GENIORS
GEN IV integrated oxide fuels recycling strategies

First INSPYRE Summer School

Hydrometallurgical Reprocessing Strategies

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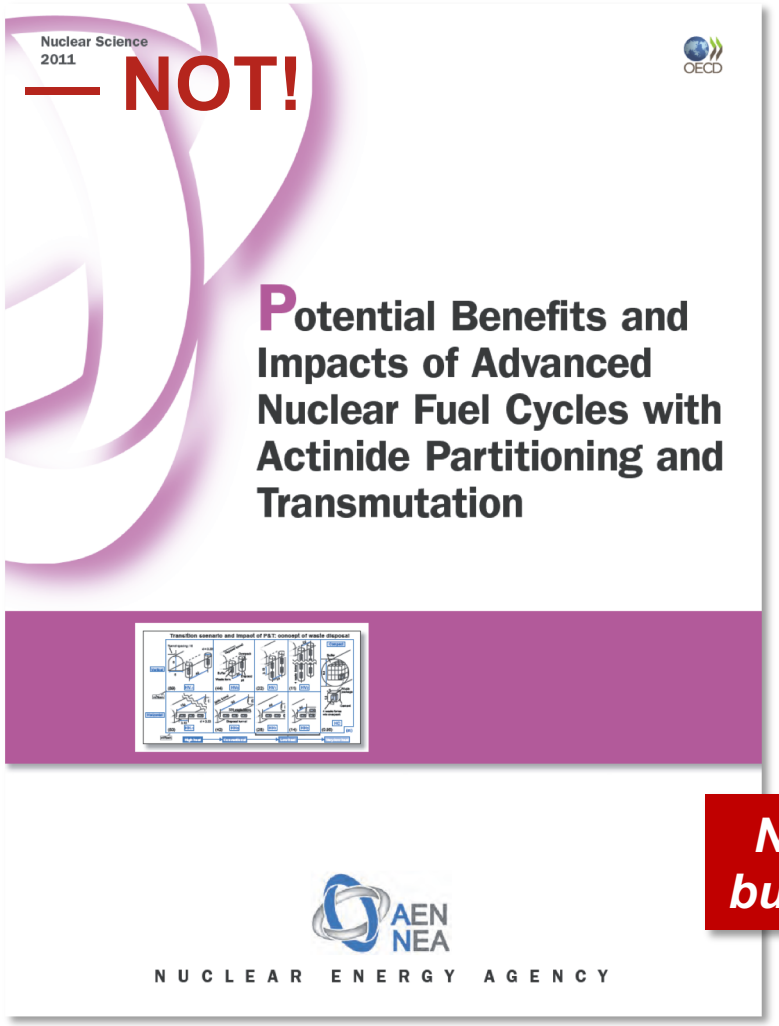
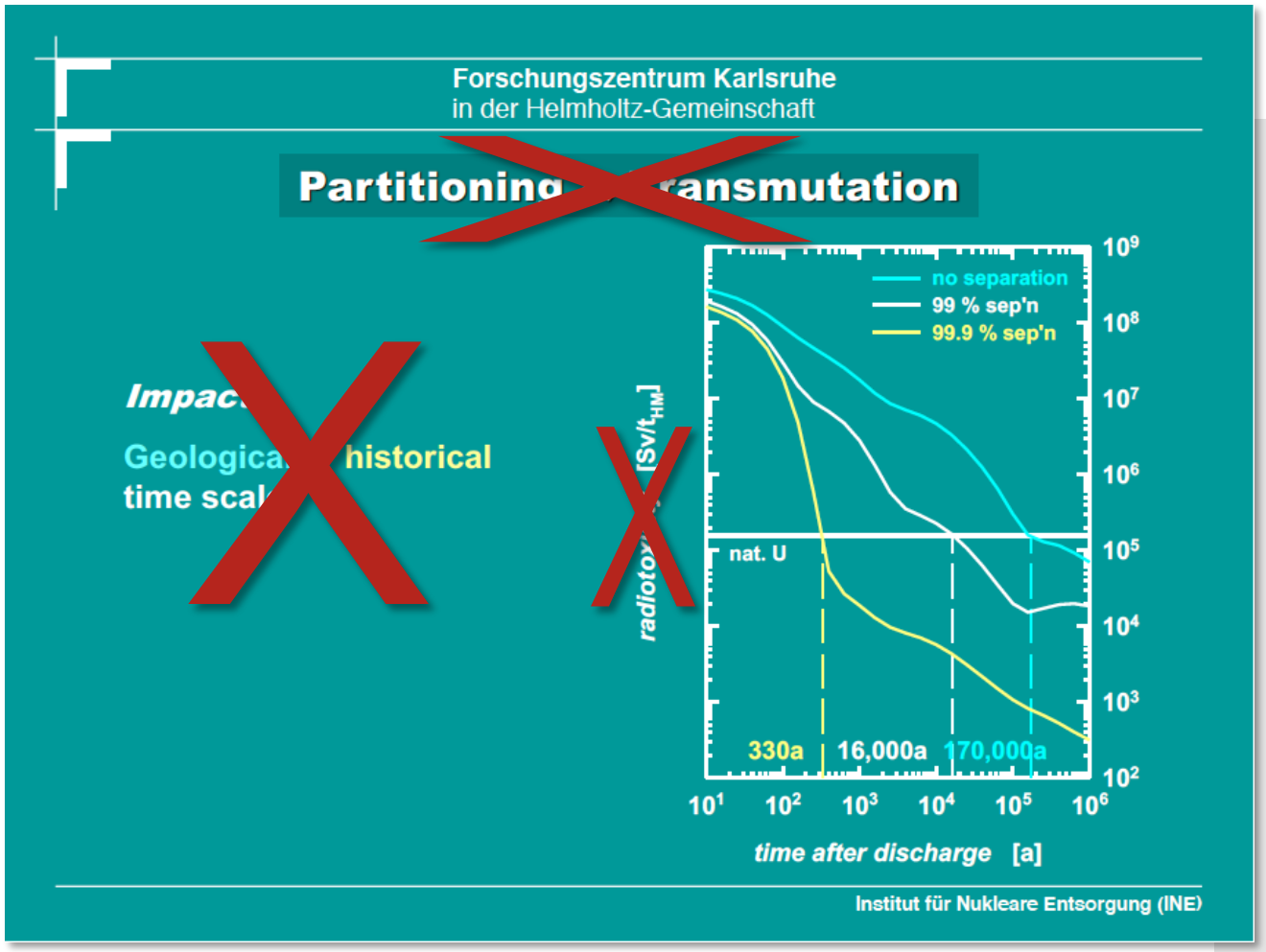
Irradiated Nuclear Fuel — Spent or Used?

- Waste or resource?
  - Only ≈ 1% of U_{nat} consumed
- German politics
  - ”Atomgesetz” amendments
    - 2002, direct disposal only
    - 2011, phase-out
  - **Spent** nuclear fuel = waste
    - Reasonable in light of nuclear phase-out
- Elsewhere
  - **Used** nuclear fuel = resource

Recycling Actinides

- Why — NOT!



