

Partitioning and transmutation

Annual report 2007

Emma Aneheim, Christian Ekberg, Sofie Englund,
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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 , ^{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. The most difficult separations to make are those between trivalent actinides and lanthanides, due to their relatively similar chemical properties, and those between different actinides themselves. These separations are necessary to obtain the desired efficiency of the transmutation process and in order not to create any unnecessary waste thus rendering the process useless. 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.

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 framework programmes from NEWPART in the 4th framework via PARTNEW and EUROPART to ACSEPT now in the 7th programme. The aims of the projects have now shifted from basic understanding to more applied research with focus on process development. However, since a further investigation on basic understanding of the chemical behaviour is required, we have our main focus on the chemical processes and understanding of how they work. Due to new recruitments we will now also work on ligand design and development. This will decrease the response time between new ligands and their evaluation.

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. De svåraste separationerna att göra är de mellan trevärdade aktinider och lantanider, på grund av deras relativt liknande kemi, samt de mellan aktiniderna själva. Dessa separationer är nödvändiga för att uppnå den önskade effektiviteten i transmutationsprocessen samt för att undvika extra avfall som skulle göra hela processen överflödig. 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.

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 från NEWPART i det 4:e ramprogrammet via PARTNEW och EUROPART till ACSEPT i 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. Dock behövs fortfarande grundläggande kunskaper varför vårt fokus fortfarande ligger på grundläggande kemiska frågor och förståelse för ingående processer. På grund av nyrekryteringar kommer vi nu även att utveckla och syntetisera nya extraktionsreagens. Detta kommer att minska svarstiden mellan tillverkning av ett nytt reagens och testen av dess effektivitet.

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Introduction

The Partitioning and Transmutation (P&T) group at Nuclear Chemistry, Department of Chemical and Biological Engineering at Chalmers University of Technology investigates the separation of different chemical elements in the 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 lot 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 electrolysis and chromatographic methods are also investigated.

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 lanthanides from trivalent actinides following the CHON principle (only containing carbon, hydrogen, oxygen and nitrogen). This search has continued but now in more close collaboration with process expertise to make sure that the molecules not only have good separation capabilities but also survive practically in a process. In addition, additional focus has been put on the whole organic system since changing the diluent the hydrolytic and radiolytic stability can be increased as well as the separation factor can be enhanced. To further work towards an industrial process Chalmers is now a partner in the 7th European Union framework programme ACSEPT (2008–2012). The number of partners has now increased from 24 in EUROPART to 36 in ACSEPT. The research can be divided into five domains (the respective domain leaders and their organisations in parenthesis):

- DM 1, Hydrometallurgical processes (Clement Hill, CEA).
- DM 2, Pyrometallurgical processes (Concha Caravaca, CIEMAT).
- DM 3, Process development (Emmanuel Gaubert, NEXIA).
- DM 4, Fuels and targets (Frodo Klaasen, SKC-CEN).
- DM 5 Education and training (Christian Ekberg, Chalmers).

Clearly there was a serious attempt to include the fuel and target community in this partitioning process but due to the cut back in funding from the EC it was decided that DM 4 should be very limited. Instead, there will be a joint proposal aiming at fuel and targets in the next call in 2008. Domain 5 is relatively new and aims at knowledge transfer between the labs, domains and the whole community.

The main experimental work at Chalmers concerns the extraction properties and other basic chemical characteristics of ligands previously synthesized in Reading, UK. Due to the retirement of Dr. Michael Hudson and the transfer of Dr. Mark Foreman from Reading to Chalmers a larger part of the development work on new ligands will now be made at Chalmers. The influence on extraction of pH, kinetics, ionic strength and media, absorbed dose and concentration of the involved species are studied in combination with modelling of the systems using e.g. solubility parameters. Recently the role of the organic diluent has been investigated as well as detailed studies on the effect of small changes in the molecular structure of the ligands used for the separation. However, Chalmers is also involved in process development and flow sheet calculations. One of our PhD students is currently working at ITU in Germany with real waste solutions to increase the experience and verify the modelling tool developed at Chalmers previously.

Research

During most part of 2007 two PhD students have worked full time in the project, Teodora Retegan and Anna Fermvik. The former is studying the effect of the diluents on the extraction as well as the effect of small changes in the molecular structure of the ligand. Also, how the extraction is affected by these factors, the chemical stability of the extracting system and efficiency of the separation.

Anna Fermvik is studying the effects of radiolysis on the already selected extracting systems. In this light, the radiolysis products are one of the most interesting issues. As a part of this work she investigates how to inhibit this radiolysis. Also, different radiation doses seem to be responsible for different extraction behaviour. This fact is closely studied. Also, besides the actinides and lanthanides, during an industrial process, other metals can be leached out from the equipment and affect the purity of the final products. This is already known, but how the extraction of these metals looks like when the extracting system has been subjected to radiolysis during the process is not known and is under investigation.

In July, Dr. Mark Foreman moved from Reading University, UK, to Chalmers. The main part of his work this year has been the design and commissioning of an organic synthesis facility in the Nuclear Chemistry group. This organic chemistry laboratory is going to be shared with the Industrial Materials Recycling group. Already some work has been performed on the synthesis of new BTBP compounds.

A diploma worker, Karin Wald, started to work in the P&T group. She is studying the behaviour of a synergic mixture often used as a model system a decade ago, alfa-bromodecanoic acid and terpyridine in tributylbenzene (TBB).

In November a new PhD student, Emma Aneheim, started her work dealing with the bridging of experimental solvent extraction and organic synthesis.

Sofie Englund is now working at OKG AB but is still involved in this project at about 10% intensity.

Daniel Magnusson and Catharina Nästrén are working in Germany (ITU) on process experiments on real high active raffinate from the PUREX process and development of targets for transmutation, respectively. They will return to Chalmers in the beginning of 2008 and finish their PhD studies.

The EUROPART project ended in July 2007 and during the year there were two meetings. A meeting was held in January in Karlsruhe and the final meeting, arranged by Chalmers, was held in June in Stenungsund.

1 BTBP chemistry

The use of nitrogen-containing heterocyclic molecules following the CHON-principle (CarbonHydrogenOxygenNitrogen) has been shown to efficiently separate actinides and lanthanides using solvent extraction. Last year, an extensive part of the chemistry of the BTBP family was presented. BTBP stands for *bis*-triazin-bipyridine, which refers to the nature of the central core common to all the molecules in the family, Figure 1-1.

The extracting properties of the molecules and their possibilities to be used in a process are dependent on factors like the diluent, solubility, kinetics, stability towards irradiation etcetera. The chemistry of the BTBPs is further presented here.

The general experimental conditions (unless otherwise stated) were:

- aqueous phase consisted of 0.01 M HNO₃ (the ionic strength was kept at 1 M by addition of NaNO₃) spiked with trace amounts of ¹⁵²Eu, ²⁴¹Am,
- organic phase consisted of the ligand at a concentration of 0.01 M dissolved in a chosen diluent (long chain alcohols, cyclohexanone preequilibrated with corresponding aqueous phase without metals, nitrobenzene),
- the experiments were carried out in triplicates,
- 500 μL of each phase were placed in 3.5 mL vials and shaken 5 minutes by hand (except for the kinetic experiments, when the time was longer) and centrifuged for 10 minutes at 800 g,
- aliquots of 200 μL were taken from each phase and activities of ¹⁵²Eu and ²⁴¹Am were measured in a HPGe detector (Ortec, Gamma Analyst GEM 23195).

Throughout the report the concepts of distribution ratio (D) and separation factor (SF) are frequently used and they are defined in equation 1 and 2:

$$D = \frac{[A]_{org}}{[A]_{aq}} \quad (1)$$

where [A]_i is the total concentration of a substance, A, in the organic phase and the aqueous phase, respectively.

$$SF = \frac{D_A}{D_B} \quad (2)$$

where D_i is the distribution of elements A and B, respectively.

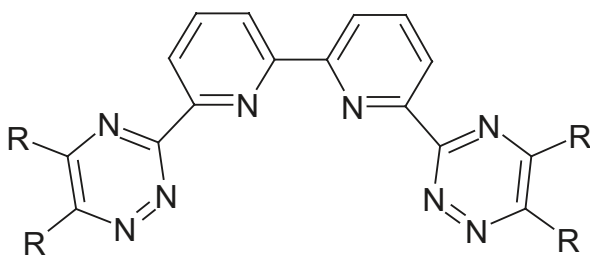


Figure 1-1. Bis-triazin-bipyridine, or BTBP core molecule.

1.1 Screening studies of MF2-BTBP

A new ligand, generically named MF2-BTBP, was synthesized and received from Reading University, UK. For patenting reasons the structure cannot be given here. The following screening tests were performed:

- Dissolution.
- Extracting capacity.
- Kinetics.

Different long chain alcohols were selected for the screening experiments to serve as a comparison base with previous studies of CyMe₄-BTBP /1, 2/, since MF2-BTBP has similar features with this ligand.

Also, a comparative kinetics study was performed.

1.1.1 Extraction and dissolution

A range of long chain alcohols (C6 to C10) were used as diluents. The extraction of Am and Eu using MF2-BTBP showed values similar to those obtained in the previous studies involving CyMe₄-BTBP /2/ but this time a clear trend was found: the log D decreases with increasing the number of carbons in the chain. The molecule dissolved reasonably quickly (5 minutes) in all the alcohols. This is not the case for the system containing CyMe₄-BTBP molecule. A comparative study is illustrated in Figures 1-2 and 1-3.

