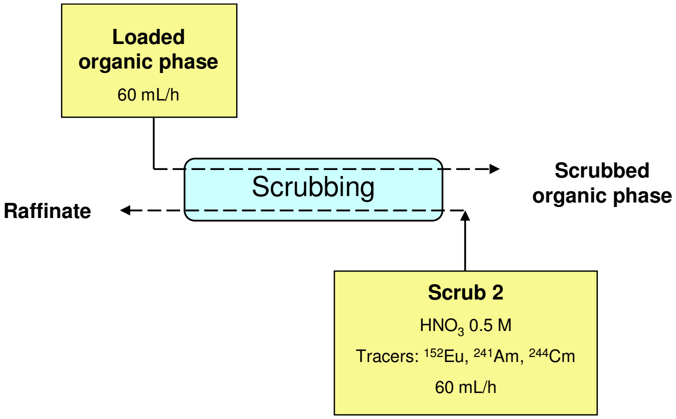


Figure 78. The composition and flow-rates of the organic and aqueous phase in the test simulating the second scrubbing step.

Table 35. The HAR elements distribution ratios in the scrubbing step of the single centrifugal contactor test.

Time	10 min	15 min	20 min	25 min	30 min	40 min	50 min	Eq
	Distribution ratios							
^{241}Am	20.0	13.2	17.9	19.9	24.2	27.3	24.3	46.3
^{152}Eu	40.6	24.5	32.3	30.3	41.1	49.0	42.0	283
Y	> 200	> 200	> 200	> 200	> 200	> 200	> 200	> 200
La	8.72	8.40	8.05	7.62	7.96	7.98	7.88	3.92
Ce	16.3	15.8	15.6	14.6	15.2	14.9	14.9	7.35
Pr	29.4	29.6	27.9	25.6	28.3	27.5	27.2	13.2
Nd	68.5	66.0	72.5	60.0	67.5	66.3	59.0	27.4
Sm*	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
Eu*	> 30	> 30	> 30	> 30	> 30	> 30	> 30	> 30
Gd*	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
Pd	2.27	3.43	> 30	> 30	> 30	> 30	> 30	> 30
Ru	≈ 5	≈ 5	≈ 5	≈ 5	≈ 5	≈ 5	≈ 5	≈ 5
Mo	0.83	0.75	0.83	0.64	0.69	0.66	0.68	0.41
Sr	0.32	0.26	0.29	0.24	0.24	0.24	0.24	0.04
Ba, Cd, Cs, Rb, Rh, Sb, Te, Zr	DL	DL	DL	DL	DL	DL	DL	DL

DL – below detection limit
* description in the text

their low concentration in the aqueous phase (below ICP-MS detection limit) thus the D-values of these metals shown in the Table 35 are taken as the lowest possible.

The concentrations of the rest of the fission products were below detection limit in both phases.

The comparison of the distribution ratios of some of the lanthanides during the test run with the equilibrium values (Figure 79) indicate that the equilibrium for these metals was not reached. The equilibrium values (dotted lines) are lower that those of the collected samples in time intervals (points) since the lower distribution ratios mean more efficient stripping.

In this case this is beneficial as the higher D-values of the Ln(III) in this section compared to the values in equilibrium assure that their major part stays in the organic solvent. If the Ln(III) were also scrubbed in this step, it would be an advantage , however it could also entail the partial loss of An(III).

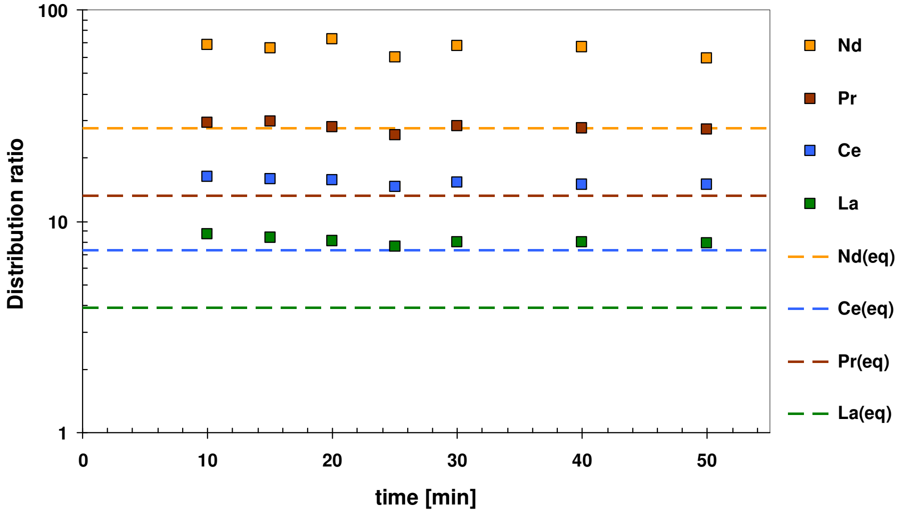


Figure 79. The distribution ratio profiles of light lanthanides in the scrubbing step.

The behaviour of the radiotracers was different compared to the stable trivalent lanthanides. The distribution ratios of ^{152}Eu and ^{241}Am in equilibrium were much higher than the values for time intervals (Figure 80). However, the radiotracers were added to the scrubbing solution, therefore they were present in the aqueous phase while the stable lanthanides were in the loaded organic phase. This means the stable metals were stripped from the organic phase while radiotracers were extracted to the organic phase.

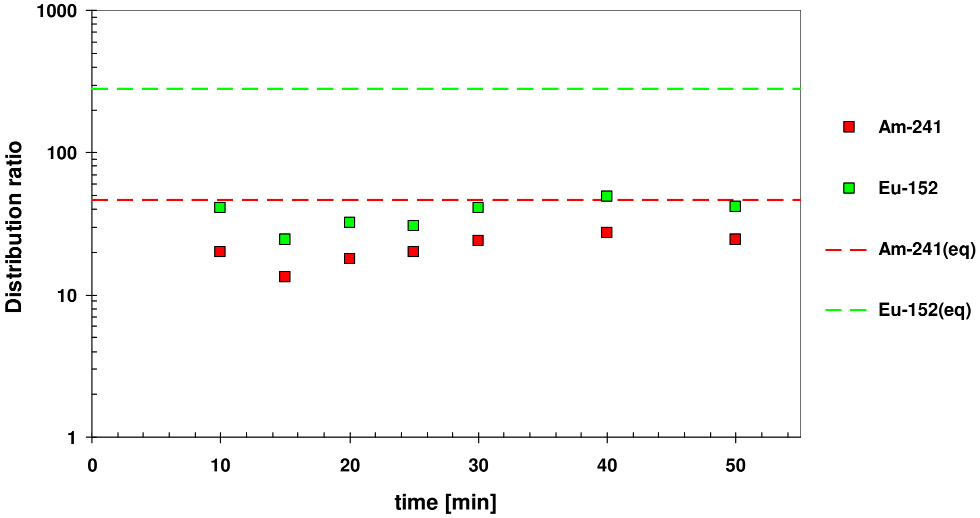


Figure 80. The distribution ratio profiles of ^{241}Am and ^{152}Eu in the scrubbing step.

4.5.3. The selective Actinide stripping step

This is the most crucial and complicated step of the whole innovative SANEX process. The intention is to selectively strip only the trivalent actinides while keeping the trivalent lanthanides in the organic phase.

The organic phase collected in the previous step was used in the following actinide stripping test (Figure 81). Three stripping solutions with different initial pH were tested. Based on the results from the batch tests (chapter 4.3 Innovative SANEX, page 83) it was decided to use the actinide stripping solutions of pH = 1.7, 1.9 and 2.0. These solutions were used one after another in order of increasing initial pH of the solution. The samples of the organic and aqueous phase were collected from the outlets after 5 and 11 minutes for each stripping solution. Once the last stripping solution (pH = 2.0) was tested, the contactor was stopped and the residual mixed phases from the contactor chamber were treated in the same way as in the extraction and scrubbing step described before.

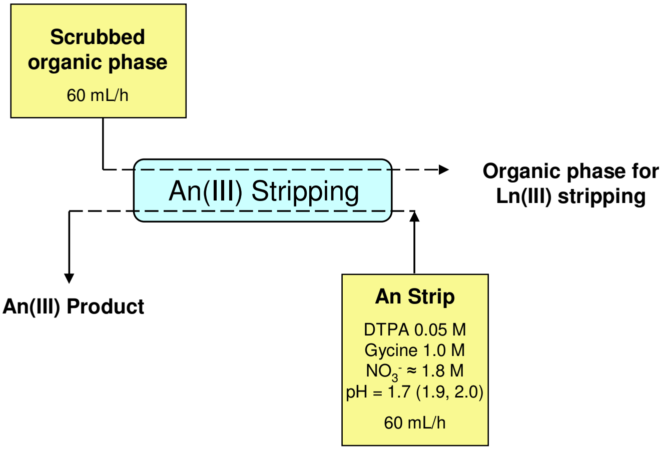


Figure 81. The composition and flow-rates of the organic and aqueous phases in the actinide stripping test.

The distribution ratios of the metals calculated from their concentrations or radioactivities in the collected organic and aqueous samples are shown in Table 36.

The trivalent lanthanides and yttrium stayed mostly in the organic phase during this test, regardless of the initial pH of the stripping solution used. Americium was effectively stripped into the aqueous phase only by the last used solution of pH_{ini}=2.0 (D_{Am}=0.42). The first stripping solution (pH_{ini}= 1.7) was not able to efficiently strip Am from the organic phase (D_{Am}=4.78). After 11 minutes from introducing the solution of pH_{ini}=1.9 the distribution ratio of Am decreased below 1 (D_{Am}=0.79), nevertheless this value was still too high to achieve good recovery of this element. Almost all ruthenium and palladium which were not removed from the organic phase in the second scrubbing step stayed in the organic phase together with the lanthanides during An-stripping. Unfortunately, molybdenum (D_{Mo}<0.5) and strontium (D_{Sr}<0.2) followed Am into the An-product. This will probably be diminished in a multi-stage test by introducing a Scrub 1 section and also by increasing the number of stages of both scrubbing sections. The concentrations of the rest of the fission products were below detection limit of the ICP-MS.

Table 36. The HAR elements distribution ratios in the actinide stripping step of the single centrifugal contactor test.

pH$_{ini}$	1.7		1.9		2.0		
Time	5 min	11 min	5 min	11 min	5 min	11 min	Eq
	Distribution ratios						
^{241}Am	15.3	4.78	1.01	0.79	0.48	0.42	0.48
^{152}Eu	163	58.1	15.7	11.4	8.29	6.36	6.10
Y	> 200	> 200	> 200	> 200	> 200	> 200	> 200
La	13.9	14.5	8.82	7.77	6.92	6.03	5.73
Ce	24.2	21.1	9.33	7.64	5.62	4.53	4.54
Pr	37.1	23.8	7.36	5.64	3.61	2.86	2.90
Nd	64.0	32.0	7.53	5.66	3.64	2.73	2.73
Sm	> 100	93.3	12.0	8.33	6.04	4.15	3.99
Eu	> 100	> 100	18.1	12.3	8.72	6.04	5.75
Gd	> 100	67.9	16.4	14.4	9.04	6.87	5.95
Ru	> 100	> 100	> 100	> 100	> 100	> 100	> 100
Pd	> 30	> 30	> 30	> 30	> 30	> 30	> 30
Mo	0.45	0.34	0.41	0.36	0.35	0.45	0.23
Sr	0.10	0.16	< 0.001	< 0.001	0.13	0.14	0.14
Ba, Cd, Cs, Rb, Rh, Sb, Te, Zr	DL	DL	DL	DL	DL	DL	DL

DL – below detection limit

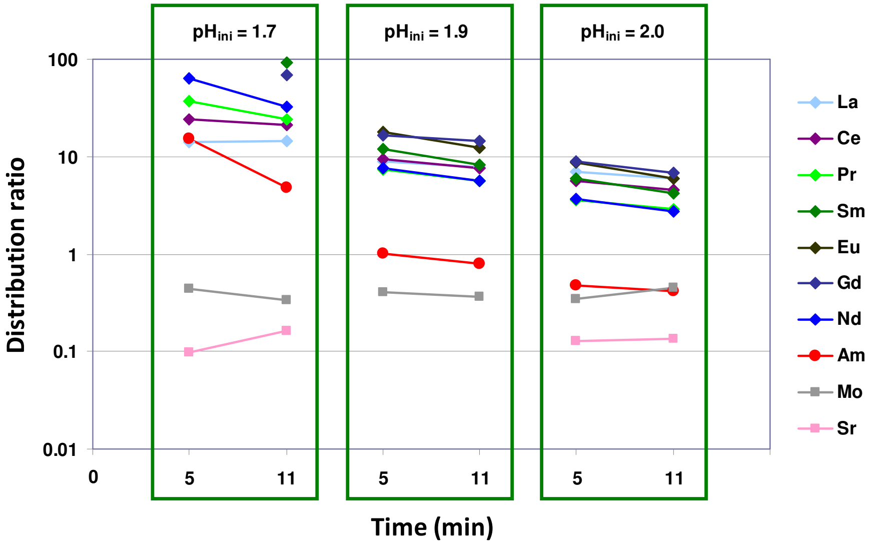


Figure 82. The distribution ratio profiles of the HAR elements in the actinide stripping step at different initial pH.

