Octanol as Diluent in a Grouped ActiNide EXtraction Process

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Abstract

Since the beginning of the development of nuclear power plants nuclear energy has played a significant role in the worldwide electricity supply. More than 20% of the total electricity in the world comes from nuclear power plants. Nuclear energy has both advantages and disadvantages. On one hand, it contributes to clean energy in terms of low greenhouse gas emissions, and on the other hand, it causes problems with radioactive waste. By the end of May 2016, 444 nuclear reactors were in operation for the worldwide electricity generation. 63 new reactors are under construction, meaning that a large amount of nuclear waste has to be handled every year. Used nuclear fuel is highly radiotoxic when it is discharged from the reactor and has to be stored for at least 100,000 years for the radiotoxicity to reach the same level as the natural uranium needed to produce one tonne of enriched fuel. The storage time could, however, be reduced to around 1,000 years if the long-lived actinides are separated from the rest of the used nuclear fuel and transmuted into the short-lived or even stable isotopes. One of the separation methods are liquid-liquid extraction, where several different processes have been developed during the years. One of them is the GANEX (Grouped ActiNide EXtraction) process, which is still under development with the purpose of extracting all the actinides together as a group from the lanthanides and the other fission products. In order to reach a promising separation, different diluents and extraction agents are under investigation.

In this work, the Chalmers GANEX process has been investigated using 6,6´-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2´]bipyridine (CyMe$_4$-BTBP) and tri-butyl phosphate (TBP) as extraction agents and 1-octanol as diluent. This system has also been compared with another system using FS13 (Phenyl Trifluoromethyl Sulfone) as diluent. Extraction of both active and inactive metal ions has been investigated. The experiments shows that both systems have a high actinide extraction and low extraction of the majority of both the lanthanides and the other fission products. In comparison with the FS13 based GANEX system the 1-octanol based GANEX system has a slightly higher extraction of both americium and curium but a lower extraction of both uranium and plutonium. The time to reach extraction equilibrium is slower for all actinides in the 1-octanol based GANEX system compared to the FS13 based GANEX system. Investigations with different volumes of TBP in the 1-octanol based GANEX system shows that the extraction of plutonium and europium increases with an increasing TBP concentration while the there is no big difference in the europium extraction.

Keywords: Solvent Extraction, GANEX, 1-octanol, CyMe$_4$-BTBP and TBP.

Contents

LIST OF ABBREVIATIONS

ADS	Accelerator Driven System
BTBP	Bis-triazine bi-pyridine
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
FS13	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
MOX-fuel	Mixed Oxide Fuel
NEA	Nuclear Energy Agency
NEI	Nuclear Energy Institute
OECD	Organization for Economic Co-operation and Development
PUREX	Plutonium Uranium Reduction EXtraction
P&T	Partitioning and Transmutation
SANEX	Selective ActiNide Extraction
SF	Separation Factor
TBP	Tri-Butyl Phosphate
tHM	Tonne of Heavy Metals
TODGA	N,N,N’,N’-tetraoctyl diglycolamide

1. Introduction and Background

The worldwide electrical energy demand is high and is increasing every day due to an increasing population [1]. Electrical energy has played an important role for both developed and developing countries [2]. Developing countries need a big amount of energy to keep developing and developed countries needs energy to maintain the industry and welfare. The electrical energy generation has, however, caused several severe environmental problems such as global warming, wild fire, flooding, depletion of the ozone layer, etc. These natural disasters are mainly caused by fossil fuel burning and greenhouse gas emissions. It has been suggested that green energy should replace the fossil fuel energy in order to approach the 2 ˚C target, meaning that the global temperature increase should not exceed 2 degrees [3]. Nuclear energy is one of the green energy alternatives [4]. By the end of May 2016, 444 reactors were in operation, worldwide, for the production of electricity and 63 new nuclear power plants are under the construction in 15 different countries [5]. In Sweden of the year 2015, 34.3% of the electrical energy comes from nuclear power plants and 10 different reactors are operable [5].

Over the years several different types of nuclear reactors have been developed. A common way of categorizing nuclear reactors and nuclear reactor engineering is by generations. Generation I reactors are prototype nuclear reactors mainly developed as a proof of concept, it was launched around 1950s and 1960s [6]. Generation II reactors are commercial reactors and the reactor type that is used worldwide today. They started to be in operation from the late 1960s [6]. Generation III reactors are basically an upgrade of the Generation II reactors with improvements like; more reliable safety system, higher thermal efficiency and modularized construction. The Generation III+ reactors are even further developed Generation III reactors with an enhanced passive safety system [6]. The Generation IV concept includes a full fuel cycle i.e. both reactor and recycling and is currently under development [6] and is expected to be in use around year 2030 [7]. The generation IV concept aims to follow six different characters; sustainability, safety and reliability, economic competitiveness, proliferation resistance and physical protection [8].

There are currently three main strategies how to deal with used nuclear fuel. The “once through” method where the nuclear fuel is only used once and then placed in a final repository. The “reprocessing” method where the used fuel will be sent to a reprocessing plant to extract the remaining uranium and plutonium to manufacture new fuel. The third option is called ′′recycling′′ and recycles not only the uranium and plutonium but also the minor actinides (neptunium, americium and curium) [9][10]. In Sweden the once through cycle is employed, many other countries are, however, indecisive on how to handle their used nuclear fuel.

1.1 Nuclear Waste

In 2014, roughly 10,000 t HM (tonne of heavy metals) of used nuclear fuel were discharged from nuclear power plants all over the world. The total amount of used nuclear fuel is around 380,500 t HM, where 258,700 t HM are stored in intermediate repository sites and the rest are still stored at the nuclear power plants [11]. Since the used nuclear fuel is highly radiotoxic is it necessary to isolate it from the environment. It takes around 100,000 years until the radiotoxicity of the used nuclear fuel reaches the same level as the natural uranium needed to produce one ton of enriched fuel [12], figure 1.1. The radiotoxicity is mainly caused by long-lived actinides [13] and in order to reduce the storage time and decrease the heat load of the final repository these long-lived actinides can be separated from the used nuclear fuel. The separated elements can then be transmuted into short-lived or stable nuclides. This method is called “P&T” (Partitioning and Transmutation) and fast reactors using ADS (Accelerator Driven System) are based on the concept of transmutation [14].

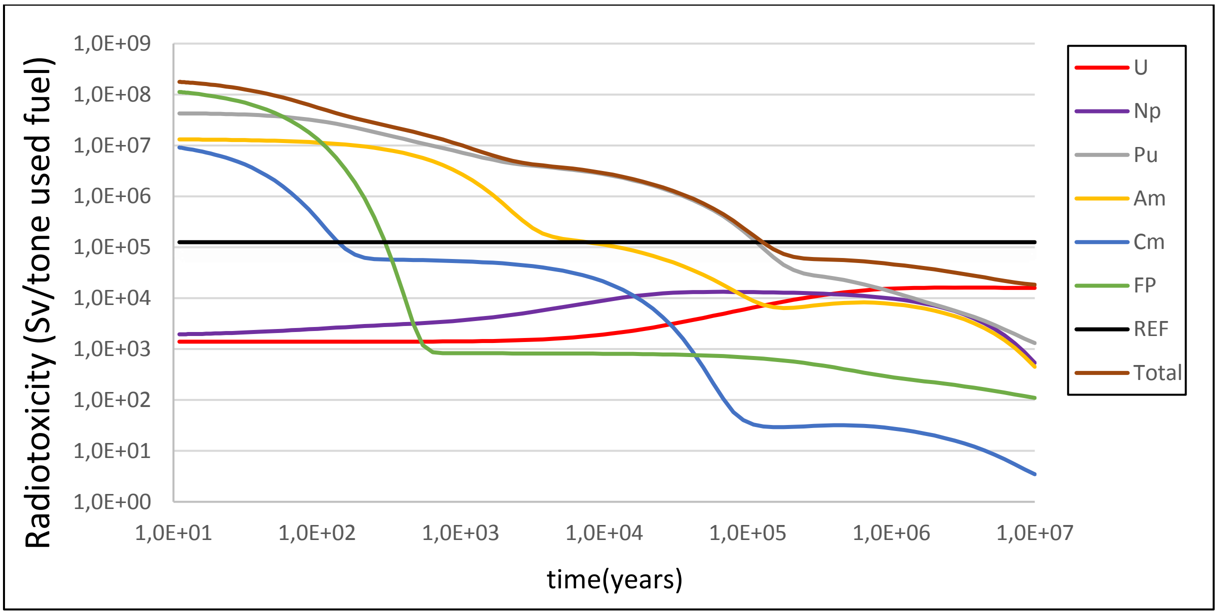

Figure 1.1. Radiotoxicity of used nuclear fuel (UO_X fuel, 4% enrichment, burnup 45 GW and 10 years cooling time) over time. The reference is the amount of natural uranium needed to produce 1 ton of enriched fuel (ICRP) [15].

1.2 Once through

The once through fuel cycle is a method were the nuclear fuel is only used once, which means that the discharged fuel will be sent to a final repository or other storage facilities instead of being reused [16]. The once though cycle requires, due to this, a large repository located e.g. underground in order to be isolated from the environment. Currently, the once through method is applied in Sweden.

1.3 Reprocessing

In the reprocessing method uranium and plutonium is recovered from the used fuel to allow for manufacturing of new fuel. Liquid-liquid extraction, also known as solvent extraction, is a common method for separation of actinides from used nuclear fuel. Solvent extraction has been used for several decades to extract uranium and plutonium from used nuclear fuel. The commonly used solvent extraction process is the PUREX (Plutonium and Uranium Reduction EXtraction) process which was originally developed in the United States of America during the Manhattan Project in the 1940s. The main purpose of the process was to produce pure plutonium streams to be used for the production of nuclear weapons [17]. The PUREX process is a reprocessing process and today the PUREX process is mainly used to produce MOX (mixed oxide) fuel [18]. After the PUREX process, long-lived actinides are, however, still present in the used fuel and it has to be stored for a long time. The pure plutonium stream produced in a PUREX process also poses a threat to the nuclear proliferation resistance, which is one of the characteristics of the Generation IV concept. Since the PUREX process does not meet the Generation IV criteria it cannot be used in a Generation IV system and an alternative process has to be developed [19].

1.4 Recycling

In the recycling method all the long-lived actinides are recovered from the used nuclear fuel, instead of only uranium and plutonium, as in reprocessing. A recycling process can decrease the long-term radiotoxicity of the used nuclear fuel [20] as well as reducing the heat load of the fuel making the final repository more volume efficient [21].

