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Research on Advanced Aqueous Reprocessing of Spent Nuclear Fuel: Literature Study

Karen Van Hecke & Patrick Goethals

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SCK•CEN
Boeretang 200
2400 Mol
Belgium

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SCK•CEN
Boeretang 200
2400 Mol
Belgium

Belgian Nuclear Research Centre
Boeretang 200
2400 Mol
Belgium

Phone +32 14 33 21 11
Fax +32 14 31 50 21

http://www.sckcen.be

Contact:
Knowledge Centre
library@sckcen.be

Abstract

The goal of the partitioning and transmutation (P&T) strategy is to reduce the radiotoxicity of spent nuclear fuel to the level of natural uranium in a short period of time (about 1000 years) and thus the required containment period of radioactive material in a repository. Furthermore, it aims to reduce the volume of α-waste requiring deep geological disposal and hence the associated space requirements and costs. Several aqueous as well as pyrochemical separation processes have been developed for the partitioning of the long-lived radionuclides from the remaining of the spent fuel. This report aims to describe and compare advanced aqueous reprocessing methods.

TABLE OF CONTENTS

1. Introduction

A disadvantage of the generation of electricity by nuclear energy is its inevitable by-product of radioactive waste. Electricity production by means of nuclear power is responsible for more than 95% of the radioactivity of the total amount of nuclear waste. Radioactive waste arises from all stages of the nuclear fuel cycle, but more than 99% of the radioactivity involved in electricity generation by nuclear power plants is concentrated within the spent fuel discharged from reactors. Public acceptance of nuclear power as a long term source of sustainable energy highly depends on the impact of the radioactive waste on the environment. The disposal of these radioactive wastes is a serious environmental problem for which there is, as yet, no universally accepted solution. It is one of the most urgent technological and political problems that face mankind worldwide.

Radioactive waste from nuclear reactors typically contains radionuclides with a wide variety of half-lives. The majority of these nuclides exhibit short half-lives ranging from fractions of a second up to a couple of years and disappear in a relatively short period of time representing only a short risk during waste handling and storage. Some radionuclides however, still exist after thousands or even millions of years, so their isolation from the biosphere must be guaranteed for a very long time for example in deep geological formations. Most of the long-lived radionuclides determining the long-term safety within a repository belong to the actinide group (Fig. 1).

With the current reprocessing technology, the time perspective for the confinement of radioactive waste in a repository decreases from the one-million to the hundred-thousand-year perspective, which is still a geological time scale. Even if 99.9% of uranium and plutonium could be separated during reprocessing, the radiotoxicity of the remaining waste would only decrease one order of magnitude (see figure 2). The toxic lifetime of vitrified high level waste is determined by the presence of minor actinides and long-lived fission products (^{99}Tc, ^{129}I, ^{79}Se, ^{93}Zr, ^{135}Cs).

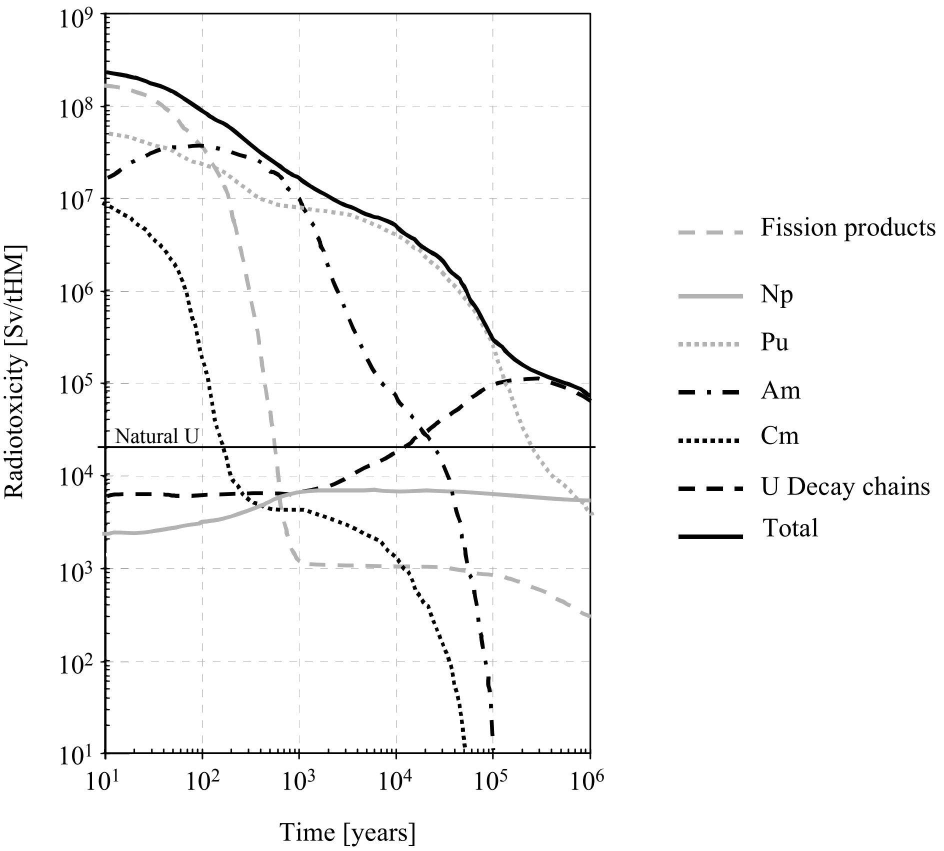


Fig. 1: Radiotoxicity inventory (ingestion) for 1 ton of spent fuel from a pressurised water reactor (PWR) with 4% 235U enrichment and burn-up of 40 GWd/tHM (tHM = Ton heavy metal = uranium mass prior to irradiation without the oxide = uranium plus transuranics plus fission products afterwards) [GOM01]

In the seventies, the idea arose of separating all the long-lived radionuclides, especially minor actinides, from the reprocessing waste, called partitioning, and to transform them into stable nuclides or nuclides with shorter half-lives, called transmutation. Transmutation should be carried out with the help of special reactors or accelerator-driven systems (ADS, with spallation target) which have high neutron fluxes. Transmutation reactions are fission (for minor actinides) and neutron capture (for long-lived fission products) reactions. For transmuting the minor actinides, neutron capture is rather undesirable because of the build-up of higher actinides. Therefore fast neutrons are more suited than thermal neutrons. The goal of this transmutation strategy is to reduce the radiotoxicity of the radwaste to the level of natural uranium in a short period of time (about 1000 years) and thus the required containment period of radioactive material in a repository.

Partitioning and transmutation (P&T) also aims to reduce the volume of α-waste requiring deep geological disposal and hence the associated space requirements and costs. However, quantitative transmutation is not feasible in one single transmutation cycle. Therefore, irradiated transmutation targets must be reprocessed several times.

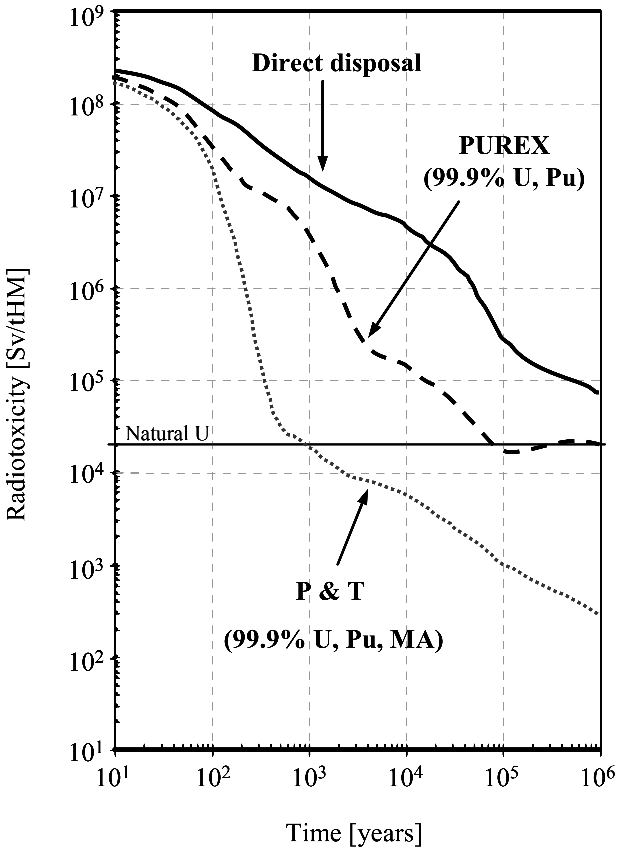


Fig. 2: Evolution of the radiotoxicity (ingestion) of 1 ton of spent fuel from a pressurised water reactor (PWR) with 4% ^{235}U enrichment and burn-up of 40 GWd/tHM, as a function of the waste management strategy [GOM01]

Many countries (e.g. Japan, Germany, France) have a research programme on P&T. Even in USA, a comprehensive development work on the separation of actinides from various wastes and scraps has been carried out, although reprocessing was already deferred for all practical purposes and also from the research programmes.

In order to obtain radioactive waste that will reach the radiotoxicity level of natural uranium after about 900 years, 99.9% of uranium, plutonium and the minor actinides (Np, Cm and Am) must be separated from the spent fuel (see figure 2). Because of their chemical similarity and their disadvantageous ratio of presence, the minor actinides americium and curium and the lanthanides, which represent about one third of the fission products and are about 20 up to 50 times more abundant, are very difficult to separate. This separation is necessary because lanthanides act as neutron poisons, i.e. they tend to absorb neutrons efficiently.

For instance, the neutron capture cross section for ^{157}Gd is > 250 000 barn. Its fission yield is, however, quite low. More important neutron poisons are ^{143}Nd (330 barn) and ^{149}Sm (> 40 000 barn). Also most lanthanide isotopes are stable and only a few are long-lived radioisotopes, so there is little incentive to transmute them, and furthermore, only a limited amount of elements can be incorporated in the targets. In addition, lanthanides do not form solid solutions in metal alloys or in mixed oxide transmutation targets, and as a result they segregate in separate phases with the tendency to grow under thermal treatment. Minor actinides tend to concentrate in these phases and this will lead to an unacceptable non-uniform heat distribution in the transmutation fuel matrix under irradiation.

Owing to the difficulty of the direct separation, it is foreseen to isolate the minor actinides by means of two extraction cycles: the first cycle should separate the trivalent minor actinides and lanthanides from the bulk of the fission products and the second cycle aims to separate selectively the trivalent actinides from the lanthanides. The resulting MA fraction should contain more than 99.9% of the trivalent actinides and approx. 0.2% of the lanthanide inventory [GEI02]. For the first purpose, a number of partitioning processes have already been developed, for instance the TRUEX and the DIAMEX process. The subsequent actinide/lanthanide separation is, however, more difficult to realise. In Europe, the SANEX (Selective ActiNide(III) EXtraction) process has been developed for this purpose. In the case of a heterogeneous fuel concept where the radionuclides that are to be transmuted are physically separated from the fuel, with transmutation targets containing a high amount of Am and/or Cm, a Ln/An separation factor of about 100 would be needed. Otherwise the target separation factor can be lower. If homogeneous MA transmutation in fast reactors or PWR is foreseen, the development of a process for the Am/Cm separation is required to provide the possibility for a specific transmutation of Am and possibly a specific conditioning of Cm. Because curium is very radioactive (decay heat) and furthermore, it is a neutron source (resulting from spontaneous fission and from α-n reaction in oxide type targets), it is very difficult to include in homogeneous transmutation fuel, where the radionuclides to be transmuted are intimately mixed with the fuel (e.g. UO_2 or MOX). Storage of the separated curium for about a century would allow most of the curium isotopes to decay. The plutonium isotopes resulting from the alpha decay of curium could then be recycled in an advanced fuel cycle. The americium/curium separation is, however, considered to be not necessary if both are conditioned in a ceramic type of matrix, which will be used in ADS type reactors. In the case of heterogeneous MA transmutation in fast reactors or PWR, the need for Am/Cm separation is still unclear.

The partitioning and conditioning (P&C) strategy is considered as an alternative to the P&T strategy. It consists in the immobilisation of the long-lived radionuclides into a stable inert matrix, either as a product for final disposal or as a product for interim storage until transmutation facilities become available. Partitioning followed by geological disposal of the actinides and long-lived fission products could reduce the volume of wastes requiring deep geological disposal and allow less expensive near-surface burial of the shorter-lived fission products. Furthermore, if the separated elements are conditioned in a specifically designed waste form, the long-term stability of such tailored waste forms would probably be easier to assure. It is not necessary to separate the americium-curium fraction in the P&C strategy.

The primary purpose of this report is to qualitatively (or semi-quantitatively) compare the performance of extractants that have been developed for the advanced aqueous reprocessing of spent fuel.

[PHL93, JOS97, KNE00, MER93, BOK89, CHR04, SER05, APO95, MAT01, IAE04, BAE98, PIL02]

2. Scheme of advanced aqueous reprocessing

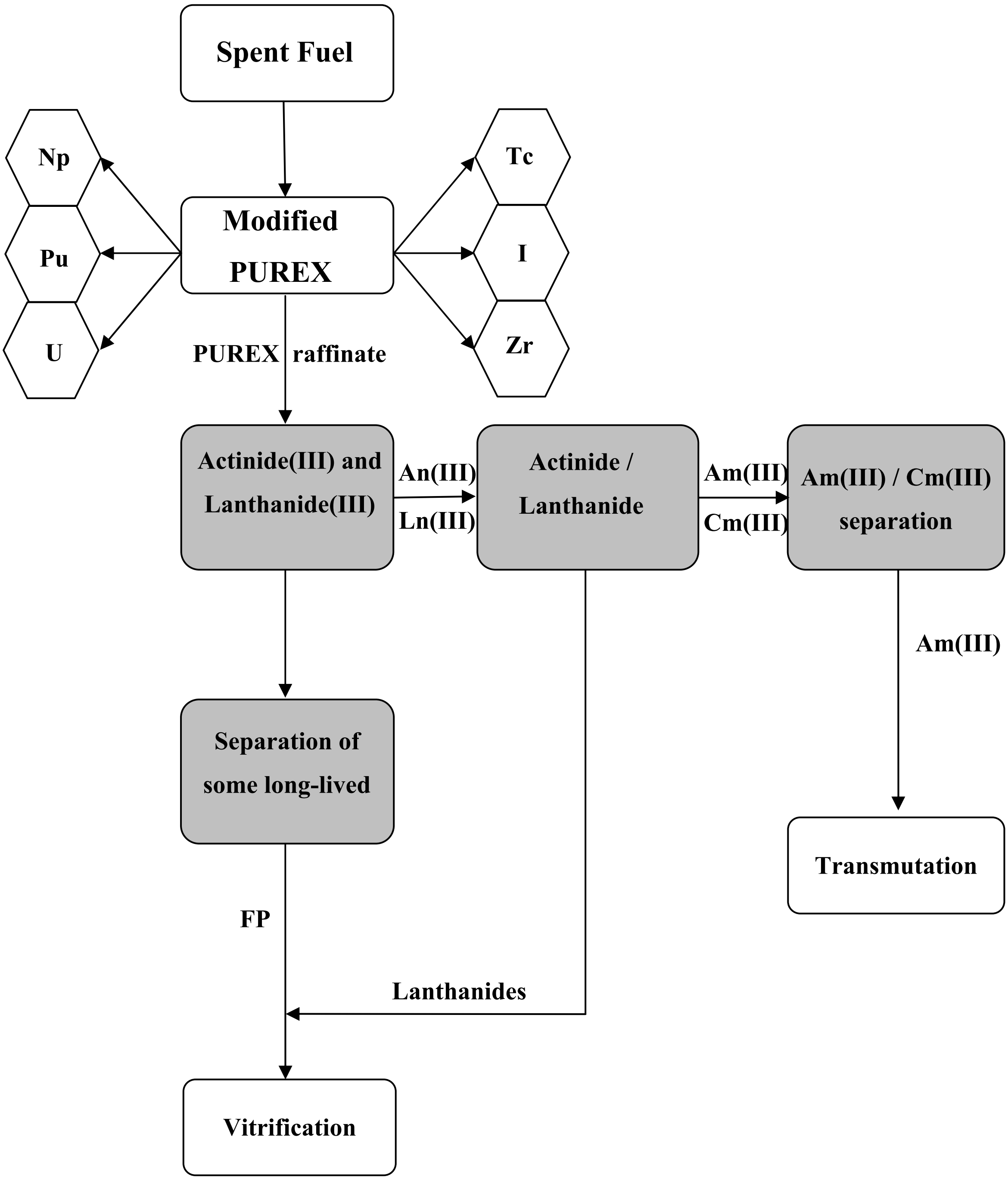


Fig. 3: Example of a general separation scheme for advanced aqueous reprocessing

3. Feed of advanced reprocessing = PUREX HLLW

The head-end of advanced reprocessing is the High-Level Liquid Waste (HLLW) typically originating in the reprocessing of spent nuclear fuel by means of the PUREX process. This HLLW is also called Highly Active Waste (HAW).

