

DE LA RECHERCHE À L'INDUSTRIE

cea den

From fuel to fuel: Dissolution, Partitioning and fuel manufacturing

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**TURNING
SPENT NUCLEAR FUEL
INTO A RESOURCE**

INTRODUCTION
THE 3 PROJECTS
EDUCATION AND TRAINING



**TURNING
SPENT NUCLEAR FUEL
INTO A RESOURCE**

INTRODUCTION



Does not preserve natural resource

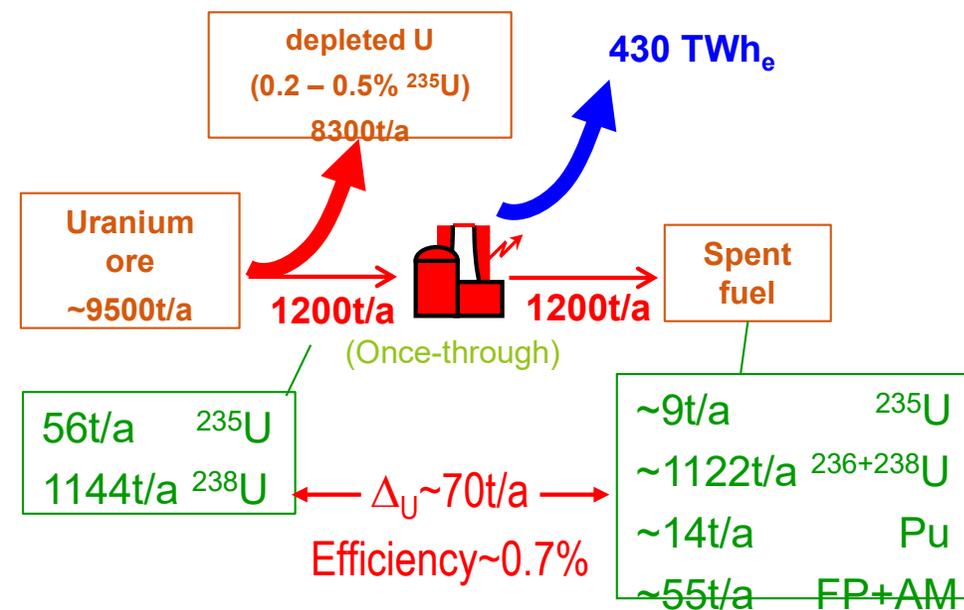
➤ Natural U is a limited resource

- Although present everywhere, U-ores of reasonable economic interest are limited (260\$/kg U)
- Minimum lifespan ~135 years (*with current consumption 56kt/y*)
- Need for preserving U-resource

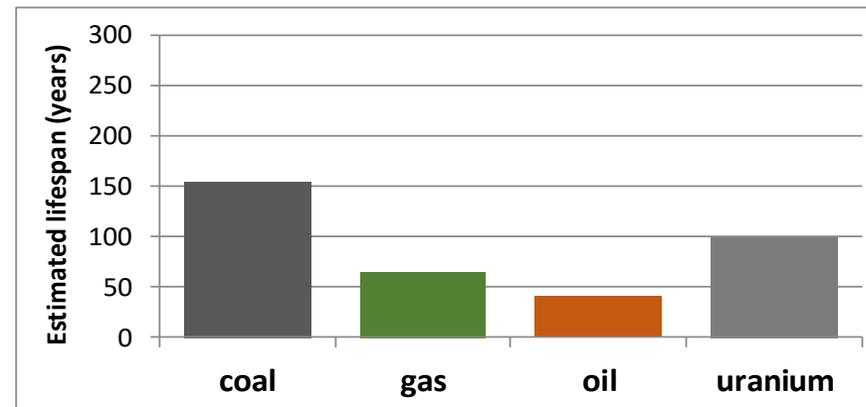
➤ Global efficiency is currently very low: ~0.7%

- ~70t from the initial ~9500t Uore

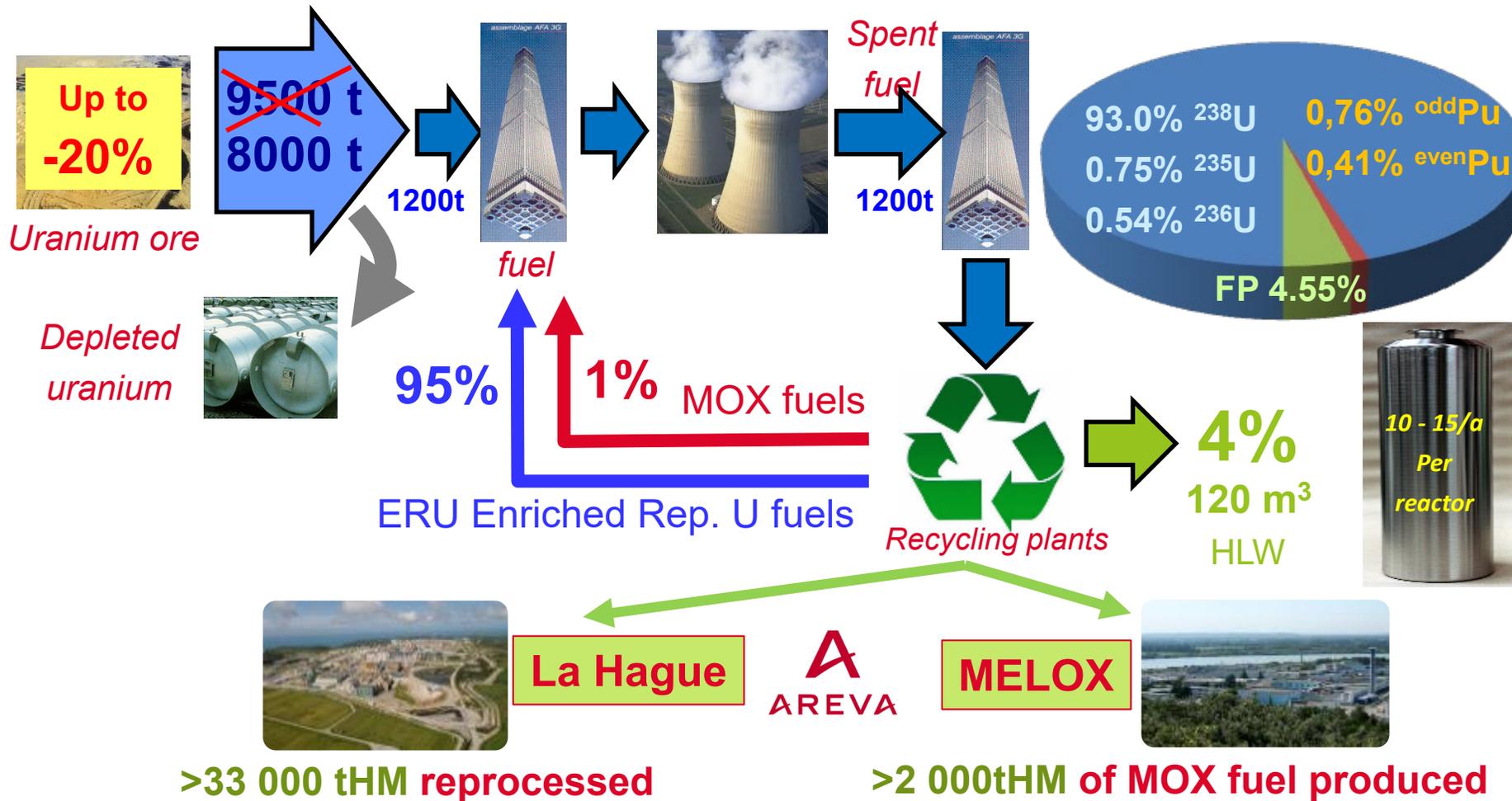
➤ Need for improving U-efficiency



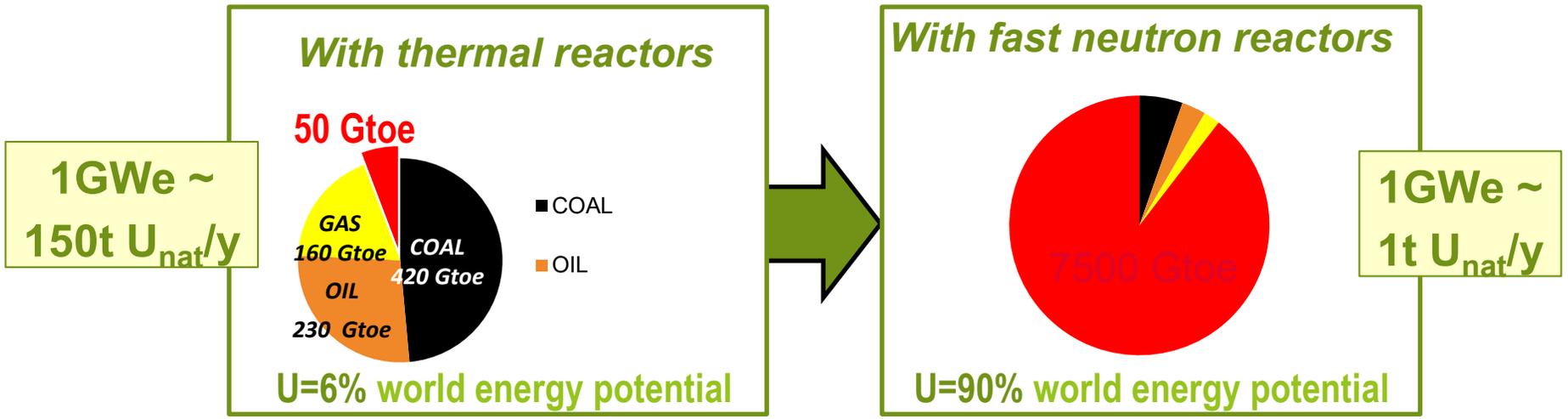
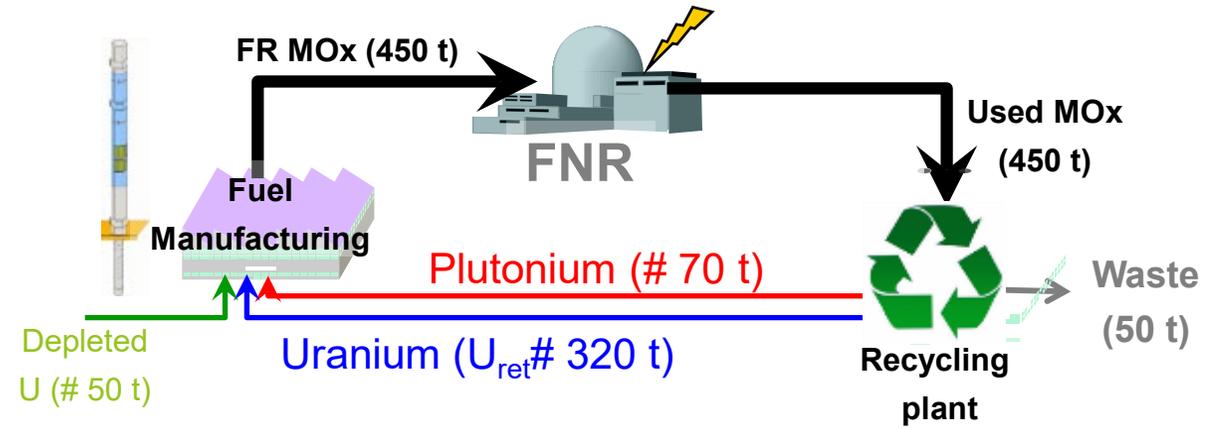
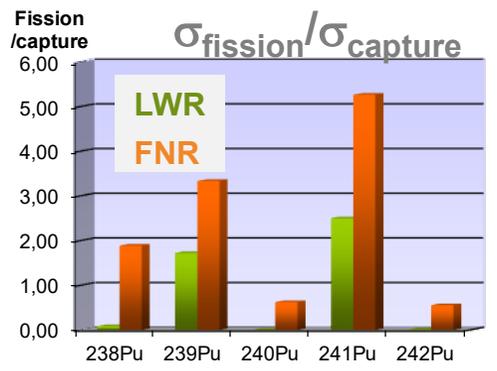
Rough estimates derived from French Fuel cycle assuming no recycling



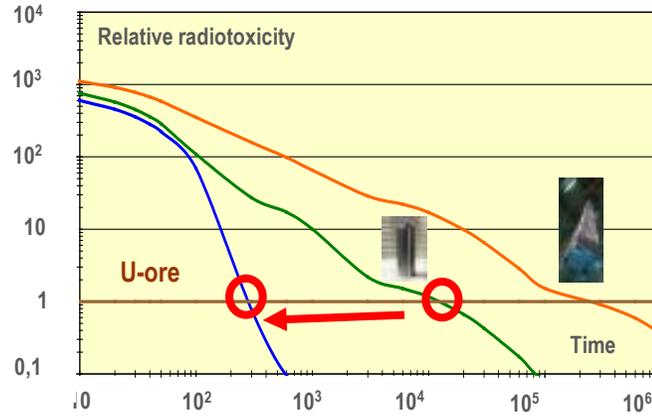
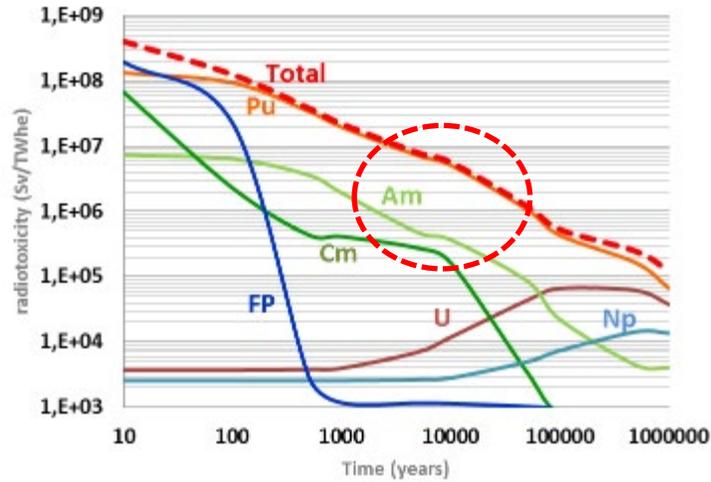
Nuclear Energy Today – Once through fuel cycle (French fuel cycle)



- 15 to 20% of French electricity yearly supplied by recycled materials
- ~1500t uranium ore yearly preserved
- No significant SNF interim storage ⇔ risk reduced