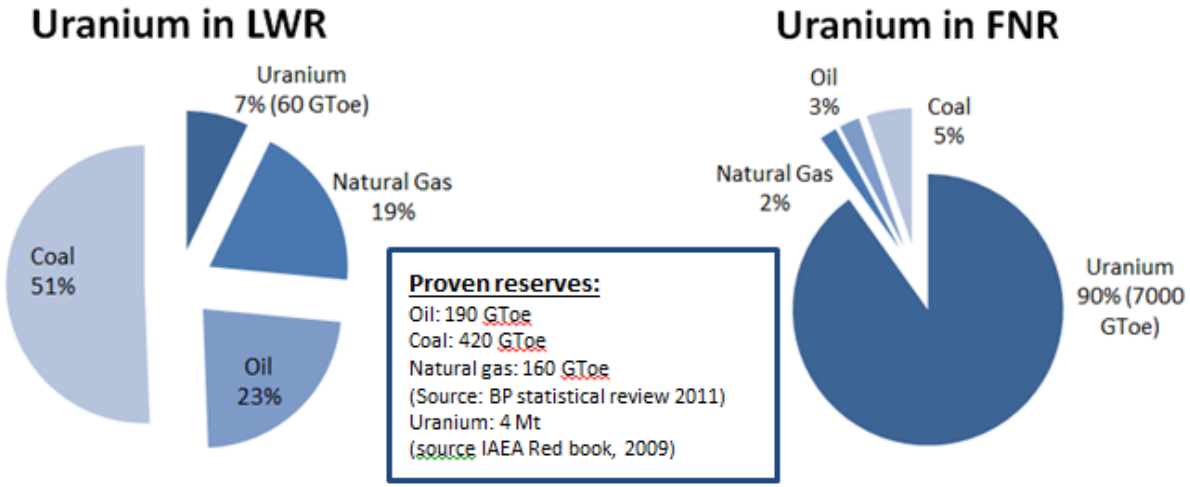


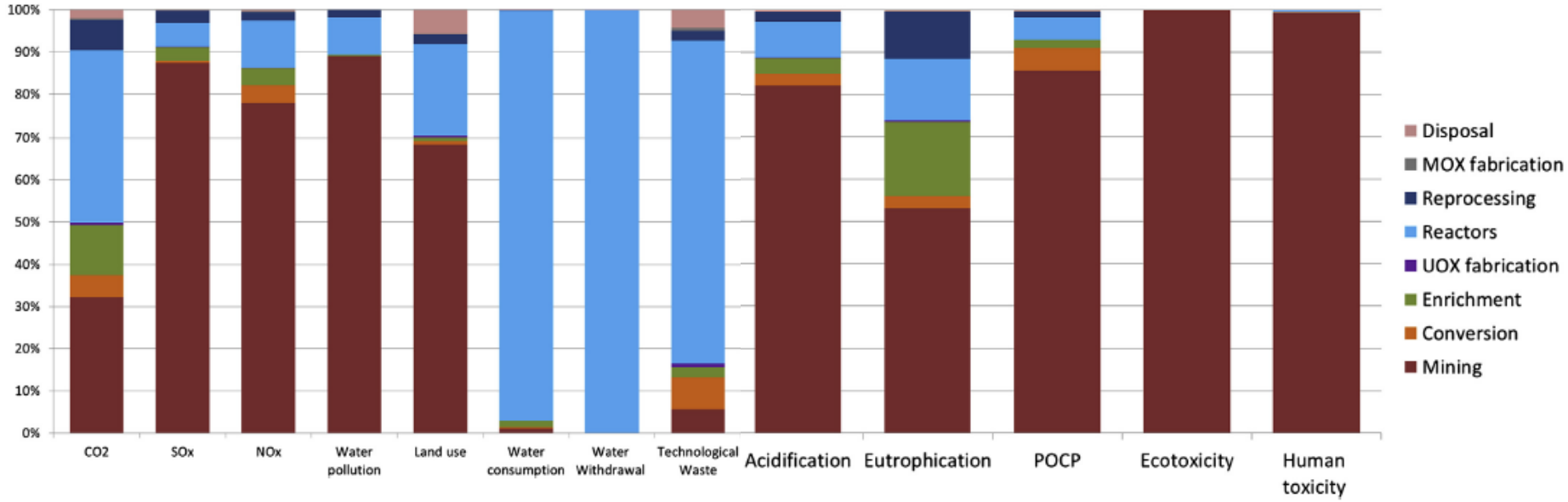
Not: what is IN the repository but what might find its way OUT

Recycling Actinides

- Why?
  - Resources “forever and a day”
  - Less mining

→ depleted U
→ Pu multi recycling





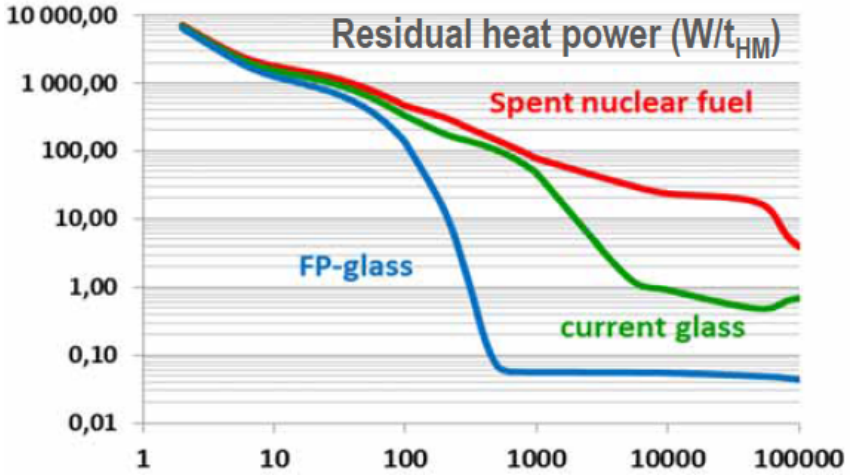
Huge impact on eco footprint!

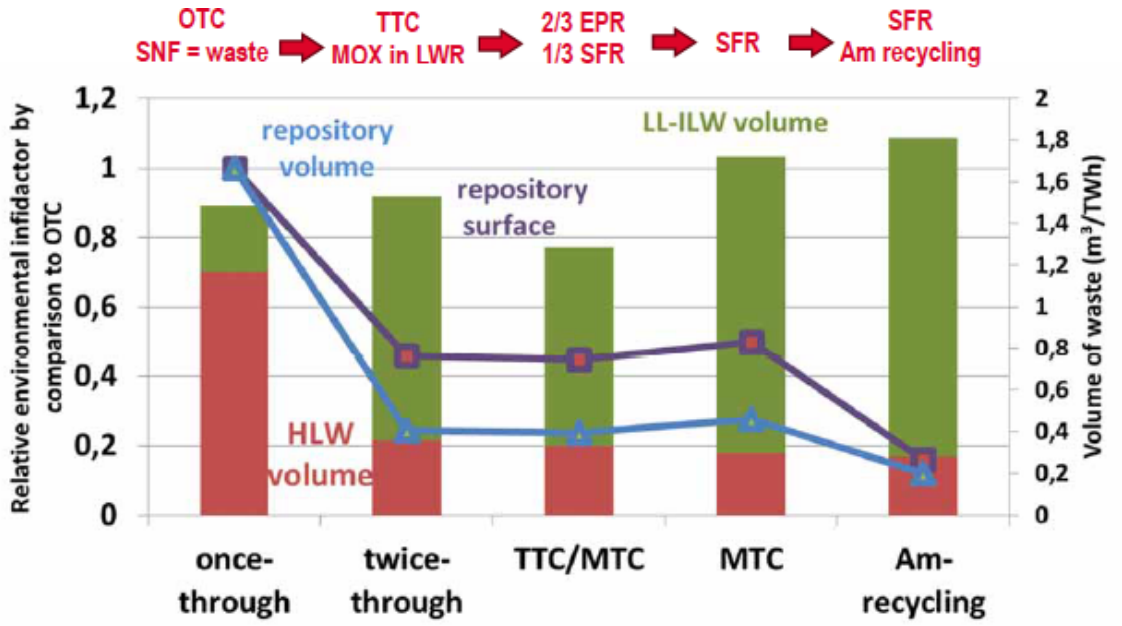
C. Poinssot et al., *Energy* **2014,** *6,* 199–211
C. Poinssot et al., *PiNE* **2016,** *92,* 234–241

