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Partitioning and Transmutation

Annual Report 2010 & 2011

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Nuclear Chemistry
Department of Chemical and Biological Engineering
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Abstract

The long-lived elements in the spent nuclear fuels are mostly actinides, some fission products (^{79}Se, ^{87}Rb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I and ^{135}Cs) and activation products (^{14}C, ^{36}Cl, ^{59}Ni, ^{93}Zr, ^{94}Nb). To be able to destroy the long-lived elements in a transmutation process they must be separated from the rest of the spent nuclear fuel for different reasons. One being high neutron capture cross-sections for some elements, like the lanthanides. Other reasons may be the unintentional production of other long lived isotopes. The most difficult separations to make are those between different actinides but also between trivalent actinides and lanthanides, due to their relatively similar chemical properties. Solvent extraction is an efficient and well-known method that makes it possible to have separation factors that fulfil the highly set demands on purity of the separated phases and on small losses. In the case of a fuel with a higher burnup or possible future fuels, pyro processing may be of higher advantage due to the limited risk of criticality during the process.

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in several European frame work programmes. These projects have ranged from NEWPART in the 4th framework via PARTNEW and EUROPART to ACSEPT in the present 7th programme. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development. One recycling route, called DIAMEX (DIAmide EXtracton) / SANEX (Selective ActiNide EXtraction) is now considered to be working on a basic scale and has been proven in hot tests and focus has moved on to more process oriented areas. However, since further investigations on basic understanding of the chemical behavior are required, we have our main focus on the chemical processes and understanding of how they work. Our work is now primarily put on the so called GANEX (Group ActiNide EXtraction) process. We have proposed a novel process along these concept lines and continue to optimise it. Areas of further basic understanding are to continue to explore the effect of dilutents on the processes and also to understand the degradation routes of both the extraction agents as well as the diluents.

Sammanfattning

De långlivade ämnena i det använda kärnbränslet består till största delen av aktinider, en del fissionsprodukter (^{79}Se, ^{87}Rb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs) och aktiveringsprodukter (^{14}C, ^{36}Cl, ^{59}Ni, ^{93}Zr, ^{94}Nb). För att kunna förstöra de långlivade ämnena i en transmutationsprocess måste de separeras från resten av det använda kärnbränslet. En av anledningarna till att detta är nödvändigt är det höga tvärsnitt för neutroninfångning som finns hos bland annat lantaniderna. Andra anledningar kan vara en önskan att inte framställa nya långlivade isotoper från nu stabila eller kortlivade ämnen. De svåraste separationerna att göra är de mellan trevärda aktinider och lantanider, på grund av deras liknande kemiska egenskaper, samt de mellan aktiniderna själva. Vätskeextraktion är en effektiv och välkänd metod som gör det möjligt att uppnå separationsfaktorer som uppfyller de högt ställda kraven på renhet i de separerade faserna och små förluster i processen. Om man i stället skulle ha ett högutbränt bränsle eller vissa möjliga framtida bränslen kan en så kallad pyroprocess vara att föredra. I detta fall är kriticitetsrisken under upparbetningen väsentligt lägre.

Chalmers tekniska högskola deltar i forskningen rörande separationen av aktinider och lantanider och mellan aktiniderna själva, genom att vara en partner i flera ramprogram finansierade av EU. Dessa projekt har sträckt sig från NEWPART i det 4:e ramprogrammet via PARTNEW och EUROPART till ACSEPT i det nuvarande 7:e ramprogrammet. Målet med arbetet har under denna tid flyttats från grundläggande förståelse till mer tillämpad forskning med processberäkningar och test med riktigt använt kärnbränsle. En processväg, DIAMEX (DIAmide EXtraction) / SANEX (Selective ActiNde EXtraction), anses nu fungera på labskala och har testats med riktigt använt kärnbränsle varför dess utveckling nu i huvudsak förs inom den mer processorienterade forskningen. Dock behövs fortfarande grundläggande kunskaper och därför ligger vårt fokus fortfarande på grundläggande kemiska frågor och förståelse för ingående processer. I nuläget arbetar vi mest kring den så kallade GANEX-processen (Group ActiNide EXtraction). Områden som vi undersöker på en grundläggande nivå är hur olika lösningsmedel påverkar extraktionerna samt hur nedbrytningen av både lösningsmedlet och extraktionsmedlet går till.

Contents

Introduction

The Partitioning and Transmutation (P&T) group at Nuclear Chemistry and Industrial Materials Recycling belongs to the Department of Chemical and Biological Engineering at Chalmers University of Technology. The group investigates the separation of different chemical elements in spent nuclear fuel, for purification and/or recovery in a future transmutation process.

Solvent extraction is used already today in *e.g.* France, UK and Russia in the reprocessing of spent nuclear fuel, *i.e.* the recirculation of uranium and plutonium back into the fuel cycle. This means that a substantial amount of expertise on how to handle highly active aqueous and organic solutions already exists. Solvent extraction is also a good technique to use considering the high efficiency of separation that can be achieved.

Internationally, other processes such as molten salt extraction and electro deposition are also investigated. These so called pyro processes are of particular interest when it comes to high burnup fuel and possible future fuel types due to the very limited risk of criticality in the developed process.

The Chalmers group has been involved in the separation for transmutation research throughout three different European Union framework programmes*;* NEWPART (1996–1999), PARTNEW (2000–2003) and EUROPART (2004–2007). During this time the focus has changed slightly although the main content has remained the same. As time has passed the main effort has been more and more focussed on process development. In the early years there was a search for suitable extracting agents for separation of trivalent lanthanides from trivalent actinides following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This separation route, the so called DIAMEX (DIAMide EXraction) / SANEX (selective Actinide EXtraction) has been tested with genuine spent fuel and is now considered to be working on an acceptable level, which is why the basic research have been redirected towards other, more complex separation schemes, like *e.g.* the GANEX (Group Actinide Extraction). In the GANEX process all the actinides are extracted together from fuel dissolution liquor. They may then either be separated from each other by selective stripping or kept together to comply with non-proliferation issues. To further work towards an industrial process, Chalmers is since 2008 also a partner in the 7th European Union framework programme ACSEPT (2008–2012). It is planned that there will be a continuation of ACSEPT in some form.

A substantial collaboration has started in Sweden between Chalmers and KTH on the issue of fuel fabrication. Presently, a fuel fabrication lab is constructed at Chalmers which will be in connection to the existing separation lab and thus the border between the fuel and separation research will be significantly decreased. The main focus will be the fabrication of oxide and nitride fuels for research purposes.

The main experimental work at Chalmers concerns the extraction properties and other basic chemical characteristics of extraction ligands. The department also house the development and synthesis of new ligands in the organic laboratory. Currently the main focus lines, as represented by our PhD students are the development of a new GANEX extraction system based on the extractants TBP and BTBP. This system has proven to work well for the collected extraction of the actinides but unfortunately the system also extracts some fission and corrosion products. Thus the main effort during the year has been to find means to suppress or pre-extract the troublesome elements. Research on the stability of the extraction agents is ongoing in most labs working with separation for transmutation. At Chalmers we have one of the most versatile irradiation sources in Europe and our studies we now takes it one step further than the traditional studies of the distribution values as a function of dose. We now, in collaboration with partners in ACSEPT focused on analytical chemistry, try to identify degradation products and thus hopefully can be able to understand the reaction mechanisms and possibly design more stable molecules. Once identified, some of the degradation products will be synthesised to investigate their properties. Apart from the extraction agent the solvent in the extraction system also contains the diluent. Previously we have presented a thesis on the effect different diluents have on the extractions. These results together with new complementary information will now allow for the possibility to describe these interactions from a more fundamental side, allowing for possible a priori optimisation of the selection of the diluent to be used.

Research

2010

During 2010 two PhD students have worked full time within the partitioning and transmutation (P&T) group. Emma Aneheim has mainly been working with most aspects of a novel GANEX extraction system. Elin Löfström-Engdahl has been working on basic thermodynamic consideration for solvent theory to help in optimisation of the future extraction systems as a continuation of the work defended by Teodora Retegan in 2009. A third phD student, Anna Fermvik is studying the effects of radiolysis on several selected extraction systems. She has, however been on maternity leave for most part of the year.

Dr. Mark Foreman is working 50% within this project and 50% with other material recycling issues. The main part of his work this year has been on synthesis of suppressing ligands for several fission and corrosion products that are extracted by the novel GANEX solvent.

A French diploma worker, Nathalie Mablie, worked in the P&T group during part of 2010. She studied the possible replacement of TBP in the GANEX process. Two other French students, Marie-Adeline Ferrero and Linda Belgacem also participated in the work of the group during an eight week project in the late spring of 2010.

Sofie Englund, a former PhD student from nuclear chemistry, is working at OKG AB but is still involved in this project at about 10% intensity.

The ACSEPT project is ongoing and during 2010 there were two meetings: a 2nd Annual Meeting in Lisbon, Portugal in March and a Half Yearly Meeting in Petten, Netherlands in September. The first meeting included presentations of work performed during the second year of ACSEPT, while the second meeting was primarily dedicated to education and training by workshops and seminars. In addition, the 1st ACSEPT International Workshop was held in Lisbon in April.

2011

During 2011 Emma Aneheim (PhD Student) has mainly been working with different aspects of a novel GANEX extraction system and Elin Löfström-Engdahl (PhD Student) has been working with solvent effects within the same system. Both have been working full time in the partitioning and transmutation (P&T) group. A third PhD student, Anna Fermvik was studying the effects of radiolysis on several selected extraction systems during the first half of 2011 until her dissertation in June. The name of her defended thesis was “Radiolytic degradation of BTBP type Molecules for Treatment of Used Nuclear Fuel by Solvent Extraction” and her opponent was Dr Bruce Mincher.

Dr. Mark Foreman’s main work within the P&T group during 2011 has been to investigate the thermal stability of different solvents using an in house constructed device. He is working 50% within this project and 50% with other material recycling issues. He has during the year been promoted to associate professor and given a tenure.

During the first half of 2011 a British project worker, Alexander Littley, was working within the P&T group under the supervision of Emma Aneheim. He studied the behaviour of technetium in the GANEX system. During the later part of 2011 a diploma-worker, Hanna Elfverson, started her work within the group investigating the replacement of cyclohexanone with hexanoic acid in the GANEX system. She will continue also during 2012 under the supervision of Elin Löfström-Engdahl.

General information

Below follow a few definitions that will be used throughout the report to minimise the need for repetition and hence increase the readability.

Extraction

Liquid-Liquid extraction is the process by which a substance (the solute) is partitioned between two immiscible liquids. These immiscible liquids are usually an organic and aqueous phase. The organic phase is usually referred to as the solvent and the solute containing aqueous phase referred to as the feed. The solvent consists of a diluent, making up the bulk of the phase and sometimes one or several extractants. The extractant is the component primarily responsible for solute extraction and can also be the diluent. Upon contacting the two phases, the extractant should remove the solute from the feed, leaving a raffinate of depleted solution.

Distribution ratio (D) is used to express the distribution of the solute between the two phases and the equation can be seen below. For a liquid-liquid extraction to work successfully the solute to be extracted must have a distribution ratio greater than 1 and any substances to be left in the raffinate must have a distribution ratio lower than 1.

$$D = \frac{[C]_{Org}}{[C]_{Aq}}$$

Where D is the distribution ratio $[C]_{Org}$ is the concentration of metal in the organic phase and $[C]_{Aq}$ is the concentration of metal in the aqueous phase. During the experiments performed, count rate (count/second) is assumed to be directly proportional to concentration and therefore the ratio of organic phase count rate to aqueous phase count rate is used to calculate distribution ratios.

The results of experiments performed will be presented in the form of D and log(D) values, where for a desired product the values should be > 1 and > 0 respectively, whereas for the undesired substances, values of < 1 and < 0 should be aimed for.

Also the concept of separation factor will be frequently used in the report and $SF_{A/B}$ = the ratio between the distribution ratios of two different substances (A and B) in the same system.

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

Standard extraction experiment

Most extraction experiments presented in this report are performed in a similar manner and therefore a standard experimental procedure is stated here and will be referred to in the text.

Almost exclusively 3.5 mL glass vials are used for the extraction experiments. The volumes most commonly used are 200–500 µL of organic phase and 200–500 µL of aqueous phase. Due to the mutual solubility of some of the diluents used (e.g. cyclohexanone) and the acidic water phases, both phases used for extraction are pre-equilibrated with the corresponding aqueous and organic solution. The organic phase usually contains 0.005–0.01 M extractant dissolved in a selected diluent and the aqueous phase normally consist of HNO_3 of various concentrations and the metals to be extracted. When radioactive isotopes are used the metals are added in trace amounts by spiking the aqueous phase with concentrated stock solutions (often 10–20 µL are added). The phases are contacted either by vigorously hand-shaking in an insulated canister in which the vials are placed or in a shaking machine connected to a thermostatic water bath. The contact time depends on the time it takes for the extraction system to reach equilibrium. After contact, the phases are left to separate either by gravitation or by centrifuging. When the phases are completely separated samples from each phase are removed for analysis and prepared in different ways depending on the detection method used.

^{241}Am and ^{152}Eu are commonly used as radiotracers to act as analogues for trivalent actinides and trivalent lanthanides, respectively.

Detection

The equipment most commonly used for analysis will only be described in detail here and in the rest of the text just referred to by name.

HPGe 1: High Purity Germanium detector for γ-radiation (Ortec, GEM 15180-S).

HPGe 2: High Purity Germanium detector for γ-radiation (Ortec, Gamma Analyst GEM 23195) with automatic sampler.

Liquid Scintillator: Liquid scintillation detector for α- and β-radiation (Wallac 1414 WinSpectral).

NaI: NaI(Tl) scintillation well detector (Intertechnique GC-4000).

ICP-OES: Thermo iCAP 6500 Inductively Coupled Plasma Optical Emission Spectrometer.

ICP-MS: ELAN 6000 Inductively Coupled Plasma Mass Spectrometer.

Spectrophotometer: Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer.

Alphaspectrometer: Ortec, Alpha Duo.

TRLFS: GmbH Pump laser (Innolas Spitlight 300-10), NarrowScan (D-R Dye Laser) (Radient Dye Lasers Accessories).

Gamma irradiation source

During 2010 the ^{60}Co-source (Gamma cell 220 from Atomic Energy of Canada ltd) at our department was recharged. The new approximate dose rate (estimated by Fricke dosimetry) is 18 kGy/h. This can be compared to the dose rate of 10 Gy/h before the recharge. The higher dose rate results in a temperature rise of the irradiated solutions. The temperature of an irradiated sample with the current source was estimated to be around 50°C. This naturally could pose a problem when comparing new and old results but care has been taken to take this into account.

Results 2010

1 BTBP-chemistry

The use of nitrogen-containing heterocyclic molecules following the CHON-principle (containing only carbon, hydrogen, oxygen and nitrogen) has been shown to efficiently separate trivalent actinides and lanthanides using solvent extraction (Ekberg et al. 2008). One of the latest groups of molecules to be designed and developed was the BTBPs, and a significant amount of the studies performed by the Chalmers group involves these molecules.

1.1 BTBP

BTBP is an abbreviation for *bis*-triazin-*bi*-pyridine, which refers to the nature of the central core common to all the molecules in the family (see Figure 1-1). This is a group of molecules that can act as tetradentate ligands to metal ions and a high selectivity towards trivalent actinides over trivalent lanthanides has been observed (Nilsson 2005, Foreman et al. 2005, Nilsson et al. 2006b).

The extracting properties of the molecules and their possibilities to be used in a process are dependent on factors like the extraction and separation ability, solubility, kinetics of extraction, stability towards irradiation, etcetera. Depending on the side groups (denoted R in Figure 1-1) and different attachments to the BTBP core-molecule these properties change (Retegan et al. 2007, Ekberg et al. 2007).

The two BTBP's referred to in this report are shown below in Figure 1-2.

Various experiments have been performed to further explore the general chemistry of the BTBP´s, mainly focussed on properties that are of importance in solvent extraction processes. Some of the different studies are presented below.

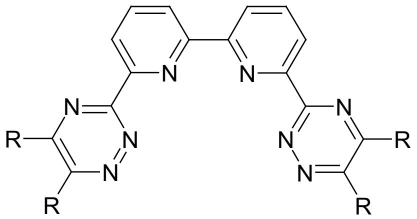
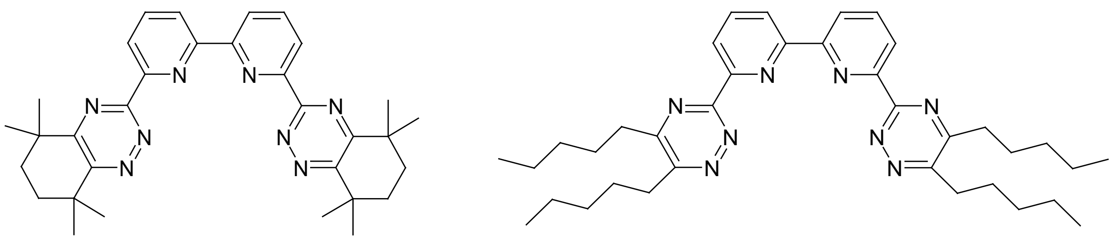


Figure 1-1. *The bis-triazin-bipyridine, or BTBP, core molecule.*



CyMe$_4$-BTBP C5-BTBP

Figure 1-2. *Molecular structures of the BTBP molecules discussed in this report: CyMe$_4$-BTBP and C5-BTBP.*

1.2 Protonation behavior of BTBP

It has previously been shown that BTP is protonated in contact with acid (Weigl et al. 2006). To investigate if this applies also for the structurally similar BTBP, several experiments were made.

An acid extraction study was performed according to the description given by Weiglet al. with a nitric acid concentration ranging from 0 to 3 M (Weigl et al. 2006). The ionic strength was, however, kept constant at 3 M using sodium nitrate, assuming full dissociation of nitric acid, even though this is an incorrect assumption at the higher concentrations. The organic phases used were either C5- or CyMe$_4$-BTBP (0.02 M) in nitrobenzene or octanol. Aqueous samples were introduced into vials with an equal volume of organic phase and then hand shaken for 10 minutes. The phases were separated by centrifugation and for each phase the acid concentrations were measured by titration with 0.1 M sodium hydroxide.

To measure the concentration of the BTBP in solution, UV-Vis spectrometry can be used since iron II and BTBP form a dark blue complex that absorbs around 600 nm. A saturated solution of FeSO$_4$ (FLUKA, purum p.a. > 99,0%) in ethanol/water 50-50 was made. Then 10 mL of ethanol was mixed with 500 µL of the FeSO$_4$ solution, 300 µL of diluents (nitrobenzene or octanol) and finally 100 µL of the sample to be measured. About 1 mL of the mixed solution was then placed in a plastic cuvette and the absorbance at 600 nm was measured with the spectrophotometer. The baseline was registered between 500 nm and 700 nm with a solution made of 10 mL ethanol, 500 µL of the FeSO$_4$ solution and 400 µL of diluent.

1.2.1 BTBP in octanol

Systems consisting of either pure octanol, C5-BTBP in octanol or CyMe$_4$-BTBP in octanol were contacted with aqueous phases with varying nitric acid concentration. After separation, the phases were titrated with NaOH to determine the proton content. As can be seen in Figure 1-3, the acid extraction of the solvent was too large to be able to draw any conclusions about the effect of the BTBP. This does, however, not necessarily mean that the BTBP does not extract any acid.

If the distribution ratio is plotted instead of the acidity of the organic phase (as in Figure 1-3), a slight nitric acid extraction due to the presence of BTBP in the organic phase can be seen (Figure 1-4). This extraction is higher for low concentration of nitric acid and then decreases. The difference in distribution ratios are however very small and hence no conclusions of protonation of the BTBP can be drawn.

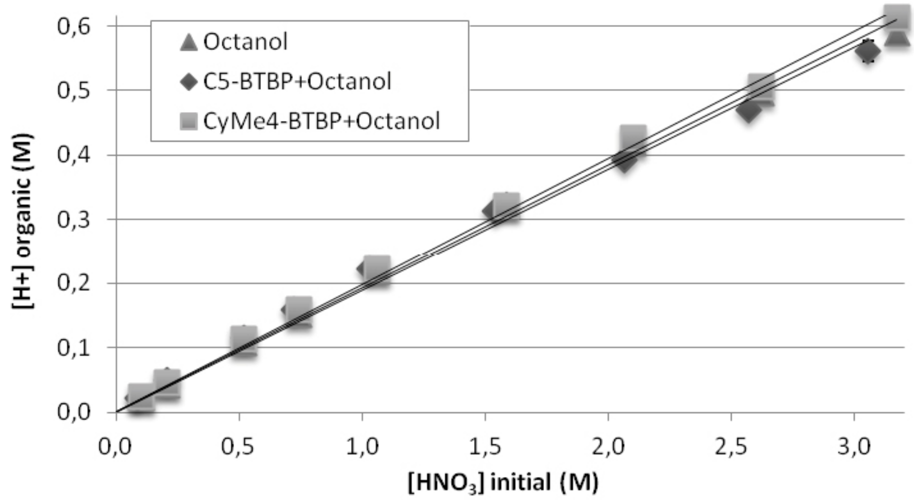


Figure 1-3. *Nitric acid extraction equilibrium data from three different organic phases: 1-octanol, C5-BTBP in octanol and CyMe$_4$-BTBP in octanol. Aqueous phase: HNO$_3$ (initial concentration plotted) + NaNO$_3$ to keep the ionic strength at 3.*

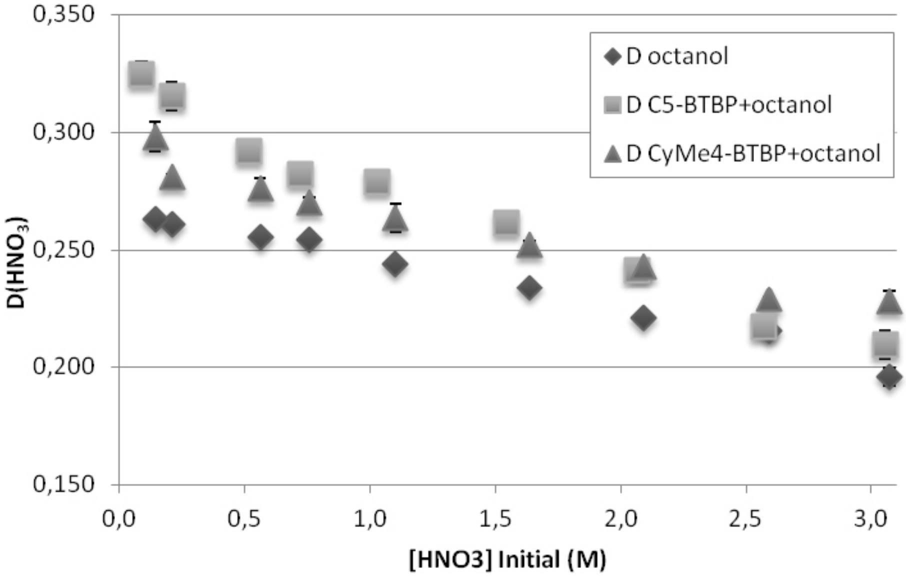


Figure 1-4. *Extraction of nitric acid at different acidities with three different organic phases pure octanol, C5-BTBP in octanol and CyMe$_4$-BTBP in octanol. Aqueous phase: HNO$_3$ (initial concentration plotted) + NaNO$_3$ to keep the ionic strength at 3.*

1.2.2 BTBP in nitrobenzene

Because of the large extraction of acid caused by the octanol in the previous experiment, another similar acid extraction test was performed but with another diluent, nitrobenzene, that does not extract as much acid. As seen in Figure 1-5 there is an acid concentration in the organic phase that reaches twice the concentration of CyMe$_4$-BTBP.

However, since HNO$_3$ does not completely dissociate (pKa=–1.4), it cannot be said whether or not it is the whole acid that is being extracted or the BTBP that is being protonated. Due to this, another set of acid extractions with similar conditions were performed but with hydrochloric acid instead, which is dissociated to a much higher degree (pKa=–6).

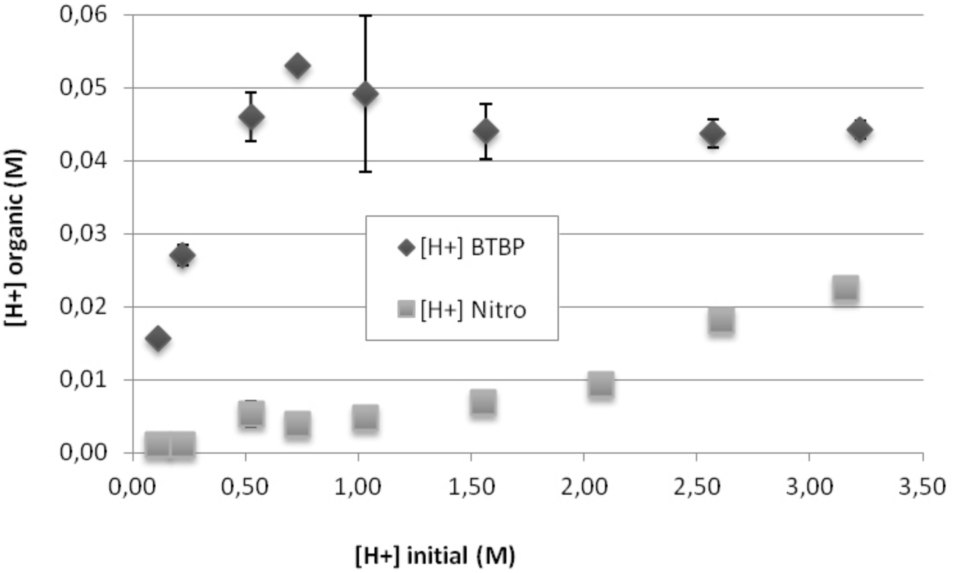


Figure 1-5. *Acid extraction by CyMe$_4$-BTBP in nitrobenzene ([H+]BTBP) corrected for the extraction by nitrobenzene and acid extraction by nitrobenzene ([H+] Nitro). Aqueous phase: HNO$_3$ (initial concentration plotted) + NaNO$_3$ to keep the ionic strength at 3.*

As seen in Figure 1-6, the acid extraction observed for the nitrobenzene/HNO_3 system is not present in the hydrochloric acid system and therefore it can be assumed that the extraction observed in the previous experiment most likely is a nitric acid extraction and not a protonation of the BTBP molecule.

A spectrophotometry measurement of the concentration of BTBP in the organic phase was also performed to see if there were any variations that could indicate that a supposedly protonated BTBP tend to stay at the phase boundary. As can be seen in Figure 1-7 this was not observed.

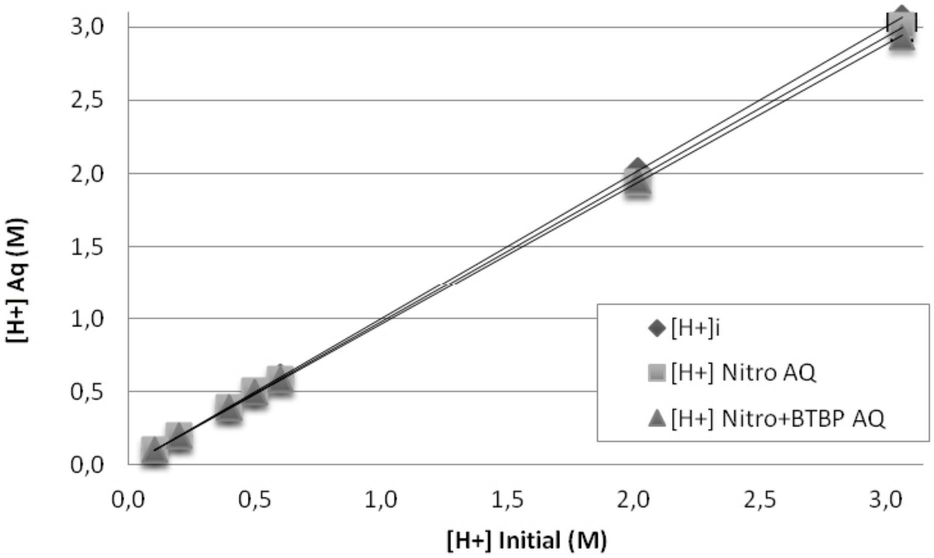


Figure 1-6. *Hydrochloric acid extraction equilibrium data. Aqueous phase, HCl (initial concentration plotted) + NaCl to keep the ionic strength constant at 3.*

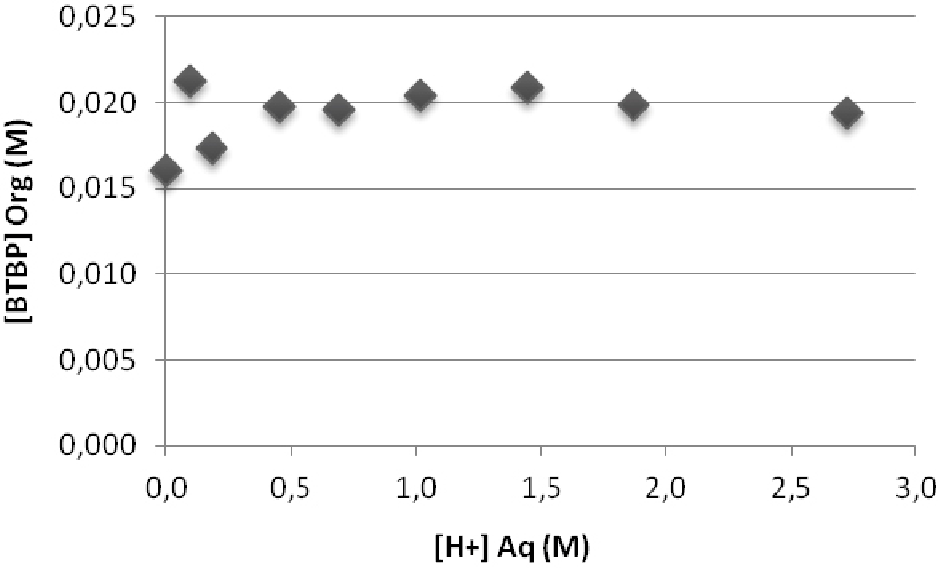


Figure 1-7. *Concentration of CyMe$_4$-BTBP in the organic phase as a function of the concentration of hydrochloric acid in the aqueous phase.*

1.3 Thermodynamics of complexation

The diluent cyclohexanone, which is normally used in the Chalmers GANEX process, is a diluent that has not previously been used for reprocessing of spent nuclear fuel. Cyclohexanone has several advantages: it is not poisonous, it follows the CHON principle and the molecule $CyMe_4$-BTBP has a relatively high solubility in the diluent. However, one of the disadvantages with cyclohexanone is the mutual solubility with water. Due to this, an investigation of the complexation of $CyMe_4$-BTBP and curium ($Cm(ClO_4)_3$)(curium used as a representative for the minor actinides) was performed in water saturated and non water-saturated, “dry” cyclohexanone. This investigation was done using Time Resolved Laser Fluorescence Spectroscopy (TRLFS). This research will proceed during 2011 and is performed in cooperation with the Technical Institute in Karlsruhe (KIT).

In the solution consisting of $CyMe_4$-BTBP, cyclohexanone and $Cm(ClO_4)_3$ the different curium species reported from literature (Trumm et al. 2010a, b) are the free, solvated, ion, the 1:1 complex where one BTBP-$CyMe_4$ forms a complex with one metal ion and finally the 1:2 complex where two ligands form a complex with one metal ion. The complexation between the ligand and the metal takes place according to the following equilibrium:

$[M(solv)]^{3+}$+ n $CyMe_4$-BTBP ↔ $[M(CyMe_4\text{-}BTBP)_n]^{3+}$

Thus, the stability constant of the complex equals:

$$K = \left(\frac{[M\ (CyMe4 - BTBP)_n]^{3+}}{[M(solv)]^{3+}\, x\ [CyMe4 - BTBP]^n} \right) \qquad \text{(Equation 1)}$$

The optical properties of the Cm(III) ion and their applications has been summarized by Edelstein et al. (2006). The fluorescence spectrum of the curium species comes from the $^6D'_{7/2} \rightarrow {}^8S'_{7/2}$ transitions in the curium ion and the fluorescence intensity of this relaxation is influenced by ligands in the vicinity of the ion. Because of this, the formation of complexed species can be monitored using the evolution of the curium fluorescence spectrum during increased ligand concentration. During such ligand titration, a small amount of ligand is added to the organic solution containing the dissolved Cm. After every ligand addition a fluorescence spectrum can be measured.

Ligand solutions for the titrations were prepared by dissolving the ligand $CyMe_4$-BTBP in the water saturated and “dry” cyclohexanone. A small volume of a stock solution of $Cm(ClO_4)_3$ (30 µL, 4 µM) was evaporated into two separate cuvettes to produce solid $Cm(ClO_4)_3$. Initially, the $Cm(ClO_4)_3$ was dissolved in the pure diluents giving the concentrations of 0.12 µM Cm. Spectra of the pure solvated ion in the different diluents were measured. Small amounts of the ligand solution were then added to the cuvettes and after every addition a spectrum was measured. When several spectra were collected, the ligand concentration was heavily increased in order to obtain very high ligand concentration and therefore the pure complexed ion. This species, which is seen as a peak around 620 nm, is known from literature to be the 1:2 complex (Trumm et al. 2010a).

The fluorescence spectra of the pure solvated curium species in the “dry” and water saturated cyclohexanone are displayed in Figure 1-8. The peak maximum for the Cm ion in the water saturated cyclohexanone is at 595.8 nm while the peak maximum for the Cm ion dissolved in the “dry” cyclohexanone is at around 598.2 nm, there is a small red shift (shift towards longer wavelengths) in the “dry” one. The red shift in the “dry” sample is due to the loss of water. The more water the shorter the emission wavelength (Edelstein et al. 2006). The spectra for the 1:2 complex in the “dry” and water saturated diluents are seen in Figure 1-9. Also here a shift is observed, but it is the water saturated solution that is red-shifted, from 618 nm for the “dry” cyclohexanone to 620 nm for the water saturated solution.

The $CyMe_4$-BTBP titrations in the “dry” cyclohexanone can be seen in Figure 1-10 and the titrations in water saturated cyclohexanone can be seen in Figure 1-11. The series correspond to various ligand concentrations. Starting from the solvated species, formation of two new peaks, pointing to the formation of two different complexes; the one around 620 nm is known from the literature (Trumm et al. 2010a) to be the 1:2 complex meaning the one around 610 nm must be the 1:1 complex. These bathocromic shifts compared to the solvated ion indicates a ligand field splitting caused by stronger complexation of the metal ion. These shifts are also in agreement with earlier achieved data for the Cm(III) complexation of the BTP (Trumm et al. 2010b) class molecules. The spectra of the pure solvated ions and the 1:2 species where used for evaluation of the titrations. From the spectra achieved from the ligand titrations the spectrum of the 1:1 complex was deconvoluted. By doing so, peak deconvolutions were performed for the various ligand concentrations obtained during the titration, and a speciation of the three species as a function of ligand concentration were achieved.

When both the dry and water saturated titrations were evaluated, a slope analyses of the stability constant, k, of the three species as a function of ligand concentration were performed. These analyses showed that there seems to have been a problem with not reaching the equilibrium. Therefore this titration has been repeated. However, the new results have not yet been evaluated.

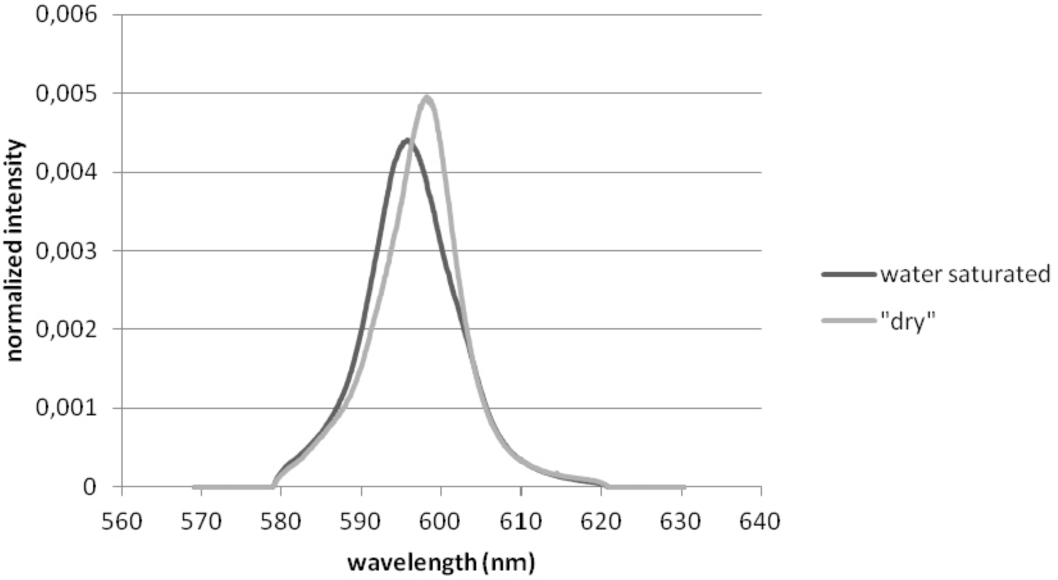


Figure 1-8. *The solvated curium ion in the water saturated and the "dry" cyclohexanone. The peak maximum for the "free" solvated curium in the water saturated cyclohexanone is at 595.8 nm, while the peak maximum in the dry cyclohexanone is slightly red shifted (shifted towards longer wavelengths) and is seen at 598.2 nm.*

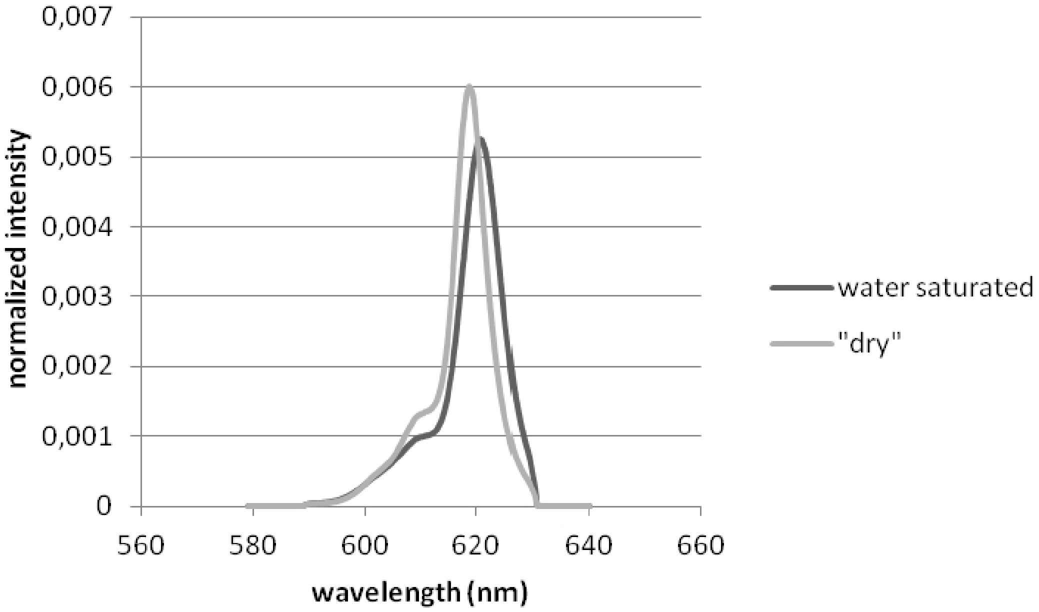


Figure 1-9. *The spectra of the 2:1 complexes in the water saturated and the "dry" cyclohexanone. When comparing the "dry" and the water saturated diluent, the water saturated complex is red.*

From the titrations a concentration of ligand where all the different curium species are present simultaneously in the solution can be chosen for proceeding to a thermodynamic evaluation. From the ligand titrations concentrations of 2.5 µM (“dry”) and 8 µM (water saturated) were chosen for this measurement. The temperature of the samples was increased in steps of 5°, with an initial temperature of 10°C and a final temperature of 60°C. After every temperature step spectra of the two solutions were collected.

Using these variations in temperature the ratio between the three species vary. In the case of an endothermic complexation the ratio of complexed curium will increase with increasing temperature, while in the case of an exothermic reaction the concentration of free solvated curium will increase with increased temperature. The same peak deconvolution gives the ratios between the solvated curium, the 1:1 complex and the 1:2 complex, but this time as a function of the temperature. By using the results from these measurements, the stability constant, k, can be calculated as a function of temperature. Using the van’t Hoff equation, Equation 2, the thermodynamic data for the different complexes can then be obtained.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (2)$$

For both the water saturated and the “dry” cyclohexanone the complexation between Cm and BTBP is increasing with increasing temperature, see Figure 1-12 (water saturated) and 1-13 (“dry”). The peak deconvolution is used to give the speciation as a function of temperature, Figure 1-15 (water saturated) and 1-16 (“dry”). The fraction 1:2 complex is increasing with increasing temperature, independently of water saturation or not. Similarly, the fraction of free curium is decreasing. These graphs are to be further analyzed in 2011.

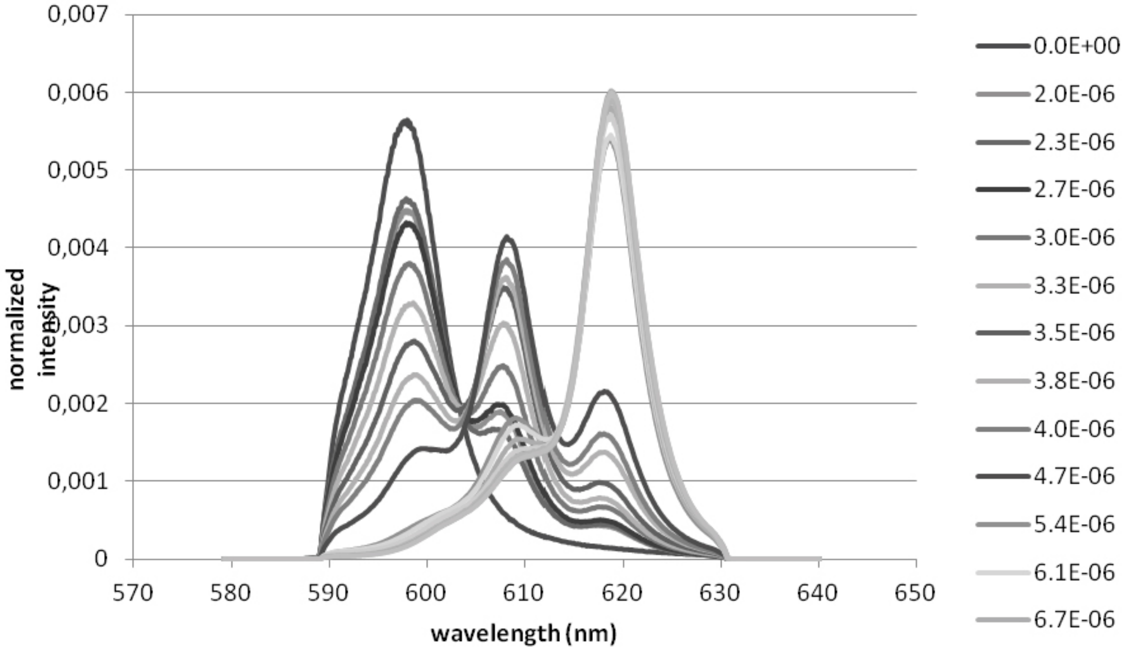


Figure 1-10. *The curium spectra in the “dry” cyclohexanone. The series correspond to ligand concentrations. As can be seen the 2:1 complex (around 620 nm) is increasing with higher ligand concentrations and an intermediate 1:1 complex can be seen around 610 nm.*

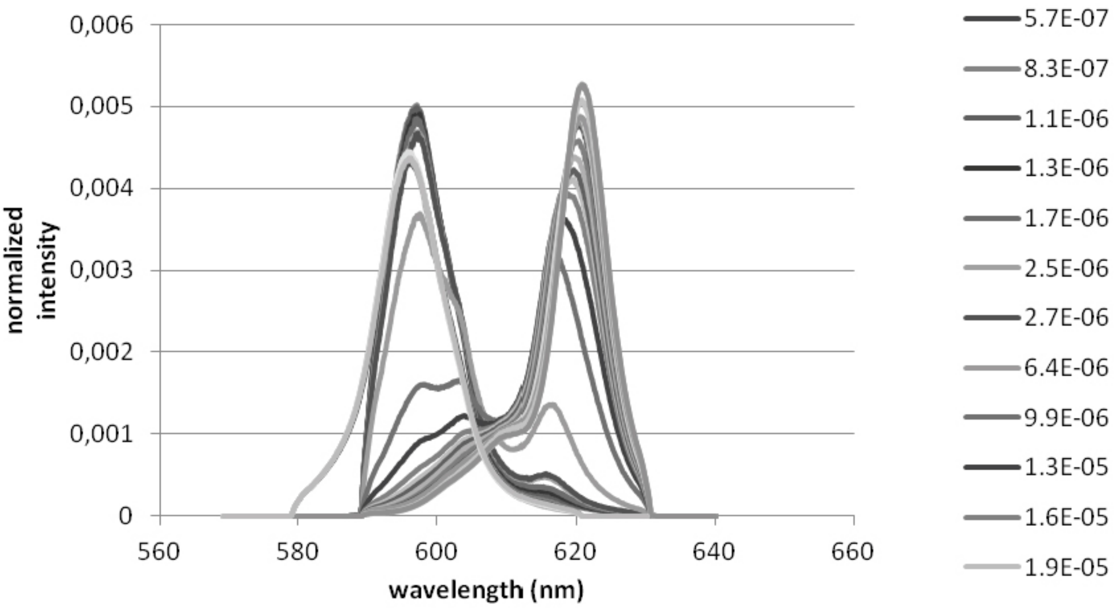


Figure 1-11. The curium spectra in the water saturated cyclohexanone. The series correspond to ligand concentration. As in the dry sample the 2:1 complex (around 620 nm) is increasing with higher ligand concentrations and an intermediate 1:1 complex can be seen around 607 nm.