4.5.4. The Lanthanide stripping step

The stripping of Lanthanides was not tested, as this step is considered to be the least problematic in the whole innovative-SANEX process. The efficient stripping could be achieved using 0.01 mol/L HNO_3 or a water-soluble ligands for Ln complexation (see chapter *Water-soluble ligands*).

4.5.5. The steady states

In the innovative-SANEX process based on TODGA/1-octanol the co-extraction of An and Ln in the first step is characterised by relatively fast kinetics. The selective stripping of actinides can also be classified as a fast kinetics system. The single centrifugal contactor tests described above must have run long enough to ensure that the steady state was reached. Reaching the steady state does not necessarily mean that the chemical equilibrium of the system was obtained. The equilibrium state means that the efficiency of the centrifugal contactor is 100%. However, very often the efficiency is much lower especially when the flow-rates of the phases are relatively high. Therefore, additional samples from the contactor chamber were collected after the test (the residual phases left in the contactor after its stopping) and treated as in a batch test. The obtained results were then compared with the results of the samples collected from the corresponding single centrifugal run (Table 37).

Table 37. Comparison of the radionuclide distribution ratios in steady state and equilibrium of the individual stages.

	Steady-state			Equilibrium		
	Ex (57min)	Sc (50min)	St 2.0 (11min)	Ex (eq)	Sc (eq)	St 2.0 (eq)
D_{Am}	-	24.3	0.42	-	46.3	0.48
D_{Eu}	> 200	42.0	6.36	> 200	283	6.10
$[HNO_3]_{aq,eq}$	2.71	0.708	pH=1.84	2.66	0.715	pH=1.88

Ex – extraction, Sc – scrubbing, St 2.0 – stripping at pH=2

The results in Table 37 indicate that in all tested steps the equilibrium was nearly reached except for radiotracers in the scrubbing step. The results of ^{241}Am in the extraction step are not included as the radiotracers were added in the following scrubbing step. The distribution ratio of Eu in the extraction step is taken from the ICP-MS results (^{153}Eu – stable isotope).

Batch tests were also carried out using the same solutions as in the single-centrifugal contactor runs. The phases were shaken for 15 minutes and the organic phase from one step was used in the subsequent step. The results of this batch tests are shown in Table 38.

Table 38. The distribution ratios of the radiotracers obtained in batch tests using the solutions from the contactor run.

	Batch test				
	Ex	Sc	St 1.7	St 1.9	St 2.0
D_{Am}	668	71.3	3.07	0.45	0.20
D_{Eu}	434	156	51.4	8.32	3.52
pH_{eq}	-	-	1.53	1.76	1.84

The distribution ratios of Am in the stripping step of the single centrifuge test (Table 37 column 4) are higher (D_{Am}=0.48) than those found in the batch test (D_{Am}=0.2, Table 38). This can be explained by the higher concentration of nitric acid (thus nitrate ions) carried over to the stripping step by the organic phase in the contactor run. It would mean a poor efficiency of a single contactor in the scrubbing step (0.5 mol/L HNO_3) thus poor acid scrubbing form the loaded solvent.

4.5.6. The influence of the aqueous/organic phase volumetric ratio

Additional batch tests were carried out in order to estimate the influence of different aqueous/organic phase volumetric ratios on the metal extraction. In the batch tests (see chapter 4.3 Innovative SANEX, page 83) the volumes of both contacted phases were identical

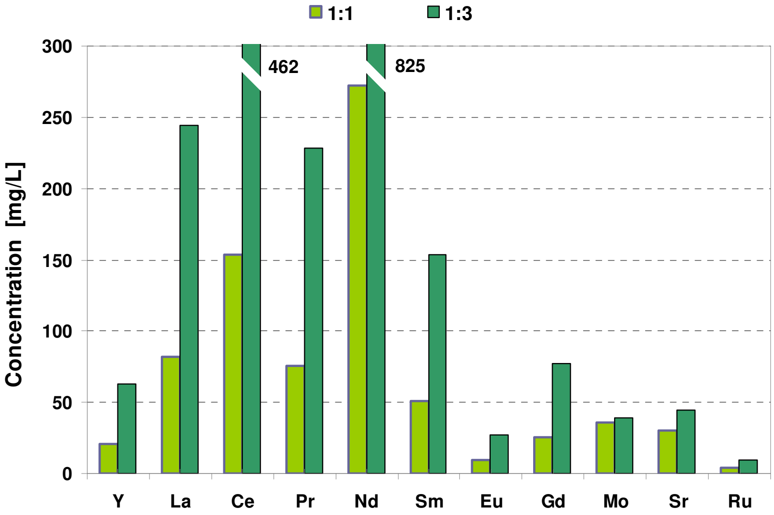
(500 µL each), resulting in V_{Aq}/V_{Org} ratio of 1. In the extraction step of the single centrifugal contactor test the flow-rate of the organic phase was adjusted to 60 mL/h while the aqueous phase flowrate was adjusted to 210 mL/h. Consequently, the phase volumetric ratio was 3.5 (3.5 times more of the aqueous phase than the organic phase inside the centrifugal contactor's mixing chamber).

The extraction step was tested by contacting the same feed as used in the single centrifugal contactor test (ITU feed mixed with 3 and 0.5 mol/L HNO_3) with the same organic phase as used in the single stage test. In one experiment the aqueous/organic volumetric ratio equalled 1, while in a second experiment the volume of the aqueous phase was 3 times higher than the organic phase volume. Figure 83 shows the concentrations of different elements in the organic (a) and aqueous phases (b) obtained from these batch tests.

The concentration of each of the less extractable fission products in the aqueous phase was not affected by the volumetric ratio of the phases (Figure 83b).

All the tested lanthanides and yttrium had relatively high distribution ratios (nearly quantitative extraction), therefore the concentration of these elements in the organic phase of the sample with a volumetric ratio of 1:3 was 3 times higher than in the organic phase of the sample with a volumetric ratio of 1:1 (Table 39). Molybdenum, strontium and ruthenium were only partly extracted, thus the concentration ratios (aq/org) differ from 3, but are higher than 1 (Table 39, column 4). Therefore, a higher flow-rate of the aqueous phase compared to the organic phase in a continuous process, thus higher volume of the aqueous phase, will increase the loading of the solvent with these metals i.e. Sr, Mo and Ru.

a)



b)

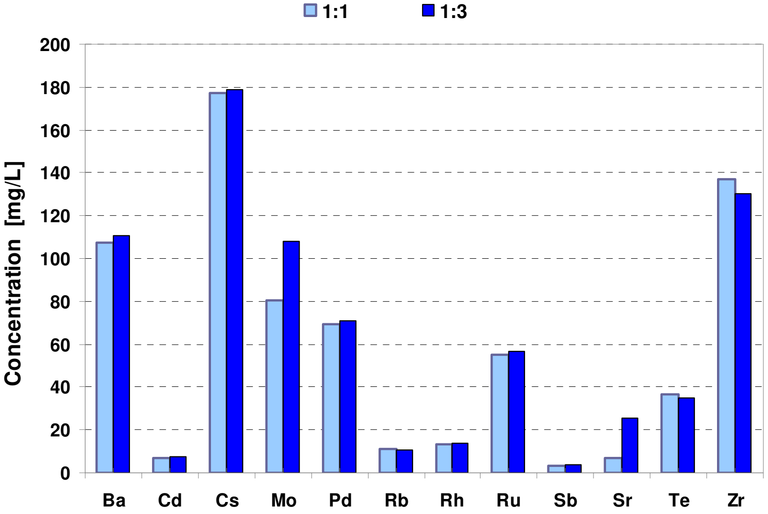


Figure 83. The concentration of HAR metals in the a) organic and b) aqueous phase of the extraction step from the batch test after equilibration.

Table 39. Comparison of the HAR metal distribution ratios of the batch samples with different aqueous/organic phase volumetric ratio.

Element	$[M]_{eq,org}$ (1:1)	$[M]_{eq,org}$ (1:3)	$\frac{[M]_{eq,org}\ (1:3)}{[M]_{eq,org}\ (1:1)}$
Y	20.8	63.0	3.0
La	81.7	244	3.0
Ce	153	462	3.0
Pr	75.7	229	3.0
Nd	272	825	3.0
Sm	50.9	154	3.0
Eu	9.87	27.0	2.7
Gd	25.1	77.1	3.1
Mo	35.8	38.6	1.1
Sr	30.1	44.7	1.5
Ru	3.95	9.23	2.3
	[mg/L]	[mg/L]	

$[M]_{eq,org}$ – metal concentration in the organic phase in equilibrium

If we compare the concentration of these elements in the organic phase of the single centrifugal contactor test (sample collected in minute 57 of the extraction step) and in the batch test (volumetric ratio of both phases equalled 1:3) they seem to be very similar. This suggests that the extraction equilibrium in the single centrifugal contactor test was achieved (Table 40).

Table 40. Comparison of the metal concentrations in the organic phase of the single centrifuge contactor test and the batch test in the extraction step.

Element	$[M]_{57min,org}$	$[M]_{eq,org}$	$[M]_{57min,org}$ / $[M]_{eq,org}$
Y	69.8	63.0	1.1
La	249	244	1.0
Ce	471	462	1.0
Pr	233	229	1.0
Nd	848	825	1.0
Sm	160	154	1.0
Eu	28.4	27.0	1.1
Gd	82.0	77.1	1.1
Mo	46.1	38.6	1.2
Sr	58.4	44.7	1.3
Ru	8.83	9.23	1.0
	[mg/L]	[mg/L]	

4.5.7. Nitric acid profiles

The nitric acid profiles of the extraction and scrubbing steps of the single centrifugal contactor tests are shown in Figure 84a and Figure 84b. These profiles indicate that the steady states for nitric acid extraction were achieved after 10 and 15 minutes for the extraction (a) and scrubbing (b) steps, respectively.

