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San Francisco, USA, 1-5 November 2010

JÜLICH FORSCHUNGSZENTRUM

One-cycle SANEX process development studies and lab-scale demonstrations

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Institut für Energie- und Klimaforschung (IEK-6), Sicherheitsforschung und Reaktortechnik, Jülich, Germany

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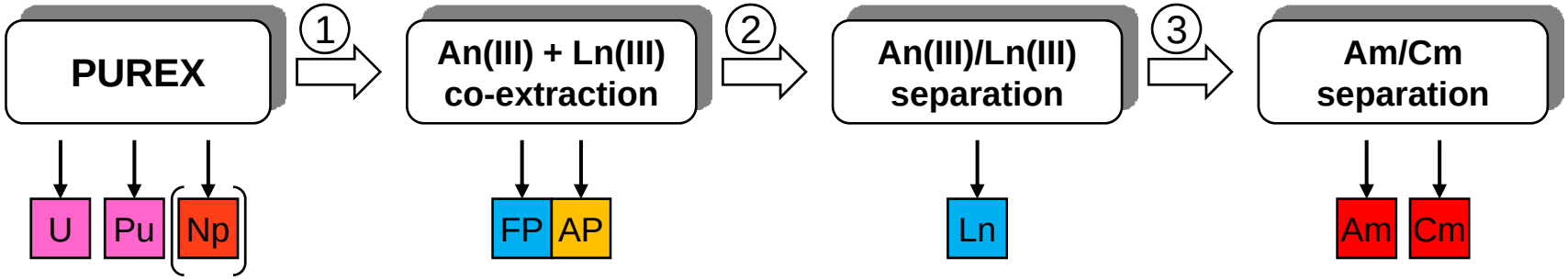
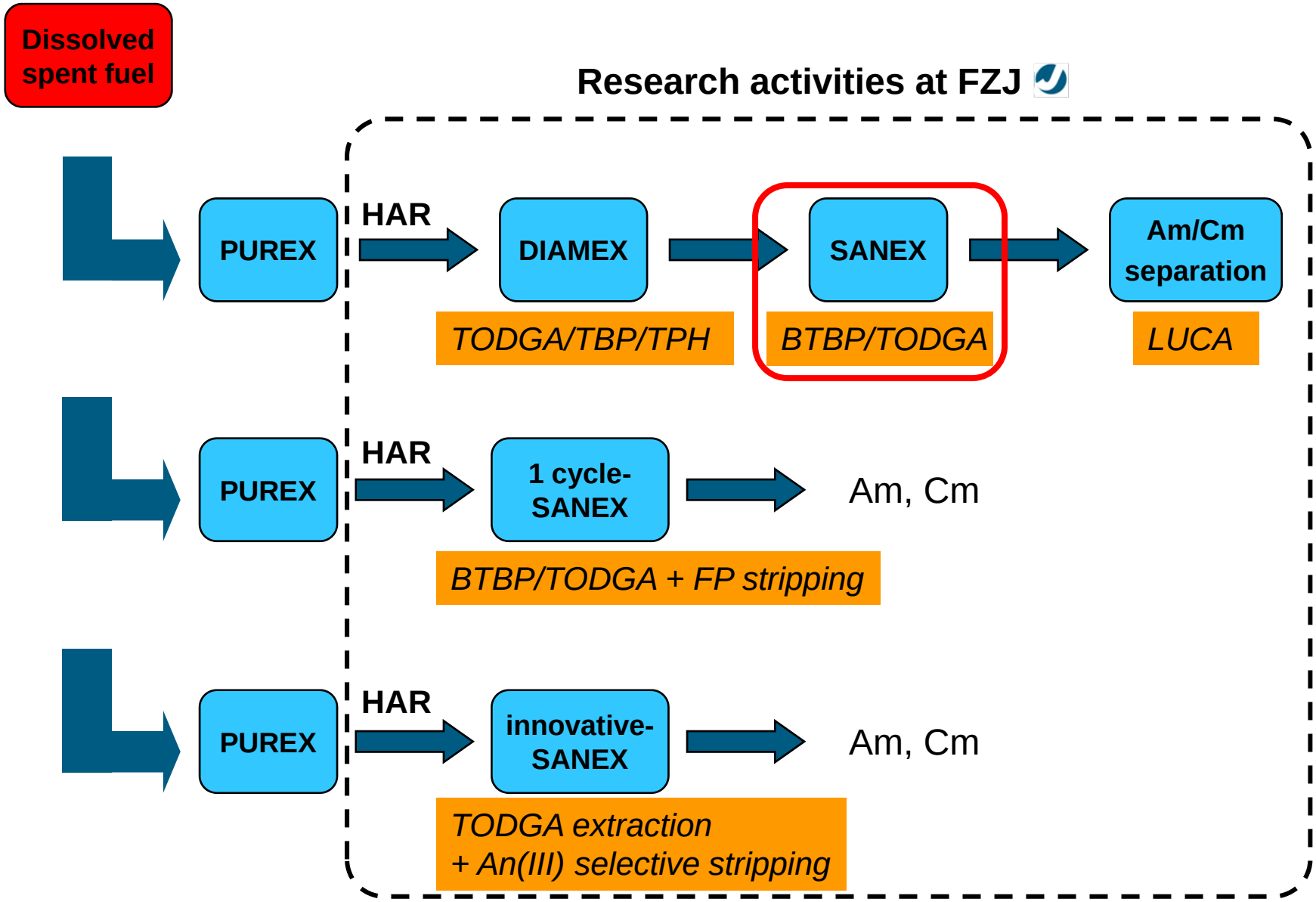
Institut für Nukleare Entsorgung (INE), Karlsruhe, Germany

