THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel

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Cover:
Radiotoxicity as a function of time for the once through fuel cycle (left) compared to one P&T cycle using the GANEX process (right) (efficiencies: partitioning from Table 5.5.4, transmutation: 99.9%). Calculations performed using RadTox [HOL12].

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Abstract

When uranium is used as fuel in nuclear reactors it both undergoes neutron induced fission as well as neutron capture. Through successive neutron capture and beta decay transuranic elements such as neptunium, plutonium, americium and curium are produced in substantial amounts. These radioactive elements are mostly long-lived and contribute to a large portion of the long term radiotoxicity of the used nuclear fuel. This radiotoxicity is what makes it necessary to isolate the used fuel for more than 100,000 years in a final repository in order to avoid harm to the biosphere. To diminish this long-term radiotoxicity of the waste, to further increase the energy utilization and to decrease the heat load of the final repository there is an advanced reprocessing option called Partitioning and Transmutation (P&T). Within P&T the transuranic elements are separated from the fission products in the used fuel and transmuted using a fast neutron spectrum. During transmutation these long lived elements are transformed to short lived or even stable ones.

The partitioning for transmutation can be realised using liquid-liquid extraction. Within this work a liquid-liquid extraction process of GANEX type has been developed and studied. The GANEX (Group ActiNide EXtraction) concept consists of two cycles; a first cycle where the uranium bulk is removed from the fuel dissolution liquor and a second cycle (the actual GANEX extraction) where the transuranic elements as well as residual uranium are extracted together as a group. Here, only the second cycle has been studied.

The GANEX solvent developed comprises of the extractants CyMe$_4$-BTBP and TBP in cyclohexanone. This solvent composition was found to be able to efficiently extract the actinides as a group from nitric acid. The actinides could also be separated from most of the fission products (including the trivalent lanthanides) with high separation factors. The few co-extracted fission products could to a large extent be managed by the addition of water soluble suppressing agents and scrubbing reagents. The solvent was found to be stable towards both hydrolysis as well as γ-radiolysis in the presence of nitric acid. The process was also shown to work under fission product loading conditions and after acid scrubbing of the solvent the actinides could be recovered as a group. In addition a single stage continuous test was performed to test the solvents suitability for process implementation.

Keywords: Solvent Extraction, Partitioning, GANEX, BTBP, TBP, Fission Products

List of Publications

This thesis is based on the work contained in the following papers, referred to by roman numerals in the text:

I. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M. R. StJ., Retegan, T., Skarnemark, G.: A TBP/BTBP-based GANEX Separation Process - Part 1: Feasibility. Solvent Extraction and Ion Exchange, 28(4), 437-458, 2010

Contribution: Main author, all experimental work

II. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M. R. StJ., Grüner, B., Hájková, Z., Kvičalová, M.: A TBP/BTBP-based GANEX Separation Process - Part 2: Ageing, Hydrolytic and Radiolytic Stability. Solvent Extraction and Ion Exchange, 29(2), 157-175, 2011

Contribution: Main author, all extraction experiments

III. Aneheim, E., Ekberg, C., Foreman, M. R. StJ.: A TBP/BTBP-based GANEX Separation Process - Part 3: Fission Product Handling. Accepted for publication in Solvent Extraction and Ion Exchange, vol. 31, 2013

*Contribution: Main author, all experimental work**

IV. Aneheim, E., Ekberg, C., Foreman, M. R. StJ.: Aqueous Complexation of Palladium to Prevent Precipitation and Extraction in a Group Actinide Extraction System. Hydrometallurgy, 115-116, 71-76, 2012

Contribution: Main author, all experimental work

V. Aneheim, E., Grüner, B., Ekberg, C., Foreman, M. R StJ., Hájková, Z., Löfström-Engdahl, E., Drew, M. G. B., Hudson, M. J.: Fission Product Interactions with Nitrogen Donor Ligands used for Spent Nuclear Fuel Treatment**,** Submitted to Polyhedron, 2012

Contribution: Main author, all extraction experiments and NMR analyses

* except ligand synthesis

VI. Aneheim, E., Ekberg, C., Littley, A., Löfström-Engdahl, E., Skarnemark, G.: Technetium chemistry in a novel group actinide extraction process. Accepted for publication in Journal of Radioanalytical and Nuclear Chemistry, Special Issue: MARC IX (published online July 2012)

Contribution: Main author

VII. Aneheim, E., Ekberg, C., Mabile, N.: Exchange of TBP for a monoamide extraction ligand in a GANEX Solvent - advantages and disadvantages. Proceedings of the 19th International Solvent Extraction Conference, p 65, Chapter 3, Ed. Valenzuela L. F., Moyer, B. A., ISBN 978-956-8504-55-7, Gecamin Ltda. Santiago Chile, 2011

Contribution: Main author, part of the experimental work

VIII. Aneheim, E., Ekberg, C., Foreman, M. R. S, Löfström-Engdahl, E., Mabile, N.: Studies of a solvent for GANEX applications containing $CyMe_4$-BTBP and DEHBA in Cyclohexanone. Separation Science and Technology, 47(5), 663-669, 2012

Contribution: Main author, part of the experimental work

IX. Aneheim, E., Bauhn, L., Ekberg, C., Foreman, M., Löfström-Engdahl, E.: Extraction experiments after radiolysis of a proposed GANEX solvent - the effect of time. Accepted for publication in Procedia Chemistry, ATALANTE 2012 – Nuclear Chemistry for Sustainable Fuel Cycles

Contribution: Main author, main experimental work

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1. Introduction and Background

Sweden, like the rest of the world's industrialized countries, is a society highly dependent on electricity and electrical energy. The main core industries such as the steel and paper industry are large consumers of electricity (15% and 14% of the total electrical energy consumption respectively) [SKO12, STÅ12] and in everyday life the average citizen depends on electricity. This dependency ranges from simple things like turning on the lights or TV at home to intensive care at hospitals in emergency situations. The emission of greenhouse gases from the combustion of fossil fuels such as coal for electrical energy production has been pointed out as the major contributor to the phenomenon of global warming. Seen in this context, nuclear power is one of the few available power sources with a large capacity and very low emissions of carbon dioxide [SAI00]. Swedish electrical energy production is based on hydropower, nuclear power, non-nuclear thermal power (e.g. waste and biomass incineration plants) and a small portion of wind power and imported energy. Of these, hydropower and nuclear power are the largest contributors, accounting for 45% and 39% respectively of the total production in 2011 [SVE12, ELÅ11]. Sweden has 10 nuclear reactors in operation, making this one of the most nuclear-dense nations in the world. World-wide, 435 nuclear reactors were in operation in the end of 2011, producing 12.3% of the total amount of electrical energy. Although nuclear power has recently experienced a slight recession after the accident at the Fukushima Daiichi power plant in Japan in March 2011, there is still large demand for energy produced without carbon dioxide emissions, and 65 new nuclear reactors were under construction around the world at the end of 2011 [IAE12]. Good as this energy alternative might be considering global warming and carbon dioxide emissions, it comes with one inevitable downside, which is the waste.

1.1 Nuclear Waste

By the end of 2011 the total amount of discharged nuclear fuel in the world reached 350,000 tonnes of heavy metal (tHM) [IAE12]. This used fuel is highly radiotoxic and needs to be stored for more than 100,000 years for the radiotoxicity to equal that of the natural uranium needed to produce the fuel [MAD04].

When uranium is used as fuel in nuclear reactors it interacts with a thermal (slow) neutron and undergoes a fission reaction. In this reaction the uranium atom is split into a number of lighter, mostly short-lived elements, so called fission products. In each fission reaction, energy and new neutrons are released. However, the uranium atom can also capture a neutron and, through successive beta decay, elements that are heavier than uranium itself, such as neptunium, plutonium, americium and curium, are created. These transuranic elements are mostly long-lived and contribute to a large portion of the long term radiotoxicity of the used fuel [WES07].

There are currently three main strategies for the used nuclear fuel cycle. One is direct disposal, also referred to as the "once-through" option, where the fuel is used only one time in the reactor and then, following some decades of interim storage, sent for final storage in a future repository. The second option is reprocessing, where the uranium and plutonium in the waste are recycled. The third option is the “wait-and-see” strategy for those who do not want to decide on either of the first two options [IAE08]. Sweden as a country has chosen the once-through option for handling the used fuel, and in 2009 Forsmark, 150km north of Stockholm, was decided on as the location of the final repository [SKB09]. This repository will be located deep down (500m) in the bedrock and the waste will be contained in large copper canisters [SKB01]. Other countries such as the UK, Russia and France have chosen the reprocessing option.

The reprocessing performed today consists of separating the plutonium and uranium present in the used fuel from the rest of the elements. This is done either to store the reprocessed uranium as a potential strategic asset or to directly recycle the materials into new fuels containing either uranium only or both uranium and plutonium, so called mixed oxide fuels (MOX). These fuels can then be used in existing thermal nuclear reactors [IAE07, IAE12]. Of all nuclear waste in the world today, 100,000 tHM has already been reprocessed at least once and the world reprocessing capacity is approximately 4,800 tHM per year [IAE12]. Recycling of the used nuclear fuel is possible since the utilization of energy from the fuel in a normal nuclear reactor is quite low, typically around 2% for a light water reactor [CHO02]. If one considers the amount of natural uranium needed to produce the enriched fuel, the energy utilization becomes even lower (< 1%). Reprocessing the uranium and plutonium once improves the use of fissile material resources by up to 25% (i.e. increases energy utilization from 2 to 2.5%). There are, however, also disadvantages to this waste-handling option. These include the cost of reprocessing, the created amount of high active waste in need of final storage and the potentially lower proliferation resistance [IAE08]. The used MOX fuel will also be highly radiotoxic – even more so in the shorter time span (up to approximately 4,000 years) – than used uranium fuel, due to a larger presence of the minor actinides americium and curium [BEA97]. The residual waste after conventional reprocessing therefore still needs to be stored for about the same time as the fuel from the once-through option. To diminish this long-term radiotoxicity of the waste, further increase energy utilization and decrease the heat load of the final repository there is a more advanced option for reprocessing, called Partitioning and Transmutation (P&T) [RED07].

1.2 The Concept of P&T

It has been suggested that not only plutonium but also the minor actinides (neptunium, americium and curium) could be separated from the rest of the used nuclear fuel, the storage time of the bulk part of the waste could be shortened to about 1,000 years [BON75, MAD00, AOK02]. Figure 1.2.1 illustrates how the different actinides and the fission products contribute to the total radiotoxicity of the used fuel. As can be seen, among the minor actinides, americium and curium contributes to the largest part of the total radiotoxicity in the time span below 100,000 years and 20,000 years respectively.

The radiotoxicity and storage time of the bulk part of the waste can be diminished by simply removing the transuranic elements. However, to be able to utilize more of the energy in the used fuel and to decrease the storage time and radiotoxicity of the entire waste fraction also the minor actinides must be transmuted. This means that, after selective separation of the elements in question, they can be used in new innovative fuels which are to be burned in nuclear reactors utilizing a fast neutron spectrum. When the minor actinides then undergo fission in these reactors they are transmuted into elements with a shorter half-life (or even stable ones) that hence have a lower radiotoxicity than the original nuclide [SAL98].

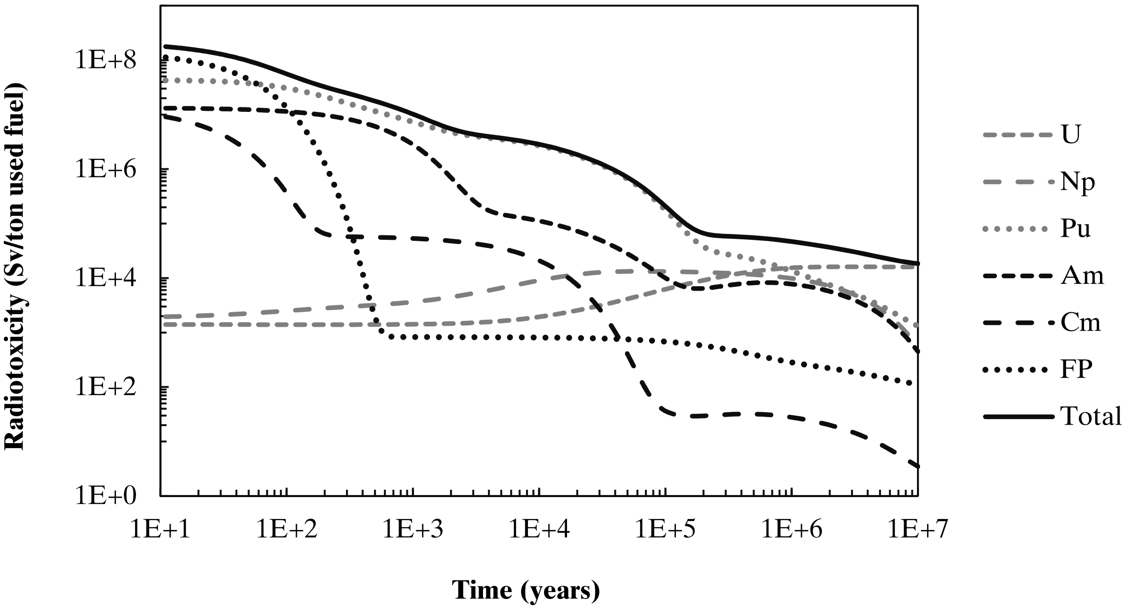

Figure 1.2.1 Radiotoxicity contribution of the fission product fraction and different actinides in used nuclear fuel (UO_X fuel (4% enrichment), 45 Gw burnup and 10 y cooling). Calculations performed using RadTox [HOL12]

Transmutation can be defined as a nuclear reaction where one nuclide transforms into another in one or several steps. This can be accomplished through radioactive decay or through reactions with accelerated particles [NAT12]. However, most transuranic elements do not easily interact with thermal (slow) neutrons like those present in an ordinary nuclear reactor, but require fast neutrons to be able to undergo a transmutation reaction [GUD00]. As mentioned above, other types of nuclear reactors than the thermal ones are therefore needed to be able to transmute future minor actinide-containing fuel. There are two major options under investigation for these future types of reactors: fast reactors and accelerator-driven systems (ADS). Fast reactors would be used for energy production as a complement to the reactors existing today, utilizing minor actinide-containing fuel. The accelerator-driven systems' main task would instead be to only transmute minor actinides to lower the radiotoxicity of the already produced used nuclear fuel. ADS fuel can, however, contain larger amounts of these minor actinides than the fast reactor fuel and therefore offers larger transmutation potential. Hence it is possible that a combination of the two could be an option for the future [MUE09].

Separation, or partitioning, of the actinides from the rest of the elements (mainly fission products) in the used fuel is a prerequisite for their effective transmutation. This is because the transmutation fuel needs to be free from both elements that can cause a build-up of new long-lived and radiotoxic nuclides and elements that have a higher neutron capture cross section than the actinides. A high neutron capture cross section means that these elements would consume the neutrons intended for the actinides and in this way prevent them from undergoing fission/transmutation. In addition, the presence of fission products in transmutation fuel would also cause unwanted non-uniform heat distribution during irradiation [CHR04].

1.3 Partitioning Processes

The partitioning of the used nuclear fuel can be performed along two main routes: the “dry route”, which utilizes pyrochemical methods, and the “wet route”, which utilizes hydrochemical methods. The pyrochemical methods have the advantage of being radiation resistant and possess a low risk of criticality. The hydrochemical processes on the other hand are well established and use an already highly developed technology [IAE08]. Thus, hydrochemical processes have become the methods of choice for most of the P&T research around the world. There are several different hydrometallurgical processes for partitioning, such as chromatographic separation, ion exchange separation and supported liquid membrane extraction [AHL04, AHL07]. However, the most common wet method, and the one that is used for industrial reprocessing today, is liquid-liquid extraction, also referred to as solvent extraction.

One of the earliest reprocessing processes was a solvent extraction process called PUREX (Plutonium Uranium Redox EXtraction). It was developed in the 1940s as part of the Manhattan project, primarily for the production of plutonium for nuclear weapons [AND60]. The PUREX process is still used today for commercial reprocessing of uranium and plutonium, although it has been modified and optimized during the past 65 years.

The partitioning and transmutation processes previously developed have usually been aimed at following a conventional PUREX process. A partitioning concept developed early on initially concerned separation of the minor actinides americium and curium together with the lanthanides from the aqueous phase after the PUREX process. In a second extraction step these actinides were then separated from the lanthanides. Processes within this concept include the American TALSPEAK (Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes) process developed in the 1960s [WEA64] and the more recent European DIAMEX (DIAMide EXtraction)/SANEX (Selective ActiNide EXtraction) process [COU00, MAD04, MAG09] (Figure 1.3.1).

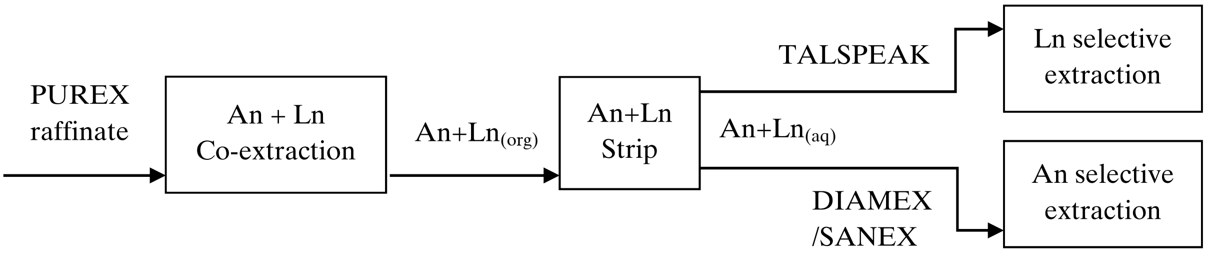

Figure 1.3.1 Schematic description of the TALSPEAK and DIAMEX/SANEX processes

A modification of this first concept has also been made in which the minor actinides and lanthanides are still co-extracted. Then, however, the minor actinides are selectively removed directly from the organic phase instead of first being stripped and then selectively extracted. Two processes within this second concept are the CTH process, which is a reversed form of the TALSPEAK process [LIL84], and the innovative SANEX process [SYP10].

There is currently another extraction concept under investigation, which is not aimed at following a conventional PUREX process but at replacing PUREX. By doing this, proliferation resistance is increased as no pure plutonium stream is created. One process within this new concept is the GANEX (Group ActiNide EXtraction) process [ADN05].

1.3.1 GANEX

The GANEX process is a homogenous reprocessing concept contrary to the previously mentioned TALSPEAK and DIAMEX/SANEX processes, which are heterogeneous reprocessing concepts. In homogenous recycling all the transuranic elements (Np, Pu, Am and Cm) are recycled together, whereas in heterogeneous recycling they are separated.

The GANEX concept consists of two cycles: a first cycle where the uranium bulk is removed from the fuel dissolution liquor and a second cycle (the actual GANEX process) where the transuranic elements as well as residual uranium are extracted together as a group. A schematic description of the GANEX concept is provided in Figure 1.3.2. The idea behind removing the uranium bulk is to create a stream of pure uranium. This stream then makes it possible to adjust the uranium concentration in the final solutions intended for fuel fabrication. Also, as uranium is present in substantially larger amounts than the other actinides, removing uranium would decrease the risk of solvent loading in the GANEX extraction. Ideally the group actinide extraction should be a one-step process where the actinides are extracted simultaneously as they are separated from the rest of the elements, such as the fission products and the corrosion and activation products, in the used fuel [ADN05, MIG07]. By implementing a GANEX process instead of a PUREX process followed by a separation method like the DIAMEX/SANEX process, the total number of necessary extraction steps can be reduced. Reducing the number of steps in a solvent extraction process is desirable as it results in limited waste streams, a reduction in the capital investment required to build an industrial plant, a decrease in plant size and lower running costs and final decommissioning costs [RIT04].

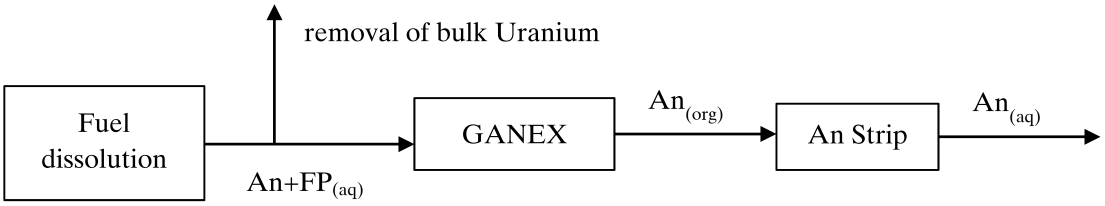

Figure 1.3.2 Schematic picture of the GANEX concept

The aim of the work presented in this thesis has been to develop a liquid-liquid extraction process of GANEX type for the partitioning and transmutation of commercial uranium fuel. By investigating both the big picture as well as the small details an attempt has been made to achieve a feasible process as well as to gain basic understanding about the extraction system used.

2. Theory

2.1 Liquid-Liquid Extraction

Liquid-liquid extraction can be described as the partitioning of a species (solute) between two immiscible liquids. These immiscible liquids most often consist of an organic and an aqueous phase. The organic phase before extraction is called the solvent (hence the commonly used name solvent extraction) and the aqueous phase containing the solute is called the (pregnant) feed. The solvent always consists of a diluent, which is the bulk phase, and sometimes also of one or several extractants. The extractant is the component that is primarily responsible for transferring the solute from one phase to another. The phase containing the extracted solute after extraction is called the extract while the depleted aqueous phase is called the raffinate [RIC93].

Solvent extraction can be performed in many different ways, and these extraction systems are often categorized into different classes: A (MX_N), B (MA_Z), C (ML_ZB_b), D (Q^+L^-) and E [RYD04]. These classes are described in Table 2.1.1

Table 2.1.1 Description of the different solvent extraction classes [RYD04]

Class	Description	Example
A	Extraction of simple inorganic molecules	MX_N = $GeCl_4$ or I_2
B	Neutral complexes between a metal ion and a lipophilic organic acid	MA_Z=$Th(RCOO)_4$
C	Neutral complexes between a metal ion and a ligand. The complexes are, however, coordinatively unsaturated and can therefore accept uncharged organic molecules as solvating agents. This class is therefore often called solvating extraction.	ML_ZB_b=$UO_2(NO_3)_2(TBP)_2$
D	Ion pair extraction. Either an anion (the most common one, with an inorganic anion and a large organic cation) or a cation exchange mechanism takes place	Q^+L^-= $R_3N^+Cl^-$
E	Other extractions	Crown ethers

In an extraction system, two processes can govern the kinetics of the extraction (i.e. how fast the solute can be moved from the feed to the extract): diffusion of the solute, extractant or formed complex across the phase boundary and the speed of the chemical reaction (complexation). If the chemical reaction takes place at the phase boundary then both these processes are favoured by a large interfacial area between the organic and aqueous phase. This in practice means smaller droplets of one phase (the disperse phase) in the other (the continuous phase). The size of the droplets can be modified by the use of e.g. surface active agents that lower the interfacial surface tension, as a low interfacial tension gives smaller droplets, but the most important factor is an effective mixing of the two phases [DAN04].

Several different expressions are used to describe the extraction processes in a solvent extraction application [RYD04]. These expressions can be used independent of the type of extraction process implemented. Consider the solvating extraction of a metal ion (M) by a ligand (L) and an uncharged organic ligand (O) (extraction class C) described in reaction 2.1:

$$M^{+} + L^{-} + \bar{O} \leftrightarrow \overline{MLO} \tag{2.1}$$

This reaction will now be used to describe the solvent extraction expressions most commonly used within this thesis. The concept of distribution ratio (D) is used to describe the total distribution of the concentration of a solute between the two phases (Equation 2.2). The distribution ratio should not be confused with the distribution constant (K_D), which describes the concentration distribution of a solute in a single definite form (Equation 2.3) [RIC93]. The separation factor (SF) describes the separation of two different solutes that are present in the same extraction system (Equation 2.4) where $D_{M1}>D_{M2}$ always renders an SF>1. According to IUPAC, the separation factor should be denoted α [RIC93] but, since this symbol is frequently used in nuclear chemistry for α-radiation, the separation factor will, in this text, only be referred to as SF.

$$D_M = \frac{[\overline{MLO}] + [\overline{ML}]}{[M^{+}] + [ML]} \tag{2.2}$$

$$K_{D,ML} = \frac{[\overline{ML}]}{[ML]} \tag{2.3}$$

$$SF_{M1/M2} = \frac{D_{M1}}{D_{M2}} \tag{2.4}$$

For a solvent extraction system aimed at separating different solutes to be considered successful, the distribution ratio of the solute to be extracted must be above one, and below one for any solute from which it is wished to be separated. The distribution ratio is affected by many factors in an extraction process, such as temperature, extractant concentration, the concentration of the counter ion in a solvating system etc. [YU98].

2.2 Complexation Chemistry

The complexation of metal ions with ligands to facilitate extraction depends on the features of both the metal ion and the complexant.

Metal ions in aqueous solution are always surrounded by coordinating water molecules where the oxygen acts as a donor atom (hydration). The number of coordinated waters largely depends on the size of the metal ions and can range from four for the small Be(II) up to nine for the large La(III) [BOC93, COT06]. Water, as well as other ligands, can associate with metal ions both in what is called an inner sphere and an outer sphere. In the inner sphere the ligand is coordinated directly to the metal ion while in the outer sphere the ligands are separated from the metal by an inner sphere ligand [CHO04]. The metal-water complex can act as a Brönstedt acid, donating protons, which means that the complex changes from coordinating only water to also comprising hydroxyl groups (hydrolysis). The acidity of the complex is dependent on factors such as the size and charge of the metal ion. Small, highly charged atoms generally create more acidic complexes, i.e. hydrolyse more easily. Plutonium as Pu^{4+} is, for example, easily hydrolysed. However, under highly acidic conditions such as in dissolved used nuclear fuel, these hydrolysis reactions do not occur. Complexation of a metal ion with any type of ligand means that the already coordinated water molecules must to some extent be replaced with organic and/or inorganic counterparts [CHO04]. The rate at which ligand exchange takes place at the metal ion can play a major role in the kinetics of a complexation reaction and hence also the following extraction. For example, nickel is known to display slow ligand exchange kinetics in many cases [KOB98].