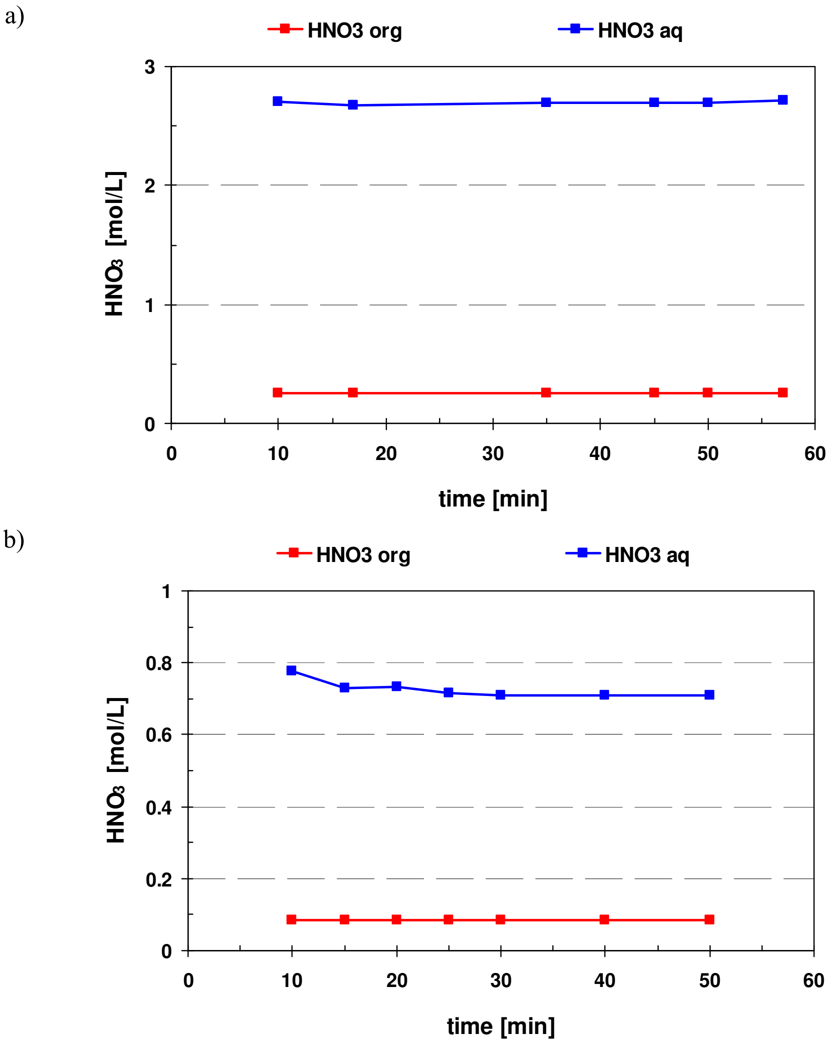


Figure 84. Nitric acid profiles of the (a) extraction and (b) scrubbing steps in the single centrifugal contactor tests.

The initial nitric acid concentration of the feed solution was 2.78 mol/L. However, summation of the HNO_3 concentration in the organic and aqueous phase in the extraction stage (e.g. the sample collected at 57 min of the test) resulted in 2.976 mol/L HNO_3. The higher concentration of the acid in the extraction step can be explained by the different flow rates of the contacted phases. The nitric acid concentration in the aqueous phase at 57 min was 2.71 mol/L. The organic phase should then contain 0.07 mol/L HNO_3 ($[HNO_3]_{feed}$ – $[HNO_3]_{57min,aq}$), but instead of that the measured value was 0.256 mol/L HNO_3, which is approximately 3.6 times more than the expected 0.07 mol/L. This is in agreement with the ratio of the phases flow-rate in the extraction step. Concluding, the higher flow-rate of the aqueous phase regarding the organic phase, the more nitric acid is extracted.

It is assumed that in the second scrubbing step the nitric acid equilibrium was not reached. The organic phase coming from the extraction step carried over 0.256 mol/L nitric acid. The HNO_3 concentration in the Scrub 2 solution was 0.513 mol/L. Therefore, the concentration of HNO_3 in the organic phase after the second scrubbing step should have equalled 0.0334 mol/L (calculated from Figure 54 – nitric acid extraction by TODGA/octanol). However the measured value was 0.083 mol/L HNO_3. In this step the flow-rates (thus also volumes of the phases) were identical, therefore the explanation can be the slow kinetics of the nitric acid scrubbing. In a continuous process this can be improved by increasing the number of stages in the scrubbing section resulting in better acid scrubbing.

4.6. Screening tests of new lipophilic and hydrophilic ligands

Extensive screening tests of new organic compounds provided by University of Twente were carried out in parallel to the work of the experimental studies described before in this thesis. The aim of these tests was to find a correlation between the structural modifications of TODGA and its extraction properties. Additionally, a number of organic ligands containing nitrogen as a central atom and malonamide and diglycolamide derivatives were screened. They extracted An(III) and Ln(III) using solvating mechanism, but also showed significant discrimination between these two groups of elements at low nitric acid concentration. Those properties would allow substituting TODGA in the innovative SANEX process with the new ligand enhancing the Ln(III)/An(III) separation.

After selective stripping of An(III) in the i-SANEX process, the organic solvent still contains Ln(III) elements which have to be removed before solvent clean-up and re-direction back to the process. The Ln(III) stripping from TODGA-based solvents can be achieved using diluted nitric acid. However, this is characterised by slow-kinetics, thus more phase contact stages have to be applied e.g. increased number of centrifugal contactors to achieve satisfactory stripping.[47] An efficient hydrophilic ligand applied in the Ln(III) stripping solution would speed up the stripping kinetics reducing the necessary number of required stages. Therefore, University of Twente also synthesised and delivered new hydrophilic ligands on which the screening tests were performed.

4.6.1. Lipophilic compounds prepared at Twente

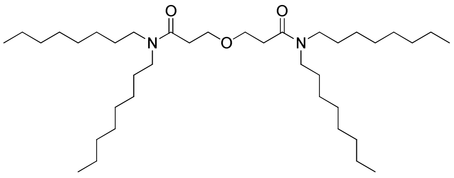
At the beginning of the 1990s, Stephan et al.[120] reported on the extraction of a number of di- and trivalent metals by diglycolamides (DGA). In the late 1990s Sasaki and Choppin[42-43] used these ligands for the extraction of actinides from acidic waste solutions. Since then attention has been drawn to DGAs resulting in extensive studies on their extraction properties with An, Ln(III) and some other fission products.[101, 121-126] It was found that the best extraction properties, solubility in aliphatic solvents and radiochemical/hydrochemical stability were represented by TODGA. The effect of structural modifications of TODGA on the extraction behaviour had not yet been studied except the replacement of the central oxygen atom by sulphur.[127] Therefore, different types of TODGA derivatives were proposed to study their extraction properties for americium(III) and europium(III), simulating the extraction of actinides(III) and lanthanides(III) from nitric acid solutions.

4.6.1.1. Extraction of Am(III) and Eu(III) with TODGA derivative ligands containing oxygen as a central atom

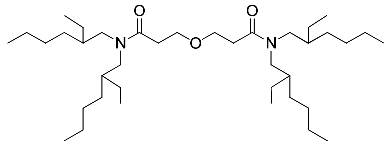
Eleven different TODGA derivative compounds with oxygen as a central atom were synthesised and delivered by the University of Twente for screening tests (Figure 85). Within these ligands only five (TWE-14, 15, 21, 22, A4) showed promising results on Am(III) and Eu(III) extraction.

The other six compounds did not extract the radiotracers (TWE-1, TWE-2, TWE-16) or were not soluble in THP nor in 1-octanol (TWE-3 – 5).

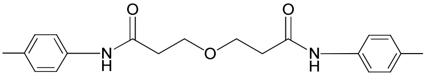
In order to study the influence of the chain length between the central oxygen atom and the moieties in the TODGA molecule responsible for the metal extraction two derivatives were synthesised, namely TWE-1 and TWE-2. The screening tests of these two compounds showed no extraction of Am(III) nor Eu(III) which is caused by the increased length (compared to TODGA) of the aliphatic chain between the two amide groups making the distance between the coordinating moieties too large.[128]



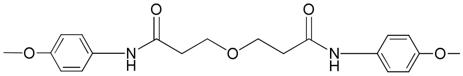
3,3'-oxybis(N,N-dioctylpropanamide)
(TWE-1)



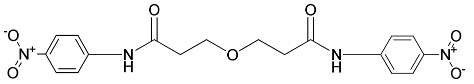
3,3'-oxybis(N,Nbis(2-ethylhexyl)-propanamide)
(TWE-2)



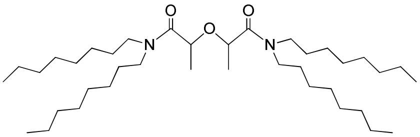
3,3'-oxybis(N-p-tolylpropanamide)
(TWE-3)



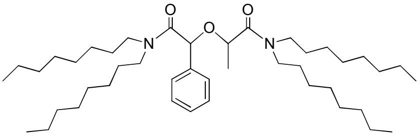
3,3'-oxybis(N-(4-methoxyphenyl)propanamide)
(TWE-4)



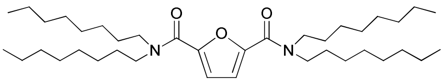
3,3'-oxybis(N-(4-nitrophenyl)-propanamide)
(TWE-5)



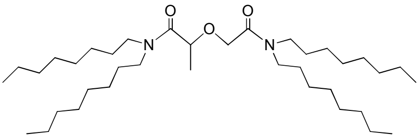
2,2'-oxybis(N,N-dioctylpropanamide)
(TWE-14)



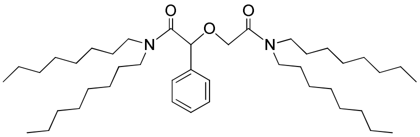
2-(2-(dioctylamino)-2-oxo-1-phenylethoxy)-N,N-dioctylpropanamide)
(TWE-15)



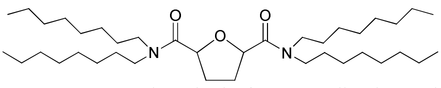
N,N,N',N'-tetraoctylfuran-2,5-dicarboxamide
(TWE-16)



2-(2-(dioctylamino)-2-oxoethoxy)-N,N-dioctylpropanamide
(TWE-21)



2-(2-(dioctylamino)-2-oxoethoxy)-N,N-dioctyl-2-phenylacetamide
(TWE-22)



N,N,N',N'-tetraoctyltetrahydrofuran-2,5-dicarboxamide
(TWE-A4)

Figure 85. Chemical structures of screened TODGA derivatives with oxygen as a central atom

The basicity of the central oxygen atom has a significant influence on the metal extraction from solutions with different nitric acid concentrations.[96] Four different ligands derived from

TODGA were synthesised by introducing additional groups to the carbon atoms next to the central oxygen atom. TWE-21 and TWE-14 had one or two additional methyl groups, respectively, and their extraction results are shown in Figure 86. The extraction of both radionuclides increased with increasing the nitric acid concentration. Taking into account the trivalent metal extraction profile and the neutral character of the DGA, it is assumed that the new ligands act as solvating extractant i.e. extracting metals as neutral species (Eq 31).

$$M^{3+} + a\overline{L} + 3NO_3^- \longleftrightarrow \overline{M(NO_3)_3(L)_a} \qquad \text{Eq 31}$$

The order of extractability is TODGA > TWE-21 > TWE-14, and only at high nitric acid concentration of 3 and 4 mol/L, the distribution ratios for TWE-21 were as high as for TODGA. The difference in metal extraction between TODGA and the new ligands is attributed to the addition of the methyl group(s) which decreases the molecule flexibility. The

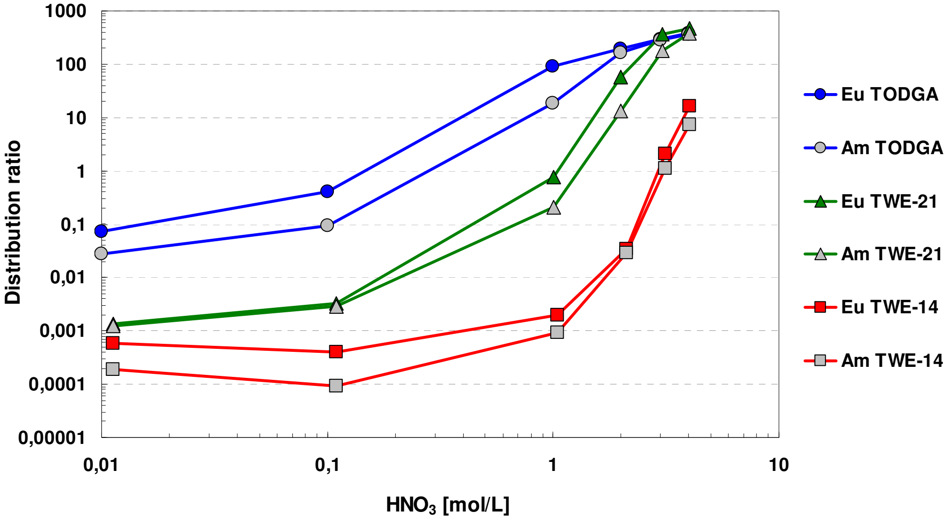


Figure 86. The extraction of ^{241}Am and ^{152}Eu by TODGA, TWE-14 and TWE-21 as a function of nitric acid concentration.