European Projects
Newpart - ACSEPT

- 1996-1999: Newpart (FP4: FI4I-CT-96-0010)
- 2000-2003: Partnew (FP5: FIKW-CT-2000-00087)
- 2004-2007: Europart (EUROpean Research Programme for the PARTitioning of Minor Actinides) (FP6: FI6W-CT-2003-508854)
- 2008-2012: ACSEPT (Actinide reCycling by SEParation and Transmutation) (FP7: FP7-CP-2007-211267)

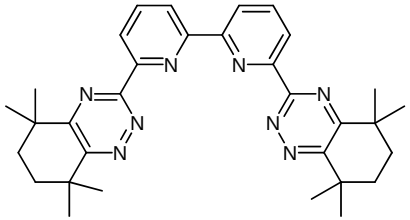


Overview of the processes

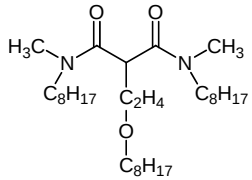


SANEX process demonstration
- An(III)/Ln(III) separation -

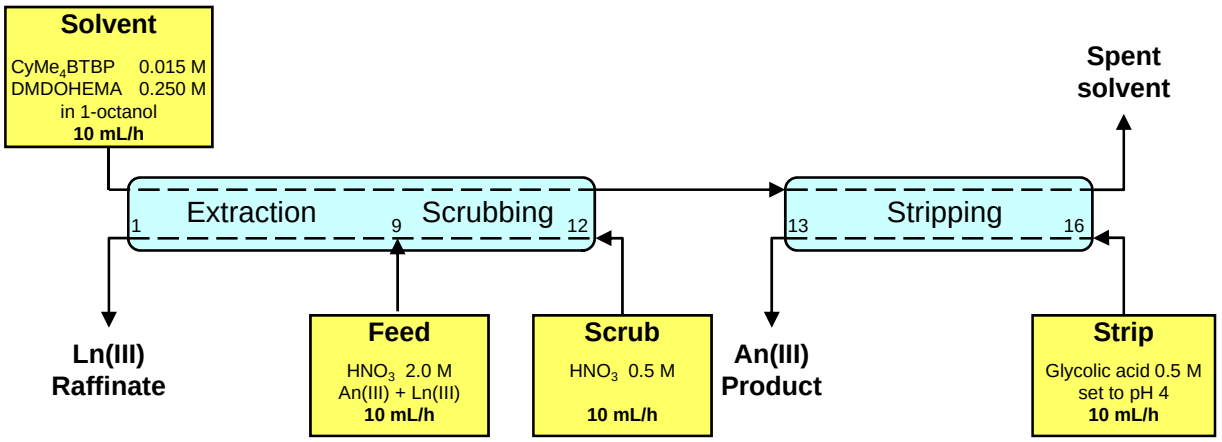
- Successful hot demonstration test at ITU 2008[1]
- Product:
  - Am(III) > 99.99 %
  - Cm(III) > 99.99 %
  - Ln(III) < 0.1 %
  - Y ~ 0.43 %
  - Gd ~ 0.32 %

