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Advances in the Application and Understanding of the CHALMEX FS-13 Process

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Cover: Process flow schematic of the CHALMEX process

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ABSTRACT

During the last year, the European demand for electricity has increased and at the same time, the production of planned electricity generation has decreased due to unexpected weather conditions and war. Combined with a limited capability to store energy, low-carbon energy producers such as nuclear power is getting renewed attention in many countries. While having benefits such as reliable, clean, affordable and safe electricity production, the main concerns regarding nuclear power usually refer to the extremely long-lived and radiotoxic final waste. The main contributor to the long-lived radiotoxicity of the spent fuel is Pu and the minor actinides (Np, Am, Cm).

The Chalmers Grouped ActiNide EXtraction (CHALMEX) process is a solvent extraction process for the recycling of minor and major actinides as a group, from spent nuclear fuel. By recycling the actinides, and using them as fuel in fast reactors, one can significantly reduce both the overall environmental impact of the nuclear fuel cycle, the lifetime- and the radiotoxicity of the final waste.

By combining the extractants TBP with CyMe$_4$-BTBP in the diluent FS-13, the CHALMEX solvent has been shown to have preferential physical properties for use in industrial processes. Separation of the actinides from a spent fuel solution is achieved in only 8 process stages. The co-separation of specific fission products is reduced by the use of masking agents and scrubbing stages. Overall, low degrees of fission product contamination is found in the actinide product stream ($<1.5\%$).The kinetics of the system has also been shown to be compatible with contacting in centrifugal contactors. Despite observation of phase entrainment under certain conditions in a centrifugal contactor, the CHALMEX process is a promising process for the actinide separation from spent nuclear fuels.

LIST OF PUBLICATIONS

I. Thea Lyseid Authen, Andreas Wilden, Jenny Halleröd, Dimitri Schneider, Fabian Kreft, Giuseppe Modolo & Christian Ekberg (2021) Batch Tests for Optimisation of Solvent Composition and Process Flexibility of the CHALMEX FS-13 Process, *Solvent Extraction and Ion Exchange*, 39:1, 1-17, DOI: 10.1080/07366299.2020.1797988

II. Thea Lyseid Authen, Andreas Wilden, Dimitri Schneider, Fabian Kreft, Giuseppe Modolo, Mark R. StJ Foreman & Christian Ekberg (2021) Batch flowsheet test for a GANEX-type process: the CHALMEX FS-13 process, *Solvent Extraction and Ion Exchange*, 40:3, 189-202, DOI: 10.1080/07366299.2021.1890372

III. Thea Lyseid Authen, Jean-Marc Adnet, Stéphane Bourg, Michael Carrott, Christian Ekberg, Hitos Galán, Andreas Geist, Philippe Guilbaud, Manuel Miguirditchian, Giuseppe Modolo, Chris Rhodes, Andreas Wilden & Robin Taylor (2021) An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, Part 2 — homogeneous recycling, *Separation Science and Technology*, DOI: 10.1080/01496395.2021.2001531

IV. Jenny Halleröd, Christian Ekberg, Thea Authen, Laura Bertolo, Mu Lin, Bohumír Grüner, Jaroslav Švehla, Christoph Wagner, Andreas Geist, Petra Panak & Emma Aneheim (2018) On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based GANEX System Containing CyMe4-BTBP and TBP, Solvent Extraction and Ion Exchange, 36:4, 360-372, DOI: 10.1080/07366299.2018.1497043

V. Thea Lyseid Authen, Behabitu Ergette Tekikachew, Mark R. StJ. Foreman, Andreas Wilden & Christian Ekberg (2022) A comparison on the use of DEHBA or TBP as extracting agent for tetra- and hexavalent 5 actinides in the Chalmers Grouped ActiNide EXtraction Process.
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CONTRIBUTION REPORT

I. Lead author. Performed all experiments, the majority of analytical procedures and wrote the manuscript.

II. Lead author. Performed all experiments, the majority of analytical procedures and wrote the manuscript.

III. First author. Wrote the first draft of the manuscript.

IV. Co-author. Performed a portion of the experimental and analytical work.

V. Lead author. Performed all experiments, analytical procedures and wrote the manuscript.

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Chapter 1

Introduction

During the winter months of 2021-22, the combination of dry, overcast weather and little wind reduced the capacity of renewable electricity production across the European continent. Even more recently, the war in Ukraine has forced the energy debate to consider Europe's energy supply and security. Combining a higher than usual electricity demand all over Europe with a high cost of natural gas, electricity prices were reaching new all-time highs throughout the winter season.[1] The Nord Pool market, for instance, saw the highest increase in electricity costs with a 46% higher price compared to the month November the year before.[2–4]

Although world leaders have agreed on decarbonisation, and renewable energy production provided more than 50% of the global electricity supply in 2021, carbon emissions are rising. The increase in emissions is directly related to an increased energy demand due to the fast electrification of society as a whole, from industries to our vehicles and to private homes. However, the vulnerability of an electricity market based largely on renewable sources has become evident.[5–8]

With an increasing demand for electricity as the world sees increasing electrification and decarbonisation, the need for a reliable and non-intermittent electricity supply is undeniable. In the UN *International Panel on Climate Change's* (IPCC) special report on possible emission pathways and system transition, nuclear power is identified as a key contributor to the production of green and affordable electricity.[9] The same was also reflected in the European Commission's *taxonomy for environmentally sustainable activities*.[8, 10, 11]

While nuclear power can claim green, steady, reliable, safe and economical electricity production, concerns are usually associated with the production and final disposal of long-lived, highly radioactive spent nuclear fuel (SNF).[12–14] In the majority of nuclear power states today, SNF is temporarily stored awaiting final disposal in a geological repository. An already proven option is to recycle the
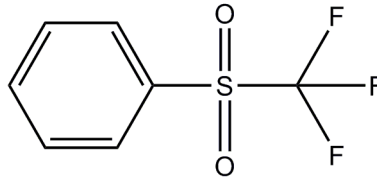
Figure 1.1: Molecular structure of phenyl trifluoro methyl sulfone (FS-13)

unused uranium and produced plutonium to manufacture so-called mixed-oxide (MOX) fuels. A third, and very promising technology, allows for the recycling of neptunium, americium and curium in addition to the uranium and plutonium. The recycling of these elements would significantly reduce the environmental impact of nuclear power, considering all impact factors in a *Life Cycle Analysis* (LCA).[15, 16] Amongst other things, recycling would reduce or even eliminate the need for mining of fresh uranium ore and reduce the final volume of highly active waste needing long-term disposal in a repository. Studies show that through the recycling of U, Pu and Am only, one can reduce the footprint of a geological repository by a factor of 7. Furthermore, a full recycle of SNF would reduce the long-term radioactivity and radiotoxicity of the waste from the 10^5 year range to the 10^3 year range.[15–18]

The Chalmers Grouped Actinide Extraction (CHALMEX) process is a solvent extraction process for the recycling of uranium, plutonium, neptunium, americium and curium as a group, without redox control. In the most recent work on the process, a focus has been on investigating a different diluent than before, namely phenyl trifluoro methyl sulfone (Figure 1.1). Although the extractants remain the same as for earlier solvents, the diluent changes the solvent characteristics, which meant that gaining a fundamental understanding of the system was the focus iof previous work on the CHALMEX process.[19–21] More specifically, Halleröd et al. investigated the extraction behaviour of the system, the solvent stability and the solvent thermodynamic properties.[22–27]

Here, the fundamental understanding of the system has remained in focus by targeting specific knowledge gaps important for the scale up of the process. These knowledge gaps include performance under varying process parameters, including acid concentrations, pH and temperatures. In addition, already identified issues such as fission product extraction and retention have been targeted. Furthermore, as an improved understanding of the CHALMEX FS-13 system was gained, attention was concentrated on the system performance when subjected to more process-relevant conditions. Such conditions are related to metal loading, masking agents, kinetics and continuous extraction in relevant contactors.

Chapter 2

Background

2.1 A brief history of nuclear power

Nuclear fission was first discovered in 1938, when the fission fragments of ^{235}U, ^{141}Ba and ^{92}Kr were detected after bombardment of uranium with neutrons, as illustrated by Equation 2.1. Lise Meitner and her nephew Otto Frisch soon realised that the huge amount of energy released in the reaction ($\sim$200 MeV) was due to the mass defect. The high energy quickly attracted the attention of researchers like Oppenheimer, who started the development of the *atomic bomb* in the Manhattan project.[28]

$$^{1}_{0}n + {}^{235}_{92}\text{U} \Longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3{}^{1}_{0}\text{n} \tag{2.1}$$
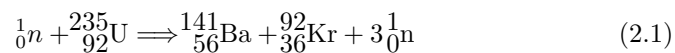
Years before nuclear power became a reality, the Manhattan project became the start of nuclear reprocessing as we know it today. To produce the atomic bomb, a significant amount of pure ^{239}Pu or ^{235}U was needed. To separate these elements, it was quickly realised that the, until then, two known oxidation states of plutonium could be exploited. Solvent extraction processes were thus pursued as the most efficient separation technique. The bismuth phosphate process became the first process used to separate uranium and plutonium from their fission products and each other.[28–31] Shortly afterwards, the bismuth phosphate process was superseeded by the REDOX process, which in turn was superseeded by the PUREX (Plutonium Uranium Reduction EXtraction) process.The PUREX process has since remained the benchmark process for nuclear reprocessing.[32]

In 1951, 9 years after the start of the Manhattan project, electricity production from nuclear fission reactions was achieved when the EBR-I fast reactor powered four 200 W lightbulbs. Three years later, in 1954, the USSR's ther-

mal, 5 MW$_e$ Obninsk APS-1 became the first nuclear reactor connected to the electricity grid.[33, 34] Today, there are more than 430 operable nuclear power reactors, producing about 390 GW$_e$, with another 55 reactors planned or under construction.[35–37]

2.2   Power production

The power production in a nuclear reactor is based on sustaining a chain reaction by utilising the 2-3 neutrons released in a fission reaction, illustrated in Figure 2.1, to induce further fission reactions. In power reactors, the chain reaction is controlled so that the neutrons released in one fission reaction, induce just one more fission reaction. Most reactors today operate in a thermal neutron spectrum: i.e. the neutrons are slowed down (moderated) to facilitate the absorption and subsequent fission of the traditional uranium fuel.[36, 38]
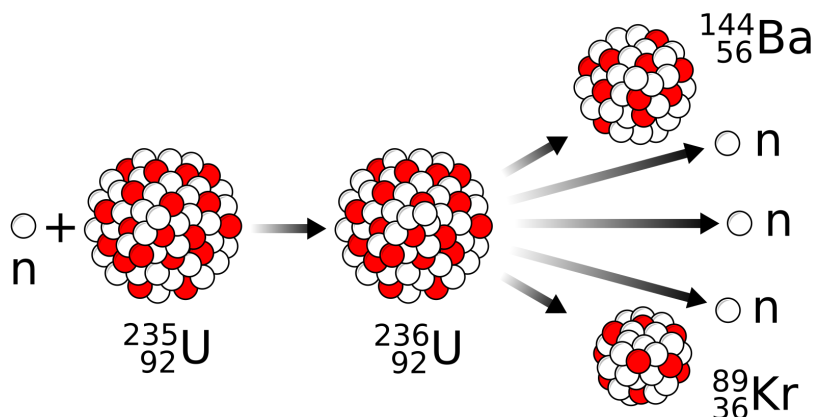

Figure 2.1: Schematic of a nuclear fission reaction. Reproduced under the CC-BY license.[30]

The most common nuclear fuel is a ^{235}U enriched UO$_2$ fuel. This is based mainly on the high fissionability of this isotope when subject to thermal neutrons.[30] Generally the fuel enrichment is between 3-5 wt% in commercial reactors. In addition, MOX fuels consisting of uranium and ^{239}Pu are not uncommon.[36] When uranium (or plutonium) undergoes fission, the energy is released as thermal energy. This energy is used to heat water into steam, which runs turbines. The turbines drive generators, which produces electricity for the grid.[36]

Some reactors can operate with unmoderated "fast" neutrons, and are referred

to as fast reactors. Fast reactors fission ^{238}U much more efficiently than thermal reactors. In addition, fast reactors allow for the use of the minor actinides (MA= Np, Am, Cm) as fuel. Pu and MA are the main contributors to the long-lived radioactivity and radiotoxicity of spent nuclear fuel, as shown in Figure 2.2.[36, 39]
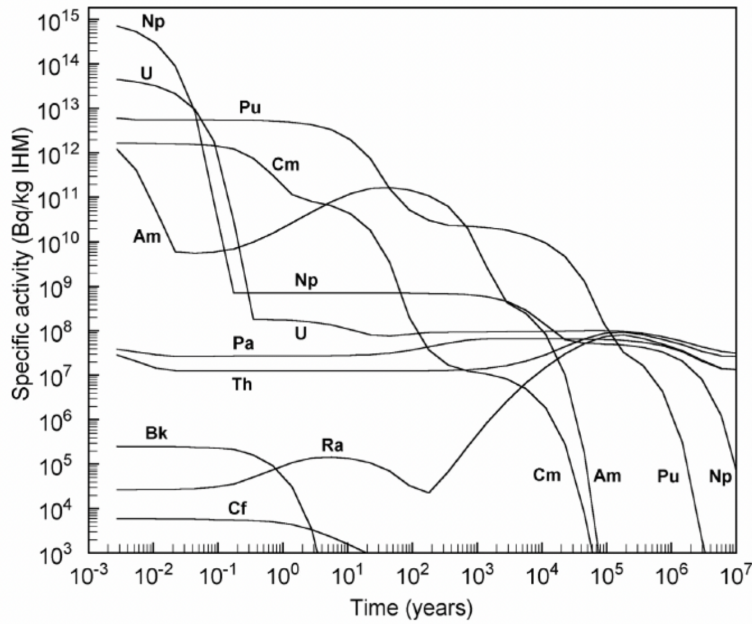

Figure 2.2: The specific activity of different radionuclides present in spent nuclear fuel as a function of time.[36] Reproduced under the CC-BY license.

2.3 Spent nuclear fuel

More than 400 different fission fragments have been observed from the fission of just ^{235}U. The masses of the fission products tend to concentrate around mass number 97 and 137, as shown by the fission yields presented in Figure 2.3.[40]

Further adding to the complexity of nuclear fuel is the fact that not all neutron absorptions lead to immediate fissioning. Some absorptions produce higher actinides, such as ^{236}U and ^{239}U, and even higher actinides through processes such as seen in Equation 2.2. Through both decay of these isotopes and subsequent neutron absorption, an intricate mixture of elements are formed by the time the fuel is taken out of the reactor.
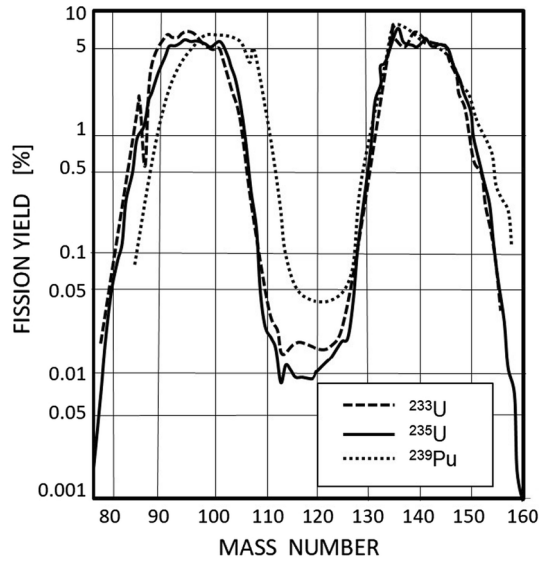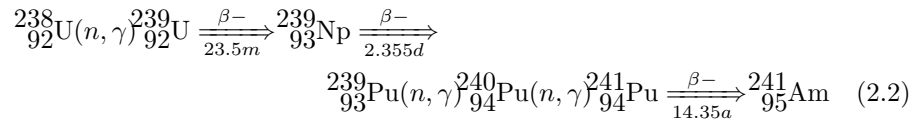
Figure 2.3: The mass distribution of fission products resulting from the fission of ^{233}U, ^{235}U and ^{239}Pu by thermal neutrons.[40]

$$^{238}_{92}\text{U}(n, \gamma)^{239}_{92}\text{U} \xrightarrow[23.5m]{\beta-} {}^{239}_{93}\text{Np} \xrightarrow[2.355d]{\beta-}$$
$$^{239}_{93}\text{Pu}(n, \gamma)^{240}_{94}\text{Pu}(n, \gamma)^{241}_{94}\text{Pu} \xrightarrow[14.35a]{\beta-} {}^{241}_{95}\text{Am} \quad (2.2)$$

2.3.1 Management options

When nuclear fuel is taken out of the reactor, it is very hot and highly radioactive and requires immediate cooling in cooling ponds. The water in the ponds provides both cooling and shielding from the high radiation. A typical cooling period is 3-5 years, after which the fuel is transferred for interim storage awaiting reprocessing or final disposal. The interim storage can be a wet storage or dry storage. Since very few countries have made progress on their final disposal sites, the "interim" storage can have a timeframe of 30-40 years and counting.[41]

Direct disposal is the approach chosen by the majority of the nuclear power states and is usually referred to as the open fuel cycle. Here, the spent fuel will be disposed of in a geological repository. The most developed concept so far is the KBS-3 concept, developed by the Swedish SKB (*Svensk Kärnbränslehantering AB*). The concept is based on a multi barrier protection system consisting of a copper canister, bentonite clay and crystalline bedrock.[42] Finland's Onkalo, a KBS-3 concept geolical repository, will be the world's first operating final disposal site for spent nuclear fuel (trials to start by 2023, disposal by 2025),

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while the Swedish authorities have recently approved the application for the Forsmark repository submitted by SKB.[42–45]

Upon removal from the reactor, more than 90% of the fuel's energy potential remains. The fuel has to be taken out of the reactor at this point due to the build-up of fission products working as neutron poisons. In the partially closed fuel cycle, the uranium and plutonium are recycled to produce MOX fuels. A number of solvent extraction processes have been developed for the extraction of uranium and plutonium. The most established industrial process, the PUREX process, was first patented in 1947 and quickly became the benchmark for uranium and plutonium separation. The PUREX process is an example of a *heterogeneous* process as it produces single element streams of material, in other words a pure uranium stream followed by a pure plutonium stream. While the heterogeneous process allows for very exact tuning of the final fuel composition, it also simplifies the misuse of the materials for weapons production, principally due to the pure Pu-stream.[46, 47]

In the closed fuel cycle, the focus is the recovery of both uranium, plutonium and either some or all of the MA. The recycling and use of these elements in advanced nuclear fuels is enabled by the operation of fast reactors.[48] This alternative is often referred to as advanced/extensive recycling. Alternatively, the minor actinides can be irradiated with fast neutrons in an accelerator-driven system (ADS), solely for the purpose of fissioning the actinides into shorter-lived elements (without electricity generation). Partitioning and Transmutation (P&T) is a collective term covering the separation of minor and major actinides from spent nuclear fuel, for transmutation in either a fast reactor or in an ADS. Aside from the electricity production aspect, there are also significant differences in the fuel/target production of the two approaches: in fast reactors, a MA content of ∼5 wt% is possible, while in the ADS option, a MA content of around 50% is possible.[49–53] By adopting the advanced recycle option, extensive studies have found a greater than 30% decrease in the final, highly active waste volume, with a significantly lower radiotoxicity, possible elimination of uranium mining, reduced heat load and increased proliferation security.[15, 16, 54]

2.4   The GANEX concept

For a more in depth analysis of the GANEX processes, see Paper III.

The Grouped ActiNide EXtraction (GANEX) concept is a two-step process for the homogeneous recovery of the major and minor actinides from a spent nuclear fuel solution. *Homogeneous* refers to the partitioning of the actinides as a group, with the primary benefit of reducing proliferation risks. In the first step, the bulk of uranium is extracted in order to reduce the loading of heavy
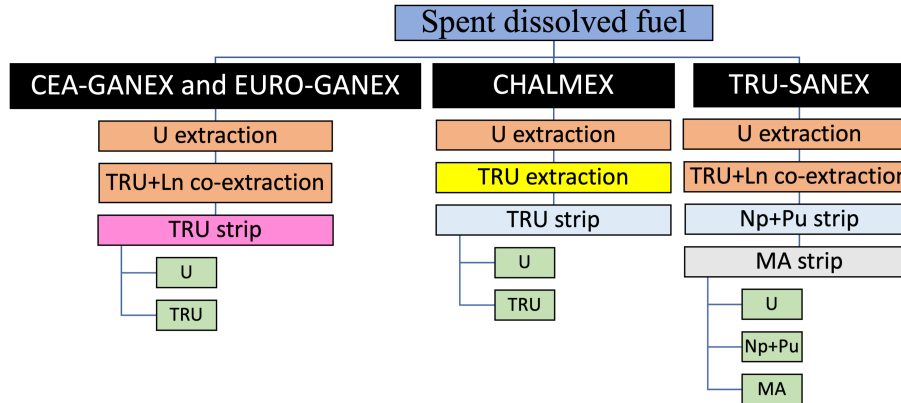
Figure 2.4: A schematic overview of the different GANEX concepts.

metals.[55] In the second step, the remaining actinides (Pu, Np, Am, Cm) are co-separated from the raffinate.

There are currently three GANEX concepts being developed, as illustrated in Figure 2.4. In the CEA-GANEX and the EURO-GANEX concepts, the actinides and lanthanides are co-separated in the second extraction step after the uranium bulk extraction. The separation of the actinides from the lanthanides occur by selective stripping, giving two product streams overall: a uranium stream and a TRU-stream (TRU= transuranic actinides).[56–62] In the CHALMEX (Chalmers GANEX) process, the same product streams are achieved, but through selective TRU extraction rather than through selective stripping[19, 63, 64]. In the final GANEX concept, three product streams are generated through the selective stripping of neptunium with plutonium and subsequently the remaining MA.[65]

In order meet the objectives of the GANEX concept, significant research efforts have been invested in general ligand development and later development of the homogeneous recycling options.[56, 66–70] The first concept was developed by the French CEA, and named thereafter: CEA-GANEX. The EURO-GANEX was later developed by the NNL as an alternative to the CEA-GANEX, and has now become the European reference process for homogeneous recycling. The CHALMEX concept was offered as a simpler alternative to the former two processes to investigate the possibility of reducing the complexity of the process by aiming for direct An separation in the extraction step.
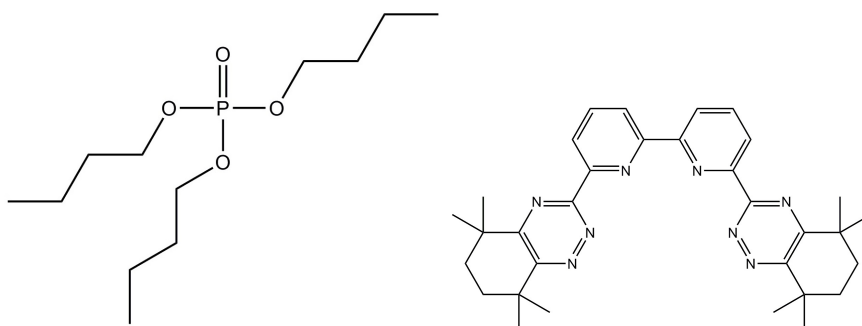
Figure 2.5: Molecular structure of (a) Tri-*n*-butyl phosphate (TBP) and (b) 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo- 1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe$_4$-BTBP).

2.4.1 CHALMEX process

The CHALMEX process differs from the other GANEX processes in that the actinides are separated from the lanthanides and other fission products directly. This is achieved by combining extractants which target the oxidation states of the actinides specifically. The well-known tri-*n*-butyl phosphate (TBP), seen in Figure 2.5a (a), is used for the extraction of Pu(IV) and U(VI), while 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), shown in Figure 2.5b, ensures the extraction of trivalent and pentavalent minor actinides.

The CHALMEX process has shown promising results at the fundamental level. Earlier work has focused on basic extraction properties and hydrolytic and radiolytic stability, while it is clear that a more applied understanding of the process is necessary in order to compare the process performance to that of the more developed EURO-GANEX and CEA-GANEX processes.

Chapter 3

Theory

3.1 Solvent Extraction

In solvent extraction, or liquid-liquid distribution, two immiscible or partially miscible liquids forms a two-phase system separated by a phase boundary. In such a system, a solute will distribute between the two liquids according to its respective solubility in each phase. A solute is the element or compound of interest, which in the case of the GANEX concept includes all the actinides, and in some cases, also the lanthanides.[71, 72]

Typically, the two phases in a solvent extraction system include an aqueous phase and an organic phase. The former is usually an acidic medium in which the solute is dissolved, often also in the presence of other unwanted species. The organic phase is usually referred to as the *solvent*, which is a collective term and includes the extractant(s) and the diluent. In some systems, organic extractants are added to the solvent to better facilitate the extraction of certain elements. For instance, metal ions typically have a high solubility in aqueous acidic medium, but due to their polar nature, they are not very soluble in organic mediums. Some organic extractants are weak acids, and can complex metals in the aqueous phase to form neutral complexes that are soluble in the organic phase, as illustrated by Equation 3.1,

$$M^{z+}_{aq} + zHA_{(aq\,or\,org)} \rightleftharpoons MA_{z(org)} + z^+_{aq} \tag{3.1}$$
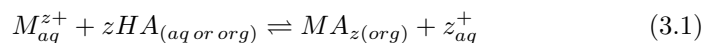
where M is a metal of charge z and HA is the weakly acidic organic extractant. Other organic ligands can act as Lewis bases. Furthermore, some metal-ligand complexes are coordinated by aqueous ligands, such as nitrates, to achieve neutrality and extractability into the organic phase.

Solute distribution between the two phases depend largely on the type and

strength of the molecular interactions between solute and the solvent and possibly other solute particles. These interactions, and by extension a solute's solubility, can be manipulated or engineered by changing the conditions of one or both of the two phases. Conditions such as pH, concentration, temperature etc., can be changed to facilitate a wanted distribution of the solute. As such, most solutes can be made more or less soluble in both phases, which demonstrates the versatility of solvent extraction as an extraction and separation method.

The distribution ratio, D, is a measure of distribution of a solute between the organic and the aqueous phase. More specifically, the total concentration of the solute in the organic phase over its total concentration in the aqueous phase gives the distribution ratio, as seen in Equation 3.2.[71]

$$D = \frac{[A]_{org}}{[A]_{aq}} \qquad (3.2)$$

If different solutes (A and B) distribute themselves differently between the two phases (different D-values), then solvent extraction techniques can be used to separate them. The separation factor (SF), Equation 3.3, gives a measure of how well separated two solutes are by dividing the D-value of one over the other.

$$SF = \frac{D_A}{D_B} \qquad (3.3)$$

3.2 Coordination chemistry and HSAB theory

Many phenomena observed in coordination theory can be at least partially explained by the *Hard-Soft Acid-Base* (HSAB) theory. In HSAB theory, the definition of Lewis acids (electron pair acceptors) is extended as being either hard or soft, based on a combination of size, charge and polarizability. Similarly, Lewis bases (electron pair donors) are also defined as being hard or soft. In principle, hard acids will form ionic complexes with hard bases, while soft acids will form covalent bonds with soft bases.

In solvent extraction systems, metals are usually dissolved in either water or an acid. If a metal ion is fully surrounded, or *coordinated*, by water molecules, it is *hydrated*. Likewise, metal ions coordinated by dissociated acid components such as nitrates are *solvated*. Such a coordination complex is an example of a reaction between a Lewis acid (metal ion) and a Lewis base (i.e. OH^-, NO_3). As explained in Section 3.1, organic ligands can either fully or partially replace the coordinated hydroxides, nitrates etc., acting like Lewis bases, to form neutral complexes with high solubility in an organic phase. However, since such ligands typically have low solubility in the aqueous phase, their coordination to the metal ion can be slow.[71]

Metals and ligands can have multiple coordination sites. The CyMe$_4$-BTBP molecule for example, is a tetradentate, organic ligand. CyMe$_4$-BTBP will attach to a metal at 4 sites to form a neutral complex. The f-group elements (lanthanides and actinides) are hard Lewis acids, where the lanthanides are slightly harder than the actinides. Some of the actinides can form stable complexes with CyMe$_4$-BTBP, and this is due to the slightly more covalent nature of the BTBP-An bond. Am(III) has 8 available coordination sites, and forms a neutral complex with two BTBP-ligand coordinated by nitrate ions in the inner sphere.[71, 73]

3.3 Chemistry of the *d*-block elements

The *d*-block elements are often referred to as the transition metals due to their partially filled *d*-subshell. Silver, copper, gold, cadmium and zinc are also considered part of the *d*-block elements. The *d*-block elements are typically associated with coloured compounds, good heat- and electricity conductivity, and high melting and boiling points. A wide range of available oxidation states is also characteristic. Due to some *d*-block elements having uneven numbers of electrons, magnetism is observed for some of the *d*-block elements.[74]

Since *d*-orbitals are spaced relatively far apart and electron repulsions are weak, the attraction between the positive nucleus and each electron is strong. In bonding, electrons from the *s*-orbitals typically engage before the *d*-electrons. Since both the *s*- and *d*-orbitals are available for bonding, the *d*-block metals exhibit several stable oxidation states. This trend is exemplified for the centre rows of the *d*-block. Elements found in the first and last row of the *d*-block are "untypical", with only 1 available oxidation state (save mercury, with 3 known oxidation states).[74]

3.4 Chemistry of the f-block elements

The lanthanides (Ln) and the actinides (An) constitutes the f-block elemental group in the periodic table, and are (typically) characterised by their gradual filling of the f-shell. The f-shell can accommodate 32 electrons, compared to the 10 electrons accommodated by the d-shell. All the lanthanides are naturally occurring elements, while only uranium and thorium can be found in natural sources. For the lanthanides, the $4f$ shell sees gradual filling across the series, with cerium's electron configuration being $[Xe]4f^15d^16s^2$. Although the lanthanides are commonly referred to as the *rare earth metals* (along with yttrium and scandium), many of these are actually quite abundant in the Earth's crust. Cerium for example, is the 26th most abundant element in the world, and

even neodymium is more abundant than gold.[75]

The lanthanides are also characterised by high neutron absorption cross sections for thermal neutrons and relatively low reactivity. The latter is related to the lanthanide electron configuration, which sees a filling of the $4f$ orbitals. These orbitals contract due to their close proximity to the relatively highly charged nucleus, which shields the from participating forming bonds and participating in reactions. In nuclear reactors, the build-up of lanthanides and other fission products is problematic as it will absorb neutrons without fissioning.

For the majority of the lanthanides, the most stable oxidation state is +3 in aqueous solutions. When considering their ionisation energies, the sum of the three first ionisation energies is generally smaller than the fourth ionisation energy, which confirms that the fourth oxidation state is chiefly unavailable for the group. Only 5 LNs exist in the +4 state: neodymium and dysprosium (only in the solid state), praseodymium and terbium (which also exist as tetrafluoride and dioxide) and finally cerium, which can exist in a range of different salts and tetravalent compounds. Cerium(IV) is often used as a non-radioactive analogue to plutonium. In water, an increasing solubility is seen with increasing atomic mass.

Most of the actinides are products of successive neutron absorption of either uranium or thorium, for example in a nuclear reactor or a nuclear detonation. The higher actinides can only be formed after absorption of heavier nuclei. In contrast to the lanthanides, all the actinides are unstable and radioactive. They are also found in a range of different oxidation states in aqueous solutions. Uranium, for instance, is most stable in the +IV and +VI states, plutonium in the +IV state, while americium and curium are most stable in the +III state and neptunium in the +V and +VI states, in aqueous solutions.

Uranium-235 and plutonium-239 have high neutron absorption cross sections for thermal neutrons and are thus suitable for use as fuel in most commercial nuclear power reactors today. Uranium-238, and the MA have high fast neutron absorption spectrums, making them suitable to use as fuels in fast reactors or as targets in ADS.

With a gradual filling of the $5f$-orbital, the actinides following thorium are typically much more reactive than the lanthanides. The $5f$-orbitals are not shielded by the nucleus like the $4f$-orbitals, and the $5f$-orbitals are largely available for participating in bonding.

3.5   CHALMEX solvent

In a spent nuclear fuel raffinate, the fuel is dissolved in high concentration nitric acid ($\sim$ 4 M). Under such conditions, uranium will exist in the +VI oxidation

state, plutonium in the +VI, americium, curium and europium in the +III, while neptunium will most likely be available in either the +V or the +V,VI oxidation states.[76]

TBP is an extractant that efficiently and preferentially separates U(VI) and Pu(IV) from the remaining fission products and actinides. TBP is a solvating extractant and a hard Lewis base, whos extraction mechanisms are well understood. 2 TBP molecules coordinate to both uranium and plutonium. The uranium complex is solvated by two nitrates, while the plutonium complex is solvated by four nitrates. TBP's process and degradation chemistry is well established. While the molecule is relatively stable towards hydrolysis and radiolytic degradation, it's main degradation products include monobutyl phosphate (MDP) and dibutyl phosphate (DBP), known to both promote crud formation and initiate red oil reactions. The risk of red oil reactions are mainly associated with the evaporators in reprocessing plants, and these risks can be reduced by removal of dissolved TBP from the nitric acid liquor, lower operating temperature of evaporators and monitoring of mass flows to detect any losses of TBP to the evaporators.[77–81]

Bis-triazin-*bi*-pyridine extractants are polyaromatic, nitrogen donor ligands that forms solvated and chelated complexes with metals. CyMe$_4$-BTBP in specific, is a tetradentate ligand which forms complexes with trivalent and pentavalent actinides solvated by nitrates in nitric acid media. Two CyMe$_4$-BTBP molecules coordinate to each actinide.[73, 82, 83] The BTBP-ligands are soft Lewis bases and forms complexes with the soft(er) actinides, such as americium, curium and to some extent neptunium. A combination of TBP and CyMe$_4$-BTBP can theoretically and directly separate the actinides from the remaining fission products.

FS-13 has in recent years been investigated as a diluent in the process. It has beneficial properties for use as a diluent in nuclear applications due to its high chemical and radiolytic stability, it's low solubility in aqueous solutions, it's low viscosity and its high density.[84–86] FS-13's polar nature provides a high solubility of CyMe$_4$-BTBP. In fundamental studies, the CHALMEX FS-13 solvent has shown very promising results for the extraction and separation of the actinides from fission products. A more than 99% recovery of plutonium and americium has been demonstrated in systems with no competing metal extraction.[26]

3.5.1 DEHBA

It is well-known that the degradation products of TBP can have severe effects in reprocessing plants. In order to mitigate such unwanted degradation products, an

alternative extracting agent has been investigated for the extraction of hexavalent uranium and tetravalent plutonium.

N,N-di-(2-ethylhexyl)butyramide (DEHBA), seen in Figure 3.1, is a monoamide that has been investigated as an extracting agent for uranium and plutonium in similar solvent extraction systems. The N,N-dialkyl monoamides extract uranium and plutonium to a comparable degree to TBP, but it's degradation products are far less problematic, namely carboxylic acids and amines.[87–89]
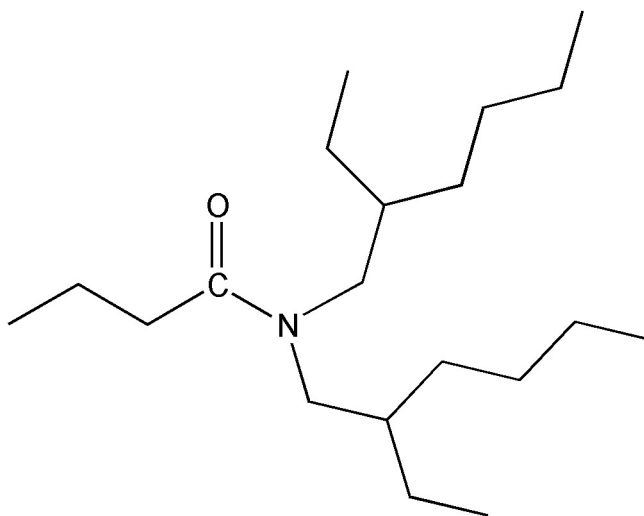
Figure 3.1: Molecular structure of N,N-di-(2-ethylhexyl)butyramide (DEHBA).

3.6   Industrial process development

The development of industrial solvent extraction processes usually includes establishing knowledge about the system's key parameters. These parameters are outlined by Rydberg et al.[71], and include:

1. Extractant screening

2. Solvent conditioning

3. Collecting distribution data

4. Extractant concentration

5. Temperature effects

6. Stage-wise separations

Steps 1-2 have already been completed for the CHALMEX process through various European frameworks.[17, 90–96] Step 3 includes collecting data such as

loading capacity and kinetics of extraction, stripping and scrubbing stages of the extraction process. Step 4 includes solvent optimisation for the expected metal concentration and investigation of the solvent's loading characteristics. Here it is also important to determine the degree of any unwanted metal extraction during loading conditions. If the extractant preferably extracts the solute of interest, a system should be operated close to the solvent's loading capacity of the solute in question. For systems in which impurities are extracted to a similar or higher degree than the wanted solute, masking agents can be considered to suppress extraction of the impurities.[71]

For the GANEX processes, the reference contactors are cascade centrifugal contactors. Centrifugal contactors are space efficient contactors taking advantage of the centrifugal force for both mixing and separation. Relative to other contacting equipment traditionally used in nuclear reprocessing (mixer-settlers, columns), centrifugal contactors are compact in size and can handle large throughputs of fissile materials.[97, 98]

Based on the collected distribution data, calculations of ideal number of stages can be performed for cascade, counter-current contactors.[98] The extraction, P, of a solute is defined as the product of its distribution ratio D and its phase ratio, θ, as seen in Equation 3.4.

$$P = D \cdot \theta \tag{3.4}$$

The fraction of solute in the raffinate (x_R) as compared to in the feed solution (x_F) is defined by ϕ, as shown in Equation 3.5. Here, n refers to the number of ideal stages in the cascade. By rearranging Equation 3.5, one can calculate the number of ideal stages needed for a required separation, as seen in Equation 3.6.

$$\phi = \frac{x_R}{x_F} = \frac{P - 1}{P^{n+1} - 1} \tag{3.5}$$

$$n = \frac{ln(P - 1) - ln(\phi)}{ln(P)} - 1 \tag{3.6}$$

Chapter 4

Experimental procedures

The experiments presented in this section were performed either at Chalmers University of Technology, Sweden or Jülich Forschungszentrum, Germany. Slightly different methods were used, both of which are described here. Please refer to A for details on the respective equipment and radionuclides used at both laboratories.

4.1 Solvent Extraction

Two compositions of the CHALMEX solvent have been used for the majority of the experiments presented in this work. Unless otherwise stated, the concentration of TBP was 30% v/v in 70% v/v FS-13. The $CyMe_4$-BTBP concentration was either 10 mM $CyMe_4$-BTBP or 25 mM $CyMe_4$-BTBP. The concentration is specified for all datasets presented. The TBP was benchtop 97% TBP purchased from Sigma Aldrich/Merck. The FS-13 was either supplied by Marshallton Research Laboratories, Inc. or HaiHang Industry Co., Ltd. $CyMe_4$-BTBP was provided by Karlsruhe Institute of Technology, or produced in-house.

Unless otherwise stated, equal volumes of organic phase and aqueous phase (no less than 400 μL) was contacted for 1 hour at 25°C. The radionuclides were added directly to the aqueous phase. After contacting, the samples were subsequently centrifuged for 5 minutes before sampling.

At Chalmers University of Technology, the experiments were always performed in triplicates and radionuclides were investigated in isolation. The exception was ^{241}Am/^{152}Eu, which were added to the same samples prior to contacting. For investigations of inactive fission products, the fission products were dissolved in groups of three to four with similar, but not conflicting isotopic masses.

At Jülich Forschungszentrum, a ^{239}Pu tracer, a ^{237}Np and a tracer consisting of ^{241}Am, ^{244}Cm and ^{152}Eu (tracer 4) were added directly to the aqueous phase. For most experiments, a ^{nat}U tracer was also added, but this was subject to

availability. Fission product solutions were prepared by dissolving and diluting fission products in nitric acid medium. The fission products were of standard bench-top quality and brand.