Recycling Actinides

→ Pu, Am recycling

- Why?
  - Less long term heat load
  - More compact HLW repository



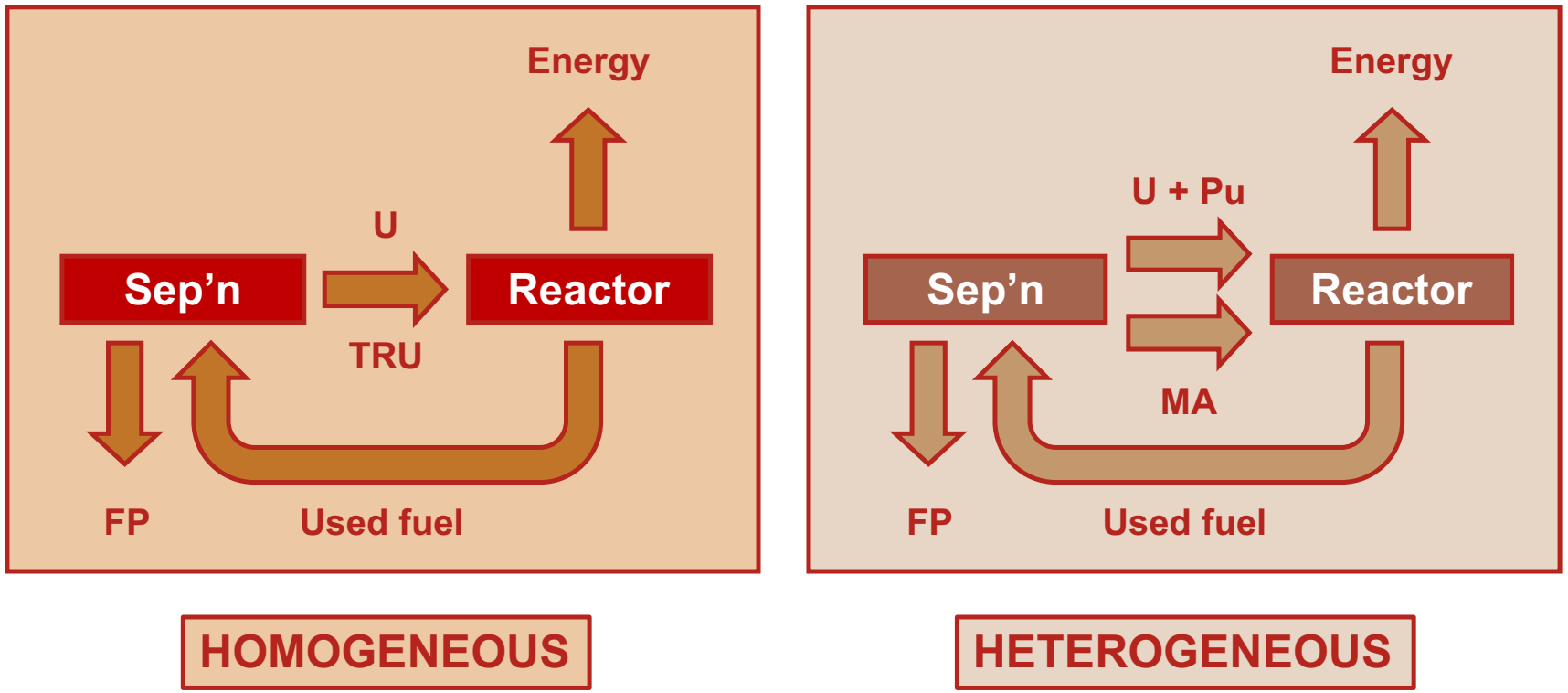


C. Poinssot et al., *Energy* **2014,** *6,* 199–211
C. Poinssot et al., *PiNE* **2016,** *92,* 234–241

Recycling Actinides

Dedicated separations for
→ homogeneous
→ heterogeneous

- How?
  - Separation
  - Fast reactor



Actinide Separations

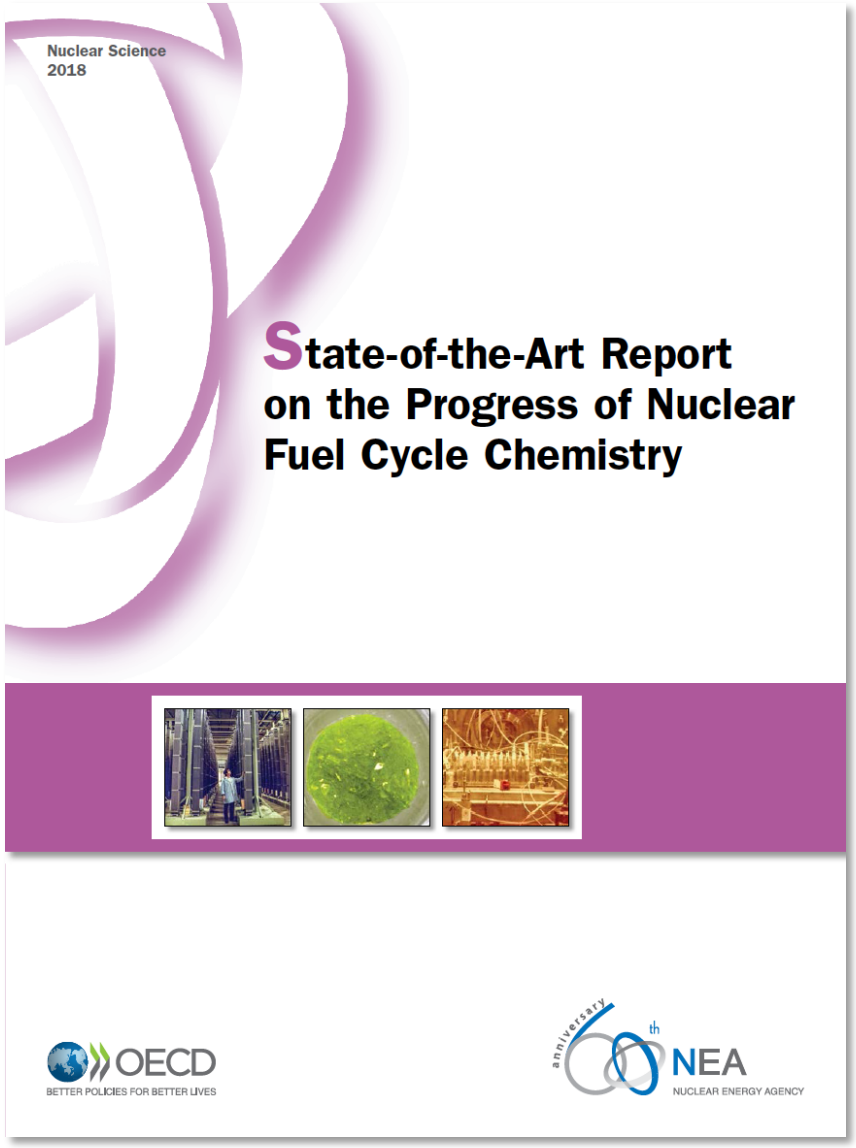
- Pyrometallurgy
  - Molten salt/liquid metal
  - Electrorefining

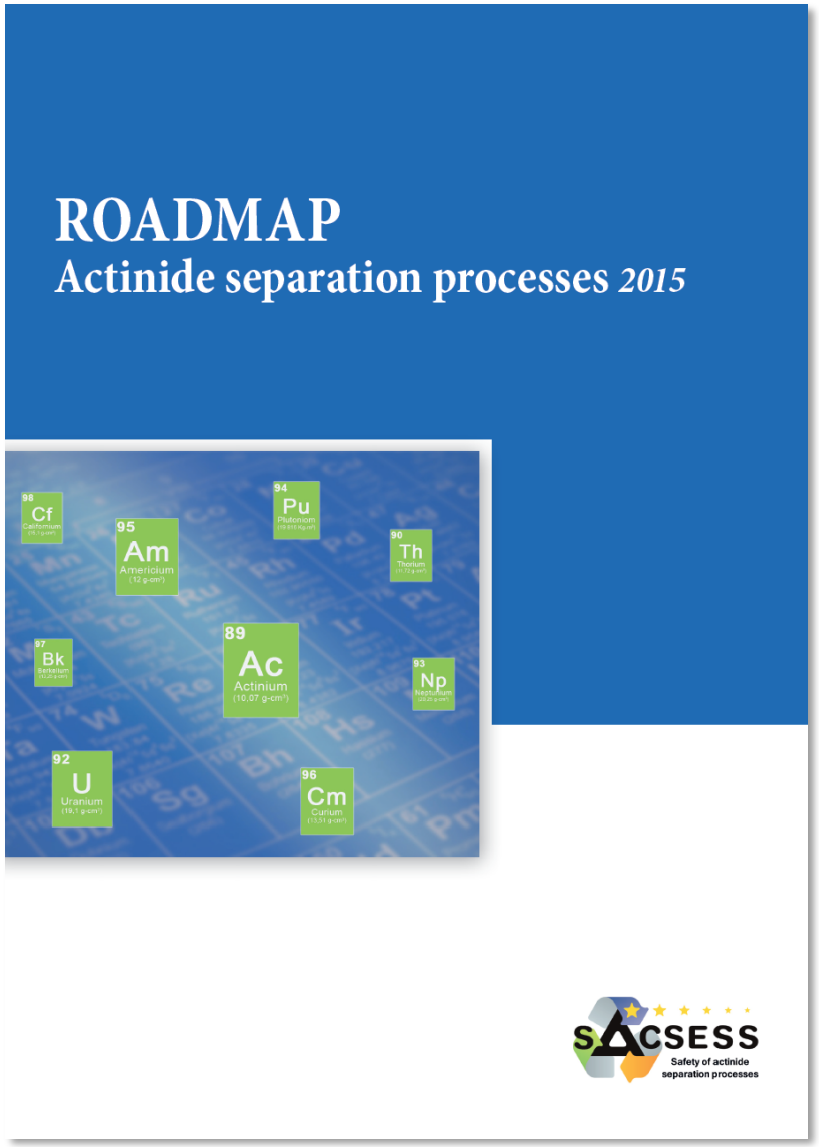
  - High temperature process
  - Innovative
  - Robust vs. radiolysis

- Hydrometallurgy
  - **Solvent extraction**
  - Aqueous/organic phase

  - Industrial experience (PUREX)
  - Excellent
    - Selectivity
    - Recovery
  - Organic phases prone to radiolytic degradation