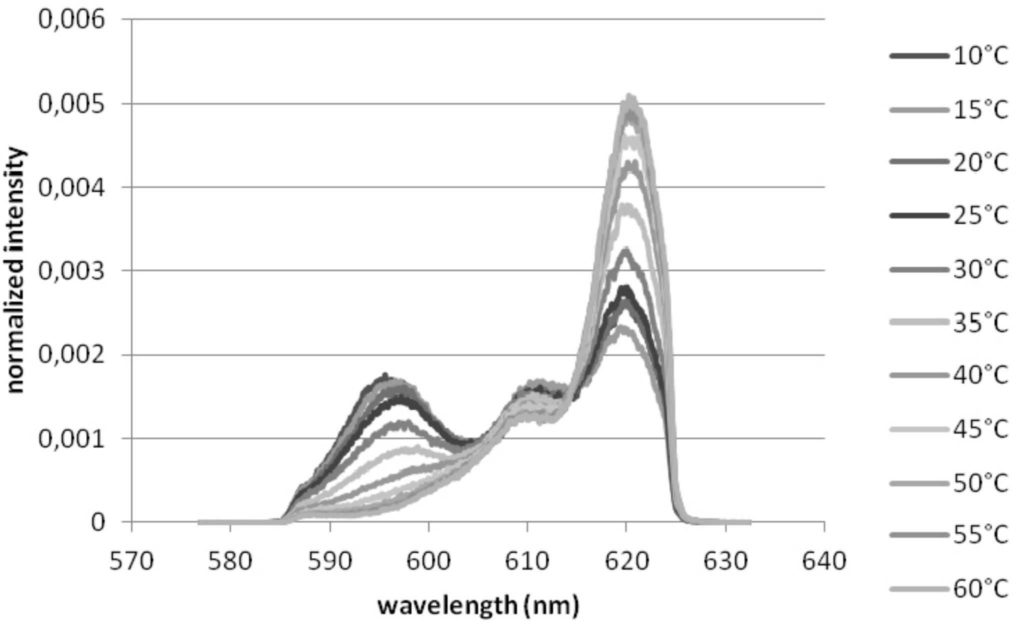


Figure 1-12. The curium spectra in 0.12 µM Cm solution with 8 µM CyMe$_4$-BTBP in water saturated cyclohexanone. The series correspond to different temperatures. As can be seen, the amount complex is increasing, while the concentration solvated curium is decreasing, with increasing temperature.

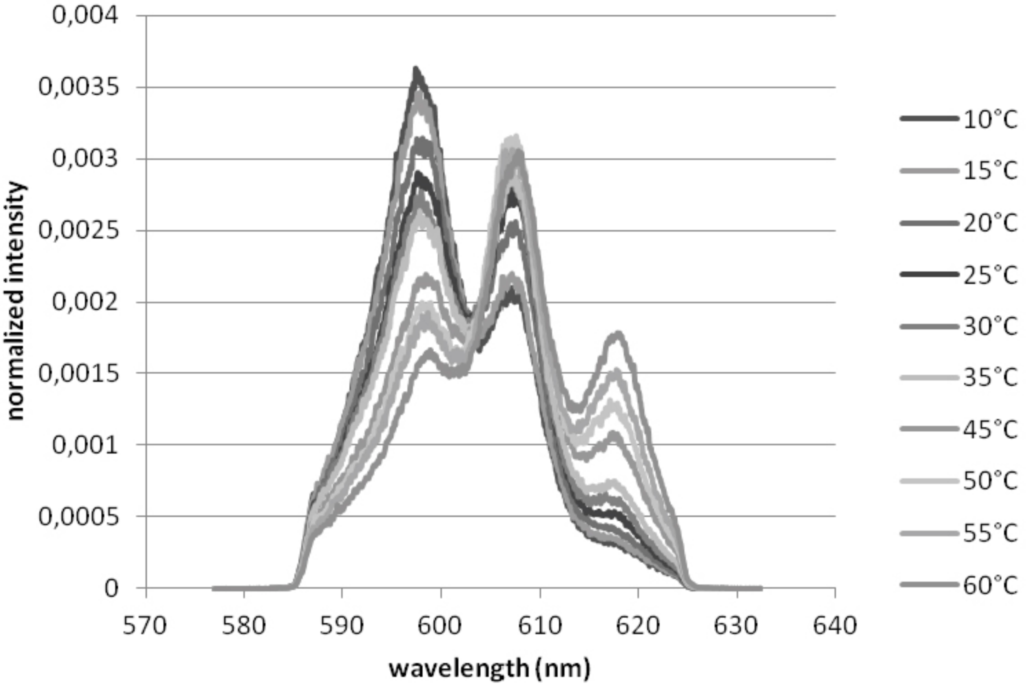


Figure 1-13. The curium spectra in 0.12 µM Cm solution and 2.5 µM CyMe$_4$-BTBP in "dry" cyclohexanone. The series correspond to different temperatures. There is no series corresponding to 40° due to problems during the measurement. The complexation increases with increasing temperature.

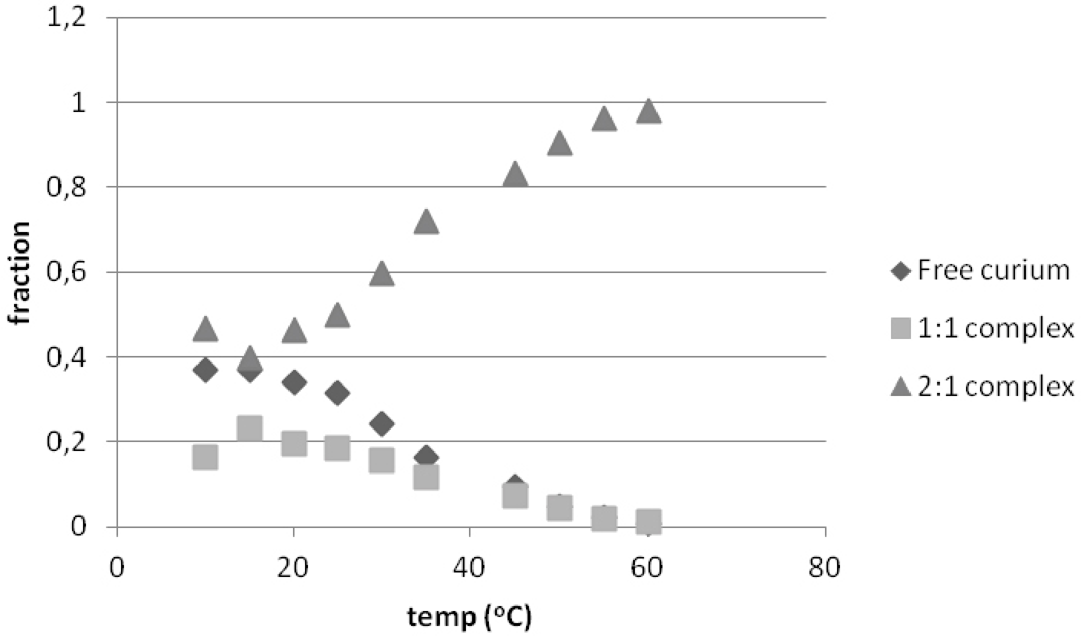


Figure 1-14. The relation between the three curium species as a function of the temperature in the water saturated cyclohexanone. At higher temperature the 2:1 complex is the dominating species. Further evaluation of the data will be performed during 2011.

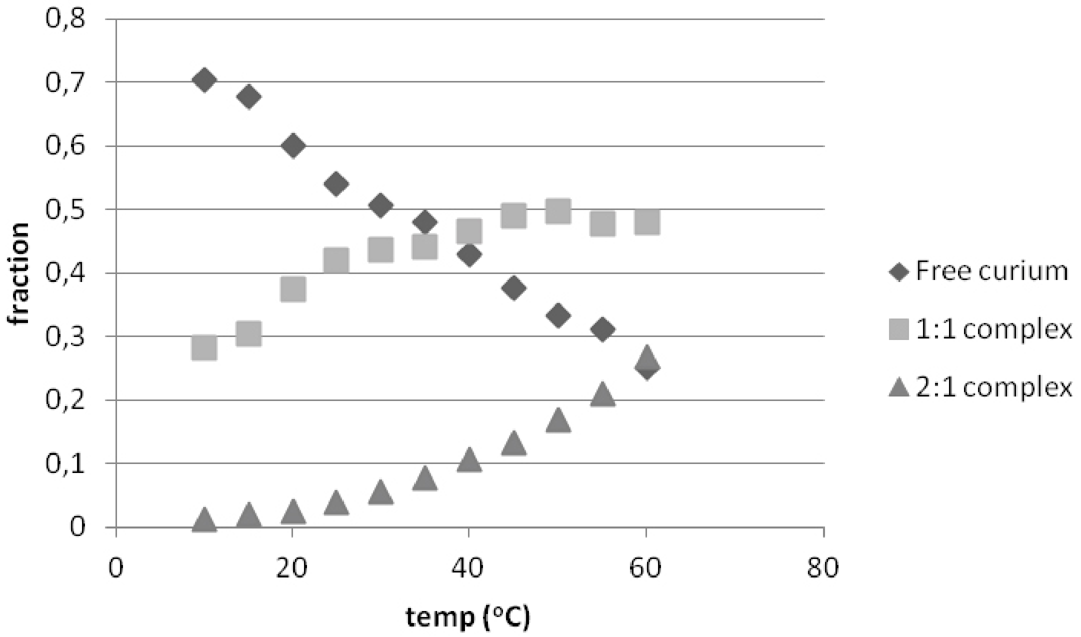


Figure 1-15. The relation between the three curium species as a function of the temperature in the "dry" cyclohexanone. At higher temperature the 2:1 complex is the dominating species. Further evaluation of the data will be performed during 2011.

The stability constants for the equilibriums:

1) Cm(III) + CyMe$_4$-BTBP ↔ [Cm(CyMe$_4$-BTBP)]

2) Cm(III) + 2 CyMe$_4$-BTBP ↔ [Cm(CyMe$_4$-BTBP)$_2$]

in the water saturated cyclohexanone were calculated using the speciation and the known Cm(III) concentration and are shown as a function of temperature in Figure 1-16 for the 1:1 complex and in Figure 1-17 for the 1:2 complex. The solubility of the water in the cyclohexanone was decreasing with a decrease in temperature. This was seen when the sample at 10°C turned cloudy and when the temperature increased turned clear. Another problem with the measurements in the water saturated system is that the graphs are non linear. This indicates that the equilibrium was not reached during the temperature variation and also these measurements are to be repeated.

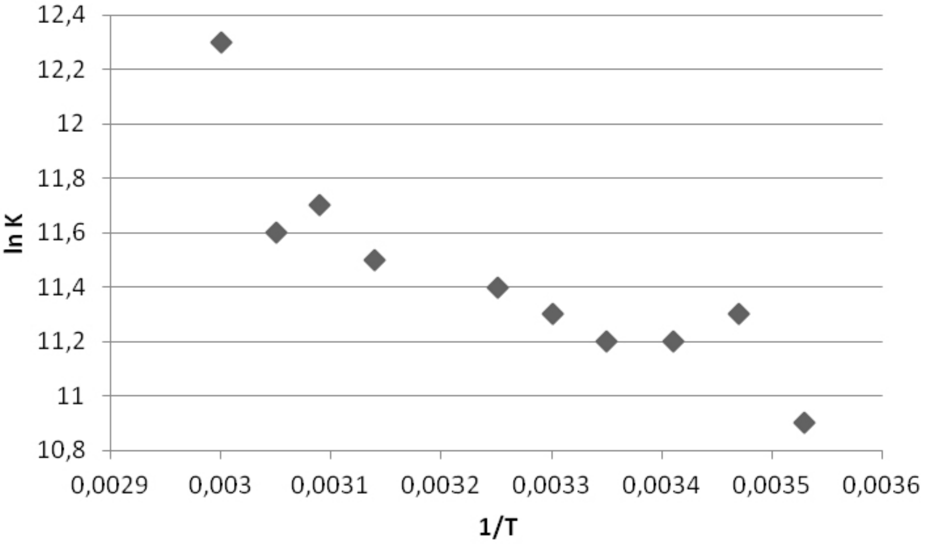


Figure 1-16. The stability constant (k) for the 1:1 complex in the water saturated cyclohexanone as a function of the temperature in Kelvin. The slightly exponential behavior of the measurements indicates non equilibrium conditions.

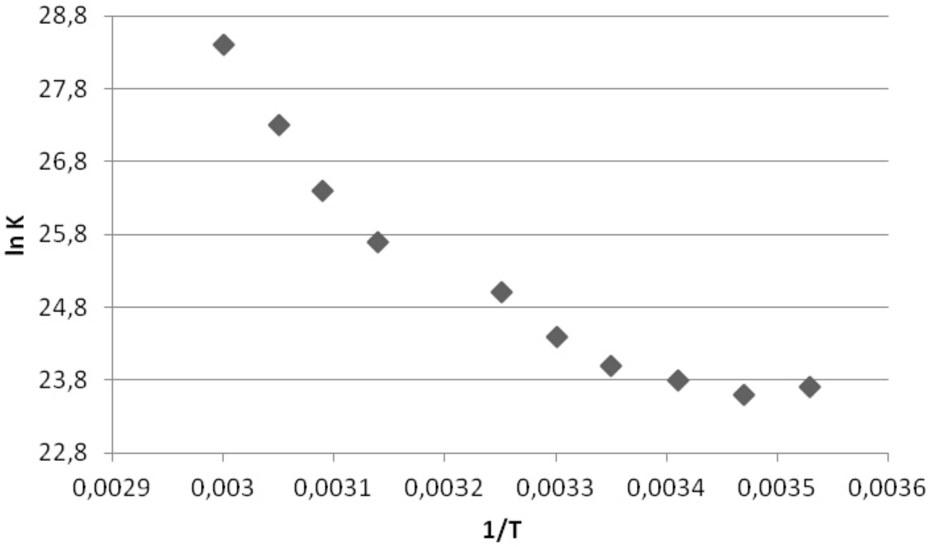


Figure 1-17. *The stability constant (k) for the 2:1 complex in the water saturated cyclohexanone as a function of temperature in Kelvin. The exponential appearance of the graph indicates non equilibrium conditions.*

The corresponding stability constants for the equilibriums in the "dry" cyclohexanone are shown in Figure 1-18 and 1-19 for the 1:1 and 1:2 complex, respectively. As can be seen, the graphs show a linear trend and the thermodynamic data for the "dry" system has been calculated from these graphs and can be seen in Table 1-1. One conclusion of this investigation is that the time for reaching the equilibrium for the complexation is longer in the water saturated system than in the "dry" diluent.

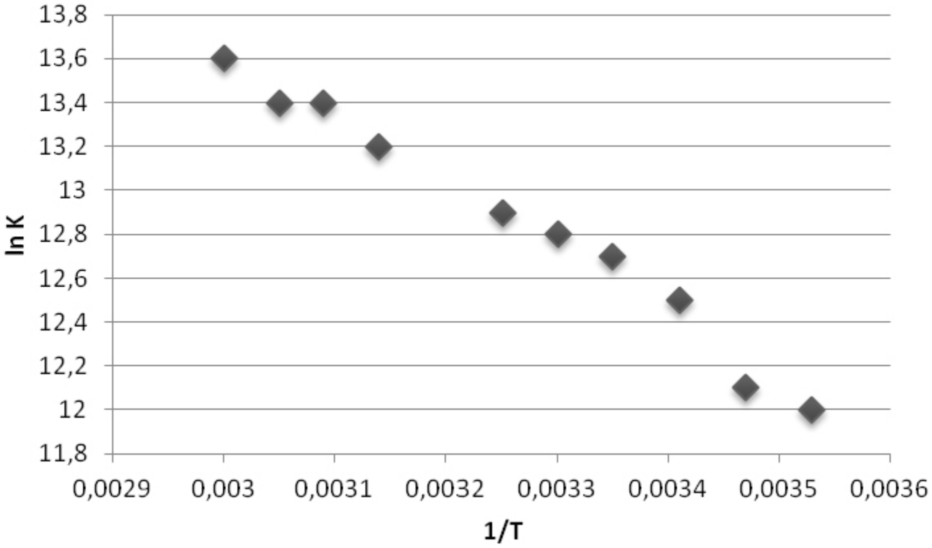


Figure 1-18. *The stability constant (k) for the 1:1 complex in the "dry" cyclohexanone as a function of temperature (T).*

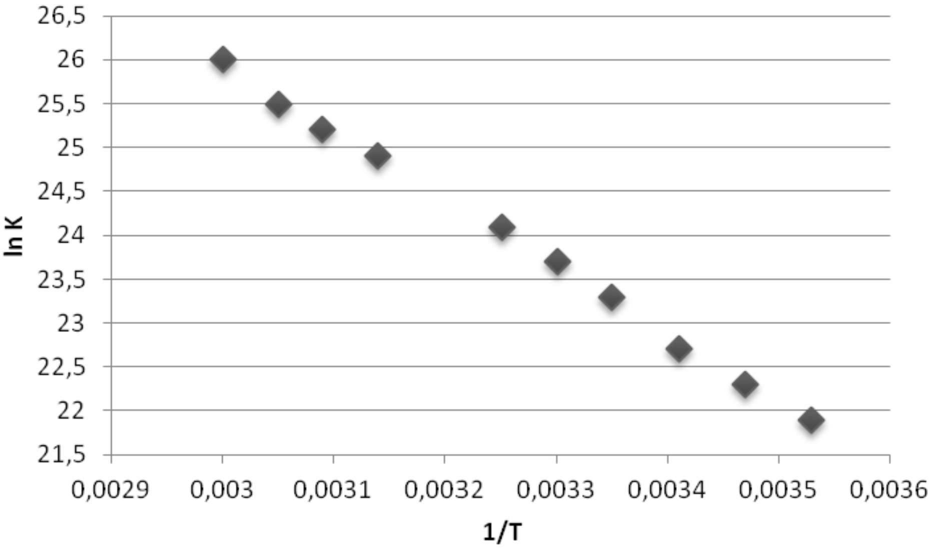


Figure 1-19. *The stability constant (k) for the 1:2 complex in the "dry" cyclohexanone as a function of temperature (T).*

Table 1-1. Thermodynamic constants for complexation in "dry" cyclohexanone.

Complex	1:1	1:2
Diluent	"Dry"	"Dry"
ΔH (kJ/mol)	24.6	64.7
ΔS (J/K·mol)	178.1	410.2
ΔG (25°C) (kJ/mol)	–27.6	–57.6

2 GANEX studies

In the 2009 annual SKB-report (Aneheim et al. 2010a) a ternary solvent extraction system for GANEX purposes was introduced. The investigations of this same system consisting of $CyMe_4$-BTBP and TBP in cyclohexanone have continued. During the last year focus was put primarily on the fission products, mostly regarding the prevention of their extraction with the ternary system by the use of water soluble complexing agents but the extraction behavior was also studied to some extent.

2.1 Experimental

The ternary system consisting of $CyMe_4$-BTBP + 30% TBP in cyclohexanone will in this section from now on be referred to as “the GANEX solvent”.

2.1.1 Extraction/Stripping

All extractions were performed according to the standard extraction experiment described in section 3 unless otherwise stated.

All stripping experiments were performed by first loading a larger quantity of the organic phase with metals from a 4 M nitric acid solution (equal phase volumes and hand-shaking for app. 10 minutes) without any pre-equilibration. The organic phase was then subsided to stripping experiments with a pre-equilibrated aqueous phase performed just like the standard extraction experiment. For all inactive metals the aqueous phase before and after loading of the organic phase was measured with ICP-OES to indirectly determine the metal content in the organic phase. Then the aqueous stripping phases were measured to determine the % of metal stripped.

2.1.2 Precipitation experiments with Pd

All precipitation experiments were performed by adding different amounts of complexing agents (organic or aqueous) to a two phase system with a well defined palladium concentration in the aqueous phase. After contacting the phases, precipitation occurred where not enough ligand was present to complex all the palladium. In this way the palladium to ligand ratio could be determined, given that even a small precipitation can be observed.

2.2 Palladium-BTBP-dependence

One of the major fission products that previously was found to be extracted with the GANEX solvent was palladium. Due to this, studies on the extraction behavior of BTBP and palladium were done to try to determine the composition of the extracted complex.

A range of different slope analyses were performed. These included regular extraction experiments varying the $CyMe_4$-BTBP concentration in the organic phase at different nitrate concentrations and with different palladium concentrations in the aqueous phase, as well as extractions with constant BTBP-concentration but varying the palladium concentration in the aqueous phase. Extractions varying the $CyMe_4$-BTBP concentration in the organic phase with the presence of the water soluble palladium complexant methionine (Aneheim et al. 2010a) in the aqueous phase were also done to ensure that no palladium precipitated during the experiment. In all these analyses the aqueous phase before and after extraction were investigated with ICP-OES. A regular extraction with varying BTBP-concentration but followed by stripping of the organic phase with dilute HCl was also performed. However, despite all these different experiments no slopes could be obtained from the data, as can be seen in Figure 2-1.

The lack of slopes in the extraction of macro amounts of palladium with $CyMe_4$-BTBP could be caused by the formation of water soluble species.

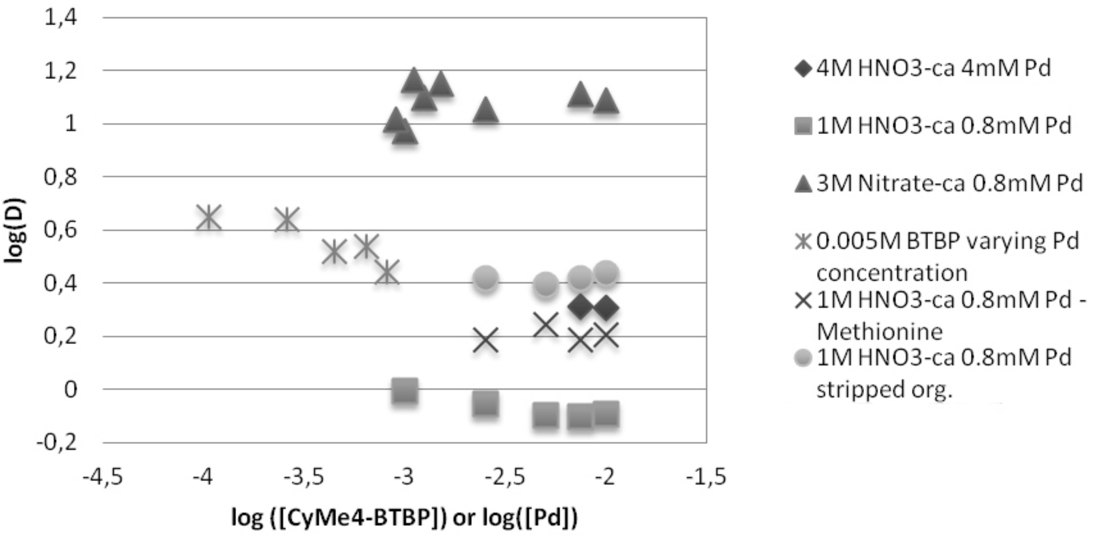


Figure 2-1. *Extraction of Pd with $CyMe_4$-BTBP in cyclohexanone (from 1 M HNO_3 where nothing else is stated).*

However, it has previously been established that palladium precipitates in the presence of ketones such as cyclohexanone. Because of this, the ligand to Pd ratio in the organic phase could be investigated by intentionally precipitating palladium with cyclohexanone.

In all the samples were not enough ligand i.e. BTBP, was present in the organic phase to complex the palladium, a black precipitate became visible after just a few minutes, while the samples containing enough ligand to complex all the Pd, no sign of precipitation was observed for several hours (see Figure 2-2) The concentrations of palladium and BTBP suggest that the extracted complex most likely have a ratio of 1:1.

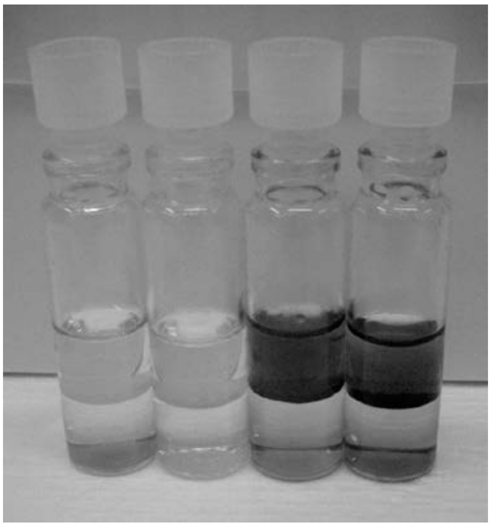


Figure 2-2. *Four different organic phases in contact with the same aqueous phase, 4.2 mM $Pd(NO_3)_2$*$2H_20$ in 1 M HNO_3. From the left: 10 m M $CyMe_4$-BTBP in cyclohexanone, 5 mM $CyMe_4$-BTBP in cyclohexanone, 3 mM $CyMe_4$-BTBP in cyclohexanone and 2 m M $CyMe_4$-BTBP in cyclohexanone.*

2.3 Fission product handling

One option to prevent or minimize the extraction of unwanted elements by the GANEX solvent is suppression of these elements in the aqueous phase. This would mean that the distribution ratio by the GANEX solvent should be suppressed to at least < 1. It is, however, even better the lower the D, since this would allow for more extraction steps increasing the actinide extraction without allowing for too much co-extraction of the unwanted fission products. Another option would be to selectively strip/scrub the undesired elements from the organic phase after extraction. To be able to remove all the undesired products in a reasonable amount of steps a stripping of > 50% would be desired.

Another technique to remove the unwanted fission products, beside stripping and suppression, is to pre extract them before the actual GANEX extraction process. A successful pre extraction need to have a distribution ratio > 1 for the fission product(s) and a D<1 for the actinides. The larger the difference from this value, however, the better, since this would mean fewer extraction steps and less actinide loss.

2.3.1 Suppression/Scrubbing

Both these methods require selective aqueous complexation and the following sections describes a number of different studies on the complexation by various molecules.

Iso Saccharinic Acid (ISA)

α-Isosaccharinic acid (ISA) (Figure 2-3 (left)) has been studied for the ability to strip and suppress the extraction of Zr, Mo and Pd with the GANEX solvent by aqueous complexation. In aqueous solution the lactone form, the isosaccharinic acid and the isosaccharinate are in equilibrium with each other in different amounts depending on the pH. Under the acidic conditions in the GANEX process, most ISA will be present in the lactone form (Figure 2-3 (right)) (Allard 2005). The lactone form of isosaccharinic acid was synthesized using a carbohydrate starting material and calcium hydroxide as a base and Lewis acid. The acid was then converted from the calcium salt to the free acid.

Tests to strip molybdenum (Mo), palladium (Pd), zirconium (Zr) as well as americium (Am), uranium (U), plutonium (Pu) and europium (Eu) from the GANEX solvent with varying concentrations of ISA in a 4 M nitrate ($NaNO_3$) solution showed that none of the actinides were stripped to any greater extent but that Mo and Zr were readily stripped as well as some of the small presence of Eu (Figure 2-4).

In the same way, tests were done to vary the pH of the aqueous stripping phase before the actual back extraction by the addition of ammonia. Nothing is gained by increasing the pH and the zirconium stripping is actually decreased, see Figure 2-5.

The nitrate concentration of the stripping solution was also varied (Figure 2-6) giving a larger stripping at lower nitrate concentrations, which could be expected. However, the effect on the stripping of the actinides also has to be investigated to determine which nitrate concentration that is ideal.

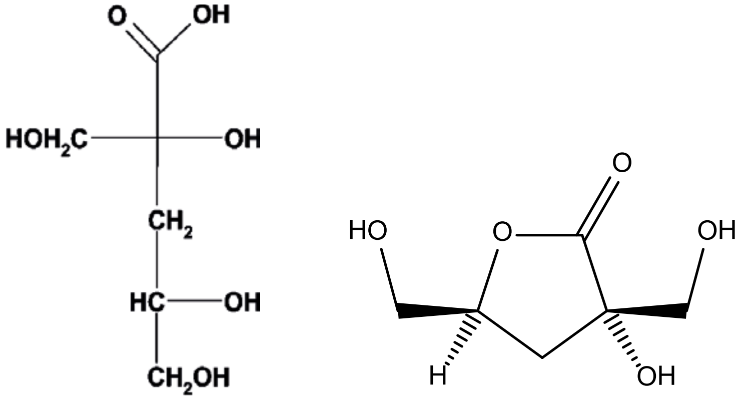


Figure 2-3. α-isosaccarinic acid (left) and the lactone form (right.

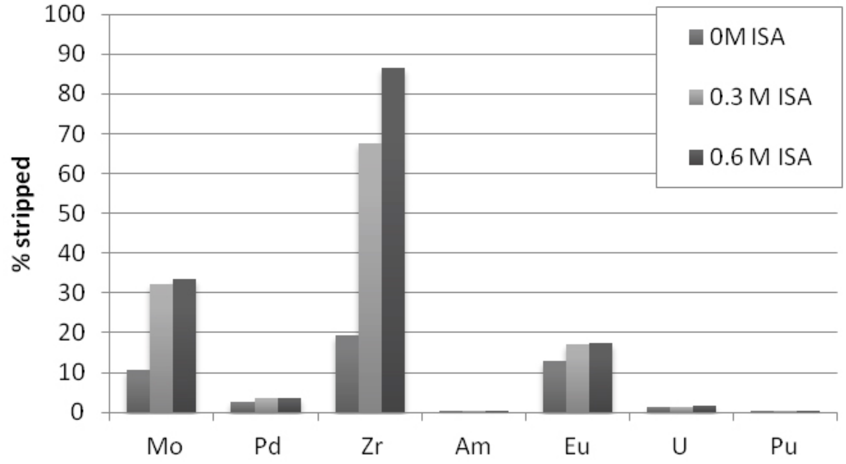


Figure 2-4. *Stripping with ISA (0, 0.3 or 0.6 M) and 4 M nitrate no pH control (pH ca 1.6).*

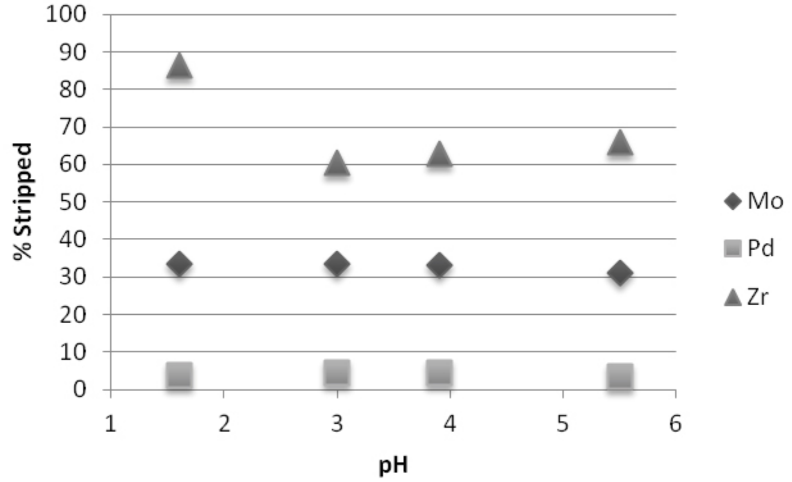


Figure 2-5. *Stripping with ISA (0.6 M) and 4 M $NaNO_3$ pH adjusted with NH_3, first series – no pH control i.e. no added ammonia.*

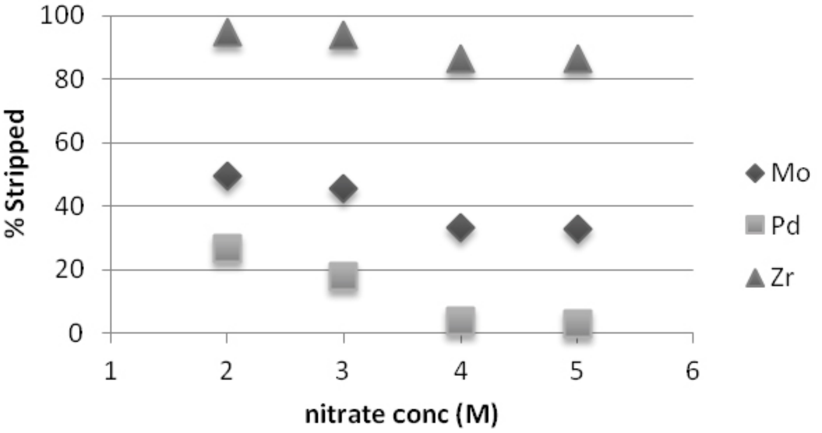


Figure 2-6. *Stripping with ISA (0.6 M) and different concentrations of $NaNO_3$ (no pH adjustment).*

It was also observed that an addition of ISA to the water phase before extraction with the GANEX solvent suppressed the extraction of Zr totally (Figure 2-7) while the extraction of Pd was only slightly lowered. The decrease in Mo distribution ratio was significant at a large addition of ISA, but never reached below the critical value of log D=0.

ISA seems like a possible alternative both for stripping and suppression of the three problematic fission products, but it is not commercially available and also the performance is not ideal. Therefore a search for other possible aqueous complexing agent sould be made.

Screening of various molecules

The molecules shown in Table 2-1 were screened both for stripping and for suppression purposes to be used against the unwanted extraction of fission products with the GANEX solvent.

The molecules were dissolved in a 4 M $NaNO_3$ solution and screened for stripping of Zr, Mo and Pd from a metal loaded GANEX solvent. The results were then compared to the performance of ISA. The molecules marked with asterisks (**) turned out to be unstable in the selected solvent extraction environment i.e. they decomposed and no data was retrieved. For the remaining compounds the results are displayed in Figure 2-8 below. As can be seen, the molecule that managed to strip the largest portion of molybdenum (> the desired 50%) was the Glucolactone. Glucolactone could also strip a large quantity of the zirconium and since it is commercially available in large quantities (due to the use as a food additive) it seems to be a better alternative than the more expensive isosaccharinic acid that needs to be synthesized in house.

The molecules in Table 2-2 were also tested as suppression agents directly in the aqueous phase in the extraction with the GANEX solvent. While many of the molecules seem to be able to suppress the extraction of zirconium, none work very well against neither molybdenum nor palladium (see Figure 2-9). The molecules from Table 2-2 that are absent in Figure 2-9 were found to be unstable in the highly acidic solvent extraction environment or to precipitate palladium as palladium black and hence no data for these were retrieved. Mannitol however also precipitated palladium but is still included in the graph. The two best alternatives when looking at both Mo and Zr suppression would be Glyceric and Fructic acid. Mannitol would also be an option if combined with e.g. bimet to stop the Pd precipitation.

To conclude this screening it can be said that glucolactone would be the better alternative to iso saccharinic acid when it comes to stripping and when it comes to suppression the good results previously reported for bimet could possibly be complemented with using glyceric acid, fructic acid or mannitol. And by combining these two methods the problem with Pd, Zr as well as Mo seems to be manageable. However, more studies need to be made.

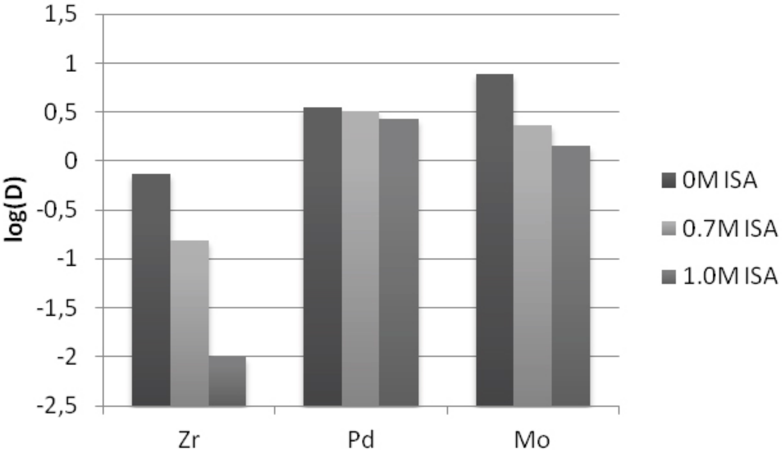
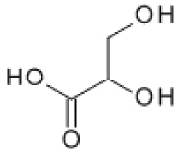
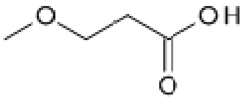
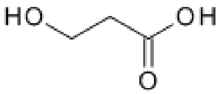
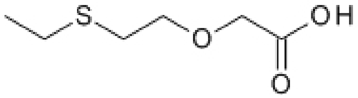
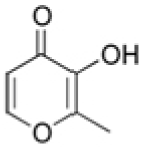
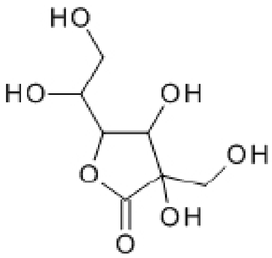
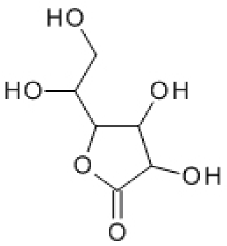
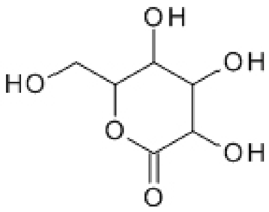
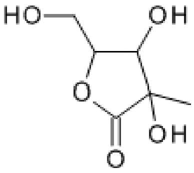
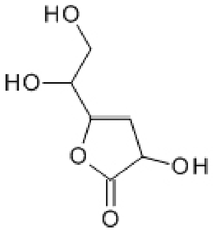
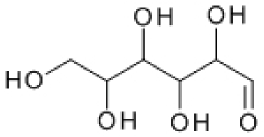
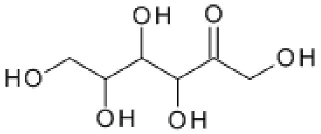
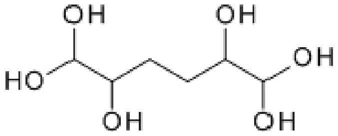


Figure 2-7. *Extraction of Zr, Mo and Pd Mo with 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from 4 M nitric acid with different additions of ISA.*

Table 2-1. Molecular structures and names of the different molecules tested for stripping of Zr, Mo and Pd from GANEX solvent (BTBP+TBP).

Molecular structure	Name
	D,L-Glyceric acid
	3-Methoxy propionic acid
	3-Hydroxy propionic acid **
	2-(2-(ethylthio)ethoxy)acetic acid **
	Ethyl-2-hydroxyethyl sulfide**
	3-hydroxy-2-methyl-4H-pyran-4-one **
	fructic acid
	hydrogenated vitamine C (Mono lactone)
	D-glucono 1,s-lactone (Glucolactone)

Molecular structure	Name
	metyl-lacton A
	metyl-lacton B
	Glucose
	Sorbose
	D-Mannitol

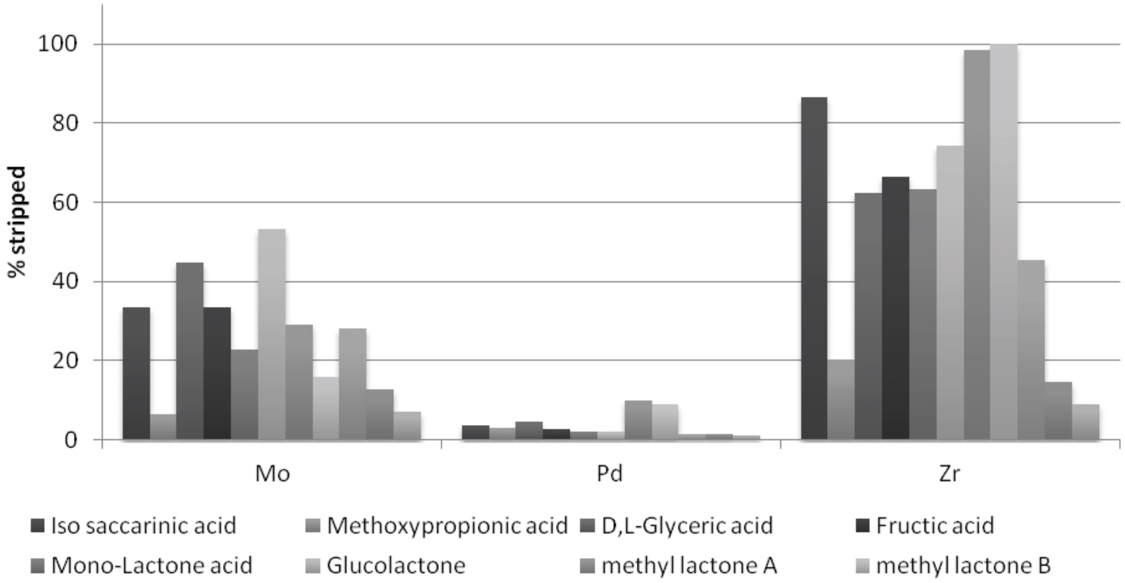


Figure 2-8. *Stripping with 0.6 M of the different molecules in 4 M $NaNO_3$ (no pH adjustment).*

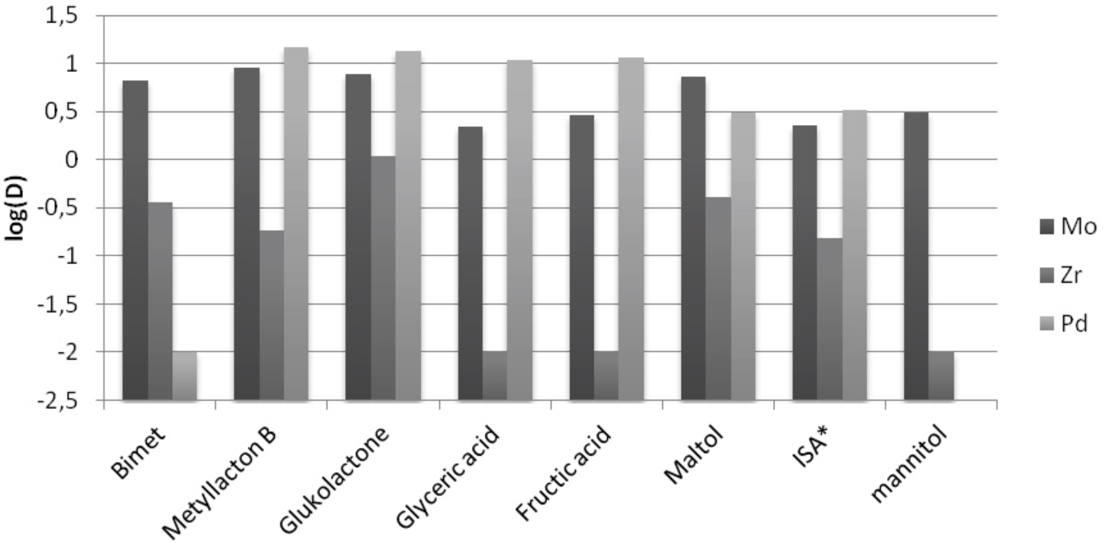


Figure 2-9. *Suppression with 0.5 M ligand in 4 M HNO_3 Mo+Pd+Zr solution. Extraction with 0.0 1 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone. (* 0.7 M ligand).*

Bimet

It was previously shown that the amino acid based molecule bi-methionine (Bimet) can suppress the extraction of palladium and also decrease the extraction of zirconium with the GANEX solvent (Aneheim et al. 2010a). Now the effect on the actinide distribution ratios and also the actinide/lanthanide separation was investigated together with the effect on some of the other problematic fission products.

