DE LA RECHERCHE À L'INDUSTRIE

cea den

GENIORS
GEN IV Integrated Oxide fuels recycling strategies

STAKEHOLDERS EVENT & TOPICAL DAY
PARTITIONING MEETS TRANSMUTATION

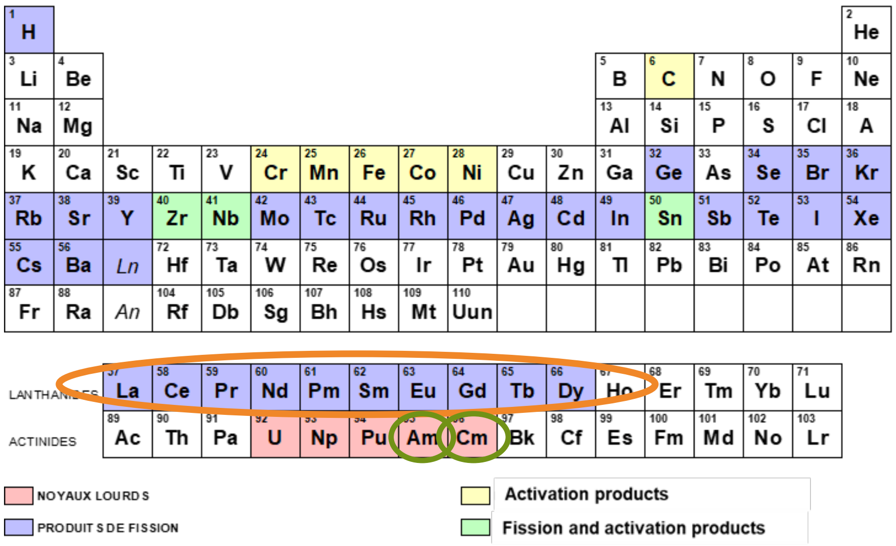
Partitioning for the 4th generation
A review of MA partitioning processes developed in Europe and in the world

M. Miguirditchian

Research Department on Mining & Fuel Recycling Processes

CEA Marcoule, Nuclear Energy Division

Tackle the issues of MA partitioning



Composition for 1 Phenix assembly after irradiation (Cooling time 1y at 85GWd/t)

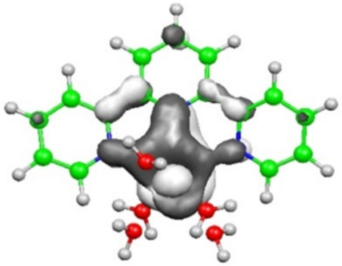
- U : 40 kg (76%)
- Pu : 8,1 kg (15,3%)
- MA (Np, Am, Cm) : 294 g (0,55%)
- FP : 4,35 kg (8,2%)

- SNF : Multi-element inventory
  - Recycle MA without :
    - Neutronic poisons (Ln : Sm, Eu…) ➔ impact on transmutation performances
    - $\beta-\gamma$ FPs ➔ impact of dose rate on fabrication processes
- Close physico-chemical properties between elements
  - MA/FP competition
  - An(III)/Ln(III) separation
- High acidity of the solution
  - M^{n+}/H^{+} competition
- Solvent radiolysis and hydrolysis
  - Chemical degradation of extracting molecules

How recycling minor actinides ?

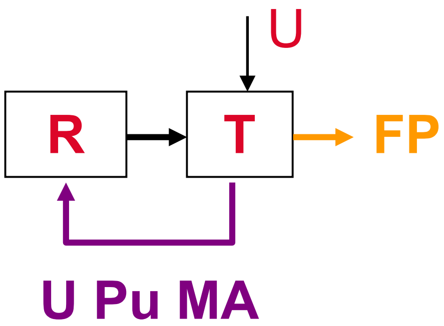
A few hundreds of new molecules

Scale : 1/100 à 1/1000



- SX as a reference option in consistency with the current industrial experience of La Hague
  - High separation yields
  - Low amount of secondary waste
  - Very significant feedback: > 25 000 t_{HM} LWR SNF reprocessed in La Hague plants
- Methodology applied for MA partitioning
  - Develop new SX processes based on new extracting or complexing molecules
  - A 3 steps methodology applied in wide cooperation framework (several EU projects … ACSEPT... SACSESS and now GENIORS!)
    - Explorative R&D and in-depths understanding of actual mechanisms
    - Batch lab experiments and process design
    - Demonstration experiments on actual SNF (5-10 kg)
      - In ATALANTE (CEA) or JRC (EU) or NNL

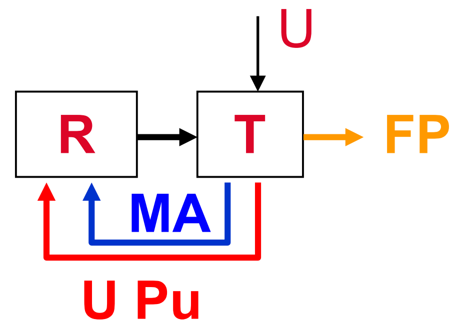
Different partitioning options for the future



Homogenous Recycling

➔ grouped recycling

GANEX processes

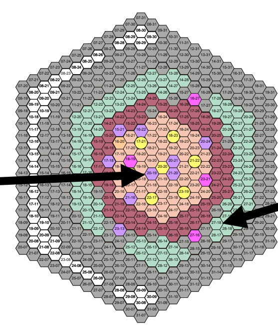


Heterogenous Recycling

➔ Enhanced partitioning

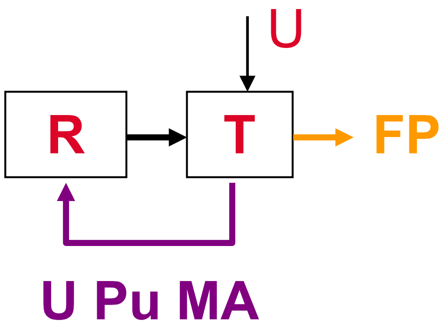
Advanced PUREX + DIAMEX-SANEX (or i-SANEX)

MA diluted ~2% in standard fuel in the whole core of GEN IV reactor



Moderated core target or blanket in periphery of the core with MA content up to 20% (MABB concept)

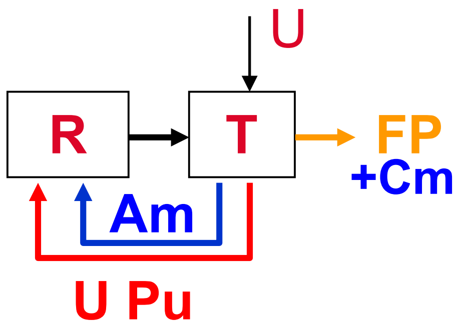
Different partitioning options for the future