4.2 Batch flowsheet tests

All the batch flowsheet tests were performed at Jülich Forschungszentrum. In the batch flowsheet tests, the aqueous phase consisted of a simulated PUREX raffinate (see Appendix B for compositions). The organic phase was the CHALMEX solvent with 10 or 25 mM CyMe$_4$-BTBP concentration. The phase ratio of the extractions was either 1:1 or 1:2. The organic phase and aqueous phase were added in a 15 mL vial and the starting volume of each phase was recorded. The phases were contacted using vortex shakers at ambient temperatures. To limit heating effects from the shaker, the vial was swapped between two equal shakers every 15 minutes. The contact time was 120 minutes for each stage.

After each contacting stage, the vial was centrifuged for 5 minutes. The lighter aqueous phase was sampled, and the remaining aqueous collected in a vial. The aqueous phase collected at the phase interface, with any entrained organic, was disposed of. The remaining volume of the organic phase was recorded, and equal amounts of scrubbing solutions were added. The above procedure repeated for all the process stages.

4.3 Centrifugal contactor tests

A single, annular centrifugal contactor (10 mm rotor, 6 mL hold-up volume, manufactured by INET, Tsinghua Univ. China) was prepared for extraction tests using the CHALMEX solvent and the simulated PUREX raffinate with added radioactive tracers (^{241}Am, ^{244}Cm, ^{152}Eu, ^{239}Pu, ^{237}Np and ^{nat}U). The solutions were pumped into the contactor using electric syringe pumps, with equal flow rates for both phases. The CHALMEX FS-13 solvent was first pumped into the centrifugal contactor with 4 M HNO$_3$ to ensure satisfactory phase separation, before changing the aqueous phase syringe to the raffinate solution.

Different flow rates and rotor speeds were investigated, in addition to phase ratios. The aqueous phase was either a simulated PUREX raffinate solution, or a 50% PUREX raffinate solution mixed with 50% 0.5 M HNO$_3$ to approximate actual process conditions. Sampling of the phases was adjusted according to the flow rate, but the sampling times were always the same for the organic and the aqueous phase.

4.4 Analytics

Due to the presence of only single radionuclides (except for Am/Eu), the analytics performed at Chalmers University of Technology were fairly straightforward. For samples containing Pu or Np, 100 μL of each phase was added to 5 mL UltimaGold scintillation cocktail and analysed using LSC. For the Am/Eu samples, 100 μL of each phase was analysed using a High Purity Germanium (HPGe) detector, for their peaks at 59.5 keV and 121.8 keV respectively. Cm was analysed by using alpha spectrometry: 10 μL was added to a 50 μL 99% acetone/1% binder solution and distributed on metal planchets, heated and burned. For the ^{nat}U samples, the aqueous phases were appropriately diluted and measured using an ICP-MS. Fission products were also measured using ICP-MS. Initial concentrations of the respective solutions were measured to enable evaluation of D-values.

In Jülich, 100-200 μL was collected for each phase for HPGe analysis of the Am/Eu radioactivities. Further 10 μL was added to 100 μL of 99% acetone/1% binder solution and distributed on metal planchets, heated and burned for alpha spectrometry. The alpha spectra yielded peaks for Np, Pu, Am and Cm. Lastly, each phase was appropriately diluted for ICP-MS analysis. The dilution of the organic phase was enabled by the use of a surfactant. All fission products were analysed using ICP-MS as a collected group.

For confirmation of oxidation states, UV-VIS spectrometry was used. Acid concentrations were confirmed by using automatic titrators. Interfacial/surface tension measurements were done using a tensiometer (SIGMA 700) and the du Nouy ring method. Densities were measured using the same tensiometer, but using a density probe of known volume and weight. All measurements were performed at ambient room temperature, between 20-22°C, and at least 3 replicate measurements were done. The error presented is the standard deviation of the measurements.

Chapter 5

Results and Discussion

5.1 Fundamental properties and performance

The results presented here are based on those published in Paper I, Paper IV and Paper V.

5.1.1 Solvent physical properties

Both density and interfacial tension play a crucial role in a solvent extraction system. Primarily, the difference in densities of the aqueous phase and the organic phase needs to be sufficiently large for the phases to separate in distinct layers. If densities are too similar, phases layering next to each other (rather than top and bottom) can occur, or phases can even be split into 3 phases.[99] Such tendencies can cause severe issues for gravitational settlers and centrifugal contactors.

In most solvent extraction systems, the heavier phase is the aqueous phase and the organic phase is the lighter phase. In the CHALMEX system, however, the density of the organic phase is the heaviest, as seen in Table 5.1. A heavier organic phase has one major advantage over lighter organic phases in systems with a high metal content: as metal is extracted by the solvent, the solvent density increases while the aqueous density decreases. Overall, the density difference between the phases will thus increase as extraction proceeds.

Solubility of either phase in the other can cause significant changes in both the solvent and the aqueous phase density. It is well-known that nitric acid is soluble in TBP, which is confirmed by the increase in density for the TBP pre-equilibrated with acid, as opposed to the pristine TBP, as shown in Table 5.1. It is also seen that the density of FS-13 changes after pre-equilibration with both water and nitric acid. FS-13 has a density of 1.41 g cm^{-3} prior to

pre-equilibration, which agrees with literature values.[84] Upon pre-equilibration, the density of the FS-13 decreases. The density of the pre-equilibrated diluent is the same for both water and nitric acid, suggesting the density difference is largely due to the solubility of water in FS-13. The density difference between the CHALMEX solvent (1.27 g cm^{-3}) and the nitric acid (1.12 g cm^{-3}), appears to be sufficient to allow spontaneous phase separation.

Table 5.1: The measured density (ρ) and interfacial tension (IFT) of the CHALMEX solvent constitutents, pristine and pre-equilibrated.

Constituent	Pre-equilibration	$\rho\,(g\,cm^{-3})$	IFT $(mN\,m^{-1})$
4 M HNO$_3$	-	1.12 ± 0.002	-
TBP	-	0.971 ± 0.002	-
TBP	MQ	0.959 ± 0.001	19.5 ± 0.60
TBP	HNO$_3$	0.997 ± 0.001	8.06 ± 0.15
FS-13	-	1.41 ± 0.002	-
FS-13	MQ	1.36 ± 0.003	12.5 ± 1.29
FS-13	HNO$_3$	1.36 ± 0.003	10.9 ± 1.72
30% TBP 70% FS-13	-	1.25 ± 0.003	-
30% TBP 70% FS-13	HNO$_3$	1.26 ± 0.01	12.8 ± 0.025
CHALMEX	HNO$_3$	1.27 ± 0.000	11.0 ± 0.23

Interfacial tension, or surface tension, is the force required to form a surface between a liquid and another phase, whether it be gas or liquid.[100] Since surface molecules of the liquid are not completely surrounded by other liquid molecules, in contrast to the bulk liquid molecules, the surface molecules have higher interaction forces with one another. A high interfacial tension between two phases means they will separate well, although this also hinders good mixing of the phases.

TBP is a surface active agent, or surfactant. Surfactants are molecules with one hydrophobic part and one hydrophilic part. The addition of a surfactant to the solvent will thus lower the interfacial tension between the organic phase and the aqueous phase by having its hydrophilic head and hydrophobic tail dissolved in the aqueous and organic phase respectively. As such, a surfactant promotes better mixing, at least up until a certain point. Here, the effect of TBP on

the CHALMEX solvent is illustrated by the decrease in interfacial tension after adding TBP to FS-13.

5.1.2 Acid extraction

It is important to understand the degree to which acid is extracted by the solvent overall, for several reasons in addition to the effect on density. Firstly, it is known that the solubility of CyMe$_4$-BTBP is dependent the dissolution of either nitrate or undissociated nitric acid.[26] Secondly, spent nuclear fuel is dissolved in nitric acid prior to reprocessing/recycling operations. Thirdly, as the extracting agent is occupied by extraction of acid molecules or protons, less ligand is available for metal complexation. Simultaneously, less nitrates are available for coordinating with metals in the aqueous phase. Lastly, an elevated acidity of the organic phase can cause issues in downstream processes, so for solvents with high degrees of acid extraction, acid scrubbing steps are usually required.[47, 101–107]

FS-13 does not extract acid to any measurable extent, as seen in Figure 5.1. This confirms that the density decrease seen for the diluent after pre-equilibration is mainly due to water solubility in FS-13. As expected, acid extraction by the CHALMEX solvent is significant and saturation of the organic phase occurs at approximately 4.9 M acid. Earlier studies have shown that the acid is extracted both as undissociated HNO$_3$, but also as protons.[26] Although acid extraction by the CyMe$_4$-BTBP molecule is not entirely unlikely, its low concentration in the solvent suggests that the majority of acid is extracted by TBP.
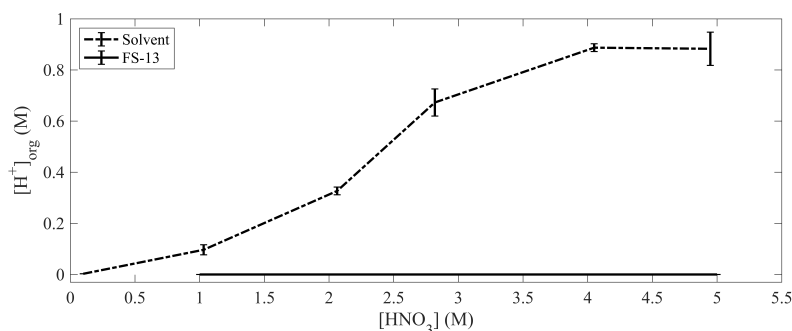

Figure 5.1: The concentration of protons in the organic phase, extracted by FS-13 and the CHALMEX solvent: 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13.

This is confirmed when considering the UV-VIS absorption spectra of FS-13, and TBP/FS-13 pristine and pre-equilibrated, as seen in Figure 5.2. The absorption spectra shows a clear dip in the absorption at 625 nm for the TBP/FS-13 solvent that has been pre-equilibrated with 4 M HNO$_3$. While no such dip is

seen in the UV-Vis spectra of pure 4 M HNO_3, the acid or water are the only possible sources of the change in absorption spectrum.
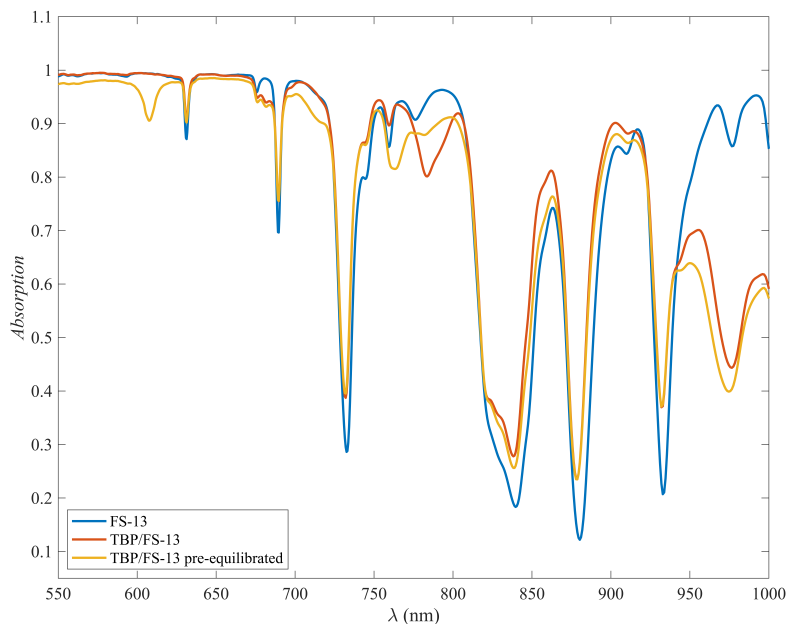

Figure 5.2: UV-VIS absorption spectrum for FS-13 and TBP/FS-13, pristine and pre-equilibrated with 4 M HNO_3.

5.1.3 Nitrate and nitric acid dependency

Increasing the nitric acid concentration increases the D-value of all the actinides and Eu, up to a nitric acid concentration of 2.5 M, as seen in Figure 5.3. At higher acid concentrations, the D-values decrease for Am, Cm and Eu, which are all extracted by $CyMe_4$-BTBP. This can indicate either saturation of the ligand with by the metal, or that the high acidities alter the $CyMe_4$-BTBP's extracting capability. The former is unlikely since only trace concentration metals were present. However, earlier studies have found that the CHALMEX solvent extracts both protons and undissociated acid.[26] Such extraction changes the polarity of the solvent, which is also known to play a major role in the solubility of Am/Cm-BTBP complexes.[73] No such trends are seen for D(Pu), which is primarily extracted by TBP and is extracted as expected by the TBP ligand. The dataset for Np is split into two series, one for Np(V) and one for Np(V,VI), as the oxidation state place a crucial role in the degree of extraction. The Np(V) is the least extractable species, shown here with D<1 for the entire acid range.

The D-ratio for Np(V,VI) however, shows a more realistic extraction behaviour for spent nuclear fuel solutions, with D≈3-4 over the nitric acid concentration range. This is due to extraction of the Np(VI) species by TBP. The oxidation state of Np is known to be difficult to control, as it is highly sensitive to a range of parameters such as nitric acid concentration, presence of nitrous acid and water-soluble organic degradation products.[76]
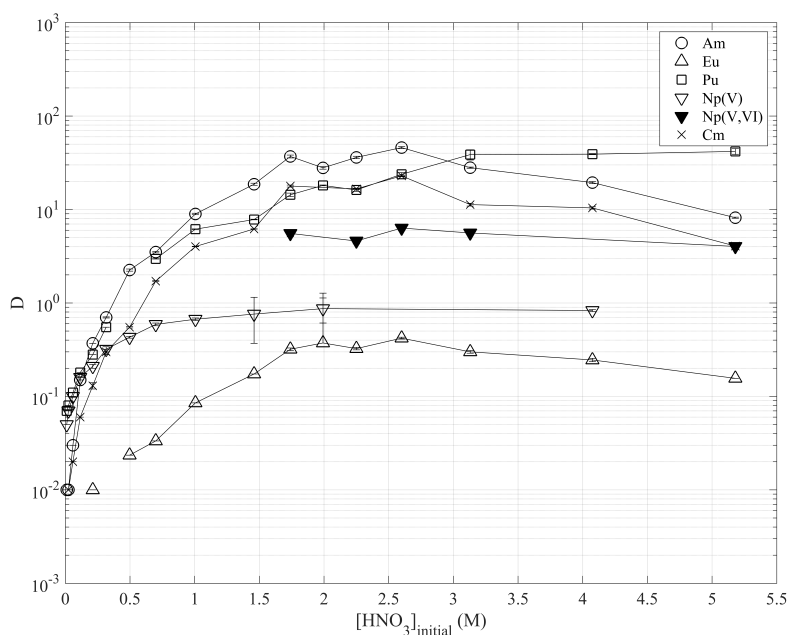

Figure 5.3: The D-values of Am, Eu, Pu, Np and Cm as a function of nitric acid concentration. The extraction was performed using the 10 mM CyMe$_4$-BTBP CHALMEX solvent.

5.1.4 Solvent optimisation

D(Pu) is shown to increase as expected with increasing TBP concentration, as seen in Figure 5.4. Although it has been shown that TBP does not extract Am or Eu, D(Am) and D(Eu) both increase as a function of % v/v TBP in FS-13. Since the CyMe$_4$-BTBP concentration was kept constant at 10 mM for these experiments, the increase in D-values can most likely be attributed to the changed solvent characteristics with increasing TBP concentration, increasing the solubility of the Am-BTBP and Eu-BTBP complexes in the organic phase. TBP is both soluble in nitric acid and is a known surfactant, which means that the polar head interacts more readily with the aqueous phase, while the organic side groups remain distributed in the organic phase. CyMe$_4$-BTBP on the other

hand is not a surfactant, and the extraction is limited by the mass transfer from the phase boundary to the bulk organic phase.

The decrease in interfacial tension from pure FS-13 to the 30% v/v TBP in 70% v/v FS-13 suggests that not only does the TBP/FS-13 solvent yield a higher solubility of the Am/Eu-BTBP complexes, but it also aids the mass transfer of the Am- and Eu-nitrate complexes across the phase boundary. This agrees with results published by Ekberg et al., who reported that the solubility of Am-CyMe$_4$-BTBP complexes in organic solvent increases with decreasing charge density of the solvent.[73]

Np(V,VI) extraction show an unexpected trend, with D-values increasing with increasing % v/v TBP up until 20 % v/v TBP, after which D(Np) drops significantly from about 4 to 1. The trend up to 20 % v/v TBP agrees with those seen for Np(V,VI) in Figure 5.3, while the D(Np) at >20% v/v TBP closely agrees with the trends seen for Np(V). This strongly suggest that the reduced D(Np) is due to a reduction of any Np(VI) to the less extractable Np(V).
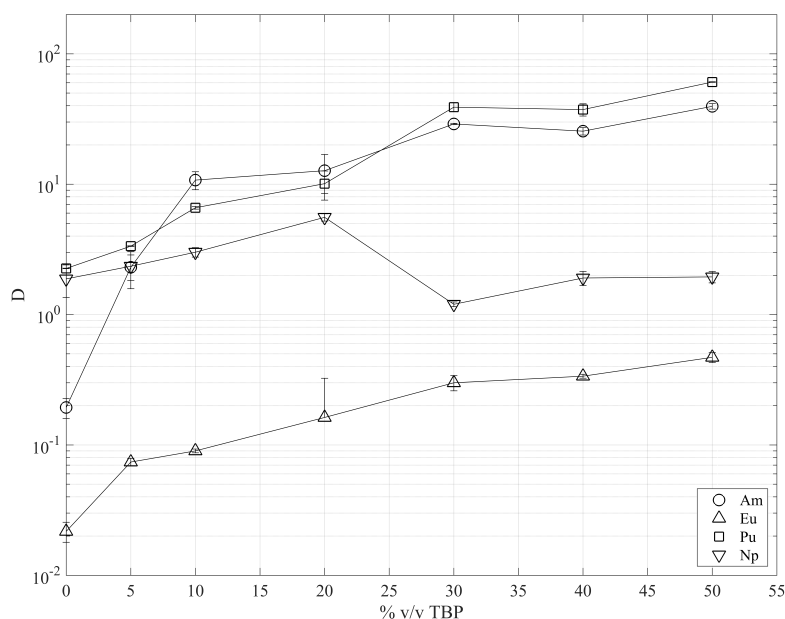
Figure 5.4: The distribution ratio of Pu, Am, Np and Eu as a function of % v/v TBP in FS-13, with a constant 10 mM concentration of CyMe$_4$-BTBP.

Also, the extraction as a function of CyMe$_4$-BTBP has been investigated for systems with different TBP concentrations. Figure 5.5 a) shows the extraction in a system with 15% v/v TBP in 85% v/v FS-13 and Figure 5.5 b) shows the extraction in a system with 50% v/v TBP in 50% v/v FS-13. D(Am) is

noticeably higher in the system with a higher TBP concentration, which is in agreement with the results in Figure 5.4. Not surprisingly, D(Am) increases with increasing CyMe₄-BTBP concentrations. Similarly, D(Pu) increases at higher CyMe₄-BTBP concentrations, although to less of a degree than D(Am). This causes D(Am) to supersede D(Pu) at a lower CyMe₄-BTBP concentrations in the 50% v/v TBP system compared to the 15 % v/v TBP system. In the 15% v/v TBP system, D(Am)>D(Pu) at 80 mM CyMe₄-BTBP concentration, while in the 50% TBP system D(Am)>D(Pu) occurs at 15 mM CyMe₄-BTBP concentration.
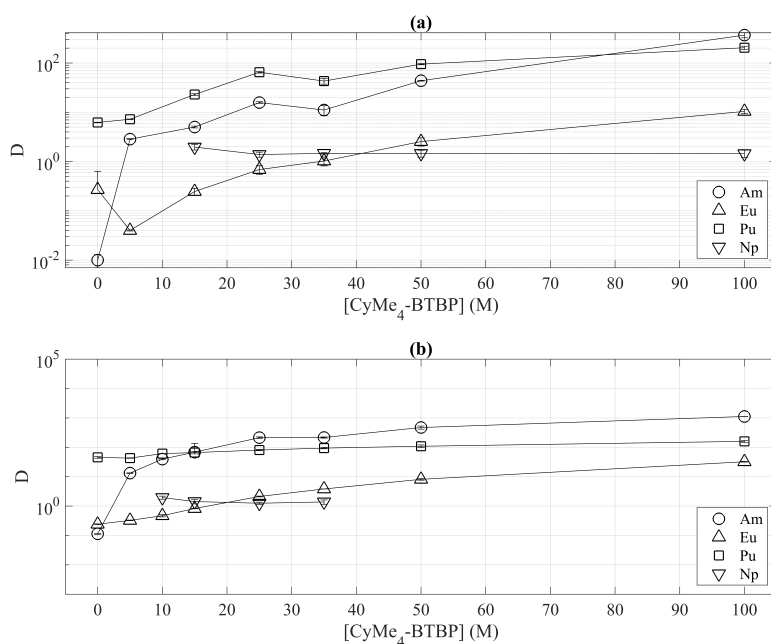
Figure 5.5: The distribution ratios of Pu, Am, Np and Eu as a function of CyMe˙4-BTBP concentration for (a) 15% v/v TBP and (b) 50% TBP.

Corresponding trends are seen for the D(Eu) and D(Np) for the two systems. While D(Eu)>D(Np) only occurs at about 40 mM CyMe₄-BTBP concentration in the 15 % v/v TBP system, it occurs at 20 mM CyMe₄-BTBP concentration for the 50 % v/v TBP system. Halleröd [27] reported that in the "standard" 30 % v/v TBP solvent, the Np/Eu inversion occurs at around 40 mM CyMe₄-BTBP concentration. It is not clear whether a Np(V) or Np(V,VI) solution was used in those experiments, but the D-values agrees with those seen for Np(V) here. The D(Np)/D(Eu) inversion is of particular importance in this system as the extraction of lanthanides is unwanted. It is therefore important to operate the process below the TBP/CyMe₄-BTBP ratio at which the D(Np)/D(Eu) inversion

occurs.

5.2 Fission products

Fission product extraction also varies significantly according to nitric acid
concentrations, as observed in Figure 5.6. The fission products Ag, Cd and Cu
all have $D > 100$ for most acid concentrations and are excluded from the data
presented. These elements are all weak acids and so their complexation with
CyMe$_4$-BTBP is not unexpected. Fission products with $D < 0.1$ for the whole
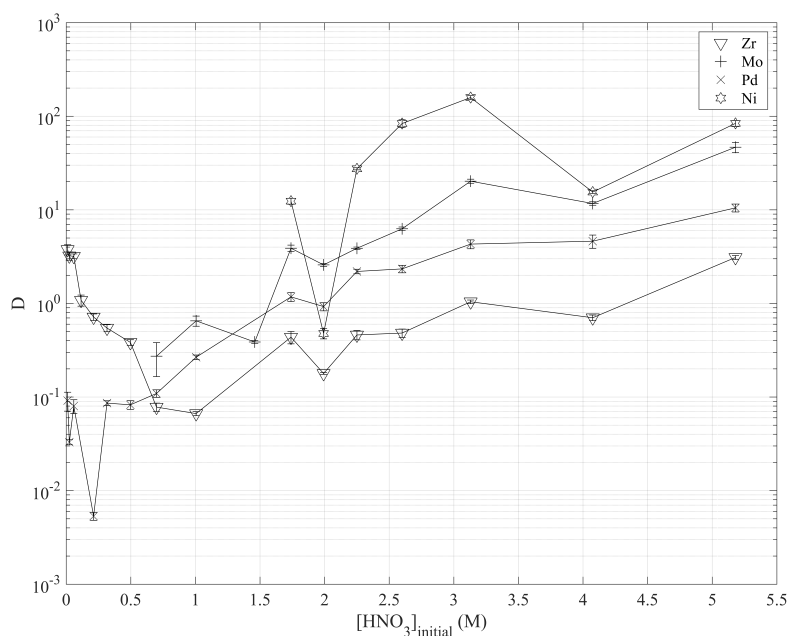acid range are also excluded.

Figure 5.6: D vs $[HNO_3]$ for selected fission products in the range of 0.01-100.
The fission products were extracted by 10 mM CyMe$_4$-BTBP CHALMEX solvent
with 30% v/v TBP, from 10^{-5} M metal solutions.

Without exception the D-values increases for all elements shown in Figure
5.6 for [HNO$_3$]> 1 M. At lower concentrations, the low D-values for all elements
except Zr can both be a result of the low nitrate concentration in the aqueous
phase, but also the lower solubility of CyMe$_4$-BTBP in the absence of acid.
It is unlikely that varying acid concentrations cause changes in the oxidation
states of the metals in question, which, if was the case, would highly influence
their extractability. Rather, it is more likely that the higher acid concentration
makes more nitrates available for solvating metal-ligand complexes. Furthermore,

higher acid concentrations are known to cause more acid extraction into the organic phase, changing the solvent properties (mainly polarity) and affecting the solubility of the complexes in the organic phase. Ni is predominantly stable in the +2 oxidation state, Zr in the +4 state, while Mo is known to have oxidation states in the range +2 to +6, although oxidation states +2 through +5 are are sensitive to oxidation in the presence of air. Pd exists as +2 oxidation state in nitric acid.[108–110]

By evaluating the fission product extraction over a range of acid concentrations, one can also determine the optimal scrubbing conditions for extracted fission products. The nitric acid concentration for the spent fuel raffinate is pre-determined at 4 M HNO_3. At this concentration, Zr, Mo, Pd, Ni, Ag and Cd extraction is significant. At nitric acid concentration of 0.5 M however, the D-ratio of Zr, Mo, Pd and Ni are all below 1, suggesting this as a suitable acid concentration for the scrubbing solution.

5.2.1 Masking agents

A study of different masking agents have been published by Aneheim et al.[64, 111] Since then, Sypula et al. (2012) found that certain polyaminocarboxylic acids worked efficiently as masking agents for similar solvent extraction systems.[112] A comparison of the most promising polyaminocarboxylic acids, bimet and mannitol as masking agents for relevant fission products is presented in Table 5.2. In addition, two novel masking agents, referred to as agent 10 and agent 13 were investigated for their efficiency in masking the troublesome fission products for the CHALMEX process. Agent 10 and agent 13 are both water-soluble, bidentate BTBP-molecules, cationic and anionic respectively, developed to function as masking agents for Pd(II), Ni(II) and Ag(I). They are evaluated as possible replacements for bimet and their structure can be seen in Figure 5.7a and 5.7b.The molecular structure of all remaining masking agents can be found in Appendix C.[113]
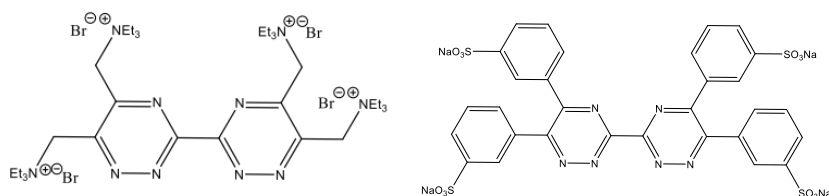

Figure 5.7: Molecular structure of (a) Agent 10 ((PhSO$_3$Na)$_2$-BT) and (b) Agent 13 ((Ch$_4$NEt$_3$X)$_2$)-BT).

Most of the polyaminocarboxylic acids show a reduction of fission product

extraction for some fission products, compared to the pristine system. EDTA and CDTA for instance, show a reduction in D-ratio to < 1 for Zr, while DTPA yields more than a tenfold reduction in D(Cd) to $D = 1.55$. In addition, CDTA yields a significant reduction for D(Cr) and D(Cu), both with concentration below the detection limit for the organic phase. Yet, the reduction of D-ratio for one element is paired with the increase in D-ratio for another fission product for the polyaminocarboxylic acids investigated. For instance, both EDTA and CDTA see an increase in D(Mo), while DTPA sees an increase in D(Pd), D(Zr) and D(Mo).

Neither agent 10 or agent 13 can compare to bimet in the reduction of D(Ag). For Pd, Agent 13 yields a D(Pd)=0.10, which is lower than that of bimet. The most noticeable benefit of Agent 13, is seen for D(Ni) however. Agent 13 is the only masking agent investigated that shows any effect on the Ni extraction, with D(Ni)=2.31 compared to D(Ni)=75.6 for pristine systems.

Table 5.2: The distribution ratios of selected metals for pristine solutions and in the presence of different masking agents. A CHALMEX solvent with 10 mM CyMe$_4$-BTBP and 30% v/v TBP was used as the extracting solvent, while 10^{-4} M of metals were dissolved in 4 M nitric acid and used as the aqueous phase.

Masking agent	Ag	Cd	Pd	Zr	Mo	Cr	Cu	Ni
Pristine	> 100 ± -	> 100 ± -	14.8 ± 0.33	1.69 ± 0.04	45.3 ± 0.89	0.10 ± 0.01	72.5 ± 1.2	75.6 ± 6.83
EDTA	> 100 ± -	> 100 ± -	11.6 ± 1.85	0.37 ± 0.04	73.9 ± 1.26	0.10 ± 0.01	12.8 ± 0.69	82.5 ± 3.5
HEDTA	> 100 ± -	> 100 ± -	> 100 ± -	42.8 ± 6.59	> 100 ± -	0.13 ± 0.01	14.4 ± 0.34	80.3 ± 4.78
DTPA	> 100 ± -	1.55 ± 0.30	> 100 ± -	39.8 ± 2.85	> 100 ± -	0.16 ± 0.08	13.1 ± 1.15	75.7 ± 9.47
CDTA	> 100 ± -	> 100 ± -	12.1 ± 2.4	0.25 ± 0.03	70.1 ± 1.1	> 0.01 ± -	< 0.01	> 100 ± -
Bimet	0.30 ± 0.04	> 100 ± -	0.23 ± 0.02	0.66 ± 0.09	6.92 ± 0.004	> 100 ± -	> 100 ± -	49.4 ± 17.5
Mannitol	> 100 ± -	> 100 ± -	7.53 ± 0.09	0.55 ± 0.04	6.70 ± 0.01	< 0.01 ± -	1.34 ± 1.16	42.3 ± 4.3
Agent 10	> 100 ± -	> 100 ± -	4.70 ± 0.78	0.50 ± 0.03	4.94 ± 0.42	0.03 ± 0.01	76.1 ± 4.0	36.9 ± 6.59
Agent 13	9.41 ± 1.06	> 100 ± -	0.10 ± 0.07	0.15 ± 0.03	10.9 ± 0.81	0.02 ± 0.005	1.03 ± 0.06	2.31 ± 0.81

For bimet, a significant reduction in D(Ag), D(Pd), D(Zr) and D(Mo) is achieved, and for all these fission products except Mo, D< 1. For the use of mannitol, a significant reduction of D(Pd), D(Zr), D(Mo) and D(Cu) is achieved. Ag, although present in low concentrations in the fuel, has shown to

be challenging to remove from the organic phase and so concerns are related to the retention and buildup of Ag during recycling and reuse of the solvent. Bimet is the only masking agent offering a sufficient reduction of D(Ag), which equals 0.30. Furthermore, the abundancy of Mo and Zr in SNF also makes its reduction in D-ratio a priority, as even a low D-ratio means a significant quantity of these metals are extracted. Both bimet and mannitol offers a considerable reduction in both Zr and Mo extraction.

Based on these results, it was concluded that both bimet was the most suitable for combination with mannitol. These masking agents will therefore be further explored in section 5.4.

5.3   DEHBA

The results presented here are based on Paper V.

DEHBA is an extracting agent for the tetra- and hexavalent actinides, namely Pu(IV) and U(VI). DEHBA yields high distribution ratios for both Pu and U, as seen in Table 5.3. For comparison, neither Np(V), Am(III) or Eu(III) are

Table 5.3: The distribution ratios of the actinides and Eu extracted by 30% v/v DEHBA in 70% FS-13

	Pu(IV)	U(VI	Np(V)	Am(III)	Eu(III)
D	11.4 $\pm$ 0.31	9.41 $\pm$ 0.51	<0.01 $\pm < 10^{-4}$	<0.01 $\pm < 10^{-4}$	<0.01 $\pm < 10^{-4}$

extracted by DEHBA to any significant degree. DEHBA has shown a higher overall extraction of lanthanides compared to TBP. With D(Eu) $< 10^{-4}$, which is the most extractable lanthanide, separation of the Pu and U from the lanthanides is achieved.[114]

Considering the DEHBA solvent's physical properties, presented in Table 5.4, it becomes apparent that the density of pure DEHBA of 0.837 g cm^{-3}, is significantly lower than the density of pure TBP (0.971 g cm^{-3}). Thus, it is not surprising that the density of the DEHBA solvent is lower than that of the TBP-solvent, with 1.12 g cm^{-3} and 1.28 g cm^{-3}, respectively, for the pre-equilibrated solvents.

A couple of elements of concern become apparent, however. The density of the pre-equilibrated DEHBA solvent is very close to the density of 4 M HNO$_4$ at 25°C, which is about 1.10 g cm^{-3} at 25°C. In a loaded aqueous phase, the density will be higher than pure nitirc acid, and phase inversion phenomena are thereby likely as the solvent is loaded with metal. Furthermore, the surface tension of the pristine- and pre-equilibrated solvent is dominated by the surface

Table 5.4: The measured density (ρ), surface tension and interfacial tension (IFT) of pure DEHBA and a 30% v/v DEHBA and 70% v/v, pristine and pre-equilibrated.

Constituent	Pre-equilibration	ρ $(kg\,m^{-3})$	Surface tension $(mN\,m^{-1})$	IFT $(mN\,m^{-1})$
DEHBA	-	0.837 $\pm$ 0.000	28.7 $\pm$0.20	-
30% v/v DEHBA 70% v/v FS-13	-	1.20 $\pm$ 0.005	27.5 $\pm$ 0.04	-
30% v/v DEHBA 70% v/v FS-13	4 M HNO$_3$	1.12	29.2	7.23 $\pm$ 0.15

tension of DEHBA. The interfacial tension of the DEHBA solvent (7.23 mN m^{-1}) against nitric acid is significantly lower than its surface tension (29.2 mN m^{-1}), and also much lower than the interfacial tension of the TBP solvent against nitric acid (12.8 mN m^{-1}). This is concerning, as a too low interfacial tension can cause challenges for the phase separation. This was also observed in the batch experiments as the solvent and aqueous phase produced a three-layered system.

The density difference between the pristine- and pre-equilibrated DEHBA solvent also suggest a significant degree of acid extraction by DEHBA. Since the density of nitric acid is lower than that of the solvent, any dissolved acid will act to reduce the density of the solvent. This was confirmed by the acid extraction experiments presented in 5.8.

A linear fit to the concentration of protons in the organic phase versus nitric acid concentration show a slope of 0.19 (R^2=0.98) for the DEHBA solvent, compared to a slope of 0.25 (R^2=0.92) for the TBP solvent until saturation is achieved. This shows that, for 1 M increase of nitric acid concentration, almost 20% of the acid is extracted by the DEHBA solvent. Likewise, a 25% extraction of available acid occurs for the TBP solvent for nitric acid concentrations below 4 M. For the process, this means that both solvents will require scrubbing of the extracted acid.

A slope analysis was performed for the extraction of Pu and U as a function of both DEHBA concentration, but also nitric acid concentration. Slope analysis is used for determining the dependency of the metal:ligand complex on a variable, such as ligand concentration or nitric acid concentration. It was found that the uranium is extracted as a 1:1 complex by DEHBA, as seen in Figure 5.9, in contrast to a 1:2 U:DEHBA complex reported by Acher et al.[115]. Acher et al. also reported that the U:DEHBA complex was coordinated by 4 nitrate ions, although extractions were performed using U(VI). Here, the slope shows a nitric acid dependency of only 0.5, as presented in Figure 5.10. The nitric
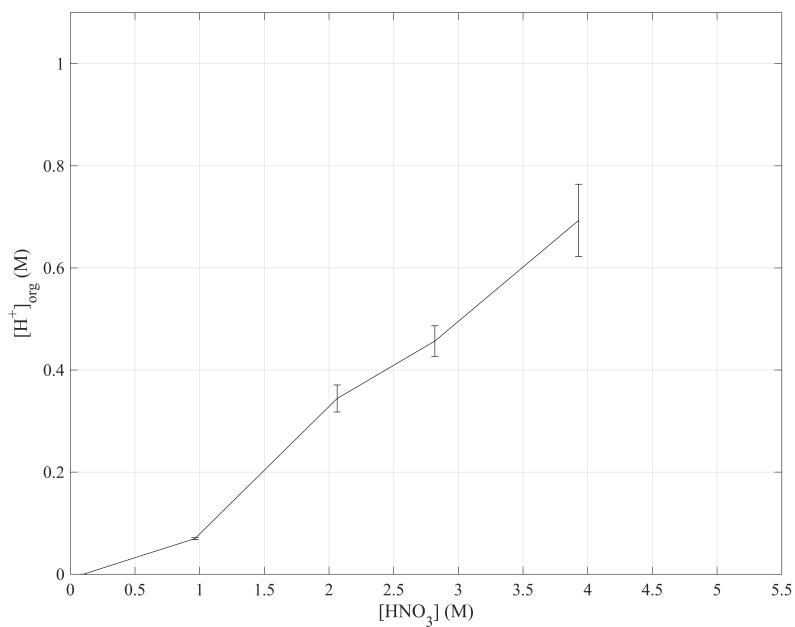
Figure 5.8: The concentration of acid in the organic phase after contacting with 4 M HNO_3.
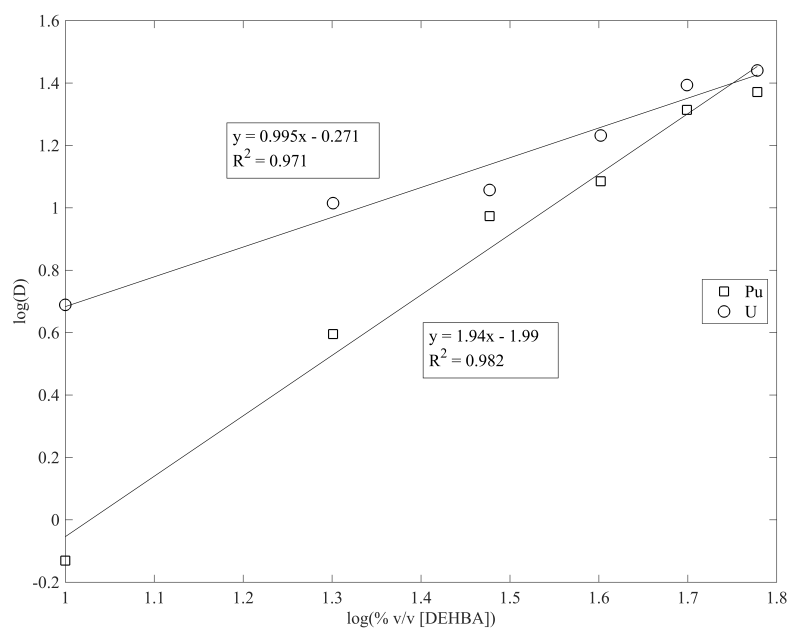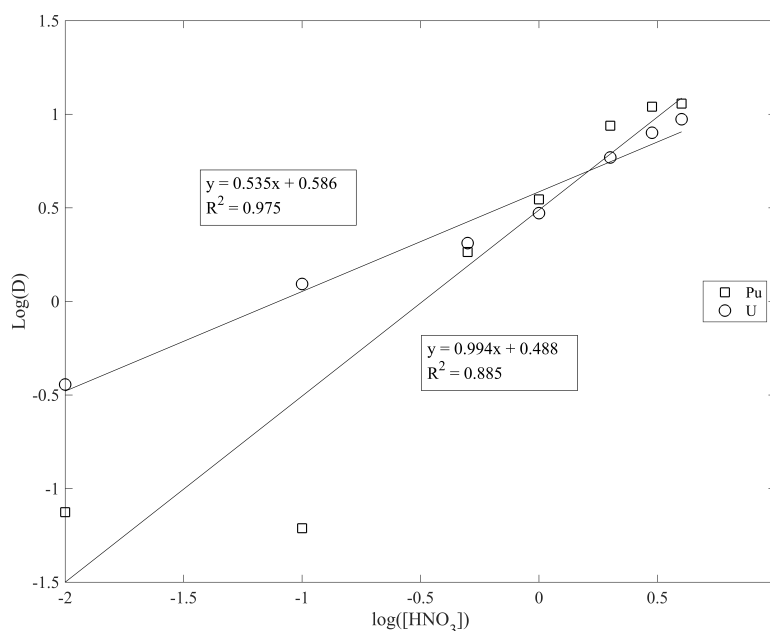

Figure 5.9: log(D) of Pu and U as a function of log(% v/v DEHBA) in FS-13. Linear regression lines have been fitted to the respective data points.

acid dependency experiments were repeated using 1 M HNO_3 and adjusting the nitrate concentration by the addition of $NaNO_3$, which produced the same slopes. This was done to reduce the effect of activity changes with increased nitrate content.

