

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

ON A SOLVENT EXTRACTION SYSTEM FOR RECYCLING USED NUCLEAR
FUEL WITH $\text{CyMe}_4\text{-BTBP}$ AND TBP AS EXTRACTING AGENTS

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Cover: Liquid-liquid extraction samples prior to and after metal extraction.

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ABSTRACT

In Sweden, as well as in many other countries worldwide, the demand for electricity and electrical energy is high. One solution to satisfy this demand in the long term could be to upgrade the nuclear power plants, including recycling of used nuclear fuel, to Generation IV. The Generation IV concept, currently at the research stage, is based on a closed nuclear fuel cycle that includes both a reactor capable of fissioning considerably more nuclides than the thermal reactors of today and a used nuclear fuel recycling process. Recycling of the used nuclear fuel would increase the energy utilization of the fuel and make the final repository more sustainable. Different types of recycling processes are under development. One of these is the Grouped ActiNide EXtraction (GANEX) process. The Chalmers GANEX process is a solvent extraction process for extracting all of the actinides present simultaneously as a group by combining two extracting agents and a diluent into one single solvent.

The original Chalmers GANEX process used cyclohexanone as the diluent, which had some drawbacks such as low flashpoint and exothermic reactions with concentrated nitric acid. In this work the focus has therefore been on a new diluent, phenyl trifluoromethyl sulfone (FS-13). Current studies have shown that a solvent based on FS-13 has several promising features such as good actinide extraction while the fission product extraction remains low, fast kinetics, efficient back-extraction using two stripping steps and high stability against both hydrolysis and radiolysis. Thermodynamic investigations have revealed that the system reacts exothermically during the metal extraction. The system also offers a high solubility of $\text{CyMe}_4\text{-BTBP}$, creating a possibility to optimise the organic phase according to the used fuel composition. The solvent was found to perform well under plutonium loading conditions, showing great promise for future use in recycling of Generation IV fuels.

Keywords: *Solvent Extraction, GANEX, FS-13, TBP and $\text{CyMe}_4\text{-BTBP}$.*

LIST OF PUBLICATIONS

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

- I. Halleröd, J., Ekberg, C., Löfström-Engdahl, E., and Aneheim, E.: Development of the Chalmers Grouped Actinide Extraction Process. *Nukleonika*, 60(4):829–835, 2016.
Contribution: Main author of the paper.

- II. 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*, 307(3):1711–1715, 2016.
Contribution: Main author of the paper and did all the experimental work.

- III. Halleröd, J., Ekberg, C., Authen, T., 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. *Submitted to Solvent Extraction and Ion Exchange*.
Contribution: Main author of the paper and did the main part of the experimental work.

- IV. Halleröd, J., Ekberg, C., Foreman, M., Löfström-Engdahl, E., and Aneheim, E.: Stability of phenyl trifluoromethyl sulfone as diluent in a grouped actinide extraction process. *Journal of Radioanalytical and Nuclear Chemistry*, 304(1):287–291, 2015.
Contribution: Main author of the paper and did all the experimental work.

- V. Halleröd, J., Ekberg, C., Authen, T. and Aneheim, E.: Optimization of a GANEX system containing of CyMe₄-BTBP and TBP in phenyl trifluoromethyl sulfone. *Manuscript*.
- Contribution: Main author of the paper and did the main part of the experimental work.*
- VI. Halleröd, J., Ekberg, C., Kajan, I., and Aneheim, E.: Solubility thermodynamics of CyMe₄-BTBP in various diluents mixed with TBP. *Accepted for publication in Solution Chemistry*.
- Contribution: Main author of the paper and did the main part of the experimental work.*
- VII. 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. Proceedings of the International Solvent Extraction Conference, ISEC, Würzburg, 2014. *(Some of the FS-13 results are also presented in Paper V.)*
- Contribution: Main author of the paper and did all the experimental work.*

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LIST OF ABBREVIATIONS

AmEx	Amine Extraction
BTBP	Bis-triazine bi-pyridine
BWR	Boiling Water Reactor
C5-BTBP	6,6'-bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridine
CHON	Carbon, Hydrogen, Oxygen and Nitrogen
CyMe ₄ -BTBP	6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine
D	Distribution ratio
DEHBA	N,N-di-2(ethylhexyl)-butyramide
DIAMEX	DIAMide EXtraction
DMDOHEMA	N,N'-(dimethyl)-N,N'-dioctyl-hexylethoxy-malonamide
EXAm	EXtraction of Americium
FP	Fission products
FS-13	Phenyl trifluoromethyl sulfone
GANEX	Grouped ActiNide EXtraction
HDEHP	di(2-ethylhexyl)phosphoric acid
HPGe	High Purity Germanium
HSAB	Hard Soft Acid Base
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICRP	International Commission on Radiological Protection

LSC	Liquid Scintillation Counting
LWR	Light Water Reactor
MOX-fuel	Mixed OXide Fuel
NEA	Nuclear Energy Agency
NEI	Nuclear Energy Institute
OECD	Organisation for Economic Co-operation and Development
PUREX	Plutonium Uranium Reduction EXtraction
PWR	Pressurized Water Reactor
SANEX	Selective ActiNide EXtraction
SF	Separation factor
SKB	The Swedish Nuclear Fuel and Waste Management Company
SSM	Swedish Radiation Safety Authority
TALSPEAK	Trivalent Actinide-Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TBP	Tri-butyl phosphate
TODGA	N,N,N',N'-tetraoctyl diglycolamide
UNEX	UNiversal EXtraction

1

INTRODUCTION

Nuclear power is one of the main sources of electricity and electrical energy both in Sweden ($\sim 40\%$) and worldwide ($\sim 20\%$) (OECD-NEA, 2017). In the late 1930s, the Manhattan Project became the starting point for industrial scale nuclear technology development in the world. The first nuclear reactors, Generation I, are early reactor prototypes that were mainly designed in the 1950s. The power level in these reactors was low and they were mainly developed as "proof of principle" (Choppin et al., 2013a). With an increasing demand for electricity, both due to global industrialisation and a growing population, the amount of electrical energy required in the world is constantly rising (Brundtland, 1987; Bradshaw, 2010). To fulfil this energy demand several different production methods can be applied and one of these is nuclear power. Positive features of using nuclear power are the low emissions of greenhouse gases for the entire life cycle (Keepin and Kats, 1988; Dones et al., 2003; Fthenakis and Kim, 2007), the high energy capacity that can be achieved using small amounts of fuel material (Grandin et al., 2010) and the long lifetime of the reactors (Teller et al., 1996).

Nuclear reactors operating at nuclear power plants today are typically called Generation II reactors. These are commercial reactors, designed to be both reliable and economical, and were mainly developed in the 1960s. This reactor generation includes, for example, boiling water reactors (BWRs) and pressurized water reactors (PWRs). However, a disadvantage with nuclear energy in general is the low energy utilization of the fuel, as only about 1% of the contained energy is used (Choppin et al., 2013b). This results in a large amount of radioactive used nuclear fuel that has to be managed. The used fuel can either be directly disposed of in a final repository (after some years of interim storage) or it can be reprocessed using what is known as the Plutonium Uranium Reduction EXtraction (PUREX) process (Anderson et al., 1960). By reprocessing plutonium and uranium, these elements can be used for the production of new fuel, called Mixed OXide (MOX) fuel. MOX fuel reduces the need for uranium mining and enrichment services by about 30%. Utilisation of energy from the fuel, however, is only increased from 1% to around 1.2% (Choppin et al., 2013b).

A number of different analyses indicate that an upgrade of nuclear power plants to enable a larger utilization of the energy present could make nuclear power a promising energy alternative for the future (Sailor et al., 2000; Bruggink and van der Zwaan, 2002; van der Zwaan, 2013). New nuclear reactors that are under development and construction, e.g. in Finland, are Generation III and Generation III+. These are essentially further developed Generation II reactors with slightly improved efficiency, fuel technology and better safety systems, among other features (Choppin et al., 2013a). Nuclear reactor systems still at the research stage are the Generation IV systems. Generation IV, although still rather undefined is in contrast to Generation II and III based on a closed nuclear fuel cycle concept and not only on a reactor construction. Reprocessing of the fuel using the PUREX process is not suitable in Generation IV systems where the requirements for proliferation resistance do not allow pure plutonium streams (Abram and Ion, 2008). Therefore, instead of an element-selective reprocessing process, alternative processes based on grouped extraction of all the actinides have been developed, e.g. the Grouped ActiNide EXtraction (GANEX) concept (Adnet et al., 2005). The separated actinides are then recycled for the production of new fuel.

In this work a GANEX process for recycling of Generation IV fuel, called the Chalmers GANEX process, has been investigated. Previously investigated Chalmers GANEX systems combining the two extracting agents 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine (CyMe₄-BTBP) and tributyl phosphate (TBP) with the diluents cyclohexanone or long-chained alcohols have shown promising extraction behaviours. However, several negative features such as low flashpoint, exothermic reaction with concentrated nitric acid, low CyMe₄-BTBP solubility and slow extraction kinetics (all connected to the diluents used), have also been found. Due to this, phenyl trifluoromethyl sulfone (FS-13) has been investigated as an alternative GANEX diluent for the CyMe₄-BTBP and TBP ligand combination. The performance of this FS-13-based GANEX solvent in terms of metal extraction and back-extraction, stability, optimization of the organic phase (including ligand solubility and plutonium loading) has been evaluated in this work.

2 | BACKGROUND

2.1 NUCLEAR ENERGY

Nuclear power today is mainly organized through the Nuclear Energy Agency (NEA). Its member countries account for approximately 84% of the world's installed nuclear capacity. In the Organisation for Economic Co-operation and Development (OECD) area, nuclear energy represents almost 19% of the electricity supply. In some countries even more nuclear energy is used; in Sweden 39.8% of the electrical energy comes from nuclear power plants, in France 72.3% and in Switzerland 31.3% (OECD-NEA, 2017). An overview of nuclear energy production in the OECD countries is shown in Table 2.1.1.

Table 2.1.1: Facts and figures concerning nuclear energy production in OECD countries in 2016 (OECD-NEA, 2017). * Preliminary data.

<i>Country</i>	<i>Number of nuclear reactors connected to the grid</i>	<i>Nuclear electricity generation (net TWh) 2016</i>	<i>Nuclear percentage of total electricity supply</i>
<i>Sweden</i>	9	60.5 *	39.8
<i>Europe</i>	130	790.4	22.3
<i>OECD America</i>	120	907.5	18.3
<i>OECD Pacific</i>	67	179.6	11

2.2 HANDLING OF USED NUCLEAR FUEL

In the commercial reactors in operation today the nuclear fuel mainly consists of uranium-238, which is enriched with respect to uranium-235. Thermal neutrons induce fission in the fissile material during operation of the reactor, Equation (2.2.1).



where FP represents the fission products produced, n represents the neutron and x the number of neutrons released per fission. The average released amount of neutrons for each fission reaction is 2.5 neutrons (Choppin et al., 2013c).

All nuclear reactors create used nuclear fuel. This fuel is highly radioactive and radiotoxic and has to be isolated from the environment for more than 100,000 years to reach a radiotoxicity equal to the natural uranium used to fabricate the fuel. The radiotoxicity is dominated by the long-lived actinides (Madic et al., 2004), as illustrated in Figure 2.2.1. The radiotoxicity of the used fuel can be decreased by irradiating some of the long-lived actinides with neutrons, and through nuclear reactions the actinides are then transformed into other nuclides that are more short-lived, or even stable. This process is known as transmutation (Salvatores et al., 1998). Transmutation can occur either naturally by radioactive decay or artificially by bombardment of the nucleus (Choppin et al., 2013b).

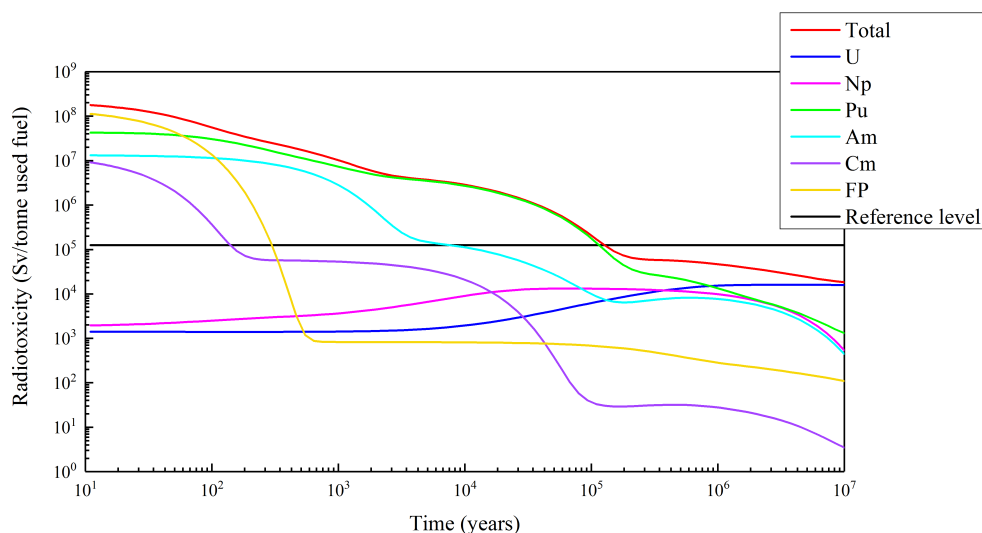


Figure 2.2.1: Radiotoxicity of used nuclear fuel (UO_X fuel, 4% enrichment, burnup 45 Gw and 10 years cooling time) as a function of time. The reference is the amount of natural uranium needed to produce 1 tonne of enriched fuel. The radiotoxicity is calculated using the International Commission on Radiological Protection (ICRP) dose coefficients, and is integrated for all prodigies from the parent nuclide, calculated using RadTox (Holm, 2012).

Most nuclear fuel cycles are based on the same fundamental steps, such as uranium mining, enrichment, fuel fabrication, use in a nuclear reactor and finally some form of used nuclear fuel waste management. There are several options for handling the used nuclear fuel; the once-through cycle and the two partitioning processes, reprocessing and recycling.

2.2.1 *The Once-Through Cycle*

In the once-through cycle, which is the method adopted in Sweden, the nuclear fuel is used once in a nuclear reactor before it is placed in an interim storage. In the interim storage the used nuclear fuel is stored temporarily in steel-lined concrete pools filled with water, which act as a natural barrier for radiation (Platzer, 1981; SKB, 2010; IAEA, 2011; NEI, 2015). After some time in the interim storage, e.g. 30 years, the used nuclear fuel is intended to be placed in the final repository. To this date no final repository has yet been established but in Sweden the Swedish Nuclear Fuel and Waste Management Company (SKB) has submitted an application to the Swedish Radiation Safety Authority (SSM) for building a final

repository (SSM, 2015). In the Swedish final repository the used nuclear fuel will be stored deep underground in the bedrock, secured by several different barriers (SKB, 2006).

An issue with the once-through fuel cycle is that in the light water reactors (LWRs) used today only around 1% of the energy in the fuel is utilized. This energy mainly comes from fission of uranium-235, but also some uranium-238 that is converted to fissile plutonium-239. This means that the major part of the actinides, i.e. a large part of the energy content, will still be present in the used nuclear fuel when the fuel is sent for final storage (Choppin et al., 2013b)

However, the advantage with the once through cycle is that it is the cheapest option and since the plutonium is embedded in the used fuel matrix, making recovery difficult, the proliferation resistance is high (Choppin et al., 2013b). Nuclear reactor Generations that follow this fuel cycle are Generation I and, in most countries, Generation II.

