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CHALMEX FS-13 investigations for process implementation

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ABSTRACT

From successive neutron absorption by uranium in nuclear reactors, transuranic elements such as neptunium, plutonium, americium and curium are produced. These elements are the main reason for the long-lived, highly radiotoxic and heat-producing nature of spent nuclear fuel. To reduce the strain on a final repository, the concept of partitioning and transmutation (P&T) has been developed. In P&T, the transuranic elements are partitioned from the nuclear fuel prior to final storage and transmuted into shorter-lived and far less radiotoxic elements. If the transmutation is facilitated in a nuclear reactor, as compared to in an accelerator driven system, further benefits include a more sustainable nuclear fuel cycle due to a reduced need for mining.

One partitioning option being developed is the Grouped ActiNide EXtraction (GANEX) process, which is a liquid-liquid extraction concept. In the Chalmers GANEX (CHALMEX) version, two extractants, tri-*n*-butyl phosphate (TBP) and 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol-[1,2,4]-triazin-3-yl)-[2,2']-bipyridine (CyMe$_4$-BTBP) are combined for the direct separation of the transuranic elements from a spent nuclear fuel solution. The extractants are dissolved in phenyl trifluoromethyl sulfone (FS-13). The focus of the work presented in this thesis has been the optimisation and evaluation of the CHALMEX system for scaled up operations. Knowledge required for later process simulations, such as distribution ratios of all relevant elements over a range of acid concentrations, has been established. A fission product handling strategy using bimet and mannitol as masking agents has been suggested, although an efficient nickel and cadmium handling strategy is still required.

List of publications and manuscripts

I. Authen, T. L., Wilden, A., Halleröd, J., Schneider, D., Kreft, F., Modolo, G. and Ekberg, C. 2020. Batch Tests for optimisation of Solvent Composition and Process flexibility of the CHALMEX FS-13 Process. *Submitted to Solvent Extraction and Ion Exchange (2019).*

Contribution: Main author and majority of experimental work.

II. Authen, T. L., Wilden, A., Schneider, D., Kreft, F., Modolo, G. and Ekberg, C. 2020. Batch flowsheet test of a GANEX-type process: The CHALMEX FS-13 process. *Manuscript*

Contribution: Main author and all experimental work.

III. Halleröd, J., Ekberg, C., Authen, T. L., Bertolo, L., Lin, M., Grüner, B., Svehla, J., Wagner, C., Geist, A., Panak, P. J. and Aneheim, E. 2018. On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based GANEX System Containing CyMe 4 -BTBP and TBP. Solvent Extraction and Ion Exchange, 36(4):1-13. DOI: 10.1080/07366299.2018.1497043

Contribution: Experimental work shared with J. Halleröd.

CONTENTS

1 | Introduction and background

Electricity production from nuclear chain reactions was initially only a byproduct of the original purpose of nuclear reactors: to produce nuclear weapons. Today, the Intergovernmental Panel on Climate Change (IPCC) has established the need for an increased portion of energy production to be supplied by nuclear power to successfully limit global warming to under 1.5°C compared to pre-industrial temperatures by the year 2050 [1-2]. In the age of global warming and the *Fridays for Future* movement, there is an increasing public focus on the need for a shift to carbon free and sustainable sources of energy [3]. Nuclear power reactors have great potential as a safe, low-carbon and non-intermittent energy producer [4].

Despite the scientifically recognised need for nuclear power to achieve the lowest impact of global warming possible, there is widespread concern regarding several aspects of nuclear power amongst the general public. The most pressing concerns regard the risk of severe nuclear accidents, the production of highly radiotoxic, long-lived waste and proliferation of nuclear weapons [5-7]. The civilian nuclear programmes have for decades addressed the concerns related to nuclear power production by developing advanced reactor systems. These reactor systems are built to be safer, cleaner and more proliferation-resistant than previous and current reactor fleets [8].

The majority of the advanced nuclear systems have been developed to operate according to what is known as the closed fuel cycle principle, and there are two concepts under revision. The first concept is based on the multi-recycle of plutonium. This includes recycling uranium and plutonium from spent nuclear fuel, much like in the already established PUREX (Plutonium Uranium Reduction EXtraction) process. The uranium and plutonium multi-recycle concept differs from the PUREX process in that it will recover unfissioned uranium and plutonium from all spent nuclear fuel (up to 10 cycles) and not only after one reactor operation cycle [9-11]. The recycled uranium and plutonium are then used for nuclear fuel production for fast reactors [12]. The second option involves a full recycle of uranium, plutonium and the minor actinides. This option has been developed to deal with both the long-lived, highly radioactive and radiotoxic waste produced and the proliferation risks that nuclear power poses.

Uranium, plutonium and the minor actinides (MA: Np, Am, Cm) are responsible for the long-lived radiotoxic characteristic of nuclear waste, as illustrated in Figure 1.1 [9, 13-15]. In the partitioning and transmutation (P&T) concept, the main objective is to extract the MA from the spent nuclear fuel to allow their transmutation. MA are extracted for transmutation in an accelerator-driven system. Here, the actinides are only transmuted and no electricity is generated in the process. Another option is to integrate all of these elements, along with uranium and plutonium, into advanced nuclear fuels. Such fuels are suitable for fast neutron reactors, in which the MA will be fissioned into shorter-lifetime, more stable isotopes. The energy of fission reaction can be harvested for electricity production. This option is commonly also referred to as the closed nuclear fuel cycle. In the P&T option, a high MA content is beneficial, while for electricity production a low MA content (~5 wt%) is required [16-17]. There are many benefits of a closed fuel cycle, including decreased (or eliminated) need for uranium mining, higher proliferation resistance, significantly reduced heat load from the final waste, up to 30% reduction in high active waste volume and hence repository volume, and significantly reduced radiotoxicity of the final waste [4, 13, 18-20].

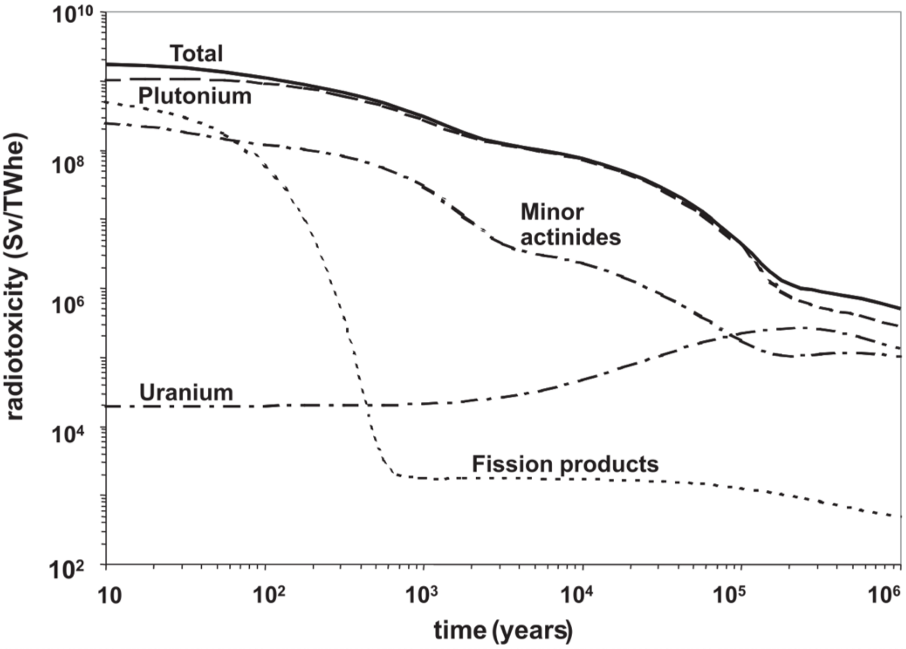


Figure 1.1. The radiotoxicity of spent nuclear waste as function of storage time. The original fuel was UOx1 with burn-up= 33 GWd/t$_{initialU}$ [15].

Several alternatives have been developed for the partitioning of the minor actinides from spent nuclear fuel. In the French reference process, the EXAm process, americium is extracted from a spent nuclear fuel raffinate and integrated into mixed oxide (MOX) fuels [21]. In the Advanced PUREX process, neptunium is recovered along with plutonium [22]. Both the EXAm process and the Advanced PUREX process are defined as heterogeneous recycling strategies, as they recover specific minor actinides in dedicated steps separate to the major actinide extraction (U, Pu). In homogenous actinide recycling, the minor actinides are co-extracted along in one process stream. In the French COEX process, efforts have been focused on coextracting uranium, plutonium and later also neptunium by co-precipitating these elements to form a product in the form (U, Pu, Np)O_2 [11].

Another homogenous minor actinide recovery concept is the Grouped ActiNide EXtraction (GANEX) process. The GANEX concept has been developed during several collaborative European projects [23-26]. In the first GANEX step, the bulk of unfissioned uranium is extracted. In the second stage, the transuranic elements are co-extracted. The work presented here has been focused on a version of the GANEX process: The Chalmers GANEX (CHALMEX) process. The main aim has been to identify and resolve issues and obstacles related to large scale process implementation of the CHALMEX process. This includes distribution ratio data for all elements over a wide range of process conditions. Such data is needed for simulation purposes (i.e. PAREX or other relevant codes [27]) and for later maloperation studies. Furthermore, such data allows for a fundamental understanding of the behaviour of the CHALMEX system as a whole.

1.1 Nuclear power

Induced nuclear fission is the basis of nuclear power production, past and present. When an atom's nucleus is hit by neutrons, the nucleus can capture a neutron and consequently undergoes a fission reaction. In a fission reaction the nucleus is split into several fragments, and the process releases energy (about 200 MeV per fission event for a heavy element such as uranium). Typically, a fission event produces a couple of heavy elements and 2-3 neutrons [28]. In a nuclear reactor the released neutrons are used to induce more fission reactions, sustaining a chain reaction. The energy release from the fission reactions is harvested and used to produce steam, which in turn drives a turbine to produce electricity.

Uranium is the most conventional fuel for nuclear power reactors. Uranium exists naturally as three isotopes with the approximate abundance of 0.01% ^{234}U, 0.72% ^{235}U and 99.27% ^{238}U and various degrees of ^{235}U enriched fuel is common. From the fission of ^{235}U more than 400 different isotopes have been identified, many of them radioactive [28]. The mass distribution of these 400 products concentrates around mass number 97 and mass number 137, as seen in Figure 1.2 [29]. From this figure, it is obvious that irradiated nuclear fuel will have a highly complex composition. Contributing to this complexity is the fact that not all neutron absorptions lead to a fission reaction. In some cases, subsequent neutron absorptions will lead to higher mass elements being formed. Minor actinides, for example, are produced from ^{238}U by its successive neutron capture. The production route of ^{241}Am is shown in Equation 1.

$$^{238}_{92}U(n,\gamma)^{239}_{92}U \underset{23.5m}{\overset{\beta^-}{\rightarrow}} {}^{239}_{93}Np \underset{2.355d}{\overset{\beta^-}{\rightarrow}} {}^{239}_{94}Pu(n,\gamma)^{240}_{94}Pu(n,\gamma)^{241}_{94}Pu \underset{14.35a}{\overset{\beta^-}{\rightarrow}} {}^{241}_{95}Am \tag{1}$$

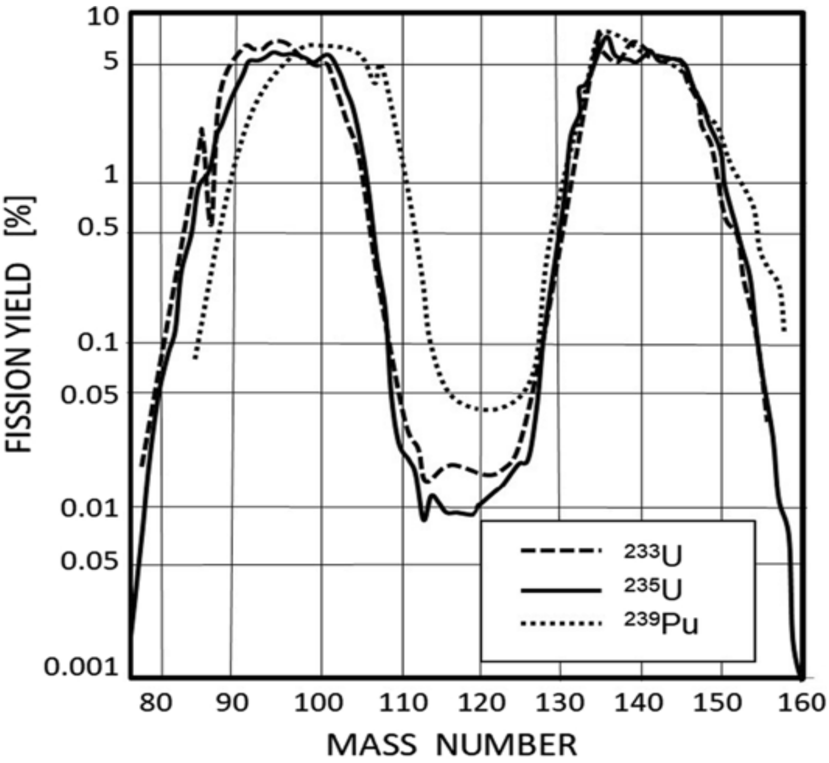


Figure 1.2. The mass distribution of fission products from the fission of ^{233}U, ^{235}U *and* ^{239}Pu *by thermal neutrons [29].*

Irradiated nuclear fuel is highly radioactive, has a lifetime of several hundreds of thousands of years and must be isolated from the Earth's biosphere. Regardless of the chosen fuel management approach, most countries have accepted the need for a final repository to store the long-lived radioactive waste produced in nuclear reactors. While actual progress in building the repository has only been made by Sweden and Finland, other countries are storing their long-lived waste indefinitely pending decision-making by politicians to actually build a final repository [30-33].

1.2 Reprocessing versus recycling

1.2.1 The PUREX process

The Plutonium Uranium Reduction EXtraction (PUREX) process is a solvent extraction process that has been the main industrial scale process for reprocessing nuclear waste since 1954. It was initially developed as a means of extracting pure plutonium and uranium from irradiated nuclear fuel for nuclear weapons production. Later, the PUREX process was used to extract the unfissioned uranium and produced plutonium with the purpose of producing Mixed OXide (MOX) nuclear fuels [34-35]. In France, the use of the PUREX process has been shown to reduce the need for uranium mining by up to 16% [7, 36].

In the PUREX process, plutonium and uranium are extracted from spent nuclear fuel by tri-*n*-butyl phosphate (TBP) in a hydrocarbon diluent, typically odourless kerosene (OK). The PUREX process produces two product streams and one waste stream: a plutonium stream, a uranium stream and a waste stream.

Today, the back-extraction of plutonium and uranium into separate streams is one of the main concerns regarding the PUREX process. This enables the direct access to materials that could be used for nuclear weapons production. Furthermore, in order to increase the sustainability of the nuclear power industry, alternatives for the recycling of all fissile and fertile material from spent nuclear fuel are being considered.

1.2.2 Grouped ActiNide EXtraction

One concept for the recycling of fissile and fertile material from spent nuclear fuel is the Grouped ActiNide EXtraction process (GANEX). In the various versions of the GANEX process, uranium is extracted in the first process step and the transuranic elements in a following step. The process was initially developed by the French CEA, and so one version of the GANEX process has been named thereafter: CEA-GANEX [37-38]. Here, both the lanthanides and the actinides are co-extracted after the initial bulk-extraction of uranium. The actinides are separated from the lanthanides by selective stripping of the actinides from the organic phase. The EURO-GANEX process follows the same principle of separation of the lanthanides and the actinides, but uses other extractants and diluents [39-44].

The recovered actinides are either integrated into accelerator targets or into advanced nuclear fuels for transmutation. When irradiated by fast neutrons, the minor actinides undergo fission and are transmuted into far less radiotoxic elements with significantly lower half-lives ($\sim10^4$ order of magnitude). Amongst other benefits, this will considerably reduce the strain on a final repository and all radioactive releases to the environment [9-10]. The GANEX process concept also aims to follow the CHON-principle in order to minimise final waste. The CHON principle is based on having organic solvent constituents made up of carbon, hydrogen, oxygen and nitrogen atoms only. This allows for incineration as a means of disposing of final organic waste.

An extensive study by Serp et al.[4] showed that in France, the front end of the nuclear fuel cycle can be completely eliminated by transitioning to a closed fuel cycle and by using already existing uranium and plutonium stockpiles. In such a scenario, France could operate their reactors for more than 8000 years without the need for supply of freshly mined uranium. A closed fuel cycle will significantly reduce NOx gas emissions, practically eliminate the SOx gas emissions and environmental- and human toxicity from nuclear power, and more than halve the greenhouse gas emissions in comparison to the single recycle process. Furthermore, transitioning to a closed, advanced reactor system fleet, such as a Generation IV (Gen IV) reactor fleet, will result in a 22.2% reduction in volume of high-level waste (HLW) produced [9].

2 | Theory

2.1 Solvent extraction

Liquid-liquid distribution, traditionally referred to as solvent extraction, is defined as *the distribution of a solute between two immiscible liquid phases in contact with each other* [36]. The principle is fairly simple: scientists exploit the different solubilities of solutes and solute complexes in aqueous and organic phases to extract specific solute(s). A key requirement is that the aqueous and organic phase are separated by a phase boundary, i.e. they are (more or less) immiscible with each other. The field of solvent extraction finds widespread application in industries such as nuclear waste reprocessing and recycling and in separation and purification processes in metallurgical and mining operations [36].

Solvent is a collective term that is used to discuss the organic phase as one unit- i.e. extractant(s) and diluent. The extractant is the ligand responsible for complex formation with the metal ion, and the diluent (if any) is a solution that contributes to beneficial properties of the extractant. Such beneficial properties can be increased solubility, change in density or change in boiling- and flashpoint, to mention a few examples [36].

Solute stability in aqueous and organic phases are governed by the strength of interactions between solute and solvent. While metal ions typically have a high stability in aqueous, acidic phases, the formation of neutral metal-ligand complexes is necessary for good solubility in the solvent phase. Such complexes have a higher stability in the more neutral organic phase, than in the polar and acidic aqueous phase [36].

Ligands can be ionic (hydrophilic) or neutral (hydrophobic) molecules. Hydrophilic ligands, such as water or nitrates, are dipolar molecules that will coordinate to the metal cation. Solvation will be used as a generic term here. To compensate for the charge of the solvated species, one or more of the solvation molecules is replaced by anionic (hydrophobic) ligands, forming an overall neutral complex that is soluble in the organic solvent. A general equation for such a *solvating extraction* mechanism is presented in Equation 2,

$$M^{n+}{}_{(aq)} + nL^{-}{}_{(aq)} + m\bar{O} \rightleftharpoons \overline{ML_nO_m} \tag{2}$$

where M is the metal ion of charge n, and L is the hydrophilic ligand and O is the hydrophobic ligand. The complexation constant for such a reaction can be represented by Equation 3.

$$\beta_n = \frac{\overline{[ML_nO_m]}}{[M^{n+}][L^-]^n[\bar{O}]^m} \tag{3}$$

Chelating ligands are a specific ligand type where chelate refers to the capability of the ligand to bind to the metal ion at more than one site. Such ligands typically form stronger complexes than their non-chelating analogues. Chelating ligands are named after how many sites they bind with. For example, a bidentate ligand binds to two sites and a tetradentate ligand binds to four sites [36]. When metal ions bind to one or more chelating ligand(s), the complex formed can be more soluble in an organic phase, resulting in extraction.