Homogenous Recycling

→ grouped recycling

GANEX processes

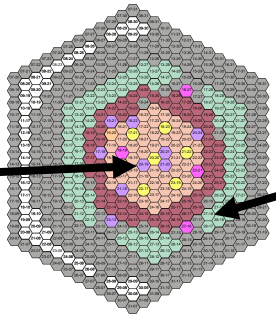


Heterogenous Recycling

→ Enhanced partitioning

Advanced PUREX
+
EXAm

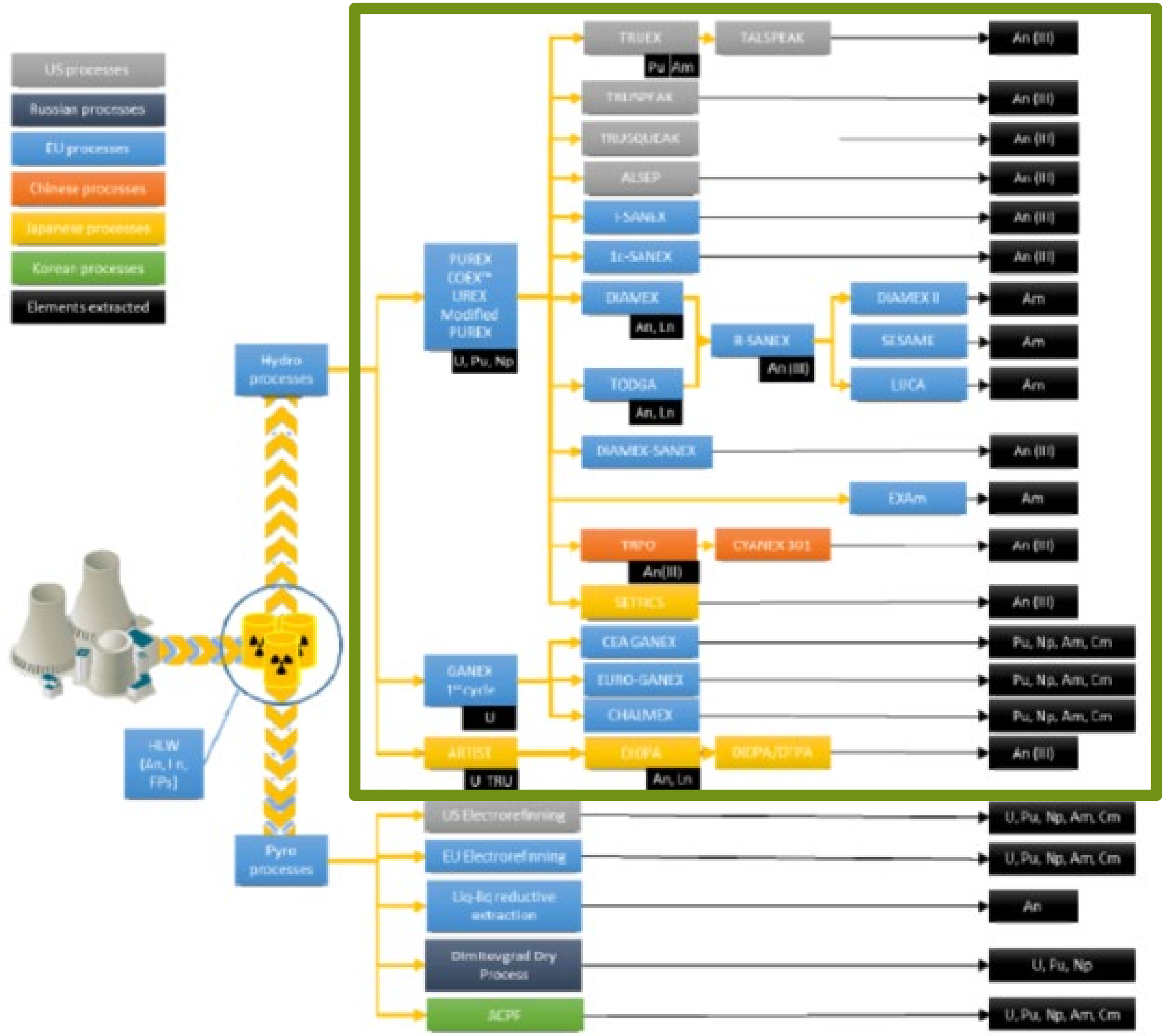
MA diluted ~2% in standard fuel in the whole core of GEN IV reactor



Moderated core target or blanket in periphery of the core with MA content up to 20% (MABB concept)

Review of MA partitioning processes

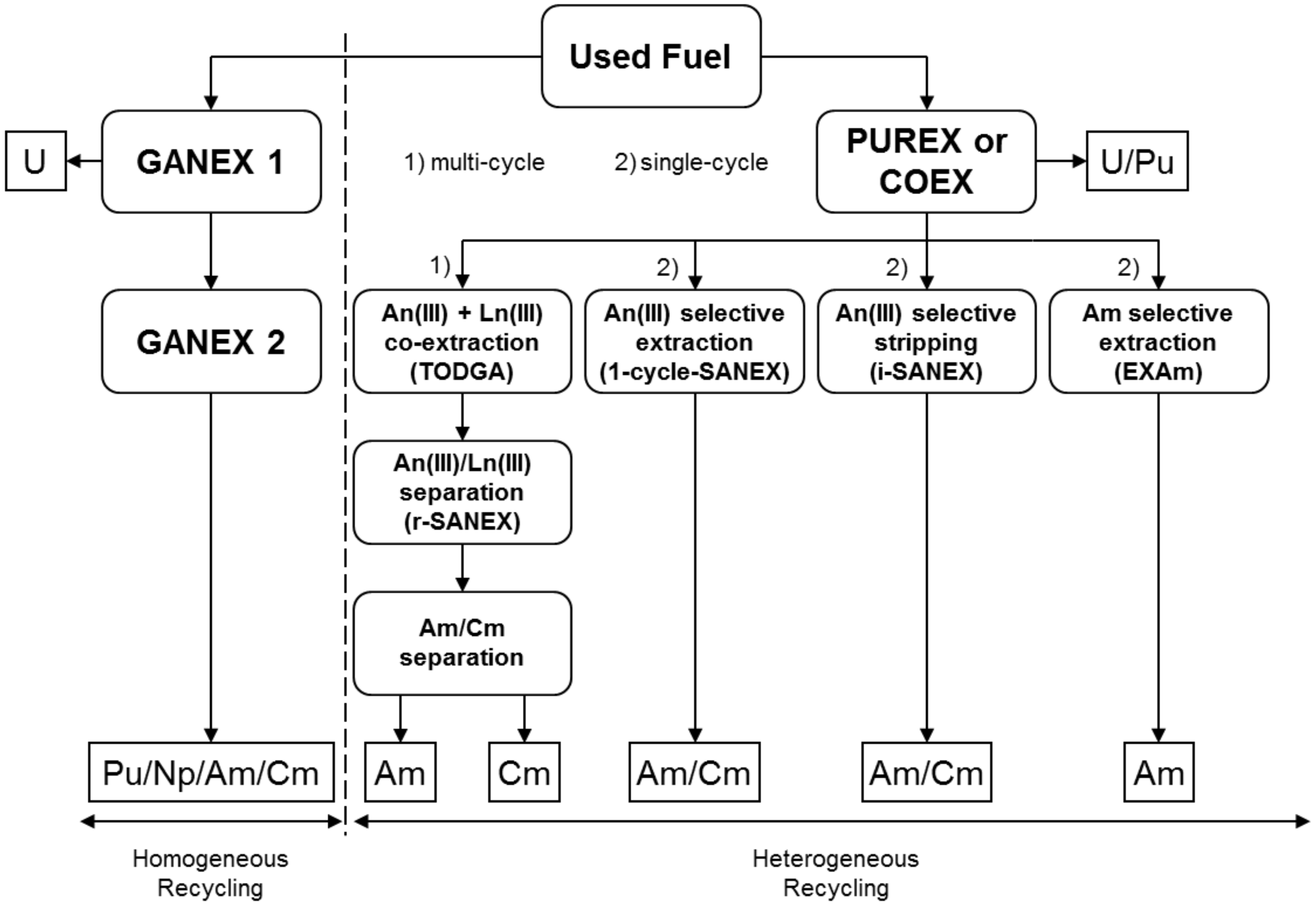
Numerous SX processes developed worldwide on MA partitioning!



Safety of actinide separation processes

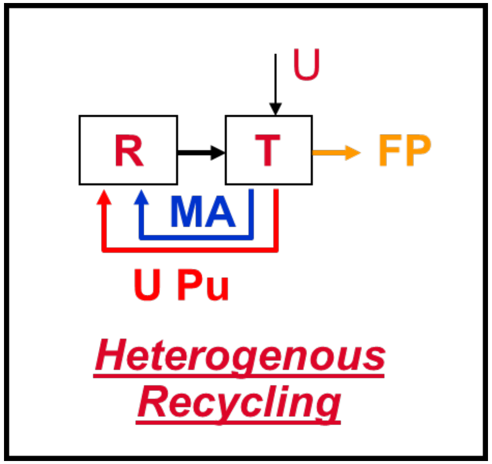
www.sacsess.eu

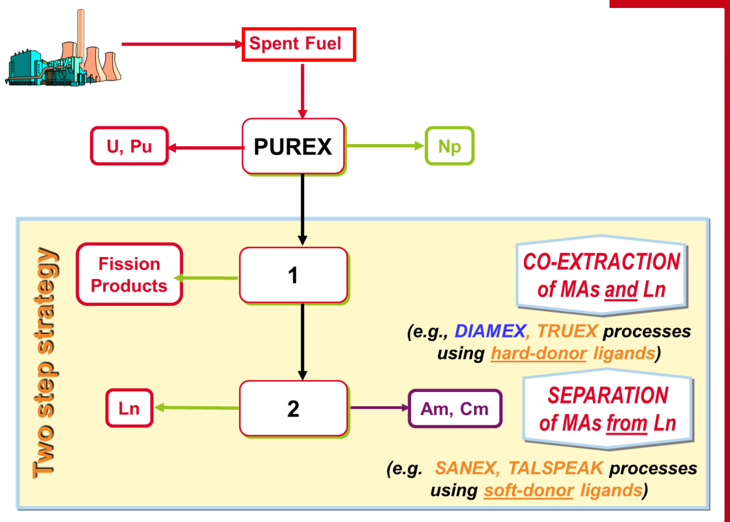
European hydrometallurgy partitioning strategy for actinide recycling