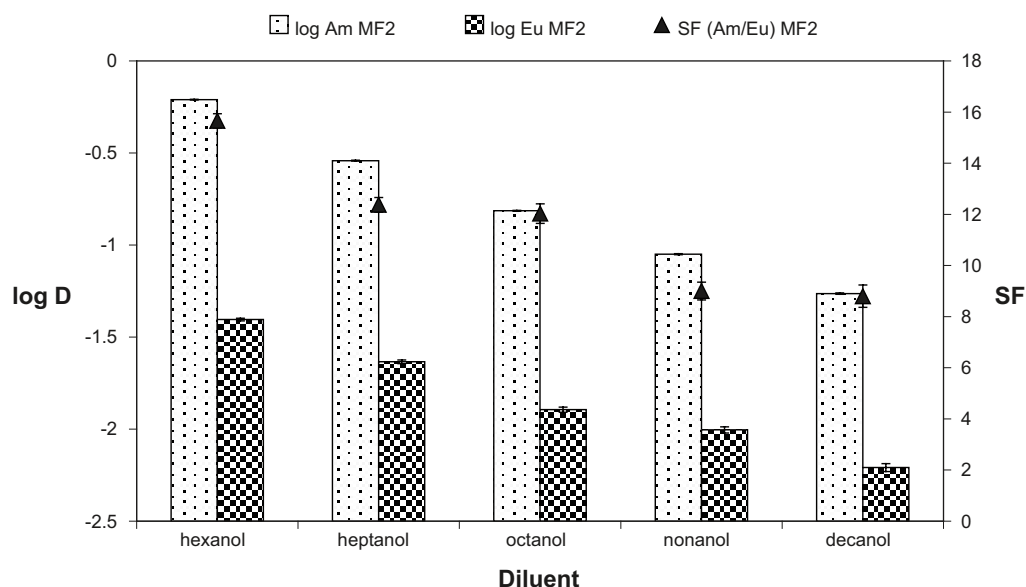


Figure 1-2. Extraction experiments using 0.01 M MF2-BTBP dissolved in long chain alcohols as organic phase and HNO₃ spiked with ²⁴¹Am and ¹⁵²Eu as aqueous phase where the [NO₃⁻] concentration was kept to 1 M with NaNO₃.

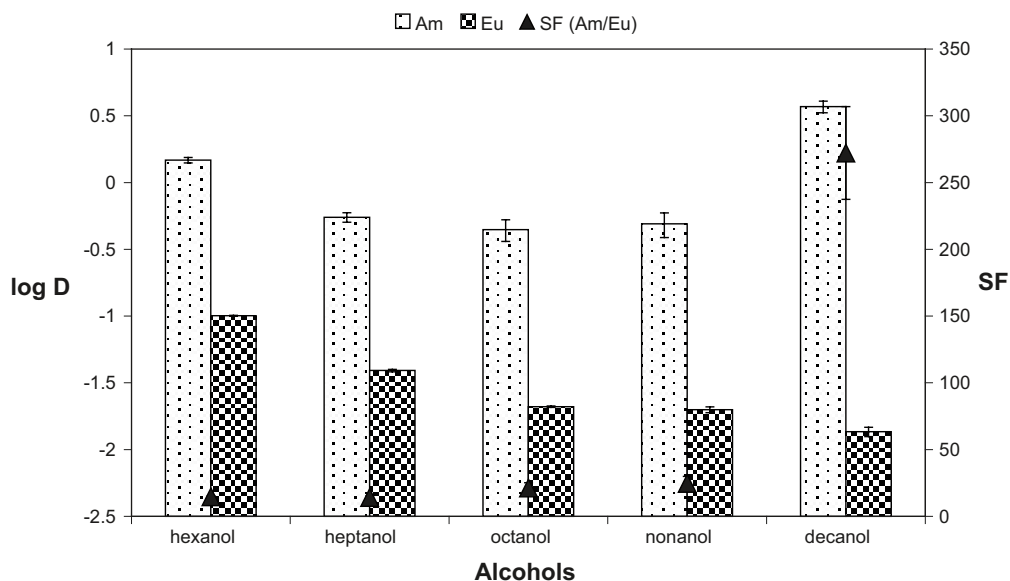


Figure 1-3. Extraction experiment using 0.01 M CyMe₄-BTBP dissolved in long chain alcohols as organic phase and HNO₃ spiked with ²⁴¹Am and ¹⁵²Eu as aqueous phase where the [NO₃⁻] concentration was kept to 1 M with NaNO₃.

1.1.2 Kinetics

A kinetics experiment was carried out, both for comparison with CyMe₄-BTBP, due to the molecular similarities, but also to investigate the performance of MF2-BTBP. In this light, the experiment was performed in the same conditions as used for the CyMe₄-BTBP molecule, where nitrobenzene was selected due to the clear performance of the system /2, 3/: fast kinetics and good extraction. The experimental conditions were similar with those described above with the aqueous phase consisting of HNO₃ spiked with ²⁴¹Am and ¹⁵²Eu as aqueous phase where the [NO₃⁻] concentration was kept to 1 M with NaNO₃. and the shaking times were: 5, 10, 15 and 20 minutes.

As it can be observed in Figure 1-4, the system did not reach equilibrium even after 20 minutes; by comparison, the system containing CyMe₄-BTBP reached equilibrium after 15 minutes. Further experiments with longer shaking times but also other diluents are planned.

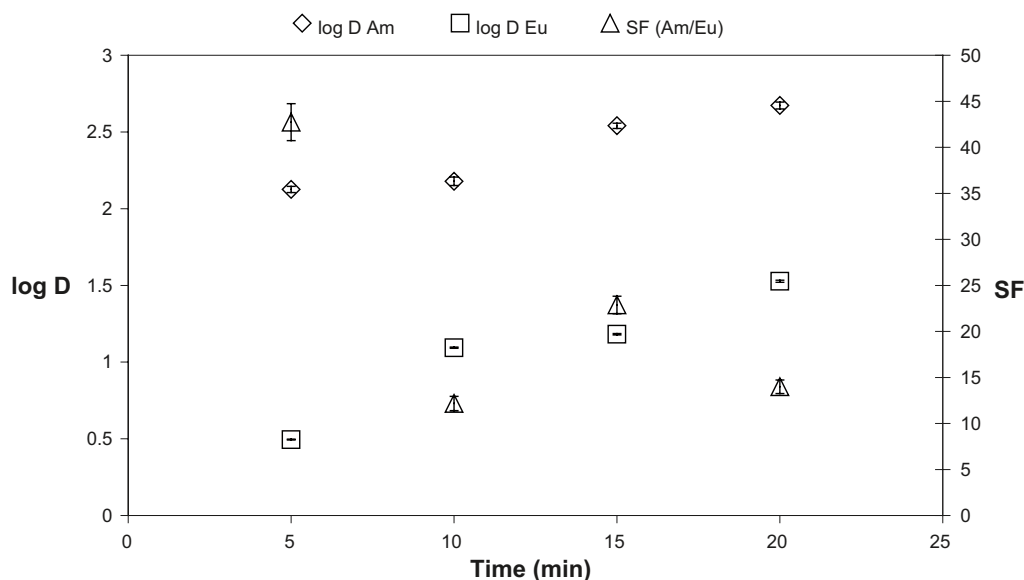


Figure 1-4. Kinetics experiment using 0.01 M MF2-BTBP dissolved in nitrobenzene as organic phase and HNO₃ spiked with ²⁴¹Am and ¹⁵²Eu as aqueous phase where the [NO₃⁻] concentration was kept to 1 M with NaNO₃.

1.2 Diluent effects

1.2.1 SF, D and kinetics studies for CyMe₄-BTP and CyMe₄-BTBP

It has been long known that changing the diluent highly affects the D (distribution ratios) and SF (separation factors) for the selected metals with different extraction mechanisms /4, 5/. However, indications have been seen previously /3/ that even with same extraction mechanism the SF may change when changing the diluent. An experiment was carried out with 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)pyridine (CyMe₄-BTP) and 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine (CyMe₄-BTBP), each of them dissolved in two different diluents: cyclohexanone and nitrobenzene.

The experimental procedure was similar with the one presented in the screening part, with the difference that the diluents selected for this experiment were cyclohexanone and nitrobenzene and the shaking time was slightly different, between 5 and 25 minutes for the cyclohexanone containing system and 5 and 40 minutes for the nitrobenzene containing system. The temperature during the experiments was $19 \pm 1^\circ\text{C}$. The experimental conditions remained the same throughout the experiment.

The extraction kinetics was very fast for both ligands dissolved in cyclohexanone and the extraction equilibrium was reached within 5 minutes for both Am and Eu, see Figure 1-5. In nitrobenzene, the kinetics was slightly slower, the equilibrium being reached after 15 minutes for CyMe₄-BTBP for both Am and Eu, and after 10 minutes for CyMe₄-BTP for Am. Eu did not reach equilibrium in this case, not even after 25 minutes as shown in Figure 1-6.