The result, given in Figure 2-10, shows that the actinide extraction and separation from the lanthanides is more or less unaffected by the addition of Bimet to the water phase, while the extraction of some of the other fission products (Ag, Rh, Sb) is suppressed. Bimet therefore still seems to be the best option to use for Pd suppression.

Mannitol

It was previously shown that mannitol could suppress the extraction of zirconium with the GANEX solvent (Aneheim et al. 2010a). Therefore the effect on the extraction of other problematic fission and corrosion products was investigated. As the result show in Figure 2-11, the extraction of Ag, Cd, Rh and Sb decreased while the extraction of Mn was not affected to any greater extent. This confirms that mannitol possibly could be used as a complementary aqueous complexing agent to bimet.

2.3.2 Pre extraction

It was previously reported that dioctyl sulfide in kerosene could extract palladium (Aneheim et al. 2010a). The effect on some of the other problematic fission products was therefore investigated. As can be seen in Figure 2-12 also silver can be extracted using dioctyl sulfide but the extraction of the rest of the fission and corrosion products is only minor.

Another extractant, trioctyl-amine (TOA), was also studied for the pre extraction of fission products. Palladium is readily extracted by TOA and also a small portion of the molybdenum, see Figure 2-13. Unfortunately also some of the uranium and plutonium is extracted. This molecule could be used for the removal of Pd and possibly also some Mo, depending on what loss of actinides that could be tolerated in the process.

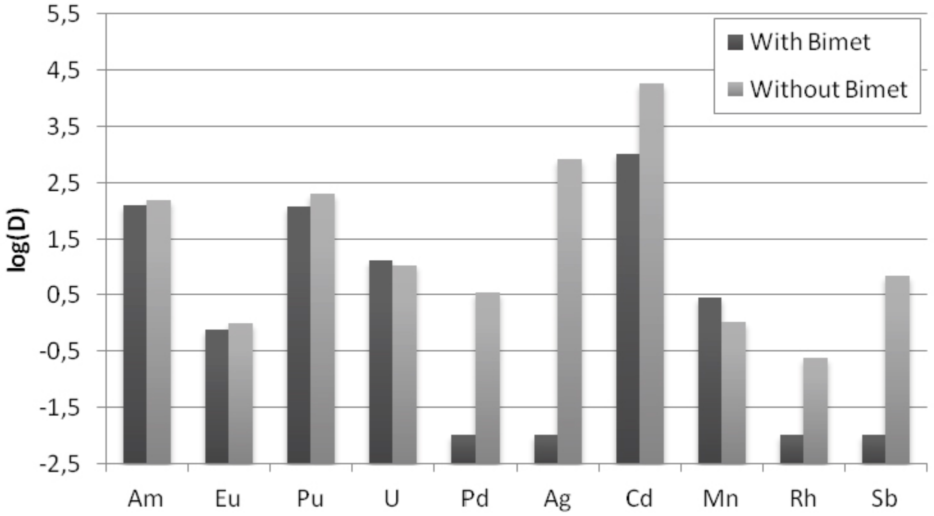


Figure 2-10. *Extraction with 0.01 M* $CyMe_4$*-BTBP and 30% TBP in cyclohexanone with and without the presence of 10 mM Bimet in the aqueous phase, consisting of 4 M* HNO_3.

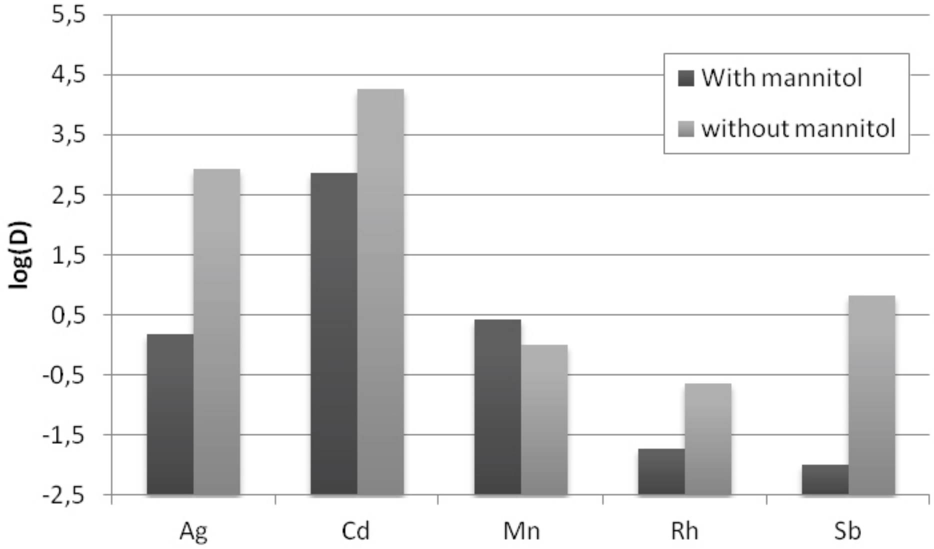


Figure 2-11. *Extraction with 0.01 M* $CyMe_4$*-BTBP and 30% TBP in cyclohexanone with and without the presence of 50 mM Mannitol in the aqueous phase, consisting of 4 M* HNO_3.

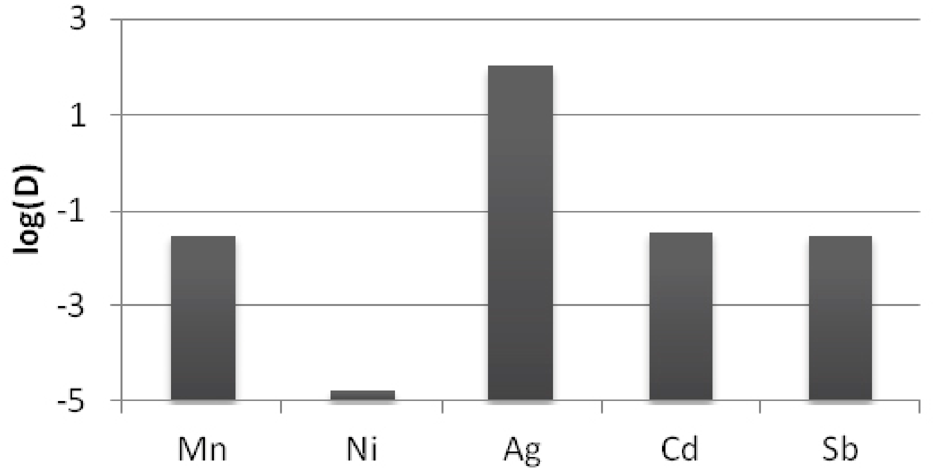


Figure 2-12. *Extraction with 0.5 M dioctyl sulfide in kerosene from a 4 M* HNO_3 *aqueous solution.*

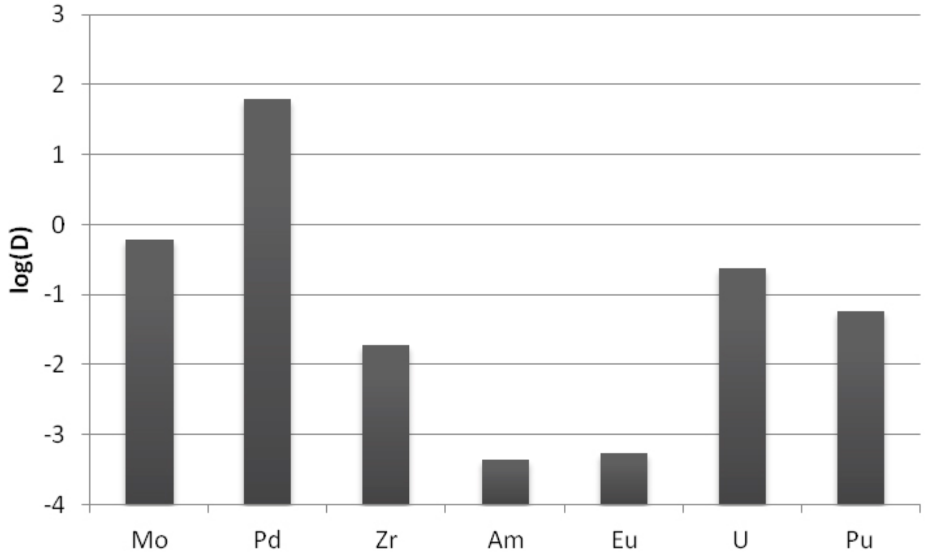


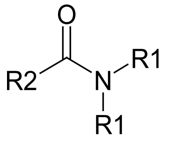
Figure 2-13. *Extraction with 0.5 M tri-octyl amine in octanol from a 4 M* HNO_3 *aqueous solution.*

2.4 DEHBA for the replacement of TBP

It has sometimes been argued that both extractants and diluents should follow the CHON principle (containing only Carbon, Hydrogen, Oxygen and Nitrogen). The use of TBP in the suggested extraction process violates this idea. However, certain monoamides, see Table 2-2, have shown to have good extracting properties for uranium and plutonium (Nair et al. 1995, 1996, Pathak et al. 2001, Prabhu et al. 1997). These molecules also follow the CHON principle Particularly the small dialkylamides like N,N-di(2-ethylhexyl)butyramide (DEHBA) or N,N-di(2-ethylhexyl)iso-butyramide (DEHiBA) (Thiollet and Musikas 1989) have shown better distribution ratios than N,N-di(octyl) butyramide (DOBA) and N,N-di(octyl)iso-butyramide (DOiBA) (Weigl et al. 2006) for uranium and plutonium and therefore seem to be good options for replacing TBP. Moreover DEHBA and DEHiBA have shown to have relatively good stability toward radiation (Nair et al. 1995) and their degradation products are harmless for the process (mostly amines and carboxylic acids) compared to those produced by TBP (dibutyl phosphoric acid and monobutyl phosphoric acid).

It was decided to test if DEHBA could replace TBP in the GANEX process, and the molecule was synthesized in house according to the procedure developed by Thiollet and Musikas (1989). All extraction experiments were performed according to the standard extraction experiment described earlier.

Table 2-2. Molecular structure of different monoamides.

	**R1**	**R2**
DEHBA	$-CH_2-CH(CH_3)-(CH_2)_3-CH_3$	$-CH_2-CH_2-CH_3$
DEHiBA	$-CH_2-CH(CH_3)-(CH_2)_3-CH_3$	$-CH-(CH_3)_2$
DOBA	$-(CH_2)_7-CH_3$	$-CH_2-CH_2-CH_3$
DOiBA	$-(CH_2)_7-CH_3$	$-CH-(CH_3)_2$

2.4.1 Americium, europium, uranium and plutonium extraction

Three sets of extractions using different amounts of DEHBA were performed and the results were compared with those obtained with TBP. Less $CyMe_4$-BTBP can be dissolved in the solution with 40% DEHBA compared to the one with 30% DEHBA suggesting that the BTBP is not soluble in DEHBA, as could be expected.

The extraction of actinides and lanthanides by the DEHBA-containing solvent is almost the same as the TBP-containing one, see Figure 2-14. The extraction of europium is however somewhat higher which is unfortunate since the distribution ratio now exceeds one, making a separation difficult. The concentration of DEHBA in the organic phase does not affect the extraction of americium, europium and plutonium. This is in accordance with the observations made in previous publications stating that these elements are extracted by $CyMe_4$-BTBP under these conditions (Aneheim et al. 2010b). It can also clearly be seen that the uranium extraction increases with the increase in DEHBA concentration as could be expected.

2.4.2 Lanthanide, corrosion and fission product extraction

Extractions of the lanthanides as well as the rest of the fission products and the corrosion products were performed at two different concentrations of DEHBA and compared to the results from the system using 30% TBP.

The distribution ratios for almost all lanthanides are higher for both DEHBA systems, compared to the one with TBP, see Figure 2-15. The same behavior can be seen for the corrosion products (Figure 2-16). It is also obvious that the distribution ratios are higher for the system with 20% DEHBA compared to that with 40% DEHBA.

When it comes to the rest of the fission products (Figure 2-17) the system with 20% DEHBA once again shows higher distribution ratios for all elements compared to that with 40% DEHBA. When looking at the comparison with the TBP system the trend however looks different. The elements that display a low distribution ratio (i.e. below log(D)=0) show higher D for the DEHBA systems than for the TBP one, while the elements with higher D show an opposite behavior.

To conclude it can be said that the GANEX solvent with DEHBA instead of TBP is equally good at extracting the actinides but unfortunately a larger portion of the lanthanides and fission products are extracted. How this extraction is affected by e.g. radiolysis, however, still has to be investigated before any final conclusions can be made on which system that is preferable.

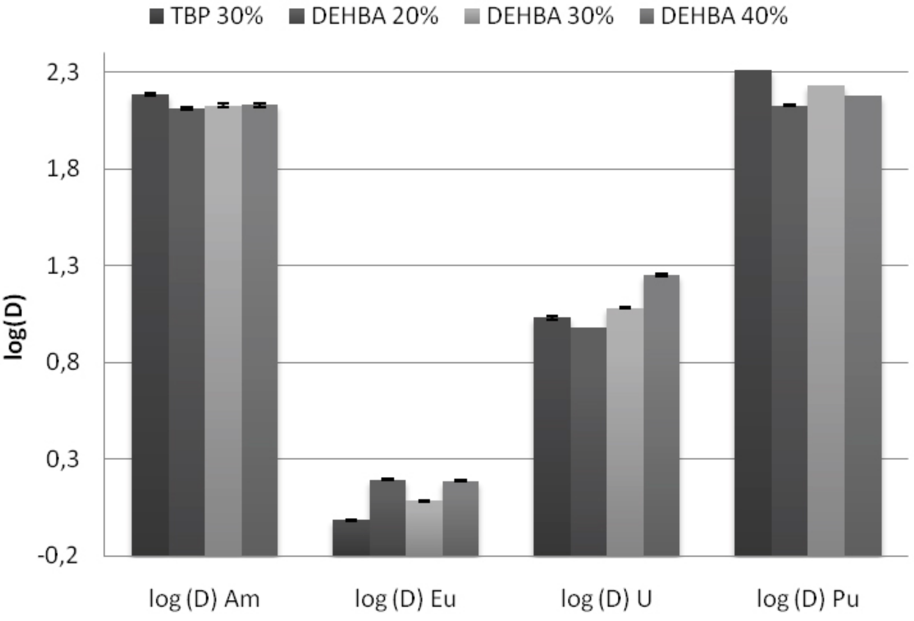


Figure 2-14. *Extraction of Am, Eu, U and Pu with 0.01 M $CyMe_4$-BTBP and different amounts of DEHBA in cyclohexanone from 4 M HNO_3, compared with corresponding results for 30% TBP in cyclohexanone.*

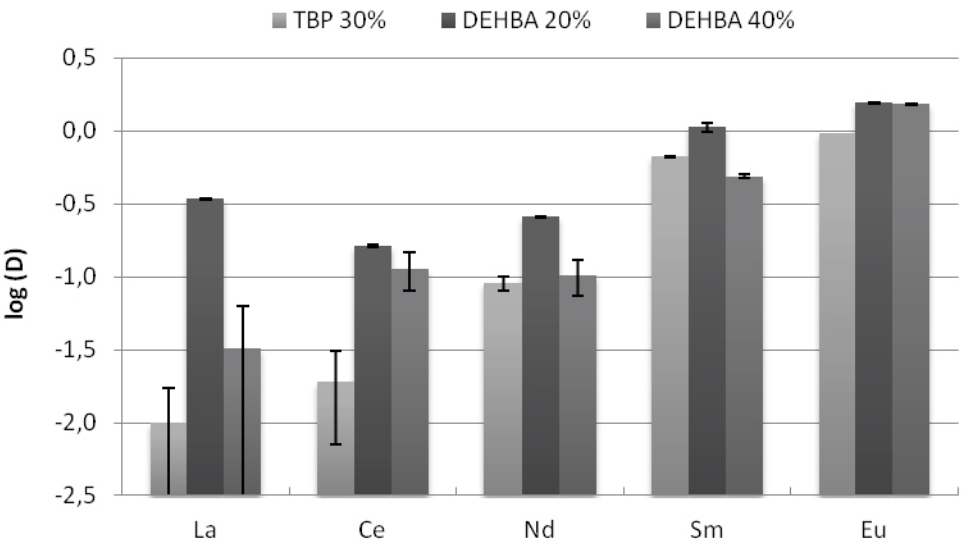


Figure 2-15. *Logarithm of distribution ratios of lanthanides according to the concentration of DEHBA in the organic phase (0.01 M BTBP in cyclohexanone), with 4 M HNO_3 as aqueous phase.*

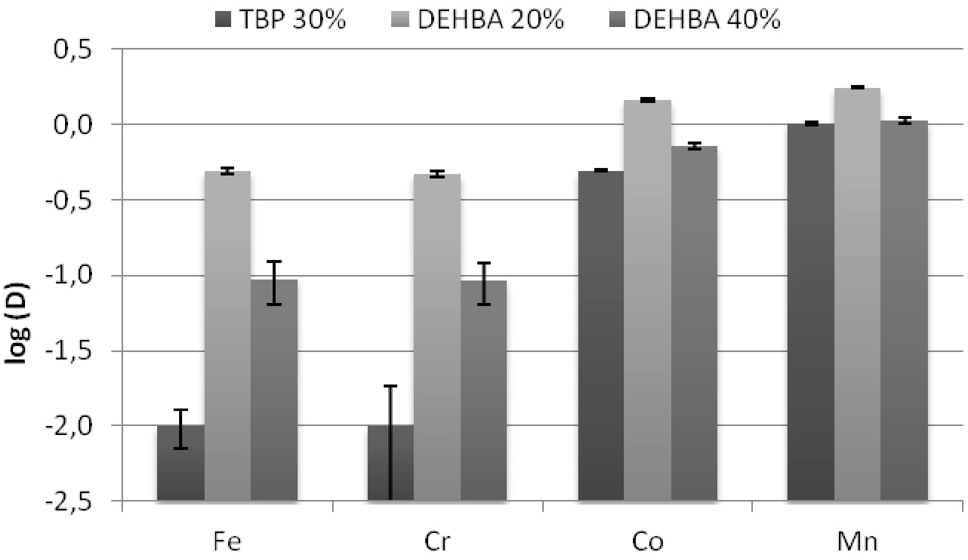


Figure 2-16. *Logarithm of distribution ratios of corrosion products according to the concentration of DEHBA in the organic phase (0.01 M BTBP in cyclohexanone), with 4 M HNO_3 as aqueous phase.*

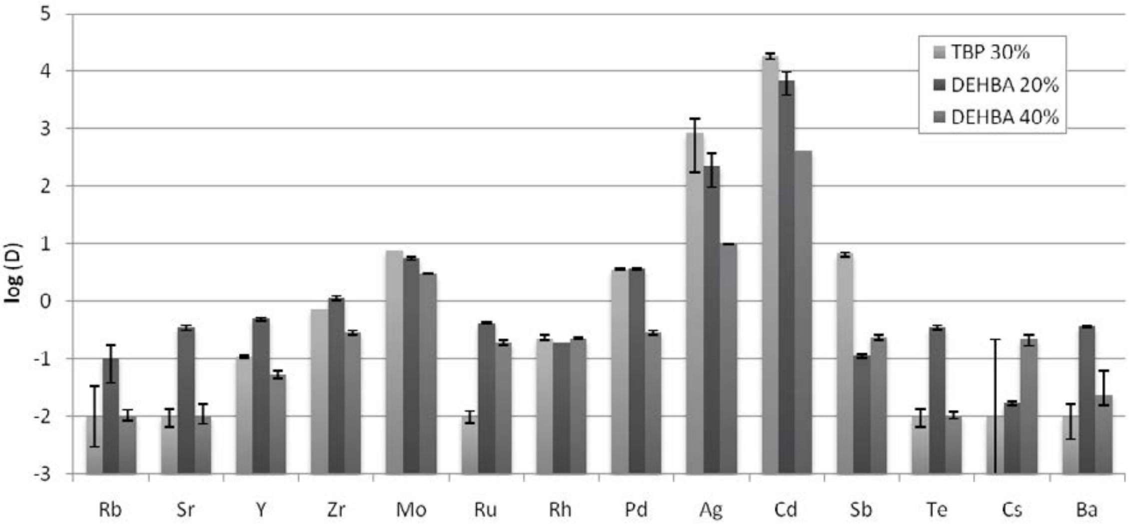


__Figure 2-17.__ Logarithm of distribution ratios of fission products according to the concentration of DEHBA in the organic phase (0.01 M BTBP in cyclohexanone), with 4 M HNO_3 as aqueous phase.

2.4.3 Hydrolytic stability

Because of the use of 4 M HNO_3 during the reprocessing of nuclear fuels, the extractants have to be resistant to acid. To test this stability, a solution of DEHBA and $CyMe_4$-BTBP in cyclohexanone as well as a solution with only DEHBA in cyclohexanone was put in contact with an acidic aqueous solution for one and four weeks, respectively. The result is displayed in Figure 2-18 (DEHBA) and 38 (DEHBA + BTBP). As can be seen the log D values for uranium and americium remain approximately the same after four weeks spent in contact with the 4 M nitric acid solution, but they drop for the plutonium. Since all other values remain relatively stable during the time of the experiment, it is possible that this drop is caused by color quenching from the organic phase. For the system containing both DEHBA and $CyMe_4$-BTBP a decrease in extraction of europium is observed as the contact time with the aqueous phase increases.

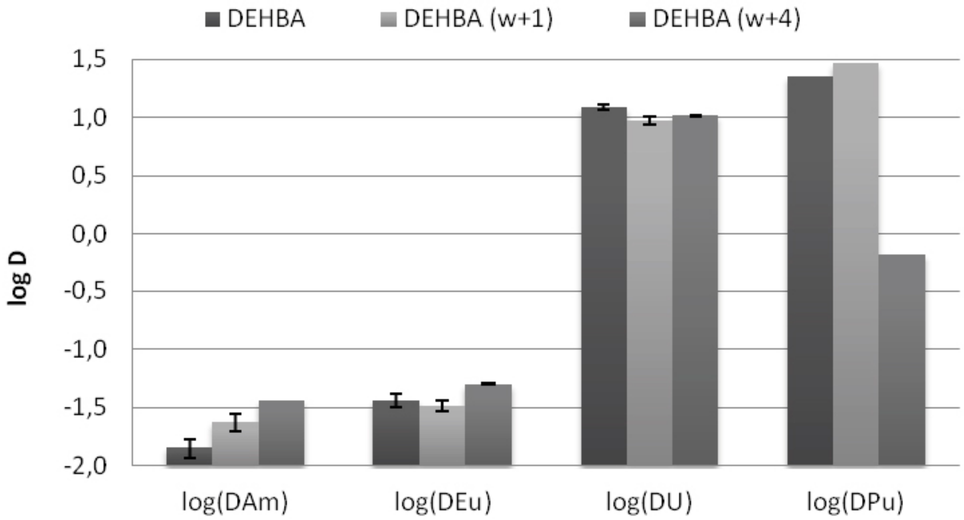


__Figure 2-18.__ The logarithm of distribution ratio of Am (III), Eu (III), U (IV) and PU (VI) according to the time passed in contact with 4 M HNO_3 by the organic phase (20% DEHBA in cyclohexanone). The label DEHBA refers to a fresh solution and w+1 and w+4 refer to solutions in contact with acid for one and four weeks, respectively.

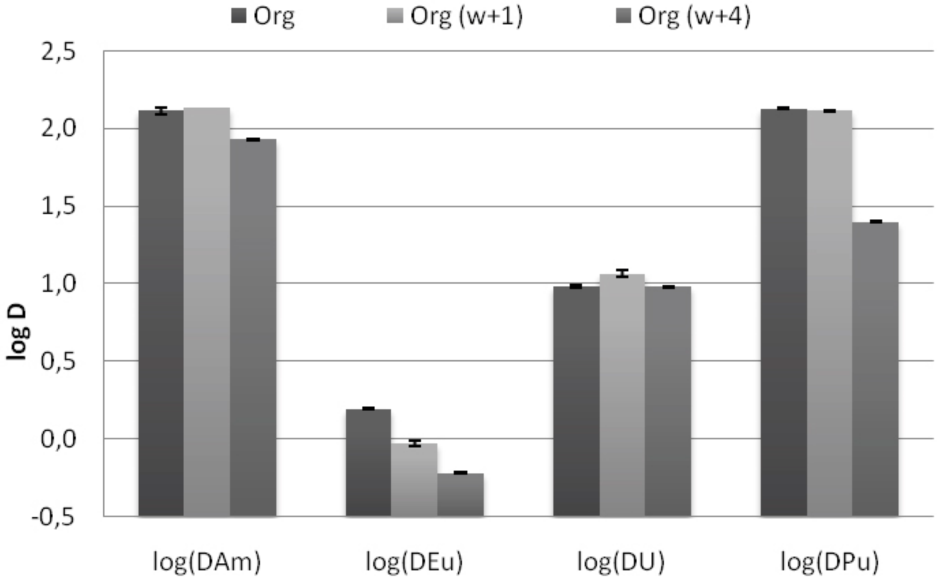


***Figure 2-19.** The logarithm of distribution ratios of Am (III), Eu (III), U (IV) and PU (VI) according to the time passed in contact with 4 M HNO_3 by the organic phase (0.01 M BTBP, 20% DEHBA in cyclohexanone). The label DEHBA refers to a fresh solution and w+1 and w+4 refer to solutions in contact with acid for one and four weeks, respectively.*

2.4.4 Acid extraction

Another reason to exchange TBP for DEHBA, besides obeying the CHON principle, is to decrease the nitric acid extraction into the organic phase, since TBP is known to extract HNO_3 in both 2:1 and 1:1 complexes (Alcock et al. 1956, Chaiko and Vandegrift 1988). Due to this the acid extraction into four different organic phases was investigated by first contacting the organic phases with acid for 15 minutes and then stripping them with MQ water for the same time. The stripped water was then titrated with 0.1 M NaOH.

As can be seen in Figure 2-20 the acid extraction caused by TBP is negligible compared to that of cyclohexanone and hence the exchange of TBP to DEHBA would not have any effect in this matter.

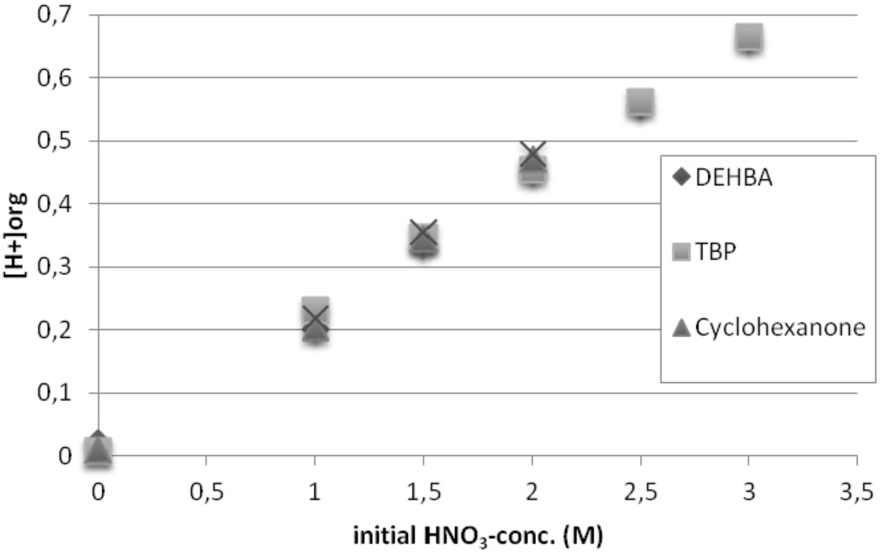


***Figure 2-20.** Acid extraction at different concentrations with four different organic phases DEHBA: 30% DEHBA in cyclohexanone, TBP: 30% TBP in cyclohexanone, Cyclohexanone: pure cyclohexanone, Cyclohexanone Pre-saturated: cyclohexanone pre-saturated with water and aqueous phases pre-saturated with cyclohexanone.*

2.4.5 Solvent effects on the rate of mass transfer

It has several times been showed that not only the extractants but also the diluents or phase modifiers affect the kinetics of an extraction system and not only the final distribution ratio of an extraction. Therefore, it is of interest to see whether the exchange of TBP for DEHBA affects the rate of extraction or not. Two kinetic screenings were performed with 30% TBP or DEHBA and 0.01 M of $CyMe_4$-BTBP in the two different diluents nitrobenzene and cyclohexanone. These two diluents were chosen since nitrobenzene earlier has shown interesting extraction properties when using $CyMe_4$-BTBP and because cyclohexanone is used in the proposed GANEX proces. The aqueous phase was in all experiments 4 M HNO_3.

The organic and aqueous phases were contacted in a mechanical shaker and then left to separate by gravitation. When the phases were completely separated, samples of 40–100 µL from each phase were removed for analysis. Samples were in all cases taken after 2.5, 5, 10, 15, 25, 35 and 50 minutes of shaking but also after 1, 2, 3 and 4 minutes when needed. If equilibrium was not reached in this time the shaking continued and new samples were taken until equilibrium had been reached. All samples were made in duplicates.

Nitrobenzene

With nitrobenzene as diluent, the TBP based GANEX process shows higher distributions ratios for both americium (Figure 2-21) and europium (Figure 2-22). A number of samples in the TBP based solvent have not been evaluated yet, but it appears as if TBP has a faster extraction than the DEHBA in this system. However, due to technical problems with the detector, all samples in these series are to be re measured. Another observation made was that the phase separation in the DEHBA based system is very slow. This can perhaps be explained with interactions between the monoamide and the nitrobenzene molecule. This study is going to be evaluated during 2011. One part of the evaluation will be to investigate the surface tension of the different diluents.

Cyclohexanone

The extraction of ^{152}Eu as a function of contact time for the two solvents with cyclohexanone as diluent is shown in Figure 2-23. The extraction with the TBP is slightly faster than the solvent using DEHBA. The TBP based solvent reaches equilibrium after around 1,200 seconds of shaking, while the DEHBA based solvent reaches equilibrium after more than 5,400 seconds. The final distribution ratio differs between the two solvents and the final value for the europium is higher in the DEHBA based solvent.

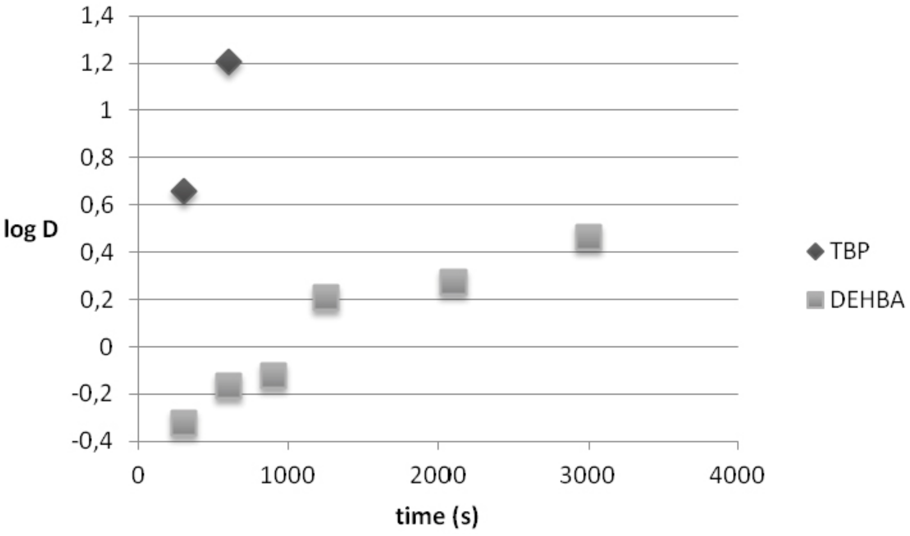


__Figure 2-21.__ The extraction of americium by either TBP or DEHBA in nitrobenzene as a function of contact time. The series denotes 30 vol% of either TBP or DEHBA. The extraction seems to be faster in the TBP based solvent.

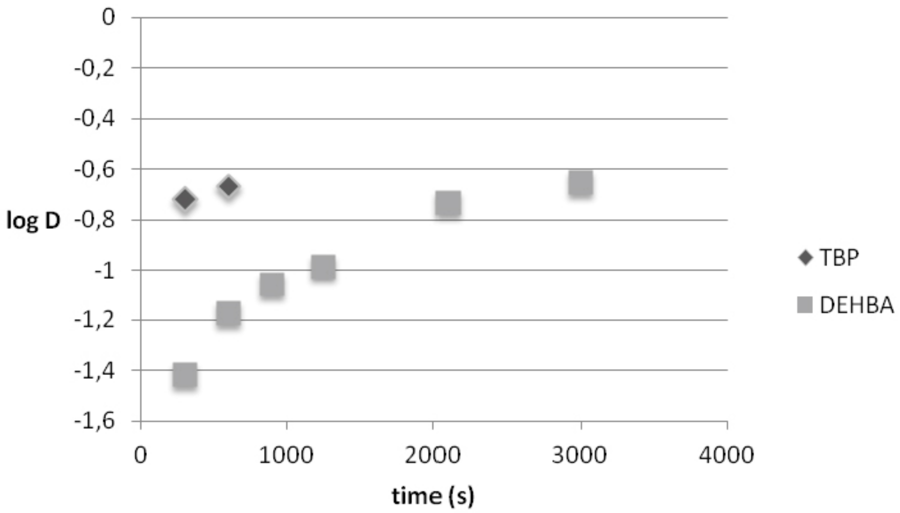


***Figure 2-22.** The extraction of europium in nitrobenzene as a function of contact time. The series denotes 30 vol% of either TBP or DEHBA. The TBP based system shows seems to have reached the equilibrium quicker than the DEHBA based solvent.*

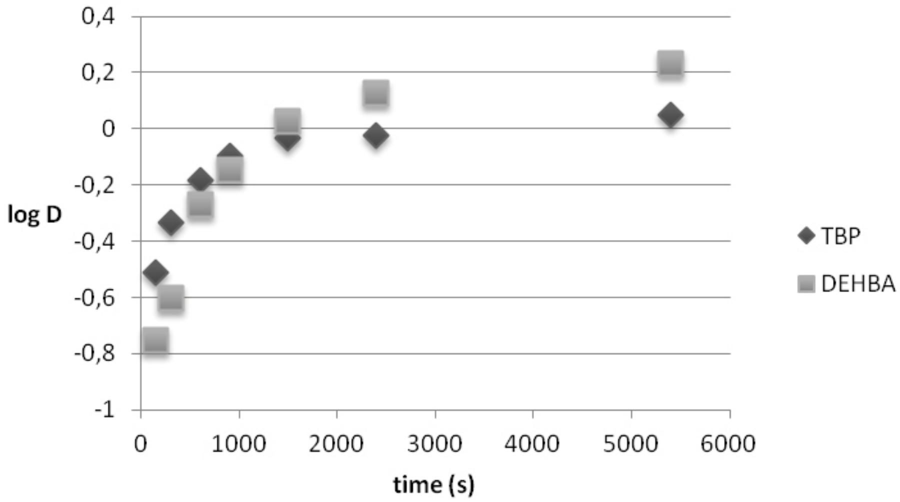


***Figure 2-23.** The extraction of europium as a function of contact time in the different GANEX solvents (30 vol% of either TBP or DEHBA in cyclohexanone). Uncertainities are so small that they are hidden behind sample points.*

The extraction of ^{241}Am is seen in Figure 2-24. Equilibrium seems to be reached for both solvents after appr. 10 minutes of shaking.

To summarize the results, When looking at the separation factors the final value for the two solvents is very similar and, in addition, the difference in rate of extraction is not very large. Thus there are other investigations that have to be done in order to determine which one of the processes that is most promising for a future GANEX process.

Unfortunately the method used in this experiment does not give any information of the rate determining step of the extraction. To achieve this information another extraction device, for example a mixer where the surface between the phases is kept constant, e.g. a Nitsch cell, is needed.

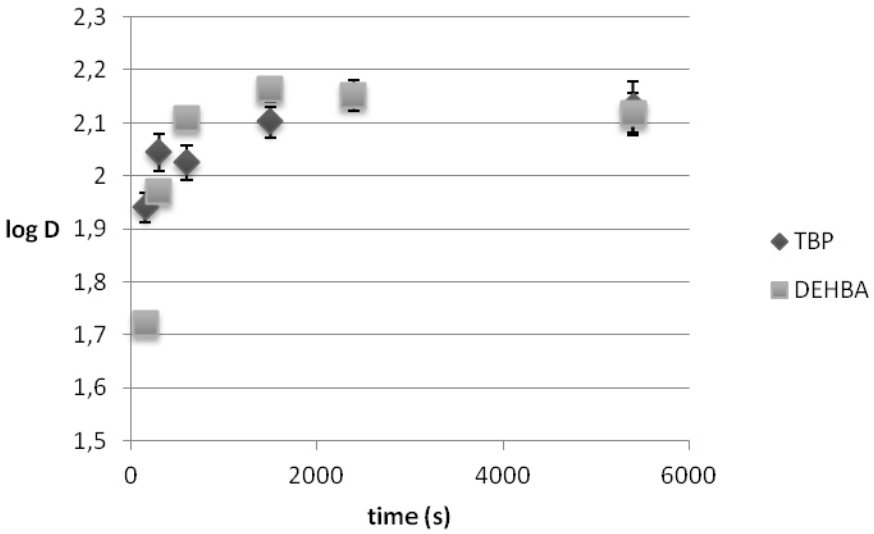


Figure 2-24. *The extraction of americium versus time in the different GANEX solvents (30 vol% of either TBP or DEHBA in cyclohexanone). The uncertainties are higher than in the europium extraction. This is due to the high, and following that, low concentration of americium in the aqueous phase.*

2.5 Plutonium loading

A plutonium loading of the TBP based GANEX solvent developed at Chalmers was performed. This was done in order to investigate the tolerance of high plutonium concentrations possibly present in the reprocessing of future transmutation fuels. Plutonium precipitation has been observed in other extraction systems under high concentrations and in a real life process this causes a risk of criticality.

A plutonium stock solution consisting of HCl (10 M) and Pu (0.41 M) was used. Since HNO_3 is to be used in the real process an attempt was made to transform 1 mL of the HCl solution to a HNO_3 solution through the addition of 1 mL $AgNO_3$ (10 M). A very heavy precipitation was formed as can be seen in Figure 2-25. Due to this, more HNO_3 was added in order to make it possible to retrieve some liquid. Extraction was performed with three different aqueous phases: undiluted (i.e. the concentration obtained after chloride precipitation and dilution), diluted 10 times and diluted 100 times. The plutonium concentration in the three aqueous phases was measured using HPGe1 and. the results can be seen in Table 2-3. The theoretical concentration of the plutonium solution after the addition of the silver nitrate solution and dilution should be 0.205 M but since the measured concentration is much lower, the conclusion can be drawn that a lot of the plutonium did co-precipitate with the silver chloride.

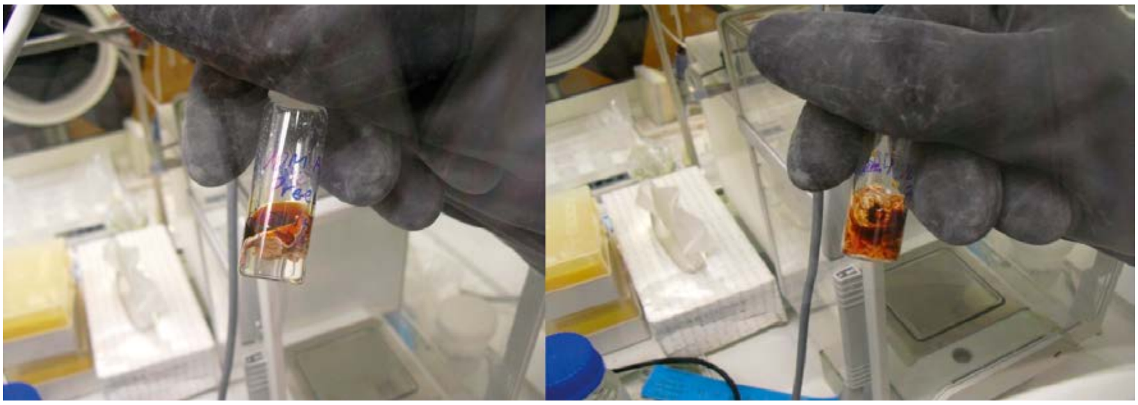


Figure 2-25. *Precipitation of AgCl when adding $AgNO_3$ to the plutonium (HCl) solution.*

Table 2-3. The results from the concentration measurements in the plutonium solutions used for extraction.

Sample	Concentration (mM)
I	34
II	3.4
III	0.34

The three plutonium solutions were vigorously mixed by hand-shaking with the same volume of organic GANEX solvent for ten minutes, and then left to separate by gravitation. Figure 2-26 displays the pure GANEX solvent to the left and the three solutions after the loading experiment to the right. Figure 2-27 once again shows the three loading extractions. From looking at the figures it is clear that the 34 mM Pu solution formed a precipitate in the organic phase. However, the 3.4 mM Pu solution did not precipitate in the organic phase and hence this amount of Pu could be handled by the solvent. Another thing that is clear from the figures is that that the organic solution changes colour from yellow (pure GANEX solvent) to green after contact with the plutonium containing aqueous phases.

2.6 Batch Hot Test of GANEX

During common extraction experiments for reprocessing the dissolved spent fuel is simulated using trace amounts of nuclides. However, in the real spent fuel the amounts of metals are much higher. Therefore it is of high interest to try the GANEX extraction system using a high metal content as well as the strong irradiation field given in a real spent fuel extraction.

A piece of old spent fuel (0.3374 g) from the Swedish reactor “Oskarshamn 1” (burn up 41,000 kWd/kg uranium in 1974 analyzed using ICP-MS in 1985, seen in Table 2-4) was dissolved in 6 M HNO_3 (1.5 ml) pre equilibrated with cyclohexanone and 30% TBP. This solution was left to dissolve in appr. 6 months. Unfortunately, some of the liquid had evaporated when sampling was made. The dissolution liquor was characterized (Figure 2-28 shows the fission product distribution) and the actinide content quantified, see Table 2-5.

A small sample (10 μL) was taken from the pre-equilibrated batch (the non pre-equilibrated one had unfortunately dried out) and was diluted with 10 mL 1 M HNO_3 to a total of 1,000 times. To be able to measure the gamma spectrum of the fuel this solution was diluted once more: 100 μL was diluted with 9.9 mL 1 M HNO_3 to a total dilution of 100,000 times. The initial HPGe analysis can be seen in Figure 2-29 and it is obvious that there is a high amount of Cs-137 present in the sample (661.6 keV). The high cesium content can be compared to the earlier analysis of the fuel (Table 2-4). Further analysis and characterization of the dissolution liquor as well as extraction experiments will be performed during 2011.

Also preliminary extractions with the GANEX solvent were made with dissolution liquor diluted 1,000 times but without any pre equilibration of the phases. From this initial extraction it could only be concluded that Am, Cm, U and Pu was extracted but also some Eu.

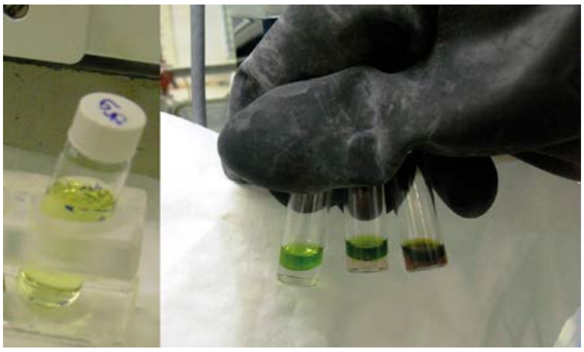


***Figure 2-26.** The loading experiments to the right, the pure organic solution to the left.*

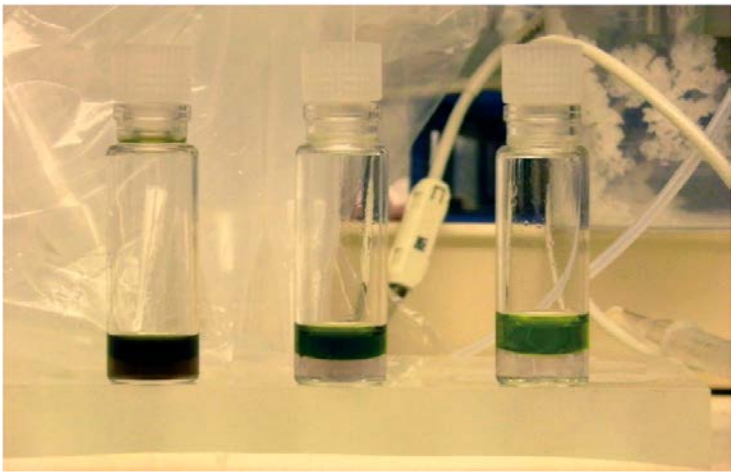


Figure 2-27. The 34 mM solution to the left, the 3.4 mM solution in the middle and the 0.34 mM solution to the right.