Very significant improvement of natural uranium efficiency



➤ Waste toxicity dominated by MA

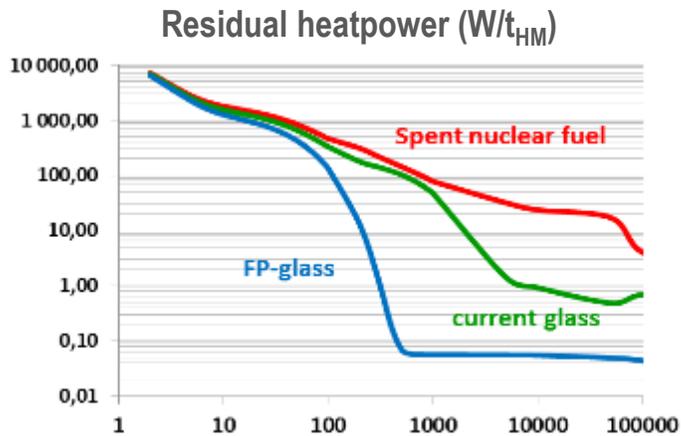
■ Recycling MA ⇔ decrease waste lifetime and toxicity

➤ Preserve the valuable repository resource

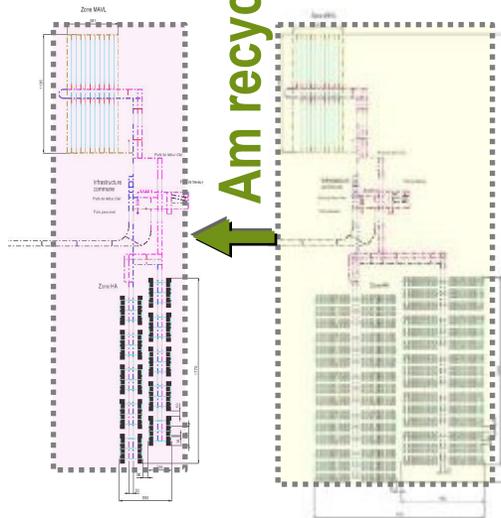
■ ↓ of the heat load ⇔ ↑ density of the repository

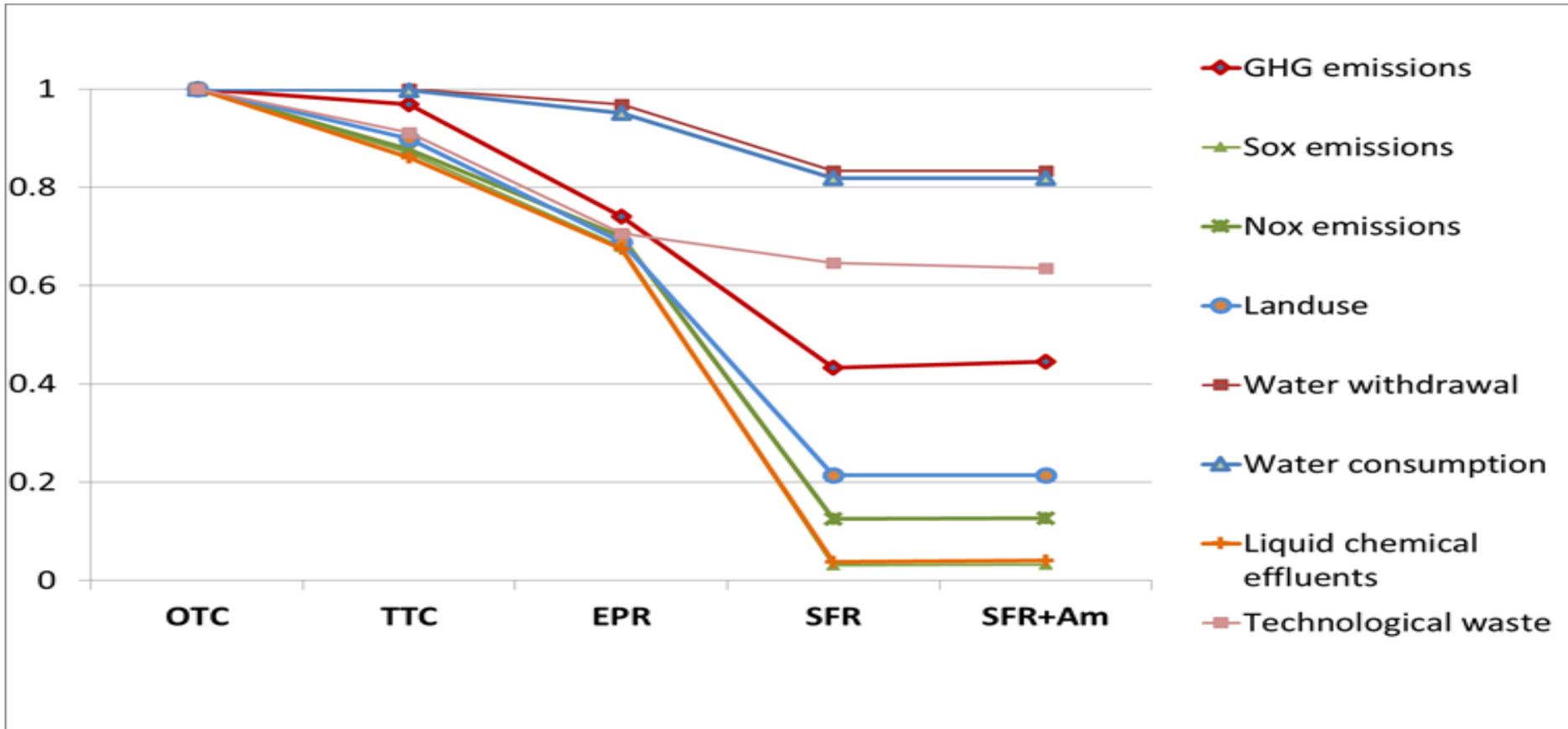
■ With Am recycling, reduction of the repository volume by a factor up to 8

■ Very significant increase of the repository "lifespan"



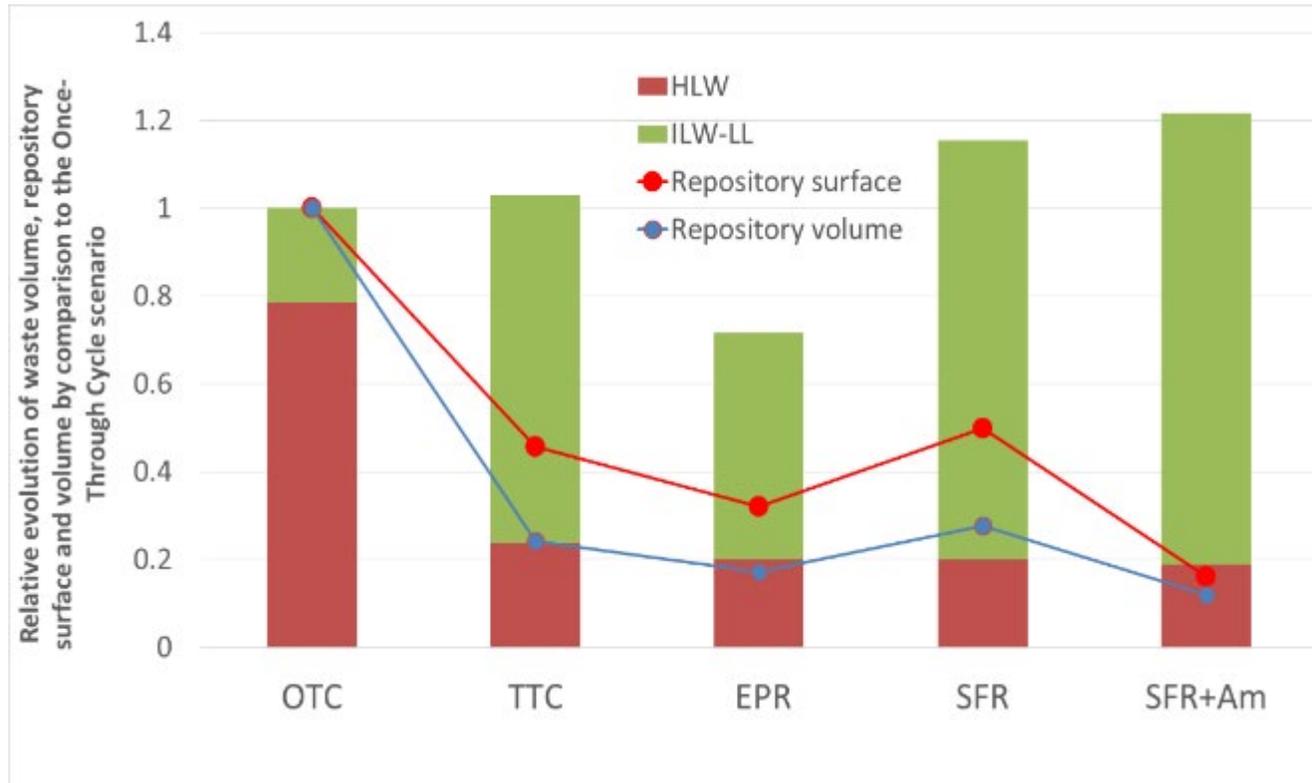
HLW: 160 ha HLW: 1200 ha





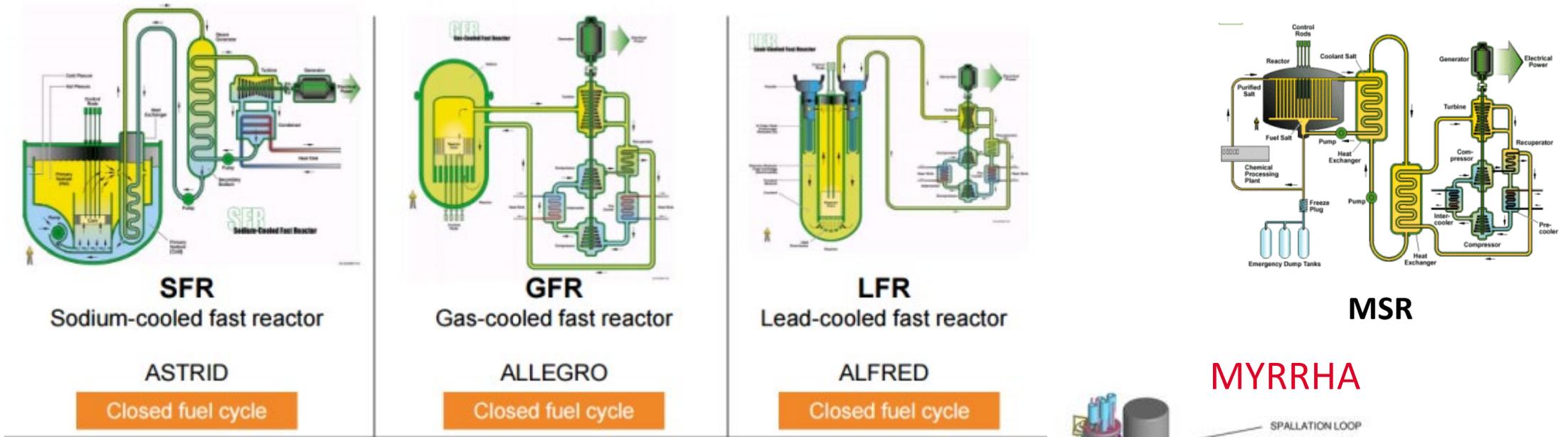
Actinides recycling significantly improve the nuclear energy environmental footprint

Ch. Poinssot, S. Bourg et al., Energy 2014, 6, 199–211
J.Serp, Ch Poinssot, S. Bourg, Energies 2017, 10, 1445.