One principle that can be applied for general consideration of most complexes is the Hard-Soft Acid-Base (HSAB) theory. This principle indicates that metal ions that are hard Lewis acids form strong complexes with ions or active groups on organic molecules that are hard Lewis bases and, in the same way, soft Lewis acids form strong complexes with soft Lewis bases. The mix of hard and soft acids and bases, however, forms weaker complexes [PEA73]. Interactions between the hard Lewis acids and the hard Lewis bases are often ionic in character. For example, the alkali metals, such as lithium, sodium, rubidium and caesium are considered to be hard Lewis acids. Organic acids and phosphorous oxides are examples of hard Lewis bases due to the fact that the coordinating atom usually is oxygen. The interactions between soft Lewis acids and soft Lewis bases, on the other hand, are more covalent in character. For example, precious metals such as silver, gold and platinum are considered to be soft Lewis acids and most organosulfur compounds, coordinating with the sulphur atom, are considered to be soft Lewis bases [KLO68, PEA73]. The HSAB theory is however not sufficient to explain the complexation behaviour of the actinides and the lanthanides. Both groups are considered to be hard Lewis acids but the hardness also varies throughout the actinide and lanthanide series. Many of the actinides as well as the lanthanides do not display a pure ionic bond character in their interactions with other species (like other hard Lewis acids) but also have a certain covalent feature. However, this covalence is larger for, e.g., the trivalent actinides compared with the corresponding trivalent lanthanides [ION01] [MIG05].

There is one type of ligands called chelates in which two or more atoms in the same molecule bind to the metal. When comparing chelating ligands with similar monodentate ligands it is found that the chelating ligands form significantly more stable complexes. The enthalpy of complex formation is more or less the same for chelating ligands as for the same amount of bonds from monodentate ones, but the increase in entropy is larger for the chelate complex rendering a total decrease in free energy [SCH52, BRE00]. One explanation for this is that more water molecules associated with the metal in the aqueous phase are released per ligand than when the ligands are not chelating. This renders an increase in the degrees of freedom in the system and therefore an increase in entropy, given that the entropy gained from the released water molecules is larger than the loss of entropy for the complexing ligand [CHO04]. For the chelating ligands, the ring size that is created is an important factor for the stability of the complex. The most stable ring formations are the five and six-membered rings, depending on the size of the metal ion [MAR96].

2.3 Actinides and Lanthanides

Most of the actinides and lanthanides differ from the main group elements and transition metals because of the presence of partially filled f orbitals. For the lanthanides, the f orbitals are strongly shielded from the atoms surroundings by the d and p orbitals and hence do not participate directly in bonding. For this reason the chemistry of the lanthanides is very much dependent on their size and charge. Their charge in solution is almost exclusively +3, which is also true for the heavier actinide elements (Am to Lr) and the difference in size between these trivalent actinides and the trivalent lanthanides is also small. Thus, separation of these elements is difficult [COT06]. However, separation, albeit difficult, is important within partitioning and transmutation since some of the lanthanides e.g. have a large neutron capture cross section.

The actinides display a contraction in ionic radii throughout the series (see Table 2.3.1), just like the lanthanides. This effect is mainly due to greater nuclear attraction than expected caused by poor shielding of the nucleus by the f orbital electrons, which results in the outer s electrons being drawn inwards. Although thorium and also actinium and lanthanum are counted as part of the actinide/lanthanide series, they lack electrons in the f orbitals and hence have slightly larger ionic radii in comparison ($r(Th^{4+})=1.05Å$ compared to $r(Pa^{4+})=1.01Å$ with CN=8 [SHA76]), as well as a somewhat different chemical behaviour. Another factor contributing to the contraction of the actinides and lanthanides, but also affecting the chemistry of the actinides at large, is the relativistic effect. This effect is caused by the heavy atomic nucleus forcing the electrons to travel close to the speed of light and therefore to increase in mass. The relativistic mass of the electrons causes the s and p orbitals to contract even further and these electrons to be stabilized, while the f and d electron orbitals are expanded and destabilized. This makes the energy of the actinide valence orbitals very similar, in some cases resulting in a violation of the Madelung rule by filling the 6d orbital with electrons before the 5f one (for electron configuration of the relevant actinides see Table 2.3.1). This effect also contributes to the stability of the unusually high oxidation states and the high tendency to form covalent bonds with oxygen in the early actinide series [COT06]. Both these phenomena are evident when studying the early f actinides in solution. In nitric acid of relative strength (as during P&T), uranium is present as U(VI) in the form of a uranyl ion, UO_2^{2+}, and the dominant oxidation state of neptunium is Np(V) in the form of NpO_2^+. In both these oxygen-containing species the two double-bonded oxygens are placed in an axial position around the central atom. Protactinium also exhibits oxidation state Pa(V) in nitric acid solution but can instead be found as a mixture of different nitrato/oxyhydroxo complexes. Plutonium has a dominant oxidation state of Pu(IV) in the form of Pu^{4+} in nitric acid, but when oxidized to Pu(VI), plutonium also forms an oxygen species, PuO_2^{2+} [MOR06, KAT86].

Table 2.3.1 Electron configuration and ionic radii for actinides relevant for partitioning and transmutation [SHA76]

Element	Electron configuration	Ionic radii for An(III) (6 coordination) (Å)
U	[Rn] $5f^3\ 6d^1\ 7s^2$	1.025
Np	[Rn] $5f^4\ 6d^1\ 7s^2$	1.01
Pu	[Rn] $5f^6\ 7s^2$	1
Am	[Rn] $5f^7\ 7s^2$	0.975
Cm	[Rn] $5f^7\ 6d^1\ 7s^2$	0.97

2.4 Fission Product Transition Metals

In a commercial nuclear reactor utilizing thermal neutrons, the fissile material in the fuel is mainly ^{235}U but also ^{239}Pu that builds up through neutron capture of ^{238}U during operation. When these elements fission, a spectrum of new nuclides, so called fission products, are formed as shown in Figure 2.4.1.

As can be seen, the fission yield stretches between elements with approximately A=75 to A=160 and is focused in two groups of mass numbers. The lighter group is centred around A~96 for uranium fission and A~101 for plutonium fission, while the heavier group is centred around A~140 in both cases. This means that a large portion of the fission products present in used nuclear fuel can be found among the 5th row transition metals: Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag and Cd. However, since the used fuel will need a certain cooling time before further processing, not all of the transition metals are relevant for partitioning and transmutation purposes. The stable isotope of niobium (^{93}Nb) is not formed during fission, so after a few years of cooling there is no niobium left in the fuel [PFE95].

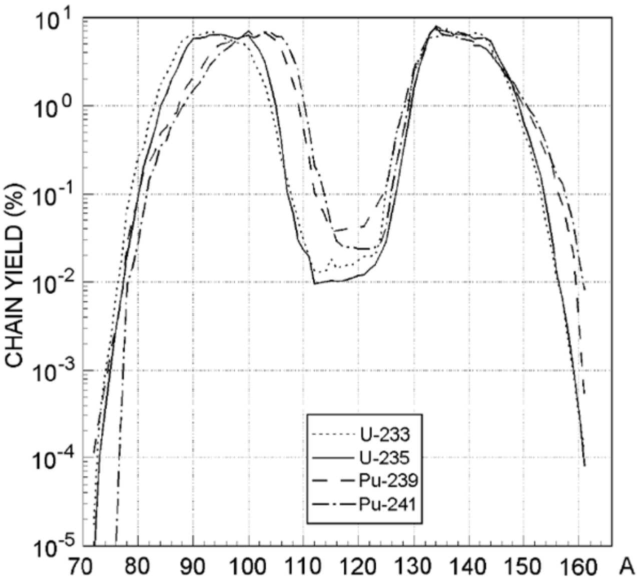

Figure 2.4.1 Chain yield curves for fission of ^{233}U, ^{235}U, ^{239}Pu and ^{241}Pu with thermal neutrons [CHO02X]

Yttrium displays chemistry very similar to the lanthanides, the other large fission product fraction, and is often even classified with them as a "rare earth metal" together with scandium. In this work yttrium will, therefore, be treated together with the lanthanides and is hence not considered further in this section.

The remaining transition metals (Zr, Mo, Tc, Ru, Rh, Pd, Ag and Cd) are, however, important to consider for separation and transmutation purposes as most of them are relatively abundant in the used fuel. Many also exhibit a complex chemistry in solution, displaying a large variety in coordination and possible oxidation states.

Starting from the right in the series, it can be concluded that the most common oxidation state for cadmium is Cd(II) and that cadmium most often forms tetrahedral complexes. Cadmium, like the other group 12 elements, lacks d orbital contributions in bonding and is hence more easily oxidized than its adjacent neighbour in group 11, silver. The most common oxidation state of silver is Ag(I), which tends to form linear complexes. The rest of the 5th row transition metals only rarely form simple $M^{2+}_{(aq)}$ ions. However, with ligands other than water (preferably π-donors), stable complexes can be formed [SHR99]. In nitrate solution and strong nitric acid, such as in fuel dissolution liquor, palladium is stable in the divalent state, while rhodium under the same conditions is only stable in the trivalent state [KOL03]. Pd(II) forms square planar complexes, as does rhodium, in the form of Rh(I). What these types of complexes have in common is that they readily undergo ligand substitution and oxidative addition [SHR99]. This is why the late transition metals are commonly used as catalysts for different chemical reactions. They can therefore also react with organic compounds, which could be problematic in a solvent extraction environment. Another problematic feature is that the platinoid ions, such as palladium, can also be easily reduced to their metallic state by other species and hence precipitate [KOL03]. Unlike palladium, ruthenium in its divalent state forms octahedral complexes with its ligands.

However, in nitric acid solution, ruthenium is present as Ru(III) in a variety of neutral and cationic nitrosyl nitrato complexes with coordination number 6, e.g. $[RuNO(NO_3)_2OH(H_2O)_2]$ and $[RuNO(NO_3)_2(H_2O)_3]^+$ [BLA81, BLA84]. The earlier transition metals, in particular, molybdenum and technetium in the 5th row, can readily assume very high oxidation states. Metals in high oxidation states typically occur as oxoanions in aqueous solution, such as the tetrahedral molybdate (MoO_4^{2-}) and pertechnetate (TcO_4^-). This means that when solvating ligands are used in a solvent extraction system, these types of ions can be co-extracted as counter ions instead of, e.g., nitrate. Among the 5th row transition metals, Mo(VI) also has a tendency to form polyoxometallates in acidic solution, and the higher the acidity, the larger the complexes formed [SHR99]. The formation of these types of polymeric species would undoubtedly influence the molybdenum extraction in a solvent extraction system. Unlike molybdenum and technetium, zirconium is commonly found in solution as highly hydrolysed tetrahedral Zr^{4+}. This is also the case in nitric acid solutions, although the atoms coordinating to zirconium are then nitrates instead.

2.5 Radiolysis

In a partitioning for transmutation process, a vast amount of ionizing radiation will be present, originating from the radioactive materials in the used nuclear fuel. This radiation will affect both the aqueous and the organic phase in a solvent extraction process. For this reason it is important that the organic molecules used for extraction are stable to radiolysis (decomposition by radiation [CHO02Y]). This, to ensure there is no significant impairment of the efficiency of the extraction system during the process. The reactions that follow the irradiation of a solvent and an aqueous phase can be either direct or indirect. In direct reactions, the ionizing radiation interacts with the molecule in question, whereas in indirect reactions, the molecule in question interacts with radicals or ions formed after a direct reaction [DAI48].

In a solvent extraction system the most common reaction is that the extractant molecules undergo indirect reactions with radicals formed by direct reactions between the ionizing radiation and the diluent or the aqueous phase. In some cases a molecule can act as a radical inhibitor by reacting with the free radicals or solvated electrons in a solution. This kind of molecule is called a radical scavenger and can protect a solvent against damage from indirect reactions after irradiation. In a component mixture it is also possible for one compound with a lower ionization potential to protect another compound with a higher ionization potential from the direct reactions with radiation by being consumed itself.

When an aqueous phase consisting of aerated strong nitric acid (as in a P&T process) is irradiated, three main types of radicals are formed: OH, NO_3 and NO_2. When organic solvents are irradiated, organic radicals, radical cations, hydrogen atoms and solvated electrons are formed upon the direct reaction with the ionizing radiation [MIN09]. When the organic phase is in contact with aerated nitric acid of a higher concentration the only reactive species that remains in the organic phase will be the radical cation [MEZ09]. The chemistry of an irradiated two-phase system is, however, very dependent on the oxygen supply and while an aerated acidic aqueous system has an oxidizing chemistry, a sealed system will be rapidly depleted of oxygen and the chemistry will change to being reducing [MIN09X]. The possible reaction between one of the radicals mentioned above and the extractant molecule could mean that the extractant would be degraded or its complex forming ability altered by changes in the molecular structure [CLA01].

2.6 Metal Processing Through Solvent Extraction

2.6.1 The Different Process Steps

Although called solvent extraction, the process usually comprises several stages focused on results other than the extraction of a solute, such as scrubbing and stripping. The most common stages encountered in a solvent extraction process are described below.

In most cases, a solvent extraction process for metal recovery is aimed at separating one or several metals from a mixture of metals. This separation is often performed in the extraction step. In this step the aqueous feed solution containing the mixture of different metals is contacted with a fresh organic solvent. The system of choice has been specifically designed to extract one or several metals of interest available in the feed mixture and to separate them from the other metals. This can be achieved through, for example, the choice of diluent and extractant(s) in the organic solvent or through the conditions of the aqueous feed solution, such as the pH.

If the feed solution is a complex mixture of metals it is not uncommon to also extract metals other than the desired one(s) in the extraction step. This undesired extraction can sometimes be decreased or prevented by the use of complexing agents in the feed solution. These ligands then form water-soluble complexes with the metals in question to keep them from transferring into the organic phase but remain in the raffinate. This is, however, not always applicable and even if so, it is still possible that the organic extract after metal extraction could contain metal impurities. This means that the second stage in a solvent extraction process is usually scrubbing. In the scrubbing step the metal containing organic extract is contacted with an aqueous scrubbing solution to which metal impurities are transferred either by the addition of water-soluble complexing agents or through the choice of conditions such as ion strength. Metal impurities are, however, not always the target in the scrubbing step; there may sometimes be a desire to remove, e.g., extracted acid from the organic phase.

After scrubbing, the extract only contains the metals of interest, with possibly some small amounts of impurities. For further processing, it is almost always desirable to have the metals in an aqueous solution. Consequently, the third stage of a solvent extraction process is most often stripping (or back extraction). In this step the extract is contacted with a strip solution to transfer the metal(s) of interest from an organic to an aqueous medium. This can be done by, for example, the use of complexing agents or through the choice of conditions, such as pH. In this step the purity usually increases further by the fact that remaining impurities from the extraction and scrubbing stay in the organic phase when the desired metals are stripped. If there are several metals of interest present in the extract and further processing requires their separation, it is sometimes possible to perform a separation in the stripping step too. This can be done by, for example, utilizing oxidizing/reducing agents to change the prerequisite for extraction for one or more of the metals, hence allowing them to be released by the organic phase and recovered in the aqueous one. The strip solution can then be removed and replaced with another one where the other metal(s) are recovered. If traces of metal impurities now remain in the organic phase, it is important to introduce a clean-up step to be able to recycle the organic solvent into the process without the accumulation of undesired metals.

2.6.2 Contacting Equipment

The choice of contacting equipment is vital for the outcome of a solvent extraction process and is dependent on the application as well as the type of extraction system used. In addition to physical properties such as kinetics, other important factors in the choice of equipment include the system's tendency to form emulsions, third phases (whereby the organic phase splits into two layers upon loading [RAO96]) and crud (a gelatinous organic/aqueous emulsion stabilized by solid particles [BOU67]). There are three main types of contacting equipment: mixer settlers, centrifugal contactors and columns [TRE56, MUR79].

Mixer settlers have a large hold-up volume and a long residence time. This makes them suitable for systems with relatively slow kinetics. As they are cheap, relatively insensitive to precipitation and crud formation and easy to scale up, they are also suitable for large-scale solvent extraction. Consequently, mixer settlers are commonly used within for example the mining industry.

Centrifugal contactors have a very short residence time, requiring systems with fast kinetics. They also have a low hold-up volume, which is practical in the case of reprocessing to avoid criticality risks during the process. In these types of processes any type of plutonium precipitation must also be avoided for criticality reasons, especially since the centrifugal contactors are very sensitive to solid impurities. As phase separation is facilitated using centripetal force rather than gravity, this enables good phase separation. Centrifugal contactors are, however, mechanically complicated and hence difficult to maintain and scale up.

Columns are usually of simple construction and can be made with a large number of theoretical ideal steps in one unit. This means that the number of steps dictates the hold-up volume of the equipment, which is not discrete per step. The residence time is in general shorter than for mixer settlers but not as short as for centrifugal contactors. Columns cannot cope with large variations in organic to aqueous ratio or flow rates and also require more difficult calculations compared with mixer settlers.

2.6.3 Flow Sheet Calculations

In a solvent extraction process it is important to be able to predict the behaviour of a system in the equipment to be used before scaling up. To do this, it is necessary to complement the experimental data obtained with flow-sheet calculations and also flow-sheet computer modelling. There are three types of schematic flow sheets that can be used for extraction: co-current extraction, counter-current extraction and cross-current extraction [COX04]. The most efficient type of flow sheet, which is also by far the most commonly used one, is counter-current extraction. The concentrations of the solute in the extract (y_n) and raffinate (x_n) in such a process with n stages can be calculated according to Equation 2.6.

$$x_F + \Theta y_F \frac{P^n - 1}{P - 1} = x_n \frac{P^{n+1} - 1}{P - 1} \tag{2.6}$$

where x_F and y_F are the feed concentrations, $P=\Theta^*D$, D is the distribution ratio and Θ is the ratio between the flow rate of the organic and the aqueous feed in the process [LLO04].

3. Development of the GANEX Process

3.1 Solvent Components

In recent years, there has been increased interest in mixed solvents for implementation in the separation of actinides and lanthanides [LUM10]. Examples of such processes include the adaptation of the DIAMEX/SANEX processes utilizing HDEHP and DMDOHEMA in TPH [MIG07] or TODGA and DMDOHEMA in kerosene [BRO12] for GANEX purposes. The GANEX extraction system that has been developed within this work combines the PUREX process with the SANEX process. One class of molecules that have been developed for SANEX purposes is the BTBP-type molecules. They have the ability to separate trivalent and pentavalent actinides from trivalent lanthanides [DRE05, RET07]. TBP on the other hand, which is utilized in the PUREX process, is known to extract uranium and plutonium [BUR58]. By combining these two molecules, it should be possible to extract all the actinides simultaneously from the used fuel and to avoid the complicated process of redox control of, e.g., plutonium and neptunium. The choice of diluent is important in this solvent composition to be able to utilize the maximum capacity of the BTBP extractant with regard to factors such as kinetics of extraction and solubility, as BTBP type molecules are known for their slow kinetics and low solubility in alkane diluents. One diluent that fulfils these demands is cyclohexanone [RET07X, EKB10].

3.1.1 BTBP-type Molecules

BTBP (*bis*-triazin-*bi*-pyridine) refers to the nature of the central core common to all the molecules in the family (Figure 3.1.1 left). This is a group of polyaromatic, nitrogen donor ligands that can act as tetradentate chelating ligands to metal ions. A wide range of BTBP-type molecules have been explored as ligands for liquid-liquid extraction within separation for transmutation [EKB08]. This is because these molecules have been observed to have a high selectivity towards trivalent actinides over trivalent lanthanides [NIL05, FOR05, NIL06], which can be explained by the larger amount of covalence in the nitrogen-An(III) bonds compared with the nitrogen-Ln(III) bonds [MIG05].

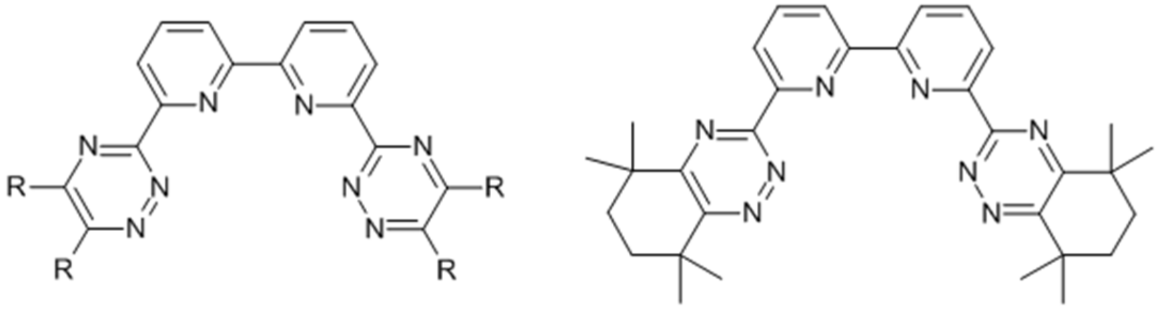

Figure 3.1.1 The bis-triazin-bi-pyridine (BTBP) core molecule(left) and the molecular structure of (6,6'Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine) ($CyMe_4$-BTBP) (right).

The BTBP-type molecules act as solvating agents in a class C extraction process. From nitric acid media, for example, which is the case in reprocessing, they extract trivalent actinides together with nitrate ions into the organic phase. The stoichiometry of a complex between BTBP molecules and a trivalent actinide in nitrate media has been shown to be $[An(BTBP)_2(NO_3)_3]$. The BTBP molecules have also been shown to extract the pentavalent actinide NpO_2^+ in what seems to be a 1:1 complex, while Th(IV) and U(VI) are known not to be extracted [RET07]. The extraction properties of the BTBP-type molecules are highly dependent on the side groups (denoted R in Figure 3.1.1 left) and different attachments to the BTBP core molecule. These properties include extraction and separation ability, solubility, kinetics of extraction and stability to irradiation [RET07, EKB07]. The BTBP molecule that was chosen for this GANEX solvent is the $CyMe_4$-BTBP (Figure 3.1.1 right). This specific BTBP has proven to be relatively stable against both high acidity and radiolysis [GEI06, RET07Y]. This can be explained by the fact that, compared with other BTBPs with straight chained aliphatic side groups, the branched rings of the $CyMe_4$-BTBP do not give opportunity for alpha hydrogen abstraction by, e.g., nitrous acid radicals in the nitric acid.

3.1.2 TBP and DEHBA

Tributyl phosphate, or TBP (Figure 3.1.2 left), is a commonly used extractant and phase modifier in solvent extraction. TBP, which is considered to be a hard Lewis base, has a well-documented ability to extract uranium and plutonium directly from dissolved used nuclear fuel [BUR58].

Metal extraction with TBP follows the solvation extraction mechanism (class C) just like the BTBP-type molecules. For example, in the case of uranyl extraction the complex has been shown to be $UO_2(TBP)_2(NO_3)_2$ [HEA56].

Despite its wide use in industrial reprocessing, there are some disadvantages connected to the use of TBP as an extractant. TBP is decomposed during both hydrolysis and radiolysis resulting in undesired decomposition products that affect the performance of the solvent. The primary degradation product is di-butyl phosphoric acid (HDBP), although mono-butyl-phosphoric acid and phosphoric acid can also be found in small amounts [SCH84, BUR59]. HDBP promotes crud formation and changes the performance of the extraction system by strong complexation with, first and foremost, plutonium, which complicates the subsequent stripping procedures [SHE58]. In the PUREX process these decomposition products are removed from the organic phase, before recirculation, in a solvent clean-up step using, e.g., sodium carbonate [HOR80].

Because of the above-mentioned drawback of the TBP molecule, the GANEX solvent was also tested, replacing TBP with a monoamide, di-(ethyl-hexyl)butyr amide (DEHBA) (Figure 3.1.2 right). DEHBA has been previously investigated as a replacement for TBP within reprocessing and has shown adequate distribution ratios towards both uranium and plutonium [PRA97]. DEHBA is degraded to almost the same extent as TBP but with possibly less problematic degradation products, the corresponding carboxylic acid and amine [CLA01].

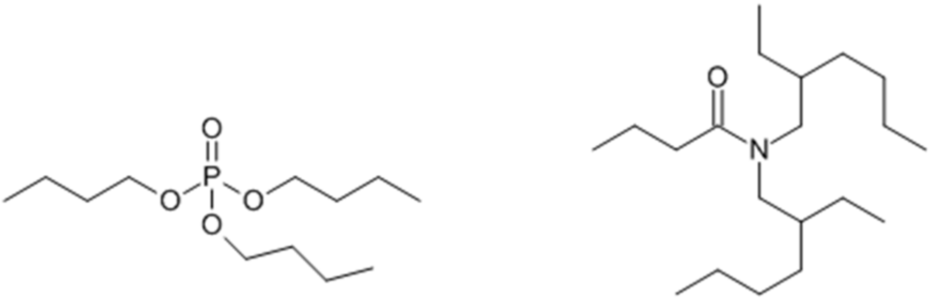

Figure 3.1.2 Molecular structures of left: tri-n-butyl phosphate (TBP), right: di-(ethyl-hexyl)butyr amide (DEHBA)

3.1.3 Cyclohexanone

The BTBP-type molecules are known to have a low solubility in alkane diluents [AND05] but a significantly higher solubility in more polar diluents like cyclohexanone. In the same way, the distribution ratios for BTBP-type molecules are higher in more polar diluents [EKB10]. It has also previously been shown that CyMe$_4$-BTBP display fast extraction kinetics when cyclohexanone is used as a diluent [RET07X]. Despite this there are, however, some other less positive features about using cyclohexanone as a diluent that must be taken into consideration. Cyclohexanone is not completely immiscible with water. The solubility of water in cyclohexanone is as high as 8.0 weight % at 25°C [MAR04]. This could give rise to solvent losses and changes in phase volume in an industrial solvent extraction process. That problem can, though, be avoided by pre-equilibrating or, if possible, recirculating the phases. Cyclohexanone is also known to extract some fission product metals, like technetium, [BOY60] and to react exothermically with concentrated nitric acid, forming adipic acid [HAM51]. Despite these downsides, using cyclohexanone as a diluent for the previously discussed GANEX solvent containing CyMe$_4$-BTBP and TBP is the best available option at present.

3.2 Investigations and Considerations

To determine whether the proposed GANEX solvent is suitable for process purposes or not, a number of different investigations must be undertaken.

3.2.1 Screening of the Extraction Behaviour

One of the first things in need of investigation is the actinide extraction, in order to see if the proposed GANEX solvent can perform its main task. In connection to this it is also important to see whether the solvent can also perform one of the most difficult separations, i.e. between the trivalent actinides and the trivalent lanthanides. If both these criteria are met, then the behaviour of the solvent can be more thoroughly studied. One vital feature is to determine if the different components in the solvent react with each other or not. If they do not react, then experiments can be conducted to see which of the possible extractants (in this case three: BTBP, TBP and cyclohexanone) extract which actinide. This also reveals if there are any major synergistic or antagonistic tendencies in the system. Although synergism can, in some respects, be desirable to increase the extraction, any types of interaction between the different solvent components also complicates the system regarding future computer modelling and understanding. It is also important to determine at an early stage how the system behaves regarding kinetics, as a very slow system is generally unsuitable for process applications.

