

TOWARDS A DIAMEX PROCESS FLOWSHEET USING HIGH ACTIVE CONCENTRATE (HAC)

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Abstract

The efficiency of MA recovery in the DIAMEX process has already been demonstrated using HAR. The next step aims at the demonstration of reprocessing from HAC as feed, in view of an industrial application. The volume reduction would reduce the size of the installation and thereby the costs of the process. The first step towards the demonstration of a DIAMEX process using HAC is the production of the genuine solutions. In ITU about 9 L HAR raffinate has been prepared, from PUREX reprocessing of 1.4 kg of MOX fuel, and characterised in order to produce HAC for the upcoming extraction tests. For this purpose, the HAR is subjected to a concentration/denitration process to obtain HAC with a final acidity compatible with the DIAMEX operating conditions, i.e. around 3 M HNO₃. This process has been tested and optimised using HAR-simulate. Promising results were found for concentration factors (CF) of 6 to 8. At CF of 39 a significant co-precipitation of lanthanides occurred.

Introduction

Partitioning and transmutation (P&T) concepts are studied world wide to reduce the long-term radiotoxicity of the nuclear waste. The essential part of P&T concepts is the efficient recovery and multi-recycling of long-lived radiotoxic elements in dedicated reactors for transmutation into stable or shorter-lived products. P&T concern all radionuclides contributing to the overall long-term radiotoxicity but due to the high radiotoxicity of the minor actinides, they are of special interest.

Today fissile uranium (U) and plutonium (Pu) are recovered by PUREX reprocessing, leaving the MAs together with the bulk of fission products in the high active waste stream – the so-called high active raffinate (HAR). The present waste management of HAR is immobilisation in borosilicate glass blocks for final storage in a deep geological repository. New advanced aqueous reprocessing schemes have therefore been developed, aiming primarily at the complete recovery of americium (Am) and curium (Cm) from HAR. The scheme developed in Europe is the combination of the DIAMEX and SANEX processes. In this scheme Am and Cm are co-separated with lanthanides in the DIAMEX process and the subsequent separation of Am and Cm from lanthanides is carried out in the SANEX process. The product fraction (containing Am and Cm) can be subjected to a subsequent Am/Cm separation process to provide the possibility for a specific recycling and transmutation of Am and possibly a specific conditioning of Cm.

The efficiency of the DIAMEX process has been demonstrated in hot tests using genuine fuel solutions, prior subjected to PUREX reprocessing. [1-3] It could be shown that 99.9% of the Am and Cm contained in the HAR feed could be recovered in a 16 stages centrifugal extractor set-up. It was also shown that potential problem elements, co-extracted by the diamide molecule, such as Zr, Mo and Pd could be efficiently directed to the DIAMEX raffinate by oxalic acid and HEDTA washing. [4] The product fraction (An and Ln) generated from DIAMEX reprocessing is now used for the development and hot testing of the SANEX process. [5-6]

The next set of experiments to be carried out within the European research co-operation, PARTNEW, aims at the demonstration of MA recovery by the DIAMEX process using high active concentrate (HAC) as feed – in view of an industrial application. The decrease in volume (compared to HAR) would reduce the size of the installation and thereby the costs of the process. Three different problems need to be solved before this process can be demonstrated; 1) the concentration/denitration process has to be designed so that MA containing precipitates is not formed; 2) as oxalic acid is added to HAC a Zr and Mo precipitate, containing also MA's might form; 3) higher metal concentration increases the risk of third phase formation in the extraction process. All phenomena are dependent on factors such as the concentration factor of HAC and the nitric acid and oxalic acid concentrations, which have to be optimised.

The first step towards the demonstration of a DIAMEX process using HAC has been the production of genuine starting solutions. In ITU about 9 L HAR raffinate has been prepared from PUREX reprocessing of 1.4 kg of MOX fuel (Burn-Up 30 GWd/THM).