The distribution ratio (D) is defined as the ratio of the concentration of all species of M present in the organic layer, compared to the concentration of all species of M in the aqueous layer. This is represented by Equation 4.

$$D = \frac{[M]_{tot-org}}{[M]_{tot-aq}} \tag{4}$$

If there is more than one metal present in the initial aqueous phase, the success in separating metal M from metal N is defined by the separation factor, expressed in Equation 5, with the constraint that M and N has SF>1.

$$SF_{M/N} = \frac{D(M)}{D(N)} \tag{5}$$

2.2 Coordination chemistry

Many metal ions, such as the actinides, are Lewis acids (electron pair acceptors) in aqueous solutions. When such metals react with a Lewis base (electron donors) a coordination complex is formed which consists of the central metal ion bonded by covalent coordinate bond(s) to the Lewis base molecule(s) or ion(s). In such a case, the Lewis base is referred to as a ligand [45]. Examples of ligands used for complexation in solvent extraction in the nuclear industry are tri-*n*-butyl phosphate (TBP) or N,N,N',N'-Tetraoctyl Diglycolamide (TODGA), presented in Figure 1.1 [40, 46-49].

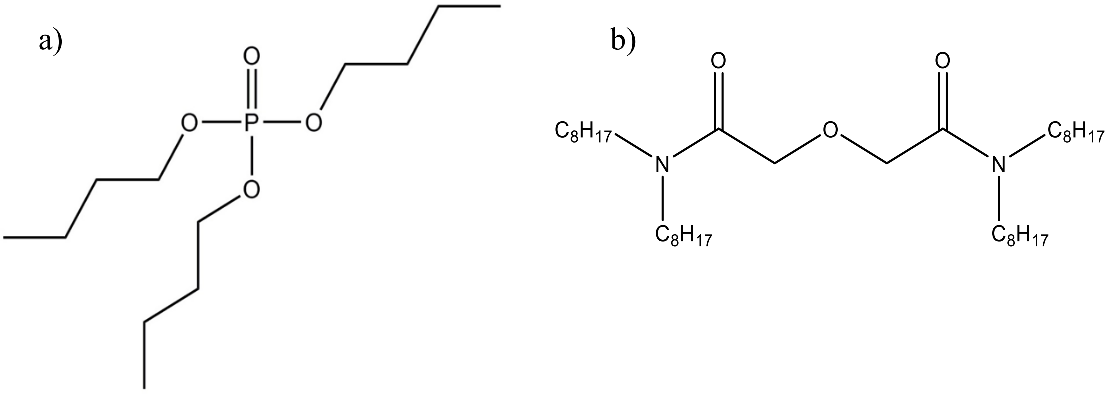


Figure 2.1. The molecular structure of a) Tri-n-Butyl Phosphate (TBP) and b) N,N,N',N'-Tetraoctyl Diglycolamide (TODGA).

Lewis acids and bases can be further defined as being either hard or soft. The hardness depends on both the size, charge and the polarizability of the species [50]. Both the actinides and the lanthanides are defined as hard acids, but an actinide-base bond has a slightly more covalent bond character than the lanthanide-base bond. This is the basis of trivalent actinide-lanthanide separation theory using nitrogen donor atoms [51].

In pure water, metal ions are surrounded by water molecules: they are hydrated. In aqueous nitric acid solutions, the metal ions are surrounded by water, nitrate(s) or a combination of the two. This is referred to as solvation. For the selective extraction of metal ions from spent nuclear fuel, the water molecules and/or nitrate ions have to be completely or partially replaced by other ligands than water. In solvent extraction processes, these ligands are organic molecules with low solubility in aqueous solutions. Such a process can be slow, and will thus affect the kinetics of the system as a whole [36]. Nitrate ions are typically associated with outer sphere complexation for BTBP complexes, but both inner and outer sphere complexes exist for TBP complexes [36].

CyMe$_4$-BTBP, seen in Figure 2.2, is a neutral tetradentate chelating ligand, i.e. it will bind to the metal ions in up to 4 sites to form a metal-anion-ligand complex. Furthermore, solvate complexes typically display varying degrees of hydrophobicity of the accessible surface, making them more soluble in organic solutions than in aqueous solutions. CyMe$_4$-BTBP is a soft base and preferentially extracts trivalent actinides over lanthanides due to the stronger covalent bond [52-54]. Nitrate anions in the inner sphere compensate the charge of the metal ion, increasing the stability of the complex as well as increasing its solubility in organic solutions by forming and overall neutral complex [55].

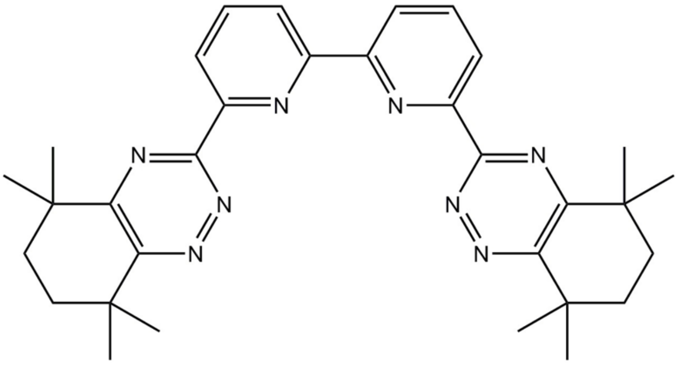


Figure 2.2. The molecular structure of 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol-[1,2,4]-triazin-3-yl)-[2,2']-bipyridine (CyMe₄-BTBP).

2.3 Chemistry of the lanthanides and actinides

Lanthanides are both found in natural ores around the world, and in spent nuclear fuel as fission products. The MA however, are produced by nuclear reactions such as successive neutron absorption of the starting material (conventionally uranium and/or plutonium). The actinides following Fm, are typically not found in conventional spent nuclear fuel. All the actinides are radioactive [56], while the lanthanides found in spent nuclear fuels exist as both radioactive and non-radioactive isotopes.

The separation of lanthanides from actinides for transmutation purposes is necessary due to the high neutron absorption cross-section of certain lanthanides (i.e. Sm, Eu, Gd and Dy [57]), making their presence in nuclear fuels/targets problematic [51]. For this purpose, only uranium and the transuranic elements up to and including curium are of interest, due the low relative occurrence of higher actinides in spent nuclear fuel and the relative short half-lives of most of these. The separation of trivalent MA and trivalent lanthanides is challenging due to the very similar size and charge of these two groups of elements. Traditionally, such separation of trivalent MA from the trivalent lanthanides has focused on either solvent extraction or ion exchange mechanisms [51].

Lanthanides exist predominantly in the +III oxidation state in aqueous solutions [51, 56]. Uranium is stable in the +IV and the +VI oxidations states and plutonium has +IV as the most stable oxidation states. Neptunium has +V as its predominant oxidations state while americium and curium are most stable in the +III oxidation state [56]. The difference in the actinide and lanthanide behaviour stems from the electron configuration. The lanthanides are associated with the gradual filling of the 4*f* shell. Due to the high charge of the nucleus the 4*f* orbitals contract, making these more stable than the 5*d* orbitals. The 4*f* orbitals penetrate the nucleus of the lanthanide(s), shielding it from participating in bonding and forming π-bonds by the $5s^2$ and $5p^6$ orbitals.

The actinides following thorium are associated with the gradual filling of the 5*f* orbitals. In contrast to the lanthanide series however, these 5*f* electrons are not affected by shielding effects and can readily participate in bonding [56].

2.4 Fission product chemistry

The fission products produced in a nuclear reactor tend to concentrate around mass number 97 and 137 [58], making the majority of the fission products *d*-block elements or lanthanides (*f*-block). Lanthanide chemistry was briefly covered in chapter 2.3, and so this section will focus on the chemistry of the d-block elements. A significant part of the work presented within this thesis will focus on the fission product extraction and possible handling strategies. The co-extraction of certain fission products is undesirable due to the high neutron capture cross sections of isotopes of Cd, Sm and ^{157}Gd [59].

Isotopes with mass number around 97 are found amongst the transition metals in the *d*-block of the periodic table. It is referred to as the *d*-block as the elements found here are associated with a gradual filling of the *d*-orbitals. Despite their position in the periodic table, zinc, cadmium and mercury are not typically associated with the transition metal due to their full *d*-orbitals. This makes the properties of these metals resemble the main group metals. Despite this, these elements will be included in this brief overview [45].

D-block elements electron orbitals are far apart, and the electron-electron repulsion is thus weak. The electron density is low near the metal nucleus, and the nuclear charge exerts strong attractive forces on bonding electrons. *D*-block metals have a tendency to first donate their s-electrons when forming bonds with other elements and molecules, due to the low ionisation energy required to do so. Most of the transition metals can however also donate *d*-electrons, which results in a range of different oxidation states. Typically, elements close to the centre of each row show the widest range of possible oxidation states, while elements in the first and last column have only one oxidation state. The exception is mercury, which has 3 possible oxidation states.

2.5 The CHALMEX process

In the CHALMEX process, the trivalent actinides are separated directly from the lanthanides and other fission products. A bis-triazin-bi-pyridine(BTBP)-type ligand, CyMe$_4$-BTBP, has been developed to extract actinides in the trivalent and pentavalent oxidation states (Figure 2.2) [52, 60-63].

CyMe$_4$-BTBP is combined with the extractant used in the well-establish PUREX process: tri-*n*-butyl phosphate (TBP) (Figure 2.1 a). TBP preferentially extracts the tetravalent and hexavalent oxidation states of plutonium and uranium. One can thus, in theory, co-extract uranium and the transuranic elements in one process step. The extraction mechanism of TBP for uranium and plutonium is presented in Equation 6 and Equation 7 respectively. The CHALMEX extractants have shown great potential in actinide extraction and separation from the lanthanides [64-69].

$$UO_2{}^{2+} + 2NO_3{}^- + 2\overline{TBP} \leftrightharpoons [\overline{UO_2(NO_3)_2 \cdot 2TBP}] \qquad (6)$$

$$Pu^{4+} + 4NO_3^{-} + 2\overline{TBP} \leftrightharpoons [\overline{Pu(NO_3)_4 \cdot 2TBP}] \qquad (7)$$

Extensive efforts have been focused on finding a suitable diluent for the CHALMEX process [65-66, 68, 70-73]. In the first version of the CHALMEX process, cyclohexanone was used as a diluent. This option was abandoned due to the low flash point of cyclohexanone (44°C), its high solubility in nitric acid, it's exothermic reaction with concentrated nitric acid and phase separation issues after extraction from solutions with high metal-content [74-75]. In recent work, phenyl trifluoromethyl sulfone (Figure 2.3 b) was investigated as a possible diluent for the CHALMEX process [71-72, 76-79]. It was developed for use in Russian reprocessing plants, and has found further use as a diluent in the American UNEX process [80-82].

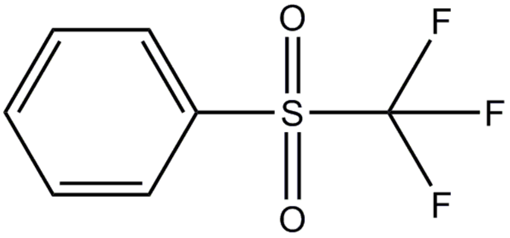


Figure 2.3. The molecular structure of phenyl trifluoromethyl sulfone (FS-13)

FS-13 meets most of the required properties for a diluent for nuclear waste reprocessing: high chemical and radiolytic stability, low aqueous solubility, and low viscosity. It is also non-toxic and it can dissolve the CHALMEX extractants [79-80, 82-83]. Due to the high density of FS-13 (1.41 g cm^{-3}), phase separation issues are avoided once the solvent is loaded by metal. The main drawback is that FS-13 does not satisfy the CHON principle.

The CHALMEX FS-13 solvent has proven to be radiolytically, chemically and thermally stable [72, 78]. It shows good separation factors for the transuranic elements and the lanthanides [68, 71, 78], and the solvent is able to handle high concentrations of plutonium (up to 40 g L^{-1}) without precipitating metal [77].

2.6 Process considerations

2.6.1 Contacting equipment

There are traditionally three types of contactors used for the continuous operation of a solvent extraction process: mixer-settlers, columns and centrifugal extractors. Although different in design and layout, they all allow for sufficient surface area of contact between the aqueous feed solution and the organic solvent and can be operated over a range of conditions [84].

A mixer-settler’s design and operating principle is fairly simple: it is typically a stirred tank with either an integrated settling chamber or it is connected to a settling unit. In the stirred tank section, the phases are rigorously mixed before the solution is allowed to settle by gravity [85]. A bank of mixer-settlers can easily be connected to one another to allow for counter-current operation. The main draw-back of mixer-settlers is the size of the units.

Columns, or towers, are differential, continuous contactors that do not operate at equilibrium. Phase mixing and separation occur instantaneously throughout the column and is facilitated by the presence of packing material (i.e. rings or saddles). In the nuclear industry, a pulsed type column is typically preferred, as it contains no moving parts (this is beneficial as it reduces mechanical stress and thus reduces maintenance need) [85]. Pulsed columns are less flexible regards to operating control (compared to mixer-settlers), they are very costly, and require a large building headroom [86].

Centrifugal contactors are considered the most space efficient contactors. They make use of centrifugal force to accelerate both the mixing and separation of the feed solution and solvent. Due to their compactness, they can handle large amounts of fissile material without raising criticality concerns [84-86]. The main disadvantage of the centrifugal contactors is the short residence time of the feed and solvent.

2.6.2 Process development

The Technology Readiness Level (TRL) is an established scale used by organisations ranging from intergovernmental departments, such as the European Commission Department of Energy, to commercial companies such as Boeing and smaller research institutions. The TRL scale is used for establishing the stage of development of new technologies and enabling the direct comparison of the readiness of new technologies to be deployed on an industrial scale. The TRL scale ranges from level 1-9, where level 1-3 is related to proof of concept research. Level 4-6 relates to proof of principle research, while levels above this relate proof of performance [24]. A summary of the definitions of each TRL is presented in Figure 2.4.

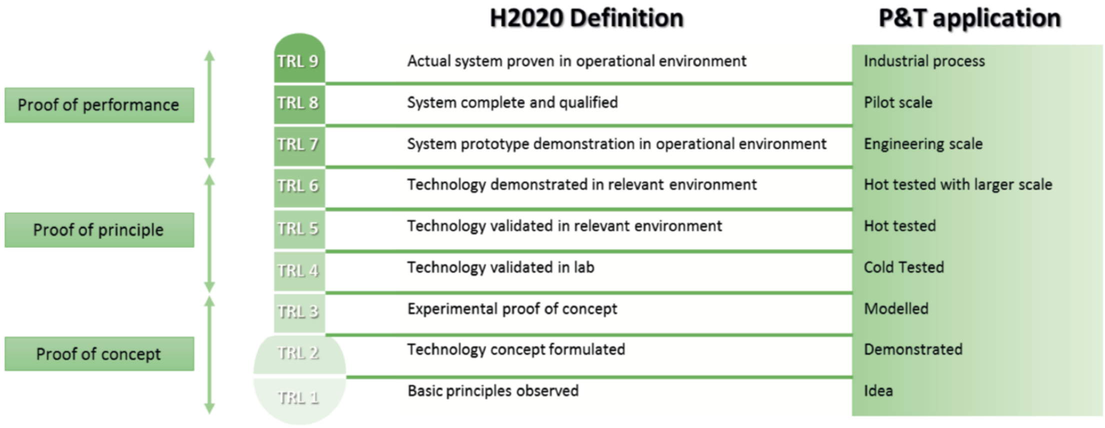


Figure 2.4. The TRL scale definition. Reproduced from Joly and Boo [23-24].

In 2015, the CHALMEX process was evaluated to be on TRL 2 to 3 [24]. The work presented in this thesis has been aimed at identifying and satisfying knowledge gaps in the CHALMEX process research to enable an increase of evaluated TRL.

3 | Materials and methods

3.1 Materials

CyMe$_4$-BTBP was obtained from KIT, Germany. The diluent, FS-13, was provided by Marshallton labs, USA or by HaiHang Industry co. Ltd., China. The origin and supplier of the radionuclides used in the experiments conducted at Chalmers University of Technology are listed below.

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

The radionuclides used in the experiments performed at Forschungszentrum Jülich had the following origin:

- ^{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

All other chemicals were laboratory grade and were supplied by Merck, Sigma-Aldrich, Aldrich or Fluka.

3.2 Solvent extraction experiments

Unless otherwise stated, all experiments were performed using a standard CHALMEX solvent composed of 10 mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13. The solvent was always pre-equilibrated with nitric acid of the same concentration as that used as aqueous phase in the extractions. In all experiments, a phase ratio of 1:1 was maintained, and a minimum of 300 µL of each phase was contacted. The radiotracers were added to the aqueous phase so that the total volume of the aqueous phase was equal to that of the organic phase. The organic and aqueous phase was contacted for 1 hour at 25°C, unless otherwise stated, which is assumed to be enough time to reach extraction equilibrium [78]. After contacting, the samples were centrifuged for a minimum of 5 minutes before sampling.

All experiments performed at Chalmers University of Technology were performed in triplicates. Americium and europium were investigated together in one system, i.e. both radionuclides were added to the same aqueous phase. Plutonium, curium, neptunium and uranium on the other hand were investigated in isolated systems, with only single elements present in the aqueous phase.

Single experiments were done at Forschungszentrum Jülich, with all elements investigated in one system; radionuclides and inactive elements were all added to the same aqueous phase and no triplicate experiments were made.

In the batch flowsheet tests, the volume of the organic phase and aqueous phase was 5 mL each. The phases were contacted in 10-12 mL vials in a vortex shaker at ambient temperatures. To limit heating effects, the sample vial was moved between two identical shakers every 15 minutes. Once one stage was complete, the vial was centrifuged for a minimum of 5 minutes. A 0.5 mL sample was collected from each phase, before the aqueous phase was completely removed. The remaining volume of the organic phase was recorded and an identical volume of aqueous phase was added. The 0.5 mL sample was used for sample preparation for γ- and α-spectrometry and ICP-MS analysis. The bulk of the removed aqueous phase was used for pH measurements and titrations.