To take all these aspects into account extractions of actinides and lanthanides have been made using both the GANEX solvent as well as the solvents different components.

3.2.2 Stability

As in a GANEX process the aqueous phase will consist of strong nitric acid (approximately 4 M), it is important that the solvent used is sufficiently stable to this acid so that it does not lose its extraction capability. Nitric acid has the possibility to both oxidise and nitrate organic molecules [ATK65], often taking the reaction route via nitrous acid (HNO_2). Nitrous acid is naturally present in nitric acid of low and adequate strength and is produced during irradiation [LON54, MIN09]. Hence, another vital factor regarding stability is the radiolysis of the solvent. The solvent in a GANEX process will be subjected to ionizing radiation, both in the form of α-, β- and γ-radiation, and it is therefore possible that either the extractants or the diluent will be degraded by indirect or direct interactions with the radiation (see section 2.5). The large amount of radiation will also result in an increase in temperature and accordingly there are three different variables that need to be taken into account when considering the stability of a solvent for partitioning and transmutation purposes; acidity, radiation and temperature.

The GANEX solvent has been subjected to long-term hydrolysis studies with nitric acid as well as radiolysis. In the radiolysis studies the solvent has undergone gamma irradiation at high dose rate and elevated temperature in contact with nitric acid, in order to try to mimic process conditions. The diluent has also been specifically investigated regarding reactions with nitric acid as well as extraction at elevated temperatures.

3.2.3 Fission and Corrosion Product Handling

In addition to the actinides, large amounts of different fission and corrosion/activation products will also be present in the aqueous phase in a GANEX process. The extraction of these with the GANEX solvent needs to be thoroughly investigated. If it is discovered in extraction tests that some fission products (FP) and/or corrosion/activation products (CP) are extracted by the GANEX solvent, this can be considered to be a problem. The focus ought to be placed on the elements that are present in high abundance in the spent fuel and that have a distribution ratio close to or above one. There are different strategies for handling this undesired extraction. Three main strategies can be identified, all of which have both advantages and disadvantages in comparison with each other: 1 – Pre-extraction, 2 – Scrubbing and 3 – Suppression (Figure 3.2.1).

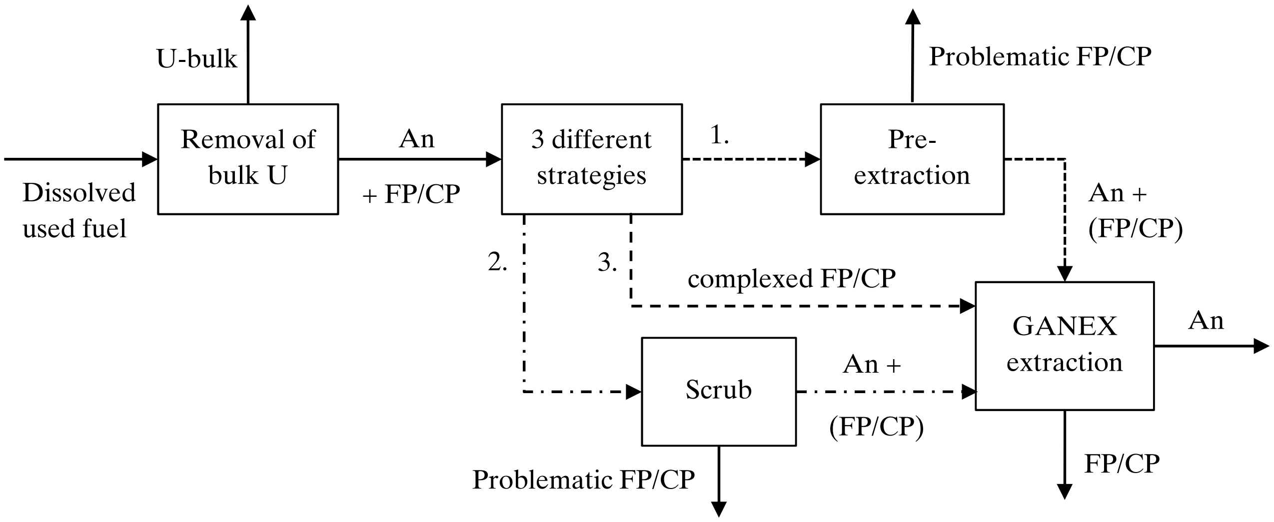

Figure 3.2.1 Schematic picture of three different ways of handling a potential fission product problem in the GANEX process: 1 Pre-extraction, 2-Scrubbing, 3-Suppression

In pre-extraction, an extraction step is introduced before the actual GANEX process in which some of the more problematic FP and CP are to be removed without affecting the actinides. However, by introducing an extra step in the process, the amount of waste generated will be larger. There is also a risk of losing some of the actinides in this pre-extraction step.

In scrubbing, some of the FP and CP are allowed to be co-extracted with the actinides by the GANEX solvent. After this, a step is introduced in order to scrub them out of the organic phase without the loss of any of the actinides. Just as in the pre-extraction scenario, the introduction of an extra step in the process is undesirable. It is also possible that the co-extraction of FP and CP inhibits the actinide extraction in the actual GANEX process, making it less effective.

In suppression, the idea is to add a complexing agent to the aqueous phase to form stable water-soluble complexes with the FP and CP in question. This will then inhibit the extraction of these metals with the GANEX solvent. With this method, no extra step is introduced in the process, but, on the other hand, new chemicals are introduced into the GANEX step, making both the extraction conditions and the waste handling (vitrification) more complicated.

In this work, the general extraction behaviour of a range of fission products has been investigated. A number of molecules have also been screened for all three handling strategies to see which offers the best solution for the specific system, or if a combination of several strategies is preferable.

3.2.4 Towards Process Implementation

When a solvent has been identified as performing adequately with regard to extraction, separation, stability etc., there are still several factors that need investigation to see if the system is suitable for process implementation.

The effect from fission product loading of the aqueous phase on, e.g., actinide extraction and kinetics of the system has to be studied. Once the actinides have been extracted and separated from undesired fission products, investigation of their stripping efficiency must also follow. This is because further processing of the actinides will have to continue from an aqueous phase.

When all parts of the process have been investigated one by one, they have to be investigated as a whole. Firstly, each part is performed in batch experiments, but following each other. This is in order to see whether one step influences the following one in a positive or negative way and, if this is the case, how this must be taken into consideration. Secondly, continuous single-stage experiments must be performed to investigate flow rates and kinetics of the system in the equipment of choice before finally moving towards multi-stage pilot scale process tests. This also allows for consideration of whether the chosen equipment really is the most suitable one.

In this work, the influence on fission product loading has been investigated with regard to both actinide extraction and kinetics. These investigations were made in preparation for a batch process test as well as a single centrifugal contactor test, which were both also performed.

4. Experimental

Many of the experiments in this work have been performed using the same standard composition of the organic phase: 0.01 M CyMe$_4$-BTBP and 30% (by volume) TBP in cyclohexanone. This solvent will therefore be referred to as “the GANEX solvent” from now on. The CyMe$_4$-BTBP was synthesized in-house according to [FOR06].

4.1 Solvent Extraction Experiments

Several different sets of extraction experiments have been performed during the course of this work. All were conducted in a similar way and hence a standard extraction experimental procedure is given here:

3.5 mL glass vials with plastic stoppers or 2 mL glass vials with plastic screw tops were used for the major part of the extraction experiments. The phases were of equal volume between 200-1000 µL. Due to the mutual solubility of the solvent(s) and the acidic water phase(s), both phases used for extraction were in most cases pre-equilibrated with the corresponding aqueous/organic solution. When radioactive isotopes were used, the metals were added in trace amounts by spiking the aqueous phase with small volumes of concentrated stock solutions (2-40 µL) after pre equilibration. The actinides (^{235}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{244}Cm), one lanthanide (^{152}Eu) and one of the corrosion products (^{63}Ni) were in all cases added in the form of radioactive tracers. The inactive metals were, unless otherwise mentioned, present in concentrations close to those that can be found in real dissolved spent fuel [GAR94, CHI96, MAL00, SER05] (Appendix A). When inactive metals were used, the metals were also present in the aqueous solutions during pre-equilibration. The phases were contacted either by vigorous hand-shaking in an insulated canister or through a mechanical shaker (IKA VIBRAX VXR) equipped with a custom-made sample holder (horizontal placement) connected to a thermostatted water bath. The contact times used were sufficient for the relevant extraction to reach equilibrium except when kinetics experiments were performed. After contact, the phases were left to separate either by gravitation or centrifugation. When the phases were completely separated, a sample from each phase was removed for radiometric analysis. When inactive metals were analysed by ICP-OES, samples were instead taken from the aqueous phase only, before (but after pre-equilibration) and after contacting. With this method, it is assumed that all metal that is not found in the aqueous phase is present in the organic phase.

The batch extraction process tests differed from the protocol described above. They were performed using large test-tubes (10 ml) with Teflon screw caps and a vortex shaker for contacting the phases (contact time in all cases 5 min; not sufficient to reach equilibrium). The phase volumes were between 1-4 ml and of equal size.

4.1.1 Centrifugal Contactor Test

The single centrifugal contactor tests were performed at IEK-6, Forschungszentrum Jülich, Germany, using a W-10 contactor manufactured by INET (Tsinghua Univ. China). The aqueous and organic phases were inserted into the centrifuge using syringe pumps and the experimental setup can be seen in Figure 4.1.1 below. The centrifuge was operated at a speed of 4,500 rpm for the extraction and acid scrub stages and at 3,500rpm for the stripping stage to facilitate efficient phase separation.

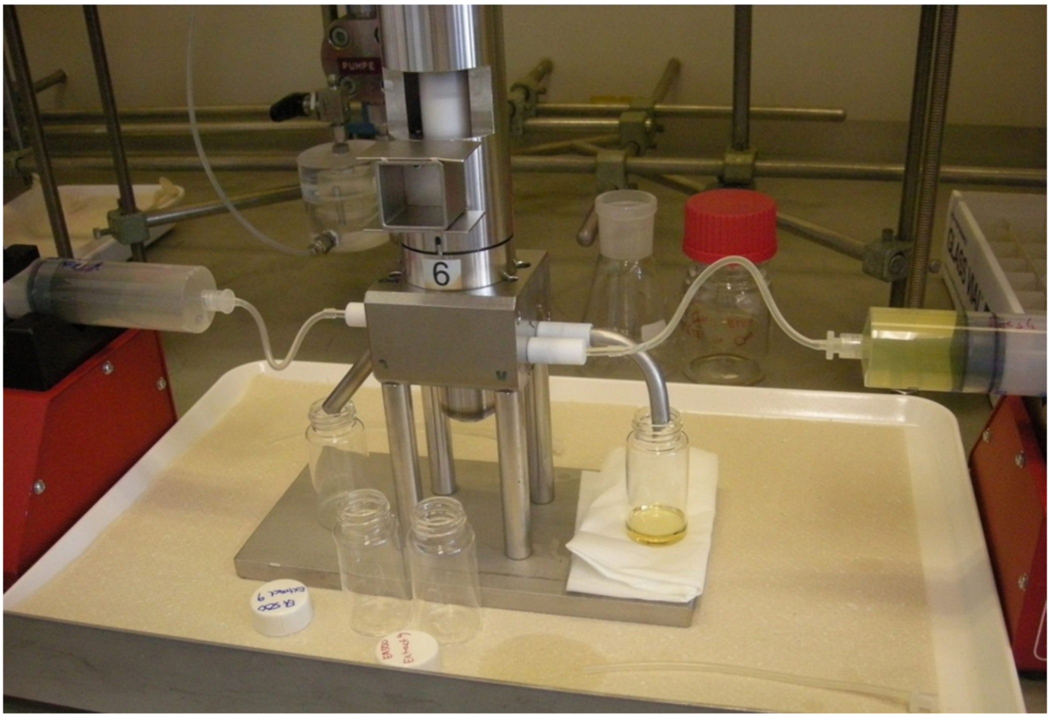

Figure 4.1.1 Experimental setup for the single centrifugal contactor test. Aqueous phase inlet and outlet to the left and organic phase inlet and outlet to the right

The two phases used for extraction were pumped into the centrifuge using the same flow rates for both phases (60 mL/h) and samples were withdrawn for analyses after certain periods of time (every 1, 2 or 5 minutes) to see when steady state was reached. Both pumps were then stopped, the flow rate lowered (30 mL/h) and the system started again. In the same way as for the higher flow rate, samples were removed on a regular basis and the system was allowed to pump until the organic phase was consumed. The centrifuge was then dismantled and the content of the mixing chamber transferred to a test tube (10 mL) that was shaken on a vortex shaker for 15 minutes to retrieve equilibrium data. After HPGe measurements and sample removal for alpha spectrometry and ICP-MS analyses, all collected organic phases were combined into one, which was also sampled. The combined organic phase was then used for the next stage in the process (acid scrub, then stripping) and the procedure repeated.

4.2 Stability

The extraction system has been investigated with regard to different aspects of stability described in this section.

4.2.2 Radiolysis and Hydrolysis

Irradiations were performed using two different ^{60}Co γ-sources: a Gammacell 220 from Atomic Energy of Canada Ltd. (located at Chalmers) and an Issledovatel (located at Instytut Chemii i Techniki Jadrowej in Warsaw, Poland). The dose rate in the Gammacell was between approximately 18 and 13 kGy/h (due to decay), rendering an elevated temperature of approximately 50°C, while in the Issledovatel the dose rate was 0.939 kGy/h and the temperature between 23°C and 25°C. Samples were irradiated in glass containers with either an organic phase only or with an organic phase in contact with an aqueous phase (in all cases 4 M HNO_3). The organic and aqueous phases were always of equal volume, contacted before insertion into the source by hand-shaking the containers and then left in stagnant contact during the irradiation. After irradiation, all extraction experiments were conducted using the irradiated organic phase and a fresh aqueous phase (pre-equilibrated with fresh organic). Reference samples were made when applicable.

For the hydrolysis tests, glass vials were filled with an equal amount of organic solvent and aqueous phase (4 M HNO_3). The phases were contacted by shaking the vials a few times before the experiments were started and before each sampling. The vials were left to stand in a semi-dark environment at room temperature and samples were withdrawn for extraction experiments after different lengths of time. Just as for the irradiated samples, extractions were performed using fresh aqueous phase pre-equilibrated with fresh organic.

4.2.3 Diluent Stability

The possible occurrence of an exothermic reaction between the diluent (cyclohexanone) and nitric acid upon heating was investigated using a home-made calorimetry machine. The calorimeter consisted of a test tube (connected to a liebig condenser) equipped on the outside with a thermostated electrical heater placed inside a thermos flask. The neck of the flask was packed with glass wool during operation to improve the thermal insulation of the reaction mixture.

The acidic water phase (4 M HNO_3) was added to the flask first and heated to the decided temperature. When the system had reached a steady state, the organic phase (30% TBP in cyclohexanone) was inserted into the flask and heating continued to keep the mixture at the desired temperature. The volume of the combined phases was at all times 8 mL, ensuring efficient heating in the lower part of the test tube. During the entire process, the supply of electrical current was monitored as well as the temperature of the flask. When the temperature increased above the set-point due to heat released from the chemical reaction in the mixture, the electrical heating was automatically stopped. Therefore an exotherm could be observed not only as an increase in temperature but also as a reduction in the average current supplied to the heater.

4.5 Analysis

In this work γ-analyses were made using HPGe (Ortec: GEM 15180-S, GEM 23195) and NaI(Tl) (Intertechnique GC-4000), α- and β-analyses with α-spectrometers (Ortec: alpha duo, Octête TM PC) and liquid scintillation spectrometry (Wallac 1414 WinSpectral), inactive metal analyses with ICP-OES (Thermo iCAP 6500) and ICP-MS (Perkin Elmer Elan 6100 DRC), organometallic complex analyses with NMR (Varian Agilent 400) and neptunium oxidation state controls were performed using spectrophotometry (Perkin Elmer Lambda 19).

For all analyses of distribution ratios of active samples, the same detector was used to measure both the organic and the aqueous phase. For α-spectrometry analyses of samples with high salt and/or sugar content in the aqueous phase, all results were corrected using internal standards also measured using HPGe (^{241}Am or ^{235}U). Liquid scintillation counting was conducted using several different cocktails: Emulsifier safe, Ultima Gold AB and HIonic. However, these were always the same for both phases when calculating distribution ratios. In some cases when the samples were highly coloured, the instrument's internal ^{152}Eu source was used to correct for colour quenching or quench curves made. For ICP-OES analyses, dilutions were made using 0.1 M HNO_3, supra pure (SP). For ICP-MS analyses, dilution was made using 1% HNO_3 (65%, SP) and for the organic samples, an addition of 2% TritonX-100 was also made. NMR analyses were performed by adding a small amount of organic sample to deuterated benzene. When aqueous samples were to be analysed, the experiments had been performed from the start using acid made from heavy water, meaning that no further sample preparation was necessary.

In all cases, any uncertainties have been calculated using error propagation based on measurement statistics. Where slopes have been given, these have always been calculated for data points with an $R^2>0.99$ and uncertainties given with 95% confidence, unless otherwise stated.

5. Results and Discussion

5.1 Actinide Extractions and An/Ln Separations

The results presented in this section are based on Paper I, and IX as well as unpublished material. In all cases, the extracted metals have been used in trace amounts.

5.1.1 General Extractions

According to the discussion in section 3.2.1, the GANEX solvent was first evaluated regarding its potential for actinide extractions as well its ability to separate actinides from the lanthanides. As can be seen in Figure 5.1.1, the actinides are readily extracted from 4 M nitric acid and could also be separated from the lanthanides, in this section represented by europium ($SF_{Am/Eu}$=160).

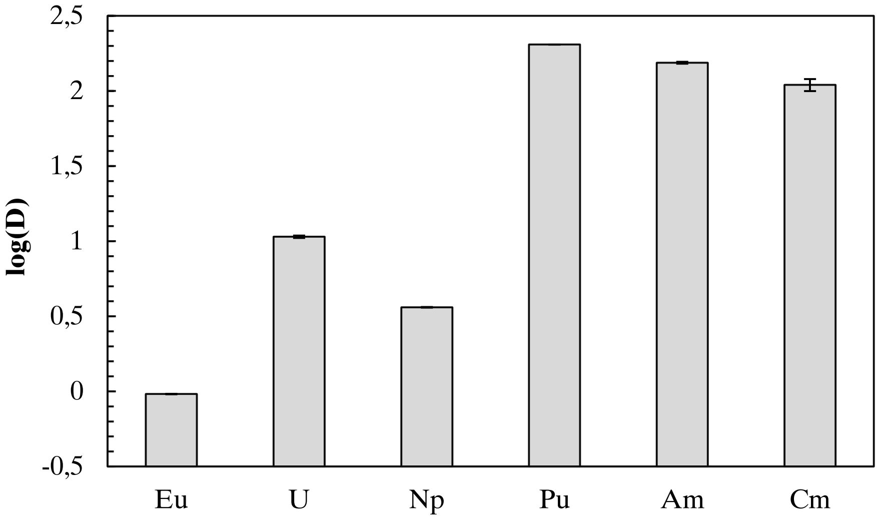

Figure 5.1.1 Extraction of actinides (^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am, ^{244}Cm) and one lanthanide (^{152}Eu) from 4 M nitric acid with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone

Not included in Figure 5.1.1 is the actinide protactinium, which, because of its very low abundance and, in particular, nuclides with a short half-life, is planned to follow the fission product fraction in a GANEX process. The extraction of protactinium with the GANEX solvent is also very small (D_{Pa}=0.33), as wanted.

As the behaviour of americium and curium is very similar due to their similarity in size and charge (according to section 2.3), most experiments in the continuation of this work have been conducted using americium only. This is due to the lower amounts of curium available as well as the fact that it is more convenient to detect gamma radiation (from ^{241}Am) compared with only alpha radiation (as from ^{244}Cm). In addition, as the Am/Cm separation factor is small ($SF_{Am/Cm}$=1.4), the obtained results for americium can be expected to also be valid for curium.

To determine which of the three possible extractants in the GANEX solvent extract the different actinides and lanthanide, an extraction experiment using four different organic phases was performed: 1- 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone, 2- 0.01 M CyMe$_4$-BTBP in cyclohexanone, 3- 30% TBP in cyclohexanon, 4- cyclohexanone. This scheme also makes it possible to detect any major synergistic or antagonistic behaviour between the different solvent components. The water phase used was in all cases 1 M HNO_3 + 3 M $NaNO_3$. The reason for not using 4 M HNO_3 as in the first experiment and the real process is that when using such a high acidity, the interfacial tension between cyclohexanone (without TBP present) and the aqueous phase becomes so low that it does not allow for phase separation. The interfacial tension when using a similar nitrate concentration but a lower acidity is, however, higher. As an example, the interfacial tension between cyclohexanone and 1 M HNO_3 is 1.18±0.03 N/m compared with 5.8±0.7 N/m for cyclohexanone and 0.01 M HNO_3+0.99 M $NaNO_3$.

The extraction results are presented in Figure 5.1.2 from where it can be concluded that there are no major synergistic or antagonistic effects in the system. This result could be expected since TLC tests also showed that BTBP (in the form of C5-BTBP) and TBP did not interact with each other in cyclohexanone.

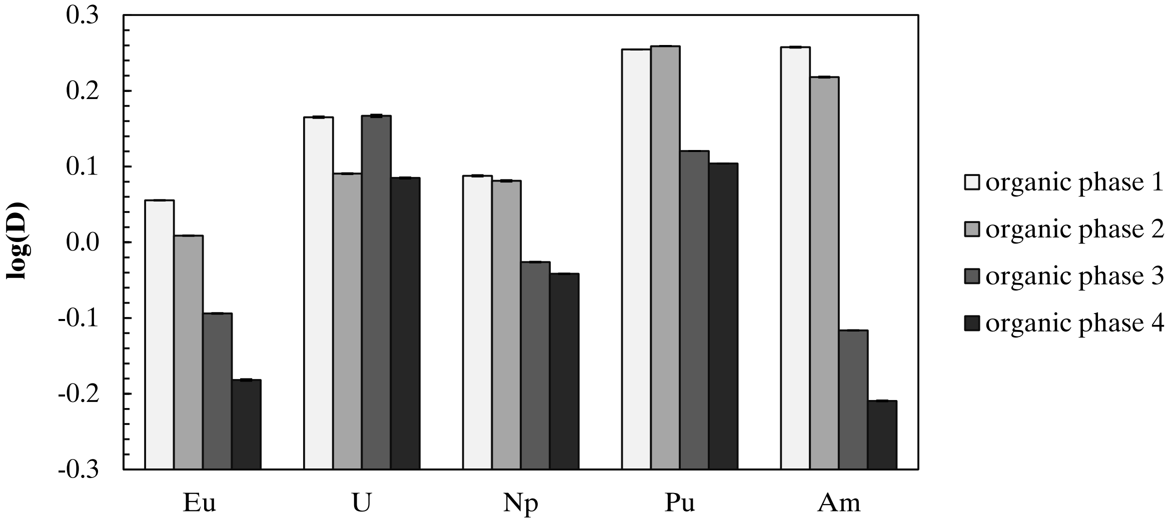

Figure 5.1.2 Extraction of ^{152}Eu, ^{235}U, ^{237}Np, ^{238}Pu and ^{241}Am from 1 M HNO_3 + 3 M $NaNO_3$ with four different organic phases: 1- 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone, 2- 0.01 M CyMe$_4$-BTBP in cyclohexanone, 3- 30% TBP in cyclohexanone, 4- cyclohexanone

It is also obvious that, as expected, both americium and europium are mainly extracted by BTBP. For both elements, distribution ratios are, however, slightly higher in the systems that have TBP present (organic phase 1 and 3) compared with the counterparts without TBP. This could be attributed to a small simultaneous extraction by TBP. Uranium is, as expected, extracted by TBP but also by the diluent cyclohexanone. Neptunium is also, to a small extent, extracted by the diluent and TBP, but mainly by BTBP. This could be expected, as the dominant oxidation state under these conditions ought to be Np(V), which has previously been shown to be extracted by CyMe$_4$-BTBP [RET07]. This was also controlled by UV-VIS spectrometry that showed a large peak for Np(V) (928 nm) but also a possible indication of a small simultaneous presence of Np(VI) (1023nm) and Np(IV) (723nm) [KAT86] in the aqueous phase before extraction (Figure 5.1.3). However, plutonium does not behave as expected and is clearly extracted by BTBP in organic phases 1 and 2. There is also an extraction by TBP (organic phase 3) as well as cyclohexanone (organic phase 4), which could be expected, but it seems that the complex formed with BTBP dominates in the GANEX solvent, as there is no real difference in distribution ratio between organic phases 1 and 2.

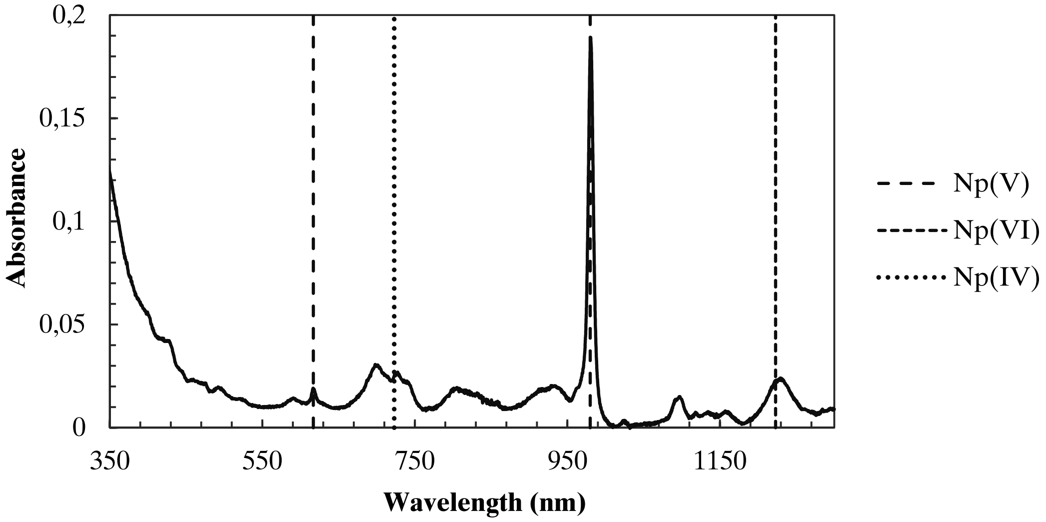

Figure 5.1.3 Spectrophotometric analysis of 1 M HNO_3 + 3 M $NaNO_3$ spiked with ^{237}Np from stock solution

5.1.2 Plutonium Behaviour

To conclude whether the plutonium extraction by CyMe$_4$-BTBP is an effect of an unexpected change in oxidation state of the plutonium or if in fact BTBP does extract tetravalent plutonium, an experiment was conducted using thenoyltrifluoracetone (TTA) extractions. TTA is known only to extract Pu(IV) [NIT88] and hence this could be used as a measure of the oxidation state of the plutonium. Extractions were made with the previously described four organic solvents as well as with TTA in toluene. To retrieve more information, the plutonium was also oxidized to Pu(VI) using ozone during the experiment.