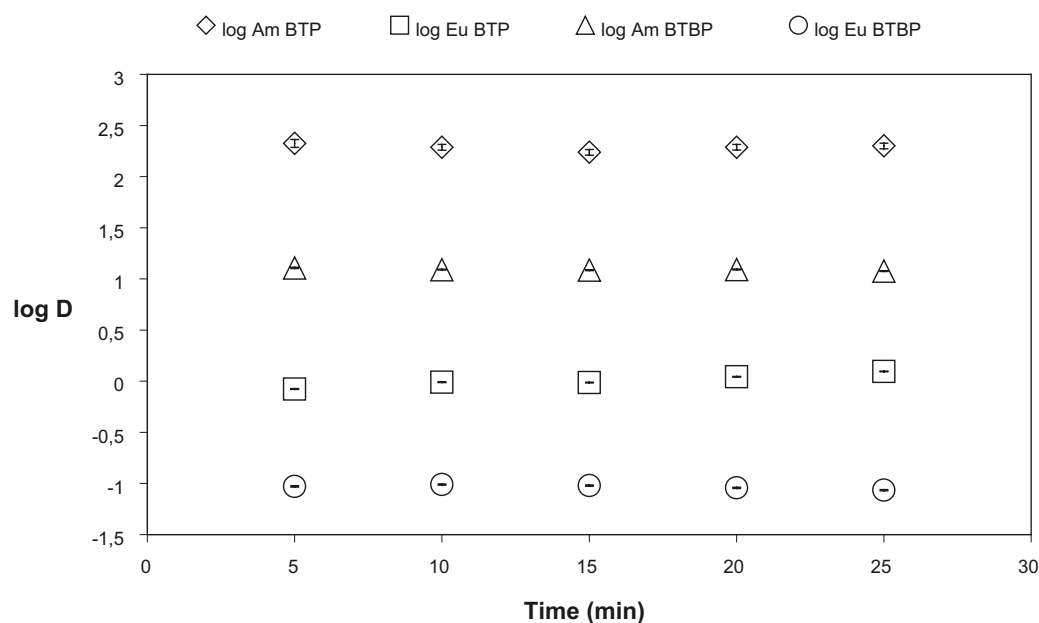


Figure 1-5. The kinetics experiments carried out with 0.01 M CyMe₄-BTP and CyMe₄-BTBP dissolved in cyclohexanone in contact with 0.01 M HNO₃ spiked with ²⁴¹Am and ¹⁵²Eu.

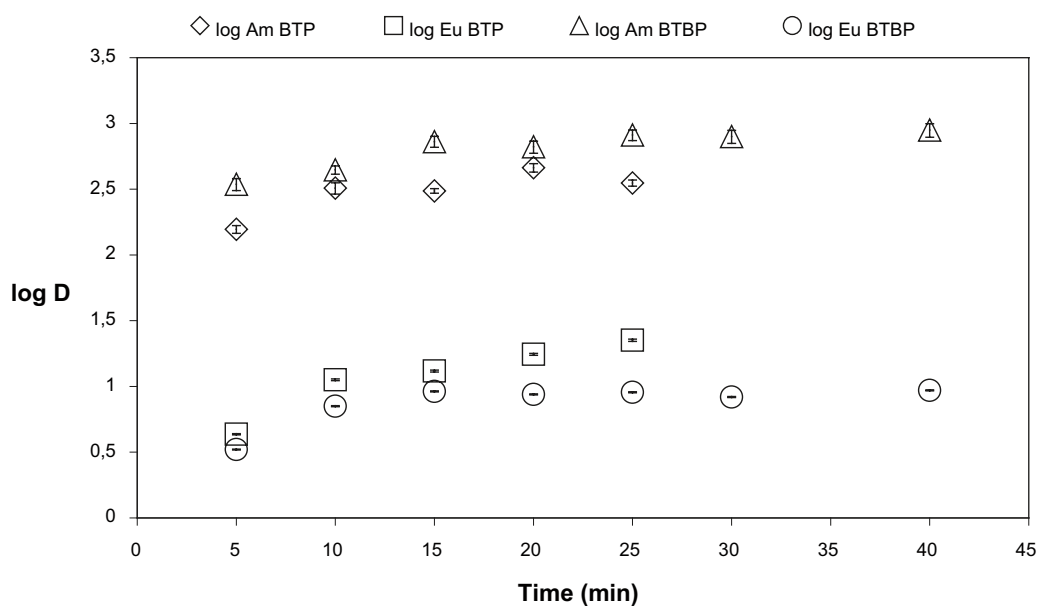


Figure 1-6. The kinetics experiments carried out with 0.01 M $\text{CyMe}_4\text{-BTP}$ and $\text{CyMe}_4\text{-BTBP}$ dissolved in nitrobenzene in contact with 0.01 M HNO_3 spiked with ^{241}Am and ^{152}Eu .

$\text{CyMe}_4\text{-BTBP}$ in nitrobenzene or cyclohexanone

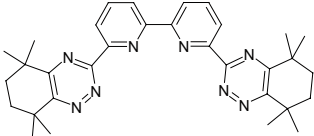
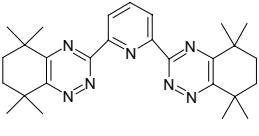
The dissolution of $\text{CyMe}_4\text{-BTBP}$ is faster in nitrobenzene than in cyclohexanone, which can probably be attributed to the polarity of the diluents: nitrobenzene ($\epsilon = 34.8$), cyclohexanone ($\epsilon = 18.2$) or due to the fact that nitrobenzene has an aromatic π system, similar with that of the BTPs and BTBPs. Cyclohexanone has a very small π system, associated with the carbonyl group. Thus the dissolution should work by the rule “like dissolve like”.

Usually the complex formation specific to BTBP molecules is 1:2 with the respect to metal:ligand ratio and three nitrates. The higher D of Am and Eu in nitrobenzene containing systems can probably be explained by the fact that an oxygen atom from the more polar nitrobenzene molecule can coordinate to the metal, thus increasing lipophilicity of the complex and easing the extraction.

As for the difference in SF between the two systems, this can also be explained by the fact that the coordinated oxygen from nitrobenzene is less selective than nitrogen towards actinides and lanthanides, therefore as nitrobenzene coordinates it is expected that D for Eu should increase towards that of Am.

Another explanation can be that the nitrates are in outer sphere complexes in the organic phase. A reason for better extraction could then be that the transfer energy of nitrate from the aqueous phase to the organic phase is less for nitrobenzene than for cyclohexanone. At present we cannot say which explanation is the correct one. An experimental matrix was designed, in order to offer a better insight upon the results and discussions, Table 1-1. /3/

Table 1-1. Experimental matrix showing the main results of the kinetic extraction using 0.01 M CyMe₄-BTBP and CyMe₄-BTP dissolved in cyclohexanone and nitrobenzene in contact with 0.01 M HNO₃ (where nitrate concentration was kept to equal 1 by adding NaNO₃) spiked with trace amounts of ²⁴¹Am and ^{152,154}Eu.

Ligands		
Diluents		
	CyMe₄-BTBP	CyMe₄-BTP
Cyclohexanone	D Am: 12.8 ± 0.18 D Eu: 0.093 ± 0.01 SF _{Am/Eu} : 136 ± 3.00 Kinetics: fast Equilibrium: 5 minutes for Am 5 minutes for Eu	D Am: 212 ± 19.00 D Eu: 0.84 ± 0.10 SF _{Am/Eu} : 253 ± 23.00 Kinetics: fast Equilibrium: 5 minutes for Am 5 minutes for Eu D
Nitrobenzene	D Am: 728 ± 69.00 D Eu: 9.2 ± 0.10 SF _{Am/Eu} : 79.4 ± 8.00 Kinetics: slow Equilibrium: 15 minutes for Am 15 minutes for Eu	Am: 322 ± 32.00 D Eu: 22.5 ± 0.40* SF _{Am/Eu} : 14.20* Kinetics: slow Equilibrium: 10 minutes for Am *after 25 minutes, not at equilibrium

CyMe₄-BTP in nitrobenzene or cyclohexanone

The solubility and polarity previously discussed can be applied without any amendments in this case, too. The difference in D for Am are not as significant as in the previous systems and this can be explained by the different complexes formed for Am 1:3 with respect to metal:ligand ratio. Thus 9 coordination sites are already taken and the coordination of one or more oxygen from nitrobenzene will not be easily done.

The D for Eu show a different trend: in cyclohexanone Eu reaches equilibrium in the same time as Am. It is assumed that also Eu forms only a 1:3 complex in this diluent. In nitrobenzene, the extraction of Eu is still increased even after 25 minutes, thus the SF in this case will decrease even further and will certainly be different than in the cyclohexanone containing system. This can probably be attributed to the fact that nitrobenzene can contribute to the extraction as described before but here it is also assumed that two different complexes between Eu and BTP can exist, 1:2 and 1:3.

CyMe₄-BTBP and CyMe₄-BTP in cyclohexanone

The D for Am are higher in the BTP case due to the fact that there are 9 coordination sites occupied by the ligand since the complex is 1:3 with the respect to metal:ligand ratio, and three nitrate groups per molecule coordinate. This way the complex is more lipophilic than one formed by CyMe₄-BTBP which only uses 8 coordination sites.