In the next step, optimisation of the concentration/denitration process have been undertaken. It must be demonstrated, that it is possible to concentrate a genuine industrial HAR, denitrate to an acidity around 3 M and add oxalic acid to a concentration of about 0.3 M without risk of precipitation or third phase formation in the following DIAMEX extraction. Initial tests on concentration/denitration of HAR simulate have therefore been carried out to prepare and optimise the concentration/denitration process for genuine HAR, which is to be carried out in a hot cell. The aim has been to control the process and to obtain a HAC simulate (6 times concentrated with an acidity of 3 M) without formation of lanthanide containing precipitates. In this paper the results of these experiments are discussed and future experimental plan is outlined.

Experimental

Reagents

All reagents and chemicals were of the analytical reagent grade. TriButylPhosphate (TBP), dodecane and formic acid were obtained from MERCK (Germany). The nitric acid solutions were prepared either from dilution of concentrated nitric acid or from Titrisol ampoules. UHQ grade water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used for all dilutions. As regards metals, all simulate solutions were prepared from commercially available nitrates: Rb (Fluka, Germany), Sr, Y, Zr, Ag, Sb, Cs, La, Ce, Nd, Sm, Eu, Gd (MERCK) Ru, Rh, Pd, Cd, Ba, Pr (Alfa Aesar, Germany), or pure metals: Te, Sn and Mo. The simulate preparation recipe is described elsewhere. [7]

Equipment and procedure

PUREX process

The centrifugal extractor equipment installed in the hot cells is described elsewhere. [8] The PUREX reprocessing was carried out using 16 extractor stages divided in four blocks with four extractors each. At the end of the experiment centrifuges and pumps were turned off simultaneously and samples were taken from the mixing chambers of each centrifuge and the two phases were separated. In addition, the feed and the collected fractions were sampled during the last 30 minutes of the experiment.

All concentrations in the aqueous samples were determined by a High Resolution ICP-MS (ThermoFinnigan Element 2). Samples taken from the organic phase were back-extracted twice with 0.1 M HNO_3 (aqueous to organic volume ratio of 2) prior to analyses.

The PUREX process flow sheet is shown in Figure 1. The process scheme was optimised so that the organic phase could be re-circulated, after conditioning with 1 M NaOH followed by acidification, in order to minimise organic waste. Dissolving 1.4 kg of commercial MOX fuel in 7 M HNO_3 produced 7 L of fuel solution used as feed for the process. Some characteristics of the original MOX fuel and the fuel solution are given in Table 1 and 2, respectively.

Figure 1. PUREX process for production of HAR. Organic phase is re-circulated after conditioning with 1 M NaOH follow by acidification

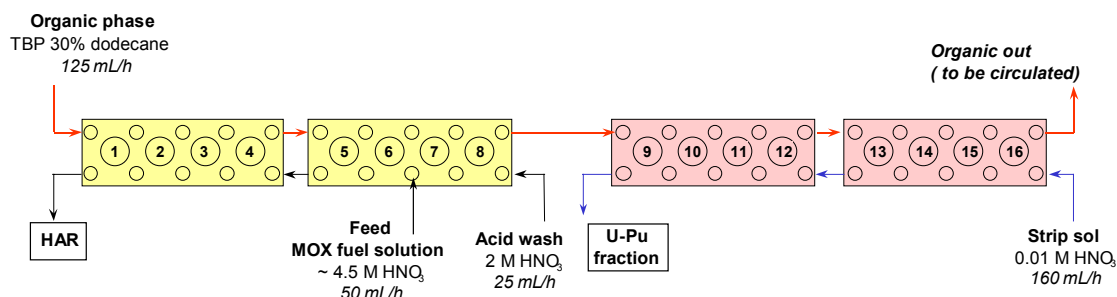


Table 1. Characteristics of the original MOX fuel

Reactor type	PWR
Average burn-up	30 GWd/tM
Fuel pin diameter	10.75 mm
Full power days	957
Discharged date	9.6.89

Table 2. Measured uranium and plutonium total concentrations and isotopic composition of the fuel solution