As can be seen in Figure 5.1.4, CyMe$_4$-BTBP extracts both Pu(IV) and Pu(VI) but with a slightly lower distribution ratio for Pu(VI) compared with Pu(IV). This trend is also valid for both the TBP as well as for the cyclohexanone extraction of plutonium. This further highlights the previously established difference between plutonium and the often-used analogue thorium, as it has been shown that Th(IV) is not extracted by BTBP-type molecules [RET07, EKB00].

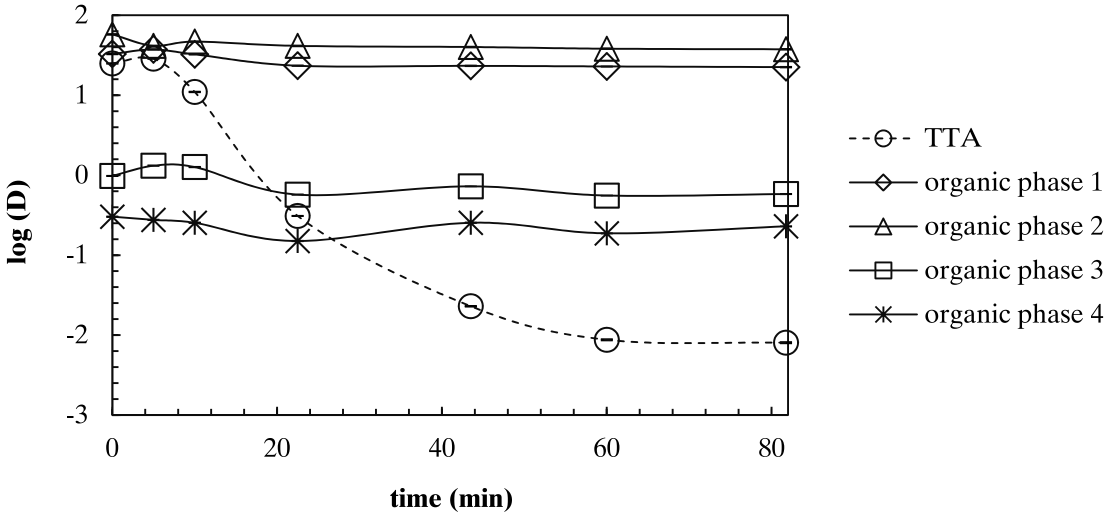

Figure 5.1.4 ^{238}Pu extractions (from 0.5 M HNO_3 + 0.5 M $NaNO_3$) performed at different times during Pu(IV)-Pu(VI) oxidation (in 3.5 M HNO_3) through ozone bubbling by five different solvents: TTA-0.25 M TTA in toluene, 1- 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone, 2- 0.01 M $CyMe_4$-BTBP in cyclohexanone, 3- 30% TBP in cyclohexanone and 4- cyclohexanone (lines added to guide the eye)

As it had now been shown that $CyMe_4$-BTBP does extract Pu(IV), a slope analysis of the plutonium extraction was performed (Figure 5.1.5). The slope was found to be 1.85±0.03 with 95% confidence. The given uncertainty is, however, only related to the linear regression and hence the achieved slope of 1.85 indicates that the number of BTBPs in the plutonium complex is two, just as for the trivalent actinides. This is also a strong indication that the oxidation state of the plutonium is Pu(IV) rather than Pu(VI), since there would not be enough room for two BTBP molecules around a plutonyl ion (PuO_2^{2+}) [RET07].

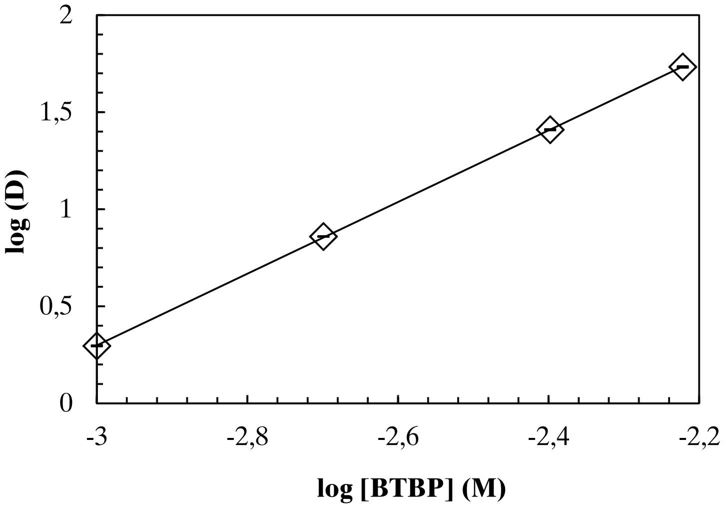

Figure 5.1.5 Extraction of ^{238}Pu from 1 M HNO_3 with different concentrations of $CyMe_4$-BTBP in cyclohexanone

5.1.3 Kinetics

The kinetics of the GANEX solvent for the actinide and lanthanide extractions were also investigated and found to be fast for all actinides and somewhat slower for the lanthanide europium (Figure 5.1.6). This behaviour has also been observed elsewhere and could hence be expected [LÖF11]. There is also an obvious difference in behaviour between uranium, which is extracted by TBP, and the rest of the elements that are extracted by BTBP. This is because no kinetic effect can be observed on the uranium extraction within the time intervals used in this experiment.

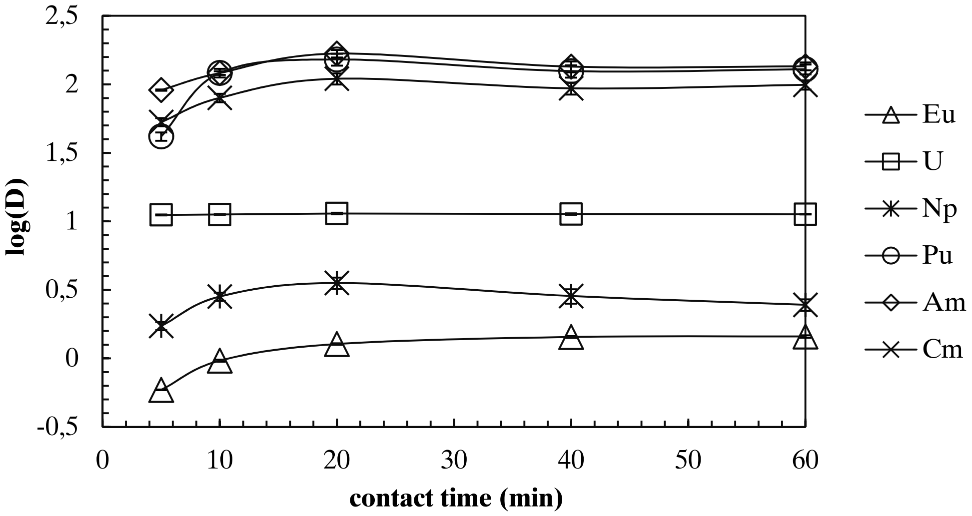

Figure 5.1.6 Extraction of actinides (^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am) and one lanthanide (^{152}Eu) from 4 M nitric acid with 0.01 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone with different contacting times (lines added to guide the eye)

5.2 Stability

The results presented in this section are based on data found in Papers II, VIII and IX as well as unpublished material.

5.2.1 Hydrolytic stability

As TBP is known to extract nitric acid (approximately 0.8 M into 30% TBP in kerosene in contact with 4 M nitric acid) [ALC56] and cyclohexanone is known to have a mutual solubility with water [MAR04], the dissolution of nitric acid into the combined GANEX solvent was studied.

The acid extraction into three different organic phases was investigated by NaOH titrations: 30% TBP in cyclohexanone, pure cyclohexanone and cyclohexanone pre-saturated with water. As can be seen in Figure 5.2.1, a large amount of nitric acid is extracted in the system and this extraction is more or less the same in all three solvents. This means that the presence of TBP does not largely affect the nitric acid extraction. Instead, the nitric acid is extracted by the cyclohexanone.

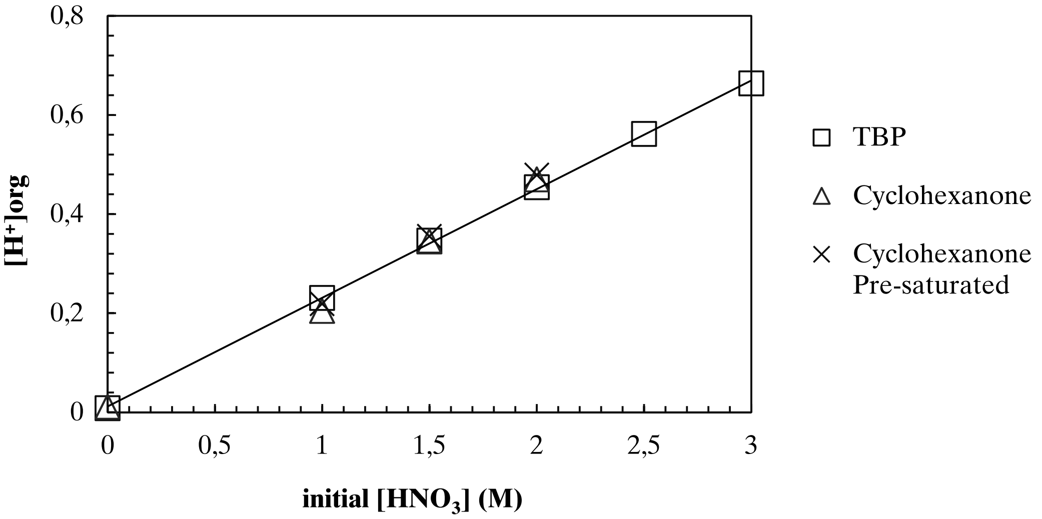

Figure 5.2.1 Acid extraction at different concentrations with three different organic phases TBP: 30% TBP in cyclohexanone, Cyclohexanone: pure cyclohexanone, Cyclohexanone Pre-saturated: cyclohexanone pre-saturated with water and aqueous phases pre-saturated with cyclohexanone

A hydrolysis test was performed to investigate the effect of the dissolved acid on the stability of the solvent during prolonged acid contact between the organic and the aqueous phase. The GANEX solvent was kept in contact with nitric acid at room temperature and after different periods of time samples from the organic phase was withdrawn and subjected to extraction tests. From the results in Figure 5.2.2, it is clear that the distribution ratios for all actinides are more or less stable over time, which means that the whole system can be considered to be hydrolytically stable in contact with strong nitric acid, even over longer periods of time.

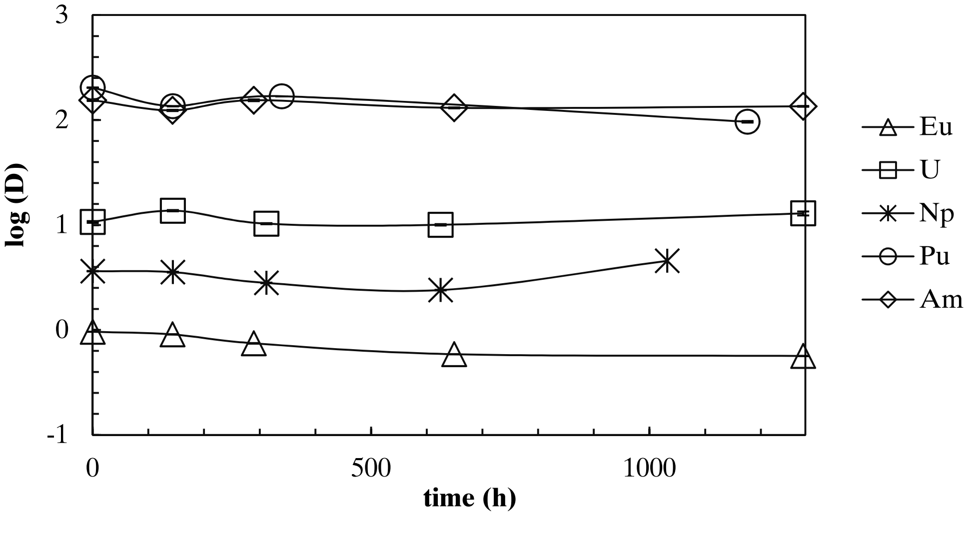

Figure 5.2.2 Extractions of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu from 4 M HNO_3 with $CyMe_4$-BTBP (0.01 M) +30% TBP after different periods of acid contact between the organic phase and 4 M HNO_3 (lines added to guide the eye)

Samples of the organic phase were also analysed with HPLC (UV detection) to determine the BTBP content (Paper II). It was observed that after a contact time of 646.5 hours between the GANEX solvent and 4 M nitric acid, the CyMe$_4$-BTBP content in the solvent had decreased to 54.5%. However, as the distribution ratios were not found to be affected to any great extent, it seems that the hydrolysis products of CyMe$_4$-BTBP also extract actinides to the same extent as the original molecule.

5.2.2 Radiolytic stability

To investigate stability to radiolysis, the GANEX solvent was irradiated in a cobalt 60-source both with and without nitric acid contact. As can be seen when comparing the results in Figure 5.2.2 and 5.2.3, the presence of nitric acid during irradiation of the solvent promotes a slightly better resistance to radiolysis. This could be caused by the radical scavenging effect of the nitric acid, removing the solvated electrons formed in the organic phase. The distribution ratios in the system containing nitric acid stay relatively stable for all extracted metals during the entire period of irradiation.

However, when comparing the radiolysis studies presented in Papers II and VIII, a discrepancy in plutonium behaviour can be observed. An explanation for this could be the large difference in latency time (the time between irradiation and extraction) between the two studies. Because of this, an investigation of the effect of latency time after irradiation in contact with nitric acid was performed. Two different series were investigated; one in which the solvent was kept in contact with the acid after irradiation (series 1) and one where the acid was removed after irradiation (series 2).

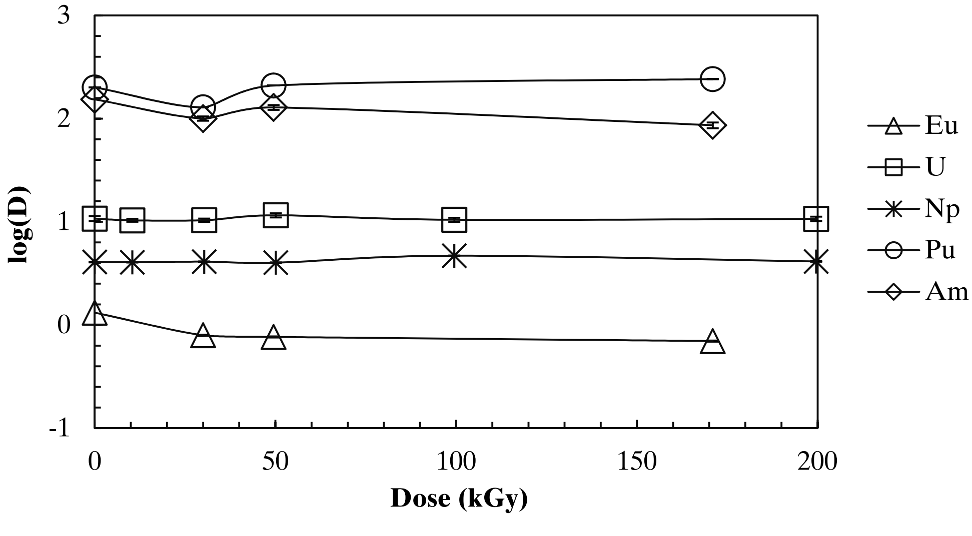

Figure 5.2.2 Gamma irradiation of 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone in contact with 4 M HNO$_3$. Dose rate approximately 0.9 kGy/h for ^{235}U and ^{237}Np extraction. Dose rate approximetly 18 kGy/h for ^{152}Eu, ^{238}Pu and ^{241}Am extraction (lines added to guide the eye)

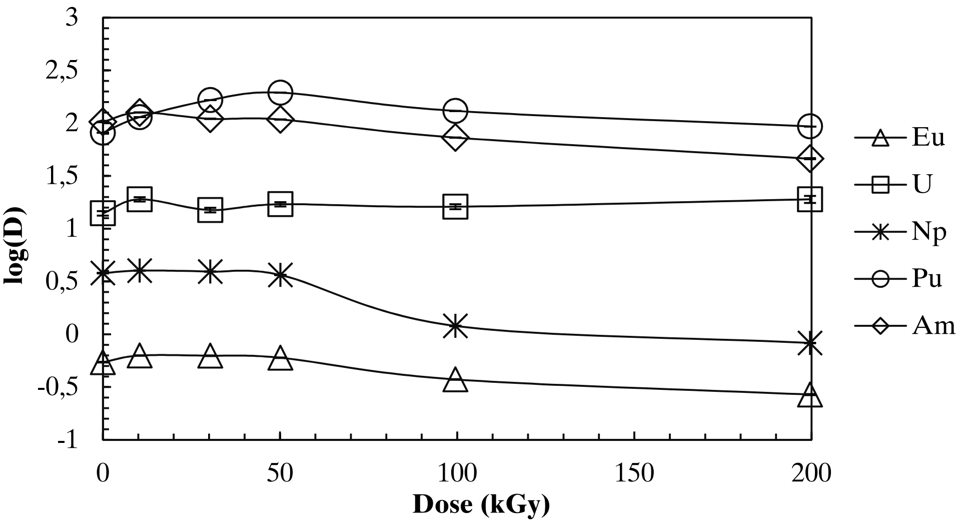

Figure 5.2.3 Extractions of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu from 4 M HNO_3 with gamma irradiated 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone Dose rate approximately 0.9kGy/h (lines added to guide the eye)

As can be seen from the results in Figure 5.2.4, the plutonium distribution ratios decreased rapidly in series 1 after removal form the irradiation source. The result is not caused by a degradation of the BTBP molecule, as the same behaviour was not observed for americium, also extracted by BTBP. Instead, the explanation could be oxidation of the plutonium from Pu(IV) to Pu(VI). In series 2, the decrease was not as prominent and more or less the same as for the reference series (solvent in acid contact at the same temperature for the same amount of time as during irradiation), leading to the conclusion that species from the acid take part in the reactions.

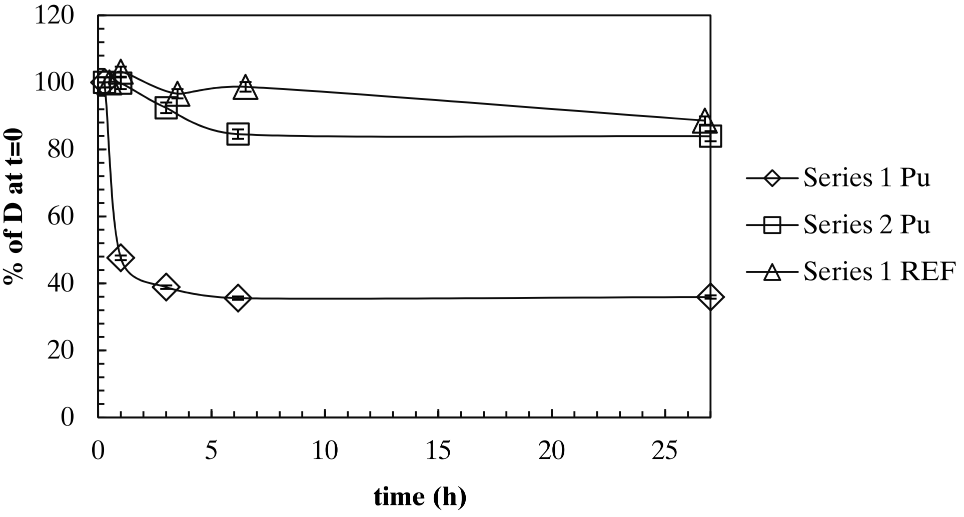

Figure 5.2.4 ^{238}Pu extractions (from 4 M HNO_3) performed at different times after removal of 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone (irradiated to 203 kGy in contact with 4 M HNO_3) from a ^{60}Co source (dose rate 13 kGy/h) or after acid contact (REF) during the same period of time and temperature. Series 1: Solvent left in contact with the irradiated acid. Series 2: Acid removed after irradiation (lines added to guide the eye)

These results highlight the importance of performing extraction experiments as soon as possible after irradiation to ensure accurate results regarding the stability of the solvent. This is because during a reprocessing process the extraction takes place during irradiation and not hours after.

5.2.3 Temperature effects

During the hydrolysis tests (section 5.2.1) the solvent was left in contact with nitric acid for several months at room temperature, without any signs of violent reactions. However, it is well known that cyclohexanone reacts exothermically with concentrated nitric acid (see section 3.1.3). Consequently, the effect of heating the solvent in contact with acid of process concentration needs further investigation. This is despite the fact that during radiolysis, the temperature inside the cobalt 60 source at the highest dose rate was around 50°C and, as could be seen in Figure 5.2.2, extractions after the solvent had been subjected to this temperature for several hours still showed high distribution ratios for the actinides.

In the previous experiments, all extractions have also been performed at room temperature. Therefore, the effect of temperature on the actual actinide and lanthanide extraction was also investigated.

Diluent Stability

To conduct this investigation, nitric acid of process concentration was heated using the electrical heater described in section 4.2.3. After the temperature had stabilized, a portion of cyclohexanone + 30% TBP was added and the temperature profile was monitored. Just like many other nitric acid oxidation reactions, the oxidation of cyclohexanone also displays a long induction time. These types of oxidations are induced by nitrous acid and therefore also highly dependent on acid concentration [CAS91]. Consequently, to induce a reaction at this low acid strength, the temperature had to be increased to approximately 53°C with an organic to aqueous ratio of 0.6. Under these conditions, however, a violent exotherm took place, as can be seen in Figure 5.2.5. After a prolonged period of heating (> 1 hour), the temperature rapidly increases to approximately 80°C and then the reaction dies off, most likely due to temporary evaporation of the solvent.

As the exothermic reaction taking place is most likely due to an autocatalytic reaction between cyclohexanone and the nitric acid, an attempt to solve the problem was made by adding a nitrous acid scavenger to the system. As can be seen in Figure 5.2.5, when adding 30 mM of sulfamic acid to the nitric acid before the start of heating, the exotherm never takes off but cools down again after a slight temperature increase of only a few degrees. When adding larger amounts of sulfamic acid (0.5 M) no temperature increase at all can be detected.

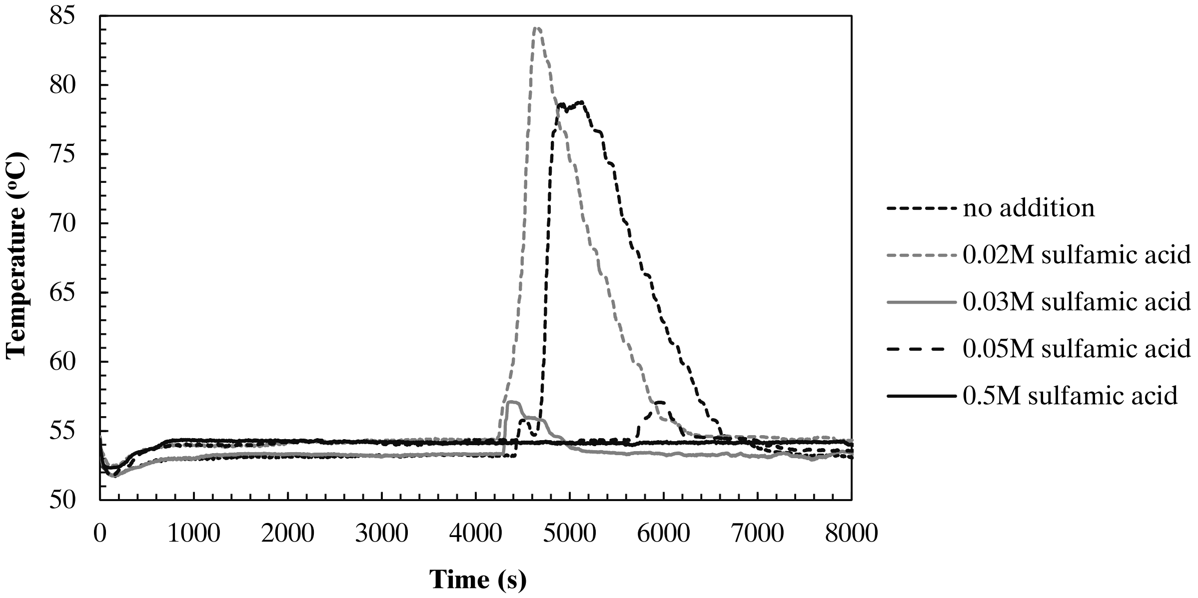

Figure 5.2.5 Temperature monitoring of 30%TBP in cyclohexanone in contact with 4 M HNO_3 (o/a ratio 0.6) upon heating to approximately 53°C

To be able to see if using sulfamic acid as an addition to the aqueous phase to stabilise the cyclohexanone affects the actinide behaviour or not, an extraction experiment was performed. As can be seen in Figure 5.2.6, the addition of sulfamic acid does not affect the actinide extraction by the GANEX solvent to any great extent.