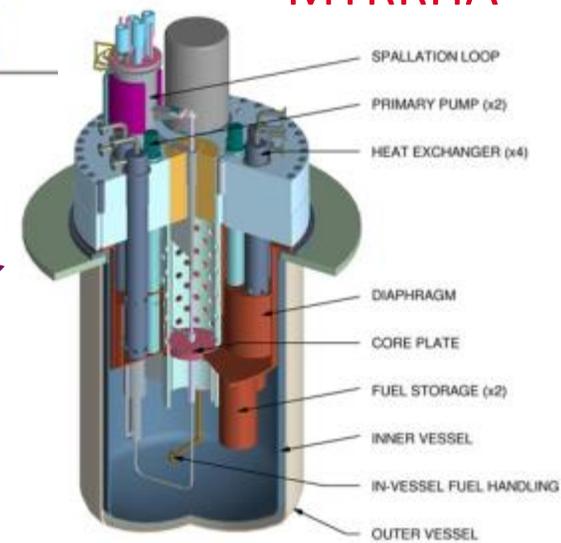
Interim storage time:
120 years

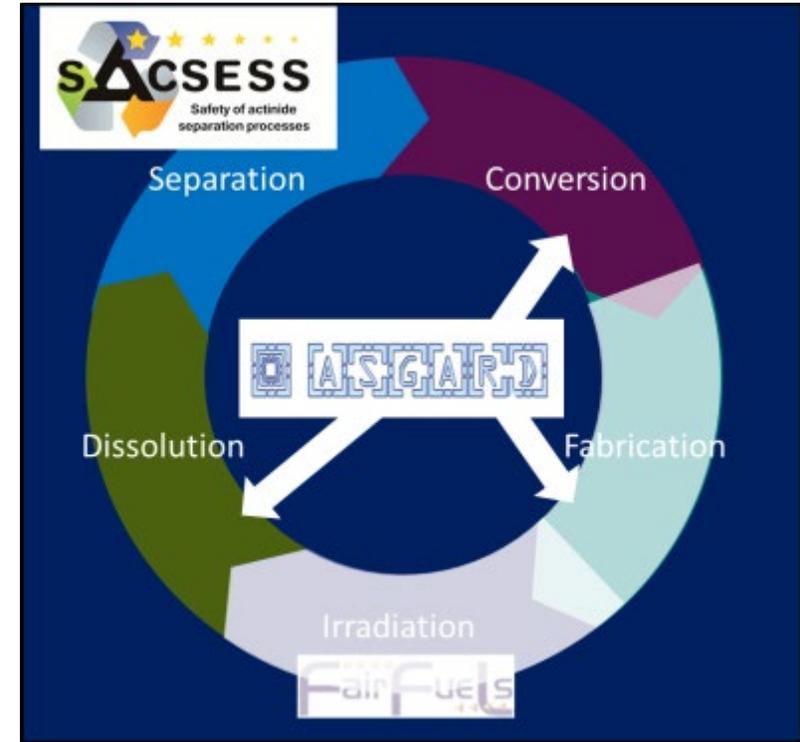
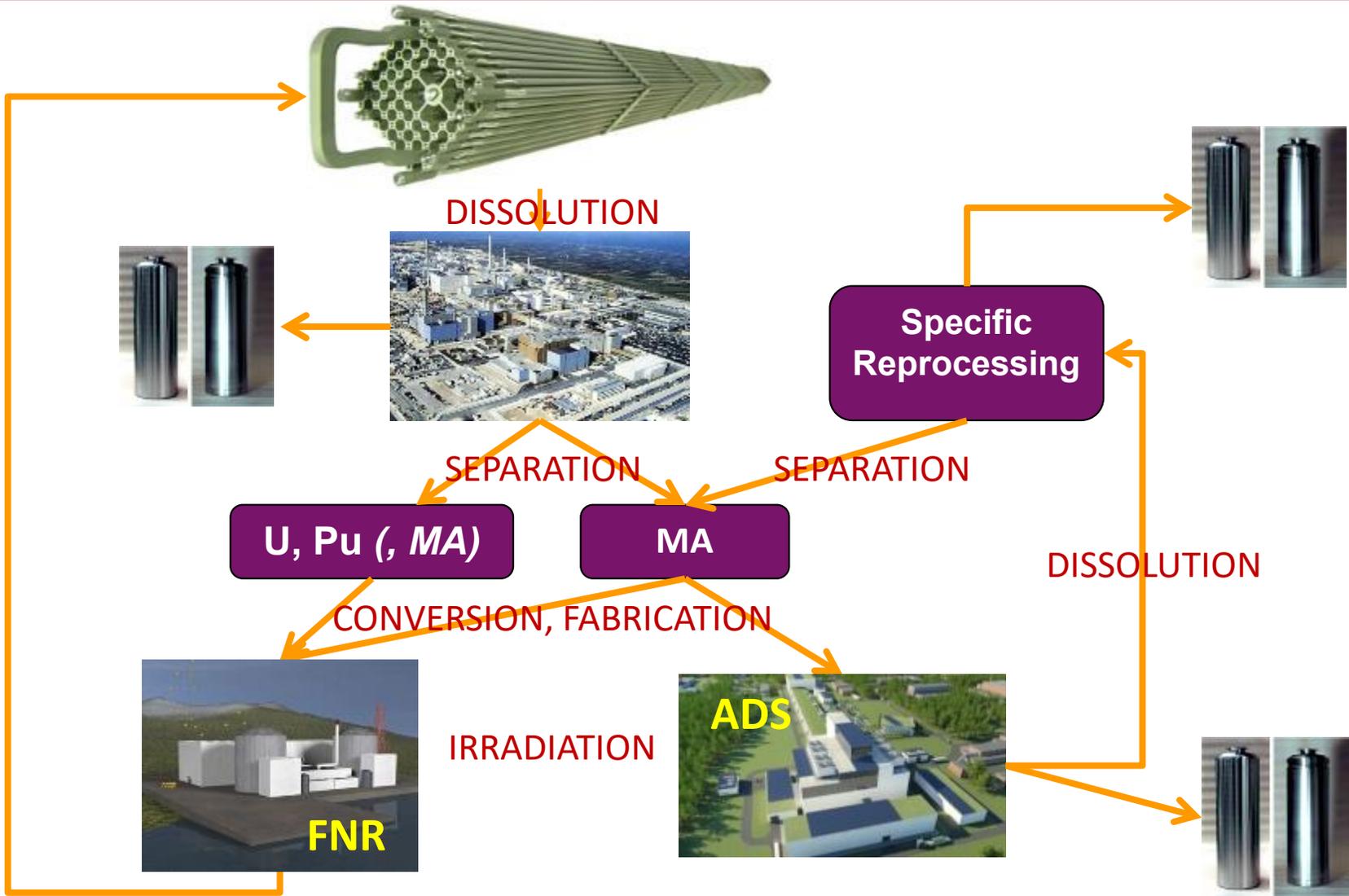
- Relative decrease of HLW vs. ILW while total volume of waste ~ constant +/- 20%
- Decrease of thermal power due to Pu-recycling → significant gain for the repository volume
- Decrease of radiotoxicity & lifetime
- Am transmutation: save the repository surface by a factor about 3 compared to SFR



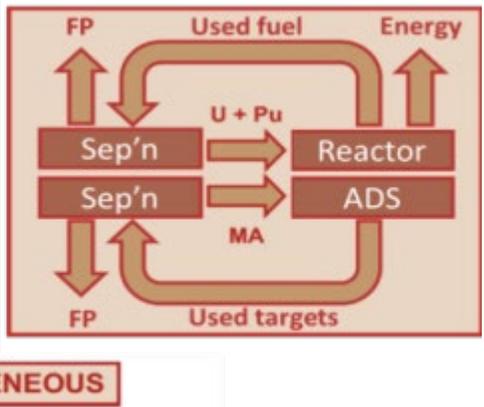
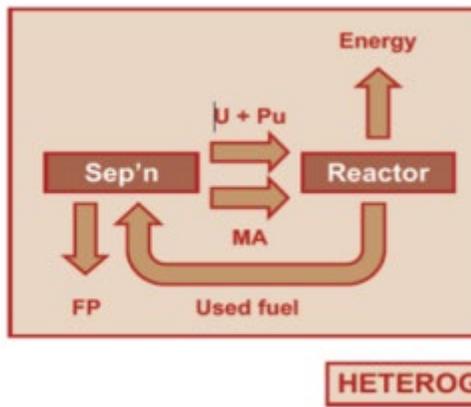
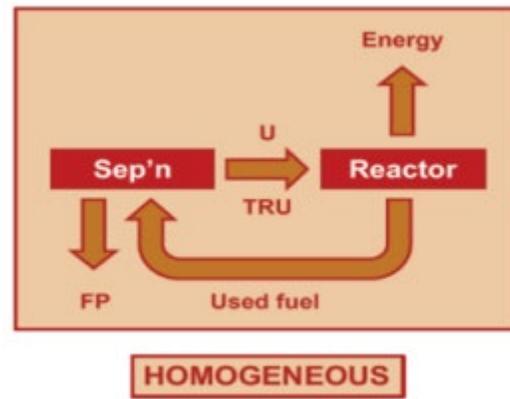
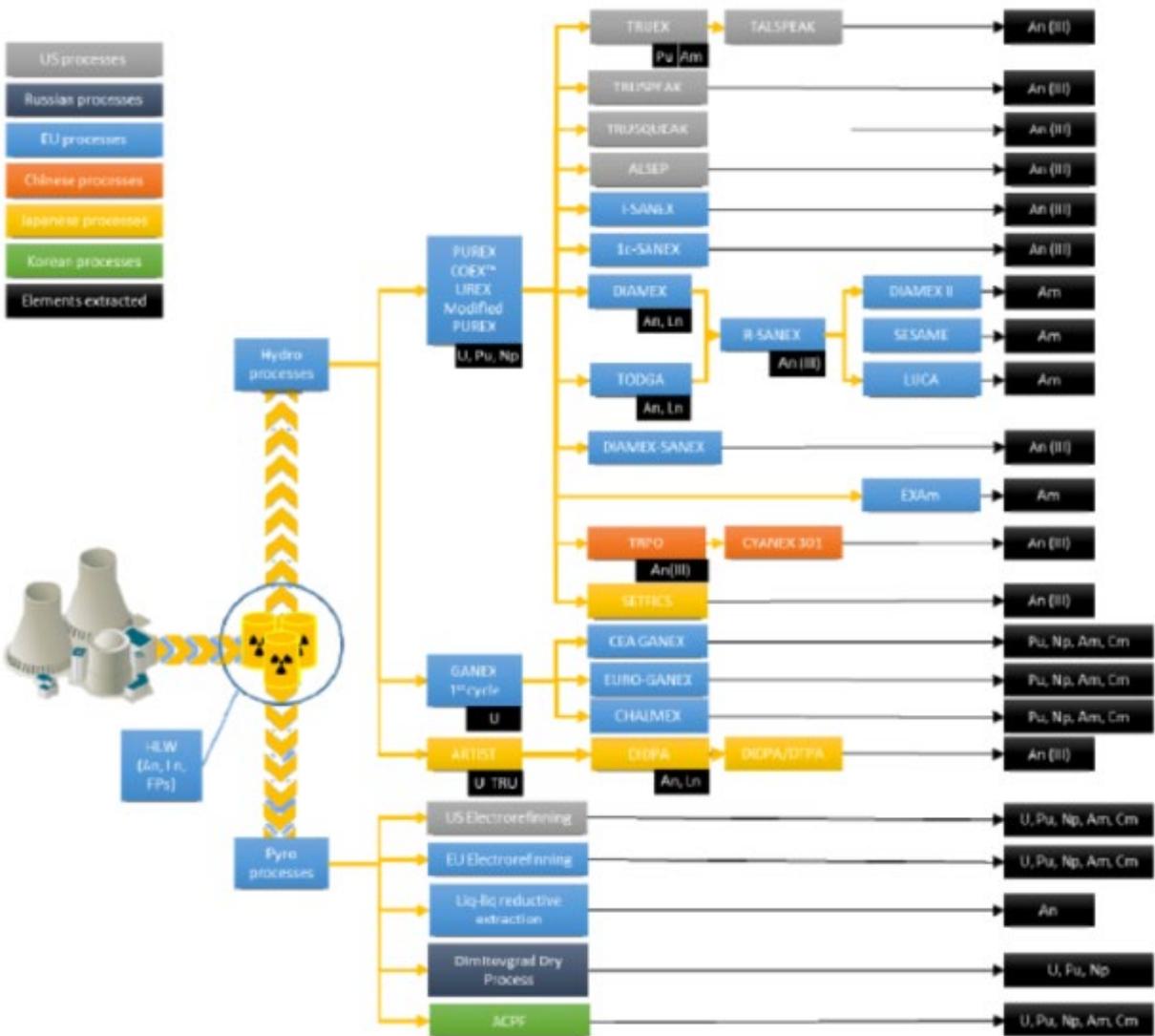
Reference fuel: carbide, nitride...

Reference fuel: MOX





Different separation process options developed worldwide for different fuel cycle strategies



But before, we need to dissolve the fuel, and after, we have to re-manufacture it!



**TURNING
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ASGARD

FROM FUEL TO FUEL

NON MOX

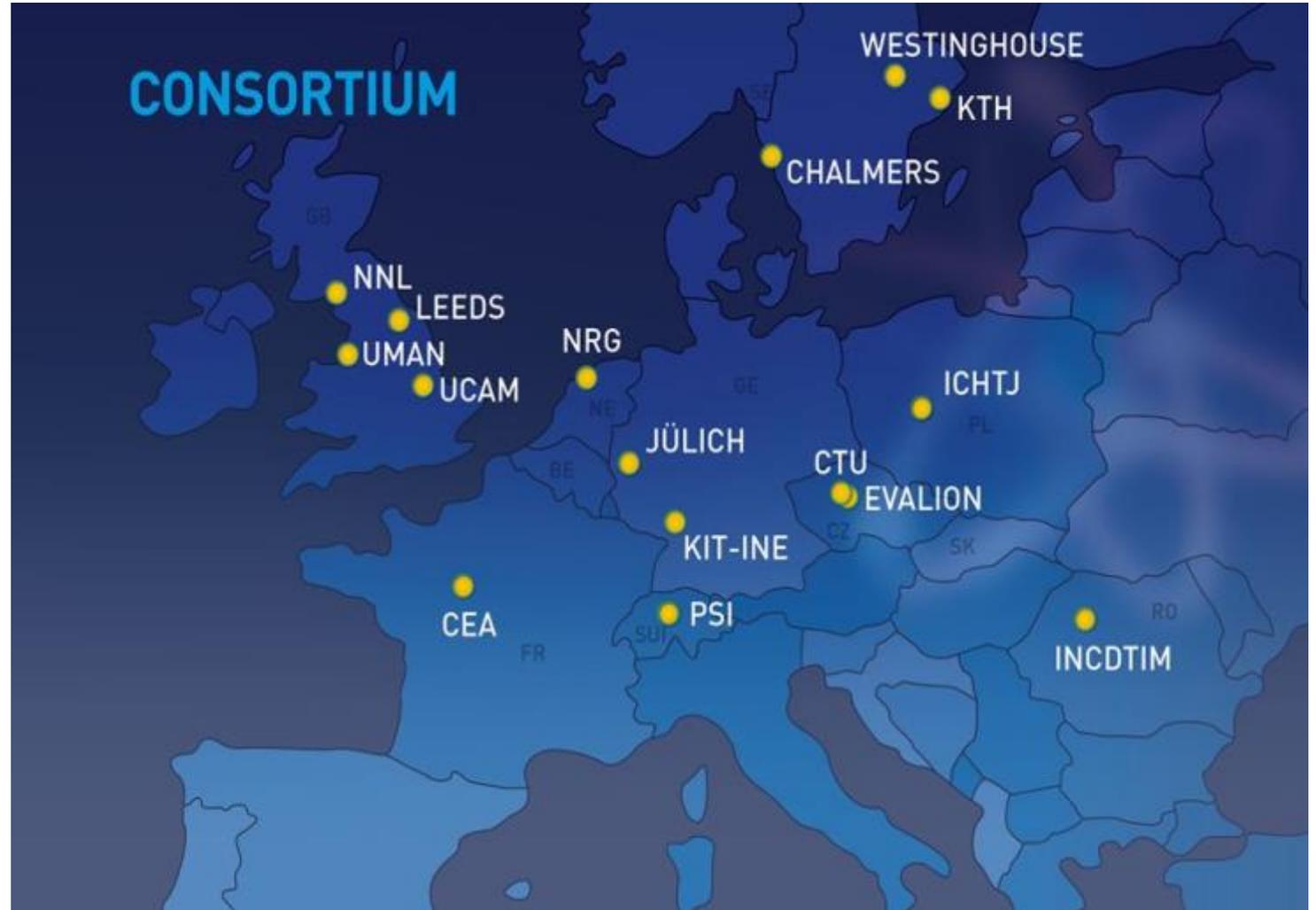


ASGLARD



**Christian Ekberg, Stephane Bourg, Eva deVisser-Tynova, Andreas Geist, Frodo Klaassen,
Teodora Retegan, Mark Sarsfield and Janne Wallenius**

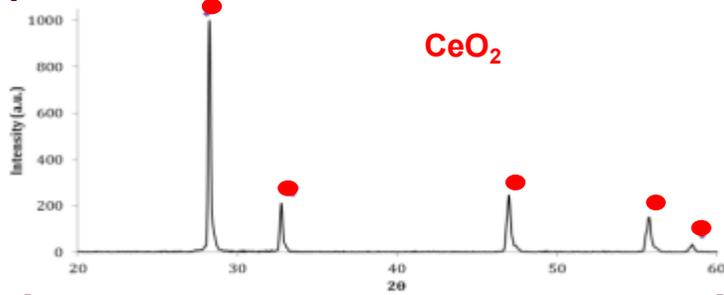
- Budget: 9365 kEuro (EC 4.9 kEuro)
- Duration: 20120101- 20151231
(4 years)
- Extended to 20150630



- Focus on the behaviour of novel nuclear fuels ranging through production, dissolution, conversion and refabrication
- Novel fuels considered are An (Am) bearing oxides, CERMET (Mo-based), CERCER (Mg based)', nitrides and carbides
- Provide extensive training and education concerning handling of nuclear material from the whole fuel