For the extraction of Pu, a dependency of 1:2 is seen for Pu:DEHBA, which is in agreement with earlier reported work. Acher et al. also showed evidence of a 1:3 dependency, which is not reproduced for the DEHBA-FS-13 solvent.[115] Also, it was found that the nitrate and nitric acid dependencies were equal for Pu .

Figure 5.10: Log(D) of Pu and U as a function of log($[HNO_3]$), extracted by 30% v/v DEHBA in FS-13. Linear regression lines have been fitted to the respective data points.

While the presence of TBP has been shown to promote the degradation of $CyMe_4$-BTBP, the presence of DEHBA appear to not play any role in the $CyMe_4$-BTBP degradation. However, it has been found that DEHBA forms water-soluble degradation products which act like masking agents for both Am and Eu.[114] Here, the effect of gamma irradiation on the extraction of Pu and U has been investigated, and the results are presented in Table 5.5. The D-ratios of both Pu and U decrease with increasing irradiation doses. Generally, the higher the dose, the lower the D-ratios. Both D(Pu) and D(U) are, however, maintained at sufficiently high levels to achieve separation from the aqueous

Table 5.5: The D-ratios of Pu and U after gamma irradiation of the DEHBA solvent, aerated and in contact with 4 M HNO_3

Dose (kGy)	D(Pu)	D(U)
5	27.2 ± 0.37	13.8 ± 0.35
20	21.6 ± 0.47	8.24 ± 0.71
75	19.9 ± 0.21	8.12 ± 0.31
100	17.5 ± 0.27	9.51 ± 0-41
250	17.7 ± 0.63	6.41 ± 0.15

phase.

Lastly, the kinetics of extraction for the DEHBA solvent was investigated. For the TBP solvent, extraction equilibrium is reached within 10 minutes of contacting. For Pu extraction by DEHBA, equilibrium is also reached within 10 minutes, as seen in Figure 5.11. The equilibrium value for D(Pu) is about 13.5,
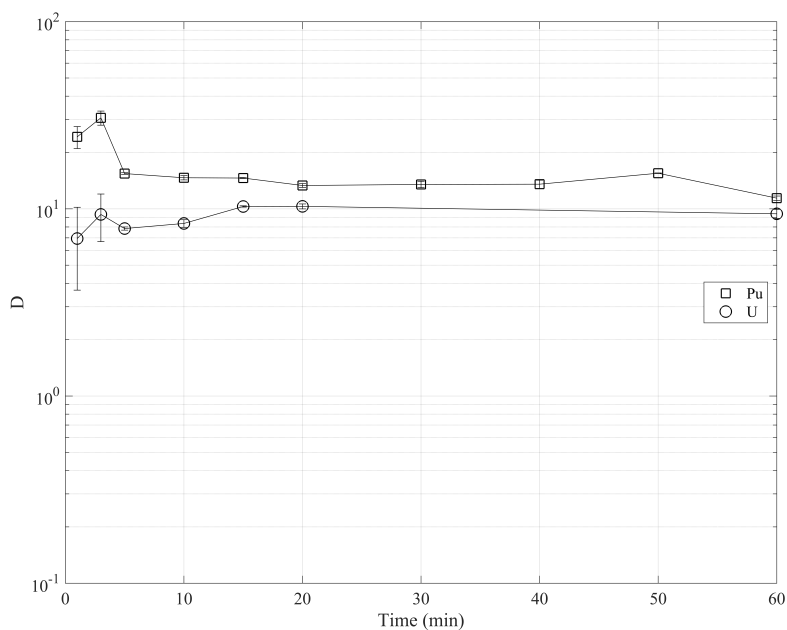
Figure 5.11: The distribution ratio of Pu and U as a function of time, extracted by 30% v/v DEHBA in FS-13.

which is significantly lower than the D(Pu)=24 after only 1 minute of contacting. Furthermore, D(Pu) after 5 minutes contact time was approximately 31. It is possible that this initial increase in D(Pu) is due to for example a competing extraction reaction with HNO_3 or NO_3^-, some unknown chemical reaction or it could simply be due to difficulties in sampling at accurate time intervals. As

the contacting times are increased, the sampling time will have a smaller and smaller effect on the D-ratio.

Similar trends are seen for the extraction of U, although to a much smaller degree than for the Pu extraction. D(U) also saw a much higher deviancy in the triplicate samples.

5.4   Metal loading

The results presented here are based on Paper I.

Extraction trends during metal loading conditions can be substantially different to those with only trace concentration metals. This can be related to interfering or competing extraction of other metals with high concentration in the aqueous solution.

With only trace level metals, a 10 mM CyMe$_4$-BTBP concentration is sufficient for An/FP separation. During metal loading conditions on the other hand, the extraction of both Am and Cm is severely reduced, as seen in Figure 5.12 (a). Meanwhile, little effect is seen on Np, Pu and U extraction. This is not entirely unexpected since the concentration of TBP (30% v/v=1.1 M) is much higher than that of Pu and U. The 10 mM CyMe$_4$-BTBP concentration however, is lower than the total concentration of extractable (by CyMe$_4$-BTBP) metal in the aqueous phase, resulting in significantly lower D-ratios for the Am, Cm and partially Np.

At higher CyMe$_4$-BTBP concentrations, as seen in Figure 5.12 (b), the Am and Cm D-values are maintained > 1 for all the raffinates investigated. One can still distinguish between the raffinates, for both CyMe$_4$-BTBP concentrations. The raffinates yielding the lowest D-values for Am and Cm are the SANEX 4.2 M raffinate and the HAW-CEA 4.3 M raffinate. This is perhaps not too unexpected when considering the raffinate metal composition in Appendix B, as these raffinates have the highest total metal concentration. Furthermore, it has overall higher concentrations of FP previously shown to be extracted by the BTBP-ligand, namely Ag, Ni, Cd, Mo, Pd, Cu and Cr.

In the presence of mannitol and bimet as fission product masking agents, the D-ratios are noticeably higher for Am and Cm, as seen in Figure 5.13. The effect on Np, Pu and U is surprisingly the opposite, however, with decreased D-ratios in the presence of masking agents. While the D-ratios for Pu and U both remain over 10 for all raffinates, D(Np) is below 10 for all the raffinates in the presence of the masking agents. Firstly, this suggests that either bimet or mannitol, or the combination, to a small degree inhibits the TBP molecule. Secondly and by extension, this also indicates that Np has been at least partially oxidized from Np(V) to Np(V, VI), which is extractable by TBP.
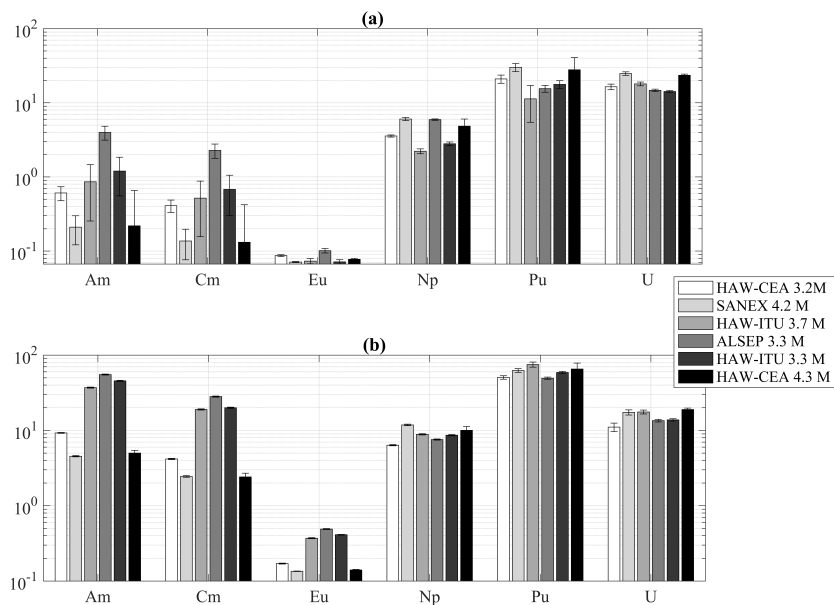
Figure 5.12: The distribution ratio of the actinides and Eu after extraction from various spent fuel raffinates using a 30% v/v CHALMEX solvent (a) with 10 mM CyMe$_4$-BTBP and (b) with 25 mM CyMe$_4$-BTBP.

Overall, the system with 25 mM CyMe$_4$-BTBP solvent and in the presence of masking agents, yields promising D-ratios for all the actinides, even for the raffinates with the highest metal content.

5.4.1 Kinetics

Since the CyMe$_4$-BTBP ligand is not surface active and its extraction of actinides depends on the mass transfer of metal-nitrate complexes to the organic phase, it is likely that the metal concentration plays a significant role in its extraction kinetics. Under trace metal concentrations, it has previously been demonstrated that the actinides extracted by CyMe$_4$-BTBP (mainly Am and Cm, to a lesser extent Np(V) and Pu) and Eu reached extraction equilibrium after 20 minutes contact time.[27] The actinides extracted by TBP on the other hand, quickly reached extraction equilibrium more or less instantly.

As expected, the kinetics of the actinide extraction by CyMe$_4$-BTBP is affected by the high metal content, as seen in Figure 5.14. Extractions using both 10 mM and 25 mM CyMe$_4$-BTBP concentrations were performed, but only the former is presented here as the trends are identical. The extraction of U and Pu reaches equilibrium within 5 minutes of contacting, while the extraction

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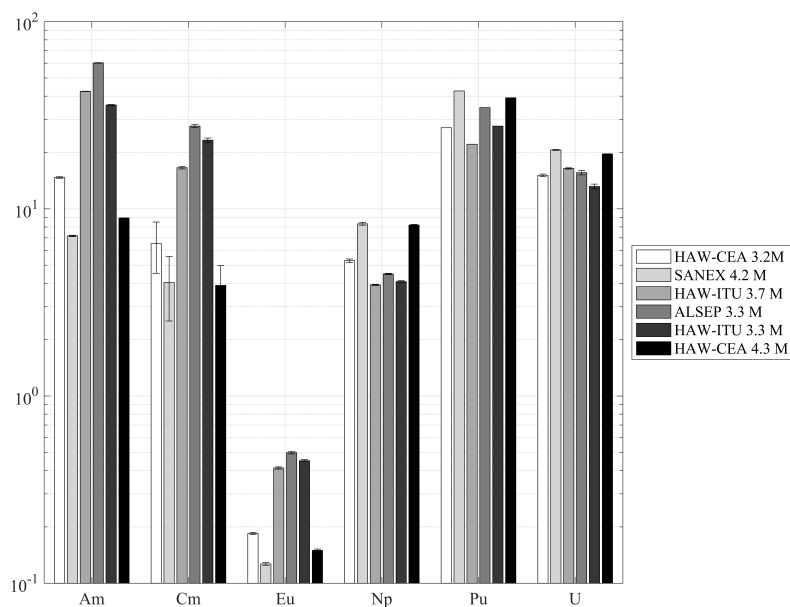
Figure 5.13: The distribution ratios of Am, Cm, Eu, Np, Pu and U in the presence of bimet and mannitol, extracted from various simulated spent fuel raffinates. The solvent had CyMe$_4$-BTBP concentration of 25 mM.

of Np reaches equilibrium within 20 minutes of contacting. D(Am), D(Cm) and D(Eu), however, do not reach equilibrium until 100 minutes of contacting. These are extremely long time scales considering the intent to use centrifugal contactors as contacting equipment for the European homogeneous An recycling processes. Still, the maximum D-ratios for Am and Cm are seen after only 10 minutes of contacting, after which the D-ratios decrease steadily. This indicates a competing extraction reaction with one or several of the fission products. It also demonstrates that the use of centrifugal contactors can actually be beneficial for the CHALMEX process, since shorter contact times yields higher D-ratios compared to the equilibrium values.

Although the trends for the 25 mM CyMe$_4$-BTBP system were equal to those of the 10 mM CyMe$_4$-BTBP system, the overall D-ratios were higher. For instance, the equilibrium value for D(Am) was 0.35 for 10 mM CyMe$_4$-BTBP, and was 4.9 for the 25 mM CyMe$_4$-BTBP system. Similarily, the equilibrium D(Np) was 4.8 and 7.6 respectively.

The extraction of the most concerning fission products as a function of time can be observed in Figure 5.15. It is apparent that Pd, Ag and Zr all reach extraction equilibrium within 10 minutes. This is surprising as both Cd and
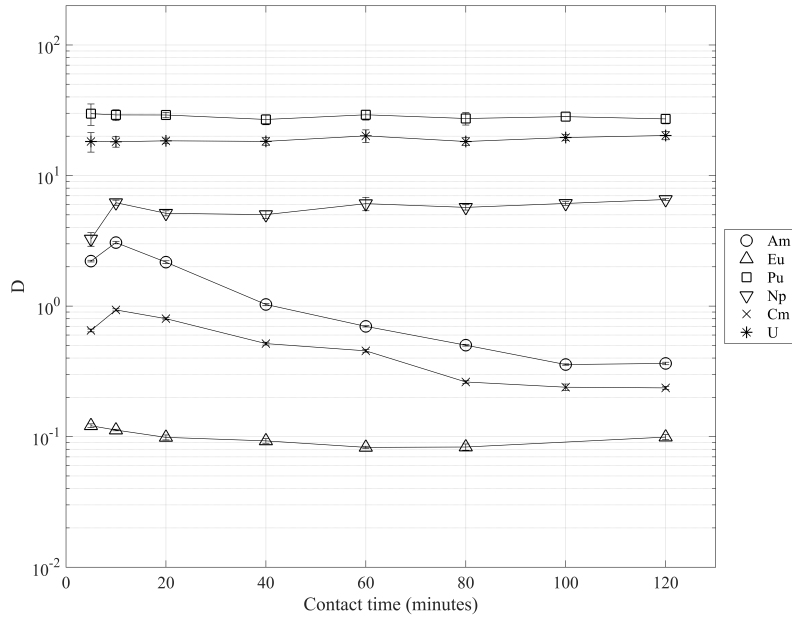
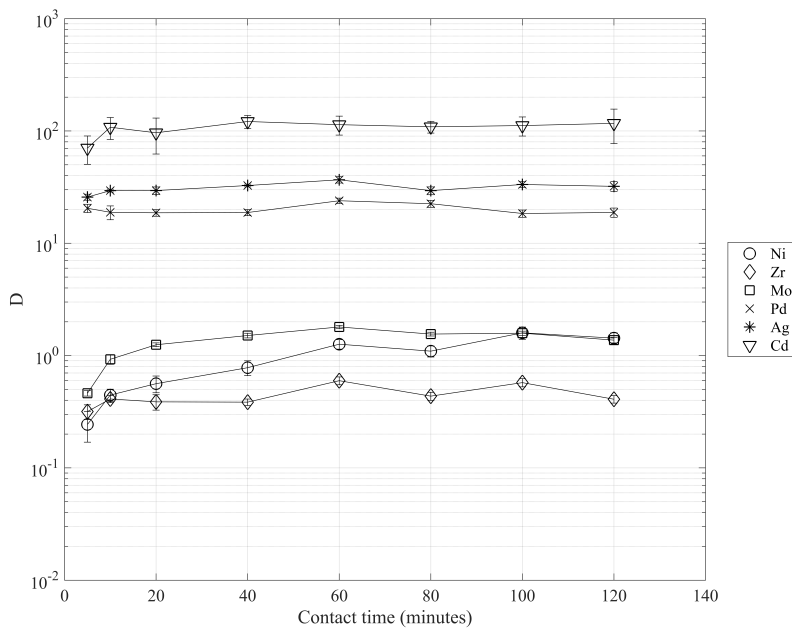Figure 5.14: The distribution ratio of the actinides and Eu as a function of time for CHALMEX solvent with 10 mM CyMe$_4$-BTBP.

Figure 5.15: The distribution ratio of selected FP as a function of time, extracted by 10 mM CyMe$_4$-BTBP CHALMEX solvent from HAW-CEA 3.2 M.

Ag are known to be extracted by the BTBP-ligand, which displayed very slow kinetics for the actinide extraction.[111, 116] Zr on the other hand is extracted by TBP, which is known to have much faster kinetics compared to CyMe$_4$-BTBP.

An interesting trend is seen for D(Ni). The slow extraction trend oppositely matches that seen for the decrease in D(Am) in Figure 5.14. As for Am, Ni does not reach extraction equilibrium until after 100 minutes of contacting. If considering the concentration of Ni in the raffinate and assuming a 2:1 complex formation with the BTBP-ligand, it is deemed very likely that the Ni extraction slowly outcompetes that of Am.

In the presence of masking agents and 25 mM CyMe$_4$-BTBP,the distribution ratios of the actinides are greatly increased, as seen in Figure 5.16.
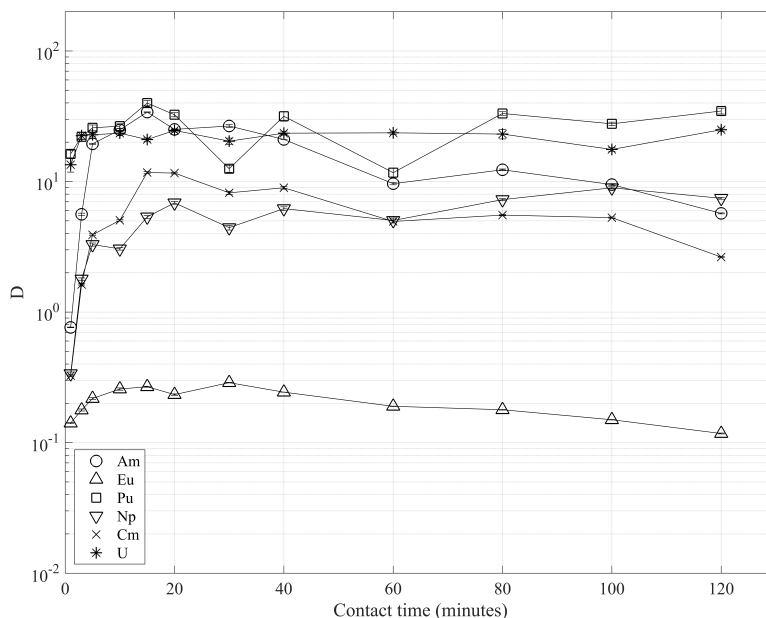
Figure 5.16: The distribution ratios of Am, Cm, Eu, Np, Pu and U in the presence of bimet and mannitol, extracted from a simulated spent fuel raffinate, as a function of time. The solvent had CyMe$_4$-BTBP concentration of 25 mM.

D(Am) and D(Cm) are much higher than those for the pristine system. Yet, the D-ratios of both Am and Cm decrease at the same rate as in the system without masking agents. This shows that the masking agents are ineffective in masking the extraction of Ni. Still, the higher ligand concentration is sufficient to ensure D> 1 for both Am and Cm. D(Pu) and D(U) are comparable to the 10 mM CyMe$_4$-BTBP system, once again showing that the majority of these actinides are extracted by TBP and that TBPs concentration is high enough

to ensure sufficient extraction. D(Np) also increases for the system with higher BTBP concentration and in the presence of masking agents. The values increase from an equilibrium value of about 7 to an equilibrium value of approximately 8. This shows that Np is indeed also extracted by the BTBP ligand, or that bimet or mannitol mask fissions products that are competing with the Np extraction.

Scrubbing

In Figure 5.6, it was shown that several of the most extracted fission products, had low D-ratios at lower nitric acid concentrations. Specifically, Zr, Mo, Pd and Ni all displayed D< 1 for nitric acid concentrations between 0.2 M and 1.5 M. This demonstrates that a scrubbing solution with a nitric acid concentration in that nitric acid range should back-extract these elements. Ag, Cd and Cu however, had D> 1000 for the entire range and are thus not expected to be back-extracted using such a scrubbing solution. Figure 5.17 shows the scrubbing as a function of time for Zr, Mo, Ni and Cu. It is clear that 0.5 M HNO_3 is
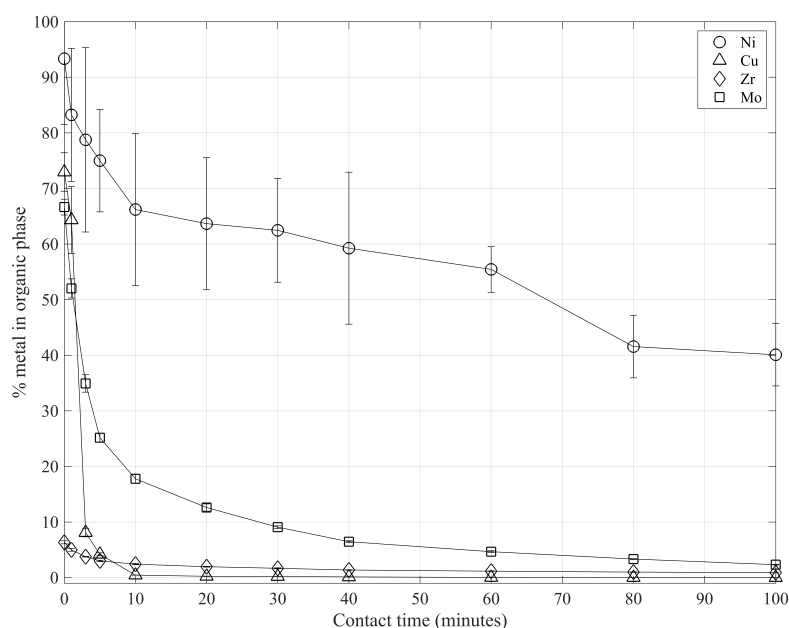
Figure 5.17: % metal in the organic phase of selected fission products as a function of scrubbing time for the CHALMEX solvent with 25 mM $CyMe_4$-BTBP, using 0.5 M HNO_3 as scrubbing solution. The extraction was from raffinate named HAW-CEA 3.2 M in the presence of mannitol and bimet.

an efficient scrubbing agent for these metals, and that the metals are quickly back-extracted from the organic phase. The majority of Cu is back-extracted

within 3 minutes (from 73% to 8% in the organic phase). Within 5 minutes, more than half of the Zr and Mo is also scrubbed from the organic phase, while for Ni, more than 80 minutes of contacting passes before half the Ni is scrubbed from the organic phase.

Stripping

The actinides are recovered to the aqueous phase in the stripping stage. Screening studies have been performed for stripping solutions previously.[27] Stripping using 0.5 M glycolic acid at different pH is presented in Table 5.6.

Table 5.6: The % metal in the organic phase for extraction, scrubbing and stripping of the actinides and Eu for which different pH stripping solutions were investigated in parallel. The solvent, 25 mM CyMe$_4$-BTBP CHALMEX solvent, extracted from the simulated spent fuel raffinate named HAW-CEA, 3.2 M in the presence of the masking agents bimet and mannitol.

	Am	**Cm**	**Eu**	**Np**	**Pu**
Extraction	96.2% ± 2%	90.4% ± 2.1%	20.4% ± 0.1%	89.2% ± 2.3%	96.0% ± 4.2%
Scrubbing	90.9% ± 0.4%	79.3% ± 2.13%	2.4% ± 1.6%	65.2% ± 2.14%	91.3% ± 4.4%
Strip pH 3.8	0.5% ± 0.01%	0.2% ± 0.01%	0.0% ± 0.01%	7.0% ± 0.17%	1.0% ± 0.04%
Strip pH 4.0	0.3% ± 0.001%	0.1% ± 0.01%	0.0% ± 0.001%	6.2% ± 0.16%	0.7% ± 0.03%
Strip pH 4.2	0.2% ± 0.002%	0.1% ± 0.01%	0.0% ± 0.001%	7.3% ± 0.09%	1.0% ± 0.05%

It is clear that small variance in the pH does not cause a significant change in the back-extraction of the actinides or Eu. The biggest difference is seen for the Np back-extraction, with a 1.1% difference for the pH 4.0 and pH 4.2. For the remaining actinides, a difference of less than 0.3% is seen between the different stripping solutions. Overall, pH 4 yields the most efficient back-extraction.

The kinetics of the stripping was investigated next, as presented in Figure 5.18. The stripping was performed after extraction from 3.2 M HAW-CEA and subsequent scrubbing using 0.5 M nitric acid. Here, time 0 minutes shows the % metal in the organic phase after the scrubbing stage. The stripping is efficient for Am, Cm, Pu and Eu, especially, with less than 1% of the metal remaining in the organic phase after 5 minutes of contacting. Np reaches <10% in the organic phase after 10 minutes contact time. This all demonstrates the efficiency of the stripping agent, and also its suitability for use in contactors with short residence times.
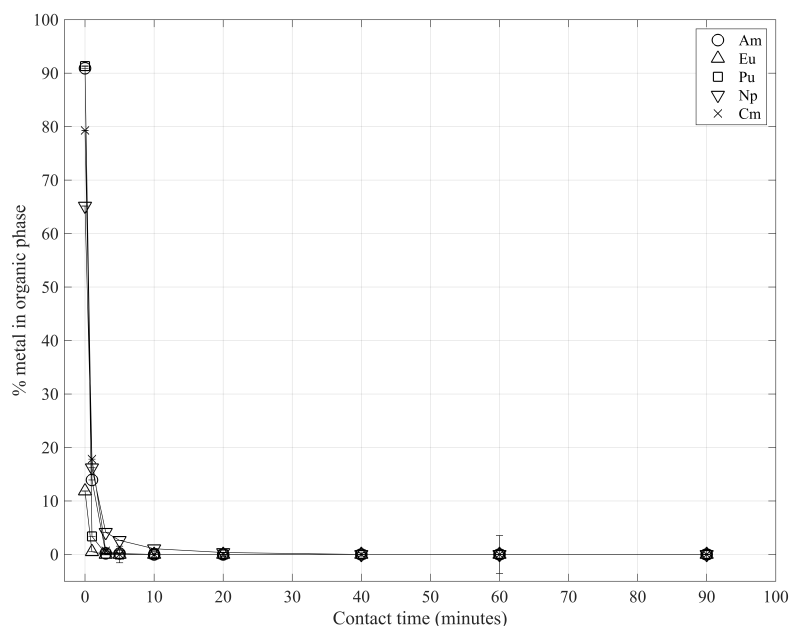
Figure 5.18: % metal in the organic phase as a function of contact time for stripping of the CHALMEX solvent with 25 mM CyMe$_4$-BTBP, using 0.5 M glycolic acid at pH 4. The extraction was from raffinate named HAW-CEA 3.2 M.

5.5 Flowsheet tests

The results presented here are based Paper II.

Several batch flowsheet tests were performed, both to enable simple flowsheet calculations, but also in preparation for single centrifugal contactor tests. The process conditions for the different batch flowsheet tests performed can be seen in Table 5.7. Changes to the flowsheets were made based on the previous flowsheet tests and also on knowledge and experiences gained from single batch experiments.

In the first flowsheet, extractions were performed using a solvent with 10 mM CyMe$_4$-BTBP and without masking agents to limit fission product extraction. The phase ratio was 1:1 for all the process stages. Both scrubbing and stripping solutions were chosen based on earlier published studies.[27, 64, 111]

The low concentration of CyMe$_4$-BTBP combined with the absence of masking agents yields low D-ratios for Am and Cm in particular in the first flowsheet test, ss can be seen in Figure 5.19. The extraction of Np, Pu and U however are maintained at high D-ratios. An unexpected result, however, is that the D-ratio during scrubbing is significantly lower for Pu (D=2.5) compared to during it's

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Table 5.7: The process conditions of the different batch flowsheet tests performed. The phase ratio refers to the ratio of extraction solvent volume to aqueous phase volume.

Flowsheet test	1	2	3
Raffinate	HAW-ITU 3.3 M	HAW-CEA 3.2 M	HAW-ITU 3.7 M
[CyMe$_4$-BTBP] (mM)	10	25	25
Phase ratio, θ	1:1	1:1	1:2
No. of scrub stages	2	2	1
No. of strip stages	2	2	1
Complexing agents	-	0.2 M Mannitol 20 mM Bimet	0.2 M Mannitol 20 mM Bimet
Scrub solution	0.01 M HNO$_3$ 0.99 M NaNO$_3$ 0.6 M glucono-lactone	0.5 M HNO$_3$	0.5 M HNO$_3$
Strip solution	0.5 M glycolic acid at pH 4	0.5 M glycolic acid at pH 4	0.5 M glycolic acid at pH 4

extraction (D=31). In terms of % metal in the organic phase, the decrease in D-ratio results in a 27% loss of Pu from the organic phase. Similarly, the other actinides also sees a significant loss from the organic phase to the scrubbing solution. A 16% loss is seen for Np, 10% for Cm, 9% for Am and less problematic, 7% loss is seen for Eu.

Glycolic acid yields D<1 for all the actinides in flowsheet 1. While Am and Cm (and any remaining Eu) are efficiently scrubbed to levels below 1% metal remaining in the organic phase. 5% of the Pu remains in the organic phase after 2 stripping stages, while 13% and 22% remains of U an Np respectively. After titrations of the stripping phases, it was calculated that strip 1 had a pH of 1.75 (starting pH=4) after contacting. This shows that a significant amount of acid remained in the organic phase after only 1 scrubbing stage. This likely affect the stripping efficiency and so another scrubbing stage was added to the next flowsheet.

In the second flowsheet test, the concentration of CyMe$_4$-BTBP was increased, masking agents were also added to the aqueous phase and the scrubbing solution was changed due to observation of third phase formation in the scrubbing stage in flowsheet 1. These changes had a pronounced effect especially on the extraction of the minor actinides, as seen in *Flowsheet 2* in Figure 5.19. D(Am) was above 40 and D(Cm) almost 13. Also D(Np) was nearly doubled from 5.5 in
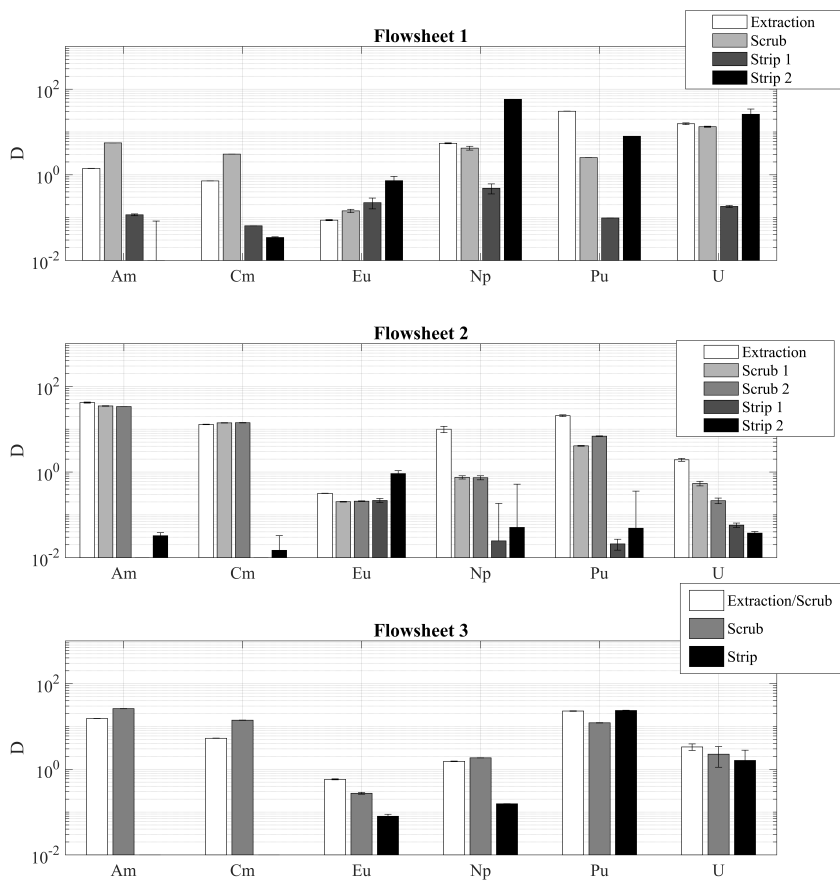
Figure 5.19: The distribution ratio of the actinides and Eu in the different flowsheet tests performed.

flowsheet 1 to 10 in flowsheet 2. The extraction of U on the other hand, showed a considerable reduction with D(U)=16 in flowsheet 1 and D(U)=1.9 in flowsheet 2. This could possibly be due to the added masking agents, although no suppression of uranium or other actinide extraction has been observed earlier.[64] Also D(Pu) sees a decrease from 31 to 21, but this only accounts for a 1.4% reduction of the total metal extraction.

For the scrubbing stages in flowsheet 2, both U and Np have D-ratios below 1. After 2 scrubbing stages, about 4% of the total uranium remain in the organic phase. It is however important to recognize that more than 99.9% of the U has been pre-extracted in the first GANEX cycle.[55, 56, 62] For Np, about 17% of the total metal remains in the organic phase. The oxidation state of Np has, however, proven tricky to control during process conditions, since it is affected by many parameters, including nitric acid concentration, the presence of nitrous acid, etc. Solvent degradation products are also known to affect Np's oxidation state. It is therefore challenging to evaluate how accurate the Np behaviour is in under simulated process conditions.

For the remaining actinides (Pu, Am, Cm), the D-ratios are above 1 for the scrubbing stages. The stripping solutions is once again shown to be effective in back-extracting the actinides, with D<0.25 for every element.

In the third flowsheet, more substantial changes were done to approach more process-like conditions. The solvent, complexing agents, scrubbing and stripping conditions were all kept the same, but the number of stages were reduced from 2 to 1 for both scrubbing and stripping. This was thought to reduce the loss of U and Np in the scrubbing stages. Also, the simulated raffinate solution was mixed 50:50 with the scrubbing solution and a phase ratio of solvent:aqueous phase of 1:2 was maintained in the extraction stage. In a centrifugal contactor flowsheet, the scrubbing stage will be introduced to the bank of contactors at a point such that it will add to flow of the raffinate solution. The phase ratio as such becomes 1:2.

While the extracted Np and U is now retained in the organic phase during the pure scrubbing stage, their D-ratios are far lower in the extraction stage for the third flowsheet. Still, with D(U)=3.3 and D(Np)=1.5, a high yield is possible by increasing the number of extraction stages. The D(U) and D(Np) are also both both maintained at above 1 during scrubbing. The major concern for the third flowsheet test is the high D-ratios for Pu (D=24) and U (D=1.6) in the stripping stage. This is likely due to insufficient acid scrubbing of the organic phase prior to the back-extraction of the actinides, which likely reduces the stripping efficiency.

5.5.1 Flowsheet calculations

Based on the results of the flowsheets in section 5.5, the ideal number of stages for each flowsheet were calculated. The calculations were based on the element with the lowest D-ratio as the "limiting" actinide, and allowing a minimum amount (99%) of extraction for that actinide. The same was done for the scrubbing stages, where the maximum loss allowed was 0.1%, and for the stripping, the actinide with the highest D-ratio was used as the "limiting" actinide.

Although the calculations are for ideal systems, they give valuable insights into which flowsheet provide more optimal conditions for the CHALMEX system. Generally, the results for the first flowsheet give many number of stages, for little gain in the recovery of especially Cm and Np, as seen in Table 5.8.

For the second flowsheet, one can see a significantly higher recovery of all the actinides compared to the first flowsheet, except for U. The number of process stages is also notably reduced from a total of 38 stages in the first flowsheet to 8 in the second. There is, however, also a higher recovery of Eu with 5.3% overall. In the third flowsheet, 10 stages were calculated in total. Here, the recovery of Pu and U are much lower than in the preceeding flowsheets however. Simultaneously, the recovery of Eu is the highest out of all the flowsheet tests, at 15.8%. Despite the high yields of the minor actinides, such a high recovery of Eu can be problematic for later fuel production. While the recovery of U is of minor concern here, the low recovery of Pu is highly problematic since spent fast reactor fuel can contain 10's of grams per litre.

Based on the results, it is clear that the second flowsheet is the most promising one. Here, the low extraction of Np causes the overall recovery to be low. In the third flowsheet however, the feed solution was 50%:50% feed solution and 0.5 M HNO_3. The scrubbing solution lowers the overall acid molarity of the feed solution, which will increase the D-ratio of Np as seen before. An adaption of the second flowsheet would thus be to lower the acidity of the feed solution in order to boost the Np extraction. In the third flowsheet, however, the major actinides are retained in the organic phase during stripping. In addition to the feed solution/scrubbing solution, only one scrubbing stage was considered. It is known that retention of the actinides can occur due to insufficient acid scrubbing, so another scrubbing can be added to the second flowsheet to optimise the recovery.

For the second flowsheet, the fission product recovery, when subject to the ideal number of stages, was calculated next. The fission products with the highest recovery yield are shown in Figure 5.20. It becomes clear that the recovered actinide stream has a very low degree of contamination of fission products. The fission product with the highest recovery was Ag, with a 1.1% total recovery.

Table 5.8: The ideal number of stages calculated for each flowsheet test and the overall recoveries of the actinides and Eu.

Flowsheet test	1	2	3
No. of extraction stages	18	3	2
No. of scrubbing stages	18	4	6
No. of stripping stages	2	1	2
% total Am recovery	94.1	99.8	99.9
% total Cm recovery	65.0	99.9	99.9
% total Np recovery	58.1	68.2	97.9
% total Pu recovery	90.3	99.6	69.8
% total U recovery	82.2	34.0	27.9
% total Eu recovery	0.99	5.31	15.8

The majority of the silver was lost during the scrubbing stage, but about 0.5% of the total Ag remain in the organic phase. For Cd, more than 99% was retained in the organic phase, demonstrating the need for a solvent cleanup stage.
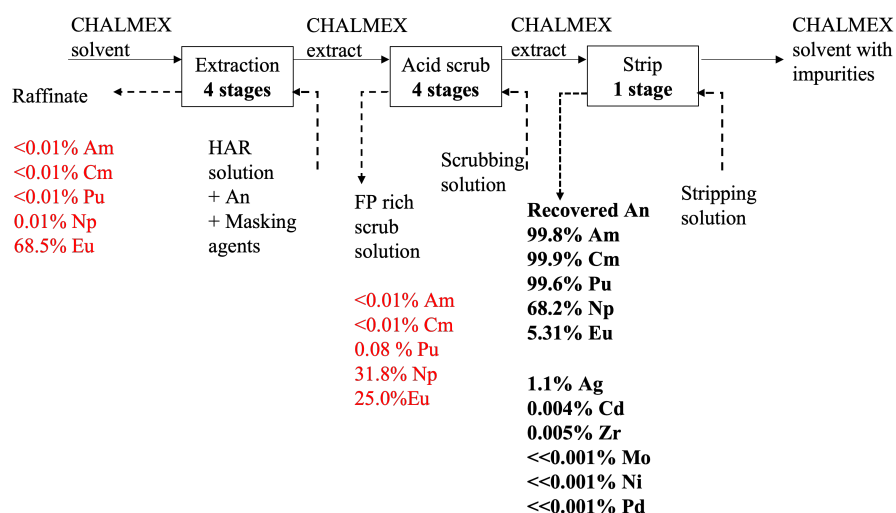
Figure 5.20: The recovery of the actinides, Eu and the most recovered FP for flowsheet 2, based on ideal number of stages.

5.6 Centrifugal contactor tests

During the first single centrifugal contactor test, separation was satisfactory at higher flow rates (60 mL/h and 30 mL/h), while phase entrainment became apparent at the slowest flow rate (10 mL/h). The conditions for both the centrifugal contactor tests are summarised in Table 5.9. It was therefore necessary to centrifuge the sample aliquots collected during the 10 mL/h flow rate. The distribution ratios of the added radioactive tracers are presented in Figure 5.21 (a) for test 1. Unsurprisingly, the higher flow rates yield lower extraction-values, due to the shorter residence time of both phases in the contactor unit at higher flow rates.

Table 5.9: The operating conditions of the two single centrifugal contactor tests (1) using 10 mM CyMe$_4$-BTBP solvent and (2) using 25 mM CyMe$_4$-BTBP solvent.