3.2.1 Centrifugal contactor test

In preparation for the single centrifugal contactor test, all sample vials were labelled and weighed (with caps) before the start of the experiment. The organic phase in the test was 10 mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13, pre-equilibrated with 4 M HNO_3. The start-up of the centrifuge test used the CHALMEX solvent as the organic phase and 4 M HNO_3 as the aqueous phase. Once phase separation had been achieved, the aqueous phase syringe was swapped with one containing the HAW-ITU 3.3 M (Appendix B) with added radiotracers, see Figure 3.1. The centrifugal contactor was operated at 3 different flow rates: 60 mL hr^{-1}, 30 mL hr^{-1} and 10 mL hr^{-1}. The sampling rate was every 2 minutes, every 5 minutes and every 30 minutes, respectively, for each of the flow rates.

The O:A ratio was kept constant during the duration of the experiment. For the slowest flow rate (10 mL hr^{-1}), phase entrainment was visible. To ensure full phase separation, the samples collected were centrifuged further before samples were taken for analytics.

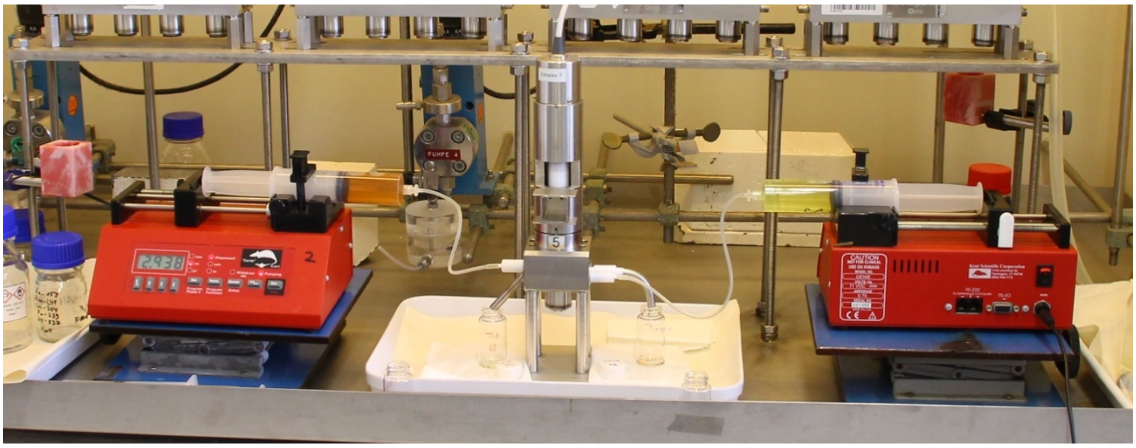


Figure 3.1. The experimental setup of the single centrifugal contactor test. Left syringe: simulated PUREX raffinate with added radiotracers. Right syringe: CHALMEX FS-13 solvent using 10 mM CyMe$_4$-BTBP and left syringe: HAW-ITU 3.3 M raffinate with added radiotracers.

3.3 Analytical methods

For a full list of all equipment used in the experiments, see appendix A.

Slightly different methods of analysis were performed at Chalmers University of Technology versus Forschungszentrum Jülich. At Chalmers University of Technology, americium and europium radioactivities were analysed by high purity germanium (HPGe) detector. Plutonium and neptunium radioactivities were analysed by liquid scintillation counting (LSC) for the beta-peak. Inactive metals were analysed by ICP-MS analysis (aqueous phase only, distribution ratios were based on mass balance calculations).

At Forschungszentrum Jülich, all elements and radionuclides were analysed by ICP-MS and the radionuclides were also analysed by alpha-spectrometry. For ICP-MS analysis, both the organic and aqueous phases were analysed. The samples with a high metal content, such as the simulated PUREX raffinates, were diluted by a factor of 10^4 in two steps. The organic phase was diluted in the presence of a surfactant (EcoSurf) to allow dissolution of the organic matter. For lower metal concentration solution, the solutions were diluted by a factor of 10^2. In all cases, americium and europium radioactivities were analysed by HPGe.

Samples for alpha spectrometry were prepared by taking and mixing 10 μL of the respective sample (organic or aqueous) with 100 μL acetone solution (ZAP-100). The mixture was then distributed on a metal planchette and placed under an IR-lamp for evaporation of the solution. Residual organic matter was removed by burning the planchette with a torch. The alpha planchettes were then inserted into the respective alpha-spectrometer and typically measured until each peak had at least 10 000 counts.

pH measurements were done during the batch flowsheet tests. A pH meter was used for online measurements during the experiment. An aliquot of the aqueous phase was also titrated against NaOH to confirm pH meter measurements.

4 | Results and Discussion

4.1 Solvent optimisation

Earlier work on the CHALMEX FS-13 system has included some solvent optimisation studies. It has, for example, been established that $CyMe_4$-BTBP over 35 mM is counterproductive for partitioning purposes, as at this concentration the europium extraction exceeds that of neptunium [79]. In Paper I [87], it is concluded that the optimal $CyMe_4$-BTBP concentration is 10 mM. This is based on maximising the separation factor between all the actinides and europium. While earlier efforts have mainly been focused on a system with $30\%_{vol}$ TBP [79], extended studies on varying the TBP concentration will be presented in this work.

Halleröd et al. [78] (Paper III) showed that the distribution ratio of all actinides increases with increased $CyMe_4$-BTBP concentration. It was also reported that both the americium and curium extraction only proceeds in solvents where both TBP and $CyMe_4$-BTBP are present. Although americium is extracted by $CyMe_4$-BTBP and not TBP, the distribution ratio of americium increases with increased TBP volume ratio in the organic phase, up to $30\%_{vol}$ TBP, as seen in both Figure 4.1 and Figure 4.2. This is most likely due to an increase in the solubility and stability of the Am-$CyMe_4$-BTBP complex in a solution with lower charge density, as reported by Ekberg et al. [55].

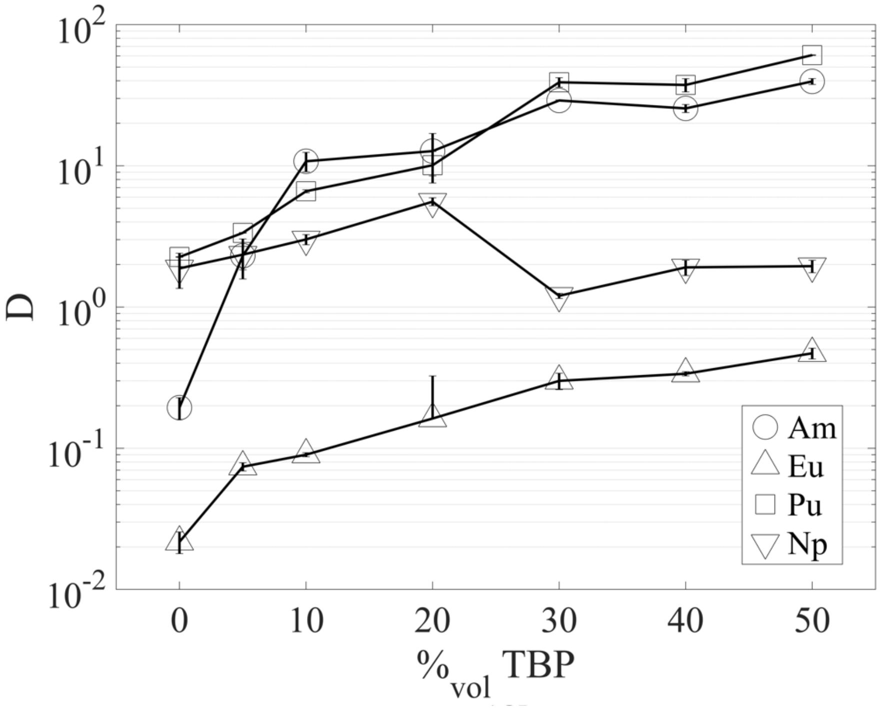


Figure 4.1. The distribution ratio (D) of Am, Eu, Pu and Np as a function of the TBP volume ratio. The $CyMe_4$-BTBP concentration was kept constant at 10 mM in all experiments. The remaining organic phase consisted of FS-13. All extractions were made from 4M HNO3. Data for $30\%_{vol}$ TBP is reproduced from Halleröd [79].

A similar trend is seen for the europium extraction, although its distribution ratio remains below 1 for all TBP volume ratios. The neptunium extraction however, shows a more unexpected trend: higher distribution ratios for lower TBP fractions. This is unexpected from PUREX chemistry. It is most likely due to a change in oxidation state, as it is known that Np(V) is less extractable by TBP compared to the tetra-and hexavalent oxidation state [22, 88]. It is also observed that the separation factor of neptunium to europium decreases with increasing TBP volume ratio. At higher TBP volume ratios, the inversion where D(Eu)>D(Np) occurs at lower and lower CyMe$_4$-BTBP concentrations. Further studies are however required to determine the extraction chemistry of neptunium.

Plutonium is extracted by both TBP and CyMe$_4$-BTBP (paper III) [78], and it is thus not surprising that D(Pu) is affected not only by both the volume ratio of TBP but also by the CyMe$_4$-BTBP concentration. In a system with 15%$_{vol}$ TBP (Figure 4.2 a), the plutonium distribution ratio increases with increasing CyMe$_4$-BTBP concentrations. It is reasonable to assume that even at 15%$_{vol}$ TBP the plutonium extraction occurs mainly by TBP extraction. At higher CyMe$_4$-BTBP the ligand is present in sufficient concentrations to be able to compete with the TBP in extraction of plutonium.

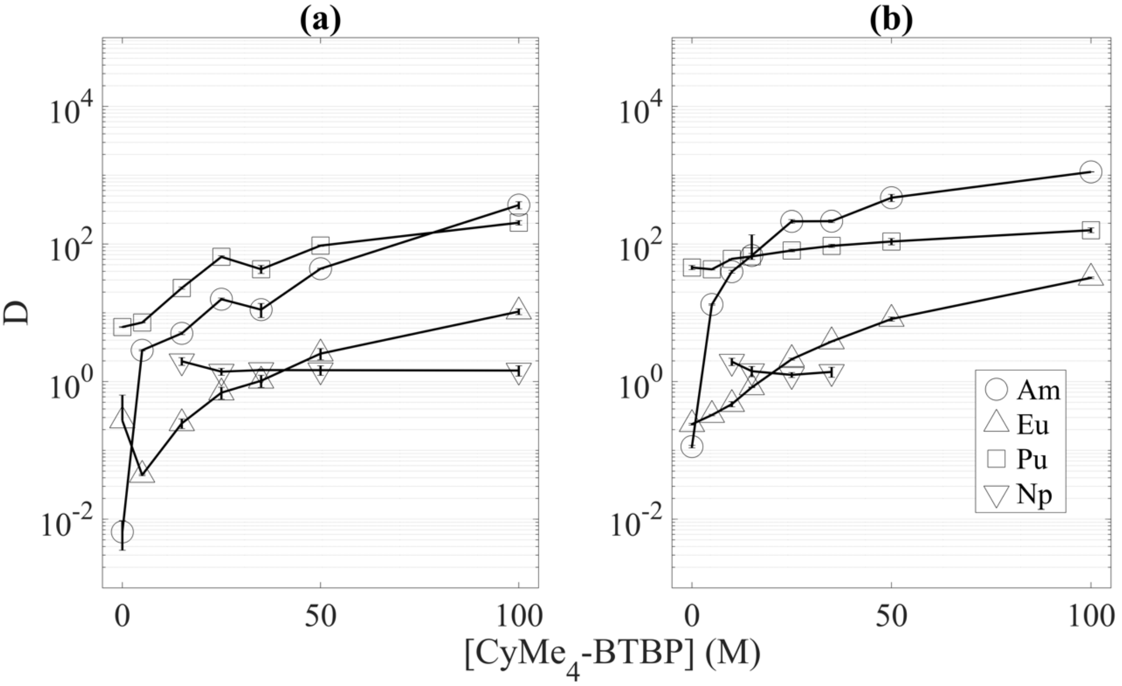


Figure 4.2. The distribution ratio (D) of Am, Eu, Pu and Np as a function of CyMe$_4$-BTBP concentration for systems with a) 15%$_{vol}$ TBP and 85%$_{vol}$ FS-13 and b) 50%$_{vol}$ TBP and 50%$_{vol}$ FS-13. The aqueous phase was 4M in all cases.

4.2 Nitric acid extraction and dependency

It is established that TBP extracts nitric acid [35, 89-90]. Acid extraction by the CHALMEX solvent has been studied, and the results are shown in Figure 4.3. For nitric acid concentrations over 1 M, a decrease in acid extraction by TBP is reported with increased acid concentration [91-92]. In Figure 4.3 however, it can be seen that the acid distribution ratio increases between 1 and 4 M initial HNO_3. Between 4 and 5 M HNO_3, the distribution ratio decreases. This is due to saturation of TBP molecules with acid, which results in a reduced distribution ratio at higher acid concentrations. For comparison, acid extraction experiments were also performed for the pure diluent, FS-13, which showed that no acid was extracted by the diluent.

Acid can be extracted by two mechanisms: by protonation of the extracting molecule or by the extraction of a non-dissociated acid molecule by hydrogen bonding to the extracting molecule. While acid extraction by $CyMe_4$-BTBP is not entirely unlikely due to the presence of 4 N-donors in the molecule, the $CyMe_4$-BTBP concentration in the solvent is so low that establishing acid extraction would be more challenging than simple acid titrations before and after contacting. This is especially true since the difference between protonation and charge neutralisation and nitric acid molecular extraction is hard to establish with certainty [93].

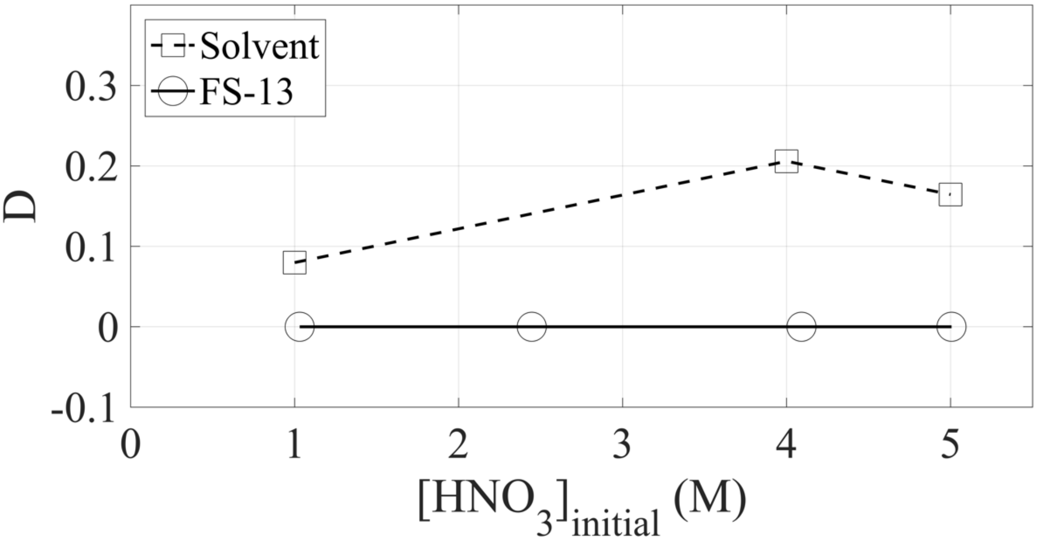


Figure 4.3. The distribution ratio (D) of acid extracted by the standard CHALMEX solvent.

The CHALMEX FS-13 solvent is dependent on acid extraction as it increases the $CyMe_4$-BTBP solubility in FS-13 [76]. This effect is possibly to protonation of the $CyMe_4$-BTBP. This is beneficial for the dissolution of $CyMe_4$-BTBP due to the polar nature of the diluent. The distribution ratios of the actinides and europium as a function of acid concentration are shown in Figure 4.4. The minor actinide extraction is found to increase with the nitric acid concentration, up to 2.5 M HNO_3. This is most likely due to two factors; the increased solubility of CyMe$_4$-BTBP in the organic phase and the increased nitrate concentration in the aqueous phase.

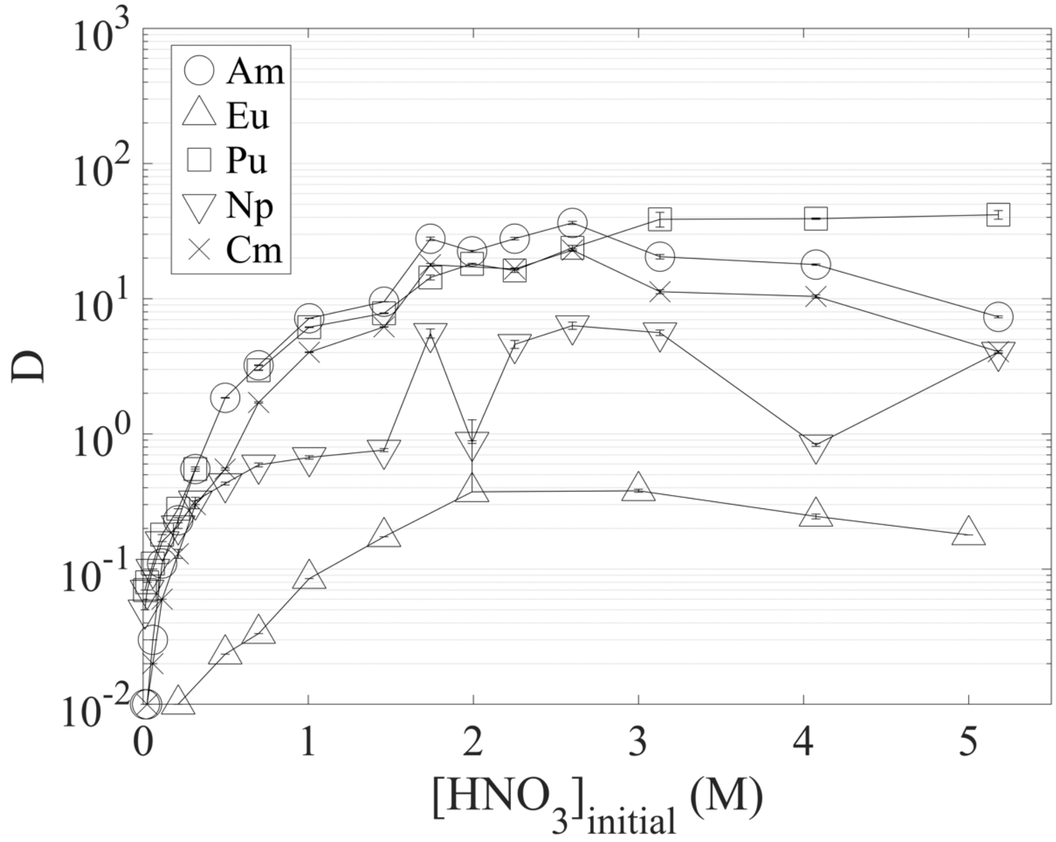


Figure 4.4. The distribution ratio (D) of the actinides as a function of nitric acid concentration, in the presence of 10^{-5} M fission products. The organic phase was 10 mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13.