Organic phase: 0.1mol/L of ligand in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu,
mixing time: 15min; T=22°C±1°.

introduction of one or two methyl groups made the central oxygen atom more basic, however due to the sterical constraints it did not result in better extraction properties compared to TODGA.[128] The ligands with additional phenyl (TWE-22) or methyl and phenyl group (TWE-15) did not extract the radionuclides as efficiently as TODGA (Figure 87). It is clear that the influence of the phenyl group is dominant and the addition of a methyl group in TWE-15 did not influence the metal extractability. It can be assumed that both sterically and electronically it has a negative influence on the extraction behaviour.[128]

In order to study the steric interactions, two TODGA derivatives containing a rigidified tetrahydrofuran (TWE-A4) or furan in the centre of the molecule (TWE-16) were synthesized. The introduction of a tetrahydrofuran ring decreased the Am(III) and Eu(III) extraction compared to TODGA (Figure 88). TWE-16 with a furan ring did not extract the radiotracers

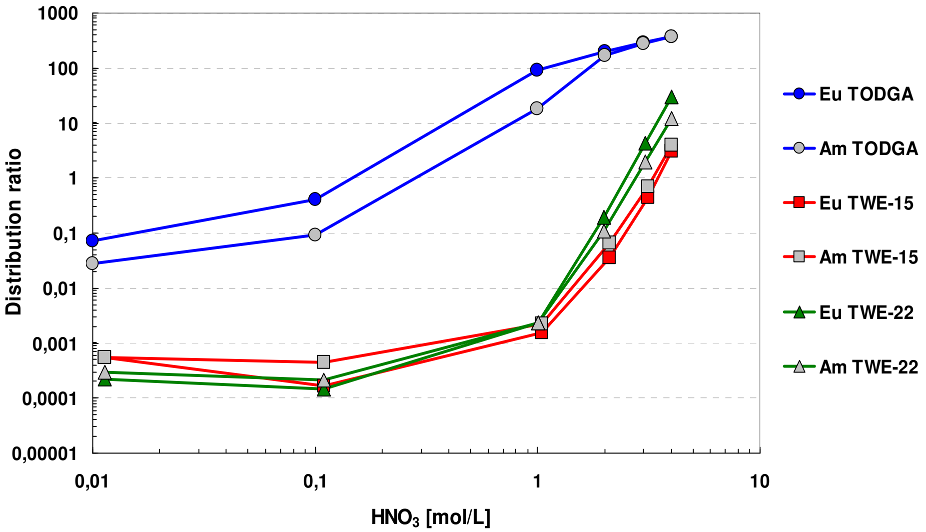


Figure 87. The extraction of ^{241}Am and ^{152}Eu by TODGA, TWE-15 and TWE-22 as a function of nitric acid concentration.

Organic phase: 0.1mol/L of ligand in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15min; T=22°C±1°.

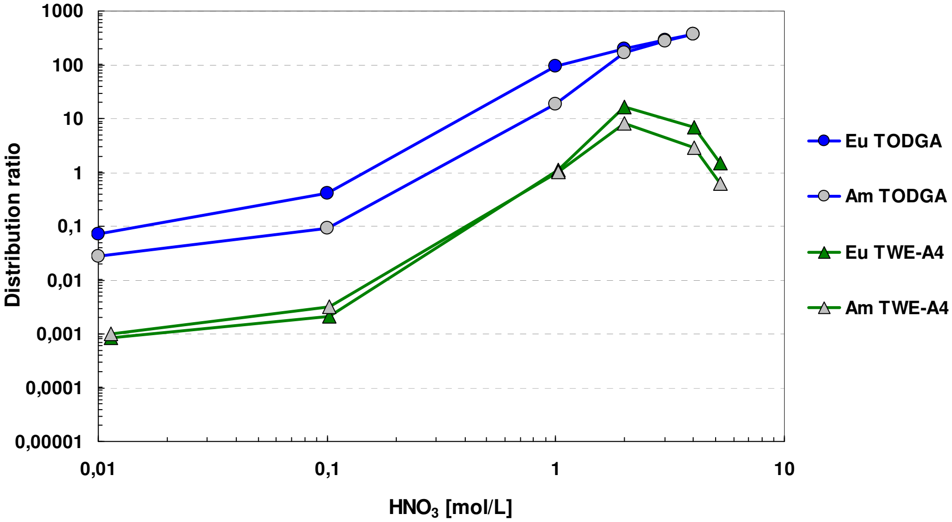


Figure 88. The extraction of ^{241}Am and ^{152}Eu by TODGA and TWE-A4 as a function of nitric acid concentration.

Organic phase:	0.1mol/L of TODGA or 0.08mol/L of TWE-A4 in TPH
Aqueous phase:	variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15min for TODGA and 60min for ligand TWE-A4; T=22°C±1°.

in the whole nitric acid concentration range tested which can be explained by lower basicity of the central oxygen atom compared to TODGA.[129]

Concerning the studies on different DGA analogues, TWE-21 showed the most promising results with respect to the process application. The extraction of Am and Eu by TWE-21 from 3 and 4 mol/L HNO_3 was as good as for TODGA (Figure 86). In addition the metal extraction for TWE-21 decreased much faster than for TODGA with decreasing the acidity of the aqueous phase. At 0.1 mol/L of nitric acid the $D_{Am,Eu}$ were approximately two orders of magnitude lower compared to TODGA. This is a benefit concerning the partitioning of high-level radioactive waste since the back-extraction step can be performed at moderately acidic conditions. In a recently developed process for An(III) partitioning from high active raffinate using TODGA as an extractant, the An(III)/Ln(III) stripping solution consisted of 0.01 mol/L and rather a large number of stages was used.[47-48]

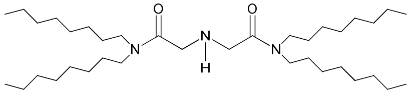
Some further studies on TWE-21 were carried out and are shown at the end of this chapter.

4.6.1.2. Extraction of Am(III) and Eu(III) with TODGA derivative ligands containing nitrogen as a central atom

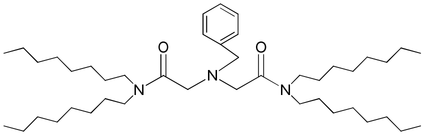
Nine new lipophilic compounds containing one additional central nitrogen atom were synthesised (Figure 89). Possessing three donor atoms they were expected to show good extractability for trivalent An and Ln. Moreover, the soft donor central nitrogen atom suggested that possibly the discrimination between trivalent actinides and lanthanides could be achieved.

Most of the ligands did not show any metal extraction from 0.01 – 4 mol/L nitric acid, resulting in $D_{Am,Eu} < 0.01$ (TWE-6 – 10, AL-1 and AL-2, Figure 89). Only two compounds, TWE-11 and TWE-17 showed moderate extraction of Am(III) and Eu(III) at low nitric acid concentration (Figure 90), although with reasonably high Am/Eu separation factor at 0.01 mol/L HNO_3, namely 8 (TWE-11) and 12 (TWE-17).

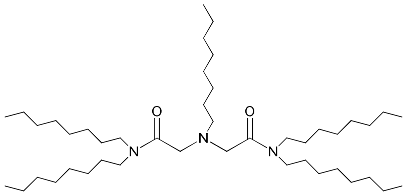
These two ligands act as tridentate chelates, but the complexed metal is coordinated by the two carbonyl oxygens and, instead of the central nitrogen atom, the additional oxygen of the third amide moiety. The metal extraction profiles in Figure 90 suggest that the ligands become de-protonated at the central N atom because of increasing D-values with lowering the acidity. Therefore, the ion-pair extraction mechanism can be proposed, however this hypothesis requires more detailed studies by slope analysis.



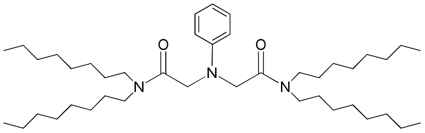
2,2'-azanediylbis(N,N-dioctylacetamide)
(TWE-6)



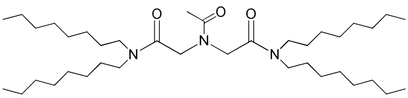
2,2'-(benzylazanediyl)bis(N,N-dioctylacetamide)
(TWE-7)



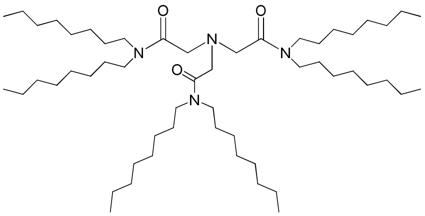
2,2'-(octylazanediyl)bis(N,N-dioctylacetamide)
(TWE-8)



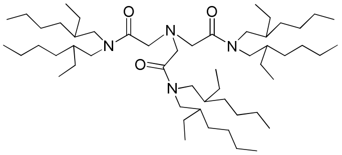
2,2'-(phenylazanediyl)bis(N,N-dioctylacetamide)
(TWE-9)



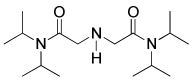
2-(N-(2-(dioctylamino)-2-oxoethyl)acetamido)-N,N-dioctylacetamide
(TWE-10)



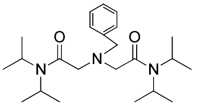
2,2’,2”-nitrilotris(N,N-dioctylacetamide)
(TWE-11)



2,2’,2”-nitrilotris(N,N-bis(2-ethylhexyl)acetamide)
(TWE-17)



2,2'-azanediylbis(N,N-diisopropylacetamide)
(AL-1)



2,2'-(benzylazanediyl)bis(N,N-diisopropylacetamide)
(AL-2)

Figure 89. Chemical structures of screened TODGA derivatives with nitrogen as a central atom

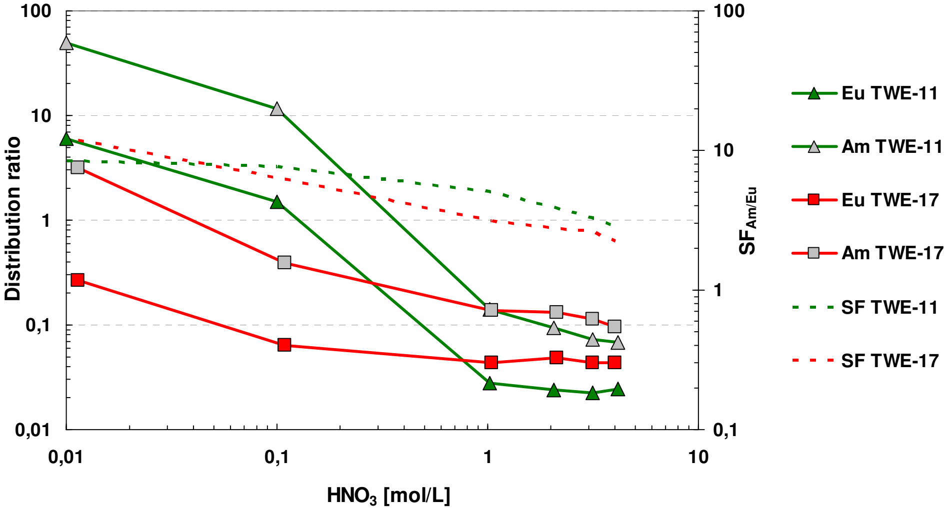


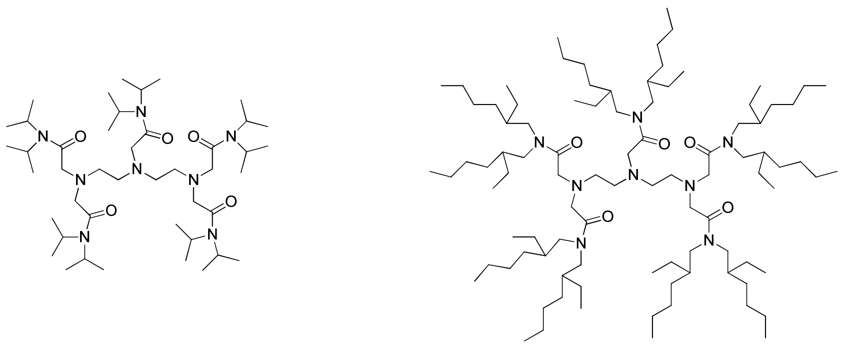
Figure 90. The extraction of ^{241}Am and ^{152}Eu by TWE-11 and TWE-17 a function of nitric acid concentration.