2.2.2 *Reprocessing*

Reprocessing is a partitioning process where the uranium and the plutonium are separated from the used nuclear fuel to create new MOX fuel, Figure 2.2.2 (Choppin et al., 2013b). The use of MOX fuels increases the utilisation of energy from uranium (Ritcey, 2004) and today MOX fuels are used, for example, in France. Nuclear reactor generations that follow this fuel cycle are in some countries Generation II, Generation III and Generation III+.

The process that is used industrially today for the recovery of uranium and plutonium for reprocessing is called PUREX. The PUREX process was one of the earliest reprocessing processes and was primarily developed during the Manhattan Project in the 1940s for the production of plutonium for nuclear weapons (Anderson et al., 1960). In this process the plutonium and uranium are both separated from the rest of the used nuclear fuel (Thomas and Spring, 1958).

However, besides the uranium and plutonium, the used nuclear fuel also contains minor actinides (neptunium, americium and curium) that contribute to the long term radiotoxicity of the used nuclear fuel (Salvatores et al., 1998; Grouiller et al., 2003), Figure 2.2.1. Due to this, the radiotoxicity of the reprocessed used nuclear

fuel is similar to the used fuel in the once-through cycle and the requirements for the final repository are not significantly changed.

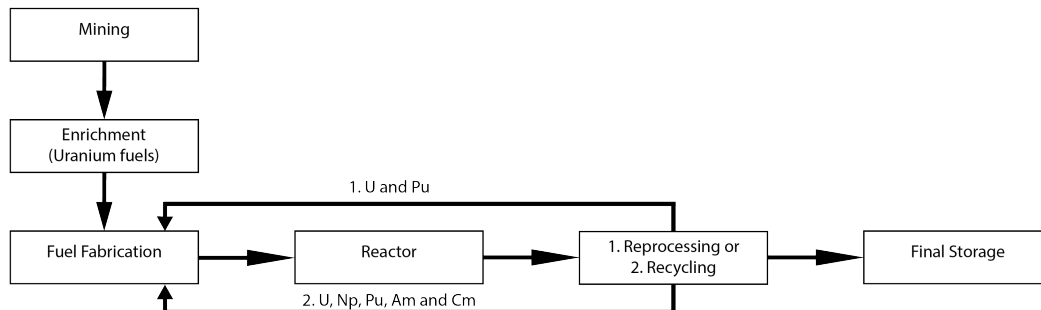


Figure 2.2.2: Schematic figure over nuclear fuel cycles "cradle to grave". 1. is a reprocessing process. 2. is a recycling process.

2.2.3 Recycling

The recycling concept follows the reprocessing concept, but instead of only separating uranium and plutonium from the used fuel, all of the long-lived actinides are separated from the fission products to make new fuel, as shown in Figure 2.2.2. By doing this the long-term radiotoxicity of the waste is decreased, Figure 2.2.1. The heat load of the waste will also be reduced, making the final repository more volume-efficient (Salvatores et al., 1998; Grouiller et al., 2003). Most fission products are short-lived elements and some of these, especially the lanthanides, have high neutron capture cross sections. Elements with high neutron capture cross section can absorb the available neutrons in the reactor. Without lanthanides and other fission products present, these neutrons have the potential to transmute the actinides in the recycled nuclear fuel, while simultaneously increasing the energy utilization (Aoki, 2002; Choppin et al., 2013b; Bond and Leuze, 1976; Madic et al., 2000). However, the chemical similarities between the minor actinides, americium and curium, and the lanthanide can make it hard to separate them from each other (Choppin, 1983).

The Generation IV systems are the only reactor concepts that follow the recycling fuel cycle. The largest differences between Generation IV reactor systems and existing Generation II and Generation III reactors are the reactor types and the recycling step. There are some established goals that should be reached for the Generation IV systems; they should be highly economic, have enhanced safety, produce

minimal waste and be proliferation resistant (Abram and Ion, 2008; OECD-NEA, 2014). To reach these goals most of the proposed Generation IV systems adopt a closed fuel cycle. Fuel recycling technology is therefore the key to a successful future Generation IV system. The PUREX process used for MOX fuel production includes separation of pure plutonium and will hence not fulfil the Generation IV requirements of proliferation resistance (Abram and Ion, 2008). Therefore an alternative recycling process has to be developed.

2.3 RECYCLING PROCESSES

Research on recycling processes has been carried out worldwide for decades. The main procedures developed are the “dry” routes and the “wet” routes.

The dry routes, also called pyroprocessing, include for example Halide volatility, where fluorides of uranium (UF_6) are separated from a mixture of fuel elements dissolved in a molten fluoride salt, eutectic in the presence of hydrofluoric acid (Choppin et al., 2013b). Another dry route is the Molten salt extraction, which similarly to Halide volatility is also based on an eutectic salt melt. With a heat-resistant solvent of low volatility, the actinides and fission products can distribute themselves between the two phases (Choppin et al., 2013b). Pyroprocessing is considered to be a potential recycling method for Generation IV nuclear fuel cycles due to its capability to treat used fuels with a high burn-up and high plutonium concentration after only a short period of cooling (GAO et al., 2011; IAEA, 2008, 2005; OECD-NEA, 2004). However, pyroprocessing is currently only at the research stage.

The wet route is based on the separation of elements through their specific capacities to form organic soluble complexes. This method is called liquid-liquid extraction and is used in many different industrial processes for separating metals (Hansson, 2013; Al-Malah, 2016). Several different recycling processes have been developed using liquid-liquid extraction.

Several of the recycling processes developed have been based on the combined partitioning of minor actinides and lanthanides from the rest of the fission products remaining in the aqueous phase after the PUREX process. This kind of raffinate treatment process, called double strata, requires a second partitioning step where the actinides and lanthanides are separated from each other. Separation processes following this concept are e.g. the American Trivalent Actinide - Lanthanide Sepa-

ration by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) process originally developed in the 1960s (Weaver and Kappelmann, 1964) and the DIAMide EXtraction (DIAMEX)/Selective ActiNide EXtraction (SANEX) process (Hill et al., 2007; Courson et al., 2000; Madic et al., 2004; Magnusson et al., 2009b) developed since the early 1990s within several European Union framework programmes. Other developed double strata processes are the EXAm and the AmEx processes designed to partition americium; not only from the fission products but also primarily from curium (Rostaing et al., 2012; Rainey, 1954). Due to e.g. high neutron emissions of the curium isotopes, curium recycling can be difficult since extra shielding would be required at every step of the fuel cycle (Chapron et al., 2015). This is why it can be desirable to separate curium from americium, which has a higher recycling potential.

Another partitioning approach for recycling of used nuclear fuels is grouped separation of the actinides, known as the GANEX process. This type of process is also compatible with the Generation IV concept. Three different GANEX processes are, or have been, under investigation within the European Union.

2.3.1 *Grouped ActiNide EXtraction Processes*

The CEA-GANEX process was developed in France and is based on an adaptation of the DIAMEX/SANEX process, combining di(2-ethylhexyl)phosphoric acid (HDEHP) and N,N'-(dimethyl)-N,N'-dioctyl-hexylethoxy-malonamide (DMDOHEMA) (Miguirditchian et al., 2007, 2008). The CEA-GANEX process separates all the transuranic elements and the lanthanides together from the fission products prior to selective actinide back-extraction. The process has been proven successful regarding both the extraction and back-extraction of neptunium, plutonium, americium and curium together as a group, with high separation factors towards lanthanides (cerium and europium). As in the CEA-GANEX process, both the EURO-GANEX process and the Chalmers GANEX process follow the concept of combining two different extracting agents.

The EURO-GANEX process follows the concept of the CEA-GANEX, separating all the transuranic elements and the lanthanides together from the fission products prior to selective actinide back-extraction. For the EURO-GANEX process the following combination of extracting agents has been proposed, DMDOHEMA and N,N,N',N'-tetraoctyl diglycolamide (TODGA). The EURO-GANEX process has been shown to successfully extract the actinides and lanthanides. However,

difficulties have however been found in separating some of the lanthanides from the actinides during the back-extraction steps (Carrott et al., 2014, 2015).

The Chalmers GANEX process differs from the CEA-GANEX and the EURO-GANEX processes as the minor actinides, after the uranium bulk removal, are separated together from both the lanthanides and the rest of the fission products in the extraction step (Figure 2.3.1). The GANEX processes developed at Chalmers University of Technology in recent years have shown promising results, both with respect to extraction and separation (Aneheim et al., 2010; L fstr m-Engdahl et al., 2013a) and hydrolytic and radiolytic stability (Aneheim et al., 2011).

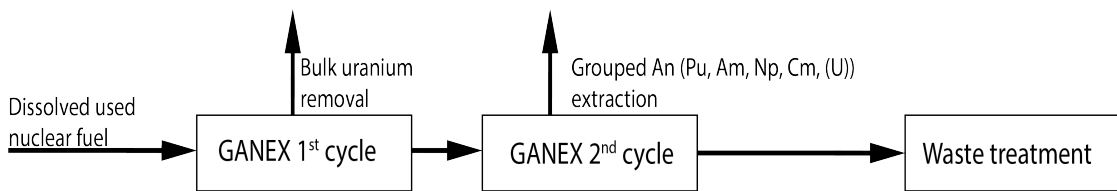


Figure 2.3.1: Schematic figure of the GANEX process.

2.4 DEVELOPMENT OF THE CHALMERS GANEX PROCESS

The Chalmers GANEX concept is based on the principle of combining two well-known extracting agents with a diluent, enabling utilization of their different properties. As is evident from the description of the CEA-GANEX and the EURO-GANEX processes, a variety of different extracting agents can be used in a GANEX process. Although extracting agents developed for other solvent extraction processes, such as N,N-di-2(ethylhexyl)-butyramide (DEHBA) have in some cases been investigated for use in the Chalmers GANEX process, the extracting agents primarily selected are CyMe₄-BTBP, and TBP (Figure 2.4.1), which are combined into a single solvent. By combining TBP with a bis-triazine bi-pyridine (BTBP) extracting agent, a system extracting most valence states of the actinides present in the used nuclear fuel can be created. This means that redox control can be avoided. In addition, the actinides can either be back-extracted selectively or can be reused directly in homogeneous recycling (OECD-NEA, 2012; Aneheim, 2012).

Several different diluents have been investigated over the years for use as GANEX solvents in the Chalmers GANEX process. Initially cyclohexanone was chosen due to its relatively fast extraction kinetics with the selected extracting agents (Retegan et al., 2007a) and good solubility of CyMe₄-BTBP (Ekberg et al., 2010).

Cyclohexanone is a cheap commercial chemical that is mass produced for the production of nylon 6 (Okushita et al., 1995). However, there are some drawbacks to using cyclohexanone. For example, cyclohexanone reacts exothermically in combination with concentrated nitric acid, forming adipic acid (Ambrose and Hamblet, 1951) and it also has a low flashpoint (44 °C). Cyclohexanone also has a comparatively high solubility in an acidic aqueous phase (Riddick et al., 1970), decreasing the stability and recycling potential of the solvent.

Due to the problems with cyclohexanone, long-chained alcohols were thoroughly investigated as an alternative diluent for a Chalmers GANEX system using BTBP-type extracting agents, as the long-chained alcohols are cheap, easily accessible and relatively stable (Löfström-Engdahl et al., 2014). For instance, 1-octanol is a standard diluent within solvent extraction. In earlier experiments investigating the actinide distribution ratios by C5-BTBP in long-chained alcohols it was discovered that a decrease in the chain length led to an increase in the distribution ratios (Löfström-Engdahl et al., 2013b). A slightly higher solubility of CyMe₄-BTBP was also found using 1-hexanol compared to 1-octanol (Ekberg et al., 2010), therefore the main focus when investigating long-chained alcohols for GANEX purposes was placed on 1-hexanol. However, the long-chained alcohols (similar to the commonly used diluent kerosene (Panak and Geist, 2013)) have a low solubility of CyMe₄-BTBP as well as comparatively slow kinetics (Löfström-Engdahl, 2014). Due to this, research investigating other more innovative solvents for the Chalmers GANEX process has been continued.

2.4.1 *Solvent Composition*

The BTBP-type ligands are polyaromatic nitrogen donor ligands that act as tetradentate ligands for metal ions, and are also soft Lewis bases (Narbutt et al., 2015). According to the Hard-Soft Acid-Base (HSAB) theory, soft Lewis bases form strong complexes with metal ions that are soft Lewis acids and, likewise, hard Lewis bases form strong complexes with hard Lewis acids. At the same time, hard metal ions and soft Lewis bases, i.e. mixed complexes, do not form such strong complexes (Pearson, 1968). One BTBP-type ligand that has been developed and synthesised to extract tri- and pentavalent actinides and separate them from the fission products, and mainly the lanthanides, is CyMe₄-BTBP (Figure 2.4.1) (Nilsson et al., 2006a,b; Foreman et al., 2005; Ekberg et al., 2008). Both actinides and lanthanides are assumed to be hard Lewis acids; the hardness varies, however, throughout the actinide and lanthanide series. The more covalent character in the complexation

of the actinides compared to the lanthanides by the N-donor BTBP-type ligands is one reason why the actinide complexation is preferred (Miguirditchian et al., 2005; Ionova et al., 2001a,b). The presence of the nitrate ion in the coordination sphere of the americium complex that compensates the charge density of the complex is another (Ekberg et al., 2015). CyMe₄-BTBP has a good resistance towards both alpha radiolysis (Magnusson et al., 2009c) and low dose rate gamma radiolysis (Retegan et al., 2007b; Panak and Geist, 2013). It is also stable under highly acidic conditions (Aneheim et al., 2011). These features make it suitable for use in a GANEX solvent. CyMe₄-BTBP is a surface active molecule, meaning that the chemical reactions in the system take place at the surface between the organic and aqueous phase. These reactions, such as complexation, can determine the extraction rate of the system (Geist et al., 2012).

In addition to CyMe₄-BTBP, the other main extracting agent used in the Chalmers GANEX solvent is TBP (Figure 2.4.1) (Aneheim et al., 2010; Löfström-Engdahl, 2014). TBP was developed to extract tetra- and hexavalent actinides (Warf, 1949; Anderson et al., 1960) and was used for plutonium and uranium extraction during the 1950s and 1960s (Burger, 1958). TBP is still used today as an extracting agent in the PUREX process. A drawback with TBP is that it decomposes to di-butyl phosphate (Schulz and Navratil, 1984). Di-butyl phosphate increases the extraction of fission products (Shevchenko and Smelov, 1958) and, due to this decomposition, extra purification steps may be needed for extraction processes using TBP.