Trivalent americium is extracted as a 1:2 CyMe$_4$-BTBP complex, in the form $[Am(CyMe_4\text{-}BTBP)_2(NO_3)]^{2+}$, with a further 2 nitrates complexing in the outer sphere forming a neutral, hydrophobic complex. The solubility and stability of these complexes have been found to increase with decreasing relative permittivity of the solvent [55]. This follows general trends in solvent extraction where the solubility of neutral, organic complexes increases in the organic phase with decreasing polarity of the solvent [36]. The americium distribution ratio presented in Figure 4.4 increases up to 2.5 M HNO$_3$, and at subsequently higher acid concentrations, the americium distribution ratio decreases. This suggests that the americium extraction is in competition with acid extraction. Competition with other metals is unlikely as all elements were only present in trace concentrations (10^{-5} M). Curium, having the same electro-negativity as americium, show the same distribution ratio trend as americium.

Europium extraction also shows similar trends to americium, although its distribution ratio never passes 0.4 in value. The remaining lanthanides were excluded from the results, as the distribution ratios were below 0.01 at all nitric acid concentrations. This agrees with the extraction trends reported by Geist et al. [94], that europium, of all the lanthanides, is the most extracted by CyMe$_4$-BTBP.

Neptunium distribution ratios show a less conclusive trend as a function of initial acid concentration compared to americium and curium. This is believed to be due to the speciation of the different neptunium stock solutions used in the experiments. Due to availability, two different neptunium stock solutions were used to determine the dependency of neptunium extraction on acid concentration. The speciation of both stock solutions was controlled and found to be Np(V) by UV-VIS spectrometry, but the clear increase in distribution ratio for the second Np stock solution is believed to be due to the presence of Np(VI). Np(VI) is highly extractable by TBP, which is clearly seen in Figure 4.4 [22]. Furthermore, neptunium's valency chemistry is highly complex and is affected by many factors. The nitric acid concentration plays a significant role, but so does the absorbed dose of the solutions, and various radiolysis products and radicals formed during spent nuclear fuel reprocessing [95]. The speciation of neptunium is therefore very challenging to control in a process [96].

Plutonium is extracted by TBP as a nitrate complex, $Pu(NO_3)_4 \cdot 2TBP$, and plutonium extraction has been reported to increase with increasing nitric acid concentrations [35, 97]. This is supported by the trends shown in Figure 4.4.

4.3 Fission Products

Previous studies have shown that the CHALMEX FS-13 solvent extracts some fission products, in addition to extracting the actinides. Of particular concern, based on both the distribution ratios but also the abundance in spent nuclear fuel, is the extraction of molybdenum, zirconium, palladium, cadmium and silver [79].

Fission product extraction as a function of nitric acid concentration was investigated to establish an understanding of the extraction mechanism. All relevant elements (fission-, corrosion- and activation products) were included in the experiments, but only the results for elements of concern are shown in Figure 4.5. No nickel extraction data has so far been reported, but nickel was included in the extraction system as it is present in spent nuclear fuel solutions as a result of the neutron activation of reactor component [98]. As can be seen in Figure 4.5, the distribution ratios of zirconium, molybdenum, palladium, silver and nickel all increase with increased acid concentration. This is believed to be due to the increasing nitrate concentration available for complex formation. At very low nitric acid concentrations, the extraction of all elements is low. As with the actinides, this is most likely a result of the low nitrate concentration of the aqueous phase and also the low solubility of CyMe$_4$-BTBP at such low acid concentration. In the preparation of the organic phases, the various organic solutions were pre-contacted with nitric acid of the same concentration that the experiment was performed with. At nitric acid concentrations below 1M, the ligand was visibly not fully dissolved, even when heated in a thermostatic bath. At nitric acid concentrations above 1 M however, the extraction is purely a factor of available nitrates for complex formation. It is also worth noting that, due to the different oxidation states of the metals in solution, the metals will also have different nitrate complexation stability constants, which again affects the extraction and thus the distribution ratios.

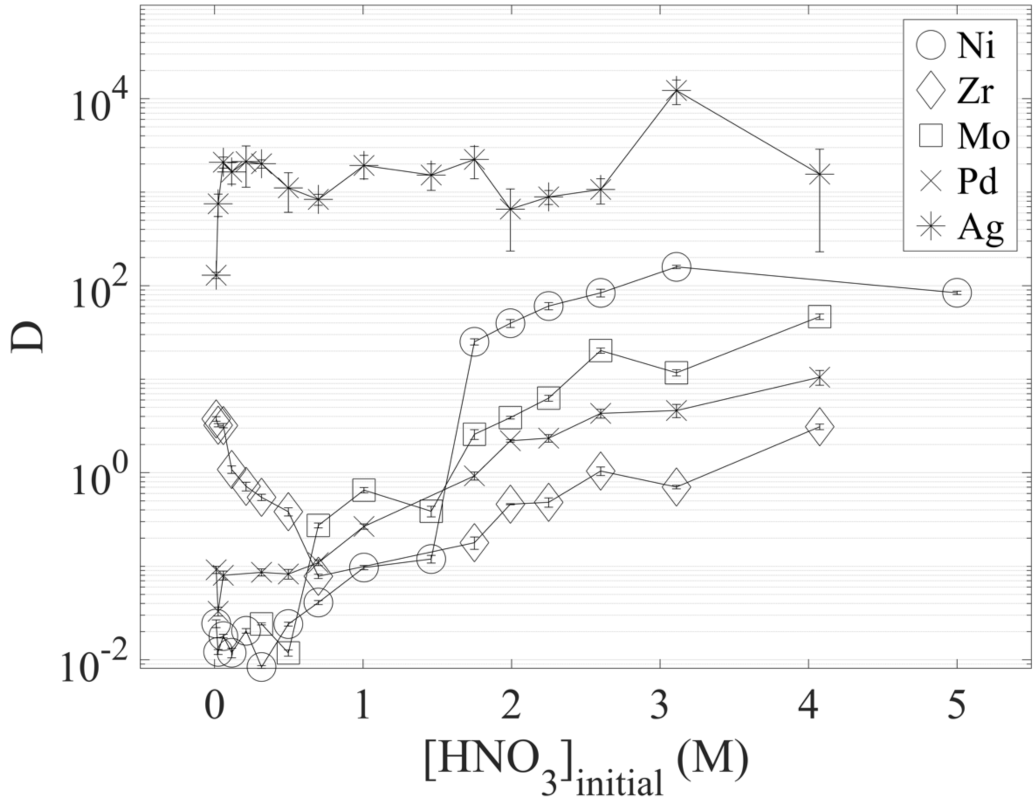


Figure 4.5. The distribution ratio (D) for Zr, Mo, Pd, Ag and Ni as a function of nitric acid concentration, with no complexing agents present. The organic phase was 10 mM CyMe$_4$*-BTBP in 30%*$_{vol}$ *TBP and 70%*$_{vol}$ *FS.13, and the aqueous phase contained* 10^{-5} *M of all investigated metals in varying nitric acid concentrations. All metals were present in the aqueous phase.*

For silver extraction, the distribution ratios are above 100 for all acid concentrations tested. This confirms the trends reported by Aneheim et al.[69], who showed that silver is extracted as a 2:2 complex and forms an inner sphere complex with CyMe$_4$-BTBP, with NO_3^- completely expelled from the inner coordination sphere. Silver is reported to have a coordination number of 4 in aqueous solutions. Each CyMe$_4$-BTBP molecule has four N-donors: one for each acceptor site on the silver ion. This validates what is shown in Figure 4.5, i.e. that D(Ag) is independent of nitrate concentration. A decrease in distribution ratio is seen from nitric acid concentration of 4 M to 5 M for the silver extraction. At distribution ratios above 100, the variation in distribution ratio is statistically arbitrary [36], as the vast majority of metal is extracted regardless. However, any variation for silver could be due to salting out effects, as earlier reported by Aneheim et al [69].

Palladium is extracted as a 1:1 complex with CyMe$_4$-BTBP, with nitrates compensating the charge of the overall complex. Some evidence has also been published for the formation of

1:2 complexes, although there are uncertainties associated with this claim [69]. Earlier slope analysis studies have shown a nitrate dependency of 2 [69]. Cadmium extraction was also studied here as a function of nitric acid. The cadmium remaining in the aqueous phase was below the detection limit of the instrument, yielding infinite distribution ratios. Cadmium was therefore excluded from the data presented in Figure 4.5.

To confirm the extraction dependence on nitrate concentration, a slope analysis was performed by plotting the log(D) value versus the log of the activity coefficients for nitric acid at respective concentrations. This is presented in Figure 4.6. The ionic activity of the aqueous phase was estimated using the activity coefficients determined by Davis et al. [99].

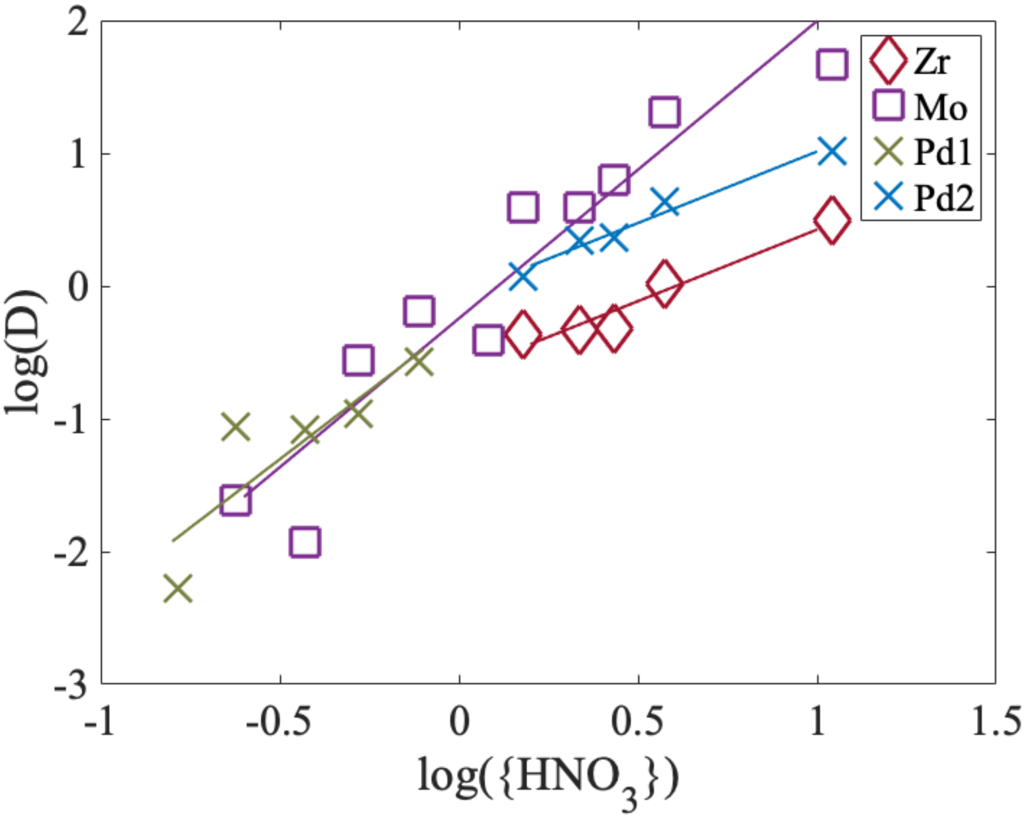


Figure 4.6. Distribution ratios (D) as a function of nitric acid activity for zirconium, molybdenum and palladium.

The results in Figure 4.6 and Table 4.1 show that the nitrate dependency of zirconium and molybdenum is 1.08 and 2.2, respectively. This is established with high confidence (R^2=0.939 and 0.899 respectively). The results for palladium are surprising, with a different nitrate dependency seen for different acid concentrations. At acid concentrations below 1 M, the palladium complex is dependent on two nitrates in its outer sphere for extraction into the organic phase, while at higher concentrations only one nitrate is complexed. Palladium typically exhibits a coordination number of 4 in aqueous solutions [100]. In low nitric acid solutions (at least) two of these coordination sites are occupied by nitrates, while at higher nitric acid concentration only one additional nitrate is coordinated. This could be related to salting in effects, despite the opposite being reported by Aneheim et. al. [69], who reported an exponential increase in the distribution ratio with increased nitrate concentration. Salting-in and salting-out effects are caused by two phenomena: the formation of hydrated salt ions, which ties up water molecules, and the increase in solubility of the organic ligand due to the disruption of hydrogen bonds in the water structure, respectively [36]. The former leads to fewer available solvation molecules, which then decreases the slope of the distribution ratio. The slopes for silver and cadmium showed that their extraction is independent of acid concentration.

Table 4.1. The results of slope analysis of $\log_{10}(D)$ *vs* $\log_{10}(\{HNO3\})$ *for Zr, Mo, Pd, Ag and Cd. The slopes of Pd show the slope at acid concentrations <1 M and slopes for acid concentrations > 1.7 M respectively. The slope of Ag and Cd were inconclusive, and the extraction appears independent of acid concentration.*

	Zr	Mo	Pd	Ag	Cd
Slope	1.08	2.2	2.06 / 1.08	-	-
R^2	0.939	0.899	0.749/ 0.972	-	-

In previous studies, the extraction of cadmium has been disregarded using the argument that it can be incorporated into the fuel as a neutron poison for controlling the reactivity of the reactor. Due to the low concentrations of cadmium in the simulated highly active raffinates (0.0170 mg/L), the high distribution ratios achieved have thus been of low priority when developing the CHALMEX process. There are however an infinite number of spent fuel compositions depending on reactor type, fuel type, operating conditions, burnup, etc. Another concern is also the build-up of cadmium in the organic phase if it is not sufficiently stripped. Handling of zirconium, molybdenum, palladium, silver, nickel and cadmium is therefore desired.

4.4 Performance and optimisation for metal loaded systems

Extraction experiments were performed on a variety of different simulated fission product solutions, compositions can be found in Appendix B. It can be seen in Figure 4.7 that the actinide extraction is significantly reduced in metal loaded systems compared to the extraction in isolated systems. The ALSEP raffinate shows the highest americium extraction, which can be attributed to the significantly lower metal content of this raffinate, including the absence of silver, cadmium, sodium, copper, aluminium and chromium. Furthermore, the content of iron in the ALSEP raffinate is much lower (6.2 mg/L) compared to the HAW-CEA raffinates (~1550 mg/L) and the SANEX raffinate (1375 mg/L). Overall, the HAW-ITU raffinates also have much lower total metal concentration compared to the HAW-CEA- and SANEX raffinates. This includes low iron concentrations (2.2-2.6 mg/L).

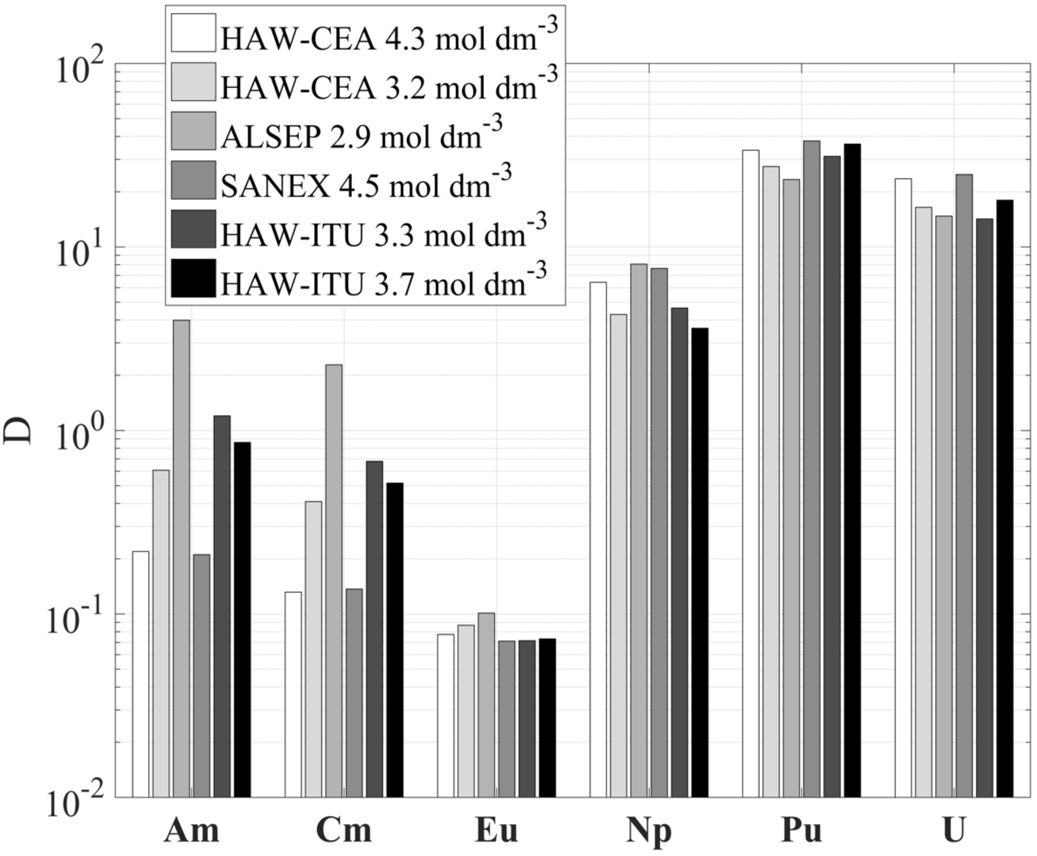


Figure 4.7. Actinide and europium extraction from simulated HAR raffinates of varying composition and acid concentrations (Appendix B). Organic phase was 10mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13.

The previous reported nitric acid dependency also has an effect on the extraction: for americium and curium, the highest distribution ratios are seen for the lower nitric acid concentration for the duplicate raffinates (HAW-CEA and HAW-ITU). The major actinides, U and Pu, both follow the trends previously reported for extraction by TBP [35, 47].

For non-loading systems it has been established that extraction equilibrium is reached after 20 minutes [78]. In systems with very high metal concentrations, and then in particular for systems with compositions similar to real spent nuclear fuel solutions, the equilibrium is not reached within 20 minutes [101]. Kinetics tests for the HAW-CEA 3.157M show that extraction equilibrium for americium is reached within 100 minutes (Figure 4.8). It is clear that both americium and curium extraction is in competition with other elements with slower kinetics.