Organic phase: 0.1mol/L of the ligand in TPH
Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu,
mixing time: 15min; T=22°C±1°.

4.6.1.3. Extraction of Am(III) and Eu(III) with diethylenetriaminepentaacetic acid (DTPA) derivatives

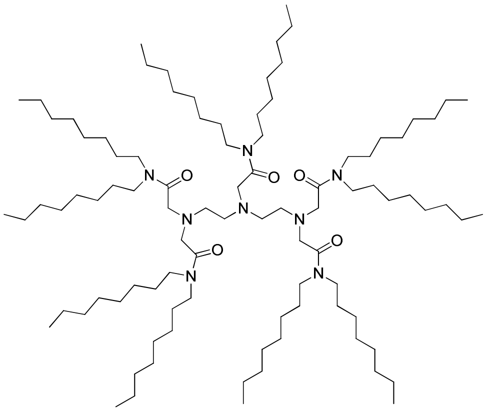
The well-known polyaminocarboxylic acid DTPA forms more stable complexes with trivalent actinides compared to trivalent lanthanides. This hydrophilic complexant was successfully applied in several processes[50, 64, 130] for An(III) recovery allowing the efficient separation from Ln(III). By substitution of its acetyl groups for aliphatic chains a lipophilic ligand could be obtained hopefully possessing the same An(III)/Ln(III) discrimination as the hydrophilic analogue (DTPA). Three different lipophilic DTPA derivatives, TWE-A1 – A3 (Figure 91), were screened for the extraction of An(III) and Ln(III), here represented by ^{241}Am and ^{152}Eu.

The TWE-A1 was poorly soluble in an aliphatic diluent TPH thus an addition of 1-octanol was necessary. The final concentration of the ligand was 0.044 mol/L, though the distribution ratio of the radiotracers did not exceed 0.1. The second DTPA derivative tested, TWE-A2 containing 2-ethylhexyl chains as a substitution for acetyl groups, showed better solubility than TWE-A1, however no metal extraction was observed ($D_{Am,Eu}$ were much below 0.01). The last tested TWE-A3 extracted Eu and Am equally well from low concentrated nitric acid with the highest D_M=11 at 0.01 mol/L HNO_3. A similar metal coordination by ligands can be proposed as for TWE-11 and TWE-17.



Diethylenetriamine-penta-N,N-diisopropylacetamide
(TWE-A1)

Diethylenetriamine-penta-N,N-di-2-ethylhexylacetamide
(TWE-A2)

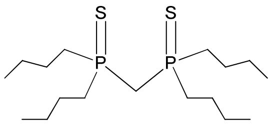


Diethylenetriamine-penta-N,N-dioctylacetamide
(TWE-A3)

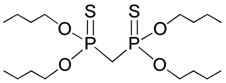
Figure 91. Chemical structures of screened DTPA derivatives

4.6.1.4. Extraction of Am(III) and Eu(III) with malonamide and diglycolamide derivatives containing sulphur and phosphorus

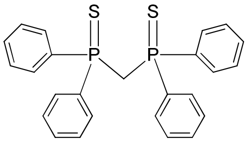
In order to enhance the An(III)/Ln(III) discrimination, a substitution of the two carbonyl oxygen atoms of malonamide and diglycolamide by sulphur was proposed. The University of TWENTE synthesised and delivered three malonamide derivatives, TWE-23 – TWE-25 and four diglycolamide analogues, TWE-27 – TWE-30 (Figure 92).



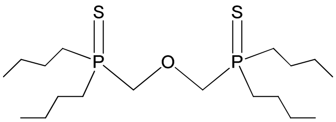
bis(dibutylphosphorothioyl)methane
(TWE-23)



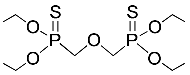
O,O,O',O'-tetrabutyl methylenediphosphonothioate
(TWE-24)



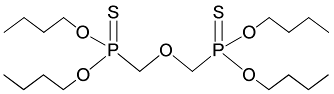
bis(diphenylphosphorothioyl)methane
(TWE-25)



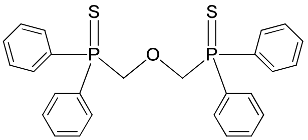
1,3-Bis(dibutylthio phosphinoyl)-2-oxapropane
(TWE-27)



O,O,O',O'-tetraethyloxybis(methylene)
diphosphonothioate
(TWE-28)



O,O,O',O'-tetrabutyloxybis(methylene)
diphosphonothioate
(TWE-29)



1,3-Bis(diphenylthiophosphinoyl)-2-oxapropane
(TWE-30)

Figure 92. Chemical structures of screened DTPA derivatives

The compounds containing phenyl groups (TWE-25 and 30) were not soluble in TPH nor in 1-octanol. The malonamide derivatives TWE-27 – 29 dissolved in TPH at a concentration of 0.1 mol/L of ligand did not extract Am and Eu from the nitric acid concentration tested ($D_{Am,Eu} < 0.01$).

The only sulphur-phosphorus containing ligand which showed good metal extraction was TWE-24. The distribution ratios of Am and Eu were >100 at the nitric acid concentration range of 0.01 – 2 mol/L with a steep decrease for higher acid concentrations (Figure 93).

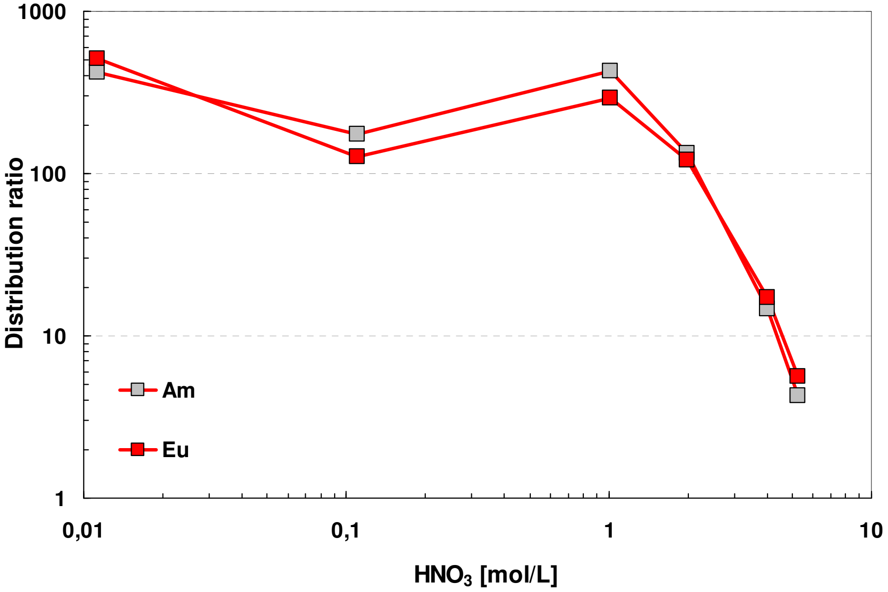


Figure 93. The extraction of ^{241}Am and ^{152}Eu by TWE-24 as a function of nitric acid concentration.

Organic phase: 0.09mol/L TWE-24 + 0.003mol/L 1-octanol in TPH

Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu,
mixing time: 60min; T=22°C±1°.

4.6.1.5. *Optimisation studies on TWE-21*

The radiotracers (^{241}Am and ^{152}Eu) extraction results of TWE-21 (Figure 86) from high nitric acid concentration were similar as for TODGA. Moreover, the diglycolamide with methyl group showed lower affinity to Am(III) and Eu(III) at nitric acid concentration ≤ 2 mol/L compared to TODGA which should facilitate their stripping into an aqueous phase. Therefore, further optimisation studies on TWE-21 were carried out.

In the first experiment the limiting organic concentration (LOC) for TWE-21 was determined at two different nitric acid concentrations and compared with TODGA. The results of this experiment are shown in Figure 94. TWE-21 at 3 mol/L HNO_3 appeared to be able to handle higher Nd concentration than TODGA with LOC = 29 mmol/L of Nd (LOC_{TODGA} = 24mmol/L). At 2 mol/L HNO_3 even more Nd was loaded into the organic phase without a

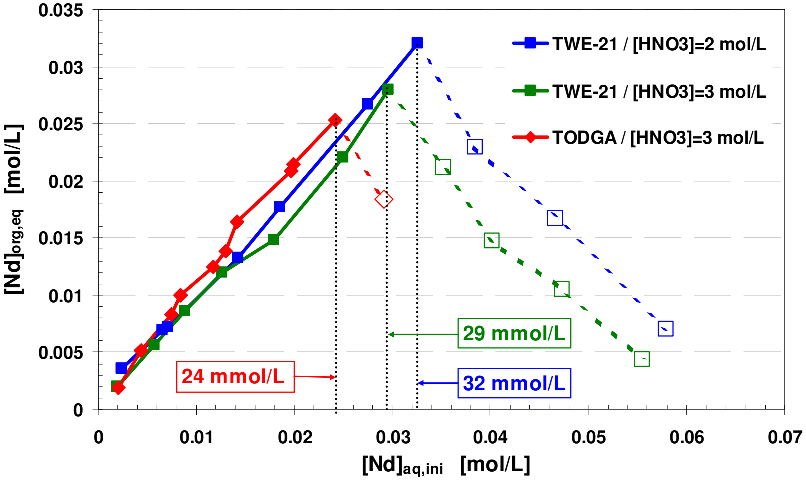


Figure 94. The extraction of neodymium by TWE-21 and TODGA as a function of its initial concentration and acidity of the aqueous phase.

Organic phase: 0.2 mol/L TWE-21 in TPH

Aqueous phase: variable Nd concentration at 2 and 3 mol/L HNO_3,
mixing time: 15min; T=22°C±1°.

third phase formation. However, this result should not be surprising as at higher nitric acid concentration more acid is extracted by the ligand, thus less ligand molecules are available to complex the metal.

After proving the good loading capacity of TWE-21, the solvent was loaded with HAR simulate solution (HAR-FZJ) for comparison with TODGA. The new ligand was tested without phase modifier and with addition of TBP nor 1-octanol. The results are presented in Table 41. The addition of a phase modifier into TWE-21 decreased the extraction of ^{241}Am and lanthanides, especially in the case of 1-octanol (column 6). At the same time less Pd was extracted compared to TWE-21 alone, however a masking agent has still to be needed for process implementation. TWE-21 extracted zirconium much better than TODGA which must be considered as a draw-back for this ligand. In this case the addition of a masking agent such as CDTA should minimise the extraction of this undesired fission product. Also slightly lower extraction of strontium was observed for the new ligand TWE-21. The rest of the fission and corrosion products were not extractable, similarly as for TODGA.

The major difference in metals extraction between TWE-21 and TODGA is for molybdenum. TWE-21 extracts this metal with D_{Mo}=27 (no presence of phase modifier) and D_{Mo}=13 for addition of TBP or 1-octanol. The last result (D_{Mo}=13) is about 50 times higher than for TODGA with the same phase modifiers ($D_{Mo}\approx 0.24$). This phenomenon was not further studied because as a next step of the ligand screening the radio- and hydrochemical stability of the new organic ligand should be determined to show whether it can be used for the process development.