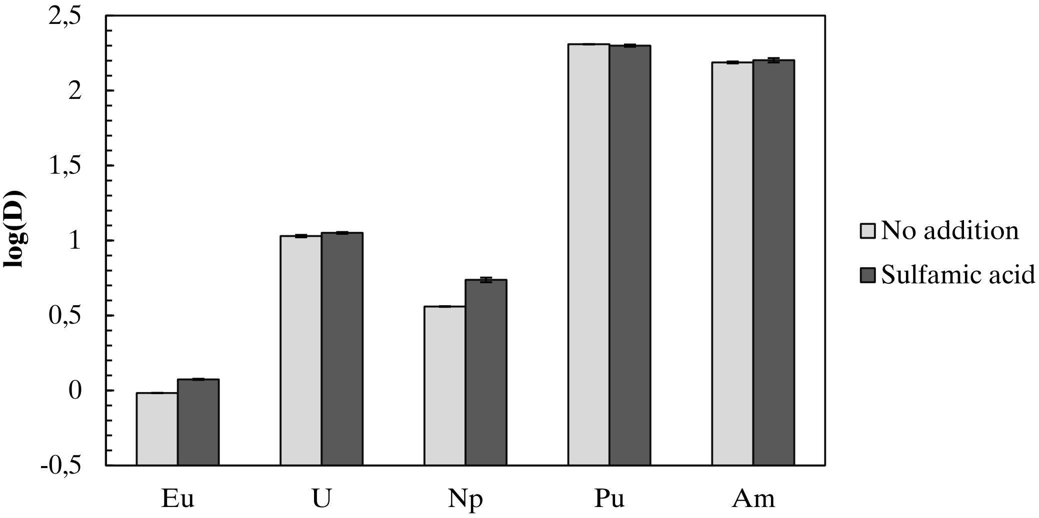

Figure 5.2.6 Comparison of the extraction of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu from 4 M nitric acid with and without the addition of 50 mM sulfamic acid with 0.01 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone

Thermodynamic Extractions

To investigate how temperature affects the actinide extractions and lanthanide separation, extractions at different temperatures between 20°C and 50°C were performed. As seen in Figure 5.2.7, the extraction decreased with an increase in temperature for all actinides, except uranium. This trend was also the case for the lanthanide europium, meaning that high separation factors could still be maintained even at elevated temperatures. However, in practical terms, this means that the temperature of this GANEX solvent extraction process should be kept as low as possible, which is also beneficial for the diluent stability. The uranium extraction was unchanged during the entire experiment, which means that the uranium extraction by TBP in this particular solvent is mainly driven by the entropy change. The decrease in the logarithm of the distribution ratio is linear for americium, curium, plutonium and europium. For neptunium, however, the slope is very low and cannot be confirmed to be linear. This behaviour indicates that there might not be any temperature dependence for this extraction, just like for uranium. An explanation could be that the BTBP behaviour is different for the actinyl ions compared with the spherical ions. It could, however, also be a change in extraction mechanism for neptunium with an increase in temperature.

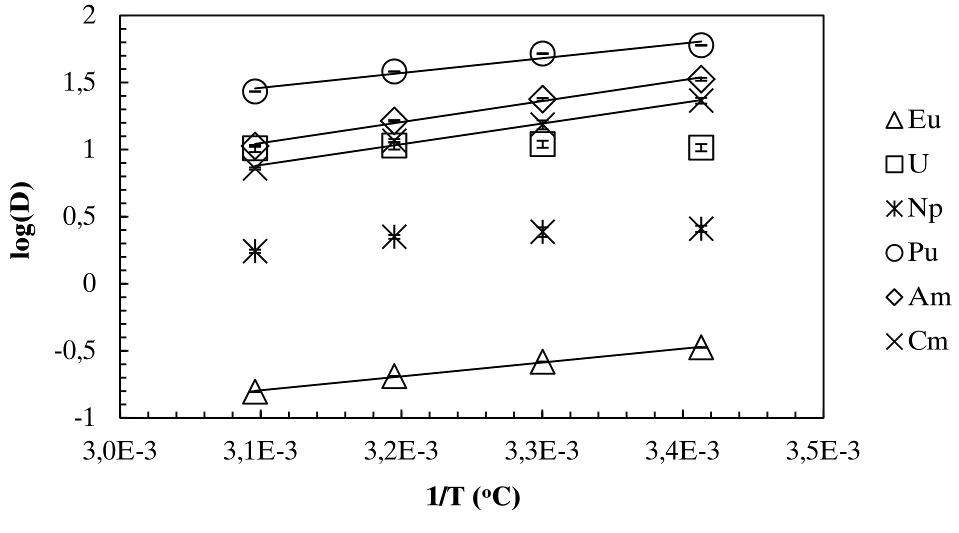

Figure 5.2.7 Extraction of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am, ^{244}Cm and ^{152}Eu from 4M nitric acid at different temperatures with 0.005 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone

In the BTBP extraction (Reaction 5.1), all metals used in the experiment were of trace amounts. Because of this both the ligand concentration and nitric acid/nitrate concentration can be assumed to be constant during the extractions (Equation 5.2 and 5.3). Therefore, the stability constant for the extraction, K$_{ex}$, can be expressed through the distribution ratio according to Equation 5.4.

$$M^{n+} + nNO_3^- + 2\overline{BTBP} \overset{K_{ex}}{\leftrightarrow} \overline{M(NO_3)_nBTBP_2} \tag{5.1}$$

$$K_{ex} = \frac{\left[\overline{M(NO_3)_nBTBP_2}\right]}{[M^{n+}] * [NO_3^-]^n * [\overline{BTBP}]^2} \tag{5.2}$$

$$[NO_3^-]^n * [\overline{BTBP}]^2 = constant = C \tag{5.3}$$

$$K_{ex} = \frac{[M(NO_3)_nBTBP_2]}{[M^{n+}] * C} = D_M * \frac{1}{C} \tag{5.4}$$

As the relation between the logarithm of the distribution ratio and the inverse temperature was found to be linear for americium, curium europium and plutonium (Figure 5.2.7), the Cp for the extraction reaction (5.1) is zero. The enthalpy and entropy of the extraction can then be determined by plotting ln(K_{ex}) against 1/T. This is according to the linear relationship below (Equation 5.5), derived from the Van't Hoffs Equation [VAN94]:

$$\ln K_{ex} = -\frac{\Delta H_n^0}{RT} + \frac{\Delta S_n^0}{R} \tag{5.5}$$

When performing the linear regression according to Equation 5.5, it can be concluded that the enthalpy as well as entropy for the extraction of americium, curium, plutonium and europium by the GANEX solvent are both negative (Table 5.2.1). This means that these extractions are driven by the change in enthalpy.

Table 5.2.1 Enthalpy and entropy of complexation for the extraction of ^{238}Pu, ^{241}Am, ^{244}Cm and ^{152}Eu from 4 M nitric acid with 0.005 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone

	ΔH° (kJ/mol)	+/-	ΔS° (J/mol*K)	+/-
Am	-30.0	1.7	-5.3	5.7
Cm	-29.6	2.3	-7.3	7.5
Pu	-26.5	1.4	-7.4	4.3
Eu	-19.9	0.6	-9.2	2.1

5.3 Fission products

The results presented in this section are based on Papers III, IV, V and VI as well as unpublished material.

5.3.1 General Extractions

Fission products of concentrations close to those that can be found in used nuclear fuel (concentrations tabulated in Appendix A), as well as corrosion products, were extracted with the GANEX solvent from 4 M HNO$_3$. The results are presented in Figures 5.3.1 and 5.3.2.

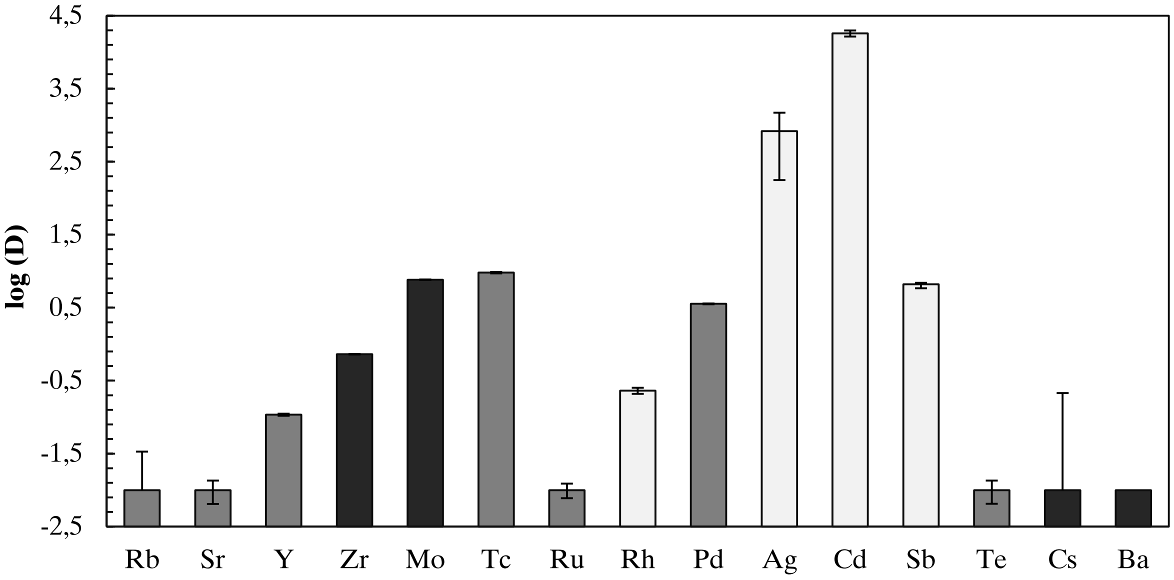

Figure 5.3.1 Extraction of fission products from 4 M nitric acid with 0.01 M CyMe4-BTBP and 30% TBP in cyclohexanone. Light grey bars - concentrations well below 100 ppm in dissolved fuel. Grey bars - concentrations between 100 and 600 ppm in the dissolved fuel. Dark grey bars - concentrations above 1,000 ppm in dissolved fuel

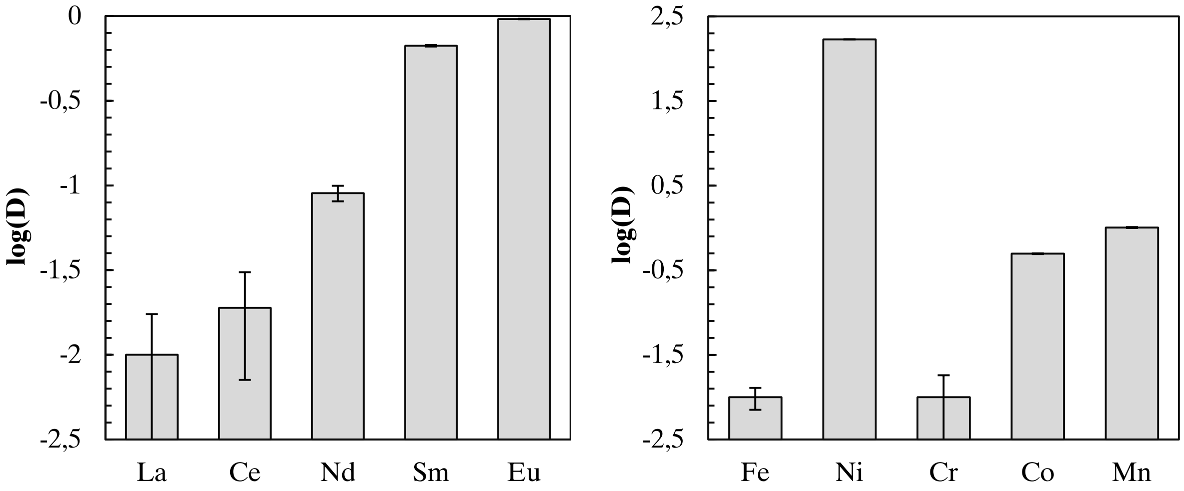

Figure 5.3.2 Extraction of lanthanides (left) and corrosion/activation products (right) from 4 M nitric acid with 0.01 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone (^{152}Eu and ^{63}Ni in trace amounts, the rest as non-radioactive metal salts)

As is evident from the experimental results, some of the fission and corrosion products are extracted by the GANEX solvent. Among the elements with the highest abundance in the spent fuel, it can be seen that both zirconium and molybdenum are extracted. Palladium and technetium, which have a medium high abundance, are also extracted. The extraction of these elements is undesirable and can be considered to be a problem that must be addressed using one or more of the methods mentioned in section 3.2.3. Even if silver, cadmium and nickel are quantitatively extracted, the abundance of them in the used fuel is very low (Ag, Cd) or uncertain (Ni). These elements are therefore unlikely to cause any major problems during the actinide extraction. In fact, it could even be positive to leave cadmium in the organic stream to act as a neutron poison for the plutonium, which means that cadmium should capture any neutrons present to prevent the fission of plutonium. This is possible, as cadmium has a very high neutron capture cross section [PFE95]. However, if these elements cannot be handled together with the other fission products, it must be ensured that they can be efficiently scrubbed out of the organic phase to avoid metal accumulation during processing. The undesired co-extraction of fission products is not uncommon within reprocessing, due to the complexity of the feed solution, and in, for example, the PUREX process, zirconium ruthenium and technetium are co-extracted with the actinides and removed later in the process by scrubbing of the organic phase [MOR06].

To better be able to tackle the issues with extracted fission and corrosion products, an experiment was performed to see which extractants in the GANEX solvent are extracting the metals in question. This investigation was performed, just as for the actinides, using four different organic phases (1- 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone, 2- 0.01 M CyMe$_4$-BTBP in cyclohexanone, 3- 30% TBP in cyclohexanone, 4- cyclohexanone) and 1 M HNO_3+3 M $NaNO_3$ as the base for the aqueous phase. The results in Table 5.3.1 show that all metals are extracted by BTBP except for technetium, which is extracted by cyclohexanone.

Table 5.3.1 Extraction of selected fission products from 1 M HNO_3+3 M $NaNO_3$ with four different organic phases: 1- 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone, 2- 0.01 M CyMe$_4$-BTBP in cyclohexanone, 3- 30% TBP in cyclohexanone, 4- cyclohexanone

	Organic phase 1		Organic phase 2		Organic phase 3		Organic phase 4	
	log (D)	+/-	log (D)	+/-	log (D)	+/-	log (D)	+/-
Ni	1.83	0.005/0.005	2.85	0.02/0.02	-2.99	0.01/0.01	-2.58	0.007/0.007
Zr	-0.30	0.002/0.002	-0.35	0.002/0.002	-2.00	0.001/0.001	-2.00	0.001/0.001
Mo	1.21	0.003/0.003	1.46	0.004/0.004	-0.99	0.02/0.02	-1.13	0.01/0.01
Tc	1.01	0.004/0.004	1.14	0.004/0.004	0.97	0.004/0.004	0.98	0.004/0.004
Pd	1.33	0.01/0.01	2.11	0.03/0.03	-0.84	0.01/0.01	-0.76	0.01/0.01
Ag	1.78	0.01/0.01	1.72	0.01/0.01	-0.79	0.02/0.02	-0.76	0.03/0.03
Cd	Q		Q		-1.11	0.05/0.06	-1.46	0.1/0.2

Q-quantitative extraction, too little metal in the aqueous phase to measure with the equipment

As can be seen in Table 5.3.1, the distribution ratios for most metals are higher for organic phase 2 than for organic phase 1, although there are no indications of interactions between TBP and BTBP. The explanation could be a diluent effect where TBP acts as part of the diluent, altering its properties. This is because the extraction by TBP/cyclohexanone in most cases is very low. To investigate how the presence of TBP affects the properties of the entire diluent, the interfacial tension between the four organic phases and one water phase was measured. As can be seen in Table 5.3.2, the addition of TBP to the solvent increases the surface tension between the two phases, strengthening the explanation that the difference in distribution ratio between organic phases 1 and 2 is an effect originating from the diluent. It is also obvious that when TBP is not in the system, BTBP lowers the surface tension compared with just cyclohexanone.

Table 5.3.2 Interfacial surface tension between four different organic phases (pure cyclohexanone, CyMe$_4$-BTBP (13 mM) in cyclohexanone, cyclohexanone + 30% TBP and CyMe$_4$-BTBP (10 mM) in cyclohexanone + 30%TBP) and 0.99 M NaNO$_3$+0.01 M HNO$_3$. The standard deviation was calculated using the "n-1" method for multiplets and technical replicates

Organic phase	Interfacial surface tension (mN/m)
Organic phase 1	4.4±0.3
Organic phase 2	2.0±0.2
Organic phase 3	4.2±0.2
Organic phase 4	3.6±0.1

An extraction experiment with the fission products that have been concluded to be extracted by BTBP was performed, varying the BTBP concentration in the GANEX solvent. The result is displayed in Figure 5.3.3. Although the metal concentrations were too high to perform adequate slope analysis, it can still be concluded that the zirconium, molybdenum and silver distribution ratios obviously vary linearly with the BTBP concentration, thus indicating a BTBP extraction.

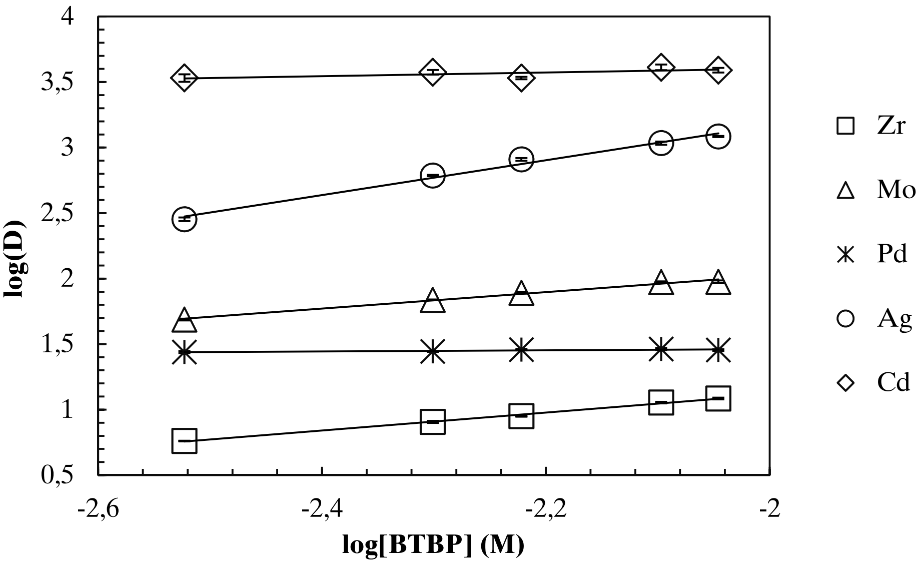

Figure 5.3.3 Extraction of fission products (0.1 mM) from 4 M HNO$_3$ with different BTBP concentrations (total FP concentration 0.7 mM) in cyclohexanone + 30% TBP

Palladium extraction, however, has a slope which is close to zero (0.04), meaning that an increased ligand concentration does not increase the extraction. This result was unexpected, as it was concluded that palladium is extracted by BTBP, and thus required further investigation (see section 5.3.2). Also the cadmium extraction was more or less independent of the BTBP concentration (slope 0.14), although this could be an artefact from the very high distribution ratios and it is therefore difficult to draw any conclusions from this.

5.3.2 Palladium

During the general fission product extractions it was discovered that without the presence of BTBP, palladium precipitated in the organic phase upon contact with cyclohexanone. It was also seen that the palladium extraction by CyMe$_4$-BTBP was not dependent on the ligand concentration. A possible explanation to this could be that a water-soluble complex was formed. To test this hypothesis, an experiment was performed utilizing the palladium precipitation upon cyclohexanone contact. A palladium-containing aqueous phase was contacted with organic phases containing different concentrations of CyMe$_4$-BTBP in cyclohexanone. By keeping the BTBP concentrations sub-stoichiometric to the palladium amount in the aqueous phase, all palladium that was not complexed by BTBP would precipitate. The remaining palladium amount in the aqueous phase could thereafter be measured. From the results in Figure 5.3.4, it is clear that a higher amount of BTBP in the organic phase increased the remaining amount of palladium in the aqueous phase. This indicates that a water-soluble complex of possible stoichiometry 1:1 (slope 0.43±0.02 with 95% confidence) is actually forming. This was also confirmed using HPLC which showed that the BTBP concentration in the organic phase decreased with an increased amount of palladium in the aqueous phase. In the same time, an increase of BTBP in the aqueous phase could be observed. Without metal present, BTBP has not been observed to be water-soluble (Paper II).

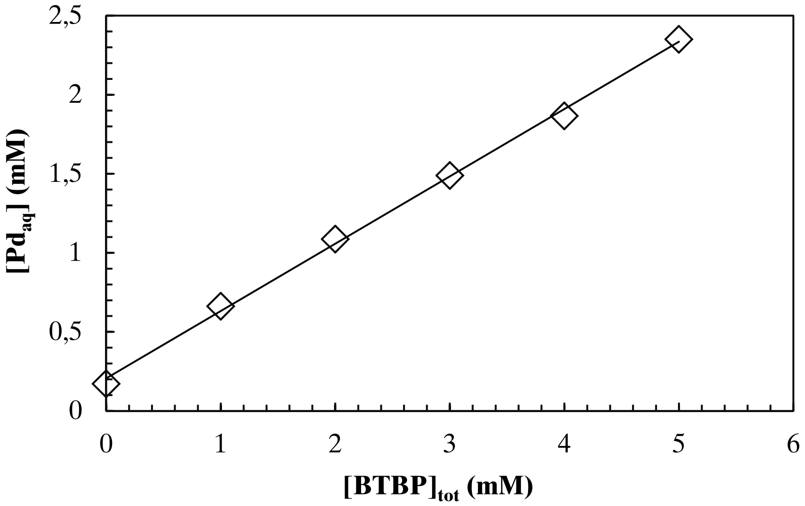

Figure 5.3.4 Remaining Pd concentration in the aqueous phase (measured with ICP-OES) after extraction of Pd (from 1 M HNO_3) with CyMe$_4$-BTBP in cyclohexanone (BTBP in deficit compared with palladium) rendering a precipitation of excess palladium

To investigate the structure of the water-soluble palladium complex in solution, NMR investigations were performed. These investigations are based on the fact that, when complexed, the ^{1}H-NMR shifts of the pyridine hydrogen on the BTBP molecule changes. Depending on the type of complex formed, if there are one or two BTBP molecules bound to the metal, the shift is different. To be able to distinguish between the different complex formations, comparisons were made with solid complexes of other metals (silver, cadmium and lead), of which the structures had previously been determined using crystallography and elemental analysis (Paper V). First it was confirmed that the structure of the dissolved solid complexes was the same as the complexes formed by solvent extraction. As can be seen in Table 5.3.3, the NMR shifts correspond well between the two complexes with different origin. It can also be concluded that silver, which is a 2:2 complex, has a different appearance compared with the 1:2 complexes with cadmium and lead. This is more easily seen in Figures 5.3.5 and 5.3.6. When comparing the shift patterns for the palladium complex (Table 5.3.3 and Figure 5.3.7) with those of the other metals, it can be seen that both in the organic and the aqueous phase, palladium seems to form a 1:1 complex with BTBP. This is due to the resemblance with the silver complex rather than with the cadmium or lead complexes. This was also confirmed using mass spectrometry of the two phases (Paper V). The fact that the group of peaks for the palladium complex has changed place in the NMR spectrum, when comparing the aqueous to the organic phase, could be explained by coordinated nitrates in the organic phase being absent in the aqueous phase.

Table 5.3.3 ^{1}H NMR shifts for the three pyridine hydrogen of CyMe$_4$- and C2-BTBP in cyclohexanone (addition of C_6D_6) or D_2O alone and in complex with various metals both formed during extraction from nitrate media and as dissolved solids in cyclohexanone

Measured compound	ppm triplet	ppm doublet 1	ppm doublet 2
CyMe$_4$-BTBP	7.95	8.33	8.72
C2-BTBP	7.94	8.34	8.71
Pb CyMe$_4$ solid complex	8.40	8.69	8.87
Pb CyMe$_4$ extraction	8.38	8.68	8.83
Ag CyMe$_4$ solid complex	8.27	8.32	8.42
Ag CyMe$_4$ extraction	8.25	8.29	8.40
Ag C2 solid complex	8.26	8.33	8.37
Ag C2 extraction	8.25	8.33	8.36
Cd C2 solid complex	8.35	8.59	8.97
Cd C2 extraction	8.39	8.60	9.01
Pd CyMe$_4$ extraction (org)	8.34	8.50	8.50
Pd CyMe$_4$ extraction (aq)	8.35	8.23	8.26

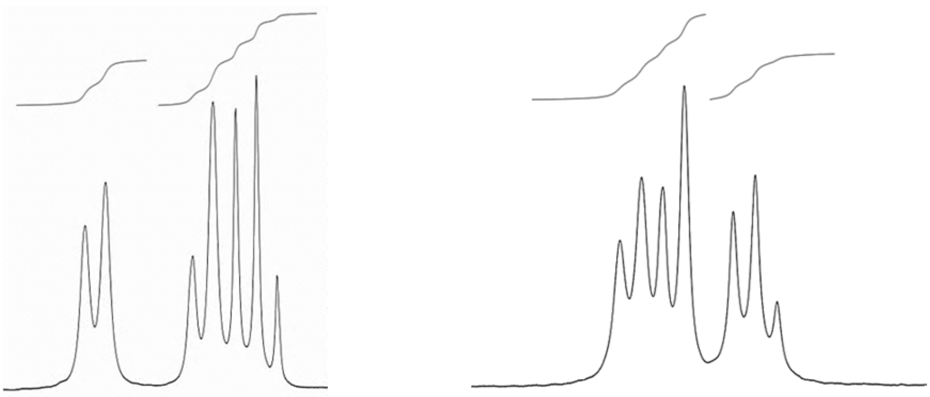

Figure 5.3.5 ^{1}H NMR spectra of solid complexes of Ag and CyMe$_4$-BTBP (left) and Ag and C2-BTBP (right) dissolved in cyclohexanone with an addition of C_6D_6 (approximately 7.5%)

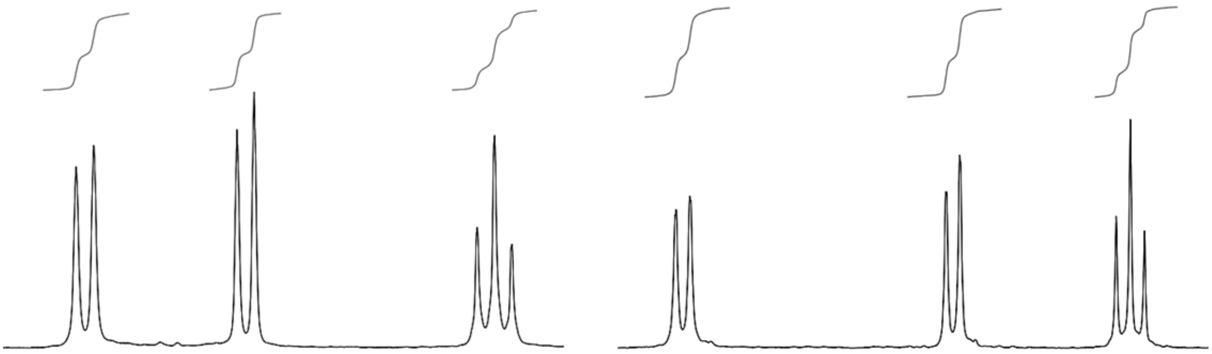

Figure 5.3.6 ^{1}H NMR spectra of a solid complex of left: Pb and CyMe$_4$-BTBP and right: Cd and C2-BTBP dissolved in cyclohexanone with an addition of C_6D_6 (approximately 7.5%)

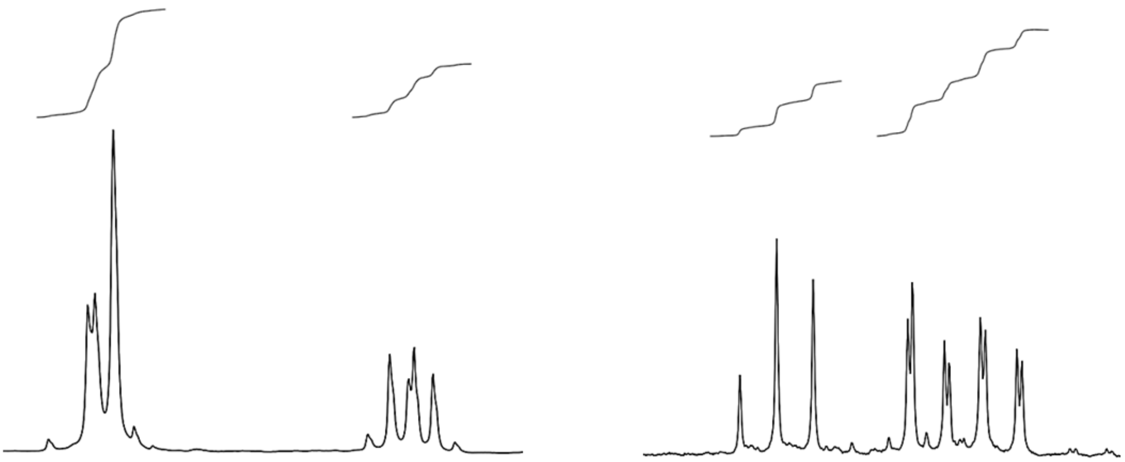

Figure 5.3.7 ^{1}H NMR spectra of CyMe$_4$-BTBP complexing Pd in (left) the organic phase (cyclohexanone with an addition of C_6D_6 (approximately 7.5%)) and (right) in 1M HNO_3 (made from D_2O). Both spectra obtained after contacting the two phases

The amount of nitrates bound in the palladium complex in the organic phase was also investigated using slope analyses. With higher nitrate activity (calculated using the Pitzer equations for mixed electrolytes [PIT73]), as in a reprocessing process, it was found that the nitrate dependence was not linear. The palladium extraction instead increased exponentially, which could indicate a salting-out effect. Consequently, the nitrate concentration had to be lowered and as the palladium concentration used was comparatively high, the ion strength was kept constant using $NaHSO_4$. The amount of nitrates associated with the extracted Pd:BTBP complex was found to be two from the slope (1.9±0.1 with 95% confidence) in Figure 5.3.8. This was also expected, as palladium under these conditions should be present in the form of Pd^{2+} (see section 2.3).