3.1. Composition of PUREX HAW solution

The major part of the HAW solution is the aqueous raffinate from the simultaneous extraction of U and Pu in the first extraction cycle of the PUREX process [KOL91]. Most fission products and minor actinides are left in this Highly Active Raffinate (HAR). However, essential fractions of problem elements like Np and Tc can follow U and Pu and must be removed in purification cycles. Raffinates or raffinate concentrates from these purification cycles are added to the HAW. Real HAW solutions have a nitric acid concentration of about 4 M, resulting from the dissolution of the fuel and the extraction of U and Pu in the PUREX process. It further contains corrosion products (dissolver, vessels), and sometimes also Gd(III) which is used in the PUREX process as a neutron poison. The solutions also contain residues of tributyl phosphate (TBP), which is predominantly destroyed to dibutyl and monobutyl phosphate and even to phosphoric acid. This HLLW is seldom a clear solution. A precipitate is deposited from the solution during mere storage in a tank. Precipitation is supported by phosphoric acid. Zirconium phosphate represents the major part of the precipitate, which further contains hydroxides, nitrates, phosphomolybdates, palladium and plutonium. The formation of the precipitate is however not avoided, if dissolved or dispersed remainders of TBP are almost fully removed from the HAW solution e.g. by washing with dodecane [KOL91, BAT78]. It is therefore desirable to wait with the addition of the basic solvent wash solutions resulting from the PUREX solvent recycling, which are not contaminated with Am, to the HAW until the TRU elements are removed.

The composition of a simulated HAW solution is shown in table 1 and corresponds to a volume of 5000 L/t UOx fuel with stainless steel cladding and an initial enrichment of 3.3%, released from a PWR after an average thermal burn-up of 33000 MWd/t_{HM} and reprocessed after a cooling down period of 150 days after release from the reactor core [CEC77, CEC78, KOL91]. The composition has been calculated considering the values given by the software code

ORIGEN, the fact that the fuel has been separated from its cladding (chop-and-leach procedure), which contained certain corrosion products, U and Pu purification cycles and solvent regeneration [CEC78].

Tab. 1: *Composition of a HAW solution (4 M* HNO_3*) [CEC77, CEC78, KOL91, KOL98A].*

Fission Products (g/l)					
Ag	1.2×10^{-2}	I	0.054	Sb	3.5×10^{-3}
As	1.75×10^{-5}	In	2.4×10^{-4}	Se	0.01
Ba	0.278	La	0.254	Sm	0.16
Br	3×10^{-3}	Mo	0.69	Sn	0.011
Cd	0.017	Nd	0.78	Sr	0.18
Ce	0.576	Pd	0.26	Tb	3.5×10^{-4}
Cs	0.544	Pr	0.24	Tc	0.16
Eu	0.036	Rb	0.066	Te	0.113
Gd	0.021	Rh	0.08	Y	0.094
Ge	7×10^{-5}	Ru	0.45	Zr	0.73

Actinides (g/l)					
U	0.95		$1.52 \times 10^{-2} \leq$	Np	$\leq 1.52 \times 10^{-1}$
Pu	9.08×10^{-3}	Am	3.06×10^{-2}	Cm	7.06×10^{-3}

Corrosion Products (g/l)					
Cr	0.096	Ni	0.047	Cu	0.02
Zn	0.024	Al	0.0021		

Products originating from U and Pu purification and solvent regeneration (g/l)			
Na	1.61	Fe	1.88

For transuranic elements extraction by certain agents, e.g. diisodecylphosphoric acid (DIDPA), the nitric acid concentration in the HAR solution has to be lowered. Lower nitric acid concentrations can be obtained by denitration with an organic reductant such as formic acid, formaldehyde, sugar, etc [CEC86]. As a result of the denitration of simulated HAR solutions by formic acid, Zr, Mo and Te were separated from the solution as precipitate [KON94].

This could be advantageous, because these elements are often co-extracted with TRU elements during advanced reprocessing. However, at an acidity below 0.5 M HNO_3, co-precipitation of lanthanides and actinides occurs [LEE95].

3.2. PUREX HAC solution

The current waste management of HAW solutions is concentration/denitration and immobilisation by means of vitrification for final storage in a deep geological repository. After the initial concentration of HAW in an evaporator, where the volume is usually reduced by a factor 10, the resulting Highly Active Concentrate (HAC) is intermediately stored for several years in expensive, cooled and ventilated stainless steel containers until part of the radioactivity has decayed. It would be beneficial if these HAC solutions could be used in the view of industrialisation of the advanced reprocessing, because the volume reduction would reduce the size of the installations to be used, and thus the costs.

The original HAC solution has a nitric acid concentration of 4 to 6 M. In order to reduce corrosion of the stainless steel containers, the nitric acid concentration is usually reduced to 1 to 2 M. Neutralisation of HNO_3 with alkali should be avoided because of the increase of the salt content in the waste. If wastes with high concentrations of nitrate salts have to be solidified, the nitrates will significantly increase the storage volume and, furthermore, affect the integrity of the vitrified waste form. Removing nitric acid or nitrate from aqueous solutions by chemical reduction is not a straightforward operation [FAN00]. Unfortunately, there is no reducing agent that can be mixed directly with a nitric acid solution at room temperature to rapidly reduce nitric acid. The reactions are kinetically controlled, not thermodynamically. A catalyst is required, high pressure, heat or another energy source needs to be applied. The mostly applied way for the removal of nitric acid is the chemical denitration with formic acid because, besides H_2O, only gaseous products (CO_x , N_2O, NH_3, N_2 and NO_x) are the result. This reaction is governed by a complex reaction mechanism, in which nitrous acid (HNO_2) is an important reaction intermediate [LON54, FAN00, CEC86]. A drawback of the process of homogeneous denitration is the relatively long induction period, which is related to the formation of nitrous acid. This induction period can be shortened by heating the solution to the boiling point [CEC86], by adding $NaNO_2$ to the reaction mixture [KUB79], or by using a catalyst. Platinum supported on

SiO_2 significantly reduces the induction period by promoting the formation of HNO_2 [GUE00]. More recently, activated carbon has been reported as an alternative catalyst, which is not prone to metal leaching due to the concentrated acid medium like platinum catalysts [MIY04]. The denitration reaction starts, sometimes violently, after the induction period and a reaction time of several hours is necessary. In average, 1.65 mol formic acid are consumed per mol HNO_3 destroyed [KOL91]. The violent start of the reaction can be prevented by adding nitrite to the reaction mixture. Prolonged reaction with excess of formic acid results in the reduction of the nitrate ion to ammonia, and a pH value as high as 9 can be obtained. The volume increase of the waste solution due to denitration is less than 5% [SHI92].

Unfortunately, precipitate formation is intensified if HAW solutions are concentrated [KOL91]. Precipitation is accelerated by temperature increase and by lowering the nitric acid concentration. The precipitate formation is particularly intensive if a HAW solution is simultaneously concentrated by evaporation and denitrated. Recently, a genuine HAC solution has been prepared and investigated at ITU [SER05]. The precipitate formed after the concentration/denitration to obtain a MOX HAC with a final concentration factor (CF) of about 10 (5 compared to industrial HAR) and an acidity of 4 M mainly composed of Sr, Zr, Mo, Sn and Ba. Minor actinides precipitation was not significant (<0.001%). If the HNO_3 concentration of a simulated HAC solution did not decrease below 2.5 M the denitration by formic acid caused the formation of < 1 g solid per kg fuel [KOL91]. The amount of solids increased to about 15 g per kg fuel if the acid concentration was suppressed to ~ 1 M. The precipitate retains a fraction of the actinides and fission products, and the fractions retained are strongly increased with decreasing resulting HNO_3 concentration in the concentrate. Precipitates resulting from the entire process of concentration and denitration to 4-5M HNO_3, interim storage and final denitration to 0.1 – 0.2 M nitric acid represent about 5% of the volume of the final denitrated HAC solution (500L/t fuel) [CEC77]. After leaching with hot 4 M HNO_3, less than 0.1% of trivalent actinides, but 2-10% of Pu (probably polymeric) remains in the precipitate. Only treatment of the precipitate with hydrogen halides, like HCl, can provide for a complete decontamination, which is important in the view of the reduction of the long-term radiotoxicity of HLW. Nitric acid wash solutions could be recycled in the denitration equipment, after the removal of Pu, but HCl solutions are more problematic because of the corrosive properties of HCl against stainless steel which is generally used as a material of equipments in reprocessing plants. To omit Pu precipitation, an extraction of Pu, Zr and Mo with 0.25 M di(2-ethylhexyl)phosphoric acid (HDEHP) in mesitylene or an extraction of Pu by TBP in advance of the final denitration has been proposed. Although the mechanism of Pu precipitation is not clearly known, the results of Shirahashi et al [SHI92] indicate that Pu is not precipitated itself by polymerisation or hydrolysis, but coprecipitated with elements such as Mo, Zr, Te and Ru. They also discovered that the precipitate can be completely dissolved in 0.5 M oxalic acid solutions. Oxalic acid is also used to dissolve the sludge (precipitate) formed in stored HLLW. It has the advantage that it can be decomposed by HNO_3 and it is little corrosive. This way TRU elements can be easily recovered.

A disadvantage of the denitration reaction with formic acid is the hazard of explosion [CEC86]. Formic acid can form explosive gas mixtures of air and formic acid. After the induction period, the denitration reaction can become violent, which results in a violent gas production. Furthermore, if noble metals are present in the HLLW solution, and the addition of the HLLW solution to the denitration reactor containing formic acid is interrupted, or to slow, the denitration can become unsteady due to catalytic decomposition of formic acid at Pd if the nitric acid concentration becomes too low. One of the reaction products of the latter reaction is H_2 gas. A strict control of the reactant flow rates should avoid any hardly development of the denitration process.

4. Separation methods for advanced aqueous reprocessing

4.1. Solvent extraction or liquid-liquid extraction

In liquid-liquid extraction, an organic extracting agent, which complexes the elements of interest very well, is dissolved in an organic solvent. Sometimes a second extracting agent is added, which performs a synergistic enhancement of the extraction capacity by completing the dehydration of the metal cation. This solution is contacted intensively with an aqueous solution containing the species of interest. The technique is based on the formation of uncharged organic metal complexes which are preferably soluble in organic solvents. The four main types of such complexes are:

- organic chelate complexes e.g. plutonium tetra-acetylacetonate ($PuAa_4$)
- inorganic metal complexes (with neutral charge) forming adducts with solvating (neutral) organic molecules like tributyl phosphate (TBP) e.g. $UO_2(NO_3)_2 \cdot 2TBP$ and $Pu(NO_3)_4 \cdot 2TPB$
- ion pair complexes between large organic cations, sometimes called liquid anion exchanger, e.g. quaternary amines like Aliquat™ • 336 and negatively charged inorganic complexes e.g. $UO_2(SO_4)_3^{4-}$
- metal complexes with organic acids, which are in fact liquid cation exchangers

[CHO95A, SUD86]

In a separatory funnel containing two immiscible liquids, a very polar aqueous phase and a very nonpolar organic phase such as hexane, the lighter phase, which is usually the organic phase will rise to the top as a distinct upper layer. If the contents of the funnel were stoppered and shaken a separation would be achieved according to the principle ‘like likes like’: the polar aqueous solvent attracts the more polar compounds and the more nonpolar compounds dissolve in the relatively nonpolar upper layer.

The extraction of a solute into the organic phase will reach an equilibrium according to the distribution law of Nernst:

$$D = \frac{C_{org}}{C_{aq}} \qquad \textit{Eq. 1}$$

D = distribution coefficient

C_{org} = concentration of the species of interest in the organic phase

C_{aq} = concentration of the species of interest in the aqueous phase

After thorough mixing of both phases, the next step is the phase separation in one organic and one aqueous phase. On a laboratory scale, this is done by removing the stopper of the separatory funnel, opening its stopcock and drawing off the aqueous layer as demonstrated in Fig. 4 or, for smaller volumes, even with a small vessel and a pipet.

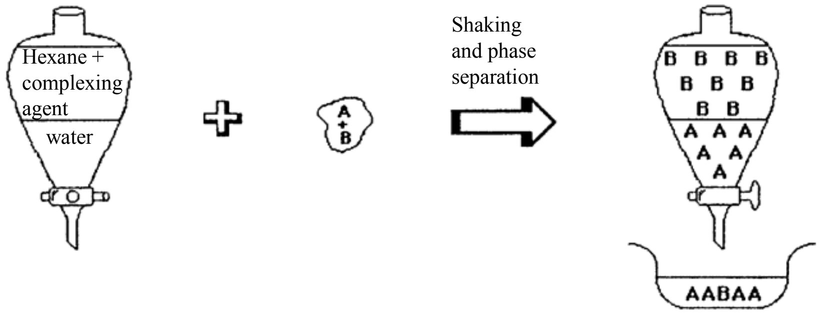


Fig. 4: *Separation of two elements, A and B. The complex of B has a high stability constant and thus B has a high distribution coefficient. A, whose complex has a very low stability constant, prefers the aqueous phase. [MCM94]*

Often the organo-metal complex will still have a certain affinity to water. In order to decrease that affinity, an ionic salt like NaCl or $Al(NO_3)_3$ can be added to the water phase. This will increase the ionic strength of the water and drive the non-polar hydrophobic compounds into the organic phase. The ions from the salt solution that has been added will attract the water molecules in an effort to solvate the ions, leading to a lower H_2O activity. This releases the water molecules from any solvation with non-polar compounds. The result of the lower H_2O activity, known as “salting-out”, is a higher distribution coefficient.

It is better to use the whole volume of extraction solution in two equal parts and do two subsequent extractions instead of one extraction with the whole volume. The first reason is that in practice it is not possible to completely separate the two phases. A small amount of the organic phase is always left which deteriorates the separation. The second extraction has a wash effect and improves the quality of separation. The enormous improvement in separation is the second and most important reason. The amount of the species left in the aqueous phase can be calculated by the following equation, which is derived from the distribution law.

$$m_a = \frac{m_t}{\left(\frac{D \cdot V_o}{V_a} + 1\right)^n} = \frac{m_t}{(P+1)^n} \qquad \textit{Eq. 2}$$

m_a = amount of the species of interest left in the aqueous phase
m_t = total amount of the species of interest
V_a = volume of aqueous phase
V_o = volume of organic phase used for one extraction
n = number of extractions

The ratio V_o/V_a is called the phase volume ratio, θ. The partition (or extraction) coefficient, P, is defined by:

$$P = D \cdot \theta = D \cdot \frac{V_o}{V_a} = \frac{m_o}{m_a} \qquad \textit{Eq. 3}$$

From the value of m_a, the decontamination factor, f_D, can be calculated by:

$$f_D = \frac{m_a}{m_t} \qquad \textit{Eq. 4}$$

Alternatively, the decontamination factor, DF, is defined by:

$$DF = \frac{m_t}{m_a} \qquad \textit{Eq. 5}$$

It can be clearly seen from Eq 2 and Eq 4 and from Fig. 5 that the improvement in separation by multiple extractions with the same total amount of organic phase is strongly dependent on the distribution coefficient.