CyMe₄-BTBP and CyMe₄-BTP in nitrobenzene

In this case, the D for Am decreases in the CyMe₄-BTP containing system whereas the D for Eu increases without reaching equilibrium, even after 25 minutes. The longer equilibrium time can probably be explained as before with more Eu:BTP species but the decrease in the Am extraction cannot yet be explained. That the selectivity goes down in nitrobenzene is as said before probably due to the coordination of the non selective oxygens from the nitro group in the diluent.

1.2.2 New diluent

A provisory list of the demands on diluents for solvent extraction /6/ was made:

- contain only carbon, hydrogen, oxygen and nitrogen,
- high flash-point,
- high boiling point and low freezing point,
- low density,
- low water solubility,
- low chemical transformation rate with water or reagents,
- not form a third phase under loading conditions, if at all,
- low rate of radiation damage at reasonable dose rates.

These demands can always be upgraded, as a function of extractants and requirements in technological set-ups (type of contactors).

Taking one of the requirements into consideration, namely the low water solubility, but also trying to stay close to the rest of the requirements, a new diluent was made and tested, Figure 1-7.

The tests were simple screening experiments following the same experimental procedure as described before. The ligand used for this particular test was $\text{CyMe}_4\text{-BTBP}$. A comparison was made between the D obtained from the new diluent and the solvents containing cyclohexanone and nitrobenzene as diluents. The values shown by the new diluent are inferior to the ones obtained with the other two diluents, thus no further experiments are considered, Figure 1-8. The kinetics is similar with the other two diluents.

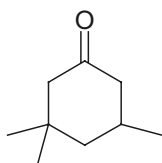


Figure 1-7. 3,3,5-trimethyl-cyclohexanone.

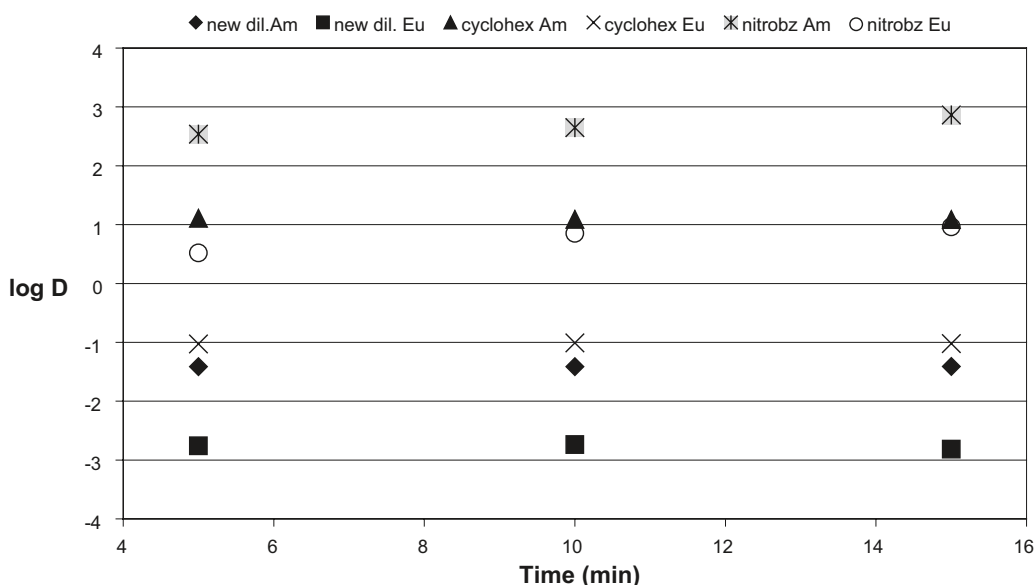


Figure 1-8. Kinetics experiment using 0.01 M $\text{CyMe}_4\text{-BTBP}$ dissolved in the new synthesized diluent, 3,3,5-trimethyl-cyclohexanone, compared with a similar solvents containing nitrobenzene or cyclohexanone as organic phase and 0.01 M HNO_3 spiked with ^{241}Am and ^{152}Eu .

1.3 Mobility of metal complexes of the BTBPs

Since little is known of the nature of the metal complex present within the organic phase a series of electrical conductivity experiments were performed using solutions of metal complexes in water saturated nitrobenzene and water saturated cyclohexanone. The aim of this study was to accept or reject the hypothesis that “in nitrobenzene the metal species (and counter ions) formed by the extraction of europium nitrate by the BTBPs are separated ion pairs which are able to move freely, while in cyclohexanone these ions are present within contact ‘pairs’ which inhibits their free movement”.

As an initial test of the equipment and experimental protocol, the conductivity of tetraethylammonium perchlorate and a series of perchlorate salts of C2-BTBP complexes (copper(II), cadmium(II) and lead(II)) were determined. In addition the conductivity of the perchlorate salt of the CyMe₄-BTBP complex of lead was measured, as illustrated in Figure 1-9. Because mobility data for the ions present within tetraethylammonium perchlorate has been presented in the literature /7/ and as this compound is readily available by the anion metathesis of tetraethyl ammonium chloride with perchloric acid, we have chosen to employ this salt as our standard within nitrobenzene.

The three metal complexes were used to test the assumption that the mobility of a *homoleptic* BTBP complex is independent on the nature of the metal at the centre of the complex.

NB. Below 100 $\mu\text{mol dm}^{-3}$ the molar conductivity of tetraethylammonium perchlorate decreased, this is thought to be due to an adsorption effect, hence those points for concentrations of this compound at less than 100 $\mu\text{mol dm}^{-3}$ were disregarded.

As hoped the metal salts are strong electrolytes in nitrobenzene, and the ionic conductivities of the BTBP complexes are very similar. Using the stokes equation and a literature value for the hydrodynamic radius of a perchlorate anion /8/ it was possible to estimate the hydrodynamic radii of the metal complexes after making the assumption that these complexes exist as *homoleptic* BTBP complexes in nitrobenzene.

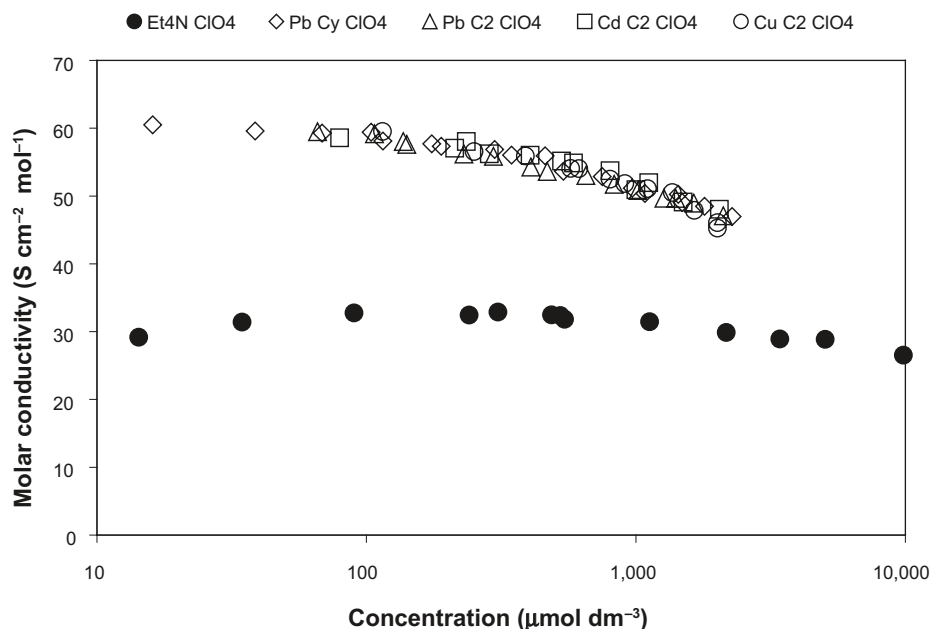


Figure 1-9. The molar conductivities of a series of perchlorate salts as a function of their concentration.

1.3.1 The nature of the nitrate salt of the europium(III) CyMe₄-BTBP complex when dissolved in nitrobenzene and cyclohexanone

A solution of the nitrate salt of the europium(III) CyMe₄-BTBP complex was made in nitrobenzene. The conductivity of this salt was measured at different concentrations. While it was found that this salt is a strong electrolyte which obeys Kohlrausch's law, it was noticed that the molar conductivity (extrapolated to zero concentration) was lower than that which would be predicted by Kohlrausch's law of independent ionic mobility. This was calculated after having made the assumption that the hydrodynamic radius of the europium complexes [Eu(CyMe₄BTBP)₂]³⁺, is identical to that of [Pb(CyMe₄BTBP)₂]²⁺. We continue to work on the problem of the abnormally low conductivity using both experimental and computational methods.

When attempts were made to repeat the study in cyclohexanone it was found that the nitrate salt of the europium(III) CyMe₄-BTBP complex and tetraethyl ammonium perchlorate were both weak electrolytes in cyclohexanone. Attempts to employ Kohlrausch's law ($\lambda_m = \lambda_m^0 - K\sqrt{c}$) created curved graphs reminiscent of that obtained using data for a known weak electrolytes (acetic acid in water) /9/. This weak electrolyte behaviour strongly suggests that contact ion pairing is immobilising the charge carrying ions.

1.4 Radiolysis

Since the separation processes where the BTBP molecules will be used take place in a high radiation flux, both the extractant and the diluent must be resistant to radiation. A number of organic systems were irradiated and the effect on extraction was studied. Solutions were placed in glass bottles in an irradiation source (Gamma cell 220, Atomic Energy of Canada Ltd) with an estimated dose rate of between 12 and 15 Gy/h. Corresponding samples were placed in a flask outside the source, at a remote distance, to act as a reference and also to investigate the possible ageing effects of the molecules. Samples were taken from the organic systems at the start of the experiments and then at different times during a longer time period.