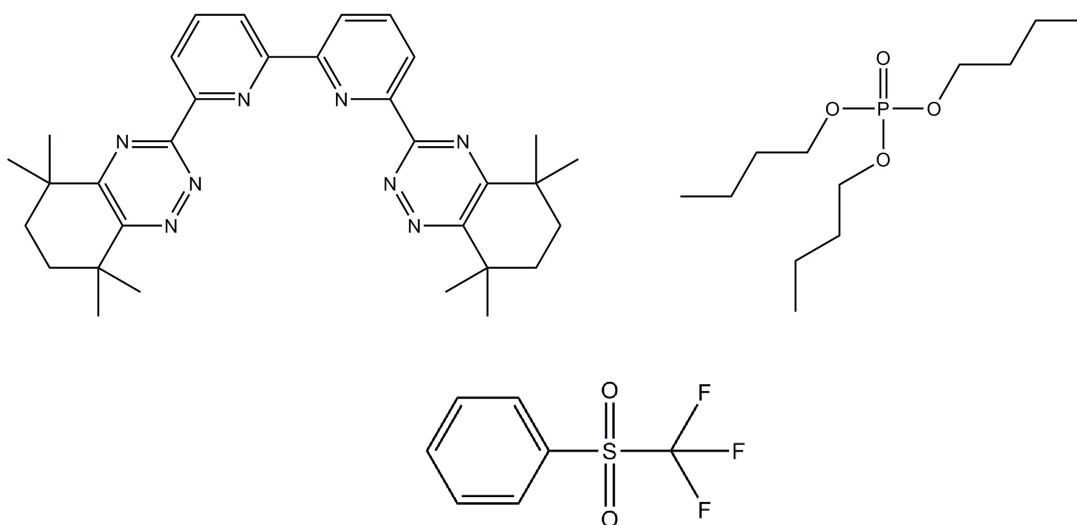


Figure 2.4.1: Molecular structure: left: 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)[2,2']bipyridine (CyMe₄-BTBP). Right: tri-butyl phosphate (TBP). Bottom: phenyl trifluoromethyl sulfone (FS-13)

Due to the problems described above using cyclohexanone and long-chained alcohols as diluents in previous Chalmers GANEX processes, the use of FS-13, illustrated in Figure 2.4.1, is now under investigation. FS-13 was originally developed for use in the UNiversal EXtraction (UNEX) process and has been proven to have a good hydrolytic stability against nitric acid and a high resistance towards radiolytic degradation (Rzhekhina et al., 2007; Romanovskiy et al., 2001). Other advantages with FS-13 are that it is a polar diluent (Sinha et al., 2011), which makes FS-13 a possible candidate for high solubility of CyMe₄-BTBP. It also has a low viscosity and a good chemical stability, together with a high density difference compared to nitric acid (1.4 g/mL and 1.1 g/mL respectively) (Law et al., 2001; Weast, 1976). The high density of the diluent creates a GANEX system with a heavy organic phase, which facilitates a system where the organic and aqueous phases can be easily separated from each other, even after metal extraction where the density difference between the phases increases. In the case where the organic phase is lighter than the aqueous phase, the density difference between the phases decreases during the metal extraction, which might cause problems in the system.

A disadvantage with using FS-13 as a GANEX diluent is the presence of sulphur and fluoride in the molecule. Due to this, FS-13 does not follow the CHON principle, meaning that the solvent is not fully combustible and hence has to be recycled

(Madic and Hudson, 1998). However, this is also the case for all GANEX solvents containing TBP.

2.5 NUCLEAR FUELS

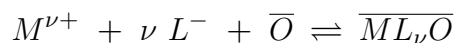
When recycling used nuclear fuel, for example using the GANEX process, the composition of the used fuel has to be considered when designing the recycling process. The composition of the used fuel depends on several different aspects, such as the type of fresh fuel used, fuel burn-up and the reactor type employed (Ando and Takano, 1999; OECD-NEA, 2011). Comparing the used fuel composition from reactors even within the same Generation, large differences can be found, e.g. a plutonium content ranging from 0.5 to 5%_{wt} in Generation II reactors (Ando and Takano, 1999; OECD-NEA, 2006, 2011; Choppin et al., 2013b). Due to these differences in the used fuel composition for Generation II reactors, where oxide-based fuels are commonly used (Degueldre et al., 2011), it is reasonable to assume that the disparity will be even larger within the Generation IV concept, where several different types of fresh fuels are under investigation (Wallenius et al., 2012). Proposed Generation IV fuel types are e.g. nitrogen- and carbon-based fuels, as well as metallic and ceramic fuels (Maschek et al., 2008; Streit and Ingold, 2005; Minato et al., 2003; Katoh et al., 2013). In addition, the recycled transuranic elements within the Generation IV concept are mixed with either recycled or depleted uranium (the use of natural uranium could also be an option) to fabricate transmutation fuel (Carmack and Pasamehmetoglu, 2008).

Many of these fresh nuclear fuel types intended for use in the Generation IV concept also have a large content of minor actinides, such as neptunium, americium and curium, in addition to a large plutonium content. It is therefore important during recycling process development, especially when aiming for the Generation IV concept, to consider both process flexibility and solvent performance under actinide loading conditions (Schreinemachers et al., 2014; Somers, 2011; Rogozkin et al., 2011; Arai et al., 1999).

3 | THEORY

3.1 LIQUID-LIQUID EXTRACTION

A liquid-liquid extraction process typically consists of two completely or almost completely immiscible phases, and the process of transferring a solute from one phase to the other phase has been investigated (Rice et al., 1993). In this work the two phases consist of one organic and one aqueous phase and the studied solutes are metal ions. The process of solvating metal extraction by a ligand and an uncharged organic ligand is illustrated in Figure 3.1.1 and is described by the reaction.



where M is the metal ion, L the ligand, O the uncharged organic ligand, MLO the final complex, and the line indicates presence in the organic phase.

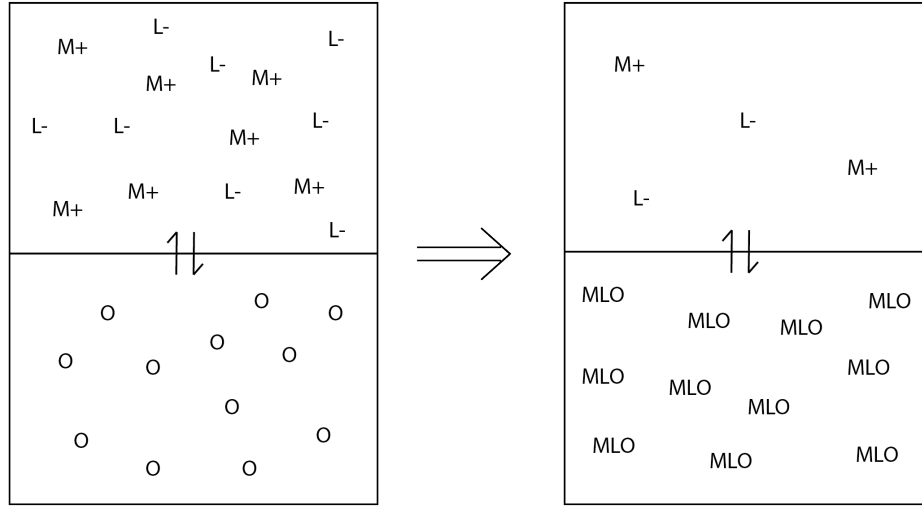


Figure 3.1.1: A schematic liquid-liquid extraction process with an upper aqueous phase and a lower organic phase, where M is the metal ion, L the ligand, O the uncharged solvating organic ligand, and MLO the formed complex. Left: the two immiscible phases before phase contact. Right: the two phases separated after phase contact. The desired metals have been transferred to the bottom organic phase and separated from the remaining metals in the aqueous phase.

There are several different expressions that describe the extraction processes in a liquid-liquid extraction system (Rydberg et al., 2004). Regardless of the type of extraction process, the following expressions can be used. The equilibrium constant, K_{ex} for the extraction in the reaction above can be described using Equation (3.1.1).

$$K_{ex} = \frac{[ML_{\nu}O]}{[M^{\nu+}] \times [L]^{\nu} \times [O]} \quad (3.1.1)$$

The metal extraction in a liquid-liquid extraction system can be described through the distribution ratio, D (Equation (3.1.2)). The distribution ratio is defined as the ratio of the total analytical concentration of the element, M, in the extract, regardless of its chemical form, in relation to the total analytical concentration of the element in the other phase, the raffinate (Rice et al., 1993). The extract containing the metal species is in this work the organic phase. For radioactive nuclides the concentration is proportional to the activity, A, of the nuclide and

therefore the distribution ratio can also be described using Equation (3.1.3)

$$D = \frac{[M]_{tot}}{[M]_{tot}} \quad (3.1.2)$$

\propto

$$D = \frac{A_{org}}{A_{aq}} = \frac{R_{org} / V_{org}}{R_{aq} / V_{aq}} \quad (3.1.3)$$

where V is the volume of the sample and R is the count rate.

The separation factor, SF, is defined as the ratio between two distribution ratios, Equation (3.1.4), and is used to describe how well two different solutes can be separated from each other. The ratio between solute M_1 and M_2 is defined so as to always be larger than 1, i.e. the distribution ratio is higher for species M_1 than for species M_2 .

$$SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (3.1.4)$$

3.2 LIQUID-LIQUID EXTRACTION PROCESSING

The common stages of a liquid-liquid extraction process, such as a GANEX process, are: 1. extraction - where the desired solute, often a metal, is transferred from one phase to the other and separated from other solutes, 2. scrubbing - where extracted impurities, acid or other contaminants can be removed and 3. back-extraction or stripping - where the desired solute is transferred from the extract into a strip solution for further processing, Figure 3.2.1. If the solvent is to be recycled in the process it is also often necessary to introduce a solvent clean-up step after the back-extraction to remove impurities and avoid accumulation of any metal that did not strip completely. In order to predict the behaviour of the studied process in the chosen extraction equipment it is necessary to complement the experimental data obtained with flow sheet calculations and flow sheet computer modelling before scaling up. There are three different types of schematic flow sheet used for solvent extraction processes; co-current extraction, counter current extraction (Figure 3.2.1) and cross current extraction (Cox and Rydberg, 2004).

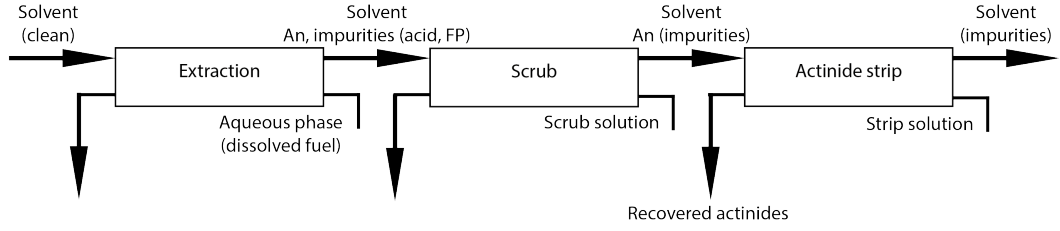


Figure 3.2.1: A schematic figure of a counter current GANEX process and the different process steps.

The counter current extraction flow sheet is both the most efficient and the most commonly used. The concentration of the solute in the extract (y_n) and the raffinate (x_n) in such a process with n number of steps can be calculated according to Equation (3.2.1)

$$x_F + \Theta \times y_F \frac{P^n - 1}{P - 1} = x_n \frac{P^{n+1} - 1}{P - 1} \quad (3.2.1)$$

where y_F and x_F are the feed concentrations, Θ is the ratio between the flow rate of the organic phase and the aqueous feed in the process, and P equals to Θ times D , where D is the distribution ratio (Lloyd, 2004). In the case where initially no metals are present in the organic phase, Equation (3.2.1) can be simplified to Equation (3.2.2).

$$x_F = x_n \frac{P^{n+1} - 1}{P - 1} \quad (3.2.2)$$

3.3 COMPLEXATION CHEMISTRY

The complexation between metal ions and extracting agents to facilitate extraction depends on several different features, both relating to the metal ion and the complexant.

In liquid-liquid extraction processes consisting of an aqueous phase containing metal ions, these metal ions are surrounded by coordinating water molecules, where

the oxygen acts as a donor atom. Depending on the size of the metal ions, various numbers of water molecules can be coordinated. For example, a small metal ion can coordinate four water molecules while a large metal ion can coordinate up to nine (Bock and Glusker, 1993; Cotton, 2006). The metal ions can coordinate with the complexant in several ways, e.g. through an inner or outer coordination sphere. In the inner coordination sphere the complexants are directly coordinated to the metal ion, in comparison to the outer coordination sphere where the complexants are separated from the metal ion by the inner sphere complexants or otherwise associated molecules such as hydration water (Choppin, 2004). Forming a complexation between a metal ion and an extracting agent means that the already coordinated water molecule has to be replaced with an organic and/or inorganic ligand (Choppin, 2004). The exchange rate between the water molecule and extracting agent is important for the kinetics of a complexation reaction, and hence is also important for the following extraction. For example, nickel is known to have slow ligand exchange kinetics in many cases, leading to a slow extraction (Kobayashi et al., 1998). One type of extracting agent is called a chelate, where two or more atoms in the same molecule bind to the metal. For the chelating extracting agents the ring size that is created is an important factor for the stability of the complex. The most stable ring formations are the five- and six-membered rings, depending on the size of the metal ion (Hancock and Martell, 1996). The disorder of the system also decreases as one chelate ligand replaces two or more water molecules, explaining the increase in stability of the formed complex in comparison to when two separate ligands replace two water molecules (Breslow et al., 2000; Schwarzenbach, 1952).

3.4 THERMODYNAMICS

When the actinide ions, M^+ , are extracted by $CyMe_4$ -BTBP in a GANEX system, n numbers of $CyMe_4$ -BTBP molecules and m numbers of NO_3^- ions bind to the metal, creating a chemical equilibrium reaction. The equilibrium constant, K_{ex} described in Equation (3.1.1), can then be expressed according to Equation (3.4.1), where $CyMe_4$ -BTBP corresponds to the uncharged organic ligand O, and NO_3^- to the ligand L^- .

$$K_{ex} = \frac{[M(NO_3)_m BTBP_n]}{[M^{3+}] \times [NO_3^-]^m \times [BTBP]^n} \quad (3.4.1)$$

In reactions where the metal concentration is very low, for example in the case of trace amounts in comparison to the ligand concentration or the concentration of nitrate, the ligand and nitrate concentrations can be assumed to be constant throughout the extraction. This also assumes that only a minor amount of the nitric acid is co-extracted into the organic phase, leading to Equation (3.4.2).

$$[NO_3^-]^m \times [\overline{BTBP}]^n = C \quad (3.4.2)$$

If it is assumed that the concentration of the complexes is equal to the thermodynamic activities, K_{ex} can be expressed through the distribution ratio, Equation (3.4.3).

$$K_{ex} = D_M \times \frac{1}{C} \quad (3.4.3)$$

The equilibrium constant can be used to calculate the enthalpy and entropy of the extraction. The equations for Gibbs free energy and Gibbs free energy isotherm, Equation (3.4.4) and Equation (3.4.5), can be combined to get the van 't Hoff equation, Equation (3.4.6).

$$\Delta G^0 = \Delta H^0 - T \times \Delta S^0 \quad (3.4.4)$$

$$\Delta G^0 = -R \times T \times \ln(K_X) \quad (3.4.5)$$

$$\ln(K_X) = \frac{-\Delta H^0}{R \times T} + \frac{\Delta S^0}{R} \quad (3.4.6)$$

where ΔG^0 is Gibbs free energy, ΔH^0 the enthalpy and ΔS^0 the entropy for a selected standard state, R is the ideal gas constant, T the temperature and K_X is the equilibrium constant for either the extraction, K_{ex} , or the solubility, K_S , at the standard temperature and pressure.

Using the van 't Hoff equation for a plot, $-\Delta H/R$ represents the slope and $\Delta S/R$ represents the intercept of the linear fit.

4

EXPERIMENTAL

The majority of the experiments performed within this work have been done using the same composition of the organic phase, combining the two ligands CyMe₄-BTBP and TBP in FS-13 as diluent. This solvent composition will from now on be called the FS-13-based GANEX solvent.

Several different sets of solvent extraction experiments have been performed during this work. They were all conducted in similar ways, from fresh solvent batches for each actinide separately and in triplicates, unless otherwise stated. The uncertainties are in all cases calculated as standard deviations from triplicate samples.