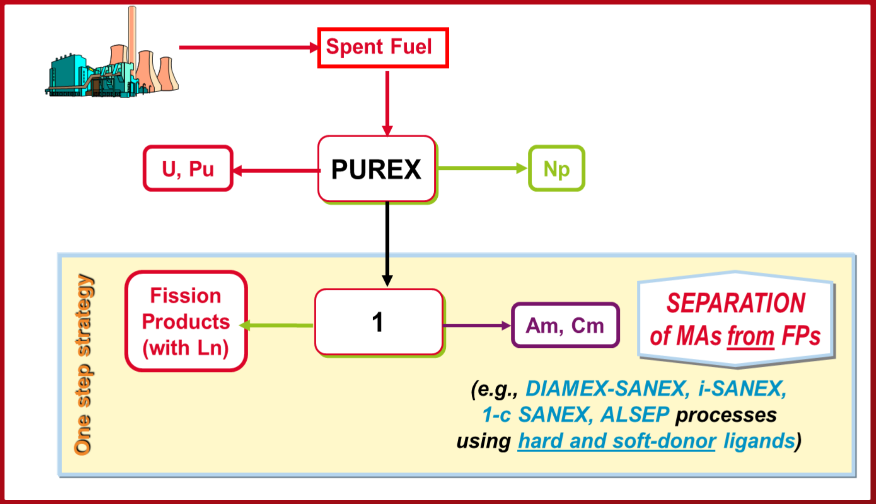


G. Modolo, A. Geist, M. Miguirditchian, « Minor actinide separations in the reprocessing of different fuels : recent advances in Europe »
Reprocessing and Recycling of Spent Nuclear Fuel - Published by Robin Taylor

MA separation

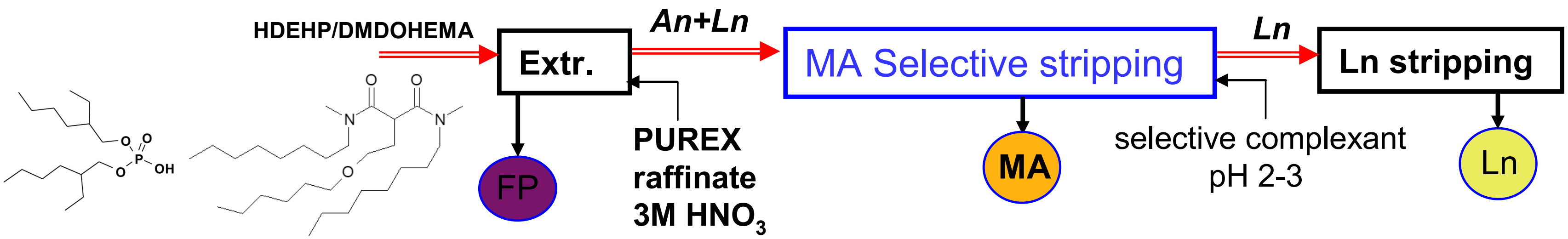




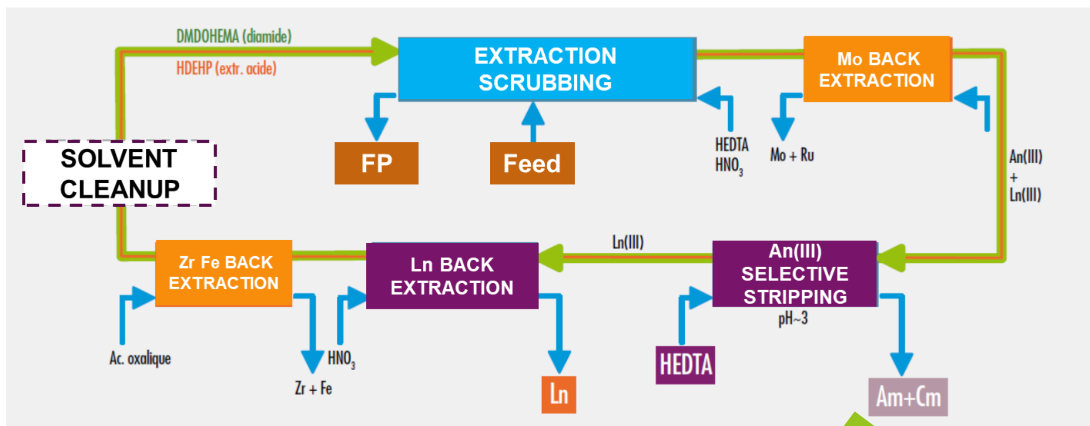


CEA DIAMEX-SANEX Process

➢ Process based on actinide separation by selective actinide stripping



- Use of mixture of HDEHP and DMDOHEMA for Am+Cm+Ln extraction
- Specific separation steps to take Mo Ru Zr Fe extraction into account
- Selective An stripping using HEDTA and citric acid at pH 3
- Demonstrated on genuine PUREX raffinates in 2000 and 2005 in Atalante facility



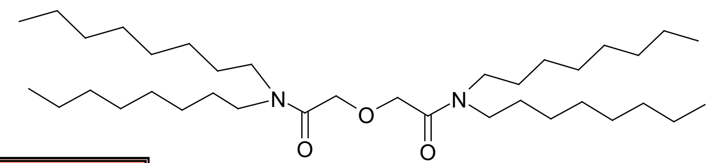
Am recovery > 99.9 %, Cm ~ 99.7 %
DF MA/Ln > 800

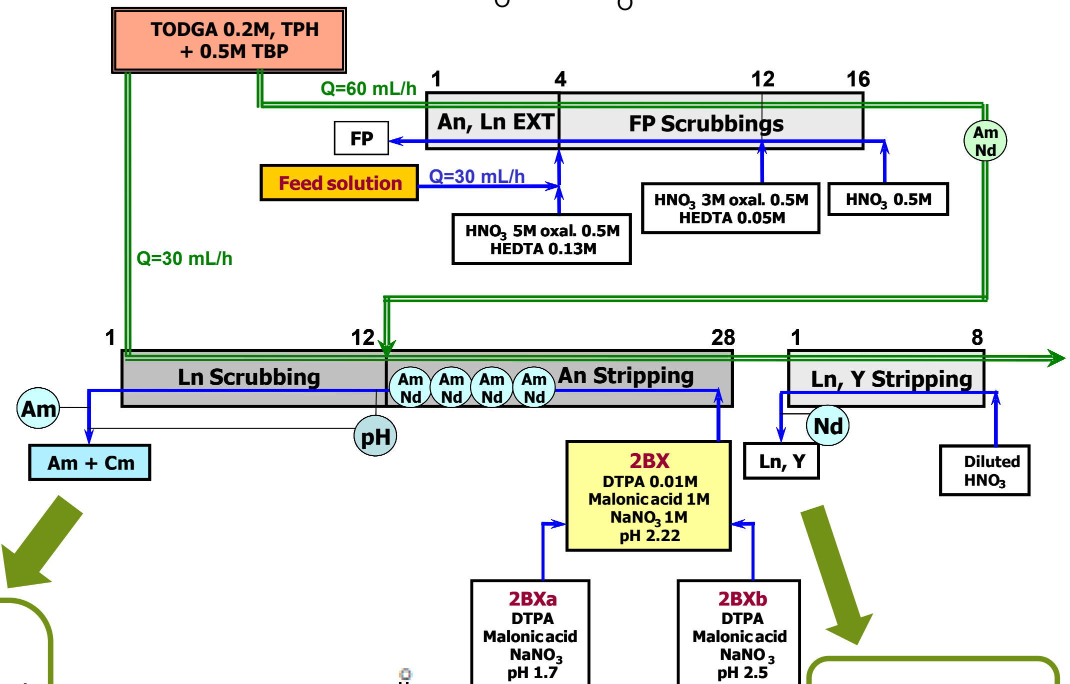
G. Modolo, A. Geist, M. Miguirditchian, Reprocessing and Recycling of Spent Nuclear Fuel - Published by Robin Taylor

i-SANEX-TODGA

➢ Process developed by CEA, based on the « japanese » TODGA

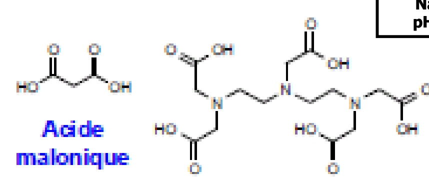
- Use of a mixture of TODGA and TBP for An+Ln co-extraction
- Selective An stripping using DTPA and malonic acid at pH 2 with a salting out agent ($NaNO_3$) to maintain Ln in organic phase
  - ☺ No need of a 2nd cationic exchanger (HDEHP)
  - ☹ Strong sensitivity to pH
- Hot test performed in 2009 on genuine PUREX raffinate in ATALANTE in the frame of the ACSEPT project