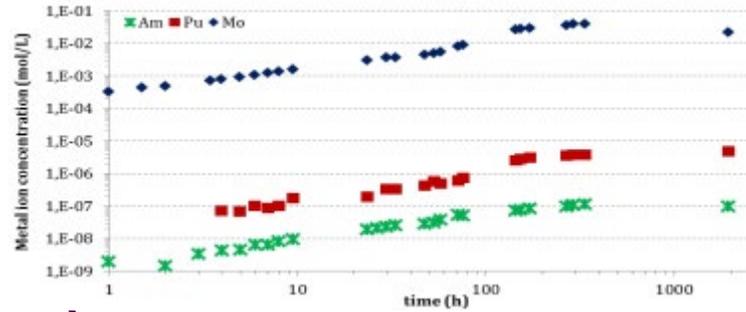
CeO₂/Mo dissolution

- CeO₂ /Mo (60/40wt.%) pellets dissolved in 20 and 100 mL 1 mol/L HNO₃ without or with Fe(III)
- CeO₂ separated from the matrix



PuO₂/Mo dissolution

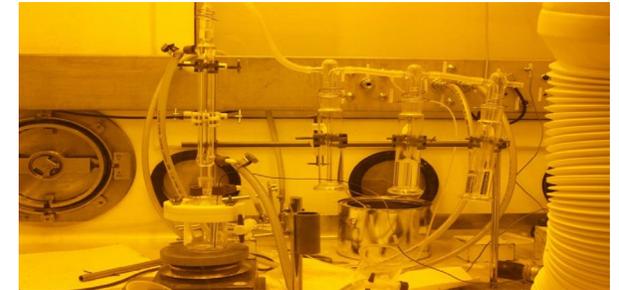
- 1 and 3 mol/L HNO₃ and 1 mol/L HNO₃/0.2 mol/L Fe(NO₃)₃, RT
- Mo dissolution – faster with Fe (III)
- Pu (Am) dissolution much slower in presence of Fe(III)
- PuO₂ could be separated from Mo matrix



Fresh fuel

(Pu_{0.8}Am_{0.2})O₂/ Mo dissolution

- Irradiated at HFR Petten (HELIOS pin 5)
- 2 steps process:
 - dissolution of Mo -matrix HNO₃ (8 M)
 - dissolution of actinides oxides HF or Ag(II)
- ❑ Samples taken during dissolution for ICP measurements
- ❑ Black residue remained – PuO₂

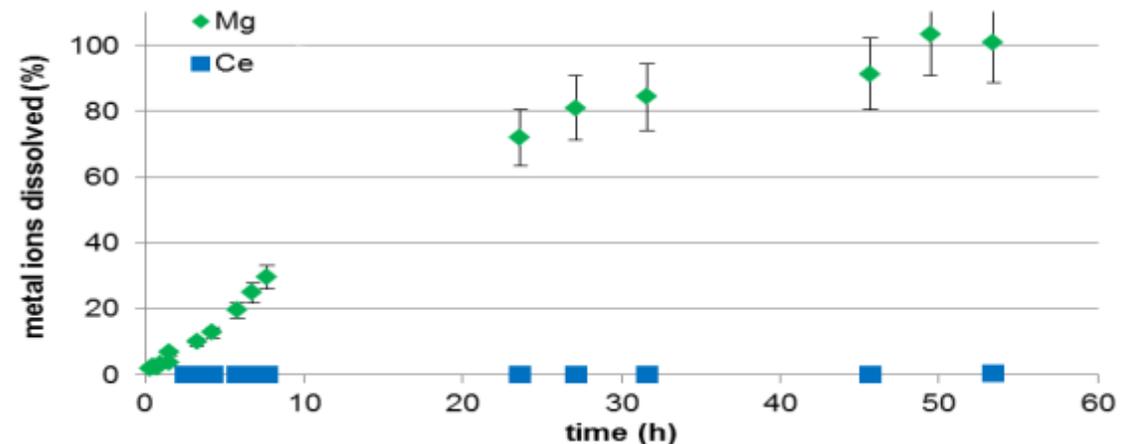


Irradiated fuel

- Experiments in 2.5 mol/L HNO₃ at 30 °C.
- Agitation speed has no effect on dissolution rate, i.e. **dissolution rate is surface controlled**
- The acid volume has no effect on dissolution rate.
- A two-stage reaction equation for the dissolution of MgO was postulated based on XRD measurements and literature review.
- The dissolution (2 M HNO₃, RT) of MgO/CeO₂ (60/40 wt.%) – MgO completely dissolved, CeO₂ remained as powder



- **Actinides can be separated from the magnesia matrix**



Sol – gel methods

Two methods

- *Internal gelation*
- *Complex Sol-Gel Process*
- UO₂/Nd microspheres prepared & characterized
- processes studied & optimised



Impregnation of solid matrixes

- Amberlite IRC-86 and Lewatit TP-207 resins tested for fabrication of UO₂/Nd microspheres
- Amberlite IRC-86 successful

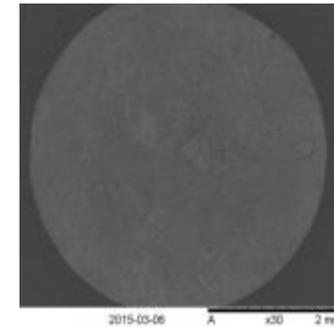


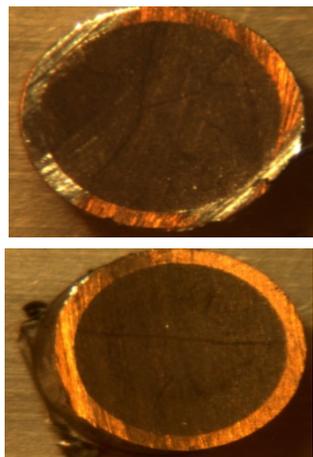
Photochemical conversion

- UO₂, ThO₂, ThO₂-UO₂, CeO₂, Eu₂O₃, (Ce,U)O₂, Eu₂O₃-UO₂ materials prepared
- Fuel pellets made



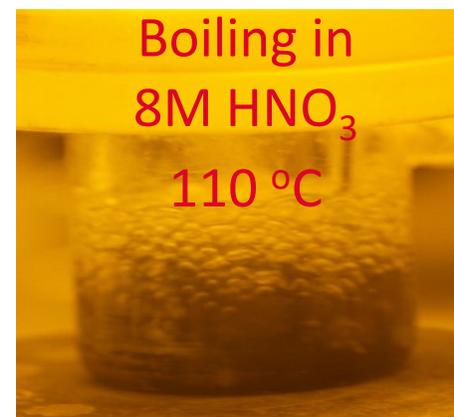
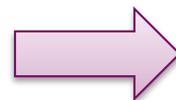
- Sol-gel beads and pellets of ZrN and (Pu,Zr)N has been manufactured
 - EXAFS show one structure for (Pu, Zr)N
- (Pu,Zr)N pellets sintered in Ar or N₂
 - The ones in N₂ has two crystal structures
 - The ones in Ar has one crystal structure
- Problems with carbon content but being solved
- The expected blackberry structure could be avoided and a smooth pellet achieved





CONFIRM pin slices
(including cladding)

- $m \approx 1.13 - 1.27 \text{ g}$
- $h \approx 4.6 - 5.2 \text{ mm}$
- $\text{Pu} \approx 400 - 440 \text{ mg}$

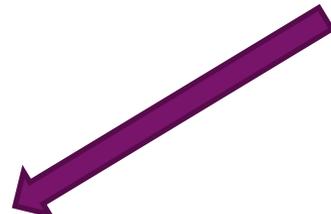
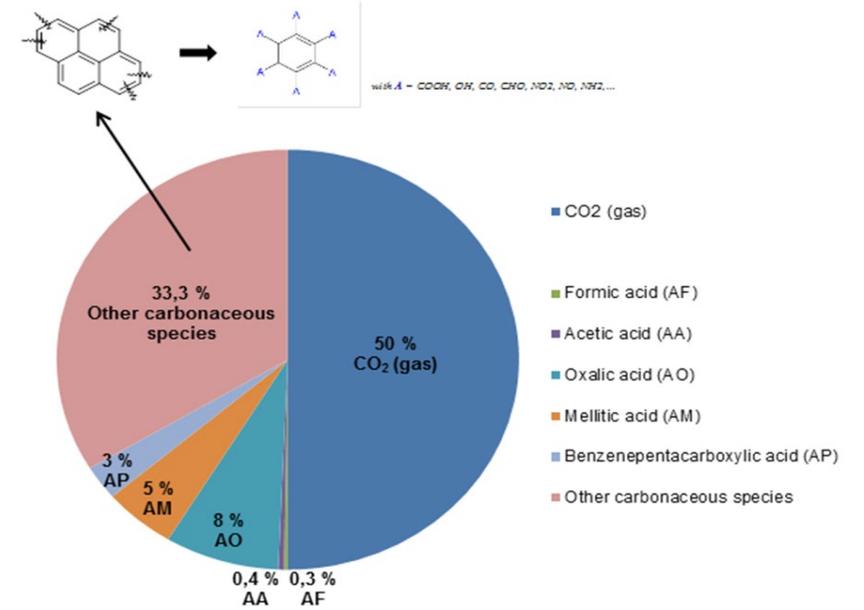
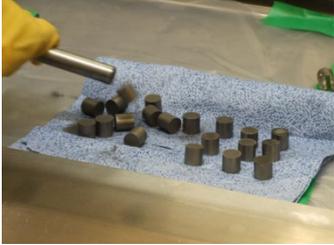


Exp. 1

	Exp. 1	Exp. 2	Exp. 3	Exp. 4
Additions	-	1 M HF*	0.8 M HF	250 mg AgO
Boiling time (h)	13	23	6	16
Liquid volume (ml)	100	100	150	100
Undissolved fuel on cladding	YES	NO (or little)	NO	YES
Solid residue (particles) (Zr cont.)	YES	YES	NO	YES
Remaining solid (clad.+fuel) (mg)	547	574	117	716

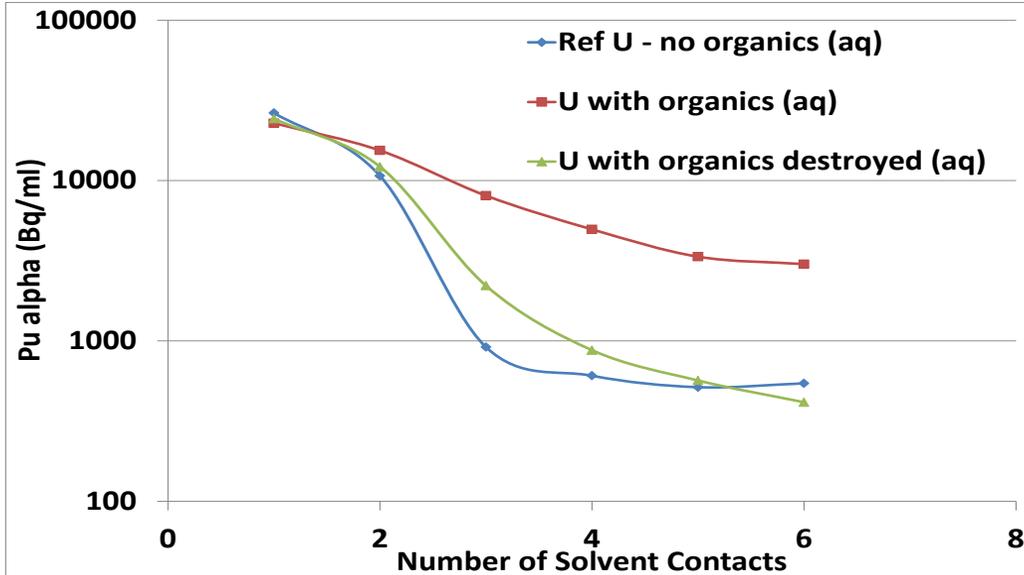
- Pin starts to dissolve from the middle
- HF necessary for complete dissolution

* added after 54h



“Uranium carbide dissolution in nitric acid: organic compounds speciation”
 S. Legand, C. Bouyer, F. Casanova, D. Lebeau and C. Lamouroux (submitted).

“Dissolution of Uranium Carbide Fuel pellets” M.J. Sarsfield, C.J. Maher, T.L. Griffiths (submitted).