4.1 BASIC SOLVENT EXTRACTION

Unless otherwise stated the organic phase used consists of 10 mM CyMe₄-BTBP (synthesised in house according to Foreman et al. (2006), or supplied from Karlsruhe Institute of Technology, Germany, or Reading University, United Kingdom), 30%_{vol} TBP (Sigma-Aldrich, 97%) and 70%_{vol} FS-13 (CarboSynth or Marshallton). Similarly the aqueous phase was in all cases, unless otherwise stated, based on 4 M HNO₃ (Sigma Aldrich, \geq 69% diluted with MilliQ-water, ($>$ 18 M Ω)). 3.5 mL glass vials with plastic lids were used for phase contacts. All samples contained equal amounts of organic and aqueous phase, between 200 - 1000 μ L. The phase contact was facilitated in a mechanical shaker (IKA, VIBRAX VXR 1,500 rpm) at 25 °C for a duration of one hour, except for kinetic studies and temperature dependence studies.

4.1.1 Actinide Partitioning

Trace amounts of the actinides and europium were added to the samples from stock solutions: U(VI)-235 (84.44% enrichment, 40 mM), Np(V)-237 (0.35 MBq mL⁻¹), Np(V, VI)-239 (extracted from a silica column loaded with Am-243), Pu(IV)-238 (0.28 Bq mL⁻¹), Am(III)-241 (0.42 MBq mL⁻¹ or 2.2 MBq mL⁻¹), Cm(III)-244 (0.23 MBq mL⁻¹) and Eu(III)-152 (23 kBq mL⁻¹ or 1.4 MBq mL⁻¹). Americium

and europium were in most cases analysed collectively, i.e. added to the same samples, according to Section 4.5.1, Gamma Spectrometry. The other actinides were analysed separately, according to Section 4.5.2, Liquid Scintillation Counting or Section 4.5.3, Alpha Spectrometry.

4.1.2 *Fission Products*

The investigations of fission product extraction were conducted as described in Section 4.1, Basic Solvent Extraction. Inactive metals of the corresponding element and concentrations consistent with a PUREX feed were used, Table A.1 in Appendix A, FISSION PRODUCTS on page 71. The elements were investigated in groups of two or three, based on similar concentrations and diverse mass weights. The samples were analysed according to Section 4.5.4, Inductively Coupled Plasma Mass Spectrometry.

4.1.3 *Back-Extraction and Scrubbing*

The back-extraction and scrubbing experiments were conducted in a similar way to the procedures described in Section 4.1, Basic Solvent Extraction, using trace amounts of the investigated metals, as described in Section 4.1.1, Actinide Partitioning. During back-extraction and scrubbing steps the aqueous phase used were 0.05 M glycolic acid (Sigma-Aldrich, 99%) set to pH 4 using ammonia (Merch, 25%) or 3.99 M NaNO₃ (Sigma-Aldrich, ≥ 99.5%) in 0.01 M HNO₃, respectively. The extraction steps were performed successively and the remaining organic phase was moved to a new clean vial prior to the next step of the experiment.

4.2 SOLVENT STABILITY

The extraction properties of the organic phase were investigated as described in Section 4.1, Basic Solvent Extraction, using trace amounts of the investigated metals as described in Section 4.1.1, Actinide Partitioning.

4.2.1 *Radiolysis*

Irradiations were performed using a cobalt-60 γ -source (Gammacell 220, Atomic Energy of Canada Ltd) with a dose rate of approximately 8.5 kGy/h (on 2015-06-29) and a temperature of 45 °C. The samples were irradiated in glass vials with plastic lids containing either only the organic phase or both the organic and

aqueous phases (equal amounts). Reference samples were stored in a tempered water bath, set to the same temperature as the γ -source for the same time periods as the respective samples. The organic phase was immediately separated from the aqueous phase after irradiation and placed in new clean vials before being subjected to further experiments.

4.2.2 *Hydrolysis*

The hydrolysis and long-term stability of the FS-13 based GANEX solvent was examined using two different batches of the solvent; one stored with aqueous phase contact and one without. Both batches were stored for up to six weeks at room temperature. Every week, samples of the organic phase were removed from both batches and placed in new clean vials before being subjected to further experiments.

4.3 CYME₄-BTBP SOLUBILITY

To examine the CyMe₄-BTBP solubility in pristine and nitric acid pre-equilibrated FS-13-based GANEX solvents containing 30%_{vol} TBP and 70%_{vol} FS-13, 1 mL of each solution was placed in a glass vial together with a large amount of solid CyMe₄-BTBP. The samples were placed in a thermostat-equipped mechanical shaker at the desired temperature and left for three days. During these three days additional CyMe₄-BTBP was added, morning and evening, until undissolved CyMe₄-BTBP was observed. The samples were then maintained at the same temperature for two additional days to allow the solid phase to settle. Each experiment was performed in triplicate and at three different temperatures; 15 °C, 25 °C and 35 °C. In the pre-equilibrated solutions organic phase and nitric acid were thoroughly mixed and centrifuged at room temperature (21 °C) before the organic phase was separated from the acid, prior to CyMe₄-BTBP dissolution. The samples were analysed according to Section 4.5.5, UV-VIS Spectrophotometer.

4.4 PLUTONIUM LOADING

The plutonium loading experiment was conducted in a similar way to that described in Section 4.1, Basic Solvent Extraction, except that the concentration of CyMe₄-BTBP in the organic phase was either 25 or 50 mM. A 4 M nitric acid stock solution containing 40 g ^{238, 239, 240, 241}Pu/L, 0.6 g ²⁴¹Am/L, and 1 g inactive Eu/L was used either directly as aqueous phase or diluted with 4M nitric acid. Phase

contact during the plutonium loading experiments was performed by contacting the phases by hand, keeping the glass vials in an insulated plastic container. Plutonium and europium were analysed according to Section 4.5.4, Inductively Coupled Plasma Mass Spectrometry, while americium and, in some samples, plutonium-239 were analysed according to Section 4.5.1, Gamma Spectrometry.

4.5 ANALYSIS

To determine the radioactivity, metal concentration, or CyMe₄-BTBP concentration, five different measurement techniques were used. Possible differences in detector efficiency when analysing the organic compared to aqueous phases were investigated for all techniques. No efficiency differences were observed.

4.5.1 *Gamma Spectrometry*

A high purity germanium (HPGe) detector was used to measure the samples containing both americium-241 and europium-152 and the plutonium loading samples (Canberra, Gamma Analyst GEM 23195 or Ortec, GEM 15180-S). 100 μ L of each sample and phase were removed and placed in new clean plastic vials. Plutonium-239 was analysed using the gamma energy of 129.3 keV, americium-241 using the gamma energies of 59.5 keV or 125.3 keV, and europium-152 using the gamma energy of 121.8 keV. The counts in the energy peak were subjected to automatic background correction using the γ -spectrometry software Genie 2000 (the Canberra detector) or GammaVision (the Ortec detector). Each sample was measured until the measurement uncertainty was below 5%.

4.5.2 *Liquid Scintillation Counting*

For measurements of the samples containing either uranium-235, neptunium-239, plutonium-238, americium-241, or curium-244, separately, a liquid scintillation counting (LSC) detector was used (Wallac 1414 WinSpectral). 100 μ L of each sample and phase were removed, placed in a 7.5 mL scintillation vial and mixed with 5 mL scintillation cocktail (Ultima Gold AB, Perkin Elmer). Experiments to examine possible quenching were performed by standard addition or by control measurements using HPGe (for example using americium). No quenching using FS-13 was observed within the sample volume range used.

4.5.3 *Alpha Spectrometry*

For the samples containing neptunium-237, or americium-241 and curium-244 simultaneously, 10 μL of each sample and phase were removed and placed on an alpha planchet. 75 μL of a coating solution (Z-100) dissolved in acetone was added on top of the sample. The alpha planchets were dried under an IR lamp (\sim 10 minutes) and organic residues were evaporated using a gas burner. The samples were analysed using alpha spectrometry (Ortec, Alpha Duo, Octête TM PC). The neptunium was analysed using the alpha energy of 4.8 MeV, americium-241 was analysed using the alpha energy of 5.5 MeV, and curium-244 was analysed using the alpha energy of 5.8 MeV.

4.5.4 *Inductively Coupled Plasma Mass Spectrometry*

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the inactive fission products and the plutonium loading samples (Perkin Elmer Elan 6100 DRC). A 0.5 M HNO_3 solution containing an internal standard of 5 ppb bismuth was used to dilute the samples to a metal concentration of 5-10 ppb. Only the aqueous phase can be measured on the ICP-MS system used, so to be able to calculate the metal extraction a reference sample was prepared containing the same amount of metal as the original sample, prior to the phase contacting. This leaves the possibility of a third phase affecting calculated distribution ratios going undetected and, due to this, mass balance calculations or control measurements using HPGe (for example with plutonium) were performed.

4.5.5 *UV-VIS Spectrophotometer*

The quantification of $\text{CyMe}_4\text{-BTBP}$ concentration in the solubility solutions was based on the ability of $\text{CyMe}_4\text{-BTBP}$ to form a blue-coloured complex with Fe^{2+} ions in solution (Ekberg et al., 2010). The absorbance of the blue complex was measured at a wavelength of 598 nm using quartz cuvettes with a 10 mm path length and a UV-VIS spectrophotometer (Shimadzu UV-1800). A solution of Mohrs salt (Sigma-Aldrich, p.a. 99%) was used as the source of Fe^{2+} ions. This solution was prepared using an excessive amount of solid Mohrs salt dissolved in 50 mL ethanol (Solveco, 95%) and 50 mL Milli-Q water, added in the order stated. A fresh iron solution was prepared prior to each measurement because the solution is sensitive towards ageing as Fe^{2+} is oxidized to Fe^{3+} .

For the UV-VIS spectrophotometry measurement 100-300 μL of the tempered solvent with dissolved $\text{CyMe}_4\text{-BTBP}$ was added to a solution containing 10 mL of ethanol and 500 μL Fe^{2+} solution. A mixture of 70%_{vol} FS-13 and 30%_{vol} TBP was then added to make up a total volume of 400 μL of added organic phase. Absorption was measured against a reference solution containing 400 μL solvent without $\text{CyMe}_4\text{-BTBP}$ in 10 mL of ethanol and 500 μL Fe^{2+} solution. Solutions with known concentration of $\text{CyMe}_4\text{-BTBP}$ were used to obtain a calibration curve prior to the measurements.

5

RESULTS AND DISCUSSION

As previously mentioned, several different Chalmers GANEX solvents have been developed over the years (Paper I). In this work, results from investigations using FS-13 as Chalmers GANEX diluent are presented.

5.1 BASIC SOLVENT EXTRACTION

During the development of a GANEX process there are several basic features of the solvent extraction system that have to be investigated. Among these features, for example, are obtained a high actinide extraction while maintaining a low fission product extraction, fast extraction kinetics and the possibility to back-extract the actinides. All experiments, unless otherwise stated, were performed as described in Section 4.1, Basic Solvent Extraction, using trace amounts of the investigated metals described in Section 4.1.1, Actinide Partitioning. All experiments were analysed according to Section 4.5, Analysis.

5.1.1 *Extraction Behaviour of the System*

Initial studies trying to evaluate the potential of FS-13 as a Chalmers GANEX diluent were performed by investigating the extraction potential of uranium, plutonium, neptunium, americium, curium and europium in the FS-13-based GANEX solvent (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP). These results are mainly presented in Paper II and Paper III. Extraction kinetics experiments, Figure 5.1.1, were performed in order to investigate the extraction potential as well as the extraction rate of the system. The time to reach extraction equilibrium was also investigated to estimate an adequate contact time of the two phases for the remainder of the experiments in this work.

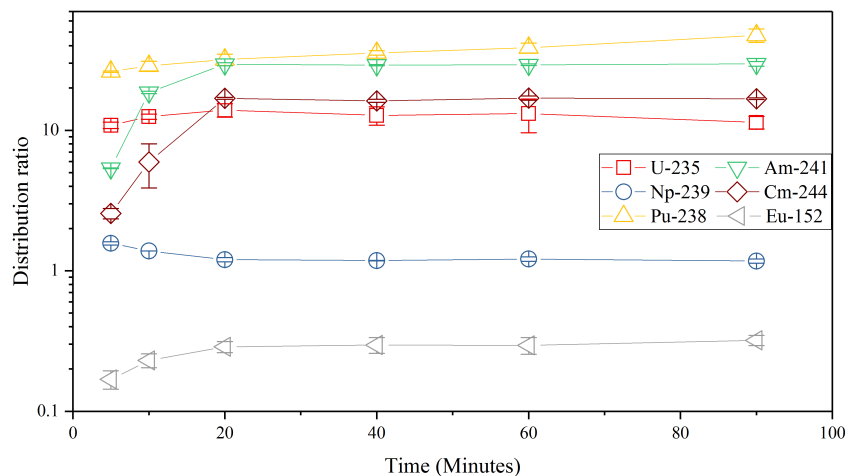


Figure 5.1.1: Distribution ratios for uranium, neptunium, plutonium, americium, curium and europium using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase (lines added to guide the eye) varying the contact time.

Uranium and plutonium extract quickly and reach extraction equilibrium more or less instantly. The neptunium extraction, however, decreases between 5 and 20 minutes, which might be due to a shift in the dominating oxidation state of neptunium. Neptunium is easily oxidised and reduced by the acidic conditions in this experiment and is most likely present in mixed oxidation states (Huizenga and Magnusson, 1951; Taylor et al., 2013). The extraction of americium and curium reaches equilibrium after 20 minutes and both metals show a significant increase in distribution ratios between 5 and 20 minutes. Europium is not extracted to any greater extent and has similar kinetics to americium and curium. Hence, all actinides and europium reached extraction equilibrium after 20 minutes, which is fast compared to other Chalmers GANEX systems with CyMe₄-BTBP as extracting agent, using the same contacting equipment (Löfström-Engdahl et al., 2014). The time to reach extraction equilibrium in a recycling process for used nuclear fuel, however, will depend on the solvent extraction equipment used. In previously investigated Chalmers GANEX solvents (discussed in Paper I), for example, for the cyclohexanone-based GANEX solvent (70%_{vol} cyclohexanone, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) and the hexanol-based GANEX solvent (70%_{vol} hexanol, 30%_{vol} TBP and 10 mM CyMe₄-BTBP), a similar phase contact time to reach extraction equilibrium has been found (Aneheim, 2012; Löfström-Engdahl, 2014).

Comparing the equilibrium distribution ratios for the FS-13-based GANEX solvent with previously investigated Chalmers GANEX solvents, values are found to be in a similar order of magnitude (Aneheim et al., 2012; L fstr m-Engdahl et al., 2014).

The FS-13-based GANEX system has high distribution ratios for plutonium and americium, slightly lower for uranium and curium, and a distribution ratio well below one for europium, Table 5.1.1. These distribution ratios correspond to a metal extraction between 93% and 98% (uranium and plutonium, respectively), after one extraction step using equal phase volumes. This is adequate for a recycling process aiming at > 99.9% extraction (Magnusson et al., 2009a) using three or more extraction steps, calculated using Equation (3.2.2) for counter current flows.

Table 5.1.1: Distribution ratios for selected actinides and europium, as well as separation factors for selected actinides over europium using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase.