Table 2-4. Content of the spent fuel according to analyses performed in 1985. Both Ce-144 and Ru-106 have relatively short half-lives, thus there are no expectations of finding these nuclides when analyzing the samples today.

Nuclide(s)	Activity (MBq /g $_{\text{Uran}}$)	$T_{1/2}$
Cs-134	923	2.06 y
Cs-137	4,130	30.17 y
Ce-144	130	284.8 d
Ru-106	157	373.6 d
Eu-154	168	8.8 y
Sr-90	2,280	28.64 y
Pu-239 + Pu-240	27	$2.411*10^4$ y, 6,563 y
Pu-238 + Am-241	118	87.74 y, 432.2 y
Cm-244	89	18.10 y

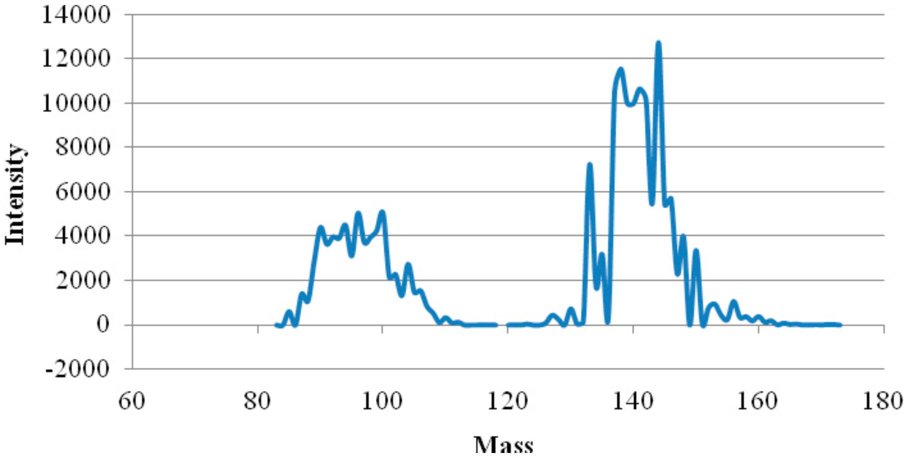


Figure 2-28. ICP-MS measurement of the spent fuel dissolution liquor. Here displaying the fission product distribution.

Table 2-5. Concentration of the actinides in the dissolution liquor. Quantified with ICP-MS using standards of U and Th.

	Mass	Conc. (M)
234-U	234	0.001363852
235-U	235	0.034720328
236-U, 236-Np	236	0.06102656
237-Np	237	0.057212208
238-U, 238-Pu	238	1.388979196
239-Pu	239	0.062829788
240-Pu	240	0.03843673
241-Pu, 241-Am	241	0.016061787
242-Pu, 242-Am	242	0.00978389
243-Am, 243-Cm	243	0.000895065

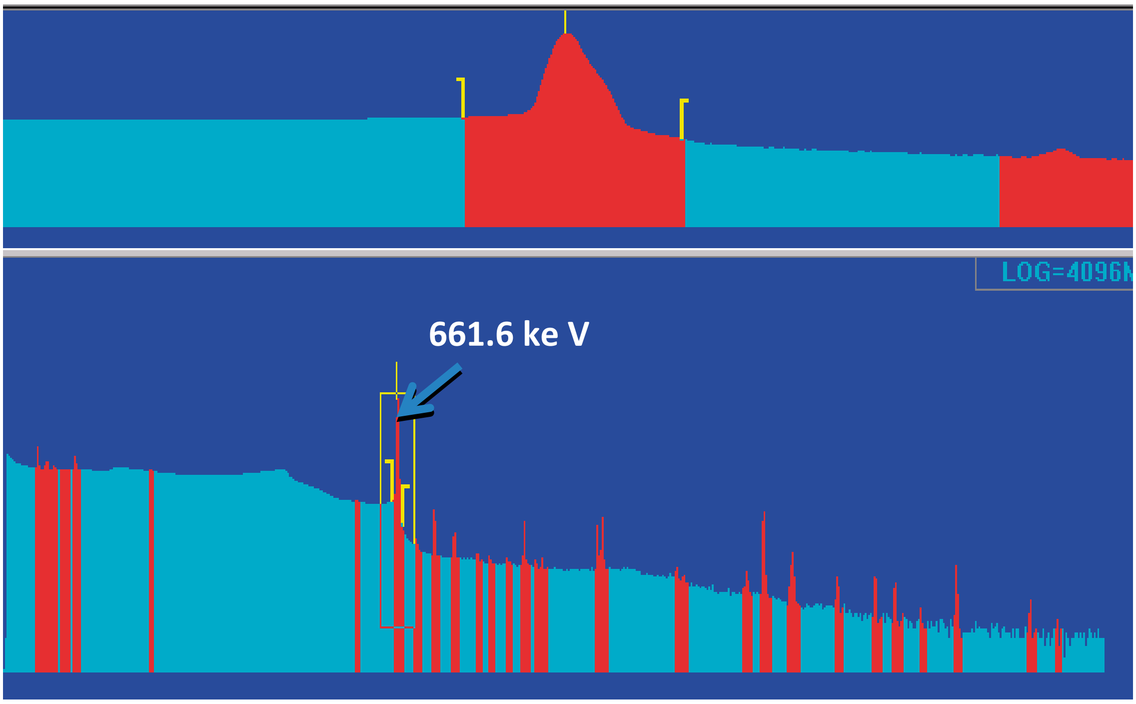


Figure 2-29. The spectrum from the HPGE measurement. As can be seen in the enlarged part of the spectrum (top picture) it is a high concentration of ^{137}*Cs in the sample.*

3 Diluent effects

During 2010 a literature review of different diluent effects was made. Below follows a summary of this review. Parts of this summary were also published in ACSEPT International Workshop (Löfström-Engdahl et al. 2010).

The fact that the choice of organic diluent is important for a solvent extraction process goes without saying. Several factors, such as e.g. price, flash point, viscosity, polarity etc each have their place in the planning of a solvent extraction system. This high number of variables makes the lack of compilations concerning diluent effects an interesting topic. Often the interest for research concerning a specific extraction system focuses on the extractant used and the complexes formed during an extraction. The diluents used are often classical ones, even if it has been shown that the choice of diluent can affect extraction as well as separation in an extraction system.

3.1 Demands on Diluents and Extractants

The choice of extractant(s) and diluent are two important aspects of a successful solvent extraction operation. In many cases the aqueous phase is acidic, basic or in other ways aggressive to the diluent and the extractant. This may affect both the long term behavior of the extraction system as well as the following chemical treatment such as scrubbing or stripping. Also a radioactive or otherwise ionizing environment can destroy the diluent or the extractant. Preferably the diluent as well as the extractant(s) should be completely incinerable in order to reduce waste production. The demands on diluents are summarised by Retegan et al. and can be read in Retegan (2007) and the properties of a usable extractant have been summarized by Andersson et al. (Andersson 2005).

3.2 Diluent categories

Since numerous organic diluents are used in different liquid-liquid extraction systems, several attempts to categorize them have been made. One classification scheme of liquids, including hydrocarbons as well as highly polar molecules such as water, was described by Marcus (2004). He uses the molecules capability of forming hydrogen bonding and from this creates five classes of liquids. Class 1 include liquids capable of forming three-dimensional networks of strong hydrogen bonds (water, polyamino alcohols, hydroxi acids etc). Class 2 includes other liquids that have both active hydrogen atoms and acceptor atoms, but rather than three-dimensional networks they prefer forming chainlike oligomers (primary alcohols, carboxylic acids, primary and secondary amines etc). Class 3 includes dipolar aprotic substances. They are diluents containing molecules with acceptor atoms but no active hydrogen atoms (ethers, ketones, aldehydes etc). Class 4 covers liquids composed of molecules containing active hydrogen atoms but no acceptor atoms (e.g. chloroform). Finally, class 5 includes liquids without hydrogen bonding capability and without donor atoms, such as hydrocarbons, carbon disulfide and carbon tetrachloride. This classification results in different outcomes relevant to solvent extraction. For example; the diluents in class 1 are highly soluble in water and could not be used as organic phase, while diluents from class 3, ketones and aldehydes, react directly with inorganic compounds, forming extractable organic complexes. One example of such extraction in absence of extractant is given by Aneheim et al. (2010b), where cyclohexanone by itself extracts metals. Ketones and aldehydes are aprotic dipolar molecules and since they only consist of donor atoms they tend not to dimerize or self-associate.

Classes of diluents used for solvent extraction purposes are aliphatic molecules e.g. hexane, aromatic ones, e.g. benzene, ketones e.g. cyclohexanone and alcohols e.g. octanol. During a screening, the aliphatic diluents are often considered in order to obtain high distribution ratios, easy handling and easy manufacturing. The aliphatic molecules are typically included in class 5 according to the Marcus classification, since they form no hydrogen bonds. Aliphatic diluents have a low polarizablity and a low dipole moment, which makes the cohesive forces in such diluents dependent on the dispersion interactions between the molecules. These interactions are weak, which means that separation of this kind of molecules is relatively easy. The energetic cost for cavity formation – formation of a hole in the liquid where a species can be placed – is proportional to the energy needed for separating the liquid molecules. This means that liquids exclusively interacting through dispersion interactions, weak attractive interactions, have a low energy cost for cavity formation. On the other hand, there is no permanent dipole moment in aliphatic diluents that can increase attractive interactions between the extracted metal-ligand complex and the diluent. Several authors have reported that aliphatic hydrocarbons are giving the most efficient extraction systems (Islam et al. 1978, Siekiersky 1961). Healy et al. described high water solubility in the organic phase as a decreasing factor for extraction (Healy 1961). Water solubility is low in aliphatic molecules and higher in polar molecules and in diluents having a high dielectric constant. This theory therefore correlates with the one proposed where aliphatic diluents, which have a low cavity cost, increase extraction. Among the aliphatic hydrocarbons the extraction seems to decrease with increasing number of carbon atoms in the chain. Siekierski et al. explained this with the solubility of the extractant in the diluents used (Siekiersky 1961).

The aromatic molecule benzene has no dipole moment. Therefore it is not supposed to extract charged species. On the other hand benzene has a slightly enhanced dielectric constant (Marcus 2004). This implies the existence of some polarisable part of the molecule. This theory has been strengthened when benzene was described as a π-electron-donor that strongly interacts with polar complexes and thereby extracts them (Sekine and Ishii 1970).

Long chained primary alcohols are included in class 2 and their interaction energy as well as their solubility in water decrease with longer aliphatic chains. Several diluent screenings have been performed using alcohols, for example by Nilsson et al. (2006a). Nilsson's results showed surprisingly that shorter aliphatic chain in the alcohol increased extraction. Nilsson et al. explained this with the higher solubility of the extractant in the diluents containing a higher concentration of OH-groups, i.e. the alcohols having a shorter aliphatic chain (Nilsson et al. 2006b). The consensus was for a long time that non-polar diluents were the most effective for extraction and it was explained by the small cost for cavity forming. However, when trying different combinations of extractants and diluents the opposite of this behavior was observed. For example, Jaber and Al-Naser (1997) tried surface active agents, such as polyethylene glycol (PEG), in combination with picrate acid for extraction. Surprisingly, this test indicated that diluents having a high dielectric constant, including high dipolarity and high water solubility (Riddick and Bunger 1970, pp 356, 398), enhanced the extraction. This effect was explained by stabilizing of the helix formed complex by high dielectric medium as well as high solubility of the picrate anions in such diluent. Also the BTBP molecules show higher extraction into polar diluents (Nilsson et al. 2006b). The mentioned studies, i.e. Jaber and Al-Naser (1997) and Nilsson et al. (2006b), are examples where the energetic cost for cavity formation is less important, since interactions with the diluent makes the extraction more favourable into media having a higher dielectric constant. This shows that the nature of the diluent plays an important role in an extraction and that possibility to interact with the diluent is sometimes more important for enhanced extraction of a species than low energetic cost for cavity formation.

4 Irradiation experiments

Since the separation processes intended for recycling of used nuclear fuel take place in a high radiation flux the solvent, *i.e.* both the extractant and the diluent, must be resistant to radiation. The radiation will be of different types, *e.g.* alpha and gamma, and the dose rate will be dependent on the isotopic concentration of minor actinides (MA) (Magnusson et al. 2009). This will in turn be dependent on the initial fuel composition and burn-up etc.

4.1 Irradiation of $CyMe_4$-BTBP

$CyMe_4$-BTBP in two different diluents, cyclohexanone and hexanol, was previously irradiated and analyzed for degradation products (Aneheim et al. 2010a). However, the irradiation was done before the recharge of the ^{60}Co source, hence the dose rate was very low and the total dose given to the solutions only reached around 20 kGy. On the contrary to C5-BTBP, which degrades substantially at these doses (Fermvik 2009, 2011), no degradation was observed for $CyMe_4$-BTBP. Therefore, a new irradiation study was done, using the much higher dose rate and thus reaching higher doses in a short time. Two solutions, containing 0.005 M $CyMe_4$-BTBP in hexanol or cyclohexanone, were irradiated with doses up to 880 kGy. Samples were taken at various times and part of the sample was used for extraction experiments, while the rest was sent to Dr. Bohumir Grüuner at the Institute of inorganic chemistry, Academy of sciences, Czech Republic, for analysis of degradation products using HPLC and LC-MS. The results from these experiments are still undergoing analysis and are hence not yet available.

4.2 Irradiation of UREA and HMTA

An irradiation study in cooperation with the research center in Jülich, Germany, was performed in order to investigate the behavior of irradiated urea, HMTA, and urea + HMTA in the process of internal gelation of uranium(VI).

Internal gelation of uranium(VI) is based on the heat-induced decay of HMTA, catalysed by urea, which causes a drastical pH increase and hydrolysis of the uranium(VI). Understanding of the mechanisms, especially in a radiolytic environment, is crucial to master the whole process. Although internal gelation of uranium(VI) solutions also with addition of e.g. neodymium(III) works fine, it has to be investigated how the system can cope with a higher radiation field caused by e.g. addition of americium(III). Irradiation experiments of HMTA and urea stock soultions with subsequent examination of radiolysis products are therefore important for this understanding.

Three sets, with three samples each, were irradiated. One set was only urea in aqueous solution, one was HMTA in aqueous solution and the third set contained a mixture of urea and HMTA. The samples were placed in the Gamma cell and removed after different periods of time. The first samples were removed after 30 minutes, the second after 5 hours and the last ones were removed after 50 hours. This corresponds to doses of approximately 9, 90 and 900 kGy.

As can be seen in Figure 4-1 the glass was colored very quickly during the irradiation. The irradiated samples are to be analyzed in the research center in Jülich during 2011.

Figure 4-1. *The three series irradiated for FZJ. Top left figure shows the HMTA series, top right shows the urea series and bottom left shows the urea+HMTA series. To the left in all pictures the reference bottle is seen.*

Results 2011

5 BTBP-chemistry

The BTBP type molecules have been found to separate actinides from lanthanides and are hence important molecules in the partitioning for transmutation research. The behaviour of several different of these molecules have been studied during 2011 (Figure 1-2, 2010 results) and (Figure 5-1).

5.1 Silver, Copper and Cadmium extraction

Since silver, copper and cadmium are troublesome elements in the proposed cyclohexanone, TBP and BTBP-CyMe$_4$ based GANEX process, the investigations of the extraction of these elements have proceeded during 2011. Also experiments with C2-BTBP have been performed in order to be able to compare the ligand side group effect on the extraction.

The silver extraction as a function of the ligand C2-BTBP concentration shows a slope of between 0.25 and 0.3 (Figure 5-2). This can be compared to the extraction of nickel presented in earlier literature (Ekberg et al. 2007). The extraction of nickel using the C2-BTBP does not follow a linear trend, instead, it shows that at low ligand concentrations there is a strong ligand concentration dependence (high slope) but at higher ligand concentrations it evens out (Ekberg et al. 2007). This so called plateau behaviour has earlier in literature been explained by that at low concentrations of ligand, the extraction is governed by the association between the metal and ligand, giving a high slope, while at higher concentrations of ligand, the extraction determining step is the solubility of the metal:ligand complex in the two phases (Ekberg et al. 2007). In the nickel study this plateau takes place at ligand concentrations above 1 mM (Ekberg et al. 2007) study concentrations of 5 mM–10 mM are used (Figure 5-2). This indicates that the experiments presented here possibly represent the plateau region.

When plotting the logarithm of the cadmium distribution ratio versus the logarithm of the ligand concentration a peculiar trend is achieved. At lower concentrations (< 5 mM), it can be seen that it is extracted with a dependence of around 0.25 (the same as silver), but when increasing the concentration (> 5 mM), a slope of 1.5 is achieved, indicating a dramatic change in extraction behaviour. Such qualitatively increase of the slope at higher ligand concentrations is also seen in the nickel extraction (Ekberg et al. 2007), but, at much higher concentrations than during this extraction. The cupper extraction shows a linear trend with a slope of 0.4.

These unexpected low slope indicate that there are water soluble complexes in the C2-BTBP-metal systems. However, this theory has not been confirmed yet.

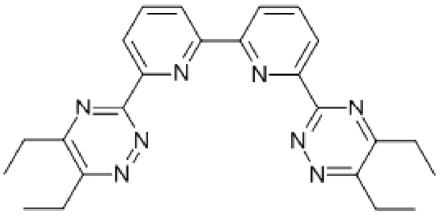


Figure 5-1. *Molecular structure of C2-BTBP.*

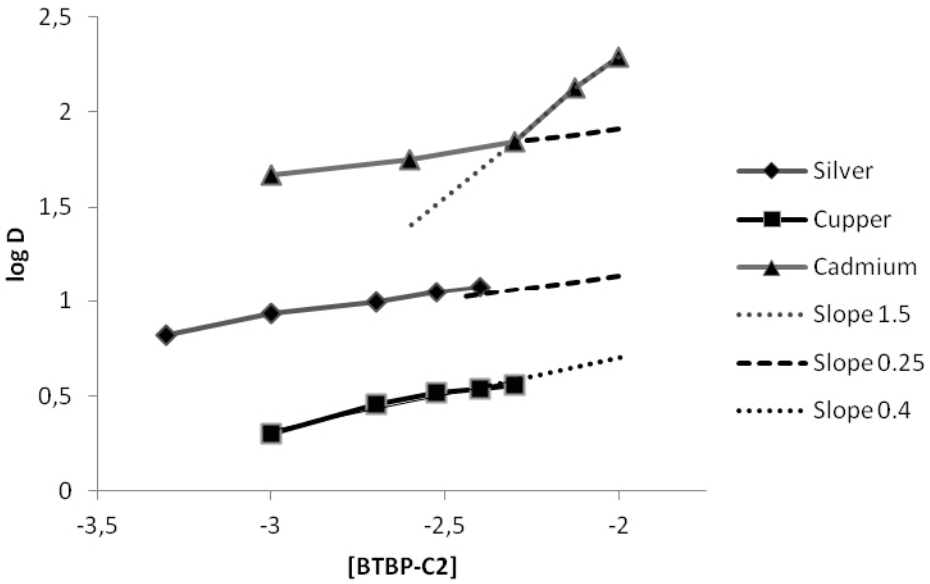


Figure 5-2. *The extraction of silver, copper and cadmium using C2-BTBP in cyclohexanone. The aqueous phase is 1 M* HNO_3*. Imaginary lines with given slopes are shown in the graph in order to guide the eye. Uncertainties are all based on double samples.*

5.1.1 A deeper look into the silver chemistry

The extractions of the pure diluents were investigated in order to see whether the diluent/solvent by its own extracts silver. The diluent cyclohexanone do not extract silver to any greater extent, and when adding TBP the extraction is even more suppressed (Figure 5-3).

The effects of the side group of the ligand were investigated using $CyMe_4$ and C2 – BTBP. As can be seen the D in the $CyMe_4$-BTBP based solvent is higher than for the C2-BTBP based system. This is the same behavior as for nickel (ref). Anyway, the slope analysis for the C2 system is 0.3 during the whole series, while close to 1 for the $CyMe_4$ system at lower ligand concentrations (< 5 mM). The slope of the $CyMe_4$-BTBP extraction is decreasing to 0.3 at higher ligand concentration (> 5 mM). This indicates that $CyMe_4$ silver complex reaches the plateau region at higher ligand concentrations than the C2 complex. This could perhaps indicate that the C2:silver complex is more hydrophilic than the $CyMe_4$:silver complex.

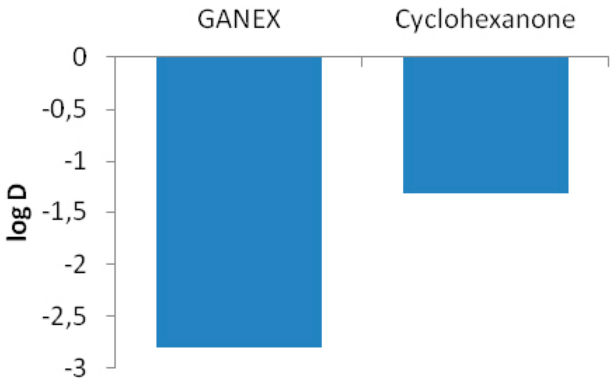


Figure 5-3. *The extraction of silver from the diluent cyclohexanone and the GANEX solvent (cyclohexanone 70% and TBP 30%).*

Evidently, the sidegroup has an effect on the governing step in silver extraction at low concentrations. However, for achieving the highest silver distributions CyMe$_4$-BTBP should be used.

Since the addition of TBP does suppress the silver extraction of the pure cyclohexanone (earlier seen in Figure 5-3) it is interesting to see if this suppression also exist when using CyMe$_4$-BTBP (Figure 5-4). Since the extraction is strongly dominated by the BTBP molecule, the influence of the TBP is so small so it can be neglected, as seen in Figure 5-5.

In order to understand whether the exchange of the cyclic ketone for a long chained alcohol affected the complexation in the silver extraction an exchange of the diluent cyclohexanone for octanol were made Figure 5-6. The extraction is slightly higher in the cyclohexanone, but at higher concentrations of the ligand it seems to be similar. One possible explanation for this is that the extracted complex is more soluble in cyclohexanone than in octanol.

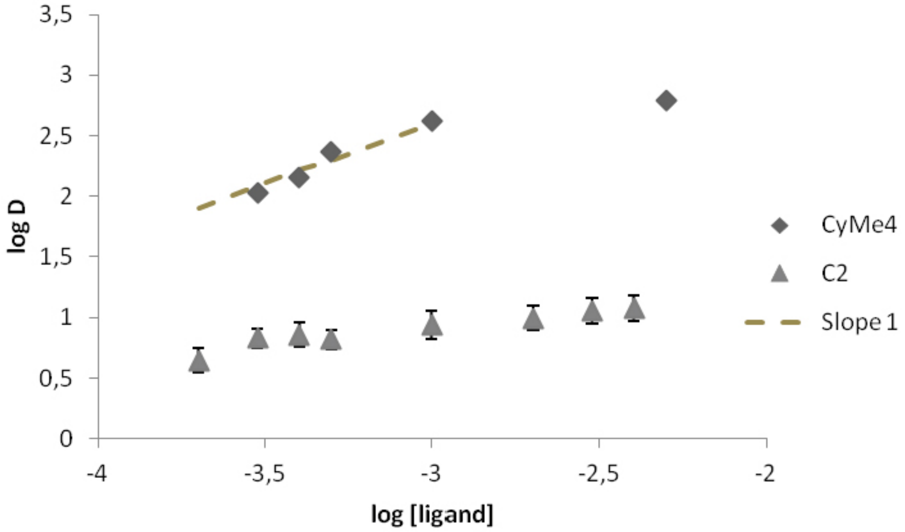


Figure 5-4. *The extraction of silver using CyMe$_4$ and C2 – BTBP in cyclohexanone. There is a different between the extraction behavior, the CyMe$_4$ extracts more, and has a higher slope at lower ligand concentrations.*

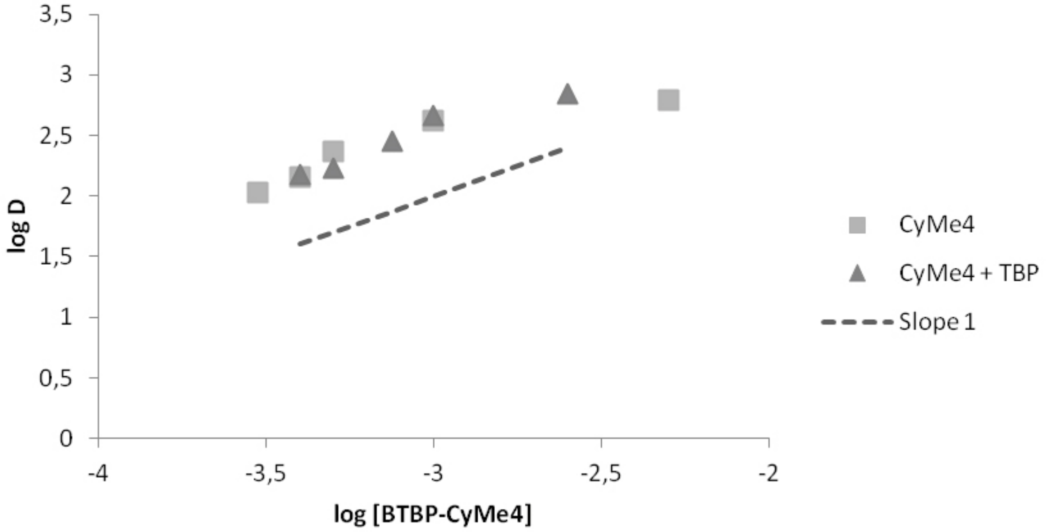


Figure 5-5. *The extraction of silver using CyMe$_4$-BTBP: in pure cyclohexanone and in the GANEX solvent. Also, a value showing the theoretic suppressing effect of the TBP is added in the graph.*

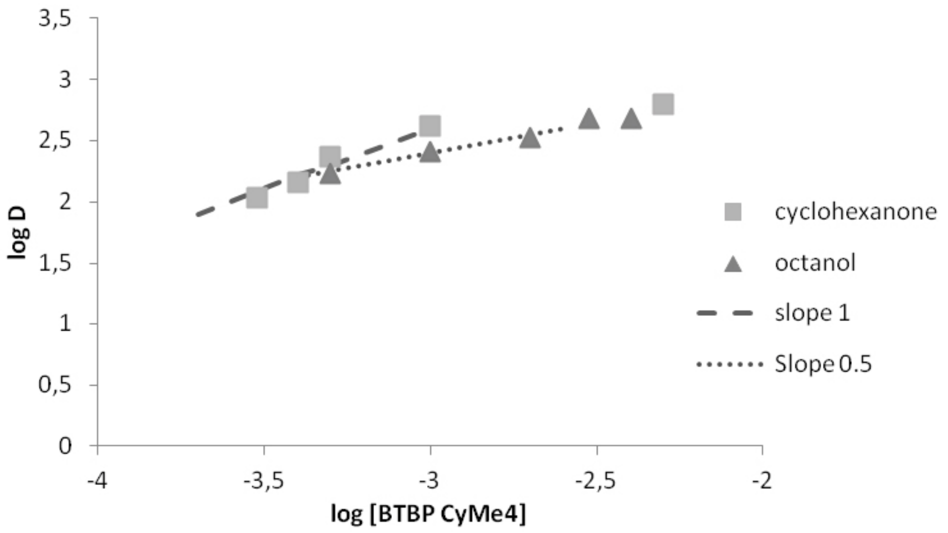


***Figure 5-6.** The extraction of silver using $CyMe_4$-BTBP in pure cyclohexanone and in pure octanol.*

5.2 Palladium Extraction

The palladium extraction behaviour has been thoroughly investigated based on the studies presented in the 2010 SKB report where it was found that no Pd-BTBP slopes could be obtained, possibly due to a water soluble complex.

5.2.1 Nitrate dependence

First of all the nitrate dependence of the palladium extraction with $CyMe_4$-BTBP in cyclohexanone was studied. In a real GANEX process the aqueous phase would consist of ca 4 M nitric acid. Due to this, extractions with varying additions of $NaNO_3$ to 1 M HNO_3 were performed up to a total nitrate concentration of 4 M.

Since the dissociation of nitric acid decreases with the increase in concentration the nitric acid is not fully dissociated ($Ka(HNO_3)=21$), at as high acidities as 1 M HNO_3. The degree of dissociation of both the HNO_3 and $NaNO_3$ is also affected by the total ionic strength of the solution. To be able to take this into account, the nitrate dependence was in this case investigated using chemical activities. The chemical activity of nitrate ions was calculated according to the equation below

$$a_j = \gamma_j x_j$$

where a is the chemical activity, γ is the activity coefficient and x is the mole fraction. The activity coefficient was in turn calculated using the PITZER equations for mixed electrolytes (Pitzer and Mayorga 1973). After simplifications (possible due to equal charges of the ions etc) the final equations used were:

$$ln\gamma_{MX} = |z_M z_X| + \frac{2\upsilon_M}{\upsilon}\sum_a m_a\left(B_{Ma} + \left(\sum mz\right) \times C_{Ma}\right) + \frac{2\upsilon_X}{\upsilon}\sum_c m_c\left(B_{cX} + \left(\sum mz\right) \times C_{cX}\right) + \sum_c\sum_a m_c m_a\left(|z_M z_X| B'_{ca} + \frac{1}{\upsilon}(2\upsilon_M z_M C_a)\right)$$

Where:

$$B_{MX} = \beta^o_{MX} + \frac{\beta'_{MX}}{2I_m}\left(1 - \left(1 + 2\sqrt{I_m}\right)e^{-2\sqrt{I_m}}\right)$$

$$B'_{MX} = \beta^o_{MX} + \frac{\beta'_{MX}}{2I_m^2}\left(-1 + \left(1 + 2\sqrt{I_m} + 2I_m\right)e^{-2\sqrt{I_m}}\right)$$

$$C_{MX} = \frac{C^{\varphi}_{MX}}{2\sqrt{|z_M z_X|}}$$

where υ_M and υ_X are the numbers of M and X ions ($\upsilon = \upsilon_M + \upsilon_X$), z_M and z_X are their respective charges and I is the ionic strength. When plotting the distribution ratio against the activity (see Figure 5-7) the dependency was clearly exponential, indicating a possible salting out effect at these high ionic strengths.

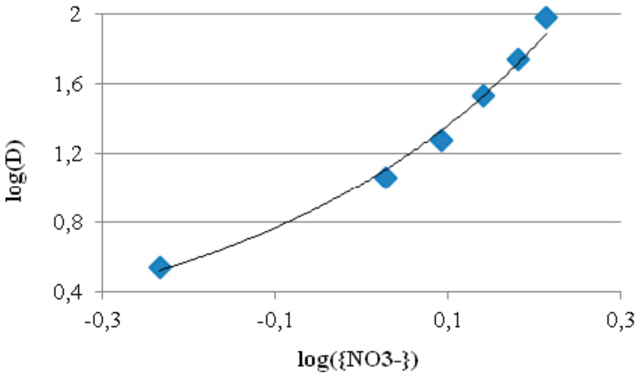


***Figure 5-7.** Distribution ratio as a function of nitrate activity after Pd (2 mM) extraction with CyMe$_4$-BTBP (0.01 M) in cyclohexanone.*

Therefore, to be able to decide the nitrate dependence of the extracted complex, process conditions were abandoned and another extraction was performed with much lower nitrate concentrations. To keep the ionic strength of the solution constant when varying the nitrate concentration sulphuric acid in the pH range of 0.04 and 0.29 (calculated based on pKa1=–3 and pKa2=2) was used. Within this range the dominating sulphate species is HSO_4^- ions. To make sure that palladium did not extract with BTBP into cyclohexanone as a sulphate complex, or was affected by the change in pH having HSO_4^- as counter ion, extractions with different concentrations of sulphuric acid (within the range mentioned) was performed. No variations of (the very low) distribution ratio could be observed (Figure 5-8). A nitrate dependency experiment could therefore be performed using $NaNO_3$ to vary the nitrate concentration adjusting the ionic strength to constant with sulphuric acid. As the slope analysis show (Figure 5-9) the nitrate dependency of the extracted complex is two. This could be expected since the charge of the palladium ion under these conditions ought to be two.

5.2.2 BTBP-Pd extraction

In section 2.2 in the results from 2010 It was suggested that the presence of a water soluble complex could be responsible for the lack of slopes when varying the BTBP concentration. To investigate the presence of a water soluble Pd-BTBP complex, another precipitation experiment was performed where organic phases with different concentrations of CyMe$_4$-BTBP (all sub-stoichiometric compared to Pd) were contacted with a palladium containing aqueous phase. Based on the previous experiments described above, an assumption was made that almost all free palladium would precipitate in the organic phase and then the remaining concentration of palladium in the aqueous phase could be determined. As can be seen in Figure 5-10, the amount of Pd in the aqueous phase increased linearly with the increased amount of BTBP in the organic phase, indicating the presence of a water soluble Pd-BTBP complex. The slope was found to be close to 0.5 meaning that for every two added BTBP-molecules to the system another single Pd atom is found in the water phase. Since Pd is in fact also extracted into the organic phase, this could mean that the Pd-BTBP complex constitution is 1:1 in both the organic and the aqueous phase in the case of a bi-phasic system.

To further confirm the presence of a proposed water soluble complex between palladium and BTBP, HPLC analyses of both the aqueous and the organic phases in normal extraction experiments were performed. It was previously proven by HPLC and MS analyses that aqueous phases, without metals, in contact with BTBP-containing organic phases never contained any traces of CyMe$_4$-BTBP (Aneheim et al. 2011). The molecule alone does hence not distribute into water, which means that any amount of BTBP found in the aqueous phase, or loss of BTBP from the organic phase should be directly connected with the presence of palladium. MS measurements were also made on the samples in order to directly identify the complex composition.

As can be seen in Figure 5-11, the amount of BTBP determined by HPLC in the organic phase steadily decreases with the increase in Pd concentration in the aqueous phase. There is also an increasing amount of BTBP found in the aqueous phase. Both these observations confirm the presence of a water soluble Pd-BTBP complex. However, the composition of the complex cannot be easily determined from these data, since the mass balance of BTBP in the organic and aqueous phase does not fit the initial concentration of ligand in the organic phase prior to contact.

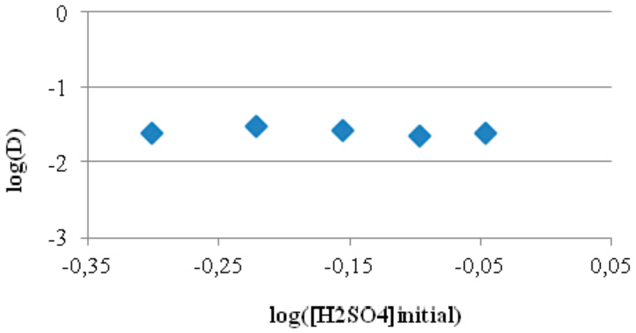


Figure 5-8. *Extraction of Pd (2 mM) from concentrations of H_2SO_4 with 0.005 M $CyMe_4$-BTBP in cyclohexanone.*

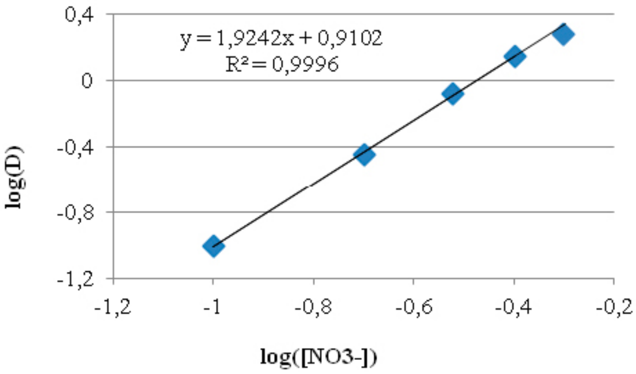


Figure 5-9. *Slope analysis of the nitrate concentrations and distribution ratio of Pd (2 mM) after extraction with $CyMe_4$-BTBP (0.01 M) in cyclohexanone with ionic strength constant (H_2SO_4).*

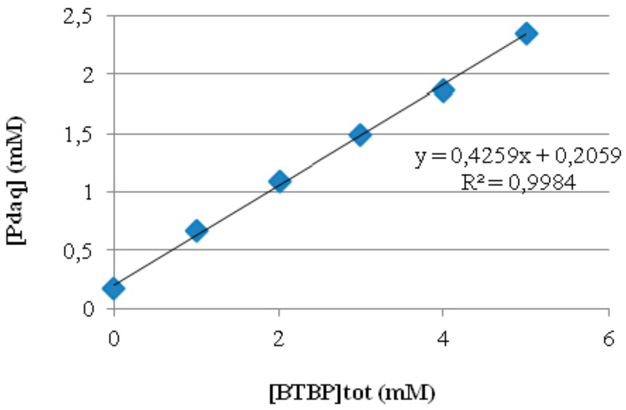


Figure 5-10. *Extraction of Pd (from 1 M HNO_3) with BTBP (in deficit) in cyclohexanone rendering a precipitation of excess palladium.*

5.2.3 NMR investigations

To try and establish the composition of the palladium complex in solution, H-NMR investigations were made comparing several different metal complexes and solutions with each other. Solid metal complexes of Ag, Cd and Pb with BTBP (structures previously determined using elemental analysis, NMR and in some cases X-ray crystallography (Aneheim et al. 2010a)) dissolved in cyclohexanone was first compared to the same metals after extraction with BTBP from 1 M HNO_3 to see that the result was the same. As can be seen in Figure 5-12, 5-13 and 5-14 they show a very similar result. These complexes have different compositions (2:1 and 1:1) and were then used for comparison to a cyclohexanone – BTBP solution after Pd-extraction to see which complex it corresponded to. As can be seen in Figure 5-15 the extracted Pd-complex is a 1:1 complex as it is very similar to the silver complex (1:1) and hence very different to both the Cd and Pb complexes (2:1). That none of the peaks are attributed to simply BTBP can also be seen in Figure 5-15 where the NMR spectrum of $CyMe_4$-BTBP in cyclohexanone is shown.

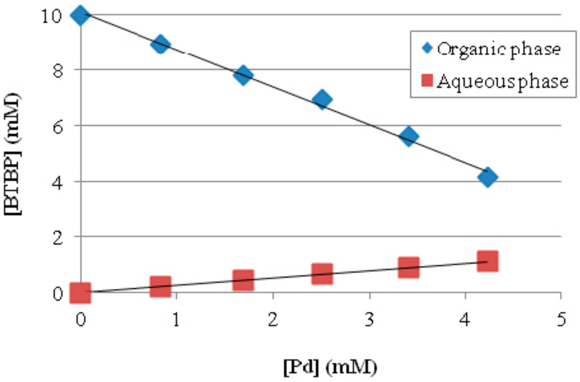


Figure 5-11. *$CyMe_4$-BTBP concentration in the organic and aqueous phase after extraction of different concentrations of palladium in 1 M HNO_3 with cyclohexanone as diluent.*

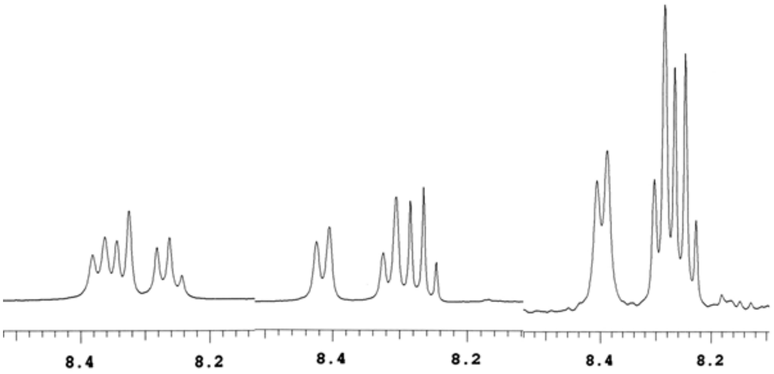


Figure 5-12. *Solid complexes dissolved in cyclohexanone (Left:C2-BTBP Middle:$CyMe_4$-BTBP) compared to Ag extracted from an aqueous phase (1 M HNO_3) with $CyMe_4$-BTBP (0.01 M) in cyclohexanone (right).*

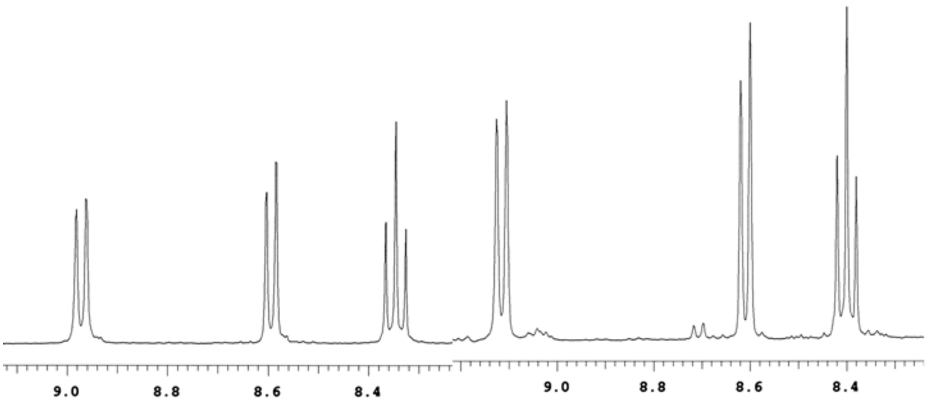


Figure 5-13. *Solid complex dissolved in cyclohexanone (Left:C2) compared to Cd extracted from an aqueous phase (1 M* HNO_3*) with* $CyMe_4$*-BTBP (0.01 M) in cyclohexanone (Right).*

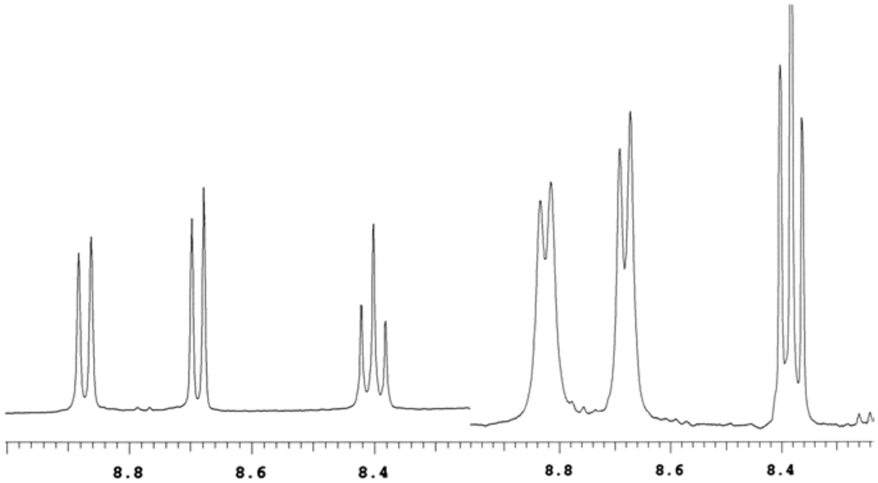


Figure 5-14. *Solid complex dissolved in cyclohexanone (Left:*$CyMe_4$*) compared to Pb extracted from an aqueous phase (1 M* HNO_3*) with* $CyMe_4$*-BTBP (0.01 M) in cyclohexanone (Right).*

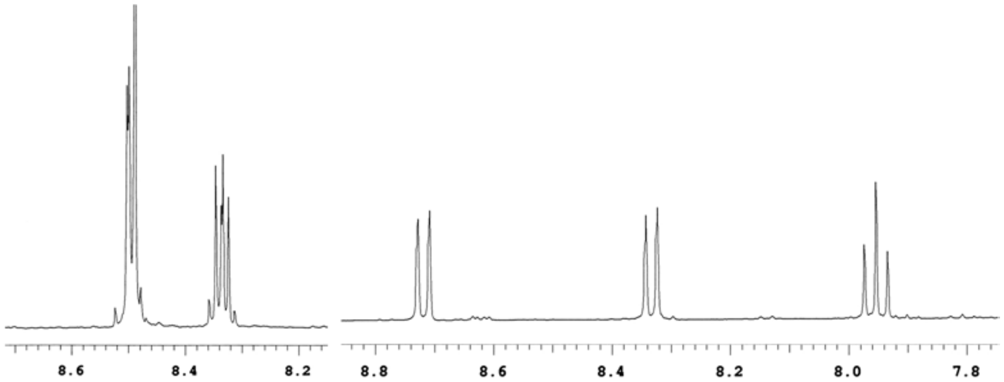


Figure 5-15. *Pd extracted from an aqueous phase (1 M* HNO_3*) with* $CyMe_4$*-BTBP (0.013 M) in cyclohexanone (Left) Pure* $CyMe_4$*-BTBP in cyclohexanone (Right).*

6 GANEX

A new novel Group ActiNide EXtraction (GANEX) system for used fuel recycling is being developed at Chalmers. The aim of the GANEX system is to exctract all actinides present in the used fuel together and at the same time ensuring that there is no pure plutonium stream created. The latter requirement is to add a greater resistance to nuclear proliferation.

