Thesis for the degree of Licentiate of Engineering

Phenyl Trifluoromethyl Sulfone as Diluent in a Grouped ActiNide EXtraction Process

Jenny Halleröd

Nuclear Chemistry
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
Gothenburg, Sweden 2015

Phenyl Trifluoromethyl Sulfone as Diluent
in a Grouped ActiNide EXtraction Process
Jenny Halleröd

Licuppsatser vid Institutionen för kemi och kemiteknik. 2015:12
ISSN: 1652-943X

Nuclear Chemistry
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone: +46 (0)31-7721000

Cover: Molecular structure of phenyl trifluoromethyl sulfone.
Thanks to Rikard Ylmén for help with the drawing.

Chalmers Reproservice
Gothenburg, Sweden 2015

LIST OF PUBLICATIONS

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

I. 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.

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 CyMe$_4$-BTBP. *Journal of Radioanalytical and Nuclear Chemistry*, DOI: 10.1007/s10967-015-4416-7.

III. Halleröd, J., Ekberg, C., Löfström-Engdahl, E., and Aneheim, E.: Development of the Chalmers Grouped Actinide Extraction Process. *Nukleonika*, DOI: 10.1515/nuka-2015-0115.

Contribution report

I, II & III — Main author of the paper and all the experimental work.

PHENYL TRIFLUOROMETHYL SULFONE AS DILUENT IN A GROUPED ACTINIDE EXTRACTION PROCESS

JENNY HALLERÖD
DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
GOTHENBURG, SWEDEN 2015

ABSTRACT

The demand for electricity and electrical energy is very high both in Sweden and in the other industrialised countries in the world. An upgrade of the nuclear power plants, including recycling of the used nuclear fuel, would make nuclear power a sustainable energy option. Over the years different types of nuclear reactors have been developed. Current research focuses on the concept of generation IV systems. The generation IV concept is based on a closed nuclear fuel cycle including both a reactor and a used nuclear fuel recycling process. Recycling of the used nuclear fuel would increase the energy utilization of the uranium and make the final repositories significantly more sustainable, with regard both to capacity and storage time. 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 extracting all the present actinides together as a group by combining two extracting agents and a diluent into one single solvent.

In this work, a GANEX solvent based on the diluent phenyl trifluoromethyl sulfone (FS-13) containing the extraction agents CyMe$_4$-BTBP and tri-butyl phosphate (TBP) has been investigated. Initial studies have shown that a FS-13-based solvent is promising, with good actinide extraction, relatively fast kinetics and a high stability against both hydrolysis and radiolysis. The two extraction agents seem to behave synergistically in the FS-13 GANEX system. This has to be further investigated for process development, and possible process optimisations can be made. The thermodynamic data shows an exothermic reaction with a slight decrease of the americium and europium extraction with an increasing temperature. The last step of the GANEX process is actinide stripping. Stripping seems feasible from the FS-13-based GANEX solvent, but this has to be further investigated, together with possible acid-scrubbing steps.

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

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

ACSEPT	Actinides reCycling by SEParation and Transmutation (European project within the 7^{th} Framework Programme)
BTBP	Bis-triazine bi-pyridine
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
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
SACSESS	Safety on ACtinide SEparation proceSSes (European project within the 7^{th} Framework Programme)
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

”For, usually and fitly, the presence of an introduction is held to imply that there is something of consequence and importance to be introduced.” – Arthur Machen

Sweden together with the other industrialised countries in the world have a high demand for electricity and electrical energy. The demand for electricity increases every day. Both industrialisation and a globally increasing population raises the amount of electric energy required (Brundtland, 1987; Bradshaw, 2010). To fulfil this energy demand several different production methods can be applied. One of these is nuclear power. A number of analyses indicate that an upgrade of the nuclear power plants, enabling a larger utilization of the present energy, could be a promising energy alternative to fossil fuel during the development of other environmentally and societally accepted sustainable energy routes (Sailor et al., 2000; Bruggink and van der Zwaan, 2002; van der Zwaan, 2013). Many people have concerns about nuclear power today. Among these concerns are the risk for accidents during operation, the long-lived radiotoxic waste and the poor utilization of the inherent energy in the fuel. From a radiotoxic point of view the used nuclear fuels have to be stored for more than 100,000 years before reaching the same level as the natural uranium needed to produce one tonne of enriched fuel. In the case of the energy utilization only about 1% of the energy contained in the fuel is used (Choppin et al., 2013a). This leaves a large amount of used nuclear fuel that has to be managed.

Over the years different types of nuclear reactors have been developed. A common way of chronological sorting nuclear reactors and nuclear reactor engineering is by the concept of reactor generations.

Generation I are the early reactor prototypes, mainly designed in the 1950s. The power level in these reactors is low and they were mainly developed as a ”proof of principle” (Choppin et al., 2013b).

Generation II are commercial reactors designed to be both reliable and economical and these were mainly designed in the 1960s. This generation, for example, includes the boiling water reactors and pressurized water reactors. The used fuel can either be aimed at direct disposal 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 (Choppin et al., 2013b). The reprocessed plutonium and uranium can be used for the production of new fuel, called Mixed OXide (MOX) fuel (Choppin et al., 2013a). MOX fuel reduces the need for uranium mining and enrichment services by about 30% (Choppin et al., 2013a). The utilisation of the energy in the uranium is only increased by 0.2%, however, giving a total amount of around 1.2% (Choppin et al., 2013a).

Generation III are essentially further developed generation II reactors with improved thermal efficiency, fuel technology and safety systems among other features. Reactors within this generation, for example, are the advanced boiling water reactor (Choppin et al., 2013b).

Generation III+ reactors basically use the same concept as previously but with further developments, mainly with respect to passive safety (Choppin et al., 2013b).

Generation IV systems are still at the research stage and are rather undefined. Generation IV, however, is based on the concept of a closed nuclear fuel cycle and not only on a reactor construction. Reprocessing of the fuel using PUREX is not suitable in generation IV systems where the requirements for proliferation resistance do not allow pure plutonium streams (Abram and Ion, 2008). Instead of a selective reprocessing process such as the PUREX process, alternative processes based on grouped extraction of all the actinides have been developed, i.e. the Grouped ActiNide EXtraction (GANEX) concept (Adnet et al., 2005). The separated actinides are then recycled for the production of new fuel.

Three different versions of the GANEX concept are under investigation within the European Union; the CEA-GANEX, the EURO-GANEX and the Chalmers GANEX (SACSESS, 2013; ACSEPT, 2013). This work has focused on the continuous development of the Chalmers GANEX process. The Chalmers GANEX process is based on the combination of two extraction ligands and one diluent. Previous versions of the GANEX process have shown promising results for nuclear fuel recycling (Aneheim, 2012; Löfström-Engdahl, 2014) but there have been problems with the diluents used. The diluents have e.g. not been stable in the chemical environment, there has been poor solubility of the extracting agents and slow kinetics. The objectives of this work has therefore been to further develop the Chalmers GANEX process. Optimisations regarding the content of the GANEX solvent have been investigated. In the current work phenyl trifluoromethyl sulfone (FS-13) has been used as diluent due to promising results in the UNiversal EXtraction (UNEX) process.

2

BACKGROUND

"In the animal kingdom, one of the keys to survival is to outwit your enemies. And when you're surrounded by carnivores, one of the best strategies is to fade into the background and disappear." – Neil deGrasse Tyson

2.1 NUCLEAR ENERGY

Nuclear power today is mainly organized through the Nuclear Energy Agency (NEA). Its member countries account for approximately 86% of the world's installed nuclear capacity. In the Organisation for Economic Co-operation and Development (OECD) area, nuclear energy represents almost 18.6% of the electricity supply. In some countries even more nuclear energy is used; in Sweden 42.6% of the electrical energy comes from nuclear power plants, in France 73.3% and in Switzerland 36.3% (OECD-NEA, 2014a). An overview of nuclear energy production in the OECD countries is displayed in Table 2.1.1.

Table 2.1.1: Facts and figures concerning nuclear energy production in OECD countries in 2013 (OECD-NEA, 2014a). * Provisional data.

Country	*Number of nuclear reactors connected to the grid*	*Nuclear electricity generation (net TWh) 2013*	*Nuclear percentage of total electricity supply*
Sweden	10	63.6 *	42.6
OECD Europe	133	833.1	23.7
OECD America	121	897.4	18.0
OECD Pacific	71	152.7	9.5

2.2 USED NUCLEAR FUEL

All nuclear reactors create used nuclear fuel. This fuel is highly 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, Figure 2.2.1, (Madic et al., 2004). 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 can then be transformed into other nuclides that are more short-lived, or even stable, 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., 2013a).

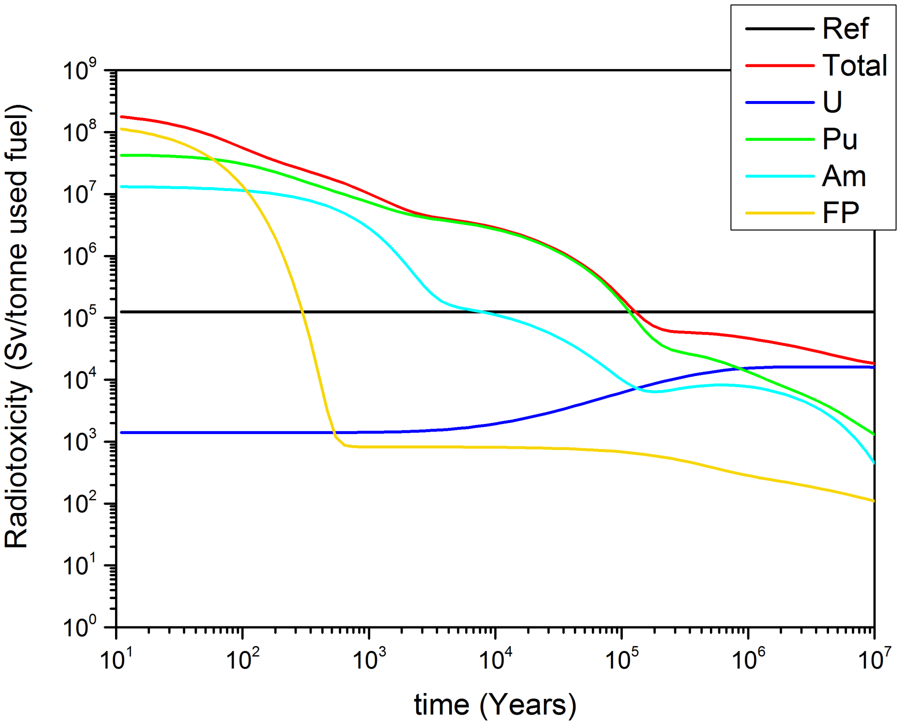

Figure 2.2.1: Radiotoxicity of used nuclear fuel (UO_X fuel, 4% enrichment, burnup 45 Gw and 10 years cooling time) as a function of time. The reference is the amount of natural uranium needed to produce 1 tonne of enriched fuel. The radiotoxicity is calculated using the International Commission on Radiological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

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

$$^{235}U \ + \ n \ \rightarrow \ FP \ + \ xn \tag{2.2.1}$$

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

2.2.1 *The Once-Through Cycle*

In the once-through cycle the nuclear fuel is used one time in a nuclear reactor before it is placed in the interim storage. In this interim storage the used nuclear fuel is stored in temporary steel-lined, concrete pools filled with water, which act as a natural barrier for radiation (NEI, 2015; IAEA, 2011). After some time, e.g. 30 years, in the interim storage the used nuclear fuel will be placed in the final repository. In the deep geological final repository the used nuclear fuel is stored underground in the bedrock, secured by several different barriers, Figure 2.2.2 (SKB, 2006). In Sweden, the Swedish Nuclear Fuel and Waste Management Company (SKB) has submitted an application to the Swedish Radiation Safety Authority (SSM) for building the final repository (SSM, 2015).