	<i>U</i>	<i>Np</i>	<i>Pu</i>	<i>Am</i>	<i>Cm</i>	<i>Eu</i>
<i>D</i> _{eq}	13 ± 2	1.2 ± 0.05	39 ± 3	29 ± 0.3	17 ± 0.6	0.3 ± 0.04
<i>SF</i> _{eq}	44 ± 6	4.1 ± 0.5	120 ± 18	84 ± 4	56 ± 6	–

The separation factors were calculated for evaluation of the actinide extraction in comparison to europium, and used as a reference for the lanthanides, Table 5.1.1. The distribution ratios of the two lanthanides terbium and dysprosium has in previous work been found to be slightly higher compared to europium using CyMe₄-BTBP as extracting agent (Geist et al., 2006). It is important to be able to separate the actinides from the lanthanides in particular due to the lanthanides high thermal neutron capture cross-section (Pfennig et al., 2006). However, due to the limited presence of these lanthanides in the used fuel, europium can still be used as a valid reference for the lanthanides. The only actinide with a low separation factor vis-à-vis europium is neptunium. The separation factor, however, is higher than in both the cyclohexanone- and the hexanol-based GANEX solvent, and is high enough to enable separation. Americium/curium separation can also be desirable in certain suggested recycling options, such as the AmEX and EXAm processes (Rainey, 1954; Rostaing et al., 2012; Chapron et al., 2015). The separation factor between americium and curium in the FS-13-based GANEX solvent is small (1.5 ± 0.2) but is in agreement with the selectivity observed for

CyMe₄-BTBP in e.g. 1-octanol (Geist et al., 2006). This indicates that americium and curium may be hard to separate from each other using this extraction system.

In Paper IV, separation factors different from Table 5.1.1 are presented. This is probably due to a lower CyMe₄-BTBP concentration than intended (8 mM instead of 10 mM), caused by insufficient dissolution of CyMe₄-BTBP in FS-13. Since CyMe₄-BTBP extracts the trivalent actinides, and to some extent the trivalent lanthanides, the distribution ratio of the elements will decrease with a decreasing CyMe₄-BTBP concentration. The separation factors presented in Paper IV (all except Am/Eu) are based on a distribution ratio of 0.1 for europium instead of 0.3, found in later work (Paper I, Paper II and Paper III) with a correct CyMe₄-BTBP concentration of 10 mM.

Fission Products

During a GANEX process high distribution ratios of the actinides alongside a low extraction of the other fission products besides the lanthanides is also desirable (Paper III). In this study, performed as described in Section 4.1, Basic Solvent Extraction, inactive metals have been used as references for the actual fission products, as described in Section 4.1.2, Fission Products. For a majority of the investigated fission products a distribution ratio below one has been found, Figure 5.1.2. Some of the fission product distribution ratios, however, are higher than, or close to, one and might become a problem in a future process. A distribution ratio of one means that the concentration of metal is equally dispersed between the two phases, which is why a distribution ratio above one is desirable for the actinides and below one is desirable for the fission products. The fission products with the highest distribution ratios are cadmium and silver. The abundance of these elements in dissolved used uranium-based ceramic fuel, however, is lower than 0.4 mM. These unwanted metals can, despite this, become a problem in a future process if they cannot be scrubbed from the solvent before recycling it in the process. Previous studies of solvents containing CyMe₄-BTBP show that the extraction of silver can easily be prevented, whereas the extraction of cadmium remains an unsolved problem (Aneheim et al., 2013, 2010). One metal with higher abundance (above 9 mM) in dissolved used fuel is zirconium. Even if the distribution ratio remain below one, the high abundance in the used fuel can still cause problems. Therefore, further studies investigating the extraction of fission products, possibly using suppression agents and/or scrubbing steps, are needed. Comparing the inactive europium, Figure 5.1.2, with the active europium, Figure 5.1.1, distribution ratios around 0.3 are

found in both cases, indicating that the different europium concentrations (~ 55 mg/L and trace amounts, respectively) do not affect the extraction system. Comparing the fission product behaviour with other GANEX systems, as well as with another Chalmers GANEX system, similar results have been obtained. In these systems promising results have been achieved using suppression agents (Aneheim et al., 2010; Sypula et al., 2012; Bell et al., 2012).

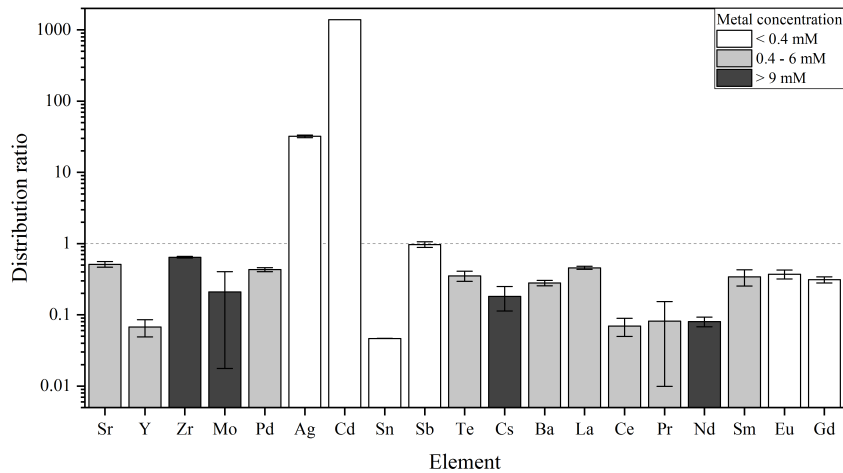


Figure 5.1.2: Distribution ratios of selected fission products using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase. White bars correspond to a metal concentration below 0.4 mM in the dissolved used fuel. Grey bars correspond to a metal concentration between 0.4 and 6 mM in the dissolved used fuel. Black bars correspond to a metal concentration above 9 mM in the dissolved used fuel. The dashed line marks $D = 1$, which is the dividing line between extraction and stripping.

5.1.2 Extraction Behaviour of the Extracting Agents

It is important to understand the behaviour of the ingoing components in the extraction system in order to predict their future behaviour in a process. Data published in Paper II and Paper III has shown that the combination of TBP and CyMe₄-BTBP is beneficial for both the americium and the curium extraction using FS-13 as diluent. The distribution ratios of americium and curium reach 0.05 and 0.4, respectively, after 1 hour of phase contacting in both the systems containing only one of the two extracting agents (70%_{vol} FS-13 and 30%_{vol} TBP or 100%_{vol}

FS-13 and 10 mM CyMe₄-BTBP). In the system containing both extracting agents (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) americium and curium, however, reach distribution ratios of 25 and 17, respectively, Figure 5.1.3.

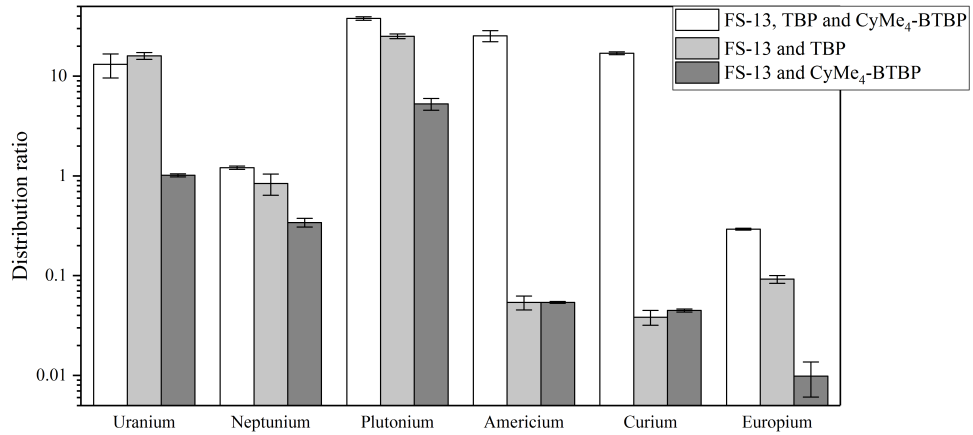


Figure 5.1.3: Distribution ratios of actinides and europium using A: 70%_{vol} FS-13 and 30%_{vol} TBP, B: 100%_{vol} FS-13 and 10 mM CyMe₄-BTBP and C: 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase.

TRLFS experiments were performed to study the trivalent actinide complexation by CyMe₄-BTBP, Paper III. Curium was found to be extracted from 4 M HNO₃ into 10 mM CyMe₄-BTBP in 100%_{vol} FS-13 as well as in 10 mM CyMe₄-BTBP in 70%_{vol} FS-13, 30%_{vol} TBP as a 1:2 complex. Thus, trivalent actinides seem to be extracted by CyMe₄-BTBP in both systems, despite the results shown in Figure 5.1.3. Due to the TRLFS results, a long-term extraction kinetics study of the system containing 100%_{vol} FS-13 and 10 mM CyMe₄-BTBP was performed, Figure 5.1.4. The extraction of europium seems to be stable throughout the experiment, with a distribution ratio of 0.05, while the extraction of americium slowly increases over time. The extraction equilibrium of americium is reached after approximately 20 hours with a final distribution ratio of 7.5. This is very slow compared to the system consisting of 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP where the extraction equilibrium of americium is reached after 20 minutes, with a distribution ratio of 29. Hence, the presence of TBP strongly affects the minor actinide extraction kinetics by CyMe₄-BTBP in FS-13 and also influences the corresponding equilibrium distribution ratio in a positive way. This is most likely not a synergistic effect but could indicate that TBP acts as a phase

transfer catalyst. A similar behaviour has also been observed when adding DM-DOHEMA (Geist et al., 2006) or TODGA (Modolo et al., 2013; Geist et al., 2012) to a CyMe₄-BTBP-containing extraction system. However, the large amount of TBP also has an impact on the physical properties of the solvent, such as the surface tension (26.6 and 28.5 mN/m, respectively) and density (1.40 and 1.28 g/mL, respectively), Paper VI.

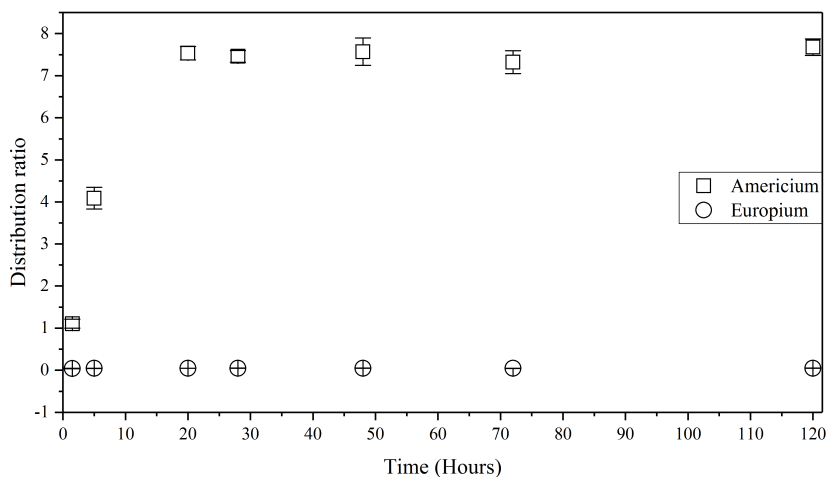


Figure 5.1.4: Distribution ratios for americium and europium using 100%_{vol} FS-13 and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase after long-term phase contacting.

The complexation data retrieved for curium and CyMe₄-BTBP in the FS-13 based GANEX solvent by TRLFS was complemented for neptunium, plutonium, americium and europium by extraction slope analysis using various concentrations of CyMe₄-BTBP, Paper III. The results for the trivalent metals, americium and europium, correspond well with the curium results (2.17 ± 0.04 and 1.96 ± 0.12 for americium and europium, respectively) indicating a 2:1 complexation between CyMe₄-BTBP and all three metals. The complexation between neptunium as well as plutonium and CyMe₄-BTBP (1.19 ± 0.15 and 0.86 ± 0.22 , respectively) on the other hand indicates a 1:1 relation. These results are expected compared to literature data on CyMe₄-BTBP-complexation (Modolo et al., 2013; Wilden et al., 2013; L fstr m-Engdahl, 2014; Aneheim, 2012; Retegan et al., 2007a). It should be noted, however, that both neptunium and plutonium, as well as europium in FS-13, are also extracted by TBP, as previously shown in Figure 5.1.3.

5.1.3 Back-Extraction

The experiments were performed as described in Section 4.1.3, Back-Extraction and Scrubbing.

The americium content in the organic phase remains high after the first back-extraction step while the plutonium content decreases to roughly 15%. The europium is also efficiently back-extracted in the first step. After the second back-extraction step, however, the content of both plutonium and americium in the organic phase is below 1%, while the europium content is below the detection limit of the detector. This shows that it is possible to efficiently remove the extracted actinides from the FS-13-based GANEX solvent in order to enable further processing. This can be compared to the cyclohexanone-based GANEX system where a low initial back-extraction was found, possibly caused by a large amount of the acidic aqueous phase being extracted into the organic phase (Aneheim et al., 2012).

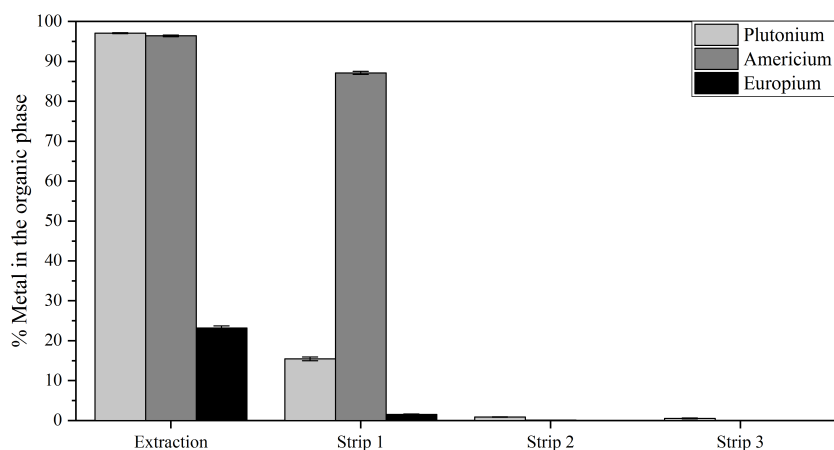


Figure 5.1.5: Amount (%) of plutonium, americium and europium in the organic phase (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) after one extraction step from 4 M HNO₃ and three back-extraction steps using 0.5 M glycolic acid with pH 4.

In order to try to increase back-extraction of americium in the first step, another experiment was attempted where the extraction step was followed by two scrubbing steps. Introducing scrubbing before the actual stripping step could possibly enhance back-extraction by removing dissolved acid from the organic phase, as

well as facilitate a possible removal of unwanted fission products from the solvent. It was found that the major part of uranium, plutonium and americium remains in the organic phase during scrubbing, while the europium content slightly decreased, Figure 5.1.5. During the back-extraction step the main part of the uranium is back-extracted into the aqueous phase, while both plutonium and americium mainly remain in the organic phase. This indicates that several back-extraction steps are needed to recover the actinides when introducing scrubbing. The reason for only investigating four subsequent steps in both studies is equipment-related, as the phase volumes are limited to maximum 1 mL per phase.

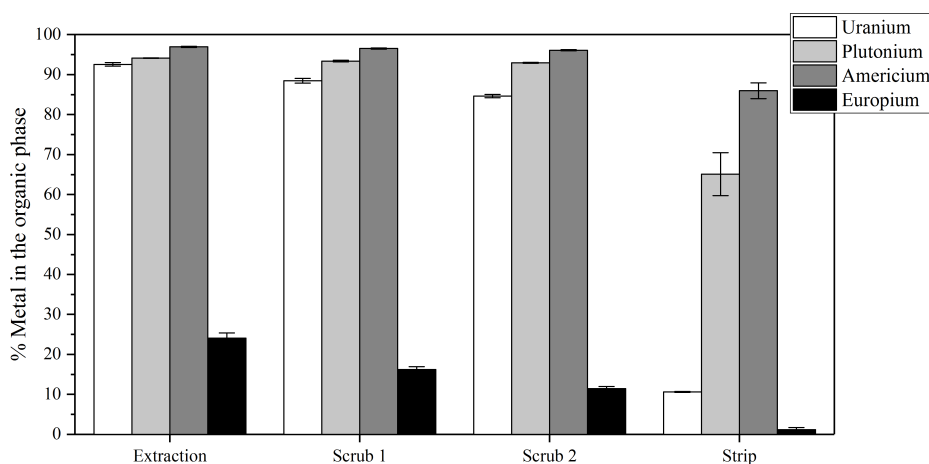


Figure 5.1.6: Amount (%) of uranium, plutonium, americium and europium in the organic phase (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) after one extraction step from 4 M HNO₃, two scrubbing steps using 3.99 M NaNO₃ in 0.01 M HNO₃ and one back-extraction step using 0.5 M glycolic acid with pH 4.

