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Development of the Chalmers Grouped Actinide Extraction Process

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Abstract. Several solvents for Grouped ActiNide EXtraction (GANEX) processes have been investigated at Chalmers University of Technology in recent years. Four different GANEX solvents; cyclo-GANEX ($CyMe_4$-BTBP, 30 vol.% tri-butyl phosphate (TBP) and cyclohexanone), DEHBA-GANEX ($CyMe_4$-BTBP, 20 vol.% *N*,*N*-di-2(ethylhexyl) butyramide (DEHBA) and cyclohexanone), hexanol-GANEX ($CyMe_4$-BTBP, 30 vol.% TBP and hexanol) and FS-13-GANEX ($CyMe_4$-BTBP, 30 vol.% TBP and phenyl trifluoromethyl sulfone (FS-13)) have been studied and the results are discussed and compared in this work. The cyclohexanone based solvents show fast and high extraction of the actinides but a somewhat poor diluent stability in contact with the acidic aqueous phase. FS-13-GANEX display high separation factors between the actinides and lanthanides and a good radiolytic and hydrolytic stability. However, the distribution ratios of the actinides are lower, compared to the cyclohexanone based solvents. The hexanol-GANEX is a cheap solvent system using a rather stable diluent but the actinide extraction is, however, comparatively low.

Key words: BTBP-ligands • DEHBA • GANEX • organic diluents • TBP • solvent extraction

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Introduction

Today, nuclear power plants render highly radiotoxic used nuclear fuel that has to be isolated from the environment. If the fuel is disposed in the final storage, it has to be stored for over 100 000 years to reach a radiotoxicity level that is equal to that of natural uranium needed to produce the fuel [1]. An alternative path to the final storage would be to separate the long-lived actinides from the used nuclear fuel for transmutation. Then, the storage time could be reduced to around 1000 years [2]. This separation would not only reduce the long-term radiotoxicity but also the heat load, making the final storage more volume efficient [3].

Several methods for the partitioning of actinides from the rest of the elements in the used fuel have been developed during the years and solvent extraction is one of the most well-established methods [4]. Today the plutonium uranium redox extraction (PUREX) process, developed during the 1940's, is widely used for the recovery of plutonium and/or uranium [5, 6].

GANEX process has since 2007 been under development at Chalmers University of Technology. The different solvent systems developed all have the common denominator that they combine two different extractants; one being from the bis-triazine bipyridine (BTBP) family and the other being either tributyl phosphate (TBP) or the monoamide *N*,*N*-di(2-ethylhexyl)butyramide (DEHBA). In the initial process cyclohexanone was used as diluent with good results [7, 8]. However, due to instability and density issues other diluents were investigated later on. These were long-chained alcohols, for example hexanol and octanol [9], and lately – fluorinated aromatic sulfone compounds such as phenyl trifluoromethyl sulfone (FS-13) [10].

Grouped actinide extraction

Three GANEX processes have mainly been developed in Europe, the EURO-GANEX, the CEA-GANEX and the Chalmers GANEX [11]. In general the GANEX process is divided into two separate steps, one where the bulk uranium is removed and one partitioning step, the actual GANEX step, where the actinides are separated from the fission products, for example lanthanides and corrosion/activation products [12]. This step occurs during highly acidic conditions. The separated actinides are then stripped for transmutation purposes.

CEA-GANEX was developed in France, combining *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) and di(2-ethylhexyl)phosphoric acid (HDEHP). The EURO-GANEX process like the Chalmers GANEX, is also under development. A combination of the following extractants has been proposed for EURO-GANEX; *N*,*N*′-(dimethyl)-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) and *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA). Different from the Chalmers GANEX, the EURO-GANEX process separates all the transuranic elements and the lanthanides together from other fission products, before selective actinide stripping [13]. The GANEX process developed at Chalmers combines two extractants and one diluent. During the years, different extractant molecules and diluents have been used but for a long period of time various bis-triazine bipyridine (BTBP) molecules have been used as one of the extractants. BTBP molecules act as tetradentate ligands for metal ions, and many of them have a high selectivity of trivalent actinide extraction over trivalent lanthanides [14, 15]. This is in general a difficult separation due to the chemical similarities between the trivalent actinides and the lanthanides. The other main extraction agent used, tributyl phosphate (TBP) extracts tetra- and hexavalent actinides [6, 16].