Uranium [mg/g]	114.7± 0.9	Plutonium [mg/g]	4.43 ± 0.02
Isotopic composition (wt.%)			
U-234	0.016	Pu-238	2.947
U-235	0.375	Pu-239	42.401
U-236	0.077	Pu-240	33.562
U-238	99.529	Pu-241	10.372
		Pu-242	10.715

Concentration-denitration

An apparatus (Figure 2) consisted of a one litre round-bottomed three-necked flask was used; this flask was sat in a combined heater/magnetic stirrer. The first neck was connected to a glass in-pipe that led to the bottom of the flask, ensuring that all liquids introduced into the flask entered at the base; this in-pipe was connected to a peristaltic pump. The second, central neck led to a 10 cm glass spacer-tube, which led to a condensing unit, which led further to a double-walled condenser, after which three Sodium Hydroxide-filled gas-traps collected the acidic gases produced in the experiment. The condensing unit allowed gas to pass through, but directed the liquid returning from the primary condenser through a second condenser to be collected at the side of the apparatus. The third neck was filled with a plastic stopper and was used only for collection of HAC samples. The nitric acid concentration in the samples was determined using a Metrohm 655 Dosimat.

Figure 2. Equipment used for concentration-denitration experiments



To test the equipment, solutions of nitric acid were concentrated and denitrated. The starting volume was normally about 250 ml of nitric acid and different concentration factors (CF) were reached. During concentration the temperature remained within 110-130°C range, it increased with the acid concentration to the azeotropic point of concentrated HNO₃ around 14.5 M, see Figure 3. The distillate was collected after condensing in a measuring flask and its volume was used to calculate the concentration factor.

The concentration factor (CF) for the concentration is defined by the following equation:

$$CF = \frac{\text{initial volume of concentrate (ml)}}{\text{final volume of concentrate (ml)}} \quad (1)$$

Denitration test was carried out by addition of concentrated formic acid to the concentrate. In Eq. 1 to 3 the reaction between nitric and formic acids is shown. [9] In strongly acidic solution (HNO₃ > 8 M), the reaction (2) is shown to prevail whereas in more diluted nitric acid solutions, mainly reaction (3) and (4) will occur.

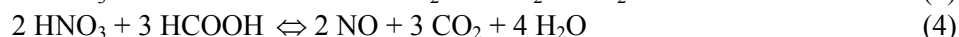
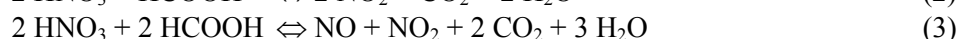
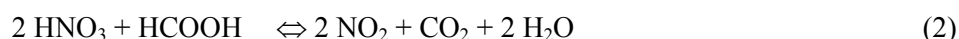
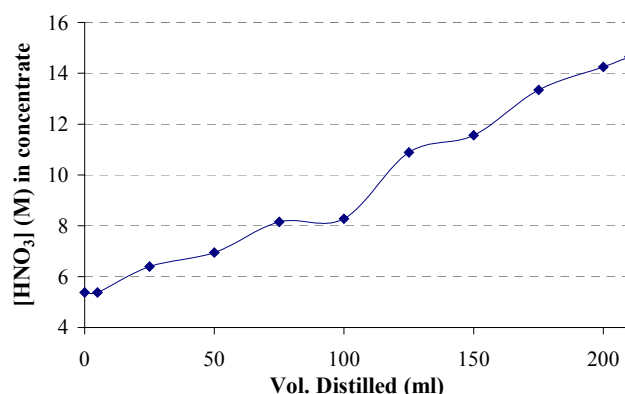


Figure 3. Nitric acid concentration of concentrate versus the amount of distillate. Starting volume 250 mL and CF= 5