Comparing the two studies, the concentration of americium left in the organic phase after one back-extraction step is more or less the same with or without the scrubbing steps, while the plutonium concentration is much higher after the acid scrub. This could possibly be caused by a beneficial complexation between the glycolic acid and the nitrate or slower extraction kinetics after the acid scrub steps. In addition the loss of actinides during the scrubbing steps makes this back-extraction alternative unsuitable for the FS-13-based GANEX system. Comparing with the cyclohexanone-based GANEX system, introducing an acid scrub signifi-

cantly enhanced the back-extraction of the actinides in the solvent (Aneheim, 2012; Aneheim et al., 2013).

5.2 SOLVENT STABILITY

Due to the promising extraction results, the stability towards irradiation, ageing and hydrolysis of the FS-13-based GANEX solvent was investigated (mainly presented in Paper III and Paper IV). Besides confirming a maintained extraction performance, investigating radiolytic and hydrolytic stability is also important to be able to estimate the lifetime of the solvent. Stable solvents will make the process more cost efficient and will also decrease the amount of organic waste. The irradiation experiments were performed as described in Section 4.2, Solvent Stability. The extraction was performed using trace amounts of the investigated metal according to Section 4.1, Basic Solvent Extraction and Section 4.1.1, Actinide Partitioning. The samples were analysed as described in Section 4.5, Analysis.

5.2.1 *Radiolytic Stability*

According to the extraction results after solvent irradiation, presented in Figure 5.2.1, no significant differences in the americium and europium extractions could be observed between the reference samples and the irradiated samples. The results indicate that the extraction properties of the solvent are maintained during irradiation in contact with the 4 M HNO₃ aqueous phase for doses up to at least approximately 160 kGy. The distribution ratios obtained correspond well with the results in Table 5.1.1 on page 30. However, HPLC measurements of the irradiated organic phase show that the CyMe₄-BTBP concentration decreases as the dose increases. Alongside the decrease in CyMe₄-BTBP concentration, two other peaks can be observed to be increasing, corresponding to two hydroxy-derivatives of CyMe₄-BTBP; (HO)-CyMe₄-BTBP and (HO)₂-CyMe₄-BTBP. The most likely position of the hydroxyl group(s) are on the pyridine rings of the BTBP. Above doses of 100 kGy there is more or less no CyMe₄-BTBP left, but the extraction ability of the system, as previously mentioned, is maintained. This indicates that the new molecules have similar extraction and complexation properties as CyMe₄-BTBP. Comparing with previously investigated GANEX solvents, both the cyclohexanone- and hexanol-based GANEX solvents largely maintain their respective extraction properties after irradiation (Aneheim, 2012; Löffström-Engdahl, 2014).

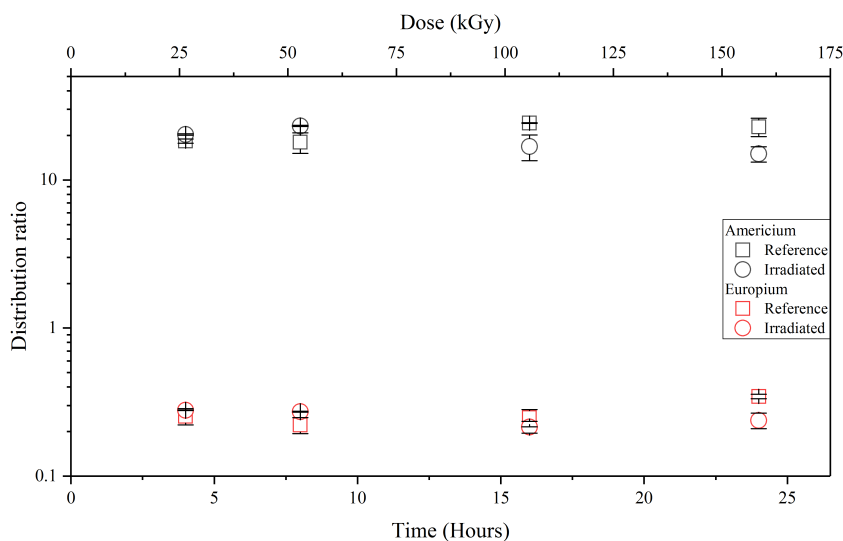


Figure 5.2.1: Distribution ratios of americium and europium after irradiation of the solvent (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) in contact with an aqueous phase (4 M HNO₃) for 24 h and a dose rate of 6.6 kGy/h.

5.2.2 Hydrolytic Stability

Both the hydrolysis and long-term stability of the FS-13-based GANEX solvent have been investigated and evaluated in terms of maintained extraction performance. These results are presented in Figure 5.2.2. In the solvent without aqueous phase contact the distribution ratio of americium is slightly increased between the second and fourth week and decreased in the fifth week. In the solvent with aqueous phase contact americium shows a stable distribution ratio for the duration of the whole experiment (6 weeks). The results show that the stability of the solvent is increased when it is stored in contact with the aqueous phase. Results from HPLC measurements also show that CyMe₄-BTBP stays intact in the aqueous phase-contacted solvent for the duration of the whole experimental period. The acidic aqueous phase could work like a scavenger, in a similar way to how the aqueous phase scavenges radicals during irradiation experiments (Mincher et al., 2009). Europium shows a stable distribution ratio for both solvents for the whole duration of the experiment. Compared with the previously investigated GANEX solvents, the cyclohexanone-based GANEX solvent degrades in contact with acid and the CyMe₄-BTBP content decreases. The actinide extraction, however, is maintained, indicating that the hydrolysis products of CyMe₄-BTBP also extract

the actinides (Aneheim, 2012). In the hexanol-based GANEX solvent the extraction of americium decreases during hydrolysis (Löfström-Engdahl, 2014).

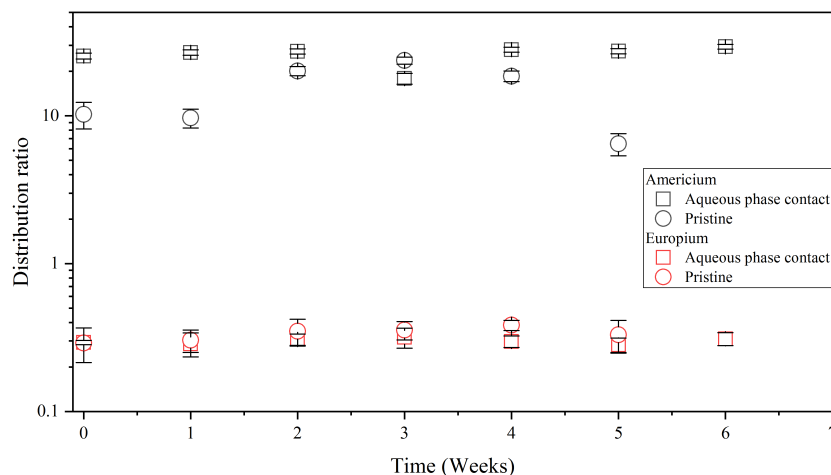


Figure 5.2.2: Distribution ratios of the investigated solvent (70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP) after ageing with and without aqueous phase (4 M HNO₃) contact.

The slow increase of the americium distribution ratio without aqueous phase contact could be due to an initially incomplete slow dissolution of CyMe₄-BTBP in the mixture of FS-13 and TBP. While the aqueous-contacted organic phase dissolved the CyMe₄-BTBP instantly, the dry organic phase was only able to slowly dissolve the CyMe₄-BTBP. This dissolution was most likely not complete until after the first two weeks of the experiments. This is further explored in Section 5.3.2, Solubility Thermodynamics.

5.3 THERMODYNAMIC INVESTIGATIONS

Studies investigating how changes in temperature effect both the actinide extraction and the solubility of CyMe₄-BTBP were performed (mainly presented in Paper III and Paper V). This is important, as a recycling process for used fuel will most likely take place at elevated temperatures.

5.3.1 Extraction Thermodynamics

To investigate how the temperature affects the trivalent actinide and lanthanide extraction with the FS-13-based GANEX solvent, experiments within a temperature interval between 20 °C and 40 °C were performed (Figure 5.3.1). The experiments in this study were performed as described in Section 4.1, Basic Solvent Extraction, using trace amounts of the investigated metals described in Section 4.1.1, Actinide Partitioning. All experiments were analysed according to Section 4.5, Analysis. The extraction of both americium and europium shows a slight decrease with increasing temperature, indicating that the extraction reaction is exothermic and that separation factors could still be maintained at higher temperatures.

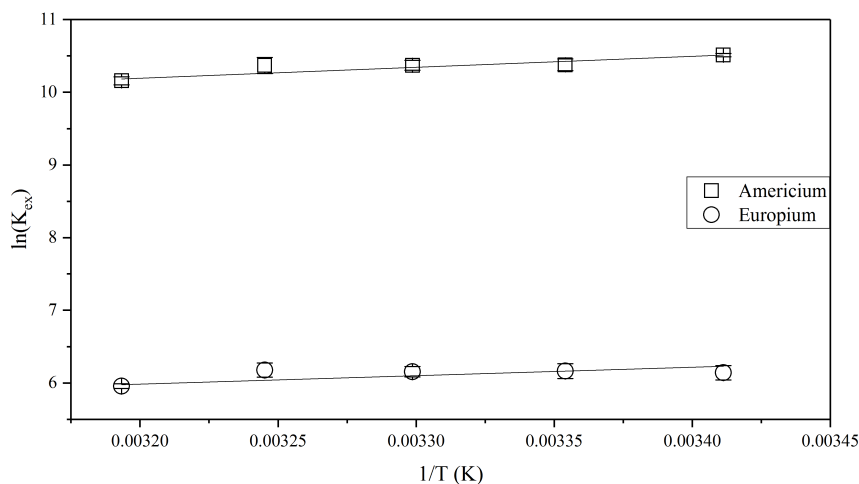


Figure 5.3.1: The natural logarithm of the extraction constant vs. $1/T$ using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase.

By performing a linear regression on the data points in Figure 5.3.1 according to the Van 't Hoff Equation (Equation (3.4.6) on page 20), the enthalpy and the entropy for the extraction of americium and europium can be calculated. For the FS-13-based GANEX system the enthalpy change is negative, while the entropy change is positive (Table 5.3.1). The increase in entropy during the extraction acts as a thermodynamic driving force for the reaction.

Table 5.3.1: Enthalpy and entropy of complexation for the extraction of americium and europium using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase.

<i>Metal</i>	ΔH^0 [kJ/mol]	ΔS^0 [J/mol K]
<i>Americium</i>	- 12.5 ± 0.4	44.6 ± 1.2
<i>Europium</i>	- 9.7 ± 0.8	18.5 ± 2.8

Thermodynamic studies have previously shown that both the cyclohexanone- and hexanol-based GANEX systems are also exothermic (Löfström-Engdahl, 2014; Aneheim, 2012). The hexanol-based GANEX system displays an increasing entropy for the extraction, just as the FS-13-based GANEX system. However, in the case of the cyclohexanone-based GANEX system the entropy change seems to depend on the aqueous phase used (Aneheim, 2012; Löfström-Engdahl, 2014).

5.3.2 Solubility Thermodynamics

The amount of extracting agent is generally important during metal extraction, and especially under loading conditions (Taylor et al., 2016; Brown et al., 2012). CyMe₄-BTBP is known to have a low solubility in many investigated diluents (Ekberg et al., 2010), which could make it problematic to use for recycling of minor actinide-containing Generation IV fuels, such as metallic U-Pu-Zr (Trybus et al., 1993; Capriotti et al., 2017). Experiments investigating the overall solubility of CyMe₄-BTBP have therefore been performed in pristine 70%_{vol} FS-13 and 30%_{vol} TBP as well as in 70%_{vol} FS-13 and 30%_{vol} TBP pre-equilibrated with 4 M nitric acid. Experiments were performed as described in Section 4.3, CyMe₄-BTBP Solubility and analyses were made according to Section 4.5.5, UV-VIS Spectrophotometer. The CyMe₄-BTBP solubility was found to increase drastically when the organic phase was pre-equilibrated with 4 M nitric acid compared to the pristine solvent, Figure 5.3.2. No aqueous phase was present during the dissolution. Similar results were also found when using cyclohexanone and 1-octanol as diluents, Paper VI.

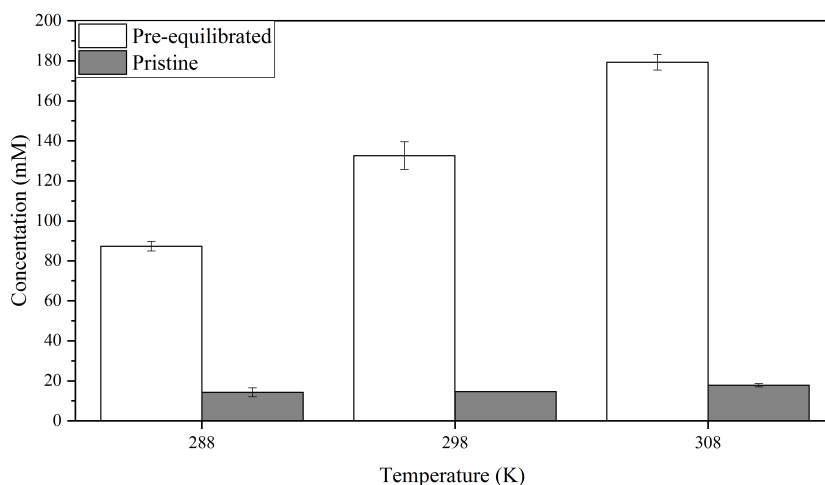


Figure 5.3.2: Solubility of CyMe₄-BTBP in 70%_{vol} FS-13 and 30%_{vol} TBP. The white bars correspond to pre-equilibrated organic phase and the grey bars correspond to pristine organic phase.

The results in Figure 5.3.2 indicate that the solubility of CyMe₄-BTBP increases with increasing temperature, both for the pristine organic phase and the pre-equilibrated. The difference in CyMe₄-BTBP solubility between the pristine organic phase and the pre-equilibrated also increases with increasing temperature. This is important, as precipitation of the extracting agent and/or complexed metal would impact the safety of the process. The higher solubility of CyMe₄-BTBP in the pre-equilibrated organic phase indicates that the aqueous phase plays a significant role in the solubility by affecting the organic phase. It has previously been shown that CyMe₄-BTBP is not soluble above the detection limit in a nitric acid aqueous phase (Aneheim et al., 2011). In addition, the pre-equilibrated organic phase was analysed using a Folded Capillary cell (Malvern, DTS1070) for presence of aqueous phase in the form of micelles or micro droplets but none above the size of 1.5-2 nm could be detected.

To further investigate the impact of the aqueous phase on CyMe₄-BTBP solubility in FS-13, single samples with 70%_{vol} FS-13 and 30%_{vol} TBP were pre-equilibrated with 4 M hydrochloric acid, Milli-Q water and 4 M NaCl dissolved in Milli-Q water. These samples were used to obtain an indication of whether the increased CyMe₄-BTBP solubility is a result of nitric acid extraction as non-dissociated HNO₃, protonation of the organic phase, or another phenomenon. The samples

containing HCl, NaCl and Milli-Q water reached a CyMe₄-BTBP solubility of 30, 20 and 15 mM, respectively. These results, which compared to the CyMe₄-BTBP solubility of 130 mM using HNO₃, are in the same order of magnitude. This indicates that it is the nitrate or extraction of non-dissociated nitric acid rather than the acidity or protonation that is crucial for the increased CyMe₄-BTBP solubility.