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SACSESS

**IMPROVING THE SAFETY OF SPENT FUEL
REPROCESSING**



SACSESS, 2013-2016

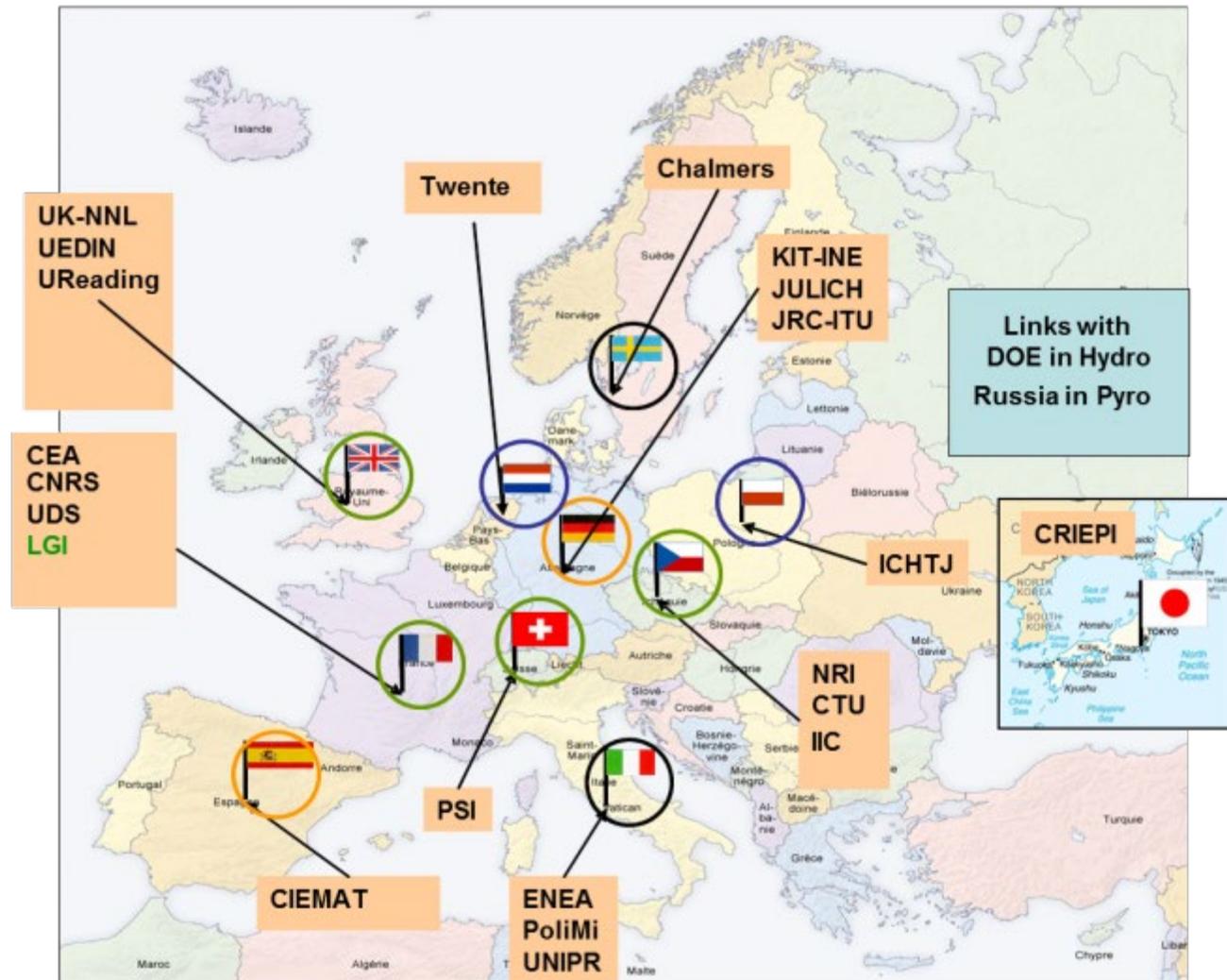
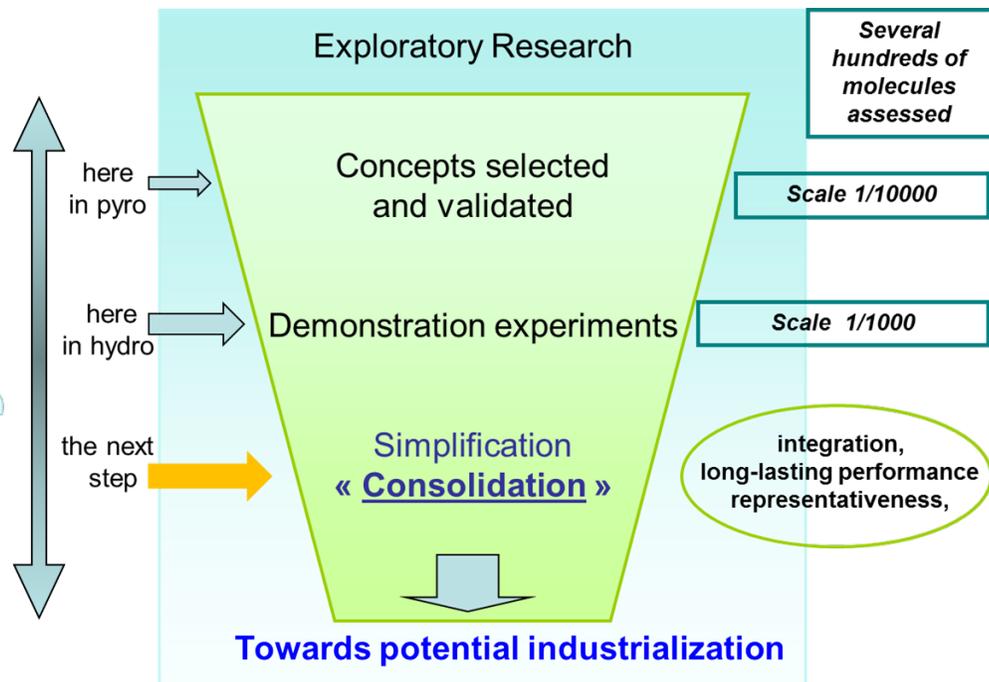
26 Partners

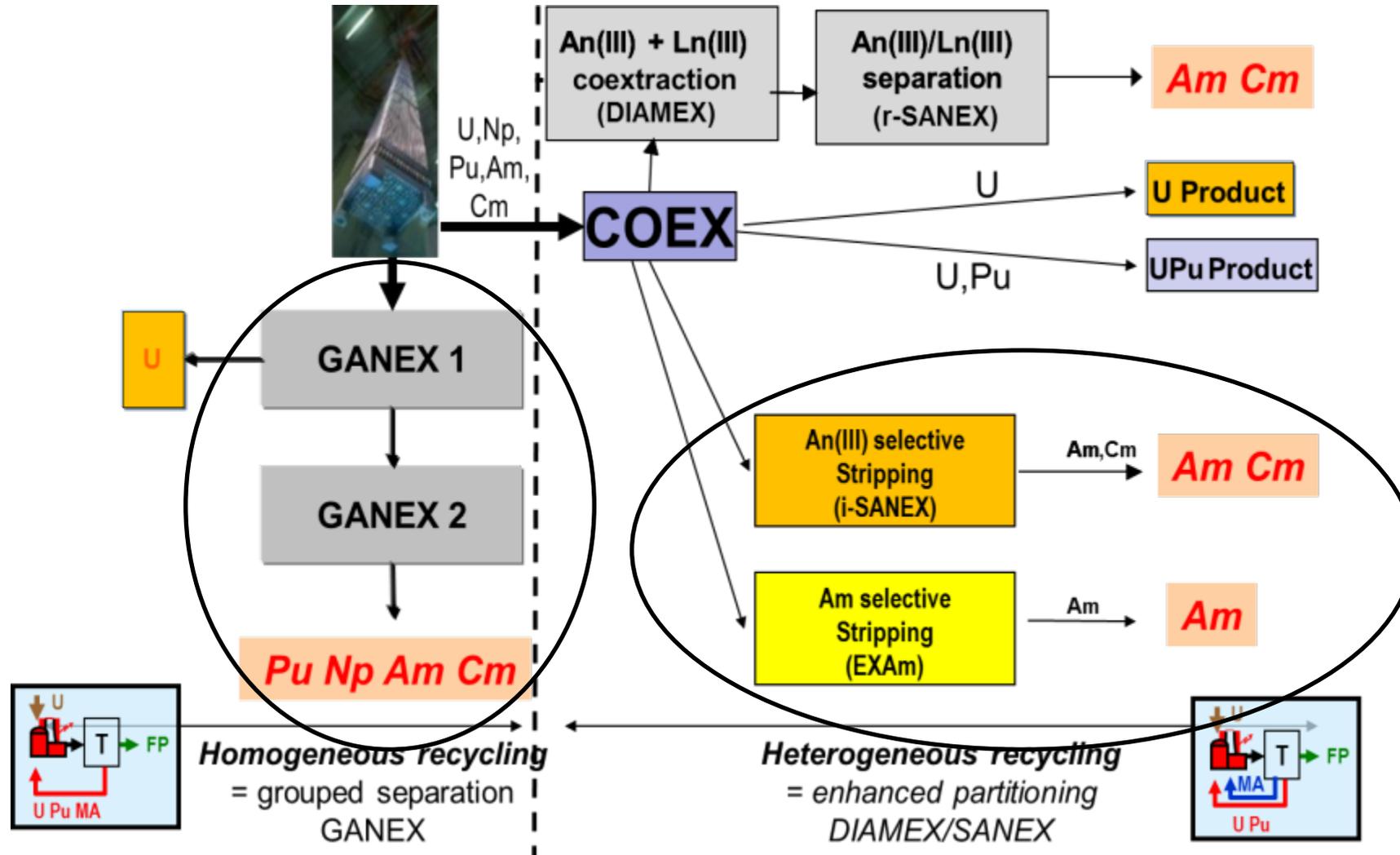
2013-2015

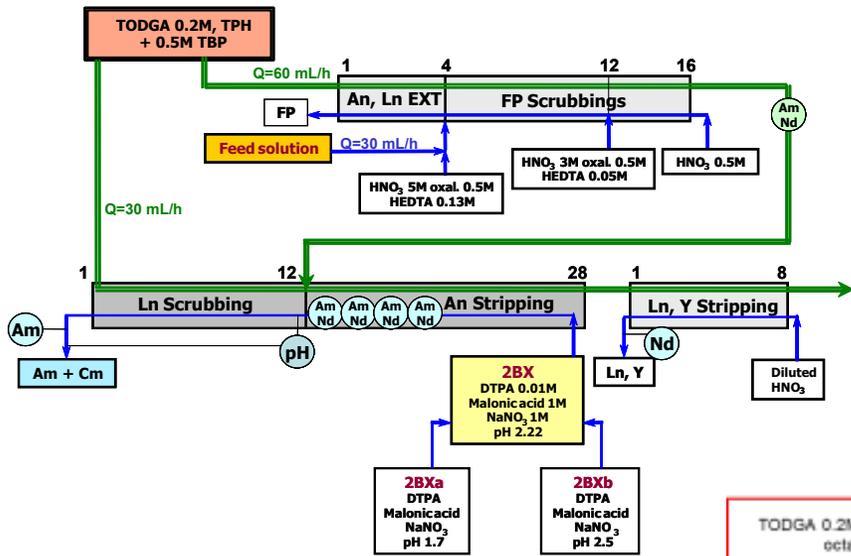
Budget 10,5 M€

Grant 5,55 M€

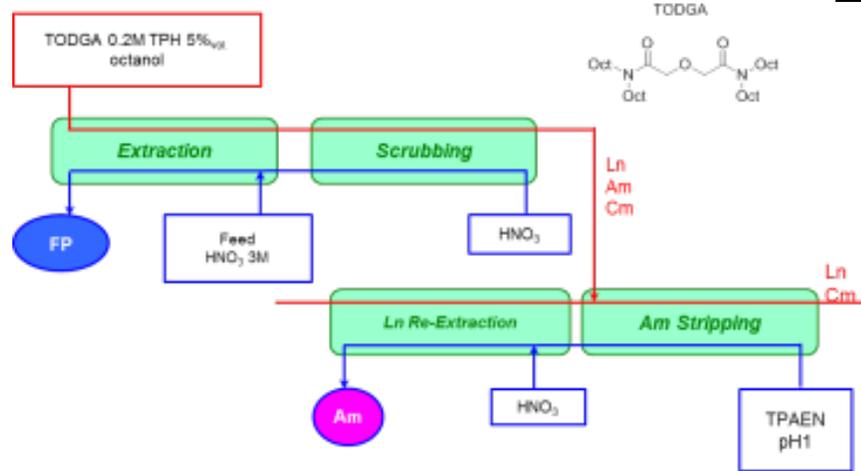
Safety issues



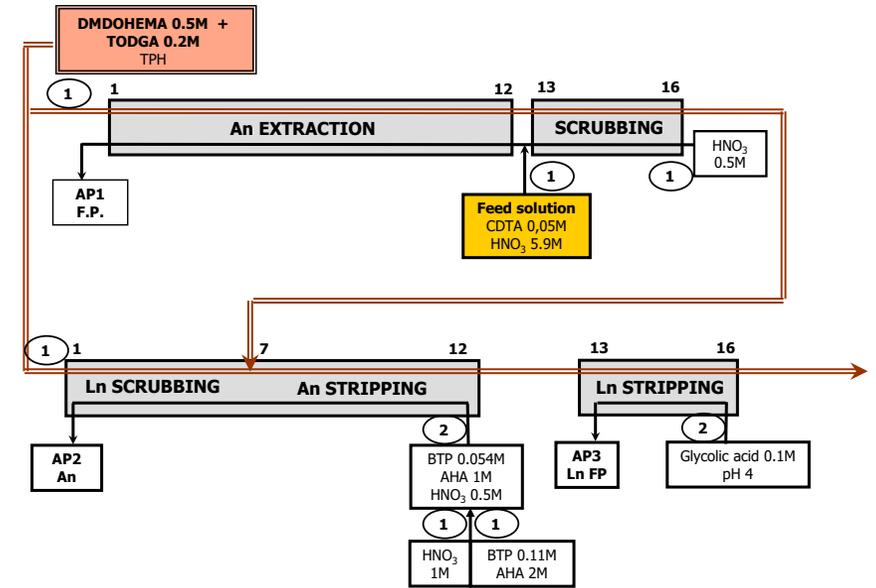




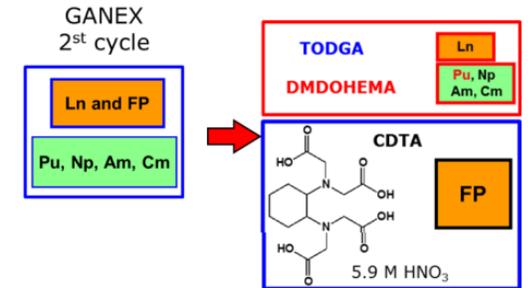
i-SANEX



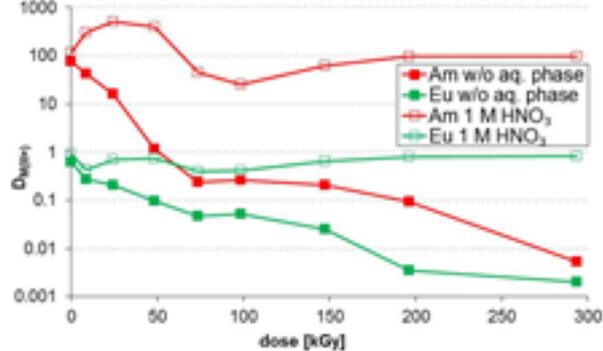
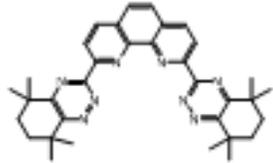
EURO-EXAM



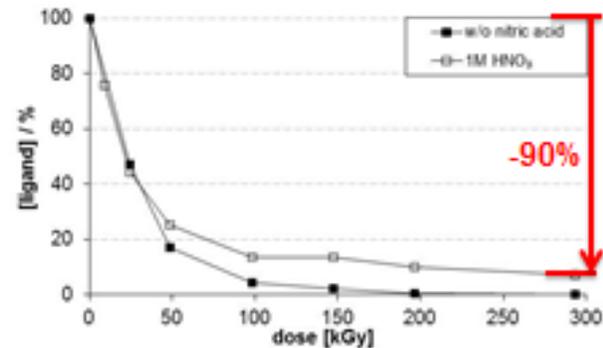
EURO-GANEX



Liquid-liquid extraction (CyMe₄BTPPhen) comparison to HPLC-DAD results



Org.: Irrad. 10 mmol/L CyMe₄BTPPhen in 1-octanol
Aq.: fresh 1.0 mol/L HNO₃ + ²⁴¹Am/¹⁵²Eu tracer



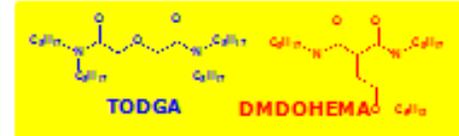
6

- Decreasing D-values with increasing dose
- HPLC-DAD shows destruction of molecule
- Nitric acid while irradiation stabilizes D-values
- 90% reduction of ligand concentration detected by HPLC-DAD
⇒ due to 1:2 complex, D-value should drop down ~ two orders of magnitude

New built species during radiolysis, able to extract An/Ln ⇒ mass spectroscopy

Loading capacity of degraded organic GANEX solvent

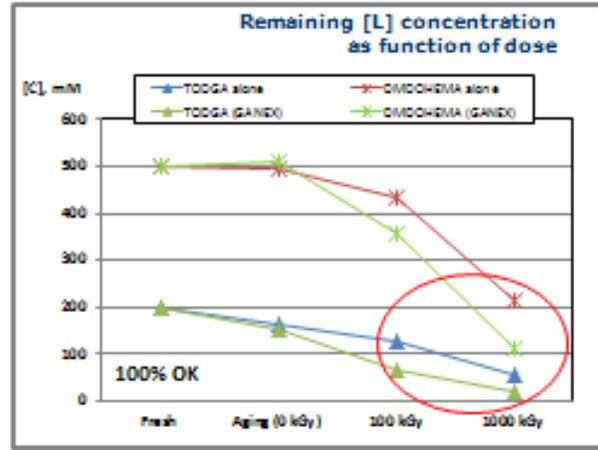
Euro-GANEX



- 0.2 mol/L TODGA
- 0.5 mol/L DMDOHEMA
- In kerosene (OK)

Loading capacity studies are needed!!!