In total three experiments with HAR simulate have been carried out leading to a CF of 6, 8 and 39. In all cases the starting volume of HAR was 2 L, initially 0.5 L were heated to 90-100°C under magnetic stirring. At this temperature 0.1 L of distillate were collected from the secondary condenser approximately every 15 minutes. After each 100 mL of collected distillate, a sample was taken and a further 0.1 L of HAR was pumped into the reaction vessel through the in-pipe. Each collected sample was analysed for nitric acid content. This procedure continued until all two litres of HAR had been introduced. The concentration continued until the desired final CF. At this point the condensation unit and secondary condenser were removed from the apparatus and a sample taken of the HAC. Heating and stirring were maintained while an addition of 10 mL formic acid was pumped into the flask through the in-pipe. The denitration reaction did not start immediately, however, once begun it was very vigorous, pumping brown NO_x gases out through the condenser and gas-traps. When reaction was judged to have fully reacted (no more NO_x gases could be seen) another 10 mL of formic acid were added, and so on until the final acid concentration was reached. A sample of HAC was taken using a glass Pasteur pipette after each addition and analysed for nitric acid content.

Results and Discussion

PUREX process

The PUREX process yielded 9 L of HAR. The aqueous concentration profile for some actinides and fission products are shown in Figure 4. Uranium and plutonium are efficiently extracted. Smaller but significant extraction of neptunium is also observed. Of the fission products technetium and zirconium are co-extracted, as the process was not optimised to direct these elements to the raffinate stream. Americium, curium and the rest of the fission products, including lanthanides (represented in Figure 4 by La) were not extracted. For stripping 0.01 M nitric acid was used. Uranium and technetium are accumulated in the back-extraction. Of the actinides, plutonium is the most efficiently stripped (see in more detail in Figure 5). The acidity profile for the process is also shown in Figure 5. To reach higher recovery rates for uranium, neptunium and technetium the back-extraction has to be optimised in terms of acidity and number of stages.

Figure 4. Aqueous concentration profiles for U, Pu, Np, Tc, Zr, La, Am and Cm. The feed and the acid wash solutions, are introduced between stages 6 and 7 and stages 8 and 9, respectively

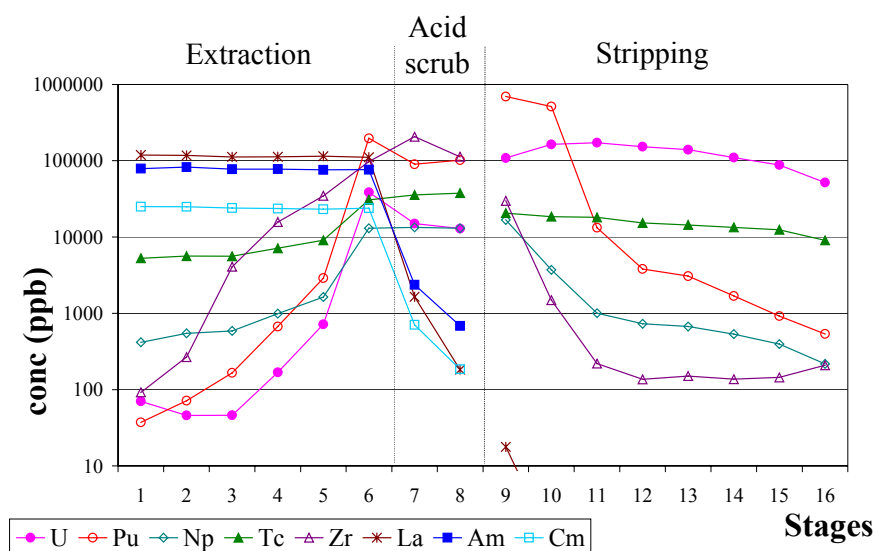
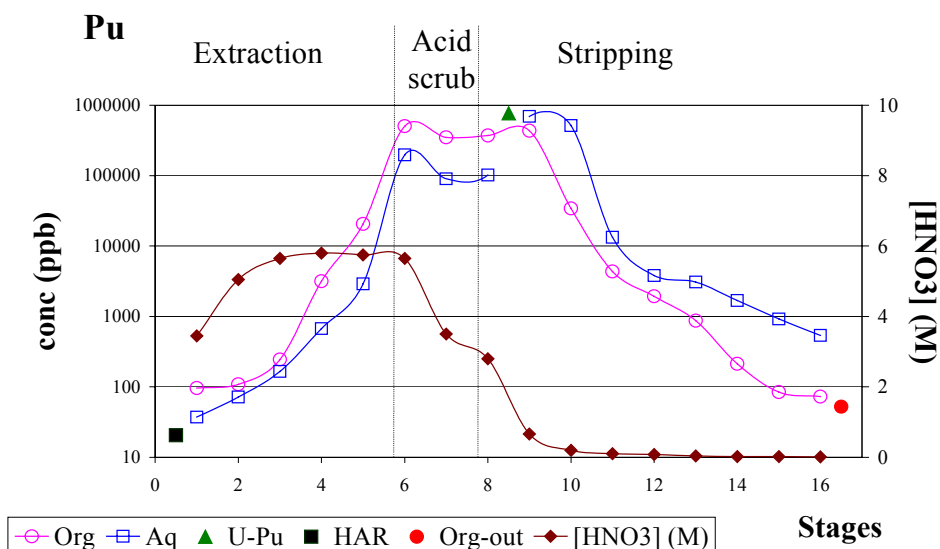