Table 41. Distribution ratios of HAR elements for three different solvents with and without presence of an organic phase modifier

	without phase modifier	TBP		Octanol	
	TWE-21	TODGA/TBP	TWE-21/TBP	TODGA/Oct	TWE-21/Oct
^{241}Am	>300	292	200	>300	87
La	11	27	10	88	3
Ce	46	41	28	>300	11
Pr	112	54	62	>300	27
Nd	237	76	136	294	62
Sm	>300	>300	>300	>300	>300
Eu	109	>300	107	>300	157
^{152}Eu	>300	>300	>300	>300	>300
Gd	130	>300	100	>300	58
Zr	126	45	172	324	183
Pd	9.1	4.0	6.1	4.8	5.8
Mo	27	0.22	13	0.24	13
Sr	0.41	0.88	0.23	1.2	0.03
Ba	-	0.019	-	< 0.01	-
Cd	0.16	0.14	-	0.07	0.18
Cr	<0.001	-	<0.001	0.04	<0.001
Cs	<0.001	<0.001	<0.001	< 0.01	<0.001
Cu	<0.001	0.024	<0.001	< 0.01	<0.001
Ni	<0.001	<0.01	<0.001	< 0.01	<0.001
Rb	0.04	0.07	-	< 0.01	0.05
Rh	0.001	0.002	0.003	< 0.01	<0.001
Ru	0.14	0.31	0.20	0.21	0.12
Sb	0.09	0.02	-	< 0.01	0.004
Te	<0.001	<0.001	0.0013	< 0.01	0.0022
Y	>1000	>1000	>1000	>1000	>1000

Organic phase: 0.2 mol/L ligand (+ 0.5 mol/L TBP or 5vol.% 1-octanol) in TPH

Aqueous phase: HAR simulate solution (HAR-FZJ), 3 mol/L HNO_3, tracers: ^{241}Am, ^{152}Eu, mixing time: 15min; T=22°C±1°.

4.6.2. Water-soluble ligands

The innovative SANEX concept assumes the utilisation of a hydrophilic complexant with high An/Ln discrimination to increase the Ln(III)/An(III) separation performance. During the actinide stripping step of the process, there is always a competition between the organic ligand (e.g. TODGA) and the hydrophilic complexant to bond the metal of interest, therefore strong complexing agents with a high solubility in water are required to selectively strip the trivalent actinide ions. Some water-soluble diglycolamides (tetraalkyl diglycolamide) have been studied by Sasaki et al.,[131-132] however, their water solubility was limited. Water-soluble N-donor ligands, containing pyridine and pyrazine rings described by Heitzmann et al.,[133-134] demonstrate the correlation of the selectivity for trivalent actinides (e.g. Am) over Ln with the N-donor groups coordinated to the cation (softness of the molecule).

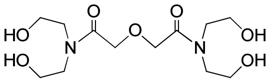
Well-known polyaminocarboxylic acids, such as EDTA or DTPA, require higher pH for their complete deprotonation which allows them to complex metals. Several new hydrophilic ligands were synthesised and delivered by University of Twente for screening tests in order to find a complexant of good solubility and metal complexation at $pH_{ini} < 2$, combined with higher affinity to trivalent actinides than lanthanides. However, the new ligands were also tested at initial pH of 2, 3 and 4 to see whether a higher Ln(III)/An(III) separation factor can be obtained compared with the polyaminocarboxylic acids mentioned previously.

New water-soluble diglycolamides with varying lengths of ethylene glycol chains on the amidic nitrogens, and two novel water-soluble ligands with the backbone similar to diglycolamide[42] and malonamide[135] but with the softer sulphur as coordinating atom instead of oxygen were screened to determinate their metal back-extraction properties.

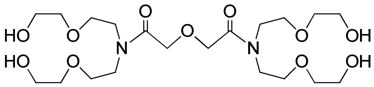
The tripodal lipophilic ligands described previously, TWE-11 and TWE-17, proved to be selective for Am(III), however, only at lower nitric acid concentration. Since for back-extraction of An(III) a low nitric acid concentration is required, also water-soluble derivatives of these ligands were synthesised to study their applicability for selective metal back-extraction.

4.6.2.1. Extraction of Am(III) and Eu(III) with water-soluble TODGA derivative ligands

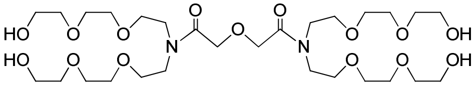
The three new hydrophilic diglycolamide ligands TWE-18 – 20 (Figure 95) were easily soluble in 0.5mol/L NH_4NO_3 up to concentration 0.1 mol/L. Since they are neutral ligands it was anticipated that the utility for metal back-extraction was possible from the pH region to acidic solutions.[131] The fourth ligand TWE-31 (Figure 95) was less soluble in the mentioned solution thus only 0.01 mol/L of this ligand was prepared.



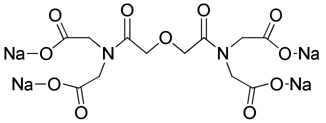
2,2'-oxybis(N,N-bis(2-hydroxyethyl)acetamide)
(TWE-18)



2,2'-oxybis(N,N-bis(2-(2-hydroxyethoxy) ethyl)acetamide)
(TWE-19)



2,2'-oxybis(N,N-bis(2-(2-(2-hydroxyethoxy) ethoxy)ethyl)acetamide)
(TWE-20)



N,N,N',N'-tetrasodiumacetate diglycolamide
(TWE-31)

Figure 95. Chemical structure of screened water-soluble TODGA derivatives

The extraction of ^{241}Am and ^{152}Eu from a solution containing TWE-18 is shown in Figure 96. The extraction experiment with 0.1 mol/L TWE-18 revealed its very strong affinity towards Am and Eu which increased with increasing the initial pH of the aqueous phase, although no discrimination between these two metals was observed. Even at initial pH = 2 over 90% (D_M<0.1) of Am and Eu stayed in the aqueous phase complexed by the hydrophilic ligand. The reference results shown in Figure 96 as red dotted lines represent the extraction of the radionuclides without the presence of the hydrophilic ligand (reference samples). The Am and Eu distribution ratios were not affected by the pH_{ini} due to the constant nitrate ions concentration provided by NH_4NO_3. TODGA used as an organic ligand in all screening tests

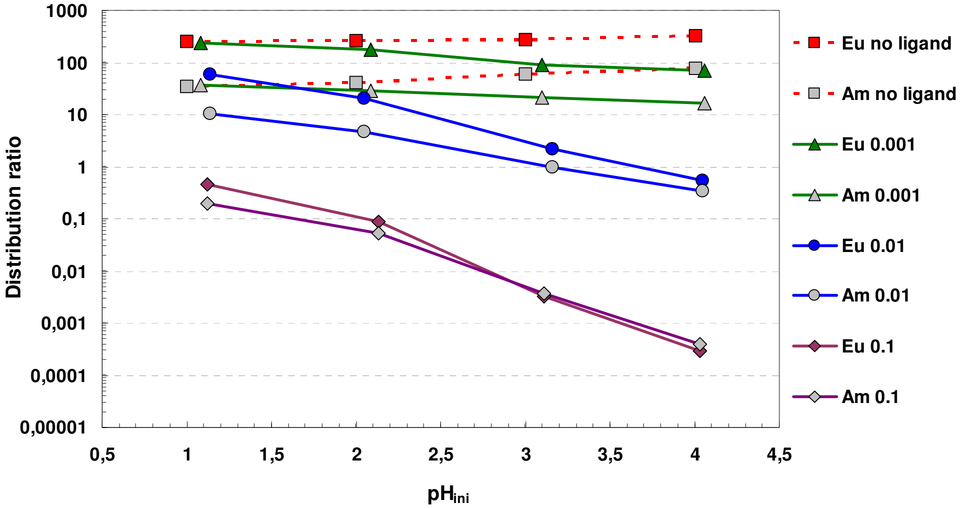


Figure 96. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH_{aq} and TWE-18 concentration in the aqueous phase.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH_{ini}, variable concentration of TWE-18, tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°.

of the water-soluble ligands is a solvating extractant, therefore its extraction properties directly depend on the NO_3^- concentration.

This high complexing efficiency of a hydrophilic ligand was further studied by varying TWE-18 concentration and the phase mixing time. In Figure 96 additional results at 0.01 and 0.001 mol/L of TWE-18 are shown. The decrease of the hydrophilic ligand concentration increased the $D_{Am,Eu}$, however the same trend as previously of better metal complexation at higher pH_{ini} was observed.

Additionally, the extraction kinetics of Am(III) and Eu(III) in a presence of TWE-18 was studied (Figure 97). The results showed that at most 5 minutes for the phase mixing time was sufficient to complex Am and Eu in the aqueous phase preventing their extraction by TODGA. The complexes of TWE-18 – metal were stable at least up to 60 minutes phase mixing time.

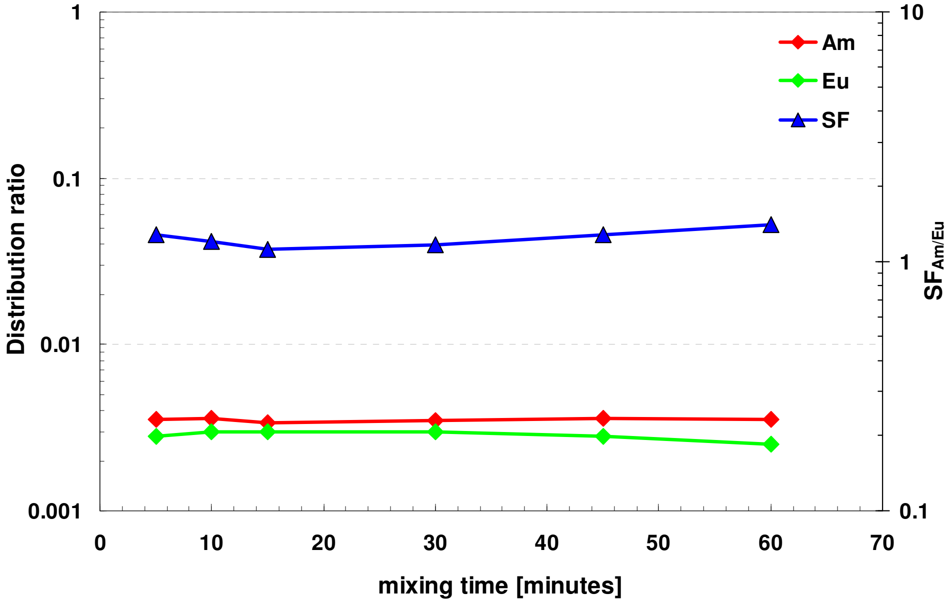


Figure 97. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the mixing time.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, 0.1 mol/L TWE-18, pH_{ini}=3, variable mixing time, tracers: ^{241}Am, ^{152}Eu; T = 22°C ± 1°

The ligands TWE-19 and TWE-20 with increased ethylene glycol chain at the DGA were much less efficient in metal complexation compared to TWE-18. Their extraction results (Figure 98) revealed weak affinity of the studied hydrophilic ligands to Am(III) and Eu(III). A colour change of the organic phase was observed after the extraction using both new hydrophilic ligands. The organic phase became darker after 60 min contact with the aqueous phase. The colour change was more pronounced with decreasing pH_{ini} of the aqueous phase containing the ligand. Possibly this effect can be explained by small ligand impurities, which were extracted into the organic phase and caused the colour change. The distribution ratios of Am and Eu for TWE-20 at pH_{ini}=2 were even higher than for the reference system where no

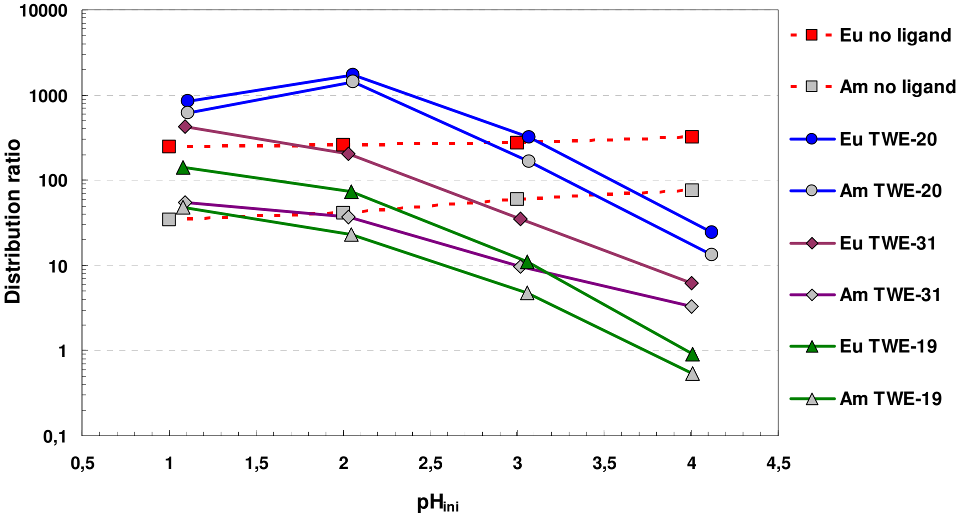


Figure 98. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH$_{aq}$.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

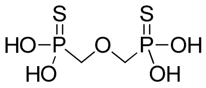
Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH$_{ini}$, 0.1mol/L TWE-19 or TWE-20 (0.01 mol/L TWE-31), tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°

ligand was used (red dotted lines) which indicates that small amounts of impurities formed even stronger hydrophobic metal complexes in the organic phase.