The natural logarithm of the solubility constant, Equation (3.4.6) on page 20, was plotted at different temperatures against 1/T, Figure 5.3.3. The solubility constant of CyMe₄-BTBP increases in both the pristine and pre-equilibrated system with increasing temperature, indicating that the solubility reaction is endothermic.

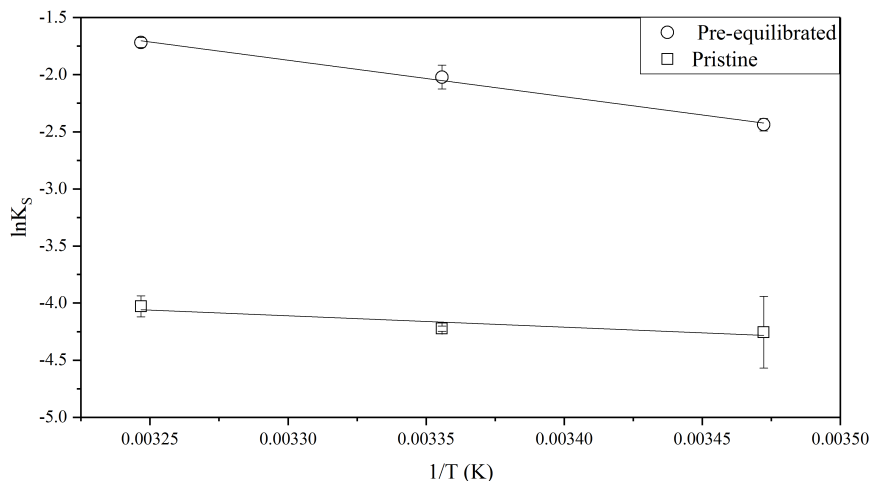


Figure 5.3.3: The dependence of the natural logarithm of the CyMe₄-BTBP solubility constant in 70%_{vol} FS-13 and 30%_{vol} TBP pre-equilibrated with 4 M nitric acid or pristine organic phase, plotted versus 1/T.

By performing a linear regression on the data points in Figure 5.3.3, according to the Van 't Hoff Equation (Equation (3.4.6) on page 20), the enthalpy and the entropy for the solubility in the two systems can be calculated, Table 5.3.2. The change in enthalpy is positive for both systems, indicating an endothermic process during the dissolution, i.e. the systems consume energy from the outer environment. Previous studies on dissolution of BTBP-type molecules in other solvents also show endothermic processes (Ekberg et al., 2010). Both the enthalpy and the entropy increase in the FS-13-based solvent with acid pre-equilibration while only the enthalpy is positive in the pristine system. The negative entropy in the pristine

system indicates either a small or no change in the status quo of the system, i.e. the molecular order of the system is decreasing.

Table 5.3.2: Enthalpy and entropy for CyMe₄-BTBP solubility using 70%_{vol} FS-13 and 30%_{vol} TBP pre-equilibrated with 4 M nitric acid or pristine organic phase.

<i>Solution</i>	ΔH^0 [kJ/mol]	ΔS^0 [J/mol K]
<i>FS-13/TBP, pre-equilibrated</i>	26.6 ± 0.3	72.1 ± 0.2
<i>FS-13/TBP, pristine</i>	8.3 ± 0.6	-6.9 ± 0.4

5.4 SOLVENT OPTIMISATION

Due to the increased minor actinide extraction found when combining CyMe₄-BTBP and TBP (presented in Section 5.1.2, Extraction Behaviour of the Extracting Agents), studies investigating the effect of solvent composition on the actinide extraction and actinide/lanthanide separation properties were conducted. The extraction experiments were performed according to 4.1, Basic Solvent Extraction, using trace amounts of the investigated metals described in Section 4.1.1, Actinide Partitioning. All experiments were analysed according to Section 4.5, Analysis.

The effect on metal extraction when varying the concentration of CyMe₄-BTBP between 10 and 100 mM in a solvent consisting of 70%_{vol} FS-13 and 30%_{vol} TBP was investigated, Figure 5.4.1. For americium it was found that the distribution ratios increased up to a concentration of 35 mM CyMe₄-BTBP, after which the extraction reached a plateau, possibly caused by the high metal extraction, making it difficult to measure any difference in the distribution ratios from 35 mM CyMe₄-BTBP onwards. The extraction of plutonium seemed to reach a maximum around a CyMe₄-BTBP concentration of 50 mM. For neptunium a slight increase in distribution ratio could be observed with an increased concentration of CyMe₄-BTBP. At 35 mM CyMe₄-BTBP the distribution ratio of europium, however, was more or less the same as that of neptunium, making separation of the two elements impossible. At even higher CyMe₄-BTBP concentrations the distribution ratio of europium exceeded the distribution ratio of neptunium.

The increasing distribution ratio of europium indicates that a higher concentration of CyMe₄-BTBP is beneficial both for lanthanide and actinide extraction. There-

fore using concentrations above 35 mM CyMe₄-BTBP in the system containing 70%_{vol} FS-13 and 30%_{vol} TBP is less relevant for actinide extraction purposes, unless the extraction of lanthanides can be suppressed or extracted metals removed from the organic phase in a later process stage.

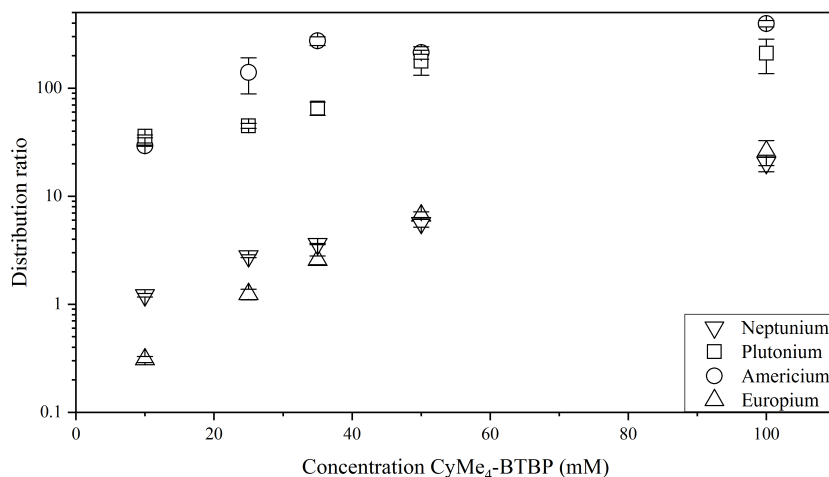


Figure 5.4.1: Distribution ratios for neptunium, plutonium, americium, curium and europium using an organic phase of 70%_{vol} FS-13, 30%_{vol} TBP and various concentration of CyMe₄-BTBP and 4 M HNO₃ as aqueous phase.

Due to the possibility to increase the actinide extraction with an increasing CyMe₄-BTBP concentration, Figure 5.4.1, a study using various amounts of TBP (10, 20 and 30%_{vol}) in FS-13 and 25 mM CyMe₄-BTBP was performed. This was done to investigate TBP's effect on the metal extraction. The extraction kinetics of plutonium seem to be only slightly affected by varying the TBP concentration within the investigated interval, Figure 5.4.2A. The extraction of americium, however, seems to become slower with a lower TBP concentration, Figure 5.4.2B. All three systems display high equilibrium distribution ratios for americium, indicating that the chosen TBP concentration mainly affects the time to reach extraction equilibrium. The equilibrium distribution ratio of europium, Figure 5.4.2C, decreases slightly with a lower TBP concentration. In contrast to what could be observed for americium, however, the time to reach extraction equilibrium does not seem to be affected, Figure 5.4.2C. A similar difference in the extraction kinetics between americium and europium was previously observed in this work, Figure 5.1.1 and Figure 5.1.4. This indicates that the extraction of the trivalent actinides and trivalent lanthanides are affected differently by the changes in the organic phase.

This could possibly be caused by the fact that europium is extracted by TBP to a greater extent compared to CyMe₄-BTBP, which could also be seen in Figure 5.1.3. TBP is known to extract lanthanides under certain conditions (Cox, 2004), but not e.g. in the previously discussed PUREX process (Anderson et al., 1960). Slope analysis on the complexation between europium and TBP indicates a 1:1 relation (0.85 ± 0.15), while no distinct complexation can be seen between americium and TBP (0.39 ± 0.08).

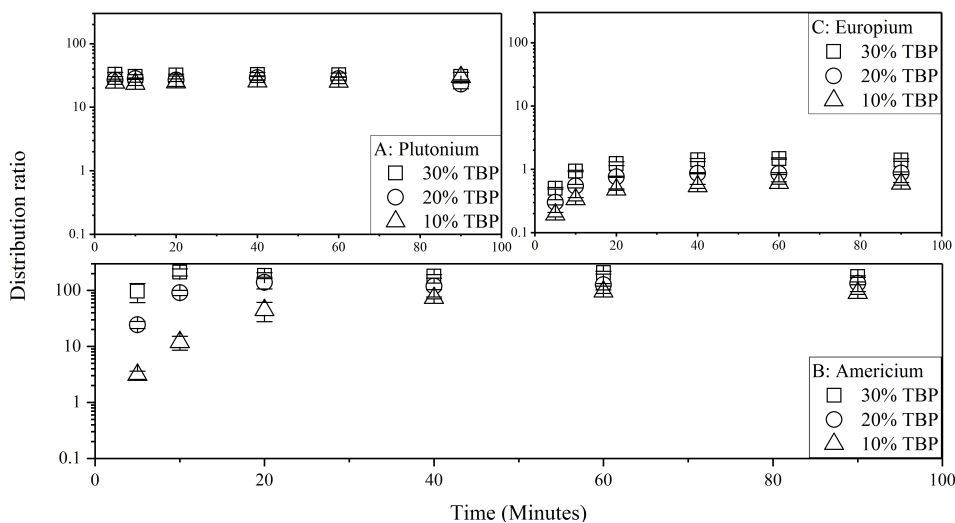


Figure 5.4.2: Distribution ratios for A: plutonium, B: americium and C: europium using 25 mM CyMe₄-BTBP, various amounts of TBP and corresponding amounts of FS-13 as organic phase and 4 M HNO₃ as aqueous phase, varying the contacting time.

5.5 PLUTONIUM LOADING

Investigating different compositions of the organic phase makes it possible to optimize the extraction properties of the system depending on e.g. metal composition of the used nuclear fuel (Paper V and Paper VII). Studies using 10, 20 and 40 g plutonium/L with a high americium content, Table 5.5.1, in 4 M HNO₃ and solvent systems consisting of 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM or 50 mM CyMe₄-BTBP were performed in order to evaluate how efficiently the systems perform under metal loading conditions. Experimental conditions are further described in Section 4.4, Plutonium Loading and analysis was according to Section 4.5, Analysis.

Table 5.5.1: Concentrations of the metals and ligands used during the plutonium loading experiments. 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM or 50 mM CyMe₄-BTBP was used as organic phase and 4 M HNO₃ as aqueous phase.

<i>Metal/Ligand</i>	<i>10 g Pu/L</i>	<i>20 g Pu/L</i>	<i>40 g Pu/L</i>
<i>Plutonium</i>	40 mM	80 mM	160 mM
<i>Americium</i>	0.6 mM	1.2 mM	2.4 mM
<i>Europium</i>	1.6 mM	3.3 mM	6.6 mM
<i>TBP</i>	1 M	1 M	1 M
<i>CyMe₄-BTBP</i>	25 mM/50 mM	25 mM/50 mM	25 mM/50 mM

In the study using a 10 g plutonium/L aqueous phase and the solvent systems consisting of 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM CyMe₄-BTBP, Figure 5.5.1A, or 50 mM CyMe₄-BTBP, Figure 5.5.1B, similar trends in extraction could be observed for both systems. It was found that high distribution ratios for both plutonium and americium could be obtained, while maintaining a relatively low distribution ratio for europium.

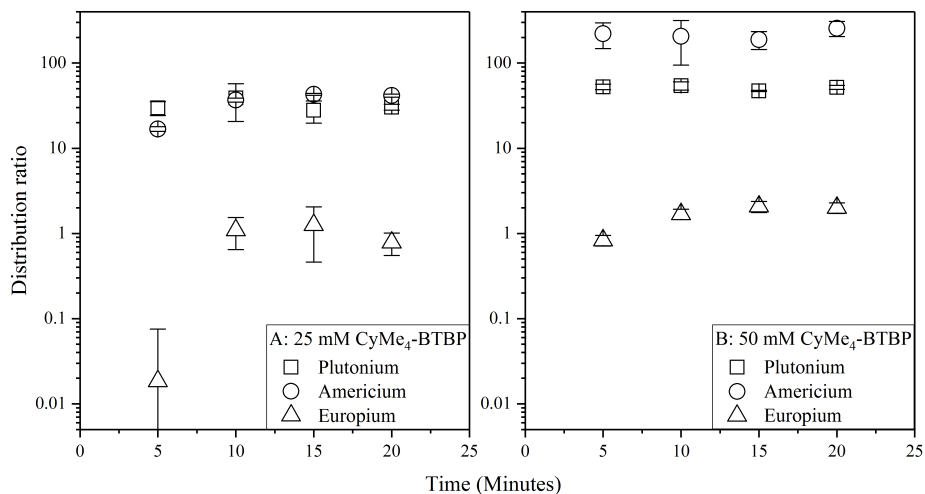


Figure 5.5.1: Distribution ratios for plutonium, americium and europium during plutonium loading (10 g Pu/L, 4M HNO₃) using 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM (A) or 50 mM CyMe₄-BTBP (B) as organic phase, varying the phase contacting time. The samples were phase contacted using shaking by hand in an insulated container.

In the study using a 20 g plutonium/L aqueous phase and the solvent systems consisting of 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM CyMe₄-BTBP, Figure 5.5.2A, or 50 mM CyMe₄-BTBP, Figure 5.5.2B, the equilibrium distribution ratios for plutonium and americium are still high. However, it takes longer for americium to reach extraction equilibrium, compared to the lower plutonium concentration. Extraction kinetics in the system containing 50 mM CyMe₄-BTBP, however, are faster compared to the system using 25 mM CyMe₄-BTBP at similar metal loading conditions. Comparing the extraction kinetics of americium in Figure 5.1.1 and Figure 5.4.2B it is evident also in this case that the extraction is faster in the system with a higher CyMe₄-BTBP concentration. Both these results indicate that CyMe₄-BTBP is surface active in the FS-13-based GANEX solvent, affecting the extraction kinetics of americium.