Figure 5. Plutonium concentration profiles (aqueous and organic), the collected effluent concentration and the acidity profile in the PUREX process. The feed and the acid wash solutions, are introduced between stages 6 and 7 and stages 8 and 9, respectively



The recoveries in the outgoing fractions as well as decontamination factors for some representative elements are tabulated in Table 3.

Table 3. Recoveries in the outgoing factors and DF in the PUREX experiment

Element	Recoveries (%)			DF
	Org-out sol	U-Pu fraction	HAR	
Zr	0.00	96.43	3.57	296
Tc	18.82	71.15	10.03	10
Cs	0.00	0.00	100.00	1
La	0.00	0.00	100.00	1
Np	0.42	92.78	6.80	15
U	15.04	84.95	0.01	15 183
Pu	0.01	99.98	0.01	7 043
Am	0.00	0.00	100.00	1
Cm	0.00	0.00	100.00	1

The decontamination factor (DF) for the extraction is defined by the Eq. (5):

$$DF = \frac{C_{\text{Feed}} \cdot M_{\text{Feed}}}{C_{\text{Raffinate}} \cdot M_{\text{Raffinate}}} \quad (5)$$

where C and M are component concentration in the solute and mass of the solute respectively.

For uranium and plutonium DF values higher than 10^4 and 10^3 respectively were determined. Neptunium and zirconium were also extracted to about 90% and technetium to about 70%. All the other lighter fission products and lanthanides, represented in Table 3 by Cs and La respectively, were completely recovered in the HAR solution.

A characterisation of the produced genuine HAR is shown in Table 4. It is around two times more diluted than an industrial HAR due to differences in the process (e.g. limitation to 16 extractor stages). As during the hot-cell tests ITU genuine HAR will be used, all simulate solutions were prepared referring to ITU composition, thus all CF reported refers to ITU levels.

Table 4. **Characterisation of ITU genuine HAR**

ITU genuine HAR concentration (mg/g)							
Rb	22	Ag	9	La	126	U	8
Sr	44	Cd	11	Ce	226	Np	3
Y	26	In	2	Pr	113	Pu	1
Zr	61*	Sn	3	Nd	422	Am	464
Mo	257	Sb	2	Pm	5	Cm	32
Tc	10*	Te	71	Sm	100		
Ru	128	Cs	517	Eu	18		
Rh	31	Ba	175	Gd	24		
Pd	123			Dy	14		

* Concentrations would be 264 and 58 mg/g for Zr and Tc, respectively, if not extracted in PUREX process.