One recycling process is the GANEX (Grouped ActiNides EXtraction) process which currently is under development. The GANEX process consists of two cycles. The first cycle were the bulk uranium is extracted from the rest of the used nuclear fuel and the second cycle were the remaining uranium as well as the other actinides are extracted from both the fission and corrosion products. There are three different GANEX processes in Europe, the CEA GANEX process, the EURO GANEX process and the Chalmers GANEX process.

The CEA GANEX process, developed in France, separates all the transuranic elements and the lanthanides from the other fission products. The actinides are then stripped selectively. In the CEA GANEX process N,N’-(dimethyl)-N,N’-dioctyl-hexylethoxy-malonamide (DMDOHEMA) and di(2-ethylhexyl)phosphoric acid (HDEHP) have been selected as extractants [22][23].

The EURO GANEX process is similar to the CEA GANEX process it, however, uses a different combination of extractants, DMDOHEMA and N,N,N’,N’-tetraoctyl diglycolamide (TODGA). The EURO GANEX process is able to extract actinides and lanthanides successfully. Some difficulties during the separation of the lanthanides from the actinides have, however, been found [24][25].

The Chalmers GANEX process, developed at Chalmers University of Technology, combining 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) and TBP (tri-butyl phosphate) in different diluents has shown promising results regarding both extraction and separation [26][27] as well as in hydrolytic and radiolytic stability [28].

1.5 Chalmers GANEX

1.5.1 Extractants

Two different extraction agents, CyMe$_4$-BTBP and TBP, have been investigated for use in the Chalmers GANEX process. The combination was chosen due to their good ability to extract the relevant actinides [29]. CyMe$_4$-BTBP, figure 1.2 left, is a BTBP (bis-triazine bi-pyridine) type ligand which are a polyaromatic nitrogen donor ligand that is able to bind metal ions as tetradentate complexes. CyMe$_4$-

BTBP has been developed and synthesised to extract tri- and pentavalent actinides. The TBP ligand, figure 1.2 right, has been used during decades and is used to extract tetra- and hexavalent actinides [15][30]. Due to this, the necessity of redox control can be avoided by using a combination of $CyMe_4$-BTBP and TBP.

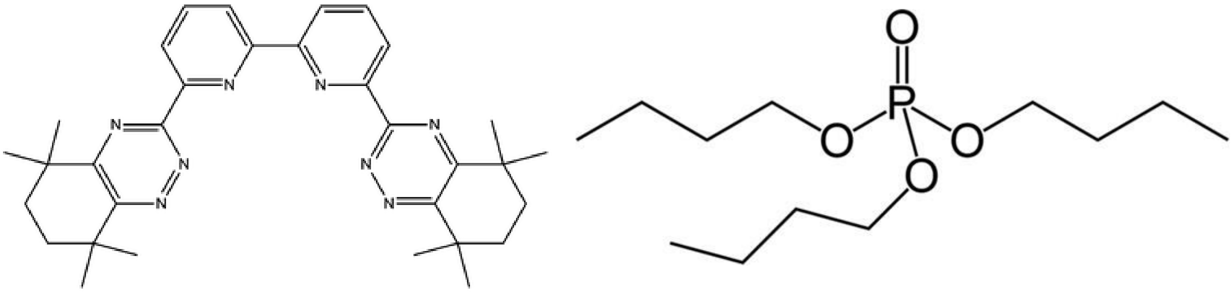

Figure 1.2. Molecular structure of 6,6´-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2´]bipyridine ($CyMe_4$-BTBP) (left) and Molecular structure of tri-butyl phosphate (TBP) (right).

1.5.2 Diluents

Several different diluents have been investigated during the development of the Chalmers GANEX process. Initially, cyclohexanone was used and has shown several advantages like a good extraction of actinides from 4 M nitric acid [32][33] and a maintained high extraction during both radiolysis and hydrolysis [26][30][31]. There are, however, some drawbacks, cyclohexanone has a low flash point (44°C) [34] and it reacts exothermically in combination with concentrated nitric acid [35]. It has a comparably high solubility within the acidic aqueous phase decreasing the stability of the diluent. Several fission products, such as e.g. technetium are to some extent extracted [33]. In this work, a 1-octanol, figure 1.3 left, based system has been investigated and compared with a FS13, figure 1.3 right, based system. The FS13 based system has shown promising preliminary results as a GANEX solvent [36]. Both 1-octanol and FS13 have a higher flash point, (81.1°C and 122°C respectively [34]), than cyclohexanone. 1-octanol has a lower density than both cyclohexanone, FS13 and nitric acid [34] that is used as aqueous phase. This might cause a problem after the metal extraction when the organic phase becomes heavier and the density between the organic and the aqueous phases decrease, making them harder to separate from each other. FS13 has a good hydrolytic stability against nitric acid as well as a good stability towards radiolysis [36] it, however, does not follow the CHON principle. The CHON principle refers to materials only consisting of carbon, hydrogen, oxygen and nitrogen. These materials can be considered to be more or less fully combustible [37].

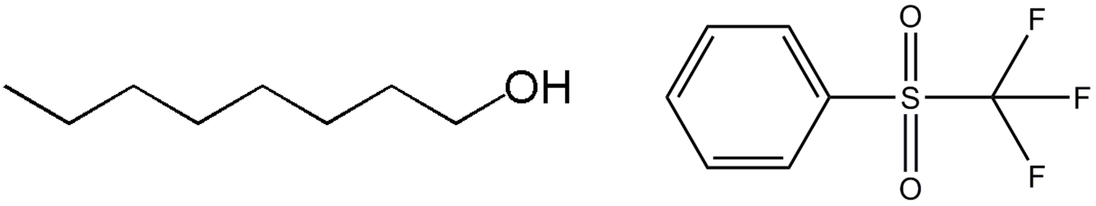

Figure 1.3. Molecular structure of 1-octanol (left) and molecular structure of phenyl trifluoromethyl sulfone (FS13) (right).

2. Theory

2.1 Liquid-Liquid Extraction

The term liquid-liquid extraction refers to the distribution of a solute in two immiscible liquid phases which, in this case, are exemplified as an organic phase and an aqueous phase. In this case, solutes consisting of metal ions are used and are originally added into the aqueous phase. The organic phase contains the diluent and the extractants. After an adequate time of phase contact, the maximum amount of metals have been transferred from the aqueous phase to the organic phase [38].

2.1.1 Distribution Ratio and Separation Factor

The metal distribution between the two immiscible liquid phases after extraction is referred to as the distribution ratio, D, which refers to the ratio of the solutes in the different phases [39].

$$Distribution\ Ratio = \frac{Metal\ concentration\ of\ solutes\ in\ \ the\ organic\ phase}{Metal\ concentration\ of\ solutes\ in\ the\ aqueous\ phase} \qquad (2.1)$$

For example:

$$Organic\ phase\colon 2HA \leftrightarrows H_2A_2$$

$$\upharpoonleft\downharpoonright$$

$$Aqueous\ phase\colon HA \leftrightarrows H^+ + A^-$$

The organic phase contains both HA and H_2A_2, the aqueous phase contains HA, A^- and H^+. According to definitions the distribution ratio of A should be:

$$D_A = \frac{[A]_{org,tot}}{[A]_{aq,tot}} = \frac{[HA]_{org}+2[H_2A_2]_{org}}{[HA]_{aq}+[A^-]_{aq}} \qquad (2.2)$$

In order to simplify the equation of the distribution ratio, it can be assumed that the solute exists in a single molecular form in the system, called nonreactive extraction systems.

The separation factor, SF, evaluates the separation of one solute from another solute. It can be calculated by using the distribution ratio of two solutes, for example:

$$SF_{A/B} = \frac{D_A}{D_B} \qquad (2.3)$$

The separation factor of solute A over solute B is defined to be larger than 1, i.e. the distribution ratio of solute A should be larger than the distribution ratio for solute B.

2.1.2 Kinetics and Equilibrium

Different chemical systems have different reaction rates as well as different matter transfer rates. The principle of solvent extraction is to transfer the formed complex (with desired solutes) from the aqueous phase to the organic phase. The equilibrium kinetics of the solvent extraction system determines the speed of the extraction approaching equilibrium, i.e. faster kinetics will accelerate the extraction approaching equilibrium [40].

There are several parameters affecting the extraction kinetics such as the temperature during extraction and the area of phase contact [40].

2.1.3 Stripping

The last step of a liquid-liquid extraction process is most often stripping of the solutes, in this case actinides, from the organic phase into an aqueous phase. An aqueous phase with a lower acidity can e.g. be used to strip the actinides from the loaded organic phase. There are, however, several difficulties in performing a successful stripping process. Two difficulties that may occur are stripping of unwanted metal ions that previously have been co-extracted and back-extraction of nitric acid. A possible solution is to add pre-wash steps [40] with a high nitrate concentration in order to make the desired metal ions (actinides) stay in the organic phase, equation 2.4, while removing acid and possibly the undesired metal ions [41].

$$M^{n+} + n\,NO_3{}^- + a\,\overline{BTBP} + b\,\overline{TBP} \leftrightarrow \overline{M(NO_3)_n(BTBP)_a(TBP)_b} \tag{2.4}$$

2.2 Lanthanides, Actinides and Fission Products

Both lanthanides and actinides are positioned close to each other in the periodic table. Most elements found in used nuclear fuel are formed due to fission reactions. New minor actinides are, however, also formed due to neutron absorption and radioactive decay in high-flux nuclear reactors, for example equation 2.5 - 2.7:

$$^{239}_{94}Pu + n \rightarrow {}^{240}_{94}Pu \tag{2.5}$$

$$^{240}_{94}Pu + n \rightarrow {}^{241}_{94}Pu \tag{2.6}$$

$$^{241}_{94}Pu \rightarrow \beta^- + {}^{241}_{95}Am \tag{2.7}$$

Where Am-241 is formed by two successive neutron absorption of Pu-239 and a beta decay of Pu-241 [42].

The lighter actinides have several oxidation states due to the small energy difference between 5f and 6d orbitals. The heavier actinides (from Am to Lr) exhibit a main oxidation state of 3+, which is the same as the lanthanides [43]. Since both the heavier actinides and all of the lanthanides have a main oxidation state of 3+ it can be hard to separate them from each other.

Apart from actinides and lanthanides also some of fission products, see figure 2.4.1, are formed in the reactor. In general, the fissile materials in commercial reactors mainly consists of U-235 and Pu-239 that is build up by neutron capture of uranium during operation, and the main fission products can be found between the masses of 75 and 160, figure 2.4.1. The most abundant fission products are: Se, Rb, Sr, Y, Zr, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Sn, Sb, Te, Cs, and Ba [44].