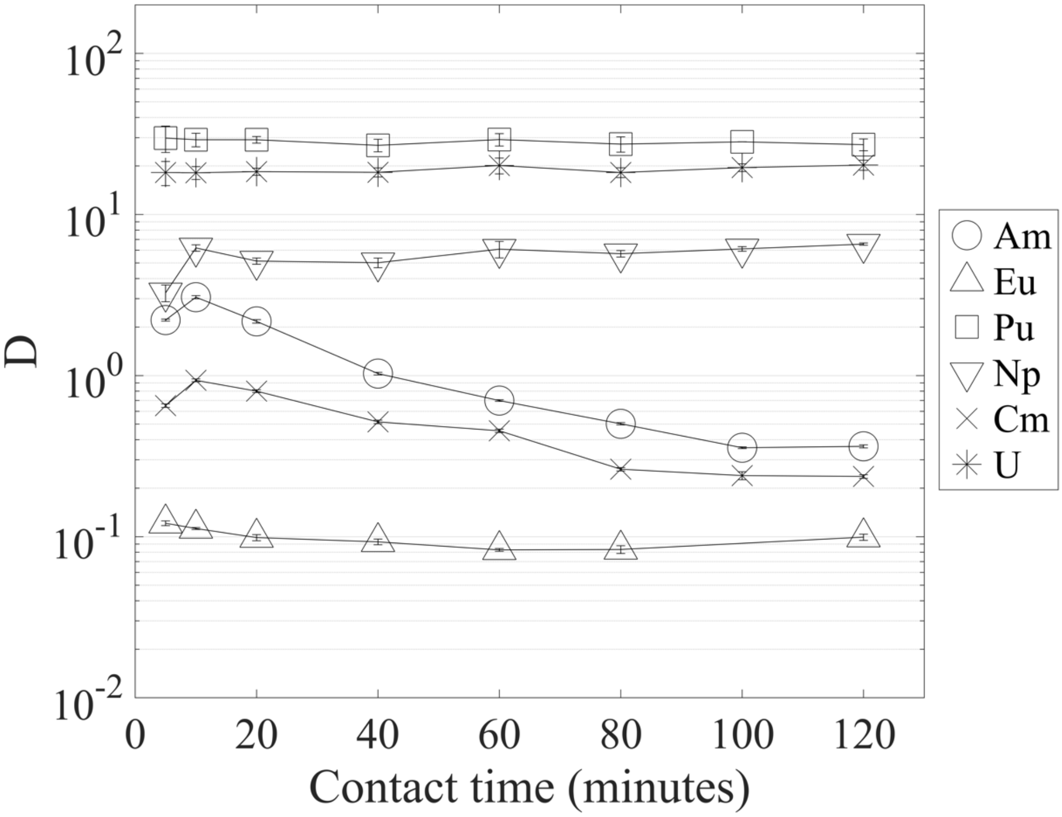


Figure 4.8. The distribution ratio (D) of Eu, U and the transuranic elements during metal loading conditions as a function of contact time. The aqueous phase was HAW-CEA 3.2 M.

The maximum americium and curium distribution ratios are both seen at 10 minute contact time, with distribution ratios of 3.07 and 0.93 respectively. In comparison, the distribution ratio of americium is 0.36 and for curium is 0.24 at equilibrium. The radionuclides that are extracted by TBP all reach equilibrium within 5 minutes, while europium and neptunium reach extraction equilibrium within 20 minutes.

Cadmium, silver and palladium all reach equilibrium within 10 minutes, as seen in Figure 4.9, which was also the general trend for most of the fission products and lanthanides. Molybdenum and zirconium, on the other hand, reach equilibrium within 40 minutes. The slowest extraction of the troublesome fission products is observed for nickel. For nickel, extraction equilibrium is reached after approximately 100 minutes. This compares well to the reduction seen in americium and curium distribution ratios over the same time period. Nickel is present at ~38 mg/L which corresponds to 0.54 mM. By assuming a 1:2 complex with CyMe$_4$-BTBP, Ni extraction can occupy 1.3 mM of CyMe$_4$-BTBP, which is sufficient to reduce the americium and curium extraction.

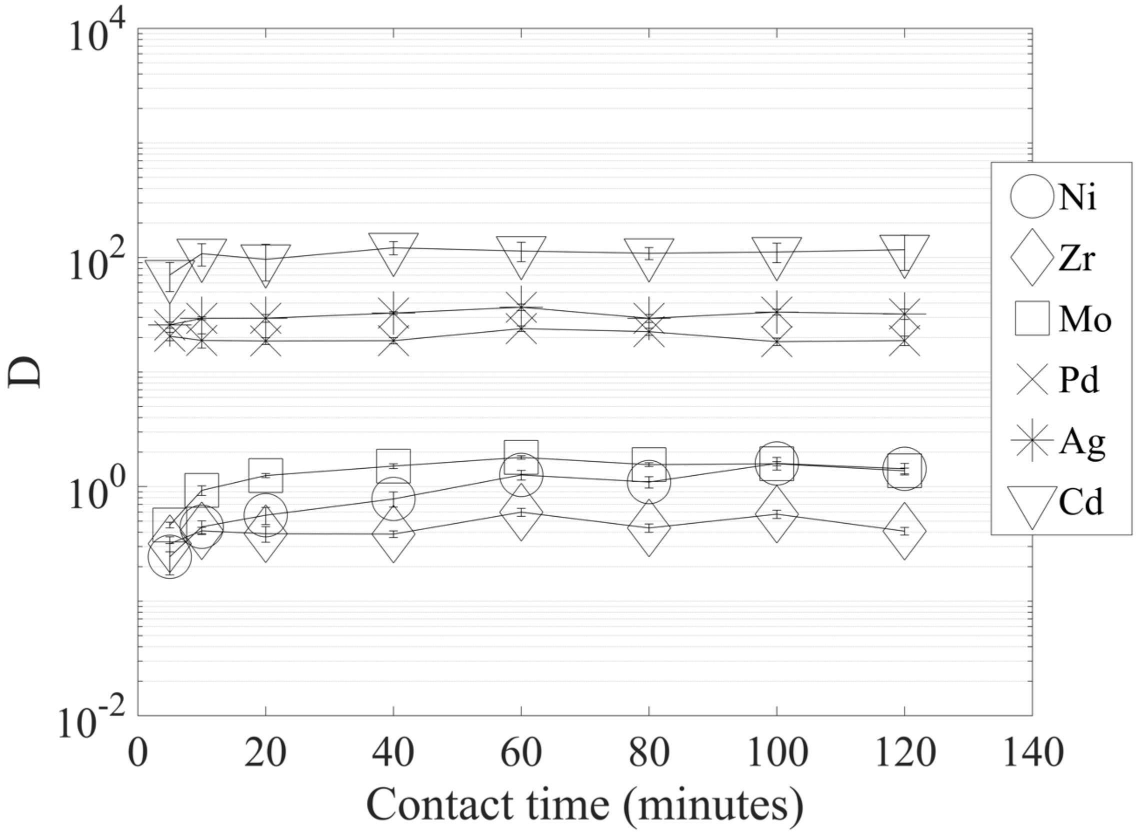


Figure 4.9. The distribution ratio of Ni, Zr, Mo, Pd, Ag and Cd as a function of time in 10 mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13. The aqueous phase was HAW-CEA 3.2 M with trace amounts of radionuclides.

Table 4.2 presents the distribution ratios of the remaining fission and corrosion products and the lanthanides after 120 minute of contacting. All elements reached equilibrium within this time. It is observed that the copper distribution ratio is significantly high to warrant concern. All copper is extracted into the organic phase within 20 minutes. However, copper is only present in small amounts in the raffinate (~0.26 mM).

Table 4.2. The distribution ratios of the remaining elements after 120 minutes contacting time. The aqueous phase was HAW-CEA 3.2 M and the organic phase was 10 mM $CyMe_4$-BTBP in $30\%_{vol}$ TBP and $70\%_{vol}$ FS-13.

	D	**±**		**D**	**±**
Cr	0.13	9.6E-03	**Sb**	0.12	6.5E-03
Fe	0.13	7.6E-4	**Te**	0.11	6.3E-03
Cu	>100	-	**Cs**	0.14	6.2E-03
Se	0.50	5.7E-02	**Ba**	0.20	9.6E-03
Rb	0.31	2.6E-02	**La**	0.18	6.9E-03
Sr	0.16	1.8E-02	**Ce**	0.14	1.0E-02
Y	0.17	1.3E-02	**Pr**	0.16	9.4E-03
Ru	0.57	1.7E-02	**Nd**	0.17	5.1E-03
Rh	0.17	7.1E-03	**Sm**	0.18	8.9E-03
Sn	0.05	1.5E-03	**Gd**	0.18	9.8E-03

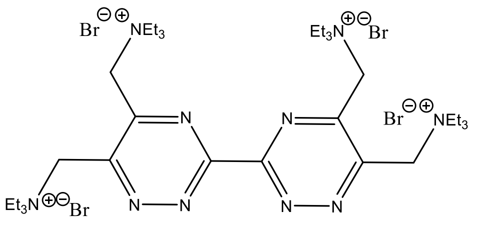
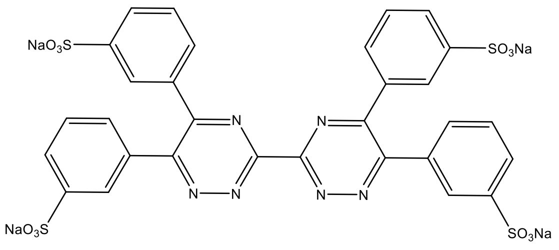
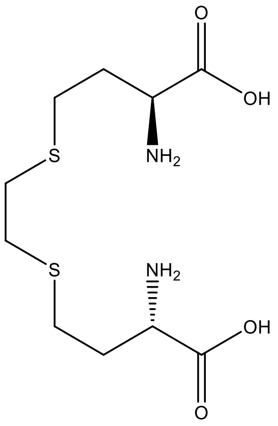
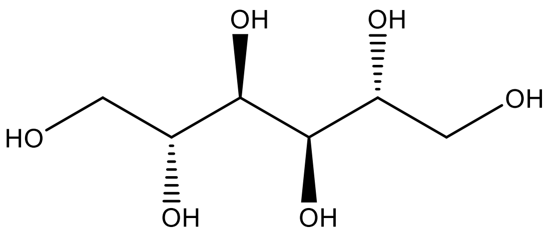
4.4.1 Fission product handling

A thorough study by Aneheim et al. [67, 69] reported several strategies for the handling of challenging fission products, including pre-extraction, scrubbing and complexation. Pre-extraction using kerosene or octanol was found to be a possible option for the removal of nickel from the aqueous phase, while scrubbing using glucono-lactone in $NaNO_3$ (4 M) efficiently removed zirconium and molybdenum from the organic phase. The complexing agents bimet and mannitol reportedly suppress the extraction of molybdenum, zirconium, palladium and silver, but not nickel or cadmium [67]. Mannitol is a complexing agent for molybdenum and zirconium, while bimet was developed for the complexation of palladium. Silver is complexed by both bimet and mannitol. The combination has no effect on the extraction of actinides [67, 101]. However, the main advantage of the CHALMEX process over the other GANEX processes is its simplicity; no redox control is required and there is direct partitioning of actinides from a spent nuclear fuel solution. Having different strategies for various fission products increases the complexity of the process, which is unwanted. One strategy to manage all the concerning elements is therefore desired.

Lewis et al. [102] reports two promising, hydrophilic anionic and cationic complexing agents for the suppression of many transition metals present in spent nuclear fuel solutions. The suppression agents, named Agent 10 and Agent 13 (Table 4.3), are bidentate bis-triazine ligands, showing promising results as hold-back agents for Pd(II), Ni(II) and Ag(I), without interacting with the actinides or the lanthanides [102]. No published data examines the effectiveness of these masking agents for other transition metals, or at different acid concentrations. Data on the effectiveness of these complexing agents under metal loading conditions is also missing. The masking Agent 10 and Agent 13 were both combined with mannitol for molybdenum and zirconium suppression, and compared.

The results, presented in Figure 4.10 (a) and (b) shows the dependency in a system with complexing Agent 10 and complexing Agent 13 respectively. All of the fission products extracted in the presence of complexing Agent 10 show an overall increase in distribution ratio with nitric acid concentration (Figure 4.10 a). However, the distribution ratio trend for Mo shows an initial increase in distribution ratio followed by a decrease between acid concentration of 3 M and 4 M. This suggests that the molybdenum extraction is in competition with the acid extraction by the solvent. The cadmium distribution ratio remains above 10^2 for all acid concentrations, appearing unaffected by the acid concentration. Little effect is seen on the nickel distribution ratio.

Table 4.3. The name and molecular structure for the masking agents used for fission product suppression.

Name	Molecular structure
Agent 10 $(PhSO_3Na)_2$-BT	
Agent 13 $(Ch_2NEt_3X)_2$-BT	
Bimet ((2S,2’S)-4,4’-(ethane- 1,2 - diylbis(sulfanediyl))bis(2- aminobutanoic acid)	
D-Mannitol ((2R,3R,4R,5R)-hexane-1,2,3,4,5,6- hexol)	

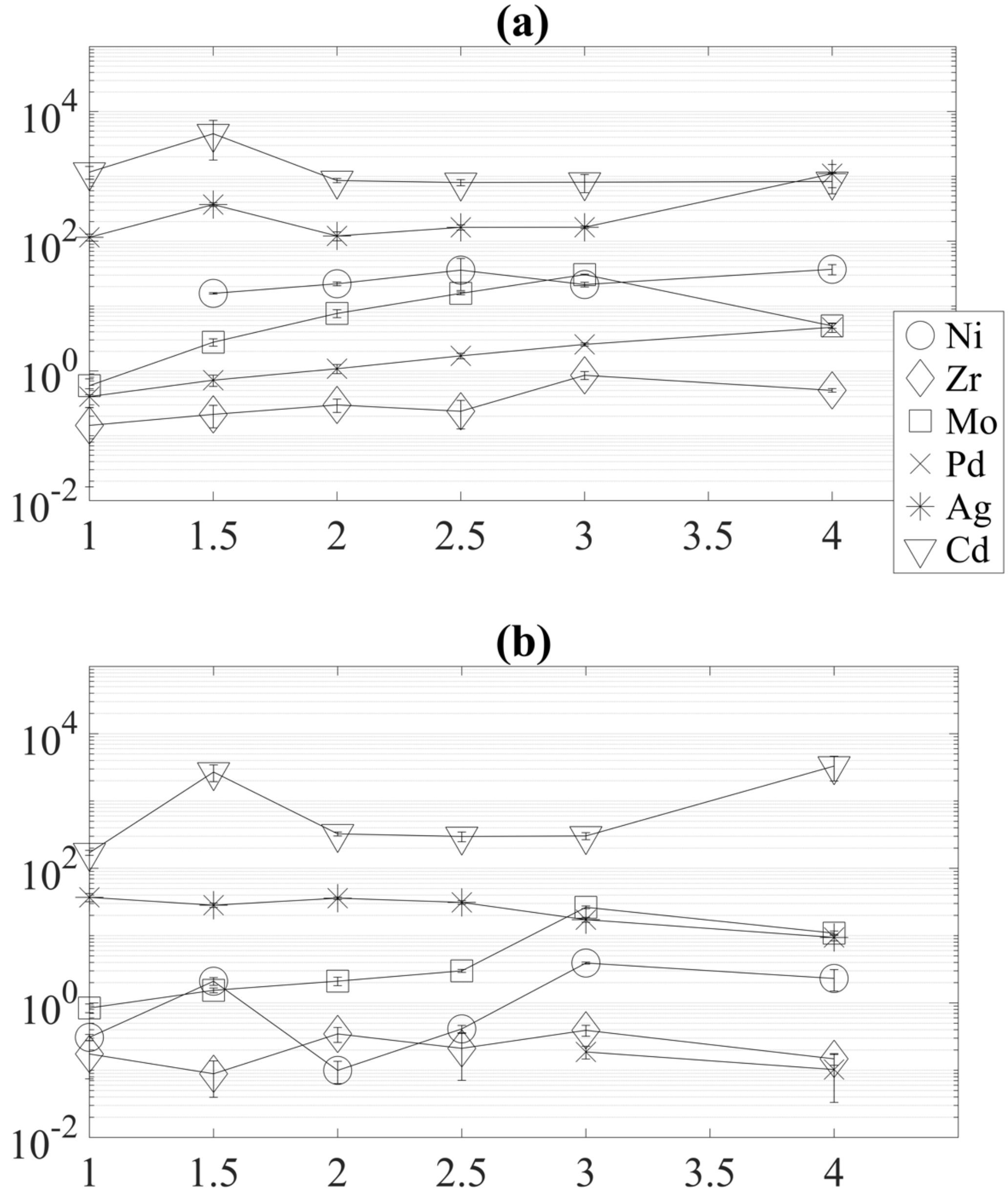


Figure 4.10. Distribution ratio (D) of selected fission products with initial concentration 10^{-5} M with (a) 20 mM Agent 10 and (b) 20 mM Agent 13, as a function of nitric acid concentration. The organic phase was 25 mM $CyMe_4$-BTBP in $30\%_{vol}$ TBP and $70\%_{vol}$ FS-13.

It is also of importance to establish the effects of the various complexing agents under metal loading conditions. The extraction from a simulated PUREX raffinate was therefore examined. The distribution ratio of palladium is reduced compared to in the trace-concentrations of metals, see Figure 4.11. D(Ni) in contrast, increases for all complexing agents. This is possibly correlated to the reduction of palladium extraction, freeing up ligand available for Ni extraction. The same can be said about the molybdenum distribution ratio, which is seen to increase for all the systems containing complexing agents. Molybdenum, however, is extracted by TBP and not CyMe$_4$-BTBP [103], suggesting that the complexing agents efficiently reduce the extraction of another element extracted by TBP. As molybdenum is typically present in high concentrations in spent nuclear fuel raffinates, it is important to have an efficient strategy for the removal of this fission product from the organic phase.

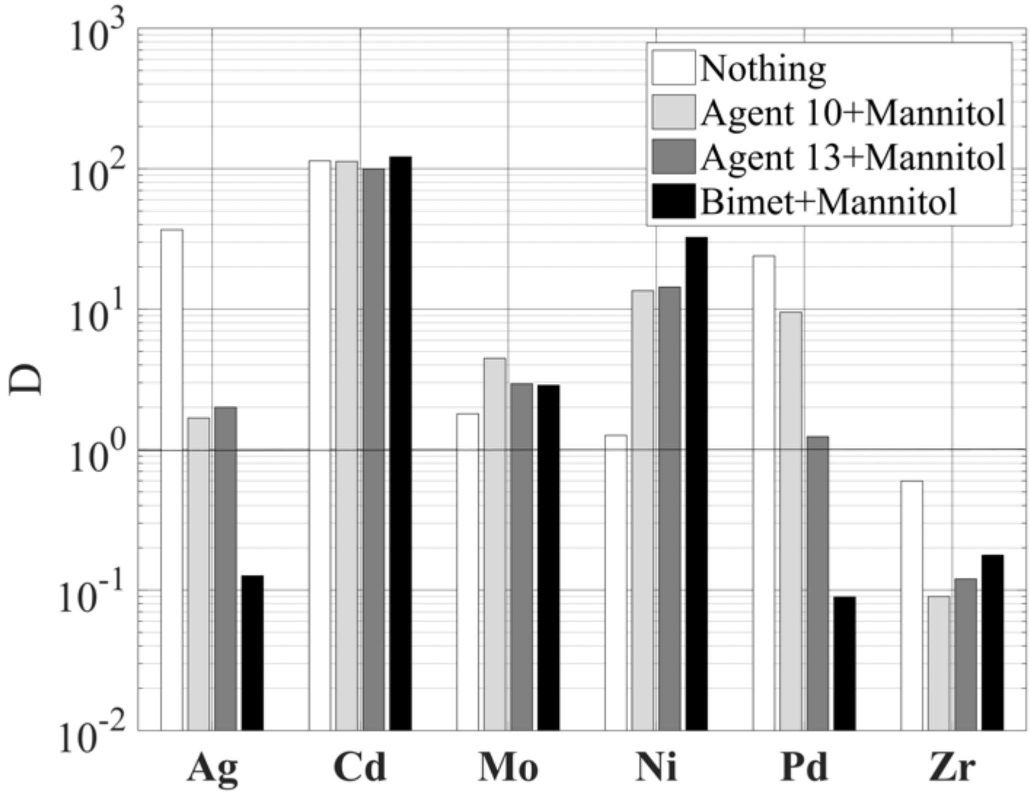


Figure 4.11. The distribution ratio (D) of selected fission products in HAW-CEA 3.2 M raffinate (Appendix B). The extraction was made using 20 mM of the different complexing agents and 0.2 M mannitol. Contact time was 1 hour for all experiments.