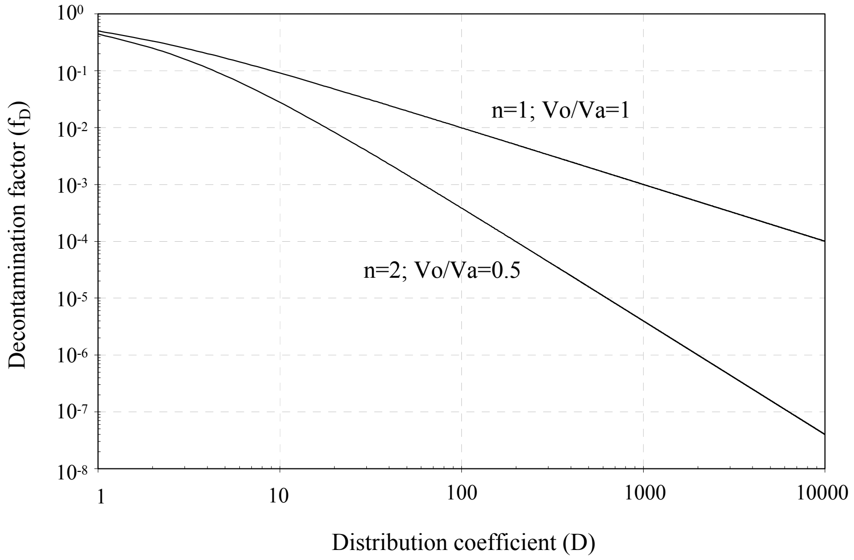


Fig. 5: Dependence of the decontamination factor, f_D, on the distribution coefficient, D, according to the distribution law for two situations: in the first separation only one extraction was performed with an equal volume of aqueous and organic phase, in the second situation the solute was extracted from the aqueous phase by two subsequent extractions, each with half of the total volume of the organic phase. The volume of the aqueous phase and the total volume of the organic phase are equal in both situations. [KÜP97]

An important characteristic of the extractant is that it should have a high selectivity for the species of interest, i. e. only the species of interest should have a high affinity for the extractant and impurities should have a distribution coefficient as small as possible. This selectivity is described by the separation factor, SF:

$$SF = \frac{D_{\text{species of interest}}}{D_{\text{impurity}}} \qquad \textit{Eq. 6}$$

[KÜP97, RYD92, CHO95A]

Especially for the separation of radioactive products, the ideal extracting agent should have the following characteristics: [MER83]

- a high capacity for those elements we want to isolate
- selectivity against other elements
- good solubility in aliphatic diluents
- good resistance to the nitric acid in which the radionuclides are usually dissolved
- good resistance to radiolysis
- thermal stability
- separation efficiency remains during several cycles (no poisoning of the extraction agent by metals)
- density differs a lot from the density of water so that fast phase separation is possible
- low tendency to form emulsions to avoid third phase formation
- low inflammability
- possibility of recycling
- the extracted isotopes can by back-extracted quantitatively under mild chemical conditions (to be avoided is the use of complexants decomposing to precipitate forming products in the aqueous phase or which could interfere with the subsequent treatment of the partitioned waste)
- does not require large amounts of salting out agents (e.g. $Al(NO_3)_3$) which put a strain on the waste stream

During the last years, it has become fashionable to use completely incinerable extraction agents to minimize the amount of residual ash produced when the reagents are destroyed subsequent to their application. These reagents do not contain other elements than carbon, hydrogen, oxygen and nitrogen (so called CHON principle). A lot of efforts have been made to develop nitrogen containing complexants in stead of organophosphorous reagents in actinide separation processes. One should, however, be aware that whatever process is employed, total process design, from reagent synthesis through process development to waste disposal, should be considered all times. Thus, although the development of incinerable extractants is a reasonable objective, it may ultimately prove equally acceptable to take advantage of the favourable characteristics of organophosphorous reagents, that is the controllable thermal and radiolytic stability, and choose a waste form more compatible with the incinerator ash generated, e.g. phosphate glass. [NAS00]

Synergistic solvent extraction systems are frequently used because the synergistic adduct (e.g. TBP or TOPO) completes the dehydration of the actinide cation and it makes the stoichiometry usually consistent and predictable. The need to dehydrate, fully or partially, the metal ion prior to extraction into the organic phase is an important factor in extractant success. A common feature of synergistic extraction systems is thus an increased extraction strength. Unfortunately, this is generally at the expense of selectivity. [CHO95B, NAS97]

It is recommended to use an alkane diluent during the first two extraction cycles of an advanced aqueous reprocessing process. This is reasoned by the higher chemical and radiation stability of paraffinic diluents in comparison with e.g. aromatic ones. Good properties are exhibited by the highly branched French diluent TPH (tetrapropyl hydrogène), which mainly consists of highly branched dodecane, namely 1,1,2,2,3,3,4,4-octamethyl-butane. In comparison with n-paraffines, the branching enhances the ability of the diluent to dissolve extractants of different types. Also the solubility of extracted complexes can be expected to be higher in TPH than in n-paraffines, which helps to avoid third phase formation. [KOL98A]

The big advantage of liquid-liquid extraction is the fact that besides a batch process it can be performed as a continuous process. Continuous processes are preferred in industry. The most common and simple liquid-liquid extraction equipment is the mixer-settler. It contains a mixing part for the efficient transfer of the solute between the two phases and a settling part for an efficient phase separation. In the uranium industry (uranium production and fuel reprocessing), a single mixer-settler may hold as much as 1000 m^3. The mixer-settlers, each corresponding to a single extraction stage, are arranged in batteries. In these batteries, the aqueous and organic phases flow counter to each other. Besides the extraction stages, there are also washing (or scrubbing) stage(s), in which the loaded organic phase will be cleaned of the impurities that were also extracted by contacting it with a clean aqueous solution. Washing is not the same as stripping. During the stripping (or back extraction) stage the desired species will be back extracted to a new aqueous phase. The composition of this aqueous phase is chosen so that the distribution coefficient of the desired species will be very low, so good stripping efficiency can be obtained using a minimum amount of aqueous phase and chemicals. If no additional purification is desired after extraction and the extractant is volatile, the organic phase may be distilled, leaving a pure solid product. Mixer-settlers provide good mixing and reasonably good phase separation performance, but unfortunately require a rather large liquid inventory (hold-up). They are also relatively sensitive to crud (impurities forming a precipitate with the decay products of the extractant, usually at the interphase border) due to the mechanical moving parts (stirrer).

In the reprocessing industry, the extraction equipment must be very reliable, have a high stage efficiency, short contact times, small hold-up, be easy to decontaminate and to service and not least be resistant to criticality. High reliability usually means simple design and few moving parts. Packed columns have this simple design. These are long columns (10-20 m with 0.3-3 m ∅) filled with small pieces of material obstructing a straight flow through the column. The aqueous phase enters the column at the upper end and the organic phase at the lower end. The flow is by gravity. However, these columns do not have high stage efficiency because this requires mechanical agitation of the two phases and a good phase separation. Good mixing is provided by a pulse generator in the pulsed column technology. These columns are divided into “settling chambers” by horizontal perforated plates (sieves). In the down movement, the aqueous phase is forced through the sieves, forming droplets. These droplets fall through the lighter organic phase, which is already separated from the phase mixture and is about ¼ of the interplate distance, and merge with the phase mixture. In the upward stroke, organic droplets form and rise through the aqueous phase until they meet the phase mixture. Pulsed columns are relatively insensitive to crud and can be critically safe for high sample throughput if neutron absorbers like hafnium are used in the sieves. They also allow short residence time of the extractant, which is beneficial for decomposition due to radiolysis. Unfortunately, pulsed columns have a poor phase separation.

A phase separation of almost 100% can be obtained with centrifugal extractors. They also effect good mixing and have very small hold-ups. The contact time of the aqueous and organic phase can be made much shorter than in mixer-settlers or columns. The small hold-up volume and the short residence time are favourable for reducing radiation decomposition. Due to the moving parts, centrifugal extractors are very sensitive to crud.

Because of the disadvantage of precipitation being a batch process, continuous solvent extraction processes were developed during the Manhattan Project. One of these processes was the PUREX (Plutonium-Uranium-Recovery by EXtraction) process. The first PUREX plants to operate on an industrial scale were built at Hanford, Washington, during the Manhattan Project. The initial plant was built before the final parameters of the extraction process were well defined. This plant was developed for the military goal of plutonium weapons production. Later, the PUREX process also became important for the reprocessing of spent nuclear fuel from the civil application of nuclear energy. Packed columns were used in the first Windscale plant at

Sellafield (UK). Pulsed columns were used at Hanford (USA), in the old Eurochemie plant at Mol (Belgium) and are currently in use in the newer La Hague (France) plants and in the THORP (Thermal Oxide Reprocessing Plant) plants at Sellafield. Mixer-settlers have been used at Savannah River (USA), in the Magnox Encapsulation Plant (MEP) at Sellafield and at La Hague. Centrifugal extractors were installed at Savannah River and at La Hague. The USA closed all reprocessing plants since they opted for direct disposal of spent fuel and they do not want to produce plutonium any more. But the PUREX process is still used in reprocessing plants in the U. K., France, Japan and Russia.

For advanced aqueous reprocessing centrifugal extractors are receiving more and more attention. This is related to their small hold-up volume and short residence time. These type of contactors are the most compact solvent extraction systems and thus minimise shielding costs.

[CHO95B, RYD92, MER83, CHO95A, CHI98A]

4.2. Solid Phase Extraction (SPE)

Solid Phase Extraction (SPE), which is also called extraction chromatography, is a technique that is ideally suited for the separation of radionuclides from a wide range of sample types. It combines the selectivity of liquid-liquid extraction with the ease of operation of column chromatography. Separation methods based on SPE, have become increasingly popular in radiochemical analysis. This is due to their simplicity, rapidity, and the savings in reagent and waste disposal costs compared to traditional methods based on ion exchange and liquid-liquid extraction, which has the additional disadvantage of being sensitive to cross contamination [PIL00]. Another possible application of extraction chromatographic resins could be their use in the front chromatographic mode for the removal of radionuclides from limited volumes of liquid waste on a technical scale, for instance by using the twin column concept developed by Wenzel [WEN94, WEN95]. A transportable frontal chromatographic unit for industrial scale decontamination purposes using fraternal twins has recently been reported [WEN04A, WEN04B]. Also for actinide recovery from PUREX HAW and other HLW solutions, SPE resins have gained interest, e.g. [LUM93, MAT95, WEI00]. Compared to U and Pu, the minor actinides are significantly less abundant in spent nuclear fuel, so the scale of a separation process for minor actinides from HAW solutions should be considerably smaller than that of the PUREX process. A partitioning process based on extraction chromatography would use only a minimum amount of organic compounds and a compact equipment to separate the minor actinides (and lanthanides) from the nitrate acidic HLLW [WEI00]. Column instability remains a significant obstacle, however, to the process-scale application of extraction chromatography [DIE99]. Most immobilized extractants tend to "bleed" from the inert matrix as the aqueous eluent transits the column [MAT01]. Furthermore, organic extractants are usually quite sensitive to radiolysis, thermolysis and/or hydrolysis.

A solid phase extraction system consists of three major components: an inert support, a stationary phase, and a mobile phase. The depiction of a portion of an SPE resin bead can be seen in Fig. 6.

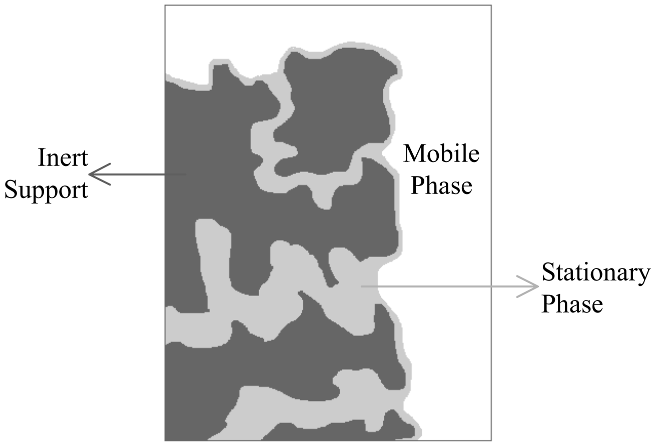


Fig. 6: Depiction of SPE surface of a porous bead. [HOR02]

The inert support can be a silica gel or a polymeric resin like polymethacrylate or polystyrene divinylbenzene copolymer ranging in size between 50 and 150 µm in diameter. These macroporous polymeric resins, having a rigid three-dimensional structure, are most suitable to incorporate large amounts of extractants due to the high specific surface area (150-900 m^2/g), high mechanical strength, and rather low solvent swelling during the impregnation process [JUA99]. In general their average pore diameter is 4-9 nm and they have a pore volume of 0.6-1.1 cm^3/g. This results in a porosity of 0.4-0.6.

The stationary phase usually consists of organic extractants. Most of these extractants are already well known from liquid-liquid extraction. Their characteristics and the way in which uncharged complexes with metals are formed are usually the same as described for liquid-liquid extraction. The extractant can be a single compound or a synergist can be added. Solvents or solvent modifiers can be used to help solubilise the extractant and to increase the hydrophobicity of the stationary phase [HOR02].

The inert support can be impregnated by means of four methods: the wet and the dry impregnation method, the modifier addition method and the dynamic column method [JUA99]. The dry method is mostly used. The extractant is dissolved in an organic solvent and porous beads are added to the solution. The solvent is then completely removed slowly by evaporation or distillation under vacuum. This method is most successful in the impregnation of hydrophilic extractants such as amines, ethers, esters and ketones. Wet impregnation means that the inert support is placed in contact with a mixture of the extractant and a pre-calculated amount of solvent (usually n-hexane or ethanol). After the resin has had the time to swell and all the liquid is absorbed, it will be submerged in a metal salt solution to form a metal-extractant complex. After completion of complex formation, the resin is washed with excessive amounts of deionised water and the metal is removed from the resin for instance by contact with acid before it is washed for a final time in deionised water. Alternatively, the metal-extractant complex is formed first in the liquid phase and then directly impregnated. Using the wet method some of the solvent remains on the surface of the inert support. In this solvent layer, the extractant molecules get the chance to move to the surface of the inert support and organise themselves into a micelle [MUR98A, MUR98B]. After application of the dry impregnation method, where the solvent has been completely removed, the extracting agent forms more or less a homogeneous layer on the surface of the inert support. If an SPE resin made according to the dry impregnation method comes into contact with an aqueous phase, only a partial micellisation will occur, i.e. only the extractant molecules on the surface are able to organise themselves in a micelle. The modifier addition method is considered to be a hybrid of the wet and dry impregnation method. A modifier such as dibutylpolypropylene glycol, which promotes the penetration of water into the polymer, is added. The solvent is evaporated as in the dry method. For impregnation of the support by the dynamic column method, the polymer resin is contacted first with the solvent until it has become fully swelled. Then it is packed into a column and a solution of the extractant is passed through the column until the inlet and outlet concentrations of the extractant are the same. The resulting resin is finally washed with water. In all of the above methods the actual mechanism of impregnation is identical and is the result of physical interactions, not covalent bond formation between the extractant and the support.

Impregnation is mostly a combination of pore filling and surface adsorption. The extractant gradually fills the pore space starting with the smallest pores and moving up to pores of about

10 nm and then surface adsorption becomes the dominant force [GUA90, JUA99]. Interaction between the extractant and support is usually quite weak, consisting of only the attractive forces between alkyl chains and/or aromatic rings of the ligand and those of the support [DIE99]. In contrast to partition chromatography, in which the partitioning solute undergoes little, if any, chemical change, the sorption of a metal in SPE involves complex chemical changes associated with the conversion of a hydrated metal ion into a neutral organophilic metal complex, just as in liquid-liquid extraction [DIE99].

In order to perform a separation, the SPE resin is slurry-packed in a glass column (this can be a capillary pipette plugged with glass wool) or in a syringe barrel, where it is trapped between two inert filters. The syringe barrels are designed to be used with either a special cap and a syringe to push the sample and solvent through the cartridge or a vacuum apparatus to pull solvent and sample through the packed resin bed into a test tube for collection. Larger glass columns are used in combination with a pump. Once the sample is on the SPE column, it can be washed to remove impurities and then eluted in a step-by-step manner with different mobile phases. In radiochemical separations the mobile phase is usually an acid solution, e.g. nitric or hydrochloric acid. Aqueous solutions containing complexing agents like oxalic acid are frequently used to enhance selectivity or the stripping of strongly retained metal ions from the column.
[HOR02, PIL00, MUR98A, MAI00, MCM94]

Radionuclides can be extracted by a solid phase extraction resin which is filled into a glass or plastic column. By using a suitable mobile phase, usually an acid, they can be eluted from the column. In Fig. 7 the breakthrough of a solute from an SPE column is illustrated.