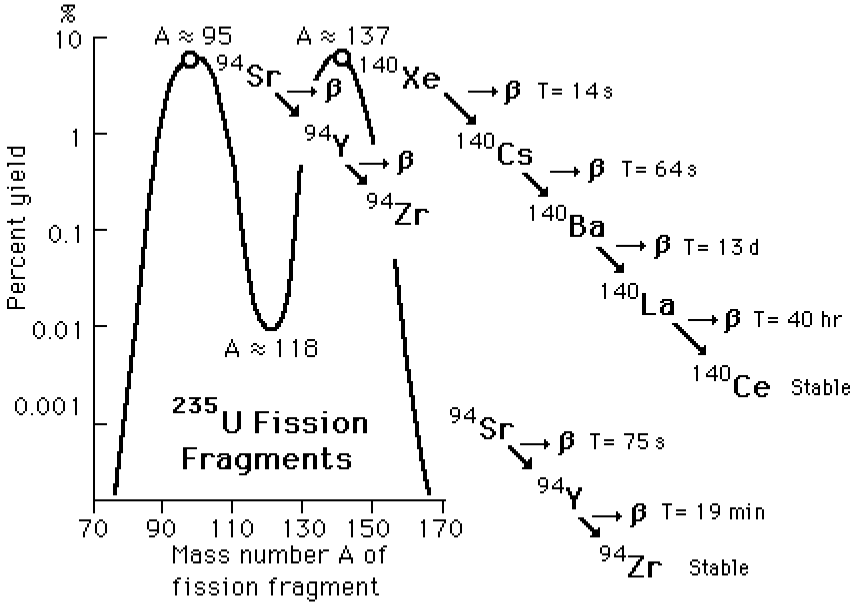

Figure 2.4.1. Fission products of uranium [45].

3. Experimental

In the majority of the experiments performed in this work, the same composition of the organic phase has been used. As extractants 10 mM CyMe$_4$-BTBP and 30%$_{vol}$ TBP were used and as diluent 1-octanol was used in most cases. This solvent composition is from now on called “the 1-octanol based GANEX system”. In some cases FS13 was used as diluent and this solvent composition is from now on called “the FS13 based GANEX system”. In all cases an aqueous phase containing of 4 M HNO$_3$ was used.

Several different sets of extraction experiments were performed during this work. All of them conducted in similar ways and with triplicate samples for the purpose of uncertainties, in this case calculated standard deviations.

3.1 Solvent Extraction Experiments

3.5 mL glass vials with plastic lids were used as phase contacting vessels. Equal amounts of the organic and aqueous phases were used, usually between 0.3 mL – 1 mL of each phase. The metals were added in trace amounts (5-10 µL) from stock solutions: U(VI)-235 (84.44% enrichment, 40 mM), Pu(IV)-238 (0.28 Bq mL^{-1}), Am(III)-241 (0.42 MBq mL^{-1} or 2.4 MBq mL^{-1}), Cm(III)-244 (0.23 MBq mL^{-1}) and Eu(III)-152 (23 kBq mL^{-1}). The extraction of lanthanides and the other fission products was performed using inactive metal ion solutions (concentrations are presented in appendix 1). The phase contact was facilitated using a shaking machine (IKA, VIBRAX VXR 1,500 rpm) at 25 ^{o}C for up to one and a half hour.

3.2 Analysis

In order to analyze the radioactive samples two different measurement methods was used, gamma spectrometry and liquid scintillation counting. The inactive samples were measured using an inductively coupled plasma mass spectrometry.

3.2.1 Gamma Spectrometry

A HPGe (high purity germanium detector) was used for the measurement of most of the samples containing americium and europium (Canberra, Gamma Analyst GEM 23195 or Ortec, GEM 15180-S). For americium the gamma energy of 59.6 keV was used and the gamma energy of 121.8 keV was used for europium. Some of the americium and europium samples were, however, measured using a NaI (Sodium Iodide) detector (Intertechnique CG, 4000 Gamma Counter). For all samples 100 uL of each phase was placed in a plastic vial and measured until the measurement uncertainty was less than 5%.

In order to guarantee the accuracy of the measurements each batch of samples were measured by the same detector.

3.2.2 Liquid Scintillation Counting

The samples containing plutonium, uranium or curium were measured using a liquid scintillation counting detector (Wallac, 1414 WinSpectral). For each sample and phase, 100 uL was removed and added into a scintillation vial (7.5 mL) and mixed with 5 mL scintillation cocktail (Ultima Gold AB, Perkin Elmer). Each sample was measured until the measurement uncertainty was less than 5%.

No quenching was observed using 1-octanol as diluent within the used concentration range.

3.2.3 Inductively Coupled Plasma Mass Spectrometry

The ICP-MS (inductively coupled plasma mass spectrometry) (Thermo Scientific, I CAPQ, ICP-MS) was used for the samples containing non-radioactive fission products. Every sample was diluted to an appropriate concentration, 10 – 50 ppb metal, corresponding to the requirement of the ICP-MS. Both the aqueous phases and the stock solutions were measured.

The concentration of the organic phase was calculated according to equation (3.1), due to ICP-MS is not able to measure the organic phase. This method is mainly based on an assumption that there is no or very little interfacial phenomena or precipitation appearing in the interface between the organic and aqueous phase, which means the solutes must be either in the organic phase or in the aqueous phase. It requests that the distribution ratio should be staying within the detection limits, usually between 0.1 and 10, and the reliability would be lost once very large or small distribution ratio is obtained.

$$\text{Concentration}_{\text{Org}} = \text{Concentration}_{\text{Stock}} - \text{Concentration}_{\text{Aq}} \tag{3.1}$$

$\text{Concentration}_{\text{Org}}$: metal concentration in the organic phase after extraction.

$\text{Concentration}_{\text{Stock}}$: metal concentration in the aqueous phase before extraction.

$\text{Concentration}_{\text{Aq}}$: metal concentration in the aqueous phase after extraction.

4. Results and Discussions

All the experiments were performed as described in section 3. The aqueous phase used in all experiments was 4 M HNO_3 and as organic phase a mixture of 70%$_{vol}$ diluent, 30%$_{vol}$ TPB and 10 mM $CyMe_4$-BTBP was used, unless otherwise stated. The uncertainties are calculated standard deviations.

4.1 Equilibrium Kinetics

The equilibrium kinetics describes the time it takes for an extraction system to reach the maximum metal extraction for the purpose of investigating the extraction rate. Equilibrium kinetics of systems using either 1-octanol (1-octanol will from now on be referred to as octanol) or FS13 as diluent were investigated.

4.1.1 Extraction of actinides and europium

The results in figure 4.1.1 show that for the octanol based GANEX system it takes around 60 minutes to reach equilibrium for all actinides except uranium which reaches extraction equilibrium more or less instantly. The distribution ratios of uranium, plutonium, americium and curium are all higher than europium. Americium and curium are the actinides with the highest distribution ratios while uranium has the lowest. Americium and curiums extraction curves have more or less the same shape which indicates that they have similar extraction properties.

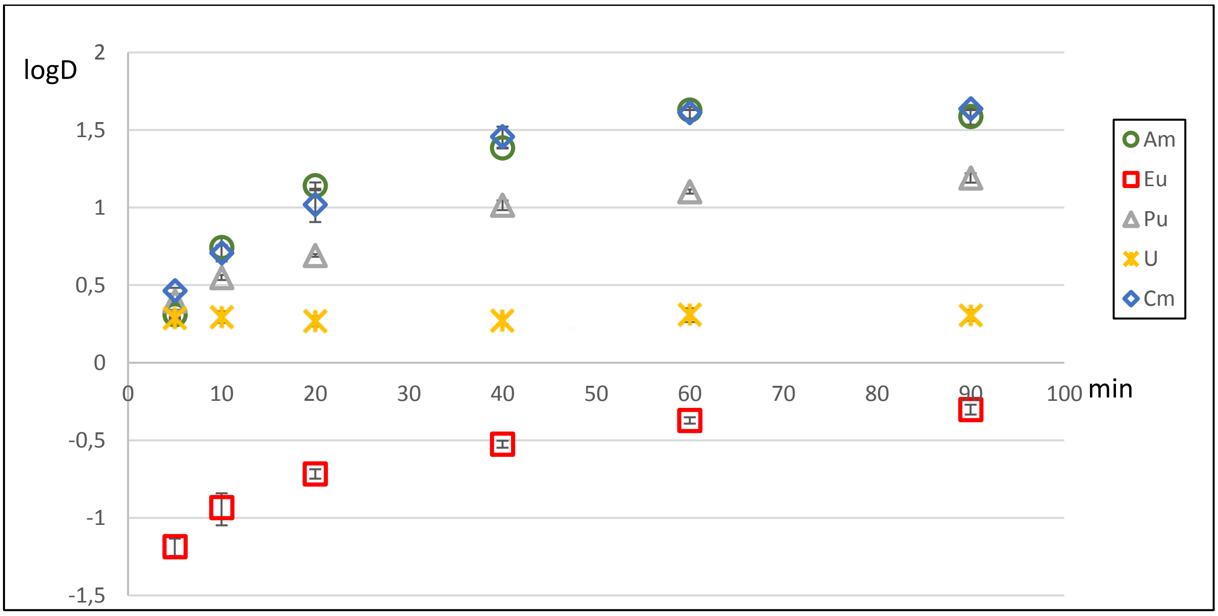

Figure 4.1.1. Logarithmic distribution ratios over time for uranium, plutonium, americium, curium and europium using octanol as diluent.

For the FS13 based GANEX system both americium and europium reaches equilibrium after around 20 minutes of phase contact time, figure 4.1.2., and the americium extraction is higher than the extraction of europium.