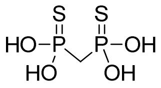
The last water-soluble TODGA derivative compound tested TWE-31 contained four sodium acetate groups and its screening results are shown in Figure 98. The extraction of Am and Eu was slightly better compared to TWE-19 indicating weaker metal complexation in the aqueous phase by TWE-31.

4.6.2.2. Extraction of Am(III) and Eu(III) with water-soluble ligands containing sulphur

The substitution of oxygen carbonyl atoms by sulphur in malonamide and diglycolamide anticipated an increase of the selectivity of the ligand for actinides(III) over lanthanides(III). In order to test this hypothesis two hydrophilic ligands were screened (Figure 99).



oxybis(methylene)diphosphonothioic
O,O-acid
(TWE-26)



methylenediphosphonothioic
O,O-acid
(TWE-32)

Figure 99. Chemical structures of screened hydrophilic ligands containing sulphur

The ligand TWE-26 was poorly soluble in 0.5 mol/L NH_4NO_3 since even in the prepared solution before the extraction test (0.03mol/L of hydrophilic ligand) small undissolved residues were visible. Therefore, the prepared solution was centrifuged and decanted for the subsequent experiment. The extraction results are shown in Figure 100 and they indicate that TWE-26 complexed Am and Eu very weakly as their distribution ratios decreased only slightly with the increasing of pH_{ini}. The drop was observed only at $pH_{ini}=1$ and 2 while for the higher values the distribution ratios stayed constant. In addition no enhanced selectivity for Am was observed compared to the system without TWE-31 since the curves for $SF_{Eu/Am}$ are nearly overlapping one another.

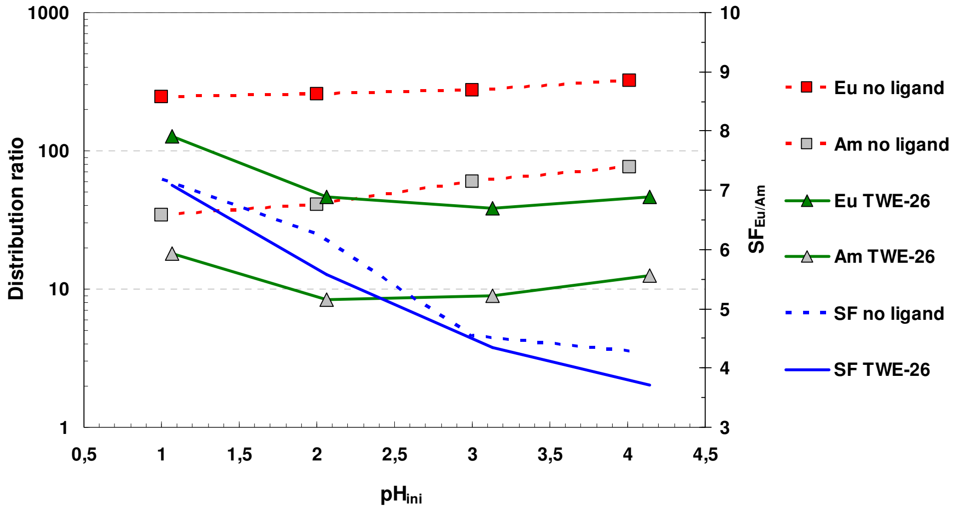


Figure 100. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH$_{aq}$.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH$_{ini}$, <0.03 mol/L TWE-26,
tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°

The second sulphur containing ligand TWE-32 (Figure 99) with a malonamide back-bone was easily soluble to the required concentration of 0.1 mol/L. At this high ligand concentration a very strong complexation in the aqueous phase was observed (Figure 101). The complexes formed between TWE-32 and Am, Eu prevent their extraction by TODGA even at the lowest pH$_{ini}$ tested (over 90% of Am and Eu was not extracted). Further decrease of the distribution ratios with increasing pH$_{ini}$ was observed resulting in over 99% of the metals retained in the aqueous phase. The effectiveness of suppressing the metal extraction by TWE-32 was additionally studied by decreasing its concentration and varying the phase mixing time.

The decrease of the hydrophilic ligand concentration increased the Am and Eu extraction by TODGA (Figure 101). In comparison to TWE-18 the sulphur containing ligand formed stronger complexes at low pH$_{ini}$, however without any significant Eu/Am separation.

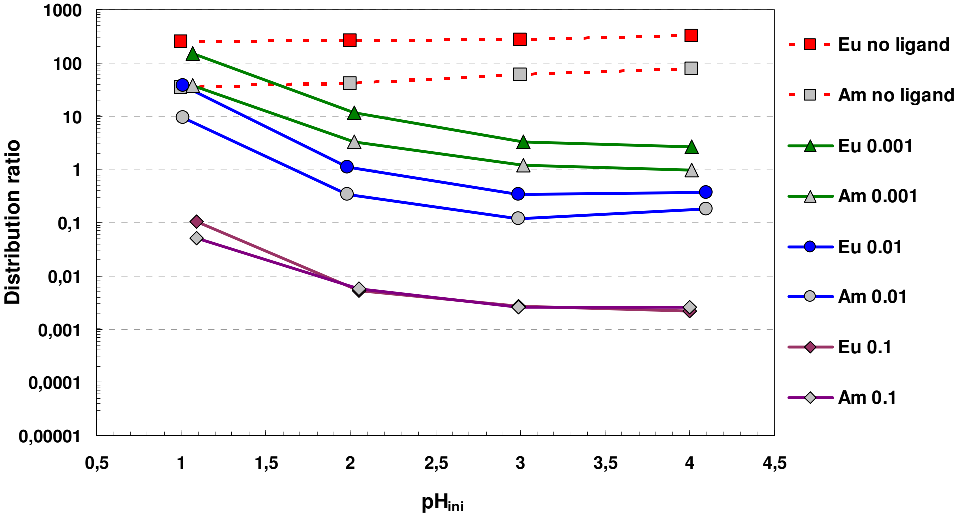


Figure 101. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH$_{aq}$ and TWE-32 concentration in the aqueous phase.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH$_{ini}$, variable concentration of TWE-32, tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°

The extraction kinetic result in the presence of TWE-32 shown in Figure 102 revealed fast complexation of Am and Eu by the ligand. The phase mixing time of five minutes was sufficient to reach the distribution ratios close to the equilibrium. Further mixing time of the phases up to 60 minutes did not change the metal distribution ratios.

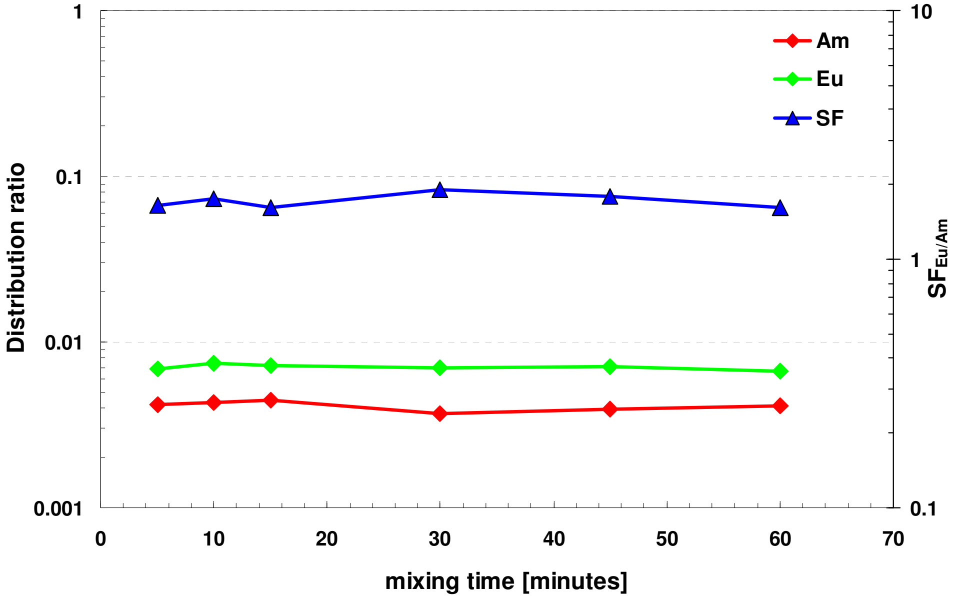


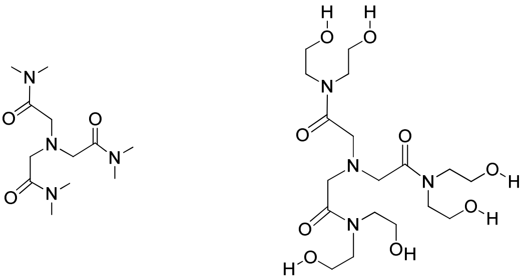
Figure 102. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the mixing time.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, 0.1 mol/L TWE-32, pH_{ini}=4, variable mixing time, tracers: ^{241}Am, ^{152}Eu; T = 22°C ± 1°

4.6.2.3. Extraction of Am(III) and Eu(III) with water-soluble tripodal ligands

The two tripodal ligands, TWE-A5 and TWE-A6 (Figure 103), were screened for their complexation with Am and Eu in the aqueous phase. The solubility of the two ligands differed thus the solution of 0.07 mol/L TWE-A5 was obtained while TWE-A6 was dissolved to the desired concentration of 0.1mol/L.



2,2',2''-nitrilotris
(N,N-dimethylacetamide)
(TWE-A5)

2,2',2''-nitrilotris(N,N-bis
(2-hydroxyethyl)acetamide)
(TWE-A6)

Figure 103. Chemical structures of screened hydrophilic tripodal ligands

The extraction results for TWE-A5 are shown in Figure 104. The increase in the pH_{ini} resulted in stronger complexation of the radionuclides by the ligand in the aqueous phase. The distribution ratios below 0.1 were observed at the highest tested pH_{ini} (pH_{ini}=4) meaning that about 90% of Am and Eu were not extracted by TODGA. However, the selectivity for Eu and Am increased comparing to the system without the hydrophilic ligand (blue dotted and continuous lines). At an initial pH = 2 the separation factor of Eu over Am reached 11 which is comparable with $SF_{Am/Eu}$=11.8 obtained for the lipophilic analogue TWE-17.

The extraction results of the second tripodal ligand, TWE-A6 (Figure 103), are shown in Figure 105. The increase of the initial pH of the aqueous phase notably increased the metal complexation. The distribution ratios were much lower compared to TWE-A5 which could result from different concentration of these two ligands in the aqueous solutions. The $SF_{Eu/Am}$ was similar as for the system with no hydrophilic ligand.

In conclusion the ligand TWE-A5 showed good discrimination for Am while TWE-A6 with its good solubility would be more suitable for stripping Am and Eu simultaneously.