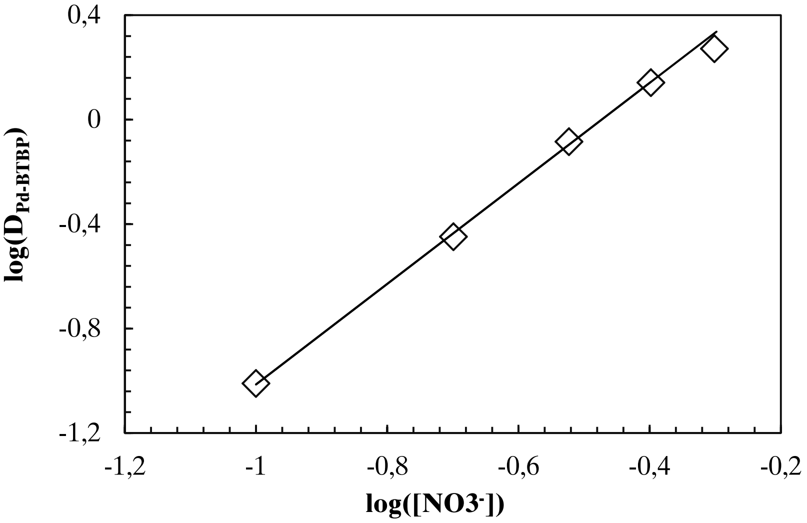

Figure 5.3.8 Distribution ratio of Pd (2 mM) after extraction with $CyMe_4$-BTBP (0.01 M) in cyclohexanone varying the nitrate concentration with ionic strength kept constant using $NaHSO_4$. Slope based on first four data points

The fact that palladium is extracted by $CyMe_4$-BTBP in cyclohexanone and also salted out into this organic phase at high nitrate activity is problematic for the proposed GANEX process. The precipitation of palladium by cyclohexanone is prevented by the complexation by BTBP. However, in a real process, the BTBP molecule would be occupied in other complexes with, first and foremost, the actinides, and might not be available to complex all the palladium. Therefore, this could also be considered to be a problem. All three of these problems mentioned can, however, be resolved by complexing the palladium with a water-soluble molecule. If this water-soluble molecule forms a sufficiently stable complex with palladium, the extraction by BTBP could be prevented as well as the precipitation by cyclohexanone. One molecule that was found to do this was bimet (Figure 5.3.9). Bimet is the combination of two moieties of the amino acid methionine. Methionine was initially investigated for the task and was found promising, but did not form sufficiently stable complexes with palladium to totally prevent extraction and precipitation, and consequently bimet was chosen. The choice was also affected by the fact that chelating molecules are known to form more stable complexes than their corresponding single ligand counterparts (see section 2.2).

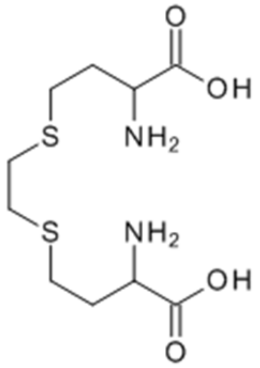

Figure 5.3.9 Molecular structure of bimet (S,S′-ethylene bis(L-homocysteine))

As can be seen from Figure 5.3.10, addition of equal or larger amounts of bimet compared with the amount of palladium efficiently prevents the precipitation of palladium black from 1 M HNO_3. This is also illustrated in Figure 5.3.11, where the remaining amount of palladium in the aqueous phase was measured at different bimet concentrations. From this, a slope could also be obtained (0.97±0.03 with 95% confidence) indicating that the formed Pd:bimet complex most likely is of 1:1 stoichiometry.

To confirm that bimet could also be used under process conditions with higher acidity in the aqueous phase, the experiment was repeated using 4 M HNO_3. As can be seen in Figure 5.3.12, bimet also efficiently prevents precipitation under these conditions and during a long contact time. The Pd:bimet complex formed in this case appears to be a 1:1 complex, based on the slope (1.0±0.5 with 95% confidence, R^2=0.97).

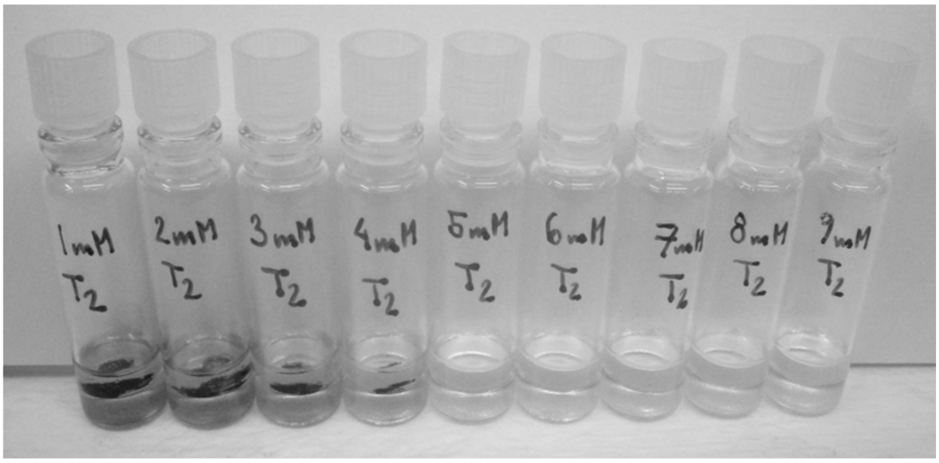

Figure 5.3.10 Organic phase: cyclohexanone. Aqueous phase: 1 M HNO_3 + 4.2 mM Pd with bimet additions of 1-9 mM at 1 mM intervals

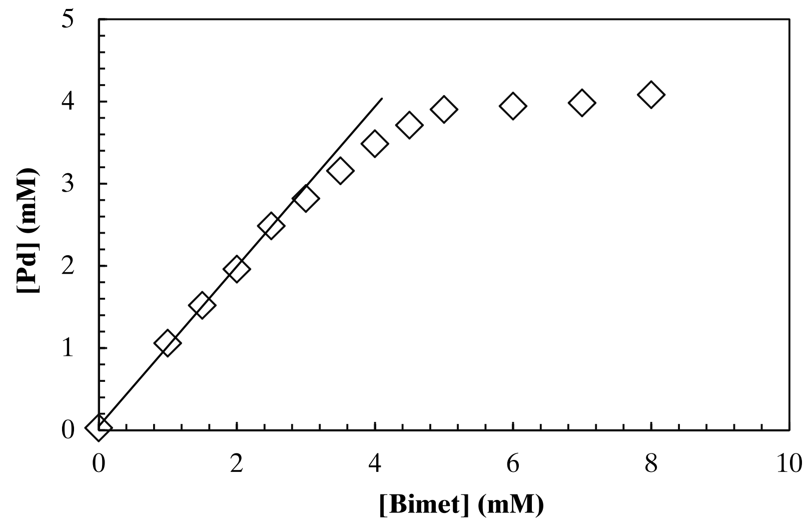

Figure 5.3.11 Remaining Pd concentration in 1 M HNO_3 after precipitating Pd with cyclohexanone, adding bimet in different concentrations. (Trendline based on the first 5 data points)

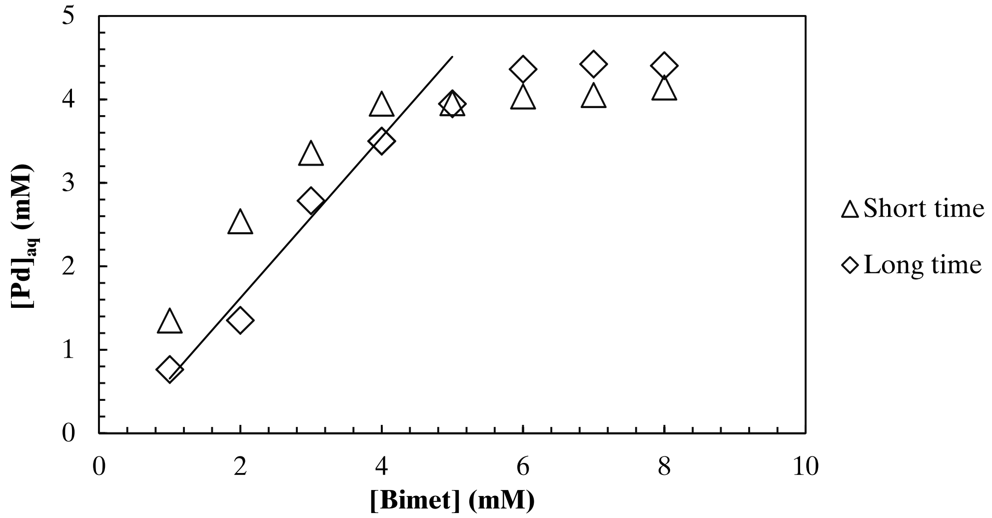

Figure 5.3.12 Remaining Pd concentration in 4 M HNO_3 after precipitating Pd with cyclohexanone, adding bimet in different concentrations. Time between preparation of solution and start of experiment: Short time= 1 h, Long time=6 days (trendline based on first 4 data points)

When extracting palladium from 4 M HNO_3 using the GANEX solvent it was found that an addition of bimet in approximately two equivalents was necessary to totally prevent extraction (Figure 5.3.13).

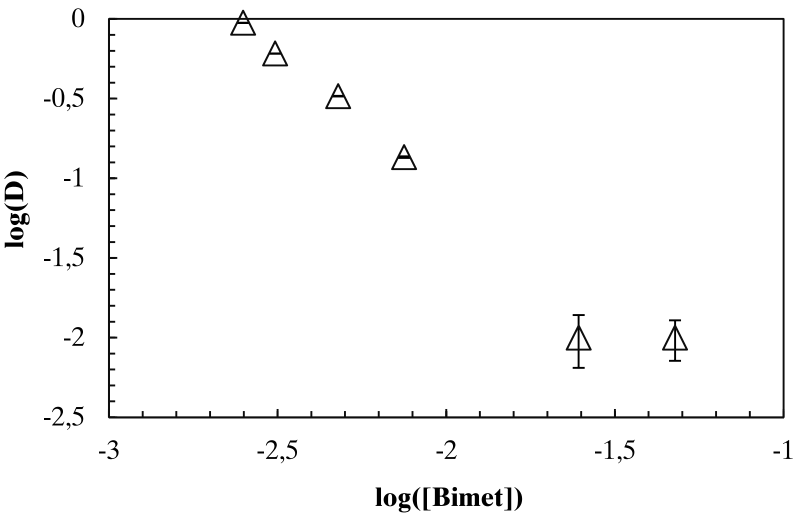

Figure 5.3.13 Extraction of Pd (4.2 mM) with 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from 4 M HNO$_3$ containing different concentrations of bimet

5.3.3 Zirconium, Molybdenum (Silver, Cadmium, Nickel and Manganese)

As could be seen in Figure 5.3.1, two fission products with high abundance in the used fuel and relatively high distribution ratios are zirconium and molybdenum. Two other fission products, silver and cadmium, displayed very high distribution ratios but are not as abundant in the fuel. From Figure 5.3.2 it was also obvious that the corrosion products nickel and manganese were extracted to a relatively high degree, although their abundance in the dissolution liquor is difficult to estimate. These six fission and corrosion products have therefore been further investigated. The focus was on zirconium and molybdenum, using the three different methods described in section 3.2.3: pre-extraction, scrubbing and suppression.

Pre-extraction

If pre-extraction were to be implemented, palladium would still be in the system and hence would also have to be taken into consideration in this step. Several molecules (dioctyl sulfide, tri-isobutylphosphine sulfide, dibutyl sulfoxide and trioctyl amine) which were believed to be efficient in the extraction of palladium, zirconium and molybdenum, were therefore investigated. All of these molecules showed efficient palladium (D_{Pd}>25) extraction, but only one, dibutyl sulfoxide, managed to also extract both molybdenum and zirconium with distribution ratios above one (D_{Mo}=3.1, D_{Zr}=12). However, when dibutyl sulfoxide was tested for actinide extraction, a considerable precipitation of uranium occurred. This, unfortunately, precluded the use of dibutyl sulfoxide in a pre-extraction process, but as the sulfoxide performed well regarding the extraction of the fission products, another sulfoxide (dodecyl methyl sulfoxide) was tested for the extraction of uranium only. This was done in order to see if the uranium precipitation could be avoided by using an unsymmetrical sulfoxide. No uranium precipitated in this extraction, but the distribution ratio was found to be too high (D_U>2) to motivate any further investigation of this type of molecule.

Essentially, it can be concluded that pre-extraction could not easily be used for the removal of zirconium and molybdenum without also affecting the actinides.

Scrubbing

A vast range of organic molecules, found in Appendix B (0.6 M), were screened for the possible effects on scrubbing zirconium and molybdenum from the GANEX solvent. Also, in this case several of the molecules managed to scrub a large portion of the extracted zirconium, but only one, gluco-lactone, could also scrub more than half of the extracted molybdenum (scrubbed(Zr)=74%, scrubbed(Mo)=53%). An attempt was made to increase the amount of gluco-lactone to investigate whether this would improve the removal of molybdenum and zirconium. However, no effect could be seen. As gluco-lactone is a food additive (E575), it is cheap and available in large amounts. Thus, zirconium and molybdenum removal with this reagent is a reasonable alternative. Experiments were therefore also performed with the other fission and corrosion products to investigate whether their scrubbing was increased by the presence of gluco-lactone. These results are shown together with the scrubbing of the actinides and lanthanides (represented by europium) in Figure 5.3.14.

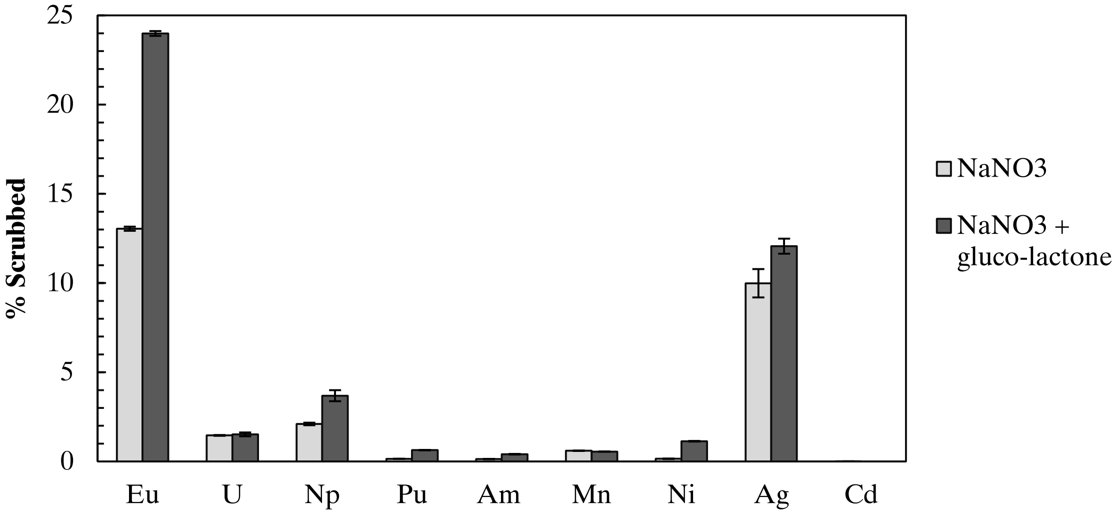

Figure 5.3.14 Scrubbing of various metals from 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone using 4 M $NaNO_3$ and 0.6 M of gluco-lactone in 4 M $NaNO_3$

As can be seen in Figure 5.3.14, the presence of gluco-lactone only slightly increases the scrubbing of all elements in question, except for europium. The scrubbing of europium is almost doubled when adding gluco-lactone, which is a positive result since this further promotes the separation of actinides from lanthanides. If a scrubbing step is necessary in the process for another reason, e.g. to increase the pH of the organic phase, then a good option would be to add gluco-lactone to this step to enhance the removal of impurities. The loss of neptunium as well as uranium is, however, slightly high during scrubbing, both with and without the addition of gluco-lactone, and therefore the use of an additional scrubbing step for the sole purpose of removing extracted fission products would not be recommended.

Suppression

Bimet and the reagents in Appendix B (0.5 M) were also tested for their ability to prevent the extraction of molybdenum and zirconium by the GANEX solvent. The molecule found to have the best combined result for molybdenum and zirconium suppression was mannitol, which is the only one able to suppress molybdenum extraction to a level below D=1 ($D_{Zr}<0.01$, $D_{Mo}=0.18$). The effect of varying the mannitol concentration was investigated (Figure 5.3.15) and while a large amount of mannitol (0.2 M) was required to fully suppress the molybdenum extraction, a smaller amount (0.05 M) was still able to reduce the distribution ratios of both zirconium and molybdenum below D=1.

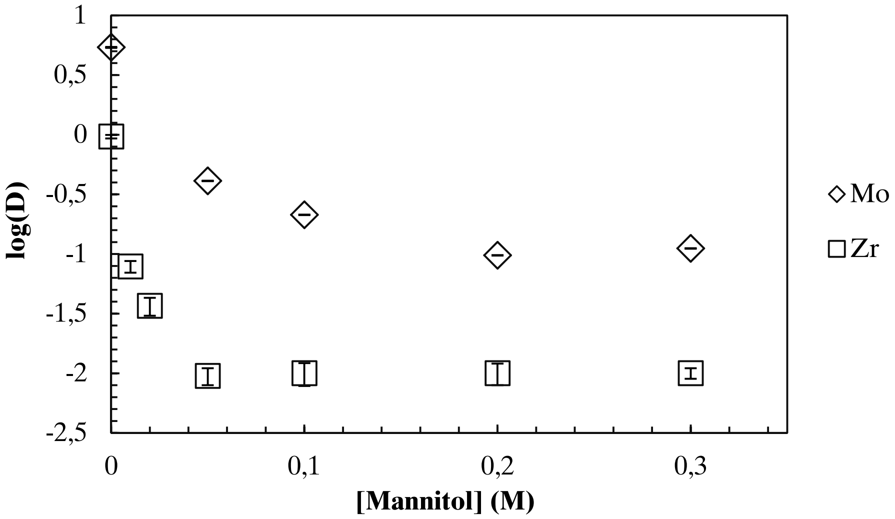

Figure 5.3.15 Molybdenum and zirconium extraction by 0.01 M CyMe$_4$-BTBP +30% TBP in cyclohexanone from 4 M HNO$_3$ with different additions of mannitol to the aqueous phase

As mannitol does not have any influence on the palladium extraction or precipitation, it would have to be combined with bimet in a process implementation. For mannitol, a desired process concentration would be 0.2 M for optimum suppression of molybdenum and total suppression of the zirconium extraction. For bimet, a suitable process concentration would be 20 mM. This concentration was chosen as it was previously established (section 5.3.2) that 10 mM is sufficient to totally suppress the palladium extraction and with a 20 mM concentration, free bimet will also be available to complex other soft metals besides palladium (such as silver) that will be present in the feed solution. A combination of the two suppressing agents was therefore tested for the extraction of actinides, fission and corrosion products to ensure that no untoward interactions between bimet and mannitol were able to disturb the solvent extraction process (Figure 5.3.16). It was found that the extraction of the actinides and lanthanides (represented by europium) was unchanged by the addition of the suppressing agents, ensuring maintained An/Ln separation factors. This combination of reagents was also able to prevent the extraction of palladium and zirconium while the extraction of molybdenum and silver was reduced (D<1). The extraction of cadmium, manganese and nickel was, however, more or less unaffected.

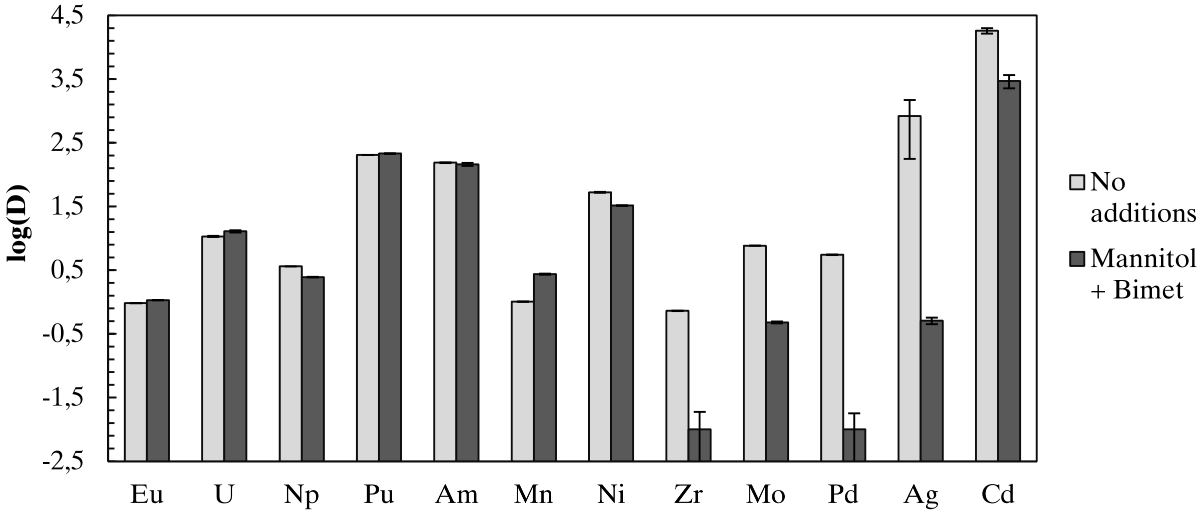

Figure 5.3.16 Extraction of various metals by 0.01 M CyMe$_4$-BTBP +30% TBP in cyclohexanone from 4 M HNO_3 with and without the addition of 20 mM bimet + 0.2 M mannitol

5.3.4 Technetium

As technetium was found not to be extracted by BTBP, like the other fission products investigated, but by cyclohexanone, the approach towards investigating technetium has been different. Firstly, the actual behaviour of the technetium extraction has been studied.

Technetium is known to be co-extracted as a pertechnetate anion together with uranium by TBP in the PUREX process [MAC79]. It is hence also possible that technetium could be co-extracted, replacing nitrate ions, by other fission product metals by BTBP. A 4 M nitric acid solution loaded with fission products (Rb, Sr, Y, Zr, Mo, Rh, Pd, Ag, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm and Te, in approximate concentrations as in Appendix A) was therefore used as aqueous phase in an extraction experiment with the GANEX solvent. The experiment was then performed twice, once with an addition of 0.1 M uranyl nitrate and once without.