The Chalmers GANEX system uses a solvent extraction method, utilising the extractants from both the PUREX and SANEX systems; TBP and Bis-Triazine BiPyridine (BTBP), respectively. The BTBP ligand used for the GANEX system is CyMe$_4$-BTBP. Whenever the notation "GANEX solvent" is used in the described results below this mean 0.01 M CyMe$_4$-BTBP +30% TBP in cyclohexanone unless otherwise stated.

6.1 Tecnetium

Technetium is one of the more common fission products formed in a light water reactor (6.1%). Currently, there exist no data on how technetium behaves in the proposed GANEX system but according to general experience this element is often troublesome due to its chemistry. It can either exist in different cationic forms or in an anionic form (TcO_4^-) depending on the chemical environment.

6.1.1 Experimental

Technetium for the experiments is extracted from a Molybdneum-99 containing ion exchange resin, acquired from Sahlgrenska University hospital and used within a week of acquisition. ^{99}Mo has a half-life of 66 hours and has therefore after a week undergone nearly 3 half-lives, making the amount of ^{99m}Tc available very small. The ^{99}Tc eluted from the molybdenum resin is in its pertechnetate form, in saline solution. HPGe analysis of the saline solution showed only a peak at 141 keV, suggesting that the eluted samples are chemically pure Tc. The concentration of pertechnetate in the saline solution was calculated to be in the region of 8×10^{-11}M.

6.1.2 Results

One of the first basic experiments usually performed when investigating the extraction of a new species is the time it takes to reach extraction equilibrium. For the case of technetium extraction using the GANEX solvent the extraction was found to be fast, see Figure 6-1.

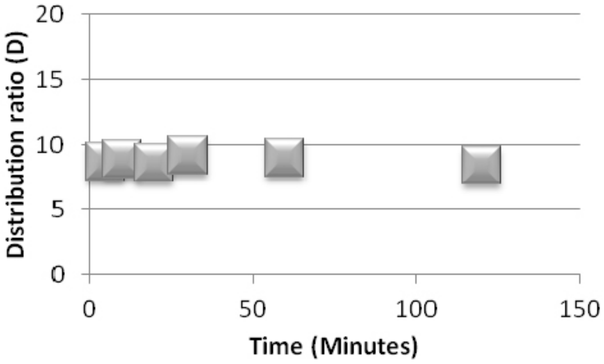


Figure 6-1. *Technetium extraction by 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone from 1 M HNO$_3$ with 3 M NaNO$_3$. Samples withdrawn over time to ensure equilibrium of extraction, shaking at 1,500 rpm.*

The GANEX solvent contains three potential extractants; CyMe$_4$-BTBP, TBP and cyclohexanone. There is a need to determine which of these that is responsible for the extraction. t is expected that cyclohexanone would extract technetium in an ion exchange mechanism where pertechnetate replaces nitrate extracted into the organic phase. It is also expected that TBP (if not present as 100% in the organic phase) would be unable to extract Tc in the absence of metals to form complexes with (Boyd and Larson 1960). The performance of BTBP on technetium is however unknown as well as the performance when combining these different extractants with each other. In this experiment, four organic solvents have been used: pure cyclohexanone (CH); 0.01 M CyMe$_4$-BTBP in cyclohexanone (BTBP); 30% TBP in cyclohexanone (TBP) and 0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone(GANEX). The aqueous phase was in all cases 1 M HNO_3 with 3 M $NaNO_3$ (the samples were not pre-equilibrated). The distribution ratios resulting from the extractions can be seen in Figure 6-2:

It can be seen that all the solutions performed similarly except for the BTBP containing cyclohexanone, which appears to have a higher Tc-extraction than the other three. It must therefore be concluded, as expected, that for technetium, cyclohexanone is the main extractant and that BTBP enhances the extraction but that effect is inhibited by the presence of TBP. This could possibly be explained by surface active properties of BTBP easing the transfer of ion-pairs into the organic phase that are cancelled out by the much larger concentration of surface active TBP in the later samples.

Effect of nitrate concentration

Since it previously was seen that nitrate ions compete with pertechnetate to be extracted by the GANEX solvent, it was tested to see if varying the nitrate concentration had any significant effect on the technetium extraction. The effect of acid concentration on the extraction and whether a high nitrate or high proton environment had a greater impact was also investigated. To achieve these results, extractions were performed using the GANEX solvent to extract technetium from varying concentrations of nitric acid and sodium nitrate. The results of this experiment can be found in Figure 6-3.

It can be seen that at low nitrate/acid concentrations, technetium is readily extracted, however, as the concentration increases; the distribution ratio for technetium slowly decreases. This effect has been previously observed with other anions and could hence be expected (Boyd and Larson 1960). The highest nitrate concentration (4 M nitric acid saturated with sodium nitrate (approx 3 M)), greatly inhibits extraction, however, there is still a positive distribution ratio for technetium. It can also be seen that there is no obvious difference between distribution ratios obtained from only acid or acid and nitrate media of the same concentration. It should however be pointed out that in all samples the acid concentration is 1 M nitric acid or more. This since it has previously been seen that in neutral salt solutions, the extraction of pertechnetate by cyclohexanone is greatly reduced (Boyd and Larson 1960).

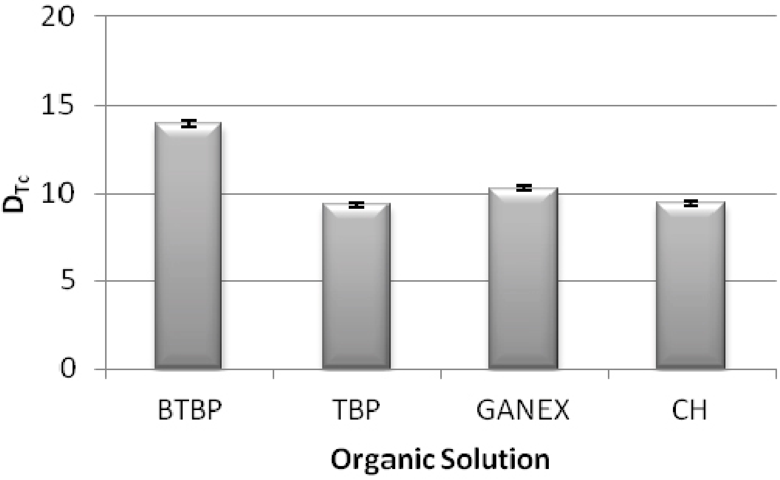


Figure 6-2. *Distribution ratios for technetium from 1 M HNO_3 and 3 M $NaNO_3$ using different organic solutions: BTBP=0.01 M CyMe$_4$-BTBP in cyclohexanone, TBP=30% TBP in cyclohexanone, GANEX=0.01 M CyMe$_4$-BTBP + 30% TBP in cyclohexanone, CH= pure cyclohexanone.*

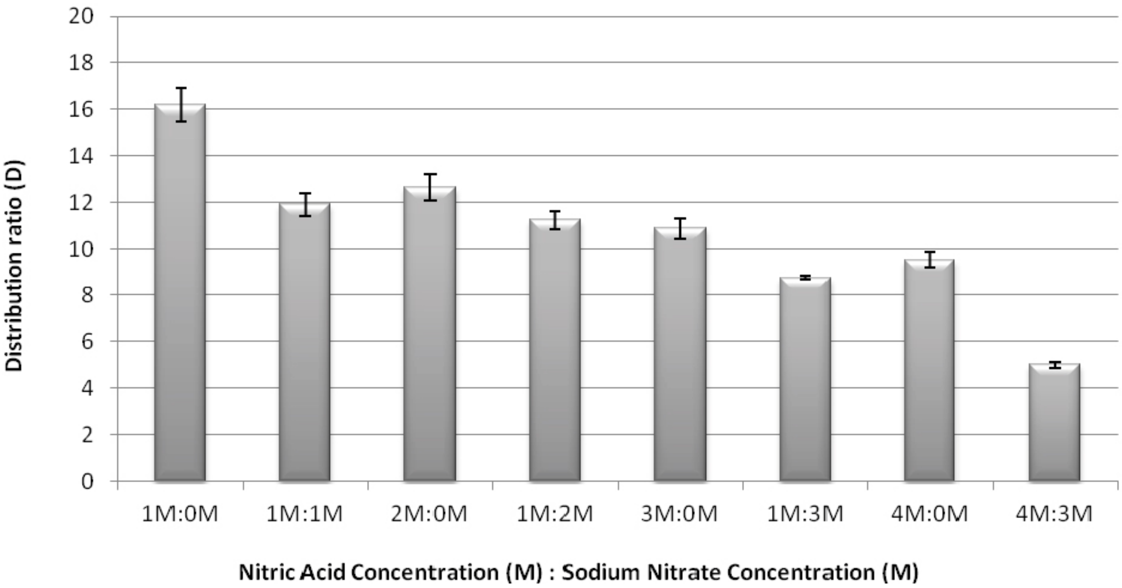


Figure 6-3. *Distribution ratios for technetium extraction with 0.01 M* $CyMe_4$*+30% TBP in cyclohexanone from varying concentrations of nitric acid and sodium nitrate* solutions.

Technetium extraction with uranium present

Since technetium is able to be extracted via ion-pair extraction by uranium and TBP, there is a possible impact of adding uranium to the aqueous phase. Despite the fact that the bulk uranium most likely will be removed from the GANEX feed in a pre-treatment step it is probable that there still will be uranium present due to the very large amounts available in the dissolution liquor, compared to the other elements. Varying concentrations of uranyl nitrate in 4 M HNO_3 was therefore used as aqueous phase when extracting technetium with the GANEX solvent. These experiments lead to the results presented in Figure 6-4.

It can be seen that the addition of uranium appears to slightly inhibit technetium extraction rather than enhancing it. This is probably due to the fact that also uranium to some extent is extracted by cyclohexanone (Aneheim et al. 2010b) and in this experiment is competing with technetium. This could be caused by the uranium ion-pair extraction favoring nitrate rather than pertechnetate. This obviously has a negative effect on the technetium extraction greater than the positive effect gained from the possible TBP extraction.

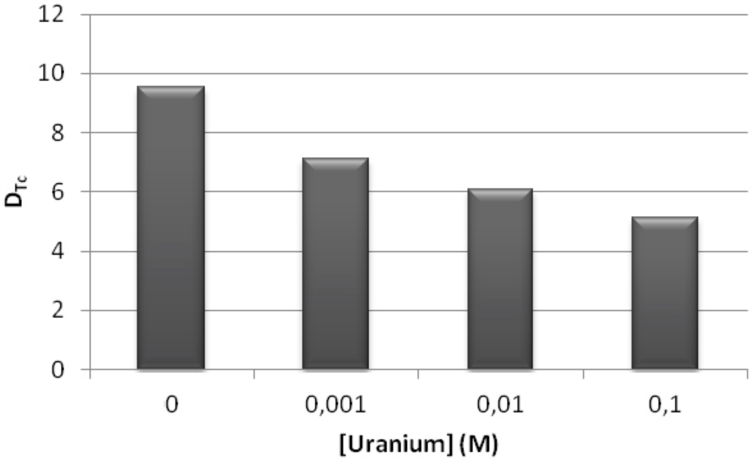


Figure 6-4. *Distribution ratios for technetium extracted by the GANEX solvent from uranium containing aqueous phases (4 M* HNO_3*).*

To see how the uranium addition is influencing the different constituents of the solvent the experiment performed with four different organic phases have been repeated but this time with an addition of uranium to the aqueous phase. The results are shown in Figure 6-5:

When comparing the results in Figure 6-2 with those in Figure 6-5 it can be concluded that in all solvents except for that containing BTBP in cyclohexanone the extraction have been greatly reduced by the presence of uranium. That the extraction by BTBP in combination with cyclohexanone is unaffected by the presence of uranium further strengthens the theory about the surface active properties of BTBP facilitating ion-pair transfer. It is possible that this mechanism demands a lower surface tension, which when adding TBP to the solvent, increases. When instead comparing the sample with pure cyclohexanone to the two solvents containing TBP (in Figure 6-5) the TBP-containing solvents display a slightly higher technetium extraction indicating that there also is an ion-pair extraction taking place between uranium and pertechnetate, facilitated by TBP.

Irradiation

Samples of pre-equilibrated GANEX solvent were irradiated in a ^{60}Co-source (dose rate: 17.9 kGy/h) for different periods of time rendering the doses presented in Figure 1-8. After a cooling period these irradiated samples were used to extract technetium from a uranium containing 4 M nitric acid phase. The cooling time varied from sample to sample, between 2–3 hours and 10 days depending on if technetium was readily available for experiments. The results of these experiments can also be seen in Figure 6-6.

It can be seen that there is a trend for the GANEX solvent to become more effective at extracting technetium when the received dose is increased. This trend starts to become evident above ca 1 MGy. The point at 108 kGy was repeated twice, once pre-equilibrated and once not, to test if it had a significant impact on the extraction. The obtained distribution ratios were very similar (D_{pre} = 4.63, $D_{not\ pre}$ = 4.85) and thus it can be concluded that pre-equilibration has minimal effects on the extraction of technetium from a uranium spiked aqueous phase. The value shown in Figure 6-6 for 108 kGy is an average of the two measured values.

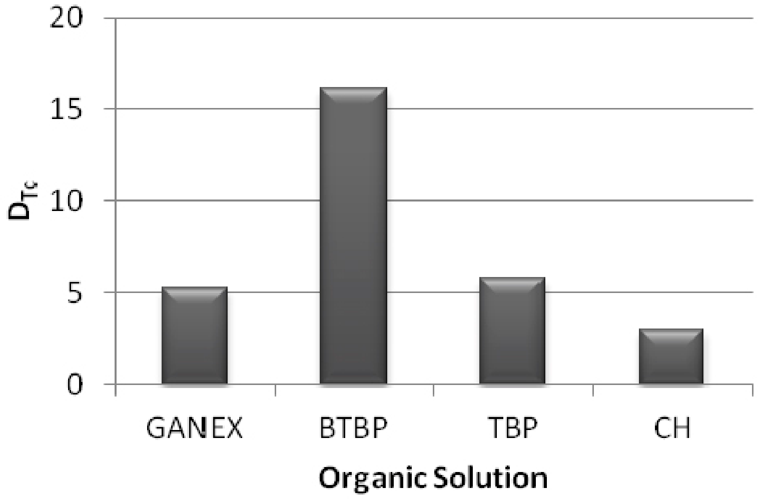


Figure 6-5. *Distribution ratios for technetium from 1 M HNO_3 + 3 M $NaNO_3$ and 0.1M uranyl nitrate using different organic solutions: BTBP=0.01 M $CyMe_4$-BTBP in cyclohexanone, TBP=30% TBP in cyclohexanone, GANEX=0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone, CH= pure cyclohexanone.*

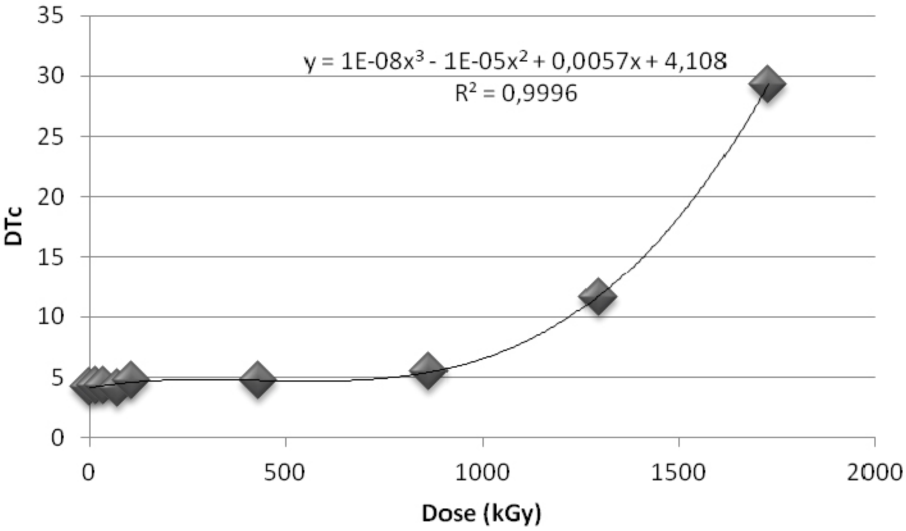


Figure 6-6. *Distribution ratios for extraction of technetium from a 0.1 M uranyl nitrate containing aqueous phase (4 $MHNO_3$) using GANEX solvents that have been irradiated with varying doses.*

Fission and corrosion product loading

All the previous experiments focus specifically on technetium and uranium only, but in the real process there will be a large number of other elements present in the dissolved spent fuel. To investigate whether technetium extraction with the GANEX solvent would increase due to ion pair extraction with other metals extracted by BTBP, a 4 M nitric acid solution, loaded with fission and corrosion products, was used as aqueous phase in an extraction experiment with the GANEX solvent. The composition of the loaded aqueous solution has been previously described in the work of Aneheim et al. (2010b). The experiment was performed twice, once with an addition of 0.1 M uranyl nitrate and once without, see Figure 6-7.

It can be seen that when comparing the system without uranium in the aqueous phase the technetium extraction is slightly reduced under fission product loading. For the uranium containing system, however, the result is slightly higher with fission product loading compared to no loading. It is also clear that the presence of uranium in the loaded system has no effect on the extraction. This could possibly mean that the extraction mechanism of the technetium under fission product loading conditions shifts from extraction by cyclohexanone to ion-par extraction with some of the fission product metals by, most likely, BTBP.

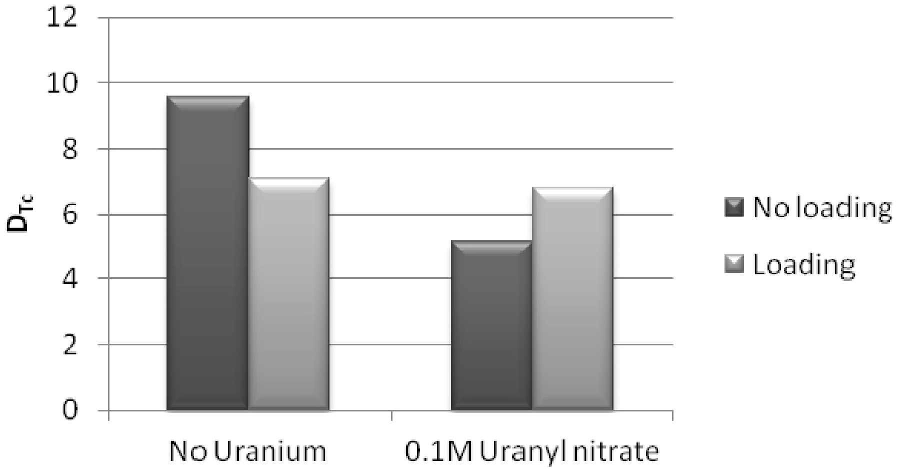


Figure 6-7. *Distribution ratios for GANEX extraction of technetium from a fission and corrosion product loaded aqueous phase with and without the addition of 0.1 M uranium.*

Inhibiting technetium extraction

As seen above, technetium is readily extracted by the selected GANEX system, with distribution ratios between 3 and 30 depending on the different conditions used. This means that in all the extractions more than 75% of the technetium is being extracted, which is clearly above an acceptable level.

As mentioned previously, one method of preventing extraction of an unwanted metal is the addition of a so called masking agent. That is a ligand which complexes the desired metal and keeps it from being extracted. Three potential masking agents are: mannitol, glucolactone and bimet. These molecules have previously been found to affect the extraction of zirconium, molybdenum and palladium by the GANEX solvent (see section 2.3 in the 2010 Results) and will therefore potentially be used in the process to mask the extraction of these unwanted fission products or to scrub them out of the organic phase. Due to this, their effect on the technetium extraction was tested. For the experiment, three different solutions of 4 M HNO_3 containing 0.1 M of bimet , mannitol and glucolactone were used as aqueous phases and the results can be seen in Figure 6-8:

It can be seen that the compounds all seem to provide some level of technetium masking, however none of them reduce extraction to desired levels.

Back-extraction of technetium

Another method of removing undesired metals from an extraction is using a scrubbing step in the process. The undesired metals are then selectively stripped from the organic phase. The scrubbing experiments were made with the GANEX solvent loaded with technetium from 4 M nitric acid both with and without the presence of uranium (0.1 M). These organic phases were then each scrubbed using three different aqueous phases: MilliQ water, 2 M HNO_3 and 4 M HNO_3. The results of the experiments can be seen in Figure 6-9:

It can be seen that MilliQ water is inefficient at back-extracting technetium from both organic phases but that the performance is slightly better from the organic phase loaded without uranium present. This is likely due to the additional technetium extraction with TBP and uranium. When increasing the nitric acid concentration in the scrub-solution, the back-extraction of technetium also increases. This is a positive result since a higher nitrate concentration in the scrub solution disfavours the scrubbing out of actinides, hence minimizing losses during a possible washing step. Another way of improving back extraction would be to lower the phase ratio and have greater amounts of the aqueous phase in relation to the organic phase, resulting in more nitrate ion competition for technetium.

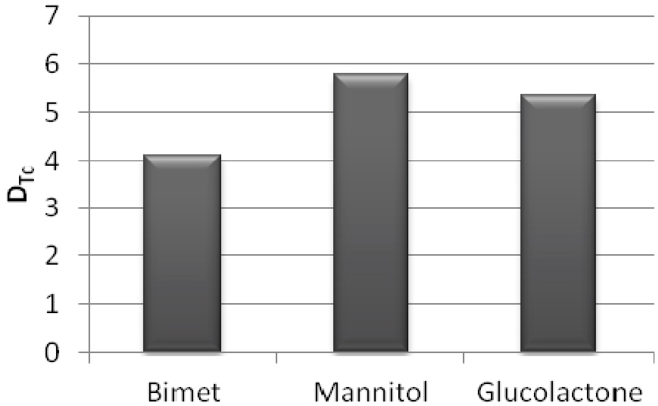


Figure 6-8. *Distribution ratios for GANEX extraction of technetium from 4 M HNO_3 in the presence of different inhibiting compounds (0.1 M).*

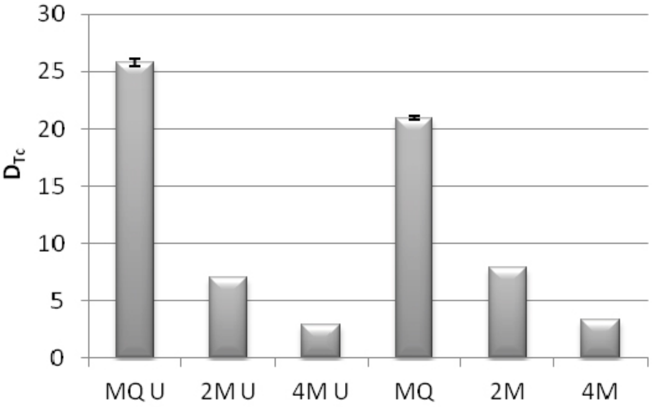


Figure 6-9. *Distribution ratios for back-extraction of technetium from two GANEX organic phases, both loaded from 4 M* HNO_3 *(one containing uranium (0.1 M) denoted U) using MilliQ water (MQ) 2 M* HNO_3 *(2 M) and 4 M* HNO_3 *(4 M).*

6.2 Nickel chemistry

Nickel is one of the corrosion products that is readily and undesirably extracted by the GANEX solvent (Aneheim et al. 2010a). Several attempts using different methods have been made to try and remove nickel from a loaded organic phase. In these experiments nickel have been used in the form of a radioactive tracer of ^{63}Ni detected by liquid scintillation.

Two different water soluble porphyrines were chosen to be investigated as scrubbing agents for nickel (Figure 6-10). They were chosen as scrubbing agents rather that masking agents due to the milder chemical conditions during scrubbing. Unfortunately neither of the aromatic sulphone compounds were found to be able to scrub out Ni from a loaded GANEX solvent. The Ni extraction was made from 4 M nitric acid and the scrubbing was performed with 5 mM of the molecule dissolved in water (compound 1 and 2) and 4 M $NaNO_3$ (compound 2). The scrubbing was attempted both in room temperature as well as at an elevated temperature (50°C) without success.

Also potassium cyanide was tested as a scrubbing reagent to see if an inorganic water soluble complex of nickel could be formed. KCN (0.1 M) in H_2O was contacted with the organic phase (after basic wash to avoid formation of $HCN_{(g)}$) but no nickel was scrubbed out.

Dimethylglyoxime is well known as a reagent which is able to bind to nickel to form a water insoluble solid. Due to this a test to see if dimethylglyoxime (ca 50 mM) dissolved in 50 mM NaOH could precipitate nickel out from a loaded GANEX organic phase was made. No precipitation was, however, found.

A mesoporous silica that acts as a metal adsorber, thiol-SAMMS, was also subsided to a test to see if, by direct contact with the loaded organic phase, nickel could be removed. This was however not the case, even after a long contact time (several days).

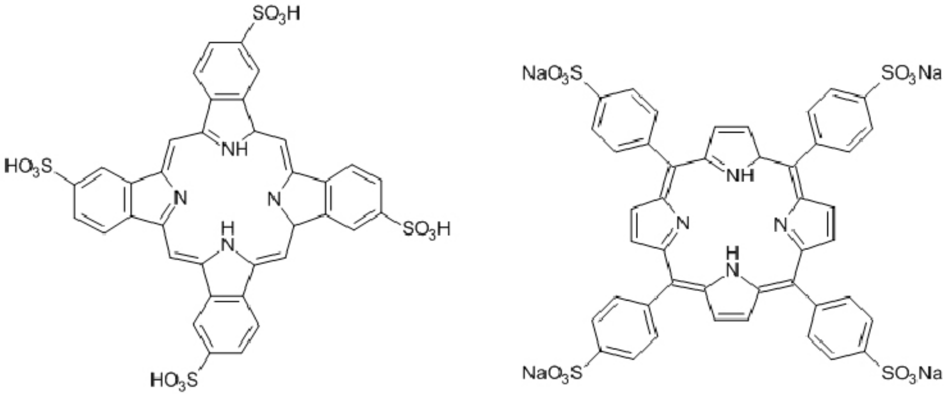


Figure 6-10. *Molecular structure of phthalocyanine tetrasulfonic acid and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin.*

6.3 Palladium chemistry

The two water soluble complexing agents methionine and bimet have been investigated to find out whether they firstly could prevent the precipitation of palladium black by cyclohexanone, and secondly inhibit the extraction of palladium with the GANEX solvent consisting of CyMe$_4$-BTBP and TBP in cyclohexanone. Previously reported results on the complexation between these two ligands and palladium have been revised and are presented below.

The immediate palladium precipitation caused by cyclohexanone was stopped by the addition of methionine, seemingly at a 1:1 ratio, after ocular inspection. As the samples were left over time, however, small amounts of precipitate formed also in the vials where the palladium to ligand ratio exceeded 1:1 up to a ratio of apparently 1:2. After measuring the remaining palladium concentration in the aqueous phase after different contact times with the organic phase and comparing it to the amount of added ligand (Figure 6-11) it could be concluded that the palladium to methionine ratio was 1:2, since the slopes were found to be close to 0.5 (0.47 ± 0.07 and 0.49 ± 0.05).

When using bimet as a complexing ligand the precipitation was stopped when the concentration of added bimet compared to that of the palladium exceeded the ratio 1:1. When ligand was added in sufficient amounts to stop palladium precipitation, this aqueous solution could stand in contact with cyclohexanone for several weeks without any additional precipitation occurring, indicating stability over time according to ocular inspection. Due to the narrow concentration ranges used it can be assumed that bimet forms a stable 1:1 complex with palladium in the water phase inhibiting any palladium precipitation. This was also confirmed by measuring the palladium concentration in the aqueous phases (Figure 6-12). The slope in this experiment was found to be close to one (0.97 ± 0.03) indicating that bimet forms a 1:1 complex with palladium.

The experiments were then repeated after increasing the nitric acid concentration of the palladium nitrate solution to 4 M. The experiments were also performed twice allowing the strong nitric acid solution containing the ligands to age, to investigate if the molecules or complexes were stable over time in this environment. Due to the slow precipitation of palladium with methionine present, the samples were left for at least 5 days before analysis. With methionine as ligand, it can be seen in Figure 6-13 that even during the short time experiment (1 hour between solution preparation and precipitation), the methionine did not manage to maintain all of the palladium in solution even when it was present in high concentrations. The previously observed 1:2 complex could however be seen here as well (slope of 0.49 ± 0.08). In the long time experiment (144 hours between solution preparation and precipitation) almost no complex seems to be formed when the ratio of palladium to methionine is less than 1:1. Above this ratio, however, some of the precipitation is obviously still stopped. By looking at the slope (0.32 ± 0.03) of this interval it can be suggested that a three times higher methionine concentration than palladium might be able to still stop the precipitation.

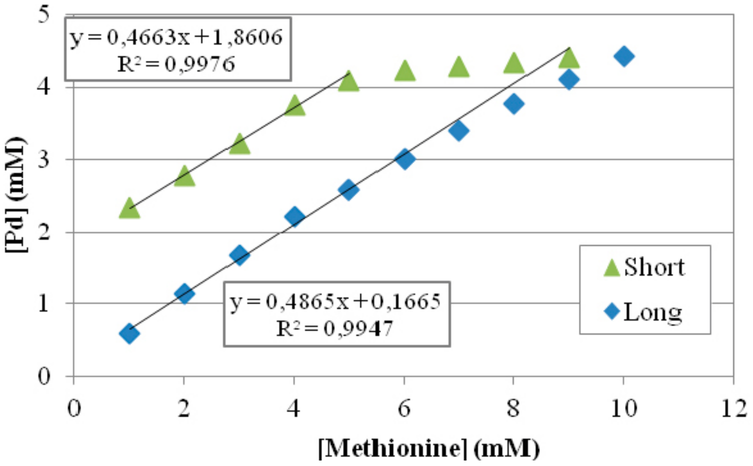


Figure 6-11. *Remaining palladium concentration an aq. phase after precipitation with cyclohexanone with addition of methionine in different concentrations. Samples removed after different precipitation times Short: 1 hour, Long: 208 hours.*

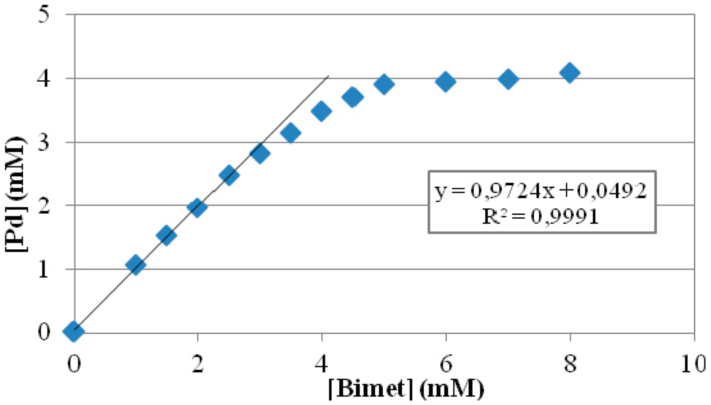


Figure 6-12. *Remaining palladium concentration (in 1 M HNO_3)phase after precipitation with cyclohexanone after addition of bimet in different concentrations.*

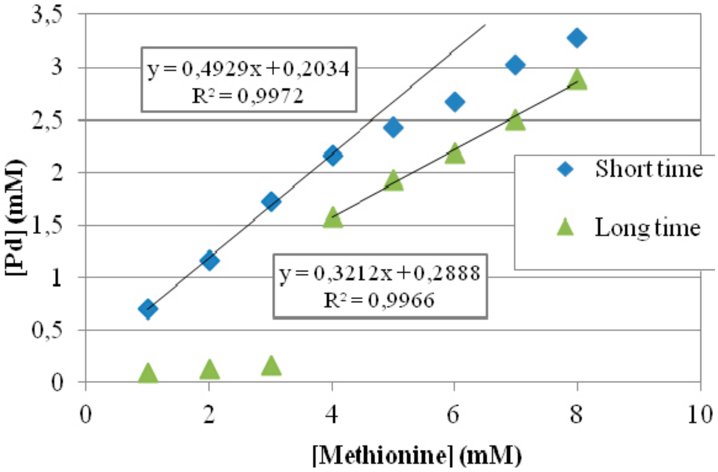


Figure 6-13. *Precipitation of Pd (ca 4 mM in 4 M HNO_3) with cyclohexanone after addition of methionine in different concentrations. Measurement of the remaining amount of Pd in the aqueous phase. Time between preparation of solution and start of experiment: Short time= 1 h, Long time= 144 h.*

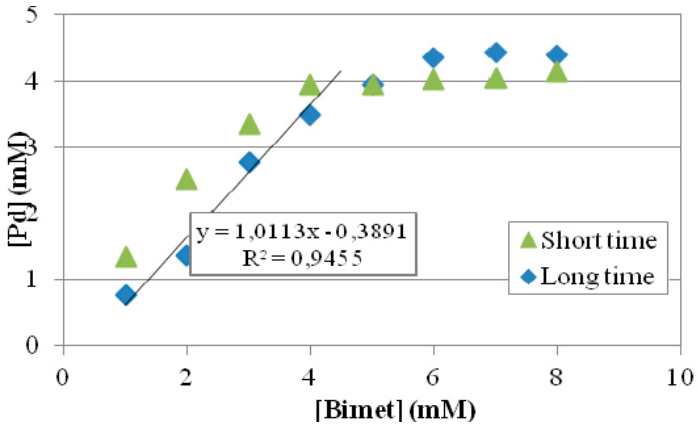


Figure 6-14. *Precipitation of Pd (in 4 M HNO_3) with cyclohexanone after addition of bimet in different concentrations. Measurement of the remaining amount of Pd in the aqueous phase. Time between preparation of solution and start of experiment: Short time= 1 h, Long time= 144 h.*

With bimet as ligand, however the precipitation is totally suppressed in both the short and long time experiment and the complex still seems to have a composition of 1:1 when looking at the slope (1.01 ± 0.69) (Figure 6-14).

6.4 Stripping/Scrubbing

In the proposed GANEX process there are several parts where stripping/scrubbing of certain substances will or can be relevant. After the group extraction of the actinides, they need to be stripped into an aqueous phase. This stripping is necessary but it is also possible to add an extra step where problematic fission products also are scrubbed out of the organic phase, either before or after the actinide stripping. This step could be possible to combine with an acid scrub, if there is a need to remove acid from the organic phase. In this section the stripping of actinides as well as scrubbing of certain fission products have been looked into.

6.4.1 An/Ln stripping

One possible stripping agent for actinides to be used in a general GANEX process is Glycolic acid. Glycolic acid solutions of different pH (adjusted with ammonia) were prepared and used for stripping from an organic phase (0.01 M $CyMe_4$-BTBP+30% TBP in cyclohexanone) loaded from 4 M HNO_3 with actinides and lanthanides.

As can be seen in Figure 6-15 despite the pH of the ingoing Stripping solution, almost nothing of the americium is stripped, only a little of the uranium, but significant amounts of the europium.

This opens the possibility of an intermediate scrubbing step to lower the acid content in the organic phase before the actual glycolic acid strip. An acid scrub with 0.01 M HNO_3 was therefore made before actinide stripping with glycolic acid of 2 different inital pH:s (Figure 6-15). As can be seen, after the acid scrub, an incoming pH of 9 on the glycolic acid solution successfully scrubs out both actinides and lanthanides. This can be compared to Figure 6-16 where without acid scrub no actinides were scrubbed out with the same initial pH of the Glycolic acid. The separation of the lanthanides from the actinindes has already taken place in the extraction step and the amounts that are being co-scubbed in this step is hence only minor.

In order to not loose any actinides in the acid scrubbing step it is however desired to keep the nitrate koncentration high. A test was therefore made to see how the pH in the acid scrub solution after contacting with the organic phase was affected by the initial nitrate concentration. As can be seen in Figure 6-17 the amount of acid scrubbed from the organic phase linearly decreases with the nitrate concentration of the aqueous phase, as expected. There is obviously a balance between the amount of acid scrubbed out of the organic phase and the loss of actinides in this step together with the effectiveness of the actinide stripping in the following step. Hence more effort have to be put into this matter to find the optimum conditions.

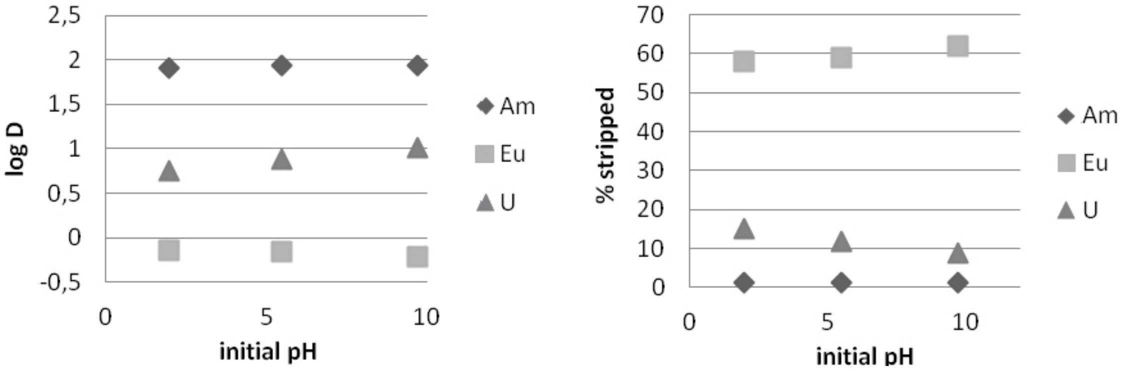


Figure 6-15. *^{241}Am ^{152}Eu ^{235}U extracted by $CyMe_4$-BTBP +30% TBP in cyclohexanone from 4 M HNO_3.*

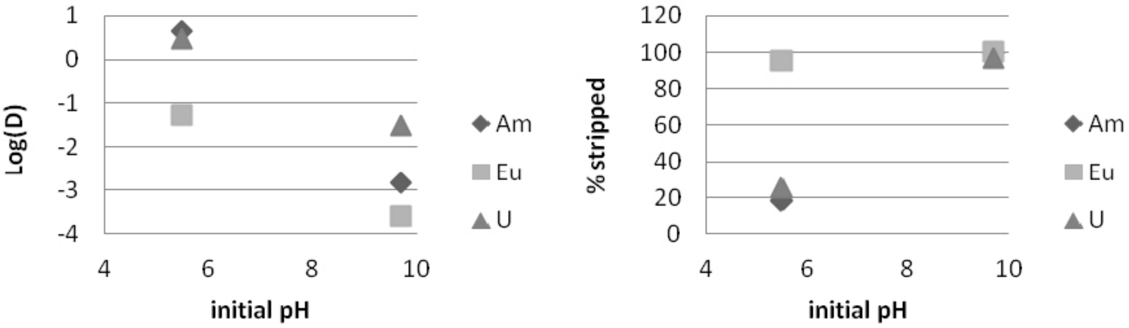


Figure 6-16. *Actinide and Lanthanide scrubbing (extraction from 4 M HNO_3 with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone) with glycolic acid of 2 different inital pH:s after an acid scrub with 0.01 M HNO_3.*

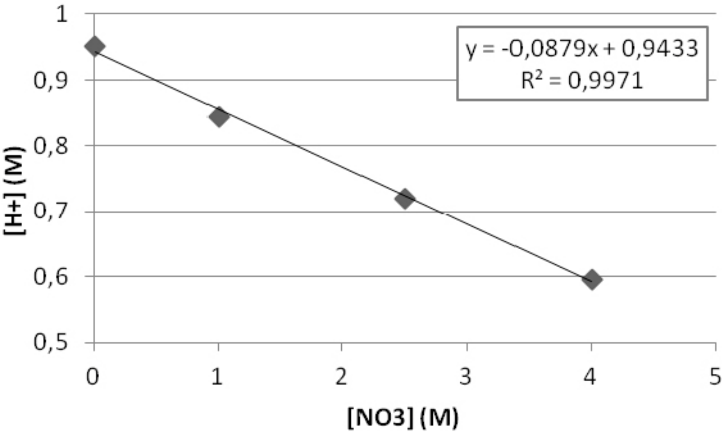


Figure 6-17. *Acid concentration in the scrub solution after scrubbing of an organic phase (30% TBP in cyclohexanone previously contacted with 4 M HNO_3) as a function of the initial nitrate concentration of the scrub solution.*

6.4.2 Fission product scrubbing

Glucolactone has previously been found to be able to scrub zirconium and molybdenum from a GANEX solvent in an initial screening of fission product (FP) scrubbing reagents (see section 2.3 in the 2010 results). Therefore the effect of glucolactone concentration on the scrubbing of Zr and Mo from a GANEX solvent (loaded from 4 M HNO_3) has been investigated. As can be seen the increased glucolactone concentration does not affect the FP-scrubbing very much and hence the lowest concentration of 0.6 M was chosen for further investigations.

The effect of adding glucolactone on the stripping of actinides, lanthanides and other troublesome fission products were investigated. Just as in a fission product scrubbing step (that could be combined with the above investigated acid scrubbing) it would be important not to loose any actinides.

It can be seen in Figure 6-19 that the addition of glucolactone only is increasing the europium scrubbing which is a positive result. It seems as if a glucolactone addition to a possible acid scrubbing step in the GANEX process would not cause any major loss of actinides compared to a scrubbing with only 4 M $NaNO_3$.