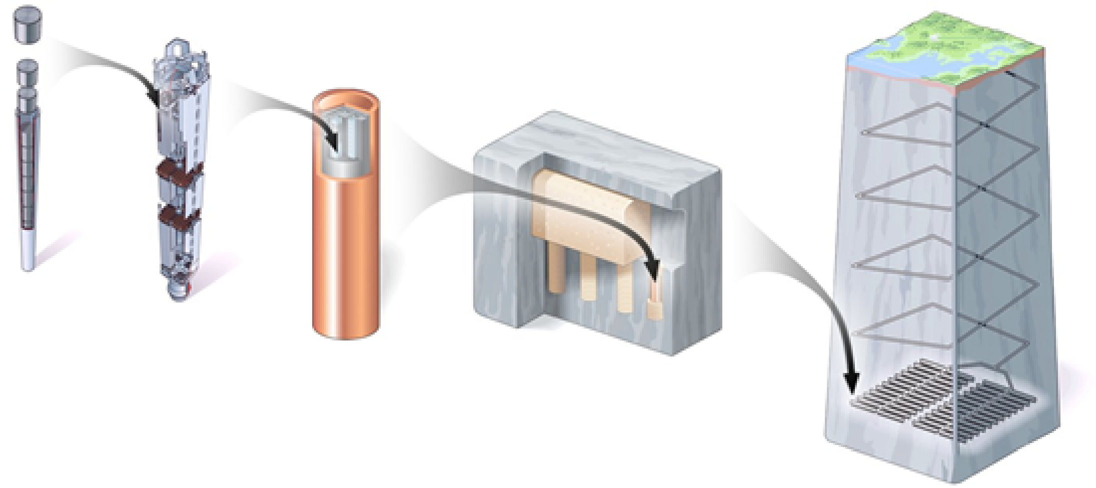

Figure 2.2.2: Schematic figure of the final repository for used nuclear fuel. From left to right: fuel pellets in a cladding tube, fuel bundle, copper canister with a cast iron insert, bore hole with bentonite clay, and an underground area (SKB, 2006).

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, is still present in the used nuclear fuel when the fuel will be sent for final storage (Choppin et al., 2013a)

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 enhanced (Choppin et al., 2013a). 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 fuel, i.e. MOX fuel (Choppin et al., 2013a). The use of MOX fuels increases the utilisation of energy from uranium (Ritcey, 2004) and MOX fuels are today 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 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). The plutonium is recovered by reduction, this reduction utilises the plutonium and uranium to be selectively separated from the rest of the used nuclear fuel (Thomas and Spring, 1958).

However, 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 once-through cycle and the storage time in a final repository is not significantly changed.

2.2.3 *Recycling*

The recycling concept follows the reprocessing concept, but instead of only separating uranium and plutonium all of the long-lived actinides are separated from the lantanides and the fission and corrosion/activation products to make new fuel. By doing this the long-term radiotoxicity of the waste is decreased (Salvatores et al., 1998) (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). The lanthanides and the fission and corrosion/activation products are short-lived elements and some of these have high neutron capture cross sections. Elements with high neutron capture cross section absorb the available neutrons. Without lanthanides and the fission and corrosion/activation products present, these neutrons have the potential to transmute the actinides recovered from the used nuclear fuel. Simultaneously the energy utilization is increased (Aoki, 2002; Choppin et al., 2013a; Bond and Leuze, 1976; Madic et al., 2000). However, the chemical similarities between the actinides 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 for the generation IV systems to reach during development; they should be highly economic, have enhanced safety, produce minimal waste and be proliferation resistant (Abram and Ion, 2008; OECD-NEA, 2014b). 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 for 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 pyro processing, are currently in the research stage and 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 that is eutectic in the presence of HF (Choppin et al., 2013a). Another dry route is the Molten salt extraction. Similar to Halide volatility, this is also based on an eutectic salt melt. With a heat resistant solvent of low volatility, the actinides and fission products can then distribute themselves between the two phases (Choppin et al., 2013a).

The wet routes, also called liquid-liquid extraction, are based on the separation of elements through their specific capacities to form organic soluble complexes. In the area of liquid-liquid extraction several different processes have been developed.

Several of the recycling processes developed have been based on the combined partitioning of minor actinides and lanthanides from the fission and corrosion/activation products remaining in the aqueous phase after the PUREX process. This kind of raffinate treatment process, called double strata, requires a second extraction step where the actinides and lanthanides are separated from each other. Separation processes following this concept are e.g. the American Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) process developed in the 1960s (Weaver and Kappelmann, 1964) or the DIAMide EXtraction (DIAMEX)/Selective ActiNide EXtraction (SANEX) process (Hill et al., 2007; Courson et al., 2000; Madic et al., 2004; Magnusson et al., 2009a) developed since the early 1990s within several European

Union framework programmes.

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 compliable with the generation IV concept. Three different GANEX processes are under investigation within the European Union.

2.3.1 *CEA Grouped ActiNide EXtraction Process*

The CEA-GANEX process was developed in France and is based on an adaptation of the DIAMEX/SANEX process combining N,N'-(dimethyl)-N,N'-dioctylhexylethoxy-malonamide (DMDOHEMA) and di(2-ethylhexyl)phosphoric acid (H-DEHP) (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 stripping. The process has been proven successful regarding both the extraction and stripping of neptunium, plutonium, americium and curium together as a group, with high separation factors towards lanthanides (cerium and europium). Both the EURO-GANEX process and the Chalmers GANEX process follow the concept of combining two different extractants, just like the CEA-GANEX.

2.3.2 *EURO Grouped ActiNide EXtraction Process*

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 stripping. For the EURO-GANEX process the following combination of extractants 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. Difficulties have however been found separating some of the lanthanides from the actinides during the stripping steps (Carrott et al., 2014, 2015).

2.3.3 *Chalmers Grouped ActiNide EXtraction Process*

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 from the lanthanides and the rest of the waste 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; Löfström-Engdahl et al., 2013a) and hydrolytic and radiolytic stability (Aneheim et al., 2011).

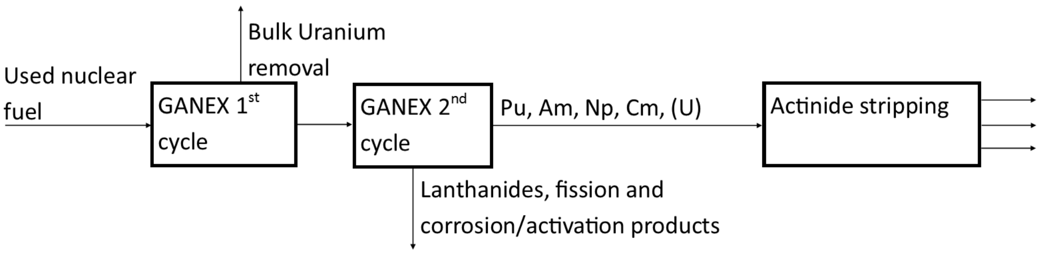

Figure 2.3.1: Schematic figure of the GANEX process.

2.4 CHALMERS GANEX SOLVENT COMPOSITION

The Chalmers GANEX concept is based on the principle of combining two well-known extractants with a diluent, enabling utilization of their different properties. There are several different extracting agents that can be used in a GANEX process. Currently the ligands mainly selected are 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine (CyMe$_4$-BTBP) (Figure 2.4.1), and tri-butyl phosphate (TBP) (Figure 2.4.2), combined into a single solvent. By combining TBP with a BTBP ligand, a system extracting most valence states of the actinides present in the used nuclear fuel can be created. With a system extracting all present valence states of the actinides, redox control can be avoided. In addition, the actinides can be stripped selectively or can be reused directly using homogeneous recycling (OECD-NEA, 2012; Aneheim, 2012).

Additional ligands developed for other solvent extraction processes have in some cases also been investigated for use in the Chalmers GANEX process.

2.4.1 *CyMe$_4$-BTBP*

The bis-triazine bi-pyridine-type (BTBP) ligands are polyaromatic nitrogen donor ligands that act as tetradentate ligands for metal ions. They have a common core of two aromatic pyridine rings, and two triazine rings but with different side groups (denominated R in Figure 2.4.1). Depending on the structure of the BTBP ligand the molecule properties, such as distribution ratio and time to reach extraction equilibrium, can change (Retegan et al., 2007a; Ekberg et al., 2007).

One BTBP type-ligand that has been developed and synthesised to extract trivalent actinides and separate them from the fission products, and mainly the lanthanides, is CyMe$_4$-BTBP (Figure 2.4.1) (Nilsson et al., 2006a,b; Foreman et al., 2005). CyMe$_4$-BTBP has a good resistance towards both alpha radiolysis (Magnusson et al., 2009b) and gamma radiolysis (low dose rate) (Retegan et al., 2007b). It is also stable under highly acidic conditions (Aneheim et al., 2011). These features makes it suitable for use in a GANEX solvent.

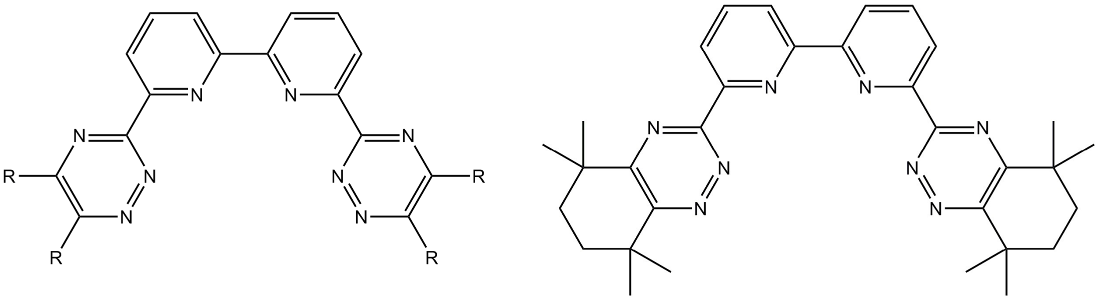

Figure 2.4.1: Molecular structure: left: BTBP-type molecules. Right:6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine (CyMe$_4$-BTBP).

CyMe$_4$-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, determine the extraction rate of the system (Geist et al., 2012).

2.4.2 *Tri-Butyl Phosphate*

In addition to CyMe$_4$-BTBP, the other main extraction agent used, TBP (Figure 2.4.2) was developed to extract tetra- and hexavalent actinides (Warf, 1949; Anderson et al., 1960).

TBP was first used for plutonium and uranium extraction during the 1950s and 1960s (Burger, 1958). TBP is a common extraction agent in the PUREX process and in later years it has become a main extractant within the Chalmers GANEX process (Aneheim et al., 2010; Löfström-Engdahl, 2014). 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). Due to this decomposition, extra purification steps may be needed for processes using TBP.

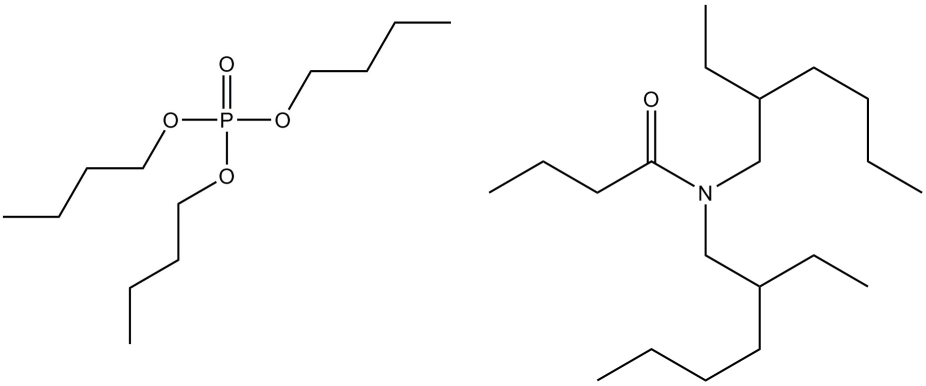

Figure 2.4.2: Molecular structures: left: tri-butyl phosphate (TPB). Right: N,N-di-2(ethylhexyl)-butyramide (DEBHA).

In addition, TBP does not follow the CHON principle (Madic and Hudson, 1998). This means that the solvent will leave a larger fraction of non-gaseous residues for waste solidification upon incineration compared to CHON solvents. The waste management of the solvent therefore has to be thoroughly investigated. An alternative to TBP could be N,N-di-2(ethylhexyl)-butyramide (DEHBA) (Figure 2.4.2). DEHBA is an amide that follows the CHON principle and decomposes into less problematic byproducts than TBP (Schulz and Navratil, 1984; Clayden et al., 2001). It has shown good extraction properties for uranium and plutonium (Nair et al., 1995; Prabhu et al., 1997)) and has also shown promise for use in GANEX processes (Aneheim et al., 2012b).

2.4.3 *Diluents*

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 extractants (Retegan et al., 2007a) and good solubility of CyMe$_4$-BTBP (Ekberg et al., 2010). Cyclohexanone is a cheap commercial chemical, mass produced for the production of nylon 6 (Okushita et al., 1995). There are some drawbacks, however, to using cyclohexanone, for example, cyclohexanone reacts exothermically in combination with concentrated nitric acid, forming adipic acid (Ambrose and Hamblet, 1951) and it 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 of the diluent.

Due to the problems with cyclohexanone, long-chained alcohols were thoroughly investigated as an alternative diluent for a Chalmers GANEX system using BTBP-type ligands, as these are cheap, easily accessible and relatively stable (Nilsson et al., 2006a; 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 increases of the distribution ratios (Löfström-Engdahl et al., 2013b). A slightly higher solubility of CyMe$_4$-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 have a low solubility of CyMe$_4$-BTBP and comparatively slow kinetics (Löfström-Engdahl, 2014). Due to this, research of other more innovative solvents for the Chalmers GANEX process has been continued.