The effect of the complexing agents is also notable for the silver extraction. A significant decrease in distribution ratio is seen for all complexing agents, although only bimet reduces the distribution ratio to below 1. The zirconium extraction is also considerably reduced, which is promising due to the high concentration in spent nuclear fuels.

As can be seen in Figure 4.12, the complexing agents have a profound effect on the actinide extraction. For all masking agents, the americium distribution ratio is above 20. Similar effects are seen for curium extraction, where the lowest D(Cm) is seen for the system with Agent 13 and mannitol, at 6.3. The most concerning result is the U distribution ratio, which is significantly reduced in the systems with Agent 10 and Agent 13 compared to the pristine and bimet system. The uranium distribution ratio is conserved for the bimet and mannitol system. Although the bulk of uranium is extracted in first a process step in the GANEX processes, it is still counter-productive to have masking agents, which reduces the extraction of any of the actinides.

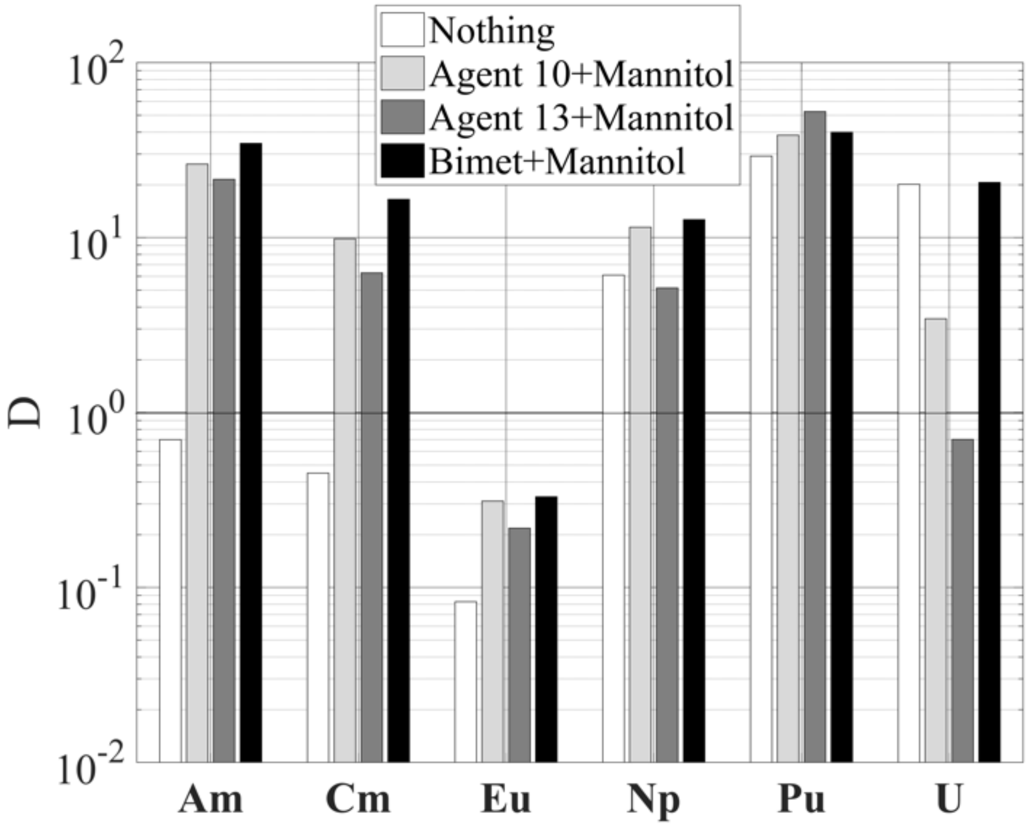


Figure 4.12. The distribution ratio of the actinides and Eu from HAW-CEA 3.2 M raffinate (Appendix B), for different systems containing no or different fission product-complexing agents.

4.5 Batch flowsheet tests

To allow for flowsheet calculations, batch flowsheet tests were conducted. In Test 1, the optimised solvent reported in Paper I [87] was used as the organic phase. After each flow sheet test, the results were used to optimise the next flow sheet test. For example, the CyMe$_4$-BTBP concentration was increased from 10 mM to 25 mM and fission product masking agents were added from Test 1 to Test 2. An acid-molybdenum scrub consisting of 0.01M HNO$_3$, 0.99M or 4M NaNO$_3$ has previously been used for dealing with any extracted molybdenum [67]. δ-glucono-lactone hydrolyses to gluconic acid in water [104], which is a known complexing agent for molybdenum [105]. A high nitrate concentration is needed to prevent the back-extraction of the actinides from the organic phase. Due to the high abundance of molybdenum (~500 mg/L) in spent nuclear fuel a significant amount is still extracted into the organic phase, despite its low distribution ratio (D=0.2-0.9). Scrubbing of Mo for the current CHALMEX system was investigated using a 0.01M HNO_3 solution with 0.99M $NaNO_3$ and 0.6M δ-glucono-lactone on two different simulated HAR solutions, where issues with precipitation became apparent. A summary of the process conditions for the different flow sheet tests are presented in Table 4.4.

Table 4.4. An overview of the 3 batch flowsheet tests that were conducted.

Flow sheet test	1	2	3
Simulated PUREX raffinate	HAW-ITU (3.3 M)	HAW-CEA (3.2 M)	HAW-CEA (3.2 M)
[CyMe$_4$-BTBP] (mM)	10	25	25
No. of scrub stages	1	2	2
No. of strip stages	2	2	2
Complexing agent	None	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	0.01 M HNO_3 0.99 M $NaNO_3$ 0.6 M glucono-lactone	0.5 M HNO_3
Strip solution	0.5M glycolic acid at pH 4	0.5M glycolic acid at pH 4	0.5M glycolic acid at pH 4

The actinide extraction in Flowsheet Test 1 (Figure 4.13, Flowsheet 1) is comparable to the one presented in Figure 4.7, with low americium and curium extraction (D(Am)=1.41 and D(Cm)=0.72) compared to non-loading systems. The most noticeable trend seen here is that plutonium is partially scrubbed from the organic phase in the scrubbing stage. Bar the americium stripping, the results are in accordance with previously reported trends, where the actinides are efficiently stripped in the first stripping stage [79].

Fission product behaviour in the flowsheet tests is reported for the elements of most concern in Table 4.5. It is seen that for Flowsheet 1, the acid/Mo scrub efficiently back-extracts molybdenum and zirconium from the organic phase. Palladium on the other hand is partially stripped along with the actinides in stripping stage 1, although the majority of the extracted palladium remains in the organic phase. From the pH of stripping stage 1, it is also obvious that there was still a significant amount of residual acid in the organic solution, that was stripped by the stripping solution. Nickel is also only partially stripped in the second strip stage. Although this allows for separation from the actinides, the potential build-up of nickel in the organic phase is concerning. Both silver and cadmium are significantly extracted, and also remain in the organic phase through all of the process steps.

In Flowsheet Test 2 (Figure 4.13), a significant increase in americium, curium and neptunium extraction is seen with D(Am)=19.4, D(Cm)=10.3 and D(Np)=16.19. This is most likely due to both the higher CyMe$_4$BTBP concentration in the organic phase and also the presence of fission product complexing agents in the aqueous phase. Europium distribution ratio remains below 0.3 for the extraction stage, yielding a high separation factor between the minor actinides and europium. Both plutonium and uranium extraction are maintained (D(Pu)=41.4 and D(U)=21.71) and similar trends are seen for plutonium in the first scrubbing stage, where more than 50% of the plutonium is scrubbed from the organic phase. In the second scrubbing stage, significant precipitation in the organic phase was observed, obstructing the sampling of the organic phase.

Different simulated PUREX solutions were used for Flowsheet 1 and Flowsheet 2. The major difference is the absence of sodium, copper, nickel, iron and chromium in the HAW-ITU raffinate. Sodium and iron are both present in high concentrations in the HAW-CEA raffinate (~1660 mg L^{-1} and ~1545 mg L^{-1} respectively), and these elements are therefore more likely to be the cause of the significant precipitation that occurred in Flowsheet Test 2. Although the organic phase could not be sampled for ICP-MS analysis, the aqueous phase was sampled. The mass balance indicated that no sodium remained in the organic phase when the precipitate was formed, while ~500 mg/of iron was misplaced from the aqueous phase and was thus present in the organic phase. The mass balance showed that no other element showed comparable deviations in mass balance. Based on this, it is assumed likely that the precipitate is caused by the formation of insoluble iron complexes.

A high iron content is expected in all spent nuclear fuel solutions. Gluconic acid complexes with iron have been reported previously [106-107]. In similar solvent extraction systems, other scrubbing solutions are used (including both a low nitric acid concentration and NaNO$_3$) in which no precipitation is seen. It is thus deemed likely that the glucono-lactone is responsible for the formation of insoluble iron complexes.

As expected, the presence of complexing agents has significant effect on the extraction of several of the troublesome fission products. Only negligible amounts of molybdenum and zirconium are extracted (D<0.05). Molybdenum extraction is however higher than in the pristine system tested in Flowsheet 1, although the first scrubbing stage removes the majority of extracted metal. A significant reduction in D(Ag) is also seen, reduced from 14.6 to 0.1. Even cadmium distribution ratio is slightly affected, although the vast majority of cadmium is still extracted. Nickel distribution ratios remain unaffected by the complexing agents.

To avoid both the scrubbing of plutonium and precipitation of iron in the scrubbing stages, the acid scrub was replaced with 0.5M HNO_3 in Flowsheet 3. As in Flowsheet 2, the actinide extraction is maintained at acceptable levels for Flowsheet 3 (Figure 4.13). Plutonium also remains in the organic phase during scrubbing. However, neptunium is seen to be partially scrubbed, with $D\sim1$. After two scrubbing stages such a D value means approximately 75% of the neptunium is removed from the organic phase. All actinides are efficiently stripped in the first stripping stage. Due to unavailability of uranium tracer, no such tracer was added in the third flowsheet.

Fission product extraction in Flowsheet 3 is, not surprisingly, comparable to Flowsheet 2 (Figure 4.2). However, a considerable difference in the effect of scrubbing solutions is seen. The 0.5 M HNO_3 scrubbing solution is effective in its scrubbing of silver, molybdenum and zirconium. Even if very low amounts of zirconium are extracted, it is all scrubbed efficiently by 0.5 M HNO_3. Despite an unmistakeable reduction in the distribution ratio of cadmium, more than 98% of the metal is still extracted, while only a small amount is removed in the scrubbing and stripping stages. The same can be seen for nickel. A different handling strategy is therefore needed for these elements.

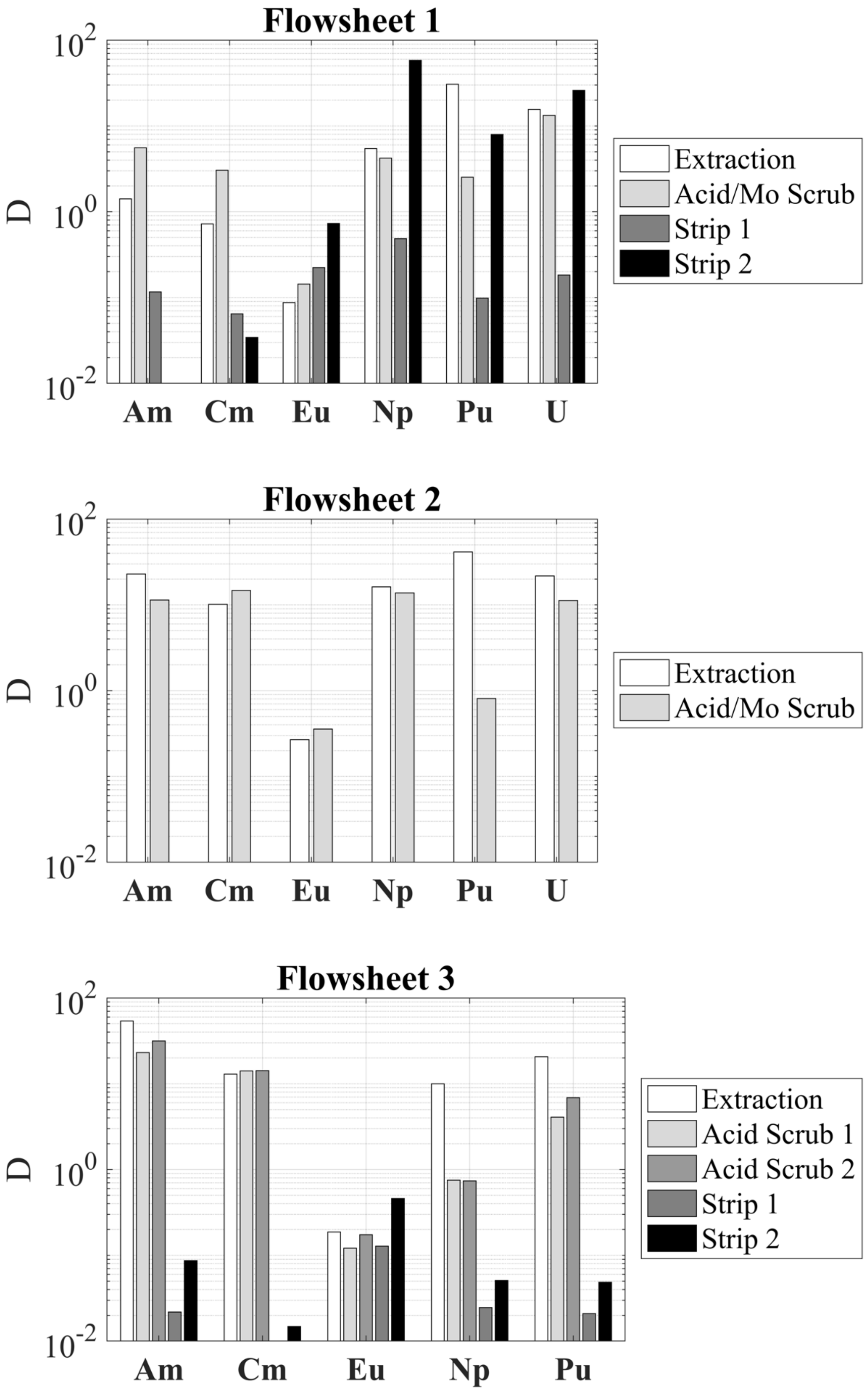


Figure 4.13. The distribution ratios (D) of the actinides and Eu for the flowsheet tests conducted using simulated PUREX raffinates.

Table 4.5. The pH and distribution ratios for selected fission products for the different flowsheet tests and stages.

	Process stage	pH	Ag	Cd	Mo	Ni	Pd	Zr
Flowsheet 1	Extraction	-	15	>100	1.7	0.5	20	0.2
	Scrub	-0.2	41.0	>100	0.4	>100	25	0.1
	Strip 1	1.8	>100	>100	0.0	>100	1.6	0.5
	Strip 2	3.9	13	>100	1.7	0.6	>100	1.4
Flowsheet 2	Extraction	-0.5	0.1	50	2.8	>100	0.0	0.0
	Scrub 1	-0.1	5.5	>100	0.1	>100	0.1	0.3
	Scrub 2	0.1	Precipitation					
Flowsheet 3	Extraction	-0.5	0.2	42	2.2	>100	0.0	0.0
	Scrub 1	0.2	0.5	24	0.0	13	0.5	0.1
	Scrub 2	0.3	0.5	16	0.3	>100	2.1	0.6
	Strip 1	0.8	2.0	>100	5.9	94	>100	3.4
	Strip 2	0.8	0.8	>100	>100	4.1	91	11

4.6 Continuous test in a centrifugal contactor

A single centrifugal contactor test was performed to assess the suitability of this type of contactor for the scaled-up operation of the CHALMEX process. Tests on the first CHALMEX solvent, in which cyclohexanone was used as a diluent, reported phase separation issues due to the similar densities of the loaded organic phase and the aqueous phase [75]. In the current system a heavy diluent is used (ρ=1.41 g cm^{-3} [80]) to evade the phase separation issue. The experimental setup is shown in Figure 3.1. The test was run over 3 different flow rates, and the results for the actinides are presented in Figure 4.14. The americium and curium distribution ratio show expected trends; lower flow rates yield higher distribution ratio due to higher residence time in the contactor. The distribution ratio at equilibrium is lower than that seen in the contactor. This supports the results presented in Figure 4.8, where a shorter contact time between the organic and aqueous phase was beneficial to maximise the Am/Cm extraction. Neptunium, plutonium and uranium distribution ratios also show expected trends. They are all extracted by the kinetically faster TBP molecule. Uranium and plutonium both reach extraction equilibrium within 1 minute, while neptunium requires 10 minutes, which is shown in Figure 4.14.