Concentration-denitration

A summary of the evolution in acid concentration in one of the performed experiments is shown in Table 5. It can be seen that the addition of formic acid reduces slightly the CF but decreases efficiently the acid concentration in the HAC solution.

It was important that the starting of the denitration reaction was controlled by means of initially adding formic acid drop-wise. The addition of concentrated nitric and formic acids produced a rapid, exothermic reaction after an induction period, in which initial by-products are formed and temperature increased. Afterwards, with decreasing reaction rate, the reaction was easily kept under control by means of small periodical additions of formic acid.

Table 5. **Evolutions of CF and acid concentration throughout experiment CF8**

Exp CF8	V (ml)	CF	[HNO ₃] (M)
Original HAR	1 900	1	4.00
HAC after concentration	200	10	10.70
HAC after denitration	250	8	3.62

In all three experiments performed precipitate was formed to varying extents (Table 6).

Table 6. **Amount of recovered precipitate in all experiments performed**

Experiment	Precipitate (mg)
CF6	<10*
CF8	120
CF39	1 500

* Estimated from the difference between HAR and HAC solutions.

The composition of the precipitates was checked by redissolution in HNO₃:H₂O₂ (1:1) and ICP-MS analyses. The results obtained were compared with the original amounts in the HAR, see Table 7.

Promising results were found for CF of 6 and 8, in which the precipitate was a mixture of Mo, Ag, and Ba with no significant co-precipitation of lanthanides. However, when higher CF was reached (CF39), significant precipitation of lanthanides was found (1 to 2% of HAR). Further experiments will be performed to check the maximum feasible CF without significant precipitation of lanthanides.

Mo and Zr are two of the major components of the precipitate at CF39. At this concentration factor, between 30-40% of these elements have precipitated from the HAR, which indicates the possibility of a pre-separation of Zr and Mo at higher CF's.

Oxalic acid has to be added to the DIAMEX feed in order to prevent co-extraction of Zr and Mo. However, it has been demonstrated that at high concentrations of oxalic acid (> 0.15 M) a precipitate mainly composed of Zr and Mo but also lanthanide containing is formed. [10] A partial pre-separation of Zr and Mo would probably improve the HAC-DIAMEX process by the possibility of lowering the concentration of oxalic acid.

Table 7. The amount of element precipitated from HAR (%) and elemental abundance in precipitate (%) for the three experiments performed, corresponding to CF of 6, 8 and 39

Element	CF6		CF8		CF39	
	Elemental precipitation from HAR (%)	Elemental abundance (%)	Elemental precipitation from HAR (%)	Elemental abundance (%)	Elemental precipitation from HAR (%)	Elemental abundance (%)
Rb	<0.015	0.2	< 0.047	0.6	3.32	0.45
Sr	<0.012	0.3	< 0.076	1.9	2.01	0.55
Y	<0.009	0.1	< 0.018	0.3	1.88	0.30
Zr	0.074	1.6	0.066	1.9	39.83	12.25
Mo	0.912*	77.5	0.050	7.0	29.84	44.77
Ru	<0.017	1.5	< 0.020	1.7	1.93	1.81
Rh	0.156	2.1	< 0.043	1.1	3.74	1.01
Pd	<0.006	0.2	< 0.017	1.2	1.85	1.35
Ag	<0.174	0.5	6.254	34.5	7.50	0.44
Cd	<0.048	0.1	< 0.207	1.4	2.93	0.21
Sn	6.713	1.7	6.868	11.7	38.62	0.71
Sb	1.338	0.6	2.886	2.7	40.03	0.41
Te	<0.069	0.4	< 0.038	1.5	29.63	13.06
Cs	<0.022	7.5	< 0.017	5.0	4.00	12.67
Ba	<0.018	2.1	0.277	26.8	1.60	1.66
La	<0.008	0.6	0.003	0.2	1.92	1.52
Pr	<0.008	0.6	< 0.000	0.0	1.97	1.39
Nd	<0.008	2.0	0.001	0.4	1.94	4.97
Eu	<0.009	0.1	< 0.000	0.0	1.78	0.22
Gd	<0.009	0.3	< 0.007	0.1	1.16	0.25

* Probably overestimated due to contamination.