Another potential diluent for the Chalmers GANEX process could be FS-13, illustrated in Figure 5.1.6.

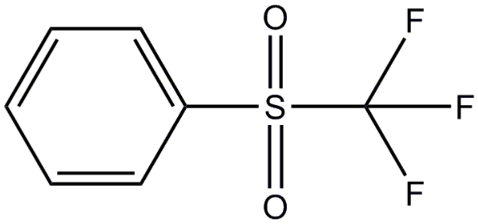

Figure 2.4.3: Molecular structure of phenyl trifluoromethyl sulfone.

FS-13 was originally developed for use in the 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 CyMe$_4$-BTBP. It also has a low viscosity and a good chemical stability, together with a high density difference compared to nitric acid (1.4 mgL^{-1} and 1.1 mgL^{-1} respectively) (Law et al., 2001; Weast, 1976). The high density of the diluent creates a GANEX system with a heavy organic phase. The heavy organic phase facilitates a system where the organic and aqueous phases can be easily separated from each other, even after metal extraction, since the density difference between the phases increases. In the case where the organic phase is lighter than the aqueous phase, density problems during the metal extraction might occur in the system.

A disadvantage with using FS-13 as a diluent is the presence of sulphur and fluoride in the molecule. Due to this, FS-13 does not follow the CHON principle. The solvent is hence not fully combustible and has to be recycled (Madic and Hudson, 1998). This is, however, also the case in all GANEX solvents containing TBP.

2.5 EXPERIMENTAL PROCEDURE FOR ASSESSMENT OF A NEW LIGAND/DILUENT

The experiments presented in this thesis follow a flowsheet to investigate extraction properties of newly synthesized ligands (Figure 2.5.1), described in *The charter assessing the extraction properties of newly synthesized ligands within EUROPART*, revised from EUROPART, the 6th European Framework Programme. This flowsheet is based on the extraction properties of ligands. The same procedure can be adapted, however, for diluent investigations.

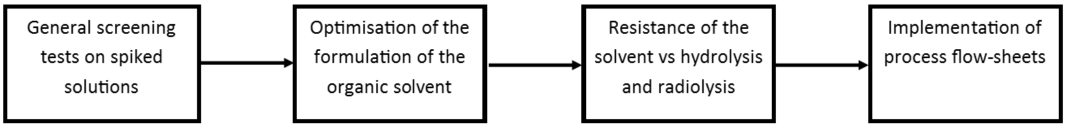

Figure 2.5.1: Flowsheet to investigate extraction properties of newly synthesized ligands. Retrieved from *The charter assessing the extraction properties of newly synthesized ligands within EUROPART*, EUROPART, the 6th European Framework Programme.

The first step aims to examine basic extraction kinetics, such as distribution ratio and back extraction. The second step is an optimisation step with the objective of proving potential industrial applications. The third step focuses on the study of the resistance towards both acidic hydrolysis and gamma-radiolysis. The fourth and last step is aimed at demonstrating the efficiency of the new solvent. Both thermodynamic and kinetic data will be required to design the process flow-sheets and to implement cold or hot tests.

3

THEORY

"It doesn't matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn't agree with experiment, it's wrong." – Richard P. Feynman

3.1 LIQUID-LIQUID EXTRACTION

A liquid-liquid extraction processes consists of two immiscible phases, here exemplified by one organic and one aqueous phase (Figure 3.1.1). Solutes, such as metals, are added to the extraction system and the process of transferring the metal from one phase to the other phase, metal extraction, is investigated (Rice et al., 1993).

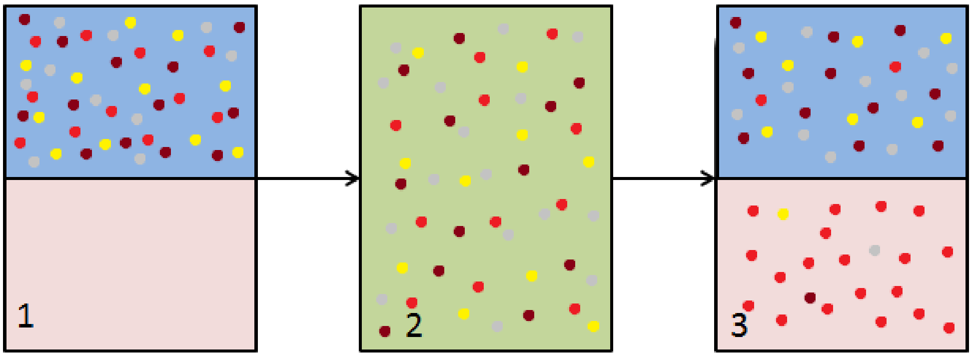

Figure 3.1.1: A schematic liquid-liquid extraction process. 1. Two immiscible phases, where the upper aqueous phase contains metals. 2. The phases are contacted to enable phase transfer of metals. 3. The phases are separated and the desired metals have been transferred to the bottom organic phase and separated from the remaining metals in the aqueous phase.

3.1.1 *Kinetics*

In a solvent extraction system, two processes can control the mass transfer rate of the solute between the phases, in other words the system kinetics. The kinetics can either be controlled by one of the chemical reactions involved in the extraction reaction (reaction controlled), or by the rate that the species diffuses through the bulk phases and the interfacial film (diffusion controlled). In the case where chemical reaction takes place at the phase boundary, both these processes are favoured by a large contact area between the two phases (Danesi, 2004).

There are several different expressions to describe the extraction processes in a solvent extraction system (Rydberg et al., 2004). Regardless of which type of extraction process is performed, these expressions can be used. The solvating extraction of a metal ion by a ligand and an uncharged organic ligand can be described as Equation 3.1.1.

$$M^{+} \ + \ L^{-} \ + \ \overline{O} \ \underset{\mathrm{k_1}}{\overset{\mathrm{k}}{\rightleftharpoons}} \ \overline{MLO} \tag{3.1.1}$$

where M is the metal ion, L the ligand, O the uncharged organic ligand, MLO the final complex and k and $\mathrm{k_1}$ the rate constants of the complexation.

3.1.2 *Distribution Ratio and Separation Factor*

The metal extraction of a solvent extraction system is described through the distribution ratio, D (Equation 3.1.2 and Equation 3.1.3). The distribution ratio is defined as the ratio of the total analytical concentration of the element, C, 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 case the organic phase. The organic phase is then separated from the aqueous phase. For radioactive nuclides, the concentration is proportional to the activity, A, of the nuclide, thus

$$D = \frac{[C]_{org}}{[C]_{aq}} \tag{3.1.2}$$

$$\propto$$

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

where V is the volume of the sample, R the count rate and ψ the detector efficiency. The efficiency of the measurement can differ depending on e.g. the volume of the samples and the geometry.

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 A and B is defined to always be larger than 1 i.e. the distribution ratio is higher for species A than for species B.

$$SF_{A/B} = \frac{D_A}{D_B} \tag{3.1.4}$$

3.2 ACTINIDE LANTHANIDE SEPARATION

The hard soft acid base (HSAB) theory can be used to describe how the differences between the acid character of the actinides and the lanthanides is one of the reasons for the separation achieved when using nitrogen donor ligands. According to the theory, soft Lewis bases form strong complexes with metal ions that are soft Lewis acids and vice versa. At the same time, hard metal ions and soft Lewis bases, i.e. mixed complexes, do not form such strong complexes (Pearson, 1968). Both actinides and lanthanides are assumed to be hard Lewis acids. The more covalent character in the complexation of the actinides compared to the lanthanides, by the N-donors in e.g. the BTBP-type ligands, is one reason why the actinide complexation is preferred (Miguirditchian et al., 2005; Ionova et al., 2001a,b). The presence of nitrate ion in the coordination sphere of the americium complex that compensates the charge density of the complex is another (Ekberg et al., 2015).

3.3 SYNERGISM AND ANTAGONISM

Synergism is a phenomenon that can be described as the creation of a whole that is greater than the simple summation of its parts, while the antagonism phenomenon can be described as two or more agents in combination having an overall effect that is less than the summation of their individual effects (Berger, 1995). The primary reason for synergism in a solvent extraction system is an increase in the hydrophobic character of the extracted metal complex upon addition of the adduct former (Rydberg et al., 2004).

In a system like the GANEX system, which contains several extraction agents, synergistic effects can be desirable in some respects to increase the extraction. Complex interactions between the extraction agents and the solutes, however, can complicate the understanding of the system and possible future computer modelling. Synergistic and antagonistic effects are also important to reveal at an early stage to be able to determine the true equilibrium kinetics of the system, since a slow extraction system is generally unsuitable for process applications.

3.4 THERMODYNAMICS

When the minor actinides, M, are extracted by CyMe$_4$-BTBP in a GANEX system n numbers of CyMe$_4$-BTBP and 3 NO$_3^-$ bind to the metal, creating a chemical equilibrium reaction according to Equation 3.4.1.

$$M^{3+} \; + \; 3\; NO_3^- \; + \; n\; \overline{BTBP} \; \rightleftharpoons \; \overline{M(NO_3)_3BTBP_n} \tag{3.4.1}$$

where the equilibrium constant for the extraction can be described according to Equation 3.4.2.

$$K_{Eq} \; = \; \frac{\overline{\{M(NO_3)_nBTBP_n\}}}{\{M^{3+}\} \; \times \; \{NO_3^-\}^3 \; \times \; \{\overline{BTBP}\}^n} \tag{3.4.2}$$

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, leading to Equation 3.4.3.

$$\{NO_3^-\}^3 \; \times \; \{\overline{BTBP}\}^n \; = \; C \tag{3.4.3}$$

where n is given by the slope of the regression line. If it is assumed that the concentration of the complexes is equal to the activities, K$_{Eq}$ can be expressed through the distribution ratio, Equation 3.4.4.

$$K_{Eq} \;=\; D_M \;\times\; \frac{1}{C} \tag{3.4.4}$$

Presuming that the enthalpy and entropy are constant for the temperature interval used under an extraction experiment, 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 3.4.5 and Equation 3.4.6 can be combined to get van 't Hoff equation, Equation 3.4.7.

$$\Delta G^0 \;=\; \Delta H^0 \;-\; T \;\times\; \Delta S^0 \tag{3.4.5}$$

where ΔG^0 is Gibbs free energy, ΔH^0 the enthalpy and ΔS^0 the entropy.

$$\Delta G^0 \;=\; -\,R \;\times\; T \;\times\; ln(K_{Eq}) \tag{3.4.6}$$

where R is the ideal gas constant and T the temperature.

$$ln(K_{Eq}) \;=\; \frac{-\Delta H^0}{R \;\times\; T} + \frac{\Delta S^0}{R} \tag{3.4.7}$$

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.

Using this method, the CyMe$_4$-BTBP GANEX system based on cyclohexanone was found to have a negative entropy change during americium extraction (Aneheim, 2012).

4

EXPERIMENTAL

"The real reason why general relativity is widely accepted is because it made predictions that were borne out by experimental observations." – Brian Greene

The majority of the experiments performed within this work have been done using the same composition of the organic phase, 10 mM CyMe$_4$-BTBP (synthesised in house according to (Foreman et al., 2006), or supplied from Karlsruhe Institute of Technology, Germany), 30%$_{vol}$ TBP (Sigma-Aldrich, 97%) and 70%$_{vol}$ FS-13 (CarboSynth or Marshallton). This composition will from now on be called the FS-13 GANEX solvent. An aqueous phase based on 4 M HNO$_3$ (Sigma Aldrich, $\geq$ 69% diluted with MilliQ-water, ($>$ 18 MΩ)) spiked with trace amounts of radionuclides has been used in all cases.

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 SOLVENT EXTRACTION EXPERIMENTS

3.5 mL glass vials with plastic lids were used for phase contacting. All samples contained equal amounts of organic and aqueous phase, between 200 – 1000 μL. Trace amounts of the actinides and europium were added to the samples from stock solutions: U(VI)–235 (84.44% enrichment, 40 mM), Np(V)–237 (0.35 MBq mL^{-1}), Np(V)–239 (extracted from a Am–243 loaded silica column), Pu(IV)–238 (0.28 Bq mL^{-1}), Am(III)–241 (0.42 MBq mL^{-1}), Cm(III)–244 (0.23 MBq mL^{-1}) and Eu(III)–152 (23 kBq mL^{-1}). Americium and europium were in most cases investigated together i.e. added to the same samples. The other actinides were investigated separately. The 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.

4.2 SOLVENT STABILITY

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 $\mathrm{kGyh^{-1}}$ 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 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 GANEX solvent was examined using two different batches of the solvent; one stored with aqueous phase contact and one without. Both batches were stored up to six weeks at room temperature.