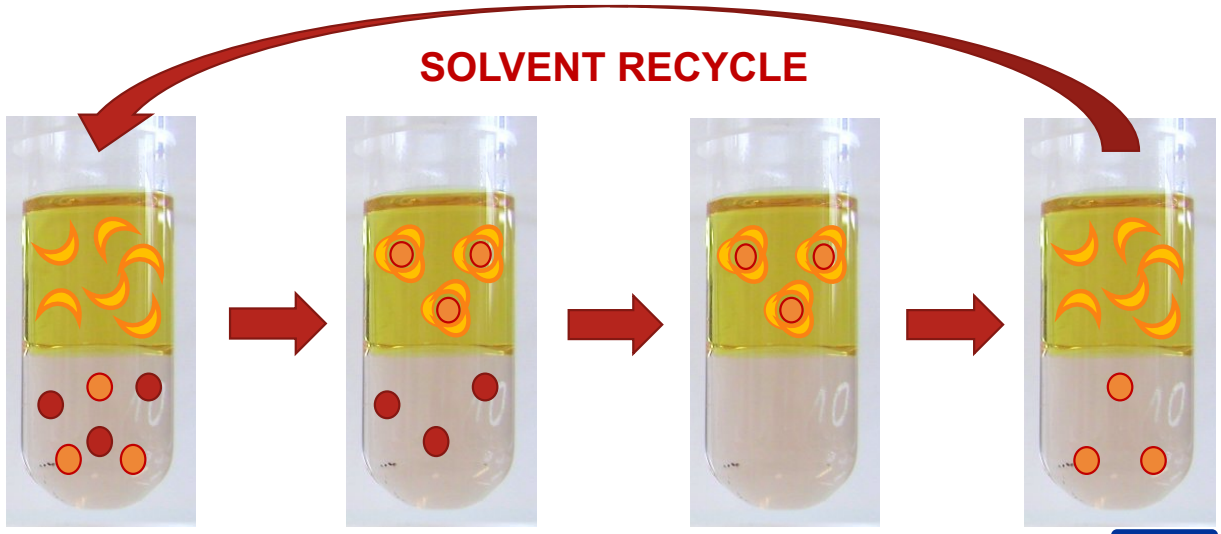
Many Options…





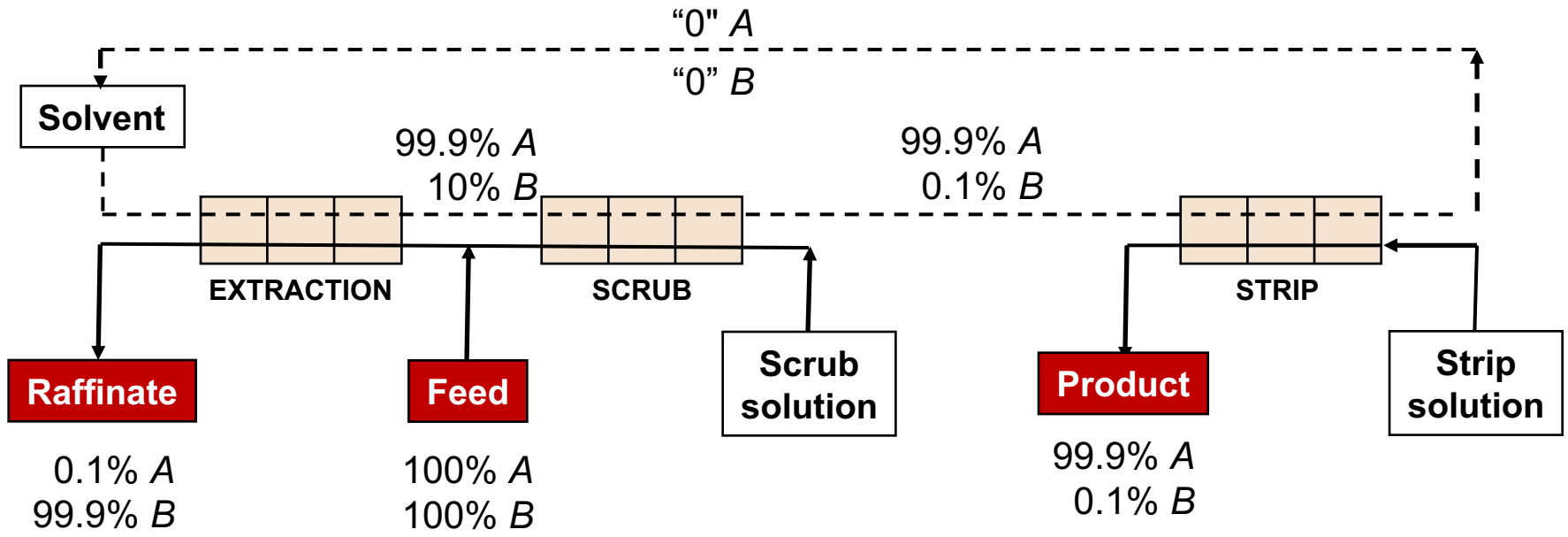
A Simple SX “Process”

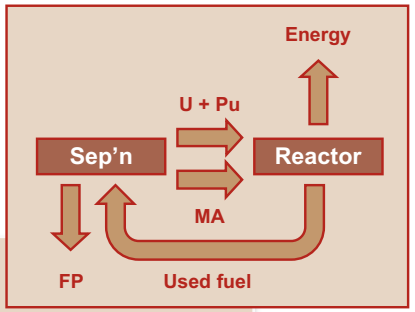
- Extraction
  - Solute transferred from aqueous to organic phase
  - Selectivity
- Back extraction (stripping)
  - Solute transferred back to a different aqueous phase
- Organic phase recycled



Actually,

- To achieve required performance, process is
  - Continuous
  - Multi-stage
  - Counter-current
  - Multi-section





HETEROGENEOUS

U, Np, Pu
Am, Cm
Ln
FP

PUREX

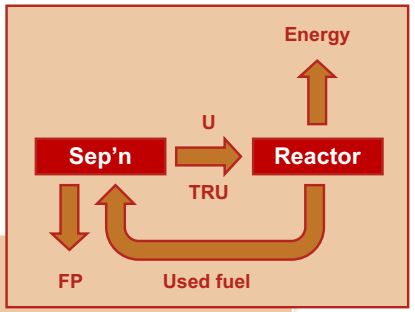
U (Np) Pu

Am
Cm
Ln
FP

SANEX

Am, Cm

FP, Ln



HOMOGENEOUS

U, Np, Pu
Am, Cm
Ln
FP

1st cycle

U

Np, Pu
Am, Cm
Ln
FP

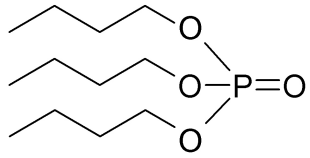
2nd cycle

Np, Pu,
Am, Cm

FP, Ln

Processes: Heterogeneous

- Strategy
  - U + Pu separated by PUREX process
  - Np(VI) extracted by TBP
  - Am(III) + Cm(III) not extracted by TBP
  - U, Np, Pu separation in modified PUREX process
  - New processes separating **Am(III)** + Cm(III) from PUREX raffinate



Extraction of Actinides with TBP in the PUREX Process

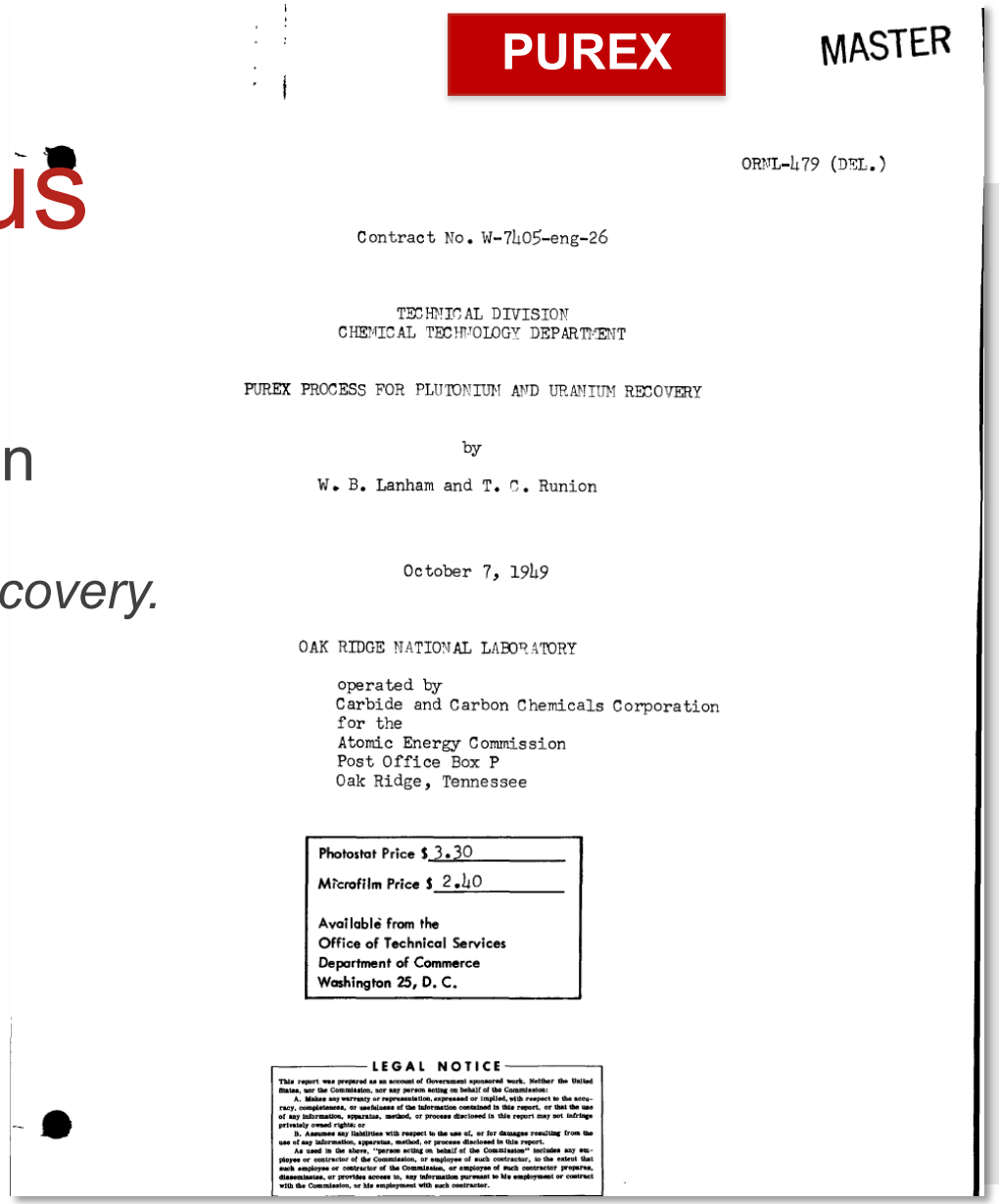
	Oxidation State			
	III	IV	V	VI
U				●
Np			●	●
Pu		●		
Am	●			
Cm	●			

● Extractible with TBP

● Not extractractible with TBP

Processes: Heterogeneous

- PUREX process
  - **P**lutonium, **U**ranium, **R**eduction, **EX**traction
    - W. B. Lanham, T. C. Runion,
      PUREX process for plutonium and uranium recovery.
      USAEC report ORNL-479 (1949)
  - a.k.a.
    - **P**lutonium **U**ranium **R**efining by **EX**traction
    - **P**lutonium **U**ranium **R**ecovery by **EX**traction


PUREX

MASTER

ORNL-479 (DEL.)