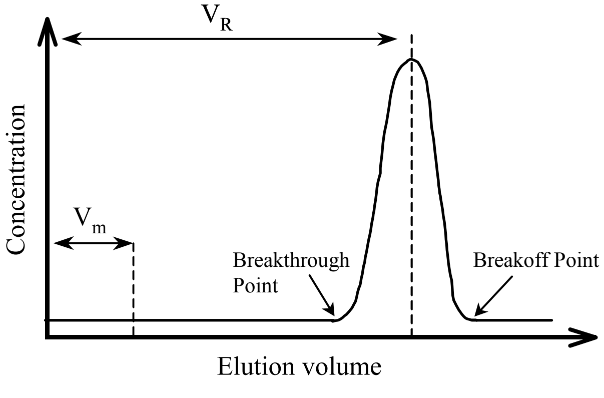


Fig. 7: Breakthrough Curve of an SPE resin

The chromatographic peak has the form of a Gauss curve. It starts at the breakthrough point. The breakthrough volume is the volume of mobile phase after which the solute starts leaving the column. V_R is the retention volume, i.e. the volume of mobile phase necessary to reach the centre of the peak. The end of the peak is called the breakoff point and the volume of mobile phase needed to reach this point is the breakoff volume. V_m is the volume of mobile phase contained in the column. It is also called the free column volume (FCV). This volume needs to be washed out before the real elution of the solute starts. The retention of the solute is therefore actually characterised by the net retention volume:

$$V_R' = V_R - V_m \qquad \textit{Eq. 7}$$

An important variable in SPE is the retention factor, capacity factor or relative retention, k'. k' is a measure of the retention of the solute relative to the volume of the mobile phase, V_m, i.e. it is the number of free column volumes necessary to reach the peak maximum. The relationship between k' and the distribution coefficient (or distribution ratio), D, as measured in a liquid-liquid extraction system is shown below:

$$k' = \frac{V_R - V_m}{V_m} = D \cdot \frac{V_s}{V_m} = \frac{D}{\beta} = \frac{m_s}{m_m} \qquad \textit{Eq. 8}$$

V_s is the volume of the stationary phase. The phase ratio, $\beta = V_m/V_s$, is a characteristic of a column containing the specific SPE resin. m_s and m_m are the amount of solute in the solid and mobile phase, respectively.

D and k' are usually not measured directly for an SPE system, but calculated from the weight distribution ratio or weight distribution coefficient, which can be easily measured by means of a batch experiment. During this experiment a certain amount of SPE resin is weighed and a certain volume of aqueous solution with a known concentration (or activity) of solute is added. The suspension is shaken extensively and then the two phases are separated and the concentration (or activity) of the solute in the aqueous phase is determined. According to the volume distribution coefficient or volume distribution ratio, D, in liquid-liquid extraction, the dry weight distribution ratio, D_w, is defined by:

$$D_w = \frac{m_s}{m_a} \times \frac{V_a}{W_r} = \frac{C_0 - C_a}{C_a} \times \frac{V_a}{W_r} = \frac{A_0 - A_a}{A_a} \times \frac{V_a}{W_r} \qquad \text{Eq. 9}$$

$$[D_w] = \mathrm{dm}^3/\mathrm{kg}$$

with: W_r the weight of the resin, C_0 and A_0 the concentration or activity in a known volume of the solute in the liquid phase before extraction, and C_a and A_a the same after extraction.

D and k‘ are then calculated according to the following equations:

$$D = D_w \cdot \frac{W_r}{V_s} \qquad \text{Eq. 10}$$

$$k' = D \cdot \frac{V_s}{V_m} = D_w \cdot \frac{W_r}{V_m} \qquad \text{Eq. 11}$$

The volume of the stationary phase per gram of resin (V_s/W_r) is obtained from its weight percent sorbed on the inert support and its density. The quantity V_m can be calculated from the weight of resin required to fill a column to a known volume and the results of a pycnometric density determination. A certain weight of the resin is filled into a volumetric flask of e.g. 100 mL and water is added to the 100 mL mark of the flask. The volume of water added can be determined by weighing the flask before and after the addition of the water. The pycnometric volume of the weighed amount of resin is thus the 100 mL – the volume water added. V_m is thus the difference of the volume of the empty column and the pycnometric volume of the amount of resin necessary to fill the column.

Details of the measurement of V_s and V_m and the calculation of D and k’ can be found in [HOR92], [HOR95] and [HOR97].

It is important to note that the concentration of the extractant in the stationary phase of an SPE resin is much higher than in solvent extraction systems, resulting in much higher D values.

Analogous to liquid-liquid extraction, the selectivity of the SPE column for one component to the other is defined by the separation factor, SF:

$$SF = \frac{D_2}{D_1} = \frac{k'_2}{k'_1} = \frac{V_{R,2} - V_m}{V_{R,1} - V_m} \qquad \text{Eq. 12}$$

For most SPE resins used in radiochemistry, the D_w value for the radionuclides is acid-dependent as is also the case in liquid-liquid extraction. Therefore, it is often necessary to change the acid concentration to elute the analytes because the k' value of the sorbed species is usually too high in the eluent used to equilibrate the column, dilute the sample and wash the column after the sample is applied to the column. The suitable acid concentration to selectively elute one or more analytes can be derived from graphs depicting the acid dependence of the D_w or k' value.

To avoid an early breakthrough and to avoid excessive cross-contamination of the elements that one is trying to separate, band spreading must be sufficiently small. Even if the extractants comprising the stationary phase exhibit very high selectivity, poor column efficiency, as manifested in excessive band spreading, can result in essentially no practical separation. Factors influencing band spreading are the specific chemical system, the particle size and porosity of the support, the extractant loading, operating temperature and mobile phase velocity.

[MAI00, HOR02, ANS04]

5. Lanthanide-Actinide(III) co-extraction

For the further partitioning of the spent fuel after its reprocessing, several processes have been developed for the separation of the group 3 elements. The most famous one, the TRUEX (TRansUranium Extraction) process, was developed in the 1980s to compensate for the lack of extraction of trivalent actinides in the PUREX process. Due to their high extraction ability of trivalent actinides from highly acidic media, bifunctional oxygen-donor extractants are preferred in the first extraction cycle of the advanced aqueous reprocessing. Such extractants possess no selectivity for trivalent actinides over lanthanides. Hence, they are co-extracted and will also accompany Am and Cm during their stripping with diluted nitric acid. Irrespective of the extractant used, Zr(IV) and Mo(VI) tend to be co-extracted with the actinides and the lanthanides in the first cycle. Their co-extraction has to be prevented, preferably by complexing these two elements in the feed stream [KOL98A].

The most important extractants for the common extraction of An(III) and Ln(III) are discussed below. They have been ordered according to the classification of the four basic classes of metal extractants [SUD86, KOL91]. According to Sudderth and Kordosky [SUD86] there are four basic classes of metal extractants on the basis of structure, extraction and stripping chemistry, and the metal species extracted. The four classes are: solvating or neutral extractants, chelating extractants, organic acid extractants and ion pairing extractants.

5.1. Solvating or neutral extractants

Up to now, solvating extractants do not separate the actinides(III) from the lanthanides(III). In the absence of particular complexants, transplutonium elements and light lanthanides exhibit a very similar extractability. [KOL91]

5.1.1. Monofunctional organophosphorous extractants

5.1.1.1. TBP

In the seventies, a solvent extraction process for the An(III)-Ln(III) co-extraction from PUREX HAC solutions, based on the PUREX reagent tributyl phosphate (TBP) has been developed at Ispra. Unfortunately even undiluted TBP extracts the trivalent An and Ln too weakly from HAW solutions. Large amounts of salting out reagents are needed for a higher extraction efficiency. After denitration to 0.1 – 0.2 M HNO_3 and addition of 0.65M $Al(NO_3)_3$ and 1.6M $NaNO_3$, $D_{Am} > 1$ is reached. Then a 30% solution of TBP in dodecane extracts 99.4% Am in three subsequent contacts. Actinides (minor actinides as well as Pu) and rare earths can be back-extracted with 0.05 M diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA) in 1M glycolic acid at pH 3, which is the aqueous phase for the TALSPEAK process. A subsequent rare earth / actinide separation was foreseen by means of the TALSPEAK process.

Because of the large amount of salting out reagents required, only HAC solutions can be treated with TBP. For the treatment of non-concentrated HAW solutions, the addition of 1.7 tons of $NaNO_3$ and $Al(NO_3)_3$ per ton spent fuel would be required. A difficult nitrate recycling process would be necessary since this amount is incompatible with the vitrification process. Furthermore, the phase ratio is unfavourable, namely org/aq = 3 and the extraction is little selective, because Ru is coextracted.

[CEC77, CEC78, KOL91]

5.1.1.2. TOPO and TRPO

The extractants trioctylphosphine oxide (TOPO) and trialkyl phosphine oxide (TRPO, $R_3P=O$ with $R=C_6\text{-}C_8$) were developed by Chinese researchers as alternative for the PUREX and TRUEX extractants, because these extractants have a better radiolytic stability and are much cheaper than TBP. TOPO has a high selectivity for tetra- and hexavalent actinides, which are usually extracted from concentrated HCl or HNO_3 solutions into 0.1 M TOPO in cyclohexane. TOPO and TRPO extract trivalent actinides and lanthanides quite well, but the HNO_3 concentration in the aqueous phase must be quite low. The An(III) and Ln(III) can be stripped by a concentrated (5 M) nitric acid solution. In the original TRPO process, two more stripping sections have been foreseen. Np and Pu were stripped with oxalic acid and U was stripped with Na_2CO_3. Recently, a simplified TRPO process has been proposed where U, Np and Pu are stripped at once with $(NH_4)_2CO_3$. The resulting solution can be acidified with concentrated nitric acid and added to the PUREX process for recovering U, Pu and Np. The stripping of trivalent

metals with concentrated nitric acid is a disadvantage, because generally low nitric acid concentrations are required for the subsequent An/Ln separation. Another disadvantage is that certain fission products e.g. Zr, Mo tend to interfere.
[ZHU94, ZHU95A, CHO95B, MAI00, ZHU89, KOL91, BAT78, LIU04]

Hot tests of the TRPO process for the removal of TRU elements from a 10 times diluted genuine HLLW solution adjusted to 0.7 M HNO_3 have been carried out by Glatz et al. [GLA95] using miniature centrifugal contactors. Iron(II) sulfamate along with hydroxylamine have been added to reduce Np(V) to Np(IV). TRU elements were almost completely extracted by 30% TRPO in dodecane and very high decontamination factors were obtained. The extracted actinides were stripped into three fractions: 5.5 M HNO_3 stripped Am + Cm, Np + Pu were stripped with 0.6 M oxalic acid and, finally U was stripped with 5% Na_2CO_3. Unfortunately, Tc, Zr and Mo were also extracted in the TRPO process. Zr was stripped together with Pu and Np and Tc and Mo were spread into all process streams. Ru, Pd and Fe were partially extracted and mainly stripped together with Am. Part of Tc and Ru were retained in the spent TRPO solvent.

5.1.1.3. Cyanex 923

5.1.1.3.1. Cyanex 923 solvent extraction process

Cyanex 923 is a commercially available trialkylphosphine oxide extractant (mixture of $R_3P=O$, $R_2R'P=O$, $RR'_2P=O$ and $R'_3P=O$ with $R=C_6$ and $R'=C_8$) similar to TRPO and TOPO. Like TRPO and TOPO, tetra- and hexavalent actinides are more strongly complexed by Cyanex 923 than trivalent actinide ions. The distribution rate of trivalent actinides is high in the acidity range of 0.5-1 M HNO_3. The extractability of An(III) decreases steadily above and below this range.
Cyanex 923 has tendency to third phase formation, particularly in the presence of large concentrations of uranium. To prevent third phase formation, U should be extracted beforehand, for instance by PUREX solvent, or a mixture of 30% Cyanex 923 and 20% of the solvent modifier TBP in n-dodecane can be used as solvent. Furthermore, other extractable elements like e.g. Fe, Cr, Al, Ni strongly compete with the An(III) extraction.
[CHR04, APO95, ANS04]

5.1.1.3.2. Cyanex 923 extraction chromatographic resin

Cyanex 923 has been applied on Chromosorb-W as inert support [ANS04]. The distribution of metal ions as a function of the nitric acid concentration was similar to the solvent extraction process. Column experiments have been carried out with simulated HLLW solutions. These experiments revealed that the reusability of the column is hampered by the accumulation of metal ions such as Fe, Cr, Al. They were not eluted, either by 8 M HNO3, water, 0.01 M EDTA or 0.03 M hydroxylammonium nitrate.

5.1.2. Bifunctional organophosphorous extractants

5.1.2.1. CMPO

5.1.2.1.1. TRUEX Process

The extractant developed by Horwitz et al. [HOR85, SCH88] for this process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). The ultimate development of the TRUEX process followed more than a decade of intensive investigation of multifunctional organophophorous extractants that combine phosphine oxide or neutral phosphonate functional groups with carbamates [NAS00].

The TRUEX process solvent consists of a standard PUREX process solvent to which CMPO is added for trivalent actinide extractions. This solvent extraction system has the capability of extracting actinides in the tri-, tetra- and hexavalent oxidation states and trivalent lanthanide fission products from nitric or hydrochloric acid media into a normal paraffinic hydrocarbon diluent (e.g. kerosene) which contains 0.2 M CMPO and 1.2 M TBP. All ions are more strongly extracted than they are by PUREX solvent. Extraction of Am^{3+} and Pu^{4+} is readily reversible by changes in the nitric acid concentration while UO_2^{2+} must be stripped from the organic phases using an aqueous complexant, typically oxalate or carbonate. The selectivity of the actinide recovery with TRUEX solvent from a HAW solution can be significantly improved by oxalate complexing. If oxalic acid is added to the HAW solution, the distribution coefficients of the actinides are little influenced, while those of Zr, Mo and Al are substantially suppressed. Unfortunately, oxalate complexing does not improve enough the separation of actinides from the platinum group metals.

A subsequent rare earth / actinide separation was foreseen by means of the TALSPEAK process. [HOR85, SCH88, NAS97, NAS00, KOL91]

A disadvantage of the TRUEX proces is that to keep the solubility of the extracted actinide nitrate CMPO complexes high enough, in other words to avoid third phase formation, the polar solvent modifier TBP has to be added to paraffinic diluents. Then the solvent can contain as much as ≥ 1.4 g-atom/l phosphorous, which is in serious conflict with the CHON principle [KOL98A]. Another drawback of the TRUEX process is the fact that acidic degradation products of the extractant complicate the efficient back extraction of the trivalent metals. Hot counter-current experiments have shown that the distribution ratios of Am(III) and Cm(III) were not low enough in all stages of a battery of centrifugal extractors for their back extraction in 0.05 M HNO_3, which caused a serious build-up in the battery [GLA94].

5.1.2.1.2. CMPO SPE resins

TRU® (TRansUranium elements) resin consists of a tri-n-butyl phosphate (TBP) solution of the bifunctional organophosphorous extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO) sorbed on an inert polymeric substrate, Amberchrom CG 71ms. This resin is derived from the TRUEX solvent extraction process and was one of the first SPE resins available. It was developed by Horwitz et al. [HOR90]. It permits the rapid and selective sorption of tri-, tetra- and hexavalent actinides from nitric acid containing media and, by a careful choice of conditions, their sequential elution. Trivalent species can be eluted with diluted HNO_3 solutions. Tetravalent Pu and Np are eluted with oxalic acid and hexavalent U is eluted with carbonate. However, the complexity of the elution sequence and the number of manipulations required to isolate the individual actinides preclude its use on a stand-alone basis in routine analysis. [HOR90, HOR93A, HOR95]

Also some resins containing only CMPO have been prepared and investigated [MAT95, WEI00]. Since TBP is only used as solvent modifier in the TRUEX process, the characteristics of these resins are much the same as for TRU resin.

The feasibility of using TRU resin for recovery of minor actinides from a neutralised cladding removal waste solution from a Hanford waste tank has been reported [LUM93]. Also the extraction and selective back extraction of U, Pu and Am from an actual PUREX HAW solution by means of a CMPO extraction chromatographic resin has been demonstrated [MAT95].