TBP ($\rho = 0.97\ \mathrm{g{\cdot}mL^{-1}}$ [17]) is a well-known extractant of plutonium and uranium, and it has been used in the PUREX processes in the last 50–60 years. In recent years, TBP became a common extractant in different GANEX solvents [7, 10, 18]. A negative feature with TBP is, however, that it does not follow the CHON principle [19]. This means that the solvent will leave a larger fraction of non-gaseous residues for waste solidification, than the CHON solvents. In addition, TBP can also decompose into dibutyl phosphate [17]. This is a problem since dibutyl phosphate increases the extraction of plutonium and fission products [20], therefore processes using TBP must include an extra purification step.

A DEHBA extractant, an alternative to the TBP, that follows the CHON principle and decomposes into less problematic by-products, has also been investigated [17, 21]. DEHBA is an amide that has shown good extraction properties for uranium and plutonium [22, 23].

The combination of a BTBP molecule with TBP or DEHBA allows for extraction of actinides in most valence states, present in the used nuclear fuel. The complicated redox control of the process is therefore avoided. It is also possible to strip the actinides selectively or to reuse them directly in homogeneous recycling [24].

BTBP ligands

All BTBP-type ligands are polyaromatic nitrogen donor molecules that have a common core of two aromatic pyridine rings and two triazine rings but with different side groups. Two BTBP type-ligands developed and synthesized to separate trivalent actinides from the fission products, mainly from lanthanides, are 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)[2,2’]bipyridine ($\mathrm{CyMe_4}$-BTBP) and 6,6′-bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2’]bipyridine (C5-BTBP) [14, 15, 25].

There are several differences between $\mathrm{CyMe_4}$-BTBP and C5-BTBP. Their solubilities in various diluents differ from one another, and the thermodynamic parameters of the extraction are also different. For C5-BTBP, the entropy change within the system is positive for americium extraction [25], while for a system containing $\mathrm{CyMe_4}$-BTBP the entropy change is negative [24].

In systems containing $\mathrm{CyMe_4}$-BTBP, it has been found that the chemical reactions that take place at the surface, such as complexation, determine the extraction rate [26]. For C5-BTBP systems the time and phase contact needed to reach extraction equilibrium has been correlated with the interfacial tension [18].

Another difference between the two extractants is that C5-BTBP is not stable under highly acidic conditions, due to α-hydrogen abstraction from the side chains, which makes it less suitable for use in a highly acidic GANEX extraction step [27].

Diluents

Some desirable properties of a diluent intended for use in a GANEX process are: good solubility of the extractants, allowing for fast reaction kinetics of the extraction system, radiolytic and hydrolytic stability, a density that provides sufficient density difference between the organic and aqueous phase, as well as reasonable cost and production capacity.

Different combinations of diluents and extracting molecules as organic phase for GANEX processes have been studied lately. At Chalmers, solvent systems combining $\mathrm{CyMe_4}$-BTBP, 30 vol.% TBP or

20 vol.% DEHBA and 70 vol.% or 80 vol.% diluent have generally been investigated.

Cyclohexanone

Cyclohexanone (ρ = 0.95 g·mL^{-1} [28]) was a diluent chosen for the Chalmers GANEX process because it well dissolves CyMe$_4$-BTBP [29] and ensures relatively fast extraction kinetics with this extractant [30]. It is also a cheap diluent that is mass produced for the production of nylon 6 [31]. However, the low flashpoint (44°C) [32] and exothermic reactions with concentrated nitric acid, forming adipic acid [33], in combination with the comparatively high solubility in the acidic aqueous phase [32] decrease the diluents stability and are the reason for further investigations of GANEX systems using alternative diluents.