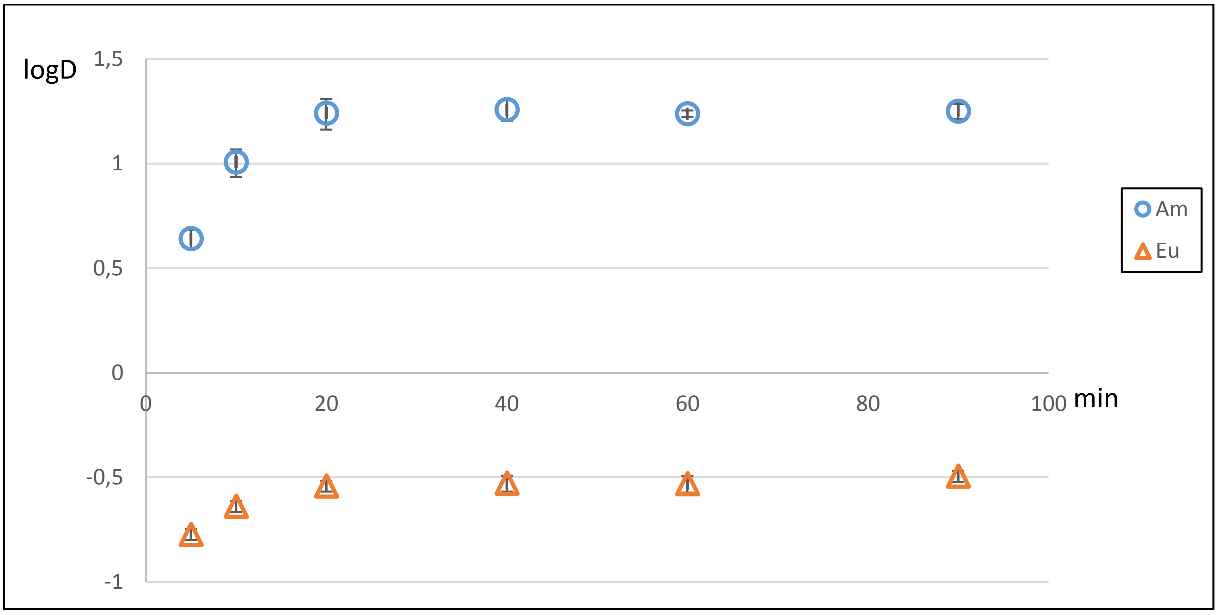

Figure 4.1.2. Logarithmic distribution ratios over time for americium and europium using FS13 as diluent.

Comparing the results using FS13 as diluent, in figure 4.1.2, with the results of the octanol based GANEX system, in figure 4.1.1, it can be seen that the extraction of americium and europium is slower in the octanol based GANEX system. The FS13 based GANEX system reaches full extraction after 20 minutes compared to the octanol based GANEX system which reaches full extraction after 60 minutes. The distribution ratios are, however, higher in the octanol based GANEX system when it has reached equilibrium, 40 and 0.5 for americium and europium respectively compared to… for the FS13 based GANEX system. Previously investigated Chalmers GANEX processes, the cyclohexanone based GANEX system and the hexanol based GANEX system, reaches full extraction after 20 minutes of phase contact time, similar to the FS13 based GANEX system[33][46].

In order to evaluate the distribution ratios of the actinides compared to europium, used as reference for the lanthanides, the separation factors were calculated, Table 4.1.1-4.1.2.

Table 4.1.1: Separation factors for selected actinides over europium in the octanol based GANEX system.

Octanol	Am/Eu	Pu/Eu	U/Eu	Cm/Eu	Am/Cm
SF	85 ± 7	31 ± 5	4 ± 0.7	87 ± 9	0.9 ± 0.02

Table 4.1.2: Separation factors for selected actinides over europium in the FS13 based GANEX system [36].

FS13	Am/Eu	Pu/Eu	U/Eu	Cm/Eu	Am/Cm
SF	84 ± 4	120 ± 18	44 ± 6	56 ± 6	1.5 ± 0.2

The two systems have similar separation factors regarding americium over europium. The octanol based GANEX system has 1.5 times higher separation factor for curium over europium compared to the FS13 based GANEX system. The separation factors for uranium and plutonium over europium are, however, around 4 and 10 times lower in the octanol based GANEX system compared to the FS13 based GANEX system. From this point of view the FS13 based GANEX system has a better capability to separate both plutonium and uranium from europium compared to the octanol based GANEX system. The octanol based GANEX system also has issues separating uranium from europium, which needs to be further investigated.

4.1.2 Extraction of fission products

In figure 4.1.3 can it be seen that the major fission products cadmium, palladium, molybdenum and cesium have a fast extraction rate and that the octanol based GANEX system reaches extraction equilibrium more or less immediately (after around 5 minutes of phase contact time). The octanol based GANEX system has a high extraction of both cadmium and palladium with distribution ratios around 1300 and 115 respectively. The molybdenum extraction is high as well with a distribution ratio of 13. The extraction of cesium is, however, low and the yttrium extraction was below the determination limit of the ICP-MS which is why it is not included in the figure.

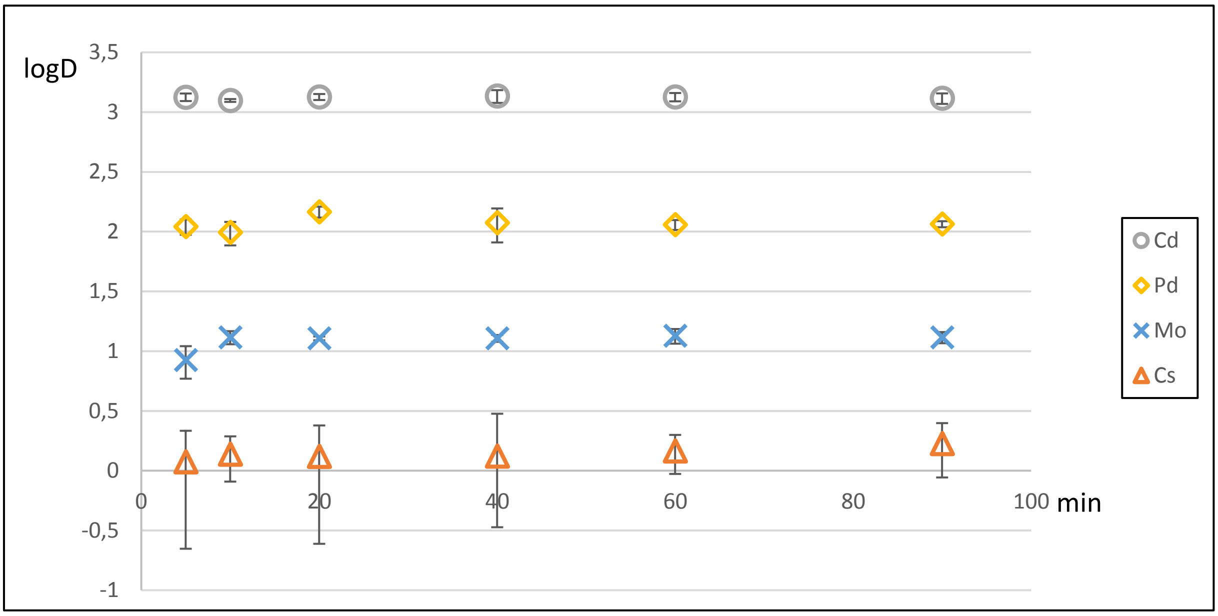

Figure 4.1.3. Logarithmic distribution ratios over time for molybdenum, cesium, cadmium and palladium using octanol as diluent.

In figure 4.1.4 can it be seen that all metal ions except molybdenum reaches extraction equilibrium more or less immediately (around 5 minutes of phase contact time) using the FS13 based GANEX system. It takes around 40 minutes for molybdenum to reach equilibrium. Compared with the octanol based GANEX system the extraction of cadmium, palladium and molybdenum are higher in the FS13 based GANEX system with distribution ratios of roughly 1400, 260 and 71 respectively. Both systems extract cesium to some extent and more or less no yttrium.

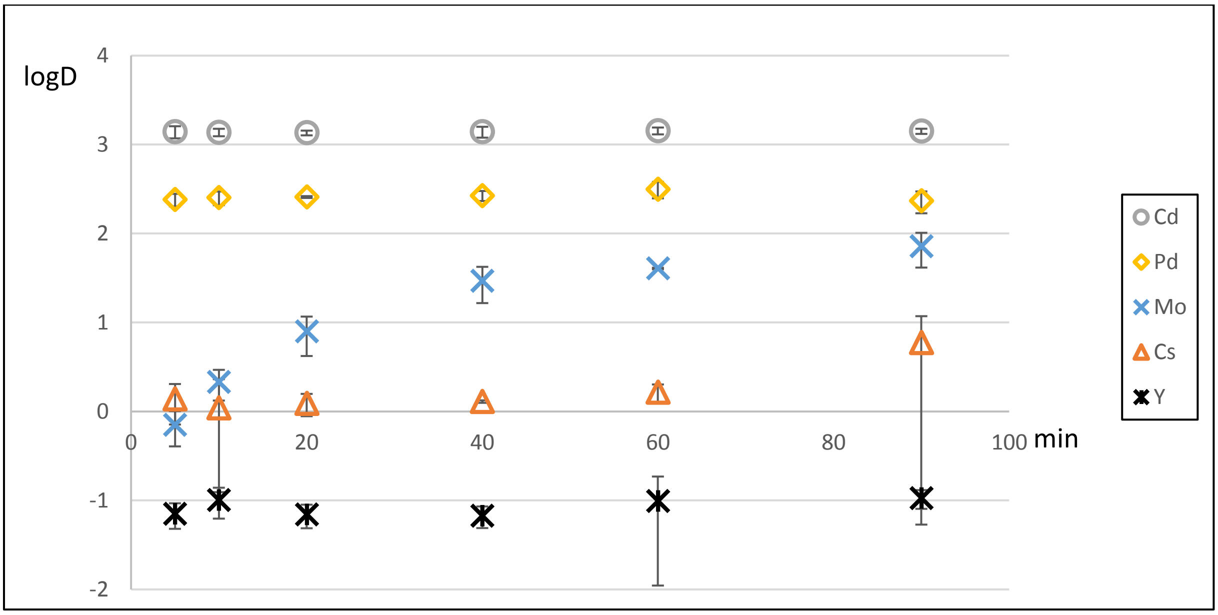

Figure 4.1.4. Logarithmic distribution ratios over time for molybdenum, cesium, cadmium, palladium and yttrium using FS13 as diluent.

Antimony and zirconium are slightly extracted in the octanol based GANEX system, figure 4.1.5. It, however, extracts silver to a considerable amount with a distribution ratio of 100 after 90 minutes of phase contact time. In the FS13 based GANEX system, figure 4.1.6, antimony reaches full extraction instantly, while zirconium reaches full extraction after 20 minutes. The extraction of silver is high in both systems and does not reach extraction equilibrium within the time-frame of this experiment.