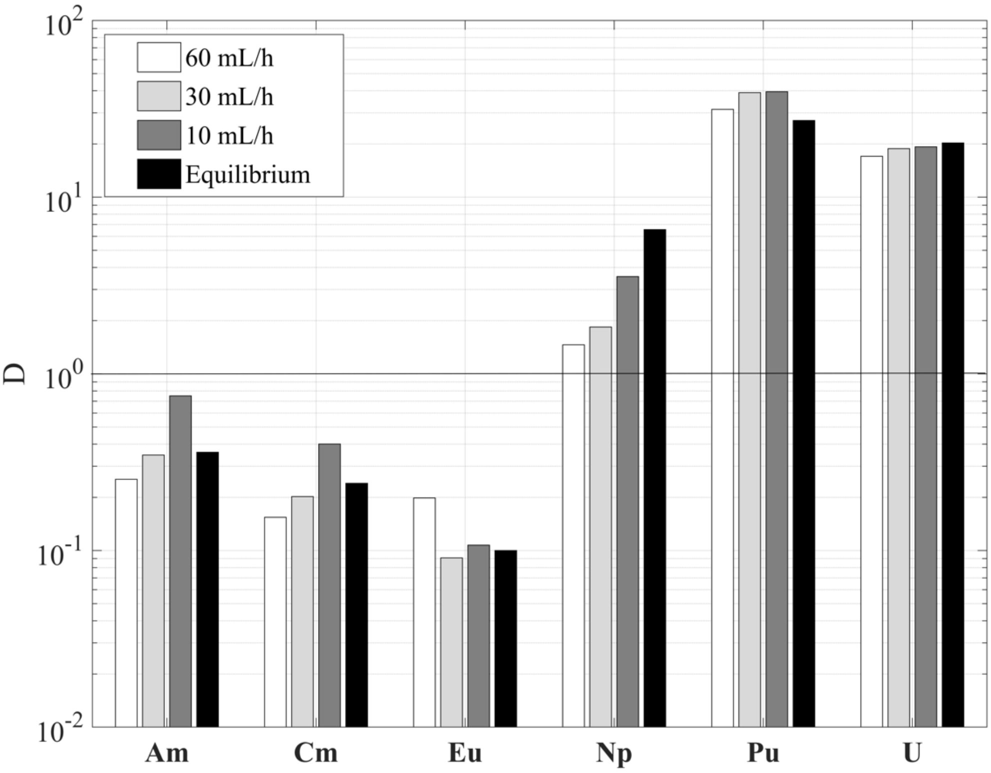


Figure 4.14. The actinide distribution ratio (D) for different flow rates in a single centrifugal contactor test. The equilibrium distribution ratios have been added for comparison.

For the lanthanides, corrosion-, activation- and fission products, the extraction is reduced compared to what was seen in the preceding batch experiments and compared to the equilibrium values, shown in Table 4.6. Only the most extracted species are seen (based on both distribution ratio and abundance in the simulated PUREX raffinate). One can also see an increasing trend, with decreasing flow rate and increasing contact time especially for the highly extracted species cadmium and palladium. Silver, cadmium, palladium and nickel have the highest distribution ratios of all the extracted elements. Their distribution ratios are high even for high flow rates showing their fast extraction kinetics. The nickel distribution ratio, however, has a lower equilibrium distribution ratio (D_{eqm}=0.4) compared to all the flow rates tested in the single centrifugal contactor (D=1.1-3.9). This suggest that nickel is competed out by another element present in the solution.

Molybdenum distribution ratios are significantly lower for all flow rates (D=0.04-0.20) compared to its equilibrium value (D_{eqm}=1.5). This is beneficial for the CHALMEX system, as molybdenum is present in relatively high concentrations (378 mg/L) and even a low distribution ratio of 1 means that a significant amount of metal is extracted. Zirconium also show lower distribution ratios in the centrifugal contactor test (D=0.20-0.27), compared to its equilibrium value (D_{eqm}=0.46). Once again, zirconium has a concentration of 464 mg/L, and so it's slow extraction kinetics can only be seen as beneficial for the CHALMEX system overall.

Table 4.6. The distribution ratios for Ag, Cd, Mo, Ni, Pd and Zr for the different flow rates and at equilibrium for the single centrifugal contactor test.

	Ag	**Cd**	**Mo**	**Ni**	**Pd**	**Zr**
60 mL/h	49	52	0.04	2.5	5.0	0.20
30 mL/h	41	61	0.06	1.1	7.0	0.21
10 mL/h	38	263	0.20	3.9	16	0.27
Equilibrium	56	486	1.5	0.4	26	0.46

5 | Summary and Conclusions

The work presented in this thesis focused on complementing already existing data on the CHALMEX FS-13 process, as well as establishing knowledge required for the progression of system evaluation. Studies have been performed to complement data-bases for future process simulations and to allow for calculations on the number of ideal stages.

In the CHALMEX FS-13 process, the extractants CyMe$_4$-BTBP and tri-*n*-butyl phosphate (TBP) are combined in phenyl trifluoromethyl sulfone (FS-13) for the homogeneous recycling of uranium, plutonium and the minor actinides from spent nuclear fuel. The optimal solvent composition was found to be 10 mM CyMe$_4$-BTBP in 30%$_{vol}$ TBP and 70%$_{vol}$ FS-13 for radionuclides present in trace levels. The optimised solvent extracts a significant amount of acid, which was also shown to compete with the americium extraction.

Acid concentration was found to have a significant effect on the distribution ratios of all investigated radionuclides (Pu, Np, Am, Cm and Eu), especially at nitric acid concentrations below 2 M. The maximum distribution ratio occurs at a nitric acid concentration of 2.5 M, while plutonium distribution ratio increases with increasing nitric acid concentration. Several fission products are extracted to a significant extent, but only silver and palladium extraction was found to be independent of nitric acid concentration.

Under more process-like conditions, the americium extraction was significantly reduced from trace level experiments. The kinetics of minor actinide extraction were also found to be much slower under metal loading conditions, and extraction equilibrium was reached only after 100 minutes of contacting for americium. Americium was seen to be competed out of the organic phase by nickel. To improve the distribution ratio of americium, the CyMe$_4$-BTBP concentration was increased and the use of bimet and mannitol as masking agents was tested. It was found that this optimised system achieved sufficient americium extraction. However, several flowsheet tests showed that both nickel and cadmium require a different handling strategy.

By using a heavy diluent (FS-13) it was also found that phase separation was much improved from the previous CHALMEX system. Centrifugal contactors are believed to be a viable option as a contacting unit for the CHALMEX FS-13 process. As successful cold-tests have been performed, TRL is now estimated to have increased from between 2-3, to between 3-4.

6 | Future work

Several alternatives should be considered for future work. Due to the very slow kinetics of the CyMe$_4$-BTBP molecule under metal loading conditions, an alternative molecule can be screened and considered for replacement.

It is also clear that several fission products need a sufficient handling strategy, as the remain in the organic phase even after the stripping stages. Alternatives include pre-extraction, or investigating other masking agents. A solvent clean-up study should be initiated, to determine if the troublesome fission products can be removed from the organic phase. Such a study should include un-irradiated solvent and irradiated solvent. Alternatives to non-CHON chemicals should also be considered, such as replacing $NaNO_3$ with NH_3NO_3.

Lastly, work should continue to allow for evaluation of the viability of the CHALMEX FS-13 process. This includes single centrifugal contactor tests to allow for McCabe Thiele calculations, for the optimised system containing masking agents. A full flowsheet test with scrubbing and stripping stages should be conducted to determine any deviations from ideal process conditions.

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8 | References

1. Rogelj, J., Shindell, D., Jiang, K., Fifita, S., Forster, P., Ginzburg, V., Handa, C., Kheshgi, H., Kobayashi, S., Kriegler, E., Mundaca, L., Séférian, R., and Vilariño, M.V., *Mitigation Pathways Compatible with 1.5°C in the Context of Sustainable*

   Development. In: Global Warming of 1.5°C. An Ipcc Special Report on the Impacts of Global Warming of 1.5°C above

   Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global

   Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty, G. Flato, et al., Editors. 2018, Intergovernmental Panel on Climate Change. p. 93-175.

2. Ipcc, *Global Warming of 1.5°C. An Ipcc Special Report on the Impacts*

   of Global Warming of 1.5°C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways,

   in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development,

   and Efforts to Eradicate Poverty., V. Masson-Delmotte, et al., Editors. 2018, World Meteorological Organization: Geneva, Switzerland. p. 32.

3. Fridays for Future. *About #Fridaysforfuture*. 2020 [cited 2020 23rd Jan]; Available from: https://www.fridaysforfuture.org/about.

4. Serp, J., Poinssot, C., and Bourg, S., *Assessment of the Anticipated Environmental Footprint of Future Nuclear Energy Systems. Evidence of the Beneficial Effect of Extensive Recycling.* Energies, 2017. **10**(9).

5. Greenpeace. *Nuclear Power*. 2019 [cited 2019 4th October]; Available from: https://www.greenpeace.org.uk/challenges/nuclear-power/.

6. The Center for Arms Control and Non-Proliferation. *Nuclear Proliferation Risks in Nuclear Energy Programs*. 2018 [cited 2019 4th Oct]; Available from: https://armscontrolcenter.org/nuclear-proliferation-risks-in-nuclear-energy-programs/.

7. Marcus, G.H., *Nuclear Power around the World.* Nature Reviews Physics, 2019. **1**(3): p. 172.

8. World Nuclear Association. *Generation Iv Nuclear Reactors*. 2019 [cited 2019 22nd Oct]; Available from: http://www.world-nuclear.org/information-library/nuclear-fuel-cycle/nuclear-power-reactors/generation-iv-nuclear-reactors.aspx.

9. Forsberg, C., *Implications of Plutonium Isotopic Separation on Closed Fuel Cycles and Repository Design.* Nuclear Technology, 2015. **189**(1): p. 63-70.

10. Camarcat, N., Lecarpentier, D., Lavaud, F., and Lemaire, P., *Plutonium Multi Recycling in Pressurised Water Reactors of the Epr Type Using Laser Isotope Separation of Pu242.* Annals of Nuclear Energy, 2019. **129**: p. 399-411.

11. Taylor, R., *Reprocessing and Recycling of Spent Nuclear Fuel*. Vol. 79. 2015, Cambridge: Woodhead Publishing.

12. Pandikumar, G., Arul, A.J., Puthiyavinayagam, P., and Chellapandi, P., *Multiple Recycling of Fuel in Prototype Fast Breeder Reactor in a Closed Fuel Cycle with Pressurized Heavy-Water Reactor External Feed.* Pramana, 2015. **85**(4): p. 667-683.

13. Rodríguez-Penalonga, L. and Moratilla Soria, Y.B., *A Review of the Nuclear Fuel Cycle Strategies and the Spent Nuclear Fuel Management Technologies.* Energies, 2017. **10**(8).

14. Schwenk-Ferrero, A., *German Spent Nuclear Fuel Legacy: Characteristics and High-Level Waste Management Issues.* Science and Technology of Nuclear Installations, 2013. **2013**: p. 1-11.

15. Madic, C. and Ouvrier, N., *Europart: European Research Program for the Partitioning of Minor Actinides from High Active Wastes Arising from the Reprocessing of Spent Nuclear Fuels*, in *Radiochimica Acta*. 2008. p. 183.

16. Osaka, M., Koi, M., Takano, S., Yamane, Y., and Misawa, T., *A Novel Concept for Americium-Containing Target for Use in Fast Reactors.* Journal of Nuclear Science and Technology, 2006. **43**(4): p. 367-374.

17. Burkes, D.E., Fielding, R.S., and Porter, D.L., *Metallic Fast Reactor Fuel Fabrication for the Global Nuclear Energy Partnership.* Journal of Nuclear Materials, 2009. **392**(2): p. 158-163.

18. Heidet, F., Kim, T.K., and Taiwo, T.A., *Impact of Minor Actinide Recycling on Sustainable Fuel Cycle Options.* Nuclear Engineering and Design, 2017. **323**: p. 434-462.

19. World Nuclear Association. *Fast Neutron Reactors*. 2019 [cited 2019 10th Oct]; Available from: https://www.world-nuclear.org/information-library/current-and-future-generation/fast-neutron-reactors.aspx.

20. Abram, T. and Ion, S., *Generation-Iv Nuclear Power: A Review of the State of the Science.* Energy Policy, 2008. **36**(12): p. 4323-4330.

21. Rostaing, C., Poinssot, C., Warin, D., Baron, P., and Lorraina, B., *Development and Validation of the Exam Separation Process for Single Am Recycling.* Procedia Chemistry, 2012. **7**: p. 367-373.

22. Taylor, R.J., Gregson, C.R., Carrott, M.J., Mason, C., and Sarsfield, M.J., *Progress Towards the Full Recovery of Neptunium in an Advanced Purex Process.* Solvent Extraction and Ion Exchange, 2013. **31**(4): p. 442-462.

23. Joly, P. and Boo, E., *Roadmap- Actinide Separation Processes*. 2015, Euroatom Research and Traning Programme on Nuclear Energy within the Seventh Framework Programme.

24. Joly, P. and Boo, E., *Roadmap: Actinide Separation Processes 2015*. 2016, SACSESS: Online.

25. Hill, C., Arnaud-Neu, F., Espertero, A.G., Desreux, J.-F., Modolo, G., Bourg, S., Malmbeck, R., Caravaca, C., Harrison, M., De Angelis, G., Uhlir, J., Ouvrier, N., and Madic, C., *Europart Sixth Framework Programme- Final Activity Report*. 2007, European Comission. p. 108.

26. Geniors Project. *About Geniors*. 2017 [cited 2018 11th Jul]; Available from: http://www.geniors.eu/about-geniors/.

27. Magnusson, D. and Malmbeck, R., *Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors.* Solvent Extraction and Ion Exchange, 2012. **30**(2): p. 115-126.

28. Choppin, G.R., Liljenzin, J.-O., Rydberg, J., Ekberg, C., Sciencedirect, Books24x, Ebook, C., and Knovel, *Radiochemistry and Nuclear Chemistry*. 4th;Fourth;4;4th; ed. 2013, Amsterdam;Boston;: Elsevier/AP, Academic Press is an imprint of Elsevier.

29. Woźnicka, U., *Review of Neutron Diagnostics Based on Fission Reactions Induced by Fusion Neutrons.* Journal of Fusion Energy, 2019. **38**(3): p. 376-385.

30. Falck, W.E. and Nilsson, K.-F., *Geological Disposal of Radioactive Waste: Moving Towards Implementation* 2009, European Commission JRC-IE.

31. OECD-NEA RWMC, *Moving Forward with Geological Disposal of Radioactive Waste*. 2008.

32. Swedish Nuclear Fuel and Waste Management Co. SKB, *Double Approval of Skb's Final Repository Application* 2019, Swedish Nuclear Fuel and Waste Management Co. SKB, : Online.

33. Posiva, *Final Disposal*, in *General Time Schedule for Final Disposal*. 2020, Posiva: Online.

34. European Nuclear Society. *Purex Process*. 2017 [cited 2017 4th Aug]; Available from: https://www.euronuclear.org/info/encyclopedia/p/purex-process.htm.

35. Irish, E.R. and Reas, W.H., *The Purex Process— a Solvent Extraction Reprocessing Method for Irradiated Uranium*. 1957, General Electric: Richland, Washington.

36. Rydberg, J., Cox, M., Musikas, C., and Choppin, G.R., *Solvent Extraction Principles and Practice*. 2nd ed. 2004, New York: Marcel Dekker.

37. Miguirditchian, M., Chareyre, L., Heres, X., Hill, C., Baron, P., and Masson, M., *Ganex: Adaptation of the Diamex-Sanex Process for the Group Actinide Separation*. 2007, United States: American Nuclear Society - ANS.

38. Adnet, J.-M., Miguirditchian, M., Hill, C., Heres, X., Lecomte, M., Masson, M., Brossard, P., and Baron, P. *Development of New Hydrometallurgical Processes for Actinide Recovery: Ganex Concept*. in *GLOBAL 2005: Proceedings of the international conference on nuclear energy systems for future generation and global sustainability*. 2005. Japan: Atomic Energy Society of Japan.

39. Bell, K., Carpentier, C., Carrott, M., Geist, A., Gregson, C., Hérès, X., Magnusson, D., Malmbeck, R., Mclachlan, F., Modolo, G., Müllich, U., Sypula, M., Taylor, R., and Wilden, A., *Progress Towards the Development of a New Ganex Process.* Procedia Chemistry, 2012. **7**: p. 392-397.

40. Carrott, M., Geist, A., Heres, X., Lange, S., Malmbeck, R., Miguirditchian, M., Modolo, G., Wilden, A., and Taylor, R., *Distribution of Plutonium, Americium and Interfering Fission Products between Nitric Acid and a Mixed Organic Phase of Todga and Dmdohema in Kerosene, and Implications for the Design of the "Euro-Ganex" Process.* HYDROMETALLURGY, 2015. **152**: p. 139-148.

41. Malmbeck, R., Magnusson, D., Bourg, S., Carrott, M., Geist, A., Heres, X., Miguirditchian, M., Modolo, G., Müllich, U., Sorel, C., Taylor, R., and Wilden, A., *Homogenous Recycling of Transuranium Elements from Irradiated Fast Reactor Fuel by the Euro-Ganex Solvent Extraction Process.* Radiochim. Acta, 2019.

42. Miguirditchian, M., Roussel, H., Chareyre, L., Baron, P., Espinoux, D., Calor, J.N., Viallesoubranne, C., Lorrain, B., and Masson, M. *Ha Demonstration in the Atalante Facility of the Ganex 2 Cycle for the Grouped Tru Extraction*. in *Proceedings of the GLOBAL 2009 congress - The Nuclear Fuel Cycle: Sustainable Options and Industrial Perspectives*. 2009. France.

43. Miguirditchian, M., Sorel, C., Camès, B., Bisel, I., Baron, P., Espinoux, D., Calor, J.-N., Viallesoubranne, C., Lorrain, B., and Masson, M. *Ha Demonstration in the Atalante Facility of the Ganex 1st Cycle for the Selective Extraction of Uranium from Hlw*. in *GLOBAL*. 2009. Paris, France: GLOBAL.

44. Taylor, R., Carrott, M., Galan, H., Geist, A., Hères, X., Maher, C., Mason, C., Malmbeck, R., Miguirditchian, M., Modolo, G., Rhodes, C., Sarsfield, M., and Wilden, A., *The Euro-Ganex Process: Current Status of Flowsheet Development and Process Safety Studies.* Procedia Chemistry, 2016. **21**: p. 524-529.

45. Atkins, P.W. and Jones, L., *Chemical Principles : The Quest for Insight*. Fourth edition. 2008: W.H. Freeman.

46. Hesford, E. and Mckay, H.a.C., *The Extraction of Mineral Acids by Tri-N-Butyl Phosphate (Tbp).* Journal of Inorganic and Nuclear Chemistry, 1960. **13**(1): p. 156-164.

47. Petrich, G. and Kolarik, Z., *The 1981 Purex Distribution Data Index*. 1981: Germany. p. 104.

48. Sasaki, Y., Sugo, Y., Suzuki, S., and Tachimori, S., *The Novel Extractants, Diglycolamides, for the Extraction of Lanthanides and Actinides in Hno3–N-Dodecane System.* Solvent Extraction and Ion Exchange, 2001. **19**(1): p. 91-103.

49. Ansari, S.A., Pathak, P.N., Manchanda, V.K., Husain, M., Prasad, A.K., and Parmar, V.S., *N,N,N′,N′-Tetraoctyl Diglycolamide (Todga): A Promising Extractant for Actinide-Partitioning from High-Level Waste (Hlw).* Solvent Extraction and Ion Exchange, 2005. **23**(4): p. 463-479.

50. Pearson, R.G., *Hard and Soft Acids and Bases—the Evolution of a Chemical Concept.* Coordination Chemistry Reviews, 1990. **100**: p. 403-425.