5.1.3. Bifunctional Diamide extractants

During the last two decades, various diamide extractants with different backbones have been investigated for the treatment of radioactive wastes, especially for the recovery of the minor actinides. Diamides exhibit a good extractability of trivalent actinides and lanthanides. In general, diamides are less effective extractants than CMPO. This desires a rather high diamide concentration in the organic phase but, on the other hand, makes the back-extraction of the trivalent actinides and lanthanides easier [KOL91]. Diamides have, compared to organophophorous extractants like CMPO, some unambiguous advantages. They fulfil the CHON principle, which means that these reagents contain only C, H, O and N atoms. On that account, they are completely incinerable to gaseous products that can be released into the air and produce no radioactive solid waste by combustion, in contrast to phosphorus-based extractants. Other advantages of diamides over organophosphorous extractants are their ease of synthesis, and thus better price, and the innocuous radiolytic and hydrolytic degradation products which do not impede the back-extraction of trivalent actinides and lanthanides with dilute acid solutions. Malonamides in particular have been studied intensively for the development of the DIAMEX solvent extraction process [CUI91A, CUI91B, CUI93, MAD94A, NIG95]. Other diamide extractants investigated include succinamides [TAN99, SHE96] and glutaramides [CHA88, CHA89]. At the Atalante 2000 conference in Avignon, France, new diamide ligands with an ether bridge between the two carbonyl groups, diglycolamides, were presented [SAS00A, SAS01].

5.1.3.1. Malonamides

5.1.3.1.1. DIAMEX process

The DIAMEX (DIAMide Extraction) process, developed in France, uses CHON compatible diamides like N,N’-dimethyl-N,N’-dibutyltetradecyl-1,3-malonamide (DMDBTDMA) as extraction agents dissolved in n-dodecane to extract transuranium elements and lanthanides. Malonamides were first reported in the 1980s by Musikas et al. [MUS87]. They are known to be some of the best bidentate diamide ligands [SAS02]. For the development of an efficient DIAMEX process, several malonamides have been synthesised and their ability to extract actinides and lanthanides from aqueous nitrate media compared [CUI91A, CUI91C, CUI93, NIG95, SPJ97, MAD98]. The conclusions of these investigations were as follows: One of the substitutents at each of the N atoms should be small, preferably methyl, to keep the carbonyl oxygen atoms accessible to the metal ions. For a series of malonamides with different R’ groups (butyl, phenyl and chlorophenyl) as the other substitutent at each of the N groups, it was shown that the less basic the malonamide is the better its extraction properties are, thus the butyl group was most adequate. Furthermore, the tendency to form a third phase decreases with increasing length of the alkyl group at the central C atom of the malonic group, and is further suppressed if the alkyl group is replaced by a long 3-oxa- or 4-oxaalkyl group. The introduction of an oxaalkyl group also enhances the extraction of transplutonium elements. As a result

DMDBTDMA has been proposed as the reference malonamide for the first DIAMEX process. Trivalent actinides and lanthanides are extracted from nitric acid solutions with an acid concentration >2 M by 0.5 M DMDBTDMA in the French TPH solvent [MUS87, MAD98, KOL98A]. The distribution ratios for the extraction of Am, Cm and Ln from HLLW containing 4 M HNO_3 were in the range of 1.5-5. Unfortunately Zr and Mo were extracted to a much higher extent. It has been suggested to complex Zr with 0.05 M ketomalonic acid and Mo with 0.1 M hydrogen peroxide [MAD98]. This way, D_{Zr} is suppressed from 35 to 0.9 and D_{Mo} from 4.5 to 0.3. Oxalic acid, suggested to be used for complexing Zr in the TRUEX process, also complexes both Zr and Mo quite satisfactorily [KOL98A]. Stripping can be easily achieved with diluted nitric acid (<1 M) solutions. The mechanism of the extraction of actinides by malonamides is not completely elucidated. According to [MAD98] it can be simple solvation of neutral actinide nitrates by neutral malonamide molecules, ion-pair formation by anionic nitrate complexes of actinide metal ions with protonated malonamide molecules, or both mechanisms can act simultaneously, in dependence of the nitric acid concentration.

Hot tests of the DIAMEX process with real HLLW have been performed in laboratory scale mixer-settlers [MAD98]. Some fission and corrosion products were also partially extracted (e.g. Fe, Ru, Zr, Mo), but all extracted species, except Ru, could be stripped excellently. The radiolytic stability of the solvent was satisfactory, if it was not aged in the loaded state. The efficiency of the DIAMEX process has also been demonstrated with centrifugal extractors in a hot test using genuine HAR solutions [CHR04]. It has been shown that 99.9% of the Am and Cm can be recovered from the HAR feed by extraction by means of a 16 stages centrifugal extractor set-up.

Recently, at CEA, Marcoule, France, new malonamides containing ether functions on the central C atom have been studied [BAR97, MAD99]. These malonamides, especially the N,N'dimethyl-N,N'dioctyl-hexylethoxy-malonamide (DMDOHEMA), exhibit better affinities for actinide and lanthanide ions in comparison with other malonamides. Spjuth et al. [SPJ00] related the better extraction properties of malonamides bearing oxyalkyl groups at the central carbon atom to their lower basicity compared to other malonamides. The competition between the metal ion and HNO_3 for extraction is less severe than with more basic malonamides. Furthermore, third phase formation occurs at higher acidities and metal concentrations compared to other malonamides. Therefore, it has been proposed that DMDOHEMA should replace N,N'-dimethyl-N,N'-dibutyl-tetradecylmalonamide (DMDBTDMA), the DIAMEX reference extractant, in a new version of the DIAMEX process [MAD99, BIS99]. According to [BER01], DMDOHEMA is more prone to radiolytic and hydrolytic degradation than the PUREX extractant TBP. However, the influence of the degradation on the solvent extraction properties is less acute for malonamides than for TBP and the cleanup of spent solvent by aqueous washings is easier for malonamides than for TBP. The decrease in extractability can be explained by a decrease in the concentration of the extractant itself and by the presence of the main degradation products, i.e. amide acids, monoamides and amines, which probably interact with the DMDOHEMA. The products of the radiolytic and hydrolytic degradation of DMDOHEMA contain at least the $C_8H_{17}(CH_3)N$ – group and thus are not soluble in water. The stability of DMDOHEMA versus radiolysis and hydrolysis appears to be sufficient to allow an efficient industrial implementation of the DIAMEX process. The partial co-extraction and incomplete stripping of Pd and Ru is the main drawback of the DIAMEX process [COU98].

5.1.3.2. Diglycolamides

5.1.3.2.1. TODGA solvent

Tetraoctyl-3-oxapentane-1,5-diamide or N,N,N’,N’-tetraoctyldiglycolamide (TODGA) has recently [SAS00A] been proposed by JAERI (Japan Atomic Energy Research Institute) scientists as a solvent extraction agent to separate neptunium, americium, curium and the lanthanides almost completely from high-level reprocessing waste. Diglycolamides (DGA) contain three oxygen atoms which vigorously capture the metal ions, so they act as tridentate ligands. Because of these three functional groups, the extraction of trivalent actinide ions is improved compared to conventional extracting agents containing only one or two functional groups. Tetravalent and hexavalent actinide extractability is also superior compared to other diamide extractants, but the enhancement of the extraction by tridentate coordination is less than for trivalent actinides, probably because in the case of U(VI), which has a planar coordination sphere, the DGA acts only as bidentate ligand [SAS02]. Even the extraction of pentavalent Np by DGA has been reported to be satisfactory [SAS98, SAS00B], although other diamide extractants exhibit very low extraction coefficients for Np(V).

The hydrophobicity of DGA extractants is controlled by the length of the carbon chains attached to the amidic N atoms [SAS00A]. DGAs containing rather short C chains, like for instance N,N,N’,N’-tetrabutyl-3-oxapentane-1,5-diamide, dissolved in chloroform, exhibit higher D values for the actinide ions than DGAs provided with a longer alkyl chain. However, they are only soluble in polar organic solvents. For the development of an efficient partitioning process, however, a fast phase separation is important, so the use of non-polar aliphatic solvents like n-dodecane or TPH (an industrial mixture of branched alkanes) is necessary. Also for the development of an efficient DGA-based extraction chromatographic material, poor water solubility of the extractant is required. The octyl chain attached to the N atoms gives enough lipophilicity to the TODGA molecule, which is depicted in figure 7.18, to dissolve satisfactorily in n-dodecane at any ratio, but in contrast only slightly in water. On the other hand, TODGA exhibits better extraction of the actinides than DGA with longer alkyl chains. Despite the presence of three polar oxygen atoms in each molecule, TODGA dissolved in n-dodecane does not form a third phase, even when equilibrated with an aqueous solution of 6 M HNO_3 [SAS01]. By means of slope analysis, it has been established that three and four TODGA molecules are involved in the extraction of Th(IV), U(VI), Pu(IV) and Am(III), Cm(III), respectively [SAS00A, SAS01].

Back-extraction of the metal ions can be performed by stripping with deionised water [SAS00A]. Because HNO_3 itself is also extracted by TODGA, repeated stripping is necessary. During the first stripping steps, the nitric acid is back-extracted, which can be observed by the low pH of the stripping solutions. After the nitric acid concentration in the organic phase has been substantially lowered, and thus the acidity of the aqueous phase is decreased, the metal ions will also leave the organic phase.

Hydrolytic effects on the extraction of actinides and lanthanides are negligible, but radiolysis is observed [SUG02]. TODGA has less radiolytic stability than malonamides. The main degradation products are amines and monoamides because the amide bonds and the bonds in the vicinity of the ether oxygen are relatively weak with respect to radiation. The radioalysis of TODGA is enhanced by n-dodecane. On the other hand, HNO_3 has no promoting effect on the radiolytic degradation of TODGA. The extraction of Am(III) was depressed, although it did not change significantly by using TODGA solvent with an absorbed dose of less than 2×10^5 Gy [SAS00A]. Thus, it is expected that the radiolytic effect on the extraction of the actinide and lanthanide ions in a partitioning process of the HLLW will be negligibly small, although radiolytic degradation products are observed.

5.1.3.2.2. TODGA resin

Two SPE resins prepared by the impregnation of TODGA on Amberchrom CG-71 have been reported [VAN04, HOR05]. The results obtained with both of these resins were similar. The TODGA resin exhibits large weight distribution ratios for the actinides as well as the lanthanides. Especially the extraction of trivalent metal ions is favoured. The latter is observed rather seldomly for other extraction chromatographic resins. The interfering coextraction of the fission products Zr, Mo and Pd can effectively be suppressed by the addition of masking reagents, such as oxalic acid and HEDTA. The TODGA resin developed by Horwitz is now commercially available from Eichrom Technologies, Inc. as DGA Resin, normal. Leaching of TODGA from the resin was very limited.

A silica-based extraction resin was prepared by impregnation of TODGA on a macroreticular styrene-divinylbenzene copolymer which is immobilized in porous silica particles [HOS04]. Using a column packed with this resin a group separation of Ln(III) and Am(III) from simulated HLLW was carried out. It was reported that the Ln(III) ions were recovered quantitatively and that the sepration from the other fission products was sufficiently. However, it should be remarked that these experiments were carried out with a HLLW simulate containing only a limited number of fission products. The TODGA/SiO_2-P resin has also been used for the separation of Mo and Zr [ZHA04, ZHA05C] and for the separation of Sr from simulated fission product solutions [ZHA05D]. High nitric acid concentrations, high temperatures as well as γ-irradiation were reported to have a significantly adverse effect on the stability of the TODGA/SiO_2-P resin [ZHA05B].

5.2. Acidic extractants (eventually combined with neutral synergists)

5.2.1.1. Diethylhexyl-phosphoric acid (HDEHP)

5.2.1.1.1. Solvent extraction

Di(2-ethylhexyl) phosphoric acid (HDEHP) is a very common, commercially available extractant. Although many other acidic organophosphorous extractants are more effective extractants, HDEHP is more suitable for large scale separations because it is only slightly soluble in aqueous solutions and unlimitedly miscible with organic diluents, its metal and sodium complexes are soluble in the organic phase (aromatic diluents) or the solubility of these complexes can be enhanced by means of a modifier (mostly TBP in case aliphatic diluents are used) and is relatively cheap [KOL91]. HAW solutions should be denitrated to obtain a pH 1-2 before treatment with HDEHP. The organic phase composition differs depending on the diluent used. Often the combination of 0.3 M HDEPH and 0.2 M TBP in n-dodecane is used as organic phase. Since HDEHP is in fact a liquid cation exchanger, back extraction can be performed with nitric acid.

Due to its poor solvent load capacity, HDEHP is only suitable if non concentrated waste solutions (5000 L/t fuel) have to be treated [CEC78]. Another disadvantage is that the impurities (derivatives of pyrophosphoric acid or diphosphoric acid ($H_4P_2O_7$)) contained in commercially available HEDHP seriously affect the extraction characteristics and hamper back extraction, even if they are only present in very limited amounts.

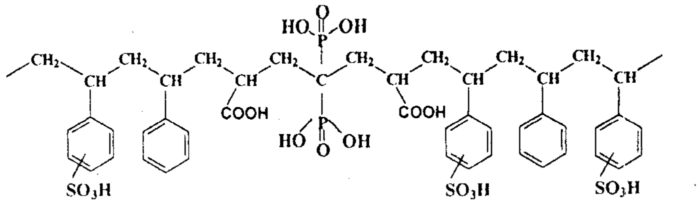
[KOL91, CEC78, NAS00]

5.2.1.1.2. Extraction chromatography

Extraction chromatographic resins with HDEHP on styrene-divinylbenzene copolymer immobilized on porous silica particles (SiO_2-P) and on XAS-7 (polystyrene) have been prepared by Wei et al [WEI00]. The preparation of the SiO2-P particles has also been described. SiO_2-P based SPE resins are usually characterized by fast kinetics (due to the small particle size), high mechanical strength, and significantly low pressure loss in a packed column. The HDEHP/SiO_2-P resin showed a fast kinetics compared to the HDEHP/XAD-7 resin, which was ascribed to the fine particle size. The adsorption of An(III) and Ln(III) significantly decreases with increasing HNO_3 concentration. The distribution coefficients of heavier Ln(III), i.e. Gd and Eu, ($D_{w,Gd} \cong 10^{-4}$ mL/g at 0.1 M HNO_3) are larger than those of Am(III) ($D_{w,Am} \cong 3.10^{-2}$ mL/g at 0.1 M HNO_3) and the lighter lanthanides. The lighter lanthanides, which form the majority of fission product lanthanides, are thus expected to co-elute with An(III).

5.2.1.2. Diphonix® resin

Methanediphosphonic acid derivatives form aqueous soluble lanthanide and actinide complexes. They have first been investigated as stripping agent to remove actinide ions quantitatively from the TRUEX process solvent [NAS00]. Further investigations of these compounds have led to the development of a multifunctional ion exchange resin, called Diphonix® (DIPHOsphinic-Ion-EXchange) resin. Diphonix® was developed by members of Argonne National Laboratory, Argonne, USA [HOR93B]. The resin is now commercially available in a variety of mesh sizes from Eichrom Industries Inc., Darien, Illinois. The resin contains geminally substituted diphosphonic acid groups chemically bonded to a styrene-divinylbenzene-based polymer matrix. The diphosphonic acid chelating group functions as the primary metal ion recognition site. Diphonix® also contains the strongly hydrophilic sulphonic acid group in the same polymer network, together with the diphosphonic acid group, to provide the polymer with the required high hydrophilicity for fast kinetics of metal species uptake.