1.4.1 C5-BTBP – extraction of Pd, Ag and Cd

Besides efficiently extracting trivalent actinides, many of the polydentate N-donor ligands also show high affinity for various transition metals, most of which are present in the HLLW solution resulting from the PUREX process. C5-BTBP in particular has proven to enable separation between metals that are generally regarded as difficult to separate, such as the separation of palladium(II) from rhodium(III) and ruthenium(II) nitrosyl /10/. The effect on extraction behaviour towards palladium (Pd), silver (Ag), and cadmium (Cd) of an irradiated organic system containing 0.005 M C5-BTBP in cyclohexanone has been investigated.

Pd, Ag, and Cd are present in the HLLW in typical concentrations of approximately 4.15, 0.20, and 0.21 mM, respectively /11/. Distribution ratios for Pd have been shown to be independent of the C5-BTBP concentration in an octanol/kerosene mixture at high nitric acid concentrations, probably due to a change in extraction mechanism /10/. Thus the acid concentration in this study was kept low, 0.01 M.

A solution containing 0.005 M C5-BTBP in cyclohexanone was placed in the gamma-irradiating cobalt source, which at the time of the irradiation had a dose rate of ~13 Gy/h. Triple samples were taken from the irradiated and the reference solution at different times during a total period of 1,341 hours, corresponding to a total dose for the irradiated samples of 17.4 kGy. The aqueous phase consisted of 0.99 M NaNO₃, 0.01 M HNO₃, and 50 μM each of Pd, Ag, and Cd.

Before conducting the extraction experiments the phases were pre-equilibrated and then 500 μL of each phase was contacted for six hours in a shaking device, sufficient time to reach chemical equilibrium. After contact, the samples were centrifuged at 800 g for five minutes and aliquots of 300 μL were taken from each phase. Samples were also taken from the pre-equilibrated

aqueous phase before contact with the organic phase. All aqueous samples were measured in an ICP-MS (Elan 6100 DRC, Perkin Elmer Sciex) and the internal standards used for the measurements were: In and Pt in 1 M ultrapure HNO₃. The difference in metal concentration in the aqueous phase before and after contact was assigned the organic phase after contact and the distribution ratios could be calculated. When comparing large and small numbers this way, of calculating D may give uncertain values.

During the experiments a dark precipitation at the interface between the phases was observed when a metal containing aqueous phase was left in contact with the organic phase. A contact experiment with Pd as the only metal present in the aqueous phase showed the same type of precipitation, confirming that Pd is reacting with the cyclohexanone. This behaviour, often referred to as palladium black, has been reported for solutions of ketones in diluents such as 1,2-dichloroethane, 1-octanol, n-dodecane, benzene, and toluene but it was not observed previously when the diluent was nitrobenzene /12/.

To determine whether or not any degradation due to ageing took place, the reference solutions were studied in terms of change in D. Figure 1-10 shows the change in distribution ratio of Pd, Ag and Cd at various times. The Ds are not increasing; hence no degradation with time is assumed. Actually, for Ag and Cd the D surprisingly rises more than one order of magnitude. This may be explained by the uncertainties connected to the method of calculating Ds by only measuring the aqueous phase. These changes in D for the reference solutions will be further studied and other measuring techniques will be used.

The effect of radiolysis upon extraction is illustrated in Figure 1-11 as the ratio (in %) between D for the irradiated solution and D for the reference solution as a function of the dose received by the irradiated solution. Uncertainty bars are based on the calculated standard deviations of the samples. The metal extraction decreases as the organic phase is being irradiated with the exception of Ag, which requires further studies. Most of the decrease occurs at low doses; hence the solution starts to degrade just as the irradiation starts. For Pd, the D for the irradiated solution goes down to around 50% of the corresponding value for the reference solution, while for Cd it decreases to around 80%.

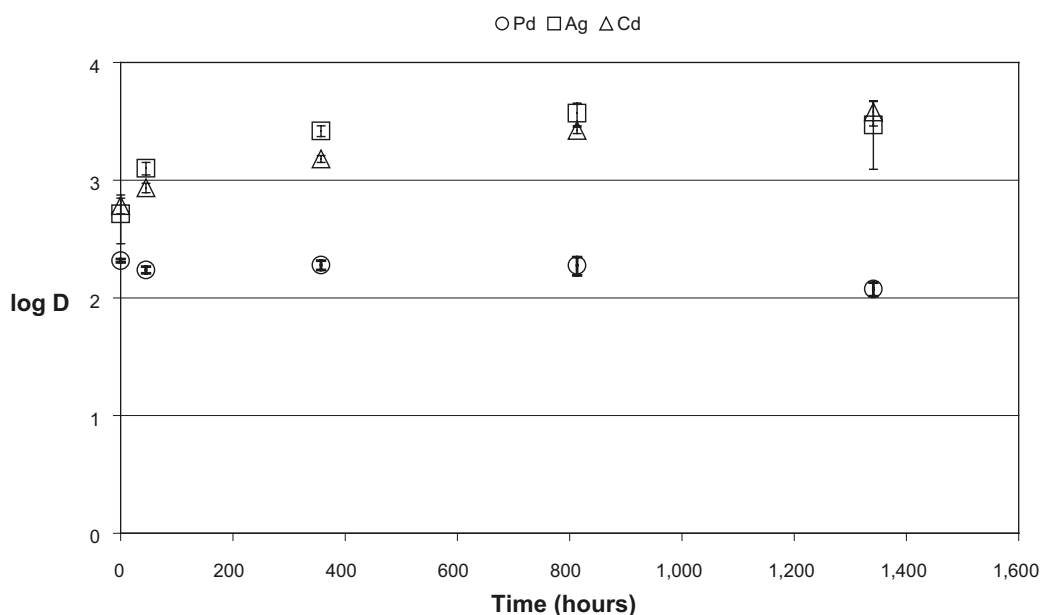


Figure 1-10. Log D for a reference solution containing 0.005 M C5-BTBP in cyclohexanone at various times.

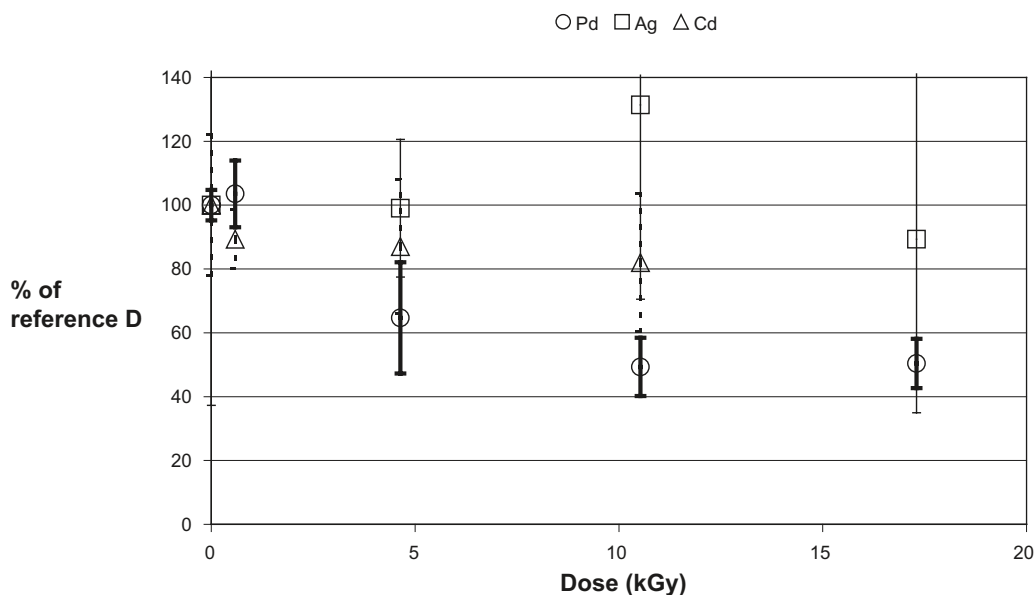


Figure 1-11. Extraction of Pd, Ag and Cd by an irradiated solution, expressed as the percentage of distribution ratio for the reference solution as a function of the received dose. Three data point were removed (two for Ag and one for Cd) due to problems with the measurements.

1.4.2 Dose rate effects

In order to investigate the dose rate dependence of radiolytic degradation, the same type of organic system was irradiated with a total received dose of ~100 kGy but with a varying dose rate. The low dose rate was ~15 Gy/h and the irradiation was performed in the ^{60}Co source at Chalmers. The high dose rate was 1.2 kGy/h and the irradiation experiments were performed in the cooling pond of the DIDO research reactor by Dr. Giuseppe Modolo at Forschungszentrum Jülich. Since the total time of irradiation at Chalmers was very long for the low dose rate solution, a reference solution was used as described above.

The organic system comprised 0.01 M MF2-BTBP in cyclohexanone. Before contact, but after irradiation, the cyclohexanone solution was pre-equilibrated with 1 M HNO_3 , which was the aqueous phase. The aqueous phase, 1 M HNO_3 , was in turn pre-equilibrated with pure cyclohexanone (not irradiated). This is important to notice, since the cyclohexanone in the samples may have degraded and does not possess the same properties as pure, fresh cyclohexanone.