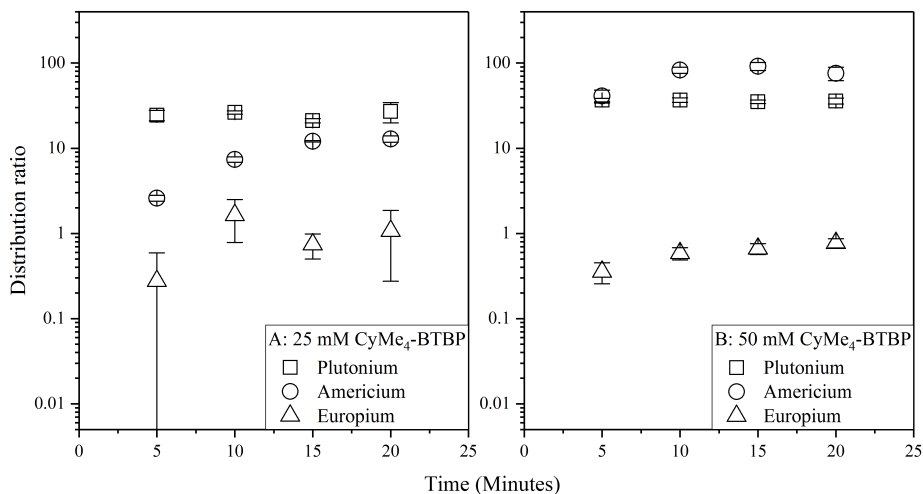


Figure 5.5.2: Distribution ratios for plutonium, americium and europium during plutonium loading (20 g Pu/L, 4M HNO₃) using 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM (A) or 50 mM CyMe₄-BTBP (B) as organic phase, varying the phase contacting time. The samples were phase contacted using shaking by hand in an insulated container.

In the study using a 40 g plutonium/L aqueous phase and the solvent systems consisting of 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM CyMe₄-BTBP, Figure 5.5.3A, or 50 mM CyMe₄-BTBP, Figure 5.5.3B, a high equilibrium distribution ratio can still be obtained for plutonium. The distribution ratio for americium, however, is low even after 20 minutes of phase contacting and extraction equilibrium was not reached during the duration of the experiment. In the solvent system containing 50 mM CyMe₄-BTBP, Figure 5.5.3B, a separation of americium from europium could still be observed, as the europium distribution ratio also is significantly decreased. In general, the europium extraction is less affected than the americium extraction by the plutonium loading, making separation between americium and europium in the 25 mM CyMe₄-BTBP and 40 g plutonium/L system more difficult, Figure 5.5.3A. This is most likely due to the previously discussed extraction of europium by TBP.

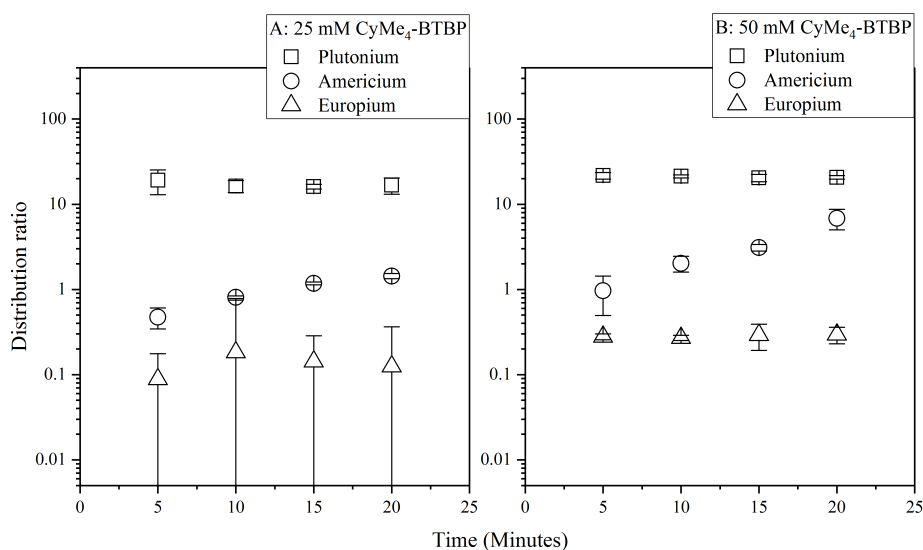


Figure 5.5.3: Distribution ratios for plutonium, americium and europium during plutonium loading (40 g Pu/L, 4M HNO₃) using 70%_{vol} FS-13, 30%_{vol} TBP and either 25 mM (A) or 50 mM CyMe₄-BTBP (B) as organic phase, varying the phase contacting time. The samples were phase contacted using shaking by hand in an insulated container.

According to Table 5.5.1, plutonium is in deficit compared to TBP in all loading experiments. In the 40 g plutonium/L experiment (160 mM), the TBP excess, however, is only around six times higher. This could be proven to be insufficient if recycling a fuel where uranium is also present. Considering only americium, the CyMe₄-BTBP concentration is in large excess for all samples except in the 40 g plutonium/L and 25 mM CyMe₄-BTBP samples. Since CyMe₄-BTBP and americium creates a 2:1 complex in FS-13, the CyMe₄-BTBP concentration is only five times higher than the americium concentration in this case. CyMe₄-BTBP in FS-13 has previously been shown to also extract plutonium in a 1:1 complex, Section 5.1.2, Extraction Behaviour of the Extracting Agents. As americium is still efficiently extracted in several of the systems where CyMe₄-BTBP is in deficit compared to both plutonium and americium combined, this indicates that americium complexation is preferred before plutonium complexation. The extraction of europium stays low in all cases, even if europium is present in higher concentrations than americium. A general observation is that extraction of all metals decreases with an increasing plutonium concentration in the aqueous phase.

For both 10 and 20 g plutonium/L loading a CyMe₄-BTBP concentration of 25 mM is sufficient to achieve > 99.9% extraction of both americium and plutonium in

three extraction steps (Equation (3.2.2) on page 18). If using 50 mM CyMe₄-BTBP the same results can be achieved in only two extraction steps. The extraction of europium in that case however becomes over 57%. For 40 g plutonium/L loading using 50 mM CyMe₄-BTBP > 99.9% extraction of americium and plutonium can be reached in four steps, while still maintaining a low europium extraction, assuming that the 20 minutes distribution ratio of americium is at equilibrium. The slow extraction kinetics of americium in this case could however become problematic in a future process.

Comparing with a plutonium loading study using a lower concentration of CyMe₄-BTBP (10 mM) in 70%_{vol} FS-13 and 30%_{vol} TBP, similar trends as in the previous study can be found for both americium and plutonium (Paper VII). The distribution ratios decrease with an increasing plutonium concentration for both plutonium and americium. However, it is not certain if the americium extraction reached equilibrium in this study as only one time point (20 minutes hand contacting) was evaluated. When comparing to the cyclohexanone-based GANEX solvent the performance of the FS-13-based GANEX solvent is more consistent during plutonium loading (Paper VII).

Table 5.5.2: Distribution ratios during plutonium-loading using 70%_{vol} FS-13, 30%_{vol} TBP and 10 mM CyMe₄-BTBP as organic phase and 4 M HNO₃ as aqueous phase. The samples have been contacted by hand for 20 minutes. The 40 g Pu/L samples are single samples.

<i>Metal</i>	<i>1 g Pu/L</i>	<i>10 g Pu/L</i>	<i>40 g Pu/L</i>
<i>Plutonium</i>	28 ± 0.08	19 ± 0.08	8.0
<i>Americium</i>	14 ± 0.07	3.0 ± 0.03	0.24

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SUMMARY AND CONCLUSIONS

Many positive features have been found when investigating FS-13 for use as diluent in a GANEX solvent with CyMe₄-BTBP and TBP as extracting agents. Among these are the phase contact time to reach extraction equilibrium for the actinides, which is approximately 20 minutes. Americium and curium, as expected, have similar extraction kinetics, indicating that they are extracted by the same extracting agent in the system. Uranium and plutonium display faster extraction kinetics, indicating that they are not extracted by the same extracting agent as americium and curium. Extraction studies investigating various combinations of FS-13 and the two extracting agents together with TRLFS studies and slope analysis have been done in order to confirm which of the two ligands extracts the separate actinides. Neptunium is extracted by both ligands separately in FS-13 and is found to form a 1:1 complex with CyMe₄-BTBP, just like plutonium, although plutonium is predominately extracted by TBP. CyMe₄-BTBP forms 2:1 complexes with americium and curium in FS-13, as expected. However, the presence of TBP in the solvent was found to be essential for achieving both fast extraction kinetics and high distribution ratios for the trivalent actinides. Using the FS-13-based GANEX solvent, high separation factors can be achieved between the actinides and europium in all cases except for neptunium. The low equilibrium distribution ratio for neptunium and low separation factor between neptunium and europium might cause problems separating neptunium from the lanthanides in a future process. Increasing the CyMe₄-BTBP concentration as expected was found to favour europium extraction and does not resolve this issue. Further studies investigating the neptunium extraction would hence be of interest for evaluating appropriateness as a GANEX solvent.

The extraction of selected fission products in the system is low, with a distribution ratio below one for most metals, allowing for separation from the actinides. A few elements (silver, cadmium and zirconium), could however cause problems in a future process and require further investigations.

In addition it has been shown to be possible to back-extract plutonium and americium with a metal recovery above 99% from the FS-13-based GANEX solvent in

two steps using glycolic acid at pH 4. Introduction of an acid scrub before back-extraction was investigated for removal of extracted unwanted fission products, as well as enhancement of the back-extraction of americium. The extracted europium content in the organic phase could be reduced from 20% to 10% but the losses of uranium, plutonium and americium during the scrubbing are too large to motivate the use of scrubbing.

By pre-equilibrating the FS-13-based GANEX solvent with nitric acid, an increase in CyMe₄-BTBP solubility up to 180 mM was observed. The FS-13-based GANEX solvent, both pre-equilibrated with nitric acid and pristine, are endothermic systems where the solubility of the CyMe₄-BTBP increases with increasing temperature of the surroundings. These features are beneficial as a solvent extraction process aimed at recycling of used nuclear fuel will take place in a highly acidic environment and also under elevated temperatures due to the inherent radiation of the used fuel. An opposite scenario, where solubility decreases with an increased temperature, could cause precipitation of the extracting agent and/or complexed metal, which would severely impact the safety of the process. Temperature-dependent experiments investigating americium and europium extraction in the FS-13-based GANEX system show a slight decrease in distribution ratio with an increase in temperature. Enthalpy and entropy calculations hence show an exothermal system.

The system has shown a good stability against radiation and hydrolysis in terms of maintained extraction performance. With higher doses, over 100 kGy, CyMe₄-BTBP was found to be completely hydrolysed. This does not, however, seem to affect the extraction of the actinides.

The possibility to use a higher CyMe₄-BTBP concentration opens up for the option to tune the solvent depending on the composition of the used fuel in need of recycling. Solvent optimization studies show that when using trace amounts of actinides, 50 mM CyMe₄-BTBP or more in the FS-13-based GANEX solvent will mainly benefit the extraction of lanthanides. Varying the concentration of TBP on the other hand mainly affects the time it takes for the system to reach extraction equilibrium. When performing investigations of solvent performance under plutonium loading conditions, including a high americium content, the preferred solvent composition was found to depend on the level of loading. The FS-13-based GANEX solvent with either 25 mM or 50 mM CyMe₄-BTBP was studied during plutonium loading of 10, 20 and 40 g plutonium/L. Comparing the two solvent systems for the same plutonium concentration it can be seen that both plutonium and

europium extraction is independent of CyMe₄-BTBP concentration. Extraction of americium, however, increases with a higher CyMe₄-BTBP concentration, both for 10 and 20 g plutonium/L loading. Upon 40 g/L plutonium loading an increase in extraction kinetics of americium can be observed for the solvent containing 50 mM CyMe₄-BTBP compared to 25 mM. The extraction of all investigated metals with the FS-13-based GANEX solvents decreases with an increase in plutonium loading.

When comparing the FS-13-based GANEX solvent with previously investigated GANEX systems using cyclohexanone or hexanol as diluent, both similarities and differences have been found. All three systems reach extraction equilibrium after roughly the same time and distribution ratios are in the same order of magnitude. The FS-13-based GANEX system has been found to resist radiolysis and hydrolysis to a greater extent than the hexanol- and cyclohexanone-based GANEX systems. A slight decrease in americium and europium extraction was found with increased temperature in all three GANEX systems. Likewise, enthalpy and entropy calculations show that all three GANEX solvents are exothermal systems. To conclude, FS-13 has been found to be a promising diluent for use in a GANEX solvent. However, further studies are needed to fully understand the FS-13-based GANEX system.

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FUTURE WORK

Future work on the FS-13-based GANEX solvent will involve both complementary and further investigations of the system.

The extraction of neptunium should be further studied, trying to increase the extraction as well as investigating the behaviour during plutonium loading. Optimisation of the organic phase in terms of CyMe₄-BTBP and TBP concentrations should be continued and for promising compositions the metal extraction of both actinides and fission products should be investigated. The extraction of some fission products, in particular silver and cadmium, is high and should be addressed in order to ensure that recycling of the solvent is feasible. Possible solutions could be to use suppressing agents and/or introduce dedicated scrubbing steps.

In addition to extraction experiments, degradation of the organic phase and subsequent detection of degradation products should be investigated in more detail. This is important for the safety assessment of the process and to be better able to establish the lifetime of the organic phase. Due to the good plutonium loading performance and high separation factor between uranium and the lanthanides, a uranium loading study would also be of interest in order to investigate the possibility of replacing the proposed two GANEX cycles with one. Over a longer time perspective, process development of the system needs to include both hot tests and enlarged scale and pilot scale tests. Recycling of the FS-13 GANEX solvent also has to be investigated due to the presence of sulphur, fluoride and phosphor. Before scale-up, computer modelling would also be useful for predicting the behaviour of the system and to be able to do this properly further investigations on the complex extraction behaviour of the system will be necessary.

If, considering to develop an entirely new GANEX solvent, designing a system that follows the CHON principle would be desirable. This could include e.g. exchanging TBP with DEHBA.

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A

FISSION PRODUCTS

Inactive metals used during the fission product extraction. The used concentrations are typical PUREX feed contents of the elements, stated in Table A.1. The data is revised from Europart, the 6th European framework program. The charter assessing the extraction properties of newly synthesized ligands within Europart.

Table A.1: Inactive metals used to simulate fission product extraction based on the feed compositions from a PUREX processes (UOX2 type spent fuel irradiated at 45 GWd/t after 4 years of cooling)

<i>Compound</i>	<i>Supplier</i>	<i>Purity</i>	<i>PUREX feed [mg/L]</i>
Sr(NO ₃) ₂	Sigma-Aldrich	≥ 99.0%	280
Y(NO ₃) ₃ × 4 H ₂ O	Fluka	> 99%	155
ZrO ₂	Aldrich	> 99%	1 245
MoO ₃	Aldrich	> 99%	1 185
Pd(NO ₃) ₂ × 2 H ₂ O	Fluka	Purum > 97%	520
AgNO ₃	May & Baker	Pro analysi > 99.9%	30
Cd(NO ₃) ₂ × 4 H ₂ O	Sigma-Aldrich	Puriss p.a ≥ 99.0%	35
SnO ₂	Riedel-deHaën	> 99%	20
Sb ₂ O ₃	Aldrich	> 99%	5
TeO ₂	Aldrich	> 99.9%	170
CsCl	Aldrich	> 99.9995%	1 265
Ba(NO ₃) ₂	Merck	Puriss p.a ≥ 99%	595
La(NO ₃) ₃ × 6 H ₂ O	Fluka	Puriss p.a ≥ 99%	425
Ce(NO ₃) ₃ × 6 H ₂ O	Fluka	Puriss p.a ≥ 99%	830
Pr(NO ₃) ₃ × 6 H ₂ O	Aldrich	> 99.9%	390

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Table A.1 – *Continued from previous page*

<i>Compound</i>	<i>Supplier</i>	<i>Purity</i>	<i>PUREX feed</i> <i>[mg/L]</i>
$\text{Nd}(\text{NO}_3)_3 \times 6 \text{H}_2\text{O}$	Aldrich	> 99.9%	1 420
$\text{Sm}(\text{NO}_3)_3 \times 6 \text{H}_2\text{O}$	Aldrich	> 99.9%	280
$\text{Eu}(\text{NO}_3)_3 \times 5 \text{H}_2\text{O}$	Aldrich	> 99.9%	55