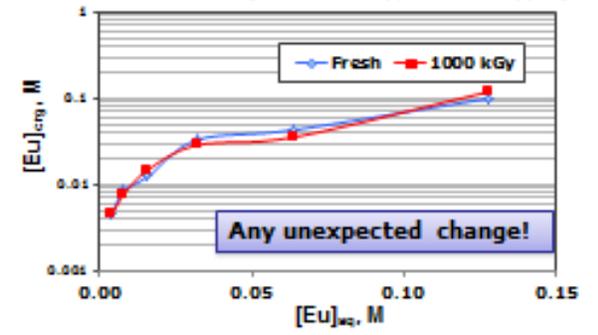
More than 50% degradation of both extracting agents.



20

CIEMAT - 2nd year SACESS Project Meeting, 20-21 April, Warsaw

Ln(III) loading capacity after irradiation (1000 kGy, 1.5 kGy/h).

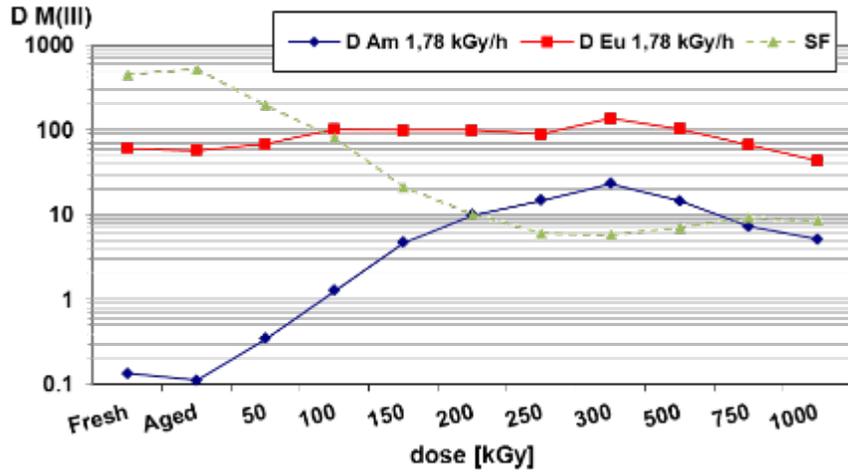


Organic Solution: 0.2 M TODGA + 0.5M DMDOHEMA in OK.
Aqueous solution: [HNO₃] = 4 mol/L and Eu(III) concentrations from 0.004 M to 0.128 M, spiked with ¹⁵²Eu (1000 Bq/mL).

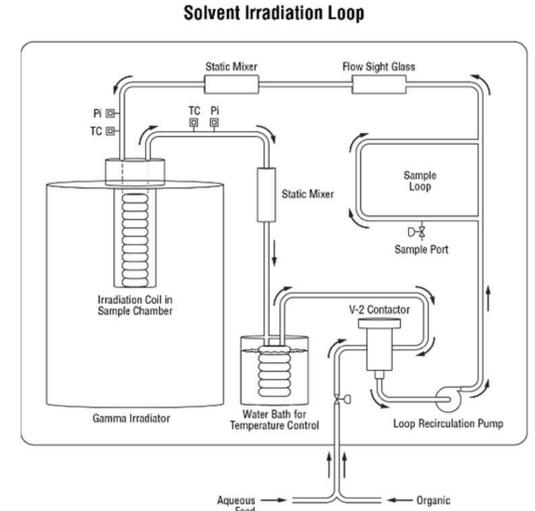
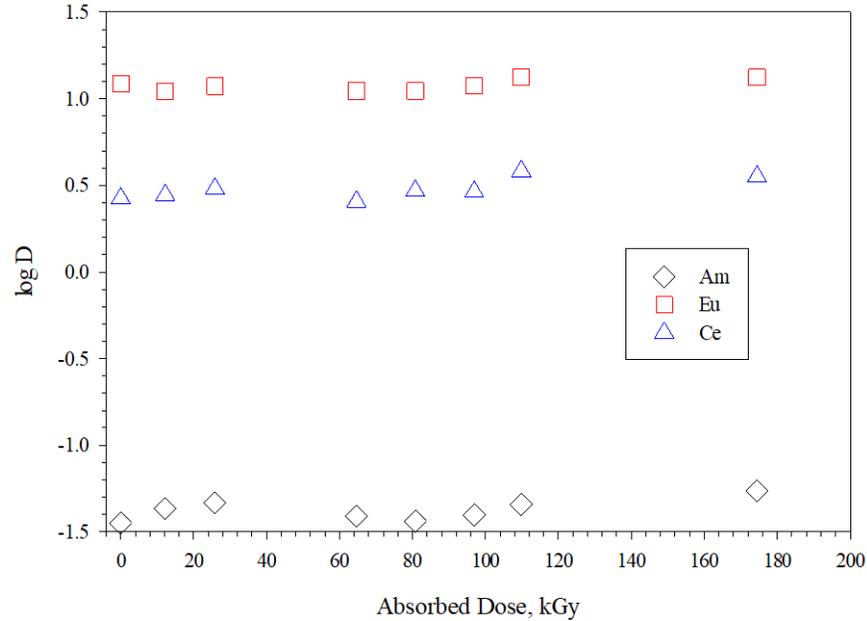
Any unexpected change!



Static tests



Dynamic tests



- Closed cap
- Aqueous phase irradiated
- Extraction



- Aerated
- Aqueous & organic phases irradiated in contact





- TODGA + TPAEN → stripping of Am selectively from Cm AND light Ln
- SF(Cm/Am) and (La/Am) ↗ with TPAEN conc.
- TPAEN concentration can be increased up to 2.5 mM
- Am stripping slow but ↗ with temperature
- Light Ln / Am separation with high concentrations of Ln

Solutions:

- 2) Re-evaluate TPAEN concentration
- 3) Temperature

- Experiments with macrocyclic ligands to improve complexation capacity of TPAEN
- Additional data acquisition (Jülich) to develop a thermodynamical model (CEA)
- Spiked test at Jülich in April and June 2016

A lot of issues to fix...
 Purity of TPAEN
 Solubility of TPAEN
 Process maybe too sensitive to some parameters (temperature...)
 To be improved! → GENIORS

TODGA 0.2M TPH
5%vol. octanol

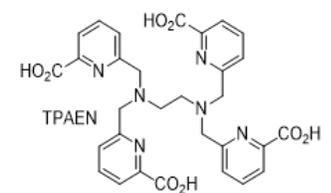
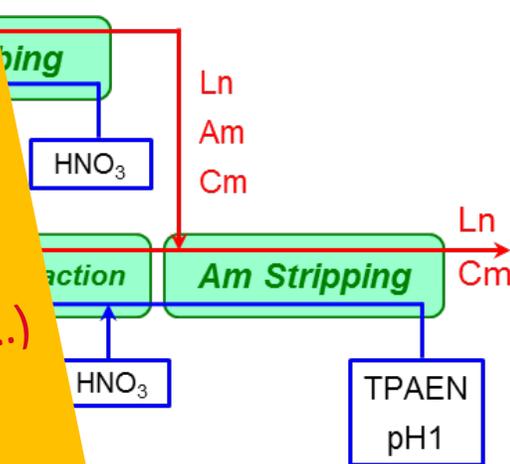
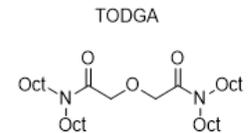




Table 7 Relative content of An and Ln in the deposits from runs 8-11

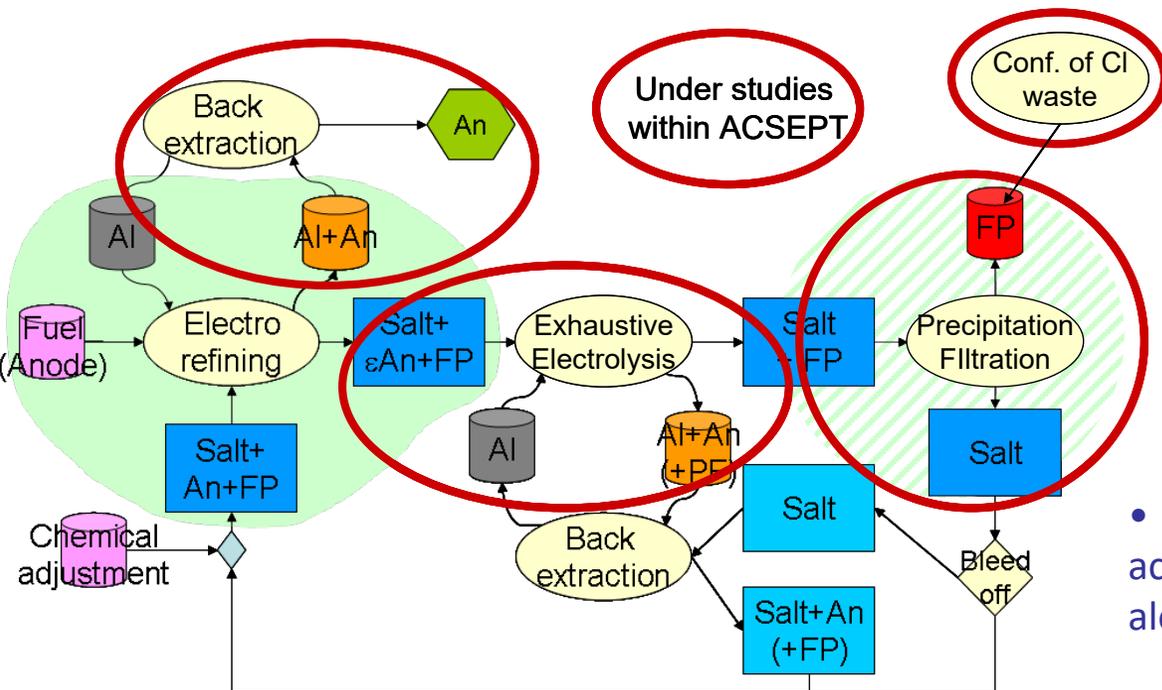
run	8	9	10	11
U	70.86	80.20	74.08	79.74
Np	1.05	0.75	0.87	0.71
Pu	28.02	18.99	24.97	19.48
Am	0.06	0.05	0.07	0.06
Cm	0.01	0.01	0.01	0.01
sum An	99.99	100.00	99.99	100.00
sum Ln	0.01	0.00	0.01	0.00

Table 6 Separation factors normalised to U for potentiostatic runs 8-11

run	8	9	10	11
potential	-1.26 V vs. Ag/AgCl			
U	1	1	1	1
Np	2.45	3.85	2.95	3.86
Pu	4.67	7.79	5.30	7.32
Am	17.3	25.3	14.8	20.5
Cm	60.4	83.2	47.3	61.4
La	1879	9294	5109	7432
Ce	3620	6612	4356	6525
Pr	1141	2800	1799	2917
Nd	1820	4008	2152	3610
Pm	1649	3394	1632	2409
Sm	2242	3008	1730	3718
Eu	2427	2903	1495	3623
Gd	2234	2932	1501	2564
Tb	2183	3071	1303	2124
Dy	2572	3191	1666	2104
Y	2145	2641	1666	2610

•Based on the IFR concept (USA), the process is centered on the selective electrorefining of solid aluminium cathode in molten chloride

- Quantitative recovery not achievable by electrorefining alone
- exhaustive electrolysis step and salt recycling under study
- Actinide back-extraction from Aluminium is deeply studied

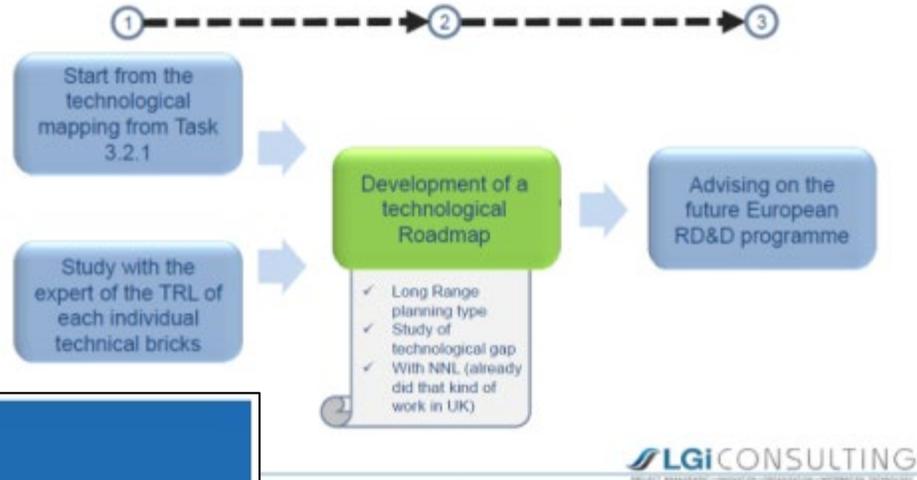


Under studies within ACSEPT

Conf. of Cl waste



Optical microscopy photographs of the transverse cuts of the Al cathodes after galvanostatic runs 1 - 5



ROADMAP
Actinide separation processes 2015

SACSESS
Safety of actinide separation processes

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 ₂ -Ph-BTP DMDOHEMA TOGDA in OK	Pu & mA product Spent solvent 2 nd cycle	DEHIBA	DEHIBA	Temperature range of operation	Pu & mA selfheating	Hydrogen generation	Long term effect of solvent on materiel
	U stripping	Ln stripping	Flowsheet equipment	Hydrazine	U product	Hydrazine	Hydrazine		FP selfheating		
	U scrubbing	An stripping 1		Fuel feed		Spent solvent 1 st cycle	CDTA		CDTA		
	U extraction	TRU scrubbing	Piping & valves	AHA	Ln product	DMDOHEMA TOGDA in OK	DMDOHEMA TOGDA in OK		U selfheating		
		TRU extract		CDTA	Nitric acid	FP raffinate	HNO ₃ /SO ₂ -Ph-BTP/AHA				
Type of studies or steps	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								

Joly, P.; Boo, E. SACSESS roadmap — actinide separation processes; 2015.

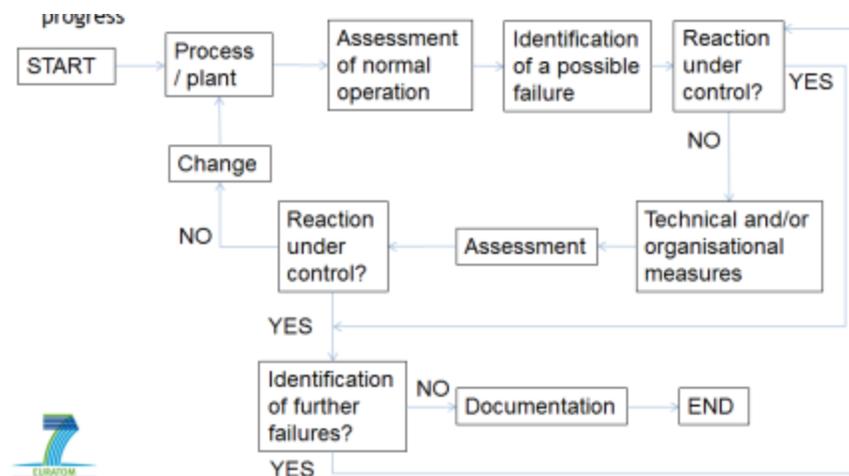
www.sacsess.eu

Global Safety

- Perform safety analyses on hydro and pyro processes to determine weaknesses in their safety and drive experimental programmes of the future to optimise against these issues
- Do this by developing tools that use tools and techniques from the partner nations
- Deploy them with the help of experts in aqueous and pyro reprocessing

The methodology is now established, based on HAZOP approach (April 2014)

Safety case studies were performed in a dedicated workshop (Sept. 2014 & Sept. 2015)





**TURNING
SPENT NUCLEAR FUEL
INTO A RESOURCE**

GENIORS

**FROM FUEL TO FUEL
MOX FOR GEN IV**



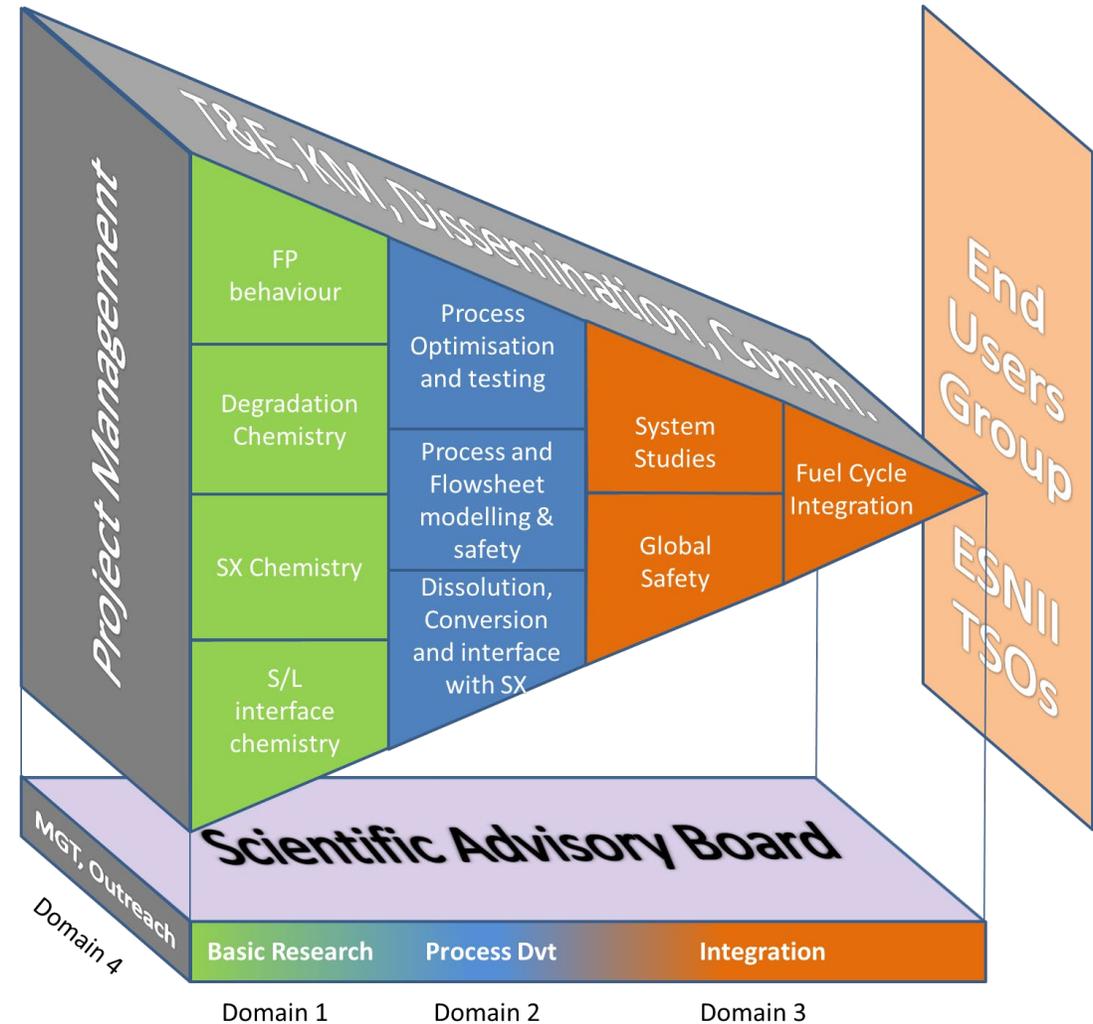
GEN IV Integrated Oxide fuels recycling strategies

6/2017 – 5/2021

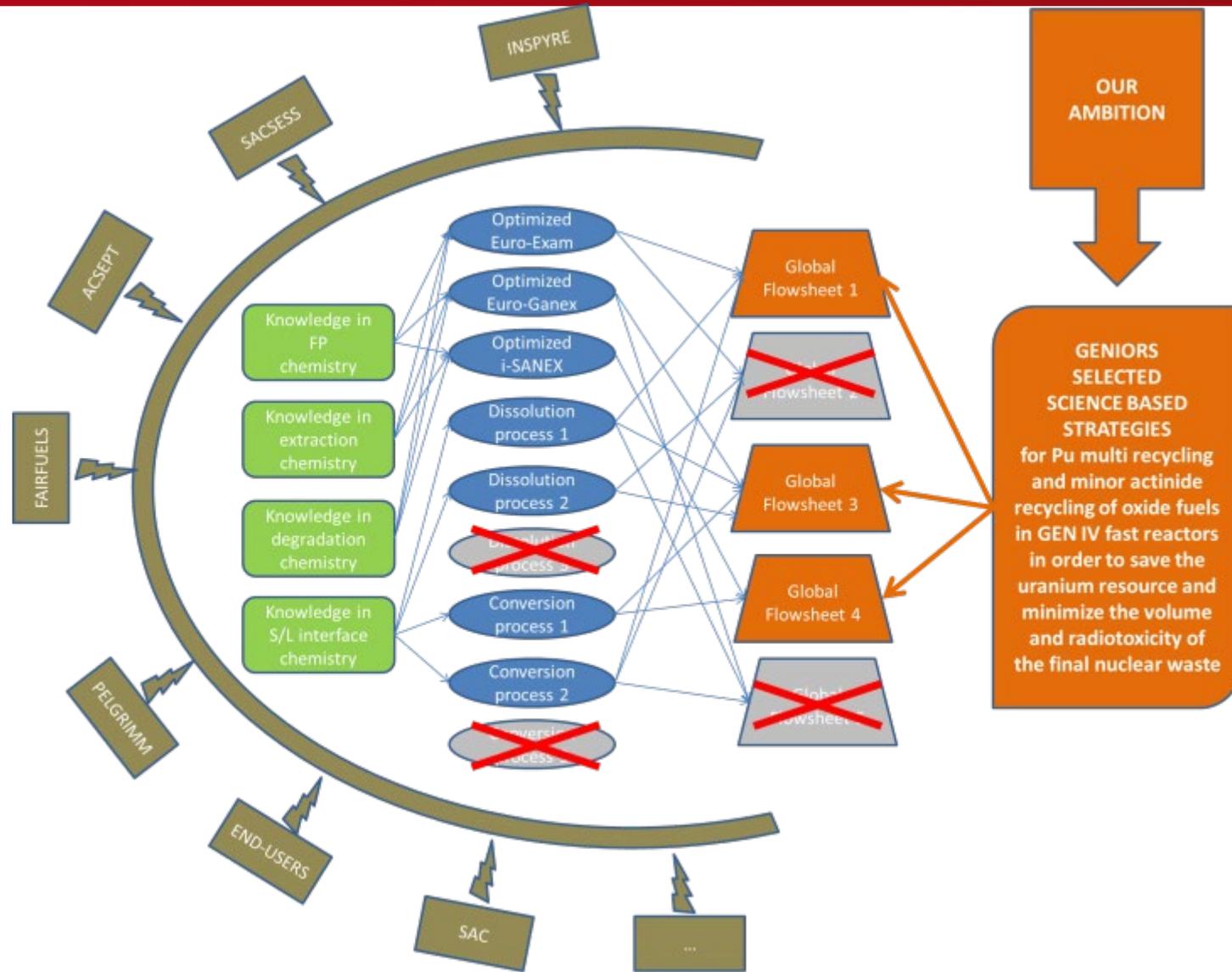
24 Partners, 11 countries

Budget 7,5M€, EU grant 5M€

CEA	JRC-ITU	UEDIN
CHALMERS	JUELICH	UNIMAN
CIEMAT	KIT	UNIPR
CNRS	LGI	ULEEDS
CTU	NNL	UREAD
ICHTJ	POLIMI	ULANC
IIC	SCK-CEN	EDF
IRSN	TWENTE	AREVA



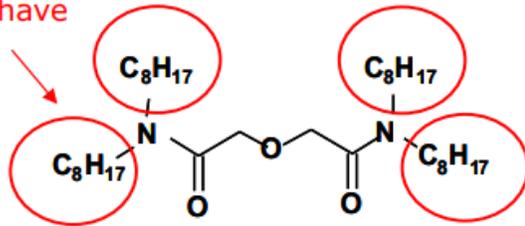
Cooperation agreement with DOE (I-NERI project),



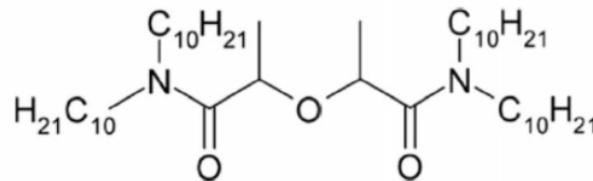


Increase the loading capacity

Side chains have an impact !!



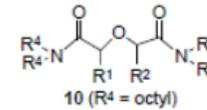
- Increased chain length strongly affects the limiting organic concentration.
- A point is reached where the organic phase seems to be stable – with Nd...
- Chain length (number of C) is limited by the increasing viscosity. Especially at high loadings



mTDDGA !

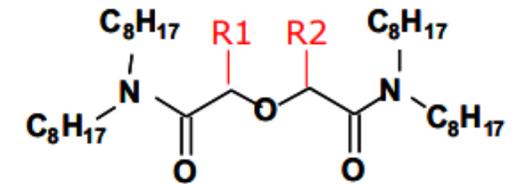
Decrease the complexation strength

Central groups makes an impact !!



10a = **TWE21**, R1 = Me, R2 = H

10b = **TWE14**, R1 = R2 = Me



- Groups inserted at central carbons exert steric hindrance and thereby affects complexation strength.
- D-values drop orders of magnitude inserting two methyl groups.





Parameter	TODGA-GANEX	mTDDGA-GANEX
Organic formulation	TODGA (0.2M) +DMDOHEMA (0.5M) mixture	Only mTDDGA (0.5M)
Diluents	kerosene	n-dodecane
Pu loading limit	~ 20 g/L	32 g/L
3rd phase formation	Yes, at high Pu and acid conc.	No, even at high Pu and acid conc.
Acidity	0.01-3.0 M	0.01-6.0 M
D value for Sr, Mo, Fe	~ 1	~0.1 (10 times lower)

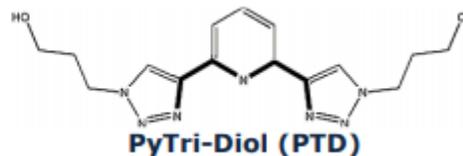
UNIVERSITY OF TWENTE.

mTDDGA could be a promising candidate for a simplified organic formulation for future EURO-GANEX process.





1. An inventory of the description of each loop as well as the current status of operation of each loop
2. An inventory of methods/methodologies of assessing the dose-rate for each loop
3. A definition of a common system to study
4. A common source of extractants, diluents and acids must be identified and used by all the partners involved.
5. A rough flowsheet will be provided by Andreas Geist (simplified flowsheet based on the Juelich process), where he will point-out where there is not sufficient data. This flowsheet is supposed to be adapted to each LOOP and reported on the outcome
6. Each Loop will report if the system can be run in the respective facilities
7. Each loop should report an estimate date for starting the test

**STRIPPING SOLVENT FORMULATION**0.08 M PTD in 0.4-0.5 M HNO₃for *i*-SANEX and EURO-GANEX processes

Process performances

- Experiments with macro-concentrations of ²⁴¹Am (1 mM), ¹⁵²Eu spike, in presence of 0.02M lanthanides for *i*-SANEX process;
- Experiments with macro-concentrations of ²⁴¹Am (1 mM) and ²³⁹Pu (10 mM), ¹⁵²Eu spike, in presence of 0.02M lanthanides for EURO-GANEX process;

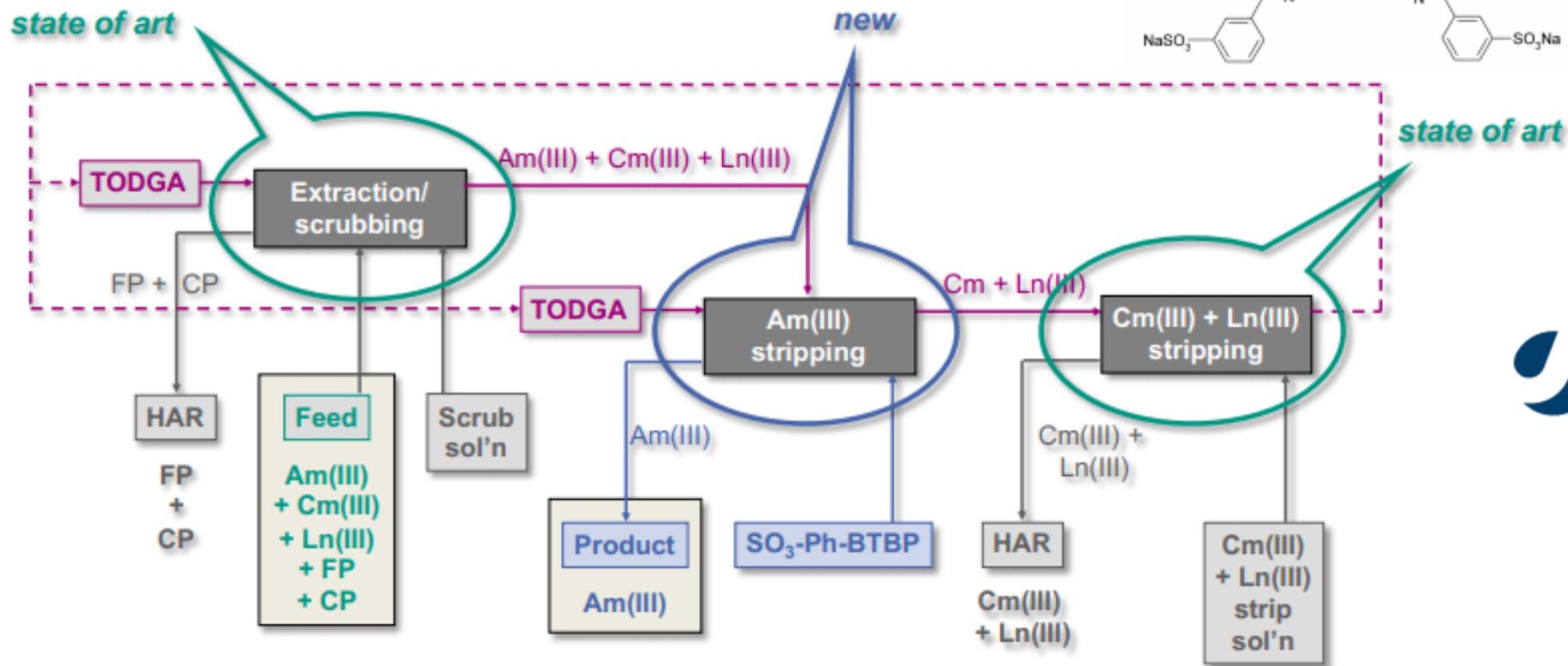
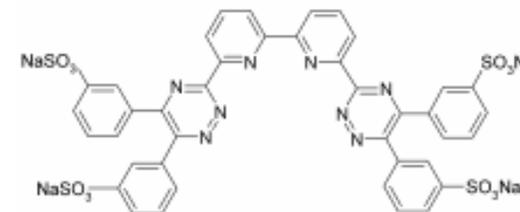
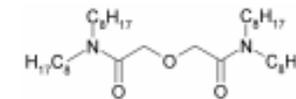
POLITECNICO
MILANO 1863UNIVERSITÀ
DI PARMA

Radiolytic stability studies

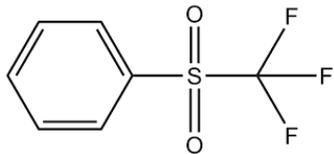
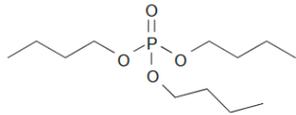
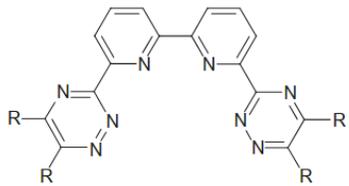
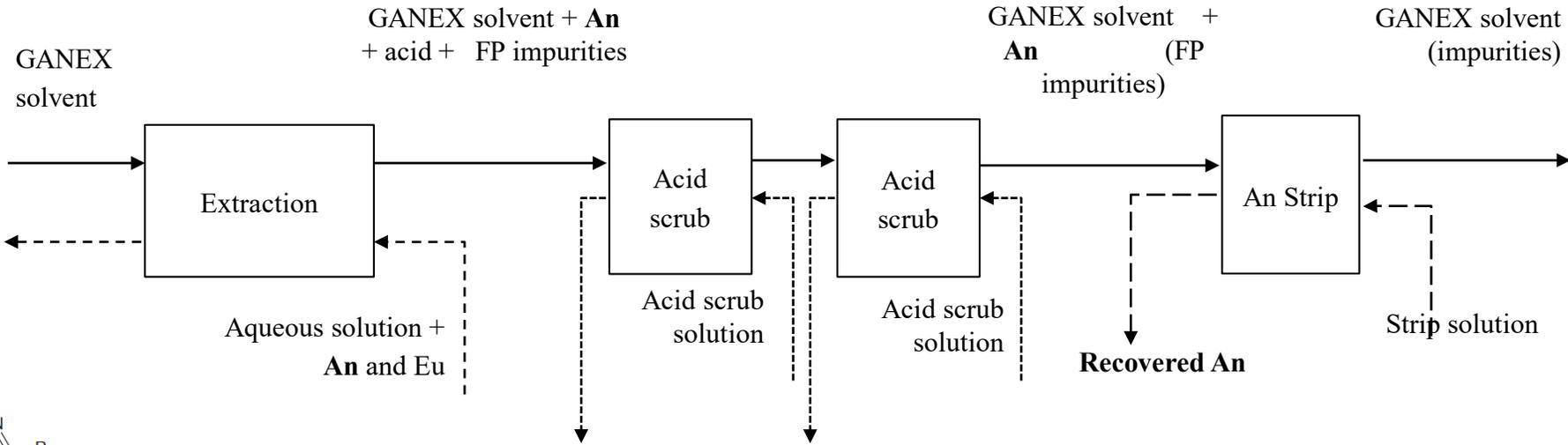
to go further in the radiochemical stability of PTD-based extracting system
to confirm the identity of the observed PTD degradation products

to study the generation of gaseous products from irradiated TODGA-PTD system

- Am(III) stripping section calculations — $SF_{Cm/Am} \approx 2.6$
 - Collaboration with JÜLICH
 - Work in progress



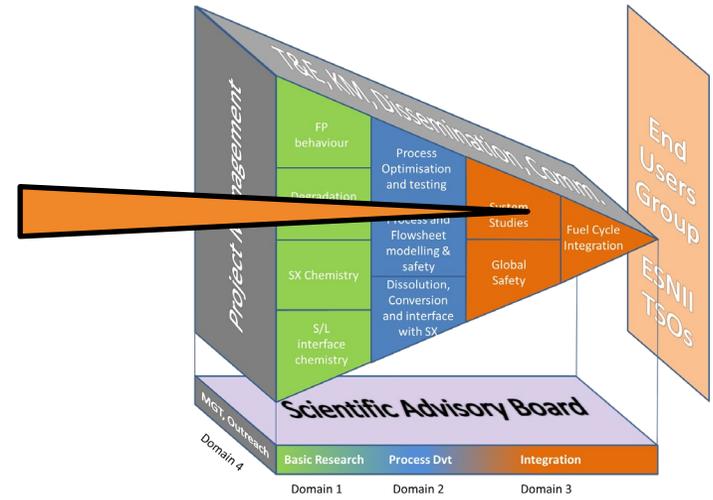
CHALMEX – a potential simpler GANEX option Batch Process Test (Real Nuclear Waste)



CHALMERS
UNIVERSITY OF TECHNOLOGY



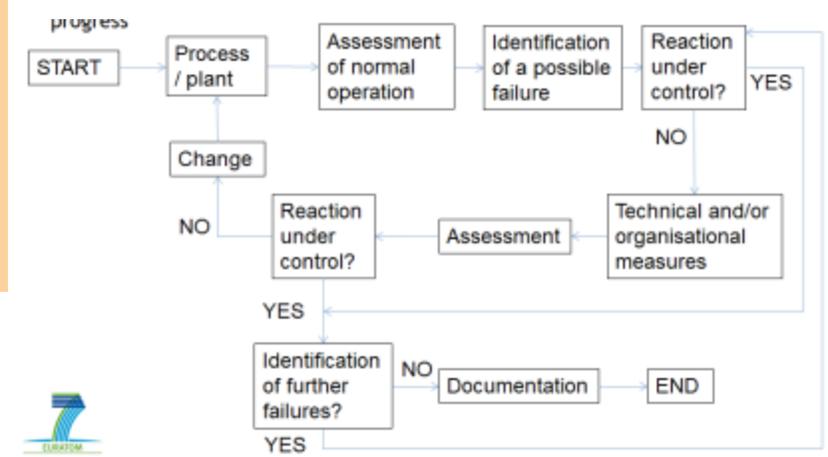
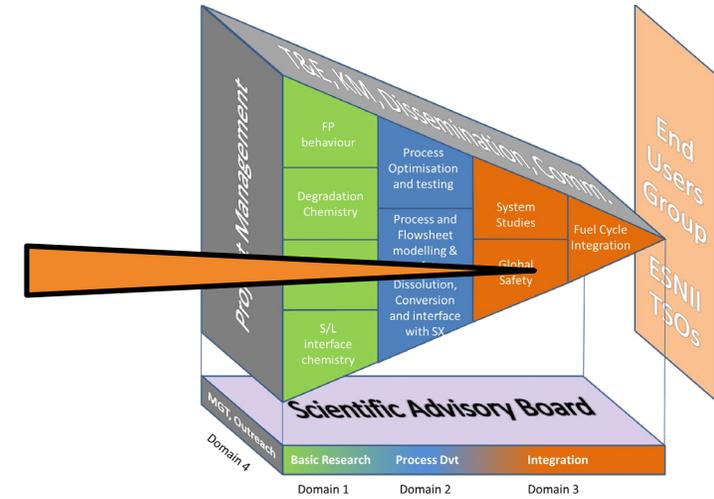
- Developing processes towards industrialisation studies
- Assessing and illustrating the holistic effects on the nuclear fuel cycle that occur from fundamental changes to the chemistry at the heart of its key processes.
- **Concept Design of a Euro-GANEX Plant**
- **Comparing SX processes for heterogeneous recycling**
- **Process Mapping Studies**
- **“Sim-plant” – engineering simulation of integrated plants**
- **Impact Studies**



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 An stripping 2	Filtr & buffer tank An stripping 1	Flow sheet major issue Piping & valves	SO ₂ /Pb-ETP DMSO/DMF TOGDMA in OR Hydracine DEHBA in OR Fuel feed AFA CDTA	Pu & mk product Spent solvent 2 nd cycle U product Spent solvent 1 st cycle U product PP raffinate	DEHBA Hydracine CDTA	DEHBA Hydracine CDTA	Temperature range of operation Cooling system	Pu & mk self-heating EP self-heating Temperature range of operation Thermolysis behaviour studies needed	Hydrogen generation Long term effect of solvent on material	Long term studies needed	
Type of studies or steps	GANEX 1 st cycle	GANEX 2 nd cycle	Technology needs	Safety and stability studies needed Radiolysis studies needed	Concentration range studies needed Flow range studies needed	Temperature range studies needed Flow range studies needed	Temperature range studies needed Thermolysis behaviour studies needed	Hydrogen generation studies needed Long term studies needed				
	EURO-GANEX in a lab			EURO-GANEX in a pilot facility								



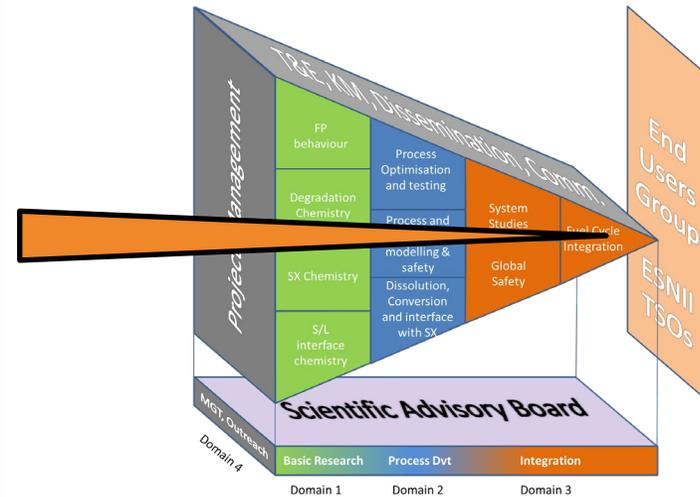
- Developing an emerging process towards industrialisation.
- Studying these requirements for both normal and mal-operations across the fuel cycle
 - Safety Review of a Euro-GANEX plant
 - Hazard Analysis and Criticality Studies
 - Quantification of Corrosions Risks in EURO-GANEX and EXAm Processes





Integrating the work done in GENIORS in a more global approach by creating synergies with other European and international initiatives and by Involving the stakeholders.

- **Clustering with other European projects and international initiatives** – including collaboration with the
- **Stakeholders/end-users Events-** Two dedicated events will be organised gathering the stakeholders potentially interested by the output of GENIORS will be organised at mid-term and at the end of the project.



Joint workshops with DOE

DGA extraction chemistry

Diluent issues

Exchanges with H2020 INSPYRE project on oxide fuel materials



**TURNING
SPENT NUCLEAR FUEL
INTO A RESOURCE**

**TRAINING
EDUCATION**

Schools

Uranium, Preston (UK) 7-8 April 2014

Plutonium, Chalmers (SE), 4-8 May 2015

Modelling, Leeds, June 2016?

SACSESS international workshop April 2015

SACSESS international workshop within
Atalante 2016, June 2016

Student Exchange

Short students presentations

Collaboration with DOE:

Scientific seminars

(Am, kinetics,

Radical Behaviour 2015)



- **A winterschool on industrial fuel fabrication**
- **A winterschool on fuel characterisation and isotopic separation (^{15}N)**
- **A summer school on plutonium chemistry together with SACSESS and CINCH**
- **Travel grants for conference participation: 18**
- **Travel and foreign labs training: 4**
- **More than 60 scientific papers**
- **Co-organising an ASGARD session at ATALANTE 2016**
- **Co-organisation of the first ASGARD international workshop at RadChem 2014**
- **Co-organising sessions at TopFuels-2015 together with PELGRIMM project**
- **Several projects in cooperation with the TALISMAN network**



The Radical Behaviour Workshop, May 2018, Würtzburg

Stakeholders event and topical day on P&T, October 2018, Antwerp

Think-tank on process safety issues, October 2018, Antwerp





THANK YOU