Flowsheet test	1	2
Feed	HAW-ITU	50% HAW-ITU 50% 0.5 M HNO$_3$
Rotor speed (rpm)	4500	3500
Aq. flow rate (mL h^{-1})	60,30,10	80,40,20
Org. flow rate (mL h^{-1})	60,30,10	40,20,10

With D-ratios ranging from 0.25 (60 mL h^{-1}) to 0.75 (10 mL h^{-1}) compared to the equilibrium D-ratio of 1.66 for Am, the extraction is significantly lower than reported for systems with only trace-level metals. Since it has been shown that extraction equilibrium is reached after approximately 100 minutes of contacting, a low D-ratio for the minor actinides is not surprising.[25] However, Am has the highest D-ratio after about 10 minutes of contacting. After 10 minutes, the D-ratio decreases until equilibrium is reached.[25] The D-ratios of both Am and Cm are below 1 for all flow rates and this is also true even for the equilibrium sample (Figure 2). This suggests that the solvent overall is not capable of extracting Am and Cm to the degree that is required for process viability. However, if an increase in americium extraction can be achieved, for example, by increasing the CyMe$_4$-BTBP concentration or by adding masking agents for the fission products, the centrifugal contactor can be suitable for the CHALMEX FS-13 process. Pu and U D-ratios are above 10 for all tested flow rates in the first single centrifugal contactor test. This is expected from the PUREX process.[26] The Np extraction increases with decreasing flow rate. Its highest D-ratio is seen at equilibrium, with D$_{eqm}$=6.6.

For the second centrifugal contactor test, performed using the 25 mM CyMe$_4$-BTBP CHALMEX solvent, severe phase entrainment was experienced for both phases when subjected to the same flow rates and rotor speeds as the first
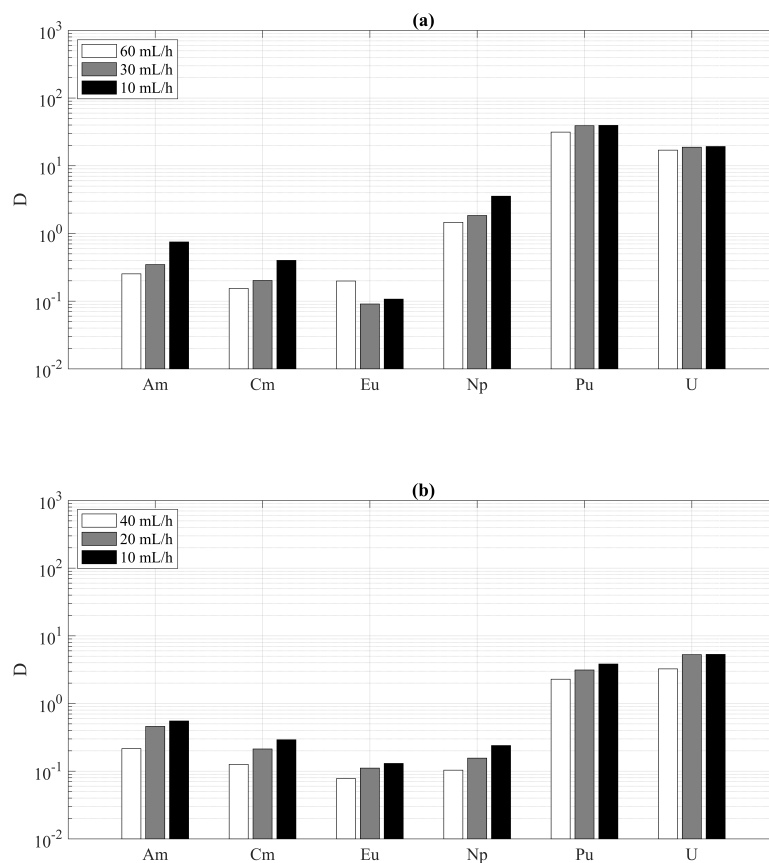
Figure 5.21: The D-ratios for the actinides and Eu for the single centrifugal contactor tests. The flow rates shows the organic flow rates. (a) Extraction using a 10 mM CyMe$_4$-BTBP solvent and a rotor speed of 4500 rpm (b) Extraction using 25 mM CyMe$_4$-BTBP and rotor speed 3500 rpm.

test. Usually, phase separation issues are due to either too high rotor speeds, a degraded teflon layer on the contactor washer, or impurities in the solvent. Solvent washing was performed in several stages and analysis was run on the washing water. No impurities were detected from GC-MS, NMR or ICP-MS analysis. Although no degradation of the washer in the centrifuge was visually observed, the centrifugal contactor was changed. Lastly, the rotor speed was changed from 4500 rpm to 3500. Although possible, it is unlikely that the poor phase distribution is due to the mixed aqueous phase. This can be assumed since in the 10 mM CyMe$_4$-BTBP test, no phase separation issues were seen for either 4 M HNO$_3$ or a simulated PUREX raffinate as the aqueous phase.

Despite sufficient phase separation being achieved after the change in conditions, the D-ratios are even lower in the second centrifugal contactor test, as seen in Figure 5.21 (b). The concentration of CyMe$_4$-BTBP is more than double that in the first contactor test, and so intuitively the D-ratios are expected to be higher. It is apparent that the lower rotor speed does not produce a fine enough droplet dispersion to facilitate a high extraction of the actinides. It is known that CyMe$_4$-BTBP is not a surface-active extractant, unlike TBP. It is therefore reliant on good phase contact, i.e. a fine droplet dispersion to allow metal extraction.

TBP on the other hand, is a highly surface-active agent, and can facilitate U and Pu extraction under poorer mixing conditions. The D-ratios for uranium (range of 3-5) and plutonium (range of 2-4) in the second centrifugal contactor test demonstrate how poor the mixing must be. One can deduce that there is a very poor droplet dispersion based on the low D-ratios.

Further investigations focused on the assumption that micelle formation could be the cause of the phase entrainment. The critical micelle concentration, *CMC*, was investigated as a function of TBP addition to the solvent. The critical micelle formation was seen at 10% v/v TBP addition to the solvent, where a clear drop in the surface tension from approximately 29 mN m^{-1} to 24 mN m^{-1} is observed. This can indicate that operating the CHALMEX system with a % v/v TBP concentration below 10% could be beneficial for centrifugal contactors.

Chapter 6

Summary and Conclusions

In this work, efforts have been focused on optimisation of the CHALMEX FS-13 process for the industrial and homogeneous recycling of the transuranic elements. These efforts have included the optimisation of parameters affecting the performance of the process, including physical properties, solvent composition, masking agents for fission products and nitrate- and nitric acid dependency. The optimised system was then applied to more process-like conditions and equipment.

Overall, the CHALMEX FS-13 has shown promising results for the extraction and separation of transuranic elements from a spent nuclear fuel raffinate. The density of the solvent was sufficiently high to promote spontaneous phase separation from nitric acid and also from simulated spent fuel raffinates with a high metal content. Furthermore, the solvent has also been shown compatible with the standard European reference raffinate solution of 4 M HNO_4 and yield high D-ratios for all the actinides.

Some co-extraction of fission products was observed. Specifically, the extraction of Ag, Cd, Pd, Zr, Mo, Pd and Ni was of main concern. The addition of bimet as a masking agent reduced the extraction of Ag, Pd and Zr to D<1, while mannitol reduced the extraction of Pd and Zr to D<1. In combination with 0.5 M HNO_3 as a scrubbing solution, an efficient separation of the actinides from the fission products was achieved, also during metal loading conditions.

During loading conditions, the extraction of Am and Cm was much slower than during extractions with trace level metals. A concentration of 25 mM CyMe$_4$-BTBP is necessary for sufficient extraction of the actinides. It is also apparent that the Am and Cm extraction competes with Ni extraction, where Am and Cm distribution ratios steadily decrease after their peaks at 10 minutes contact time. D(Ni) on the other hand, increases at the same rate as Am/Cm decreases.

Based on the process flowsheet tests, an optimised flowsheet has been suggested. This flowsheet consists of 4 extraction stages with 25 mM CyMe$_4$-BTBP, 30% v/v TBP and 70% v/v FS-13. Ideal calculations based on equilibrium extraction data showed that 4 number of scrubbing stages in combination with 1 stripping stage would yield an overall recovery of 99.6% Pu, 99.8% Am, 99.9% Cm and 68.2% Np. The main losses were to the scrubbing stages, including 31.8% Np. The product stream, however, contained negligible amounts of fission products. Any fission products not scrubbed (Ag, Cd), remained in the aqueous phase also during stripping conditions. A solvent clean up stage is thus suggested to regenerate the solvent.

Lastly, the hydrodynamics of the CHALMEX process was investigated in a single centrifugal contactor as preparations for a flowsheet tests. While the initial tests of the solvent were promising, phase separation issues were experienced during the latest test. Decreasing the rotor speed of the centrifuge solved the phase separation issues, but did not generate sufficient phase contact for facilitating extraction by the CyMe$_4$-BTBP molecule. It was suggested that the phase entrainment could be due to the formation of micelles due to the high concentration of TBP. A lowering of the TBP concentration could thus be useful.

Overall, it can be concluded that the CHALMEX process can provide an elegant and simple alternative to the other homogenenous recycling options, with only 8 ideal stages in total. This is provided that issues with phase separation in centrifugal contactors are solved, or other contacting equipment is used. Furthermore, a verification of the suggested process flowsheet is necessary for continuous extractions.

Chapter 7

Suggestions for Future Work

It is suggested that future work on the CHALMEX process focuses on the hydrodynamic challenges during centrifugal contactor operation. Investigations can be focused on micelle formation and even investigating the effect of rotor speed and flowrate on the droplet dispersion and coalescence.

The hydrodynamic properties and behaviour of a <10% v/v TBP should be considered. If favourable, the properties and behaviour of the system needs to be established. Extraction properties, fission product extraction, acid dependency, loading capacity etc. are all necessary.

Further flowsheet optimisation should also be prioritised. A combination of lowering the acidity of the feed solution and optimising the number of scrubbing stages is advised. This should increase the extraction of Np, while also ensuring the back-extraction of U and Pu. Any effect on the extraction and recovery of Eu should be observed.

Lastly, once phase separation issues have been solved for the solvent, extraction tests during continuous conditions are necessary. Successive continuous flowsheet tests in centrifugal contactors and process simulation are also suggested.

Chapter 8

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Appendix A

List of equipment

Table A.1: List of equiment used at Chalmers Univeristy of Technology and Jülich Forschungszentrum, respectively.

Equipment	Chalmers University of Technology	Jülich Forschungszentrum
Shaker	IKA Vibrax VXR 1,500 rpm	I.Heidolph Instruments GmbH Co. KG, Schwabach II.IKA Vibrax VXR 2,200 rpm
Centrifuge	Wifug, LABOR 50M, 4500 rpm	Hettich EBA 8S
HPGe	Canberra, Gamma Analyst GEM 23195	Eurisys EGC35-195-R
Alpha spectrometer	Ortec, alpha Duo Octête TM PC	Ortec Octête-PC
ICP-MS	Perkin Elmer Elan 6100 DRC	Perkin Elmer NexION 2000
LSC	Wallac 1414 WinSpectra	-
Titrator	Metrohm 905 Titrando	Metrohm 905 Titrando

List of Radionucldes

Chalmers University of Technology

- ^{241}Am: Extracted from ^{238,239,240,241}Pu source

- ^{239}Np: Silica column, produced in-house from ^{241}Am source

- ^{238}Pu: AEA Technology Inc., Harwell, UK

- ^{238,239,240,241}Pu: Studsvik, Studsvik, Sweden

- ^{237}Np: AEA Technology Inc., Harwell, UK

- ^{152}Eu: IFE, Kjeller, Norway

- ^{nat}U: IFE, Kjeller, Norway

Forschungszentrum Jülich

- ^{244}Cm: Oak Ridge National Laboratory, Oak Ridge, Tn, USA

- ^{241}Am: Isotopendienst M. Blaseg GmbH, Waldburg, Germany

- ^{239}Pu: Forschungszentrum Jülich laboratory stock solution

- ^{nat}U: Forschungszentrum Jülich laboratory stock solution

- ^{237}Np: Forschungszentrum Jülich laboratory stock solution

- ^{152}Eu: Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany

Appendix B

Simulated SNF raffinates

Table B.1: The compositions and nitric acid concentrations of the various simulated PUREX raffinates, measured by ICP-MS and given in mg L^{-1}.

Element	HAW-CEA (3.2 M)	HAW-CEA (4.3 M)	ALSEP (2.9 M)	SANEX (4.5 M)	HAW-ITU (3.3 M)	HAW-ITU (3.7 M)
Se	9.7	10.0	-	6.3	-	-
Rb	54.4	60.1	79.9	47.6	50.3	43.4
Sr	142.4	154.6	184.2	129.5	82.6	69.3
Y	74.6	81.0	109.5	68.6	60.0	50.9
Zr	676.1	736.0	629.8	488.7	464.3	380.2
Mo	548.0	599.2	384.6	501.7	377.8	325.4
Ru	320.3	346.3	271.5	290.7	353.0	95.9
Rh	62.2	68.6	0.9	55.9	66.0	17.8
Pd	86.9	192.7	5.4	159.5	157.3	150.8
Ag	6.88	10.4	-	6.7	2.8	4.1
Cd	14.1	15.8	-	14.8	16.3	13.9
Sn	9.8	8.5	11.2	0.1	3.6	3.8
Sb	3.3	3.4	-	2.1	0.5	1.2
Te	88.7	97.1	61.5	82.1	80.0	66.5
Cs	452.8	481.0	630.7	413.4	215.9	181.3
Ba	225.0	247.8	-	209.4	421.3	351.7
La	197.3	213.2	293.3	183.5	195.5	163.0
Ce	474.3	514.7	561.2	432.6	283.8	236.4
Pr	184.8	203.0	182.4	168.4	168.6	141.6
Nd	92.2	661.0	974.4	543.6	728.6	610.7
Sm	122.1	132.9	193.3	108.7	86.5	72.4
Eu	28.1	31.8	41.1	25.2	17.4	14.8
Gd	21.1	23.9	40.3	19.9	66.0	55.2
Na	1237.5	1661.9	-	1126.5	-	-
Cu	16.5	21.0	-	14.6	-	-
Ni	38.4	37.1	-	33.8	-	-
Fe	1545.0	1545.0	-	1375.4	-	-
Al	4.7	5.0	-	5.0	2.2	2.6
Cr	76.7	80.3	-	69.4	-	-

Appendix C

List of molecules

Table C.1: The name and molecular structure of compounds referred to within this work.
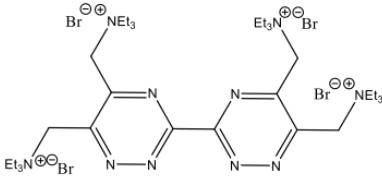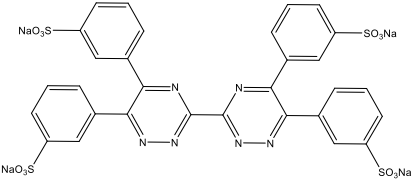
Name	Molecular structure
Agent 10	
Agent 13	

Table C.2: (2)continued...The name and molecular structure of compounds referred to within this work.
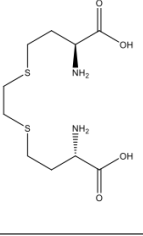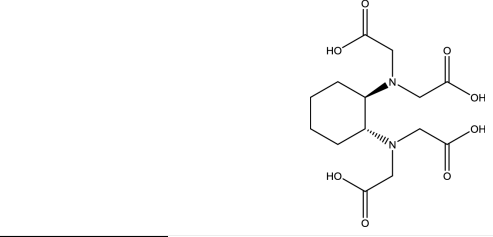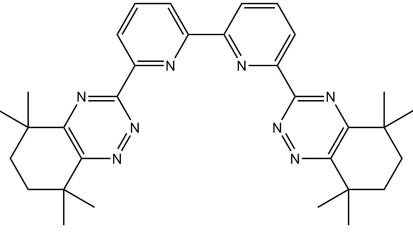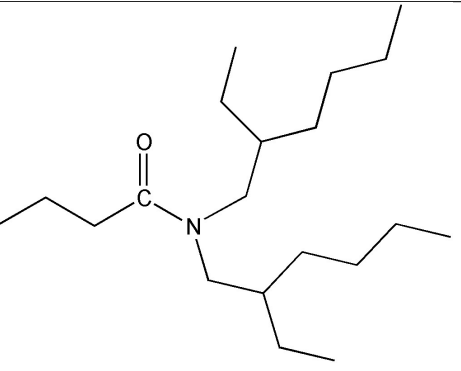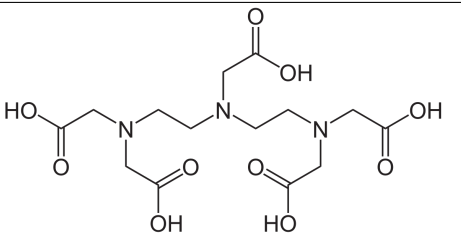
Name	Molecular structure
Bimet	
CDTA	
CyMe$_4$-BTBP	
DEHBA	
DTPA	

Table C.3: (3)continued...The name and molecular structure of compounds referred to within this work.
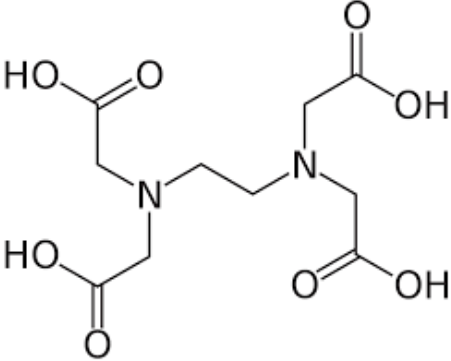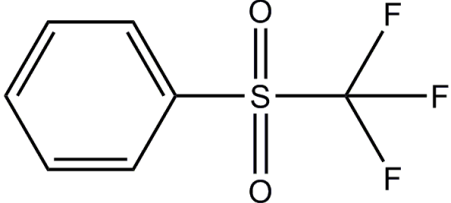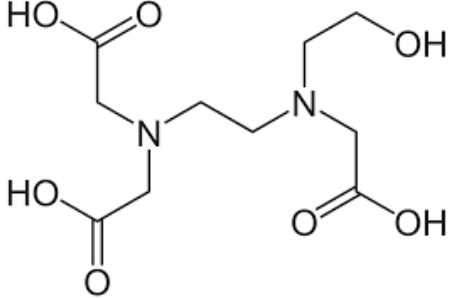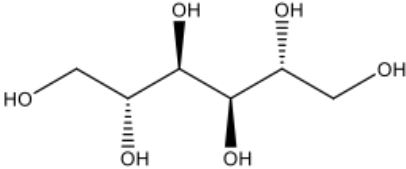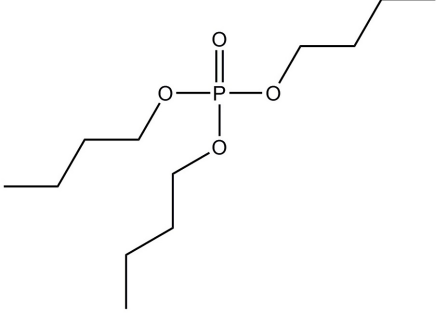
Name	Molecular structure
EDTA	
FS-13	
HEDTA	
Mannitol	

Table C.4: (4)continued...The name and molecular structure of compounds referred to within this work.

Name	Molecular structure
TBP	

Batch Tests for Optimisation of Solvent Composition and Process Flexibility of the CHALMEX FS-13 Process

Thea Lyseid Authen, Andreas Wilden, Jenny Halleröd, Dimitri Schneider, Fabian Kreft, Giuseppe Modolo & Christian Ekberg

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Batch Tests for Optimisation of Solvent Composition and Process Flexibility of the CHALMEX FS-13 Process

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ABSTRACT

Studies have been performed with the purpose of determining the optimal solvent composition of a Chalmers grouped actinide extraction (CHALMEX) solvent for the selective co-extraction of transuranic elements in a novel Grouped ActiNide EXtraction (GANEX) process. The solvent is composed 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) and tri-n-butyl phosphate (TBP) in phenyl trifluoromethyl sulfone (FS-13). The performance of the system has been shown to significantly depend on the ratios of the two extracting agents and the diluent to one another. Furthermore, the performance of the determined optimal solvent (10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13) on various simulated PUREX raffinate solutions was tested. It was found that the solvent extracts all transuranic elements with high efficiency and good selectivity with regard to most other elements (fission products/activation products) present in the simulated PUREX raffinate solutions. Moreover, the solvent was found to extract a significant amount of acid. Palladium, silver, and cadmium were co-extracted along with the TRU-radionuclides, which has also been observed in other similar CHALMEX systems. The extraction of plutonium and uranium was preserved for all tested simulated PUREX raffinate solutions compared to experiments using trace amounts.

Introduction

Several of the advanced nuclear power systems, often referred to as Generation IV (GEN IV) systems, are comprised of fast neutron reactors, fuel recycling, and novel fuel fabrication closing the fuel cycle and making it more sustainable.[1,2] By irradiating long-lived actinides in a fast reactor, one can transmute these into considerably less radiotoxic elements and isotopes, while also significantly reducing the lifetime of the final highly active waste. Through this process, not only the amount and volume of long-lived, highly radioactive waste is minimised, the need for uranium mining is also significantly

decreased.[3,4] The latter has a huge environmental footprint on non-radioactive indicators, such as atmospheric pollution, greenhouse gases, and water consumption.

The focus within EU research over the past decade with respect to separation processes has been the development of several Grouped ActiNide EXtraction (GANEX) processes for the co-extraction of all transuranic elements from spent nuclear fuel.[5–11] These processes all include a primary cycle for the bulk extraction of uranium,[12] followed by a second cycle for transuranic element extraction.[13] Three different second-cycle GANEX processes are currently being investigated: CEA-GANEX,[13] EURO-GANEX,[10] and Chalmers-GANEX (CHALMEX).[14–18] The former two are based on the principle of extracting actinides and lanthanides together, for a subsequent selective stripping of the actinides. The latter, the CHALMEX process, differs by selectively co-extracting the actinides from spent nuclear fuel, thus potentially reducing the number of process steps.[17,18] A bis-triazinyl-bi-pyridine molecule has been developed for extracting trivalent and pentavalent actinides: 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, Figure 1a) with a good An(III)/Ln(III) selectivity.[19] A separation factor of over 100 was achieved for the separation of americium from europium. In addition, CyMe$_4$-BTBP has good radiolytic and hydrolytic stability.[19–25]

Tri-n-butyl phosphate (TBP, Figure 1b) is combined with CyMe$_4$-BTBP to extract the tetra- and hexavalent actinides. The chemistry of TBP is well known from its extensive use in current reprocessing routes (PUREX process). It specifically extracts plutonium (Pu(IV)) and uranium (U(IV,VI)), with generally low distribution ratios for fission products.[26–29] TBP has been demonstrated thermally stable,[30,31] although the small amounts of radiolytic and hydrolytic degradation products have proven challenging. Attempts have been made to replace the use of TBP with other extracting agents that follow the CHON principle, such as di(2-ethylhexyl)butyramide (DEHBA) and di (2-ethylhexyl)iso-butyramide (DEHiBA). These efforts were abandoned due to low D(Pu)-values for the CHALMEX system. This can be compensated for
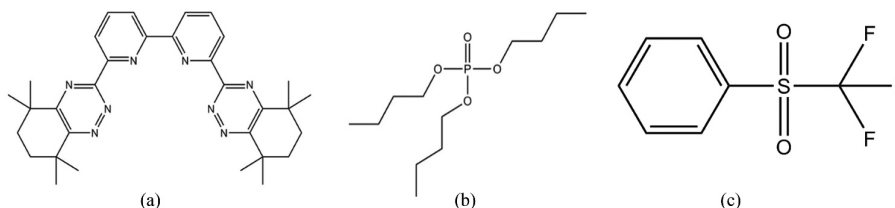

Figure 1. Molecular structure of a) CyMe$_4$-BTBP (6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8--tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine), b) TBP (tri-n-butyl phosphate), and c) FS-13 (phenyl trifluoromethyl sulfone).

by increasing the CyMe$_4$-BTBP concentration, but this will also increase D (Eu), yielding poor SF(Am/Eu).[16,32–34] On the other hand, TBP can handle large concentrations of plutonium, allowing a low enough CyMe$_4$-BTBP concentration to ensure D(Eu) below 1. By combining TBP and CyMe$_4$-BTBP in a suitable diluent, the need for redox control of the process is significantly reduced, if not eliminated.[18]

Several studies have been performed to decide on a diluent for the CHALMEX solvent.[18,35–38] The most recently used diluent is phenyl trifluoromethyl sulfone (FS-13), shown in Figure 1c. It has high thermal-, hydrolytic-, and radiolytic stability and yields a high solubility of CyMe$_4$-BTBP.[39–41] The actinide distribution ratios are maintained at gamma doses of up to approximately 160 kGy, and the CHALMEX FS-13 solvent was shown to have higher radiolytic stability compared to the CHALMEX cyclohexanone solvent.[39,42] FS-13 itself does not extract any metals, although the solvent as a whole (CyMe$_4$-BTBP, TBP, and FS-13) yields good separation factors for uranium, plutonium, and americium towards the lanthanides (i.e., europium), with extraction equilibrium reached within 20 minutes.[14,17] More problematic is the low extraction of neptunium(V,VI) ($SF_{Np/Eu}$ = 4.1, D(Np) = 1.2) and the high extraction of curium ($SF_{Am/Cm}$ = 1.7, D(Cm) = 17), cadmium (D > 1000) and silver (D > 30).[14] Curium extraction and incorporation in MOX-fuel is unwanted because of the significant shielding the fuel factory will require due to the neutron emission of curium. Despite low distribution ratios of both zirconium (D ~ 0.65) and molybdenum (D ~ 0.20), they are also of concern due to their high concentration in spent nuclear fuel.[14,17]

In previous work, a solvent using a composition of 30% v/v TBP and 70% v/v FS-13 has been used, based on the TBP concentrations used in the PUREX process. CyMe$_4$-BTBP concentrations have been varied between 10 and 50 mM corresponding to an extraction capacity of 1–100 g/L cations. In this paper, the optimisation of the extractant concentrations in the CHALMEX FS-13 solvent is presented. Furthermore, the performance of the optimised solvent on various simulated PUREX raffinate solutions is described. TBP is known to extract nitrates, as do a previous CHALMEX solvent using cyclohexanone as a diluent.[33] As the currently investigated CHALMEX solvent is now comprised of a different diluent, this work presents a study on the new solvent's nitric acid extraction. Understanding these aspects of the CHALMEX process is of scientific interest due to the importance for later process development.

Materials and methods

Materials

CyMe$_4$-BTBP was supplied by Karlsruhe Institute of Technology, Karlsruhe, Germany, and FS-13 by Marshallton Labs, King, NC, USA. Nitric acid (65%

suprapur) was bought from Merck, and TBP (97%) from Aldrich. The radio-tracers used in the solvent composition experiments have the following origins:

- ^{241}Am (extracted from ^{238,239,240,241}Pu source)
- ^{239}Np silica column (produced in-house from ^{243}Am stock)
- ^{238}Pu (AEA Technology Inc., Harwell, UK)
- $^{238, 239, 240, 241}$Pu (Studsvik, Studsvik, Sweden)
- ^{237}Np (AEA Technology Inc., Harwell, UK)
- ^{152}Eu (IFE, Kjeller, Norway)

The radiotracers used for the simulated PUREX raffinate testing were obtained from:

- ^{244}Cm: Oak Ridge National Laboratory, Oak Ridge, TN, USA
- ^{241}Am: Isotopendienst M. Blaseg GmbH, Waldburg, Germany
- ^{239}Pu: Forschungszentrum Jülich laboratory stock solution
- ^{nat}U: Forschungszentrum Jülich laboratory stock solution
- ^{237}Np: Forschungszentrum Jülich laboratory stock solution
- ^{152}Eu: Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany

Batch solvent extraction studies and analytical procedures

TBP volume ratios from 10% v/v to 50% v/v were investigated, using a fixed CyMe$_4$-BTBP concentration of 10 mM. Later, the ligand concentration was varied for different fixed TBP volume ratio systems. A minimum of 300 µL of both organic and aqueous phase (4 M HNO$_3$) was contacted in a mechanical shaker (IKA, Vibrax, VXR 1500 rpm), at 25°C. An organic-to-aqueous phase ratio of 1 was maintained in all experiments. The contacting time was 60 minutes, as this has previously been verified as sufficient time to reach equilibrium in the studied system.[15] Trace amounts of ^{241}Am(III), ^{152}Eu(III), ^{237}Np(V) or ^{239}Np(V, VI), and ^{238}Pu(IV) or ^{238,239,240,241}Pu(IV) were added to the respective aqueous phases prior to contacting. The extraction of americium and europium was investigated in one system, while neptunium and plutonium were investigated in individual systems. The samples were centrifuged for a minimum of 5 minutes (Wifug, LABOR- 50 M, 4500 rpm). A 100 µL aliquot was taken from each phase for analysis. Am/Eu radioactivities in each phase were analysed using a high purity germanium detector (HPGe) (Canberra, Gamma Analyst GEM 23195), while Pu and Np radioactivities were analysed on a liquid scintillation counter (Wallac 1414 WinSpectral). All experiments were performed in triplicate.

Solvent performance using simulated PUREX raffinates and analytical procedures

The experiments were performed as described above, although trace amounts of ^{241}Am(III), ^{152}Eu(III), ^{237}Np(V), ^{244}Cm, ^{239}Pu, and ^{nat}U were added to the raffinate together instead of being investigated in isolated systems. The phases were contacted in an IKA, Vibrax, VXR shaker (2200 rpm). The samples were centrifuged for 5 minutes after contacting (Hettich EBA 8S). Aliquots of 200 μL from each phase were sampled for HPGe (Eurisys EGC35-195-R germanium coaxial N-type detector) analysis (Am/Eu activities), 20 μL for ICP-MS analysis (Perkin Elmer NexION 2000, all elements) and 10 μL for alpha spectrometry (Ortec Octête-pc eight chamber alpha measurement system equipped with PIPS detectors) (Am/Pu/Np/Cm). To enable dissolution of the organic phase for ICP-MS analysis, a surfactant (10% *EcoSurf*) was added in the dilution stage. A sample of each of the original aqueous solutions was also analysed by ICP-MS for mass balance calculations. Six different simulated PUREX raffinates that were available in laboratory stock from previous flow sheet tests were used, and their composition and acidity are listed in Table 1.

Acid extraction

Equal volumes of the pre-equilibrated solvent and nitric acid of varying concentrations were contacted in a mechanical shaker (IKA, VIBRAX, VXR 2200 rpm) for 15 minutes at 20°C. The solvent was subsequently contacted with the same amount of MQ water for the same amount of time. An aliquot of the water was then titrated with 0.1 M NaOH, using a Metrohm 905 Titrando titrating machine, as was the initial aqueous phase. An aliquot of the organic solvent was added to MQ water and stirred on high speed for at least 5 minutes before being titrated for mass-balance calculations.

[,]Results and discussion

Solvent optimisation: TBP and CyMe₄-BTBP

The extraction of americium, europium, neptunium, and plutonium was studied as a function of the TBP/FS-13 volume ratio with a constant concentration of 10 mM CyMe₄-BTBP. The range of TBP ratios correspond to concentrations 0 M to 1.79 M. Figure 2 shows that the extraction of americium(III) increases with increasing TBP volume ratio up to 30% v/v TBP. The distribution ratios then remain fairly constant at values of around 30. As the trivalent Am and Eu are extracted by CyMe₄-BTBP and not by TBP,[15,17] this is believed to be due a better solubility of the Am/Eu complexes in the TBP/FS-13 mixture compared to pure FS-13. Ekberg et al.,[43] found that both the stability and the solubility of such complexes increases with

Table 1. The composition and acid concentration of the various simulated spent nuclear fuel solutions, measured by ICP-MS.

ICP-MS (mg/L)						
Element	HAW CEA (3.2 M HNO$_3$)	HAW CEA (4.3 M HNO$_3$)	ALSEP (2.9 M HNO$_3$)	SANEX (4.5 M HNO$_3$)	HAW-ITU (3.3 M HNO$_3$)	HAW-ITU (3.7 M HNO$_3$)
Se	9.7	10.0	-	6.3	-	-
Rb	54.4	60.1	79.9	47.6	50.3	43.4
Sr	142.4	154.6	184.2	129.5	82.6	69.3
Y	74.6	81.0	109.5	68.6	60	50.9
Zr	676.1	736.0	629.8	488.7	464.3	380.2
Mo	548.0	599.2	384.6	501.7	377.8	325.4
Ru	320.3	346.3	271.5	290.7	353	95.9
Rh	62.2	68.6	0.9	55.9	66	17.8
Pd	86.9	192.7	5.4	159.5	157.3	150.8
Ag	6.8	10.4	-	6.7	2.8	4.1
Cd	14.1	15.8	-	14.8	16.3	13.9
Sn	9.8	8.5	11.2	0.1	3.6	3.8
Sb	3.3	3.4	-	2.1	0.5	1.2
Te	88.7	97.1	61.5	82.1	80	66.5
Cs	452.8	481.0	630.7	413.4	215.9	181.3
Ba	225.0	247.8	-	209.4	421.3	351.7
La	197.3	213.2	293.3	183.5	195.5	163
Ce	474.3	514.7	561.2	432.6	283.8	236.4
Pr	184.8	203.0	182.4	168.4	168.6	141.6
Nd	592.2	661.0	974.4	543.6	728.6	610.7
Sm	122.1	132.9	193.3	108.7	86.5	72.4
Eu	28.1	31.8	41.1	25.2	17.4	14.8
Gd	21.1	23.9	40.3	19.9	66	55.2
Na	1237.5	1661.9	-	1126.5	-	-
Cu	16.5	21.0	-	14.6	-	-
Ni	38.4	37.1	-	33.8	-	-
Fe	1545.0	1545.0	6.2	1375.4	-	-
Al	4.7	5.0	-	5	2.2	2.6
Cr	76.7	80.3	-	69.4	-	-

decreasing charge density of the solvent. Increasing the ratio of TBP to FS-13 in the solvent can therefore account for an increase in Am distribution ratio with increasing TBP ratio. Wisnubroto et al.,[44] theorised that the activity of uncomplexed CMPO is reduced by hydrogen bonds with TBP through H$^+$ or H$_2$O. CyMe$_4$-BTBP contains N-donor atoms available for such hydrogen bonds. This theory explains the role that not only increased TBP fraction plays on the solubility of CyMe$_4$-BTBP, but also that of acid extraction.

The europium(III) extraction shows a similar trend to the americium extraction, with an increase up to 30% v/v TBP. Europium distribution ratios remain below 1 for all investigated TBP/FS-13 ratios, showing the high selectivity of CyMe$_4$-BTBP for trivalent actinides over lanthanides. Separation factors of up to 97 were found. Plutonium(IV) extraction slightly increased with increasing TBP concentration, as would be expected from the well-known PUREX chemistry,[28] from distribution ratios of around 4 for 5% v/v TBP up to $D = 60$ for 50% v/v TBP. The distribution ratio Pu of 2.26 for 0% v/v TBP also confirms that plutonium is extracted by CyMe$_4$-BTBP as reported earlier.[15] Due to the significant increase in both americium and plutonium extraction above 30% v/v TBP, while higher TBP concentrations do not yield
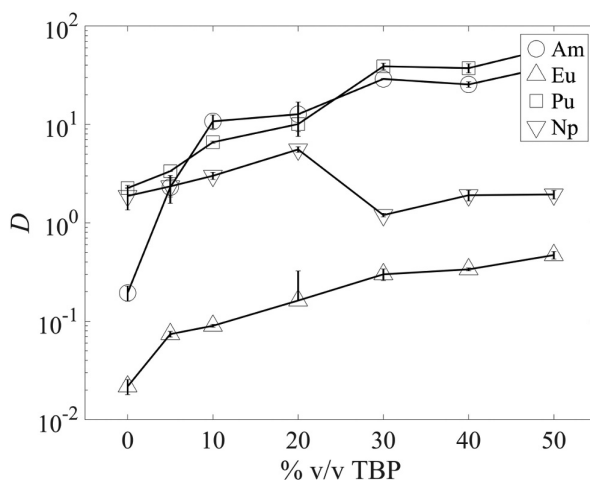
Figure 2. Distribution ratios, (*D*), of trace amounts of Am, Eu, Pu, and Np as a function of the TBP/FS-13 volume ratio and an addition of 10 mM CyMe$_4$-BTBP. The aqueous phase was 4 M HNO$_3$ with addition of trace amounts of the radionuclides. Am/Eu were investigated in one system, all other radionuclides were investigated in isolation. Data for 30% v/v (all radionuclides) was reproduced from Halleröd.[13]

further improvement, 30% v/v TBP was chosen as the optimal TBP volume ratio.

Neptunium(V,VI) extraction did not show a clear trend as a function of the TBP/FS-13 volume fraction. Distribution ratios were generally between 1.2 and 5.5, but were lower for the higher TBP volume fractions, which would not be expected from PUREX chemistry. The decrease in neptunium extraction could be due to a change in its oxidation state, as the pentavalent oxidation state is known to be less extractable with TBP compared to the tetra-, and hexavalent oxidation states.[45] The $P = O$ group of the TBP molecule is a potential reducing agent, and so it is possible that TBP acts as a reducing agent for any Np(VI) present in the system. Another possibility is the reducing effect by TBP by-products or degradation products, such as dibutyl phosphate, monobutyl phosphate, or ethyl hexyl phosphate.[46–48] Furthermore, the extraction of neptunium has been shown to be highly dependent on the nitric- and nitrous-acid concentrations, and small variations can impact the neptunium's distribution.[45,49] In the mixed CyMe$_4$-BTBP/TBP system, neptunium is mainly extracted by CyMe$_4$-BTBP and not TBP,[18] due to the dominant Np(V) oxidation state under the applied experimental conditions. Further speciation studies would thus be needed to fully understand the extraction behaviour of neptunium in the studied system.

Figure 3 shows the Pu, Np, Am, and Eu distribution ratios as a function of the CyMe$_4$-BTBP concentrations (up to 100 mM) in 15% v/v (Figure 3a), 30% v/v (Figure 3b) and 50% v/v (Figure 3c) TBP in FS-13. In all systems,
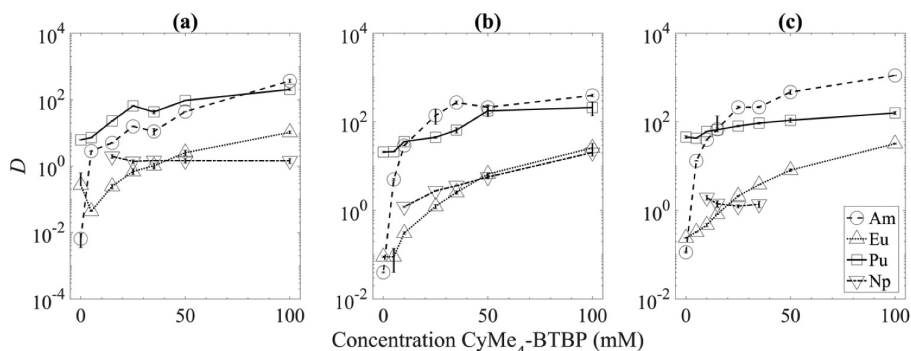
Figure 3. Distribution ratios (*D*) for Pu, Np, Am, and Eu as a function of the $CyMe_4$-BTBP concentration in **(a)** 15% v/v TBP and 85% v/v FS-13; **(b)** 30% v/v TBP and 70% v/v FS-13; **(c)** 50% v/v TBP and 50% v/v FS-13. The aqueous phase was 4 M HNO_3 with addition of trace amounts of the radionuclides for all the investigated systems. Am/Eu were investigated in one system, all other radionuclides were investigated in isolation. Data points for 10-, 25-, 35-, 50-, and 100 mM $CyMe_4$-BTBP in system (a) with 30% v/v TBP and 70% v/v FS-13 were reproduced from Halleröd.[13]

increasing the $CyMe_4$-BTBP concentration enhances the extraction of all the investigated elements (Np, Pu, Am, and Eu). Interestingly, the separation of neptunium and europium is inverted for higher $CyMe_4$-BTBP concentrations: europium is more efficiently extracted than neptunium. This behaviour appears to occur at lower $CyMe_4$-BTBP concentrations for increasing TBP fractions. As neptunium is one of the target nuclides for the extraction process, it is beneficial to keep the separation factor between neptunium and europium as high as possible. The highest separation factor between neptunium and europium is consistently seen at 10 mM $CyMe_4$-BTBP concentration, irrespective of TBP concentration. Therefore, 10 mM $CyMe_4$-BTBP concentration was chosen for further studies.

