EUROPART:European Research Programme for Partitioning of Minor Actinides within High Active Wastes Issuing the Reprocessing of Spent Nuclear Fuels

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OUTLINE

I. Introduction

Today, after the reprocessing of spent nuclear fuels, the nuclear wastes containing the FPs and the Minor Actinides (MAs = Np, Am and Cm) are vitrified. The vitrified wastes will be in the future disposed of in deep geological repository, but the definition of such a repository is complex owing to the radiotoxicity of the wastes which is high to more than 10^5 years. After ~ 200 years, the radiotoxicity is essentially due to MAs. So the Partitioning of MAs from the wastes followed by their nuclear destruction can simplify the definition of deep geological repository.

So, the aim of EUROPART is the definition of MAs Partitioning processes.

Two chemical domains have been selected:

i) Hydrometallurgy and

ii) Pyrometallurgy.

The work has been organised in Work Packages (WP):

5 for Hydro, and 4 for Pyro.

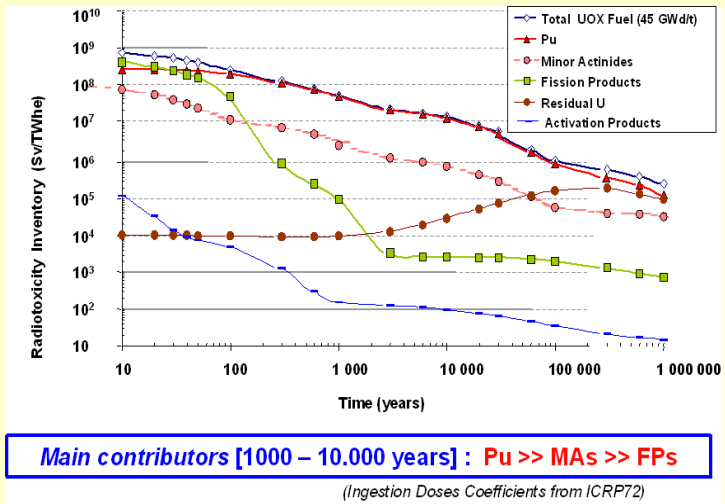


Figure 1. Radiotoxic inventory of an UOX spent fuel (45GWd/t).

II. Research Programme and Recent Results

II.1. Research Programme and Work Package organisation

II.1.1. Hydrometallurgy

- **The target for WP1 and WP2 is the Partitioning of trivalent MAs (Am and Cm) from HAR or HAC issuing the reprocessing of spent UOX or MOX fuels. Research done is in continuity with that done in FP-5: PARTNEW for WP1 and CALIXPART for WP2,**

- **The target for WP3 and WP4 is the partitioning of all the actinides contained within new fuels, like those of ADS facility. Research done is in continuity with PARTNEW for WP3 and CALIXPART for WP4.**

- **The objective of WP5 is the definition of co-conversion methods of partitioned actinides to prepare new fuels (oxides, carbides and nitrides).**

- **The work in each WP is organised in several Tasks which are listed below.**

WP1 and WP2 list of Tasks

- **Task 1: Molecular modelling of complexation and extraction,**
- **Task 2: Synthesis and characterisation of ligands,**
- **Task 3: Study of their extracting properties (thermodynamics, kinetics),**
- **Task 4: Determination of the structures of the ligands and their metallic complexes at molecular and supramolecular levels,**
- **Task 5: Study of the stability of the ligands vs radiolysis and hydrolysis,**
- **Task 6: Scaling-up of the synthesis for the ligand(s) selected for process development,**
- **Task 7: Design of process flowsheet(s),**
- **Task 8: Realisation of cold test(s) of the processes,**
- **Task 9: Preliminary hot test(s) of the processes.**

WP3 and WP4 list of Tasks

- **Task 1: Molecular modelling of complexation and extraction for both liquid-liquid extraction and chromatography,**
- **Task 2: Synthesis and characterisation of ligands,**
- **Task 3: Study of their extracting properties (thermodynamics, kinetics),**
- **Task 4: Determination of the structures of mixtures of ligands and of their metallic complexes at molecular and supramolecular levels,**
- **Task 5: Study of the stability of the of mixtures of ligands *vs* radiolysis and hydrolysis,**
- **Task 6: Scaling-up of the synthesis for the ligand(s) selected for process development,**
- **Task 7: Design of process flowsheet(s),**
- **Task 8: Realisation of cold test(s) of the processes,**
- **Task 9: Preliminary hot test(s) of the processes.**

WP5 list of Tasks

- **Task 1: Determination of the performances of the co-conversion method, including: the kinetics of the reactions, the yields of co-conversion, as functions of the operating conditions, such as the composition of the aqueous solution(s), the concentration of the reagent added, the temperature, etc..,**

- **Task 2: Chemical, physical and structural characterisations of the compounds formed after separation from the aqueous solution(s),**

- **Task 3: Study of the conversion method(s) of the solid(s) formed from the solution(s) into the final compounds (oxide, nitride, carbide),**

- **Task 4: Chemical, physical and structural characterisations of the final compounds (oxide, nitride, carbide) prepared, with an assessment of their suitability to prepare fuel(s).**

II.1.2. Pyrometallurgy

- **The work is this domain is organised into 4 WP s,**

- **For WP6, the work concerned the determination of basic properties of actinides and of some FP elements into: i) molten salts (halides: chlorides and fluorides), ii) molten metals,**
- **The work to be done within the WP7 concerns the definition of pyrometallurgical process development and also the creation of experimental facilities to test pyrochemical processes,**
- **For WP8, the work concerns the definition of solid matrices for the confinement of spent molten salts,**
- **The work done in WP9 is related to the study of fuel cycle systems involving pyrometallurgical process(es).**

WP6 list of Tasks

- **Task 1:** **Completion of the determination of basic properties of An (from U to Cf if possible) and FPs in Molten Salts and Molten Metals media taking into account the experimental procedures,**

- **Task 2:** **Compilation, comparison and analysis of thermodynamic data**

WP7 list of Tasks

- **Task 1:** **Process development for the partitioning of actinides from HLLW issued from UOX and MOX fuel reprocessing by the PUREX process based on several separation concepts, e.g. electrolysis, precipitation, liquid-liquid extraction with metallic solvents, with the aim to demonstrate the feasibility of high An recovery yields (99.9 %) with sufficient decontamination factors *vs* fission products (FP).**

- **Task 2:** **Process development for the treatment of spent fuels (SF) from advanced dedicated fuel cycles based on several separation concepts, *e.g.* electrolysis, precipitation, liquid-liquid extraction with metallic solvents, with the aim to demonstrate the feasibility of high An recovery yields (99.9 %) with sufficient decontamination factors *vs* fission products (FP).**

- **Task 3:** **Modelling of the processes and design of experimental devices (including their modelling) for process implementation.**

WP8 list of Tasks

- **Task 1:** **Selection of solid matrix(ces) for wastes conditioning,**
- **Task 2:** **Determination of the chemical and physical properties of the selected matrix(ces),**
- **Task 3:** **Determination of the resistance *vs* aqueous leaching of the MS wastes conditioned within the selected matrix(ces),**
- **Task 4:** **Study of conversion method(s) of the chloride salt wastes into oxides for subsequent conditioning of the radioactive wastes within a glass matrix.**

WP9 list of Tasks

- **Task 1:** **Identification of all the steps involved for each process,**
- **Task 2:** **Calculation of the fluxes of all the media involved within the process(es), including the fluxes of wastes. These fluxes could be normalised *vs* a produced quantity of electricity (TWhe),**
- **Task 3:** **Design of flow-sheet diagrams for the processes.**

- **II.2.1** **Hydrometallurgy**
- **WP1**

Computer modelling of extractants and of their metallic complexes.