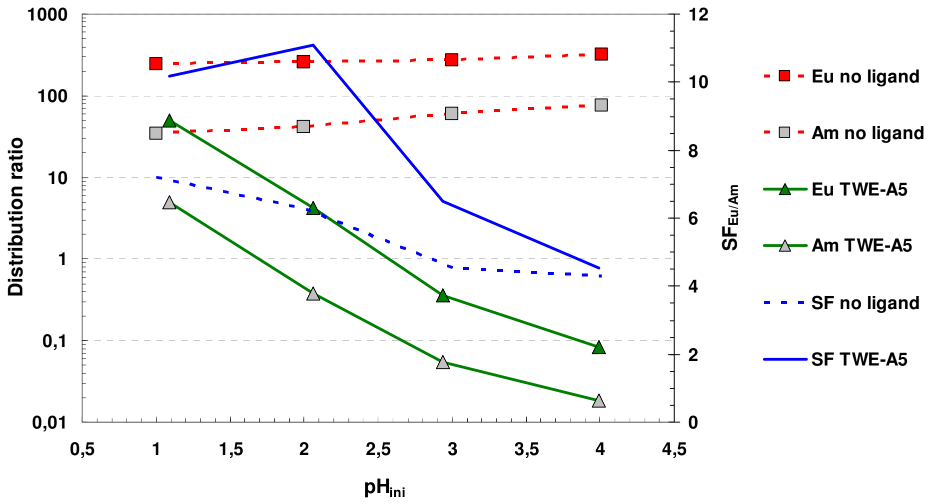


Figure 104. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH_{aq}.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH_{ini}, 0.07 mol/L TWE-A6,
tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°

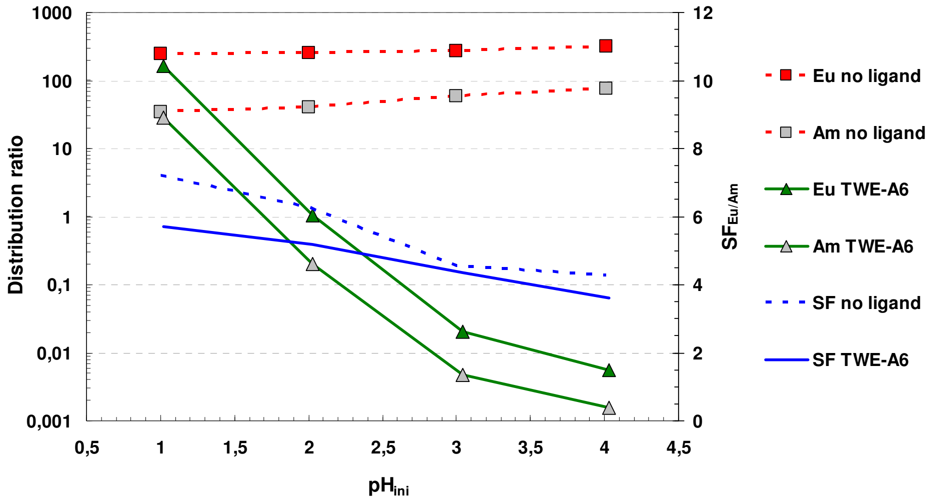


Figure 105. The extraction of ^{241}Am and ^{152}Eu by TODGA as a function of the initial pH_{aq}.

Organic phase: 0.2 mol/L TODGA + 5vol.% 1-octanol in TPH

Aqueous phase: 0.5 mol/L NH_4NO_3, variable pH_{ini}, 0.1 mol/L TWE-A6,
tracers: ^{241}Am, ^{152}Eu, mixing time: 60 min; T = 22°C ± 1°

5. Conclusions

5.1. Summary

The primary sources of long-term radiotoxicity in nuclear spent fuel, such as plutonium and the minor actinides (neptunium, americium and curium) necessitate very restricted storage conditions of the used fuel in order to minimise the impact of it onto the environment. Furthermore, the minor actinides constitute just a small part of the total mass of the spent fuel (~0.1%, LWR) thus their recovery and possible transmutation would decrease the necessary storage time and help to increase public acceptance towards nuclear energy.

Recovery of plutonium is already today performed in the PUREX process together with uranium and neptunium (advanced PUREX). Additional partitioning of minor actinides from the PUREX raffinate is quite simple, however due to the similarity of An(III) and Ln(III) these two groups of elements are usually separated together. Transmutation of separated An(III) containing significant quantities of Ln(III) is not efficient since some lanthanides (Gd) possess large neutron cross-section (*neutron poisons*) thus would significantly decrease the An(III) transmutation. Further separation of An(III) is a very challenging task and requires highly selective extractants or hydrophilic complexing agents. In this work the main emphasis was put on the development of a novel innovative-SANEX process where co-extraction of An(III) and Ln(III) follows the selective An(III) stripping using a hydrophilic complexing agent.

The first objective of this study was to screen polyaminocarboxylic acids for their complexing properties towards An(III)/Ln(III) in a reversed-TALSPEAK process (An(III) selective stripping). The obtained results showed that DTPA and TTHA were the most efficient stripping agents under known conditions with high Eu/Am separation factors of 75 and 374, respectively. These two complexants were further used in DIAMEX-SANEX process for An(III) selective stripping. In that process a neutral extractant (TODGA) was mixed with an acidic extractant (HDEHP). TODGA was responsible for An(III)/Ln(III) co-extraction while HDEHP for complexation of Ln(III) while An(III) were selectively stripped into the aqueous phase using a hydrophilic complexing agent (DTPA or TTHA). The separation factor of Eu/Am obtained using DTPA was not sufficient for selective An(III) stripping ($SF_{Eu/Am} < 8$) whereas using TTHA a high $SF_{Eu/Am}$=22 was achieved. Unfortunately, subsequent stripping of Ln(III) was not possible even by using hydrochloric acid.

Innovative-SANEX process proposed in this work was based on TODGA as an extractant with TBP or 1-octanol as an organic phase modifier. Screening tests of different buffers (buffered An(III) stripping solution) and polyaminocarboxylic acids (selective An(III) complexant) were performed. The best An(III) stripping performance was obtained using glycine and DTPA with $SF_{Eu/Am}$=16 (TODGA+TBP) and 17 (TODGA+octanol). The solvent mixture of TODGA + TBP was already studied for simultaneous An(III)/Ln(III) separation from PUREX raffinate.[46-47] However, the new solvent TODGA + 1-octanol required more fundamental studies such as nitric acid extraction. The obtained results showed that solvent consisted of TODGA + 1-octanol extracts two times less nitric acid (0.22 mol/L) compared to TODGA + TBP (0.42 mol/L) from 3 mol/L HNO_3 (PUREX raffinate acidity). This difference is even more pronounced for acid extraction from initial concentration of 0.5 mol/L HNO_3 (the acidity of the second scrubbing solution prior to selective An(III) stripping). The new solvent containing 1-octanol extracted three times less nitric acid (0.013 mol/L) than the solvent with TBP (0.042 mol/L). Such a significant decrease in nitric acid extraction is of a great importance since the extracted nitric acid prevents an efficient An(III) separation from Ln(III) (poor selective An(III) stripping). The comparison of the calculated acid extraction constant (K_H=0.49) with results obtained by other researchers proved that the nitric acid extraction is mainly controlled by TODGA and not by the diluent since the range of order of K_H is independent of the system used.

Screening tests aiming at oxalic acid substitution (Zr complexing agent) resulted successfully in the use of CDTA to prevent Zr extraction by TODGA during An(III)/Ln(III) co-extraction ($D_{Zr} < 0.01$). Moreover, CDTA was also able to prevent Pd extraction by its complexation in the feed solution ($D_{Pd} = 0.07$). The extraction kinetics of Zr in a presence of CDTA in the aqueous phase was very slow resulting in slow extraction of this metal into the organic phase where thermodynamically more stable complexes of Zr-TODGA were formed. Nevertheless, in a technical process the phase contact time (in case of centrifugal contactors) is short thus CDTA would efficiently suppress Zr extraction ($D_{Zr} < 0.01$).

The potentiometric titration studies on Zr complexation by CDTA confirmed very high stability constants ($\log\beta_{110}$=23.83) proving that CDTA is a very strong complexing agent not only for Ln(III) but also for Zr. The complexation of Zr by EDTA, the second efficient Zr complexant found in our screening test, was also studied using potentiometric technique. The stability constant of EDTA-Zr complexes are also very high ($\log\beta_{110}$=24.07). However, a direct comparison of the constant stabilities obtained for CDTA-Zr with those for EDTA-Zr was not possible since a sodium salt of EDTA was used (poor EDTA solubility in water). Sodium cations coming from Na_2EDTA dissociation can also be complexed by EDTA influencing the constant stabilities of that ligand with Zr.

The extraction, scrubbing and stripping conditions developed for the proposed i-SANEX process using batch tests were applied in a single centrifugal contactor run. CDTA was used as a making agent for Zr and Pd. Quantitative co-extraction of An(III) and Ln(III) was achieved with small Pd extraction ($D_{Pd} = 0.042$) while Zr concentration was below detection limit ($D_{Zr} < 0.001$). In the scrubbing step the extracted Sr was partly scrubbed from the organic phase. Good An(III) separation was achieved in the final An(III) stripping step using DTPA in solution of pH=2.0 ($SF_{Eu/Am}$=15).

Parallel with the work mentioned above screening tests of lipophilic and hydrophilic ligands provided by the University of Twente were performed aiming in understanding the correlation between the structural modifications of TODGA derivatives and their extraction properties (lipophilic ligands) and affinity towards An(III) and Ln(III) of the hydrophilic complexants (water-soluble ligands). Lipophilic ligands TWE-11 and TWE-17 showed better affinity to An(III) compared to Ln(III) at low nitric acid concentration with reasonably high $SF_{Am/Eu}$ of 8 (TWE-11) and 12 (TWE-17). Also TWE-24 extracted Am and Eu with high efficiency from HNO_3 < 1 mol/L, but without any discrimination between these two elements. Comparable properties to TODGA were obtained with the ligand TWE-21. However, this new ligand extracts Am and Eu weaker at low HNO_3 concentration compared to TODGA which is an advantage since the metal stripping with diluted acid would be more efficient. Comparable tests showed that TWE-21 extracts Mo to higher extent than TODGA, but an organic phase modifier is not necessary as no third phase formation was observed for just TWE-21 dissolved in TPH.

Within all tested water-soluble ligands TWE-18, TWE-32, TWE-A5 and A6 showed efficient and fast Am/Eu complexation in the aqueous phase thus their application in stripping solutions would enhance Ln(III) stripping performance.

5.2. Outlook

The performance of the proposed innovative-SANEX process still needs to be tested using battery of centrifugal contactors on spiked and genuine feed solution. The selective stripping of An(III) could be improved by application of novel hydrophilic complexant 2,6-bis(1,2,4-triazin-3-Yl)-pyridine developed in Karlsruhe, Germany.[136] This would allow stripping of An(III) at moderate acidity (0.5 mol/L HNO_3) thus buffering of the stripping solution would not be needed. A very efficient separation of Eu from Am can be obtained using this new hydrophilic complexant with value $SF_{Eu/Am} = 460$.

The new proposed CDTA complexant for Zr and Pd suppression was already tested aiming to the GANEX process using batch tests.[106] Additional studies to determine complex stabilities of these elements with CDTA at high nitric acid concentration (acidity of PUREX raffinate solution) possibly by microcalorimetry would bring more light on the remarkable complexing properties of CDTA.

Further studies on the novel organic ligand provided by University of Twente, TWE-21, should be performed. Determination of the radio and hydrolytical stabilities of TWE-21 should provide an answer on the possible substitution of TODGA in the proposed innovative-SANEX process. An increased molybdenum extraction by TWE-21 requires more detailed studies since additional scrubbing step to remove this metal could be necessary.

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- M. Sypula, A. Wilden, C. Schreinemachers, G. Modolo, Separation of An(III) from PUREX raffinate as an innovative SANEX process based on a mixture of TODGA/TBP, proceedings of the First ACSEPT International Workshop, 31 March - 2 April 2010, Lisbon, Portugal.
- M. Sypula, A. Wilden, G. Modolo, A. Geist, Innovative SANEX process for actinide(III) separation from PUREX raffinate using TODGA-based solvents, proceeding of the 19th International Solvent Extraction Conference, 3 – 7 October 2011, Chile.
- A. Wilden, M. Sypula, G. Modolo, A. Geist, Direct actinide(III) separation from PUREX raffinate using a BTBP/TODGA solvent, proceeding of the 19th International Solvent Extraction Conference, 3-7 October 2011, Santiago, Chile.
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