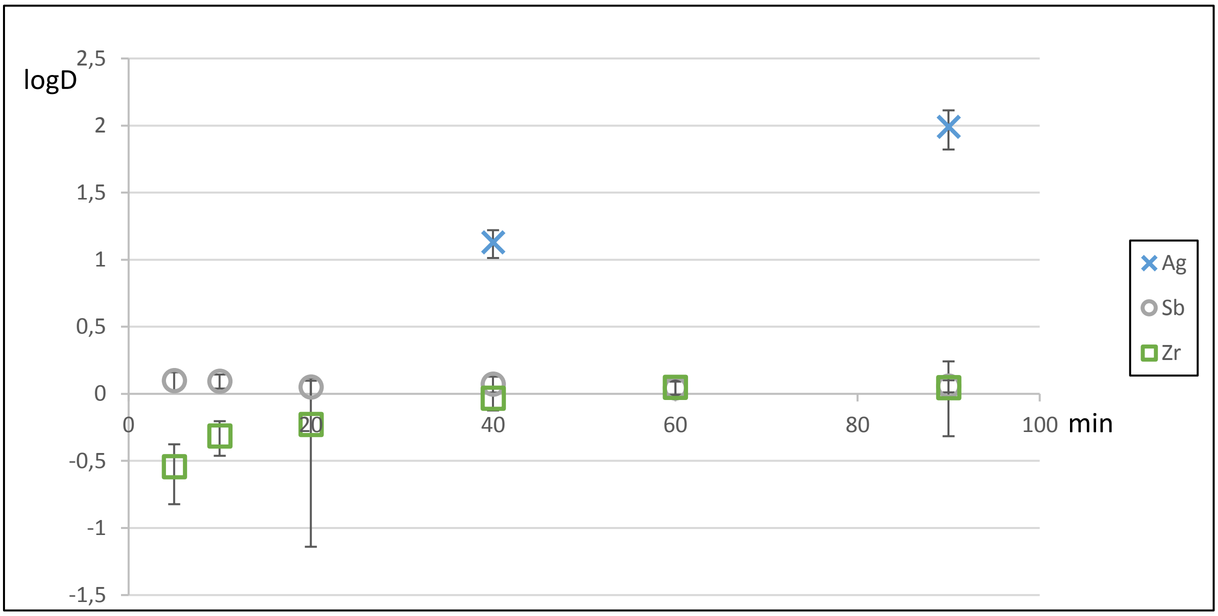

Figure 4.1.5. Logarithmic distribution ratios over time for silver, antimony and zirconium using octanol as diluent.

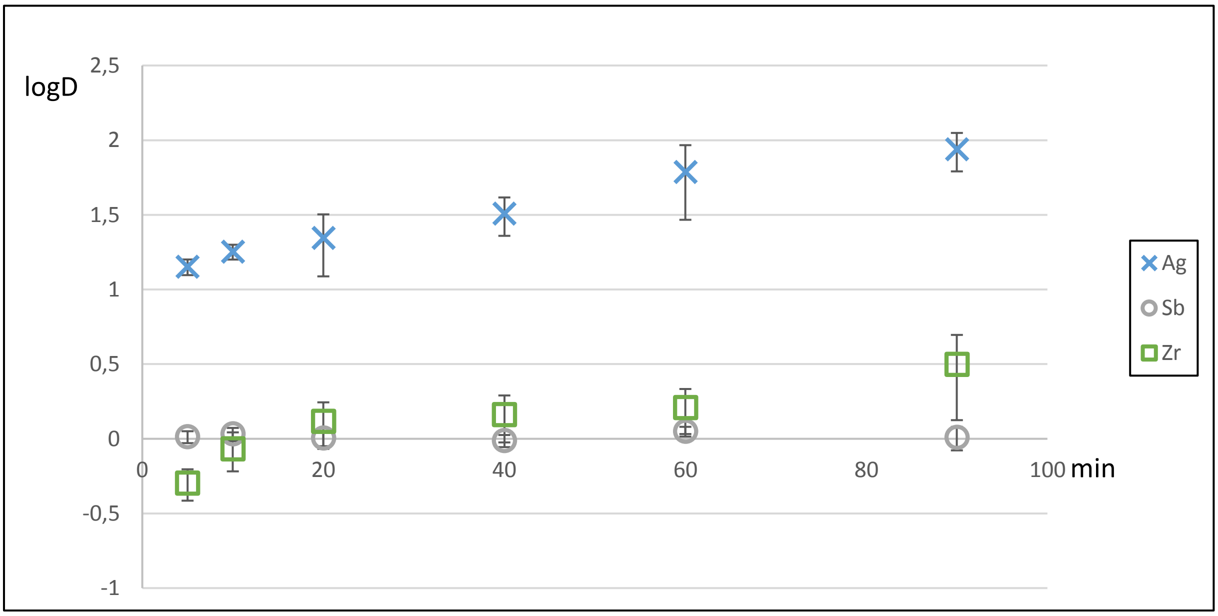

Figure 4.1.6. Logarithmic distribution ratios over time for silver, antimony and zirconium using FS13 as diluent.

Cadmium, palladium, molybdenum and silver will, to some extent, be extracted and might cause problems during the separation process due to the high distribution ratios.

But however, these four metals have very large distribution ratios which were calculated only according to the measurements of metal concentrations in aqueous phase, which means very low metal concentrations in aqueous phase were obtained. It was very difficult to distinguish if the majority of metal ions are in the organic phase or in the interface between the organic and aqueous phase in terms of either interfacial phenomena or precipitation. Although very large distribution ratios for these four metals were obtained it cannot be ensured that they were extracted the large amount by the organic phase.

The extraction of lanthanides, figure 4.1.7-4.1.10, is low in both systems and will most likely not be a problem in either system.

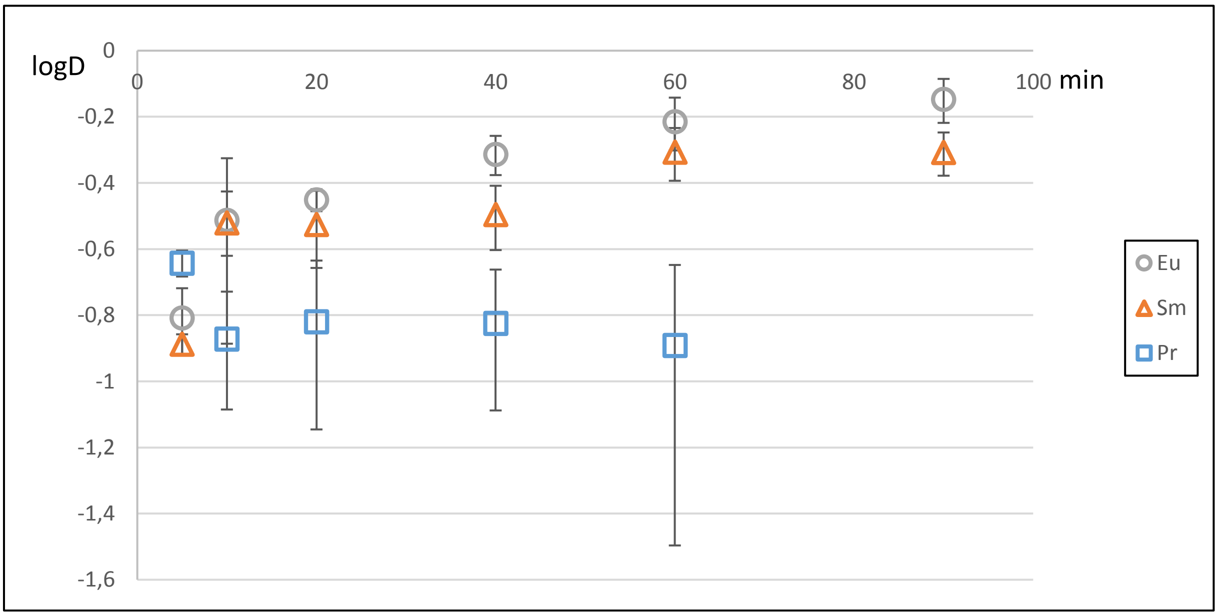

Figure 4.1.7. Logarithmic distribution ratios over time for europium, samarium and praseodymium using octanol as diluent.

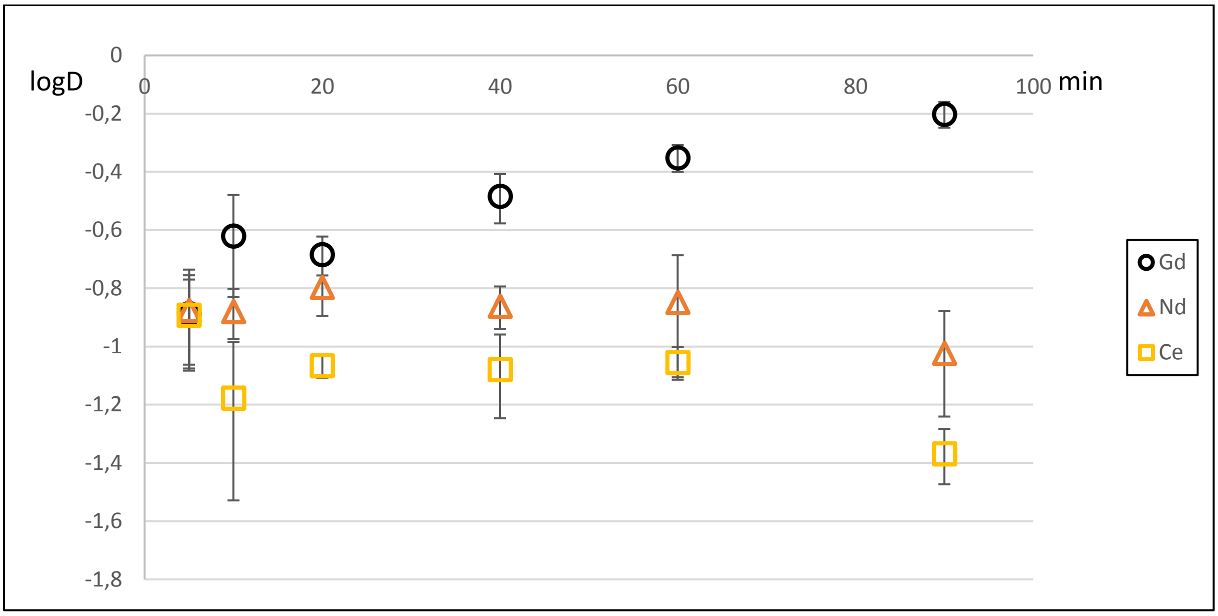

Figure 4.1.8. Logarithmic distribution ratios over time for gadolinium, neodymium and cerium using octanol as diluent.