Long-chain alcohols

Long-chain alcohols have been thoroughly investigated as diluents for BTBP-type ligands [9, 25] as they are among others cheap, easily accessible and relatively stable. 1-Octanol for instance is a standard diluent within solvent extraction. When actinide distribution ratios were investigated in long-chained alcohols (using C5-BTBP and a low-acidic aqueous phase, 0.99 M $NaNO_3$ and 0.01 M HNO_3) it was discovered that the distribution ratios increased with a decrease in chain length, being equal to 5.74 for hexanol and 1.21 for decanol [34]. Hexanol also displays a slightly higher solubility of CyMe$_4$-BTBP compared to octanol [29], which is why the main focus was put on 1-hexanol when investigating long--chained alcohols for GANEX purposes. However, the comparatively slow kinetics and low solubility of CyMe$_4$-BTBP in these types of diluents [18], led to investigations of other more innovative solvents for the Chalmers GANEX process.

Phenyl trifluoromethyl sulfone

Phenyl trifluoromethyl sulfone (FS-13), is a heavy (ρ = 1.4 g·mL^{-1}) polar diluent [35]. The high density ensures a good phase separation during metal extraction. FS-13 also displays a good chemical stability [36] and a low viscosity [35]. It was originally developed for the universal extraction (UNEX) process where it showed a high resistance against radiation and good stability against nitric acid [37, 38]. Due to FS-13 polarity a high solubility of BTBP-type ligands can also be reached. These features make it interesting for use in the Chalmers GANEX process despite the present high cost and low production volumes.

Another negative feature with FS-13 in comparison with the long-chained alcohols and cyclohexanone is that it contains sulfur and fluorine, and hence does not follow the CHON principle. This is also the case when using TBP as one of the extractants, however the amount of TBP is small in comparison to the diluent.

Extraction

A measure of extraction ability of metals in solutions is the distribution ratio, D. This is the ratio of the concentrations of a given element in the organic phase to that in the aqueous phase, Eq. (1).

$$D = \frac{[C]_{org}}{[C]_{aq}} \tag{1}$$

The ratio of two distribution ratios is defined as the separation factor, SF, Eq. (2). From the definition, SF > 1, therefore if $D_A > D_B$, D_A becomes the numerator while if $D_A < D_B$, D_B becomes the numerator.

$$SF = \frac{D_A}{D_B} \tag{2}$$

As mentioned earlier the interfacial tension is an important factor in the liquid-liquid extraction process. If the interfacial tension is lowered during mixing, the interfacial area of the phases increases [39]. This can increase the rate of mass transfer in the system, under the right circumstances [40]. A drawback is that a lower interfacial tension may complicate the phase separation and slow down the extraction [39]. However, for a fully developed extraction process using centrifuges, a lower interfacial tension system can be preferred anyway.

Methodology

Metal extraction experiments have generally been performed using small (0.2–1.5 mL) equal volumes of the different GANEX solvents and the aqueous phases. Phase contact has been performed either in a mechanical shaker (IKA, VIBRAX VXR 1500 rpm) at 25°C (standard for later investigations) or by shaking the vials by hand in an insulated canister at room temperature.

The GANEX solvents investigated generally consist of 10 mM BTBP, 30 vol.% TBP or 20 vol.% DEHBA and 70 vol.% or 80 vol.% of diluent. CyMe$_4$--BTBP and C5-BTBP were synthesized in house, according to [41].

For the GANEX experiments the aqueous phase used normally consists of 4 M nitric acid spiked with trace amounts of radioactive metals (^{152}Eu, $^{235/238}$U, $^{237/239}$Np, $^{238/239}$Pu, ^{241}Am, ^{244}Cm). The determination of the concentration of actinides and europium was mainly performed as the following: for the americium and europium samples, 100 μL sample of each phase was collected for gamma spectrometry (HPGe, Canberra, Gamma Analyst GEM 23195). ^{152}Eu was analyzed at a gamma energy of 121.8 keV and ^{241}Am – at a gamma energy of 59.6 keV. For the plutonium, uranium and neptunium-239, 100 μL samples of each phase were mixed with 5 mL scintillation cocktail (Ultima Gold AB, PerkinElmer) for liquid scintillation detection (Wallac 1414 WinSpectral). For the neptunium-237 and curium, 10 μL samples of each phase were collected and placed on an alpha planchet, and 50 μL of a coating solution (Z100) dissolved in acetone was added on the top of the sample. The alpha planchets were evaporated under an IR lamp (~10 min) and the organic residues were removed using a gas burner. The samples were analyzed with alpha spectrometry (Ortec, Alpha Duo, Octête TM PC) at the alpha energies of 4.8 MeV and 5.8 MeV for ^{237}Np and ^{244}Cm, respectively.