A slope analysis was performed on the distribution data in Figure 2, based on extraction as a function of % v/v TBP, and the slopes and R^2 values can be seen in Table 2. A 1:1 relationship is seen for Am:TBP complex, and similar trends are seen for the Eu:TBP ratio. Surprisingly, the ratio between D(Pu) and TBP concentration is found to be 1.27. In the PUREX process, TBP is known to extract plutonium as a 2:1 complex. Earlier work has shown that $CyMe_4$-BTBP also extracts plutonium independently of TBP, but the slope found here for TBP extraction may suggest a parallel adduct formation with nitric acid, as

Table 2. The slope and consequent R^2 for americium, europium plutonium, and neptunium extracted by 10 mM $CyMe_4$-BTBP and varying ratios of TBP/FS-13 from nitric acid media.

	Am	Eu	Pu	Np
Slope	1.12	0.83	1.27	0.62/0.98
R^2	0.92	0.95	0.94	0.94/0.84

proposed by Ochin et al.[15,50] Two slopes were also distinguished for the neptunium extraction: before and after the suspected reduction. The slopes (0.62 and 0.98, respectively), suggest the opposite, however: an oxidation of Np(V) to Np(VI). A slope of 0.62 indicates a low dependency of extraction on TBP, which would be expected by Np(V), while at higher TBP ratios (30% v/v and above) an increase in TBP dependency is seen, which suggests a greater proportion of Np exists as Np(VI) and is extracted by TBP. These results confirm earlier statements that further investigations into the extraction of Np in the current system is required.

Slope analysis for the extraction of actinides by CyMe$_4$-BTBP has earlier been published by our group for systems with 30% v/v TBP.[15] We showed that americium, curium, and europium are all extracted as 2:1 complexes with CyMe$_4$-BTBP, while plutonium is extracted as a 1:1 complex. Here, we see that in systems with lower TBP fractions (15% v/v), the same complex formation is seen with slopes of 2.20, 1.82, and 1.08 for americium, europium, and plutonium, respectively (Table 3). At 50% v/v TBP, however, a decrease in CyMe$_4$-BTBP:TBP ratio is seen for americium, europium, and plutonium, with slopes of 1.49, 1.59, and 0.42 respectively. This can be explained by the higher concentration of TBP, which also extracts these elements. However, it is more likely that the reduced slope is due to the complete extraction of the radiotracers at such high concentrations. In contrast to earlier reported neptunium trends here, neptunium is found to be independent of the CyMe$_4$-BTBP concentration, once again suggesting either Np(IV) or Np(VI) as the main oxidation state.

Acid extraction

A range of studies have shown that TBP extracts nitric acid.[28,50–53] Depending on the system, both increasing and decreasing distribution ratios for acid extraction are seen by TBP for acid concentrations above 1 M.[52,54,55] In Figure 4 it is seen that $D(HNO_3)$ increases up until 4 M HNO_3, after which it decreases again. Further extraction experiments showed no acid extraction by the pure FS-13 diluent. Although acid extraction by the CyMe$_4$-BTBP ligand is not unlikely due to its four N-donors, the low concentration of CyMe$_4$-BTBP (10 mM) suggests that the bulk extraction of acid rather occurs

Table 3. The slope and R^2 for the extraction of americium, europium, plutonium, and neptunium as a function CyMe$_4$-BTBP concentration in systems with 15% v/v and 50% v/v TBP.

		Am	Eu	Pu	Np
15% v/v TBP	Slope	2.20	1.82	1.08	−0.13
	R^2	0.91	0.99	0.88	0.41
50% v/v TBP	Slope	1.49	1.59	0.42	−0.09
	R^2	0.99	0.96	0.99	0.13
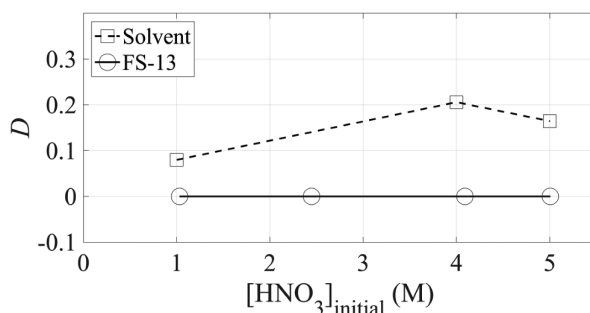
Figure 4. Distribution ratio (*D*) of HNO₃ extraction by preequilibrated organic solvent (10 mM CyMe₄-BTBP) in 30% v/v TBP and 70% v/v FS-13 as a function of initial nitric acid concentration.

by TBP. Similar trends for acid extraction by TBP are reported by Ochkin et al.[50] The high extraction of nitric acid by the solvent demonstrates the need for an acid scrub step in the CHALMEX process.

Performance of the optimised solvent on various simulated PUREX raffinates

Loading effects are not unanticipated in the current system due to the low concentration of CyMe₄-BTBP (10 mM). 30% v/v TBP corresponds to a concentration 1.07 M. In conventional PUREX raffinates, a plutonium inventory of 1 g/L (0.004 M) is typically expected. In Gen IV reactor systems, a plutonium inventory of 20 g/L (0.08 M) or even higher is predicted. By assuming the conservative 2:1 complex formation between TBP and plutonium, TBP is still present in high enough concentrations to sufficiently extract plutonium. Americium will be present in far lower concentrations compared to plutonium, namely 1 g/L (0.004 M). With a 2:1 complex with CyMe₄-BTBP, this will be borderline what the solvent can extract, especially since plutonium is also extracted by the BTBP ligand. Nonetheless, it is of significance to establish if the solvent preferentially extracts the actinides, or if the actinide extraction competes with other elements. Furthermore, in these experiments only trace amounts of the actinides are used, and so loading effects by the actinides cannot occur.

Figure 5 shows the distribution ratios of Am, Cm, Eu, Np, Pu, and U for different simulated PUREX raffinate compositions and acid concentrations, extracted by the optimised solvent of 10 mM CyMe₄-BTBP in 30% v/v TBP and 70% v/v FS-13. A significant reduction of the americium and curium extraction, in particular, compared to previously published results for isolated systems is seen.[17] This reduction in extraction with certain feed solution is probably caused by loading effects of the solvent, especially due to a reduction in free CyMe₄-BTBP concentration. The three feed solutions showing the highest americium and curium extraction (ALSEP 2.9 M, HAW-ITU 3.3 M,
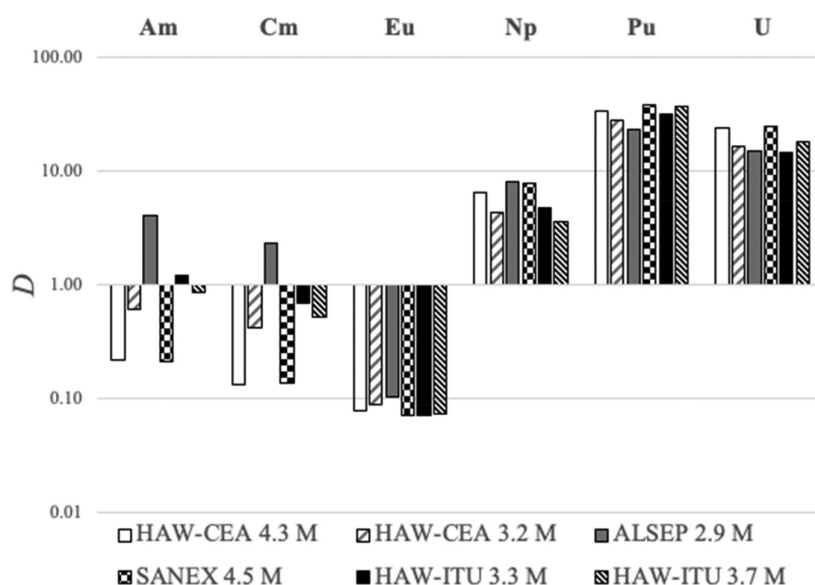
Figure 5. Distribution ratios (D) for Am, Cm, Eu, Np, Pu, and U extraction from various simulated PUREX raffinate solutions and different acid concentrations. Trace amounts of the radionuclides were added to each of the simulated PUREX raffinates prior to contacting with the organic phase. The organic phase was 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13.

and HAW-ITU 3.7 M) have a significantly lower metal content in total, compared to the other feed solution. The extraction of both uranium and plutonium is maintained at acceptably high levels (D(U,Pu) > 10), but it is reduced compared to non-metal-loaded systems. Little disparity is seen for the neptunium extraction.

The extraction of fission products presented in Figure 6 shows that the solvent co-extracts cadmium, palladium, and silver, causing further loading of the solvent. The ALSEP raffinate gives the best minor-actinide extraction of all raffinates, which is attributed to the lack of both silver and cadmium in the ALSEP raffinate. Despite the presence of silver and cadmium in both the ITU raffinates, the concentrations were low (Table 1) and were significantly less than the total capacity of CyMe$_4$-BTBP. The palladium concentration is below 1.90 mM for all the investigated raffinates. This suggests that the minor-actinide extraction is restrained by the preferential extraction of other elements in addition to cadmium, palladium, and silver.

Europium extraction is typically used as an analogue for all the lanthanides. The extractability of lanthanides follows the trend reported for CyMe$_4$-BTBP by Geist et al.,[21] with the highest extraction of Eu. None of the lanthanides are of concern, based on their low distribution ratios (D < 0.1), also confirming the use of europium as a representative analogue for the lanthanides. Molybdenum and
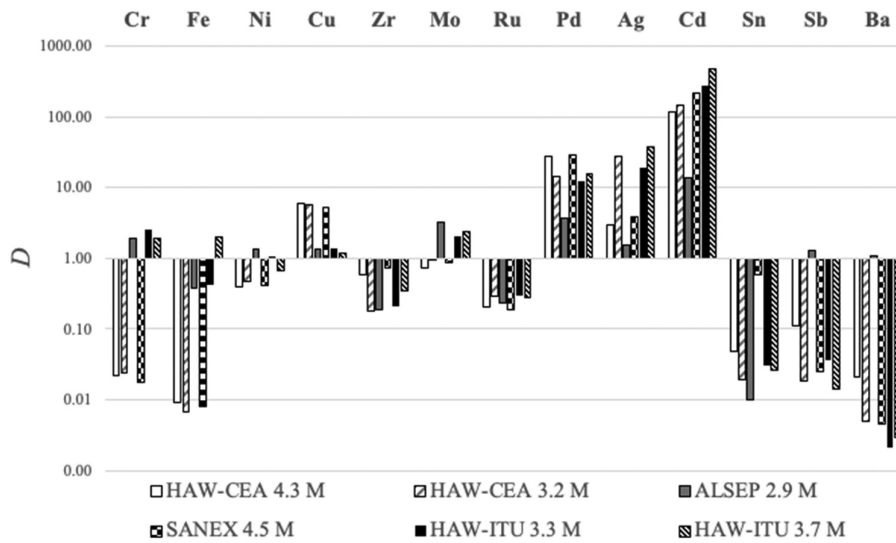
Figure 6. All distribution ratios (D) > 0.1 for the fission product extraction by 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13 from different simulated PUREX raffinate solutions and acid concentrations.

zirconium, however, are present in high concentrations in the raffinates, and even at low distribution ratios, a significant amount of these elements is extracted by the solvent.

Molybdenum concentrations ranged from 3.4–6.2 mM in the various raffinates and Mo had an average extraction percentage over 50%. Molybdenum typically exists as MoO$_4^{2-}$ in spent nuclear fuel solution, and is extracted by TBP at higher TBP fractions.[31,56,57] Goletskii et. al.,[58] have shown that TBP only extracts Mo to a significant degree at fractions above 50% v/v in nonpolar diluents. It has also been demonstrated that Mo-extractability is highly dependent on nitric acid concentration, where low acid concentrations favours higher molybdenum extraction up until 4 M HNO$_3$, after which the distribution ratios increase again, and so it is reasonable to assume that Mo is extracted by CyMe$_4$-BTBP.[59] Complementary experiments with 30% v/v TBP and 70% v/v FS-13 in the absence of CyMe$_4$-BTBP confirmed that Mo is not extracted by TBP in the CHALMEX FS-13 solvent (D (Mo) = 0.04), but is rather extracted by CyMe$_4$-BTBP. The extraction of Mo is nonetheless of concern due to the possibility of Mo accumulation downstream in the process. The same concerns apply to zirconium extraction. Zirconium exists as zirconium(IV) in spent fuel raffinates[31] and is extracted by TBP, which was also confirmed by complementary experiments. Although the distribution ratio of zirconium is lower than that of molybdenum (D(Zr) ranges from 0.18 to 0.74), its concentration range in the raffinates is 4.2–8.1 mM. With an extraction percentage range of about 14% to 37%, a significant amount of zirconium can follow the stream of uranium and the transuranic elements.

Previous studies performed on a different CHALMEX solvent, showed that most of the elements of major concern mentioned here are extracted by $CyMe_4$-BTBP.[60] A possible strategy to avoid solvent loading with unwanted fission and corrosion products would be complexing these elements in the aqueous phase to suppress their extraction by $CyMe_4$-BTBP. The use of appropriate masking agents would therefore increase the free $CyMe_4$-BTBP concentration and advance the minor-actinide extraction. Two such complexing agents were shown to be effective in complexing several of the problematic fission products for an earlier CHALMEX solvent: bimet and mannitol.[60] However, experimental confirmation for the effects for the current CHALMEX solvent is needed.

Conclusions

The optimised CHALMEX FS-13 solvent was developed based on maximising americium and plutonium extraction, in addition to keeping the separation factor between neptunium and europium at its maximum. The optimised solvent is composed of 10 mM $CyMe_4$-BTBP in 30% v/v TBP and 70% v/v FS-13 when extracting trace amounts of radionuclides. It was also shown that the solvent co-extracts certain fission and corrosion products (Ag, Cd, Pd, Mo, and Zr) causing significant loading of the solvent, especially $CyMe_4$-BTBP, thereby decreasing the extraction efficiency for trivalent actinides. It is deemed likely that the increase in BTBP concentration combined with suppression of the aforementioned elements will increase the trivalent actinide extraction.

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Batch flowsheet test for a GANEX-type process: the CHALMEX FS-13 process

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ABSTRACT

The Chalmers grouped actinide extraction (CHALMEX) process is focused on the co-separation of actinides from all other elements in spent nuclear fuel solution, with the ultimate purpose of transmuting the actinides into shorter-lived and less radiotoxic elements. Based on solvent extraction equilibrium distribution data of actinides and fission products, a preliminary flowsheet was developed and tested in batch mode. The flowsheet consists of one extraction step with the CHALMEX FS-13 solvent (25 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13), using hydrophilic masking agents (20 mM bimet and 0.2 M mannitol) in the aqueous phase for the complexation of troublesome fission products. Two nitric acid scrub steps (0.5 M HNO$_3$) were efficient in removing co-extracted acid, all molybdenum and the majority of silver. Two stripping stages (0.5 M glycolic acid at pH 4) were efficient in recovery of the actinides from the organic phase. The need for a solvent clean-up stage for the removal of nickel, cadmium, iron and the remaining silver from the organic phase was demonstrated. Based on the distribution data, it was calculated that a 99.9% recovery of americium is possible using only 3 ideal extraction stages, 3 ideal scrubbing stages and 2 ideal stripping stages.

Introduction

The recycling of plutonium and the minor actinides (Np, Am, Cm) for integration into advanced nuclear fuels is of interest due to their suitability for transmutation in fast nuclear reactors. Another option is the transmutation of the transuranium elements (TRU: Np, Pu, Am, Cm) in accelerator-driven systems.[1,2] Transmuting the TRU significantly reduces the long-term radiotoxicity and long-term heat generation of the final, highly radioactive waste.[3] The trivalent minor actinides (Am and Cm) and pentavalent Np have however proven challenging to separate from the trivalent lanthanides due to the similar chemical properties of the two groups of elements. One approach has

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been to develop a solvent extraction process for Grouped ActiNide EXtraction (GANEX), while another approach focuses on the selective actinide extraction producing (near) pure elemental product streams.[4,5]

The overall aim of GANEX processes is to separate all actinides as a group from the fission and corrosion products present in used nuclear fuel, preferably without the need for redox control. The GANEX concept is based on a two-cycle process: the bulk uranium is extracted in the first cycle and TRU in the second cycle. The first GANEX cycle has been demonstrated on genuine spent nuclear fuel, using mixer settlers, resulting in a 99.99% recovery of uranium and with satisfying decontamination factors from the other actinides and fission products.[6] In the second GANEX cycle, ligands are used which are specifically designed to either co-extract TRU and lanthanides, or to selectively extract only the TRU from the spent nuclear fuel solution. By dispensing with the separation of a pure plutonium product stream, the proliferation resistance of such a GANEX process is improved.[4] Several GANEX versions are studied internationally. In two versions of the GANEX process, the CEA – and EURO-GANEX processes, the TRU and lanthanides are co-extracted in the second cycle. The separation of the TRU from the lanthanides occurs in the stripping stage, where the TRU are selectively stripped from the organic phase.[7–14] In more recently proposed systems, the second cycle GANEX actinide recovery is achieved through the use of a single diamide of heterocyclic dicarboxylic acid or a single heterocyclic dicarboxamide.[15,16]

The Chalmers GANEX (CHALMEX) process is another version of the second cycle GANEX process. It combines the extractants 6,6′-bis -(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzene-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine (CyMe4-BTBP, Figure 1a) and tri-n-butyl phosphate (TBP, Figure 1b) in the fluorinated diluent phenyl trifluoromethyl sulfone (FS-13, Figure 1c). In contrast to the CEA-GANEX and EURO-GANEX processes, the CHALMEX process aims to achieve direct TRU/fission product separation by extracting only the TRU elements from the spent nuclear fuel solution without any redox control or modification.[17–21] The affinity of
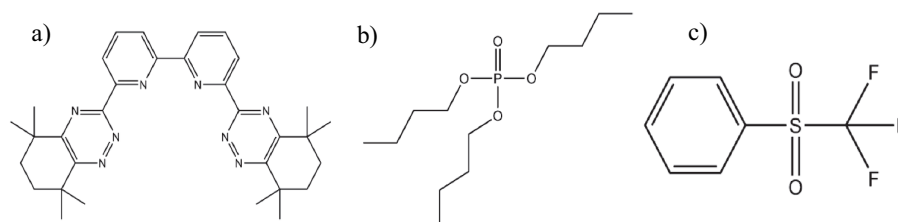

Figure 1. (a) 6,6′-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzene-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine (CyMe4-BTBP) (b) Tri-n-butyl phosphate (TBP) (c) Phenyl trifluoromethyl sulfone (FS-13).

the extracting ligand for the trivalent actinides (An(III)) over trivalent lanthanides (Ln(III)) is explained by a higher degree of covalency in bonds between the soft N-donors in CyMe$_4$-BTBP and An(III), compared to that of Ln(III) and the ligand.[22–24] The CHALMEX process has shown promising results in its actinide-lanthanide separation, even during plutonium loading conditions. Extraction equilibrium is reached for all target radionuclides within 20 minutes when these are present in trace levels in isolated systems.[17,18,21,25–27]

Previous studies on the CHALMEX FS-13 process have focused on the scrubbing of co-extracted acid from the organic phase and the stripping of transuranic elements in isolated systems only.[26] For the current solvent (CyMe$_4$-BTBP and TBP in FS-13), no published studies focus on more process-like conditions, such as extraction, scrubbing and stripping under simulated processconditions. In our previous study, we showed that an optimised CHALMEX solvent (10 mM CyMe$_4$-BTBP, 30% v/v TBP and 70% v/v FS-13) co-extracts palladium, silver and cadmium to a significant extent.[28] Furthermore, the solvent was shown to be ineffective in extracting the An(III) from a simulated raffinate solution, with distribution ratios < 1, most likely as a result of solvent loading. The concentration of CyMe$_4$-BTBP has therefore been increased to 25 mM in the experiments presented here, in order to ensure minor actinide extraction. The TBP/FS-13 ratio has been kept at 30% v/v for TBP, as was shown satisfactory for both uranium and plutonium extraction.[28]

Another study has reported on the complexation of fission products, specifically molybdenum, zirconium and palladium, in the aqueous phase using mannitol and bimet (Figure 2).[19] Although efficient in masking zirconium, palladium and silver, the extraction of cadmium, molybdenum and nickel is
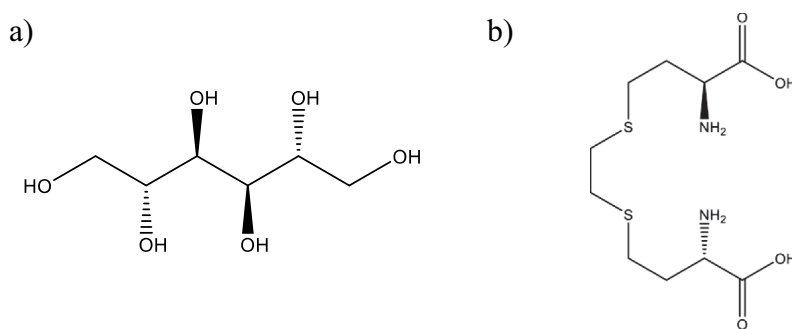

Figure 2. (a) 2 R,3 R,4 R,5 R)-hexane-1,2,3,4,5,6-hexol (D-mannitol) b) (2S,2′S)-4,4′-(ethane- 1,2 - diylbis(sulfanediyl))bis(2-aminobutanoic acid) (bimet).

still problematic, and so back-extraction of these elements in the scrubbing stages is desirable. Preliminary screening of different scrubbing solutions has been performed and 0.5 M HNO_3 has been determined to be the most suitable scrubbing solution for the back-extraction of silver, molybdenum, palladium and zirconium.[29]

Since the CHALMEX process aims to separate plutonium, trivalent and pentavalent actinides from fission products, it is of importance to investigate the route of all fission products in the process. Such process data will demonstrate whether sufficient actinide/fission product separation is achieved, or if the fission products are back extracted with the actinides causing an impure product stream. The actinides can be back extracted by using 0.5 M glycolic acid at pH 4 as a stripping solution.[26] Earlier assessments have estimated the CHALMEX process to Technology Readiness Level 2–3 (TRL 2–3), based on the absence of both computer simulations and cold tests defining fundamental data for the experimentation.[30] Although the work here is considered a cold test of the process which supports the progress of the process' TRL, computer simulations that could produce an official TRL increase are still lacking. This is of importance not only for comparative purposes with the other GANEX processes, but also an important official stage in the process development as it allows for calculation of the number of ideal stages for all process steps.

In this paper, the testing of a batch flowsheet using the aforementioned scrubbing and stripping solutions is presented. The ultimate purpose is to determine whether the fission product management strategy of the CHALMEX process is sufficient to ensure acceptable partitioning of plutonium and the MA from the fission products.

Materials and methods

Batch flowsheet testing

A full schematic representation of the process steps tested is shown in Figure 3, where each stage represents a single batch experiment. In the test, 5.00 mL of
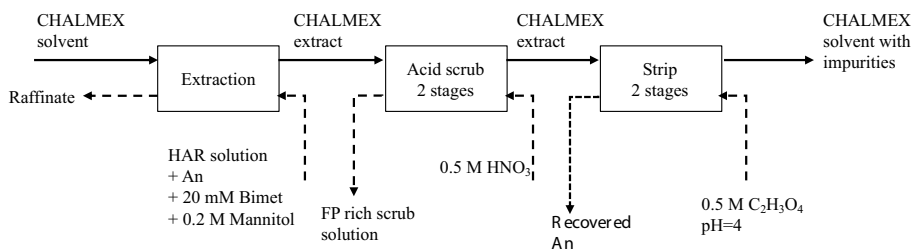

Figure 3. Suggested flowsheet for the CHALMEX FS-13 process. Each box represents one batch-contacting unit, with 90-minute contact time.

Table 1. The composition (mg L^{-1}) of the simulated raffinate solution in 3.2 M HNO_3. The simulated raffinate solution composition was based on 5000 L t^{-1} dissolved UO_x fuel with initial 3.5% ^{235}U enrichment, thermal burnup of 33,000 MWd t_{HM}^{-1} and 3 years cooling.

Se	Rb	Sr	Y	Zr	Mo	Ru	Rh	Pd	Ag	Cd	Sn	Sb	Te	Cs
9.7	54.4	142.4	74.6	676.1	548.0	320.3	62.2	86.9	6.8	14.1	9.8	3.3	88.7	452.8
Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Na	Cu	Ni	Fe	Al	Cr	-
225.0	197.3	474.3	184.8	592.2	122.1	28.1	21.1	1237.5	16.5	38.4	1545.0	4.7	76.7	-

pre-equilibrated (4 M HNO_3) solvent (25 mM $CyMe_4$-BTBP in 30% v/v TBP and 70% v/v FS-13) has been contacted with a simulated raffinate solution (see Table 1 for composition) with a nitric acid concentration of 3.2 M HNO_3 (4.70 mL). The sample was spiked with a mixed ^{241}Am (281 kBq mL^{-1})/^{152}Eu (278 kBq mL^{-1})/^{244}Cm (151 kBq mL^{-1}) tracer, 100 μL ^{239}Pu tracer (323 kBq mL^{-1}), and 100 μL ^{237}Np tracer (30 kBq mL^{-1}), in a test tube with volumetric markings. The radionuclides were obtained from the following sources:

- ^{244}Cm: Oak Ridge National Laboratory, Oak Ridge, Tn, USA
- ^{241}Am: Isotopendienst M. Blaseg GmbH, Waldburg, Germany
- ^{239}Pu: Forschungszentrum Jülich laboratory stock solution
- ^{237}Np: Forschungszentrum Jülich laboratory stock solution
- ^{152}Eu: Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany

The simulated raffinate solution was prepared by introducing 0.2 M D-mannitol (Difco laboratories, Michigan, USA) and 20 mM bimet (produced in-house according to Kanesaka et al.[31]) to the aqueous phase prior to contacting with the extractant phase for masking of selected fission products (Mo, Zr, Pd). $CyMe_4BTBP$ was supplied by Karlsruhe Institute of Technology, Karlsruhe, Germany and FS-13 by HaiHang Industry Co., Ltd., Jinan City, China. TBP (97% purity) was supplied by Aldrich (Steinheim, Germany). After the initial contacting and centrifugation, 500 μL samples of organic and aqueous phase, respectively, were each collected for analysis. The remaining aqueous phase was removed, and the remaining volume of organic phase was recorded. An equal volume to the remaining organic solution of acid/fission product scrub solution was added. The scrub solution was 0.5 M HNO_3 (diluted from 65% HNO_3 SupraPur, Merck). The contacting, centrifugation and sampling procedure was repeated for the scrub and for both stripping stages. A 0.5 M glycolic acid (99.5%, Merck) solution (adjusted to pH 4 by adding NaOH) was used as the strip solution.[26] Each stage was contacted for 90 minutes at ambient temperatures using Heidolph reax top test tube shakers (Heidolph Instruments GmbH Co. KG, Schwabach) to reach extraction equilibrium at each stage. To limit heating effects from the shakers, the sample vial was swapped between two identical

shakers every 15 minutes. The sample vial was centrifuged (Hettich EBA 8S) for 5 minutes to ensure full phase separation after each stage.

Analysis

A 200 μL sample of each phase was analysed by gamma spectrometry (Eurisys EGC35-195-R germanium coaxial N-type detector) to determine americium and europium radioactivities. Similarly, a 10 μL was collected from each phase for alpha spectrometry (Ortec Octête-pc eight chamber alpha measurement system equipped with PIPS detectors) to determine ^{237}Np, ^{239}Pu, ^{241}Am and ^{244}Cm radioactivities. The 10 μL sample was added to 100 μL of a mixture of 1% ZAP lacquer in acetone, and the liquid was then distributed on a metal planchet. The planchet was first allowed to dry under an IR lamp, and the planchet was next heated with a gas torch to burn off any residual organic matter. The planchet was then inserted into the alpha spectrometer and the measurement was allowed to proceed until a minimum of 10,000 counts per peak was recorded. A 20 μL sample of each phase was also collected and diluted by a factor of 10^4 for ICP-MS analysis. ICP-MS measurements of all elements were conducted using a Perkin Elmer NexION 2000, Perkin Elmer LAS GmbH, Rodgau, Germany. The aqueous phase was diluted in 1% v/v suprapur HNO_3, while the organic phase was diluted in 1% v/v SupraPur HNO_3 containing 2% v/v of the surfactant EcoSurf (Carl Roth, Karlsruhe, Germany), to allow dissolution. All pH measurements were made on the aqueous phases during the experiment using a Metrohm pH Meter 691. To confirm the pH measurements later, the aqueous solutions were titrated against NaOH using a Metrohm 905 Titrando automatic titrator.

Calculations

Number of ideal stages

Calculations for the ideal number of stages in a cascade counter-current operation for solvent extraction purposes can be made according to the same principles as for distillation and gas absorption.[32] The extraction, P, of a solute can be calculated from Equation 1, where θ is the phase ratio (O:A).

$$P = D \cdot \theta \qquad (1)$$

The fraction of a solute remaining in the aqueous phase compared to in the organic phase, given by the symbol φ, can be calculated using Equation 2.

$$\varphi = \frac{x_R}{x_F} = \frac{P - 1}{P^{n+1} - 1} \qquad (2)$$

Here, x is the concentration of solute in the aqueous phase, subscript F refers to feed solution, while R refers to the raffinate. By rearranging Equation 2, the number of ideal stages, n, can be calculated according to Equation 3.

$$n = \frac{\ln(P - 1) - \ln(\varphi)}{\ln(P)} - 1 \qquad (3)$$

Results and discussion

Batch flowsheet tests were conducted according to the flowsheet shown in *Figure 3*. The distribution ratios of the radionuclides in each process step are shown in *Figure 4*. The combination of increased CyMe$_4$-BTBP concentration and masking agents allows for significant extraction of the An(III), compared to what has been reported earlier, due to the increased free CyMe$_4$-BTBP concentration. The distribution ratio of Am *(D = 32)* is significantly higher than was reported in previous systems where 10 mM CyMe$_4$-BTBP was used in the absence of masking agents.[28] As mentioned above, the CyMe$_4$-BTBP concentration was increased for the system tested here, as 10 mM CyMe$_4$-BTBP was not concentrated enough to ensure sufficient An(III) extraction due to the preferential extraction of fission products over americium and curium.[28] The *D*-values of neptunium and plutonium are both > 1.

An increase in *D*-value is also seen for the curium extraction, for which a distribution ratio of 13 is obtained. The distribution ratio of plutonium *(D = 21)* is consistent with the previously reported values for the CHALMEX FS-13 system. TBP is a well-established extracting agent for plutonium and two TBP molecules form an extractable complex with plutonium. In contrast
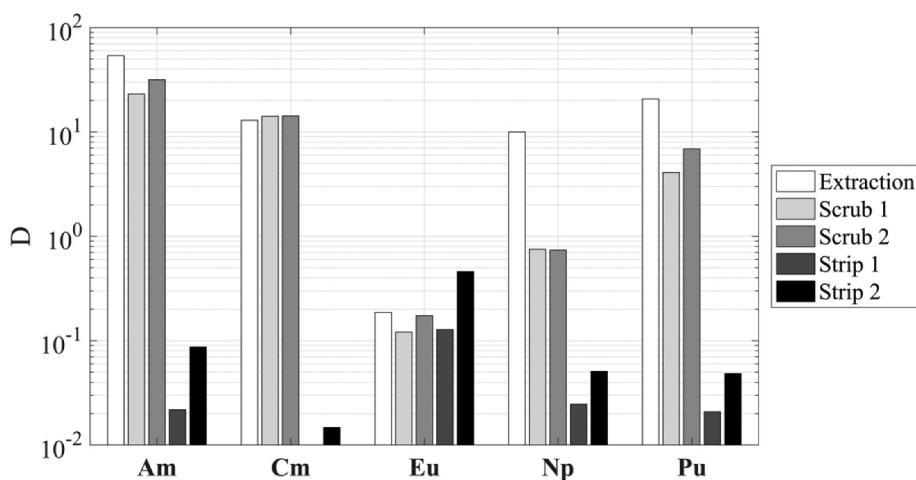
Figure 4. The distribution ratio, *D*, of the radionuclides investigated in the batch flowsheet test. The extraction was performed by contacting the feed aqueous phase (simulated raffinate solution with addition of radiotracers) with the CHALMEX FS-13 solvent comprising 25 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13. The acid scrub was 0.5 M HNO$_3$. 0.5 M glycolic acid adjusted to pH 4 using NaOH was used as the stripping solution. Distribution ratios below 0.01 are not shown.

to uranium, plutonium is also extracted by the BTBP-ligand which explains the higher D-value of plutonium compared to uranium in PUREX systems.[18,28,33–35] The neptunium distribution ratio ($D = 10$) is consistent with work recently published,[28] although this is in contrast to work published by Halleröd et al., who reported $D(Np) = 1.2$.[18] The difference is most probably due to differences in speciation of the neptunium stock solutions. In the present work, the neptunium speciation was monitored as Np(V) using UV-VIS spectrometer; the earlier publications assumed the presence of mixed oxidation states (without verification).[18] Neptunium's valence chemistry is highly variable, and is known to be affected by a range of conditions, including acid concentration ($[H^+]$) and the presence of nitrous acid (HNO_2).[36–38] In concentrations of both 3.2 M HNO_3 and 4 M HNO_3, neptunium is known to undergo a spontaneous disproportionation reaction to form a mixture of Np(V) and Np(VI), with a mole fraction of more than 0.75 of Np favouring the Np(VI) state.[39] The neptunium used in Halleröd et al.[18] was milked from a $^{243}Am/^{239}Np$ column using HCl, and HCl is known to be a reducing acid. It is possible that the presence of HCl either reduced any Np(VI) that might have been formed back into Np(V), or that HCl hinders the disproportionation reaction by interacting with any formed nitrous acid, which is a potent catalyst for the reaction.[39]

From Figure 4, it can be seen that americium, curium, and plutonium largely remain in the organic phase during the acid/fission product scrubbing stages. Neptunium, in contrast, is readily back extracted by 0.5 M HNO_3. This is unexpected as literature shows that in 0.5 M HNO_3, Np will still exist with mole fractions of above 0.65 for Np(VI) and less than 0.35 for Np(V)[39] . Both Np(IV) and Np(VI) have been shown to remain in the organic phase during such scrubbing conditions in similar systems, while Np(V) is readily back-extracted and has low distribution ratios at low acid concentrations.[13,40] It also is known that Np(V) in nitric acid media readily (but slowly) oxidizes due to the presence of dissociated nitrates, forming the more TBP-extractable Np(VI) species. It has also been reported that extracted Np(VI) in TBP-dodecane media, is reduced to the less extractable Np(V) by the presence of either U(IV) or nitrous acid in the organic phase. In addition, the presence of both H_2O and acids in the organic phase has been shown have an impact on neptunium speciation.[41,42] Further studies are suggested to understand both the forward- and the back-extraction mechanism and speciation of neptunium in the CHALMEX FS-13 system.

Most of the remaining actinides are stripped in the first stripping stage. Approximately 2.3% of the americium activity was recorded in the organic phase compared to the aqueous phase after the first stripping stage, giving a distribution ratio of 0.02. The curium activity in the organic phase was below the detection limit after the first stripping stage, implying that practically all curium was removed from the organic phase. Plutonium had a distribution

ratio of 0.02 after the first stripping stage, confirming the suitability of glycolic acid as a stripping agent. Despite the loss of neptunium in the scrubbing stages, the remaining fractions in the organic phase are stripped along with the other actinides.

The number of ideal stages required to extract 99.99% americium from the feed in a counter-current cascade operation was calculated according to Equations 1–3. It was calculated that under identical conditions, 3 ideal stages of batch extraction will be required to extract 99.99% of the americium initially present in the spent fuel solution. For 99.99% extraction of both curium and neptunium, 4 extraction stages are required. For plutonium, 3 stages will be required for a 99.00% extraction.

By allowing less than 0.01% loss of americium in the scrubbing stages, a maximum of 3 scrubbing stages were calculated. For 3 scrubbing stages, a 0.03% loss of curium, 37% loss of neptunium and 3% loss of plutonium was found. For the overall recovery of 99.9% of americium, 2 stripping stages are required. Applying the number of stages for each process stage to obtain 99.9% americium recovery, the overall recovered percentages of the remaining actinides were calculated using Equation 2. The possible recovery, assuming ideal stages, is 61% for neptunium, 99% for curium and 94% for plutonium.

For comparison, both the CEA-GANEX and the EURO-GANEX processes have been hot-tested with genuine spent nuclear fuel, the former using mixer-settlers and the latter using centrifugal contactors.[10,11] The CEA-GANEX was demonstrated using 57 process stages in total and the EURO-GANEX using 32 process stages. Both processes were able to recover >99% of the Pu, Np and Am. The CEA-GANEX study also reported a high degree of Pd (44.0%), Fe (32.5%) and Sm (18.0%) contamination of the actinide stream. In a heterogeneous recycling option such as the TRU-SANEX process, a 32 stage flowsheet was tested using centrifugal contactors and a surrogate feed.[43]

Even though the results for the CHALMEX process presented here are for ideal conditions and a simulated spent fuel raffinate, the total number of 8 process stages offer a significant simplification of the process flowsheet compared to each of the aforementioned processes. This is advantageous not only for capital costs of a plant, but also operational costs related to solvents and waste management. Furthermore, an actinide stream free from fission product contaminants is beneficial for fuel manufacture.

The distribution ratios for all fission products with $D > 0.1$ in the extraction stage are shown in Table 2, along with the titrated acidity for each process step. Nickel, cadmium and molybdenum are significantly extracted, with distribution ratios of > 100, 41.8 and 2.2 respectively in the extraction stage. Nickel is present in the raffinate at 38.4 mg L^{-1}, which corresponds to 0.65 mM. Cadmium is present at 14.1 mg L^{-1} (0.12 mM), while molybdenum is present at 548 mg L^{-1} (5.7 mM). Both nickel and cadmium are largely seen to remain in the organic phase during both the scrubbing steps and the stripping steps

Table 2. Distribution ratios, *D*, for all inactive (fission products) elements with *D* > 0.1 in the batch flowsheet test. The extracting solvent was 25 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13. The scrub solution was 0.5 M HNO$_3$ and the strip solution 0.5 M glycolic acid at pH 4. The table also shows the pH calculated from titrations of the aqueous phase after each contacting stage.

Process stage	pH	Fe	Ni	Cu	Mo	Ag	Cd	Sn
Extraction	− 0.5	0.1	> 100	1.0	2.2	0.2	41.8	0.2
Scrub 1	0.2	24	13	0.84	0.004	0.5	23.6	0.3
Scrub 2	0.3	52	> 100	1.0	0.3	0.5	15.5	0.4
Strip 1	0.4	29	94	9.0	5.9	2.0	> 100	7.6
Strip 2	0.8	42	4.1	1.9	> 100	0.8	> 100	3.1

Table 2, causing only low contamination of the actinide product. On the other hand, this causes concern for build-up of these elements in the organic phase, demonstrating the need for a solvent clean up stage. Meanwhile, molybdenum is efficiently removed from the organic phase during the two scrubbing stages. Due to the high distribution ratios of the actinides, molybdenum does not require any further handling.

Iron is the element present in the highest concentration in the raffinate solution used here, at 1545 mg L^{-1} (27.7 mM). Typically, the iron content of PUREX raffinates are considerably lower, as either U(IV) or hydrazine are used as reducing agents instead of ferrous iron.[44] Nevertheless, an earlier CHALMEX solvent showed issues with solvent loading by iron, and so a high iron content raffinate was chosen to determine if the CHALMEX FS-13 solvent could suffer similar difficulties. It is seen that iron loading issues are avoided with the current solvent.[45] However, even with *D* = 0.1, a significant amount of iron (~ 2.5 mM) is extracted by the CHALMEX FS-13 solvent. Neither the scrubbing solution, nor the stripping solution back-extracts the extracted iron. Reports on the UNEX process, which also uses FS-13 as a diluent, show success in reducing both the iron and zirconium extraction by complexing them with fluoride ions.[46,47]

The remaining elements with extraction distribution ratios above 0.1 are copper, silver and tin. Despite the low abundance in the simulated raffinate, silver is an efficient neutron poison and its presence in nuclear fuel is unwanted.[48] Although 75% of the extracted silver is scrubbed in the two scrubbing stages (*D* = 0.5), the 25% remaining in the organic phase upon stripping largely remain in the solvent. As with cadmium and nickel, this further demonstrates the need for a solvent clean-up stage.