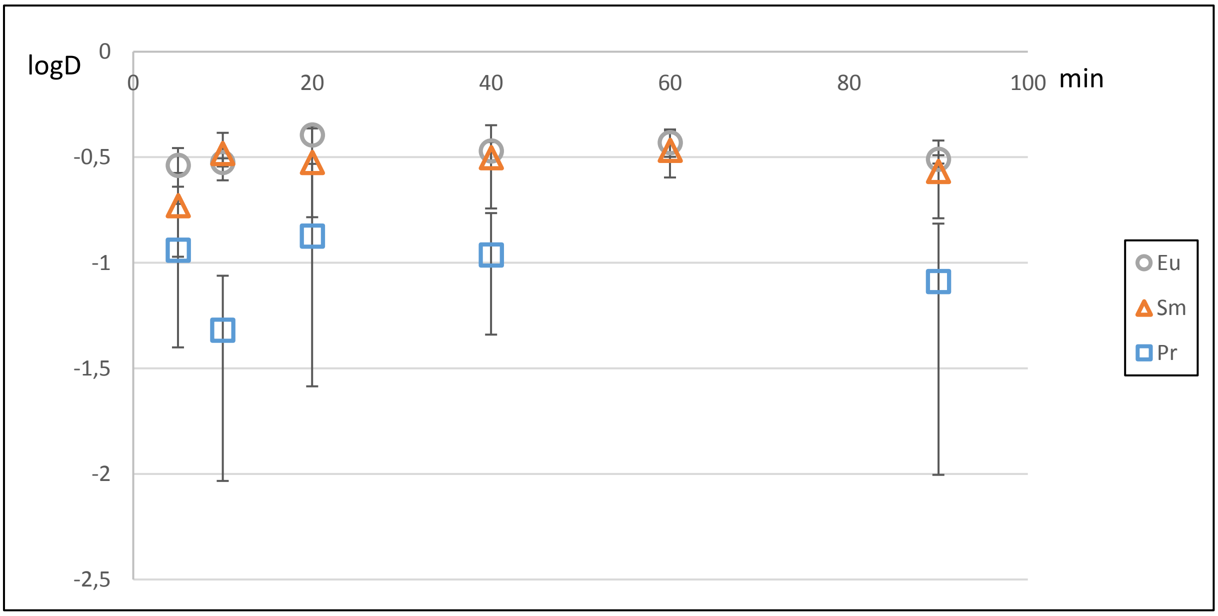

Figure 4.1.9. Logarithmic distribution ratios over time for europium, samarium and praseodymium using FS13 as diluent.

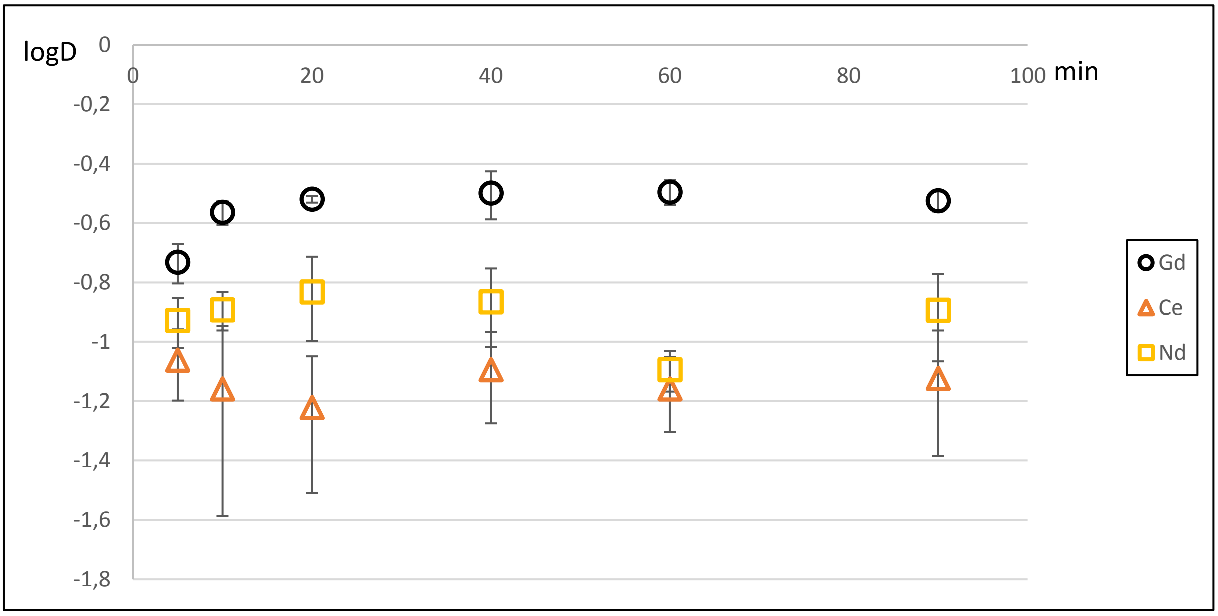

Figure 4.1.10. Logarithmic distribution ratios over time for gadolinium, neodymium and cerium using FS13 as diluent.

Although some of the metals the lanthanides have very small distribution ratios that are staying out of the detection limits, it does not affect the result as long as it can be confirmed that the majority of these metal ions are in the aqueous phase during the extraction, it does not matter in this work whether the small amount of metal ions were extracted by the organic phase or not.

4.2 Separate Ligand Extraction

Separate ligand extraction experiments has been performed to investigate the properties of the two different extraction agents. In addition to the octanol based GANEX system (70%$_{vol}$ octanol, 30%$_{vol}$ TBP and 10 mM CyMe$_4$-BTBP) three different organic phases have been investigated, system 1: octanol and 10 mM CyMe$_4$-BTBP; system 2: 70%$_{vol}$ octanol and 30%$_{vol}$ TBP; system 3: pure octanol.

In figure 4.2.1 can it be seen that americium does not reach extraction equilibrium while europium, however, reaches equilibrium after 40 minutes of phase contact time for system 1. The americium extraction is increasing during the entire experiment and reaches a distribution ratio of roughly 16.6 after 90 minutes. This is lower than for the octanol based GANEX system where a distribution ratio of around 40 is reached after 60 minutes. Europium is extracted to some extent and reaches a distribution ratio of roughly 0.15, which is lower than the octanol based GANEX system where a distribution ratio around 0.5 is reached.

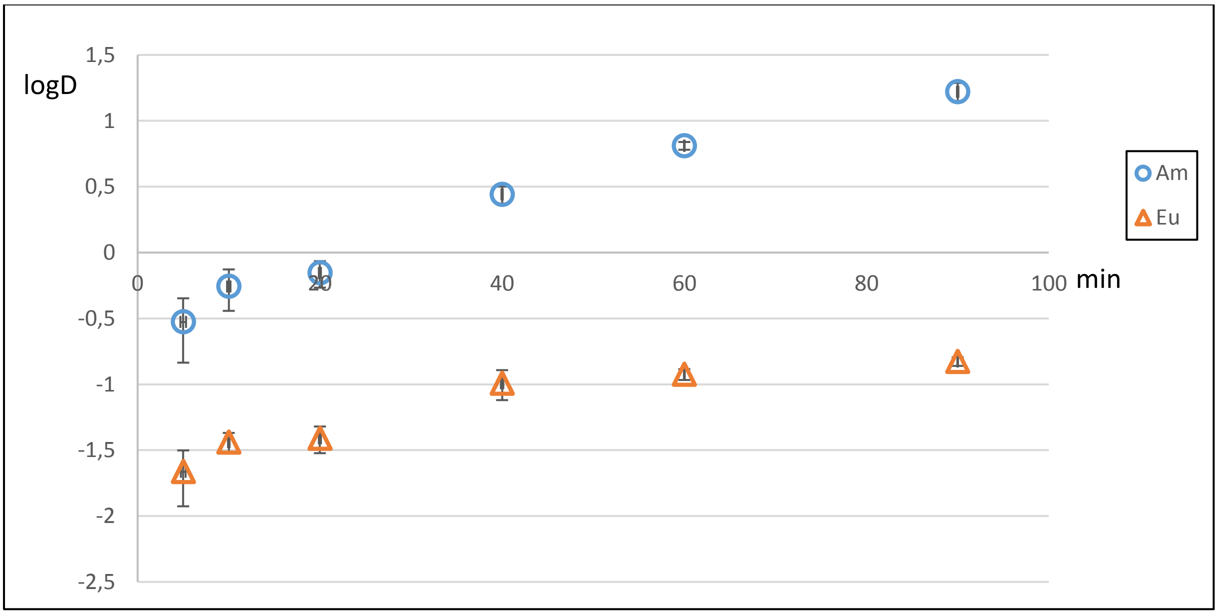

Figure 4.2.1. Logarithmic distribution ratios over time for americium and europium in system 1 (octanol and 10 mM CyMe$_4$-BTBP as organic phase).

In figure 4.2.2 (system 2 and system 3) it can be seen that the extraction of both americium and europium is low and extraction equilibrium is reached more or less immediately in both systems. The extraction of americium is lower in the pure octanol system (system 3) than in any of the other systems. No europium extraction could be observed for system 3 during the measurement, indicating that octanol extracted either no or only a small amount of europium.

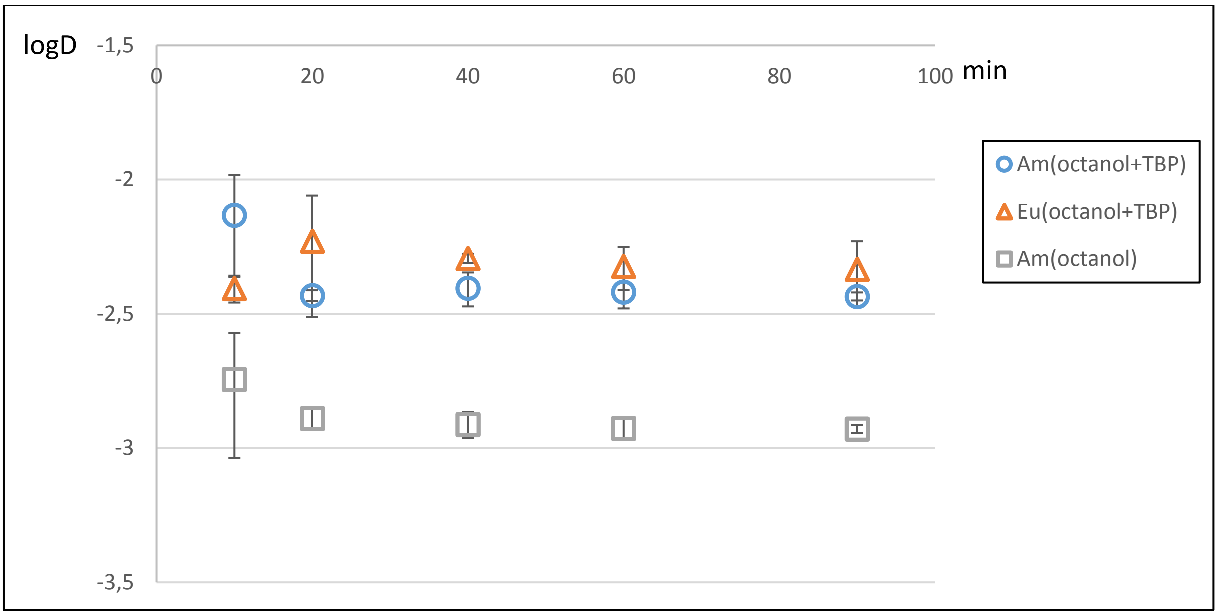

Figure 4.2.2. Logarithmic distribution ratios over time for americium and europium in system 2 (70%$_{vol}$ octanol and 30%$_{vol}$ TBP as organic phase) and system 3 (pure octanol as organic phase).