4.3 ANALYSIS

The determination of the radioactivity of the actinides and europium was performed using three different measurement techniques. Possible efficiency differences between the organic and aqueous phases were investigated for all three techniques. No efficiency differences were observed.

4.3.1 *Gamma Spectrometry*

A high purity germanium detector (HPGe) was used to measure the amounts of americium and europium (Canberra, Gamma Analyst GEM 23195 or Ortec, GEM 15180–S). 100 μL of each sample and phase were removed and placed in new clean plastic vials. The americium was analysed using a gamma energy of 59.6 keV and the europium using a 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%.

4.3.2 *Liquid Scintillation Counting*

For measurements of the samples containing either plutonium, uranium, some of the americium samples or neptunium-239 a liquid scintillation counting detector (LSC) was used (Wallac 1414 WinSpectral). 100 μL 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 of the samples have been performed. No quenching using FS-13 was observed within the concentration range used.

4.3.3 *Alpha Spectrometry*

For the neptunium-237 and curium samples, 10 μL of each sample and phase were removed and placed on an alpha planchet and 50 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 evaporated using a gas burner. The samples were analysed with alpha spectrometry (Ortec, Alpha Duo, Octête TM PC). The neptunium was analysed using an alpha energy of 4.8 MeV and curium was analysed using an alpha energy of 5.8 MeV.

5

RESULTS AND DISCUSSION

"However beautiful the strategy, you should occasionally look at the results." – Winston Churchill

As mentioned earlier, several different Chalmers GANEX solvents have been developed over the years (Paper III). Four systems have mainly been investigated: cyclo-GANEX (CyMe$_4$-BTBP, 30%$_{vol}$ TBP and cyclohexanone), DEHBA-GANEX (CyMe$_4$-BTBP, 20%$_{vol}$ DEHBA and cyclohexanone), hexanol-GANEX (CyMe$_4$-BTBP, 30%$_{vol}$ TBP and hexanol) and in the present work FS-13 GANEX (CyMe$_4$-BTBP, 30%$_{vol}$ TBP and FS-13). For the extraction of actinides the distribution ratio is highest in the two cyclohexanone-based solvents. The extraction of the lanthanides, however, is also relatively high. The separation factor for the uranium/europium extraction is low in the DEHBA-GANEX system as well as in the hexanol-GANEX system, indicating that the bulk uranium would need to be separated in a separate step before the actual GANEX extraction in both of these cases. The extraction of neptunium is rather low in all of the previously investigated systems. The results from investigations of the FS-13 GANEX system are presented below.

5.1 SOLVENT EXTRACTION EXPERIMENTS

All experiments were performed as described in Section 4.1, Solvent Extraction Experiments and analysed according to Section 4.3, Analysis.

5.1.1 *Equilibrium Kinetics*

The extraction results from uranium, plutonium, neptunium, americium and europium in the FS-13 GANEX solvent are mainly presented in Paper II. Equilibrium kinetics experiments, Figure 5.1.1, were performed to investigate the extraction rate of the system. In all cases, the extracted metals have been used in trace amounts.

The time to reach extraction equilibrium was investigated to estimate an adequate contact time of the two phases for the remainder of the experiments.

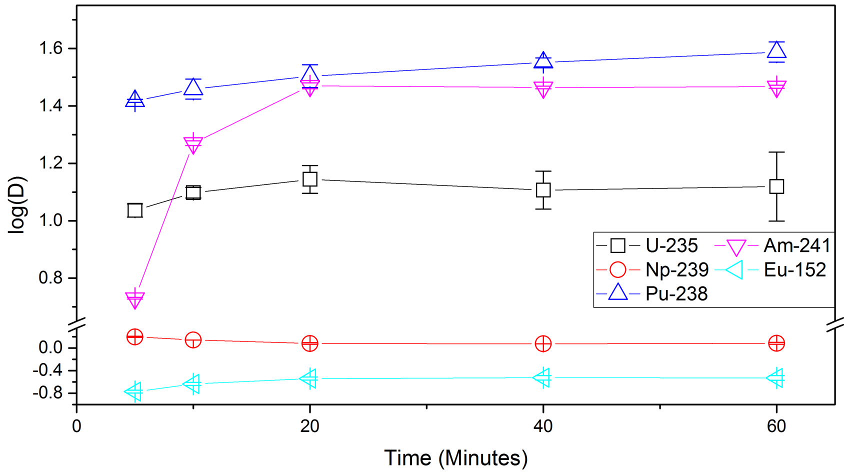

Figure 5.1.1: Logarithmic distribution ratios over time for uranium, neptunium, plutonium, americium and europium in 70$\%_{vol}$ FS-13, 30$\%_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 was used in all cases as aqueous phase (lines added to guide the eye).

The results in Figure 5.1.1 show that it takes around 20 minutes to reach final equilibrium for uranium, plutonium, neptunium and americium together with europium. The distribution ratio after five minutes is, however, already high for both uranium and plutonium. After 20 minutes the extraction of uranium seems to decrease slightly over time. Concomitantly the extraction of plutonium seems to slightly increase. Both the decrease and the increase are, however, within the error margins. The slight decrease in distribution ratio for neptunium from the start of the experiment could be a result of a shift in neptunium oxidation state, as neptunium is easily oxidised and reduced. Neptunium is most likely present in mixed oxidation states (Huizenga and Magnusson, 1951), which may influence the extraction. The distribution ratio of americium increases slowly during the first 20 minutes of the extraction, indicating that the CyMe$_4$-BTBP extraction is slower than the TBP extraction. All experiments after the equilibrium kinetics experiment presented in Figure 5.1.1 have been performed with 60 minutes of phase contact to ensure that equilibrium has been reached.

Previously investigated GANEX solvents (discussed in Paper III), for example the cyclohexanone GANEX solvent as well as the hexanol GANEX solvent (Löfström-Engdahl, 2014), have a phase contact time of 20 minutes to reach equilibrium (Aneheim, 2012). In comparison, the time to reach equilibrium for the FS-13 GANEX solvent is the same. Other long-chained alcohol solvents containing $CyMe_4$-BTBP but no TBP have a much longer phase contact time to reach equilibrium (over 130 minutes) (Löfström-Engdahl, 2014).

To evaluate the actinide extraction in comparison to europium, the reference for the lanthanides, the separation factor was calculated, Table 5.1.1. The small separation factor between americium and curium indicates that the obtained results for americium can be expected to also be valid for curium. Neptunium is the only actinide with a low separation factor with respect to europium. It is high enough, however, to be able to enable a separation.

Table 5.1.1: Separation factor for selected actinides over europium and americium over curium in FS-13.

	U/Eu	*Np/Eu*	*Pu/Eu*	*Am/Eu*	*Cm/Eu*	*Am/Cm*
SF	44 ± 6	4.1 ± 0.5	120 ± 18	84 ± 4	56 ± 6	1.5 ± 0.2

In Paper I, separation factors different from Table 5.1.1 are presented. This is probably due to a lower $CyMe_4$-BTBP concentration than intended, caused by insufficient dissolution of $CyMe_4$-BTBP in FS-13. Since $CyMe_4$-BTBP extracts the trivalent actinides, and to some extent the trivalent lanthanides, the distribution ratio of the elements will decrease with a decreasing $CyMe_4$-BTBP concentration. The separation factors presented in Paper I (all except Am/Eu) are based on a europium distribution ratio of 0.1 instead of 0.3, found in later work (Paper II, Paper III) with a correct $CyMe_4$-BTBP concentration of 10 mM. This will be further discussed in Section 5.2.1, Radiolytic and Hydrolytic Stability.

5.1.2 *Stripping*

The last step of a successful liquid-liquid extraction process are to be able to back-extract the actinides into a new aqueous phase, in order to reuse the actinides to produce new nuclear fuel. In this case 0.01 M HNO_3 was used to investigate stripping of americium from the FS-13 GANEX solvent to an aqueous phase with low nitrate concentration in two successive steps.

The results presented in Figure 5.1.2 show that two stripping steps is not enough to reach an adequate back-extraction level. For the samples containing 35 mM CyMe$_4$-BTBP and 25 mM CyMe$_4$-BTBP roughly 16% of the americium was stripped. In the 10 mM CyMe$_4$-BTBP samples roughly 3% of the americium was stripped. The slightly high value in the second stripping step for the 25 mM CyMe$_4$-BTBP samples might be due to samples not being entirely phase separated, since the expected value should be between 10 mM CyMe$_4$-BTBP and 35 mM CyMe$_4$-BTBP.

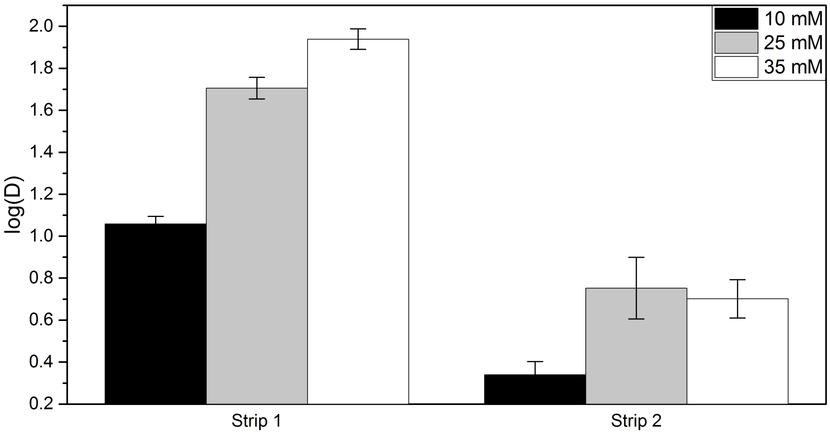

Figure 5.1.2: Logarithmic distribution ratios of americium extraction from an organic phase (70%$_{vol}$ FS-13, 30%$_{vol}$ TBP and 10 mM CyMe$_4$-BTBP) to a 0.01 M HNO_3 aqueous phase.

A low initial stripping is also the case with the cyclo-GANEX, where a large amount of the acidic aqueous phase is extracted into the organic phase (Aneheim et al., 2012b). The insufficient stripping of the FS-13 GANEX solvent could be caused by a similar dissolution of acid into the organic phase during extraction and pre-equilibration. Preliminary washing experiments of the FS-13 GANEX solvent after acid contact with MQ water show a low pH (< 2) in the wash phase even after four contacts. In the cyclo-GANEX system an acid scrub step, containing 0.01 M HNO_3, 0.99 M $NaNO_3$ and 0.6 M gluco-lactone, was introduced before the stripping. This scrub step was performed twice to remove as much acid as possible

(Aneheim, 2012; Aneheim et al., 2013). These types of acid scrub steps might also be a possible solution to increase the stripping of the FS-13 GANEX system.

5.1.3 *Separate Ligand Extraction*

In earlier studies using other diluents no synergistic effect between the two extraction agents CyMe$_4$-BTBP and TBP has been found. For future modelling purposes, possible synergistic effects must be investigated in the FS-13 GANEX system as well.

To determine which of the two possible extractants (CyMe$_4$-BTBP and TBP) extract the different actinides and europium in the FS-13 GANEX solvent an extraction experiment was performed using four different organic phases: 1: 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP and 10 mM CyMe$_4$-BTBP, 2: 100%$_{vol}$ FS-13 and 10 mM CyMe$_4$-BTBP, 3: 70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP and 4: pure FS-13. This experiment also makes it possible to detect if the diluent itself extracts any of the metals and if there are any synergistic or antagonistic behaviour between the different solvent components.

Extraction of all the metals is highest in the FS-13 GANEX solvent, system 1 (FS-13 with TBP and CyMe$_4$-BTBP), Figure 5.1.3. Extraction of neptunium is slightly low (D = 1.21) but as the extraction of europium is also low (D = 0.29) this still renders a separation factor of 4.1. To reach an adequate extraction of neptunium a possible solution could be to use a higher concentration of CyMe$_4$-BTBP. This is further discussed in Section 5.1.4, Solubility and Complex Stoichiometry. In system 2 (FS-13 with TBP), Figure 5.1.4, mainly plutonium and uranium are extracted and to some extent neptunium, as expected. The distribution ratio of plutonium is significantly lower in system 2, however, compared to system 1. This indicates an extraction by both TBP and CyMe$_4$-BTBP in system 1. The neptunium extraction is also lower in system 2 compared to system 1 (0.84 compared to 1.21 respectively). Since neptunium most likely is present in mixed oxidation states (Huizenga and Magnusson, 1951; Taylor et al., 2013), it could be extracted both by TBP and CyMe$_4$-BTBP . In system 3 (FS-13 with CyMe$_4$-BTBP) it appears as if only plutonium, uranium and to some extent neptunium obtain distribution ratios that are not close to zero, Figure 5.1.5. This indicates that CyMe$_4$-BTBP in this setting is extracting both tetra- and hexavalent ions, something that has previously been shown (Aneheim et al., 2012a), and that neptunium is indeed present in mixed oxidation states. What is surprising in system 3, however, is the almost complete lack of extraction of the trivalent actinides. This lack of trivalent actinides extraction using CyMe$_4$-BTBP has not been observed in previously investigated CyMe$_4$-BTBP systems (Geist et al., 2006; Löfström-Engdahl, 2014; Trumm et al., 2011; Harwood et al., 2011; Aneheim et al., 2010). CyMe$_4$-BTBP and TBP hence seem to behave synergistically in the FS-13 GANEX system with regard to the extraction of trivalent actinides in system 1. Synergism should be further investigated to find optimal relations between the extracting agents. The extraction of all elements in system 4 (pure FS-13) is very low, Figure 5.1.6, showing that FS-13 in itself does not act as an extracting agent. The extraction of europium is low in all four systems.