Discussion

Extraction capability

When comparing the extraction of actinides and lanthanides using four of the most investigated GANEX solvents; cyclo-GANEX (CyMe$_4$-BTBP, 30 vol.% TBP and cyclohexanone), DEHBA-GANEX (CyMe$_4$-BTBP, 20 vol.% DEHBA and cyclohexanone), hexanol-GANEX (CyMe$_4$-BTBP, 30 vol.% TBP and hexanol) and FS-13-GANEX (CyMe$_4$-BTBP, 30 vol.% TBP and FS-13) it can be concluded that they all extract the actinides and can separate them from the lanthanides (Figs. 1 and 2, Table 1).

Extraction in the two cyclohexanone based solvents are clearly the highest but this also accounts for the lanthanides that have relatively high distribution ratios. The separation factors are low for U/Eu extraction in the DEHBA-GANEX and hexanol-GANEX system and indicate that the bulk uranium would need to be separated in a separate step before the actual GANEX extraction in this case. FS-13 has high separation factors for all actinides except neptunium, which is similar as for the cyclo-GANEX. Also, the extraction of neptunium is rather low in all four systems. Since neptunium is easily oxidized and reduced, it is most likely present in mixed oxidation states [44], which may influence the extraction. Due to this it is hard to know in which oxidation state the neptunium is present.

Stability

The stabilities of the different GANEX solvents have been examined through radiolysis and hydrolysis, Table 2. The hexanol and FS-13 based solvents were irradiated up to 24 hours with a dose rate of approximately 7 kGy·h^{-1}. The hydrolysis study was performed simultaneously under the same time and temperature conditions. Cyclo-GANEX was irradiated for 16 hours at a dose rate of 18 kGy·h^{-1}. The hydrolysis was performed in room temperature for 144 hours. In both cases radiolysis and hydrolysis were performed in contact with 4 M nitric acid.

FS-13-GANEX has more or less the same distribution ratio of americium after both the radiolysis and hydrolysis study. Hexanol-GANEX resists hydrolysis better than radiolysis but displays a decrease in americium extraction in both studies. The extraction of americium also decreases in the cyclo-GANEX system after irradiation but stays the same after hydrolysis. Distribution ratios in the

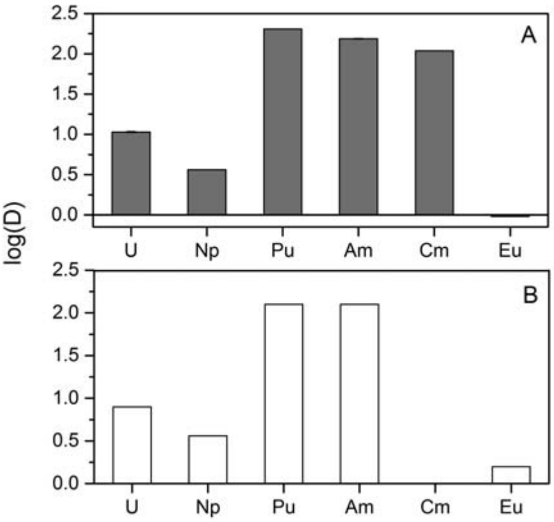

Fig. 1. Actinide and europium extraction from 4 M HNO$_3$. (A) cyclo-GANEX and (B) DEHBA-GANEX [42, 43]. There is no curium extraction data for the DEHBA-GANEX system.

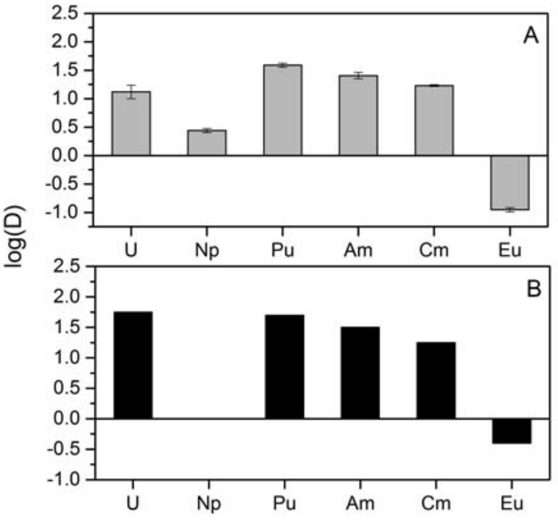

Fig. 2. Actinide and europium extraction from 4 M HNO$_3$. (A) FS-13-GANEX [10] and (B) hexanol-GANEX [18]. There is no neptunium extraction data for the hexanol-GANEX system.