It is obvious from the results in Figure 5.3.17 that the addition of uranium, without fission products in the aqueous phase, appears to inhibit the technetium extraction rather than to enhance it. This is probably due to the fact that uranium to some extent is also extracted by cyclohexanone and that this extraction is competing with the technetium extraction. This could be caused by the uranium ion-pair extraction favouring nitrate rather than pertechnetate. Also, when varying the uranium concentration during technetium extraction with the GANEX solvent, a clear

dependence on the decrease in technetium distribution ratio (D_{Tc}) with the increase in uranium concentration in the aqueous phase ($[U]_{aq}$) was found:
$\log(D_{Tc})=-0.072\log([U])+0.638$ with $R^2 = 0.999$

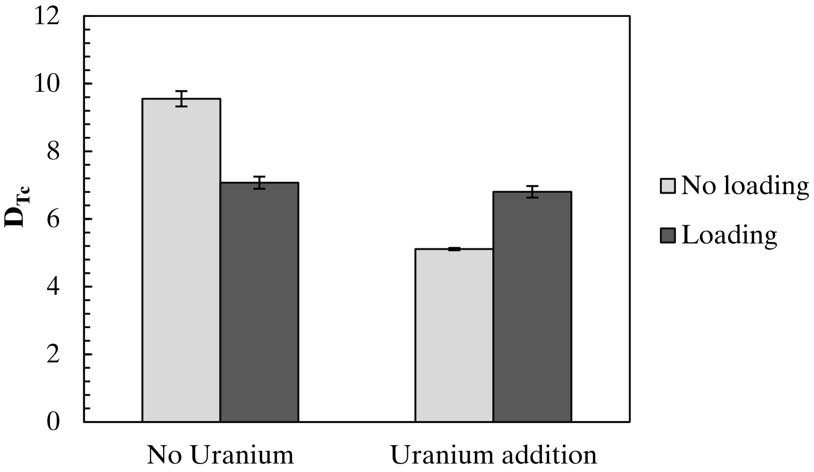

Figure 5.3.17 ^{99m}Tc extraction by 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from 4 M HNO_3 both with and without fission product loading (Rb, Sr, Y, Zr, Mo, Rh, Pd, Ag, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Te (conc. as in Appendix A)) as well as with and without uranyl nitrate addition (0.1 M) to the aqueous phase

When, instead, comparing the experiments with and without fission product loading, it can be seen that without uranium in the aqueous phase the technetium extraction is slightly reduced under loading conditions. For the uranium-containing system, however, the extraction is slightly higher with fission product loading than with no loading. It is also clear that the presence of uranium in the loaded system has no effect on the extraction. This could possibly mean that the extraction mechanism of the technetium under fission product loading conditions shifts from extraction by cyclohexanone to ion-par extraction, with some of the fission product metals extracted by, most likely, BTBP. Although this fission product extraction by BTBP to a large extent can be circumvented, as discussed in sections 5.3.2 and 5.3.3, this result could be an indication that there might also be a pertechnetate co-extraction with the actinides extracted by BTBP.

Since it was previously shown that nitrate ions seemed to compete with pertechnetate for extraction by the GANEX solvent, the effect on the technetium extraction of varying the nitrate concentration was investigated. The effect of acid concentration on the extraction and consideration of whether a high nitrate or high proton environment had any impact was also studied by using both pure nitric acid as well as a combination of nitric acid and sodium nitrate. To be able to compare the different aqueous phases, the nitric acid/sodium nitrate concentrations have been recalculated to nitrate activity in a similar way to that described in Paper V. The results of this experiment can be found in Figure 5.3.18.

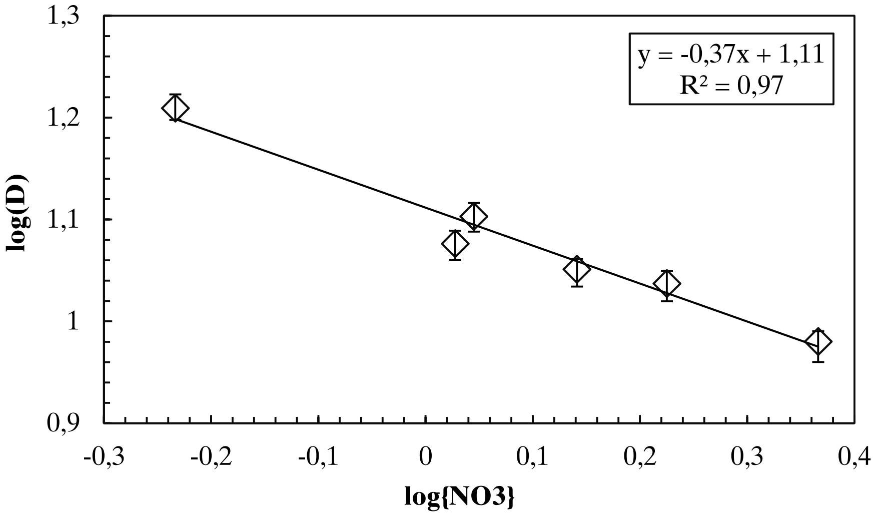

Figure 5.3.18 ^{99m}Tc extraction by 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from aqueous phases with varying nitrate activity. The nitric acid concentration was in all cases 1 M or higher

It can be seen that with low nitrate activity, technetium is readily extracted but as the activity increases the distribution ratio for technetium slowly decreases. This effect has been previously observed with cyclohexanone in combination with other anions and could hence be expected [BOY60]. As all data points fit the straight line, it can also be concluded that there is no obvious difference between distribution ratios obtained from acid only or acid and nitrate media of the same concentration. It should, however, be pointed out that in all samples the nitric acid concentration is 1 M or more. This is because it has previously been seen that in neutral salt solutions, the extraction of pertechnetate by cyclohexanone is reduced [BOY60]. The highest nitrate concentration tested (4 M nitric acid saturated with sodium nitrate) decreases the technetium extraction to D_{Tc}=5.0, which means that it might be possible to wash the technetium out of the organic phase using several highly concentrated nitrate scrub steps.

5.4 Replacing TBP with DEHBA

The results presented in this section are based on Papers VII and VIII.

When comparing actinide extraction and An/Ln separation between the GANEX solvent and solvents where the TBP has been replaced with different amounts of DEHBA, it can be seen that the distribution ratios for all solvents are quite similar (Figure 5.4.1). The europium distribution ratios are, however, higher for all DEHBA-containing solvents compared with the TBP one, resulting in a higher total lanthanide extraction in these types of solvents. When comparing the solvents with different amounts of DEHBA to each other, it can be concluded that the uranium extraction is increased with an increasing amount of DEHBA, as expected. It is also obvious that the solvent containing 20% DEHBA displays uranium distribution ratios almost as high as the one with 30% TBP, and the solvent containing 20% DEHBA with

10 mM CyMe$_4$-BTBP in cyclohexanone was therefore chosen for further investigation. This solvent will from now on be called the DEHBA solvent.

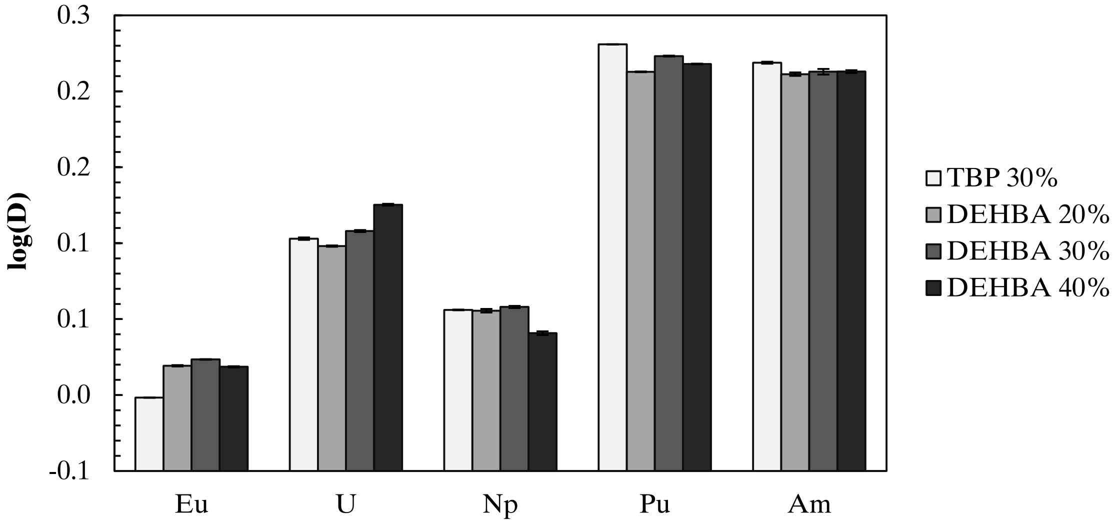

Figure 5.4.1 Extraction from 4 M HNO_3 with 0.01 M CyMe$_4$-BTBP + DEHBA/TBP in cyclohexanone

The hydrolytic and radiolytic stability of the DEHBA solvent was investigated in the same way as the GANEX solvent (Figure 5.4.2). The DEHBA solvent seems overall to be quite stable to irradiation in contact with nitric acid up to a dose of 300 kGy (dose rate: 18 kGy/h). The trends are very similar to those observed in the hydrolysis experiments but not as pronounced. Hence, it appears that the irradiation itself does not introduce any additional degradation behaviour that differs from that caused by hydrolysis. The decrease of D_{Am} and D_{Eu} in the DEHBA solvent during hydrolysis is much more pronounced than in the GANEX solvent and the plutonium behaviour is also different (the distribution ratio increases with time).

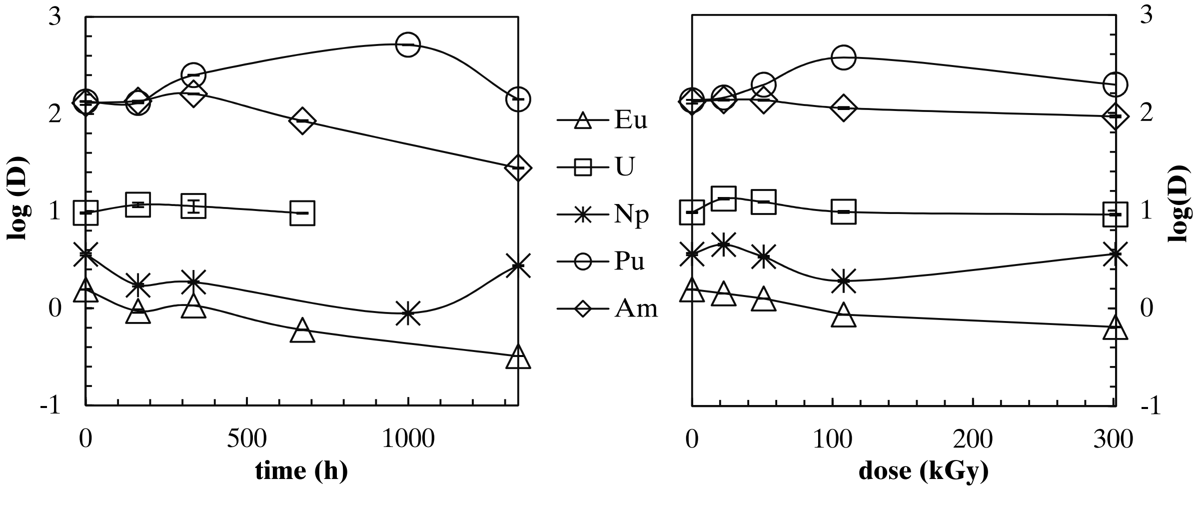

Figure 5.4.2 Left: Hydrolysis of 0.01 M CyMe$_4$-BTBP + 20% DEHBA in cyclohexanone in contact with 4 M HNO_3 and Right: Gamma irradiation of 0.01 M CyMe$_4$-BTBP + 20% DEHBA in cyclohexanone in contact with 4 M HNO_3. Dose rate approximately 18 kGy/h (lines added to guide the eye)

When comparing the overall stability behaviour of the DEHBA solvent with that of the GANEX solvent, it can be concluded that the long time performance (hydrolysis) is more complicated but that the radiolytic stability (short time scale) is almost equally good.

Extractions of the lighter lanthanides as well as the rest of the fission products and the corrosion products have been performed with the DEHBA solvent in the same way as for the GANEX solvent. For almost all elements that have a low distribution ratio for both solvents (i.e. below one), the distribution ratio is higher for the DEHBA solvent than for the GANEX solvent, rendering an overall higher extraction of impurities for this solvent. The difference in distribution ratio between the DEHBA solvent and the GANEX solvent could be explained by a difference in miscibility between the two phases. When investigating this using the extraction of tritiated water, however, the difference between the two solvents is negligible (D_{3H}(TBP)=0.122 and D_{3H}(DEHBA)=0.120). The difference could hence possibly be explained by a diluent effect.

To conclude, it can be said that the replacement of TBP by DEHBA in the GANEX solvent is possible, but as the DEHBA solvent display a more complicated hydrolytic behaviour and an elevated fission and corrosion product extraction, work was continued using the initial GANEX formulation with TBP.

5.5 Process Optimizations

The results presented in this section are mainly based on hitherto unpublished material.

5.5.1 Loading

In a GANEX process, the aqueous phase will be highly loaded with fission products. A loading experiment was therefore carried out to investigate the effect upon extraction of the actinides and their separation from the lanthanides with the GANEX solvent. A 4 M nitric acid metal solution loaded with fission products (Rb, Sr, Y, Zr, Mo, Rh, Pd, Ag, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm and Te) to a total metal concentration of >9000 ppm (approximate concentrations as in Appendix A) was used as aqueous phase.

The results are shown in Figure 5.5.1 and, as can be seen, the distribution ratio for americium and plutonium as well as europium is decreased. The drop in distribution ratio was smaller for plutonium than for americium and europium, most likely due to the extraction of plutonium by cyclohexanone and/or TBP. The decrease in americium, plutonium and europium distribution ratios results in increased An/Ln separation factors and is most likely caused by fission product extractions by BTBP. This could also be confirmed when performing similar experiments with a new loading solution of the same composition but with the addition of 20 mM bimet and 0.2 M mannitol (according to section 5.3.3). In this case the distribution ratios for the elements extracted by BTBP increased upon addition of the fission product suppressing agents to the loading solution (increase(D_{Am})=51±12%, increase(D_{Pu})=67±3% and increase(D_{Eu})=27±2%). This increase was, however, not sufficient to reach the same extraction levels as without fission product loading.

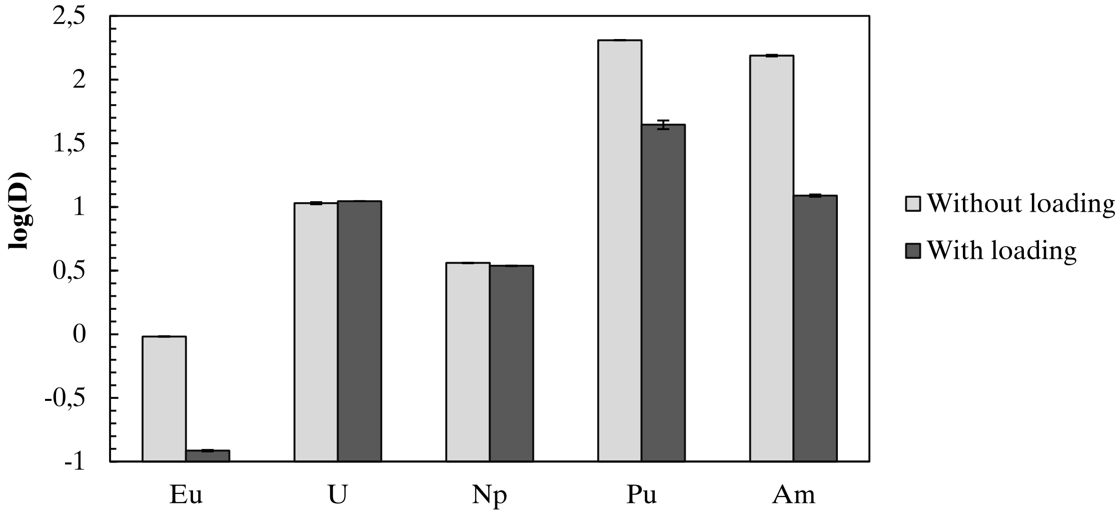

Figure 5.5.1 Extraction of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu from a 4 M nitric acid - metal loaded aqueous phase with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone. Total metal concentration: >9000 ppm

The distribution ratio for uranium is, however, unaffected by the loading conditions. This could be expected since uranium is extracted by the TBP, which is present in large volumes in the solvent and does not extract any major amounts of fission products. What is more surprising is that the distribution ratio of neptunium is not affected by the metal loading either. Since it was shown in section 5.1.1 that neptunium was extracted by the BTBP and not by the TBP, a decrease in extraction would be expected just as for americium, plutonium and europium. It is possible, however, that the oxidation state of neptunium is shifted during extraction due to interactions with other metals in the mixture. This was investigated using spectrophotometry and, as can be seen in Figure 5.5.2, the ratio between the Np(V) (928 nm) and Np(VI) (1023nm) absorbance in the loaded solution is much lower than in the pure acid, indicating a shift in oxidation state towards Np(VI).

As the loading results were promising, it was decided that a continuous single centrifugal test should be performed at Forschungszentrum Jülich, using an existing simulated high active PUREX raffinate (HAR) solution with addition of the actinides (the composition of the raffinate solution can be found in Appendix C [MOD07]). Consequently, extractions with the GANEX solvent and this loading solution, including fission product suppression agents (bimet and mannitol) as well as the cyclohexanone stabilizing agent (sulfamic acid), were performed. Surprisingly, the actinide extraction from the HAR solution was found to be very low. For this reason, a kinetics test was performed and, as can be seen in Figure 5.5.3, the actinide extraction decreases over time.

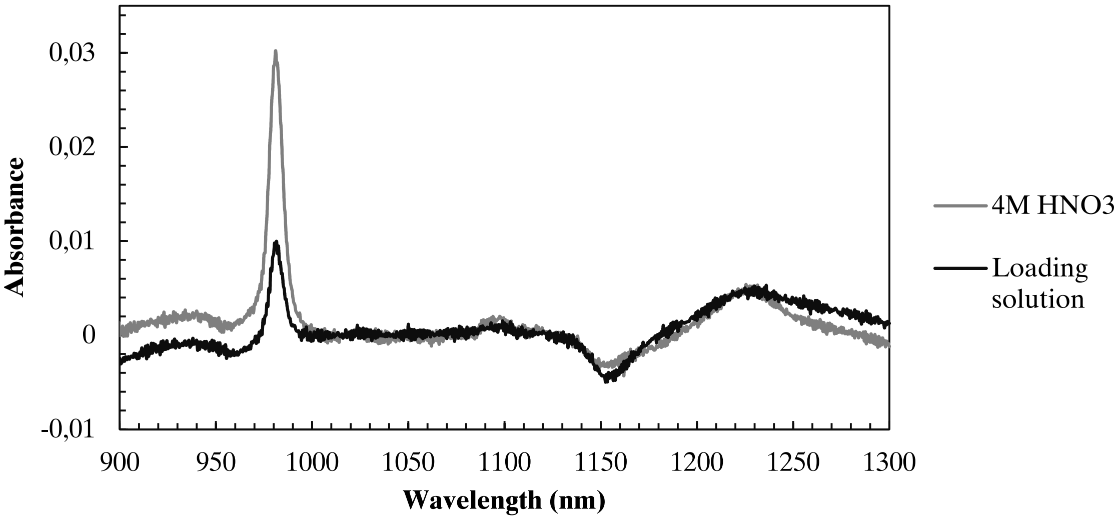

Figure 5.5.2 Spectrophotometric measurements of 4 M HNO_3 as well as 4 M HNO_3 loaded with fission products both spiked with ^{237}Np

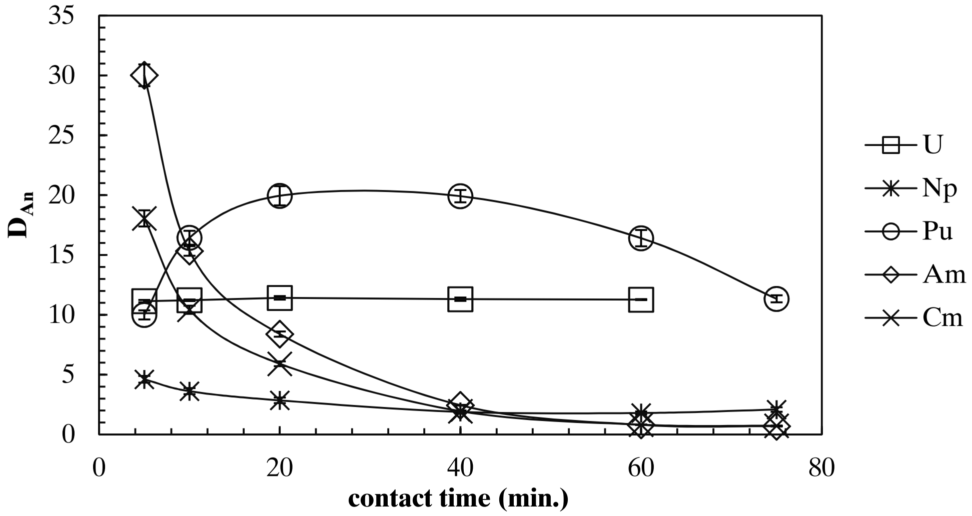

Figure 5.5.3 Extraction of actinides (^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am) at different contacting times with 0.01 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone from a 3.2 M nitric acid HAR solution (Appendix C) with additions of 20 mM bimet, 0.2 M mannitol and 50 mM sulfamic acid (lines added to guide the eye)

One major difference between this HAR solution and the previously used loading solution was a large presence of iron (previously used for redox control in the PUREX process) as well as the presence of ruthenium, which was left out of the other loading solution due to limited resources. When studying the kinetics behaviour of the fission products (and iron), a clear increase in extraction can be observed for three elements (Figure 5.5.4): iron, ruthenium and selenium. This extraction of mainly iron but also ruthenium causes a loading of the organic solvent with a drop in actinide distribution ratios in consequence. The selenium concentration in the HAR solution is, however, so low that this extraction only plays a minor role in the solvent loading.

To investigate whether this problem could be circumvented during the continuous centrifuge test, a new kinetics extraction was performed, this time with the aqueous HAR solution diluted ten times to decrease the loading. Under these conditions, the solvent was not loaded and the actinides were found to be extracted as desired.

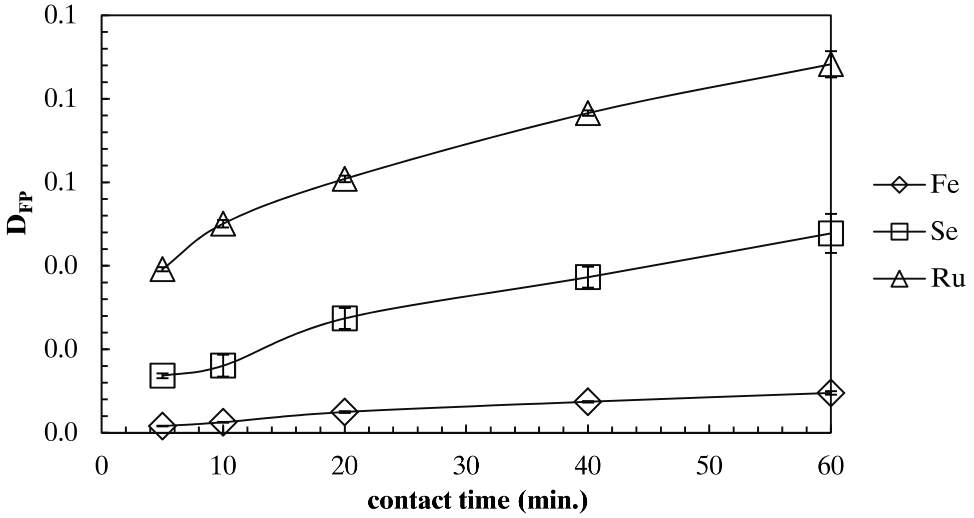

Figure 5.5.4 Extraction of fission products at different contacting times with 0.01 M $CyMe_4$-BTBP and 30% TBP in cyclohexanone from a 3.2 M nitric acid HAR solution (Appendix C) with additions of 20 mM bimet, 0.2 M mannitol and 50 mM sulfamic acid (lines added to guide the eye)

Besides the loading of fission products from the used fuel, the aqueous phase in a GANEX process will also contain relatively large amounts of plutonium, typically around 1 g/L [MAL00]. As in other GANEX solvents, precipitation upon high plutonium loading have been reported [BRO12] this was also investigated regarding the GANEX solvent in question. When the GANEX solvent was contacted with aqueous solutions of varying plutonium content, no apparent precipitation was observed at approximately 0.8 g/L Pu, while at 8 g/L a precipitate rapidly formed. These numbers indicate that this solvent might be able to handle adequately large amounts of plutonium to reprocess commercial used uranium oxide fuel.

5.5.2 Batch extraction

As a preparation for the continuous tests, a batch extraction test with all necessary steps discussed in section 2.6.1 following each other was performed. The extraction system was set to be the GANEX solvent as organic phase, with an aqueous phase consisting of the HAR solution (Appendix C) with an addition of trace amounts of actinides and europium as well as suppressing agents for the management of palladium, zirconium and molybdenum (bimet (20 mM) and mannitol (0.2 M)), and sulfamic acid (50 mM) for cyclohexanone stabilization. As the concentrated HAR solution was used for the extraction step, a short contact time was used to enable actinide extraction and to minimize the iron loading, according to the results in section 5.5.1. The same contact time was then also used for all the following steps.

It was decided that the actinides were supposed to be stripped as a group using glycolic acid. Glycolic acid of a higher pH has previously been shown to display faster stripping kinetics for this type of molecules than simple dilute nitric acid, which is another commonly used method [GEI06]. However, when the actinide stripping from the GANEX solvent was investigated it was discovered that the stripping was very low. The large amount of extracted acid (previously shown in section 5.2.1) was believed to be the reason for this and hence an acid scrub step was introduced before the stripping. For the acid scrubbing in this batch extraction test, 0.01 M HNO_3+0.99 M $NaNO_3$ + 0.6 M gluco-lactone (to increase molybdenum removal from the organic phase) was used and the step was performed twice to remove as much acid as possible. In the last step, the stripping, the actinides could then be removed from the organic phase using 0.5 M glycolic acid set to pH4 using ammonia. A schematic description of the whole batch extraction process can be found in Figure 5.5.5.