$pK_1 = 1.5$, $pK_2 = 2.5$, $pK_3 = 7.2$, $pK_4 = 10.5$

Fig. 4.9: Structure of the Diphonix resin.[CHI97]

Because of the presence of both diphosphonic and sulphonic acid groups, Diphonix resin can be considered as a dual-mechanism resin, characterised by a hydrophilic cation exchange group allowing for access (mostly non-specific) of ions into the polymeric network, and by another ligand group responsible for the resin specificity (recognition) toward target metal ions. The ability to complex actinides and lanthanides is mainly attributed to the high acidity of the diphosphonic acid group. This strong acidity of the diphosphonic acid group and its tendency to chelate actinides through either ionised or neutral diphosphonic acid ligands, thanks to the remarkable coordinating properties of the P=O groups, makes possible the formation of metal complexes of high stability under conditions too acidic for appreciable complexations by other acidic ligand such as carboxylic and monophosphonic acids to occur. Diphonix resin shows a remarkable affinity for actinides, especially the tetra- and hexavalent ones [HOR93B]. The resin is also effective in sorbing other multivalent ions, such as Al(III), Cr(III) and especially Fe(III).[CHI93] This is a drawback for actinide separations from complex waste solutions, especially if they contain concentrations of these transitions metals much higher than those of the actinides, as it limits the selectivity of the resin for actinides, particularly for americium. Some of these limitations can be overcome through appropriate redox (e.g. Fe(III)→Fe(II)) and complexation (e.g. by using oxalic acid) chemistry. The actinide species are so strongly retained by the resin that the only effective stripping agents are compounds belonging to the family of aqueous soluble diphosphonic acids like HEDPA (1-hydroxyethane-1,1-diphosphonic acid), which contain the same functional group as the resin. The stripping chemistry is in this case based on the mass action of an excess of ligand in the aqueous phase. If a further separation of the actinides is required, after stripping, the aqueous diphosphonic acid has to be thermally degraded (assisted by catalysts) for further processing of the actinides. This leads to solutions

containing high concentrations of phosphoric acid, which can generate problems in the next separation steps. Alternatively, stripping can be avoided by destroying the whole resin through wet oxidation. This difficult recovery of the actinides is a serious drawback with regard to its large-scale application for the advanced reprocessing of spent fuel.
[CHO95B, CHI97, HOR93B, CHI93, NAS94, CHI94A, HOR94, CHI94B, CHI95B, CHI96A, ALE98, CHI00, HOR99, ALE99]

5.2.1.3. Dipex resin

The utility of the diphosphonate groups, used in the Diphonix resin, has been further expanded with the preparation of lipophilic bis(2-ethylhexyl) derivatives of methane, ethane and butane diphosphonic acids as extractants for solvent extraction and SPE. The first derivative, P,P'-di(2-ethylhexyl) methane diphosphonic acid (H_2DEH[MDP]), is the extractant used in the extraction chromatographic resin Dipex. Its major application is the matrix separation and enrichment of actinides for analysis of environmental samples [NAS00].

Actinide® resin was developed by Horwitz et al. [CHI96B, HOR97] as a further development of the Diphonix® resin [HOR93B]. The Diphonix resin is not an SPE resin, but an ion exchange resin and will be introduced in the corresponding section. The extractant on the Actinide resin, P,P’-di(2-ethylhexyl)methane diphosphonic acid (Dipex) contains a diphosphonic acid functional group like the Diphonix resin. The inert support is Amberchrom CG 71ms. Actinide resin is readily applicable to the separation and preconcentration of actinides, as a group, from complex matrices because of its very strong affinity for actinides in the tri-, tetra- and hexavalent oxidation states and its superior selectivity for actinides over other cations. The distribution coefficients for the actinides are so high that it is almost impossible to elute them from the SPE resin. The easiest way to recover the actinides is to elute the whole actinide-Dipex complex from the inert support with isopropanol. The disadvantage is that this organic extractant needs to be disturbed by means of wet oxidation before further separations can be performed thus giving rise to considerable amounts of phosphoric acid. [HOR97, MAI00]

6. Separation of trivalent actinides from lanthanides

The difficult actinide (III) / lanthanide (III) separation has to be performed in a second extraction cycle. Since the mass of the lanthanide fission products is much higher than the mass of the transplutonium elements, selective extraction of the small mass of the latter elements would be preferable. The possibility of extracting transplutonium elements from acidic solutions, preferably with a nitric acid concentration between 0.1 and 1M, is considered as a significant advantage. At lower nitric acid concentrations precipitates will be formed, which would hinder extraction operations.

Lanthanide/actinide separations often depend upon the slightly stronger interaction of the trivalent actinides with ligands containing soft donor bases (S, Cl or N), or with amine extractants in contact with aqueous solutions containing high concentrations of chloride or thiocyanate. Some authors believe this is due to an enhanced covalent bonding contribution in the actinide complexes, but the question of the role of covalency effects with soft donors in An(III) vs. Ln(III) complexation still deserves further study. It has recently been demonstrated that bonds between polydentate N-bearing ligands and An(III) and Ln(III) ions include some definite covalence, which is visible in the fact that enthalpy is the driving force behind the reactions [MAD02]. This results in heat being released during the reaction. The covalence of the bonds is higher for An(III) ions than for Ln(III) ions, which explains the greater affinity of N-donor extractants for An(III).

Extractants which incorporate S as a soft donor atom have the disadvantage that they often have a poor stability when contacted by acidic solutions, particularly nitric acid. In general f-elements are poorly extracted by simple thio extractants. Ligands containing multiple soft donor atoms often exhibit the highest selectivity for trivalent actinides over lanthanides. While dialkylphosphinic and monothiophosphinic acids exhibit little lanthanide/actinide selectivity, dialkyldithiophosphinic acids extract actinides at least 1000 times more strongly than lanthanides. Enhancing size-selective complexation and developing ligands with the optimum mix of hard and soft donor groups seem to be the key factors required for more efficient separation process of trivalent actinides and lanthanides. Advances in the basic science of actinide solution chemistry (e.g. solvation reactions) will undoubtedly result in the development of more efficient separation processes.[CHO95B, NAS97, NAS00]

6.1. Solvating extractants

6.1.1. CMPO

6.1.1.1. SETFICS solvent extraction process

The SETFICS process is to consider as an improved TRUEX process. It has recently been developed at JNC [KOM98]. The TRUEX solvent is used as organic phase. In analogy with the reversed TALSPEAK process, diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA) has been used as stripping reagent. Trivalent An and Ln are co-extracted by TRUEX solvent. Instead of stripping these trivalent f-elements together with dilute HNO_3, An(III) are selectively stripped into the aqueous phase by a solution of DTPA and the salting-out reagent $NaNO_3$. Am and Cm form more stable complexes with DTPA, a N-bearing extractant, than Ln(III), especially the lighter lanthanides such as La, Ce, Pr, Nd, Pm and Sm, which form the majority (>95%) of the lanthanide fission products.

6.1.1.2. MAREC extraction chromatographic process

The MAREC (Minor Actinides Recovery from HLLW by Extraction Chromatography) uses two separation columns packed with SiO_2-P/CMPO resin [ZHA03, WEI04]. An, Ln and some other fission products (Zr, Mo and Pd) are sorbed on the first column from HLLW with a HNO_3 concentration of about 3 M. After column washing with 3 M HNO_3, the actinides, Zr, Mo, Pd, Y and heavier lanthanides (Eu, Gd, Tb-Lu) are co-eluted with 0.05 M DTPA at pH 2. No salting-out reagent is used. The lighter rare earths are subsequently eluted with diluted HNO_3 or water. Then, concentrated nitric acid is added to the An fraction to adjust the HNO_3 concentration to 3 M. Hereby most metal-DTPA complexes are destroyed because DTPA is only a weak acid. The resulting solution is introduced into the second SiO_2-P/CMPO column. In the washing step with 3 M HNO_3 Pd and DTPA are washed out. The An(III) and heavier rare earths are eluted with diluted HNO_3 and finally, Zr and Mo are eluted with oxalic acid or DTPA. Because the resin will be directly exposed to a continuously high radiation level and concentrated nitric acid, the resistance of the SiO_2-P/CMPO resin against nitric acid, temperature and γ-radiation has recently been investigated [ZHA05]. The influence of nitric acid either 3 or 0.02 M at 25°C or at

80°C on the stability of the resin was minimal. However, γ-radiation showed a serious effect on the stability of the resin. CMPO was leaked from the resin and the uptake of Nd was significantly lowered.

6.1.2. TPTZ

6.1.2.1. SANEX-TPTZ

2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) is a terdentate heterocylic nitrogen-donor ligand. When an organic cation exchanger, which is a lipophilic anion of an organic acid, like dinonylnaphtalenesulphonic acid (HDNNS) or α-bromocapric acid (or 2-bromodecanoic acid) is used in synergy, An(III) can be selectively extracted. These lipophilic anions (A) must be present in the system for the formation of an extractable complex of the type $An(III)A_3 \cdot TPTZ$. Trivalent actinides are not efficiently extracted by neither 2-bromodecanoic acid, nor by TPTZ alone [HAG99]. Furthermore, 2-bromodecanoic acid is quite unselective. Although 2-bromodecanoic acid is not in accordance with the CHON principle, this acid was selected because of its low pK_a, due to the presence of the electron withdrawing Br in the alpha position relative to the carboxylate group, and its commercial availability.

Decanol is used as diluent when α-bromocapric acid is used and t-butylbenzene or CCl_4 is taken as diluent when HDNNS is used. The pH of the aqueous phase must be in the range of 1-2. Separation factors of ~ 10 for the separation of Am and Cm from Ce, Nd, Eu or Gd are reported. [KOL91, KOL98A, HAG99]

The SANEX-TPTZ process has been demonstrated in counter-current experiments by means of a 16 stage mixer-settler battery [VIT86]. The feed solutions contained trace amounts of Am and Eu and variable amounts of Ce. The organic phase was 0.03 M TPTZ + 0.05 M HDNNS diluted in CCl_4, because CCl_4 allows faster phase disengagement in the settler compartment. The nitric acid concentration in the aqueous phase was 0.125 M. Eight or ten of the sixteen stages were scrub stages where 0.125 M HNO_3 + 0.03 M TPTZ was used as scrub solution. At least 99.5% of the Am(III) was extracted into the organic phase, but unfortunately, depending on the Ce concentration also 2-10% Eu and 2-11% Ce were co-extracted. The main drawback of the SANEX-TPTZ-process is that pH adjustment is needed.

In order to suppress the aqueous solubility of protonated forms of TPTZ, alkyl groups have been introduced at the 4-position of the 2-pyridyl rings. The extraction efficiency is also improved by this structure change [KOL98A, MAD98].

6.1.3. terPy

2,2':6',2"-terpyridine (terPy), which is also used in synergy with 2-bromodecanoic acid, is a tridentate N donor extractant, able to provide an An(III)-Ln(III) separation. TerPy itself has poor extractive properties, but it forms a synergistic system in combination with 2-bromodecanoic acid [AND03]. The acid will release its hydrogen ion and its corresponding anionic form will neutralise and complex the metal ions. The function of terPy is to improve the extraction by increasing the lipophilicity and removing water of hydratation.

Its separation efficiency for the Am-Eu pair is similar to that of TPTZ [KOL98A, HAG99]. However, it is a weaker extractant for both An(III) and Ln(III). The optimum total concentration of extractant is between 0.1 and 0.5 M in TPH or t-butylbenzene with a concentration ratio of terPy/2-bromodecanoic acid of 2/3.

Unfortunately, protonated terPy has a rather high solubility in the aqueous phase. Depending on the pH of the aqueous phase, all three nitrogens may have a hydrogen ion attached to themselves [AND02]. Due to its bad protonation behaviour, terPy is considered to be unsuitable for an industrial separation process [AND03].

6.1.4. BTP

6.1.4.1. SANEX-BTP

Recently, Kolarik et al. [KOL98A, KOL99A, KOL99B, MAD99] discovered the amazing properties of the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (named BTPs, Bis Triazine Pyridine) for the trivalent actinide / lanthanide group separation. Very soon after that discovery, the SANEX-BTP process was developed within the framework of the NEWPART project. Very efficient separations have been obtained with 2,6-bis(5,6-n-propyl-1,2,4-triazin-3-yl)pyridine (*n*Pr-BTP), which is considered as the reference molecule of the bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines. About 20 vol% of a modifier like 2-ethyl-1-hexanol or butyraldehyde is used to attain an appropriate solubility of *n*Pr-BTP in the non polar TPH diluent. The advantages of BTP extractants are that they are CHON molecules and that they are capable to extract Am from a An(III)/Ln fraction with moderate nitric acid concentration. Nevertheless, problems with the stability of the *n*Pr-TBP extractant have been observed.

Other nitrogen-bearing extractants (e.g. TPTZ, TerPy) are generally used in a synergetic mixture with an acidic extractant. Nonetheless, in the case of BTPs, these extractants can be used on their own because BTP molecules extract An(III) as nitrates. Furthermore, the feed of the SANEX-*n*Pr-BTP can be acidic (about 1 M HNO_3), which is an enormous advantage. BTP molecules are almost planar polydentate N-donors. The more electron-donor N-atoms in coordination with the metal ion, the greater the difference in affinity for An(III) and Ln(III) ions is likely to be. The affinity of BTP molecules for trivalent actinide ions is more than hundred times higher than for lanthanide ions. Compared to other nitrogen bearing ligands, BTP molecules have a very low basicity, which can be the explanation for the better extraction performances at high nitric acid concentration. Since Am(III) and Eu(III) are extracted as complexes of the type $M(NO_3)_3{\cdot}3L$, their distribution ratios increase strongly with the activity of nitrate ions in the aqueous phase and with the concentration of BTP in the organic phase.

Counter-current hot solvent extraction experiments revealed a strong sensitivity of the *n*Pr-BTP extractant towards air oxidation and acidic hydrolysis. The main hydrolysis products are alcohols and ketones. The stability of other BTP compounds has been investigated. *i*-propyl-BTP and *i*-Butyl-BTP exhibit a higher stability against decomposition than *n*Pr-BTP, but *n*-Butyl-BTP decomposed much faster than *n*Pr-BTP after the phase contact. Therefore, the *n*-Butyl compound was only briefly investigated. Hydrolysis could apparently be hindered by branching of the alkyl groups on the α position of the triazine rings. The *i*-Butyl compound is a more powerful extractant than *n*Pr-BTP and *n*-Butyl-BTP. However, the separation efficiency of these three BTP extractants was similar ($\alpha_{Am/Eu} \sim 130$). *i*-propyl-BTP is susceptible to radiolysis. Because heavier compounds, which are more lipophilic, are formed due to radiolysis, the spent solvent is unsuitable to recycling. Furthermore, its chemical synthesis is tedious, it has a low solubility in organic diluents and slow extraction kinetics. Extraction experiments in a stirred cell revealed that the rate determining step in the Am(III) extraction by *n*Pr-BTP is a slow chemical complexation reaction at the aqueous/organic phase interface [GEI00]. The extraction kinetics of *n*-Butyl-BTP, *i*Pr-BTP and *i*-Butyl-BTP is too slow for practical applications. Distribution equilibrium is only attained after a shaking time as long as ≥ 3 h. Several attempts have been made to accelerate the extraction kinetics by using co-extractants, such as TBP or DMDOHEMA. These modifiers, however, lowered the selectivity towards An(III). Furthermore, if the following solvent is used: 0.01 M *i*Pr-BTP + 0.5 M DMDOHEMA in *n*-octanol, glycolic acid is needed to enhance the kinetics of the back-extraction, whereas with *n*Pr-BTP solvent (0.04 M *n*Pr-BTP in TPH containing 30 vol% *n*-octanol) the back-extraction can be performed with diluted nitric acid.
[KOL98A, KOL99A, KOL99B, HIL00, HIL02, HIL04]

The SANEX-*n*Pr-BTP process has been tested on genuine HLLW in continuous counter-current extraction experiments, using a centrifugal extractor battery (16 stages) installed in a hot cell [SÄT00]. The representative MA/Ln fraction was obtained from dissolved commercial LWR fuel which was submitted subsequently to a small scale PUREX process followed by a DIAMEX process. The nitric acid concentration of this low acidic MA + Ln mixture was adjusted to 1 M HNO_3 with concentrated nitric acid. The organic phase consisted of 0.04 M *n*Pr-BTP dissolved in TPH containing 30 vol% of octanol. The concentrations of Am and Cm in the aqueous phase decreased by several orders of magnitude. Np and U were efficiently washed out by acid scrubbing, but Pu was co-extracted. The lanthanides were almost not extracted and, furthermore, their co-extraction is efficiently reduced by the acid scrubbing. All actinides were back-extracted in the strip section. A MA fraction almost free of lanthanides was obtained. The recovery of Am was reasonably good (99.1%), but the recovery of Cm (97.5%) has to be improved. Tc, Mo and Pd were accumulated in the organic phase.