It is also worth noting that the pH of the aqueous phases low at each stage in the process. The pH of the acid scrubbing solutions after contacting with the organic phase show a pH as expected from pristine 0.5 M HNO$_3$, suggesting little to no acid has been back extracted. After the second stripping stage the pH was titrated to 0.8. This suggests that there are significant amounts of residual acid in the organic phase and that this is scrubbed by the stripping solution along with the actinides.

Conclusions

The proof of concept of the CHALMEX FS-13 process was successfully demonstrated in a batch flowsheet test. It was shown that the TRU element's distribution ratios are sufficiently high in the extraction process step to allow 99.99% extraction of americium from a simulated raffinate solution in 3 extraction stages. Americium, curium, and plutonium remain extracted in the scrubbing stages, while neptunium is partially back extracted, demanding further studies to optimise the scrubbing conditions. Stripping of the actinides was successfully achieved using glycolic acid at pH 4. For an overall recovery of 99.9% americium in the CHALMEX FS-13 process a theoretical number of 3 extraction stages, 3 scrubbing stages and 2 stripping stages were calculated, assuming ideal conditions. Such experimental conditions yield an overall 99% recovery of curium, 61% recovery of neptunium and 94% recovery of plutonium. Nickel, cadmium and molybdenum have the highest distribution ratios of the fission products. Iron is also a cause for concern, due to the very high abundance in spent nuclear fuel solution. While molybdenum is sufficiently scrubbed by 0.5 M HNO_3, a solvent clean-up stage is required to remove iron, nickel and cadmium from the organic solvent, and any residual acid in the organic phase.

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An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, Part 2 — homogeneous recycling

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An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, Part 2 — homogeneous recycling

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ABSTRACT

The hydrometallurgical separation concepts for the recycling of irradiated nuclear fuels developed in Europe are presented and discussed. Whilst Part 1 of the review focused on concepts for heterogeneous recycling of minor actinides, this article focuses on group recycling of transuranic actinides, which would support homogeneous recycling scenarios. Most of these concepts were developed within European collaborative projects and involve solvent extraction processes separating all the actinides (U-Cm) in two cycles. The first cycle uses a monoamide extractant to recover uranium leaving all the transuranic actinides in the aqueous raffinate with the fission products. The second cycle aims for a group recovery of the transuranium elements and several strategies have been proposed for this stage. In this review article, the various solvent extraction processes are summarised and the key features of the process schemes are compared.

Introduction

Nuclear power reactors provide a safe, low-carbon and non-intermittent production of electricity. In 2019, 26.7% of the EU's total net electricity generation was generated by 109 nuclear power reactors across 16 member countries.[1] However, whilst the potential contribution nuclear energy can make towards a sustainable, low carbon future is being increasingly recognised,[2] the challenges remain related to safe, secure, long term management of the spent nuclear fuels (SNF) that are highly radioactive over long timescales.[3] Altogether, close to 58,000 tHM SNF had been produced and stored by the end of 2016 in the EU [4–7] whilst globally, around 10,000 tonnes of SNF are generated per year.[8] Although SNF can be interim stored safely for extended periods, ultimately there are only two options for spent fuel management (SFM): direct disposal or recycling. Direct disposal in a deep geological repository (DGR), called the open or once through fuel cycle, is the accepted strategy for many countries such as Finland, Sweden, Germany and the United States.[9,10] SNF recycling, based on reprocessing to recover re-usable nuclear

materials and fabrication of new fuels from the reprocessed products, has been implemented industrially in some countries, e.g. France, Russia, UK and Japan. This is referred to as the closed nuclear fuel cycle and there are variations on the closed fuel cycle depending on which materials are recycled and whether the materials are recycled once or multiple times.[11] The advantages of recycling have been described elsewhere but, as might be expected, relate to improved use of natural resources, less wastes with reduced radiotoxicity for disposal leading to a smaller DGR and a smaller environmental footprint for nuclear energy.[3,9,12–16]

Europe has a long experience of reprocessing SNF with facilities of varying scales in Belgium, France, Germany, Russia and the UK.[17] France and the UK have operated commercial scale reprocessing plants at La Hague and Sellafield, respectively, with more than 36,000 and 65,000 tonnes of used nuclear fuel reprocessed at these sites.[18,19] All these reprocessing programmes have used or still use the PUREX process [20–22] to separate fissionable materials, uranium and plutonium, from irradiated fuel. Uranium and plutonium can

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be recycled in present-day light water reactors (LWRs) either as reprocessed uranium oxide (RepU) fuels or mixed oxide (MOX) fuels.

Advanced fuel cycles, however, offer the prospect of multi-recycling of U and Pu which can substantially increase the benefits in terms of uranium utilisation and resource preservation.[9,12,23] Compared to other fuel cycle options, SNF multi-recycling in advanced fuel cycles has potential advantages of comprehensively addressing issues related to sustainability, such as public acceptance, proliferation resistance, flexibility for reprocessing of non-oxide and high-burnup fuels and the most efficient use of the DGR. The latter is supported by recycling minor actinides (MA = Np, Am, Cm) to reduce the heat loading and radiotoxicity of the final wastes.[9,16,24,25]

The multi-recycling of uranium, plutonium and MA in advanced nuclear fuel cycles can be via either homogeneous or heterogeneous routes, see Fig. 1.[26,27] In heterogeneous recycling (often termed the partitioning and transmutation or P&T scenario), uranium, plutonium and potentially neptunium [28] are recovered, usually by the PUREX process for the production of MOX fuels.[29] The other MA, americium and curium, are then recovered from the PUREX high level waste (HLW) stream and converted to MA fuels or targets which can be transmuted in the reactor or accelerator driven system (ADS). In this scenario, the (U,Pu) and MA fuels are separated in different stages in the reprocessing plant and the refabricated fuels are distributed heterogeneously in the reactor core.

In the homogeneous recycling option, uranium and the transuranic elements (TRU = Np, Pu, Am, Cm) are contained within a single fuel type and distributed homogeneously throughout the reactor core. These fuels typically have between 1 – 5 wt% MA compared to 10–20 wt% MA in the MA fuel in the heterogeneous recycle scenario.[30] The homogeneous mode with grouped actinide recycling is beneficial in that there is no pure stream of plutonium, this adds additional barriers against risks of proliferation.[11] Whilst the homogeneous route is perhaps more straightforward with regards to fuel fabrication and reactor physics, the separations chemistry is more complicated than the heterogeneous reprocessing. Therefore, advanced fuel cycle R&D programmes commonly pursue both heterogeneous and homogeneous options.[9,11,27,30]

The development of the chemical separations processes needed for the reprocessing (or partitioning) of the actinides is widely recognised as a key enabler of advanced fuel cycle technologies. In Europe, the development of the chemical separations required for such strategies was triggered by two French waste management acts (1991 and 2006) [31,32] and has found support from EURATOM-funded research programmes since the early 1990s. Continuously evolving from initially small programmes, a sequence of programmes dedicated to developing actinide separation processes and the related chemistry was executed: NEWPART (1997–1999),[33,34] PARTNEW (2000–2003),[35] EUROPART (2004–2007),[36] ACSEPT (2008–2012),[37] SACSESS (2013–2016),[38–40] and the latest programme, GENIORS (2017–2021).[41] These programmes have made substantial progress in developing the separation technologies for both LWR and FR spent fuel recycling towards the point at which they can be deployed and our previous paper [26] discussed the actinide separation processes developed in Europe addressing heterogeneous recycling. This paper reviews and assesses the respective processes for homogeneous recycling, once again focusing on the development in Europe.
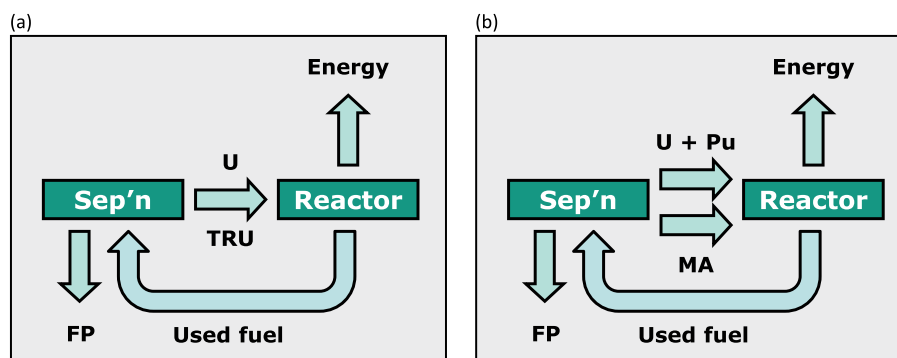

Figure 1. Schematic illustration of (a) homogeneous and (b) heterogeneous recycling. FP = fission products (redrawn from ref.).[26]

Recycling strategies

The discussion so far has focused on how multi-recycling in FRs can derive optimum benefits from nuclear energy generation related to sustainability and waste management and how this multi-recycling can be achieved either in a heterogeneous or homogeneous mode. The heterogeneous recycling mode is primarily related to the aqueous reprocessing (hydrometallurgical) routes, involving:

(a) An initial separation of U and Pu using the PUREX process or some variation thereof. If desirable, neptunium can be recovered with the U and Pu relatively easily.[28]

(b) A new extraction process to recover either americium and curium or americium alone from the aqueous HLW stream.

The different strategies for heterogeneous recycling of MA are described in the preceding paper.[26] Homogeneous recycling, on the other hand, can be achieved either by an aqueous route or by a non-aqueous pyrometallurgical processing of SNF in high temperature molten salt media.[42,43] Indeed, pyro-processing is well suited to homogeneous recycling of FR fuels (metals, nitrides, oxides), being resilient to radiation from high burn up and short cooled FR fuels, based on electrorefining or reductive extraction that is adapted to the metal fuels often considered for FRs and naturally producing a low purity mixed actinide product.[44] However, pyro-processing is generally a low throughput batch process and, as such, was originally developed as part of the Integral Fast Reactor programme in the United States.[45] Further discussion of the pyrochemical routes for homogeneous recycling are beyond the scope of this paper but the interested reader is referred to references.[11,42,46–49]

Aqueous separation processes for homogeneous recycling

The basic requirement for homogeneous recycling is that it requires the recovery of the TRU elements as a group. Uranium could be co-recovered with the TRU or separated on its own in a dedicated solvent extraction cycle (or other process such as crystallisation).[11,50] From this initial assumption, some secondary characteristics of the process become evident as well:

- A new extractant is required since tributyl phosphate (TBP), as used in the PUREX process, is not able to extract trivalent minor actinides.

- Adherence to the "CHON principle[1]" of degradable ligands in the process is preferred, ideally for both phases.

- Efficient extraction of TRU actinide ions in oxidation states III (Am, Cm), IV (Pu, Np) and VI (Np, potentially U and Pu) is required.

- The process must be able to cope with high concentrations of plutonium (~10 times that of the conventional PUREX process for thermal oxide fuel reprocessing) without third phase or precipitate formation. Also, with high plutonium concentrations, methods avoiding Pu recovery by reductive stripping (as used in the PUREX process) are preferred due to potential re-oxidation of Pu (III) by nitrous acid and the consequent need for excessive levels of reductants, such as U(IV), to maintain plutonium in the trivalent state.[51]

- Minimisation or preferably elimination of hazardous reagents, such as hydrazine, is advisable.

- At some point in the process there must be selectivity in either the organic or aqueous phases for trivalent actinides over trivalent lanthanides otherwise effective decontamination from lanthanides (which are neutron poisons in the reactor) will not be achievable.

- Fast chemical and/or mass transfer kinetics are required for compatibility with next generation solvent extraction equipment such as centrifugal contactors.[52]

- Ligands, particularly in the organic phase, must be sufficiently stable towards radiolysis and hydrolysis and extractants must be sufficiently soluble in the diluent to enable extraction of rather high concentrations of TRU elements.

In Europe, substantial challenges were met in early projects, NEWPART, PARTNEW and EUROPART, developing ligands that were able to achieve the challenging An(III)/Ln(III) separation [53,54] and this led to defining and testing "reference" processes for heterogeneous recycling in the later projects, namely ACSEPT and SACSESS.[43,55,56] The learning from these early projects was exploited, initially in the ACSEPT project, to start development of a European option for homogeneous recycling.[57] This pan-European development was in parallel to French efforts and indeed the first strategies for homogeneous recycling were developed by the French Alternative and Atomic Energies Commission (CEA) and tested in their ATALANTE facility at Marcoule.[43,58–60] The process was termed

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[1]Ligands that contain carbon, hydrogen, oxygen and nitrogen only and, therefore, should be fully decomposable to gases.
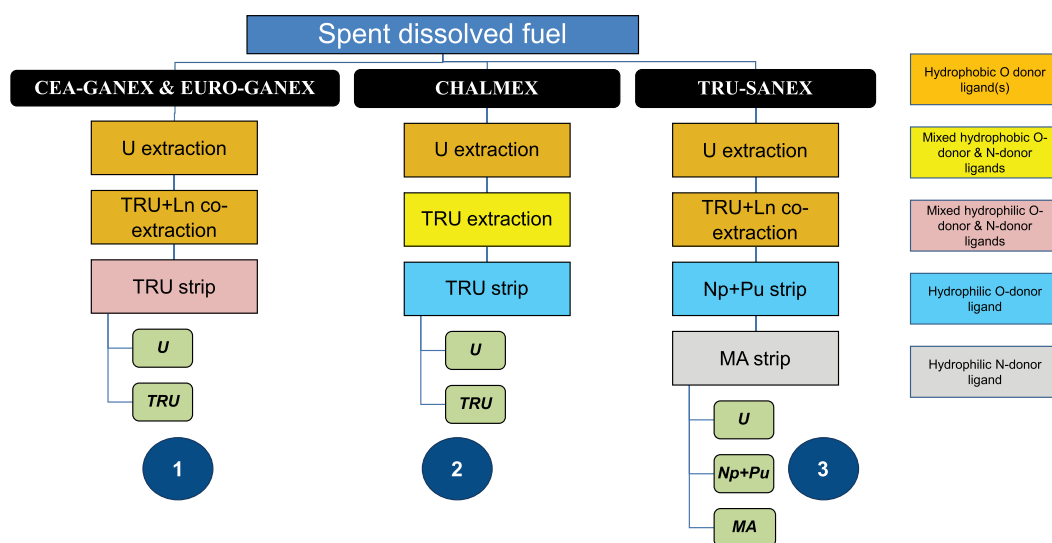
Figure 2. A schematic overview of GANEX solvent extraction processes for homogeneous recycling developed in Europe. The colour scheme indicates the kind of extracting or complexing agents used (see legend).

GANEX (Grouped ActiNide Extraction) and, as of today, three GANEX options exist for homogeneous recycling and a fourth process variant for heterogeneous recycling has also been reported. These four GANEX-variants fall into three basic strategies, depending on how they recover the TRU actinides, as indicated in Fig. 2:

(1) Co-extraction of TRU and lanthanides followed by selective stripping of TRU
(2) Selective extraction of TRU
(3) Co-extraction of TRU and lanthanides followed by selective and sequential stripping of, firstly, Np and Pu and then trivalent MA

All three strategies presume an initial separation of most or all of the uranium to reduce the volume and complexity of the TRU recovery cycle. Figure 2 also indicates the types of ligands (O – or N-donor ligands in organic or aqueous phases) proposed for each strategy.

In brief, the GANEX process was first developed by the CEA and designed as a 2-cycle solvent extraction process, where the bulk uranium is extracted in the primary stage (GANEX-1),[61] while the TRU/fission product separation is achieved in the secondary GANEX-2 stage – this has been termed CEA-GANEX.[59] In the ACSEPT project alternatives to CEA-GANEX were investigated and the

EURO-GANEX cycle was developed and tested [62–64] as well as the initial formulation of the Chalmers-GANEX (CHALMEX).[65–68] In the CEA-GANEX and the EURO-GANEX processes, the actinides (An) and lanthanides (Ln) are co-extracted from the GANEX 1st cycle (GANEX-1) raffinate. The actinide/fission product separation is achieved through subsequent selective stripping. In the CHALMEX process, the An/Ln separation occurs by the selective extraction of An.[65–67] It is clear that the CHALMEX option, at least superficially, offers a simpler and more elegant solution to the challenge of recovering TRU actinides as a group. However, it is concomitantly more challenging from the process chemistry perspective and, for reasons that will become apparent later, the EURO-GANEX is considered to be the current reference process for the GANEX 2nd cycle (GANEX-2).

The individual processes will be briefly described below, focusing on aspects such as their basic principles, development status (technology readiness), upstream and downstream compatibilities, generation of secondary wastes and process safety. In line with our previous review,[26] decontamination factors achieved in lab-scale process demonstration trials are not reported (stricter purity requirements can quite easily be met by e.g. increasing the number of stages); such data are found in the original literature. Acronyms for extracting and complexing agents, together with their molecular structures, are explained in the Appendix.

Uranium extraction (GANEX-1 cycle)

The GANEX 1st cycle is common for all the variants of the GANEX processes and is aimed at the bulk recovery of uranium from a dissolved spent nuclear fuel solution. This is necessary as a high purity uranium product is required to enable tuning of the U/TRU ratios in the final fuel. It also reduces the volume (mass) of material that must be processed in the next cycle and simplifies the chemistry – since uranium is present as the very stable, linear, hexavalent dioxo-cation, UO_2^{2+}, which is quite different to the other An^{3+} and An^{4+} cations. The uranium separation is achieved by a solvent consisting of a N,N-dialkylamide that is selective for U(VI), N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) in an aliphatic diluent such as hydrogenated tetrapropylene (TPH) or Exxsol D-80. N,N-dialkylamides have several advantages including adherence to the CHON-principle, high hydrolytic and radiolytic stability and a high loading capacity for uranium. DEHiBA degrades into carboxylic acids and secondary amines, which have little to no effect on the separation of uranium from the raffinate. DEHiBA delivers high values for $D_{U(VI)}$, high U(VI)/Pu(IV) separation factors (~80) without need of redox agent, and high decontamination factors (DF) for most fission products in nitric acid media.[43,61,69,70]

Two laboratory scale hot tests with SNF have been performed on the GANEX-1 cycle. The flowsheet was initially developed at the CEA in France and tested in lab-scale mixer-settlers in the ATALANTE facility at Marcoule with thermal oxide fuel.[43,61,71] Later, the flowsheet was adjusted by use of the CEA's PAREX model [72] and tested in centrifugal contactors at the Joint Research Centre (JRC) in Karlsruhe at the end of the ACSEPT project.[43,64] In both cases the aim was to generate the highly active (HA) raffinate stream for testing the GANEX-2 cycle although CEA have looked further at the optimisation of the GANEX-1 cycle, particularly the scrubbing step. Nevertheless, both tests gave good results that are summarised in Table 1. The flowsheet for the JRC hot test was based on dissolved FR fuel and so had a different U:Pu ratio in the feed. The results of the JRC test with respect to Np, Pu and Tc

Table 1. Key properties and results from the GANEX-1 hot tests at CEA and JRC [43,61,64].

Property	CEA hot test	JRC hot test
U in feed (g/L)	176	103.1
Pu in feed (g/L)	2.5	22.7
U in raffinate (%)	<0.002	0.06
Pu in U product (%)	0.024	0.38
Np in U product (%)	0.33	5.8
Tc in U product (%)	2.4	24.5
Contactor type	Mixer-settlers	Centrifugal contactors
Total stages	28	32

Table 2. Comparison of key features of CEA-GANEX and EURO-GANEX cycles (data from [43,59,64]).

	CEA-GANEX	EURO-GANEX
Developed by	CEA (France)	ACSEPT project (FP7)
Date of hot test	2008	2013
Fuel for hot test	LWR	DFR
Pu content in HAF	≈2 g/L	10 g/L
Equipment	Mixer-settlers	Centrifugal contactors
No. of stages	48	32
CHON?	Aqueous phase only	Organic phase only
Organic phase	DMDOHEMA + HDEHP	TODGA + DMDOHEMA
Diluent	Industrial (TPH)	Industrial (Exxsol D-80)
FP scrubbing/ holdback	Citric acid (Mo,Tc) HEDTA (Pd)	CDTA (Zr,Pd)
Actinide strip	pH 3	0.5 mol/L HNO_3
Actinide strip agents	HEDTA + citric acid + hydroxyurea	AHA + SO_3-Ph-BTP
Pu stripping	Complexation	Complexation
Ln(III) decontamination	5% in An product	<0.06 % in An product
Np recovery	~99%	99.90%
TRL (at system level) [75]	4–5	4–5

decontamination were not as good as the CEA test. This is probably attributable to the use of short residence time centrifugal contactors and fewer scrubbing stages in the JRC test. Optimisation of the hydrazine scrubbing is evidently required. As with the PUREX process,[73] technetium (Tc) co-extraction with uranium was also a significant factor and accounted for in the PAREX model.[74] The technical maturity for this cycle has been assessed through application of the widely used technology readiness level (TRL) assessment by the OECD-NEA.[75] Although it is noted that this assessment was made at the "system level" and so parts of the process (so-called "critical technology elements") may actually be at a lower level, GANEX-1 was assessed to be at TRL 5 (which was defined as "*Technology component or process step validated at bench scale under relevant conditions. Process models developed. Proof of principle hot tests using spent fuel*" [11,75]).Table 2

GANEX-2 cycle scheme 1: selective actinide stripping

The most developed formulation of the GANEX 2nd cycle is given in Scheme 1. This involves the co-extraction of TRU actinides and the trivalent lanthanides (together with some problematic fission products such as Mo, Zr, Tc, Fe) from the GANEX-1 aqueous raffinate. The co-extraction of the lanthanides is inevitable if an O-donor ligand is used as the extracting agent due to the chemical similarity of the trivalent actinides and lanthanides. The actinides are then selectively stripped from

the organic phase by suitable hydrophilic ligands containing a soft donor ligand (usually N-donors). The lanthanides remain in the organic phase and are stripped in the next stage before the lean solvent is recycled.

CEA-GANEX

The GANEX-2 cycle was first proposed by CEA based on an adaptation of their DIAMEX-SANEX process [58,59]; this being a process already developed and tested for separation of minor actinides.[31,76] Therefore, the organic phase was based on the combination of the malonamide N,N'-dimethyl-N,N'-dioctyl-2-(2-hexylethoxy) malonamide (DMDOHEMA) and di-(2-ethylhexyl)phosphoric acid (HDEHP) diluted in an aliphatic diluent (TPH). N-(hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was added to the aqueous feed and the scrub solution to suppress fission product extraction (specifically palladium) but molybdenum and technetium (as well as Zr, Fe) were nevertheless co-extracted with the TRU actinides. A dedicated scrubbing section was thus added to the flowsheet to scrub molybdenum and technetium at pH 2–3; pH adjustment was with citric acid. The actinide stripping section was also operated at pH 3 using a solution of HEDTA, citric acid and hydroxyurea. Hydroxyurea was added as a reducing agent for Np(VI) – plutonium being stabilised in the tetravalent state in the presence of HEDTA and citric acid. At this high pH, lanthanides were retained in the organic phase by complexation with HDEHP. The lanthanides and other residual contaminants (zirconium, iron) were finally stripped from the solvent with a mixture of TEDGA and oxalic acid before the solvent recycling.[43]

This CEA-GANEX cycle has been tested with SNF at the Atalante facility (Marcoule, France).[59] A LWR fuel was used (the aqueous raffinate from their GANEX-1 hot test described above) and the flowsheet test was performed in 48 stages of miniature mixer-settlers in a hot cell. Losses of TRU actinides were <0.5% with generally good fission product decontamination factors obtained. The exceptions were some middle lanthanide elements which contaminated the actinide product. Using their PAREX solvent extraction simulation capabilities,[31] this was later shown to be due to an under-estimation of some of the fission product concentrations in the feed and simulations were run that predicted how this could be rectified in future. The CEA-GANEX was, therefore, the first process demonstration of the GANEX concept and was shown to be a viable option for the GANEX-2 cycle.

EURO-GANEX

European projects had already made substantial progress in developing processes for An(III) recovery, particularly based on applications of the diglycolamide extractants – mainly N,N,N',N'-tetra-n-octyl-diglycolamide (TODGA).[55,77–79] Adapting these developments for the GANEX-2 cycle was seen as the logical place to start with early work based on a combination of TODGA and TBP.[80] However, in experiments with process concentrations of plutonium (as opposed to trace spiked solutions) precipitates were observed with TODGA and its dodecyl analogue (TDdDGA) alone in diluent or with TBP, octanol and N,N-dihexyloctanamide (DHOA) as phase modifiers.[81] Addition of the malonamide DMDOHEMA, was found to provide sufficient capacity for plutonium before a conventional third phase was observed (up to 35 g/L with 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA with extraction from 3 mol/L HNO$_3$); no precipitation occurred with DMDOHEMA [81] which acts as a co-extractant.[82] Screening of different TODGA:DMDOHEMA ratios settled on 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in an odourless kerosene diluent as the most suitable formulation. The third phase boundary was later defined as a function of nitric acid concentration showing this solvent had sufficient capacity for plutonium concentrations of ≥10 g/L for [HNO$_3$] ≤6 mol/L.[83] Consequently, 10 g/L Pu was set as the target for future flowsheet design.

Spiked batch distribution experiments confirmed the expected efficient co-extraction of Pu(IV), Am (III) and Ln(III).[83] Spiked batch distribution experiments also confirmed the sulphonated bistriazinyl pyridine ligand (SO$_3$-Ph-BTP), 2,6-bis(1,2,4-triazin-3-yl)-pyridine, developed for selective stripping of An(III) from Ln(III) in the i-SANEX process [84,85] also worked for the EURO-GANEX solvent.[63] Further experiments with process concentrations of Pu(IV) (1–10 g/L) defined suitable acid and SO$_3$-Ph-BTP concentration ranges that would deliver good separation factors whilst maintaining $D_{Pu,Am}<1$ and $D_{Eu}>1$. A second hydrophilic molecule, acetohydroxamic acid (AHA), was added as this was expected to act as a complexant for Pu(IV) [81,86] and reductant for Np(VI) [87] but it was also shown to promote stripping with the SO$_3$-Ph-BTP although the reasons for this effect are still unclear.

Fission product decontamination is a key challenge with any reprocessing flowsheet and the EURO-GANEX process is no exception. CDTA (trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid), developed for the i-SANEX cycle, was also shown to hold back

zirconium and palladium in the aqueous phase when applied to the EURO-GANEX system.[88] E.g. for 0.05 mol/L CDTA, 3 mol/L HNO$_3$, 17 g/L Pu, D$_{Zr}$ and D$_{Pd}$ decreased from 11.3 to 1.2 and 250 to 0.05 respectively whilst D$_{Pu}$ remained sufficiently high (35). Further data on problematic fission and corrosion products were reported, specifically focusing on Fe, Sr, Tc, Mo, Ru.[63] Iron showed a steep increase in distribution ratio above 1 mol/L HNO$_3$ due mainly to extraction with DMDOHEMA. Strontium showed a maximum in D$_{Sr}$ around 2 mol/L HNO$_3$ whereas for technetium extraction, primarily due to TODGA, D$_{Tc}$ decreased across the HNO$_3$ range but remained $\gg$1 even at 4 mol/L HNO$_3$. Similarly, D$_{Mo}$ was above 1 across the HNO$_3$ range although there was some reduction in a HA raffinate (HAR) simulant compared with the single component solution and with CDTA. Ruthenium distribution ratios were less than one but varied with mixing time of the solutions and are likely to be affected by changes in speciation. In fact, TODGA-based flowsheet trials often report some retention of ruthenium in the organic phase.[78,79] Ruthenium PUREX chemistry, for comparison, is known to be very complicated.[89,90]

The behaviour of neptunium in the EURO-GANEX system was given specific attention due to the known complexity of neptunium solvent extraction and redox chemistry.[28,91] The order of extractability of the different neptunium oxidation states was shown to be Np(IV) >Np(VI)>1> Np(V) on extraction from <3 mol/L HNO$_3$. Of particular interest was that whilst Np(IV) and (VI) were quite stable, the Np(V) oxidation state proved to be very unstable in the organic phase with respect to disproportionation, a feature which it was realised could be exploited in flowsheet design. An increased rate of Np(V) disproportionation in the organic phase compared to the aqueous phase was similarly seen in earlier studies in TBP.[92]

A flowsheet was designed and tested using a surrogate feed with realistic concentrations of plutonium (10 g/L) in the feed.[62] 16 centrifugal contactor stages of extract-scrub were followed by 12 stages of TRU actinide stripping and 4 stages of lanthanide stripping. CDTA was added to the feed (0.05 mol/L) which was 5 mol/L HNO$_3$ to promote neptunium disproportionation and extraction. A double strip was employed to selectively strip TRU from Ln(III) using 0.5 mol/L AHA with two different concentrations of SO$_3$-Ph-BTP to minimise Ln (III) stripping in low plutonium stages. Plutonium was well controlled through the flowsheet with a DF of ~14,000 but ~30% neptunium was lost to the HA raffinate and the TRU product contained ~7% of europium (used as an exemplar lanthanide). A flowsheet model developed in the CEA's PAREX simulation code was

validated from this test and used to refine the flowsheet design ready for a hot test. The hot test was run at the end of the ACSEPT project at the JRC, Karlsruhe, using a feed from dissolving spent Dounreay Fast Reactor (DFR) fuels.[64] Following the GANEX-1 cycle, the EURO-GANEX cycle was run in two parts using a 16 stage miniature centrifugal contactor cascade contained in a hot cell. Changes from the surrogate test included raising the feed acidity to 5.9 mol/L HNO$_3$ to promote neptunium oxidation to Np(VI), reducing the scrubbing stages and simplifying the strip to a single solution (1 mol/L AHA + 0.055 mol/L SO$_3$-Ph-BTP in 0.5 mol/ L HNO$_3$). The trial was very successful in demonstrating the EURO-GANEX concept – 99.9% Np, Pu and Am ions were recovered with 0.06% lanthanide contamination. The improved neptunium extraction in the initial extract-scrub was attributed to the flowsheet changes plus the nitrous acid generated from radiolysis catalysing the Np(V) oxidation most effectively.[28,93,94]

The subsequent European SACSESS project was focused on the safety of the reference separation processes, including EURO-GANEX.[38,39] One of the objectives for the SACSESS project was to perform a process safety review of the EURO-GANEX flowsheet under normal and potential maloperation conditions. For this purpose, a safety assessment methodology was developed based on the experience of the project collaborators across Europe and this methodology [95] was then utilised to carry out a review of the EURO-GANEX flowsheet at a SACSESS project meeting based on a workshop style approach.[38] A key maloperation identified was the loss of scrub acid from the initial extract-scrub contactor as this was likely to cause the accumulation of plutonium, americium and other species across the contactor leading to potential criticality or radiological hazards within the plant. Therefore, an experimental simulation of this maloperation was carried out in laboratory scale centrifugal contactors.[96] Following the establishment of steady state with the flowsheet under normal operating conditions, the scrub acid was reduced to 0.05 mol/L (from 0.5 mol/ L). Surprisingly, plutonium accumulation was not observed, and the plutonium remained in the solvent product with almost no change to the profile. The organic phase, however, did change colour from red-brown to green and UV-vis absorption spectroscopy confirmed a change in the solvent phase speciation and that the process was reversible. This effect was proposed to be caused by hydrolysis of Pu(IV) due to the low acidity, that was then limited in its extent by the solvent shell around the hydrolysed plutonium preventing it from polymerising to form a colloid,

as occurs in the aqueous phase.[97] It was concluded that the EURO-GANEX process was robust to at least this type of maloperation and, whilst wider studies are obviously needed, this is a potentially advantageous, if unexpected, feature of the system.

The resistance of the EURO-GANEX system against radiation has also been addressed during SACSESS and GENIORS [98–100] projects, by performing a wide variety of gamma irradiation experiments to simulate the most relevant process conditions. The studies demonstrated that although there is an important reduction in TODGA and DMDOHEMA concentration after 1 MGy adsorbed gamma dose, the system retains excellent extraction performance after 500 kGy and is still sufficient after 1 MGy, without compromising lanthanide loading capacity (i.e. the limiting organic concentration, LOC). A total of 14 degradation compounds (DCs) were identified, nine from TODGA and five from DMDOHEMA, leading to a complicated mixture where at least three of those compounds could form insoluble aggregates. Regarding fission products, the irradiated EURO-GANEX solvent only showed a slight increase in fission product extraction, with the exception of zirconium and palladium. However, irradiation of CDTA containing aqueous phases, up to relatively low doses (5–50 kGy), indicated a loss of the masking ability for zirconium and palladium due to the formation of some insoluble products. There was also some loss of selectivity in actinide stripping (in 1 mol/L HNO₃) from a loaded and irradiated (1 MGy) EURO-GANEX solvent and retention of residual lanthanides in the solvent requiring more stages for back extraction of lanthanides into dilute nitric acid in the lanthanide strip. Most of the effects were explained by the extraction properties of DCs formed on irradiation.[100–102] In general, it was found that the aqueous phase containing SO₃-Ph-BTP and AHA was less stable to radiolysis than the organic solvent but, as the aqueous phase is not recycled, the results indicate that after a low-moderate absorbed dose (40–50 kGy) the concentration of SO₃-Ph-BTP remaining is still enough to preserve an effective An/Ln separation if other factors such as AHA hydrolysis and pH are controlled.[99,103,104] Furthermore, the studies to date do not show any evidence of effects due to DCs of SO₃-Ph-BTP or AHA. Whilst further studies are still needed, particularly in the presence of plutonium, the long term operation of the EURO-GANEX system with irradiated nuclear fuels seems realistic, particularly when the impacts of the solvent clean-up process are considered; although improvements to the masking agent strategy for zirconium and palladium may be necessary.

GANEX-2 cycle scheme 2: selective actinide extraction

The simplest formulation of the GANEX 2nd cycle is given in Scheme 2. This involves the selective extraction of TRU actinides leaving the trivalent lanthanides as well as all other fission products in the GANEX-2 aqueous raffinate. This is only possible by judicious choice of extractants; particularly avoiding O-donor ligands such as diglycolamides that can co-extract lanthanides, but also finding extractants that have capacity to extract the larger amounts of Pu(IV) ions present. Following extraction, the actinides are then stripped group-wise from the organic phase by suitable hydrophilic O-donor ligands before the lean solvent is recycled.

The CHALMEX process

The CHALMEX process was developed by Chalmers University of Technology (Sweden), as an alternative strategy for the GANEX 2nd cycle.[65–68,105–111] The objective was to develop a simpler process, which could reduce the number of process steps, potentially reducing costs of a recycling plant.[38] While significantly less developed than the strategies outlined for Scheme 1, the CHALMEX process has shown promising results in its actinide/lanthanide separation characteristics.

By combining the well-known extractant TBP with 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP), the solvent can theoretically extract the actinides with oxidation states ranging from +III to +VI, without the co-extraction of lanthanides and fission products and without redox control of plutonium.[65–67] While the process chemistry of TBP is well established after decades of use in the PUREX process, the chemistry of CyMe₄-BTBP is less well-known. It has been found to be stable towards both hydrolysis and radiolysis, but a complete mapping of degradation products formed under process conditions is lacking and studies are in progress.[112–114] Both alpha and gamma-radiation induced degradations of CyMe₄-BTBP have been investigated.[66] It has been established that the ligand degrades readily when subjected to both types of radiation but extraction properties remain almost unaffected when irradiated in contact with nitric acid. It has also been suggested that the stability of the extractant towards radiolysis is dependent on the diluent having a similar shape: for cyclic extractant molecules, a cyclic diluent leads to higher radiolysis resistance, at least at low irradiation doses.[115]

CyMe4-BTBP is also the reference molecule for the regular (r) and 1-cycle (1 c) SANEX processes [116–118] and has gone through hot tests on genuine spent nuclear fuel with good results.[43,55,56]

Phenyl trifluoromethyl sulfone (FS-13) is used as a diluent in the process. Both Russian and American research efforts have focused on its use as a diluent in the UNEX (Universal Solvent Extraction) process.-[119–125] FS-13 is chemically inert and stable towards both hydrolysis and radiolysis. A major advantage of the diluent is its high density (~1.4 g/cm^3), which resolves any phase separation/inversion issues experienced in systems with more similar densities between organic and aqueous phases. Other advantageous chemical and physical properties include low aqueous solubility, low viscosity and it is non-toxic. FS-13 has a relative permittivity of approximately 30.8 F/m at 298 K [126] and high dielectric constants have been shown to be beneficial for americium extraction as it increases the solubility of CyMe4-BTBP and hence the distribution ratio of Am. The separation factor of Am/Eu, however, increases exponentially with decreasing relative permittivity.[127]

The initial feasibility studies of the CHALMEX process were promising. A good separation factor of the actinides from the lanthanides was seen within only 10 minutes of contacting (SF$_{Am/Eu}$ = 160, SF$_{Pu/Eu}$ = 210, SF$_{Np/Eu}$ = 3.5). All fission products that were extracted, except samarium and zirconium, were extracted by CyMe4BTBP and the most problematic fission products extracted included Ag, Cd, Mo Zr and Pd. The extraction of some corrosion products (Ni, Co, Mn) was also found to be an issue.[65,107]

To prevent the extraction of some of these fission products, different strategies were considered including pre-extraction, scrubbing and suppression. Pre-extraction is generally undesired due to the increase in final waste volume it would produce by adding another process stage. Both scrubbing and suppression are more attractive choices as they can be combined with already existing process steps. Finally, it was concluded that a combination of the masking agents bimet and D-mannitol added directly to the GANEX-1 raffinate successfully reduced the extraction of Mo, Zr and Pd.[65,105] Palladium was then of concern as it is known to precipitate when in contact with a pure cyclic ketone (or rather the presence of enol impurities),[128] such as the original diluent of choice, cyclohexanone.[65,67,105] No such reaction is known for cyclic sulfones like FS-13. Gluco-lactone can be added to the acid scrub step to back-extract any molybdenum or zirconium.[106]

The process feasibility has been demonstrated by batch scale tests [107] and the solvent has been tested for use in centrifugal contactors in single stage centrifugal contactor experiments.[106] Elemental calculations on number of ideal, counter-current process stages have been performed with promising results: a 99.9% recovery of Am was estimated using 3 extraction stages followed by 3 scrubbing stages and 2 stripping stages. However, to date, no counter-current flowsheet tests have been carried out.
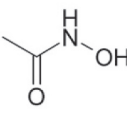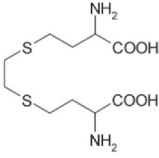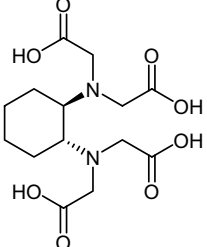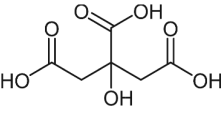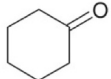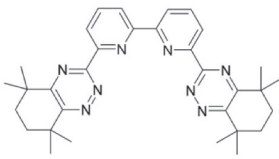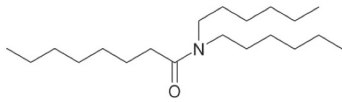
GANEX-2 cycle scheme 3: split actinide stripping

The third application of the GANEX strategy for the 2nd cycle is given in Scheme 3. This is basically a variation of Scheme 1. It involves the co-extraction of TRU actinides and the trivalent lanthanides from the GANEX-1 aqueous raffinate. The actinides are then selectively stripped from the organic phase by suitable hydrophilic ligands but, in this case, a split stripping strategy is adopted whereby firstly the multi-valent TRU ions (Np, Pu) are stripped and then the trivalent MA are stripped (Am, Cm). This gives two products that can be used for heterogeneous recycling or re-combined for homogeneous recycling. The lanthanides remain in the organic phase and are stripped in the next stage before the lean solvent is recycled. This strategy is included in this review of homogeneous recycling since it is a straight forward variation of the GANEX concept rather than a specific MA separation from PUREX HAR; options that were discussed in the preceding paper.[26]
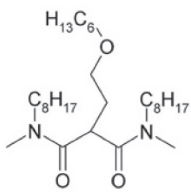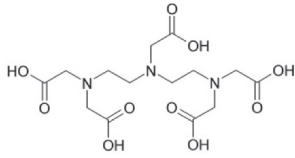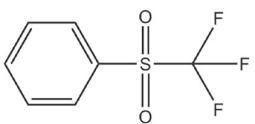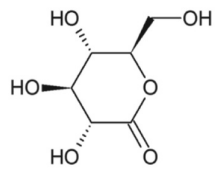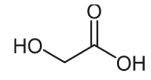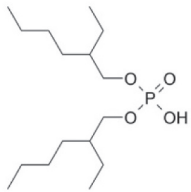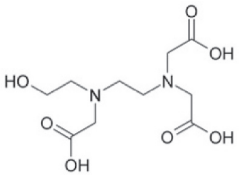
TRU-SANEX

Earlier papers in the development of the EURO-GANEX cycle had reported stripping of TRU actinides from the EURO-GANEX solvent with AHA and SO$_3$-Ph-BTP both independently and together.-[63,81] The mixture of the two reagents was the optimum combination for grouped stripping of Np-Cm. However, it was clear that, at low acidity, AHA could strip Pu(IV) and Np(IV), by complexation, and Np(VI), by reduction to Np(V), without interacting with the trivalent ions, whilst SO$_3$-Ph-BTP was designed to selectively strip the trivalent actinides from trivalent lanthanides. These selectivities are nicely illustrated by a comparison of reported stability constants – data have previously been reported for a wide range of actinide and lanthanide AHA complexes (e.g. logβ_1 values of 6.19, 5.85, 7.94, 4.83 and 14.2 for Eu(III), Am(III), U(VI), Np(V) and Pu(IV) respectively) and for curium and europium SO$_3$-Ph-BTP complexes (logβ_3 (Cm) = 12.2; logβ_3

Table 3. Table of process ligands.