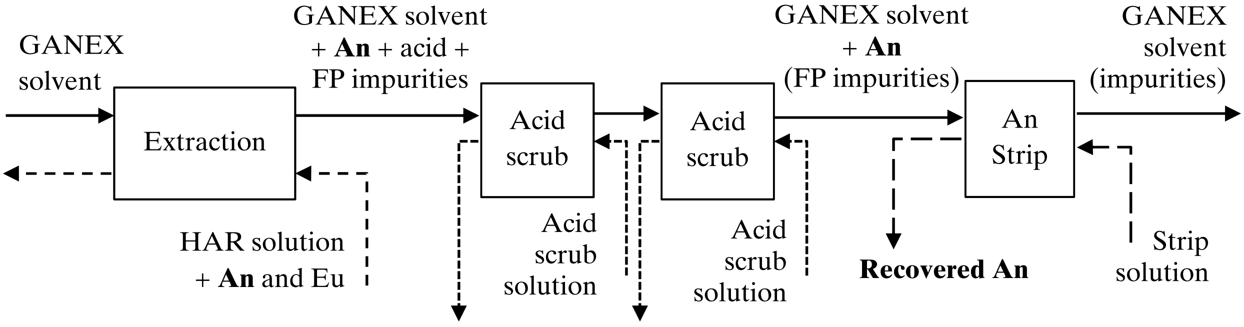

Figure 5.5.5 Schematic picture of the batch extraction experiments with the different process steps

The actinide and europium distribution ratios from all four process steps are displayed in Figure 5.5.6. As can be seen, the actinide distribution ratios are above logD=1 for the extraction step as well as in both scrubbing stages, resulting in good actinide recovery with minor losses. As the distribution ratio for all actinides is also very low in the stripping stage, this mean a more or less quantitative recovery of actinides from the organic phase. For europium, however, distribution ratios throughout the different process steps are very low, resulting in large separation between actinides and lanthanides, as desired. When calculating the total recovery of actinides over the four different process steps (Table 5.5.1), it can be concluded that 70% or more of all actinides are recovered in a one-stage process. Also less than 1% of europium is found among the actinides. When looking at the rest of the fission products (Table 5.5.2), it can be concluded that selenium, molybdenum and ruthenium are the only ones that are found among the actinides in the strip solution in quantities over 1% of the initial concentration. Most products are either not extracted or removed in the acid scrub stages. Some elements are, however, extracted and remain in the organic raffinate after the final strip stage. To get rid of these elements (especially nickel, ruthenium and cadmium) and to be able to re-use the organic phase, an efficient solvent clean-up must be developed.

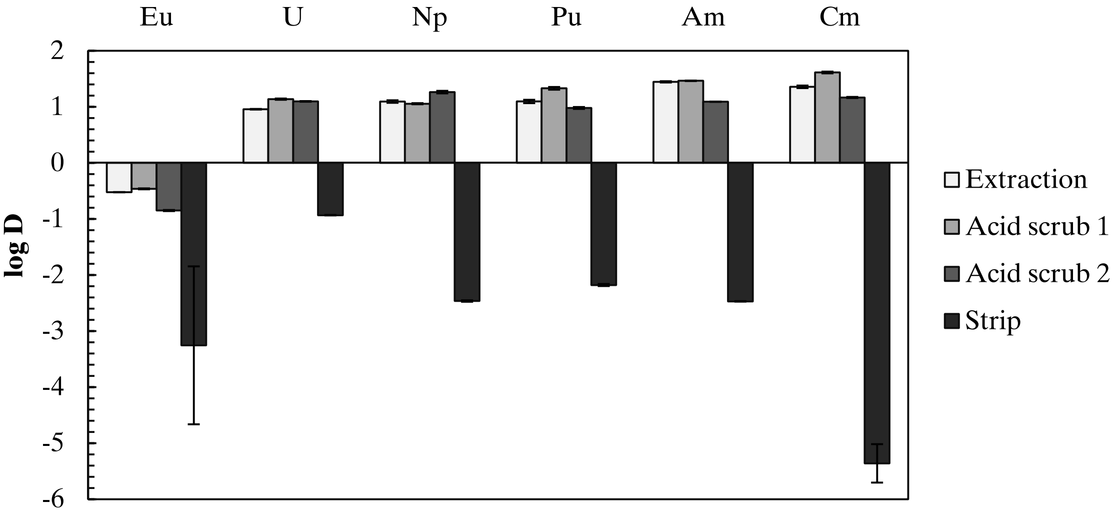

Figure 5.5.6 Extraction with 0.01 M CyMe$_4$-BTBP and 30% TBP in cyclohexanone of ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am, ^{244}Cm and ^{152}Eu from the 3.2 M HNO$_3$ HAR solution (Appendix C) with additions of 20 mM Bimet, 0.2 M Mannitol and 50 mM sulfamic acid

Table 5.5.1 An and Ln recovery in the strip solution after one extraction and two acid scrub steps in the batch process test

Element	% of initial
Eu	0.73
U	69.6
Np	80.4
Pu	79.6
Am	86.0
Cm	87.6

5.5.3 Continuous extraction

As it could be concluded in section 5.5.2 that the batch process test was successful, a single centrifugal contactor test was now performed. However, during the first test with the same solutions as in the batch process test (except for a dilution of the HAR solution 1:10), it was discovered that the difference in density between the organic and aqueous phase was too small to facilitate efficient phase separation in the equipment. To make the test viable, the densities of the aqueous phases were raised using salt additions.

Table 5.5.2 Fission product inventory in the strip solution and organic raffinate after one extraction and two acid scrub steps in the batch process test

Element	% of initial in strip solution	% of initial in org raffinate
Se	2.6	2.4
Fe	0.00	2.5
Na	0.00	0.00
Al	0.00	0.00
Cr	0.00	0.05
Ni	0.09	93
Rb	0.00	1.0
Sr	0.05	1.1
Y	0.00	0.00
Zr	0.38	0.76
Mo	3.6	5.4
Ru	2.0	10
Rh	0.01	0.03
Pd	0.13	0.78
Ag	0.06	3.3
Cd	0.24	86
Sn	0.47	0.37
Sb	0.29	0.04
Te	0.12	1.4
Cs	0.00	0.00
Ba	0.05	54*
La	0.01	0.02
Ce	0.00	0.08
Pr	0.00	0.00
Nd	0.02	0.00
Sm	0.28	0.00
Eu	0.73	0.00
Gd	0.47	0.00

* Number most likely an artefact from the surroundings; this has previously been shown for Ba in ICP-measurements [HED10]

This rendered a slightly different extraction system, though still using the GANEX solvent as organic phase. The HAR solution was diluted 1:10 with an addition of bimet (20 mM), mannitol (0.2 M) and sulfamic acid (50 mM), as before, but also 3 M $NaNO_3$ to increase the density. In the same way, the density of the acid scrub solution (0.01 M HNO_3+0.99 M $NaNO_3$ + 0.6 M gluco-lactone) was raised by an addition of 3 M $NaNO_3$. It was also decided to only use one acid scrub stage due to time constraints. To increase density of the stripping solution, 1 M Na_2SO_4 was added to the 0.5 M glycolic acid solution before adjusting the pH to 4. This was because a nitrate addition would hinder stripping of the actinides. For each stage, two different flow rates (60 mL/h and 30 mL/h, same for both phases) were used to evaluate the kinetics of the system in the centrifugal contactor. The results for the actinides and europium are shown in Table 5.5.3. It is obvious that for americium and plutonium, both flow rates render results far from the equilibrium values.

Table 5.5.3 Distribution ratios for ^{235}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{152}Eu in the single centrifugal contactor test

Steady State (60 mL/h)	Eu	U	Np	Pu	Am
Extraction	0.18	46	16	39	3.3
Scrub	5.8	70	11	1900	530
Strip	0.50	0.09	0.43	65	260
Steady State (30 mL/h)	**Eu**	**U**	**Np**	**Pu**	**Am**
Extraction	0.24	45	17	23	6.9
Scrub	5.2	130	47	560	260
Strip	0.26	0.08	0.07	1.2	5.1
Equilibrium	**Eu**	**U**	**Np**	**Pu**	**Am**
Extraction	1.2	48	31	290	110
Scrub	2.15	150	15	770	110
Strip	0.004	0.04	0.03	0.05	0.24

The stripping is especially slow, which could be attributed to an insufficient acid scrub of the organic phase due to only one acid scrub step rather than the two steps in the batch process test. It is also clear that the lower flow rate (30 mL/h) gives a better result for the extraction and stripping stages for all elements. The combined results for both uranium and neptunium are, however, rather good, once again indicating that there is a possible shift in oxidation state of the neptunium which also shifts the extraction mechanism. Nevertheless, it can be concluded that the centrifugal contactor in question is not suitable for this system as the phase contact is not sufficient to reach values close to equilibrium, especially for americium. CyMe$_4$-BTBP in another solvent has been previously tested in similar equipment and was in that case also proven to be rather slow [MAG09]. Hence these results are not unexpected. Another type of centrifugal setup, such as the AKUFVE [RYD69], where the mass transfer is facilitated in a mixing chamber and only phase separation in the centrifuge, would possibly be a better alternative. Although centrifuges are the preferred equipment for partitioning and transmutation due to criticality risks, hot tests within nuclear reprocessing have already been conducted using, e.g., miniature mixer settlers [MIG09, MIG09X]. The commercial PUREX process at La Hague, France, is operated using pulsed columns, which shows that there are options other than centrifuges that would be more suitable for this system. This would, of course, require thorough calculations to avoid criticality.

5.5.4 Flow sheet calculations

Using the equations for counter current extraction described in section 2.6.3, the outcome of a multi-stage process can be calculated on the basis of single-stage batch or centrifugal contactor experiments. The final outcome of the process can be optimized by changing the amount of steps (n) as well as the organic to aqueous ratio (Θ) in each stage of the flow sheet. This optimization is illustrated for the extraction step of the batch process test in Figures 5.5.7 and 5.5.8. It is clear from Figure 5.5.7 that five extraction stages are sufficient to quantitatively extract the actinides, although at this phase ratio a substantial amount of europium is also extracted. To decrease the europium extraction, the phase ratio can be lowered, still maintaining high actinide extraction, according to Figure 5.5.8.

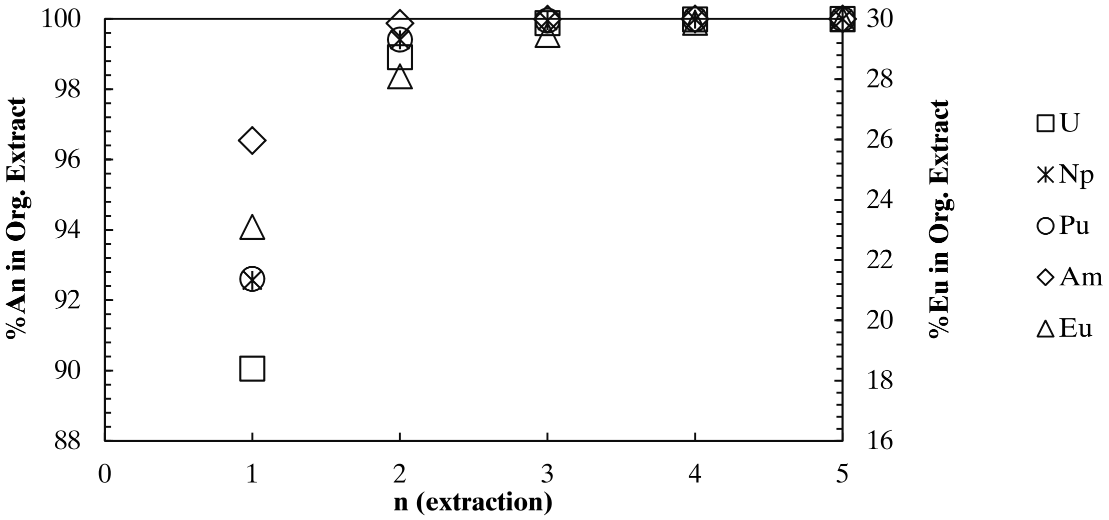

Figure 5.5.7 % of actinides and europium in the organic extract as a function of the number of extraction steps, n, with Θ=1

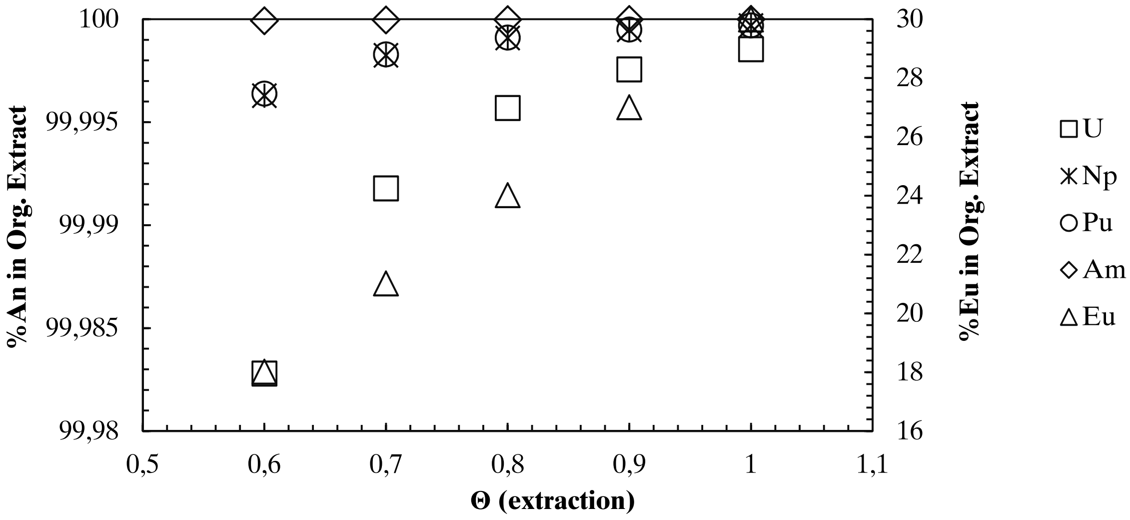

Figure 5.5.8 % of actinides and europium in the organic extract as a function of the organic to aqueous volume, Θ, with n=5

This type of manual optimization was now performed for the different stages in the batch extraction flow sheet (Figure 5.5.5). The phase ratio was set at Θ=0.6 in all stages (an even lower value would be beneficial but too large a difference in phase ratio can sometimes be difficult to handle practically) using 7 extraction steps, 6 acid scrub 1 steps, 6 acid scrub 2 steps and 1 strip step. The results from the optimized calculations can be seen in Table 5.5.4. The deviation from 99.99% actinide recovery in all cases results from the strip stage. To recover more of the actinides, another fresh strip solution could be used in a second strip stage or the organic phase could be recirculated. However, this recirculation could not be performed before remaining fission products in the organic phase had been removed (mainly nickel and cadmium), which would also be likely to result in loss of the actinides. The only fission products found together with the actinides in the aqueous strip solution in quantities larger than 1% of their initial concentration are molybdenum, ruthenium and selenium with 6%, 4% and 2% respectively. For the full fission product data see Table 5.5.5.

Table 5.5.4 Flow sheet calculations based on batch process test data using Θ=0.6, 7 extraction steps, 6 acid scrub 1 steps, 6 acid scrub 2 steps and 1 strip step

Element	% of initial in aqueous strip
Eu	0.32
U	93.5
Np	99.8
Pu	99.6
Am	99.8

Using the data obtained from the single centrifugal contactor test in the same way, it can be concluded that with Θ=0.6, 15 extraction steps (data from flow rate 60 mL/h), 3 acid scrub steps (data from flow rate 30 mL/h), and 1 strip step (data from flow rate 30 mL/h), a large quantity of uranium and neptunium can be recovered (Table 5.5.6). Unfortunately, the americium and plutonium recovery is rather minor, while the europium contamination is high. The actinide extraction can, however, be more or less quantitative for all actinides despite the kinetically slow system and non-optimal contacting equipment. The low americium and plutonium recovery is due to insufficient stripping. This is, as previously mentioned in section 5.5.3, most likely a result from both slow stripping kinetics and an inadequate acid scrub of the organic phase.

Table 5.5.5 Flow sheet calculations based on batch process test data using Θ=0.6, 7 extraction steps, 6 acid scrub 1 steps, 6 acid scrub 2 steps and 1 strip step

Element	Impurity in Aq strip (% of initial)	Impurity in Org after strip (% if initial)
Se	4.1	2.3
Fe	0.00	1.5
Na	0.00	0.00
Al	0.00	0.00
Cr	0.00	0.00
Ni	0.17	99.8
Rb	0.46	0.00
Sr	0.05	0.63
Y	0.00	0.00
Zr	0.60	0.73
Mo	6.2	5.6
Ru	2.3	7.0
Rh	0.00	0.02
Pd	0.14	0.53
Ag	0.07	2.3
Cd	0.47	99.5
Sn	0.53	0.25
Sb	0.27	0.02
Te	0.17	1.2
Cs	0.00	0.00
Ba	0.14	86*
La	0.00	0.00
Ce	0.00	0.00
Pr	0.00	0.00
Nd	0.01	0.00
Sm	0.10	0.00
Eu	0.32	0.00
Gd	0.19	0.00

*An artefact from the surroundings in the experimental data (see Table 5.5.2)

Table 5.5.6 Flow sheet calculations based on single centrifugal contactor data using Θ=0.6, 15 extraction steps, 3 acid scrub steps and 1 strip step

Element	% of initial extracted	% of initial in aqueous strip
Eu	11	9.1
U	100.0	95
Np	100.0	96
Pu	100.0	58
Am	100.0	25

6. Summary and Conclusions

In this work, a novel liquid-liquid extraction system for implementation in a Group ActiNide Extraction (GANEX) process has been developed, tested and evaluated.

The GANEX solvent is comprised of CyMe$_4$-BTBP and TBP in cyclohexanone. This solvent composition was found to be able to efficiently extract the actinides (U, Np, Pu, Am and Cm) as a group from 4 M nitric acid. The two ligands (BTBP and TBP) were also found to not react and to extract independent of each other. The actinides could be separated from most of the fission products (including the trivalent lanthanides) and corrosion/activation products with high separation factors. The solvent is also adequately stable to both hydrolysis at room temperature as well as γ-radiolysis in the presence of nitric acid up to a total dose of 200 kGy. However, cyclohexanone was found to be unstable in the presence of 4 M nitric acid upon prolonged heating, resulting in an exothermic reaction. To prevent this, sulfamic acid (a nitrous acid scavenger) could be added to the acid before contact. The actinide extraction was, however, also found to be decreased during an increased solvent temperature, and the whole process would therefore work best if cooled. An attempt was made to replace TBP with DEHBA but as there was no improvement in the solvent performance, the following studies were made using the original solvent. The extraction of the fission products palladium, zirconium and molybdenum by the GANEX solvent was found to be manageable by combining the two water-soluble complexing agents bimet and mannitol in the aqueous feed. The complexation of palladium by CyMe$_4$-BTBP was found to be extra problematic due to water solubility of the complex. The complexation of palladium with bimet, however, prevents both the Pd:BTBP complexation as well as the precipitation of palladium black that otherwise is initiated by the presence of cyclohexanone. As molybdenum suppression by mannitol was not complete, gluco-lactone was found to increase the molybdenum removal in a subsequent acid scrub step of the solvent. An acid scrub step was found necessary as the GANEX solvent extracted large amounts of nitric acid, which compromised the actinide group stripping using glycolic acid. Another major fission product, technetium, was found to be extracted as pertechnetate by cyclohexanone in the solvent. However, under fission product loading conditions, it appears that the extraction mechanism changes to co-extraction with, most likely, CyMe$_4$-BTBP. When continuing to investigate the solvent from a process perspective it can be concluded that it is possible to extract the actinides from a water phase loaded with fission products. However, large quantities of iron suppress the extraction with an increase in contact time. A batch process test could therefore only be performed with an HAR solution with large iron content if the contact time was kept short and the extraction not was allowed to reach equilibrium. The results showed an adequate actinide extraction and lanthanide separation as well as a successful group actinide stripping after two successive acid scrub steps. This means that the solvent show promise for the homogenous recycling of used nuclear fuel. Based on the batch process data, flow sheet calculations were also performed to optimize the number of steps as well as the phase ratio for a possible continuous system. Single centrifugal contactor tests were also performed on all the process steps (extraction, acid scrub and stripping), which, after adjustment of the phase densities, were completed successfully. However, the data showed that equilibrium was far from being reached in all stages (especially the stripping) for americium and plutonium and this type of equipment can therefore be concluded to be unsuitable for this solvent.

All in all, what has been performed in this work is a proof of concept rather than development of a finished product. It has been shown that it is possible to perform a GANEX process by extracting the actinides in the same time as they are separated from the lanthanides as well as the rest of the fission products.

7. Future Work

Future work based on the findings presented in this thesis could be performed along two different paths, where one does not exclude work on the other. One path would be to conduct more detailed studies and optimizations of the existing system, while the other would be to try and find another system based on the same foundation as the first one, in order to increase the process viability.

For the existing system, the rather complex radiolysis behaviour of the GANEX solvent needs further investigation. Efforts must be made to identify degradation products, investigate the chemistry of plutonium in the irradiated system and to decipher in detail the difference between the hydrolysed and irradiated systems. A deeper investigation of the neptunium chemistry would also be interesting, as many findings point towards Np(V) oxidation to Np(VI), resulting in a changed oxidation mechanism. Technetium is another substance that need further investigation to see if there is any co-extraction of pertechnetate with the actinides and CyMe$_4$-BTBP, and if so, how to handle this. A more process-oriented investigation would involve testing the system in other more suitable contacting equipment, using a loading solution without the large iron addition.

When changing the system, the most important feature would be to try and find an innovative diluent with better stability properties than cyclohexanone. This diluent should either promote plutonium extraction by TBP rather than BTBP or allow for a larger solubility of BTBP to increase the loading capacity of the solvent, thereby increasing the error margins of the process. An alternative would be to replace the CyMe$_4$-BTBP with another similarly stable molecule that has larger solubility in alkane diluents. This would then allow for replacement of cyclohexanone with, e.g., octanol and at the same time increase the loading capacity.

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Appendix A

Table A1 Concentrations of fission products and corrosion products (measured with ICP-OES) used in the extraction experiments, where indicated

Substance	Conc. (ppm)	Conc. (mM)
Ba	480	3.5
Ce	930	6.6
La	480	3.5
Nd	1360	9.4
Cs	1200	9.0
Rb	100	1.2
Sm	230	1.5
Sr	240	2.7
Te	1470	11.5
Y	110	1.2
Ag	60	0.5
Cd	30	0.3
Rh	40	0.4
Sb	10	0.08
Sn	1	0.008
Co	300	5.1
Cr	260	5.0
Fe	270	4.8
Mn	330	6.0
Zr	1500	16
Pd	450	4.2
Mo	650	6.8
Ru	400	3.9

Appendix B

Table B1 Molecular structures and names of the different organic oxo-species tested for suppression and scrubbing of Zr, Mo and Pd from the GANEX solvent (CyMe$_4$-BTBP+TBP in cyclohexanone). Names within brackets are those used in the text.

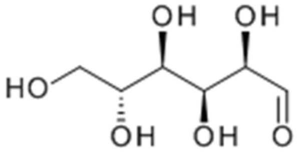
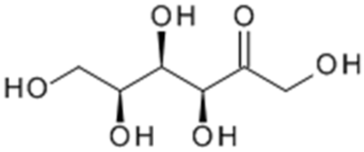
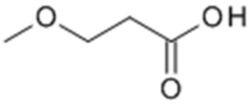
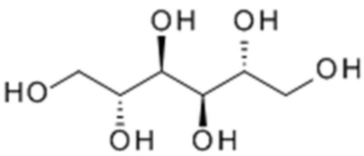
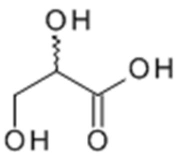
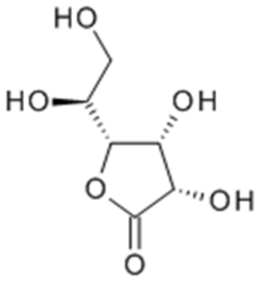
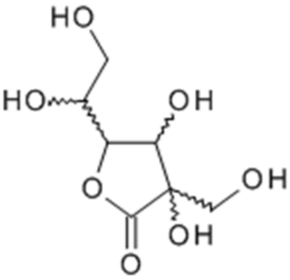
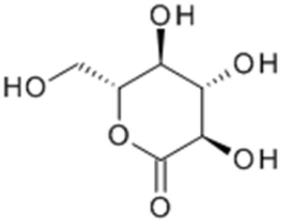
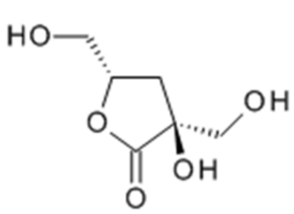
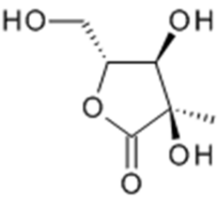
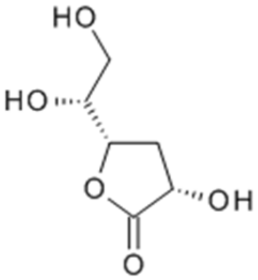
Molecular structure	Name
	D-Glucose (Glucose) (2*R*,3*S*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexanal Acros Organics 99+%
	L-Sorbose (Sorbose) (*3S,4R,5S*)-1,3,4,5,6-Pentahydroxyhexan-2-one Acros Organics 98%
	3-Methoxypropionic acid (m-Propionic acid) Aldrich 99%
	D-Mannitol (Mannitol) (2*R*,3*R*,4*R*,5*R*)-Hexan-1,2,3,4,5,6-hexol Difco laboratories ”certified” reagent
	D,L-Glyceric acid (Glyceric acid) 2,3-Dihydroxypropanoic acid ABCR 40% in H_2O

Table B2 Molecular structures and names of the different lactones tested for suppression and scrubbing of Zr, Mo and Pd from the GANEX solvent (CyMe$_4$-BTBP+TBP in cyclohexanone). Names within brackets are those used in the text.

Molecular Structure	Name
	L-gulono-1,4-lactone (Gulono-lactone) ((3S,4S,5R)-5-[(1S)-1,2-dihydroxyethyl]-3,4-dihydroxy-oxolan-2-one) In-house synthesis
	Fructic acid (Fructic acid) (5-(1,2-dihydroxyethyl)-3,4-dihydroxy-3 (hydroxymethyl)dihydrofuran-2(3H)-one) In-house synthesis
	D-glucono 1,5-lactone (Gluco-lactone) (3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-one Acros Organics 99%
	α-iso-saccharinic acid (ISA) ((2*S*,4*S*)-2,4,5-Trihydroxy-2-(hydroxymethyl)pentanoic acid) In-house synthesis
	2-C-methyl-L-ribonolactone (Ribono-lactone) (3R,4R,5R)-3,4-dihydroxy-5-(hydroxymethyl)-3-methyldihydrofuran-2(3H)-one In-house synthesis



Metasaccarinic acid (MESA)

(3-deoxy-D-*arabino*-hexono-1,4-lactone)

In-house synthesis

Appendix C

Table C1 Composition of the synthetic HAR solution (in 3.2 M HNO_3)

Element	mg/L
Ag	12.6
Na	2034
Al	2
Nd	718
Ba	264
Ni	47
Cd	17
Pd	123
Ce	518
Rb	65
Cr	91
Pr	219
Cu	19
Rh	80
Cs	556
Ru	388
Y	102
Sb	4.4
Eu	33
Se	9
Fe	1900
Sm	146
Gd	35
Sn	11
La	218
Sr	167
Mo	672
Zr	1165
Te	481