51. Ullmann, H., K. A. Gschneidner, J., Eyring, L., Choppin, G.R., and (Eds.)., G.H.L., *Handbook on the Physics and Chemistry of Rare Earth. Vol. 18: Lanthanides/Actinides: Chemistry. North Holland, Amsterdam, London, New York, Tokyo 1994; 674 Seiten. Isbn: 0–444–81724–7.* Crystal Research and Technology, 1995. **30**(8): p. 1146-1146.

52. Nilsson, M., Ekberg, C., Foreman, M., Hudson, M., Liljenzin, J.O., Modolo, G., and Skarnemark, G., *Separation of Actinides(Iii) from Lanthanides(Iii) in Simulated Nuclear Waste Streams Using 6,6′-Bis-(5,6-Dipentyl-[1,2,4]Triazin-3-Yl)-[2,2′]Bipyridinyl (C5-Btbp) in Cyclohexanone.* Solvent Extraction and Ion Exchange, 2006. **24**(6): p. 823-843.

53. Foreman, M.R.S.J., Hudson, M.J., Geist, A., Madic, C., and Weigl, M., *An Investigation into the Extraction of Americium(Iii), Lanthanides and D-Block Metals by 6,6′-Bis-(5,6-Dipentyl-[1,2,4]Triazin-3-Yl)-[2,2′]Bipyridinyl (C5-Btbp).* Solvent Extraction and Ion Exchange, 2005. **23**(5): p. 645-662.

54. Adam, C., Kaden, P., Beele, B.B., Müllich, U., Trumm, S., Geist, A., Panak, P.J., and Denecke, M.A., *Evidence for Covalence in a N-Donor Complex of Americium(Iii).* Dalton Transactions, 2013. **42**(39): p. 14068-14074.

55. Ekberg, C., Löfström-Engdahl, E., Aneheim, E., Foreman, M., Geist, A., Lundberg, D., Denecke, M., and Persson, I., *The Structures of Cyme4-Btbp Complexes of Americium(Iii) and Europium(Iii) in Solvents Used in Solvent Extraction, Explaining Their Separation Properties.* Dalton transactions. 2015. **44**.

56. Cotton, S., *Lanthanide and Actinide Chemistry*. 2007: Wiley.

57. Magill, J., Pfennig, G. and Galy, J. *Karlsruher Niklidkarte. (7th edition). 2009*. European Commission Joint Research Centre Institute for Transuranium Elements: Lage, Germany. ISBN 92-79-02175-3.

58. Choppin, G., Liljenzin, J.-O., Rydberg, J., and Ekberg, C., *Chapter 21 - the Nuclear Fuel Cycle*, in *Radiochemistry and Nuclear Chemistry (Fourth Edition)*. 2013, Academic Press: Oxford. p. 685-751.

59. Tsibulya, A., Kochetkov, A., Kravchenko, I., and Nikolaev, M., *Proposal to Represent Neutron Absorption by Fission Products by a Single Pseudo-Fragment*. 1991.

60. Drew, M.G.B., Foreman, M.R.S.J., Hill, C., Hudson, M.J., and Madic, C., *6,6 '-Bis-(5,6-Diethyl-[1,2,4]Triazin-3-Yl)-2,2 '-Bipyridyl the First Example of a New Class of Quadridentate Hetercyclic Extraction Reagents for the Separation of Americium(Iii) and Europium(Iii).* INORGANIC CHEMISTRY COMMUNICATIONS, 2005. **8**(3): p. 239-241.

61. Retegan, T., Ekberg, C., Fermvik, A., Foreman, M.R.S., and Skarnemark, G. *A Comparative Study of Some Btp and Btbp Class Extractants*. in *International Solvent Extraction Conference* 2008. Tucson, Arizona, USA: ISEC.

62. Nilsson, M., Andersson, S., Drouet, F., Ekberg, C., Foreman, M., Hudson, M., Liljenzin, J.-O., Magnusson, D., and Skarnemark, G., *Extraction Properties of 6,6′-Bis-(5,6-Dipentyl-[1,2,4]Triazin-3-Yl)-[2,2′]Bipyridinyl (C5-Btbp).* Solvent Extraction and Ion Exchange, 2006. **24**(3): p. 299-318.

63. Miguirditchian, M., Guillaneux, D., Guillaumont, D., Moisy, P., Madic, C., Jensen, M.P., and Nash, K.L., *Thermodynamic Study of the Complexation of Trivalent Actinide and Lanthanide Cations by Adptz, a Tridentate N-Donor Ligand.* Inorganic Chemistry, 2005. **44**(5): p. 1404-1412.

64. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M.R.S.J., Grűner, B., Hájková, Z., and Kvičalová, M., *A Tbp/Btbp-Based Ganex Separation Process—Part 2: Ageing, Hydrolytic, and Radiolytic Stability.* Solvent Extraction and Ion Exchange, 2011. **29**(2): p. 157-175.

65. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M.R.S.J., Retegan, T., and Skarnemark, G., *A Tbp/Btbp-Based Ganex Separation Process. Part 1: Feasibility.* Solvent Extraction and Ion Exchange, 2010. **28**(4): p. 437-458.

66. Aneheim, E., Ekberg, C., Foreman, M.R.S., Löfström-Engdahl, E., and Mabile, N., *Studies of a Solvent for Ganex Applications Containing Cyme4-Btbp and Dehba in Cyclohexanone.* Separation Science and Technology, 2012. **47**(5): p. 663-669.

67. Aneheim, E., Ekberg, C., and Foreman, M.R.S.J., *A Tbp/Btbp-Based Ganex Separation Process – Part 3: Fission Product Handling.* Solvent Extraction and Ion Exchange, 2013. **31**(3): p. 237-252.

68. Halleröd, J., Ekberg, C., Löfström-Engdahl, E., and Aneheim, E., *Development of the Chalmers Grouped Actinide Extraction Process.* Nukleonika, 2015. **60**(4): p. 829-835.

69. Aneheim, E., Grüner, B., Ekberg, C., Foreman, M.R.S., Hájková, Z., Löfström-Engdahl, E., Drew, M.G.B., and Hudson, M.J., *Fission Product Interactions with Nitrogen Donor Ligands Used for Spent Nuclear Fuel Treatment.* Polyhedron, 2013. **50**(1): p. 154-163.

70. Retegan, T., Ekberg, C., Fermvik, A., and Skarnemark, G. *The Effect of Diluents on Extraction of Actinides and Lanthanides*. in *Scientific Basis for Nuclear Waste Management XXX*. 2007. Warrendal, PA, USA.

71. Halleröd, J., Ekberg, C., and Aneheim, E., *Phenyl Trifluoromethyl Sulfone as Diluent in a Grouped Actinide Extraction Process: Extraction Properties of the Solvent Components Tbp and Cyme4-Btbp.* Journal of Radioanalytical and Nuclear Chemistry, 2016. **307**(3): p. 1711-1715.

72. Halleröd, J., Ekberg, C., Foreman, M., Engdahl, E.L., and Aneheim, E., *Stability of Phenyl Trifluoromethyl Sulfone as Diluent in a Grouped Actinide Extraction Process.* Journal of Radioanalytical and Nuclear Chemistry, 2015. **304**(1): p. 287-291.

73. Lofstrom-Engdahl, E., Aneheim, E., Ekberg, C., Foreman, M., Hallerod, J., Skarnemark, G., Chalmers University Of, T., Department Of, C., Biological Engineering, N.C., Chalmers Tekniska, H., and Institutionen För Kemi- Och Bioteknik, K., *Extraction Thermodynamics of Am(Iii) and Eu(Iii) Using Cyme4-Btbp in Various Organic Diluents.* JOURNAL OF CHEMICAL THERMODYNAMICS, 2014. **76**: p. 64-69.

74. Hamblet, C.H. and Mcalevy, A., *Adipic Acid Process*, U.S.P. Office, Editor. 1951: USA.

75. Aneheim, E., Ekberg, C., Modolo, G., and Wilden, A., *Single Centrifugal Contactor Test of a Proposed Group Actinide Extraction Process for Partitioning and Transmutation Purposes.* Separation Science and Technology, 2015. **50**(10): p. 1554-1559.

76. Halleröd, J., Ekberg, C., Kajan, I., and Aneheim, E., *Solubility Thermodynamics of Cyme 4 -Btbp in Various Diluents Mixed with Tbp.* Journal of solution chemistry, 2018. **47**(6): p. 1021-1036.

77. Halleröd, J., Ekberg, C., Foreman, M., Löfström-Engdahl, E., and Aneheim, E., *Plutonium Loading of Ganex Solvents with Phenyl Trifluoromethyl Sulfone and Cyclohexanone as Diluents.* International Solvent Extraction Conference Proceedings 2014.

78. Halleröd, J., Ekberg, C., Authen, T.L., Bertolo, L., Lin, M., Grüner, B., Švehla, J., Wagner, C., Geist, A., Panak, P., and Aneheim, E., *On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based Ganex System Containing*

Cyme4-Btbp and Tbp. Solvent Extraction and Ion Exchange, 2018. **36**(4): p. 360-372.

79. Halleröd, J., *On a Solvent Extraction System for Recycling Used Nuclear Fuel with Cyme4-Btbp and Tbp as Extracting Agents* in *Department of Chemistry and Chemical Engineering* 2018, Chalmers University of Technology Gothenburg, Sweden.

80. Romanovskiy, V.N., Smirnov, I.V., Babain, V.A., Todd, T.A., Herbst, R.S., Law, J.D., and Brewer, K.N., *The Universal Solvent Extraction (Unex) Process. I. Development of the Unex Process Solvent for the Separation of Cesium, Strontium, and the Actinides from Acidic Radioactive Waste.* Solvent Extraction and Ion Exchange, 2001. **19**(1): p. 1-21.

81. Herbst, R.S., Law, J.D., Todd, T.A., Romanovskiy, V.N., Smirnov, I.V., Babain, V.A., Esimantovskiy, V.N., and Zaitsev, B.N., *Development of the Universal Extraction (Unex) Process for the Simultaneous Recovery of Cs, Sr, and Actinides from Acidic Radioactive Wastes.* Separation Science and Technology, 2003. **38**(12-13): p. 2685-2708.

82. Belova, E.V., Nazin, E.R., Skvortsov, I.V., Sokolov, I.P., Rodin, A.V., Stefanovsky, S.V., and Myasoedov, B.F., *Thermal Stability and Radiation Resistance of Trifluoromethyl Phenyl Sulfone in the Presence of Nitric Acid.* Radiochemistry, 2016. **58**(5): p. 486-490.

83. Law, J.D., Herbst, R.S., Todd, T.A., Romanovskiy, V.N., Babain, V.A., Esimantovskiy, V.M., Smirnov, I.V., and Zaitsev, B.N., *The Universal Solvent Extraction (Unex) Process. Ii. Flowsheet Development and Demonstration of the Unex Process for the Separation of Cesium, Strontium, and Actinides from Actual Acidic Radioactive Waste.* Solvent Extraction and Ion Exchange, 2001. **19**(1): p. 23-36.

84. Arm, S. and Phillips, C., *3 - Chemical Engineering for Advanced Aqueous Radioactive Materials Separations*, in *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, K.L. Nash and G.J. Lumetta, Editors. 2011, Woodhead Publishing. p. 58-94.

85. Mccabe, W.L., Smith, J.C., and Harriott, P., *Unit Operations of Chemical Engineering*. 7. ed. ed. Mcgraw-Hill Chemical Engineering Series. 2005: McGraw Hill.

86. Todd, T.A., Wood, D.J., Brewer, K.N., Olson, A.L., and Law, J.D., *Waste, Nuclear, Reprocessing and Treatment Technologies*, in *Encyclopedia of Chemical Processing and Design* J.J. McKetta and G.E. Weismantel, Editors. 1998, Marcel Dekker, Inc. : New York, USA.

87. Authen, T.L., Wilden, A., Hallerod, J., Schneider, D., Kreft, F., Modolo, G., and Ekberg, C., *Batch Tests for Optimisation of Solvent Composition and Process Flexibility of the Chalmex Fs-13 Process* 2020: Submitted to Solvent Extraction and Ion Exchange.

88. Zhang, H., Liu, Z.-Y., Zhou, X.-M., and Li, L., *The Complex Reaction Kinetics of Neptunium Including Redox and Extraction Process in 30% Tbp—Nitric Acid System.* Journal of Radioanalytical and Nuclear Chemistry, 2017. **312**(2): p. 173-180.

89. Burns, P.E. and Hanson, C., *Distribution of Nitric Acid between Tri-N-Butyl Phosphate and Water.* Journal of Applied Chemistry, 1964. **14**(3): p. 117-121.

90. Olander, D.R., Donadieu, L., and Benedict, M., *The Distribution of Nitric Acid between Water and Tributyl Phosphate - Hexane Solvents.* AIChE Journal, 1961. **7**(1): p. 152-159.

91. Zhang, Y., Valiente, M., and Muhammed, M., *Extraction of Nitric and Phosphoric Acids with Tributyl Phosphate.* Solvent Extraction and Ion Exchange, 1989. **7**(2): p. 173-200.

92. Naito, K. and Suzuki, T., *The Mechanism of the Extraction of Several Proton Acids by Tri-N-Butyl Phosphate.* The Journal of Physical Chemistry, 1962. **66**(6): p. 983-988.

93. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M., Littley, A., Löfström-Engdahl, E.N., Mabile, N., and Skarnemark, G., *Partitioning and Transmutation Annual Report 2010 & 2011*. 2013, Nuclear Chemistry, Department of Chemical and Biological Engineering: Gothenburg, Sweden.

94. Geist, A., Hill, C., Modolo, G., Foreman, M.R.S.J., Weigl, M., Gompper, K., and Hudson, M.J., *6,6′-Bis(5,5,8,8-Tetramethyl-5,6,7,8-Tetrahydro-Benzo[1,2,4]Triazin-3-Yl) [2,2′]Bipyridine, an Effective Extracting Agent for the Separation of Americium(Iii) and Curium(Iii) from the Lanthanides.* Solvent Extraction and Ion Exchange, 2006. **24**(4): p. 463-483.

95. Chatterjee, S., Bryan, S.A., Casella, A.J., Peterson, J.M., and Levitskaia, T.G., *Mechanisms of Neptunium Redox Reactions in Nitric Acid Solutions.* Inorganic Chemistry Frontiers, 2017. **4**(4): p. 581-594.

96. Precek, M., Paulenova, A., and Mincher, B.J., *Reduction of Np(Vi) in Irradiated Solutions of Nitric Acid.* Procedia Chemistry, 2012. **7**: p. 51-58.

97. Gopakumar, G., Sreenivasulu, B., Suresh, A., Brahmmananda Rao, C.V.S., Sivaraman, N., Joseph, M., and Anoop, A., *Complexation Behavior of the Tri-N-Butyl Phosphate Ligand with Pu(Iv) and Zr(Iv): A Computational Study.* The Journal of Physical Chemistry A, 2016. **120**(24): p. 4201-4210.

98. Carboneau, M. and Adams, J., *National Low-Level Waste Management Program Radionuclide Report Series. Volume 10, Nickel-63*. 1995, Lockheed Idaho Technologies Co.

99. Davis, W. and De Bruin, H.J., *New Activity Coefficients of 0–100 Per Cent Aqueous Nitric Acid.* Journal of Inorganic and Nuclear Chemistry, 1964. **26**(6): p. 1069-1083.

100. Solov'ev, V.P., Stuklova, M.S., Koltunova, E.V., and Kochanova, N.N., *Coordination Numbers of Central Atoms in Coordination Compounds.* Russian Journal of Coordination Chemistry, 2003. **29**(9): p. 660-668.

101. Aneheim, E.H.K., *Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel*. Doktorsavhandlingar Vid Chalmers Tekniska Högskola. Ny Serie: 3432. 2012: Chalmers University of Technology.

102. Lewis, F.W., Harwood, L.M., Hudson, M.J., Müllich, U., and Geist, A., *Efficient Masking of Corrosion and Fission Products Such as Ni(Ii) and Pd(Ii) in the Presence of the Minor Actinides Am(Iii) Using Hydrophilic Anionic or Cationic Bis-Trazines.* Chemical Communications, 2015. **51**: p. 9189-9192.

103. Sato, T., Watanabe, H., and Suzuki, H., *Liquid-Liquid Extraction of Molybdenum(Vi) from Aqueous Acid Solutions by Tbp and Topo.* Hydrometallurgy, 1990. **23**(2): p. 297-308.

104. Pocker, Y. and Green, E., *Hydrolysis of D-Glucono-.Delta.-Lactone. I. General Acid-Base Catalysis, Solvent Deuterium Isotope Effects, and Transition State Characterization.* Journal of the American Chemical Society, 1973. **95**(1): p. 113-119.

105. Spence, J.T. and Kallos, G., *Molybdenum(V) and Molybdenum(Vi) Complexes with Gluconic Acid.* Inorganic Chemistry 1963. **2**(4): p. 710-713.

106. Warwick, P., Evans, N., and Vines, S., *Studies on Metal Gluconic Acid Complexes*. 2008.

107. Zhang, X., Atsumi, H., Matsuura, H., and Tsukihashi, F., *Influence of Gluconic Acid on Dissolution of Si, P and Fe from Steelmaking Slag with Different Composition into Seawater.* ISIJ International, 2014. **54**(6): p. 1443-1449.

Appendix A

The following equipment was used during the experimental procedures and analytical measurements performed at Chalmers University of Technology:

- Shaking machine: IKA, VIBRAX VXR 1500 RPM
- Centrifuge: WIFUG Lab Centrifuges LABOR-50M, 4500 rpm
- High Purity Germanium detector: Canberra, Gamma Analyst GEM 23195 with software that automatically corrects for background (Genie 2000).
- Liquid Scintillation Counter: Wallac 1414 WinSpectral
- ICP-MS: Thermo Scientific iCAP Q

The following equipment was used during the experimental procedures and analytical measurements performed at Forschungszentrum Jülich:

- Shaking machine: IKA, VIBRAX, VXR 2200 rpm
- Vortex mixer: Heidolph Reax top test tube shaker
- Centrifuge: Hettich EBA 8S
- High Purity Germanium detector:
    - Eurisys EGC35-195-R germanium coaxial N-type detector
    - Ortec GEM-F5930 coaxial semi planar p-type detector
- ICP-MS: Perkin Elmer NexION 2000
- Alpha spectrometer: Ortec Octête-pc eight chamber alpha measurement system equipped with PIPS detectors
- pH meter: Metrohm pH Meter 691
- Titration machine: Metrohm 905 Titrando
- Centrifugal contactor: Annular centrifugal contactor with 10 mm rotor and a hold-up volume of 6 mL (incl. tubing), manufactured by INET (Tsinghua Univ. China)

Appendix B

Table B.1. The composition in mg L^{-1} of the simulated PUREX raffinate. The molarity refers to the nitric acid concentration of the solution.

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