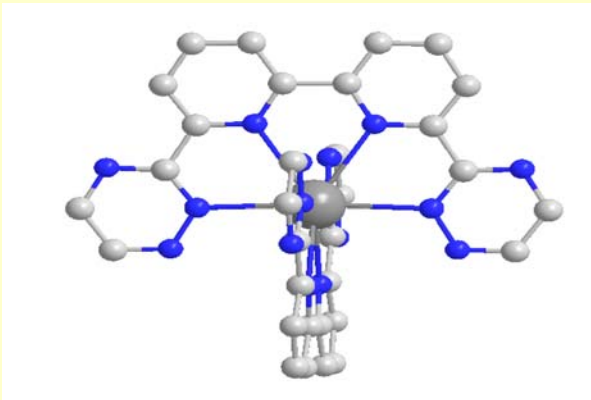


Figure 2. Model of a *bis*-complex between a lanthanide ion and a bis-pyridine-bis-1,2,4-triazine (BTBP) ligand.

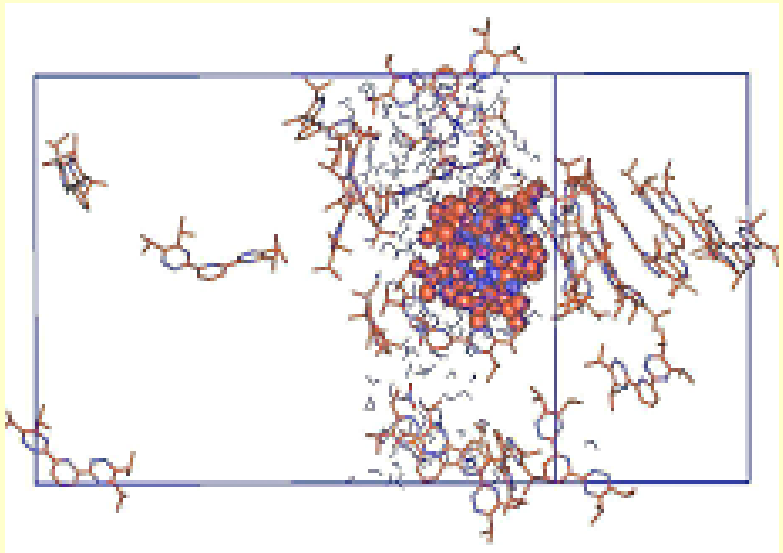
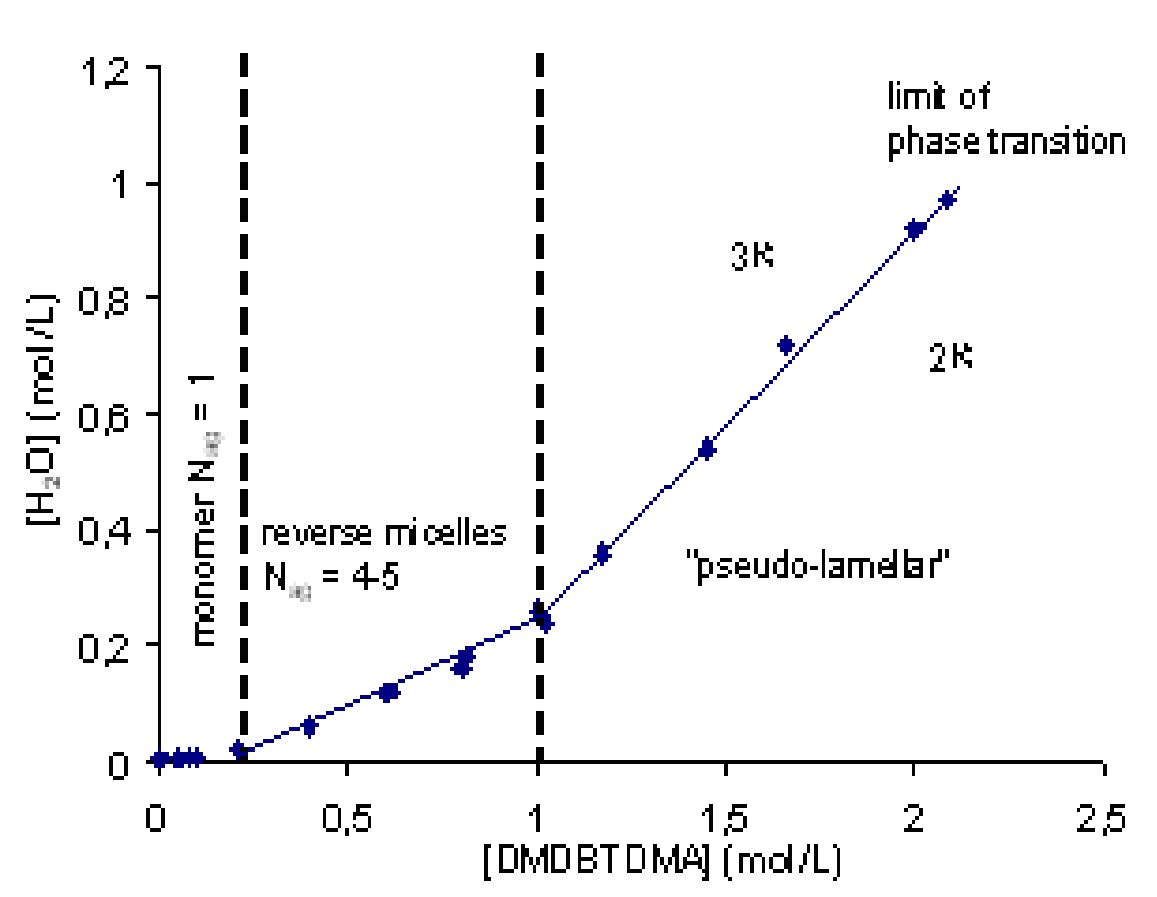
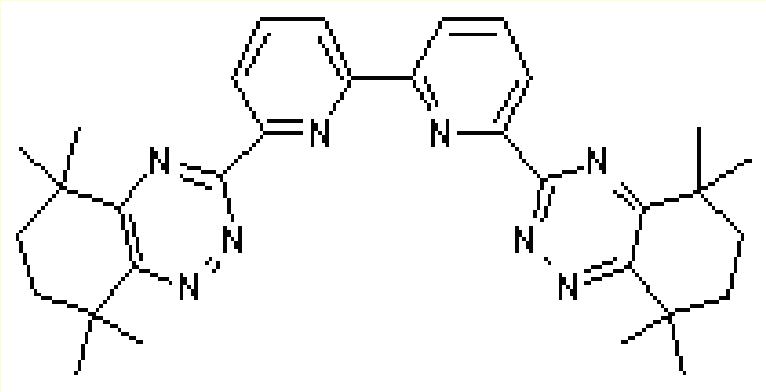


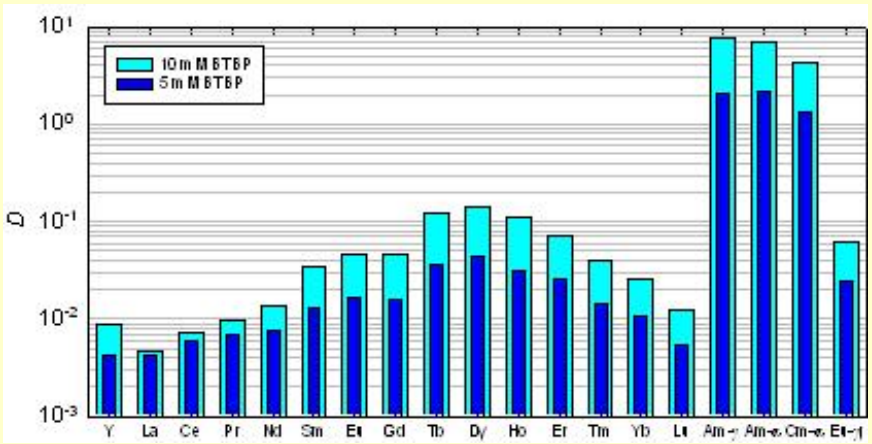
Figure 3. Dynamic simulation of $Eu(BTP)_3^{3+}$ + 24 free BTP molecules into a mixture of 95/5 vol.%(chloroform/water).

- **WP1**
- **Supramolecular organisation of diamide solvents loaded with some solutes**

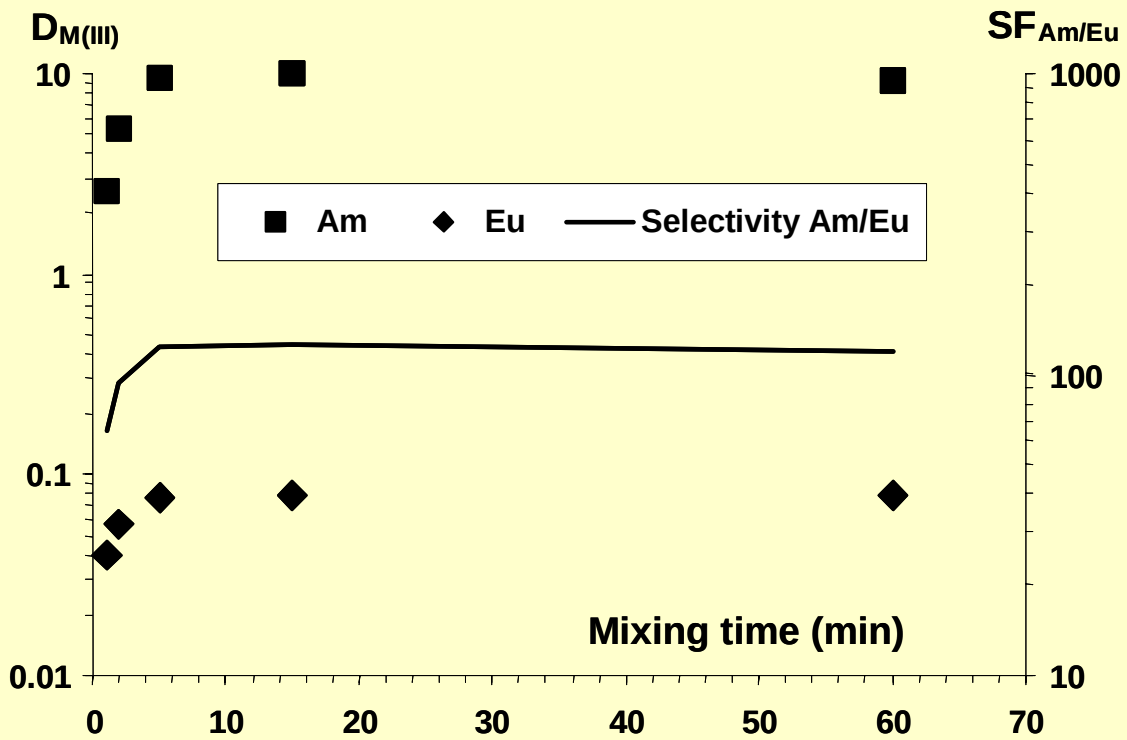




- **Figure 5. 2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazy-3-yl)-[2,2']bipyridine.**



- **Figure 6. Comparison of distribution ratios of Ln(III) and An(III) for an aqueous equilibrium nitric acid concentration of 0.88 M.**



Organic solution: **[CyMe4-BTBP]ini = 0.01 mol/L in the "*n*-octanol/[DMDOHEMA] = 0.25 mol/L" mixture, pre-equilibrated with molar nitric acid. Vorg = Vaq = 700 mL. Temperature = (25 ± 0.5)°C.**

Aqueous solution: 152Eu(III) and 241Am(III) trace level in a surrogate SANEX-MOX feed: [HNO3] = 1 mol/L + [Ln(III)]tot = 8.8 m mol/L.

- **Figure 7. Kinetics of extraction of Am(III) and Eu(III) by CyMe4-BTBP from a surrogate SANEX-MOX feed.**

- **WP1**

- **Cold test of the DIAMEX process (DMDOHEMA extractant) using HFM**

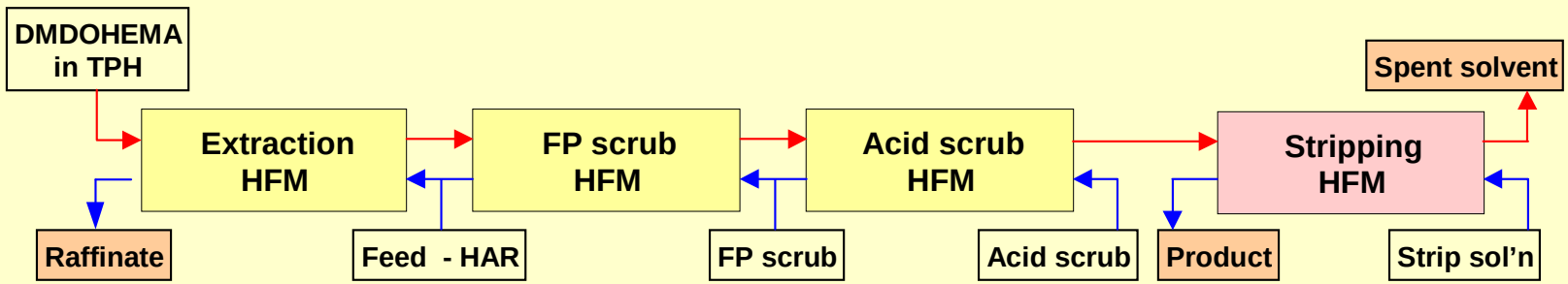
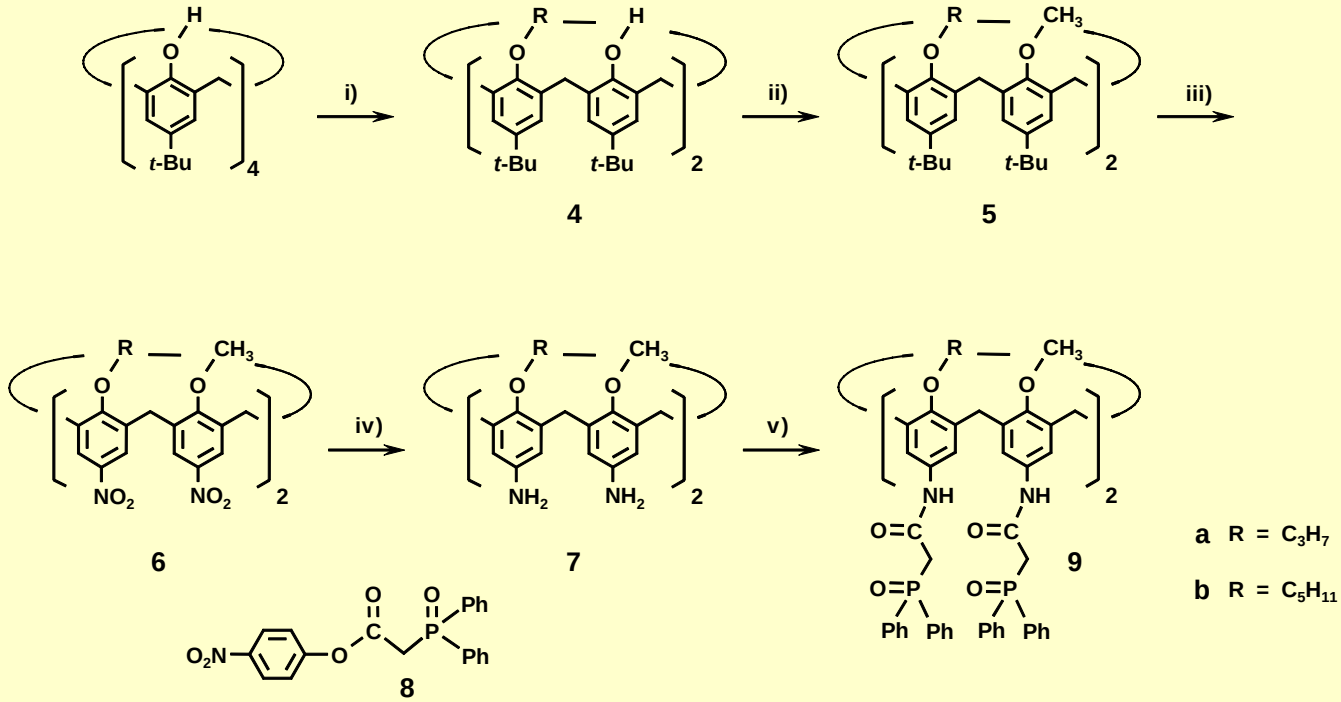


Figure 8. The Hollow Fibre Module (HFM) microplant established during the DIAMEX extraction experiment.

- **WP2 and WP4**
- **Synthesis of new ligands**



i) R-Br, K_2CO_3, CH_3CN; ii) MeI, NaH, DMF; iii) HNO_3, CH_2Cl_2;
iv) Raney-Ni, H2, toluene; v) 8, $NEt_{3(}$cat), $CHCl_3$

Figure 9. Synthesis scheme for the preparation of CMPO-calix[4]arenes.

- **WP2 and WP4**
- **Synthesis of new ligands**

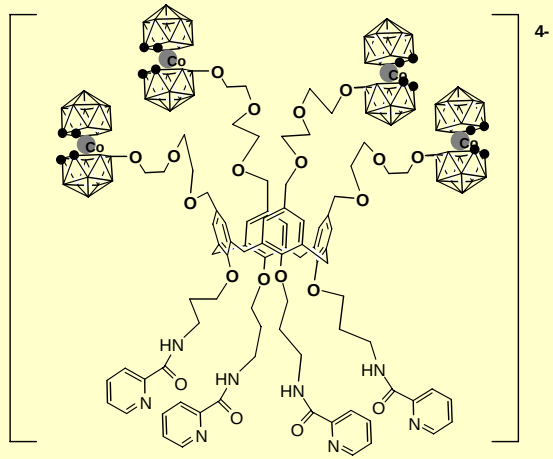


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Figure 11. New cosan-calix[4]rene.

Synthesis is based on two step procedure

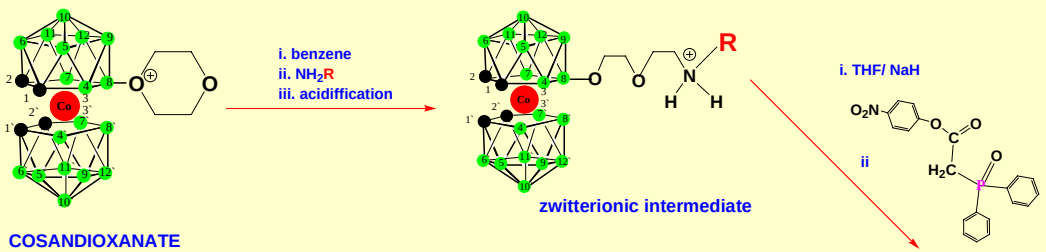
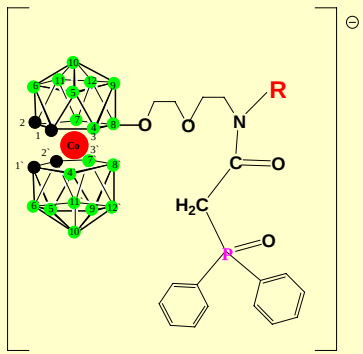


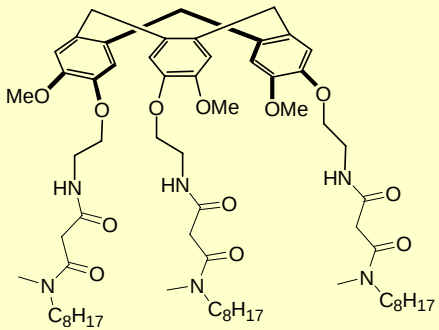
Figure 10. Synthesis scheme of cosan-CMPO.



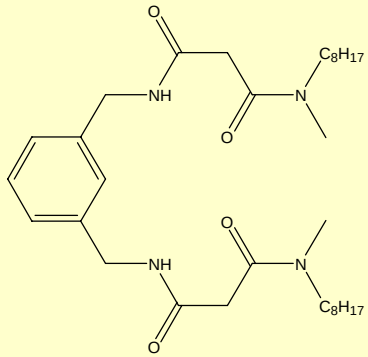
R= *t*-Oct

- **WP2 and WP4**

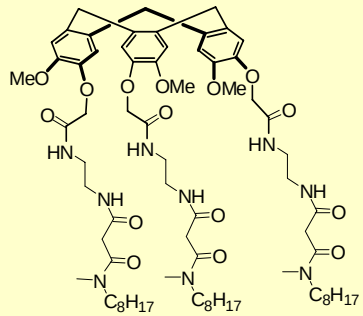
- **Synthesis of new ligands and extraction properties**



UAM-077



UAM-079



UAM-090

HNO_3 (M)	Ligand					
	10^{-2}M UAM-077		$1.5 \cdot 10^{-2}$M UAM-079		10^{-2}M UAM-090	
	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}
3	0.017	0.015	0.012	0.010	0.12	0.45
4	0.018	0.018	0.017	0.016	-	-
5	0.016	0.018	0.015	0.014	-	-

- **WP3**
- **Extraction of Am(III) and Eu(III) with solid extractants**

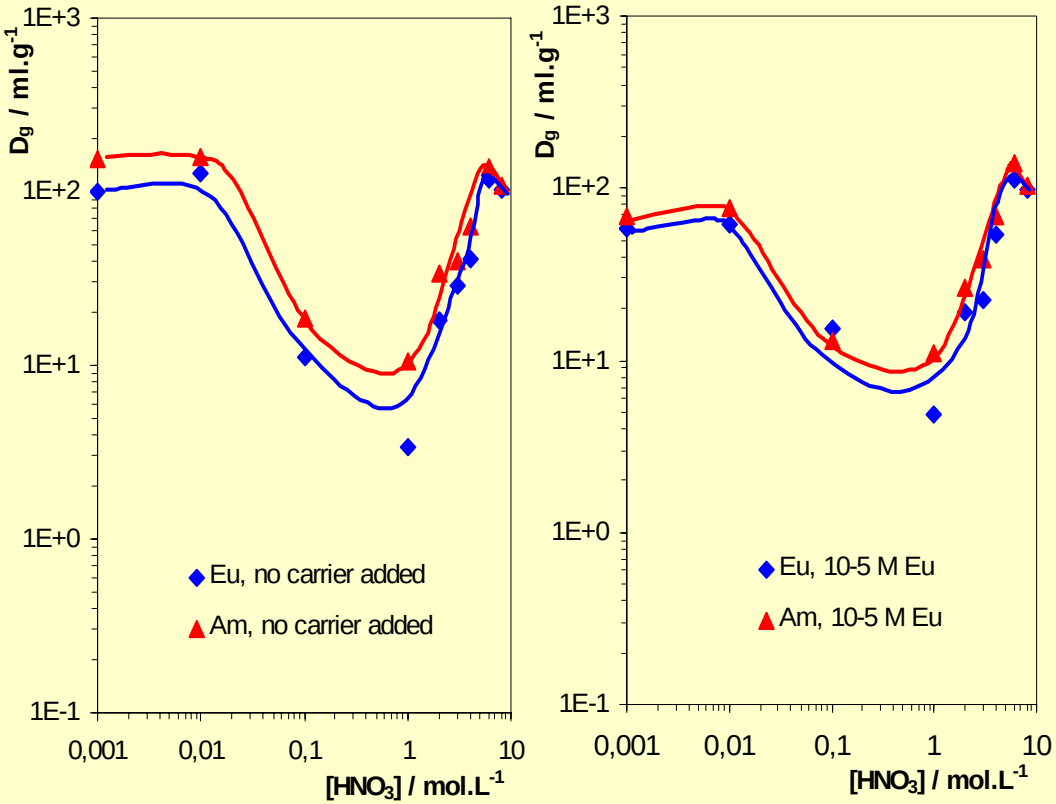


Figure 13. Dependence of weight distribution ratios D_g of Eu and Am on DMDOHEMA–PAN(HNO_3) solid extractant on nitric acid concentration in absence of any carrier or in the presence of 10^{-5}M Eu carrier. (0.1 M $NaNO_3$ + HNO_3, V/m = 250 mL/g, 20 hrs contact time).

- **WP3**
- **Chromatographic separation**

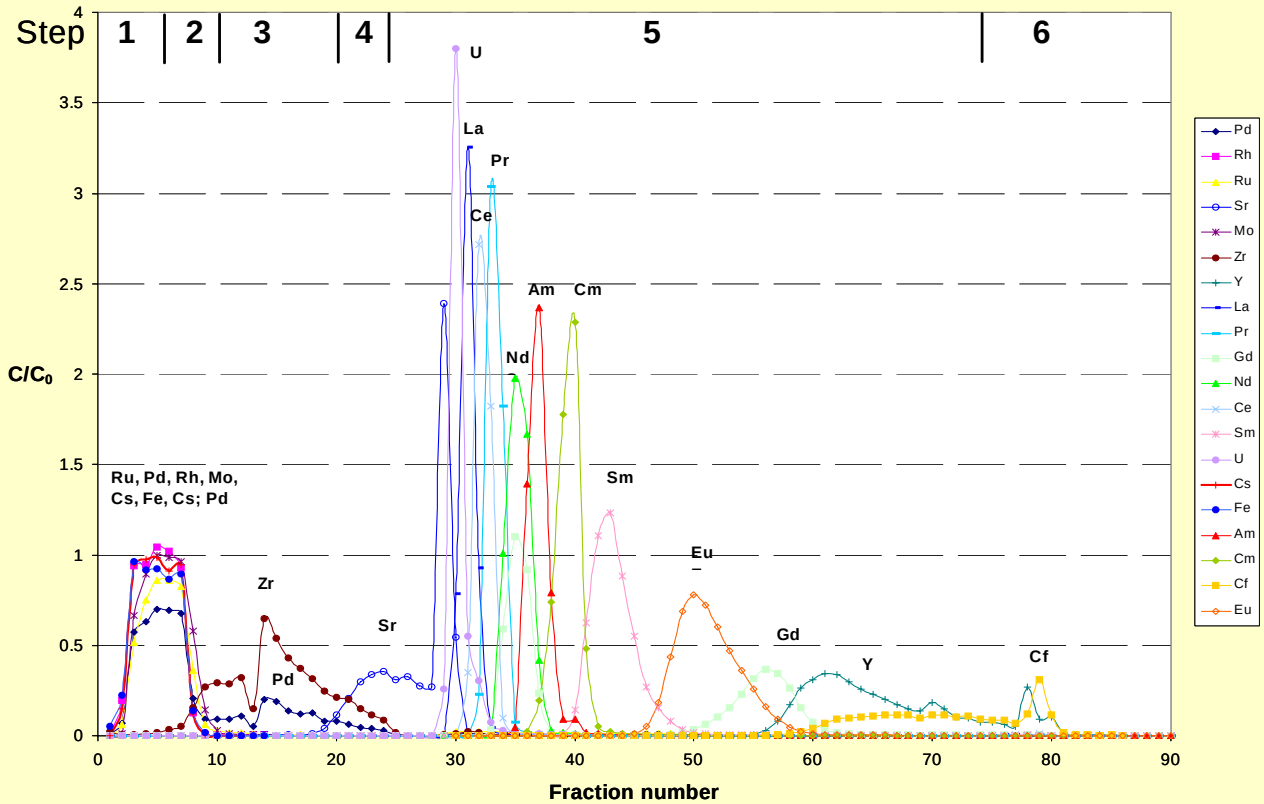


Figure 14. Chromatographic separation of a synthetic HAR by a TODGA column.

- **WP3**
- **Modified PUREX process for U/Pu splitting**

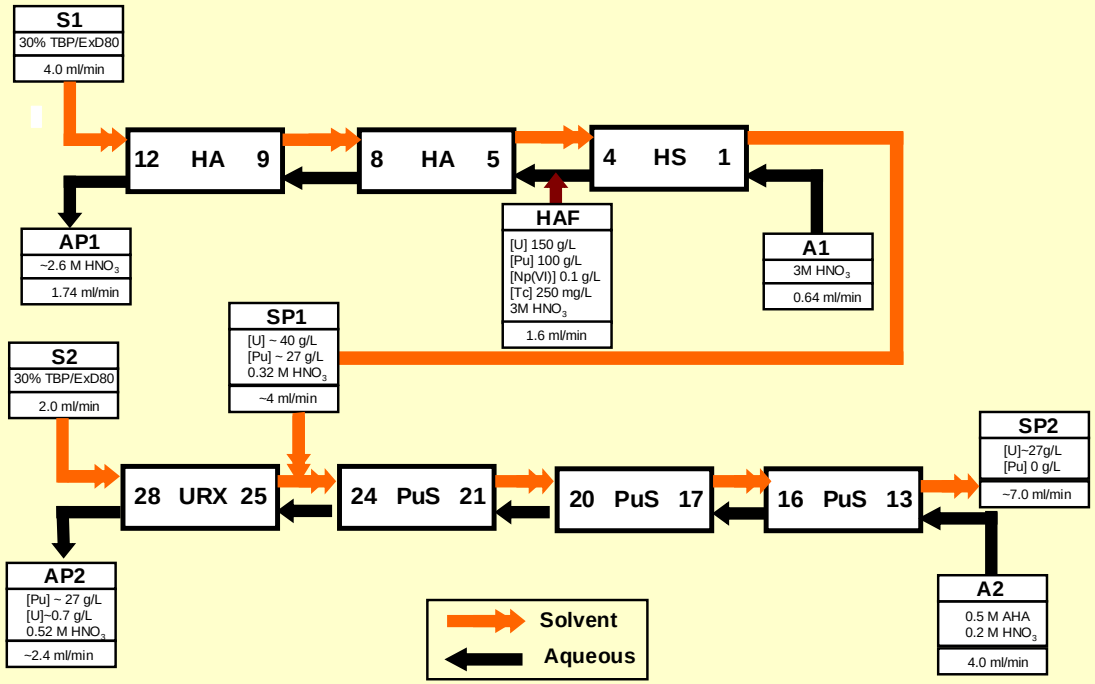


Figure 15. Schematic of flowsheet for the third U/Pu split trial.

- **WP5**
- **Sol-gel and coprecipitation techniques**

Figure 16. Zr/Y/Ce gel beads, T_{bath} = 80 °C, dried at T_{amb}.

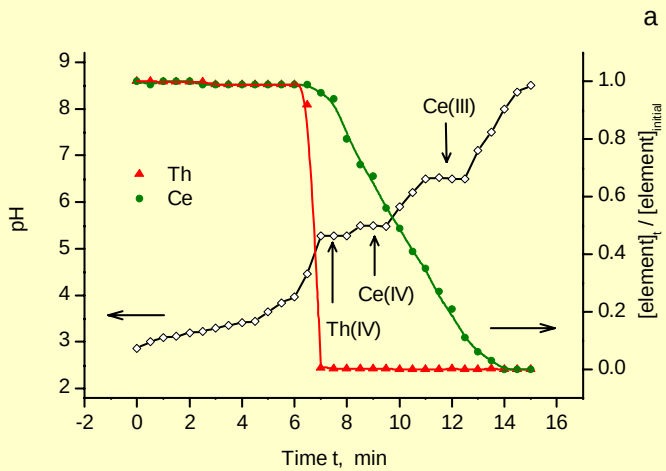
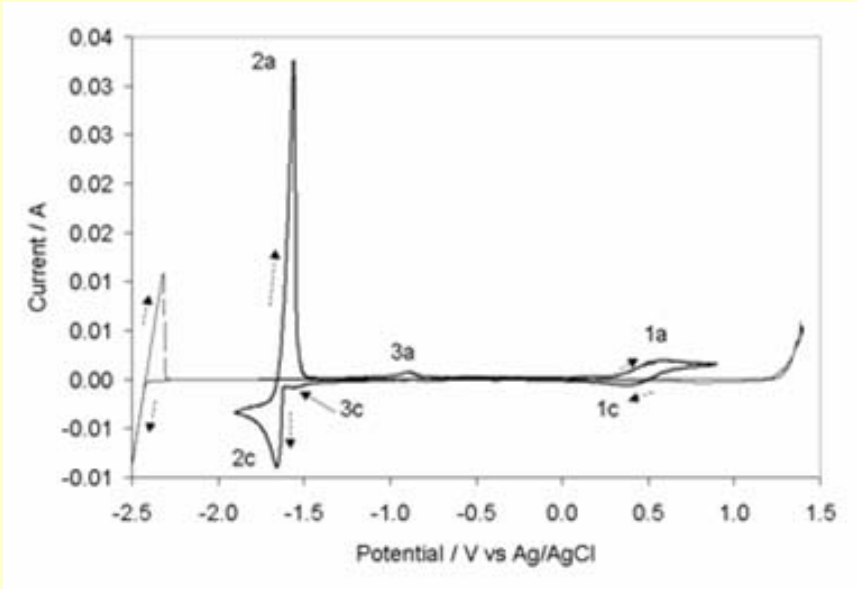


Figure 17. Coprecipitation of ThO_2-50 % CeO_2 powder. Evolution of the pH and element concentration during precipitation.

II.2. Recent results

- **II.2.2. Pyrometallurgy**
- **WP6**

Study of electrochemical properties of Np in LiCl-KCl eutectic melt



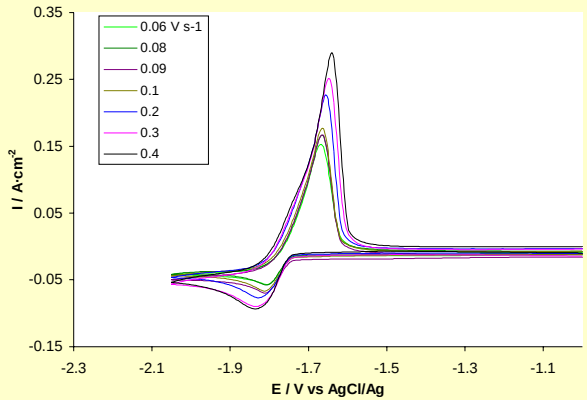


Figure 18. Cyclic voltammogram for Np in LiCl-KCl – left: full scale; right: study of the Np(III)/Np(0) couple.

- **WP7**
- **Electrorefining of An metallic alloy**

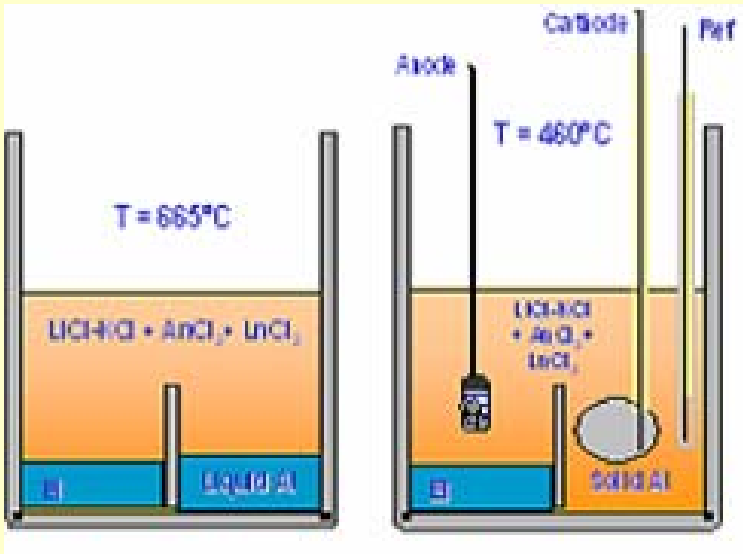


Figure 19. Experimental set-up used in the electrorefining experiments and aluminum cathode

- **WP7**
- **Liquid-liquid reductive extraction**

M	D_M	$S_{Am/M}$
Pu	197 ±30	0,73 ±0,21
Am	144 ±20	1
Ce	0,142 ±0,01	1014 ±213
Sm	0,062 ±0,006	2323 ±488
Eu	<0,013	>11000
La	<0,06	>2400

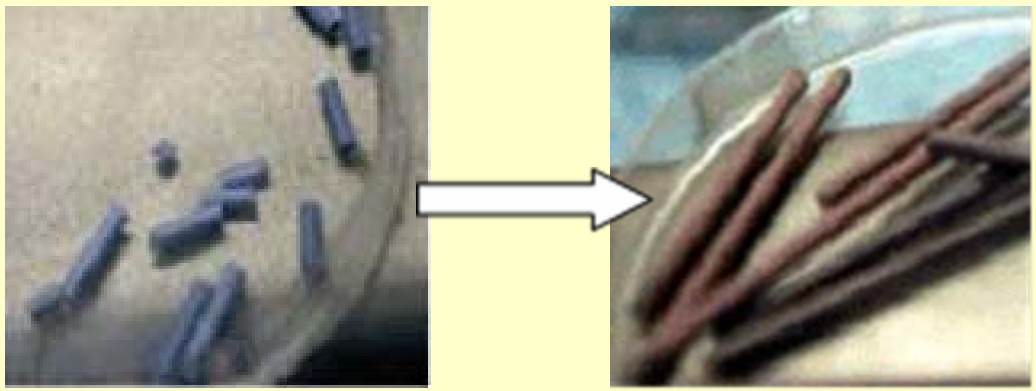


Figure 20. Mass distribution coefficients ($D_M=X_{metal}/X_{salt}$) of actinides and lanthanides with Al/Cu and separation factors with Am (D_{Am}/D_M). Pictures: salt before and after extraction (blue colour mainly due to Pu and brownish colour mainly due to remaining Sm & Eu)

- **WP7**
- **New facilities for studying pyrochemical processes**

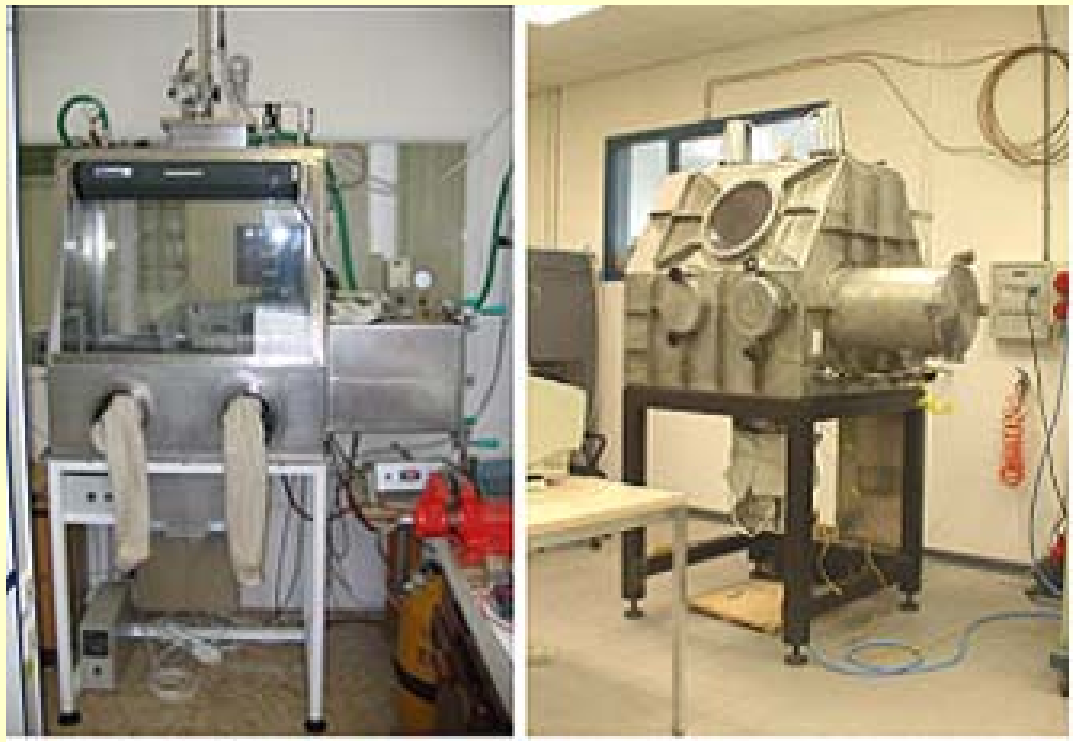


Figure 21. Built-in electrolyser for fluoride media at NRI (left) and PYREL II electrolyser facility at ENEA (right).

- **WP8**
- **Sodalite is a matrix studied for the confinement of spent chloride salt**

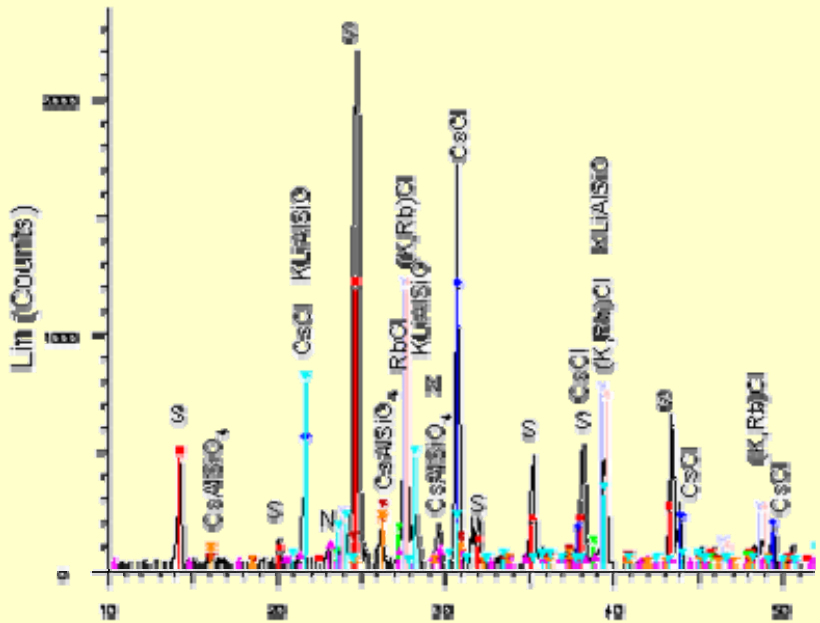


Figure 22. XRD of Cs, Rb, Li, K –doped sodalite sample synthesized at 700 °C for 48 h by reaction between salt and nepheline (S = sodalite, N= nepheline, $KLiAlSiO_4$ = potassium lithium aluminum silicate).

- **WP9**

Figure 23. System for the pyrochemical treatment of ADS spent fuel.

III. General information
III.1. Partnership (1/2)

N°	Partner	Country
1	CEA-DEN, Marcoule	France
1’	CEA-DSM, Saclay	France
2	Nexia Solutions	United Kingdom
3	Chalmers University, Göteborg	Sweden
4	CIEMAT, Madrid + UVA	Spain
5	CTU, Prague	Czech Republic
6	ECPM-CNRS, Strasbourg	France
7	EDF, Paris	France
8	ENEA –Casaccia, Roma	Italy
9	FZJ, Jülich	Germany
10	ICMAB-CSIC, Barcelona	Spain
11	IIC. Rez	Czech Republic
12	INE-FZK, Karlsruhe	Germany

Partnership (2/2)

N°	Partner	Country
13	ITU, Karlsruhe	(JRC, located in Germany)
14	JGU, Mainz	Germany
15	Katchem, Prague	Czech Republic
16	NRI, Rez	Czech Republic
17	PoliMi, Milano	Italy
18	UAM, Madrid	Spain
19	ULG, Liège	Belgium
20	ULP, Strasbourg	France
21	UNIPR, Parma	Italy
22	UREAD, Reading	United Kingdom
23	UT-SMCT, Twente	Netherlands
24	ICHTJ, Warszawa	Poland
25	CRIEPI	Japan
26	ANSTO	Australia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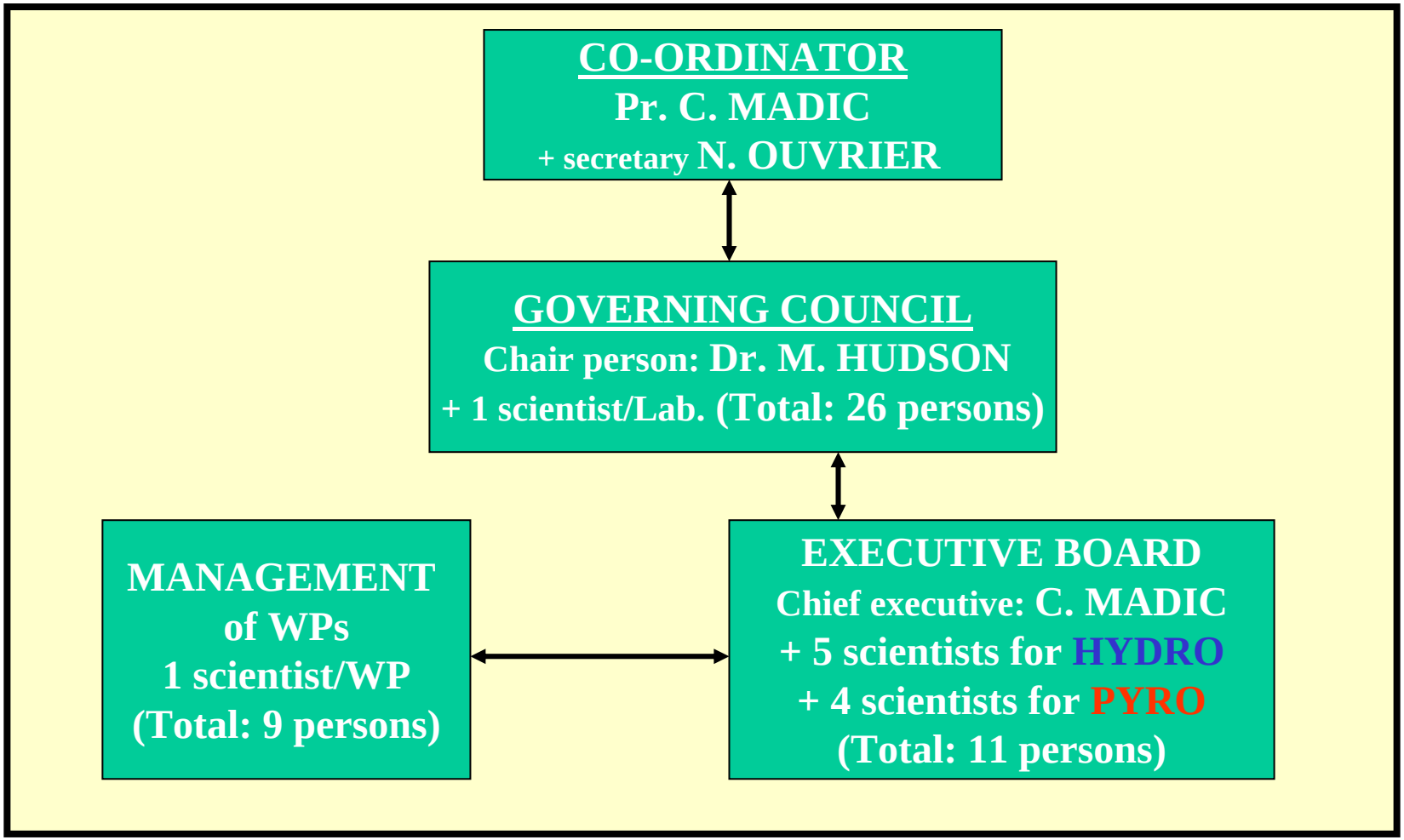
Partners

III. 2. Organisation of EUROPART



List of the WP leaders

WP N°	WP leader	Partner Laboratory
WP1	Dr. Clément HILL	1 (CEA-Marcoule, F)
WP2	Dr. Françoise ARNAUD	6 (CNRS-Strasbourg, F)
WP3	Amparo. G. ESPARTERO	4 (CIEMAT, Madrid, SP)
WP4	Pr. Jean-François DESREUX	19 (ULG, Liège, B)
WP5	Dr. Giuseppe MODOLO	9 (FZJ, Jülich, DE)
WP6	Dr. Rikard MALMBECK	13 (ITU, Karlsruhe, DE)
WP7	Dr. Stéphane BOURG	1 (CEA-Marcoule, F)
WP8	Dr. Giorgio DE ANGELIS	8 (ENEA-Casaccia, I)
WP9	Dr. Jan UHLIR	16 (NRI, Rez, CZ. Rep.)

III. 3. Other information

III.3.1. Collaborations

- **Foreign organisations:**
  - **DOE: Am/Cm separation,**
  - **KRI (St Petersburg, Russia) and Kiev University (Kiev): ISTC and STCU programmes on calixarenes.**
- **European projects**

  ACTINET network

  EUROTRANS

III.3.2. Education, training and dissemination of knowledge

During the half-yearly meetings, 2 conferences are given by important scientists.

The results obtained are published in International journals and presented during Conferences.

EUROPART web-site: www.europart-project.org

III.3.3. Exploitation of knowledge

The new processes developed will be proposed in the future to industrial: COGEMA and BNFL.

Conclusion

The studies carried out within the two first years of EUROPART have lead to significant progress for the separation of actinides and lanthanides particularly by hydrometallurgical means. In the two domains of hydrometallurgy and pyrometallurgy the combined academic and industrial research has been fruitful and successful for both fundamental research and process development. In the last year of the programme increasing efforts will be related to process developments and there will be more hot-tests. Much more work needs to be carried out and it is hoped that the studies here will lead to other projects within FP-7. The combined facilities within Europe are essential for continued development of P&T. The results obtained within EUROPART will consolidate the European P&T strategy. So, the results of EUROPART will certainly be considered by decision makers, like in France: in 2006 a political decision related to the future of nuclear wastes will be done by the Parliament, as decided by the Law of December 1991.