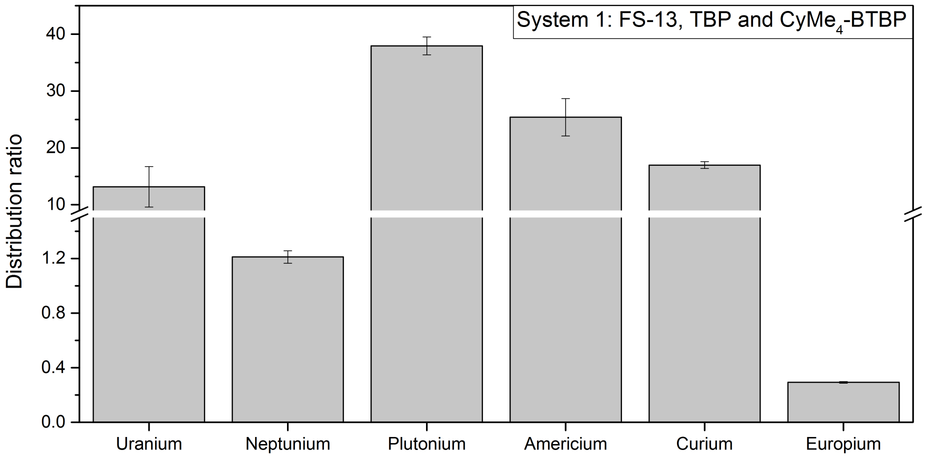

Figure 5.1.3: Distribution ratios of uranium, neptunium, plutonium, americium, curium and europium in system 1: 70 $\%_{vol}$ FS-13, 30 $\%_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

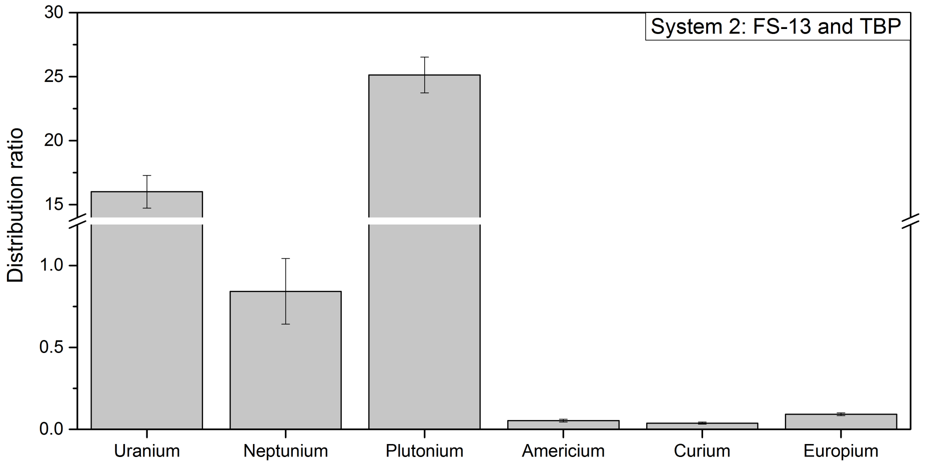

Figure 5.1.4: Distribution ratios of uranium, neptunium, plutonium, americium, curium and europium in system 2: 70 $\%_{vol}$ FS-13 and 30 $\%_{vol}$ TBP as organic phase and 4 M HNO_3 as aqueous phase.

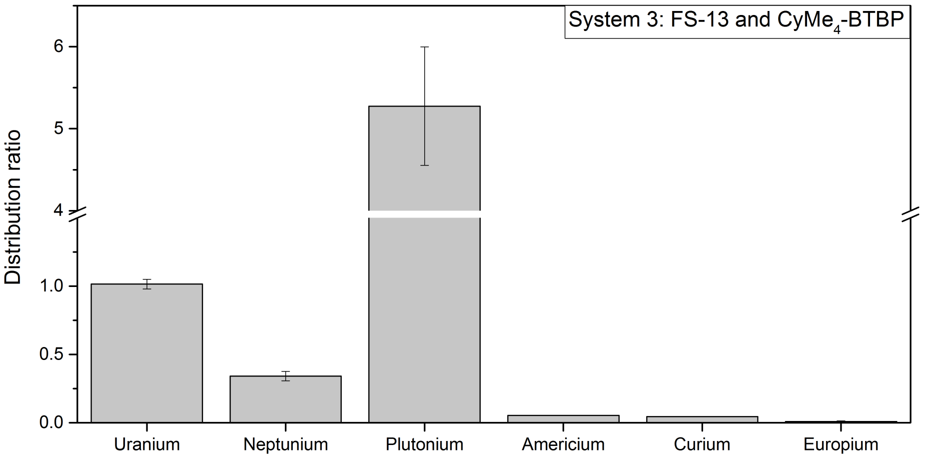

Figure 5.1.5: Distribution ratios of uranium, neptunium, plutonium, americium, curium and europium in system 3: FS-13, 10 mM $CyMe_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

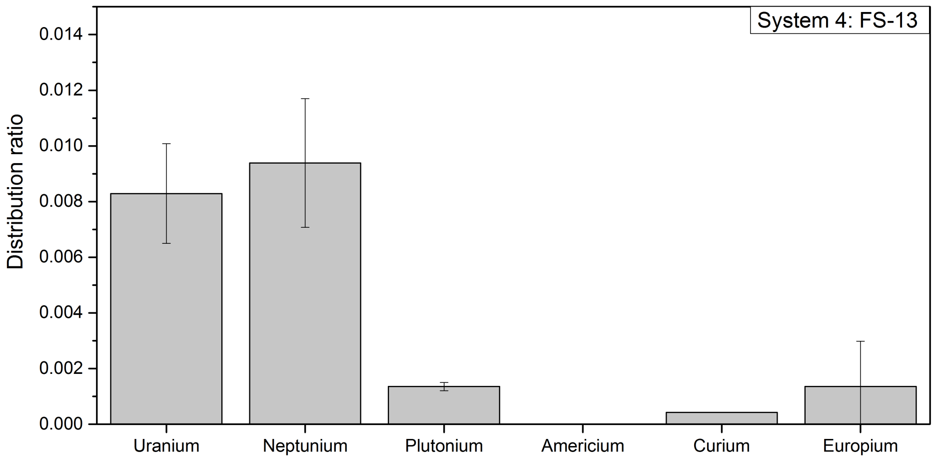

Figure 5.1.6: Distribution ratios of uranium, neptunium, plutonium, americium, curium and europium in system 4: pure FS-13 as organic phase and 4 M HNO_3 as aqueous phase.

To investigate the effect of TBP in the extraction process, experiments with a system only containing 5% TBP was performed. The results, presented in Figure 5.1.7, show a lower extraction of americium, while plutonium and europium are extracted to almost the same extent as with 30% TBP in the solvent. However, the time to reach extraction equilibrium seems to have been prolonged for both plutonium, americium and europium (from 20 minutes in the FS-13 GANEX solvent, Figure 5.1.1 on page 25, to 40 minutes), indicating that TBP has a positive effect on the overall extraction kinetics of the system. This is due to the change in the organic phase caused by using different amounts of TBP, not only changing the organic phase composition but possibly also changing parameters like the surface contact area during the solvent extraction experiments. The low americium extraction indicates a strong synergistic effect between TBP and $CyMe_4$-BTBP using FS-13 as diluent.

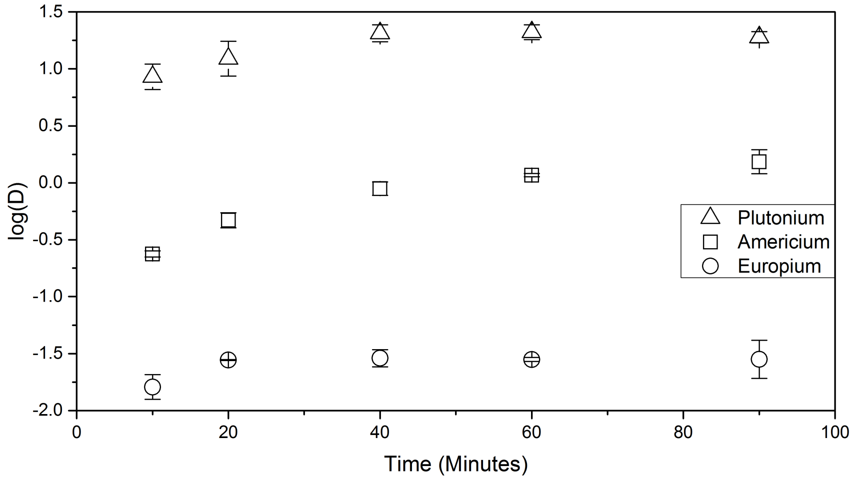

Figure 5.1.7: Logarithmic distribution ratios of plutonium, americium and europium in 95% FS-13, 5% TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

5.1.4 *Solubility and Complex Stoichiometry*

The extraction curves will at some point reach an equilibrium where the dissolved amount of CyMe$_4$-BTBP will not affect the actinide extraction, i.e. the distribution ratio will not increase with increased CyMe$_4$-BTBP concentration. In Figure 5.1.8 the extracted amounts of plutonium, americium and europium are presented for different concentrations of CyMe$_4$-BTBP.

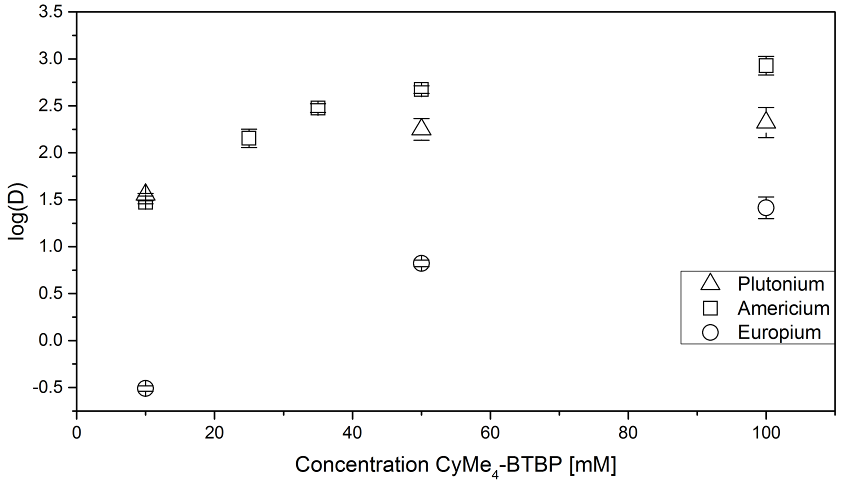

Figure 5.1.8: Logarithmic distribution ratios of plutonium, americium and europium in 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP with different amounts of CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

Equilibrium constants for the americium extractions during the increasing CyMe$_4$-BTBP concentration, shown in Figure 5.1.8, have been calculated and found to be constant up to 35 mM. The results in Figure 5.1.8 also show that the plutonium samples reached extraction equilibrium around a concentration of 50 mM CyMe$_4$-BTBP and that an increase of CyMe$_4$-BTBP does not affect the extraction further. The extraction for americium seems to increase with an increase in the CyMe$_4$-BTBP concentration, indicating that an even higher CyMe$_4$-BTBP concentration would increase the americium extraction even more. However, this is also the case with europium, meaning that a higher CyMe$_4$-BTBP concentration is beneficial both for lanthanide and actinide extraction, therefore rendering a concentration over 50 mM CyMe$_4$-BTBP in FS-13 irrelevant for actinide extraction purposes.

In Figure 5.1.9 data for the complexation between CyMe$_4$-BTBP and americium are presented. The slope is 1.81 ± 0.10 ($R^2 = 0.99$). This indicates a 2:1 relation between CyMe$_4$-BTBP and americium, meaning that two CyMe$_4$-BTBP molecules are needed to extract one americium nuclei. The 2:1 complexation relation between CyMe$_4$-BTBP and americium has previously been observed in cyclohexanone-based and hexanol-based GANEX systems (Löfström-Engdahl, 2014).