The separate ligand extraction results are summarized in table 4.2.1. It can it be seen that CyMe$_4$-BTBP is the extraction agent that mainly contributes to both the americium and europium extraction. The distribution ratios of americium and europium are much higher when the solvent combines CyMe$_4$-BTBP and TBP compared with the systems only using one of the extraction agents. This indicates that TBP affects the composition of the organic phase which results in an increased extraction of the metals.

Table 4.2.1: Distribution ratio for americium and europium in the different octanol systems (the extraction of europium in pure octanol system is below the detection limit of HPGe).

Organic phase composition	D-Am	D-Eu
Octanol, CyMe$_4$-BTBP and TBP	39 ± 5	0.5 ± 0.04
Octanol and CyMe$_4$-BTBP	17 ± 3	0.2 ± 0.01
Octanol and TBP	(4 ± 0.1) * 10^{-3}	(5 ± 1) * 10^{-3}
Octanol	(1 ± 0.04) * 10^{-3}	

4.3 Varying TBP volume in the octanol based GANEX system

Previous GANEX studies have shown that TBP not only extracts plutonium but also effects the americium extraction [29][33]. A study investigating the extraction using various volumes of TBP in the organic phase of the octanol based GANEX system was therefore performed.

In figure 4.3.1 and 4.3.2 it can be seen that a larger volume of TBP increases the extraction of plutonium. Extraction equilibrium are, however, not reached during the phase contact time for the systems containing less than 30%$_{vol}$ TBP. The 30%$_{vol}$ TBP system seems to be approaching equilibrium (after 60 minutes) faster than the other systems. The 15%$_{vol}$ TBP and the 10%$_{vol}$ TBP systems have similar distribution ratio curves, while the 20%$_{vol}$ TBP system seems to follow a similar trend but with a higher distribution ratio. This indicates that CyMe$_4$-BTBP mainly contributes to the plutonium extraction when the TBP volume is less than 15%$_{vol}$. The phase contact time required to reach extraction equilibrium seems to decrease with a TBP concentration higher than at least 20%$_{vol}$.

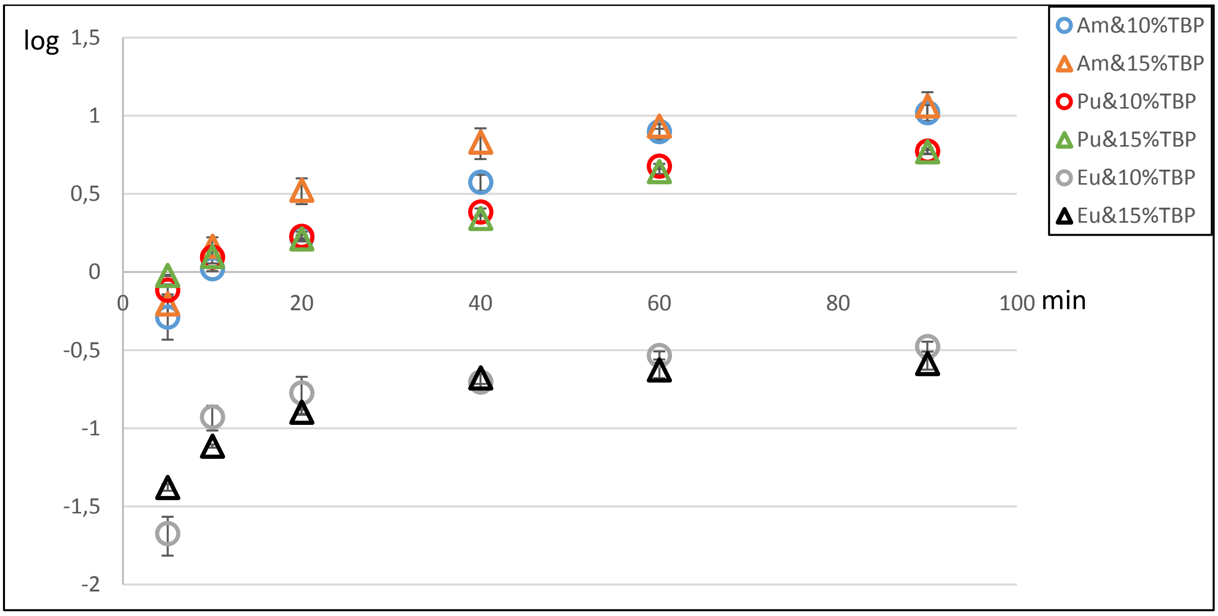

Figure 4.3.1. Logarithmic distribution ratios over time for americium, plutonium and europium using octanol as diluent and various volumes of TBP (10% and 15%).

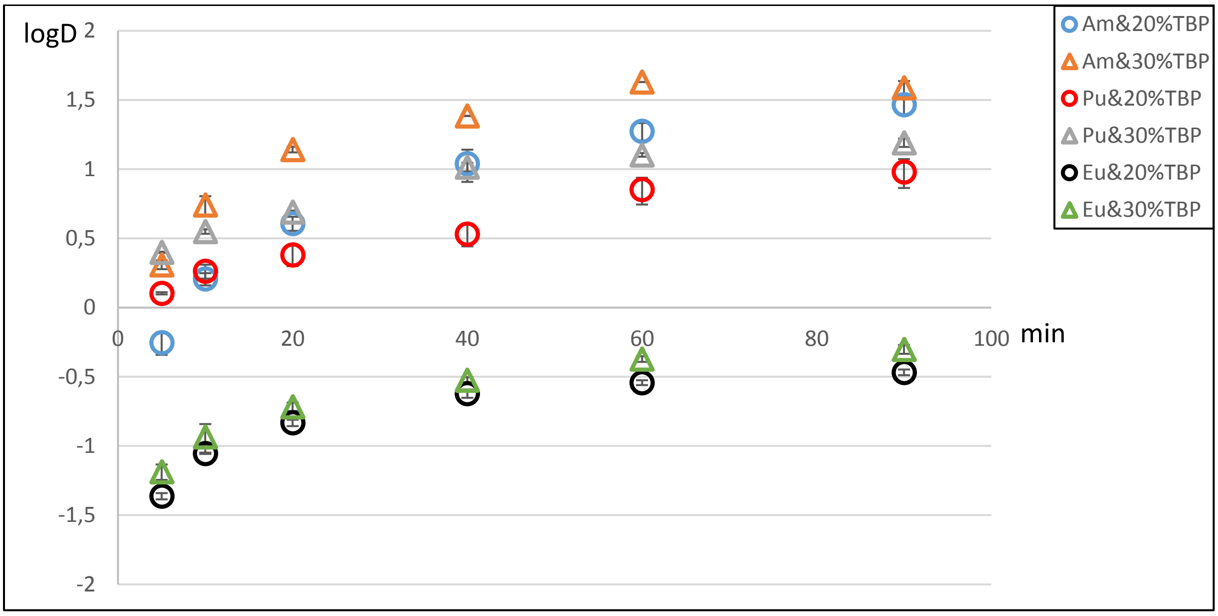

Figure 4.3.2. Logarithmic distribution ratios over time for americium, plutonium and europium using octanol as diluent and various volumes of TBP (20% and 30%).

The extraction of americium behaves similar to the plutonium extraction in the various TBP systems, a larger volume of TBP increases the extraction. Americium only reaches equilibrium in the 30%$_{vol}$ system and it is reached after approximately 60 minutes. The extraction of americium is increased with an increased volume of TBP, which indicates that TBP is involved in the extraction of americium. The 10%$_{vol}$ TBP and the 15%$_{vol}$ TBP systems both have similar distribution ratios of americium. The TBP volumes does not seem to affect the extraction of europium.

Both americium and plutonium can be extracted to a larger extent than europium with different amounts of TBP. Both have similar extraction trends and the distribution ratios are increasing with an increasing volume of TBP.

A relation between the increasing concentration of TBP in the organic phase and higher separation factors between plutonium and americium over europium can be observed, table 4.3.1. However, it should be noted that extraction equilibrium for americium and plutonium has not been reached for the volumes of TBP < 30%. There is some differences in the data for 30% TBP compared to table 4.1.1, possibly due to different measurement methods, the data is collected both from HPGe and NaI detectors, the differences are, however, within the margin of error.

Table 4.3.1. Separation factor for americium and plutonium over europium in octanol based system using various volumes of TBP.

SF	10% TBP	15% TBP	20% TBP	30% TBP
Am/Eu	31 ± 6	45 ± 15	86 ± 17	122 ± 65
Pu/Eu	18 ± 2	23 ± 3	28 ± 8	40 ± 8

4.4 Stripping

The last step of a Chalmers GANEX separation process is stripping of the actinides. In previous experiments, extraction of nitric acid by TBP have been observed [31]. During stripping, the nitric acid might be back-extracted into the aqueous phase and increase the acidity. The higher nitric acid concentration of the aqueous phase could complicate the stripping, suppressing the back-extraction of the actinides [41].

In this work, 0.01 M $HNO_3$was used as aqueous phase for the stripping process. Pre-washing steps before the stripping has been added in some experiments in order to scrub out the nitric acid from the organic phase before the actinide stripping step. Previous experiments with the cyclohexanone based GANEX system using a scrub solution containing 0.01 M HNO_3, 0.99 M $NaNO_3$ and 0.6 M gluco-lactone has efficiently been able to remove a major part of the nitric acid from the organic phase [47]. In previous studies, it has been found that gluco-lactone can increase the scrubbing of molybdenum. An observed side-effect was increased scrubbing of europium with the addition of gluco-lactone to the scrub solution [47].

In this work, three different groups of scrubbing experiments were performed with three scrub steps each.: group 1: three successive stripping steps using 0.01 M HNO_3; group 2: two wash steps using 0.01 M HNO_3 and 0.99 M $NaNO_3$ followed by a stripping step using 0.01 M HNO_3; group 3: two wash steps using 0.01 M HNO_3, 0.99 M $NaNO_3$ and 0.6 M gluco-lactone followed by a stripping step using 0.01 M HNO_3.

In figure 4.4.1 and figure 4.4.2 it can be seen that group 1 stripped both americium and europium. The europium concentration was reduced to less than 5% after the first stripping step and more or less all europium was stripped after the second stripping step. Americium needed three successive stripping steps to reach a strip larger than 95%. Insufficient stripping of americium has been observed in other Chalmers GANEX systems [36].