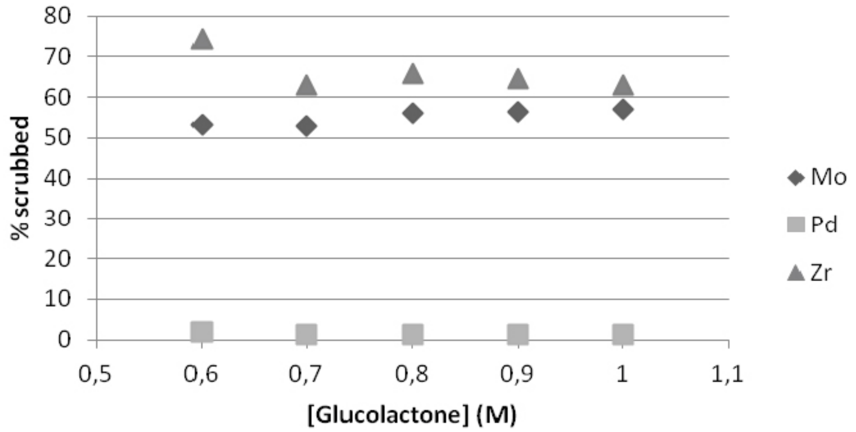


Figure 6-18. *Effect of glucolactone concentration (in 4 M $NaNO_3$) on the scrubbing of Zr and Mo (extraction from 4 M HNO_3 with 0.01 M $CyMe_4$-BTBP + 30% TBP in cyclohexanone).*

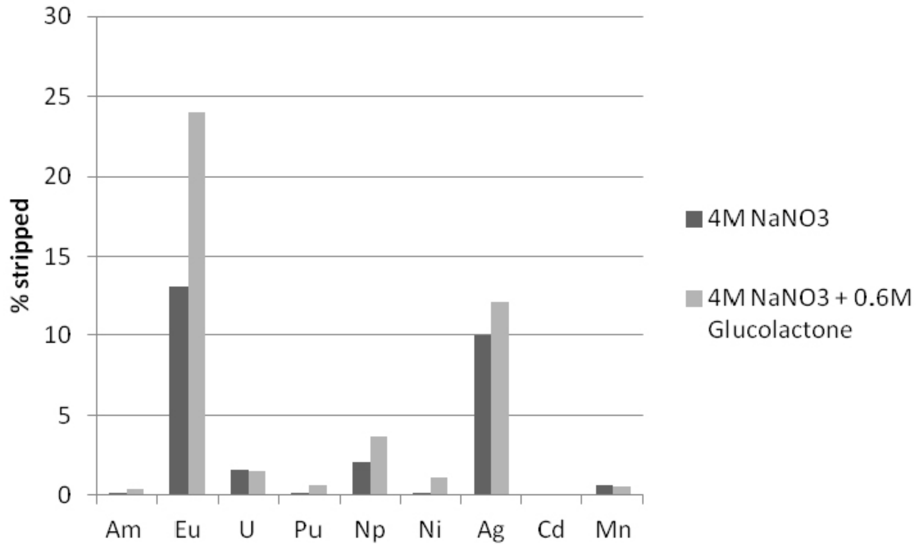


Figure 6-19. *Effect of glucolactone addition to 4 M $NaNO_3$ on the scrubbing of Actinides, Lanthanides and different fission products.*

7 Diluents and Solvent Effects

7.1 Effect of Solvent and Metal concentration on the Time Needed for Reaching Extraction Equilibrium

The time of phase contact needed for reaching extraction equilibrium in the two proposed GANEX solvents (TBP based (CyMe$_4$-BTBP (here 5.17 mM), TBP (30% vol) and cyclohexanone (70% vol)) and DEHBA based (CyMe$_4$-BTBP (here 5.17 mM), DEHBA (30% vol) and cyclohexanone (70% vol))) has shown to be shorter for actinides than for lanthanides (Löfström-Engdahl et al. 2011). Since this difference makes the separation of the actinides from the lanthanides higher at short contact times, it can be one way of improving this separation (Löfström-Engdahl et al. 2011). However, in the study presented in literature (Löfström-Engdahl et al. 2011), the actinides and lanthanides are only present in trace amounts. In a real process however, what is important is the rate of mass transfer. Therefore, three different concentrations (0.01 mM, 0.1 mM and 1 mM) of inactive Eu(NO$_3$)$_3$ were prepared in 4 M HNO$_3$. The phases were contacted using a shaking machine with constant speed (a modified IKA Vibrax VXR Basic, 1,500 rpm). Samples were withdrawn after 5, 10, 20, 40 and 80 minutes of phase contact. After that all the experiments were in equilibrium (or close to). All samples were made in doublets on different occasions. However, the uncertainties based on the counting statistics is very small, so the uncertainties presented in the graphs are therefore based on a "Cause and Effect" diagram (Andersson 2005), where the uncertainty in each distribution ratio is calculated to be less than 3%. Therefore this number is used as a standard uncertainty.

7.1.1 The TBP based GANEX solvent

The concentration of metal in the TBP based solvent influences the time it takes to reach equilibrium for the europium. Also, before reaching equilibrium, the distribution ratios are lower in the aqueous phases containing more (Figure 7-1). Anyway, at the equilibrium extraction, the distribution ratio is similar in all the three systems.

The americium extraction in the TBP based solvent also shows a difference in the distribution ratios as well as the time needed for reaching equilibrium, following the same trend as in the europium experiment (Figure 7-2). Higher metal concentration gives lower extraction before reaching equilibrium but it seems not to be a difference in equilibrium distribution in the three metal containing systems. These various trends are to be analyzed during 2012.

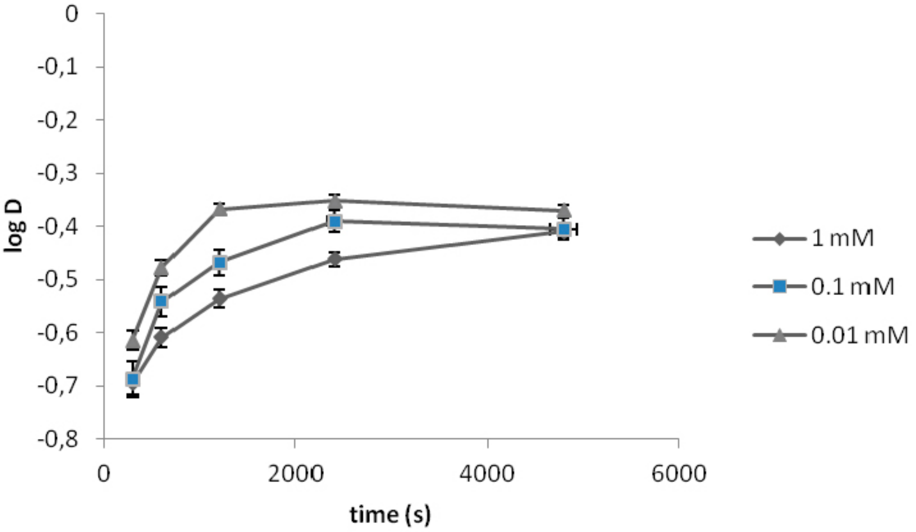


Figure 7-1. Europium extraction as a function of time. The series corresponds to concentration of inactive europium in the aqueous phases. Uncertainties are 3% (based on Andersson 2005) distribution ratio and all samples are doublets. The series "no europium" is from Löfström-Engdahl et al. (2011) and refere to a system with metals in trace amounts.

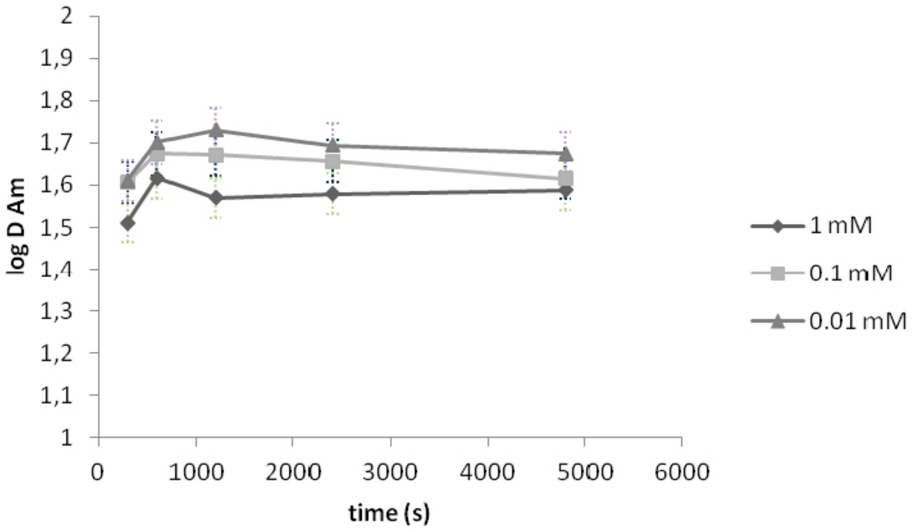


Figure 7-2. *Americium extraction as a function of time. The series corresponds to concentration of inactive europium in the aqueous phases. Uncertainties are 3% (Andersson 2005).*

The distribution ratios for americium are decreasing after reaching a peak after around 10–20 minute of phase contact in the metal containing systems. This decrease can perhaps be explained with the europium extraction and the concurrence between the metals. Since the americium extraction is the faster one (Löfström-Engdahl et al. 2011), it will in the beginning be extracted more, and when time goes by and the europium keeps on extracting, there will be a concurrence situation. Naturally, this effect is not seen when using only trace amounts of the metals and has not been seen previously in the literature, and will be further investigated (Löfström-Engdahl et al. 2011).

7.1.2 The DEHBA based GANEX solvent

In the DEHBA based solvent the europium extraction seems to be quite different. There seems to be slightly lower distribution ratios for the cases with the highest metal concentration both during the extraction as well as after equilibrium has been reached. Anyway, the 0.1 and 0.01 mM systems are almost identical. All the systems reach equilibrium simultaneously (between 40 and 80 minutes of shaking) and the equilibrium distribution ratios seem not to differ.

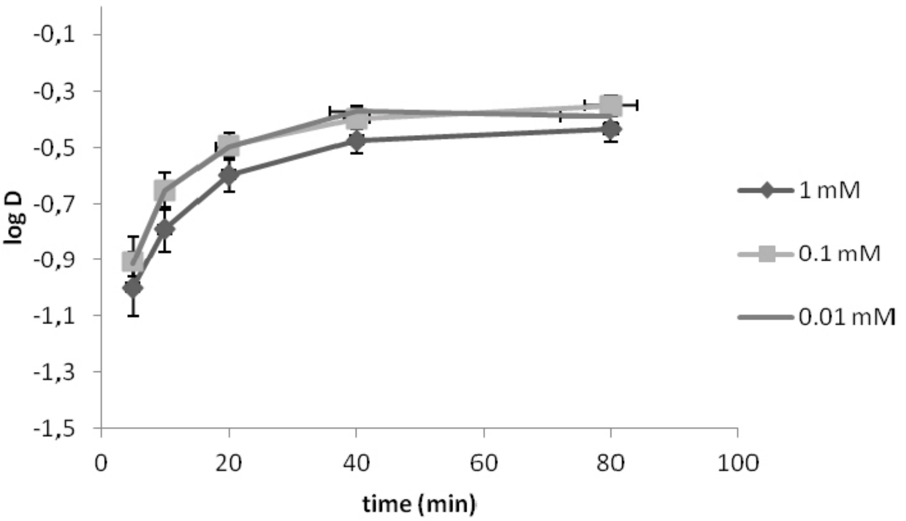


Figure 7-3. *Europium extraction as a function of time. The series corresponds to concentration of inactive europium in the aqueous phases. Uncertainties shown based on the sample preparation, sampling as well as counting and are 3% (Andersson 2005).*

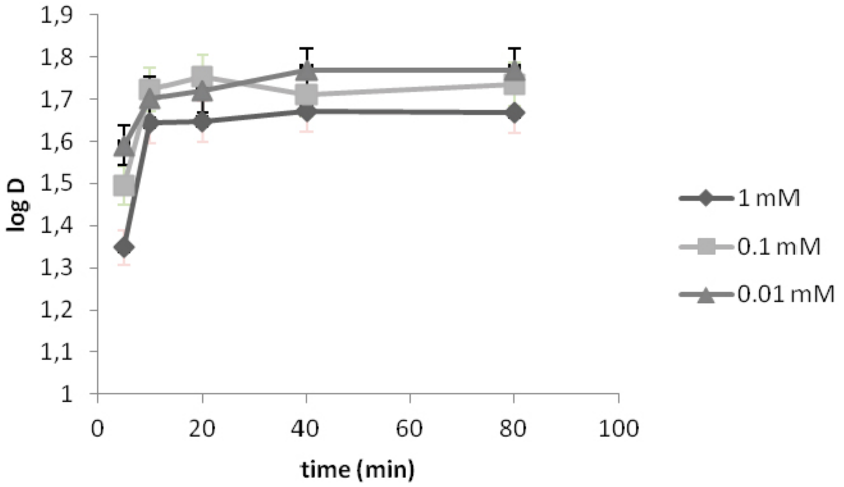


Figure 7-4. *Americium extraction as a function of time. The series corresponds to concentration of inactive europium in the aqueous phases. Uncertainties are based on "different day's doublets" and are so small that they cannot be seen.*

However, in the Am extraction, the series with 0.1 mM and 0.01 mM are nearly identical. However, the 1 mM series shows slightly lower distribution ratios, and also slightly lower equilibrium distribution ratio. The concurrence that occurs in the TBP system is indicated in the 0.1 mM system. But surprisingly, it is not seen in the 0.01 mM system. This could perhaps indicate that this system is as not as sensitive as the TBP system for an increased metal concentration.

7.1.3 Separation

The DEHBA based solvent offers slightly higher separation factors than the TBP based solvent in all the systems. This is depicted in Figures 7-5 and 7-6.

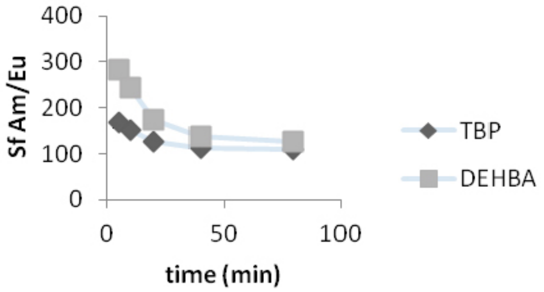


Figure 7-5. *Separation of Am from Eu in the TBP and DEHBA based systems 0.01 mM inactive Eu.*

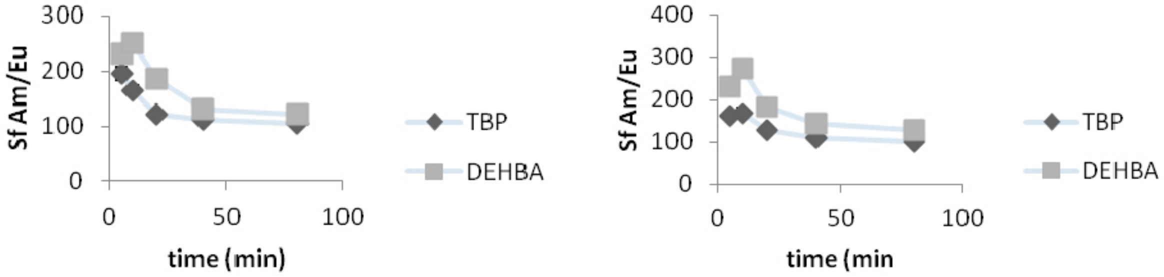


Figure 7-6. *Separation of Am from Eu in the TBP and DEHBA based system (0.1 mM, left) and 1 mM inactive Eu (right).*

7.2 Alternative diluents for proposed GANEX processes

As stated previously, cyclohexanone has traditionally been used in the GANEX process developed at Chalmers. The cyclohexanone offers relatively high solubility of the ligand, as well as a reasonable fast rate of extraction. However, there are also some disadvantages with the use of cyclohexanone, for example the low flash point (44°C) and that it degrades in the contact with the acid used during the extraction process. Therefore, alternative diluents have been investigated during 2011.

7.2.1 Hexanoic acid

Since one problem with the formulated GANEX process is the low solubility of the $CyMe_4$ BTBP ligand in the solvent it would be of high interest to find a diluent where the dissolution of the ligand would increase. The ligand is a weak base, and therefore, carboxylic acids where tried as diluents since this exchange was thought to increase the solubility of the ligand. The three acids used were hexanoic – octanoic – and nonanoic acid. The first test performed was a solubility test of the $CyMe_4$ BTBP in the three diluents. This was followed by a test where the acids where contacted with a 0.25 M Na_2CO_3 solution. This was done since sodium carbonate is used as a scrubbing agent in the PUREX process, and is thought to be used as that in GANEX processes as well. An ocular inspection where performed in order to see if there were gas formation (CO_2) and whether the aqueous and organic phases separated. The most suitable diluent, hexanoic acid, was selected for further extraction studies. Initially, the pure diluent was tested so that it does not extract in the absence of extractant. The extractions were performed using the radiotracer ^{241}Am and various different acid concentrations. Anyway, no extraction was seen. This experiment was followed a kinetic analysis showing that there is no influence of the addition of TBP to the system.

Several actinides (^{235}U, ^{238}Pu, ^{244}Cm and ^{241}Am) and the lanthanide ^{152}Eu where extracted in trace amounts using “GANEX III”. In order to compare the system with the cyclohexanone based GANEX the other elements were extracted using the same $CyMe_4$-BTBP concentration as in that process (10 mM). Also, the rest of the lanthanides were extracted (Ce, Nd, Sm, and La). Fission products were also extracted (Rb, Sr, Y, Zr, Mo, Ru, Rh, Pd, Ag, Cd, Sb, Te, Cs, Ba) as well as corrosion/activation products (Fe, Ni, Cr, Co and Mn). In order to rule out extraction of the pure diluent, the lanthanides, fission and corrosion/activation products were also extracted without any $CyMe_4$ present.

To investigate whether a competition occurred between plutonium and americium also an extraction of ^{241}Am in the presence of ^{238}Pu where performed. The americium content was analysed using HPGe. The same experiment was performed using ^{244}Cm, but the curium content was analysed using alpha spectrometry. After seeing that a concurrence occurred, indicating that the plutonium mainly is extracted by the $CyMe_4$ BTBP and not by the TBP as previously assumed, the Pu was extracted using only 30% TBP in 70% HA and in pure HA.

The more suitable diluent of the three carboxylic acid tested was hexanoic acid. It had the highest solubility of the ligand, and it appeared clear and phase separated when mixed with Na_2CO_3. The other two diluents appeared cloudy. The results from the initial test for the solubility of the $CyMe_4$ BTBP and the addition of 0.25 M Na_2CO_3 are seen in Table 7-1.

The initial extraction of ^{241}Am at various acid concentrations showed that no diluent extraction of americium was taking place (Table 7-2) The time of phase contact needed for reaching equilibrium is around 40 minutes in the solvent containing TBP and similar in the one without TBP. As contrary to the proposed cyclohexanone based solvent, the lanthanide and actinide extraction need the same time of phase contact for reaching equilibrium (both with and without TBP). Therefore, the separation factor is increasing with time, reaching it highest value when the systems are in equilibrium. However, in a future process a contact time of 40 minutes is impossible.

Table 7-1. The results from the initial tests of the three proposed diluents.

	f.p.	price (sek/kg)	initial solubility test	appearance after Na_2CO_3 addition
hexanoic acid	102	500	> 25 mM	clear, phases separated
octanoic acid	110	250	less than HA	cloudy
nonanoic acid	140	5,000	less than HA	cloudy

Table 7-2. The extraction of ^{241}Am into pure HA at various acid concentrations. The boarder for stripping/extraction is log D=0. As can be seen, no extraction is taking place.

[HNO_3]	log D Am
0.5	–2.83467
1	–2.52535
2	–3.3604
3	–3.17148
4	–2.92909

The extraction of actinides was done in several steps. The extraction of ^{241}Am, ^{244}Cm, ^{238}Pu, ^{235}U and the lanthanide ^{152}Eu as pure species are seen in Figure 7-9. As can be seen, the Pu and Am have high distribution ratios (> 100), while the uranium does not show as high distribution ratio (2.2). It is surprising and also promising that there is such a difference between the Cm distribution ratio (D_{Cm}=5.4) and the americium distribution ratio (D_{Am}=100). In this system there is a clear separation of these elements with a separation factor of almost 20. However it should be noted that the detection methods are different (alpha-spectrometry and gamma analyses (HPGe)) which could be a contributing factor to the result, which hence must be looked further into.

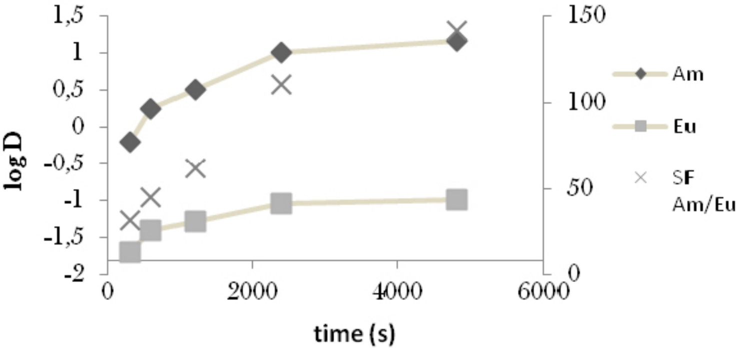


Figure 7-7. Extraction of Am-241 and Eu-152 and their separation as a function of time. Solvent is HA and 17 mM CyMe$_4$ BTBP.

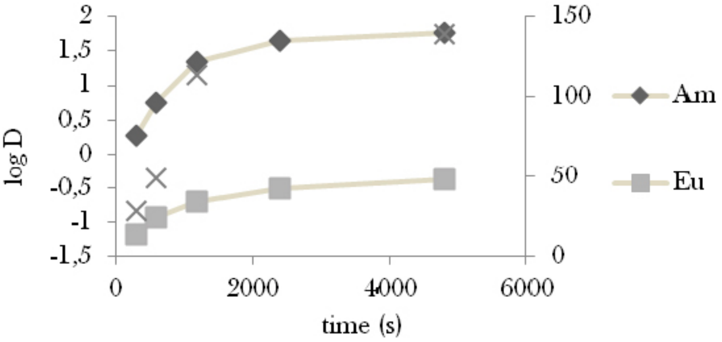


Figure 7-8. Extraction of Am-241 and Eu-152 and their separation as a function of time. Solvent is 70% HA, 30% TBP and 17 mM CyMe$_4$ BTBP.

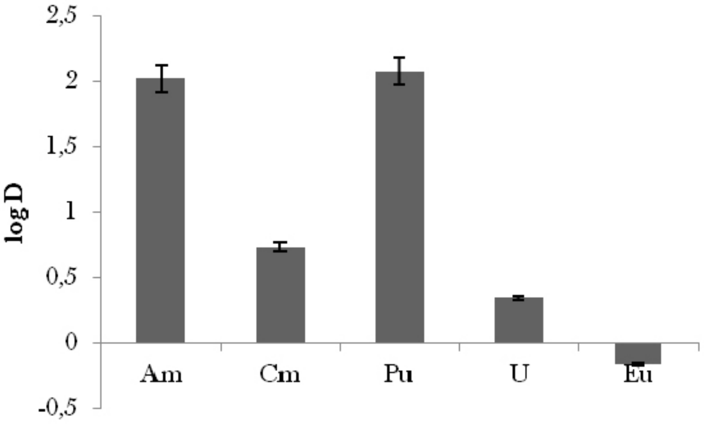


Figure 7-9. The results from the extractions of actinides and the lanthanide Eu-152 as the only elements present in the system. The uncertainties of the values are 5%, based on the sample preparation uncertainties and doublet samples. The uncertainties from the counting statistics are so small that they cannot be seen.

In order to investigate how much of the Pu that is extracted from the various pure diluents, the TBP and how much that is extracted by the CyMe$_4$-BTBP. The results from these extractions are that only a small fraction of the Pu is extracted by the TBP and no Pu at all is extracted by the HA (Figure 7-10). Since the Pu extraction is performed mainly by the CyMe$_4$-BTBP it is also of interest whether it influences and suppresses the Am, Cm and Eu extraction, which is something unwanted in the real process (suppression of Am and Cm extraction), while the suppression of the Eu extraction is wanted and also have been seen under metal loading conditions in the cyclohexanone based GANEX solvent. Therefore, extractions of Cm and Am in the presence of Pu was performed. Clearly the presence of Pu suppresses the extraction of both Cm, Am and Eu (Figure 7-10).

Extraction of lanthanides

None of the Lanthanides are extracted by the pure HA alone (Figure 7-10–7-13).

The extraction of fission products are similar to the one in the GANEX solvent based on cyclohexanone. The most troublesome metals are Ag, Cd and Pd, while Mo is close to being extracted. However, one difference between the two different GANEX solvents is that the HA not extractby itself.

The extraction of corrosion/activation products is not high. The only trouble here is the Co and Mn. However, both of them are having distribution ratios between 0.6–0.7 thus being below one.

7.2.2 Sulfur-based diluents for GANEX purposes

After making a search of the literature, sulphones were identified as possible future diluents for GANEX purposes. Examples of this class of compound could have relative dielectric constants comparable with nitrobenzene while having low toxicities and being very stable. While trifluoromethyl phenyl sulphone (Figure 7-14) is sold commercially, diisoamyl sulphone can be made as a freely flowing liquid after the addition of tributyl phosphate (Figure 7-14).

Results from the extractions with the two diluents are shown in Figure 7-15. The diisoamyl sulphone had to be mixed with TBP to obtain a clear liquid. As can be seen americium is extracted with this diluent, however, not to any greater extent. With pure FS-13 the americium extraction is also very minor but when the FS-13 is mixed with TBP the performance improves.

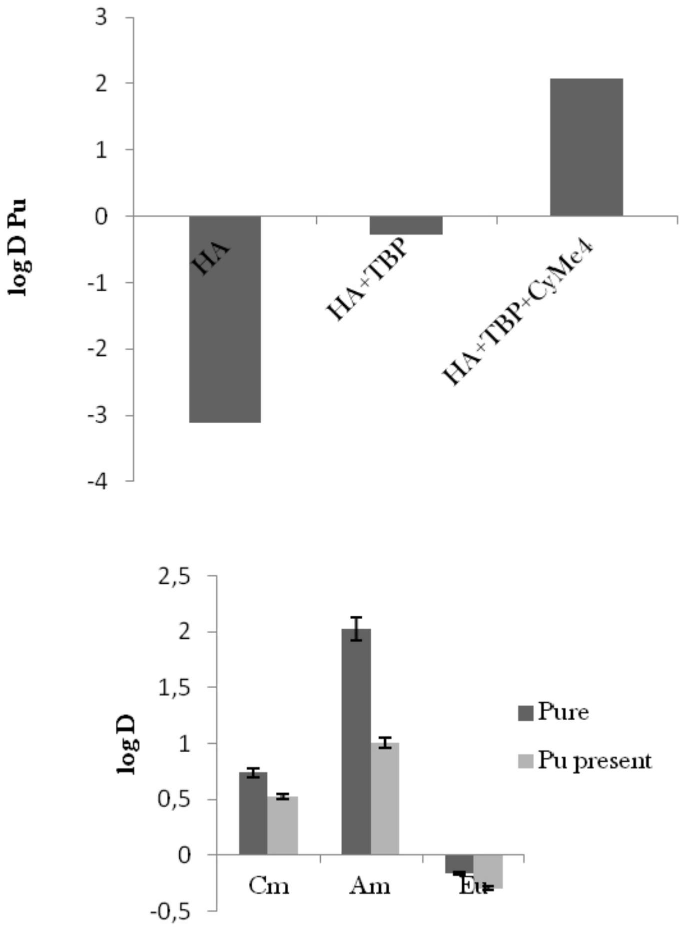


Figure 7-10. *Extraction of Pu in pure hexanoic acid, hexanoic acid and TBP and the whole ternary solvent (left). The effect of plutonium addition on the actinide extraction, as can be seen the extraction of Am, Cm and Eu is suppressed. The uncertainities are 5% and based on sample preparation. The uncertainties of the counting statistics are so small that they cannot be seen.*

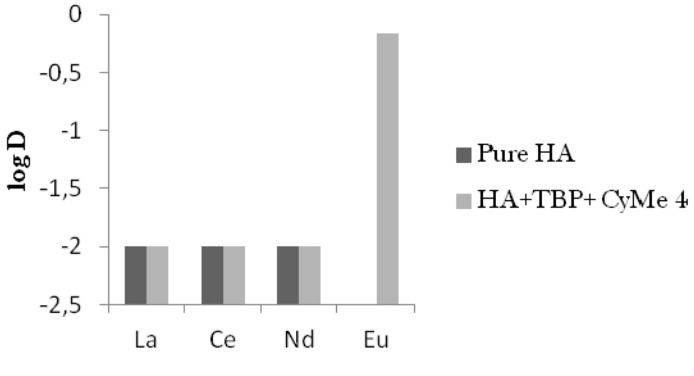


Figure 7-11. *The extraction of lanthanides by the pure diluent and the solvent +CyMe$_4$ BTBP. As can be seen it is only the Eu that is extracted to any higher extent. Where non extraction is seen the log D value is set to –2.*

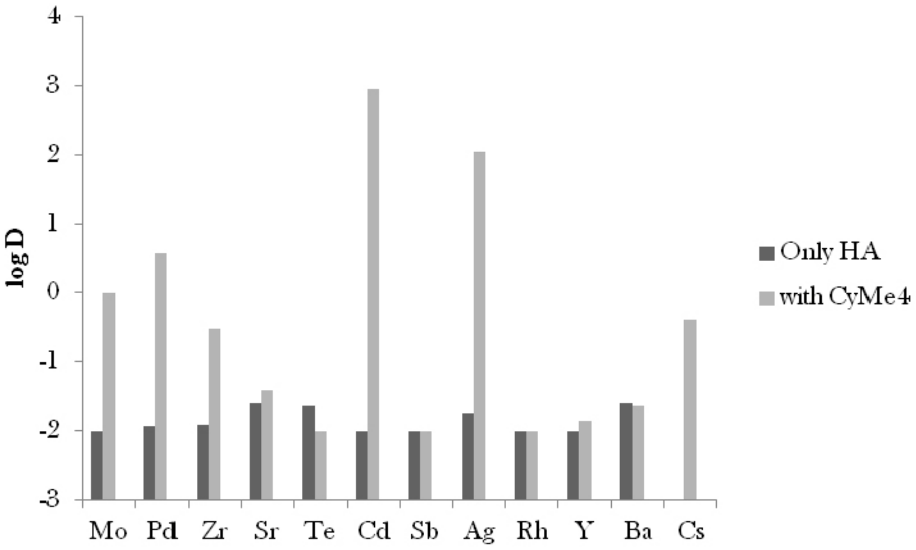


Figure 7-12. *The extraction of fission products. As can be seen the most troublesome products are Ag, Cd, Pd and Mo. It can also be seen that the diluent does not extracts by itself. Where no extraction is seen the log D value is set to –2.*

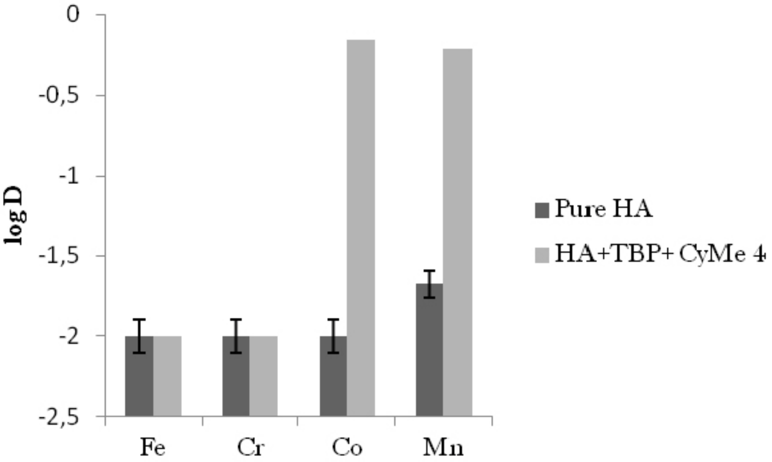


Figure 7-13. *The extraction of corrosion and activation products. Where non extraction is seen the log D value is set to –2.*

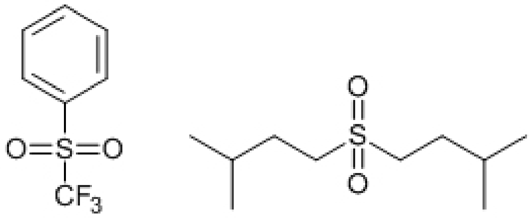


Figure 7-14. *Molecular structure of trifluoromethyl phenyl sulphone (left) and diisoamyl sulphone (right).*

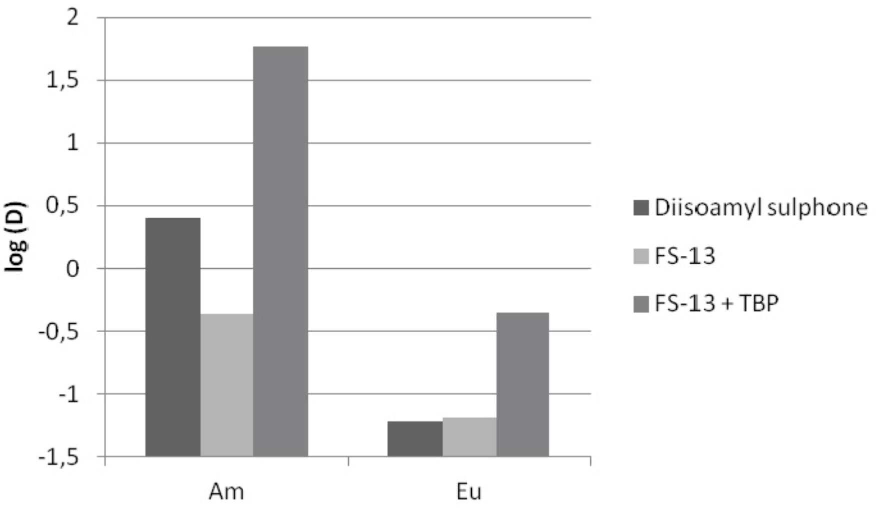


Figure 7-15. *Extraction of Am-241 and Eu-152 from 4 M HNO_3 with diisoamyl sulphone + 30% TBP saturated with $CyMe_4$-BTBP (< 10 mM), FS-13 saturated with $CyMe_4$-BTBP (ca 20 mM) and FS-13 saturated with $CyMe_4$-BTBP +30% TBP.*

7.3 Stability of Diluents

It was found that when cyclohexanone and nitric acid were left together under adiabatic conditions that a sudden exothermic reaction occurs with little warning. This exothermic reaction can cause the contents of the sample tube to be ejected when the water in the mixture boils. An experimental rig was created to study the exothermic reactions between nitric acid and diluents, in this experimental rig a test tube containing both nitric acid and the diluent is surrounded with resistors and placed inside a small dewar flask. The temperature of the mixture is monitored using a temperature dependant resistor (thermistor) which is also used to allow the mixture to be maintained at a constant temperature using a simple on-off thermostat. The voltage output from the thermistor and the voltage applied to the heating element were recorded using a digital oscilloscope. As a test of the equipment a test tube of water was allowed to reach a constant temperature before the addition of a paper bag containing finely divided iron powder (these pads are marketed as hand warmers for placement inside gloves). Below is shown a graph of the power input as a function of time.

It can be seen that the pad emits heat, and when the thermistor output is added to the graph it can be seen that the heating pad did cause moderate overheating of the system.

When the experiment was repeated using cyclohexanone (8 ml) and a non radioactive mixture of fission products in nitric acid (4 M). Using a 154 Ω heater the following trace was obtained. It is clear that the mixture starts to generate its own warmth and is able to heat up above the set point. The experiment was terminated before any violent event could occur.

After the equipment was improved and rebuilt a series of runs were performed using both super pure nitric acid and a simulated PUREX raffinate with cyclohexanone. An example of such an experiment is shown in Figure 7-19. The test tube contained 6 M nitric acid (6 ml) and cyclohexanone (6 ml).

Here it is clear that within one hour a violent reaction starts to occur, I suspect that on a large scale that once such a reaction starts inside a solvent extraction plant it will be difficult if not impossible to bring it under control.

A series of experiments (Figure 7-20) were performed in which different volumes of cyclohexanone were added to 8.8 ml of the fission product mixture in nitric acid (4 M). It was soon clear that the size of the exotherm depends on the amount of cyclohexanone added to the mixture. Also with the larger volumes (> 1 ml) of cyclohexanone the induction time between the addition of the cyclohexanone and the thermal runaway was smaller than it was with small (< 1 ml) cyclohexanone volumes.

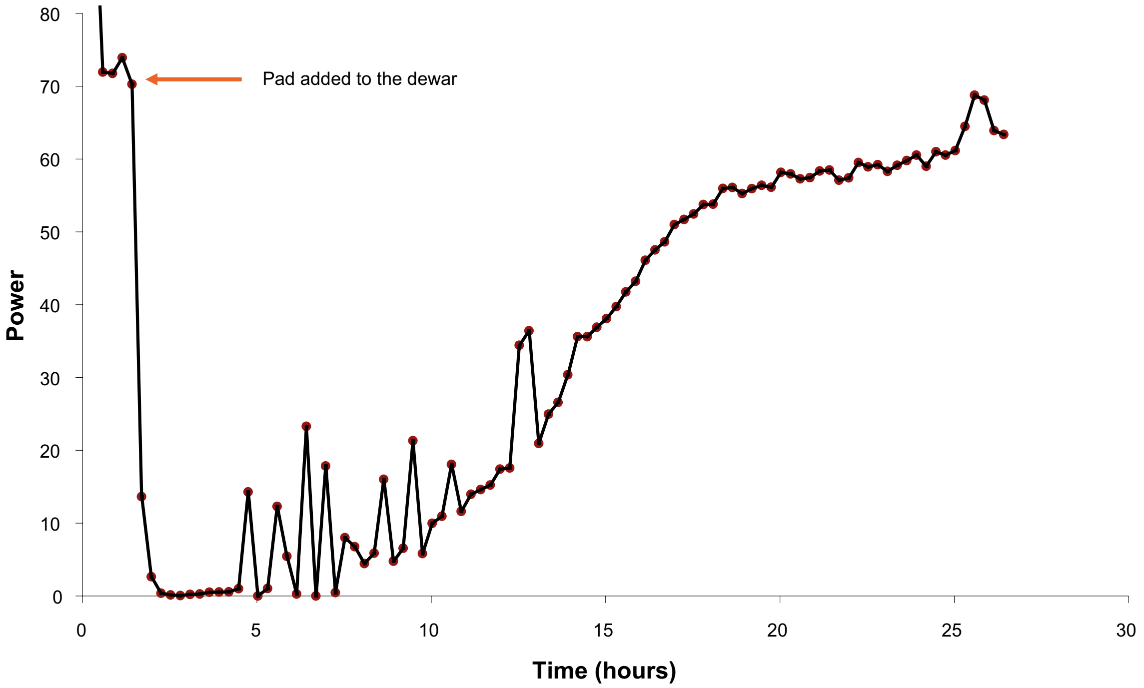


Figure 7-16. *The effect of the additional thermal power on the thermostatted system, showing a decrease in the electrical power required to maintain a constant temperature.*

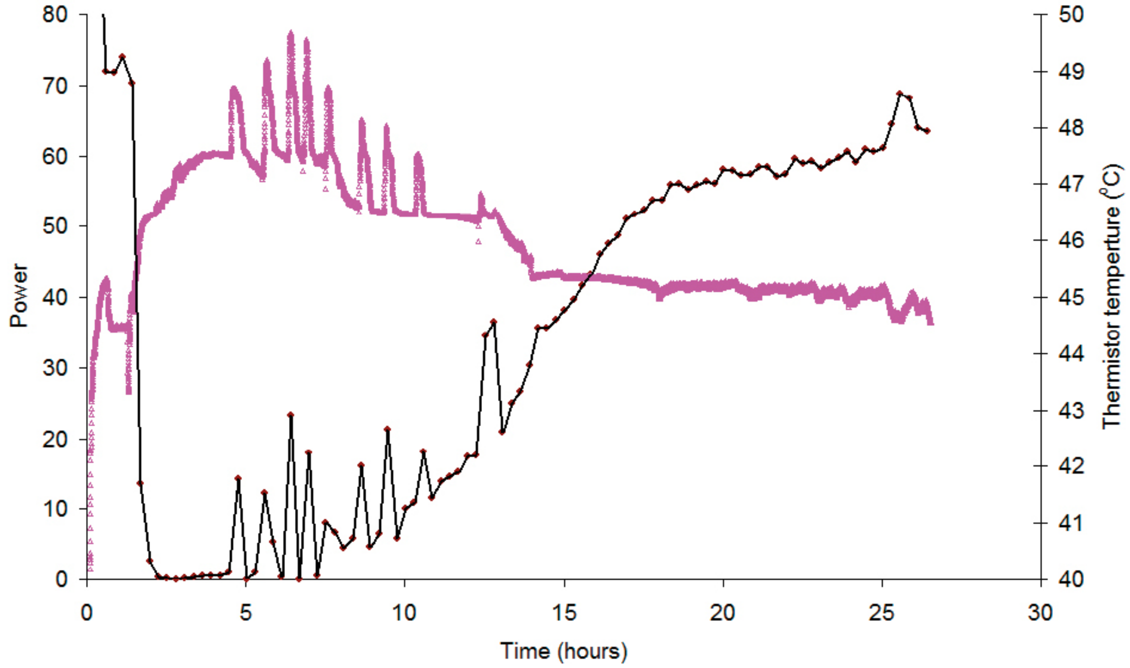


Figure 7-17. *The effect of the additional thermal power on the thermostatted system, showing a decrease in the electrical power required to maintain a constant temperature with the purple line for the temperature (showing the slight overshoot) included.*

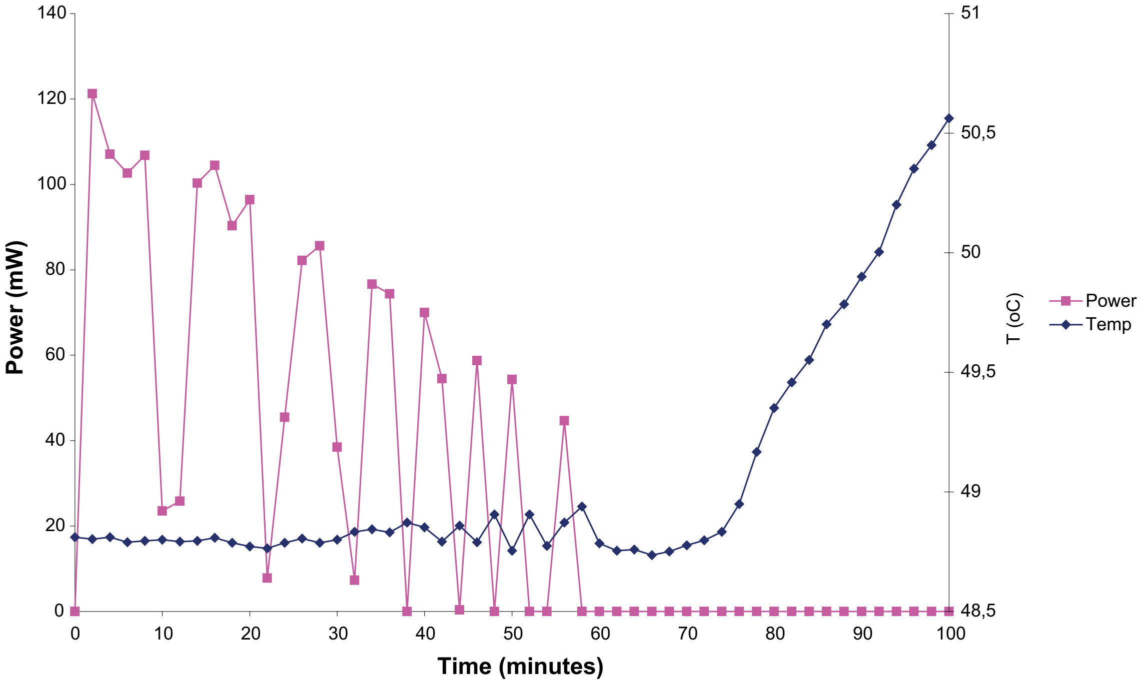


Figure 7-18. *The first test with cyclohexanone, nitric acid and an inactive fission product mixture.*

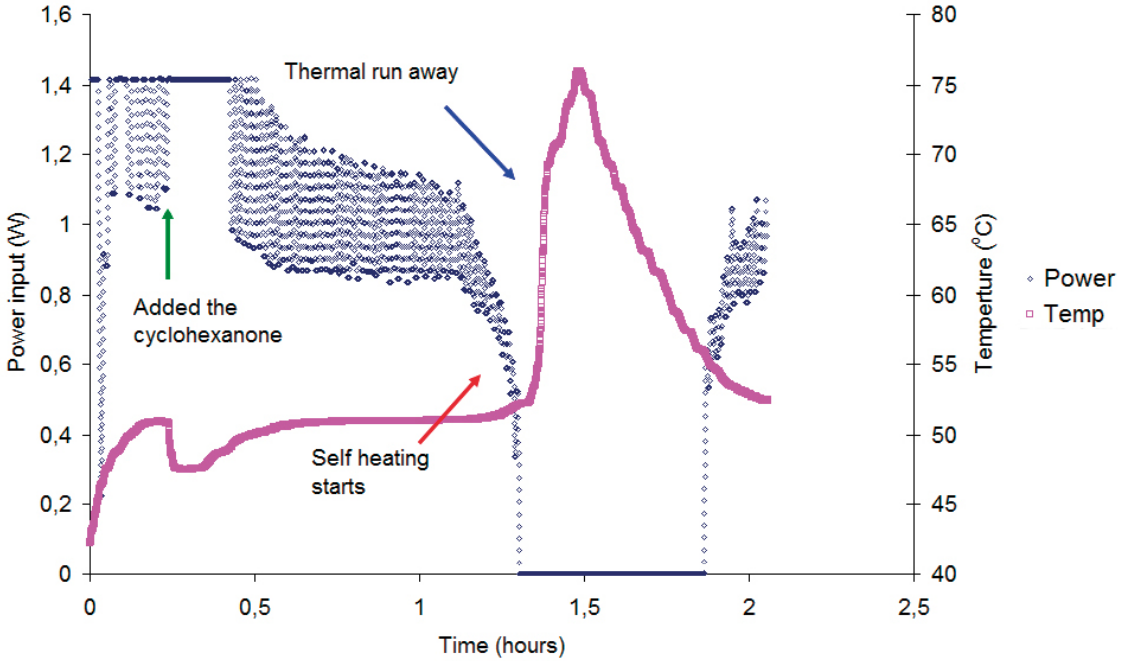


Figure 7-19. *An experiment in which cyclohexanone (6 ml) was combined with 6 M nitric acid (6 ml), the mixture was held at 50°C. Within one hour a violent exothermic reaction occurred.*

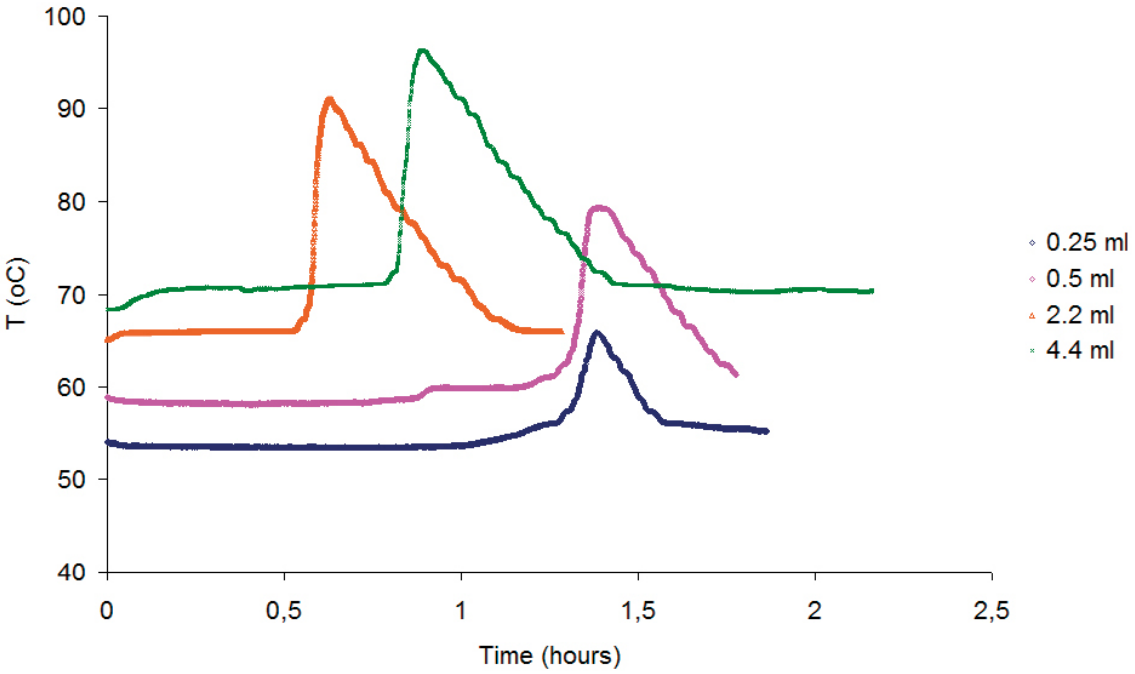


Figure 7-20. *The temperature against time for a simulated fission product mixture dissolved in 4 M nitric acid (8.8 ml) with different amounts of cyclohexanone added to it. The data has been adjusted such that zero time is the moment that the cyclohexanone is added, the lines have been separated by 5°C from each other for clarity. All reactions were kept at 55°C.*

It can also be seen below in Figure 7-21 that when the mixture is preheated to higher temperatures that the time between the addition of the cyclohexanone and the violent reaction is shorter. At the lowest temperatures the exothermic reaction occurs over such a long time that it is less noticeable and the peak temperature reached is far lower.