Product:
> 99.8 % Am(III)
> 99.9 % Cm(III)
< 2 %mass Ln

Am < 0.01%
Cm < 0.02%



Acide malonique

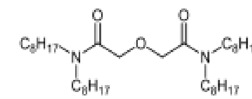
DTPA

G. Modolo, A. Geist, M. Miguirditchian, Reprocessing and Recycling of Spent Nuclear Fuel - Published by Robin Taylor

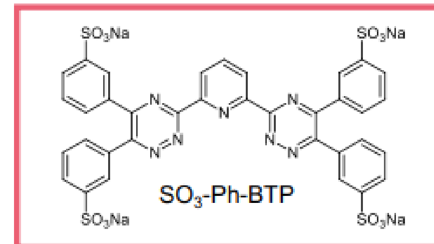
i-SANEX Process

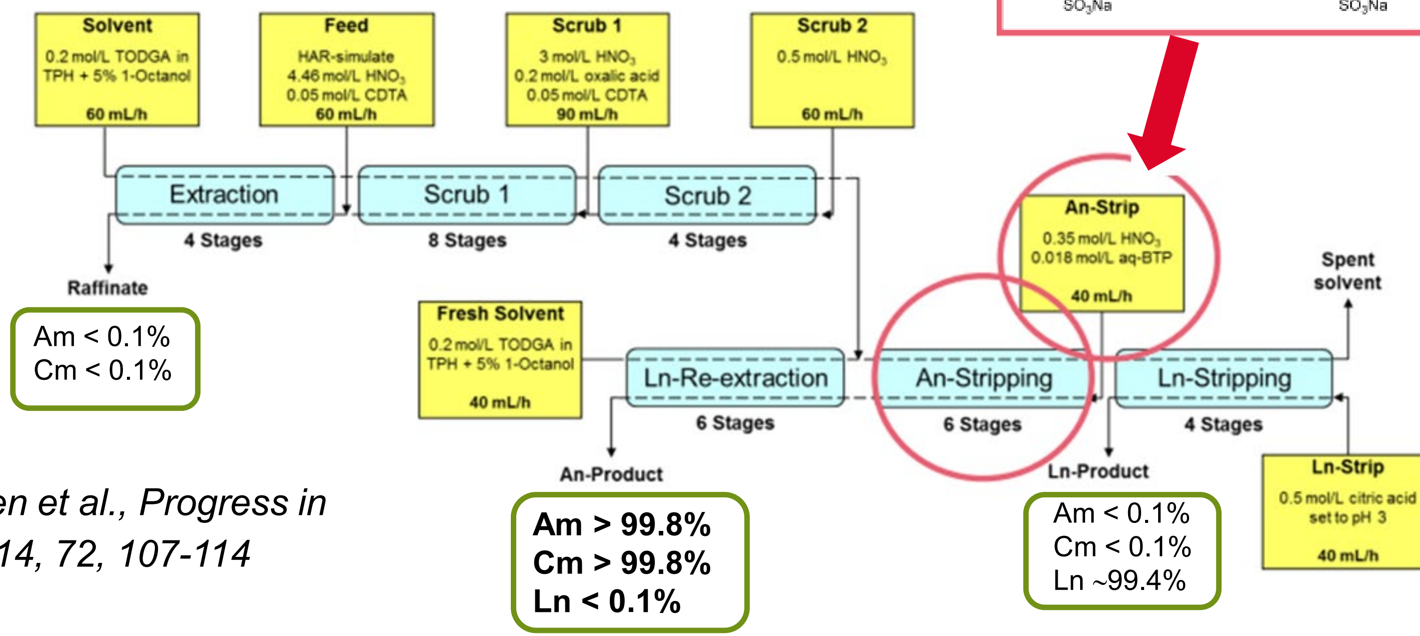
➢ Process developed by Jülich and KIT in the frame of ACSEPT

- Mixture of TODGA + 5% octanol in TPH for An+Ln co-extraction
- Selective An stripping using hydro SO_3-Ph-BTP at 0.35M HNO_3
  - ☺ Stripping at high acidity, no need to control the pH
  - ☹ Stability and potential downstream effect of SO_3-Ph-BTP, no CHON
- Spiked test performed in 2012 at Jülich on a surrogate PUREX raffinate



TODGA





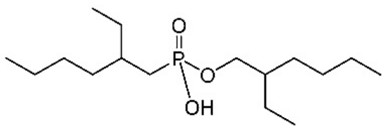
G. Modolo, A. Wilden et al., Progress in Nuclear Energy, 2014, 72, 107-114

ALSEP Process

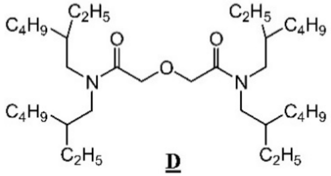
➢ **Process developed by US DOE based on a reverse-TALSPEAK process (similar to DIAMEX-SANEX process)**

- Mixture of T2EHDGA and HEH[EHP] for An+Ln co-extraction
- Selective An stripping using DTPA and citric acid at pH 2-3
  - $SF_{Ln/Am}$ ~30
- Spiked test performed in 2017 at ANL and planned at Jülich in centrifugal contactors on a surrogate PUREX raffinate in 2019
- Am/Cm separation studied at DOE by Am(III) oxidation and selective extraction of Am(VI)
  - Oxidation of Am(III) by sodium bismuthate
  - Selective extraction by DAAP or a monoamide

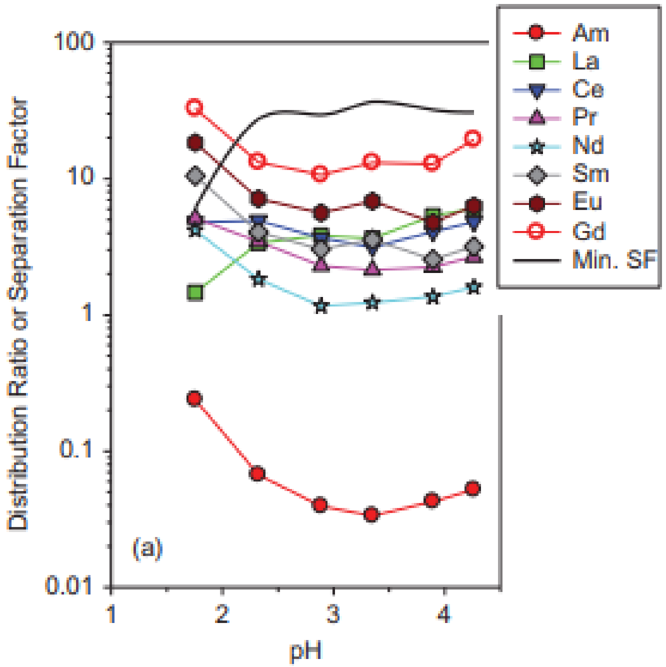
B. Mincher et al., SX-IX, 2014, 32, 153-166



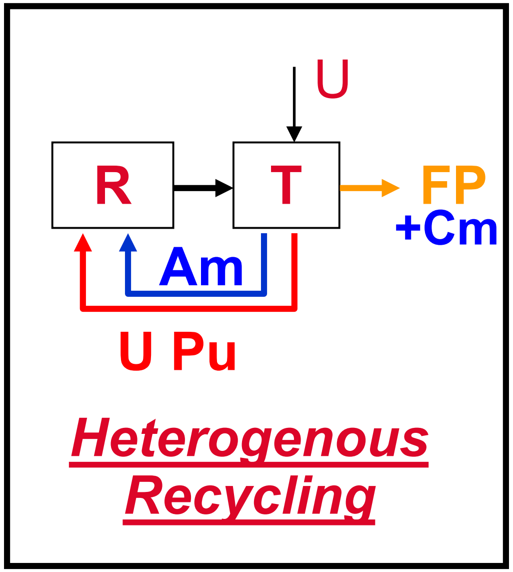
HEH[EHP]



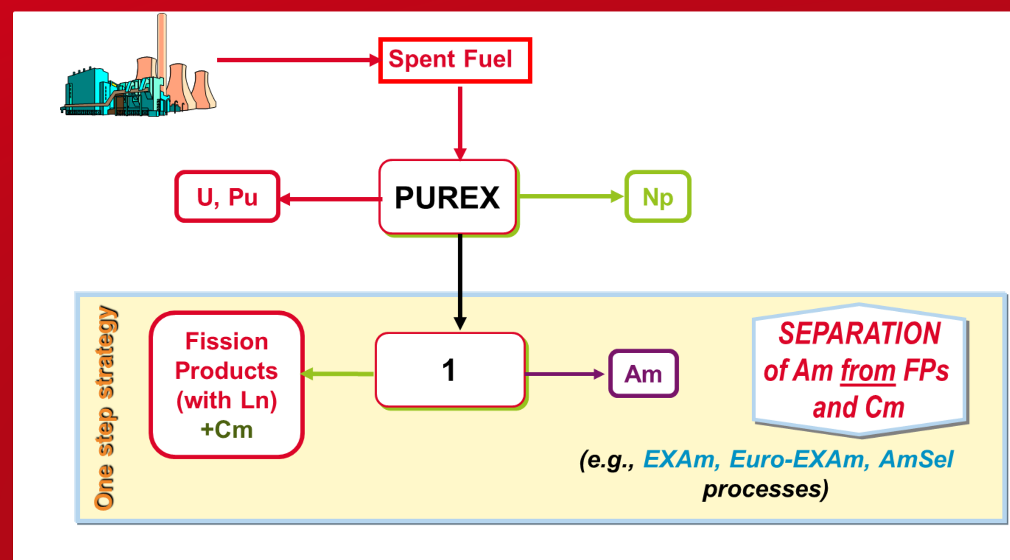
T2EHDGA



G. Lumetta et al., SX-IX, 2014, 32, 333-347
A. Guelis, I&EC, 2014, 53, 1624-1631



Am separation

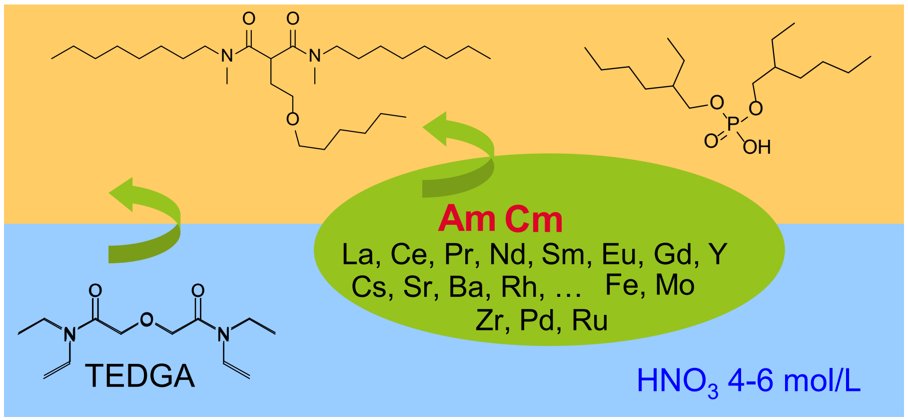


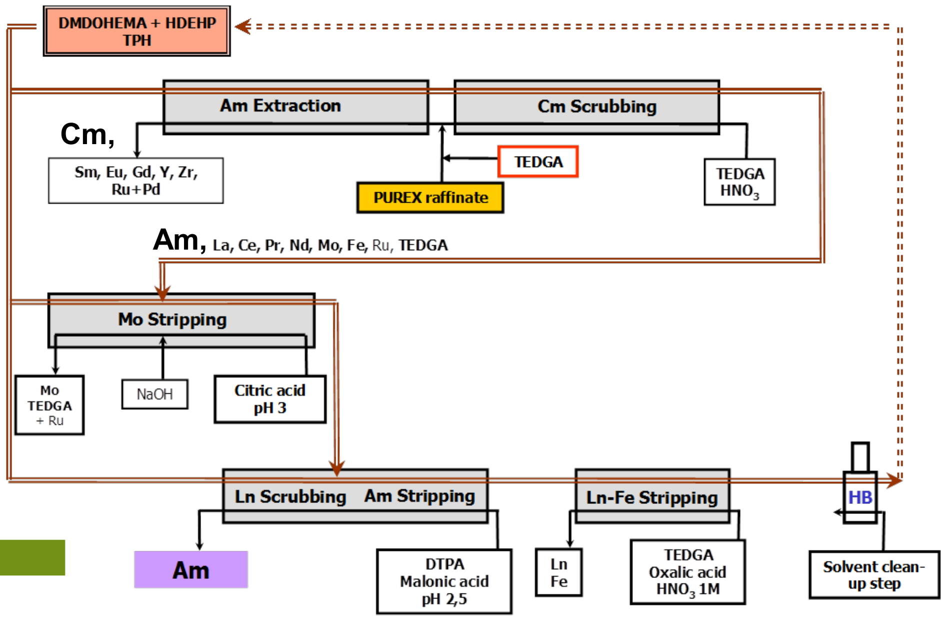
CEA EXAm: the sole-Am recycling

➢ Adaptation of DIAMEX-SANEX process for the sole Am recovery

- Selective Am(III) and light Ln extraction by HDEHP+DMDOHEMA solvent from 5M HNO_3
  - Addition of TEDGA to increase Am/Cm selectivity from 1.6 to 2.5
- Selective Am stripping by DTPA + malonic acid at pH 2.5
- Validated in 2010 after a hot test performed in mixer-settlers on a genuine PUREX raffinate in ATALANTE facility
- Adaptation of the EXAm process to treat a PUREX HAC (x3)
  - Hot test performed in 2015 allowed to recover 2.4 g of Am (DF Am/Cm ~ 50)

[DMDOHEMA]=0.6M in TPH + [HDEHP]=0.3M





M-J. Bollesteros et al. Procedia Chemistry, 2012

V. Vanel et al, Procedia Chemistry, 2016

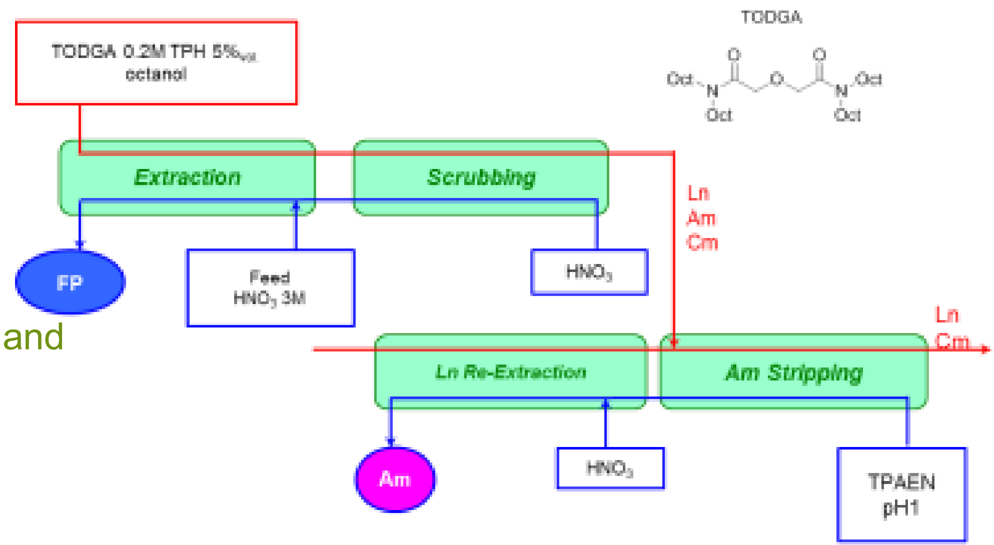
~ 98.5 % Am(III)
DF Am/Cm ~ 500
DF Am/Nd ~ 340

EURO-EXAm

Safety of actinide separation processes

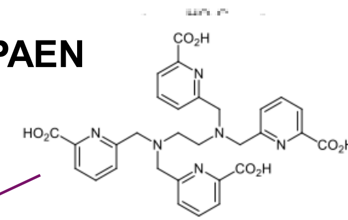
Adaptation of i-SANEX for Am selective extraction

- Mixture of TODGA + 5% octanol in TPH for An+Ln co-extraction
- Selective Am stripping using TPAEN at pH 1
  - ☺ Good Am/Cm selectivity (SF ~ 4)
  - No need of a 2nd cationic exchanger and no need of TEDGA nor pH buffer
  - ☹ Difficult Am/Light Ln separation
  - Low solubility of TPAEN aq. phase

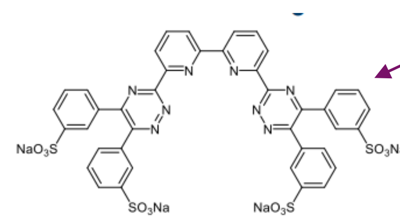


- Spiked test performed in 2015 in Jülich on a surrogate PUREX raffinate
  - Solubilities issues during the spiked test

TPAEN



- Alternative solution studied in GENIORS with SO_3-Ph-BTBP
  - ☺ Medium Am/Cm selectivity (SF ~ 2.5)
  - Good Am/Light Ln selectivity
  - High solubility
  - ☹ No CHON compound



SO_3-Ph-BTBP

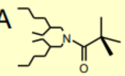
→ ***AmSel Process***

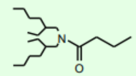
KIT Karlsruhe Institute of Technology
JÜLICH Forschungszentrum
GENIORS GEN IV Integrated Oxide fuels recycling strategies

SELECT Process

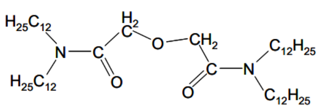
➤ **Multi-step approach to separate Am, developed at JAEA (Japan)**

- MA+RE and MA/RE separation steps tested on genuine raffinate
- Am/Cm separation tested on a spiked solution

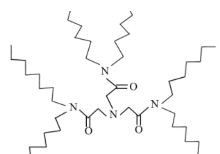
DEHDMPA


DEHBA


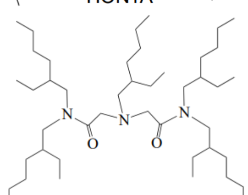
Am, Cm, Ln > 99,9%

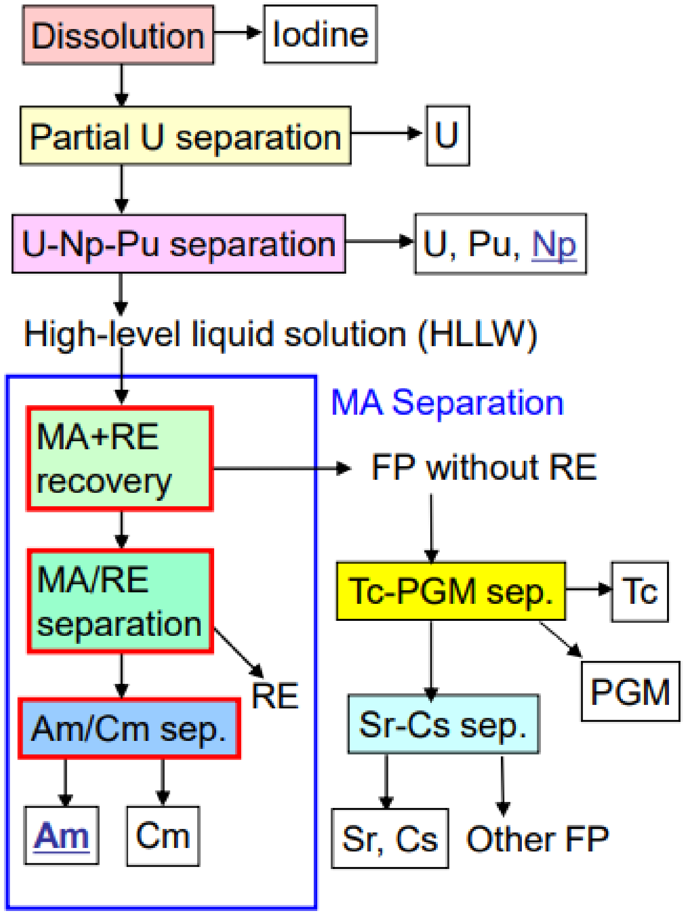

TDdDGA

$SF_{Am/Eu}$ ~ 6
Am ~ 94.5%, Cm ~ 78%
La ~ 0.1% Nd ~ 16%

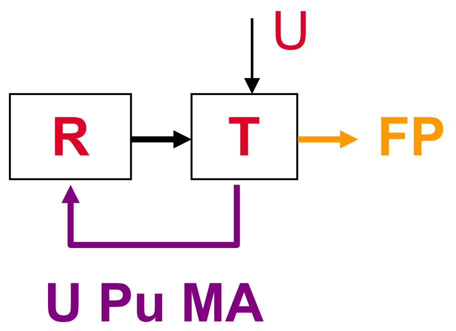

HONTA*

$SF_{Am/Cm}$ ~ 5.5
$SF_{Am/Cm}$ ~ 41 with TEDGA
Am > 99% with Cm ~ 9.6%


ADAAM(EH)**



H. Suzuki, T. Matsumura, et al., J. Nucl. Sci. Technol., in press.



Homogenous Recycling

MA group separation

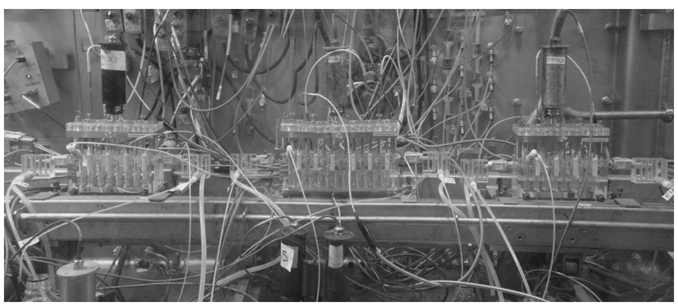
2-step GANEX concept :

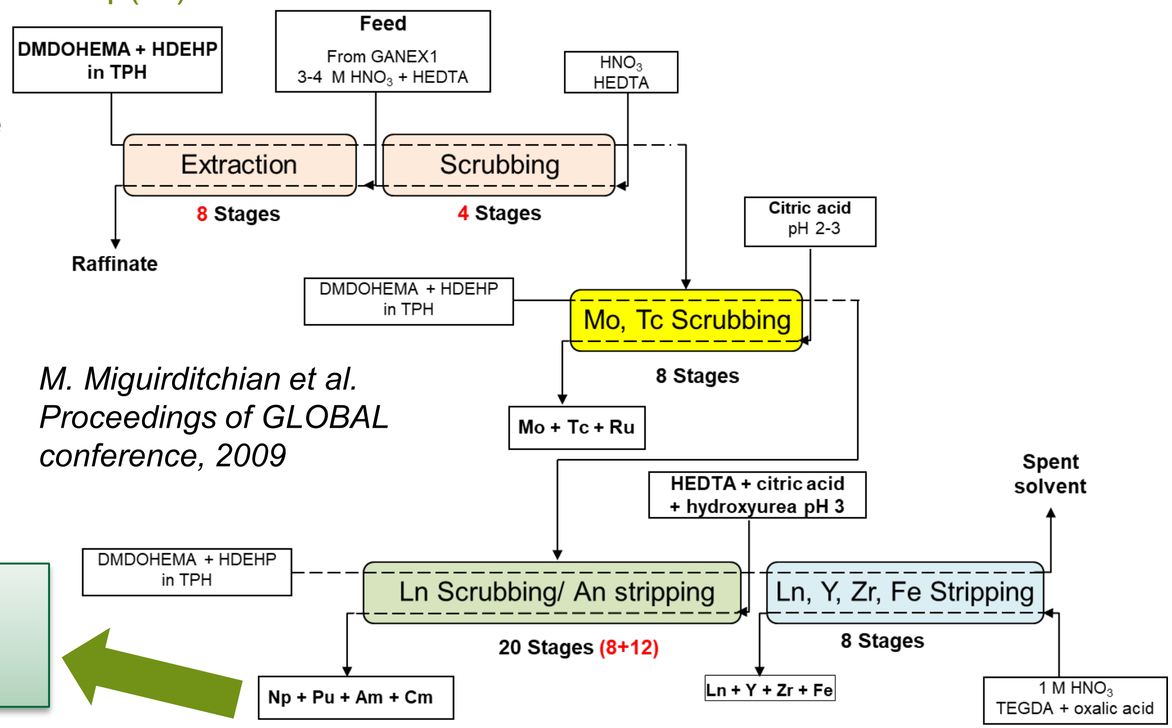
- Selective U separation by the monoamide DEHiBA (GANEX 1)
- Transuranium group separation

CEA GANEX 2

➢ Adaptation of DIAMEX-SANEX process to the group actinide separation

- Use of a mixture of HDEHP and DMDOHEMA to extraction TRU and Ln
  - Increase of [HDEHP] to increase loading capacity (due to high Pu content)
  - Increase of [HNO_3] to extract Np(VI) along with Pu, Am, Cm
- Selective An stripping by HEDTA+ citric at pH 3
  - Addition of hydroxyurea to reduce Np(VI)
- Hot test performed in 2008 on a genuine PUREX raffinate in 48 mixer-settlers





M. Miguirditchian et al. Proceedings of GLOBAL conference, 2009

99.8% < Actinide recovery < 99.9%
DF An/FP ~ 20-40

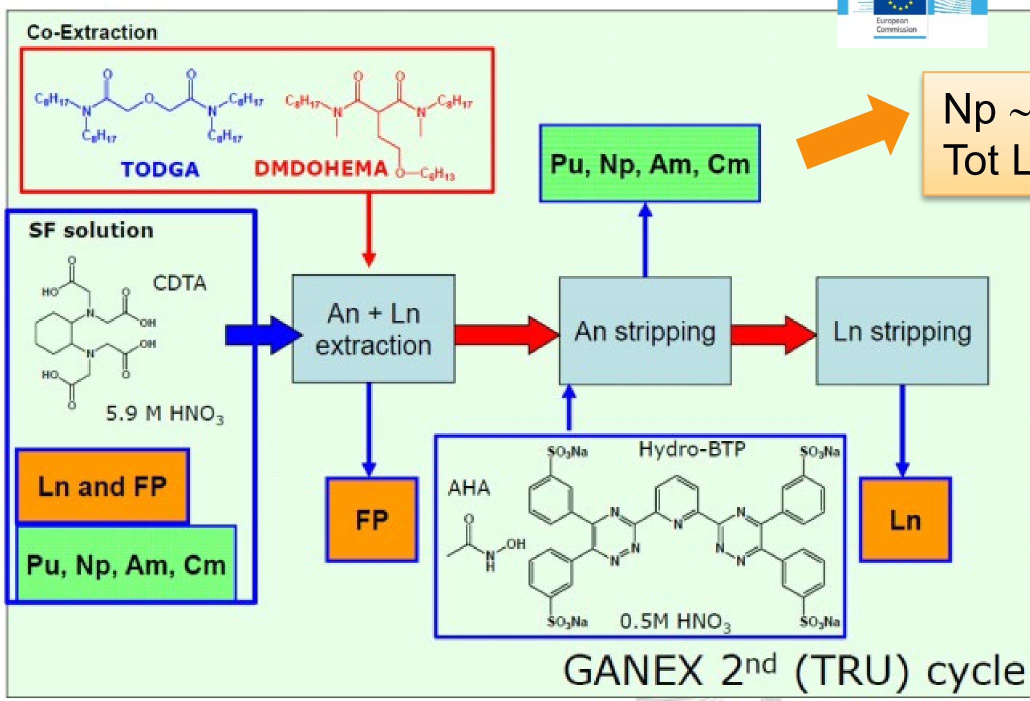
EURO GANEX

➢ Development of group separation process based on TODGA solvent

- Use of a mixture of TODGA and DMDOHEMA to avoid Pu precipitates
  - Possible to extract high concentration of Pu along with Np, Am, Cm and Ln
- Actinide/Lanthanide separation by selective An stripping with AHA and SO_3-Ph-BTP
- Spiked tests at NNL and a hot test performed on a genuine GANEX 1 raffinate in centrifugal contactors in 2012 at JRC

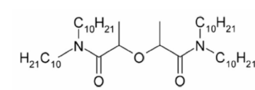
NATIONAL NUCLEAR LABORATORY

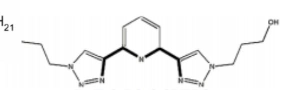
M. Carott et al. Hydrometallurgy, 2017
R. Taylor et al, Procedia Chemistry, 2016



Np ~ 99.91%, Pu ~ 99.85%, Am ~ 99.9%
Tot Ln ~ 0.06%

- Alternative solution studied in GENIORS
  - Substitution of TODGA+DMDOHEMA by MeTDDGA and SO_3-Ph-BTP by PyTriDiol





PyTri-Diol (PTD)

  - CHALMEX process
    - $CyMe_4$BTBP + TBP in FS-13

Conclusion

- Efficient partitioning processes of MA have been developed and qualified
  - DIAMEX-SANEX, 1c-SANEX, i-SANEX, ALSEP, EXAm,… for heterogenous mode
  - GANEX processes for homogeneous mode
- Priority is now put on Pu multi-recycling and we need a strong international collaboration to keep developing MA partitioning processes
  - Improvement of Euro-EXAm
  - Improvement of i-SANEX and EURO-GANEX with promising mTDDGA and PyTriDiol molecules
  - Study the impact of these new partitioning processes on the conversion step
    - Impact of PTD, AHA, SO_3-Ph-BTBP on actinide conversion
- Study the impact of a lower FP decontamination on the MA transmutation performances to develop more compact and cost-effective processes
  - Find a compromise by better linking P&T studies

GENIORS
GEN IV Integrated Oxide fuels recycling strategies

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A. Geist (KIT)
R. Taylor (NNL)
R. Malmbeck (JRC)
T. Todd (INL)
G. Lumetta (PNNL)
T. Matsumara (JAEA)

Thank you for your attention

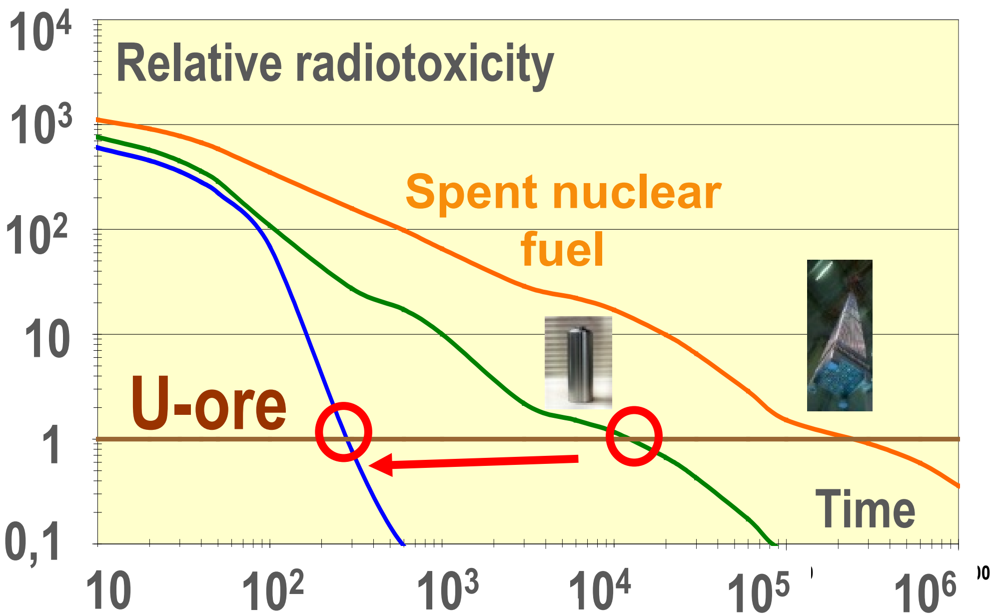
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | 30207 Bagnols-sur Cèze Cedex

Etablissement public à caractère industriel et commercial | R.C.S Paris B 775 685 019

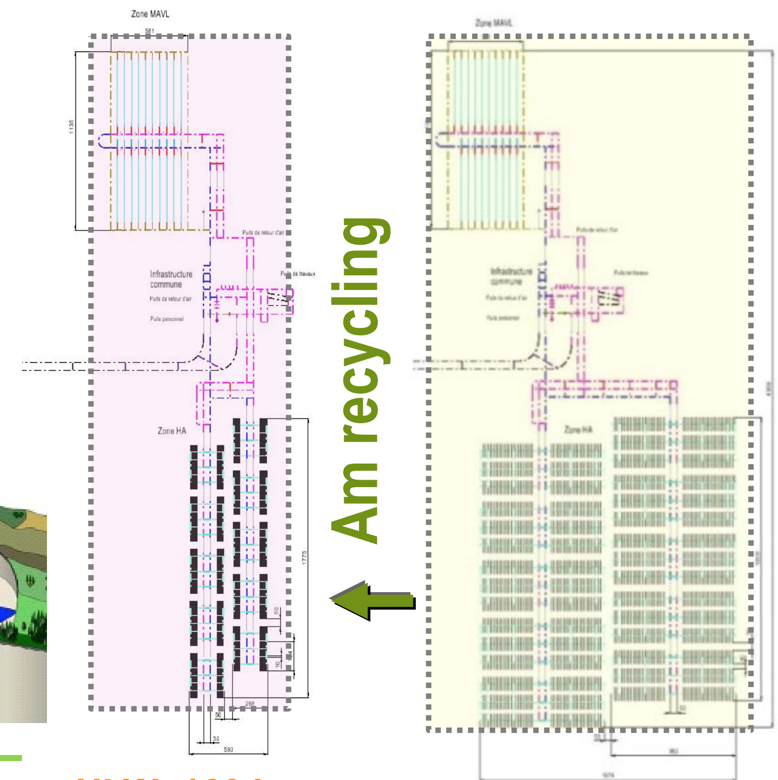
Nuclear Energy Division
Research Department on Mining and
Fuel Recycling Processes

Recycling the minor actinides, a potential contribution for decreasing the waste burden

- Recycling MA ⬄ decrease waste lifetime and toxicity

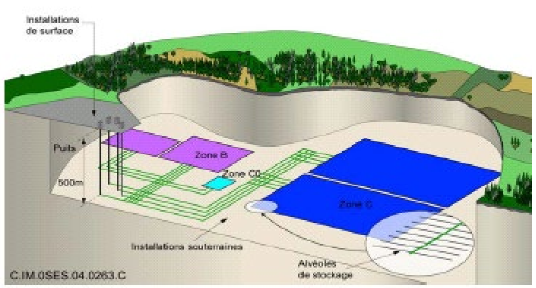


- Recycling MA ⬄ preserve the "*repository resource*"
  - ↘ of the heat load ⬄ ↗ density of the repository
    - Interest in the sole-Am recycling
  - Strong ↗ of repository "lifespan"



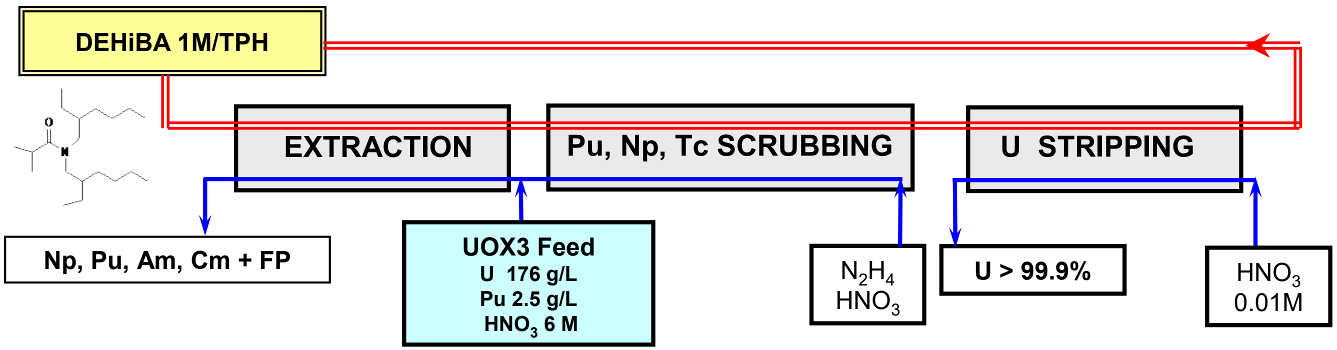
HLW: 160 ha

HLW: 1200 ha

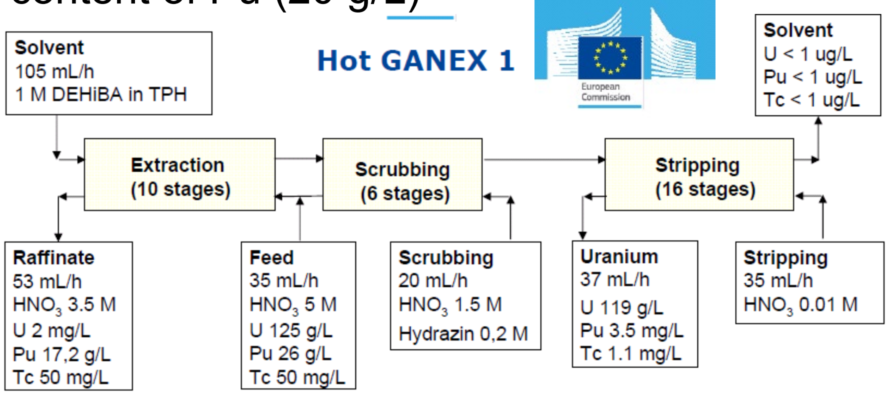


GANEX 1 HOT TESTS

- HA test first performed at CEA (ATALANTE, CBP) in 2008 on genuine spent fuel in 28 mixer-settlers
  - Uranium recovery >99.99% with high DF (Np, Pu, Tc, Ru, Cs)



- HA test performed at ITU in 2012 within ACSEPT contract in 16 centrifugal contactors with high content of Pu (20 g/L)



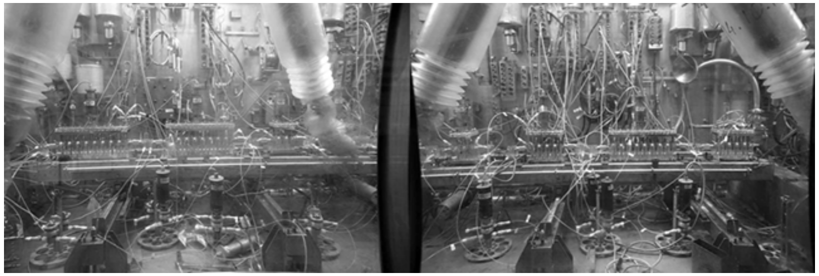
mg/L	Feed	**Raffinate**	Loaded organic	U fraction	Organic out
U	101300	**10**	36500	48000	21
Pu	20200	**18300**	9.2	24	0
Am	320	**240**	0	0	0
Cm	Below Detection Limit				
Np	17	**13**	0.25	0.4	0
Tc	41	**18**	3.2	3.5	1.6

Np almost completely routed with the raffinate
Small Tc losses to the U fraction

EXAm HAC test results

➢ 1st EXAm hot test on a HAC (dec-2015)

- Good hydrodynamic behaviour
- Needs an accurate process monitoring
- Compromise between Am recovery and Am/Cm decontamination factor



Performances :

- ***2.4 g of Am recovered***
- ***DF (Am/Ln) ≈ 2000***
- ***DF (Am/Cm) ≈ 50***
- ***Loss of Am in the raffinate ~ 10 %***
- ***Loss of Am in the Mo output < 0.01 %***

Element	Purity (%)
Am	95,5
Cm	0,6
Y	0,0
La	0,0
Ce	0,2
Pr	0,1
Nd	1,4
Sm	0,0
Eu	0,0
Fe	0,3
Mo	0,1
Zr	0,0
Pd	0,7
Ru	1,1

- Am very well recovered from fission products but decontamination towards Cm lower than expected
  - Due to a inaccurate modelling of Cm extraction in presence of TEDGA in these conditions
  - 40 stages of Cm scrubbing would have been required to reach 98% Am recovery and DF (Am/Cm) ≈ 500