In group 2 a large part of the americium (around 90%) remain in the organic phase during the first wash step. After the second washing step a majority of the americium (around 76%) is still maintained in the organic phase. Europium on the other hand, is more or less completely washed out of the organic phase (only around 2% is left) after two washing steps.

Group 3 renders similar results as group 2. The addition of the gluco-lactone, however, seems to increase the amount of both scrubbed out americium and europium.

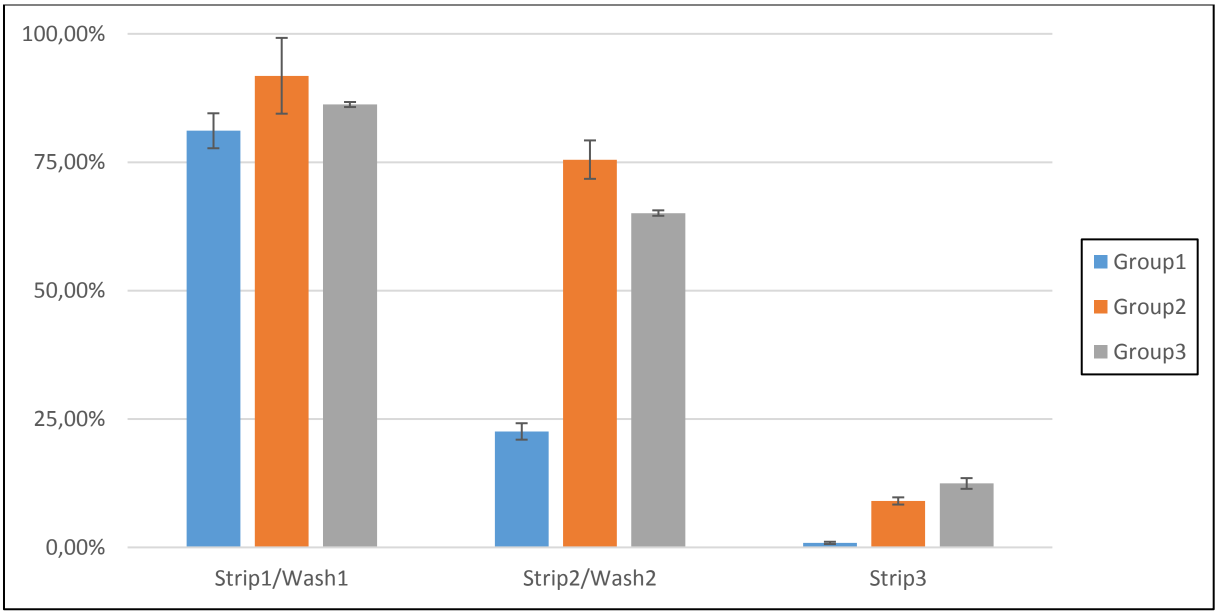

Figure 4.4.1. The amount americium left in the organic phase after each stripping/wash steps.

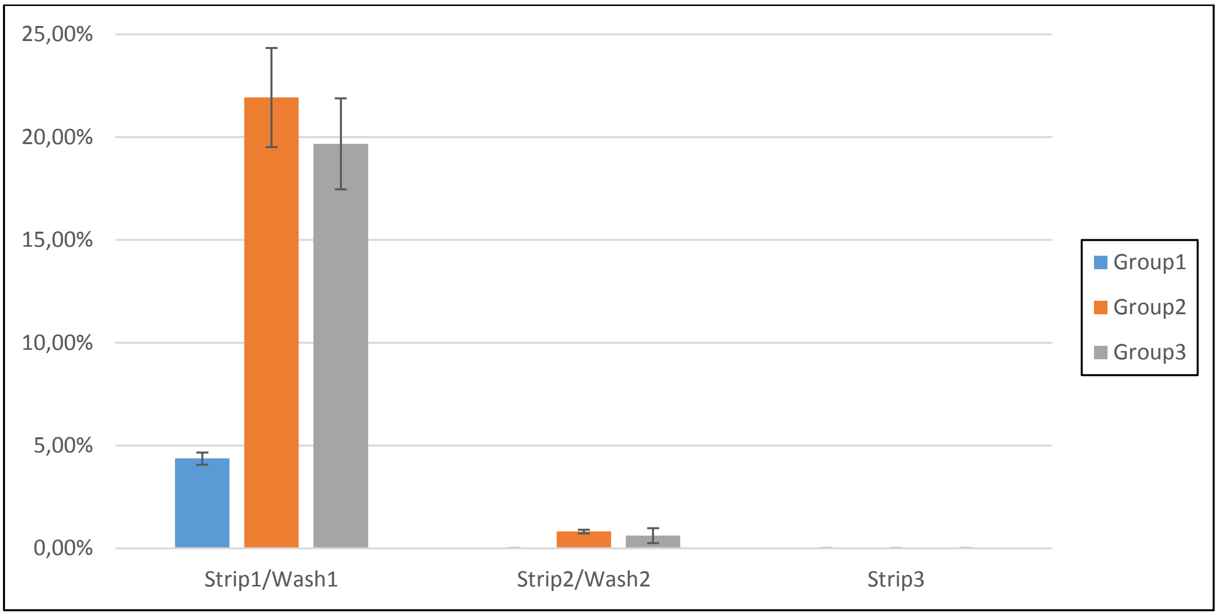

Figure 4.4.2. The amount europium left in the organic phase after each stripping/wash steps.

According to figure 4.4.1 and figure 4.4.2 two washing steps using 0.01 M HNO_3 and 0.99 M $NaNO_3$ are insufficient in suppressing the americium stripping. A higher concentration of $NaNO_3$ should be investigated to evaluate the suppression of americium stripping during the nitric acid scrub steps. The amount americium left in the organic phase after the stripping step is, however, low indicating that an pre-acid scrub is necessary to achieve a successful stripping process.

5. Summary and Conclusions

Previous investigations have shown some drawbacks of the selected diluents involved in the Chalmers GANEX process, e.g. not stable in the chemical environment, poor solubility of the extractants and slow equilibrium kinetics. An alternative diluent, octanol, has in this work been investigated and compared primarily to the FS13 based GANEX system.

Octanol and FS13 both have their advantages and disadvantages as diluents in a GANEX process. First of all, octanol has a lower flash point (81.1 ˚C) than FS13 (122 ˚C), octanol has a slightly lower density than the nitric acid used as aqueous phase. This might become a problems during the metal extraction where the organic phase gets loaded with metals and might become heavier than the aqueous phase. FS13 contains sulfur and fluoride and does hence not follow the CHON principle.

Both the octanol and FS13 systems have a high americium extraction while the europium extraction is low. The octanol based system has a higher extraction of both americium and europium than the FS13 based system, while both systems have a similar separation factor of around 85 for americium over europium. The americium extraction reaches, however, equilibrium faster in the FS13 based system than the octanol based system, 20 minutes and 60 minutes respectively.

The extraction of lanthanides are in both systems low, which indicates that the lanthanides will not be a problem in the separation system. Several other fission products, cadmium, palladium, molybdenum and silver might be, however, extracted to a high extent. Solutions to this problem, like adding suppressing agents or scrubbing out the fission products before stripping, should be further investigated.

In the octanol based GANEX system the extraction of curium and americium are high while the extraction of uranium is low. Compared with the FS13 GANEX based system the octanol GANEX system has a much lower separation factor of uranium over europium.

Both the extraction of americium and the extraction of plutonium increases with an increasing volume of TBP in the organic phase, from $10\%_{vol}$ to $30\%_{vol}$, during the extraction process. The europium is more or less unaffected, which indicates that the separation factors of both americium and plutonium over europium will increase with an increasing volume of TBP.

During the separate ligand extraction it can be seen that $CyMe_4$-BTBP contributes to the majority of the americium and europium extraction. TBP on the other hand accelerates the extraction as well as extracts a small amount of both metal ions.

Two wash steps using 0.01 M HNO_3 and 0.99 M $NaNO_3$ are sufficiently able to remove more than 98% of the europium from the organic phase while maintaining around 70% of the americium in the organic phase. A stripping step following the wash step using 0.01 M HNO_3 stripped around 60% of the remaining americium. A more efficient nitric acid scrub step, maintaining the americium in the organic phase is, however, needed to facilitate a successful stripping system.

6. Future work

During the experiments in this work, some problems needing further investigation have been found, as well as some uncompleted work.

First, the probable high distribution ratios of the fission products (palladium, cadmium, silver and molybdenum) have to be further investigated as well as the possibility of scrubbing out the fission products before stripping or suppressing the extraction. The low separation factor of uranium over europium in the octanol based system should also be further investigated. Different concentration of CyMe$_4$-BTBP, various volumes of TBP in the organic phase and different temperatures during the phase contact should be investigated. During this work, solutions containing 10 mM CyMe$_4$-BTBP and TBP volumes between 10%$_{vol}$-30%$_{vol}$ has been investigated. Solutions containing higher concentrations of both CyMe$_4$-BTBP and TBP should, however, be investigated in order to attempt to optimize the process. Finally, in order to keep as much of the americium as possible in the organic phase during the scrubbing steps, higher concentration (e.g. 4 M) of $NaNO_3$ should be investigated.

7. Acknowledgements

First of all I am so glad approaching the end of thesis diploma work and master program study, during these two years I acquired a lot of different knowledge and made many friends.

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Appendix 1

	Elements	PUREX feed(mg/L)	Involved Compounds	Real Mass(mg)
Fission Products	Se	20	SeO_2	0.248
	Rb	120	$RbNO_3$	1.856
	Sr	280	$Sr(NO_3)_2$	5.452
	Y	155	$Y(NO_3)_3.4H_2O$	4.803
	Zr	1245	ZrO_2	13.370
	Mo	1185	MoO_3	13.980
	Rh	80	$RhCl_3$	1.320
	Pd	520	$PdCl_2$	6.912
	Ag	30	$AgNO_3$	0.373
	Cd	35	$Cd(NO_3)_2.4H_2O$	0.777
	Sn	20	Sn	0.170
	Sb	5	Sb_2O_3	0.099
	Te	170	TeO_2	1.800
	Cs	1265	CsCl	14.690
	Ba	595	$Ba(NO_3)_2$	9.015
Lanthanides	La	425	$La(NO_3)_3.6H_2O$	15.80
	Ce	830	$Ce(NO_3)_3.6H_2O$	25.90
	Pr	390	$Pr(NO_3)_3.6H_2O$	13.10
	Nd	1420	$Nd(NO_3)_3.6H_2O$	43.50
	Sm	280	$Sm(NO_3)_3.6H_2O$	10.90
	Eu	55	$Eu(NO_3)_3.5H_2O$	17.17
	Gd	40	Gd_2O_3	9.80