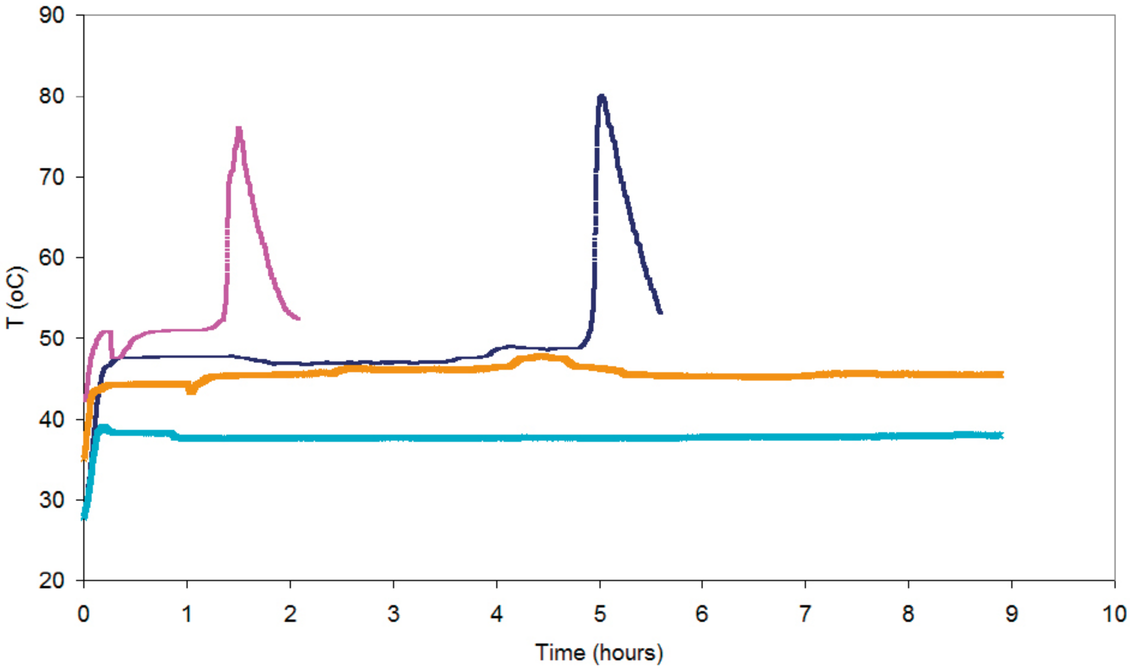


Figure 7-21. *Super pure nitric acid heated with cyclohexanone using different set points for the temperature controller. Other than the temperature all other conditions were the same for each run.*

As cyclohexanone is a solvent which has a particularly low stability against nitric acid, an experimental run was performed with nitrobenzene. As expected this solvent was very resistant to the action of the nitric acid. The nitro group deactivates the benzene ring against further attack by nitric acid. The production of explosions such as TNT requires prolonged treatment of aromatics such as toluene with mixtures of nitric and sulphuric acids. Such a mixture of acids is required to generate the NO_2^+ cation which is required for the conversion of an arene into a nitroarene. It is important to understand that while many explosives contain nitro groups, not all nitro compounds are explosives. For example a range of useful nitro group containing drugs have been in use since the mid 20th century, these drugs include sedatives, antibiotics and antiparasite agents (Strauss 1979).

In common with nitrobenzene octanol was found to be very stable against nitric acid in the same test. During an eight hour exposure of octanol to nitric acid no exothermic reactions occurred.

The alternative diluent (hexanoic acid) was treated with the fission product mixture, during this treatment nothing untoward occurred.

When the non enolisable ketone (fenchone) was heated with 4 M nitric acid nothing happened

It was understood that cyclohexanone reacts with nitric acid to form oxidation products such as adipic acid. In the past the adipic acid required for the production of nylon 66 was made by the oxidation of cyclohexanone using nitric acid. Because of this oxidation process it was decided to concentrate on adipic acid formation.

As adipic acid is a very involatile compound the products of the oxidation reaction were treated with methanol, tosic acid and a dehydration reagent (2,2-dimethoxypropane). An internal standard (Heptanedioic acid, pimelic acid) was present in the methanol. After the methyl ester formation the acid was neutralised with a small excess of triethyl amine before the reaction mixture was concentrated down. After concentration the residue was dissolved in ethyl acetate, the organic extract was washed with water before the water was removed (with anhydrous sodium sulphate). After dilution with acetone the samples were injected into gas chromatography machines.

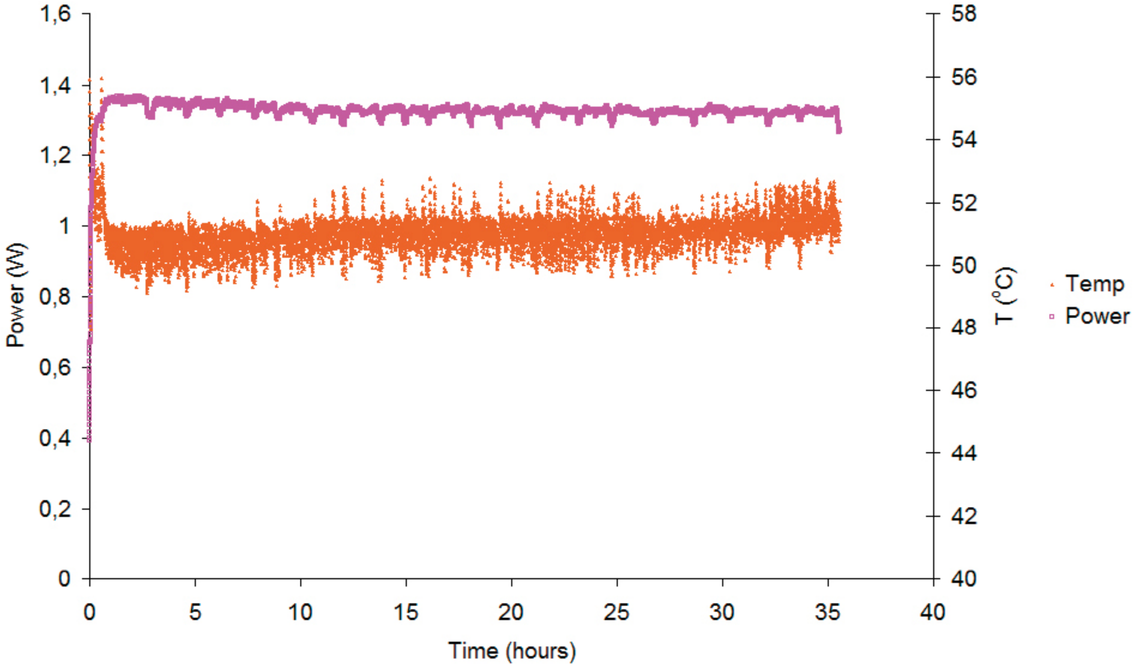


Figure 7-22. *The results of an experiment where nitrobenzene was heated with a non radioactive simulated fission product mixture in nitric acid, the orange curve is the temperature while the power delivered to the thermostated test tube is the magenta trace.*

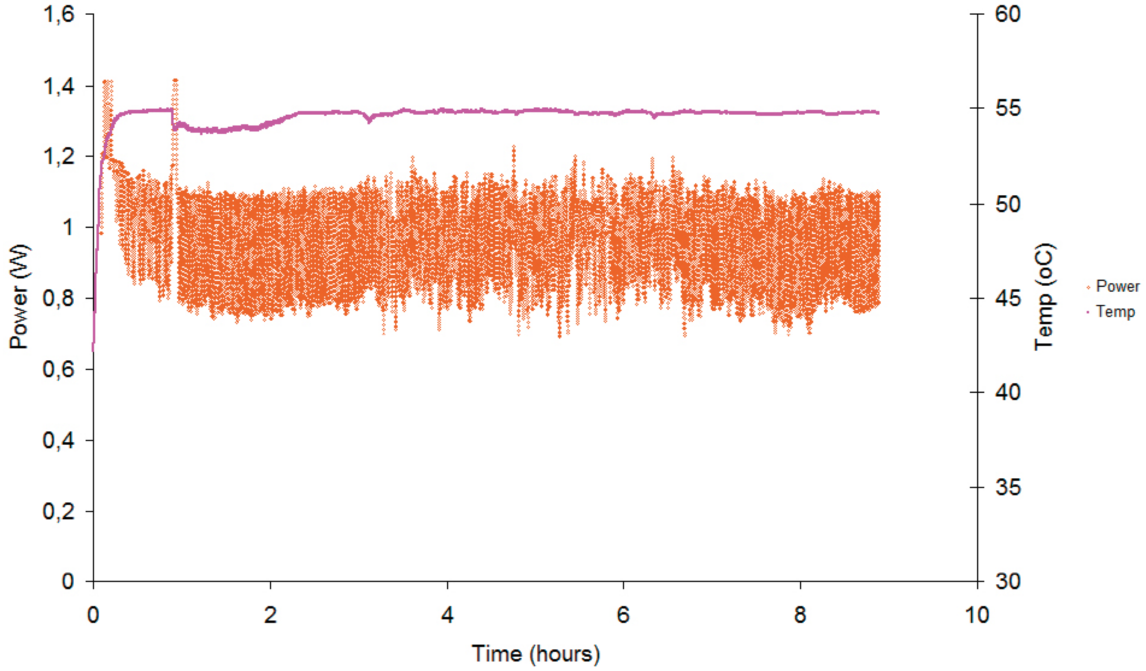


__Figure 7-23.__ The results of an experiment where octanol was heated with a non radioactive simulated fission product mixture in nitric acid, the orange curve is the temperature while the power delivered to the thermostated test tube is the magenta trace.

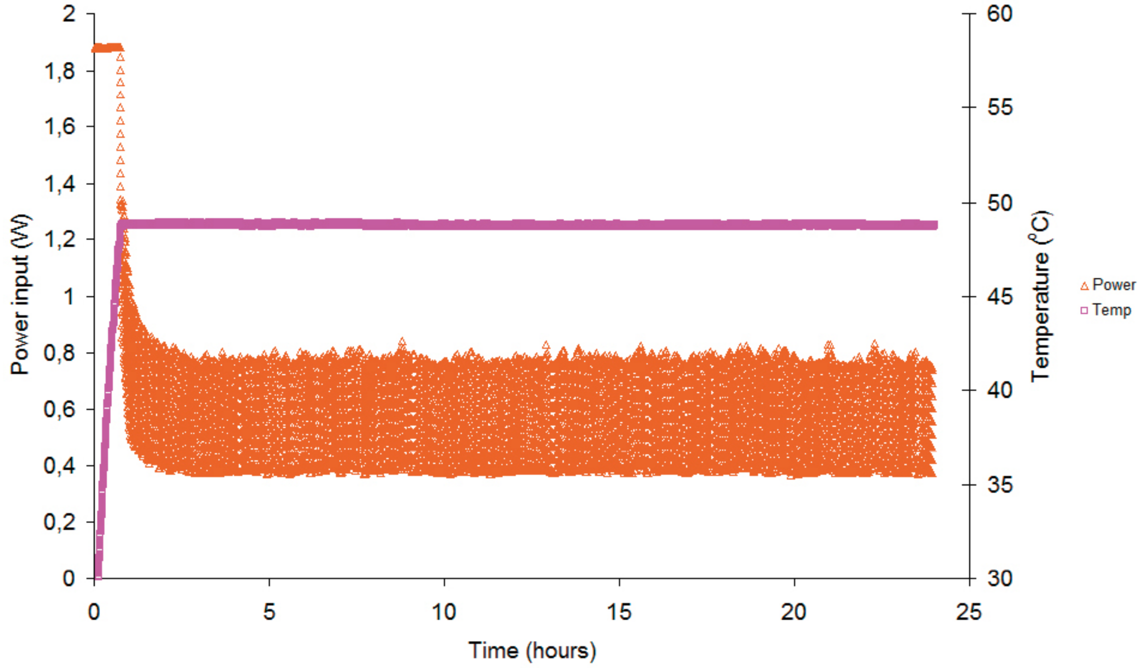


__Figure 7-24.__ The results of an experiment where hexanoic acid was heated with a non radioactive simulated fission product mixture in nitric acid, the orange curve is the temperature while the power delivered to the thermostated test tube is the magenta trace.

A test of the method was made using pure adipic acid and it was found that the ratio of the peak due to dimethyl adipate to dimethyl pimelate was proportional to the amount of adipic acid added to the vial in which the derivatisation was performed. As adipic acid has been shown to form coordination polymers with lanthanides (Borkowski and Cahill 2004) and uranium (Borkowski and Cahill 2003) it has clear potential to disturb a solvent extraction system, thus its removal from the organic phase is very desirable.

Encouraged by this work we were then able to use this method to examine a sample of cyclohexanone which was heated with nitric acid. It was found that heavy organic phase obtained by the heating of cyclohexanone and nitric acid was very complex. The mixture was allowed to stand for a week before being re-examined with gas chromatography, it was found that the chromatogram was identical thus suggesting that the compounds are stable in an acetone solution. Using a GC-MS (Gas Chromatography Mass Spectrometer) it was possible to identify several of the peaks in the chromatogram.

A small volume of the heat treated cyclohexanone was shaken with sodium hydrogen carbonate solution in an attempt to purify it. This reagent was chosen as it is closely related to the aqueous sodium carbonate used in PUREX plants to remove dibutyl hydrogen phosphate from the organic phase. I reason that any process which uses tributyl phosphate (TBP) will need to use a sodium carbonate washing stage to prevent the accumulation of dibutyl hydrogen phosphate in the organic phase.

It is clear that the peak due to the dimethyl adipate is now smaller indicating that the adipic acid has been partly removed from the cyclohexanone. The peak due to the [1,1'-bi(cyclohexylidene)]-2-one is still present, as this aldol condensation product of cyclohexanone with its self is neither acidic or basic it is likely to remain in the organic phase. The washing step was repeated yielding a still cleaner organic phase.

It is clear that the adipic acid is now absent from the cyclohexanone phase and a series of other peaks are now absent also. The exothermic conversion of cyclohexanone to adipic acid is thought to occur via intermediates such as 2-nitrosocyclohexanone and 2-nitro-2-nitrosocyclohexanone (van Assett and van Krevelen 1963).

2-Nitrosocyclohexanone can be formed by the action of an alkyl nitrite on the acetate ester of the enol form of cyclohexanone (cyclohex-1-en-1-yl acetate) (Lindsay Smith et al. 1985). It has also been suggested by Lindsay Smith et al. that the reaction may occur via the following sequence of steps.

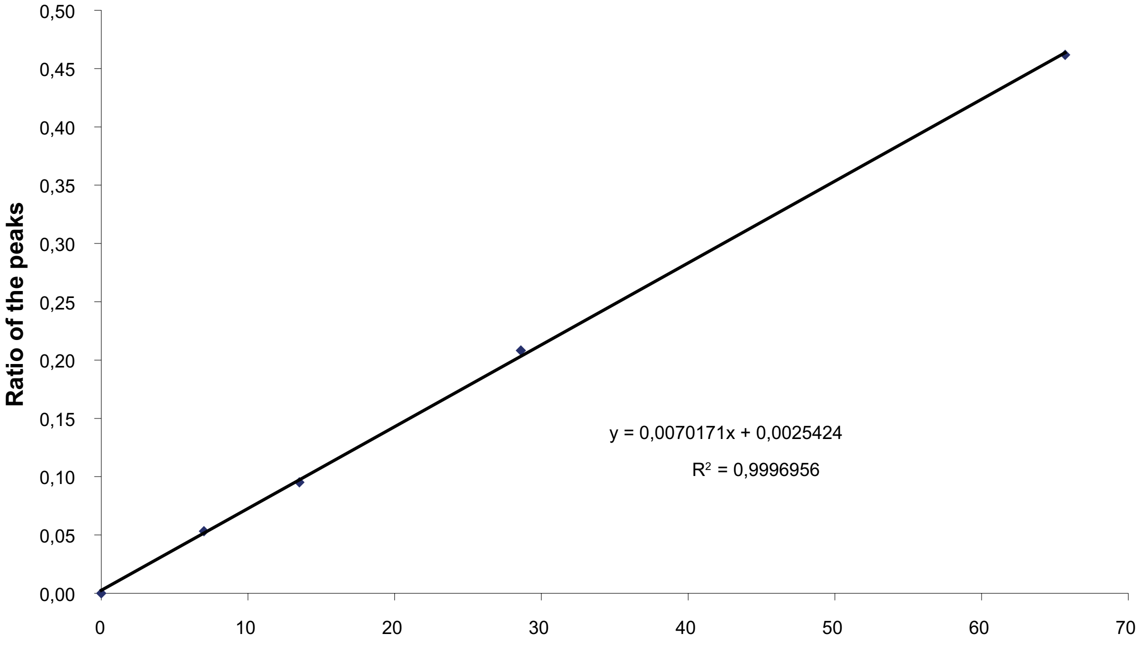


Figure 7-25. *Calibration chart for adipic acid.*

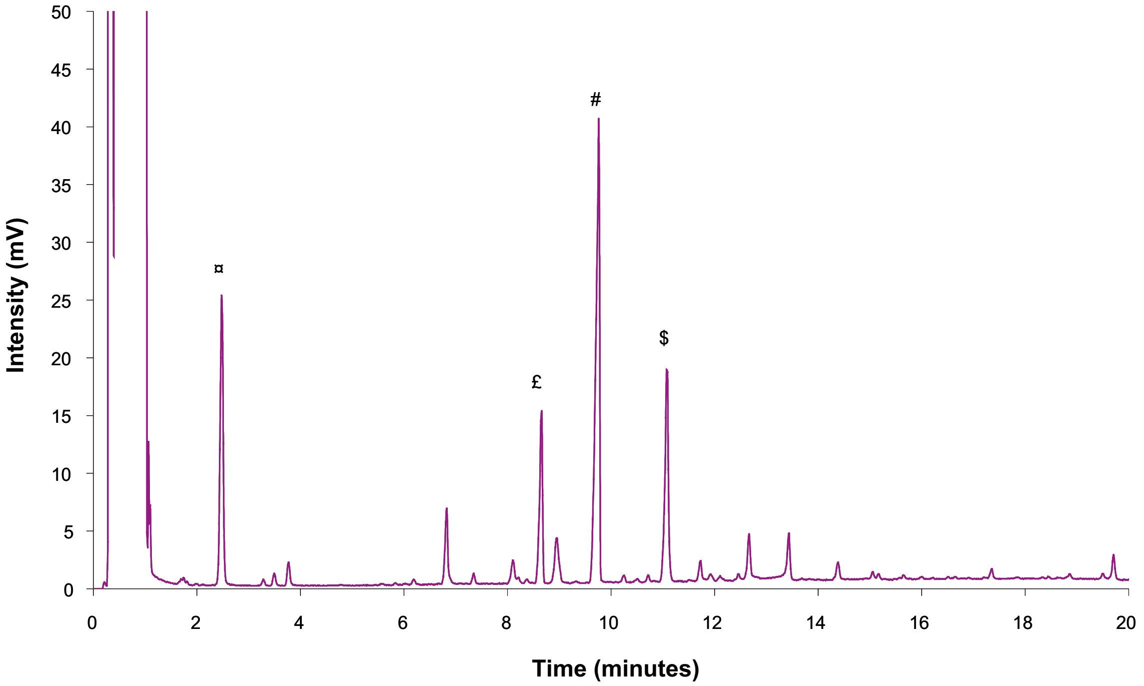


Figure 7-26. *Chromatogram of the products of cyclohexanone with nitric acid after treatment with acidic methanol. Key ¤ 1,1-dimethoxycyclohexane, £ dimethyl adipate, # dimethyl pimelate (internal standard) and $ [1,1'-bi(cyclohexylidene)]-2-one.*

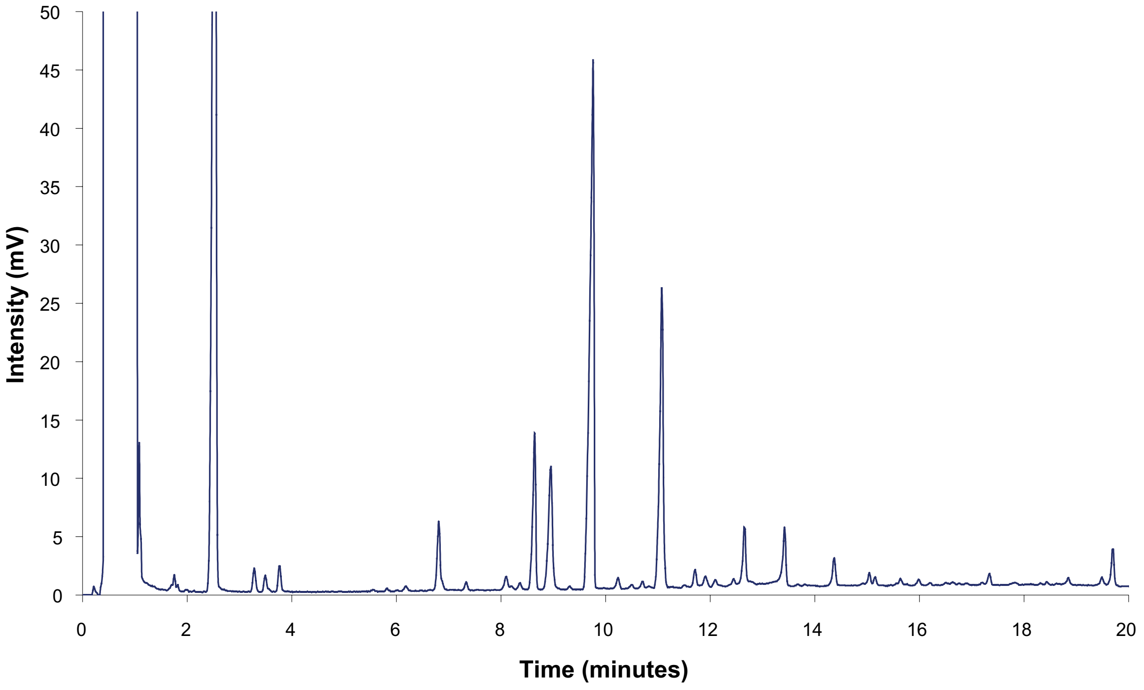


Figure 7-27. *Chromatogram of the products of cyclohexanone with nitric acid after washing once with sodium hydrogen carbonate after treatment with acidic methanol.*

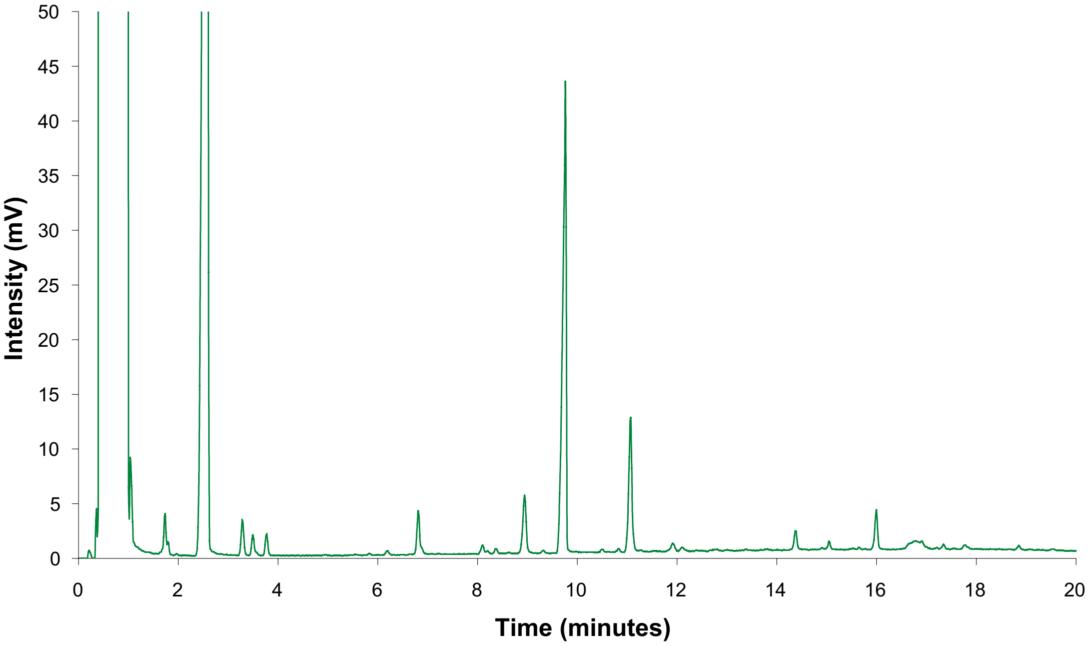


Figure 7-28. *Chromatogram of the products of cyclohexanone with nitric acid after washing twice with sodium hydrogen carbonate after treatment with acidic methanol.*

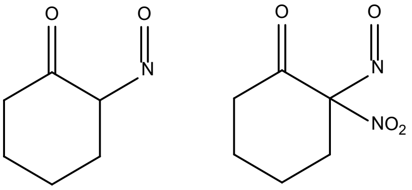


Figure 7-29. *2-Nitrosocyclohexanone and 2-nitro-2-nitrosocyclohexanone.*

As the oxidation process occurs via a series of intermediates and typically shows an induction time before the evolution of heat, it is possible that by removal of the intermediates that the reaction can be retarded. It has been shown that the adipic acid can be removed by shaking with sodium hydrogen carbonate.

It is well known that nitroalkanes are acidic (pKa of a typical nitroalkane is 9 (Casey et al. 1990, p 245)) and the presence of the ketone group is likely to decrease the pKa of the compound thus making it more acidic. For example a typical ketone has a pKa of 19 to 20 while a typical 1,3-diketone has a pKa of 9 (March 1992, p 251) This may make it possible to wash some of the reactive intermediates out of the cyclohexanone using an alkaline washing step.

Carbonic acid (H_2CO_3) has two pKa values (Atkins 1990, p 952), these are 6.4 and 10.3 hence it was reasoned that it should be possible to wash nitro compounds containing the $CHNO_2$ group from the organic phase into an aqueous phase.

This prediction was based on an examination of the literature which revealed that the pKa of 2-nitrocylohexanone has been measured in acetonitrile (Kelly-Rowley et al. 1995). Due to the different in solvent between water and acetonitrile the pKa values from this paper can not be used directly. These measurements were made in anhydrous acetonitrile using the complex of a sodium cation and 15-crown-5 as the counter ion. The measurements were made by titration using anhydrous picric acid with tetraethyl ammonium perchlorate as a supporting electrolyte. A series of compounds had their pKa measured under these conditions.

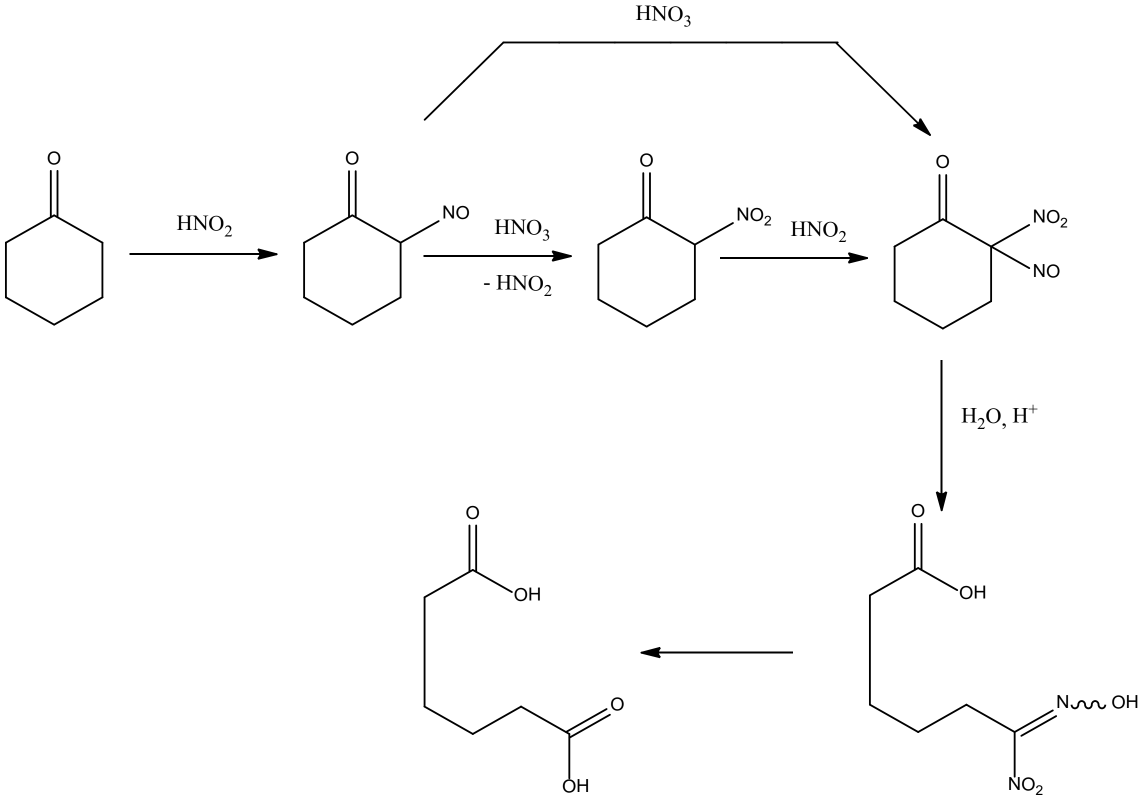
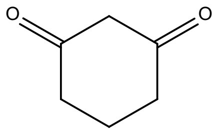
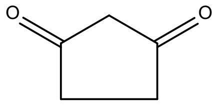
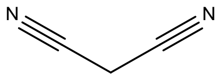
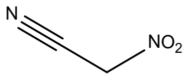
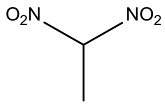
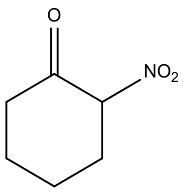


Figure 7-30. *Reaction mechanism according to Hamblet and McAlevy (1951).*

Table 7-3. pKa values for carbon acids where the methylene or methane is adjacent to two electron withdrawing groups.

Compound	pKa
	20.7
	19.2
	21.2
	15.9
	16.9
	20.4

This data suggest that the nitroketone is at least as acidic as a typical 1,3-diketone such as ACAC (acetylacetone). This suggests to me that it will be possible to wash the nitroketone out of the organic phase using aqueous sodium carbonate solution. An experiment was performed in which the stripping of 2-nitrocyclohexanone from cyclohexanone was studied using gas chromatography. It was found that within one minute that the vast majority of the nitrocyclohexanone was removed from the cyclohexanone. This observation suggests that it may be possible to increase the stability of the cyclohexanone by preventing the accumulation of the reactive intermidates by treating the solvent with an aqueous base. It is hoped that this treatment can be combined with the solvent cleanup stage commonly used in PUREX plants to also prevent the accumulation of dibutyl hydrogen phosphate in the organic phase.

Unfortunately, it was more difficult to obtain data for α-nitrosyl ketones. One notable paper (Aksnes 1960) on these compounds indicates that nitrosyl acetone has a pKa of 8.2 which suggests that it will be possible to wash these compounds from the organic phase using sodium carbonate.

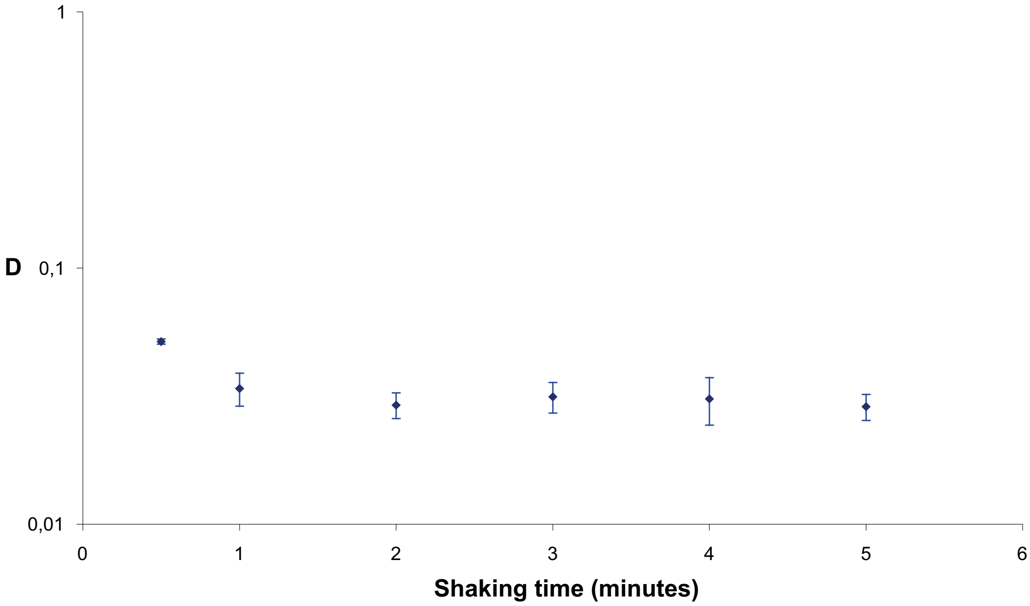


Figure 7-31. *A graph of the distribution ratio for 2-nitrocyclohexanone as a function of the contact time (hand shaking) in small glass vials.*

8 Irradiation experiments

Since the separation processes intended for recycling of used nuclear fuel take place in a high radiation flux the solvent, *i.e.* both the extractant and the diluent, must be resistant to radiation. The radiation will be of different types, *e.g.* alpha and gamma, and the dose rate will be dependent on the isotopic concentration of minor actinides (MA) (Magnusson et al. 2009). This will in turn be dependent on the initial fuel composition and burn-up etc.

8.1 Irradiation of CyMe$_4$-BTBP

CyMe$_4$-BTBP in two different diluents, cyclohexanone and hexanol, was previously irradiated and analyzed for degradation products (Aneheim et al. 2010a). However, the irradiation was done before the recharge of the ^{60}Co source, hence the dose rate was very low and the total dose given to the solutions only reached around 20 kGy. On the contrary to C5-BTBP, which degrades substantially at these doses (Fermvik et al. 2009, 2011), no degradation was observed for CyMe$_4$-BTBP. Therefore, a new irradiation study was done, using the much higher dose rate and thus reaching higher doses in a short time. Two solutions, containing 0.005 M CyMe$_4$-BTBP in hexanol or cyclohexanone, were irradiated with doses up to 880 kGy. Samples were taken at various times and part of the sample was used for extraction experiments, while the rest was sent to Dr. Bohumir Grüuner at the Institute of inorganic chemistry.

8.1.1 High dose rate irradiation of CyMe$_4$-BTBP

Irradiation of 0.005 M CyMe$_4$-BTBP in both hexanol and cyclohexanone has been performed using a high dose rate, with the aim to identify degradation products resulting from the radiolysis. A higher dose rate leads to a higher temperature in the source, around 50°C. Therefore reference solvents were placed in a water bath and samples were taken at the same time as for the irradiated solvents. Samples were removed from both the irradiated solvents and from the heated solvents at various points during a total period of 49 hours and 5 minutes, which equals a dose of 883.5 kGy. Part of the sample is used for extraction experiments, while the other part is sent to IIC (See collaborations section) and used for degradation analysis. All samples were allowed to cool to room temperature before conducting extraction experiments.

Color observations

Both solvents were characteristically yellow at the start of the irradiations. The reference solutions, kept in the water bath, kept their color throughout the whole experiment, but the irradiated solutions displayed color changes. At the first sampling point, after one hour (~18 kGy), the hexanol solvent had started to darken, and this proceeded until the sampling point at 24.3 h (~437 kGy), when the solvent had become light yellow again, even lighter than the reference solution. But then the lightening of the solvent coincided with formation of white crystals, which was not observed here with the CyMe$_4$-BTBP. At the second sampling point, after 2.5 h (44 kGy), also the cyclohexanone based solvent started to darken. It continued to get darker as the irradiation proceeded, but never started to lighten again. The solvent was left in the gamma source for an additional 24 hours to observe possible color change, but still no lightening.

Cyclohexanone as diluent

The reference solution appears to be more or less stable, but the irradiated solvent is clearly degrading. D_{Am} decreases from 5.3 down to 0.02 (Figure 8-1), and $SF_{Am/Eu}$ decreases from 111 down to 5 (Figure 8-2). This means that the decrease in extraction is much larger for Am than for Eu, a behavior previously reported for C5-BTBP degradation. Figure 8-3 shows how the BTBP concentration and D_{Am} change with dose, expressed as % of start value. The curves have similar shapes but the D_{Am} values are a bit below [BTBP] values.

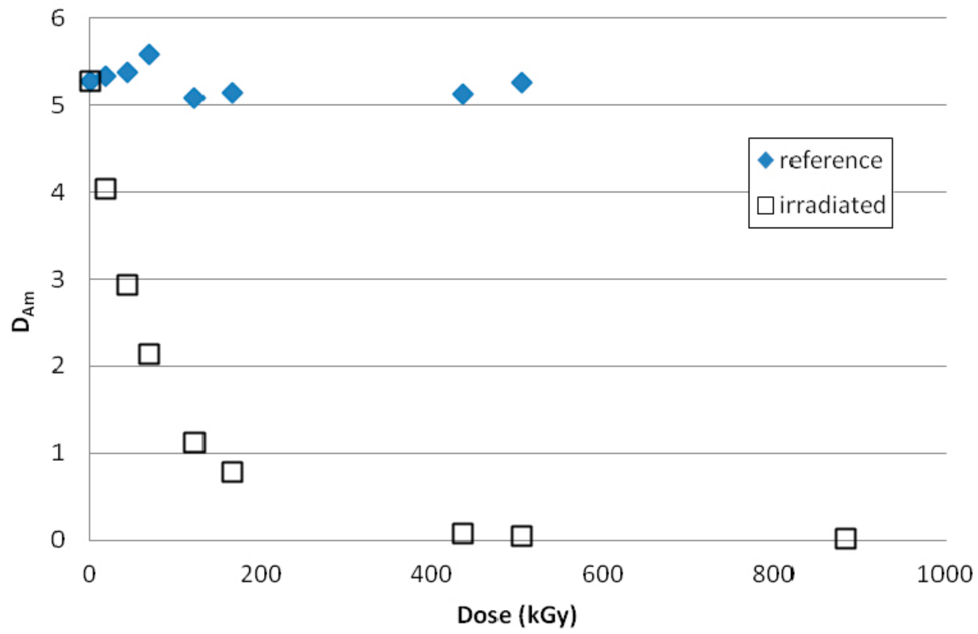


Figure 8-1. *D_{Am} as a function of the dose for a solvent initially containing 0.005 M CyMe$_4$-BTBP in cyclohexanone. The irradiated sample was irradiated in a ^{60}Co source with a dose rate of 18 kGy/h. The reference sample was placed in a thermostatic water bath at 50°C for the corresponding time.*

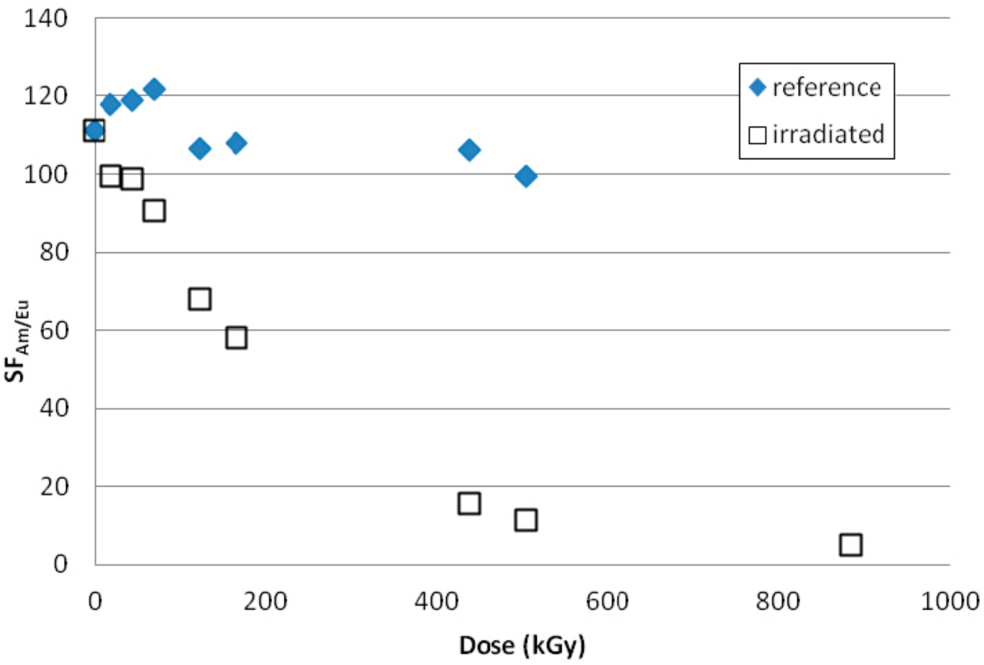


Figure 8-2. *$SF_{Am/Eu}$ as a function of the dose for a solvent initially containing 0.005 M CyMe$_4$-BTBP in cyclohexanone. The irradiated sample was irradiated in a ^{60}Co source with a dose rate of 18 kGy/h. The reference sample was placed in a thermostatic water bath at 50°C for the corresponding time.*

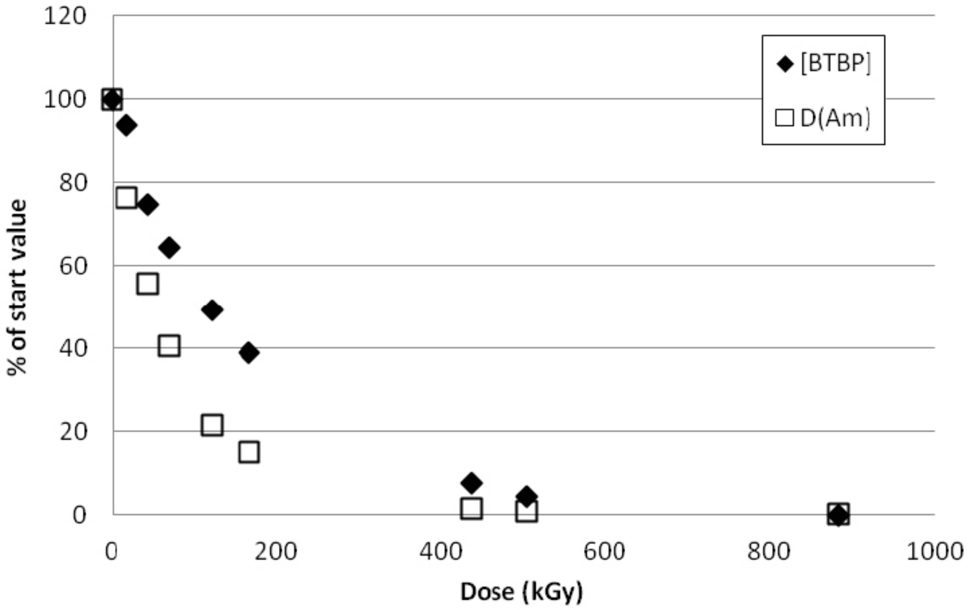


Figure 8-3. *Decrease in BTBP concentration and D_{Am} as a function of the dose for a solvent initially containing 0.005 M CyMe$_4$-BTBP in cyclohexanone. Values plotted as % of start value.*

Hexanol as diluent

When comparing a solvent with hexanol as diluent to the results for the solvent with cyclohexanone as diluent (previous section) the same behavior is observed (Figure 8-4–8-6). The reference solution appears to be stable, but the irradiated solvent is clearly degrading. Already after around 100 kGy there is no CyMe$_4$-BTBP left in the solvent and no metal extraction. For some reason the reference distribution ratios are lower than expected. The solvent with hexanol as diluent is degrading faster than corresponding solvent with cyclohexanone as diluent.