A counter-current mixer-settler hot test with a synthetic DIAMEX raffinate has been carried out in the hot cells in the ATALANTE facility in Marcoule [MAD00B, HIL00]. Am and Cm were quantitatively extracted (>99.85%). However, only 98% of the Am and 91% of Cm were recovered during the back-extraction step. Much of the Fe, Ru and Pd present in the acidic aqueous feed solution entered the organic phase so that eventually the extraction of Am and Cm could be inhibited because the BTP extractant is sequestered by a transition metal [DRE06]. Only 0.97% of the Pd was mixed with the MA in the stripping solution. Probably the back-extraction of Pd was not quantitative. 70% of the Fe(III) was found in the organic solvent and 7% ended up in the raffinate. For the lanthanides, decontamination factors increase with a decrease in atomic number. About 3% of the Gd was found in the An(III) stripping solution, whereas less than 0.05% of La was present in that solution. The An(III) solution contained less than 5 mass% Ln, which is one of the objectives of the SANEX process.

Also a once-through, single-module counter-current solvent extraction test with miniature hollow fibre modules has been performed using the *n*Pr-BTP extractant [GEI02]. Am was extracted to 99.95% from the synthetic feed solution into the organic phase and only approx. 1% of the lanthanides were co-extracted.

First attempts to the theoretical investigation of the actinide-BTP complexes have been conducted by means of quantum chemistry methods, molecular mechanics and molecular dynamics methods [DRE98, GUI00]. The structure of Ln·(*n*Pr-BTP)$_3$ crystals has been determined using X-ray diffraction [DRE01]. It has been confirmed that the complex is composed of three ligands directly bonded to the metal ion. The BTP molecules act as tridentate ligands. They coordinate via the N in the pyridine as well as via the triazinyl N atoms in the 2-position. Cm and Eu complexes with *n*Pr-BTP have been characterized by means of EXAFS (extended X-ray absorbtion fine-structure spectroscopy), TRLFS (time-resolved laser-induced fluorescence spectroscopy) and quantum-chemical investigations [DEN05, GOM05]. According to the EXAFS study, the number of coordinating N atoms directly bound to the metal cations is 9. The coordination structure of $\mathrm{Cm}\cdot(n\mathrm{Pr\text{-}BTP})_3$ and $\mathrm{Eu}\cdot(n\mathrm{Pr\text{-}BTP})_3$ is the same. The metal cation complexes coordinated with three ligads have the same coordination structure. Furthermore, bond lengths are the same in both (Am and Cm) complexes. This result was supported by quantum-chemical calculations. In all calculations, the BTP ligand is nearly planar. This means that the selectivity of *n*Pr-BTP for An(III) over Ln(III) is not of structural origin. Besides, there was no evidence for directly coordinated nitrate groups. The results of the TRLFS measurements revealed that the extracted Cm species always contains three ligands, independend on the ligand-to-metal ratio. Contrary to Cm, the $\mathrm{Eu}\cdot(n\mathrm{Pr\text{-}BTP})_3$ species is only formed at high ligand-to-metal concentration ratios. The fact that $\mathrm{Cm}\cdot(n\mathrm{Pr\text{-}BTP})_3$ is formed at much lower ligand-to-metal concentration ratios is consistent with *n*Pr-BTP's high selectivity for An(III) over Ln(III) in solvent extraction.

According to Nilsson et al. [NIL06], the radiolysis of BTP molecules can be inhibited by the addition of nitrobenzene to the solvent. The nitrobenzene scavenger is supposed to react with solvated electrons and α-hydroxy alkyl radicals, which are radiolysis products of the alcohol diluent. It is, therefore, believed that the solvated electrons and α-hydroxy alkyl radicals are important intermediates for the radiolysis of BTP molecules. Furthermore, the radiolysis products of BTP are heavier than the initial BTP molecule [HIL02] which is also an indication that α-hydroxy alkyl radicals may play the major role. Unfortunately, nitrobenzene can not be used in an industrial separation process because of safety reasons.

[KOL98A, COR98, KOL99A, KOL99B, MAD02]

D. Warin [WAR06] has suggested very recently to use CyMe4-BTP in *n*-octanol for the development of a SANEX process. This molecule is more stable than the older BTPs. The addition of DMDOHEMA as a phase transfer catalyst is recommended. Unfortunately, there is almost no literature about this compound available at the moment.

6.1.4.2. R-BTP resin

At IRI in Japan, silica-based SPE resins have been made by impregnating some R-BTP molecules into a macroreticular styrene-divinylbenzene copolymer which is immobilized in porous silica particles. Am(III) can strongly and selectively be sorbed from nitric acid solutions up to 3M using *i*Bu-BTP. In contrast, *n*Bu-BTP has only affinity for Am from nitrate solutions with low acidity. Leakage of the R-BTP extractants has been investigated. Leakage increased with increasing nitric acid concentration and is believed to be caused by protonation of the extractant. The branched *i*Bu-BTP is much more stable against leakage than *n*Bu-BTP.
[HOS06]

6.1.5. BTBP

New Bis Triazine Bis Pyridine (BTBP) ligands, which are structurally related to the BTP family, have been prepared at the University of Reading very recently.

At the FISA 2006 conference, 2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazy-3-yl)-[2,2']bipyridine, which is called CyMe$_4$-BTBP is reported to be very effective for the An(III)/Ln(III) separation [MAD06, WAR06]. Because the kinetics of metal extraction was very slow, the malonamide DMDOHEMA has been used as phase transfer catalyst. This molecule has been selected for the design of a SANEX process. A hot test will be carried out at ITU, Karlsruhe. Unfortunately, there is no detailed literature currently available.

6.2. Acidic extractants (eventually combined with neutral synergists)

6.2.1. Diethylhexyl-phosphoric acid (HDEHP)

6.2.1.1. TALSPEAK

A more efficient, but considerably more complex, approach to actinide/lanthanide group separations was the TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorous

Reagent Extraction from Aqueous Komplexes) process developed by Weaver and Kappelmann [WEA64]. Ln(III) cations are extracted by 0.5 M di(2-ethylhexyl) phosphoric acid (HDEHP) from a 1 M lactic acid (or glycolic acid [CEC78]) solution at pH 3, to which 0.05 M diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA) is added. The lactic acid serves as a pH buffer, to promote dehydration of the metal ion, improves kinetics, and acts as a co-extractant. The extracted Ln(III) species may have one bonded lactate. The DTPA complexes of the actinides remain in the aqueous phase. Separation factors for Ln(III) from Am(III) and Cm(III) are larger than 100. Since the actinides are strongly complexed in the aqueous solution, the complexing properties must be reduced to retrieve them. This can be done by reducing the pH by acid addition. However, the solubility of DTPA is low at low pH and precipitation will occur. Precipitation of DTPA prevents recycling of the aqueous solution.

Denitration is necessary since HDEHP has to be considered as a liquid cation exchanger and thus lanthanide ions are only extracted at low acidity. A sufficient concentration (1 M) of an hydroxycarboxylic acid (e.g. lactic acid) must be present because at lower concentrations the attainment of the distribution equilibrium can take hours [KOL91]. Furthermore, by using DTPA to complex Am in the aqueous phase large amounts of secondary radwaste are created [ZHU95B]. This waste is especially troublesome, since it is α-contaminated and contains complexing agents that might promote migration from a final waste repository [PER84].
Eventually, DTPA and lactic (or glycolic) acid could ultimately be destroyed by hot concentrated nitric acid [CEC78]. Besides, the HDEHP solvent loading capacity is rather limited and its clean-up is difficult. The effectiveness of the An(III)/Ln(III) separation is deteriorated when DTPA is destroyed by radiation [KOL91].

[WEA64, WEA68, NAS97, CHO95B, PER84]

6.2.1.2. Reversed TALSPEAK

The reversed TALSPEAK process has been developed to overcome the drawback of the large amounts of troublesome secondary waste created by the TALSPEAK process [PER84].
Trivalent actinides and lanthanides are first extracted together by 1 M HDEHP diluted in an aliphatic kerosene diluent at 0.1 M HNO_3 and separated from each other by selective stripping of the actinides, using a mixture of 0.05 M DTPA and 1.5 M lactic acid. Because a part of the lanthanides and yttrium are stripped together with the actinides a seven stage scrub with 1 M HDEHP has to be included.

When ammonia is used for pH adjustment of the aqueous phase, the extraction of ammonia by HDEHP reduces the pH and hence the distribution ratios of the trivalent actinides increase. This way, the actinides can be re-extracted from the DTPA/lactic acid solution using 1 M HDEHP. By this means, the aqueous DTPA/lactic acid solution remains essentially intact and can be recycled after pH and DTPA and lactic acid concentration adjustment. Only a small excess of aqueous solution, which is the result of the addition of water containing ammonia, must be withdrawn. Finally, the actinides and lanthanides can be stripped from the organic solvent with 6 M HNO_3. The solvent can be recycled after scrubbing with a small stream of distilled water to remove excess HNO_3. In order to prevent a too high build-up of metals (especially Fe) and to reduce the content of solvent degradation products, the HDEHP solvent must be purified, after neutralisation with ammonia, with 0.5 M ammonium carbonate and mannitol (to remove iron), re-acidified with 6 M HNO_3 and scrubbed with water.

The pH of the aqueous DTPA/lactic acid solution (pH 3.63) must be carefully chosen to give an optimal pH in the scrub section (pH 3.05). A too high pH gives insufficient scrubbing of the lanthanides and a too low pH an appreciable extraction of the actinides, leading to recirculation within the battery and eventually intolerable actinide losses into the lanthanide stream. Furthermore, the elements Zr, Nb, Mo, In, Sn, Pa, Th, U, Np, Pu and the main part of iron should be removed in advance of the reversed TALSPEAK process, for instance by extraction with 1 M HDEHP at 6 M HNO_3 or by means of the TRUEX process. Ru, Tc and Pd can be removed by extraction with 50% TBP. Otherwise, these elements would interfere with the separation and as they are not strippable with HNO_3, they are liable to build-up in the solvent. Besides, the solvent clean-up is rather difficult.

6.2.1.3. PALADIN process

This process has recently been developed at CEA [HER99, MAD00] . The organic phase is a mixture of extractants: HDEHP and a malonamide (see 5.1.3.1). First, trivalent actinides and lanthanides are extracted by the malonamide as metal nitrate from HAW solutions with a nitric acid concentration 3-5 M. In the next step only the trivalent actinides will be stripped with a DTPA solution. In this step, with much lower acid concentration in the aqueous phase, the metal ions in the organic phase are complexed by HDEHP.

This process has the drawback that two different extractants are used in the organic phase, which will complicate the solvent clean-up and that the pH of the aqueous phase must be carefully adjusted. Furthermore, numerous ions are co-extracted. [MAD00]

6.2.2. Diisodecylphosphoric acid (DIDPA)

Diisodecylphosphoric acid (DIDPA) is an acidic extractant which is quite similar to the HDEHP used in the TALSPEAK process. By extraction with DIDPA, all transuranium elements including Np can be separated from HAW with a HNO_3 concentration of about 0.5 M. The DIDPA process proposed by Morita [MOR95] is a two-cycle solvent extraction process. In the first cycle all actinides and lanthanides are extracted from 0.5 M HNO_3 into DIDPA solvent consisting of 0.5 M DIDPA and 0.1 M TBP in n-dodecane. Addition of TBP makes the phase separation faster, but decreases the distribution ratios little. H_2O_2 is added to the aqueous phase during extraction in order to reduce Np(V) to Np(IV), which is readily extractable. Trivalent actinides and lanthanides are then stripped with 4 M HNO_3. In the next back-extraction step, the tetravalent species Pu and Np are stripped with 0.8 M oxalic acid. The final step of the first extraction cycle is the stripping of hexavalent U with 1.5 M Na_2CO_3. The stripped trivalent actinides and lanthanides are directed to the second solvent extraction cycle. After adjustment of the acidity to 0.5 M HNO_3, the trivalent species are re-extracted by DIDPA solvent. Similar to the reversed TALSPEAK process, Am and Cm are now selectively stripped by 0.05 M DTPA. The lanthanides, which remained in the organic phase, are subsequently stripped with 4 M HNO_3. The separation factor between Am and Sm in the selective back-extraction with DTPA is smaller than in the reversed TALSPEAK process, but an An/Ln separation would still be possible.

The first cycle of this process has been tested with real HLW (1.2 L, 200 Ci) using mixer-settler equipment [KUB84] and using centrifugal extractors [MOR96]. The mixer-settler test gave a satisfactory result for the recovery of Am and Cm from HLW. Only the Np recovery was insufficient because no H_2O_2 was added [MOR85]. The Np extraction by DIDPA has been further optimized [MOR87, MOR88] until a recovery of 99.96% was obtained [MOR91]. The experiments with the centrifugal extractor battery revealed that with some improvements centrifugal extractors can also yield good recovery of the actinides. The HLW was diluted to adjust the acidity to 0.5 M and to increase the volume.

The stability of DIDPA to radiolysis is comparable to that of HDEHP and better than TBP. Furthermore, one of the advantages of DIDPA is that the influence of radiolysis is smaller than with neutral extractants. The most influential degradation product of DIDPA is its monoester monoisodecylphosphoric acid (MIDPA), which is also an acidic extractant and its behavior is similar to DIDPA. When neutral extractants, e.g. TBP, are used, acidic degradation products with different properties are formed. [MOR95, SHI94]

A disadvantage of the DIDPA process is that the distribution ratio of Fe is very high in a wide range of nitric acid concentration. An emulsion is formed in the DIDPA solvent when the Fe concentration in the organic phase becomes high [MOR95]. Emulsification is also likely to occur in the back-extraction of U. Due to the risk of emulsification, large volumes should be treated which makes the scale of the extractors larger.

6.2.3. Dithiophosphinic acids

6.2.3.1. SANEX with acidic S-bearing extractants / ALINA

Moderate separation factors for the separation of Am from Eu can be obtained using very pure dithiophosphinic acid extractants like Cyanex 301 (mainly composed of bis (2,4,4-trimethyl-pentyl) dithiophophinic acid (73-85 wt%), dicyclohexyldithiophosphinic acid and diphenyl-dithiophosphinic acid. Commercially available Cyanex 301 contains about 15% impurities like monothiophosphinic acid, which extracts lanthanides. Therefore purification of the dithiophosphinic acid is very important to selectively extract trivalent actinides [MOD98B]. High separation factors for the Am/Eu separation ($SF_{Am/Eu} > 5000$) can be obtained in the pH range of 3-4 and at an ionic strength of 1 M $NaNO_3$ [CHE96A, ZHU96A, ZHU96B, MOD98A]. While thio derivatives of dialkylphosphoric acids are susceptible to oxidation and decomposition, the chemical stability of Cyanex 301 has been proved excellent in solvent extraction systems with up to 2 M HNO_3 [SOL93]. The radiolytic degradation products of bis (2,4,4-trimethyl-pentyl)-dithiophophinic acid are dialkylmonothiophosphinic acid, dialkylphosphinic acid and some other phosphorous compounds [CHE96B]. Purified Cyanex 301 can still separate An(III) from Ln(III) till a radiation dose of 1×10^5 Gy. At higher doses, the colour of the organic phase changes, strange smells were observed and H_2SO_4 is formed, which decreases the pH of the aqueous phase. An(III) distribution rates are more decreased than those of the lanthanides, making their separation impossible.

Because most reprocessing waste solutions are much more acidic, the pH needs to be stabilised with buffers (formic acid) and about 1 M $NaNO_3$ has to be used as salting out agent. To avoid this disadvantage, Modolo synthesised dithiophosphinic acids which are much more acidic than Cyanex 301 [MOD98B, MOD99]. Good results have been obtained with bis(chlorophenyl)-dithiophosphinic acid (BCPDTP) and TBP or TOPO as the synergist dissolved in an aromatic solvent. An aromatic solvent like toluene is necessary because the aromatic extractant, which is a solid, doesn't dissolve well in nonpolar solvents as n-dodecane. No selectivity was obtained without synergist, which causes selectivity by steric hindrance. This extractant was the first which was able to perform an actinide/lanthanide separation in very acidic medium (until 1.5 M HNO_3). This separation method, called the ALINA (Actinide Lanthanide INtergroup separation from Acidic solutions) process, has already been successfully tested on a laboratory scale at Forschungszentrum Jülich with a 16-stage mini-centrifugal extractor battery. A solution containing 97% of the trivalent actinides and only 3% of the lanthanides was obtained from a simulated waste solution that would arise from the DIAMEX process. Aromatic dithiophosphinic acids are more stable to hydrolysis and radiolysis than Cyanex 301 [MOD02]. Hydrolysis can be stabilized with the aid of HNO_2 scavengers like hydrazine. The degradation products have no significant influence on the extraction.