Table 1. Separation factors for selected actinides over europium in four different GANEX systems. Data for cyclo-GANEX is retrieved from Ref. [7], DEHBA-GANEX from Ref. [43], hexanol from Ref. [18] and FS-13 from Ref. [10]

	Cyclo-GANEX	DEHBA-GANEX	Hexanol-GANEX	FS-13-GANEX
U/Eu	11 ± 1	4.5 ± 0.5	5 ± 0.4	44 ± 6
Np/Eu	3.8 ± 0.5	2.8 ± 0.5	–	4.1 ± 0.5
Pu/Eu	212 ± 22	10.5 ± 2	186 ± 19	124 ± 18
Am/Eu	160 ± 16	10.5 ± 2	121 ± 14	93 ± 1
Cm/Eu	113 ± 13	–	–	56 ± 6

Table 2. Logarithmic distribution ratios of americium. The uncertainties are standard deviations from triplicate samples. Data for cyclo-GANEX are retrieved from Ref. [43], for hexanol from Ref. [18] and for FS-13 from Ref. [10]

	Cyclo-GANEX	Hexanol-GANEX	FS-13-GANEX
Reference	2.19 ± 0.02	1.50 ± 0.05	1.40 ± 0.06
Radiolysis	1.74 ± 0.02	0.57 ± 0.04	1.18 ± 0.05
Hydrolysis	2.09 ± 0.02	0.84 ± 0.04	1.34 ± 0.06

cyclo-GANEX system are also decreased, however, still high compared to the hexanol-GANEX.

The data for DEHBA-GANEX are excluded from Table 2 due to their similarities to cyclo-GANEX. Since both systems are based on cyclohexanone, their stabilities do not substantially differ from each other [43].

The degradation of cyclohexanone in contact with the acidic aqueous phase makes cyclohexanone challenging as a diluent in systems containing 4 M nitric acid as the aqueous phase despite maintained high actinide extractions, since it will require a rigorous solvent clean-up. The instability of cyclohexanone also poses a challenge in designing a safe process.

System comparisons

All four investigated GANEX-systems have different negative and positive properties. The best feature of cyclohexanone based systems is the high actinide extraction. FS-13 is an expensive diluent while both hexanol and cyclohexanone are cheap. The high density of FS-13 makes the organic phase in the FS-13-GANEX system heavier than the aqueous phase. This is beneficial when working with metal loading, as the density difference between the phases increases upon extraction. This is the opposite to the cyclohexanone based systems where the density of the organic phase is very close to that of the aqueous one, and even more so after metal extraction, making phase separation difficult. This was evident in a recent centrifugal contactor test of the cyclo-GANEX system [45]. The radiolytic and hydrolytic stability of the FS-13-GANEX is the best of all four examined systems and makes it an interesting diluent for the future.

Conclusions

Several different promising GANEX systems have been proposed. They are under development at the Chalmers University of Technology. The hexanol-GANEX has problems with low ligand solubility, making actinide loading very difficult, and causing a decrease in extraction after irradiation and hydrolysis. Both cyclohexanone based GANEX systems have good actinide extraction properties but also a rather high lanthanide extraction, especially for the DEHBA-GANEX. The major drawbacks are the degradation of the solvent during radiolysis and hydrolysis, as well as the small differences in density between the phases, which makes cyclohexanone an unsuitable diluent for a large scale GANEX process. Right now, the most promising option is the FS-13-GANEX system due to its stability against radiation and hydrolysis, and high density of the solvent. The FS-13 based system does not reach the same actinide distribution ratios as the cyclohexanone based systems but they are still sufficient. The separation factors, also high for all actinides, indicate that FS-13 is a promising GANEX diluent.

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