Low dose rate experiments

Triple samples were taken from the irradiated solutions and triple or double samples were taken from the reference solutions. 500 μL of organic phase was contacted for 5 minutes (vigorous manual shaking) with 500 μL aqueous phase with trace amounts of ^{152}Eu , ^{241}Am and ^{244}Cm . The samples were then centrifuged for 10 minutes at 800 g and aliquots of 200 μL from both phases were taken and analysed with two different HPGc detectors (Ortec, Gamma Analyst GEM 23195 and EG&G Ortec).

NB. The contact time of 5 minutes manual shaking may be insufficient in order to reach equilibrium. But the time has been kept the same for all sampling points.

High dose rate experiments

400 μL of organic phase was contacted for 1 hour (shaking machine) with 400 μL aqueous phase with trace amounts of ^{152}Eu and ^{241}Am . Aliquots of 200 μl were taken from both phases and measured.

Results

The system that was exposed to the low dose rate did not show a trend of either decreasing or increasing distribution ratios but instead the ratio between D for the irradiated solution and D for the reference solution was around 1 at all sampling points. This indicates that the solution is rather resistant towards radiolysis. When studying the behaviour of the reference solution it fluctuates around the starting value, indicating stability in time (no ageing). Figure 1-12 illustrates the ratio between D_{Am} for the irradiated solution and D_{Am} for the reference solution at various doses. The system that was exposed to a higher dose rate showed a slow decrease in distribution ratio; hence, the system seemed to be more affected by the higher dose rate which was also expected. Further studies will be made to assess the different radiolysis products as a function of the dose rate.

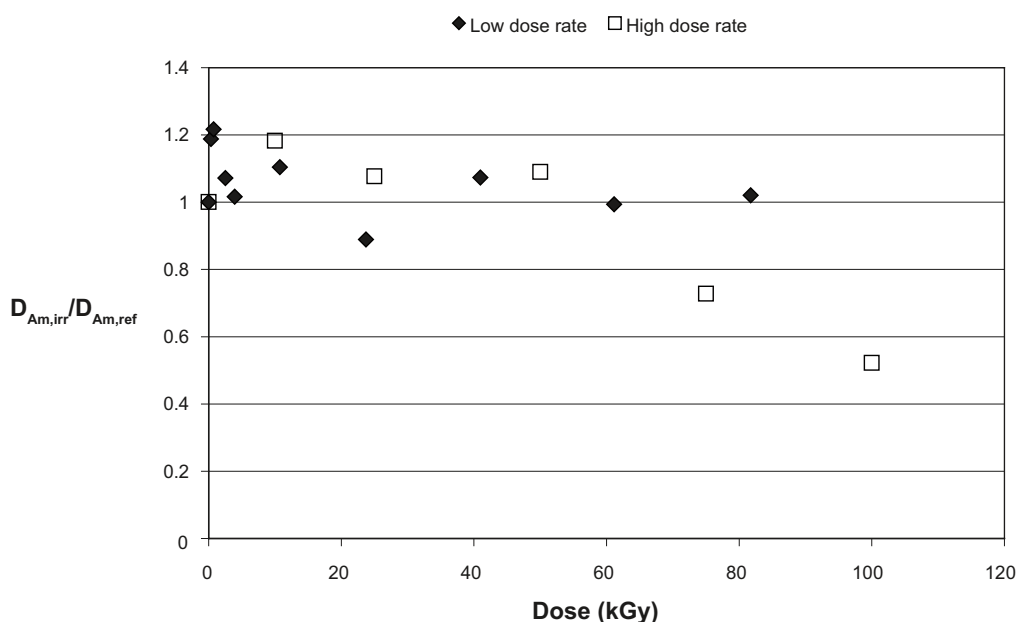


Figure 1-12. Ratio between D_{Am} for the irradiated solution and D_{Am} for the reference solution plotted against the received dose. The black marker represents the low dose rate ($\sim 15 \text{ Gy/h}$) while the white marker represents the high dose rate ($\sim 1.2 \text{ kGy/h}$).

2 Synergic extraction of Eu

The synergic extraction of europium by terpyridine (Terpy) and α -bromodecanoic acid (HA) in different diluents has been studied. An earlier study /13/ showed interesting results for an organic system with tributylbenzene (TBB) as diluent, and this study was the basis for the current experiments.

The ratio between Terpy and HA in TBB was varied and an optimal ratio was determined, giving the maximum extraction of Eu. In addition to the curve for the synergic system the figure also displays the curve for extraction with just HA, no Terpy added.

The first step in the study aimed at determining whether or not the system showed the same behaviour with higher concentrations of Eu as with trace amounts, which was used in the old study. The reason of increasing the concentration of Eu, was that the measuring techniques aimed to be used in the current study would be ICP-OES (iCAP 6000, Thermo Scientific), where the detection limit for Eu is 1–10 ppb, but also to enable NMR measurements.

In the new study the concentration was increased to 0.005 M, and inactive europium in the form of $\text{Eu}(\text{NO}_3)_3$ (^{151}Eu (47.8%) and ^{153}Eu (52.2%)) was used. When increasing the metal concentration, also the Terpy and HA concentration must be increased. The concentration of Terpy was increased to 0.05 M and the HA concentration was increased to values giving similar $[\text{HA}]/[\text{Terpy}]$ ratio as the old study. The aqueous phase contained 0.005 M $\text{Eu}(\text{NO}_3)_3$, 0.01 M HNO_3 and 0.97 M NaNO_3 .

In order to validate the results from the ICP-OES radiometrical analysis was done at the same time. All the samples were spiked with traces of active $^{152,154}\text{Eu}$.

Experimental

250 μl of each phase was contacted during 10 minutes of manual shaking. According to the previous experiments this should be sufficient to reach chemical equilibrium. To ensure the phase separation the samples were centrifuged and aliquots of 100 μl were taken from each phase and analyzed with a NaI(Tl) well type detector (Intertechnique GC-4000). The experiment was carried-out in duplicate samples.

Results and discussions

Figure 2-1 shows the extraction curves for the experiment with higher Eu concentration and for the experiments using just trace amounts of Eu. During the experiments a third phase formation was observed in the vials containing the highest concentration of HA. Therefore the last data point in each series is uncertain.

It was obvious that the maximum extraction of Eu did not occur at the same $[\text{HA}]/[\text{Terpy}]$ ratio for the higher concentration of Eu as it did when using just trace amounts. If instead the extraction is plotted as a function of $[\text{HA}]$, Figure 2-2, the maximum value of extraction coincides for the two different studies.

Further experiments were carried out with other diluents, while all the other experimental conditions remained constant, as described above. Three diluents were used: kerosene, toluene and cyclohexane. Kerosene proved to form a third phase when contacted with the aqueous phase so no extraction data could be obtained for this system.

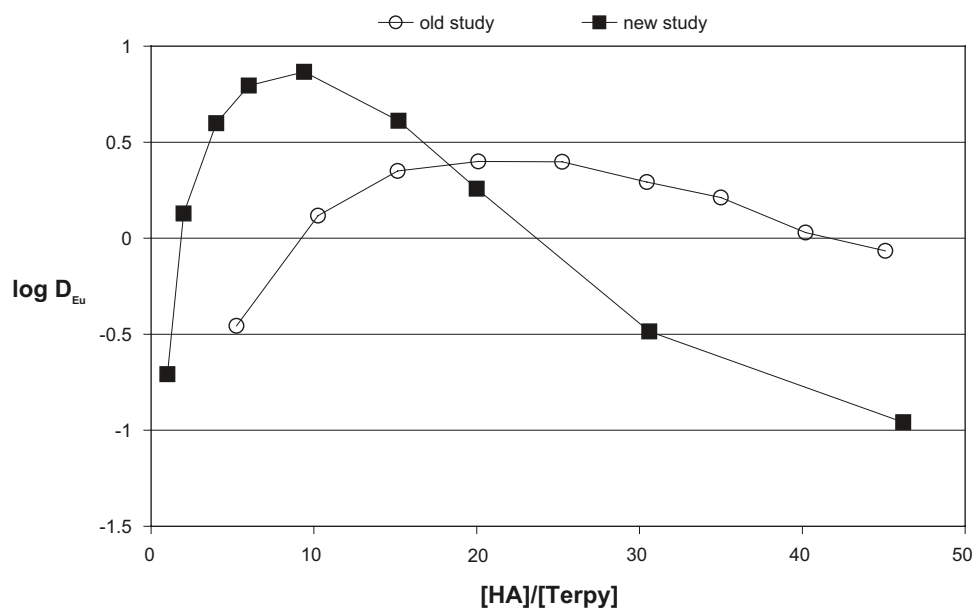


Figure 2-1. Extraction curve for the old and new study, with varying $[HA]/[Terpy]$ ratio on the x-axis. In the old study the Terpy concentration was kept constant at 0.02 M and the concentration of Eu was limited to trace amounts. In the new study the Terpy concentration was 0.05 M and the Eu concentration was 0.005 M (inactive) + traces of active Eu. $[HA]$ was varied to achieve various ratios between $[HA]$ and $[Terpy]$.

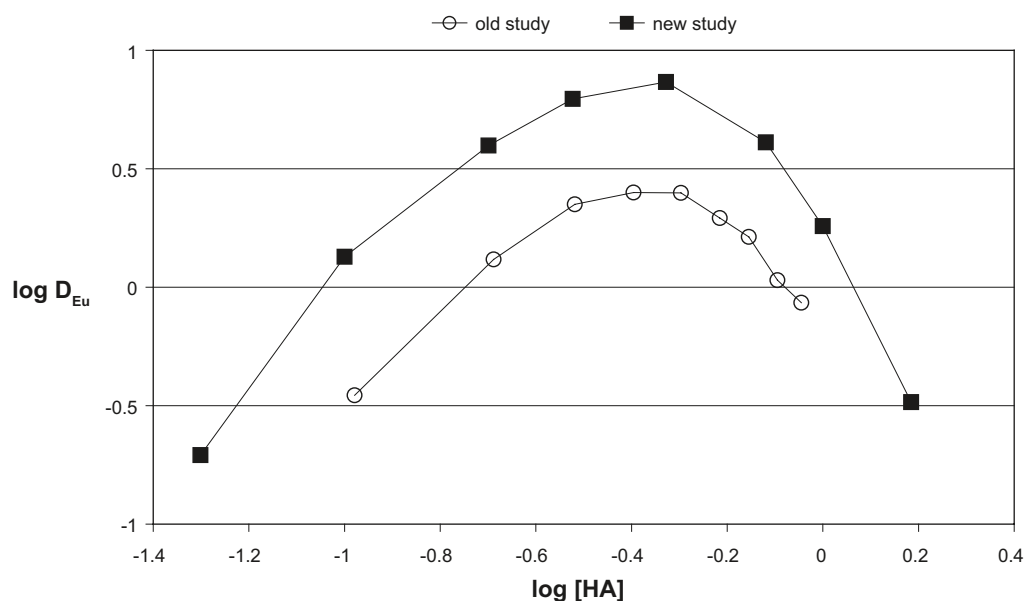


Figure 2-2. Extraction curve for the old and new study, with $\log [HA]$ on the x-axis.

Figure 2-3 illustrates the extraction curves at various $[HA]/[Terpy]$ ratios for TBB, toluene and cyclohexane. TBB and toluene appear to give the same shape of the curve but the distribution ratios for TBB are much higher. The maximum extraction with cyclohexane as diluent has not been established yet, the figure needs to be complemented with experiments with lower HA concentrations. From the available results the extraction of europium reaches the highest value with cyclohexane as diluent.

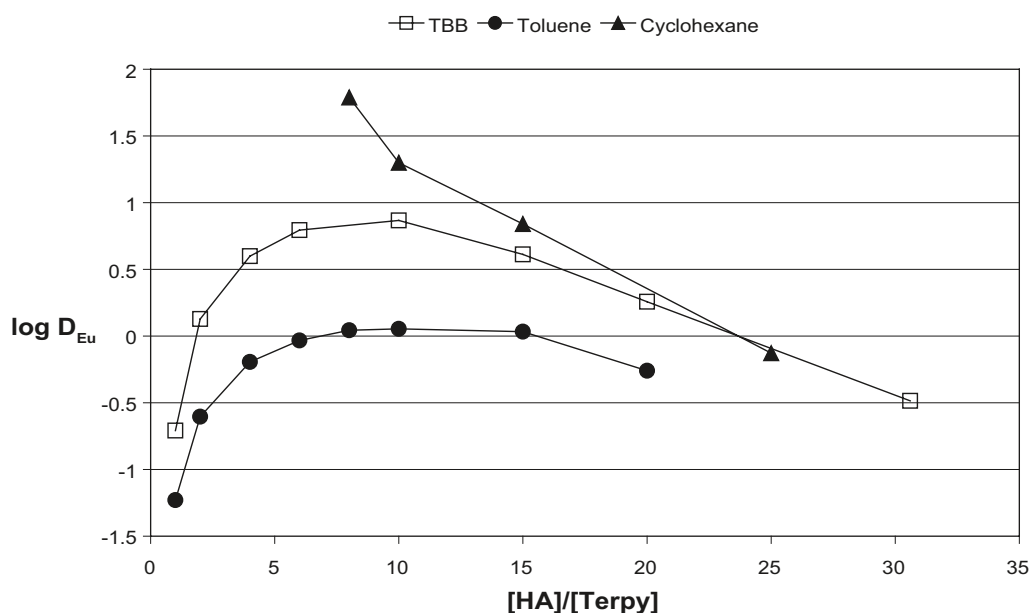


Figure 2-3. The extraction of Eu as a function of the ratio between $[HA]$ and $[Terpy]$. $[Eu] = 0.005 M$, $[Terpy] = 0.05 M$ and $[HA]$ is varied from 0.05 to 1.5 M (not all concentrations for all three diluents).

For TBB and toluene, corresponding experiments were made with just inactive Eu, no spike added, and measurements were made with ICP-OES spectrometer. The samples were diluted 1:100 with internal standard (IS) containing Gd in 1 M HNO_3 . Because the BTBPs clogged the capillary tubes of the ICP-OES, it was not possible to directly determine the Eu contents of the organic phase. Measurements were instead carried out for the aqueous phases before extraction and the resulted stripping phase. Thus, the organic phase was stripped using 2 M HNO_3 as stripping agent. The stripping was made during 10 minutes of manual shaking. Distribution ratios (D) were subsequently calculated according to Equation 3. There is an obvious drawback in this method of calculating the D due to the possible comparison of large and small numbers, however, for the cases investigated here, this is not a problem:

$$D = \frac{[M]_{Aq}^{Stripping}}{[M]_{Aq}^{After}} \quad (3)$$

Samples were also taken from the aqueous phase before contact, enabling an alternative way to calculate the distribution ratio. The difference in metal concentration in the aqueous phase before and after contact was assigned the organic phase after contact and the distribution ratios could be calculated, according to Equation 4.

$$D = \frac{[M]_{Aq}^{Before} - [M]_{Aq}^{After}}{[M]_{Aq}^{After}} \quad (4)$$

Figure 2-4 to 2-5 show the distribution curves using three different measurement techniques; radiometric detection with Na(I) and two ways to calculate distribution ratio from ICP-OES data for aqueous phases.

Different behaviour of the extraction system as function of different diluents has been observed. Further investigations of this system are on the way and will be reported at a later time.

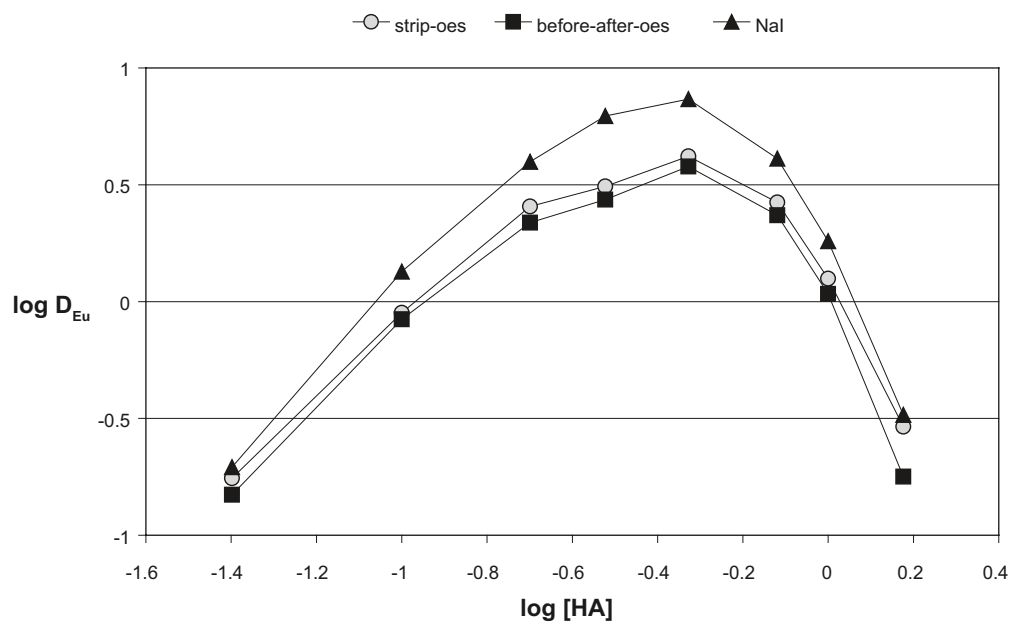


Figure 2-4. Extraction curves for a TBB based system using a) radiometric measurement in NaI(Tl) detector; b) ICP-OES analysis of aqueous phase before and after contact and c) ICP-OES analysis of aqueous phase and stripping phase.