Conclusions

Nine litres of genuine HAR has been produced by the PUREX process. The HAR has been characterised and there is a factor of two more diluted than industrial HAR

An apparatus for concentration and denitration of HAR has been set-up and successfully tested. In experiments using HAR simulate it was shown that already at a CF of 6 a non-containing lanthanide precipitate is formed. The work performed till now indicates that somewhere in between a CF of 8 and 39 significant co-precipitation of lanthanides will occur. This CF will be the maximum possible to use.

At high CF's the major components of the precipitate are Zr and Mo, up to 40% are removed from the HAC at a CF of 39. This indicates the possibility, at higher CF's, of a partial pre-separation of these elements, which are problematic in the DIAMEX process.

REFERENCES

- [1] M. Malmbeck, O. Courson, G. Pagliosa, K. Römer, B. Sätmark, J-P. Glatz, P. Baron (2000), *Partitioning of Minor Actinides from HLLW Using the DIAMEX Process. Part 2 – “Hot” Continuous Counter-Current Experiment*, Radiochimica Acta, 88, 865.
- [2] C. Madic, P. Blanc, N. Condamines, P. Baron, L. Berthon, C. Nicol, C. Pozo, M. Lecomte, M. Philippe, M. Masson, C. Hequet, M.J. Hudson (1994), *Actinide Partitioning from HLLW Using the DIAMEX Process*, The Fourth International Conference on Nuclear Fuel Reprocessing and Waste Management, RECOD94, London.
- [3] B. Sätmark, O. Courson, R. Malmbeck, G. Pagliosa, K. Römer, J-P. Glatz (2000), *Separation of Minor Actinides from a Genuine MA/Ln Fraction*, Actinide and Fission Product Partitioning and Transmutation, Proc. of 6th Information Exchange Meeting, Madrid, Spain, 11-13 Dec, p 279-286.
- [4] O. Courson, R. Malmbeck, G. Pagliosa, K. Römer, B. Sätmark, J-P. Glatz (2000), *Partitioning of Minor Actinides from HLLW Using the DIAMEX process. Part 1 – Demonstration of Extraction Performances and Hydraulic Behaviour of the Solvent in a Continuous Process*, Radiochimica Acta, 88, 857-864.
- [5] B. Sätmark, O. Courson, R. Malmbeck, G. Pagliosa, K. Römer, J-P. Glatz (2000), *Separation of Minor Actinides from a Genuine MA/Ln Fraction*, 6th International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Madrid, 11-13 Dec.
- [6] C. Hill, X. Heres, J-N. Calor, D. Guillaneux, B. Mauborgne, B. Rat, P. Rivalier, P. Baron (1999), *Trivalent Actinides/Lanthanides Separation Using Bis-Triainyl-Pyridines*, GLOBAL99, 29 Aug, Jackson Hole, Wyoming, USA.
- [7] Heits, *Zusammensetzung und Herstellung von HAW/HAWC – Simulaten*, Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen MBH, Oct. 1982.
- [8] J-P. Glatz, C. Song, X. He, H. Bokelund, L. Koch (1993), *Partitioning of Actinides from HAW in a Continuous Process by Centrifugal Extractors*, Special Symposium on Emerging Technologies in Hazardous Waste Management, Atlanta, Ed. Tedder D. W., ACS, Washington DC.
- [9] L. Cécille, M. Kelm (1985), *Chemical Reactions Involved in the Denitration Process with HCOOH and HCHO*, Denitration of Radioactive Liquid Waste, Radioactive Waste Management Series-European Commission, Proc. R&D Program on Radioactive Waste Management and Disposal, Eds. L. Cécille, S. Halaszovich, KFJ Jülich, 10-11 December 1985, Germany. ISBN 0-86010-854-6.
- [10] G. Modolo (2002), Personal communication, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany.