

No *P* No *T* — European Projects on Actinides Separation (with a focus on hydrometallurgy)

Andreas GEIST



Separation Strategy

French SPIN (séparation, incinération) programme; 1991 law

- PUREX
 - U, Np, Pu
- An(III) + Ln(III) co-sep'n
 - DIAMEX
- An(III)/Ln(III) sep'n
 - **challenge**
 - **“new extractants”**
 - **“soft donor”**
- Am(III)/Cm(III) sep'n
- Cs, Sr sep'n
 - obsolete

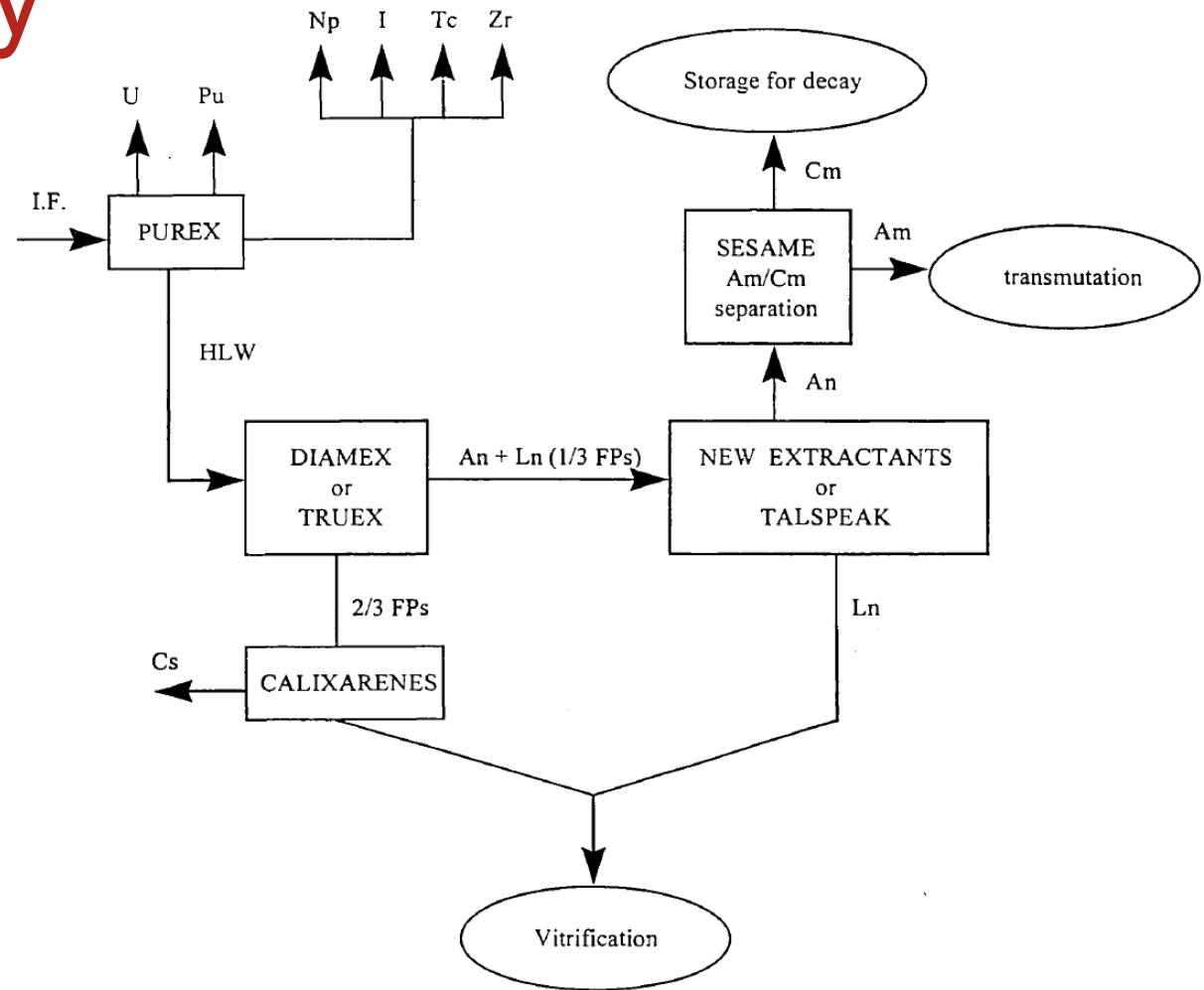


FIGURE 1 : General flow chart of operations required for the separation of long-lived radionuclides

Ambitious Goals...



	Scientific feasibility	Technical feasibility
SEPARATION of Np	1995	2002
DIAMEX	1994	2002
SANEX	2001	2005
SESAME	2000	2005
SEPARATION of Cs	1995	2005

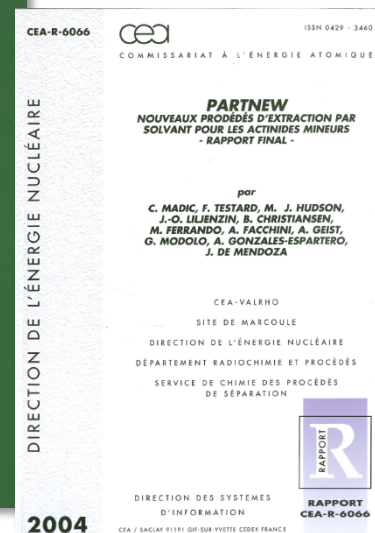
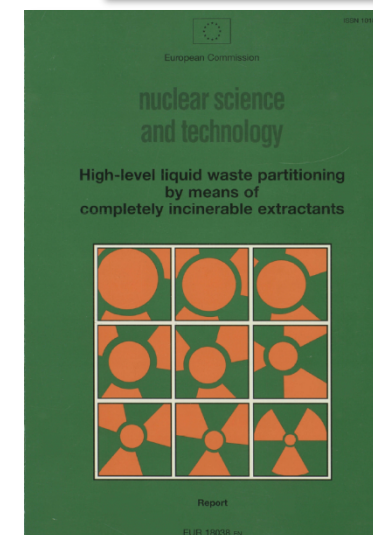
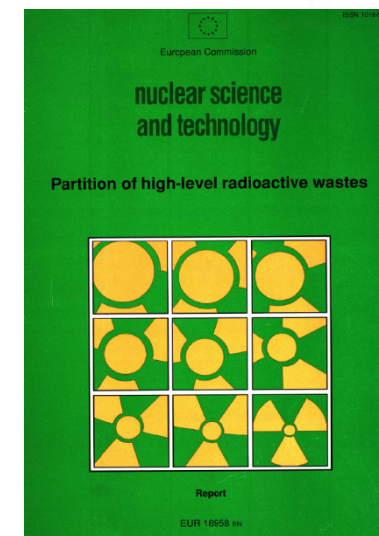


P. Bernard, B. Barré, N. Camarcat, GLOBAL 1999

European Research Programmes

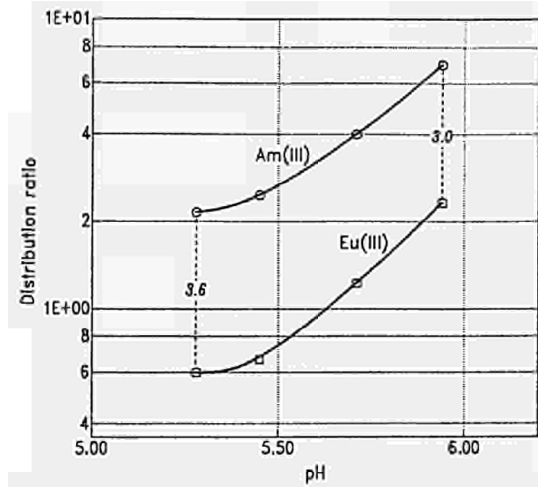


- From early 1990s on...
 - Z. Kolarik et al.
 - C. Madic, M. Hudson
 - C. Madic et al., **NEWPART**
 - C. Madic et al., **PARTNEW**
 - C. Madic et al., **EUROPART**
 - S. Bourg et al., **ACSEPT**
 - C. Ekberg et al., **ASGARD**
 - S. Bourg et al., **SACSESS**
 - S. Bourg et al., **GENIORS**



FP3 1990–1994

Z. Kolarik, R. Schuler, **U. Müllich**,
Partition of high-level radioactive waste
Contract FI2W-CT90-0047
Final report EUR 16958 (1996).



J. F. Dozol et al.,
**New macrocyclic extractants for radioactive waste treatment:
ionisable crown ethers and functionalised calixarenes**
Contract FI2W-CT90-0062
Final report EUR 17615 (1997). *Macrocycles*

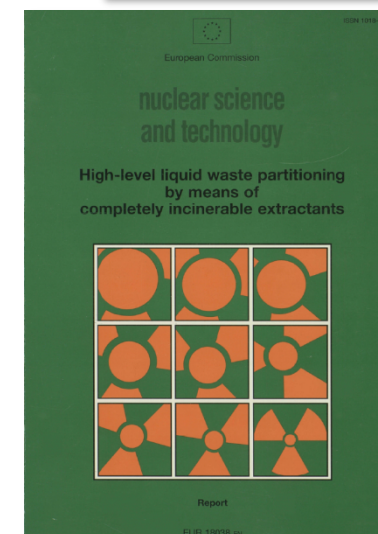
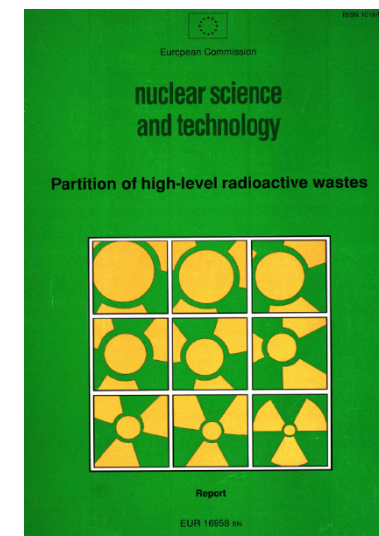
C. Madic, M. J. Hudson,
**High-level liquid waste partitioning by
means of completely incinerable extractants**
Contract FI2W-CT91-0112
Final report EUR 18038 (1998).

“CHON”

**hot
DIAMEX
tests**

F. Teixidor et al.,
**New trends in the separation of ^{137}Cs , ^{90}Sr and transplutonium
elements from radioactive HLW by borane and heteroborane anions**
Contract CIPA-CT93-0133
Final report EUR 18217 (1998). *COSANs*

$SF_{\text{Am/Eu}} \approx 10$



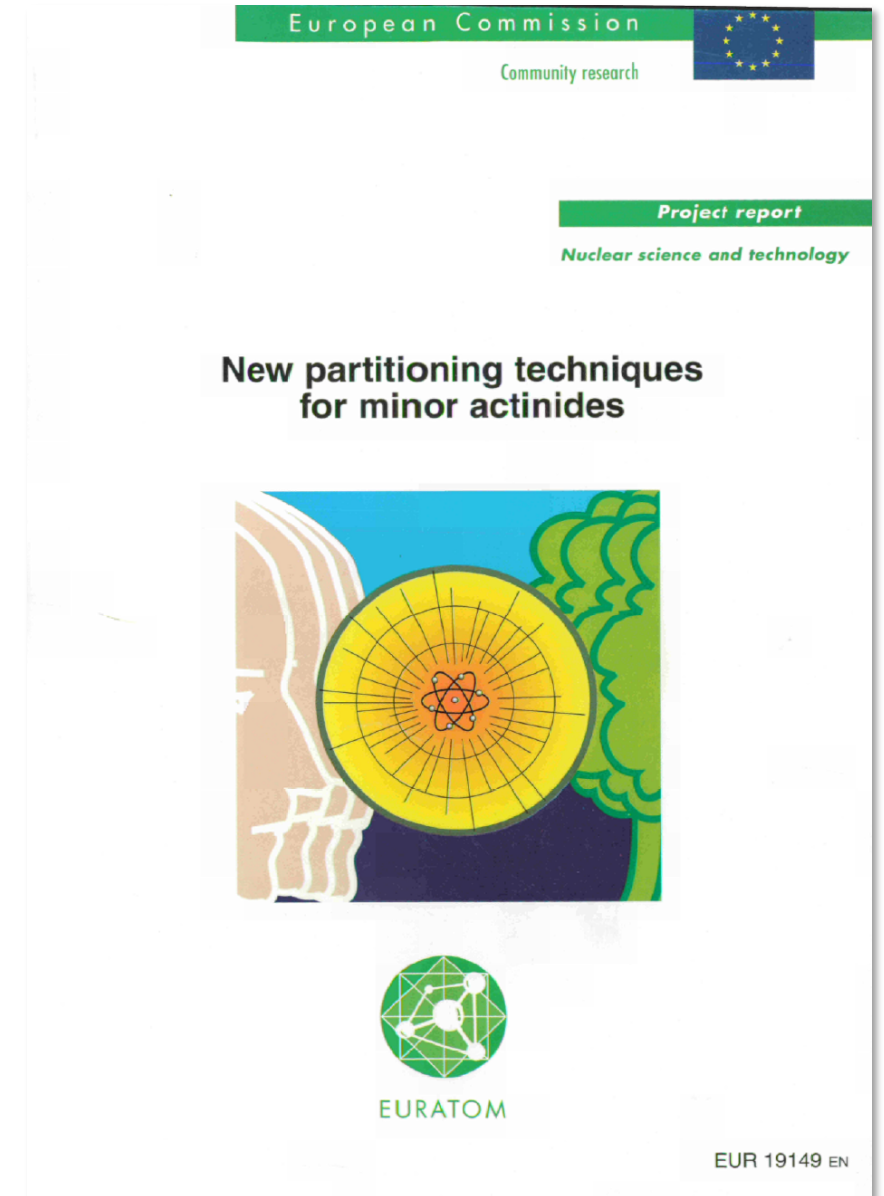
FP4 1994–1998

C. Madic et al. (eight partners)
NEWPART (New partitioning techniques for minor actinides)
Contract FI41-CT-96-0010, 01/05/1996–30/04/1999
Final report EUR 19149 (2000).

J. F. Dozol et al.,
Extraction and selective separation of long-lived nuclides by functionalised macrocycles
Final report EUR 19605 (2000). *Macrocycles*

G. Wipff et al.,
Development of technologies on efficient decontamination of radioactive wastes based on new organophosphorus ionophores
Final report EUR 19951 (2001). *Macrocycles*

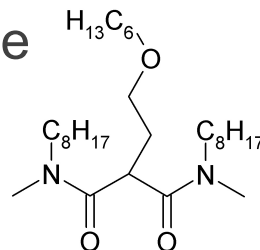
F. Teixidor et al.,
Selective separation of M^{1+} , M^{2+} , and M^{3+} radionuclides, namely of Cs, Sr, and actinides, from nuclear waste by means of chelating hydrophobic cluster anions
Final report EUR 19956 (2002). *COSANs*



NEWPART — Breakthrough

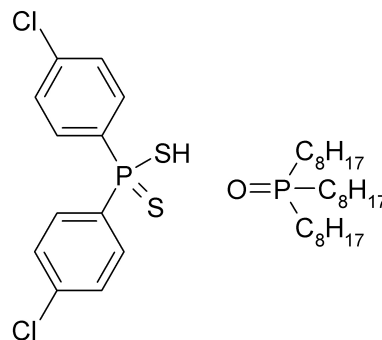
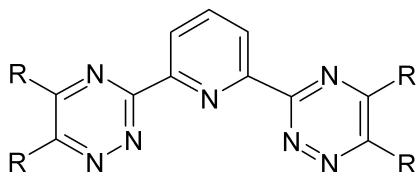
• DIAMEX

- DMDOHEMA introduced
- Current reference diamide



• SANEX

- “New extractants”
- Extraction from $> 0.5 \text{ mol/L HNO}_3$
- Selectivity for Am(III) and Cm(III) over **all** Ln(III)



SOLVENT EXTRACTION AND ION EXCHANGE, 17(1), 23-32 (1999)

SELECTIVE EXTRACTION OF Am(III) OVER Eu(III) BY 2,6-DITRIAZOLYL- AND 2,6-DITRIAZINYLPYRIDINES¹

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ABSTRACT

2,6-Di(5-alkyl-1,2,4-triazol-3-yl)-pyridine and 2,6-di(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine type compounds extract Am(III) 2-bromohexanoate and nitrate from acidic solutions ($\leq 1 \text{ M HNO}_3$) with an appreciable efficiency and selectivity, yielding Am(III)/Eu(III) separation factors of ≤ 150 .

INTRODUCTION

Separation of actinides from high-level radioactive wastes and their subsequent transmutation to short-lived radionuclides can largely facilitate nuclear waste management. A partitioning process for actinide separation, most appropriately based on solvent extraction, must include the separation of Am and Cm from fission lanthanides. Selective extraction of the small mass of Am(III) and Cm(III) over the 60 times larger mass of lanthanides(III) is the most efficient mode of the operation. It is highly preferable to apply extractants soluble in essentially paraffinic diluents that are able to extract the transplutoniides(III) from acidic solutions, containing $>0.05 \text{ M}$ nitric acid. The necessary selectivity for Am(III) and Cm(III) can be attained by using extractants that bind the extracted ions through “soft-donor”, i. e. nitrogen or sulfur, atoms. Our work is concentrated on N-donor extractants, which promise a higher chemical stability than sulfur compounds.

¹ Work performed within the European Commission's research programme on nuclear fission safety, shared cost action, contract No. F141-CT96-0010.

SOLVENT EXTRACTION AND ION EXCHANGE, 17(1), 33-53 (1999)

SYNERGISTIC SELECTIVE EXTRACTION OF ACTINIDES(III) OVER LANTHANIDES FROM NITRIC ACID USING NEW AROMATIC DIORGANYLDITHIOPHOSPHINIC ACIDS AND NEUTRAL ORGANOPHOSPHORUS COMPOUNDS

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Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

ABSTRACT

New aromatic dithiophosphinic acids (R_2PSSH) with $R = C_6H_5$, ClC_6H_4 , FC_6H_4 and $CH_3C_6H_4$ were synthesized, characterized and tested as potential separating agents for trivalent actinides over lanthanides. The extraction of Am(III), Eu(III) and other lanthanides was carried out from nitric acid medium with mixtures of R_2PSSH s and neutral organophosphorus compounds. There was no detectable extraction when R_2PSSH s were used alone as extractants for either Am(III) or Eu(III) ($D_{Am, Eu} < 10^{-3}$) under the experimental conditions used in this study. High separation factors ($D_{Am}/D_{Eu} > 20$) with $D_{Am} > 1$ were achieved in the nitric acid range $0.1 - 1 \text{ mol/L}$ by means of a synergistic mixture of bis(chlorophenyl)dithiophosphinic acid + tributylphosphate (TBP), trioctylphosphine oxide (TOPO) or tributylphosphine oxide (TBPO). The high radiation resistance (up to 10^6 Gy absorbed γ -doses) of the extractants was also demonstrated.

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E-mail: g.modolo@fz-juelich.de



FP5

C. Madic et al. (eleven partners)

PARTNEW

(Nouveaux procédés d'extraction par solvant pour les actinides mineurs)

Contract FIKW-CT200-00087, 01/09/2000–31/08/2003

Final report CEA-R-6066 (2004).

H. Boussier et al.,

PYROREP

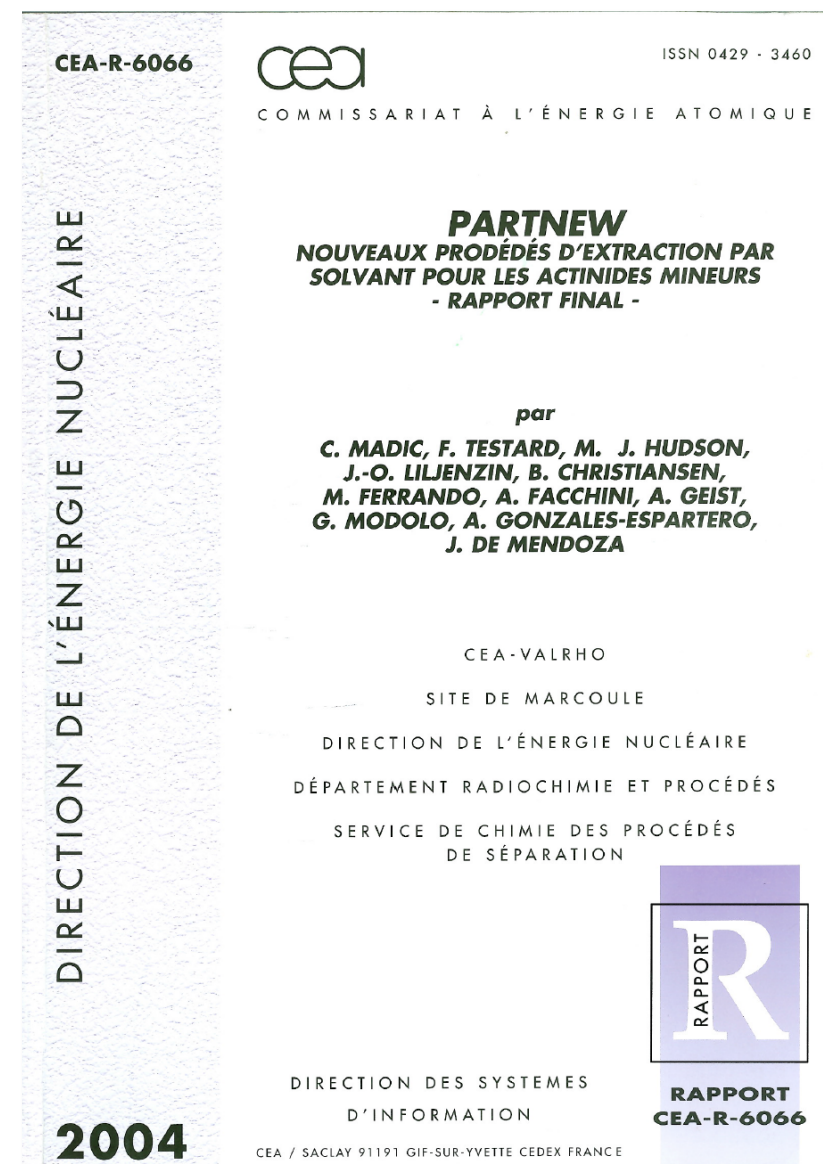
(Pyrometallurgical reprocessing research programme)

Contract FIKW-CT-2000-00049, 01/09/2000–31/08/2003

F. Arnaud-Neu et al.,

CALIXPART

(Selective extraction of minor actinides from high activity liquid waste by organized matrices) *Macrocycles*



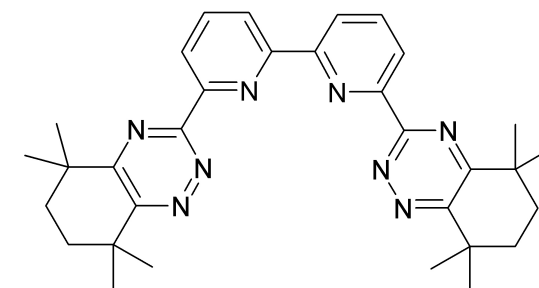
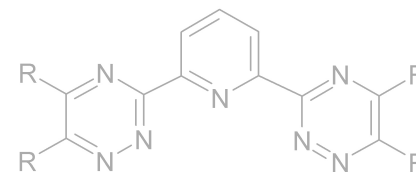
PARTNEW — Evolution

- DIAMEX

- From HAR to HAC — towards a more compact plant
- Hot demonstration @ ITU

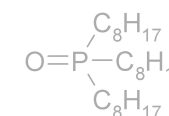
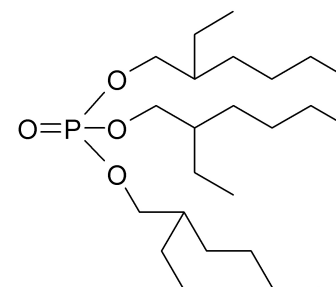
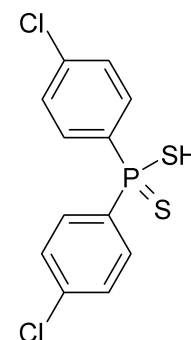
- SANEX

- Kolarik's BTP unstable
- CyMe₄-BTBP developed @ Reading, UK
 - Current reference molecule



- Am(III)/[Cm(III) + Ln(III)] separation

- LUCA system & test @ Jülich



European research programme for the partitioning of minor actinides

- Integrated project, merging former
 - PARTNEW
 - PYROREP
 - CALIXPART
- 26 partners
 - Hydrometallurgy
 - Pyrometallurgy
 - Co-conversion



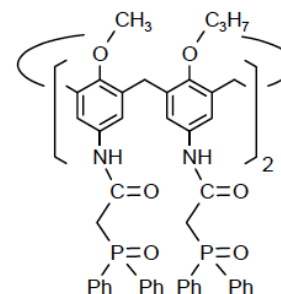
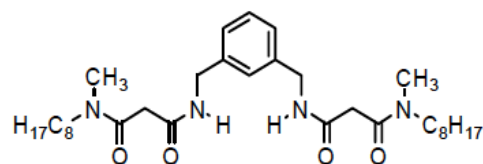
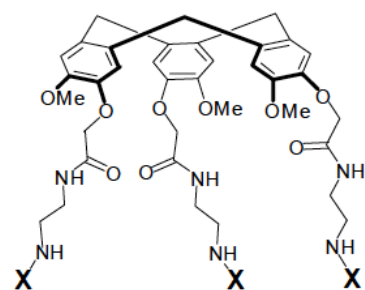
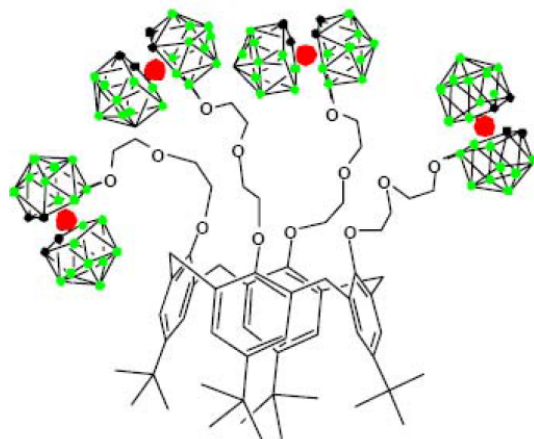
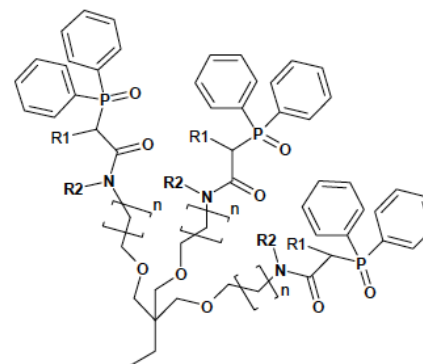
FP6



— Dissipation

European research programme for the partitioning of minor actinides

- > 100 new molecules
 - “pre-organisation”
 - “bigger is better” – but wasn’t



EUROPART
(Contract Number: FI6W-CT-2003-508 854)

FINAL ACTIVITY REPORT

Authors : Clément Hill, Françoise Arnaud-Neu, Amparo Glez Espartero, Jean-François Desreux, Giuseppe Modolo, Stéphane Bourg, Rikard Malmbeck, Concha Caravaca, Mike Harrison, Giorgio De Angelis, Jan Uhlir, Noël Ouvrier and Charles Madic

Reporting period: 01/01/04 – 30/06/07
Date of issue of this report: 10/08/07– Rev. 1: 30/11/2007

Start date of project : 01/01/04 Duration: 42 Months
Project Coordinator: Charles Madic
Project Coordinator Organisation: CEA Revision: 1

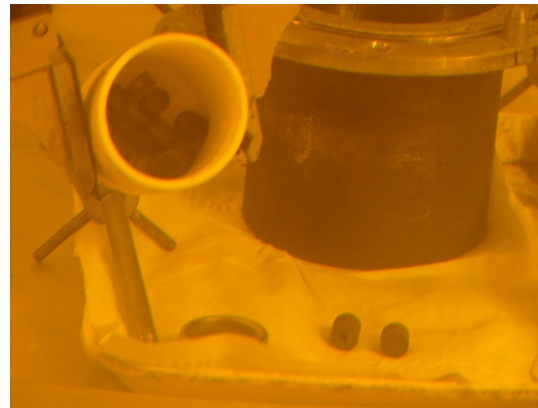
Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Sixth Framework Programme (2002-2006)

Dissemination Level	
PU	Public
RE	Restricted to a group specified by the partners of the EUROPART project
CO	Confidential, only for partners of the EUROPART project



Actinide recycling by separation and transmutation

- Head-end steps
 - Dissolution of different fuel types assessed
 - Conceptual studies + experimental work
- Pyrometallurgy
 - Options for exhaustive electrolysis and actinide back-extraction from aluminium
 - Options for salt purification and waste conditioning
- Hydrometallurgy
- 34 partners



www.acsept.eu

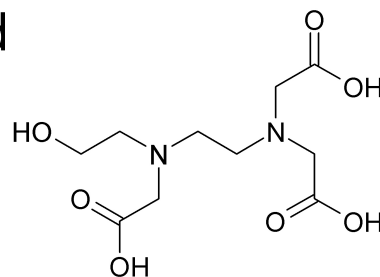
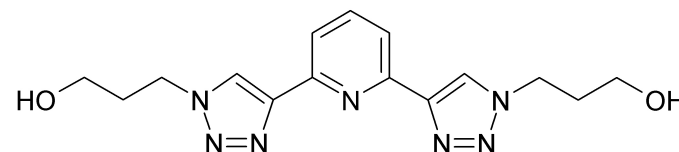
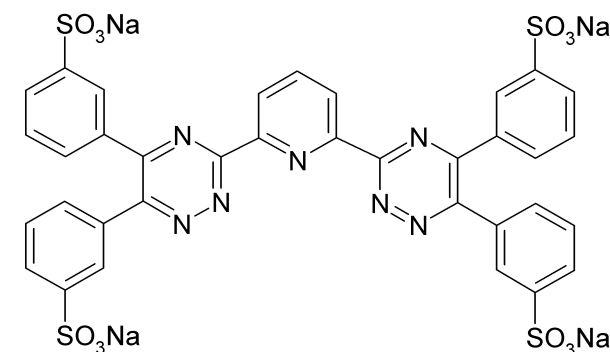
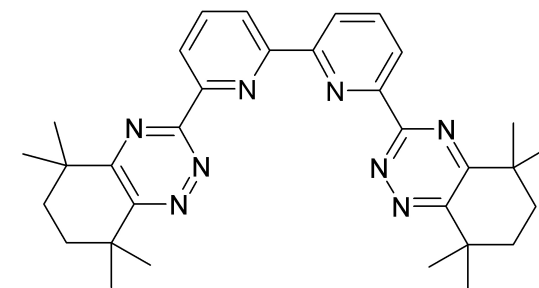
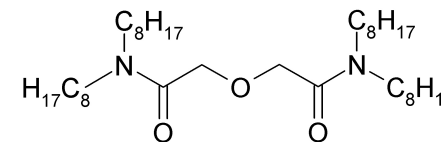
FP7 ACSEPT — Refocus

innovative solutions
for sustainable nuclear energy

Actinide recycling by separation and transmutation

- Hydrometallurgy
 - ≈ 140 new molecules synthesised and screened
 - Small molecules, based on proven cores
 - Best candidate ligand families considered as identified**
 - Four reference flow-sheets developed in ACSEPT
 - r-SANEX
 - i-SANEX
 - 1c-SANEX
 - EURO-GANEX**
 - 3 hot tests, 1 spiked

homogeneous
recycling





Safety of actinide separation processes

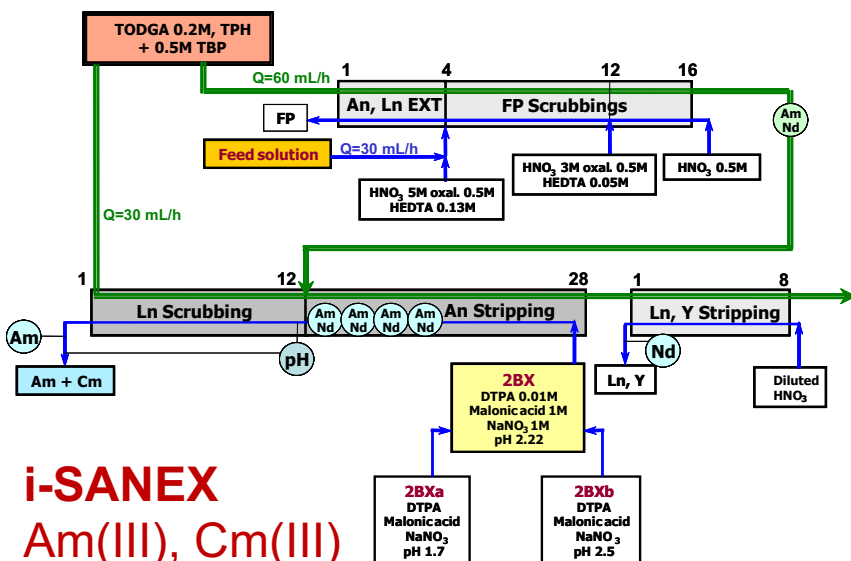
- Four Domains
 - Hydrometallurgy
 - Pyrometallurgy
 - **Global safety and system studies**
 - Management, T&E
- Reference SX systems (from ACSEPT)
 - **No new molecules**
 - Consolidate
 - Study safety
 - Increase TRL
- 26 partners



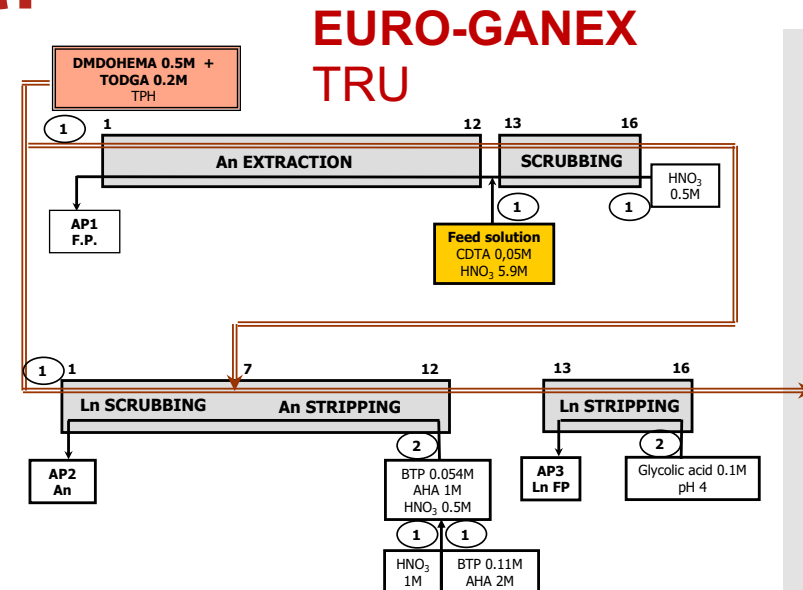
www.sacsess.eu

Safety of actinide separation processes

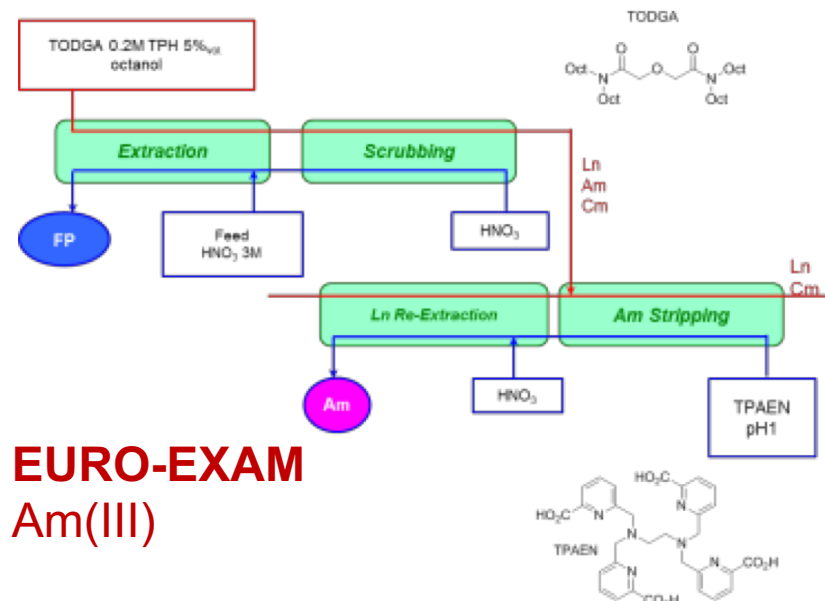
- Reference flow-sheets
 - To be optimised towards
 - **Safety**
 - TRL



i-SANEX
Am(III), Cm(III)



EURO-GANEX
TRU



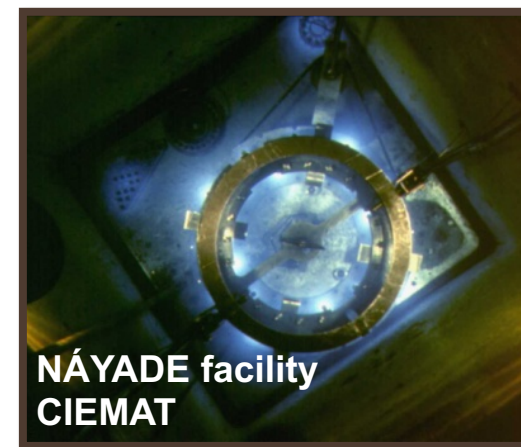
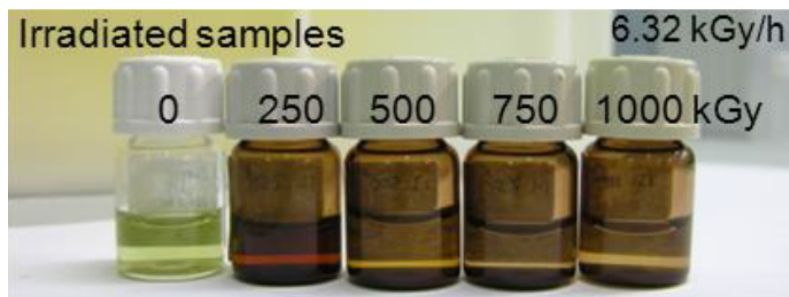
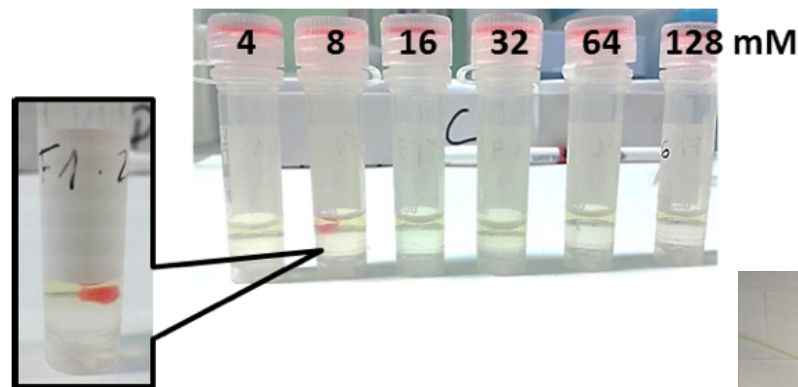
EURO-EXAM
Am(III)

FP7 — Safety First!

Safety of actinide separation processes

Safety of actinide separation processes

- Malop studies
- Stability studies
 - Chemical stability
 - **Radiation stability**



collaboration



Safety of actinide separation processes



- How to continue?

Status	4/4	4/6	1/3	3/8	2/6	0/5	0/5	0/1	1/4	0/1	0/1
Steps or studies needed	All step together	All step together	Filter & buffer tank	SO ₃ -Ph-BTP	Pu & mA product	DEHIBA	DEHIBA		Pu & mA selfheating		
		An stripping 2		DMDOHEMA TOGDA in OK	Spent solvent 2 nd cycle						
	U stripping	Ln stripping		Hydrazine	Hydrazine				FP selfheating		
	U scrubbing	An stripping 1	Flowsheet equipment	DEHIBA in OK	U product	CDTA	CDTA	Temperature range of operation	Cooling system	Hydrogen generation	Long term effect of solvent on materiel
	U extraction	TRU scrubbing	Piping & valves	AHA	Spent solvent 1 st cycle	DMDOHEMA TOGDA in OK	DMDOHEMA TOGDA in OK				
Type of studies or steps		TRU extract		CDTA	Ln product				U selfheating		
			Nitric acid		FP raffinate	HNO ₃ /SO ₃ -Ph-BTP/AHA	HNO ₃ /SO ₃ -Ph-BTP/AHA				
	GANEX 1 st cycle	GANEX 2 nd cycle	Technological needs	Safety and stability studies needed	Radiotoxicity studies needed	Concentration range studies needed	Flow range studies needed	Temperature range studies needed	Thermodynamic behaviour studies needed	Flammability and explosion studies needed	Long term studies needed
EURO-GANEX in a lab			EURO-GANEX in a pilot facility								

Figure 16: Review on the EURO-GANEX process (LGI, 2015)

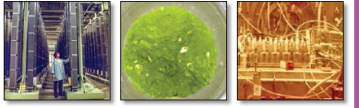
ROADMAP

Actinide separation processes 2015

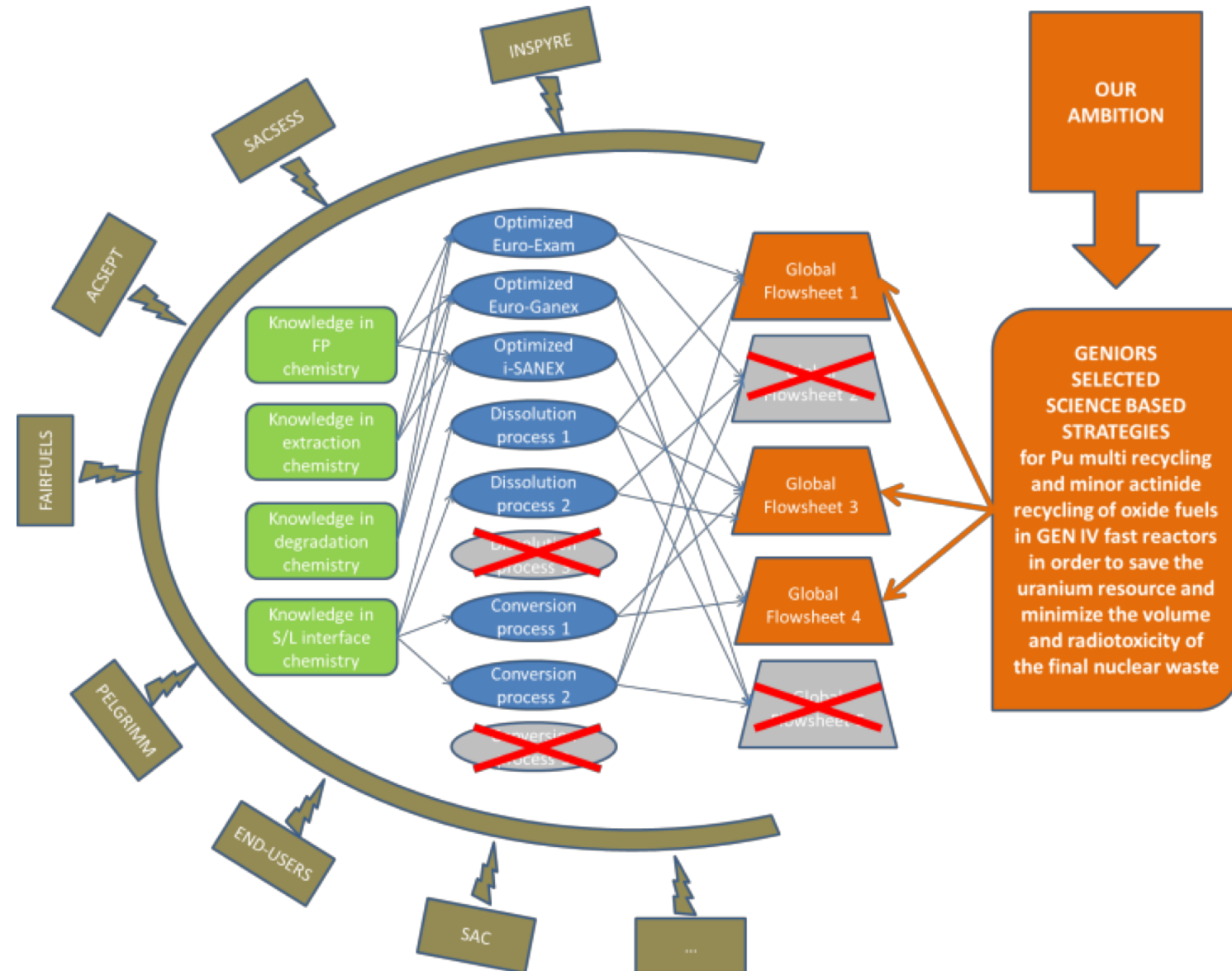
State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry

Nuclear Science 2018

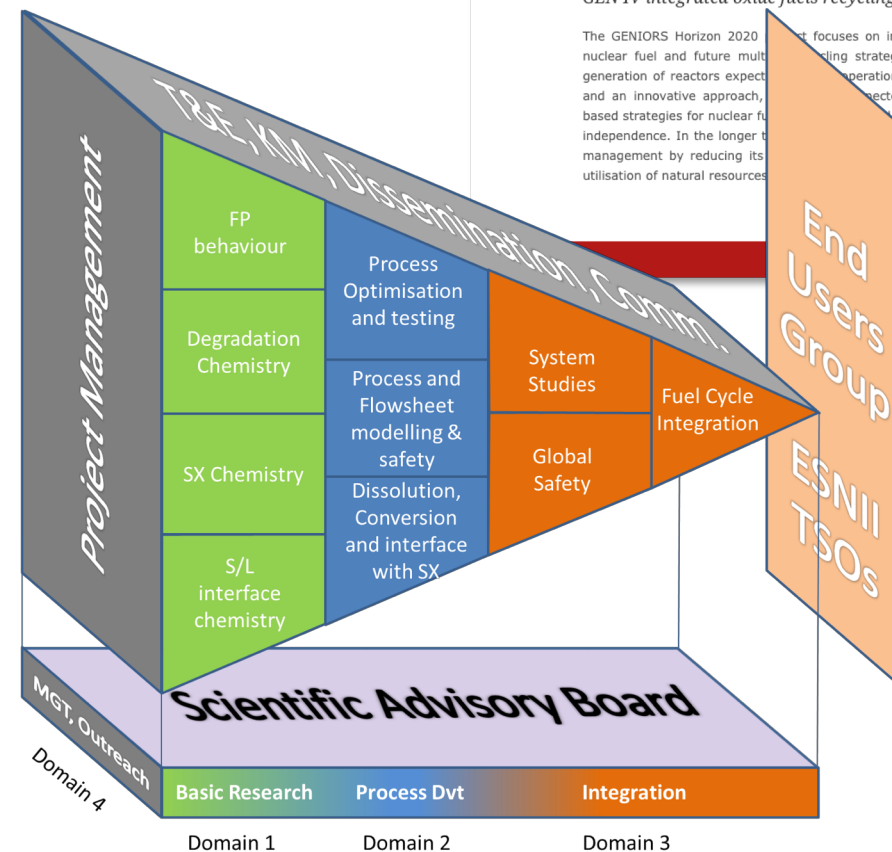


OECD
BETTER POLICIES FOR BETTER LIVES

60th anniversary
NEA
NUCLEAR ENERGY AGENCY



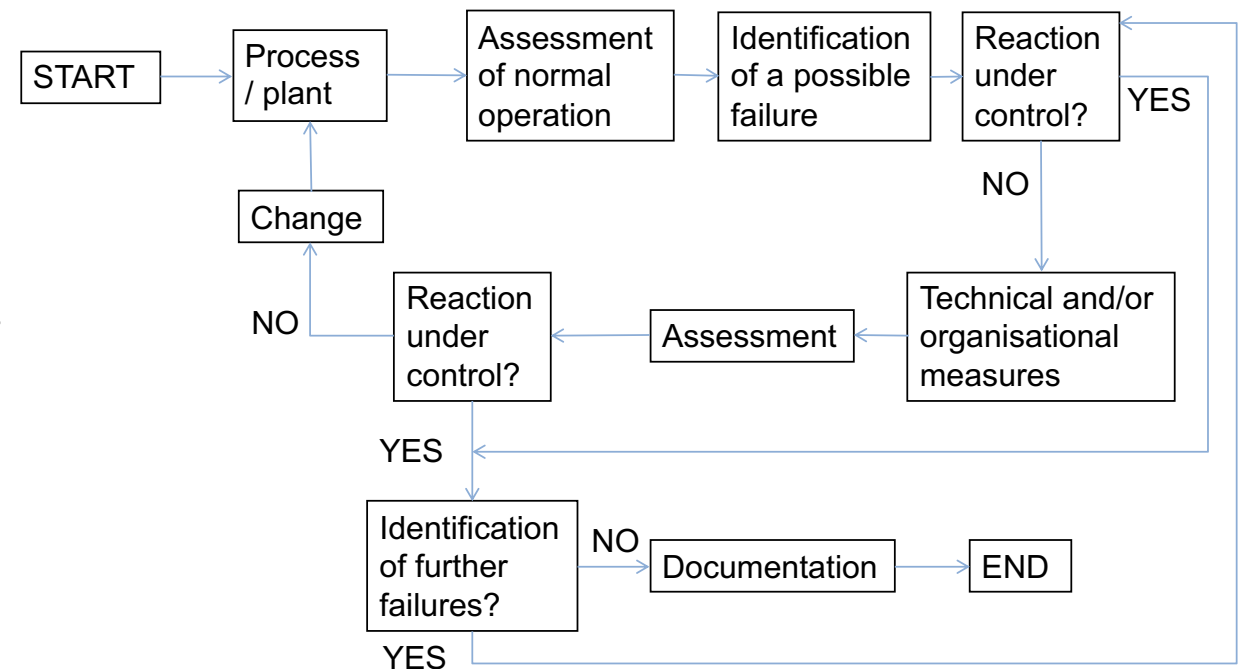
- Four Domains — only hydrometallurgy
 - Basic research
 - Process development
 - System integration
 - Management, T&E
- Focus on
 - Safe operation
 - Integration
 - TRL improvement
- 24 partners



www.geniors.eu

— Integration

- Consolidated suite of flow-sheets
 - Heterogeneous recycling
 - Homogeneous recycling
- Safe and stable operation
 - Reliable models
 - Equilibrium
 - Process
 - Radiolysis & degradation products
 - mimicking process environment
 - Solvent clean-up
 - Gas (H₂) generation
 - Safety review



— Integration

- TRL improvement
 - Comparing process options
 - Impact studies
 - EURO-GANEX plant concept design
 - Process mapping studies
 - “Sim plant” — engineering simulation

- Integration
 - Putting together the pieces
 - Dissolution
 - Separation
 - Conversion
 - DOE collab
 - Exchange with INSPYRE

• Closing the fuel cycle

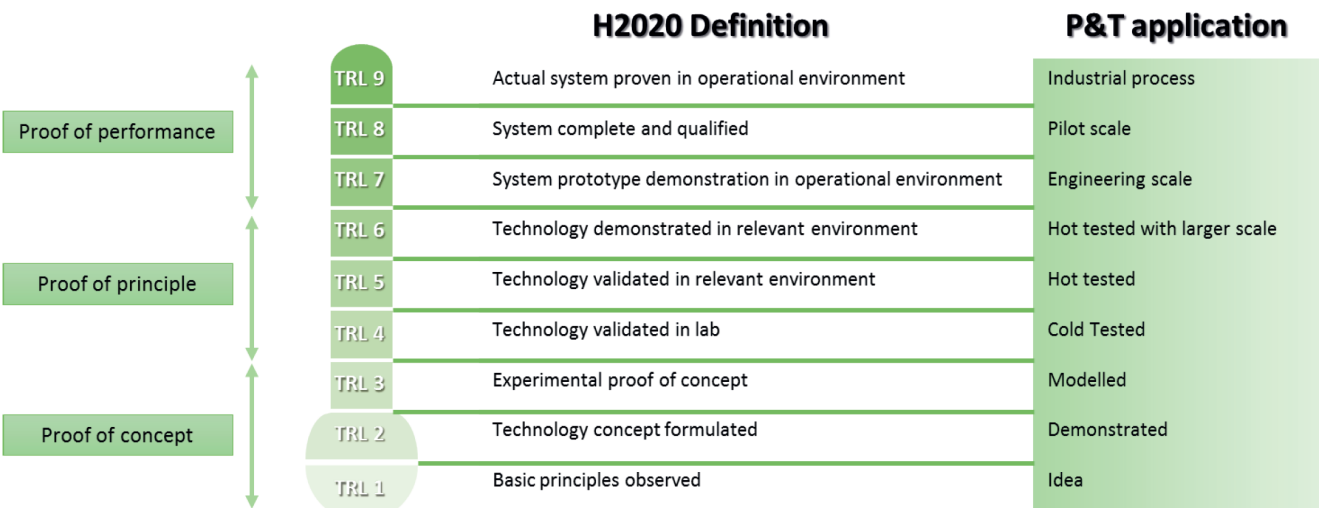




Figure 3: TRL Scale (LGI, 2014)

FP7

Advanced fuels for Generation IV reactors: reprocessing and dissolution

- New reactor concepts, novel fuels and their reprocessing
 - Studied in several European countries
 - However, by different scientific communities
 - Weak interaction
- Irradiation — separation: ASGARD closes the cycle
- Fabrication and dissolution
- Separation
 - MgO matrix
 - Mo matrix



		
DM 2	DM 3	DM 4
Oxides	Nitrides	Carbides
WP 2.1	WP 3.1	WP 4.1
WP 2.2	WP 3.2	WP 4.2
WP 2.3	WP 3.3	WP 4.3



Conclusions

- Continuous line of European Programmes
 - Since early 1990's
 - Constant progress
 - Initially focussing on chemistry ("better" extractants...)
 - Reference systems identified
 - Safety
 - Integration
 - TRL
 - Towards industrialisation
- Not only science & technology has evolved...