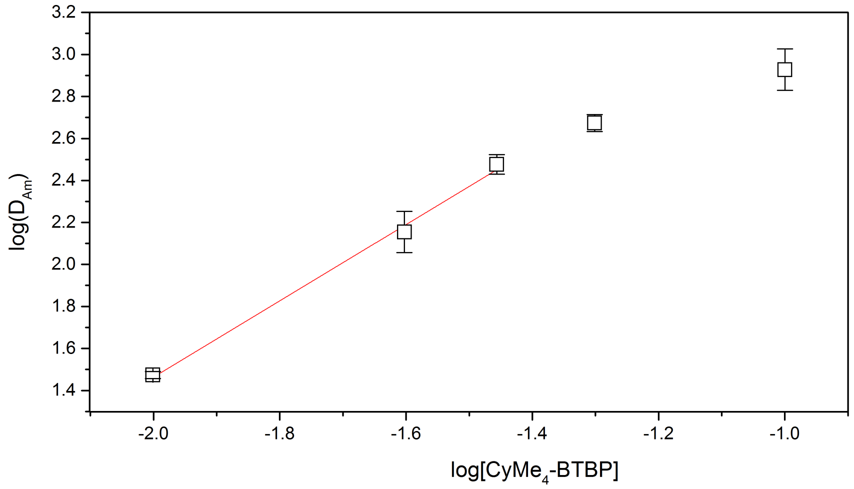

Figure 5.1.9: Logarithmic distribution ratios of americium as a function of the CyMe$_4$- BTBP concentration in the extraction system using 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase. The R^2 for the linear regression (the red line) is 0.99 and the slope is 1.81 ± 0.10.

5.1.5 *Thermodynamic Investigations*

To investigate how the temperature affects the extraction with the FS-13 GANEX solvent experiments within a temperature interval between 20 °C and 40 °C were performed (Figure 5.1.10). 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.

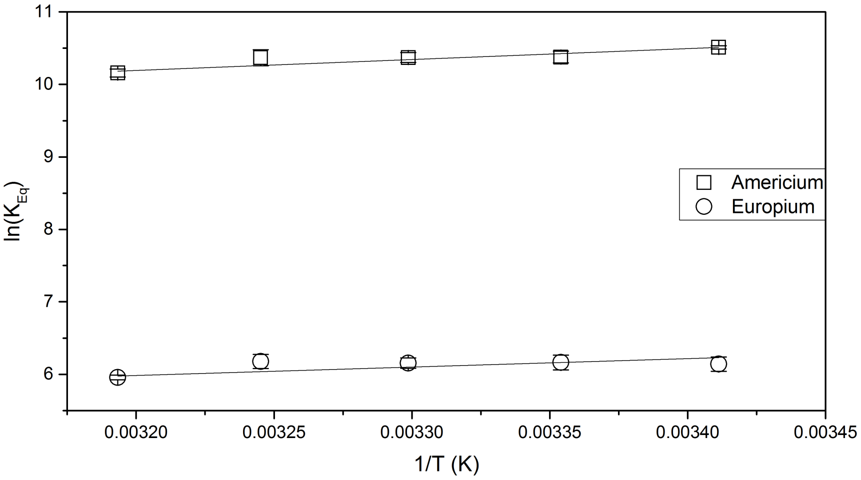

Figure 5.1.10: The logarithm of the equilibrium constant vs. 1/T. Using $70\%_{vol}$ FS-13, $30\%_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

By performing a linear regression on the data points in Figure 5.1.10, according to Van 't Hoff Equation (Equation 3.4.7 on page 20) the enthalpy and the entropy for the extraction of americium and europium can be calculated. For the FS-13 GANEX system the enthalpy is negative, while the entropy is positive (Table 5.1.2). The increase of the entropy during the extraction acts as a thermodynamic driving force for the reaction.

Table 5.1.2: Enthalpy and entropy of complexation for the extraction of americium and europium. Using $70\%_{vol}$ FS-13, $30\%_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

	ΔH^0 *[kJ × mol^{-1}]*	ΔS^0 *[J × (mol × K)$^{-1}$]*
Americium	- 12.5 ± 0.2	44.6 ± 0.6
Europium	- 9.7 ± 0.4	18.5 ± 1.4

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

5.2 SOLVENT STABILITY

The irradiation experiments were performed as described in Section 4.2, Solvent Stability, the extraction was performed according to Section 4.1, Solvent Extraction Experiments and analysed as described in Section 4.3, Analysis.

5.2.1 *Radiolytic and Hydrolytic Stability*

Due to the promising extraction experiments, the stability towards irradiation, ageing and hydrolysis of the FS-13 GANEX solvent were investigated (mainly presented in Paper II). According to the irradiation results presented in Figure 5.2.1, no significant differences in the americium and europium extractions can be observed between the reference samples and the irradiated samples. The results indicate that the solvent is stable towards irradiation in contact with the 4 M HNO_3 aqueous phase for doses at least up to roughly 160 kGy. The distribution ratio for americium is calculated to be 19 ± 3.6 and for europium 0.25 ± 0.03 throughout the entire experiment, giving a separation factor of 75 ± 9, which corresponds well with the results in Table 5.1.1 on page 26.

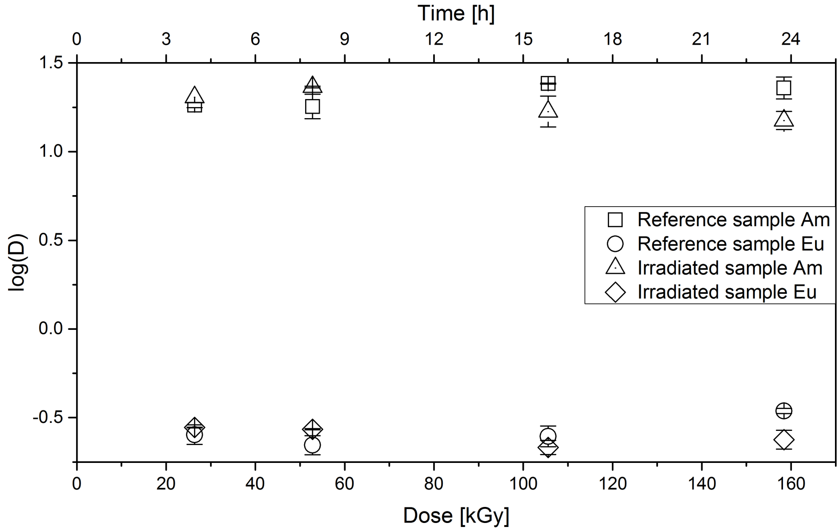

Figure 5.2.1: Logarithmic distribution ratios of americium and europium after irradiation of the solvent in contact with aqueous phase using $70\%_{vol}$ FS-13, $30\%_{vol}$ TBP and 10 mM $CyMe_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase for 24 h and a dose rate of 6.6 $kGyh^{-1}$.

Both the hydrolysis and long-term stability of the FS-13 GANEX solvent have been investigated and evaluated. 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 show 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. The acidic aqueous phase could work like a scavenger similarly 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 duration of the whole experimental period.

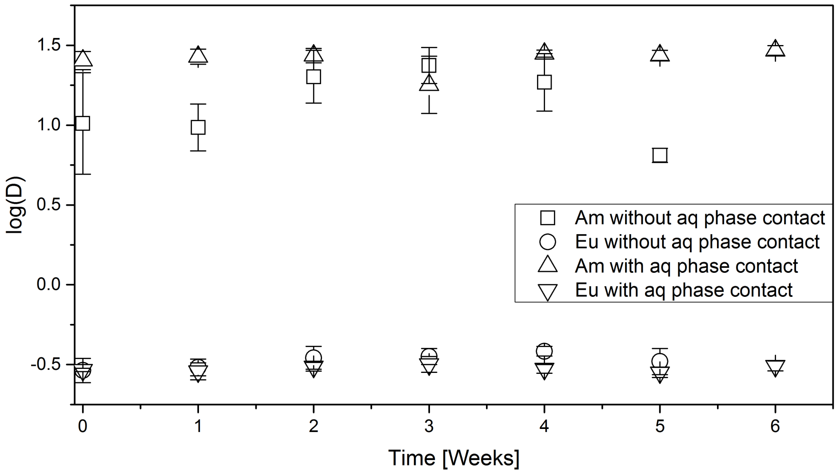

Figure 5.2.2: Logarithmic distribution ratios of the investigated solvent with and without aqueous phase contact using 70%$_{vol}$ FS-13, 30%$_{vol}$ TBP and 10 mM CyMe$_4$-BTBP as organic phase and 4 M HNO_3 as aqueous phase.

The slow increase of the americium distribution ratio without aqueous phase contact could be due to slow dissolution of CyMe$_4$-BTBP in the mixture of FS-13 and TBP. While the aqueous contacted organic phase dissolved the CyMe$_4$-BTBP instantly, the dry organic phase was able to slowly dissolve the CyMe$_4$-BTBP completely during the first two weeks of the experiments. This phenomenon has been investigated further after this experiment and a correlation between the solubility of CyMe$_4$-BTBP and an organic phase pre-equilibrated with nitric acid has been observed. After contacting the FS-13 GANEX solvent with 4M HNO_3 it is possible to dissolve $>$ 100 mM of CyMe$_4$-BTBP (something further explored in the previous Section 5.1.4, Solubility and Complex Stoichiometry), while without nitric acid contact 10 mM is difficult to dissolve completely. This increase of CyMe$_4$-BTBP solubility is probably due to nitric acid extraction by TBP (Zhang et al., 1989). The high uncertainty for the first week sample, week zero, without aqueous phase contact most likely depends on undissolved CyMe$_4$-BTBP particles that followed the organic phase from the aged organic stock solution to some of the extraction samples, where it then dissolved, influencing the americium extraction. All previous experiments were repeated to ensure that the data was retrieved with the correct CyMe$_4$-BTBP concentration. The stability experiment was not repeated due to the long duration of the experiment.

Compared with the previously investigated GANEX solvents, the cyclo-GANEX solvent degrades in contact with acid and previous experiments show a decrease of CyMe$_4$-BTBP content. The actinide extraction is the same after four weeks, however, indicating that the hydrolysis products of CyMe$_4$-BTBP also extract the actinides. The cyclo-GANEX solvent is also stable towards radiation, except for americium where a small decrease in the extraction has been observed (Aneheim, 2012). In the hexanol-GANEX, the extraction of americium decreases during both hydrolysis and radiolysis studies. However the ligand stability was shown to be better in the hydrolysis studies (Löfström-Engdahl, 2014).

6

CONCLUSIONS

"The strongest arguments prove nothing so long as the conclusions are not verified by experience. Experimental science is the queen of sciences and the goal of all speculation." – Roger Bacon

During previous investigations of diluents for use in a Chalmers GANEX solvent, several problems have been found. The diluents have for example not been stable in the chemical environment, there has been poor solubility of the extracting agents and slow kinetics. The objective of this work has therefore been to further develop the Chalmers GANEX process. Optimisations regarding the content of the GANEX solvent have been investigated. In this work an alternative Chalmers GANEX solvent based on FS-13 has been investigated and compared to previously studied GANEX diluents, such as cyclohexanone and hexanol. Both advantages and disadvantages have been discovered.

Among the positive features of the FS-13 GANEX solvent is the short time to reach extraction equilibrium. The phase contact time of 20 minutes is equal to both the cyclo-GANEX and hexanol-GANEX solvents. The cyclo-GANEX and hexanol-GANEX systems both have higher separation factors between the actinides and europium than the FS-13 based one, except in the case of uranium. The higher separation factor between uranium and europium in the FS-13 system indicates that the bulk uranium step might not be needed. This would create a safer process involving fewer steps. It has also been concluded that TBP in FS-13 extracts the tetra- and hexavalent actinides, as does CyMe$_4$-BTBP. TBP and CyMe$_4$-BTBP in combination in FS-13, however, display a synergistic extraction of the trivalent actinides. This complex extraction behaviour is a drawback compared to the other GANEX systems, as this might complicate future computer modelling of the system. The FS-13 system, however, shows a good stability against radiation and hydrolysis compared to both the hexanol-GANEX and cyclo-GANEX systems where decreasing actinide extraction and solvent degradation was found. By pre-equilibrating the FS-13 based organic phase with nitric acid, an increase of CyMe$_4$-BTBP solubility has been observed. Creating a system with a higher CyMe$_4$-BTBP concentration resulted in a higher extraction of plutonium and americium. This would also provide a possible solution for increasing the otherwise low distribution ratio of neptunium. However, the extraction of europium was also increased, resulting in the conclusion that a system containing 50 mM CyMe$_4$-BTBP or more will mainly benefit the extraction of lanthanides and other fission products. Complexation between CyMe$_4$-BTBP and americium was found to be a 2:1 relation, the same as in the hexanol-GANEX. Temperature-dependent experiments show a slight decrease of the americium and europium extraction with an increase of the temperature. This is the same for all three GANEX systems. Enthalpy and entropy calculations hence show, in all three GANEX solvents, an exothermal system. Two successive stripping experiments were performed and the back-extraction in the FS-13 GANEX solvent was found to be low, with a small percentage of the actinides present being back-extracted. This was, however, also the case for the cyclo-GANEX process before an acid scrub was added before the stripping.

Several positive features have been found using FS-13 as a diluent in a GANEX solvent. Further studies need to be performed to fully understand the system. The biggest drawback with the FS-13 GANEX system is the insufficient back-extraction of americium. If this could be solved using additional scrubbing steps, however, FS-13 could then have the potential to be a promising GANEX diluent during further studies.

7

FUTURE WORK

"The future will belong to those who have passion and are willing to work hard to make our country better." – Paul Wellstone

Future work on the FS-13 GANEX solvent involves both complementary and further investigations of the system. Experiments only performed using americium have to be investigated using all the actinides and the extraction of other fission products than europium has to be investigated. The synergistic effects between CyMe$_4$-BTBP and TBP should be further investigated, with the purpose of finding an optimal TBP percentage in the FS-13-based GANEX solvent. Studies on the possible acid extraction of the organic phase would be of interest to reveal how it affects the stripping step and whether acid scrubbing steps need to be added. Due to the high separation factor between uranium and europium, a uranium loading experiment would also be of interest, in addition to a plutonium loading experiment to investigate the effect on americium extraction. Over a longer time perspective the system needs to be propagated to include hot test, an enlarged scale and pilot scale. Recycling of the FS-13 GANEX solvent also has to be investigated due to the presence of sulphur, fluoride and phosphor in the solution. Computer modelling would also be useful for understanding the system and to do this further investigations on the complex extraction behaviour of the system will be necessary.

In case of a new start, developing a new GANEX solvent, systems using a diluent following the CHON principle would be desirable. Long-chained alcohols could be examined in combination with different BTBP-type molecules with higher solubility, such as e.g. 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)- 4-tert-butyl-[2,2']bipyridinyl (t-Bu-CyMe$_4$-BTBP). Systems exchanging TBP with DEHBA would also be of interest.

8

ACKNOWLEDGEMENTS

"Knowledge is in the end based on acknowledgement." – *Ludwig Wittgenstein*

Last but not least there are so many people I would like to thank for helping me with my work and for being there for me during this time.

My examiner, Gunnar Skarnemark, you have so far been the examiner of all my academic work and you took me on even if you were retiring. Even if you moved to Germany, it was always easy to get in touch and to get all kinds of help and answers.

My supervisor, Christian Ekberg, for all the help with my work and for giving me the opportunities to travel, build a network and meet a lot of new people.

My co-supervisor, Emma Aneheim, you have been there for such a long time now. You have not only helped me with my PhD studies (like leading a blind through a very dark darkness); you also helped me with my Masters thesis.

All the participants of SACSESS, for all the feedback and brainstorming about my work, and for all the fun during the meetings and all the new friends I made.

All my co-workers, the department would be nothing without you. You all make work a fun place to go to.

Elin and Marcus, all the fun, all the discussions (both work-related and not) and all the help you have given me.

My family, mum, dad, Andreas, Lily and the new little life, Ernst. You are all amazing and have given me so much support and energy. You have all been a part

of making this possible for me.

My extended family, for being there, not mainly for me but for my various family members and for sharing their lives and making them happy.

My friends, I would never have managed this without you. All the fun times you have given me, love and support. You have all been stress releasers, free zones and totally awesome!

Jakob, mitt vinterland, the other piece of my puzzle. Thank you for being a part of my life and letting me be a part of yours. I would never have been able to do this without you and your love, you are my Nirvana.

The Swedish Nuclear Fuel and Waste Management Company (SKB) and the European Union seventh Framework Project SACSESS (no. 323282) are both acknowledged for funding this work.

BIBLIOGRAPHY

Abram, T. and Ion, S. (2008). Generation-iv nuclear power: A review of the state of the science. *Energy Policy*, 36(12):4323–4330.

ACSEPT (2013). Final Report Summary - ACSEPT (Actinide reCycling by SEParation and Transmutation). http://cordis.europa.eu/result/rcn/56366_en.html. 2015-06-24.

Adnet, J., Miguirditchian, M., Hill, Cand Heres, X., Lecomte, M., Masson, M., Brossard, P., and Baron, P. (2005). Development of new hydrometallurgical processes for actinide recovery: GANEX concept. In *Proceedings of GLOBAL*.

Ambrose, M. and Hamblet, C. (1951). Adipic acid process. US Patent 2,557,282.

Anderson, H., Newton, M., Asprey, L., and Richmond, C. (1960). Solvent extraction process for plutonium, United States Patent Office, Patent no 2,924,506. Technical report, Applied 08-05-1947. Patented 09-02-1960.

Aneheim, E. (2012). *Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel*. PhD thesis, Chalmers University of Technology.

Aneheim, E., Bauhn, L., Ekberg, C., Foreman, M., and Löfström-Engdahl, E. (2012a). Extraction experiments after radiolysis of a proposed GANEX solvent-the effect of time. *Procedia Chemistry*, 7:123–129.

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

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

Aneheim, E., Ekberg, C., Foreman, M. R., Löfström-Engdahl, E., and Mabile, N. (2012b). Studies of a solvent for GANEX applications containing CyMe$_4$-BTBP and DEHBA in Cyclohexanone. *Separation Science and Technology*, 47(5):663–669.

Aneheim, E., Ekberg, C., and StJ. Foreman, M. R. (2013). A TBP/BTBP-Based Ganex Separation Process–Part 3: Fission Product Handling. *Solvent extraction and ion exchange*, 31(3):237–252.

Aoki, S. (2002). Research and development in Japan on long-lived nuclide partitioning and transmutation technology. *Progress in Nuclear Energy*, 40(3):343–348.

Berger, M. R. (1995). *Synergism and Antagonism between chemical Carcinogens*, chapter 2, pages 23–49. Springer.

Bond, W. and Leuze, R. (1976). Removal of actinides from high-level wastes generated in the reprocessing of commercial fuels. In *Transplutonium 1975.*

Bradshaw, M. J. (2010). Global energy dilemmas: a geographical perspective. *The Geographical Journal*, 176(4):275–290.

Bruggink, J. and van der Zwaan, B. (2002). The role of nuclear energy in establishing sustainable energy paths. *International Journal of Global Energy Issues*, 18(2-4):151–180.

Brundtland, G. H. (1987). *Report of the World Commission on Environment and Development:"Our Common Future"*. Oxford University Press, Oxford.

Burger, L. (1958). Uranium and plutonium extraction by organophosphorus compounds. *The Journal of Physical Chemistry*, 62(5):590–593.

Carrott, M., Bell, K., Brown, J., Geist, A., Gregson, C., Hères, X., Maher, C., Malmbeck, R., Mason, C., Modolo, G., et al. (2014). Development of a new flowsheet for co-separating the transuranic actinides: the "EURO-GANEX" process. *Solvent Extraction and Ion Exchange*, 32(5):447–467.

Carrott, M., Geist, A., Hères, X., Lange, S., Malmbeck, R., Miguirditchian, M., Modolo, G., Wilden, A., and Taylor, R. (2015). Distribution of plutonium, americium and interfering fission products between nitric acid and a mixed organic phase of TODGA and DMDOHEMA in kerosene, and implications for the design of the "EURO-GANEX" process. *Hydrometallurgy*, 152:139–148.

Choppin, G., Liljenzin, J.-O., Rydberg, J., and Ekberg, C. (2013a). *Radio chemistry and nuclear chemistry*, chapter 21. Elsevier, 4 edition.

Choppin, G., Liljenzin, J.-O., Rydberg, J., and Ekberg, C. (2013b). *Radio chemistry and nuclear chemistry*, chapter 20. Elsevier, 4 edition.

Choppin, G., Liljenzin, J.-O., Rydberg, J., and Ekberg, C. (2013c). *Radio chemistry and nuclear chemistry*, chapter 11. Elsevier, 4 edition.

Choppin, G. R. (1983). Comparison of the solution chemistry of the actinides and lanthanides. *Journal of the Less Common Metals*, 93(2):323–330.

Clayden, J., Greeves, N., Warren, S., and Wothers, P. (2001). *Organic Chemistry*. Oxford University Press.

Courson, O., Lebrun, M., Malmbeck, R., Pagliosa, G., Römer, K., Sätmark, B., and Glatz, J.-P. (2000). Partitioning of minor actinides from hllw using the diamex process. part 1-demonstration of extraction performances and hydraulic behaviour of the solvent in a continuous process. *Radiochimica Acta International journal for chemical aspects of nuclear science and technology*, 88(12):857.

Danesi, P. R. (2004). *Solvent Extraction Principles and Practice*, chapter 5. Marcel Dekker, New York, 2 edition.

Ekberg, C., Aneheim, E., Fermvik, A., Foreman, M., Löfström-Engdahl, E., Retegan, T., and Spendlikova, I. (2010). Thermodynamics of Dissolution for Bis (triazine)- Bipyridine-Class Ligands in Different Diluents and Its Reflection on Extraction. *Journal of Chemical & Engineering Data*, 55(11):5133–5137.

Ekberg, C., Dubois, I., Fermvik, A., Retegan, T., Skarnemark, G., Drew, M., Foreman, M., and Hudson, M. (2007). Extraction Behavior of Nickel (II) using some of the BTBP-Class Ligands. *Solvent Extraction and Ion Exchange*, 25(5):603–617.

Ekberg, C., Löfström-Engdahl, E., Aneheim, E., Foreman, M. R. S., Geist, A., Lundberg, D., Denecke, M., and Persson, I. (2015). The structures of CyMe$_4$-BTBP complexes of americium (III) and europium (III) in solvents used in solvent extraction, explaining their separation properties. *Dalton Transactions*, 44(42):18395–18402.

Foreman, M., Hudson, M., Drew, M., Hill, C., and Madic, C. (2006). Complexes formed between the quadridentate, heterocyclic molecules 6,6'-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III). *Dalton Transactions*, 13:1645–1653.

Foreman, M. R. S. J., Hudson, M. J., Geist, A., Madic, C., and Weigl, M. (2005). An Investigation into the Extraction of Americium (III), Lanthanides and D-Block Metals by 6, 6'-Bis-(5, 6-dipentyl-[1, 2, 4] triazin-3-yl)-[2, 2'] bipyridinyl (C5-BTBP). *Solvent extraction and ion exchange*, 23(5):645–662.

Geist, A., Hill, C., Modolo, G., Foreman, M. R. S. J., Weigl, M., Gompper, K., and Hudson, M. J. (2006). 6, 6?-bis (5, 5, 8, 8-tetramethyl-5, 6, 7, 8-tetrahydro-benzo [1, 2, 4] triazin-3-yl)[2, 2?] bipyridine, an effective extracting agent for the separation of americium (iii) and curium (iii) from the lanthanides. *Solvent extraction and ion exchange*, 24(4):463–483.

Geist, A., Magnusson, D., and Müllich, U. (2012). A kinetic study on the extraction of Americium (III) into CyMe$_4$-BTBP. In *Twelfth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation (12-IEMPT), Prague, Czech Republic*, pages 24–27.

Grouiller, J.-P., Pillon, S., de Saint Jean, C., Varaine, F., Leyval, L., Vambenepe, G., and Carlier, B. (2003). Minor actinides transmutation scenario studies with PWRs, FRs and moderated targets. *Journal of nuclear materials*, 320(1):163–169.

Harwood, L. M., Lewis, F. W., Hudson, M. J., John, J., and Distler, P. (2011). The separation of americium (iii) from europium (iii) by two new 6, 6'-bistriazinyl-2, 2'-bipyridines in different diluents. *Solvent Extraction and Ion Exchange*, 29(4):551–576.

Hill, C., Arnaud-Neu, F., Espartero, A., Desreux, J., Modolo, G., Bourg, S., Malmbeck, R., Caravaca, C., Harrison, M., De Angelis, G., Uhlir, J., Ouvrier, N., and Madic, C. (2007). EUROPART Final Activity Report, Contract Number: F16W-CT-2003-508 854.

Holm, M. (2012). RadTox, a computer program for assessing radiotoxicity curves for used nuclear fuel. Master's thesis, Chalmers University of Technology, Göteborg, Sweden.

Huizenga, J. R. and Magnusson, L. B. (1951). Oxidation-Reduction Reactions of Neptunium (IV) and -(V)^1. *Journal of the American Chemical Society*, 73(7):3202–3206.

IAEA (2011). Nuclear Technology Review. Technical report, IAEA, Vienna.