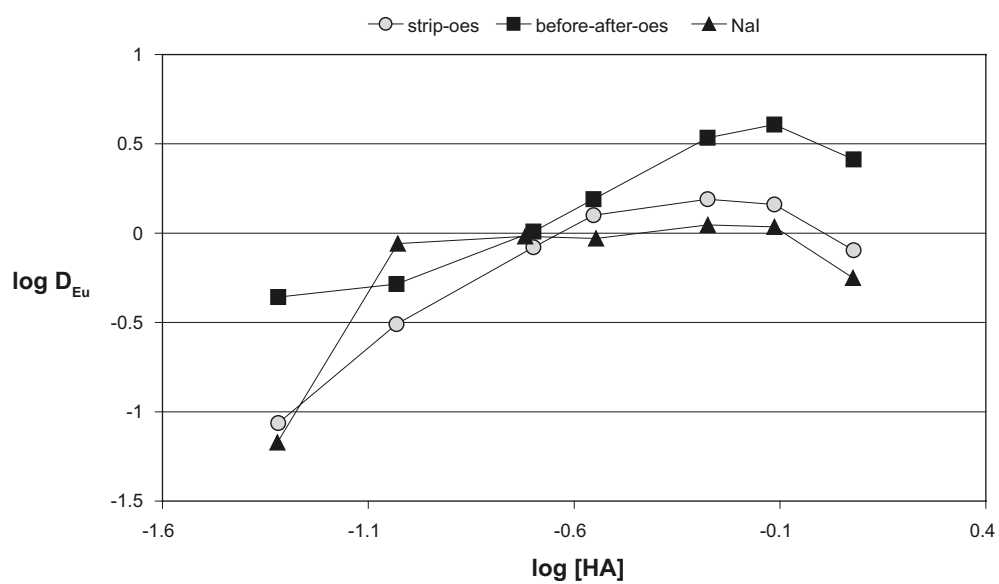


Figure 2-5. Extraction curves for a toluene based system using a) radiometric measurement in NaI(Tl) detector; b) ICP-OES analysis of aqueous phase before and after contact and c) ICP-OES analysis of aqueous phase and stripping phase .

Collaborations

The following laboratories are involved in ACSEPT:

- Commissariat à l'énergie atomique (CEA) France.
- Alcan centre de chercheurs de Voreppe, France.
- Compagnie generale des materieres nucleaires SA, France.
- Centro de investigaciones energeticas, medioambientales y tecnologicas-CIEMAT, Spain.
- CINC solutions BV, Netherlands.
- Centre national de la recherche scientifique (CNRS), France.
- Consejo superior de investigaciones cientificas, Spain.
- Ceske Vysoke uceni technicke v Praze, Czech Republic.
- Charles Univesity in Prague, Czech Republic.
- Electricite de France SA, France.
- Ente per le nuovo technologie, l'energia e l'ambiente, Italy.
- Forschungszentrum Jülich, Germany.
- Forschungszentrum Karlsruhe, Germany.
- Instytut Chemii I Techniki Jadrowej, Poland.
- Funda to privada institute Catala d'investigacio quimca (ICIQ), Spain.
- Institute of inorganic chemistry academy of sciences of Czech Republic.
- Commission of the European communities-directorate general joint research centre – JRC, Belgium.
- NEXIA solutions limited, UK.
- Nuclear research and consultancy group, Netherlands.
- Nuclear phisics institute ASCR, Czech Republic.
- Politecnico di Milano, Italy.
- Paul Sherrer Institute, Switzerland.
- Rijksuniversiteit Groningen, Netherlands.
- Chalmers University of Technology, Sweden.
- The University of Edinburg, UK.
- Universite de Liege, Belgium.
- Universita degli studi di Parma, Italy.
- The university of Reading, UK.
- Universite Louis Pasteur, France.
- Universiteit Twente, Netherlands.
- Australian nuclear science and technology organisation ANSTO, Australia.
- Central research institute of electric power industry, Japan.
- Universite Pierre et Marie Curie – Paris 6, France.
- Instituto tecnologico e nuclear, Portugal.

A more intense collaboration with Chalmers exists with:

- Forschungszentrum Jülich, Germany
- University of Reading, UK
- Institut für Mikroelektronik Mainz, Germany
- Kernchemie, Johannes Gutenberg-Universität, Germany
- CEA, France
- National Institute of Cryogenics and Isotopic Separation, Romania

International and national scientific exchange

January 2007, half yearly EUROPART meeting in Karlsruhe, Germany. Participants: C Ekberg, A Fermvik.

21–29th of April 2007. Study tour for the students taking our basic Nuclear Chemistry course. This year they visited e.g. Technical University in Prague, Rez Nuclear Research Institute (Tcheck Republic); National Institute of Isotope Separation (ICSI) Rm. Valcea, Nuclear Fuel Factory Pitesti, Cernavoda Nuclear Power Plant (CANDU 6 Type) (Romania); Silver Mine in Freiberg (Germany). Participants: C Ekberg, G Skarnemark, T Retegan, A Fermvik, J Holm, K Larsson and 13 students.

June 2007, ACTINET Summer School, ITU, Germany. Actinide behaviour in Natural Environment. Participants: A Fermvik and T Retegan.

June 2007, final EUROPART meeting in Stenungsund, Sweden. Participants: C Ekberg, A Fermvik, T Retegan, G Skarnemark, E Aneheim, S Englund.

August 2007, International Conference on Rare Earth Elements, BauTou, China. Participants: C Ekberg, S Englund.

October 2007, 15th Symposium on separation science and technology for energy applications, Gatlinburg USA. Participant: C Ekberg.

Articles and publications

During the past year several reports and articles have been published or submitted for publication.

Published

Ahlström P-E, Blomgren J, Ekberg C, Englund S, Fermvik A, Liljenzin J-O, Retegan T, Skarnemark G, Eriksson M, Seltborg P, Wallenius J, Westlen D: Partitioning and Transmutation. Current developments – 2007. A report from Swedish reference group for P&T. Technical report, Svensk Kärnbränslehantering AB (2007), (07-04), 1-91, ISSN 1404-0344.

Retegan T, Ekberg C, Fermvik A, Skarnemark G: The Effect of Diluents on Extraction of Actinides and Lanthanides, in Scientific Basis for Nuclear Waste Management XXX, edited by D.S. Dunn, C. Poinssot, B. Begg (Mater. Res. Soc. Symp. Proc. 985, Warrendale, PA, 2007), 0985-NN14-05.

Retegan T, Ekberg C, Dubois I, Fermvik A, Johnsson Vass T, Skarnemark G: 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(4) (2007).

Retegan T, Ekberg C, Englund S, Fermvik A, Foreman M R S, Skarnemark G: The Behaviour of Organic Solvents Containing C5-BTBP and CyMe₄-BTBP at Low Irradiation Doses, Radiochim. Acta, 95, 637-642 (2007).

Teodora Valeria Retegan, Licentiate thesis “The influence of Diluents and Side Groups of the Ligands on Liquid-Liquid Extraction of Actinides and Lanthanides”, Published by Chalmers Reproservice, Technic. Rep. 2007:2.

Fermvik A, Ekberg C, Retegan T, Skarnemark G: Radiolysis and Ageing of C2-BTP in Cinnamaldehyde/Hexanol mixtures, in Scientific Basis for Nuclear Waste Management XXX, edited by D.S. Dunn, C. Poinssot, B. Begg (Mater. Res. Soc. Symp. Proc. 985, Warrendale, PA, 2007), 0985-NN03-20.

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Submitted

Ekberg C, Fermvik A, Retegan T, Skarnemark G, Foreman M R S, Hudson M J, Englund S, Nilsson M: An Overview and Historic Look Back at the Solvent Extraction Using Nitrogen Donor Ligands to Extract and Separate An(III) from Ln(III). Submitted to Radiochim. Acta. (2007).

Retegan T, Ekberg C, Fermvik A, Foreman M R S, Skarnemark G, A comparative study of some BTP and BTBP class ligands, Submitted to International Solvent Extraction Conference (ISEC) 2008.

Fermvik A, Ekberg C, Foreman M R S, Retegan T, Skarnemark G; The Effect of Irradiation on Extraction of Various Metals by C5-BTBP, Submitted to International Solvent Extraction Conference (ISEC) 2008.

Retegan T, Ekberg C, Skarnemark G, Fermvik A, Foreman M R S; CHON-principle, a viable alternative for separating the actinides from lanthanides for further transmutation?, Submitted to 2nd International Nuclear Chemistry Congress, Cancun, Mexico 2008.

Future work

The future work will continue along the suggested path of the ACSEPT project. However, we will 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.

- 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 investigations of the decay products and their effects.
- Investigation of the effect of the diluents on the extraction, stripping and selectivity.
- Optimised selective stripping from a possible GANEX (Grouped ActiNide EXtraction) process.
- Investigation of the dissolution behaviour of selected transmutation fuels.
- Hopefully we will be able to get a new irradiation source for basic stability testing of ligands.

Sofie Englund is now working for OKG AB but will continue in our group part time as a co-project leader.

Daniel Magnusson will come back to Chalmers after his three years at ITU. He will finalise his PhD thesis and verify the computer program developed during his first year at Chalmers.

Teodora Retegan will continue the existing work on basic chemical understanding of nitrogen donor ligands both for the DIAMEX and SANEX processes. The main focus will be on ligand-diluent interaction for understanding of the selectivity of the ligands. Attempts will be made to correlate the extraction behaviour to some more easily measured chemical property such as heat of dissolution. The PhD exam is scheduled for January 2009.

Anna Fermvik, will study the effect of radiation on the extractant molecules used and what effect the products of radiolysis will have on the extraction. The Licenciate exam is scheduled for May 2008.

Emma Aneheim will study development of new extracting ligands and ligands for selective stripping of actinides and lanthanides.

Catharina Nästren will investigate dissolution and other chemical behaviours of fuels for transmutation purposes.

Mark Foreman will work on new synthesis routes for making new ligands and optimise their production.

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