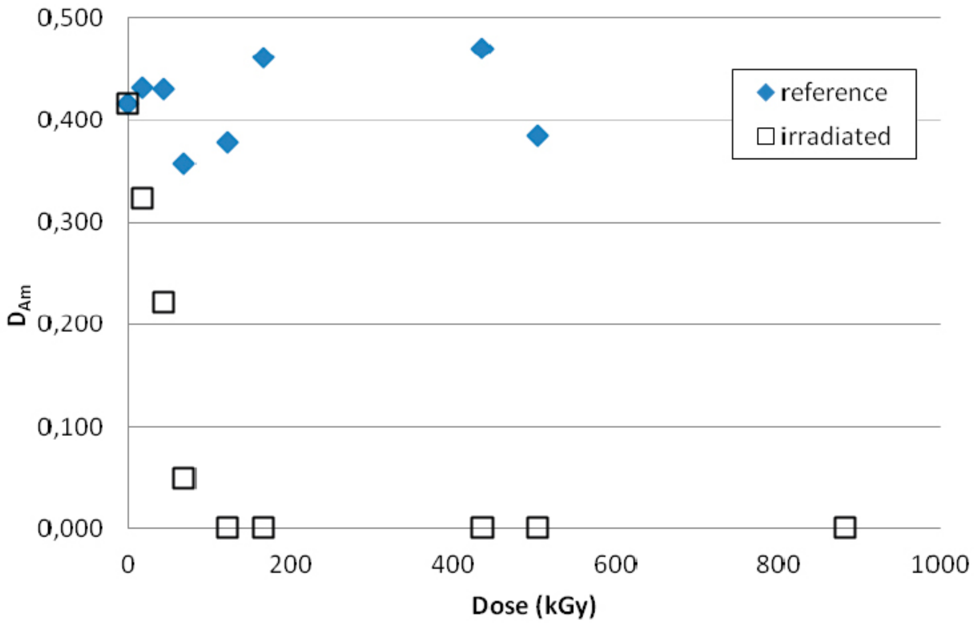


Figure 8-4. *D_{Am} as a function of the dose for a solvent initially containing 0.005 M CyMe$_4$-BTBP in hexanol. The irradiated sample was irradiated in a ^{60}Co source with a dose rate of 18 kGy/h. The reference sample was placed in a thermostatic water bath at 50°C for the corresponding time.*

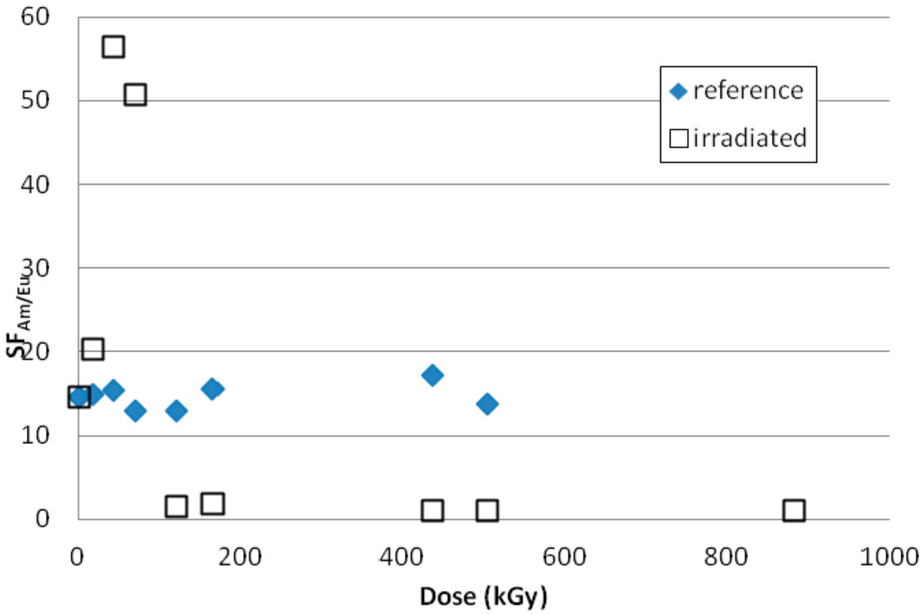


Figure 8-5. $SF_{Am/Eu}$ as a function of the dose for a solvent initially containing 0.005 M $CyMe_4$-BTBP in hexanol. The irradiated sample was irradiated in a ^{60}Co source with a dose rate of 18 kGy/h. The reference sample was placed in a thermostatic water bath at 50°C for the corresponding time.

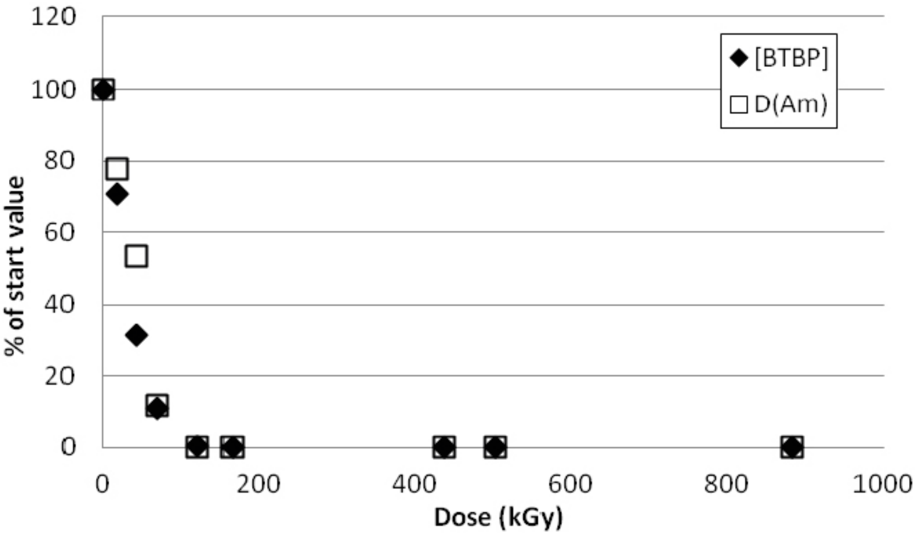


Figure 8-6. Decrease in BTBP concentration and D_{Am} as a function of the dose for a solvent initially containing 0.005 M $CyMe_4$-BTBP in hexanol. Values plotted as % of start value.

8.2 Comparison between alpha and gamma radiolysis

The extraction capacity of a solvent containing C5-BTBP in cyclohexanone after being irradiated with alpha particles was compared to a corresponding solvent irradiated with gamma radiation. In both cases the irradiation took place in the presence of an aqueous phase consisting of 0.01 M HNO_3 and 0.99 M $NaNO_3$. A ^{60}Co source was used for the gamma irradiation while the source of alpha particles was the alpha emitter ^{241}Am extracted into the organic phase. The dose rate in the gamma source was 0.939 kGy/h and the alpha dose rate started at 8 Gy/h and decreased down to 1 Gy/h at the end of the experiment as the distribution of americium between the phases changed. This much lower dose rate for the irradiation with alpha particles results in a much longer irradiation time, 6,800 hours to reach 30 kGy compared to 3 for the solvent irradiated with gamma radiation. Thus the ageing and hydrolysis of the solvent contributes to the overall degradation of the solvent irradiated with alpha particles. The decrease in D_{Am}, displayed as percent of the initial value, is illustrated as a function of the dose in Figure 8-7. Up to 10 kGy the two curves follow each other and no clear difference can be observed. However, at higher doses the solvent irradiated with alpha particles gives lower distribution ratios, probably due to the influence of ageing and hydrolysis.

8.3 GANEX related irradiations

8.3.1 CA-BTP radiolytic stability

The molecule CA-BTP (Figure 8-8) has been reported to have a large solubility in the organic phase compared to $CyMe_4$-BTBP (Trumm et al. 2011) and was hence investigated for the possible replacement of the latter in the BTBP+TBP GANEX solvent.

To see if the replacement would at all be possible the radiolytic behavior of CA-BTP in octanol was investigated. A solution of < 10 mM Ca-BTP in octanol was irradiated both alone and in the presence of 1 M nitric acid. The reason for the uncertain concentration is that the provided sample contained an impurity that was insoluble in the organic phase and due to this the concentration in all samples was lower than intended. This impurity did however dissolve when the organic phase was pre equilibrated and hence seems to be water soluble. However, the concentration of CA-BTP should most likely still be the same in each sample given that the impurity was homogeneously distributed in the sample. The result from the irradiation is displayed in Figure 8-9. As can be seen the CA-BTP is degraded without the presence of acid but when the acid is present the distribution ratios stays stable.

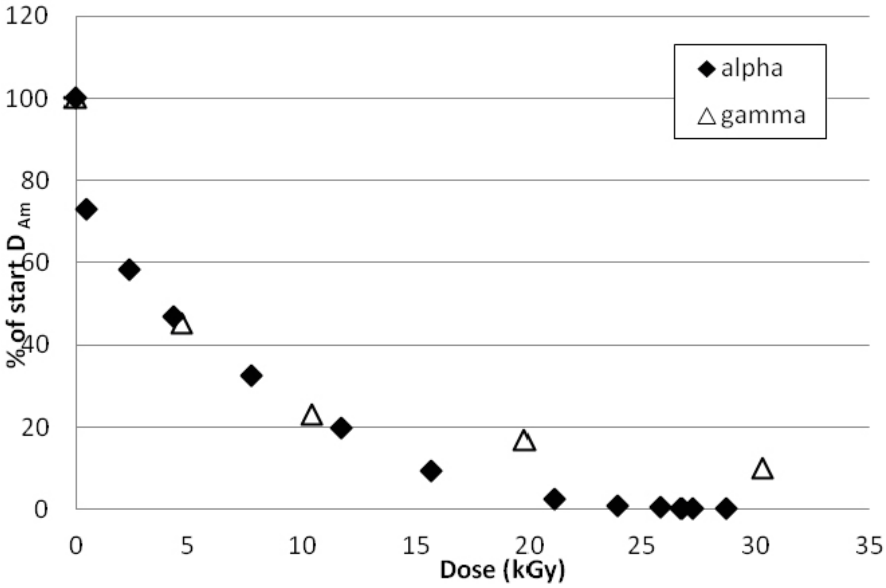


Figure 8-7. *Change in distribution ratio of Am expressed as % of the initial D as a function of the received dose. The irradiation source was either alpha or gamma radiation. The initial D_{Am} was 30.6 for the alpha experiments and 26.4 for the gamma experiments.*

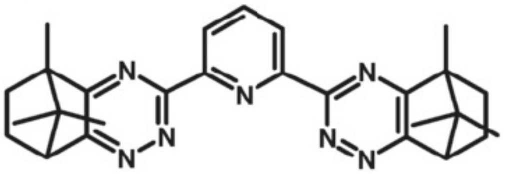


Figure 8-8. *Molecular structure of CA-BTP.*

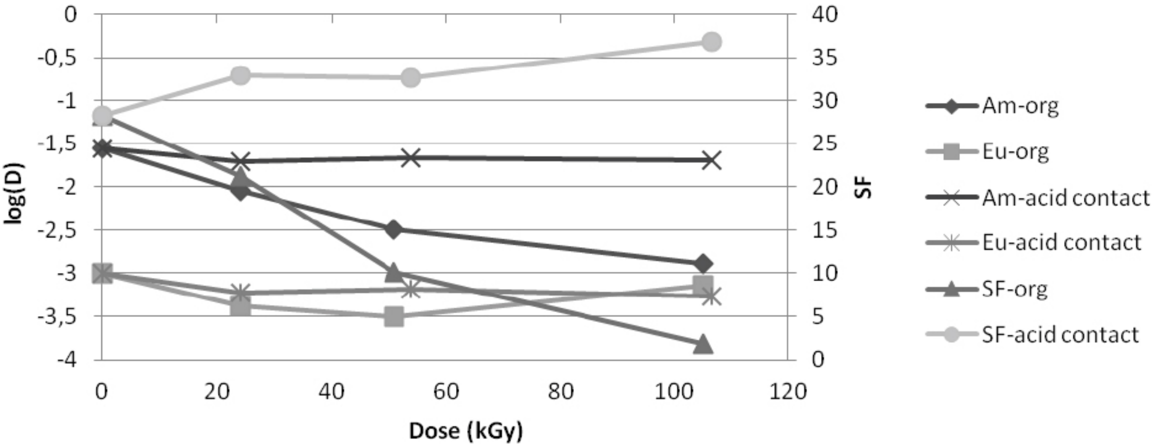


Figure 8-9. *Irradiation (18 kGy/h) of < 10 mM CA-BTP in octanol in the presence of an equal amount of 1 M* HNO_3.

Due to the successful results in the irradiaton test an attempt was made to replace CA-BTP for CyMe$_4$-BTBP in the GANEX solvent. Extractions were performed from 4 M nitric acid and the diluent used were cyclohexanone with 30% TBP. To increase the very low distribution ratios displayed in the irradiaton test the concentration of CA-BTP was increased. At a concentration of app. 0.1 M CA-BTP a precipitate formed during the extraction. The concentration was therefore lowered to 50 mM and 10 mM. It is possible that a precipitate formed in the 50 mM samples as well but very little. In any case the distribution ratios were found to be very low (see Table 8-1) and since the concentration cannot be increased without forming a precipitate the replacement of CyMe$_4$-BTBP with CA-BTP in the GANEX solvent does not seem to be a viable option.

8.3.2 Radiolysis of the DEHBA+BTBP GANEX solvent

A radiolysis experiment of the BTBP+DEHBA GANEX solvent has been performed. As can be seen in Figure 2-9 the solvent display a good stability towards radiolysis in contact with nitric acid up to 200 kGy.

Table 8-1. Distribution ratios and separation factors of Eu and Am with CA-BTP in cyclohexanone with 30% TBP. Extractions were performed from 4 M $\mathbf{HNO_3}$**.**

conc.	D Am	D Eu	SF (Am/Eu)
10 mM	0.052542	0.063543	0.826706
50 mM	0.30595	0.051162	5.979328

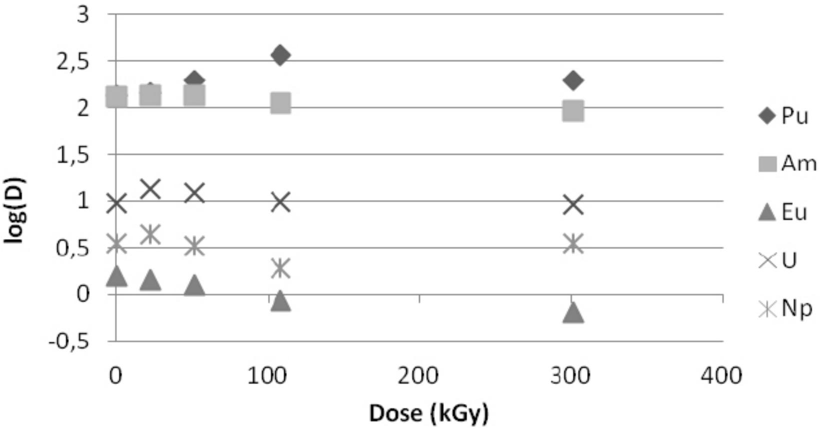


Figure 8-10. *Gamma radiolysis (18 kGy/h) of 0.01 M $CyMe_4$-BTBP+ 20% DEHBA in cyclohexanone in contact with 4 M HNO_3.*

8.4 Effect of storage temperature and time after irradiation

Experiments were conducted giving a high total dose with a high dose rate to a BTBP containing solvent ($CyMe_4$-BTBP in cyclohexanone) to facilitate degradation of the molecule. After this the effect of different storage conditions was investigated by storing the samples in three different environments for up to one week; room temperature, fridge (ca 4°C) and freezer (ca –15°C). After different times extractions were performed to observe the amount of BTBP degradation. As can be seen in Figure 2-9, 2-10 and 2-11 the distribution ratios and separation factor stays more or less stable in the different storage environments even though the molecule received enough irradiation to start degrading.

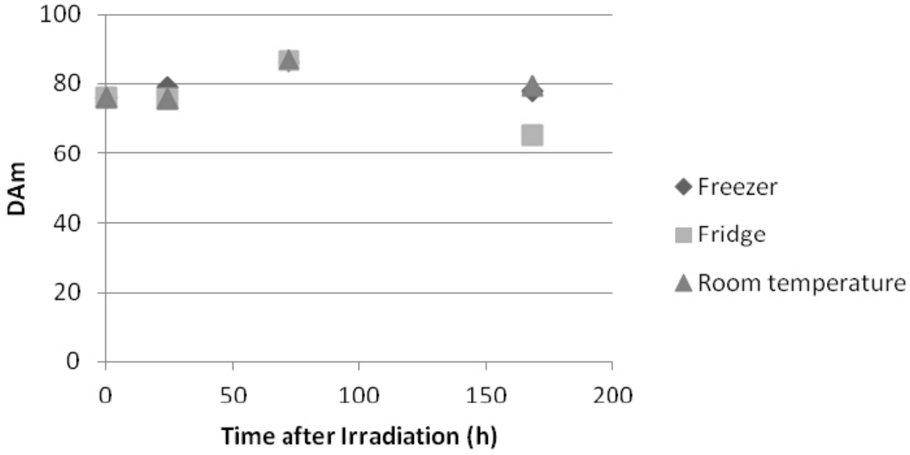


Figure 8-11. *Am extraction after irradiation of $CyMe_4$-BTBP in cyclohexanone to different doses and storage at different temperatures.*

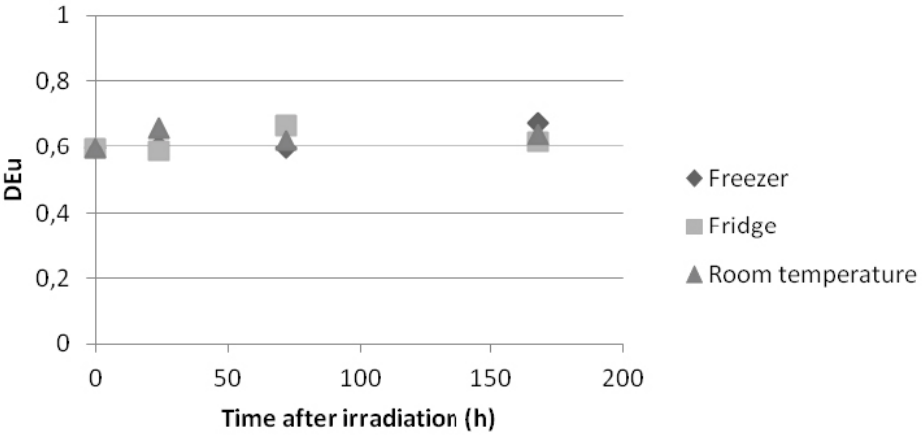


Figure 8-12. Eu extraction after irradiation of $CyMe_4$-BTBP in cyclohexanone to different doses and storage at different temperatures.

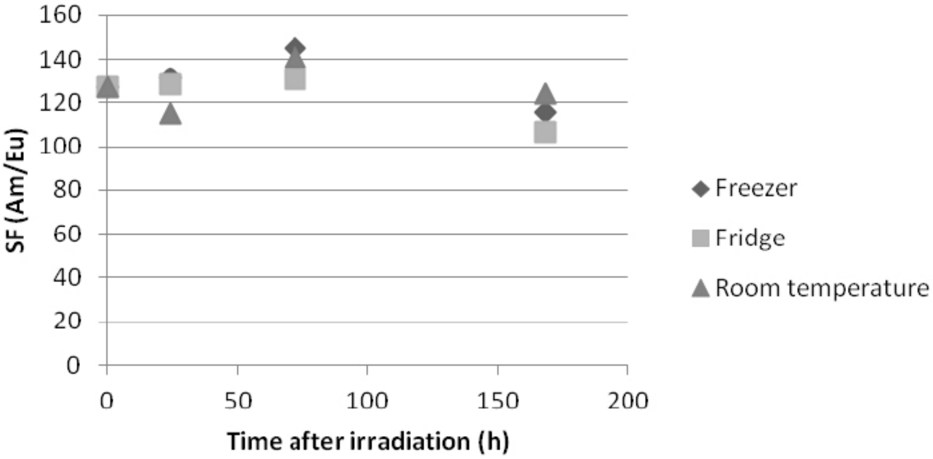


Figure 8-13. Am/Eu Separation Factors after irradiation of $CyMe_4$-BTBP in cyclohexanone to different doses and storage at different temperatures.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

Aksnes G, 1960. Nucleophilic displacements on phosphorus. Reaction of hydroxyl ion and isonitroso acetone with organofluorophosphorus compounds. Acta Chemica Scandinavica 14, 1515–1525.

Alcock K, Grimley S S, Healy T V, Kennedy J, McKay H A C, 1956. Extraction of nitrates by tributyl phosphate (TBP). I. System TBP + diluent + H_2O + HNO_3. Transactions of the Faraday Society 52, 39–47.

Allard S, 2005. Investigations of α-D-isosaccharinate: fundamental properties and complexation. PhD thesis. Chalmers University of Technology, Sweden.

Andersson S E C, 2005. Extraction properties of some nitrogen-containing extractants and determination of nitrate complex formation for lanthanides and selected actinide using solvent extraction. PhD thesis. Chalmers University of Technology, Sweden.

Aneheim E, Ekberg C, Fermvik A, Foreman M, Löfström-Engdahl E, Retegan T, Skarnemark G, Špendlíková I, 2010a. Partitioning and transmutation. Annual report 2009. SKB R-10-07, Svensk Kärnbränslehantering AB.

Aneheim E, Ekberg C, Fermvik A, Foreman M R S, Retegan T, Skarnemark G A, 2010b. A TBP/BTBP-based GANEX separation process. Part 1: Feasibility. Solvent Extraction and Ion Exchange 28, 437–458.

Aneheim E, Ekberg C, Fermvik, A, Foreman M R S, Grüner B, Hájková Z, Kvičalová M A, 2011. TBP/BTBP-based GANEX separation process – Part 2: Ageing, hydrolytic and radiolytic stability. Solvent Extraction and Ion Exchange 29, 157–175.

Atkins P W, 1990. Physical chemistry. 4th ed. Oxford: Oxford University Press.

Borkowski L A, Cahill C L, 2003. Topological evolution in uranyl dicarboxylates: synthesis and structures of one-dimensional UO2(C6H8O4)(H2O)2 and three-dimensional UO2(C6H8O4). Inorganic Chemistry 42, 7041–7045.

Borkowski L A, Cahill C L, 2004. Two novel three-dimensional Nd-adipates: influence of hydrothermal reaction temperature on framework topology. Inorganic Chemistry Communications 7, 725–728.

Boyd G E, Larson Q V, 1960. Solvent extraction of heptavalent technetium. Journal of Physical Chemistry 64, 988–996.

Casey M, Leonard J, Lygo B, Procter G, 1990. Advanced practical organic chemis- try. Glasgow: Blackie.

Chaiko D J, Vandegrift G F, 1988. A thermodynamic model of nitric acid extraction by tri-n-butyl phosphate. Nuclear Technology 82, 52–59.

Edelstein N M, Klenze R, Fanghänel T, Hubert S, 2006. Optical properties of Cm(III) in crystals and solutions and their application to Cm(III) speciation. Coordination Chemistry Reviews 250, 948–973.

Ekberg C, Dubois I, Fermvik A, Retegan T, Skarnemark G, Drew M G B, Foreman M R S, Hudson M J, 2007. Extraction behavior of nickel(II) using some of the BTBP-class ligands. Solvent Extraction and Ion Exchange 25, 603–617.

Ekberg C, Fermvik A, Retegan T, Skarnemark G, Foreman M R S, Hudson M J, Englund S, Nilsson M, 2008. An overview and historic look back at the solvent extraction using nitrogen donor ligands to extract and separate An(III) from Ln(III). Radiochimica Acta 96, 225–233.

Fermvik A, 2008. The effect of radiolysis of BTBP type molecules on distribution ratios. Lic. thesis. Department of Chemical and Biological Engineering, Chalmers University of Technology.

Fermvik A, Berthon L, Ekberg C, Englund S, Retegan T, Zorz N, 2009. Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate. Dalton Transactions 32, 6421–6430.

Fermvik A, Gruner B, Kvičalová M, Ekberg C, 2011. Semi-quantitative and quantitative studies on the gamma radiolysis of C5-BTBP. Radiochimica Acta 99, 113–119.

Foreman M, Hudson M, Geist A, Madic C, 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, 645–662.

Hamblet C H, McAlevy A, 1951. Adipic acid process. Patent 2,557,282, United States Patent Office.

Healy T V, 1961. Synergism in the solvent extraction of di-, tri- and tetravalent metal ions – II. Synergic effects in so-called inert diluents. Journal of Inorganic and Nuclear Chemistry 19, 328–339.

Islam F, Rahman H, Ali M, 1979. Solvent extraction separation study of Ti(IV) Fe(III) and Fe (II) from aqueous solutions with di-2-ethyl hexyl phosphoric acid in benzene. Journal of Inorganic and Nuclear Chemistry 41, 217–221.

Jaber A M Y, Al-Naser A-E, 1997. Liquid–liquid extraction of some lanthanide metal ions by polyoxyalkylene systems. Talanta 44, 1719–1728.

Kelly-Rowley A M, Lynch V M, Anslyn E V, 1995. Molecular recognition of enolates of active methylene compounds in acetonitrile. The interplay between complementarity and basicity, and the use of hydrogen-bonding to lower guest p*K*as. Journal of the American Chemical Society 117, 3438–3447.

Lindsay Smith J R, Richards D I, Thomas C B, Wittaker M, 1985. The role of vanadium(V) in the oxidation of cyclohexanol to adipic acid by nitric acid. Journal of the Chemical Society, Perkin Transactions 2, 1677–1682.

Löfström-Engdahl E, Aneheim E, Ekberg C, Foreman M, Skarnemark G, 2010. Diluent effects in solvent extraction. In Proceedings of the First ACSEPT International Workshop, Lisbon, Portugal, 31 March–2 April 2010.

Löfström-Engdahl E, Aneheim E, Skarnemark G, Ekberg C, 2011. Solvent effects on the extraction rate in proposed GANEX processes. In Proceedings of the19th International Solvent Extraction Conference, Santiago de Chile, 3–7 October 2011.

Magnusson D, Christiansen B, Foreman M R S, Geist A, Glatz J-P, Malmbeck R, Modolo G, Serrano-Purroy D, Sorel C, 2009. Demonstration of a SANEX process in centrifugal contactors using the $CyMe_4$-BTBP molecule on a genuine fuel solution. Solvent Extraction and Ion Exchange 27, 97–106.

March J, 1992. Advanced organic chemistry: reactions, mechanisms and structure. 4th ed. New York: Wiley.

Marcus Y, 2004. Principles of solubility and solutions. In Rydberg J, Cox M, Musikas C, Choppin R G (eds). Solvent extraction principles and practice. 2nd ed. New York: Marcel Dekker, 25–79.

Nair G M, Mahajan G R, Prabhu D R, 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, 323–330.

Nair G M, Mahajan G R, Prabhu D R, 1996. Dioctyl butyramide and dioctyl isobut- yramide as extractants for uranium(VI) and plutonium(IV). Journal of Radioanalytical and Nuclear Chemistry 204, 103–111.

Nilsson M, 2005. Screening investigations of novel nitrogen donor ligands for solvent extraction. PhD thesis. Department of Chemical and Biological Engineering, Chalmers University of Technology, Sweden.

Nilsson M, Andersson S, Drouet F, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Magnusson D, 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, 299–318.

Nilsson M, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Modolo G, 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, 823–843.

Pathak P N, Kumbhare L B, Manchanda V K, 2001. Effect of structure of N,N dialkyl amides on the extraction of U(VI) and Th(IV): a thermodynamic study. Radiochimica Acta 89, 447–452.

Pitzer K S, Mayorga G, 1973. Thermodynamics of electrolytes. I I. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. The Journal of Physical Chemistry 77, 2300–2308.

Prabhu D R, Mahajan G R, Nair G M, 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, 113–117.

Retegan T, 2007. The influence of diluents and side groups of the ligands on liquid– liquid extraction of actinides and lanthanides. Lic. thesis. Chalmers University of Technology, Sweden.

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

Riddick J A, Bunger W B, 1970. Organic solvents: physical properties and methods of purification. 3rd ed. New York: Wiley.

Sekine T, Ishii T, 1970. Studies of the liquid–liquid partition systems VII. The solvent extraction of mercury(II) chloride, bromide, iodide and thiocyanate with some organic solvents. Bulletin of the Chemical Society of Japan 43, 2422–2429.

Siekierski S, 1961. The influence of diluents on extraction of europium and thorium nitrates by tri-n-butylphosphate. Journal of Inorganic and Nuclear Chemistry 24, 205–214.

Strauss M J, 1979. The nitroaromatic group in drug design. Pharmacology and toxicology (for nonpharmacologists). Industrial & Engineering Chemistry Product Research and Development 18, 158–166.

Thiollet G, Musikas C, 1989. Synthesis and uses of the amide extractants. Solvent Extraction and Ion Exchange 7, 813–827.

Trumm S, Lieser G, Foreman M R S, Panak P J, Geist A, Fanghänel T, 2010a. A TRLFS study on the complexation of Cm(III) and Eu(III) with 4-t-butyl-6,6′-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridine in a water/2-propanol mixture. Dalton Transactions 39, 923–929.

Trumm S, Panak P J, Geist A, Fanghänel T, 2010b. A TRLFS Study on the Complexation of Cm^{III} and Eu^{III} with 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in water/methanol mixture. European Journal of Inorganic Chemistry 19, 3022–3028.

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

van Asselt W J, van Krevelen D W, 1963. Preparation of adipic acid by oxidation of cyclohexanol and cyclohexanone with nitric acid: Part I. Reaction mechanism. Recueil 82, 51–67.

Weigl M, Geist A, Müllich U, Gompper K, 2006. Kinetics of americium(III) extrac- tion and back extraction with BTP. Solvent Extraction and Ion Exchange 24, 845–860.

Collaborations

The following laboratories are involved in ACSEPT:

- ALCAN /ALCAN Centre de Recherches de Voreppe
- ANSTO /Australian Nuclear Science and Technology Organisation
- AREVA /Compagnie Générale des Matières Nucléaires-AREVA NC
- CEA /Commissariat à l'Energie Atomique
- CHALMERS /Chalmers Tekniska Hoegskola Aktiebolag
- CIEMAT /Centro de Investigaciones Energeticas, Medioambientales y Tecnologicas
- CINC /CINC Solutions BV
- CNRS /Centre National de la Recherche Scientifique
- CRIEPI /Central Research Institute of Electric Power Industry
- CSIC /Consejo Superior de Investigaciones Cientificas
- CTU /Czech Technical University Prague
- CUNI /Univerzita Karlova V Praze (Charles University in Prague) http://www.acsept.org/acsept.php?page=partner&npart=EDF&tree0=Members&tree1=Partner%20Details&orig=membersbyname&mem=By%20name
- ENEA /Ente per le Nuove Tecnologie, l'Energia e l'Ambiente
- FZJ /Forschungszentrum Juelich Gmbh
- KIT-INE /Karlsruhe institute of Technology
- ICHTJ /Instytut Chemii i Techniki Jadrowej
- ICIQ /Fundacio Privada Institut Catala d'Investigacio Quimica
- IIC /Institute of Inorganic Chemistry Academy of Sciences of Czech Republic
- ITN /Instituto Tecnologico e Nuclear
- JRC /Commission of the European Communities – Directorate General Joint Research Centre
- NNL /National Nuclear Laboratory (Great Britain)
- NRG /Nuclear Research and Consultancy Group http://www.acsept.org/acsept.php?page=partner&npart=NRI&tree0=Members&tree1=Partner%20Details&orig=membersbyname&mem=By%20name
- POLIMI /Politecnico di Milano
- PSI /Paul Scherrer Institut
- RUG /Rijksuniversiteit Groningen
- TWENTE /Universiteit Twente
- UEDIN /The University of Edinburgh
- ULG /Université de Liège
- ULP /Université Louis Pasteur
- UNIPR /Universita degli Studi di Parma
- UPMC /Université Pierre et Marie Curie – Paris VI
- UREAD /The University of Reading.

A more intense collaboration with Chalmers exists with:

- CEA, France
- Forschungszentrum Jülich, Germany
- Institute of inorganic chemistry, Academy of sciences, Czech Republic
- Instytut Chemii I Techniki Jadrowej, Poland
- Karlsruhe Institute of Technology, Germany
- NNL /National Nuclear Laboratory (Great Britain).

Scientific exchange

2010

21–26th of March: American Chemical Society, 239th half yearly conference in San Francisco, USA
Participants: Emma Aneheim, Christian Ekberg, Elin Löfström-Engdahl.

29–31st of March: ACSEPT half yearly meeting in Lisbon, Portugal
Participants: Emma Aneheim, Christian Ekberg, Elin Löfström-Engdahl.

1–2nd of April: ACSEPT 1st International Workshop, AIWO, Lisbon, Portugal.
Participants: Emma Aneheim, Christian Ekberg, Elin Löfström-Engdahl.

16–18th of June: The Swedish Chemical Societies "Oorgandagar" in Uppsala (SLU), Sweden
Participants: Emma Aneheim, Elin Löfström-Engdahl.

30th of August –3rd of September: ACTINET Practical summer school in Orange/Marcoule France
Participants: Emma Aneheim, Elin Löfström-Engdahl.

20–22nd of September: ACSEPT half yearly meeting in Petten, Netherlands
Participants: Emma Aneheim, Christian Ekberg, Elin Löfström-Engdahl.

10–13st of October: Study trip to Oskarshamn (Clab/Äspö), Ågesta and Forsmark.
Participants: Emma Aneheim, Christian Ekberg, Elin Löfström-Engdahl.

1–5th of November: OECD/NEA 11th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, San Francisco, USA
Participants: Christian Ekberg.

2011

4–7th of April-: ACSEPT 3rd Annual Meeting in Manchester, Great Britain
Participants: Emma Aneheim , Elin Löfström-Engdahl, Christian Ekberg, Mark Foreman.

13–15th of June: The Swedish Chemical Societies "Oorgandagar" in Stenugnsund, Sweden
Participants: Emma Aneheim (1 poster), Elin Löfström-Engdahl(1 poster), Christian Ekberg.

21–25th of August: Norway study trip organised by the department (visits to the Halden Reactor, Nuclear Facilities at Keller, University of Oslo etc)
Participants: Emma Aneheim, Christian Ekberg.

21–23rd of September: ACSEPT Half Yearly Meeting in Uddevalla, Sweden, arranged by the P&T group with the help of Charlotte Bouveng and Carina Svenheden
Participants: Emma Aneheim, Elin Löfström-Engdahl, Christian Ekberg, Mark Foreman.

2–7th of October: the International Solvent Extraction Conference (ISEC) in Santiago Chile
Participants: Emma Aneheim (1 oral presentation 1 poster), Elin Löfström-Engdahl (1 oral presentation 1 poster), Teodora Retegan (1 poster), Christian Ekberg. Both Elin and Emma were also awarded the ISEC scholarship to help finance the trip.

Articles and publications

During the past year several reports and articles have been published, submitted for publication or are still in preparation.

Published

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

Ekberg, C., Aneheim, E., Fermvik, A., Skarnemark, G.: “Using ^{211}At as internal alpha radiolysis source allowing for simple detection of radiolysis products”, Radiation Physics and Chemistry, **79**, 454-456 (2010).

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

Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M., Gruner, B., Hajkova, Z., Kvivalova, M.: “A TBP/BTBP-based GANEX Separation Process – Part 2: Ageing, Hydrolytic and Radiolytic Stability”. Accepted in Solvent Extraction and Ion Exchange (Issue 2, Volume 29).

Fermvik, A., Gruner, B., Kvicalova, M., Ekberg, C.: “Semi-quantitative and quantitative studies on the gamma radiolysis of C5-BTBP”, Radiochimica Acta, **99**. 113-119 (2011).

Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M.R.S.: “Development of a Novel GANEX Process”, ACS Symposium Series, Vol. 1046, Nuclear Energy and the Environment, Ch 10, 119-130 (2010) Editor(s): Chien M. Wai and Bruce J. Mincher.

Fermvik, A., Nilsson, M., Ekberg, C.: “Radiolytic Degradation of Heterocyclic Nitrogen Containing Ligands from Low Dose-Rate Gamma Sources”, ACS Symposium Series, Vol. 1046, Nuclear Energy and the Environment, Ch 18, pp 215-229 (2010) Editor(s): Chien M. Wai and Bruce J. Mincher.

Proceedings from: 10th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mito, Japan, Oct. 2008 ISBN: 978-92-64-99097-5. Poster paper III14 “Partitioning and transmutation in Scandinavia – Chalmers Group”, E. Aneheim, C. Ekberg, A. Fermvik, M. St.J. Foreman, J-O. Liljenzin, T. Retegan, G. Skarnemark.

Proceedings from: 10th OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mito, Japan, Oct. 2008 ISBN: 978-92-64-99097-5. Poster paper III17. “Development of Equipment for Pilot Scale Tests of Processes for Partitioning and Transmutation”, E. Aneheim, C. Ekberg, A. Fermvik, M. St.J. Foreman, T. Retegan, G. Skarnemark.

Proceedings from: OECD/NEA 11th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, San Francisco, USA. “Development of a novel GANEX process.” E. Aneheim, C. Ekberg, A. Fermvik, M.R.S. Foreman (not yet published).

Löfström-Engdahl, E., Aneheim, E., Ekberg, C., Foreman, M., Skarnemark, G.: “Diluent effects in solvent extraction”, Proceedings of the First ACSEPT International Workshop Lisbon, Portugal 2010.

Aneheim, E. “Development of a novel GANEX Extraction System for Partitioning and Transmutation Purposes”. Licenciate Thesis, Chalmers University of Technology, Göteborg (2010) Technical report 2010:09, ISSN 1652-943X.

Blomgren, J., Karlsson, F., Pomp, S., Aneheim, E., Ekberg, C., Fermvik, A., Skarnemark, G., Wallenius, J., Zakova, J., Grenthe, I., Szabó, Z.: “Partitioning and Transmutation Current developments – 2010, A report from the Swedish reference group for P&T-research”, Swedish Nuclear Fuel and Waste Management Co. SKB Report TR-10-35.

A TBP/BTBP-based GANEX Separation Process – Part 2: Ageing, Hydrolytic and Radiolytic Stability.
Emma Aneheim, Christian Ekberg, Anna Fermvik, Mark Foreman, Bohumir Gruner, Zuzana Hajkova, Magda Kvivalova. Solvent Extraction and Ion Exchange. Issue 2 Vol. 29 pp. 157–175, 2011.

E xchange of TBP for a Monoamide Extraction Ligand in a GANEX Solvent – Advantages & Disadvantages.
Emma Aneheim*, Christian Ekberg, Nathalie Mabile.
Paper for ISEC 2011 (peer reviewed).

Submitted/Accepted

Studies of a solvent for GANEX applications containing CyMe$_4$-BTBP and DEHBA in Cyclohexanone
Emma Aneheim*, Christian Ekberg, Mark R.S. Foreman, Elin Löfström-Engdahl, Nathalie Mabile
Accepted in Separation Science and Technology.

Aqueous Complexation of Palladium to Prevent Precipitation and Extraction in a Group Actinide Extraction System
Emma Aneheim[a,b], Christian Ekberg[a,b], Mark R.StJ. Foreman[a,b]
Accepted in Hydrometallurgy.

Fermvik, A., Gruner, B., Kvicalova, M., Ekberg, C., *Radiolysis of C5-BTBP in cyclohexanone irradiated in the absence and presence of an aqueous phase*.

Future work

The future work will continue along the suggested path of the ACSEPT project. However, we will do as previous years and use the complementary funding from the SKB to focus more on the basic scientific issues arising from the more process oriented studies. This building of knowledge is also the role of a University. The new fuel fabrication lab is now built and opens great opportunities to couple the recycling process development to the fabrication of new innovative fuels for the Generation IV system. Using the new gamma irradiation source (18 kGy/h) with our developed ^{211}At alpha irradiation technique we have the possibility to study radiolysis effects in detail, both for the ligands and the diluents. A more thorough study of the degradation of both diluents and extractants will be performed. Methods for cleaning the solvent from these products in a process environment will be undertaken. Our planned work can be listed as follows:

- Partitioning of actinides (different oxidation states, Th-Cm) for advanced dedicated future fuel cycles, like for example ADS nuclear systems. The co-extraction of actinides of different oxidation states will be studied. Mixtures of ligands, bitopic extractants and chromatographic techniques will be used.
- Studies on the radiolytic and hydrolytic stability and detailed investigations of the decay products, their production pathways and their effects on the extraction.
- Basic studies of formed metal-ligand interactions as a function of the diluent used.
- Investigation of the effect of the diluents on extraction, stripping and selectivity.
- Continue to develop and optimise the extraction system for our novel GANEX (Grouped ActiNide EXtraction) system.
- Continue the development of a selective stripping from our GANEX process.
- Study purification of extraction liquid from degradation products.
- Start our work in the borderline between the separation process and the fuel fabrication.

Anna Fermvik is now working for Vattenfall AB but will act as part time supervisor in matters dealing with radiolysis Further collaboration with Prof. Mats Johnsson at KTH and Dr. Bohumir Gruner at Academy of Sciences of the Czech Republic will focus on understanding degradation routes of both the extractant and the diluent.

Emma Aneheim will defende her theisis dealing with her studies of our novel GANEX extraction system including suppression of unwanted extraction and stripping of the actinides.

Elin Löfströn-Engdahl will continue basic studies of diluent effects on complexes and extraction and attempt to develop a predictive theory to BTBP based systems.

A new PhD student will probably be hired to continue the work on our extraction process.

Mark Foreman will work on developing synthesis routes for making new ligands and optimise their production as well as the general problems for a process development.