Ionova, G., Ionov, S., Rabbe, C., Hill, C., Madic, C., Guillaumont, R., and Krupa, J. (2001a). Mechanism of trivalent actinide/lanthanide separation using bis (2, 4, 4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) and neutral O-bearing co-extractant synergistic mixtures. *Solvent Extraction and Ion Exchange*, 19(3):391–414.

Ionova, G., Ionov, S., Rabbe, C., Hill, C., Madic, C., Guillaumont, R., Modolo, G., and Krupa, J. C. (2001b). Mechanism of trivalent actinide/lanthanide separation using synergistic mixtures of di (chlorophenyl) dithiophosphinic acid and neutral O-bearing co-extractants. *New Journal of Chemistry*, 25(3):491–501.

Law, J., Herbst, R., Todd, T., Romanovskiy, V., Babain, V., Esimantovskiy, V., Smirnov, I., and Zaitsev, B. (2001). The universal solvent extraction (UNEX) process. II. Flowsheet development and demonstration of the UNEX process for the separation of cesium, strontium, and actinides from actual acidic radioactive waste. *Solvent Extraction and Ion Exchange*, 19(1):23–36.

Löfström-Engdahl, E. (2014). *On the Diluent and Solvent Effects in Liquid-Liquid Extraction Systems based on Bis-triazine-bipyridine (BTBP) ligands*. PhD thesis, Chalmers University of Technology.

Löfström-Engdahl, E., Aneheim, E., Ekberg, C., Foreman, M., and Skarnemark, G. (2013a). Comparison of the extraction as a function of time in two GANEX solvents: Influence of metal loading, interfacial tension, and density. *Solvent Extraction and Ion Exchange*, 31(6):604–616.

Löfström-Engdahl, E., Aneheim, E., Ekberg, C., Foreman, M., and Skarnemark, G. (2014). A Comparison of Americium Extractions as a Function of Time using Two Bis-Triazine-Bipyridine Ligands in Long-Chained Alcohol Diluents. *Separation Science and Technology*, 49(13):2060–2065.

Löfström-Engdahl, E., Aneheim, E., Ekberg, C., and Skarnemark, G. (2013b). A reinterpretation of C5-BTBP extraction data, performed in various alcohols. *Journal of Radioanalytical and Nuclear Chemistry*, 296(2):733–737.

Madic, C., Hudson, M., Liljenzin, J., Glatz, J., Nannicini, R., Facchini, A., Kolarik, Z., and Odoj, R. (2000). New Partitioning Techniques for Minor Actinides. Final Report, NEWPART EUR 19149. *Nuclear Science and Technology.*

Madic, C. and Hudson, M. J. (1998). High level liquid waste partitioning by means of completely incinerable extractants. Technical Report EUR 18038, European Commission Contract No.FI2W-CT91-0112.

Madic, C., Testard, F., Hudson, M., Liljenzin, J.-O., Christiansen, B., Ferrando, M., Facchini, A., Geist, A., Modolo, G., Gonzalez-Espartero, A., and De Mendoza, J. (2004). PARTNEW New Solvent Extraction Processes for Minor Actinides, Final Report, Report CEA-R-6066.

Magnusson, D., Christiansen, B., Glatz, J.-P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., and Sorel, C. (2009a). Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors. *Radiochimica Acta International journal for chemical aspects of nuclear science and technology*, 97(3):155–159.

Magnusson, D., Christiansen, B., Malmbeck, R., and Glatz, J.-P. (2009b). Investigation of the radiolytic stability of a CyMe$_4$-BTBP based SANEX solvent. *Radiochimica Acta International journal for chemical aspects of nuclear science and technology*, 97(9):497–502.

Miguirditchian, M., Chareyre, L., Hérès, X., Hill, C., Baron, P., and Masson, M. (2007). GANEX: adaptation of the DIAMEX-SANEX process for the group actinide separation. Technical report, American Nuclear Society, 555 North Kensington Avenue, La Grange Park, IL.

Miguirditchian, M., Chareyre, L., Sorel, C., Bisel, I., Baron, P., and Masson, M. (2008). Development of the GANEX process for the reprocessing of Gen IV spent nuclear fuels. In *Proceedings Atalante*, pages 19–23.

Miguirditchian, M., Guillaneux, D., Guillaumont, D., Moisy, P., Madic, C., Jensen, M. P., and Nash, K. L. (2005). Thermodynamic study of the complexation of trivalent actinide and lanthanide cations by ADPTZ, a tridentate N-donor ligand. *Inorganic chemistry*, 44(5):1404–1412.

Mincher, B. J., Modolo, G., and Mezyk, S. P. (2009). Review article: the effects of radiation chemistry on solvent extraction: 1. conditions in acidic solution and a review of tbp radiolysis. *Solvent Extraction and Ion Exchange*, 27(1):1–25.

Nair, G., Mahajan, G., and Prabhu, D. (1995). Extraction of uranium (VI) and plutonium (IV) with some high molecular weight aliphatic monoamides from nitric acid medium. *Journal of radioanalytical and nuclear chemistry*, 191(2):323–330.

NEI (2015). Used nuclear fuel storage. http://www.nei.org/issues-policy/nuclear-waste-management/used-nuclear-fuel-storage. 2015-08-26.

Nilsson, M., Andersson, S., Drouet, F., Ekberg, C., Foreman, M., Hudson, M., Liljenzin, J.-O., Magnusson, D., and Skarnemark, G. (2006a). Extraction Properties of 6, 6'-Bis-(5, 6-dipentyl-[1, 2, 4] triazin-3-yl)-[2, 2'] bipyridinyl (C5-BTBP). *Solvent Extraction and Ion Exchange*, 24(3):299–318.

Nilsson, M., Ekberg, C., Foreman, M., Hudson, M., Liljenzin, J.-O., Modolo, G., and Skarnemark, G. (2006b). Separation of Actinides (III) from Lanthanides (III) in Simulated Nuclear Waste Streams using 6, 6'-bis-(5, 6-dipentyl-[1, 2, 4] triazin-3-yl)-[2, 2'] bipyridinyl (C5-BTBP) in Cyclohexanone. *Solvent Extraction and Ion Exchange*, 24(6):823–843.

OECD-NEA (2012). Homogeneous versus heterogeneous recycling of transuranics in fast nuclear reactors. Technical Report ISBN 978-92-64-99177-4, Organisation for Economic Co-operation and Development - Nuclear Energy Agency.

OECD-NEA (2014a). Organisation for Economic Co-operation and Development – Nuclear Energy Agency; Nuclear Energy Data. http://www.oecd-nea.org/ndd/pubs/2014/7197-bb-2014.pdf. 2015-07-13.

OECD-NEA (2014b). Technology Roadmap Update for Generation IV Nuclear Energy Systems. https://www.gen-4.org/gif/upload/docs/application/pdf/2014-03/gif-tru2014.pdf. 2015-07-13.

Okushita, H., Yoshikawa, M., and Shimidzu, T. (1995). Pervaporation of cyclohexane/cyclohexanone/cyclohexanol mixture through polyoxyethylene grafting nylon 6 membrane. *Journal of membrane science*, 105(1):51–53.

Pearson, R. G. (1968). Hard and soft acids and bases, HSAB, part ii: underlying theories. *Journal of Chemical Education*, 45(10):643.

Prabhu, D., Mahajan, G., and Nair, G. (1997). Di (2-ethyl hexyl) butyramide and di (2-ethyl hexyl) isobutyramide as extractants for uranium (VI) and plutonium (IV). *Journal of radioanalytical and nuclear chemistry*, 224(1-2):113–117.

Retegan, T., Ekberg, C., Dubois, I., Fermvik, A., Skarnemark, G., and Wass, T. J. (2007a). Extraction of actinides with different 6, 6'-bis (5, 6-dialkyl-[1, 2, 4]-triazin-3-yl)-[2, 2']-bipyridines (BTBPs). *Solvent Extraction and Ion Exchange*, 25(4):417–431.

Retegan, T., Ekberg, C., Englund, S., Fermvik, A., Foreman, M., and Skarnemark, G. (2007b). The behaviour of organic solvents containing C5-BTBP and CyMe$_4$-*btbp* at low irradiation doses. *Radiochimica Acta*, 95(11):637–642.

Rice, N., Irving, H., and Leonard, M. (1993). Nomenclature for liquid-liquid distribution (solvent extraction)(iupac recommendations 1993). *Pure and applied chemistry*, 65(11):2373–2396.

Riddick, J. A., Bunger, W. B., and Sakano, T. (1970). Techniques of chemistry. In *Organic solvents*, volume 2. Wiley-Interscience New York.

Ritcey, G. M. (2004). *Solvent Extraction Principles and Practice*, chapter 7. Marcel Dekker, New York, 2 edition.

Romanovskiy, V., Smirnov, I., Babain, VA andTodd, T., Herbst, R., Law, J., and Brewer, K. (2001). The universal solvent extraction (UNEX) process. I. Development of the UNEX process solvent for the separation of cesium, strontium, and the actinides from acidic radioactive waste. *Solvent Extraction and Ion Exchange*, 19(1):1–21.

Rydberg, J., Musikas, C., Choppin, G., and Sekine, T. (2004). *Solvent Extraction Principles and Practice*, chapter 4. Marcel Dekker, New York, 2 edition.

Rzhekhina, E., Karkozov, V., Alyapyshev, M. Y., Babain, V., Smirnov, I., Todd, P., Law, J., and Herbst, R. (2007). Reprocessing of spent solvent of the UNEX process. *Radiochemistry*, 49(5):493–498.

SACSESS (2013). SACSESS: Safety of ACtinide Separation proceSSes. http://www.sacsess.eu/. 12 March 2014.

Sailor, W. C., Bodansky, D., Braun, C., Fetter, S., and van der Zwaan, B. (2000). A nuclear solution to climate change? *Science*, 288(5469):1177.

Salvatores, M., Slessarev, I., Ritter, G., Fougeras, P., Tchistiakov, A., Youinou, G., and Zaetta, A. (1998). Long-lived radioactive waste transmutation and the role of accelerator driven (hybrid) systems. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 414(1):5–20.

Schulz, W. and Navratil, J. (1984). *Science and Technology of Tributyl Phosphate. Vol. 1.* CRC Press Inc.

Shevchenko, V. and Smelov, V. (1958). The effect of mono-and dibutyl phosphates on the extraction of plutonium with tributyl phosphate. *The Soviet Journal of Atomic Energy*, 5(5):1455–1459.

Sinha, P., Kumar, S., Kamachi Mudali, U., and Natarajan, R. (2011). Thermal stability of UNEX/HCCD-PEG diluent FS-13. *Journal of Radioanalytical and Nuclear Chemistry*, 289(3):899–901.

SKB (2006). Long-term Safety for KBS-3 Repositories at Forsmark and Laxemar – A First Evaluation, Main Report of the SR-Can Project. Technical Report TR-06-09, Svensk Kärnbränslehantering AB, Stockholm, Sweden.

SSM (2015). Slutförvar för använt kärnbränsle. http://www.stralsakerhetsmyndigheten.se/start/slutforvar/Slutforvar-for-anvant-karnbransle/. 2015-09-29.

Taylor, R., Gregson, C., Carrott, M., Mason, C., and Sarsfield, M. (2013). Progress towards the full recovery of neptunium in an advanced purex process. *Solvent Extraction and Ion Exchange*, 31(4):442–462.

Thomas, J. R. and Spring, S. (1958). Solvent extraction process for plutonium, United States Patent Office, Patent no 2,924,506. Technical report, Applied 26-07-1949. Patented 26-08-1958.

Trumm, S., Geist, A., Panak, P. J., and Fanghänel, T. (2011). An improved hydrolytically-stable bis-triazinyl-pyridine (btp) for selective actinide extraction. *Solvent Extraction and Ion Exchange*, 29(2):213–229.

van der Zwaan, B. (2013). The role of nuclear power in mitigating emissions from electricity generation. *Energy Strategy Reviews*, 1(4):296–301.

Warf, J. C. (1949). Extraction of cerium (IV) nitrate by butyl phosphate. *Journal of the American Chemical Society*, 71(9):3257–3258.

Weast, R. C., editor (1975-1976). *Handbooks of Chemistry and Physics*, chapter D, page 238. CRC Press, Cleveland, Ohio, 56 edition.

Weaver, B. and Kappelmann, F. (1964). TALSPEAK: A new method of separating americium and curium from the lanthanides by extraction from an aqueous solution of an aminopolyacetic acid complex with a monoacidic organophosphate or phosphonate. Technical report, Oak Ridge National Lab., Tenn.

Zhang, Y., Valiente, M., and Muhammed, M. (1989). Extraction of nitric and phosphoric acids with tributyl phosphate. *Solvent extraction and ion exchange*, 7(2):173–200.