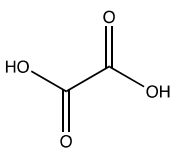| Compound	Acronym	Name
	AHA	Acetohydroxamic acid
	bimet	(2S,2'S)-4,4'-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)
	CDTA	trans-1,2-Diaminocyclohexane-*N,N,N',N'*-tetraacetic acid
	Citric acid	(2-Hydroxypropane-1,2,3-tricarboxylic acid)
	Cyclohexanone	Cyclohexanone
	CyMe$_4$-BTBP	6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine
	DHOA	Di-*n*-hexyl *n*-octanoamide
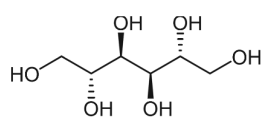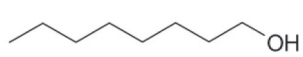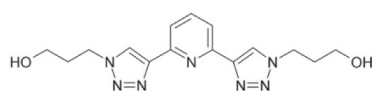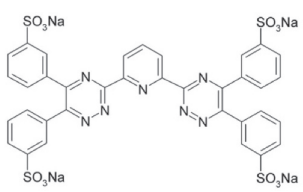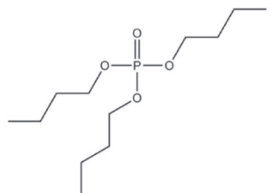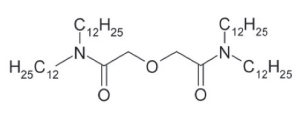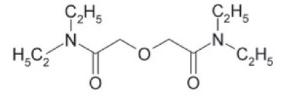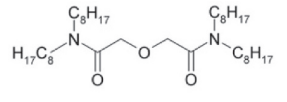
(*Continued*)

Table 3. (Continued).

Compound	Acronym	Name
	DMDOHEMA	*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxy-ethyl)-malonamide
	DTPA	diethylenetriaminepentaacetic acid
	FS-13	(Trifluoromethyl)sulfonyl benzene
	Gluco-lactone	Gluco-lactone
	Glycolic acid	2-Hydroxyethanoic acid
	HDEHP	Di-(2-ethylhexyl)phosphoric acid
	HEDTA	N-(hydroxyethyl)ethylenediaminetriacetic acid

(*Continued*)

Table 3. (Continued).

Compound	Acronym	Name
	Mannitol	D-mannitol
	Octanol	1-Octanol
	Oxalic acid	Oxalic acid
	PTD	2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine
	SO₃-Ph-BTP	2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-pyridine tetrasodium salt
	TBP	Tributyl phosphate
	TDdDGA	*N,N,N′,N′*-tetra-*n*-dodecyl diglycolamide
	TEDGA	*N,N,N′,N′*-tetraethyl diglycolamide
	TODGA	*N,N,N′,N′*-tetra-n-octyl diglycolamide

(Eu) = 10.2).[86,129–133] This raised the interesting possibility of adapting the EURO-GANEX flowsheet to produce separate (Np, Pu) and (Am, Cm) products by separate sequential strip sections using firstly AHA and then SO_3-Ph-BTP (the AHA strip needs to be first since the SO_3-Ph-BTP will strip tetravalent as well as trivalent actinides). This variation was termed "TRU-SANEX" to highlight its hybrid nature between the GANEX and SANEX processes.[134] Results from a flowsheet test confirmed the concept with only small cross-contamination between the two products. Interestingly, <10% neptunium was lost to the aqueous raffinate which is less than the simulant EURO-GANEX test (~30%) but not as good as the hot test (<0.1%). Since the extract-scrub-section in the TRU-SANEX test was based on the hot test, this gives a rough indication of the impact of (a) the flowsheet changes and (b) radiolytically generated nitrous acid in promoting neptunium conversion to extractable Np(VI) and Np(IV) oxidation states.

Comparing the process schemes

Looking at the different process schemes (Fig. 2), Scheme 2 appears the simplest since it selectively extracts the actinides at the initial extract-scrub stage. However, all three schemes are based on two cycles of solvent extraction and each cycle contains extraction, scrubbing and stripping stages, spent solvent regeneration cycles and various auxiliary equipment; for example, the engineering design may include evaporators, buffer storage or conditioning tanks, reagent tanks, connecting pipework, etc. Also, the solvent extraction process is only one part of the reprocessing plant – upstream and downstream processes for fuel preparation, dissolution, product finishing and waste management must also be considered in order to make a proper evaluation of the "simplicity" of any particular separation process. Beyond the assessment of the technologies themselves, other factors also affect the choice of separation process such as: technology readiness; safety; environmental impacts (particularly on the DGR); proliferation resistance and physical security challenges; socio-economic benefits, including public acceptability; national policies and fuel cycle scenarios.[9] Thus, evaluating the different process schemes requires consideration of many aspects which have economic implications to the viability of the flowsheet at an industrial scale. However, in the context of this article we can

highlight certain features of the different processes for each scheme that enable comparisons at the technical level.

GANEX-1

The process based on the monoamide DEHiBA for selective uranium extraction has been tested twice now with SNF.[61,64] Good results have been obtained although the slightly worse recoveries and decontamination factors in the JRC hot test, which used centrifugal contactors, point to some kinetic issues with the hydrazine scrubbing stage for technetium, neptunium and plutonium control.[64] Also, the rather low uranium saturation in the JRC hot test leads to excessive solvent and aqueous flows that should be minimised from the waste management perspective.

Nevertheless, whilst optimisation challenges remain, the concept is considered to be proven. Further physico-chemical data needed for building predictive process models are outstanding needs (see for example [73]).

Scheme 1 (CEA-GANEX and EURO-GANEX)

Two processes have been demonstrated with SNF – CEA-GANEX and EURO-GANEX – which confirm the technical feasibility of options that meet the challenging goals related to developing advanced reprocessing options for homogeneous recycling.[43] These two cycles are compared in Table 3. The EURO-GANEX option offers some significant advantages, notably:

- Actinide stripping in the acidic region (no need for pH adjustment)
- No phosphate wastes from the solvent management
- Compatibility with centrifugal contactors has been demonstrated at the lab scale

Note that both CEA-GANEX and EURO-GANEX meet the requirement to avoid plutonium reduction despite the addition of reducing agents[2][135]

However, in its current form the EURO-GANEX cycle also has various drawbacks:

- The sulphonated BTP reagent in the aqueous phase adds to waste volumes and is incompatible with vitrification processes for HLW immobilisation.

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[2]In EURO-GANEX, AHA can reduce Pu(IV) to Pu(III), most probably via hydroxylamine which is a product of the acid hydrolysis of AHA, but excess AHA stabilises Pu(IV) and the reduction reaction occurs too slowly under process conditions to be of any practical concern, at least under normal operations. In CEA-GANEX, Pu(IV) is stabilised by HEDTA and citric acid despite the addition of hydroxyurea. Both AHA and hydroxyurea act as reducing agents for Np(VI) ions in these GANEX-2 cycles.

- The combination of two extractants in the organic phase complicates solvent formulation, clean up and recycling and process simulation.
- Incomplete control of some fission products; notably molybdenum, technetium and ruthenium.
- No solvent clean up process has been developed yet for used solvent recycling.

Scheme 2 (the CHALMEX process)

The CHALMEX process has to date been developed at the fundamental level. Latest studies have moved into the process development side through single stage centrifugal contactor experiments and a "flowsheet" simulation by sequential batch experiments. Clearly, the process flowsheet needs testing in a counter-current mode with a realistic simulant before it can be compared directly with the Scheme 1 options. The CyMe₄BTBP, although very successful in selectively extracting MA, is also known to have slow kinetics and low solubility in diluents. These issues are partially addressed by use of the FS-13 diluent but it is unclear whether this is suitable for industrial applications. As in the EURO-GANEX and CEA-GANEX processes, the CHALMEX process combines two extractants in the organic phase, of which the well-known TBP molecule degrades into problematic byproducts that can complicate the solvent management. CHALMEX also relies on a series of aqueous phase ligands (bimet, D-mannitol and gluco-lactone) of which one (bimet) contains sulphur.

Scheme 3 (the TRU-SANEX process)

As has been emphasised already, this is a relatively simple adaptation of EURO-GANEX and so does not have, *per se*, pressing, unique R&D needs. However, an innovative and potentially transformative development would be if this Scheme could be extended to a "TRU-EXAm" mode; that is recovery of (Np, Pu) followed by Am alone – leaving curium in one of the waste streams.

Outlook

The GANEX-1 cycle is necessary and has wider applicability for uranium recovery. Flowsheet optimisation, basic data generation and process simulation that lead to process scale up are obvious future directions. R&D needs for the EURO-GANEX process are also quite clear and the GENIORS project is already looking at a CHON replacement for the SO₃-Ph-BTP ligand [136,137] and a modified DGA ligand that could replace the combined TODGA and DMDOHEMA organic phase.[138]

CHALMEX would benefit from a focus on flowsheet testing and a safety review, similar to that trialled on the EURO-GANEX process in the SACSESS project.[38] All processes need solvent recycling capabilities and integration with upstream (fuel dissolution) and downstream (product finishing) stages. More in-depth safety studies, such as gas generation and thermal stability of proposed solvents, are also an essential next stage. Process modelling and simulation capabilities [139,140] are another generic need in order to more efficiently design flowsheets and also to probe sensitivities to process upsets.[141]

Conclusions

As with the heterogeneous recycling option, several solvent extraction processes addressing homogeneous recycling have been developed and demonstrated in Europe. These essentially fall into three schemes for separating the TRU actinides, all of which are preceded by a common uranium extraction cycle. The following conclusions are drawn, based on the current state of the art:

The principles of the uranium extraction (GANEX-1) cycle have been demonstrated although work is still required to optimise the process, prove the decontamination factors (particularly in short residence time centrifugal contactors) and move towards process scale up, underpinned by process models and simulation with comprehensive sets of basic physico-chemical data.

Scheme 2 appears the most complex to develop into a working process, although it is potentially the most elegant concept with the fewest number of stages. However, in its current form (the CHALMEX process) it uses a mixed organic phase, various aqueous phase complexants and a fluorinated diluent. Significant further work is required to take this option towards a process demonstration with SNF and a design that is industrially deployable.

Two promising options exist for Scheme 1, both of which have been tested with SNF and demonstrate good results. Nevertheless, questions remain around both CEA-GANEX and EURO-GANEX. For the CEA-GANEX process, testing with elevated Pu content fuels, the compatibility with centrifugal contactors (particularly in the stripping stages) and the need for a high pH strip are concerns. For the EURO-GANEX process, the replacement of the SO₃-Ph-BTP ligand with a CHON ligand, simplification of the organic phase to a single extractant and verification of DFs for some problematic fission products are key R&D directions. The big advantage of the EURO-GANEX cycle is it has been proven for actinide stripping in the acidic region.

Scheme 3 is just a variant on the EURO-GANEX cycle and, whilst further testing would be needed to confirm the DFs for this TRU-SANEX cycle, its development can be assumed to be at a similar status to the EURO-GANEX cycle. Whether a heterogeneous recycling option that was based on GANEX rather than PUREX chemistry is advantageous would depend on extraneous factors related to the deployment of advanced fuel cycles in a particular country.

For nearly all separation processes, significant quantities of experimental data and experience have already been accumulated – particularly the CEA-GANEX and GANEX-1 cycles – such that now addressing the outstanding key technology gaps should become the main focus, e.g. process scale up, integration with upstream and downstream stages and solvent management (recycling within the process and solvent destruction at end of life). No processes yet have complete suites of validated process models readily available for flowsheet design in normal and off-normal (maloperation) operations, although some simulations have been performed (notably within the CEA's PAREX code which is a mature and proprietary code for modelling solvent extraction operations in nuclear fuel reprocessing plant [72]).

So far, the developments discussed in this review have been pursued on the laboratory scale only. There are clearly important knowledge gaps that need to be filled before these processes would be ready for possible industrial applications. As well as those already noted, safety studies, including gas generation and impacts of maloperations; scale up; process monitoring and control technologies are certainly desirable to raise the technological readiness of the process. The likely disadvantages of TRU fuels with their higher activities and masses, due to the combined plutonium and MA content, in the recycle fuel fabrication plant must be considered in order to optimise the whole recycle system rather than parts of the system. Beyond, technology readiness, how these processes fit into advanced, sustainable, economic and proliferation-resistant nuclear fuel cycles, supporting future low carbon generation, must be analysed.[11]

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On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based GANEX System Containing CyMe$_4$-BTBP and TBP

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ABSTRACT

A Grouped ActiNide EXtraction (GANEX) process for the extraction of actinides from used nuclear fuel for transmutation purposes has been investigated. The studied solvent consists of phenyl trifluoromethyl sulfone (FS-13), CyMe$_4$-BTBP, and TBP, a combination that has previously shown promising results. The time to reach extraction equilibrium for the system has been found to be less than 20 min. A 2:1 complex has been found between CyMe$_4$-BTBP and americium (III) or curium(III), whereas plutonium(IV) and CyMe$_4$-BTBP create a 1:1 complex. The extraction of fission product is low in the system.

Introduction

Nuclear power is an important electricity source and accounts for a large proportion of the electricity produced in the OECD countries (America, 18.3%; Europe, 22.3%; Pacific, 11%).[1] One of the major problems related to nuclear power is the production of the radiotoxic used nuclear fuel. This fuel has to be isolated from the environment and stored in a final repository for around 100,000 years to reach the same radiotoxicity as natural uranium.[2] Today, two main strategies are in use for handling the used nuclear fuel.[3] One strategy is direct disposal, or the "once through" fuel cycle, where the fuel is used once in the reactor and then left for disposal in the final repository.[4] The other option is "Reprocessing" to recover plutonium and uranium from the used nuclear fuel using the solvent extraction PUREX process.[5,6] A further development of this concept is to recover not only plutonium and uranium but also the rest of the long-lived actinides, such as americium, curium, and neptunium. Reusing the long-lived actinides as fuel instead of disposing them will not only increase the energy usage of the used fuel, but also decrease the heat load of the used fuel, making the final repository more volume efficient, [7,8] and will decrease the long-term radiotoxicity of the used fuel.[3,9,10]

Several different separation processes for long-lived actinide recovery have been developed over the years. [11–13] In this study, the process known as the Grouped ActiNide EXtraction (GANEX) process has been investigated. The aim of the GANEX process is to simultaneously remove all the actinides from the dissolved used nuclear fuel.[14] This renders a possible single process for separation of the actinides from both the lanthanides and the rest of the fission and corrosion/activation products.

The basic concept of a GANEX process is a grouped extraction where all the actinides together are separated from the fission products and corrosion/activation products. A typical GANEX process
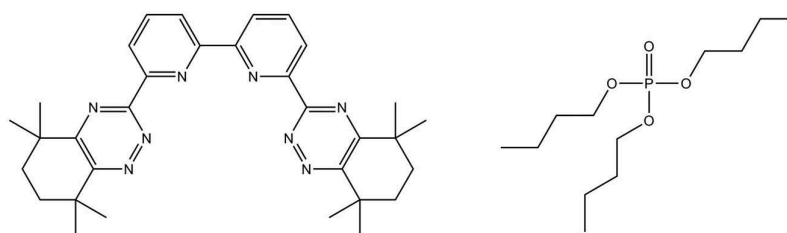
Figure 1. Molecular structure: left, 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2′]bipyridine (CyMe$_4$-BTBP); right, tri-butyl phosphate (TPB).
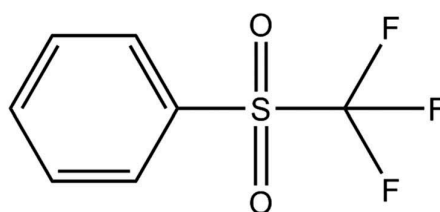
Figure 2. Molecular structure of phenyl trifluoromethyl sulfone (FS-13).

involves two successive steps. The first step is where the bulk uranium is removed, [15] and the second step is where the transuranium elements (TRUs) are removed.[16,17] At Chalmers University of Technology, a GANEX process that uses the concept of combining two well-known extractants with a diluent has been developed. This enables the utilization of the specific properties of both extracting agents. The chosen ligands are 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),[18,19] designed to extract tri-butyl and pentavalent actinides without extracting trivalent lanthanides,[20] and tri-butyl phosphate (TBP) (Figure 1), which is mainly for extracting tetra- and hexavalent actinides.[21] Combining these two extracting agents enables the necessity of redox control to be avoided, and it is possible to strip the actinides selectively or to reuse them directly in a homogeneous recycling.

Over the years, many different chemicals have been investigated for use as diluents in the Chalmers GANEX system.[22–24], Lofstrom-Engdahl2014a. Owing to various issues, these chemicals have been shown not to be suitable, and there is hence a need to investigate alternative chemicals as substitutes. In this work, phenyl trifluoromethyl sulfone (FS-13) has been investigated as a GANEX diluent, as shown in Figure 2. FS-13 was originally developed as a diluent in the UNiversal EXtraction (UNEX) process and has a good stability against nitric acid and high resistance against radiation. [25,26] Other properties indicating that FS-13 could be a good GANEX diluent are a low viscosity, a high density of $1.4 \text{ g} \cdot \text{mL}^{-1}$ [27] (making the organic phase heavier than the aqueous), the polarity of the molecule, and a good chemical stability.

Experimental methods

The experiments within this work have mainly been performed using the same composition of the organic phase, 10 mM CyMe$_4$-BTBP (synthesized in house according to Foreman et al. [18]), 30%$_{vol}$ TBP (Sigma-Aldrich, 97%), and 70%$_{vol}$ FS-13 (CarboSynth, $\geq$ 99% or Marshallton, $\geq$ 99%). An aqueous phase consisting of 4 M HNO$_3$ (Sigma Aldrich, $\geq$ 69% diluted with MilliQ-water, $>$18 MΩ) has been used in all cases.

All solvent extraction experiments within this work have been conducted in similar ways, unless otherwise stated, using freshly prepared solvent batches and separate samples for each actinide. All experiments were performed in triplicate. The uncertainties are, in all cases, calculated as standard deviations from triplicate samples.

For phase contact, 3.5 mL glass vials with plastic lids have been used. All samples contained equal amounts of organic and aqueous phases, 300–1000 μL. Trace amounts of the actinides and europium were added to the samples from stock solutions: U(VI)-235 (84.44% enrichment, 40 mM), Np((V, IV)-239 (extracted from an Am-243-loaded silica column), Pu(IV)-238 (0.28 MBq mL^{-1}), Am(III)-241 (0.42 MBq mL^{-1}), Cm(III)-244 (0.23 MBq mL^{-1}), and Eu(III)-152 (23 kBq mL^{-1}). Americium and europium were in most cases investigated together, i.e. added to the same samples. The other actinides were investigated separately. The fission product experiments were performed using inactive metal solutions of the corresponding elements, as listed in Table 1. Concentrations were chosen to represent fission products present in a PUREX feed. Phase contact was, in all cases, facilitated in a mechanical shaker (IKA, VIBRAX VXR 1,500 rpm) at 25°C for a duration of 1 h, unless otherwise stated.

Analysis

The samples containing both americium-241 and europium-152 were measured using a high-purity germanium detector (HPGe)(Canberra, Gamma Analyst GEM 23195, or Ortec, GEM 15180-S), using gamma energies of 59.5 keV and 121.8 keV, respectively. All samples containing plutonium-238, uranium-235, neptunium-239, americium-241, or curium-244, separately, were measured using a liquid scintillation counting (LSC) detector (Wallac, 1414 WinSpectral). Experiments to examine possible quenching of the samples have been performed. No quenching using FS-13 has been observed within the concentration range studied. All samples containing both americium-241 and curium-244 were measured using an alpha spectrometer (Ortec, Alpha Duo, Octête TM PC) using alpha energies of 5.5 MeV and 5.8 MeV, respectively. The inactive metals were measured on an inductively coupled plasma mass spectrometer (ICP-MS)(Perkin Elmer Elan 6100 DRC). Only the aqueous phase can be measured on the ICP-MS used, and the metal extraction was hence determined by measuring the aqueous phase prior to and after the phase contact. Each sample was

Table 1. Inactive metals used to simulate fission product extraction.

Compound	Supplier	Purity	PUREX feed Concentration (mg L^{-1})
Sr(NO$_3$)$_2$	Sigma-Aldrich	$\geq$ 99.0%	280
Y(NO$_3$)$_3$ $\times$ 4 H$_2$O	Fluka	> 99%	155
ZrO$_2$	Aldrich	> 99%	1 245
MoO$_3$	Aldrich	> 99%	1 185
Pd(NO$_3$)$_2$ $\times$ 2 H$_2$O	Fluka	Purum > 97%	520
AgNO$_3$	May & Baker	Pro analysis > 99.9%	30
Cd(NO$_3$)$_2$ $\times$ 4 H$_2$O	Sigma-Aldrich	Puriss p.a $\geq$ 99.0%	35
SnO$_2$	Riedel-deHaën	> 99%	20
Sb$_2$O$_3$	Aldrich	> 99%	5
TeO$_2$	Aldrich	> 99.9%	170
CsCl	Aldrich	> 99.9995%	1 265
Ba(NO$_3$)$_2$	Merck	Puriss p.a $\geq$ 99%	595
La(NO$_3$)$_3$ $\times$ 6 H$_2$O	Fluka	Puriss p.a $\geq$ 99%	425
Ce(NO$_3$)$_3$ $\times$ 6 H$_2$O	Fluka	Puriss p.a $\geq$ 99%	830
Pr(NO$_3$)$_3$ $\times$ 6 H$_2$O	Aldrich	> 99.9%	390
Nd(NO$_3$)$_3$ $\times$ 6 H$_2$O	Aldrich	> 99.9%	1 420
Sm(NO$_3$)$_3$ $\times$ 6 H$_2$O	Aldrich	> 99.9%	280
Eu(NO$_3$)$_3$ $\times$ 5 H$_2$O	Aldrich	> 99.9%	55
Gd$_2$O$_3$	Aldrich	> 99.9%	40

measured until the measurement uncertainty was below 5%. No differences in the efficacy between the different detectors were observed.

Analytical HPLC was used to determine the remaining amount of CyMe$_4$-BTBP in the samples after both radiolysis and aging. The measurement system used consisted of a Merck-Hitachi HPLC system (LaChrom 7000 series) equipped with a Pump L7100, a DAD 7450 detector, an Intelligent Injector L7250, and an interface. Chromatographic conditions were as follows: column, Merck Purospher STAR RP-C 8e Endcaped (5 μm, 250 × 2 mm I.D.); mobile phase, Solvent A: 80 mM aqueous triethylamine acetate (TEAA, pH 8.2) and Solvent B: CH$_3$CN; isocratic elution with mixing, A: 22%, B: 78%; flow rate, 0.3 mL/min; detection, DAD (220–350 nm); and selected wavelength, 235 nm. The samples with a volume of 25 μL were syringed twice into two different vials, and the volume was adjusted to 1.0 mL by adding acetonitrile. The injection volumes were 3 μL. The data represent mean values from six injections made from two vials of each sample. The calibration curve was constructed using the nonirradiated reference sample with a concentration of 10 mM CyMe$_4$-BTBP (aged under the same conditions as the irradiated samples) and data from four to five injections of volumes between 1 and 10 μL. The calibration curve has a linear fit over the whole range of R^2= 0.9969.

Mass spectrometry (Thermo-Finnigan Fleet Ion Trap Instrument) with atmospheric pressure chemical ionization (APCI) in positive mode was used to identify the decomposition products in the samples after irradiation. All the samples and their corresponding reference solution were stored in a freezer at −33°C, both before and after analyses. Then, 25 μL of each sample was diluted to a volume of 1.0 mL by adding acetonitrile. Infusion from the syringe into an ion source was used. Experimental conditions for the MS interface were as follows: flow rate from a syringe infusion pump, 10 μL/min; sheath gas flow, 20 L/min; auxiliary gas flow, 9 L/min; source voltage, 4.17 kV; vaporizer temperature, 400°C; capillary temperature, 250°C; capillary voltage, 3 V; mass range from 50 to 1000 mass units; and [M + H]$^+$ peaks were observed.

During the Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) measurements, Cm(III) (10^{-7} M) was extracted from 4 M HNO$_3$ into organic phases composed of 10 mM CyMe$_4$-BTBP in (a) 100%$_{vol}$ FS-13 or (b) 70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP. Phase contacting time was 1 h or 4 h. The separated organic phase was transferred into a quartz cuvette (1 cm path length) and measured (T = 25°C). TRLFS studies were performed using a Nd:YAG laser-pumped (Continuum Surelite Laser) dye laser system (NARROWscan D-R Dye Laser) with a repetition rate of 10 Hz. Cm(III) was excited using a wavelength of λ = 396.6 nm. Following spectral decomposition by a spectrograph (Shamrock 303i, 1199 lines mm^{-1}), the spectra were recorded by an Intensified Charge-Coupled Devices (ICCD) camera (iStar Gen III, ANDOR) with an integrated delay controller. The fluorescence signal was detected after a delay time of 1 μs to discriminate scattering light and short-lived fluorescence of organic compounds.

Results and discussion

Kinetics of actinides and europium (representing the lanthanides) extraction were investigated to evaluate the time it takes for the system to reach equilibrium compared to other systems using the same equipment, as shown in Figure 3.

Uranium and plutonium extract quickly and reach equilibrium more or less instantly. Neptunium extraction however decreases between 5 and 20 min, which might be due to a shift in the dominating oxidation state of neptunium. Neptunium is easily oxidized and reduced by the acidic conditions in this experiment and is most likely present in mixed oxidation states. [28,29] Americium and curium extraction reach equilibrium after 20 min and show a significant increase in the distribution ratio increase between 5 and 20 min. Europium is not extracted to any greater extent and has similar kinetics to americium and curium. Hence, all actinides and europium reached equilibrium after
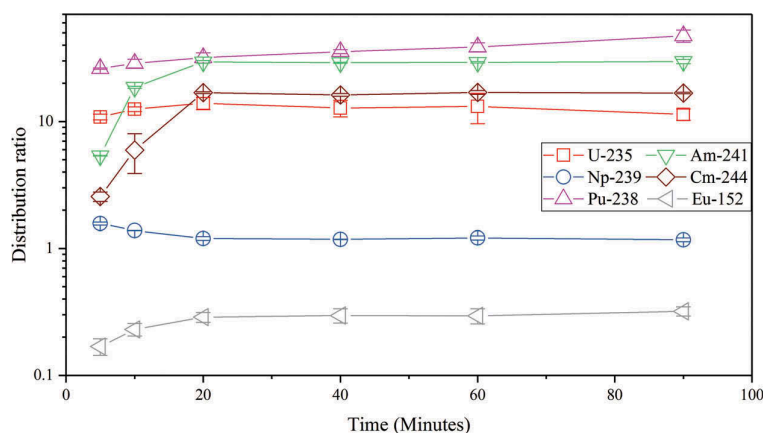
Figure 3. Distribution ratios over time for uranium, neptunium, plutonium, americium, curium, and europium in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ (lines added to guide the eye).

Table 2. Distribution ratios for selected actinides and europium, as well as separation factors for selected actinides over europium in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase.

	U	Np	Pu	Am	Cm	Eu
D_{Eq}	13 ± 2	1.2 ± 0.05	39 ± 3	29 ± 0.3	17 ± 0.6	0.3 ± 0.04
SF_{Eq}	44 ± 6	4.1 ± 0.5	120 ± 18	84 ± 4	56 ± 6	–

20 min, which is fast compared to other GANEX systems with CyMe$_4$-BTBP as an extracting agent, using the same equipment. [30]

The results in Figure 3 also provide information about the metal equilibrium distribution in the two phases, as listed in Table 2. The system has high distribution ratios for plutonium and americium, slightly lower ratios for uranium and curium, and a ratio well below one for europium. Comparing these distribution ratios with previously investigated GANEX systems using other diluents, it is found that the values are found to be in a similar order of magnitude. [30–32] Desirable distribution ratios should render a high metal extraction, while still maintaining a feasible actinide stripping. Neptunium has a rather low distribution ratio, and therefore further investigations are needed to successfully extract neptunium together with the other actinides in this system.

Separation factors were calculated for evaluation of the actinide extraction in comparison to europium, used as a reference for the lanthanides, as listed in Table 2. The only actinide with a low separation factor toward europium is neptunium. The separation factor is high enough, however, to enable separation. Americium/curium separation can also be desirable in certain suggested reprocessing options, such as the Amine Extraction (AmEX) process.[33] The separation factor between americium and curium is, however, small (1.5 ± 0.2), in agreement with the selectivity observed in an octanol diluent.[19] This indicates that americium and curium may be hard to separate from each other.

It is important to understand the behavior of the ingoing components in the extraction system in order to predict their future behavior in a process. A previously published study has shown that the combination of TBP and CyMe$_4$-BTBP is beneficial for both americium and curium extraction using FS-13 as the diluent[34]. The distribution ratios of americium and curium reach 0.05 and 0.4, respectively, after 1 h of phase contacting in both the systems containing only one of the two extracting agents (70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP or 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP). In the system containing both extracting agents (70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP) americium and curium, however, reach distribution ratios of 25 and 17, respectively, as shown in Figure 4.
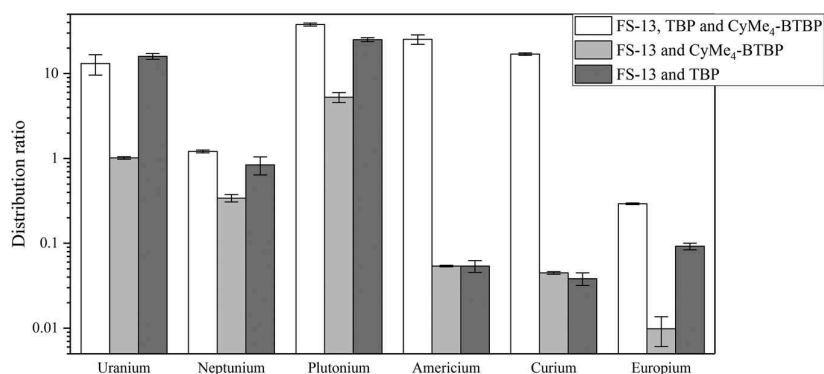
Figure 4. Distribution ratios of actinides and europium using A: 70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP; B: 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP; and C: 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP as the organic phase and 4 M HNO$_3$ as the aqueous phase. Data retrieved from Halleröd et al. [34].
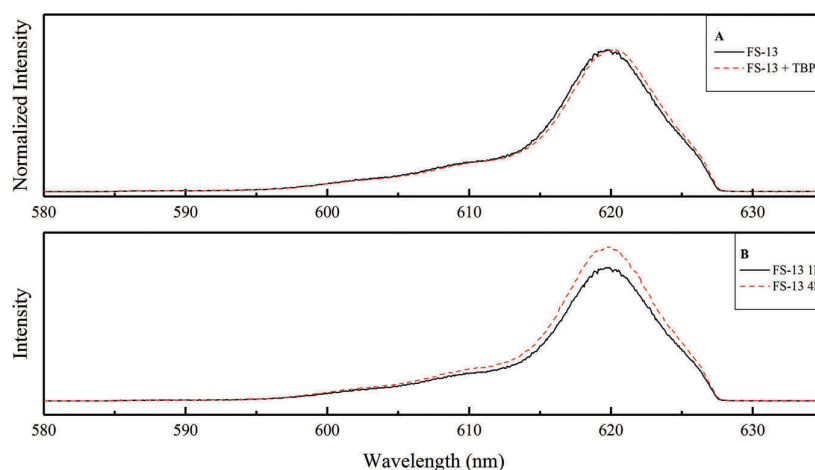
Figure 5. Graph A: normalized fluorescence spectrum of Cm(III)-CyMe$_4$-BTBP complexes in the organic phase using 100%$_{vol}$ FS-13 or 70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP and 4 M HNO$_3$ as the aqueous phase. Graph B: fluorescence spectra of Cm(III)-CyMe$_4$-BTBP-complexes in the organic phase using 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP and 4 M HNO$_3$ as aqueous phase after 1 h and 4 h phase contacting.

TRLFS experiments were performed to confirm the extraction of trivalent actinides as 1:2 complexes. Cm(III) was extracted from 4 M HNO$_3$ into 10 mM CyMe$_4$-BTBP in 100%$_{vol}$ FS-13 or 10 mM CyMe$_4$-BTBP in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP. Organic-phase samples were investigated by TRLFS. Similar emission spectra were found in both cases (Figure 5A), showing an emission maximum at a wavelength of 620 nm. The spectra match the spectrum of the [Cm(CyMe$_4$-BTBP)$_2$(NO$_3$)]$^{2+}$ complex in octanol.[35]

Thus, trivalent actinides seem to be extracted by CyMe$_4$-BTBP in both systems despite the results shown in Figure 4.[34] Further time-resolved investigations of the system containing 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP were performed with varied phase contact times (1 h and 4 h). The fluorescence emission spectra (Figure 5B) show emission intensity increasing with time, indicating slow extraction kinetics.

Owing to the TRLFS results in Figure 5B, a long-term extraction kinetics study of the system containing 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP was performed, as shown in Figure 6. The
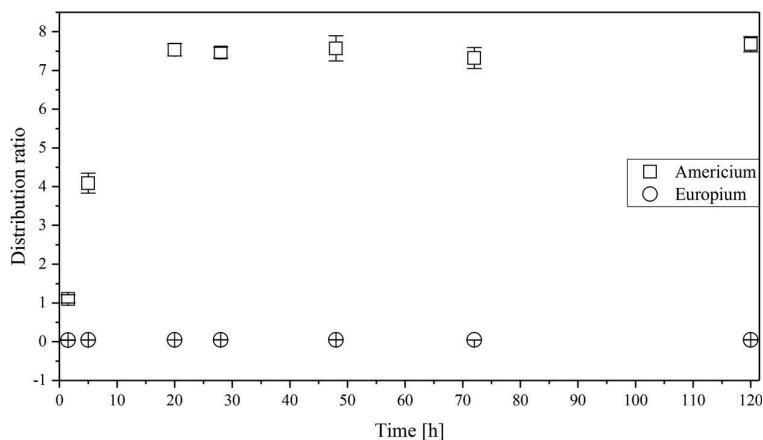
Figure 6. Long-term distribution ratios for americium and europium in 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase.

extraction of europium seems to be stable throughout the experiment, with a distribution ratio of 0.05, whereas the extraction of americium slowly increases over time. Americium extraction equilibrium is reached after approximately 20 h with a final distribution ratio of 7.5. This is slow compared to the system consisting of 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP: americium extraction equilibrium is reached after 20 min, with a distribution ratio of 29, as shown in Figure 3. Hence, the presence of TBP strongly affects the minor actinide extraction kinetics by CyMe$_4$-BTBP in FS-13 and also influences the corresponding equilibrium distribution ratio in a positive way. This indicates that TBP acts as a phase transfer catalyst. Similar behaviors have also been obtained when adding diMethyldiOctyl-hexaethoxy-malonamide (DMDOHEMA)[19] or N, N, N', N'-tetraoctyldiglycolamide (TODGA).[36,37]

To be able to compare the complexation data retrieved for curium and CyMe$_4$-BTBP by TRLFS with other metals, the complexation between CyMe$_4$-BTBP and plutonium, americium, curium, and europium was investigated by extraction slope analysis using various concentrations of CyMe$_4$-

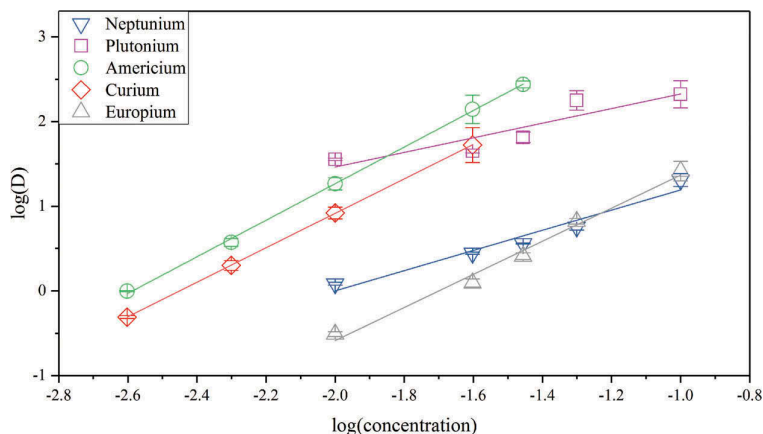**Figure 7.** Distribution ratios as a function of CyMe$_4$-BTBP concentration for the extraction of plutonium, americium, and europium in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase.

BTBP, as shown in Figure 7. The results for the trivalent metals, americium, curium and europium, correspond well with the curium results obtained by TRLFS (2.16 $\pm$ 0.04, 2.03 $\pm$ 0.01, and 1.96 $\pm$ 0.12, respectively), indicating a 2:1 complexation between $CyMe_4$-BTBP and all three metals. The complexation between $CyMe_4$-BTBP and plutonium (0.86 $\pm$ 0.22), on the contrary, indicates a 1:1 relation. It should be noted, however, that plutonium (IV) in FS-13 is also extracted by TBP, as previously shown in Figure 4. The influence of TBP in the system, however, has to be investigated further.

After concluding that the actinide extraction and lanthanide separation of the GANEX system using FS-13 as diluent is satisfactory, the stability properties of the system had to be investigated. The extraction of americium and europium in the system consisting of 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM $CyMe_4$-BTBP has previously been found to be stable during both radiolysis and hydrolysis.[38] In this work, however, HPLC measurements of the irradiated organic phase show that the $CyMe_4$-BTBP concentration decreases with an increasing dose, as listed in Table 3. With increased dose, the HPLC chromatograms show that when the $CyMe_4$-BTBP amount decreases, two other peaks increase correspondingly. These observed peaks (m/z = 551.33 and 567.25) have, by complementary MS measurements, showed the presence of two main degradation products, which could be assigned to two compositions corresponding to the hydroxyderivatives of BTBP, (HO)-$CyMe_4$-BTBP and (HO)$_2$-$CyMe_4$-BTBP. The most likely position of the hydroxyl group(s) is on the pyridine ring of the BTBP. Although after 200 kGy none of the $CyMe_4$-BTBP remains, the extraction ability of the system is, as previously mentioned, maintained. This indicates that the new molecules have similar extraction and complexation properties to $CyMe_4$-BTBP.

During the hydrolysis studies, shown in Table 4, no decrease in the amount of $CyMe_4$-BTBP could be observed. Although the measurements at weeks 4 and 5 could not be accurately measured due to small sample sizes, it is reasonable to believe that the $CyMe_4$-BTBP concentration is constant during the entire investigated time interval. This is likely as no apparent decrease in the $CyMe_4$-BTBP concentration can be observed between week 2 and week 6.

Temperature changes might occur during the separation and transmutation process, both due to heat released during the phase contacting and from irradiation. This could have an effect on the performance of the process, in terms of for example precipitation of the extracting agent and/or the complexed metal, and must therefore be investigated. Due to this, the metal extraction within a temperature interval between 20°C and 40°C has been investigated, as shown in Figure 8. Within

Table 3. $CyMe_4$-BTBP stability during irradiation using 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM $CyMe_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

Dose [kGy]	c [mmol L^{-1}]	%	± (%)
0	10.0	100	3.3
50	3.7	37	1.8
100	0.27	2.7	3.8
200	0.00	0.0	0.0
500	0.07	0.7	2.2

Table 4. $CyMe_4$-BTBP stability over 7 weeks at room temperature (20–22°C) using 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM $CyMe_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

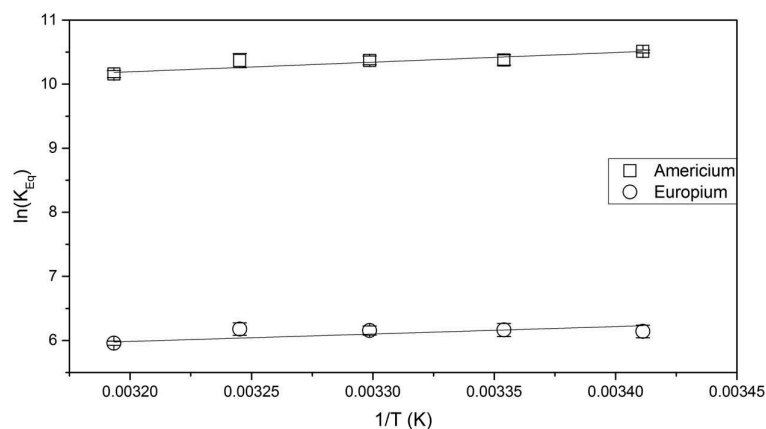| Age [weeks]	c [mmol L^{-1}]	%	± (%)
0	10.0	100	3.3
1	9.3	93	2.9
2	9.5	95	1.6
3	10.0	100	0.2
6	9.7	97	4.5
7	9.7	97	1.9

Figure 8. The logarithm of the extraction equilibrium constant vs. 1/T. Using 77%$_{wt}$ FS-13, 23%$_{wt}$ TBP, and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase.

the temperature interval, it is not likely for the extraction reaction and speciation to change.[39] A slight decrease with an increasing temperature is observed for the extraction of both americium and europium, indicating that the extraction reaction is exothermic. Similar slopes indicate selectively is maintained at higher temperatures.

Presuming that enthalpy and entropy are constant for the investigated temperature interval, ΔH^0 and ΔS^0 for the extraction of americium and europium can be calculated from the data points in Figure 8. This is carried out by performing a linear regression where the van't Hoff equation, Eq. 1, states that $-\Delta H^0/R$ represents the slope and $\Delta S^0/R$ represents the intercept of the linear fit.

$$ln(K_{Eq}) = \frac{-\Delta H^0}{R \times T} + \frac{\Delta S^0}{R} \qquad (1)$$

where K_{Eq} is the extraction equilibrium constant, T is the temperature, and R is the ideal gas constant.

The calculated enthalpy is negative, whereas the entropy is positive for both americium and europium (Table 5). Extraction is driven by both enthalpy and entropy. Similar results have been found for other GANEX systems studied using different diluents.[40,41]

During a GANEX process, high extraction of the actinides alongside a low extraction of the fission products is desirable. In this study, inactive metals have been used as references for the actual fission products, and for a majority of the investigated fission products, a distribution ratio below 1 has been found (Figure 9). Some of the fission product distribution ratios are, however, higher or close to 1 and might become a problem in a future process. The fission products with the highest distribution ratios are cadmium and silver, for which the abundance in the used fuel, however, is lower than 100 ppm. These unwanted metals can, despite this, be a problem in a future process if they cannot be scrubbed out. One metal with higher abundance (above 1000 ppm) in the used fuel is zirconium. Even if the distribution ratio remains below one, the high concentration can still cause problems. The distribution ratio of

Table 5. Enthalpy and entropy of complexation for the extraction of americium and europium using 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase.

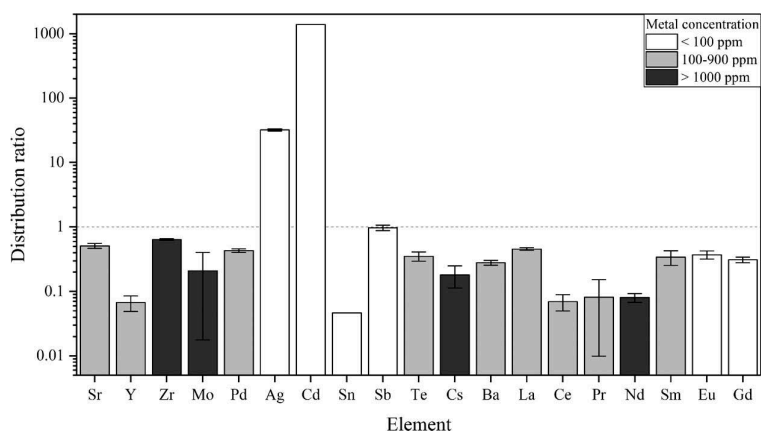|	ΔH^0 [kJ mol^{-1}]	ΔS^0 [J mol^{-1} K^{-1}]
Americium	− 12.5 ± 0.4	44.6 ± 1.2
Europium	− 9.7 ± 0.8	18.5 ± 2.8

Figure 9. Distribution ratios of selected fission products in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO$_3$ as aqueous phase. White bars correspond to a metal concentration below 100 ppm in the dissolved used fuel. Gray bars correspond to a metal concentration between 100 and 900 ppm in the dissolved used fuel. Black bars correspond to a metal concentration above 1000 ppm in the dissolved used fuel. The dashed line marks D = 1, which is the dividing line between extraction and strip.

europium is high compared to other lanthanides present with a high abundance in the used fuel. Further studies into the decreasing extraction of fission products through possible suppression agents and stripping steps are therefore needed. Similar fission product behavior has been observed in another GANEX system with CyMe$_4$-BTBP and TBP in cyclohexanone.[22] Comparing the inactive europium (Figure 9) with the active europium (Figure 3), distribution ratios of around 0.3 are found in both cases, indicating that the inactive metals can be used as substitutes for the active fission products.

Conclusions

A solvent extraction system containing 10 mM CyMe$_4$-BTBP and 30%$_{vol}$ TBP in 70%$_{vol}$ FS-13, intended for use within separation for transmutation, has been investigated with regard to actinide extraction kinetics, complex formation properties, radiolysis behavior, thermodynamic properties, and fission product extraction, with promising results.

All investigated actinides and europium reached full extraction after 20 min, which is comparably fast for a solvent containing 10 mM CyMe$_4$-BTBP. As expected, americium and curium have similar extraction kinetics, indicating that they are extracted by the same ligand, CyMe$_4$-BTBP. Uranium and plutonium, however, display faster extraction kinetics, indicating that they are not extracted by the same ligand as americium and curium but predominantly by TBP. Neptunium is most likely extracted by both ligands. High separation factors can be achieved between the actinides and europium in all cases except for neptunium. The low equilibrium distribution ratio for neptunium and the low separation factor between neptunium and europium might cause problems in a future process.

A previous study investigating various combinations of FS-13 and the two extracting agents has shown that the combination of TBP and CyMe$_4$-BTBP extracts the minor trivalent actinides, whereas neither of the extracting agents seems to extract the minor trivalent actinides on their own. TRLFS studies investigating the complexation between CyMe$_4$-BTBP and curium showed the formation of a 2:1 complex, both in 100%$_{vol}$ FS-13 and in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP, indicating that the trivalent actinides are indeed extracted by CyMe$_4$-BTBP. TRLFS also indicated that this complex formation was very slow. Extended-duration kinetic extraction studies of CyMe$_4$-BTBP and americium in 100% FS-13 confirmed these results, with extraction equilibrium reached after 20 h. The equilibrium distribution ratio is however lower than with TBP present in the extraction system. Supplementary

slope analysis also shows that americium and europium form a 2:1 complex with CyMe$_4$-BTBP in FS-13, whereas plutonium forms a 1:1 complex.

Previous radiolysis stability studies have shown that the extraction of americium and europium by CyMe$_4$-BTBP and TBP in FS-13 is unaffected up to at least 500 kGy. Analysis of the irradiated solutions now shows that after 200 kGy, despite maintained distribution ratios, all of the CyMe$_4$-BTBP present reacted and formed (HO)-CyMe$_4$-BTBP and (HO)$_2$-CyMe$_4$-BTBP.

Studies investigating the temperature dependence of americium and europium extraction show a slight decrease in the distribution ratios for both elements with increasing temperature, indicating an exothermic extraction reaction. Enthalpy and entropy calculations for the extraction of americium and europium show that the enthalpy is negative in both cases, whereas the entropy is positive. This increase of entropy during the extraction acts together with the enthalpy as a thermodynamic driving force for the reaction.

The extraction of selected fission products in the system is low, with a distribution ratio below 1 for most metals. A few elements, such as silver, cadmium, zirconium, and molybdenum, could however cause problems in a future process and require further investigations.

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1 # Title page

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17

18 # A comparison on the use of DEHBA or TBP as extracting

19 # agent for tetra- and hexavalent actinides in the

20 # CHALMEX Process

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28 The Chalmers Grouped ActiNide EXtraction (CHALMEX) process is a solvent extraction

29 process for the homogeneous recycling of spent nuclear fuel. The use of TBP for the extraction

30 of tetra- and hexavalent actinides can be problematic for several reasons, including troublesome

31 degradation products causing crud formation, decreased extraction yield and the possibility of

32 explosive red oil reactions. Here, the substitution of TBP by a N,N-dialkyl monoamide,

33 DEHBA, is investigated. The findings suggest that DEHBA can be a suitable extracting agent

34 for use in the CHALMEX solvent, although identified drawbacks needs to be further

35 investigated.

36 ## Keywords

37 GANEX, CHALMEX, DEHBA, SPENT NUCLEAR FUEL RECYCLING

38 ## Introduction

39 The recovery of tetra- and hexavalent actinides, predominantly uranium and plutonium, from

40 irradiated nuclear fuel using the extractant tri-*n*-butyl phosphate (TBP) has been done on an

41 industrial scale at since the early 1950's.[1, 2] TBP's high affinity and loading capacity for

42 U(VI) and Pu(IV) made it the benchmark molecule for the separation of uranium and plutonium

43   from fission products in the *P*lutonium *U*ranium *R*eduction *Ex*traction (PUREX) process.[1, 3,

44   4] The molecule's structure can be seen in Figure 1 a). TBP has a high resistance towards both

45   radiolysis and hydrolysis. Its degradation products are primarily mono-butyl phosphate and

46   dibutyl phosphate, and other less abundant degradation products. They are known to cause both

47   red oil reactions and promote crud formation. Both aspects can have serious implications in

48   reprocessing plants.[5-9] Furthermore, the presence of phosphor in the molecule is often

49   referred to as being problematic in modern processes, in which the aim is typically to develop

50   CHON-abiding processes. Adhering to the CHON-principle (only molecules containing C, H,

51   O and N) allows for complete incineration of the final, spent solvent, thus minimizing the

52   volume of the final waste.[10] However, the Chalmers GANEX (CHALMEX) diluent, phenyl

53   trifluoromethyl sulfone (FS-13), which is seen in Figure 1 b), is both fluorinated and sulfonated.

54   Here, solidifying the final organic waste has been suggested as a treatment option.[11]

55

a)   b)
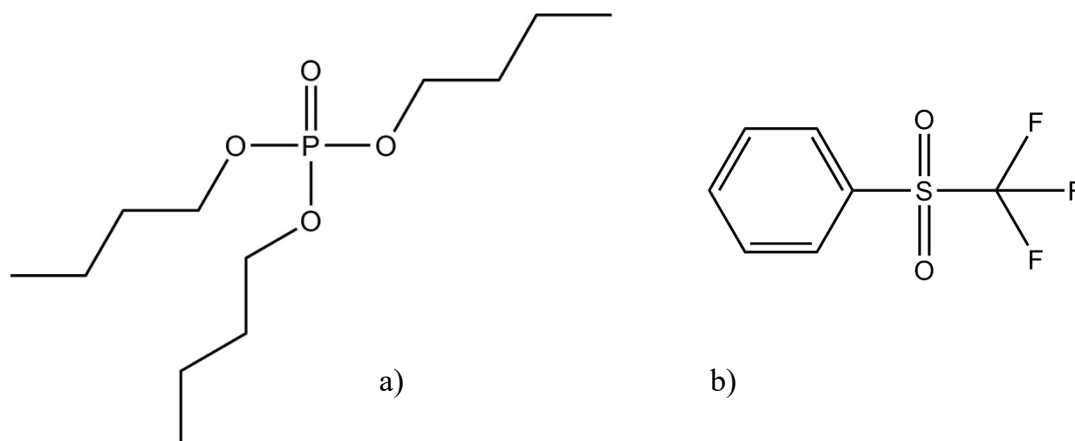
56
57   **Fig. 1** The molecular structure of a) tri-n-butyl phosphate (TBP) and b) phenyl trifluoro methyl

58   sulfone (FS-13).

59   Possible alternatives to TBP as an extracting agent have received a lot of research efforts in the

60   past decades. A promising group of extractants include the N,N-dialkyl monoamides, and

61   especially the monoamide N,N-di-(2-ethylhexyl)butyramide (DEHBA), as seen in Figure

62   2.[12-16] Not only has the monoamide class of extractants been shown to be comparable or

63   better than TBP in terms of U(VI) and Pu(IV) separation from the fission products, they also

64   have comparable radiolytic stability, compared to TBP.[17-23] One additional benefit of the

65   N,N-dialkyl monoamide extractants are the less problematic degradation products. While TBP

66   does not extract the lanthanides to any significant extent in the CHALMEX system, DEHBA

67 yields D-ratios>1 for both Sm and Eu. Similar trends are seen for the corrosion products, where

68 DEHBA consistently yielded higher D-ratios than TBP. Especially for Co and Mn, the D-ratios
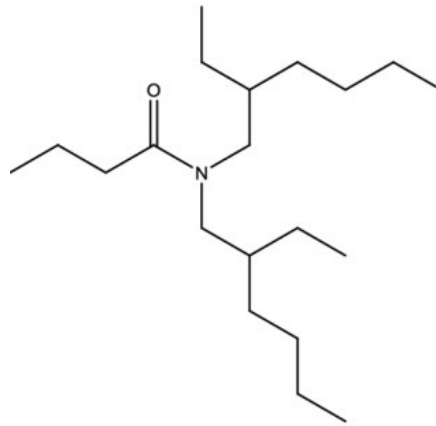
69 were >1. For the fission product extraction however, DEHBA yields lower D- ratios than TBP

70 for all the fission products with D>1 (Mo, Pd, Ag, Cd and Sb), except for Zr.[24]

71 **Fig. 2** The molecular structure of N,N-di-(2-ethylhexyl)butyramide (DEHBA).

72 GANEX 1st cycle has been proven to recover more than 99.99% of the uranium, and so the

73 main focus in this work is the ability of DEHBA to recover plutonium.[25, 26]

Theory

75 The surface tension is a measure of the force required to form a surface on a liquid. Since liquid

76 molecules at the surface are surrounded by fewer liquid molecules than the bulk liquid

77 molecules, the surface molecules interact with each other to a higher extent than in the bulk

78 liquid. Interfacial tension is practically the same force as surface tension, but between two

79 liquids rather than between a liquid and air as for surface tension.

80 Both surface tension and density are important parameters to consider in solvent extraction as

81 they play an important role in the formation and size of droplets. Generally, the smaller the

82 droplet, the greater the surface area of contact between the two liquids and also the greater the

83 mass transfer rate, at least up to a certain point. At one point the droplet size becomes so small

84 that the droplets starts behaving more like individual spheres and the rate of mass transfer will

85 start to decrease again.[27]

86   Density is an important parameter for the coalescence and separation of the organic and the

87   aqueous phase. A sufficiently different density in a two-phase system will cause the two phases

88   to spontaneously separate into two distinct layers. For systems with too similar densities

89   between the phases, different phenomena can occur: phases can be "layered" vertically, i.e.

90   side by side, or formation of a three-phase system can happen. In the latter you'll see parts of

91   the heavy phase layered over the aqueous phase. It is also important to keep in mind that in

92   solvent extraction processes in which the metal content is high, the density of the organic phase

93   will increase as extraction proceeds, while it will decrease for the aqueous phase. In systems

94   with a heavier aqueous phase and lighter organic phase, the density difference will thus

95   decrease.[28]

96   Surface active agents (surfactants) are molecules with a polar- and non-polar part, or

97   hydrophobic and hydrophilic respectively. In a solvent extraction system, a surfactant can be

98   added to lower the surface tension. The surfactant will then dissolve its hydrophobic part in the

99   organic phase, and its hydrophilic part in the aqueous phase. In systems in which the surfactant

100   is also an extractant, an increase in surfactant/extractant concentration is typically associated

101   with an increased rate of extraction.[29]

Experimental

103   Unless otherwise stated, the DEHBA solvent constitutes 30% v/v DEHBA and 70% v/v FS-

104   13, and the TBP solvent 30% v/v TBP and 70% v/v FS-13, pre-equilibrated with 4 M HNO3.

105   Physical properties of the solvents were measured using a tensiometer (Sigma 700, Attension,

106   using a du Noüy ring). Each measurement was repeated at least twice, and the average

107   measured value is reported here. Surface tension was measured against air, while interfacial

108   tension (IFT) was measured between the solvent and 4 M HNO_3. All measurements were

109   performed at room temperature of 295K.

110   The DEHBA solvent was irradiated using a ^{60}Co gamma-source (Gamma cell 220, Atomic

111   Energy of Canada ltd).To replicate process conditions, the solvent was irradiated aerated and

112   in contact with 4 M HNO_3. After irradiation, the organic phase was used for extractions from

113   4 M HNO_3 immediately after collection.

114   For the acid extraction experiments, equal volumes (500 µL) of the respective organic phases

115   were contacted with an equal volume nitric acid with concentrations ranging from 0.01 to 4

116   M (5 M for the TBP solvent) using an IKA Vibrax VXR, 1500 rpm shaker. The contact time

117   was 15 minutes and the temperature controlled by a thermostatic bath (Grant Instruments,

118   TC120 Heated Circulating Bath) at 298K. Both initial acid concentration and the resulting

119   acid concentration after contacting with the organic phase were titrated at least twice. The

120   organic phase was then contacted with MQ water for 5 minutes, and the MQ water was

121   titrated for mass balance purposes. Errors were taken as the mass balance deviation.

122   Batch solvent extraction was performed always using a phase ratio $\Theta=1$ and a minimum

123   volume of each phase of 400 µL. Contacting was done using an IKA Vibrax VXR, 1500 rpm

124   shaker and thermostatic bath. The radionuclides were added at trace concentrations and all

125   radionuclides were investigated in isolated systems, except for Am and Eu which were

126   investigated together. All data points represent the average of triplicate samples, where the

127   uncertainty is taken as the standard deviation of the series. Unless otherwise stated, the

128   temperature was kept at 298K. Save for the kinetics experiments, the contact time was 1 hour

129   for all the experiments which was enough to reach extraction equilibrium. After contacting,

130   the samples were centrifuged for 5 minutes to ensure complete phase separation.

131   *Analysis*

132   Both ^{238}Pu and ^{237}Np were analysed by taking a 100 µL aliquot of each phase and measuring

133   them using a liquid scintillation counter (LSC, Wallac 1414 WinSpectral). The samples were

134   dissolved in 5 mL Ultima Gold. The aqueous phase of the ^{nat}U-samples was diluted and

135   measured using ICP-MS. 100 µL of each phase of the ^{241}Am/^{152}Eu system was measured on a

136   high purity germanium detector (HPGe).

137   **Results and discussion**

138   The physical properties such as density, surface tension and interfacial tension plays a crucial

139   role in solvent extraction. Here, the mentioned parameters have been measured for various

140   versions of both the DEHBA- and the TBP-solvent, and the results are presented in Table 1.

141   DEHBA has a lower density than TBP, and when diluted in FS-13 the solvent density of the
142   DEHBA solvent showed a lower density than the TBP solvent for the pre-equilibrated system.
143   The density difference is significant with 1.28 g cm-3 for the TBP solvent and 1.12 g cm-3 for
144   the DEHBA solvent, while the density difference is less pronounced for the pristine solvents
145   with 1.26 g cm-3 for the TBP-solvent and 1.20 g cm-3 for the DEHBA solvent. The density of
146   nitric acid is approximately 1.14 g cm-3 at 298K and so the density difference to the pre-
147   equilibrated DEHBA solvent is only 0.02 g cm-3.[30] This can be a source of issues with phase
148   separation under process conditions. Especially considering that metal extraction will cause a
149   density increase of the solvent and a density decrease of the aqueous phase. This may in the
150   worst case even lead to phase inversion, and so further hydrodynamic tests are necessary to
151   determine the suitability of the DEHBA solvent for reprocessing applications.

152   The surface tension of the different solvents appears to be dominated by the extracting agent
153   added. For both solvents, the surface tension is closer in value to that of the pure extractant,
154   rather than to that of the pure diluent. The lower surface tension for FS-13 is somewhat
155   surprising as it is not known to be very surface active despite its polar nature.

156   Interfacial tension (IFT) is perhaps more interesting than the surface tension, as the former
157   shows the force between the solvent and the nitric acid (4 M). In contrast to earlier work
158   reported on DEHBA and TBP in cyclohexanone, the interfacial tension of the TBP solvent is
159   higher than that of the DEHBA solvent, while for n-dodecane it is the other way around. It has
160   previously been shown that DEHBA has a much larger IFT towards nitric acid compared to
161   TBP, which indicates a much higher degree of surface activity for TBP.[16, 31] Here, the
162   higher interfacial tension of the TBP solvent can indicate that the interaction between TBP and
163   FS-13 to some degree prevents the TBP molecule acting like a surfactant, through e.g. micelle
164   formation. Micelle formation is a phenomenon in which the concentration of a surfactant
165   becomes so high that they self-assemble in colloidal aggregates. The lower IFT for the DEHBA
166   solvent also suggests a quicker mass transfer rate compared to the TBP solvent.

167   **Table 1** The density, surface tension and interfacial tension measured for various versions of
168   the DEHBA- and TBP-solvent respectively.

Solvent	Density (g cm^{-3})	Surface tension (mN m^{-1})	IFT (mN m^{-1})

DEHBA	0.837	28.70	-
30%DEHBA+70%FS-13	1.20	27.46	-
30%DEHBA+70%FS-13, pre-equilibrated	1.12	29.19	7.23
TBP	0.971	25.5	-
30%TBP+70%FS-13	1.26[a]	28.5 [a]	
30%TBP+70%FS-13, pre-equilibrated	1.28 [a]	25.8	12.8
FS-13	1.41	22.9	-

169   [a]Values reproduced from Halleröd et al.[32]

170   In earlier published work, it was found that DEHBA extracts acid to the same extent as TBP,

171   although it was mainly attributed to extraction by the diluent cyclohexanone. In later work,

172   acid extraction by TBP was investigated, and found to be relatively high, while no acid is

173   extracted by the current FS-13 diluent.[33] Published results have also found that nitric acid

174   extraction by TBP occurs by both a 1:2 and a 1:1 complex formation for HNO3:TBP.[34, 35]

175   Here we show that the acid extraction by DEHBA is indeed comparable to the acid extraction

176   by TBP, at least at 2 M   [HNO3], as shown in Figure 3. A slope analysis of the log(HNO3) vs

177   log(D(DEHBA)) yields no conclusive dependency with a slope of 0.73 and R2=0.85. This

178   indicates mixed complexes of HNO3-DEHBA. At [HNO3]>2M, extraction is still significant,

179   but the extraction by TBP exceeds that of DEHBA. For both solvents, the acid extraction is a

180   function of the acid concentration, although it appears that the acid extraction of TBP reaches

181   its maximum at 4 M HNO3. This exemplifies that also for the DEHBA solvent, an acid

182   scrubbing step is required in the flow sheet.

183
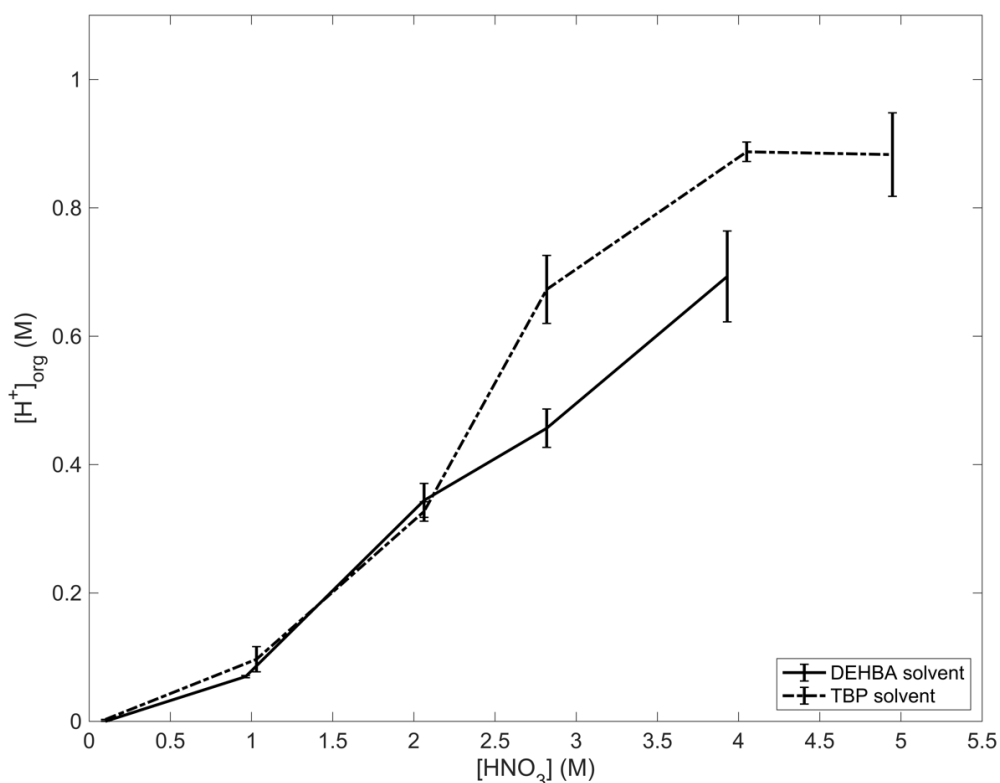
Fig. 3 [H+] extracted by the organic phase versus initial acid concentration. Data points

for TBP solvent at 1, 4 and 5 M HNO3 are reproduced from [33].

Extraction tests were performed for all the actinides of interest, irrespective of expected

oxidation state in the spent nuclear fuel raffinate. The results at equilibrium are presented in

Table 2. As expected none of the trivalent or pentavalent actinides are extracted to any

significant degree, with D-ratios<0.01 for Np(V), Am(III) and Eu(III). It has previously been

found that Np(VI) is extractable with D>1 by DEHBA from nitric acid solutions with nitrate

concentration above 1 M, while D-ratios of Np(V) remained <1 for the nitric acid range

investigated.[36] While the oxidation state of Np(V) was confirmed by UV-VIS for these

experiments, the speciation of Np has been shown to spontaneously distribute between Np(V,

VI). Furthermore, Np is sensitive to both oxidizing and reducing agents (i.e. nitrous acid)

temperature- and acid concentration changes, and so it's speciation is challenging to control

under processing conditions.[37-42] In conclusion, it is expected that the Np oxidation state

will be a mixture of +5 and +6 in spent nuclear fuel raffinate.

For both Pu(IV) and U(VI), distribution ratios are 11 and 9.4, respectively, at equilibrium. This

yields a high separation factor over the lanthanides, here represented by Eu(III). Compared to

200 TBP, the D-ratios are once again comparable. Halleröd et al.[43] reported D(Pu) of

201 approximately 12 and D(U) of approximately 10.5, while D(Am) and D(Eu) were <0.1. The

202 D-ratios of Np cannot be directly compared as Np(V,VI) was used for the extraction by TBP

203 in FS-13.

204 **Table 2** The distribution ratios measured for Pu, U, Np, Am and Eu for the extraction by the

205 DEHBA solvent.

|	Pu(IV)	U(VI)	Np(V)	Am(III)	Eu(III)
D	11.4 ± 0.31	9.41 ± 0.51	$<0.01 \pm <10^{-4}$	$<0.01 \pm <10^{-4}$	$<0.01 \pm <10^{-4}$

206

207 Pu has been shown to form both a 2:1 and a 1:1 complex with TBP. In the CHALMEX FS-13

208 system, the slope of Pu extraction as a function of TBP concentration is 1.27, which could be

209 a product of co-extraction by CyMe4-BTBP or adduct formation with nitric acid.[33] For the

210 DEHBA solvent, the slope of Pu extraction shows a 2:1 complex formation, as seen in Figure

211 4. This agrees with results published earlier. In the same publication, evidence for a 3:1

212 complex was also presented, which is not seen for the CHALMEX system.[44] For uranium, a

213 slope of 1 is seen which suggests a 1:1 complex formation with the DEHBA ligand, while

214 thorough study by Acher et al. showed that uranium is coordinated by two DEHBA molecules

215 and 4 nitrate ions.[44]

216
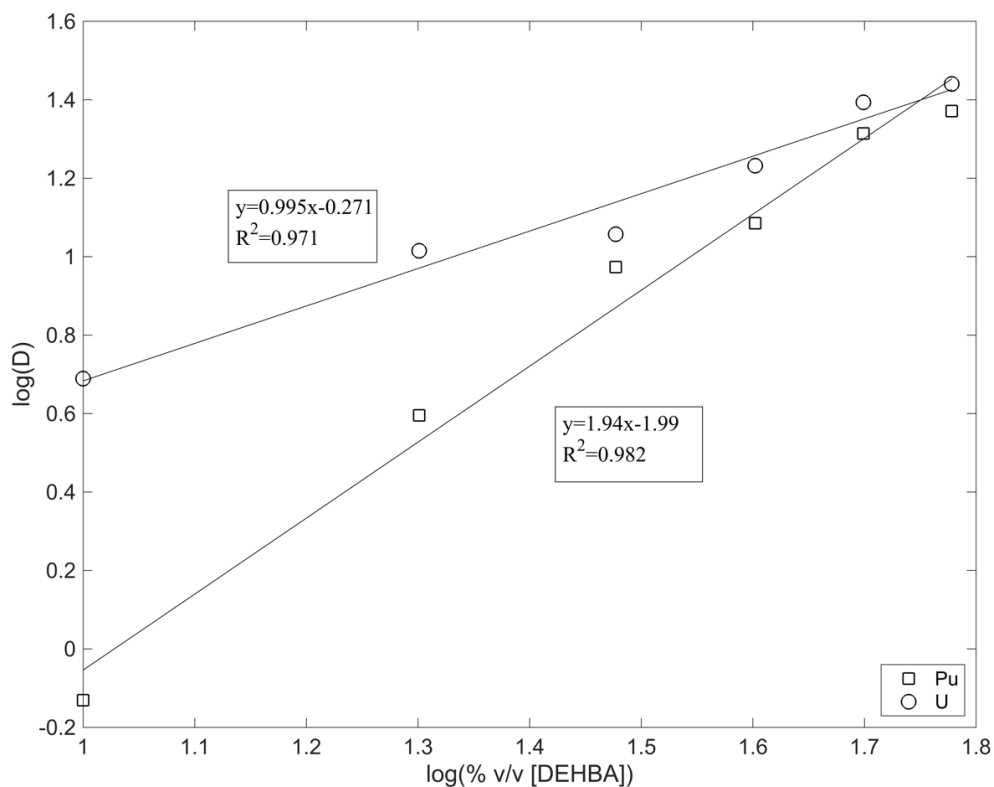
Fig. 4 The distribution ratio (D) of Pu and U as a function of % v/v DEHBA in FS-13. A linear fit to the data points, with equation and R^2, is also displayed.

The nitric acid dependency was also investigated, and the results are presented in Figure 5. As can be seen, the D-ratios increases with increasing nitric acid for both U and Pu. The slope of D(Pu) is steeper (0.994) compared to the slope of D(U) (0.535), suggesting a stronger dependency on the nitrate content of the aqueous solution. The same tests were performed by changing the nitrate concentration only (using NaNO3), which yielded the same slopes for both U and Pu. This confirms that the extraction is dependent on the nitrate concentration, rather than the acid concentration.
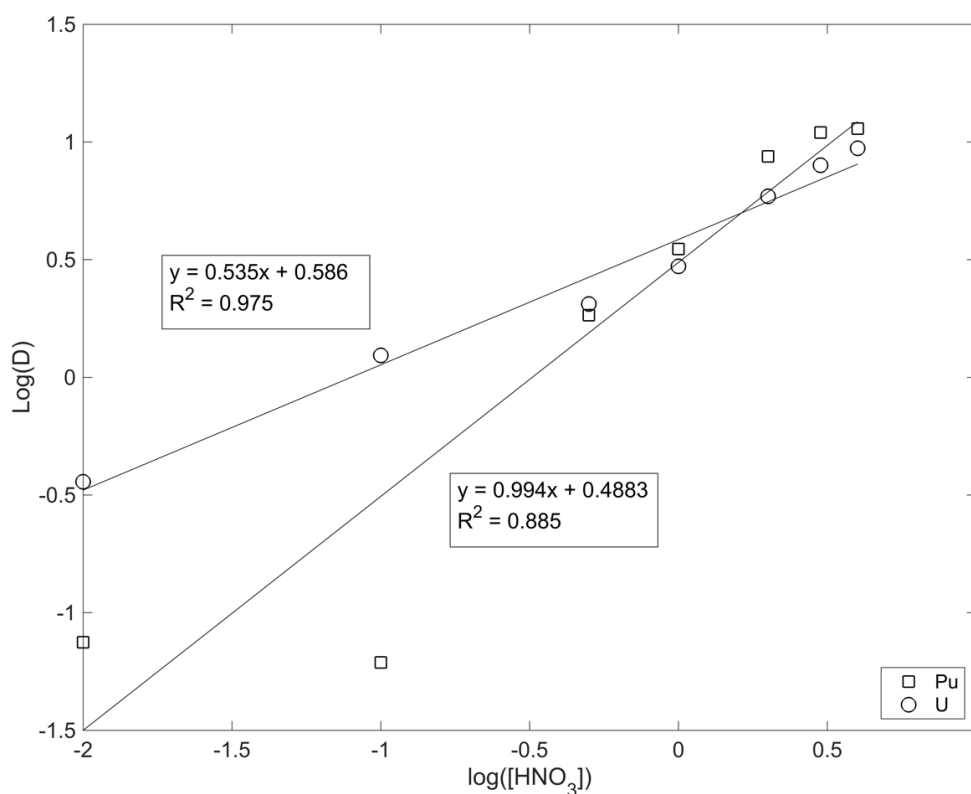
Fig. 5 The log(D) of Pu and U vs. log([HNO₃]), with linear regression lines fitted to the data points. Line equations with R^2 values are also shown.

Earlier studies have shown that the presence of TBP in the solvent more readily promotes the hydrolytic degradation of the BTBP-molecule.[17] For comparison, no BTBP degradation products were detected in the DEHBA solvent for the same conditions and exposure time. Although not relevant for the extraction of the tetra- and hexavalent actinides, the degradation of CyMe4-BTBP led to a significant decrease in both Am and Eu D-ratios. A decrease of Am and Eu D-ratios was seen also for the DEHBA solvent, which was attributed to water soluble DEHBA degradation products acting like masking agents for Am and Eu. For both solvents, a more problematic decrease in Np D-ratios was seen as hydrolysis progressed, mainly due to the low original D(Np).[17]

Similar, though accelerated, trends were seen for the radiolytic stability of the DEHBA solvent, whether it be linked to the loss of extracting agent or the presence of water soluble "complexing agents" (DEHBA degradation products), as shown in Table 3. For Pu, a higher D-ratio than the equilibrium value (Deqm=11.4) is observed for all doses. The highest D-ratio is seen after only 5 kGy, with D=27.2, with consistently decreasing D-ratios with increasing doses. For the

243 distribution ratio of U, the observations are less consistent. At 5 kGy, D=13.8, which is higher
244 than its equilibrium value (Deqm=9.41).

245 **Table 3** The D-ratios of Pu and U respectively after gamma irradiation of the DEHBA solvent
246 in contact with 4 M HNO_3.

Dose (kGy)	D(Pu)	D(U)
5	27.2 ± 0.37	13.8 ± 0.35
20	21.6 ± 0.47	8.24 ± 0.71
75	19.9 ± 0.21	8.12 ± 0.31
100	17.5 ± 0.27	9.51 ± 0.41
250	17.7 ± 0.63	6.41 ± 0.15

247

248 For the extraction of uranium and plutonium as a function of time, a surprising trend is seen in
249 Figure 6 for both nuclides. The standard deviations of the triplicates were generally below 5%
250 for all dose rates, except for D(Pu) at t=1 min, for which the uncertainty was 13% and D(U) at
251 t=3 min and t=10, for which the uncertainties were 11% and 25% respectively. The
252 uncertainties make little to no difference in the trends seen for either Pu or U. The highest D-
253 ratios are seen after 3 minutes of contacting, before the D-ratios drop to values close to their
254 equilibrium values. This is quite unexpected behavior, but it could be partially due to
255 difficulties in ensuring accurate contact times. Another possibility is that unknown and less
256 controlled chemical reactions are happening during the first minutes of contacting. If so, it is
257 probably a reaction between the metal and the solvent, as the solvent is already pre-equilibrated
258 with 4 M nitric acid. Further investigations are required to investigate this behaviour to finally
259 conclude on its cause. Overall, the distribution ratios are high for the DEHBA solvent and can
260 be compared to those of the TBP solvent published by Halleröd et al.[43] Both ligands reach
261 extraction equilibrium within 5 minutes of contact time.
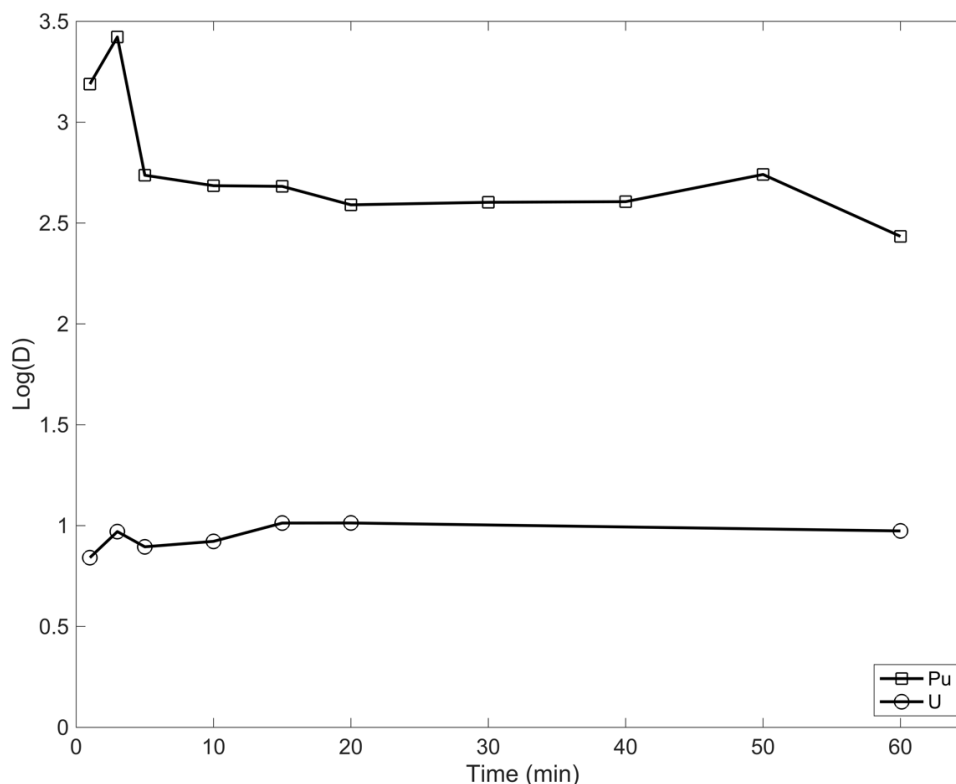
262

263 **Fig. 6** The log(D) of Pu and U as a function of contact time (min). The extraction was by the
264 pre-equilibrated DEHBA solvent from 4 M HNO₃.

Conclusions

266 In this study, a comparison of DEHBA and TBP was made for the extraction of the tetravalent
267 and hexavalent actinides, namely U(VI) and Pu(IV). While the ligands are comparable for most
268 of the evaluation criteria investigated here, some differences were identified. The acid
269 extraction by the TBP solvent is higher than that of the DEHBA solvent at [HNO3] > 2 M. The
270 only real concerns for the DEHBA solvent the low density and the low interfacial tension
271 between the solvent and 4 M nitric acid. Both these properties can cause serious phase inversion
272 issues and/or phase separation issues under process conditions.

Acknowledgements

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