Contract No. W-7405-eng-26

TECHNICAL DIVISION
CHEMICAL TECHNOLOGY DEPARTMENT

PUREX PROCESS FOR PLUTONIUM AND URANIUM RECOVERY

by

W. B. Lanham and T. C. Runion

October 7, 1949

OAK RIDGE NATIONAL LABORATORY

operated by
Carbide and Carbon Chemicals Corporation
for the
Atomic Energy Commission
Post Office Box P
Oak Ridge, Tennessee

Photostat Price $ 3.30
Microfilm Price $ 2.40

Available from the
Office of Technical Services
Department of Commerce
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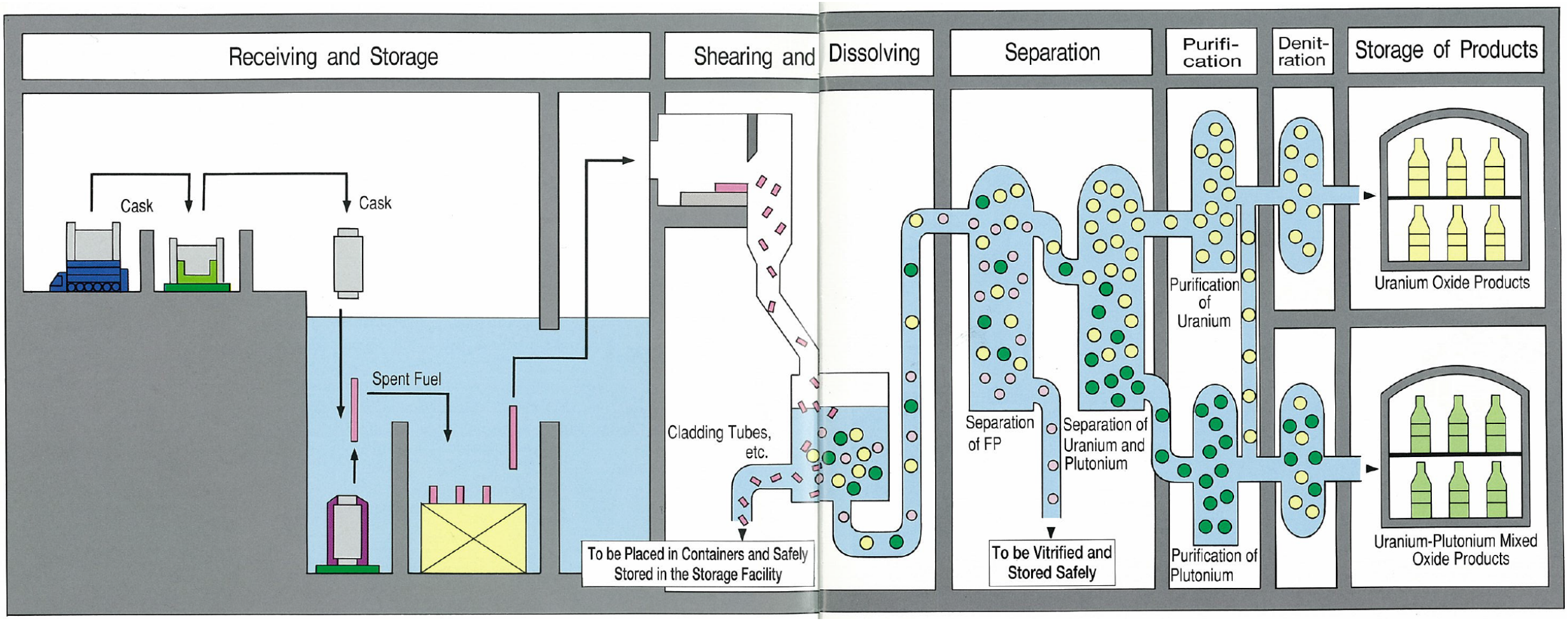
PUREX

Processes: Heterogeneous



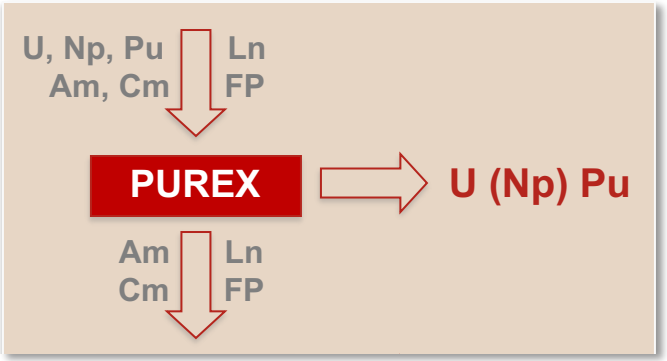
Processes: Heterogeneous

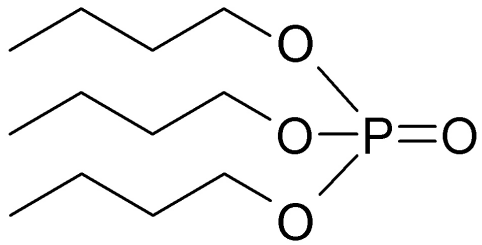
- Extracting agent, TBP (tri-*n*-butyl phosphate)

- U(VI) and Pu(IV) co-extracted
  - $UO_2(NO_3)_2 \cdot 2TBP$
  - $Pu(NO_3)_4 \cdot 2TBP$

- Pu stripped by reduction to Pu(III)
- U stripped into dilute HNO_3

- TBP purified and recycled





Processes: Heterogeneous

- Np extractable as Np(VI)
  - $2\ NpO_2^+ + 3\ H^+ + NO_3^- \rightleftharpoons 2\ NpO_2^{2+} + HNO_2 + H_2O$

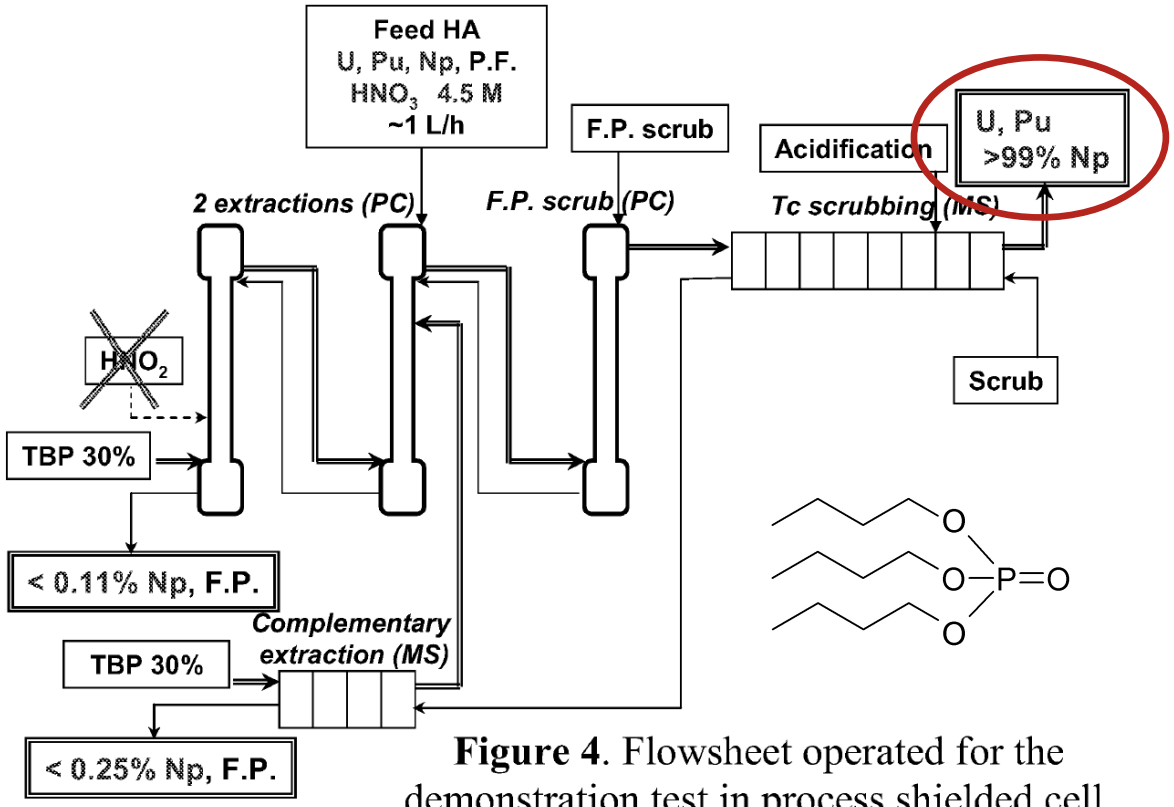
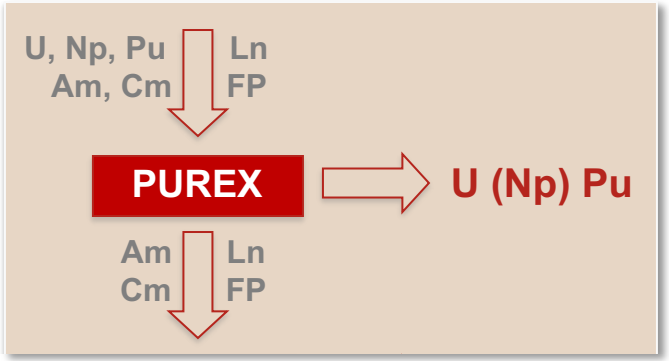


Figure 4. Flowsheet operated for the demonstration test in process shielded cell.



B. Dinh et al.,
Proc. ISEC 2009, 581–586

Processes: Heterogeneous

- Am(III) + Cm(III) separation from PUREX raffinate
  - Selective Actinides Extraction (SANEX)

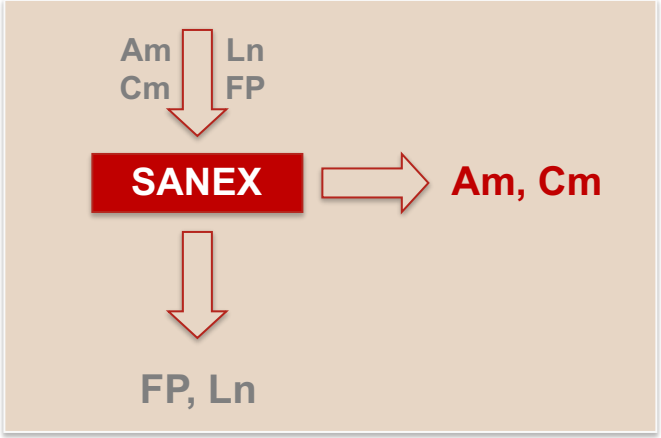
1. An(III) + Ln(III) co-extraction

$$M^{3+} + 3\,NO_3^- + m\,\overline{X} \rightleftharpoons \overline{M(NO_3)_3X_m}$$

2. Selective An(III) stripping

$$\overline{An(NO_3)_3X_m} + n\,\mathbf{L} \rightleftharpoons An\mathbf{L}_n^{3+} + 3\,NO_3^- + m\,\overline{X}$$

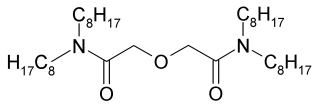
$$\overline{Ln(NO_3)_3X_m} + n\,\mathbf{L} \rightleftharpoons Ln\mathbf{L}_n^{3+} + 3\,NO_3^- + m\,\overline{X}$$



B. Weaver, F. A. Kappelmann, *USAEC report ORNL-3559,* 1964
G. Persson et al., *Solvent Extr. Ion Exch.* **1984,** 2, 89–113
X. Hérès et al., *GLOBAL 2009*
C. Poinssot et al., *ATALANTE 2012*

A. Geist et al., *Solvent Extr. Ion Exch.* **2012,** *30,* 433–444
A. Wilden et al., *Solvent Extr. Ion Exch.* **2015,** *33,* 91–108
E. Macerata et al., *JACS* **2016,** *138,* 7232–7235
G. L. Lumetta et al., *Solvent Extr. Ion Exch.* **2017,** *35,* 377–395

SANEX



Solvent
0.2 mol/L TODGA
5 % 1-octanol
in TPH
56 mL/h

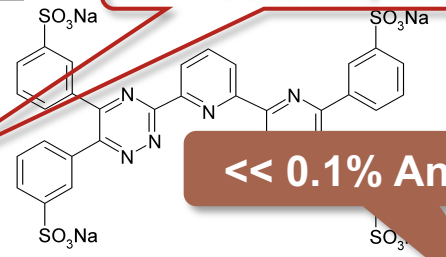
Feed
4.5 mol/L HNO_3
0.05 mol/L CDTA
61 mL/h

Scrub 1
3 mol/L HNO_3
0.05 mol/L CDTA
0.2 mol/L oxalic acid
86 mL/h

Scrub 2
0.5 mol/L HNO_3
60 mL/h

Extraction — 4 Stages
Scrub 1 — 8 Stages
Scrub 2 — 4 Stages

≈ 100% An, Ln



<< 0.1% An

Raffinate

≈ 0.01% An

≈ 99.9% An
< 0.1% Ln
0.4% Ru, 0.3% Sr

Solvent
0.2 mol/L TODGA
5 % 1-octanol
in TPH
40 mL/h

Loaded solvent
40 mL/h

An Strip
0.35 mol/L HNO_3
18 mmol/L SO_3-Ph-BTP
40 mL/h

Spent solvent

Ln Re-extr. — 6 Stages
An Strip — 6 Stages
Ln Strip — 4 Stages

An Product

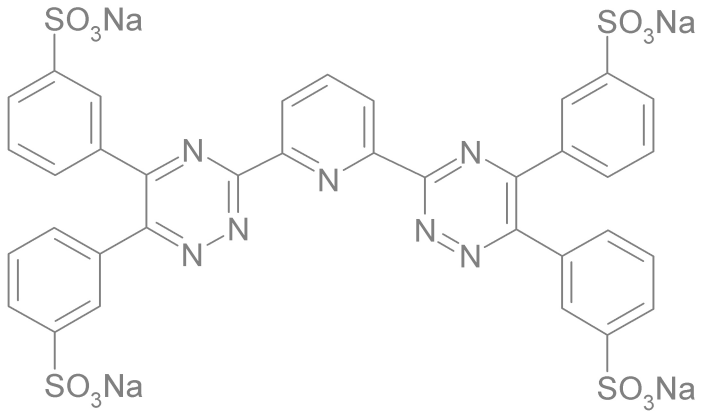
Ln Raffinate

0.05% An

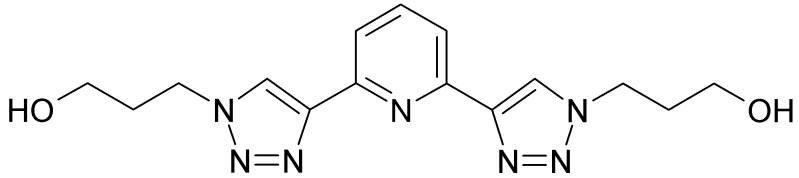
Ln Strip
0.5 mol/L citric acid
set to pH3
with NH_3
40 mL/h

SANEX — Progress

- SO_3-Ph-BTP
  - Contains sulphur
  - Waste issue



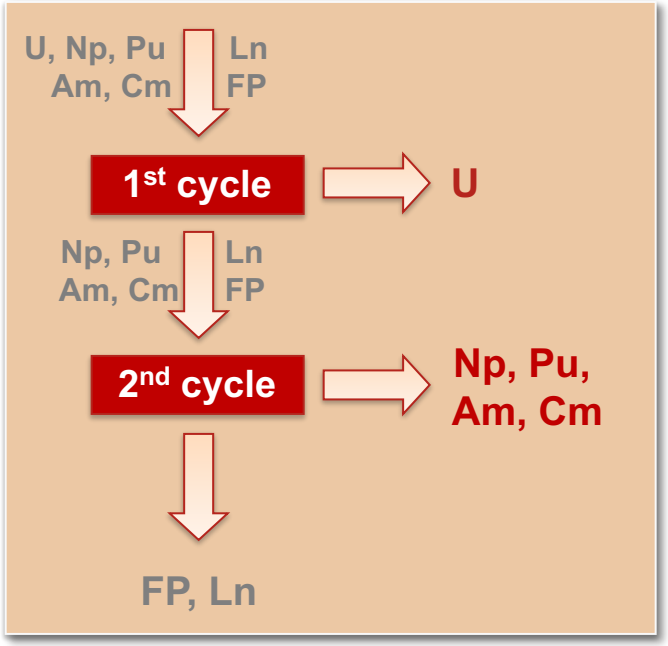
- PTD
  - *CHON*
  - Combustible to gases
  - Studied in GENIORS
    GEN IV integrated oxide fuels recycling strategies



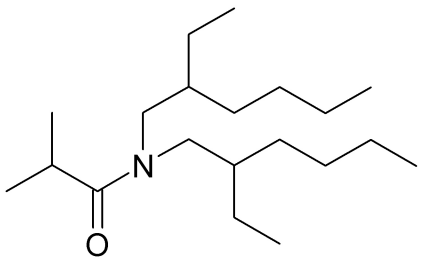
E. Macerata et al., *J. Amer. Chem. Soc.* **2016,** *138* (23), 7232–7235
C. Wagner et al., *Inorg. Chem.* **2017,** *56* (4), 2135–2144

Processes: Homogeneous

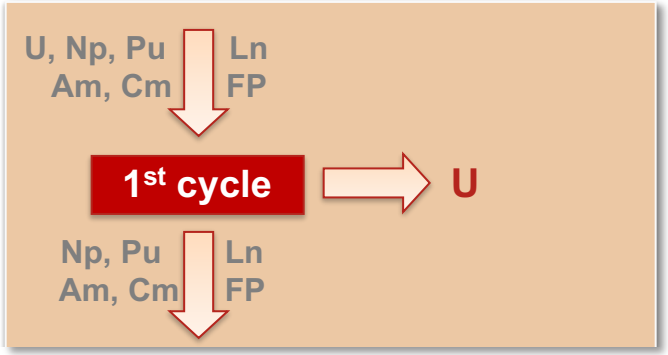
- GANEX (grouped actinides extraction) process
  - 1st cycle, U extraction
  - 2nd cycle, TRU extraction
    - No pure Pu anywhere
    - Added proliferation resistance
  - Initially developed at CEA Marcoule
    - Hot tests
  - Advanced during CSEPT innovative solutions for sustainable nuclear energy project
    - System development
    - Pu-active test
    - Hot tests



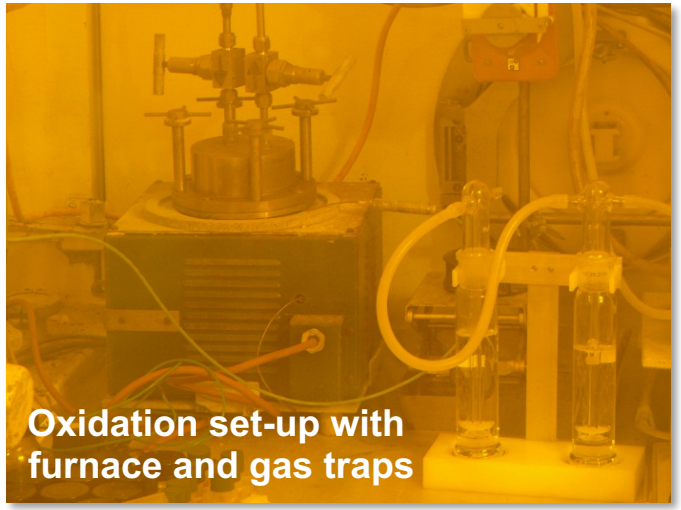
GANEX 1st Cycle



- Extracting agent, DEHiBA
  - Extracts U(VI)
  - Rejects Pu(IV) and others
- Hot tests
  - CEA Marcoule, LWR UOx fuel
  - JRC Karlsruhe, FR $U_{80}Pu_{20}$ nitride, carbide fuel

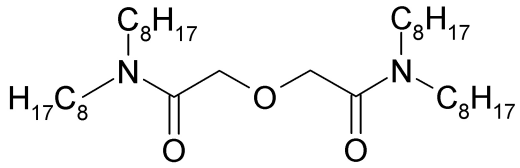


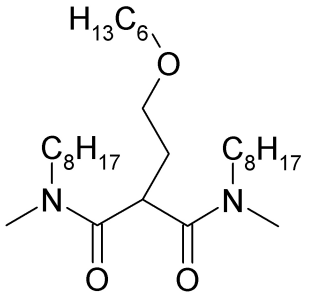

Fuel pellets before oxidation


Oxidation set-up with furnace and gas traps

M. Miguirditchian et al., *GLOBAL 2009*
R. Malmbeck et al., *Radiochim. Acta* **2019** (accepted)

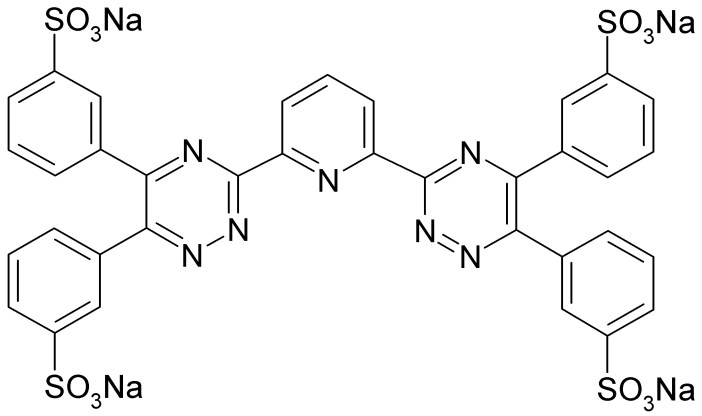
EURO-GANEX

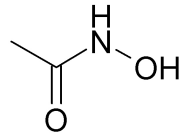




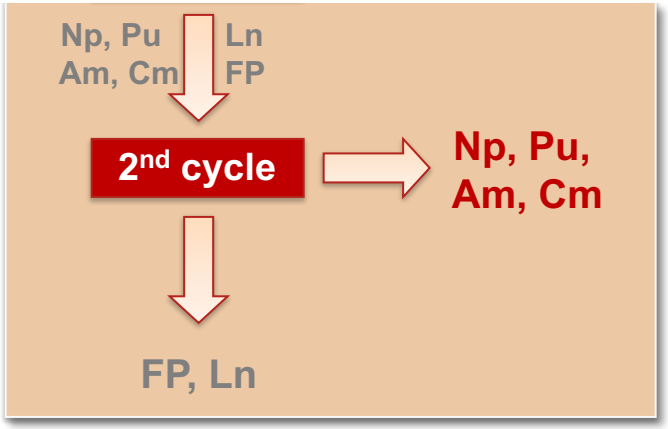
- Advanced 2nd cycle

- Extracting agents
  - TODGA & DMDOHEMA
    → TRU & Ln co-extraction





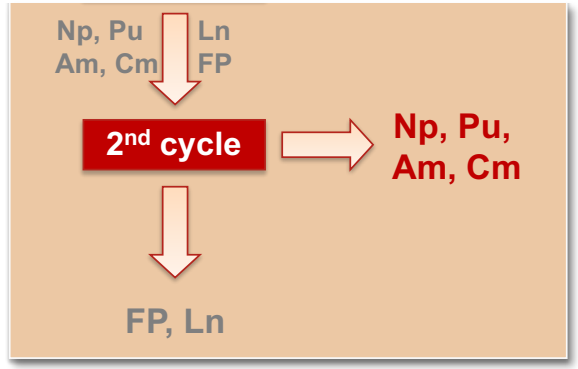
- Stripping agents
  - SO_3-Ph-BTP → Am, Cm
  - AHA → Np, Pu

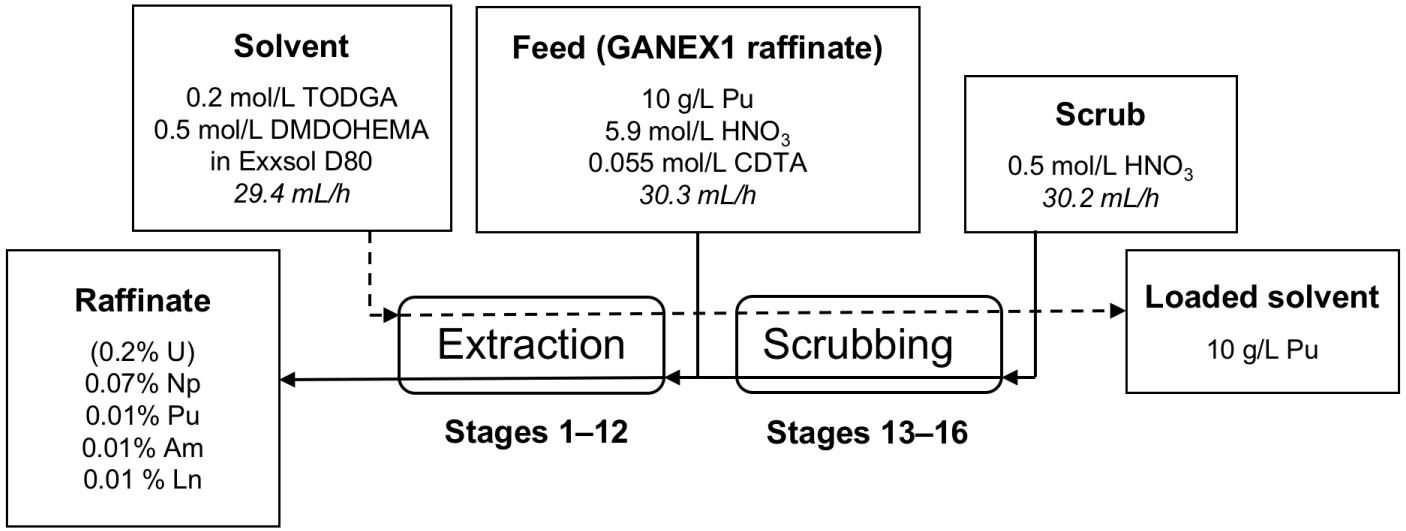


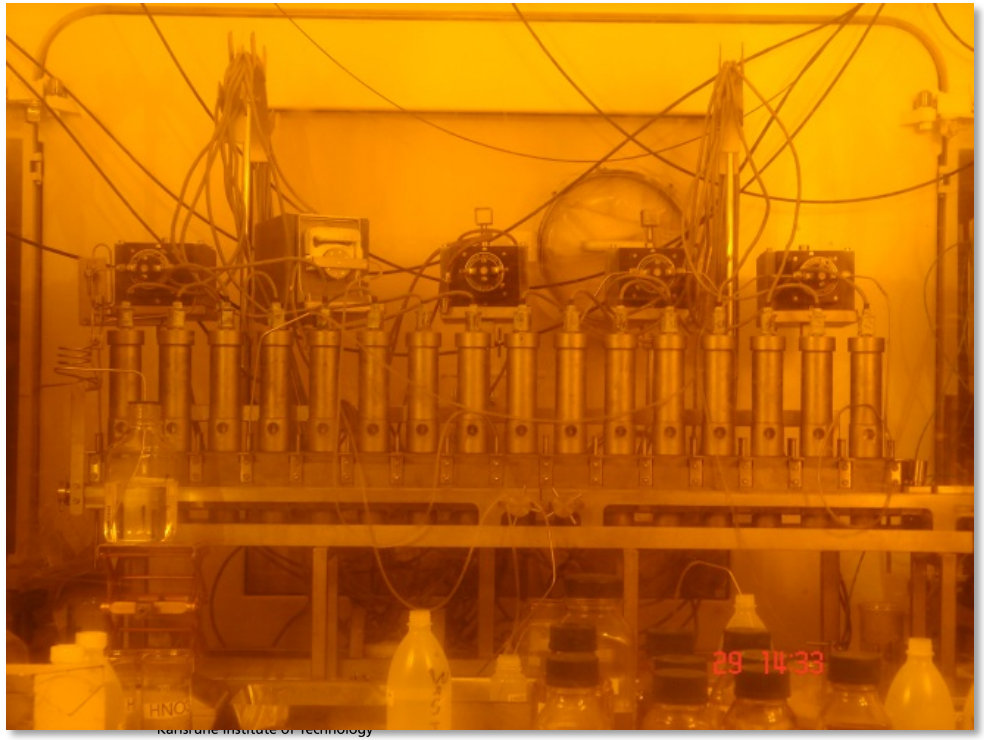
J. Brown et al., *Solvent Extr. Ion Exch.* **2012,** *30* (2), 127–141
M. Carrott et al., *Hydrometallurgy* **2015,** *152*, 139–148
M. Carrott et al., *Solvent Extr. Ion Exch.* **2013,** *31* (5), 463–482

EURO-GANEX

- Day 1, extraction
  - Preparation of loaded solvent



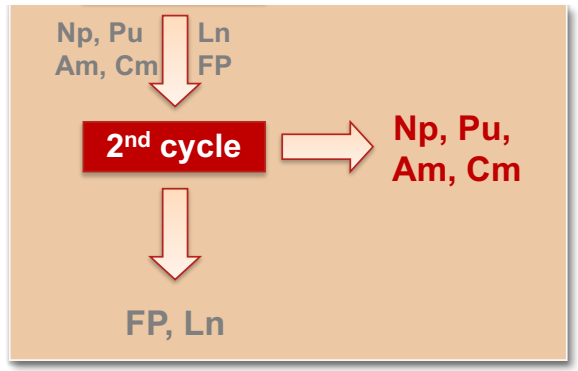


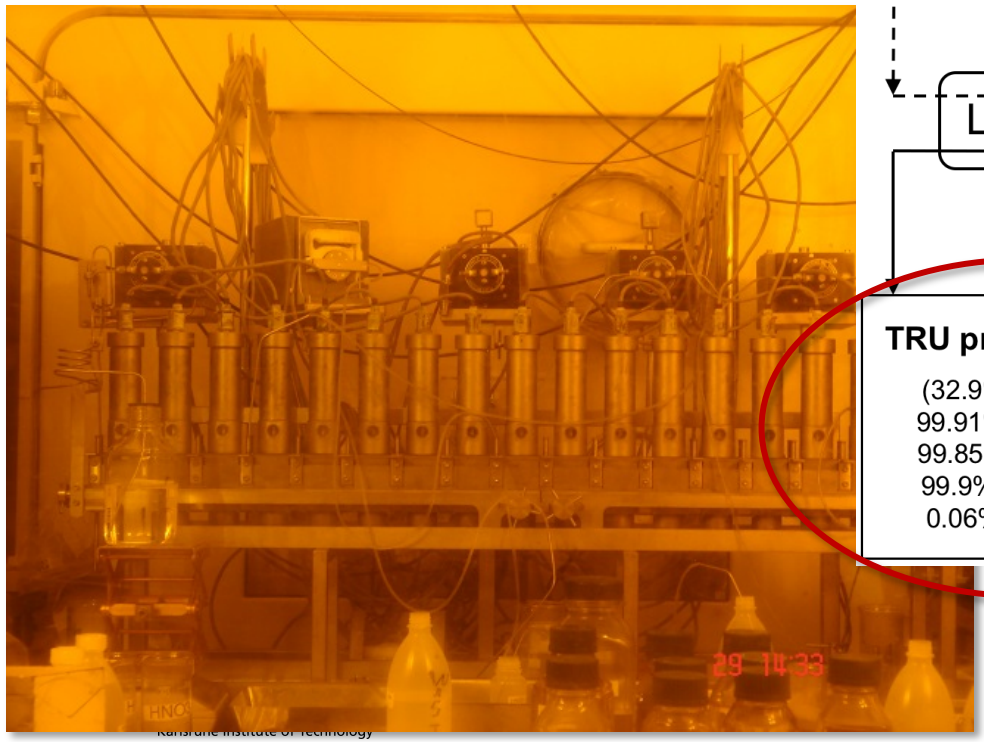


M. Carrott et al., *Solvent Extr. Ion Exch.* **2014,** *32* (5), 447–467
R. Malmbeck et al., *Radiochim. Acta* **2019** (accepted)

EURO-GANEX

- Day 2, TRU back extraction





Solvent
0.2 mol/L TODGA
0.5 mol/L DMDOHEMA
in Exxsol D80
29.8 mL/h

Loaded solvent (from day 1)
10 g/L Pu
29.8 mL/h

Spent solvent
(10% U)
0.04% Np
0.08% Pu
0.03% Am
0.03% Ln

Ln Re-extraction
Stages 1–6

TRU Stripping
Stages 7–12

Ln Stripping
Stages 13–16

TRU product
(32.9% U)
99.91% Np
99.85% Pu
99.9% Am
0.06% Ln

0.03% U
15% Zr
60% Mo

TRU strip
0.5 mol/L HNO_3
0.055 mol/L SO_3-Ph-BTP
1 mol/L AHA
57 mL/h

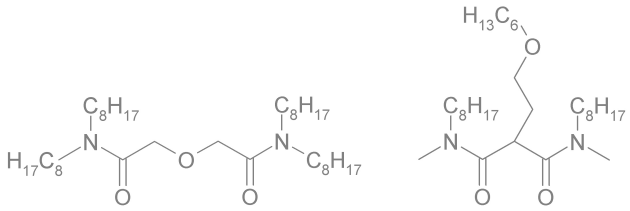
Ln product
(57.2% U)
0.05% Np
0.07% Pu
0.07% Am
99.9% Ln

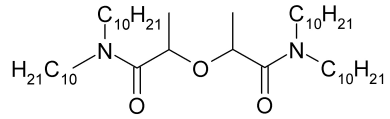
Ln strip
0.01 mol/L HNO_3
57 mL/h

M. Carrott et al., *Solvent Extr. Ion Exch.* **2014,** *32* (5), 447–467
R. Malmbeck et al., *Radiochim. Acta* **2019** (accepted)

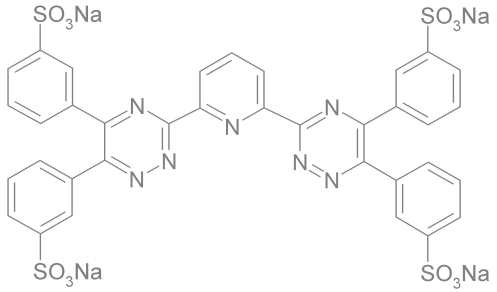
EURO-GANEX — Progress

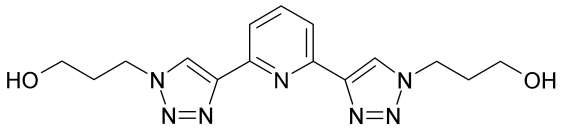
- Simplified solvent
  - Only one extracting agent





- CHON stripping agent
  - SO_3-Ph-BTP → PTD





- Improved Zr, Mo scrubbing

R. Malmbeck et al., *J. Radioanal. Nucl. Chem.* **2017,** *314* (3), 2531–2538

Conclusions

- Hydrometallurgy (solvent extraction)
  - Offers solutions for
    - Homogeneous
    - Heterogeneous
- Continuous improvement
  - Simplification
  - Safety
  - TRL
- International collaboration

Acknowledgements

Anna L. SMITH @

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Investigations Supporting MOX Fuel Licensing in ESNII Prototype Reactors

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