The main drawback of this process is the generation of S and P bearing wastes. A solvent clean-up process is not yet defined.

[ZHU95B, ZHU96A, CHE96A, CHE96B, CHE97, MOD98A, MOD98B, MOD99]

6.2.3.2. Cyanex 301 SPE resin

Extraction chromatographic resins containing Cyanex 301 have been prepared and investigated by Maischak [MAI00, MAI01]. Styrene-divinylbenzene copolymer immobilized on porous silica particles (SiO_2-P) was a better inert matrix than Amberchrom (polymethacrylate) or XAD-7 (polystyrene). The preparation of the SiO_2-P particles has been described by Wei et al [WEI00]. Better extraction of Am and thus better separation factors were obtained with the SiO_2-P resin. A similar resin has been prepared by Wei [WEI00]. The results of the experiments by Maischak and Wei were consistent. Similar to the SANEX process, the feed should have a pH of 3-4.5 and about 1 M $NaNO_3$ is used for salting out. Since lanthanide ions have distribution coefficients below 1 under these conditions, hence they are not sorbed by the resin. Am can be eluted with a more concentrated HNO_3 solution. The disadvantage of this resin is that the Am/Ln separation is very sensitive to solvent impurities and/or radiolytic or hydrolytic degradation products [WEI00]. Therefore, the Am/Ln separation doesn't work with trace concentrations of lanthanides because these small amounts will be extracted by the impurities (mainly monothiophosphinic acid). Even after a short contact period (packing and washing of a glass column) with very diluted nitric acid (pH 4) the resin was slightly green coloured and lanthanides, although present in macroconcentrations (0.01 M) were partially co-eluted with Am [MAI00]. Also with 4 weeks old Cyanex 301/ SiO_2-P resin, Ln(III) were eluted together with Am(III) [WEI00].

6.3. Ion-pairing extractants

6.3.1. Triisooctylamine

In 1961 the first solvent extraction system for the separation of An(III) and Ln(III) was published by scientists of Oak Ridge National Laboratory [MOO61]. Trivalent actinide elements are preferentially extracted from dilute hydrochloric acid – concentrated lithium chloride solutions with triisooctylamine dissolved in xylene. This process has been abandoned because of the difficulties encountered with the viscous and highly corrosive hydrochloric acid – lithium chloride solutions [MOO64].

6.3.2. Aliquat™ • 336

6.3.2.1. Solvent extraction

Different solvent extraction systems with the quaternary amine (quat) liquid anion exchanger commercially (Henkel) available as Aliquat™ • 336 dissolved in xylene using an aqueous solution of salts like NH_4SCN [MOO64, GER65] for the lanthanide/ actinide group separation have been described in detail by Weaver [WEA74]. Aliquat™ • 336 (tricaprylylmethyl-ammonium chloride), a cationic surfactant, is a technical grade mixture of trioctyl- and tridecyl-methylammonium chlorides, with C_8 predominating, having long-chain aliphatic groups to give increased organic solvent solubility and decreased aqueous solubility [HOR95]. It can be easily converted into its thiocyanate salt. The solvent extraction method described by Moore [MOO64] uses 30% Aliquat 336 in xylene and 0.6 M ammonium thiocyanate with 0.1 M sulfuric acid as the aqueous phase. The soft donor SCN^- accounts for the An(III) extraction. Because of the greater stability of the negative actinide(III) thiocyanate complexes, they are preferentially extracted by Aliquat™ • 336, which is a liquid anion exchanger. This separation method is closely related with the earlier developed anion exchange method, where thiocyanate was used as eluent [PEN60]. An advantage of liquid-liquid extraction using Aliquat 336 is the very fast metal exchange kinetics. Equilibrium was attained in less than one minute [MOO64], in contrast with the anion exchange method. The latter method therefore required slow flow rates, which promotes the radiolytic decomposition of the thiocyanate to produce free sulfur and gas bubble formation causing mechanical problems. Addition of dilute mineral acids like sulfuric acid to the ammonium thiocyanate aqueous phase resulted in a markedly improved An-Ln separation and besides, hydrolysis problems are avoided [MOO64]. Also nitric acid could be used, but it has the disadvantage of slowly oxidising the thiocyanate ion. The use of diethylbenzene as diluent has been investigated because it is more radiation resistant. It was as efficient as xylene. Doubtless, many other diluents could be used, although the addition of modifiers will be necessary with kerosene and some aliphatic compounds.

The use of formic acid instead of dilute mineral acids has been proposed by Chiarizia et al. [CHI95A] to avoid the presence of corrosive or oxidizing agents. Furthermore, formic acid can be destroyed without leaving any inorganic residue. The addition of 0.01 M hydroxylammonium formate as a reducing agent to protect thiocyanate from oxidation has been recommended by Chiarizia et al.

Also the extraction and separation of An(III) and Ln(III) from nitrate solutions has been investigated [HOR66, CHI95A]. It was found that trivalent actinides and lanthanides were efficiently extracted only in the presence of high concentrations of salting out agents ($LiNO_3$ and/or $Al(NO_3)_3$ and at very low aqueous acidity. Also very low Am/Eu separation factors were reported.

Quaternary ammonium salts containing a (substituted) benzyl group have been investigated because it was expected that metal extraction would be less sensitive to the aqueous acidity, caused by competitive acid extraction [CHI95A]. Due to the inductive electron withdrawing effect of the benzyl group, the positive charge of the quaternary N is increased. This lowers the nucleophilic character of the reaction centre of the quaternary ammonium salt ($\equiv N^+X^-$), which makes it less favorable for hydrogen bonding of the aqueous acid. This was confirmed by experimental results but, unfortunately the Am/Eu separation factor was much lower than with Aliquat™ • 336.

Unfortunately, Aliquat™ • 336 degrades rapidly to a tarry material after short contact times with highly radioactive solutions [JAR91].

6.3.2.2. TEVA resin

Actinide (III)/lanthanide separations can also be performed by means of extraction chromatography on Eichrom's TEVA resin. TEVA® (for TEtraVAlent actinides) resin, developed by Horwitz et al. [HOR95], is Amberchrom CG-71ms (Supelco) impregnated by means of the dry impregnation method with Aliquat™ • 336. The TEVA resin is highly selective for tetravalent actinides from a wide rage of nitric and hydrochloric acid concentrations. Also the pertechnate anion, TcO_4^-, is strongly retained. By using solutions containing 1 M ammonium thiocyanate and 0.1 M formic acid as eluent it is also possible to achieve a separation of the trivalent actinides, which are now well extracted, from the lanthanide elements, which will pass through the column.
[HOR95, SMI95]

A similar SPE resin, which consists of 33.3 wt.% unpurified Aliquat™ • 336 on Plaskon (a trifluorochloroethylene polymer), was prepared by Huff [HUF67]. The logarithmic relationships between the distribution coefficients of the trivalent actinides and lanthanides and the NH_4SCN concentration (0.1-3 M) give a family of straight lines with a positive slope of about 2. The logarithmic representation of the relationship between the distribution coefficients and the Aliquat™ • 336 concentration at constant ammonium thiocyanate concentration results in lines with a slope of approximately 1, which indicates that the metal to ligand ratio of the extracted species is equal to 1, which is consistent with data obtained in the liquid-liquid extraction system described by [GER65]. With this resin a separation factor of about 60 can be realized for Eu and Am. It should be mentioned that the sample solutions (in hydrochloric acid) were evaporated to dryness and redissolved in a small volume of the eluent. In contrast with the liquid-liquid extraction system described by [MOO64], a decrease in extraction was observed with increasing acidity of the aqueous phase.

Due to the low radiation resistance of Aliquat™ • 336, the application of these extraction chromatographic resins for the reprocessing of highly radioactive waste is not recommended.

6.4. An(III)/Ln(III) separations from basic solutions

Russian scientists have investigated the use of alkaline solutions to effect separations of the trivalent actinides and lanthanides. Alkylpyrocatechols such as (α,α-dioctylethyl) pyrocatechol, DOP, have been shown to be useful actinide selective extractants from alkaline aqueous solutions in which complexants suppress hydrolysis of the cations. Generally, for An(III)/Ln(III) systems, the extraction of the An(III) cations by DOP increases with increasing pH while that of the Ln(III) cations decreases. The largest separation factor reported for the Eu/Am pair for this method was 70. Quaternary amines, such as Aliquat™ • 336 (tricaprylylmethylammonium chloride) can also be used, but the separation factors between trivalent cations are usually less than four. To separate a mixture of Am(III) and Cm(III), the Am(III) can be oxidised by chemical or electrolytic means to Am(VI) at pH 10. In a solution of 0.5 M $Na_4P_2O_7$, the americium reduces to Am(V) and remains in the aqueous phase while the Cm(III) extracts in an organic phase of 1-phenyl-3-methylpyrazol-5-one (PMBP) in chloroform. A separation factor of 10^3 is reported. [KAR88, KAR92, CHO95B]

7. Americium/curium separation

Both elements are chemically so similar that very special radiochemical and/or electrochemical techniques have to be used for their separation. The electrochemical oxidation process called "SESAME" process is the only one in the world which can, in principle, separate Am/Cm in one process step [BAE98]. Most Am/Cm separations are based on the oxidation of Am(III) to the +VI or +V oxidation state. Curium remains in the +III state under strong oxidizing conditions. The separation can thus be carried out with several extraction agents. It is, however, difficult to stabilize Am in the higher oxition states. If multistage separation techniques are accepted, advantage can be taken of the small separation factors obtained with some extractants [BAR03].

7.1. SESAME Process

The SESAME (Selective Extraction and Separation of Americium by means of Electrolysis) process has been developed in France at CEA/Marcoule. Am(III) in nitric acid solutions can be oxidized to Am(VI) by electrolysis in the presence of heteropolyanions (e.g. heteropolytungstate) acting as catalyst. The hexavalent americium can then be separated from trivalent curium by means of an extraction with for instance TBP. The SESAME process exhibits a great efficiency for the Am/Cm separation. However, its industrialisation is faced with difficulties such as the instability of Am(VI), the generation of secondary solid wastes (heteropoly anions). Furthermore, it is difficult to develop a multi-stage process.

At Hitachi, Japan a similar process is under development using ammonium persulphate for the oxidation of Am(III) to Am(VI).

[MAD00, IAE04, MAD02B]

7.2. Countercurrent chromatography

Am and Cm have been separated by means of countercurrent chromatography (CCC). CCC is a multi-stage solvent extraction technique, which is based ont the retention of one phase (the so-called stationary phase) of a two-phase liquid system in a rotating coil column under the action of centrifugal forces, while the other liquid phase (mobile phase) is being continuously fed

through the column. CCC is often carried out with a planetary centrifuge. Functionally, this consists of a helical coil of inert tubing (e.g. Teflon) which rotates on its planetary axis and simultaneously rotates eccentrically about another solar axis. The effect is to create zones of mixing and zones of settling which progress along the helical coil at dizzying speed. The Am(III)/Cm(III) separation has been performed by using a diamide extractant (e.g. DMDOHEMA). The diamide solvent, which acts as the stationary phase, is filled in the spiral column in the stationary mode. After the rotation is started (i.e. in the dynamic mode), the nitric acid aqueous phase is continuously fed through the column. The Am/Cm sample is loaded onto the column by means of an injection loop after the hydronamic equilibrium between both liquid phases has been reached. An efficient Am/Cm separation by CCC can be realized by optimizing the composition of the mobile and stationary phase, the rotation speed of the column, the column length and the flow rate of the mobile phase.
[MYA05]

7.3. Anion exchange chromatography

Transplutonic elements are only slightly sorbed on anion exchangers from HCl or HNO_3 media, but the presence of alcohol in the media enhances the anion exchange of these elements, especially in nitric and sulphuric acid. The sorption of transplutonic elements increases with increased alcohol content and the binding with the resin is stronger in HNO_3 media than in H_2SO_4 media. The greater the atomic number, the stronger the sorption. Often applied, particularly for analytical purposes, is the separation of americium and curium from nitric acid-methanol medium.
[HAI73, GUS73A, GUS73B, HOL76]

7.4. Am(V) precipitation

This precipitation process has been developed at the end of the 1960s in the USA and is today under development at JNC in Japan. After the Am(III) and Cm(III) mixture is dissolved in a 2 M K_2CO_3 solution, Am(III) will be chemically or electrochemically oxidized to Am(V), which will precipitate as the solid crystalline double carbonate of Am(V) and potassium, $K_5AmO_2(CO_3)_3 \cdot nH_2O$. Cm(III) remains in solution. The main drawbacks are the quite large Am

losses with Cm, the large amounts of secondary wastes and the fact that it exists only one stage for the process.
[MAD00, IAE04]

8. Conclusions

At the Institute for Transuranium Elements, Karlsruhe, different advanced aqueous reprocessing processes have been tested on genuine HAW solutions [CHR04]. Five different processes for the simultaneous extraction of An(III) and Ln(III) have been tested: TRUEX, DIDPA, TRPO, DIAMEX (DMDBTDMA and DMDOHEMA)and CYANEX 923. For the subsequent An(III)/Ln(III) separation, SANEX-Cyanex , SANEX-ALINA and SANEX-BTP solvent extraction processes have been demonstrated on genuine fuel solutions. All five process for the simultaneous extraction of An(III) and Ln have extracted Am and Cm very efficiently. The most efficient extraction was obtained with CMPO (TRUEX process). However, due to accumulation of Am and Cm in the TRUEX solvent in the back-extraction section, only a low amount of these elements were recovered in the stripping solution. This is likely caused by the high nitric acid concentration in the loaded organic solvent. The recovery can possibly be improved by acidity reduction. The recovery in the DIDPA process is believed to be achievable by optimisation of flow rates, acidy of the feed, etc. Excellent recovery was obtained by the TRPO, DIAMEX and CYANEX 923 processes. *n*Pr-BTP showed the best performance for the separation of Ma from Ln. The highest Am/Eu separation factor was obtained with a feed containing 1 M nitric acid.

The above mentioned comparison of several solvent extraction processes for the simultaneous An+Ln separation from a PUREX HAR solution revealed that the DIAMEX process, as well as the TRPO and the CYANEX 923 process performed very well. Probably also the TRUEX and the DIDPA process can be improved by further optimisation. The DIAMEX process has, however, some clear advantages over the other processes which use phosphor bearing extractants. Diamide extractants can be incinerated at the end of their use, since they fulfil the CHON principle. Furthermore, their chemical synthesis is straightforward, which is important for their large-scale use. The diamides, as well as their actinide complexes, are compatible with aliphatic diluents (e.g. TPH). In contrast, TBP has to be added to the TRUEX solvent in order to prevent third phase formation. The radiolysis and hydrolysis products of the diamide extractants do not interfere with the extraction nor with the back-extraction.

Very good An(III)/Ln(III) separations have been obtained with the SANEX process. Extraction agents containing N-donor atoms are preferred because they are consistent with the CHON principle. According to Baestlé [BAE98] the secondary waste issue may become the bottleneck of their applicability in industrial facilities. Furthermore, S-bearing extractants are, in general, less stable than N-bearing extractants. The affinity of BTP molecules for trivalent actinide ions is more than hundred times greater than for lanthanide ions, which makes them very promising extractants. Other nitrogen-bearing extractants (e.g. TPTZ, TerPy) are generally used in a synergetic mixture with an acidic extractant. Nonetheless, in the case of BTPs, these extractants can be used on their own because BTP molecules extract An(III) as nitrates. In addition, the separation can be performed in a nitric acid medium with a concentration of about 1 M, which is an enormous advantage.

Currently, the combination of the DIAMEX process and the SANEX-BTP process seemes to be the best to achieve an efficient minor actinide recovery from spent nuclear fuel. For use at an industrial scale, the organic extractants involved in the separation processes have to withstand extreme conditions because HAW solutions are very radioactive and very acidic.

The DIAMEX process, using DMDOHEMA, which is sufficiently resistant against radiolysis and hydrolysis, is considered to be mature for further development towards industrial application, even for the treatment of HAC solutions. Due to insufficient stability of the BTP molecules, the SANEX-BTP process cannot yet be proposed for industrial development.

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