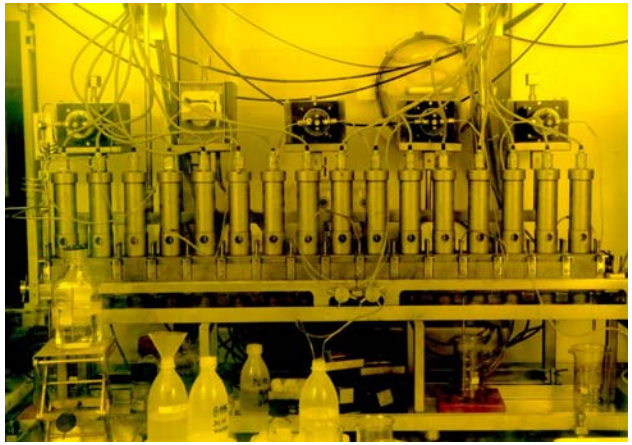


$CyMe_4BTBP$



DMDOHEMA



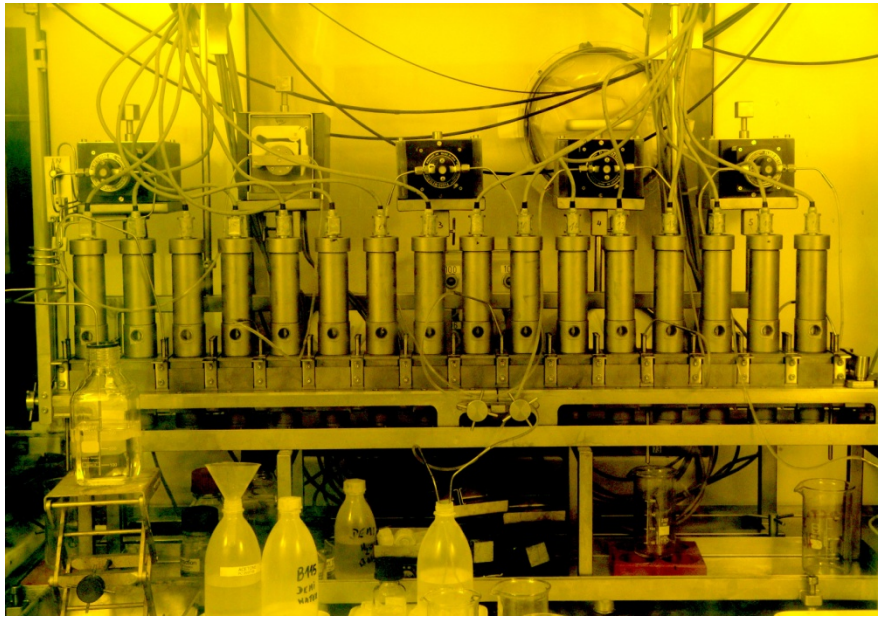


[1] Magnusson, Modolo et al. Solv. Extr. Ion Exch. 27 (2), 97-106, **2009**.

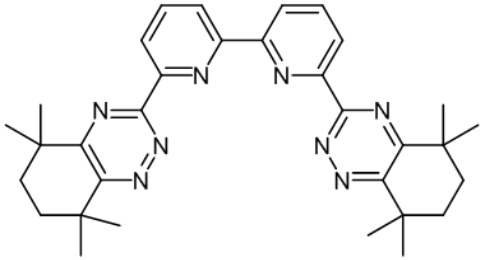
Experimental setup at FZJ and ITU

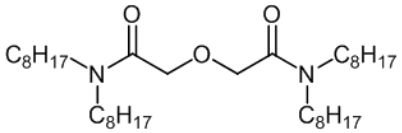
- FZJ centrifugal contactors
- INET, Tsinghua University Beijing, China
- 10 mm rotor diameter
- 4 batteries with 4 stages

- ITU centrifugal contactors
- BXP012 type, Rousselet-Robatel, France
- 12 mm rotor diameter
- 16 stages with full flexibility
- Installed in a hot cell



SANEX-process for An(III)/Ln(III) separation from a simulated DIAMEX raffinate[2]





Solvent
$CyMe_4BTBP$ 0.015 M
TODGA 0.005 M
in 1-octanol
10 mL/h

Spent solvent

1 Extraction 12 Scrubbing 16

17 Stripping 24

Ln(III) Raffinate

Feed
HNO_3 1.3 M
An(III) + Ln(III)
10 mL/h

Scrub
HNO_3 0.7 M
10 mL/h

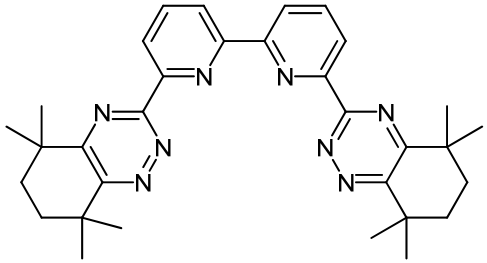
An(III) Product

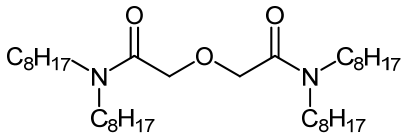
Strip
Glycolic acid 0.5 M
set to pH 4
10 mL/h

Element	Conc. [mg/L]	Nuclide	Activity [MBq/L]
Ce	383		
Eu	129	^{152}Eu	3.3
Gd	85	^{241}Am	2.5
La	205	^{244}Cm	2.4
Nd	716	^{252}Cf	1.6
Pr	192		
Sm	142		
Y	55		

[2]Modolo, G. et al., Tenth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mito, Japan, **2008**.

SANEX-process for An(III)/Ln(III) separation from a simulated DIAMEX raffinate[2]





Solvent
$CyMe_4BTBP$ 0.015 M
TODGA 0.005 M
in 1-octanol
10 mL/h

An(III) < detec. limit
Ln(III) < detec. limit

Spent solvent

1 Extraction 12 Scrubbing 16

17 Stripping 24

Ln(III) Raffinate

Ln(III) > 99.9 %
^{152}Eu ~ 99.9 %
^{241}Am ~ 0.08 %
^{244}Cm ~ 0.32 %
^{252}Cf < detec. limit

Feed
HNO_3 1.3 M
An(III) + Ln(III)
10 mL/h

Scrub
HNO_3 0.7 M
10 mL/h

An(III) Product

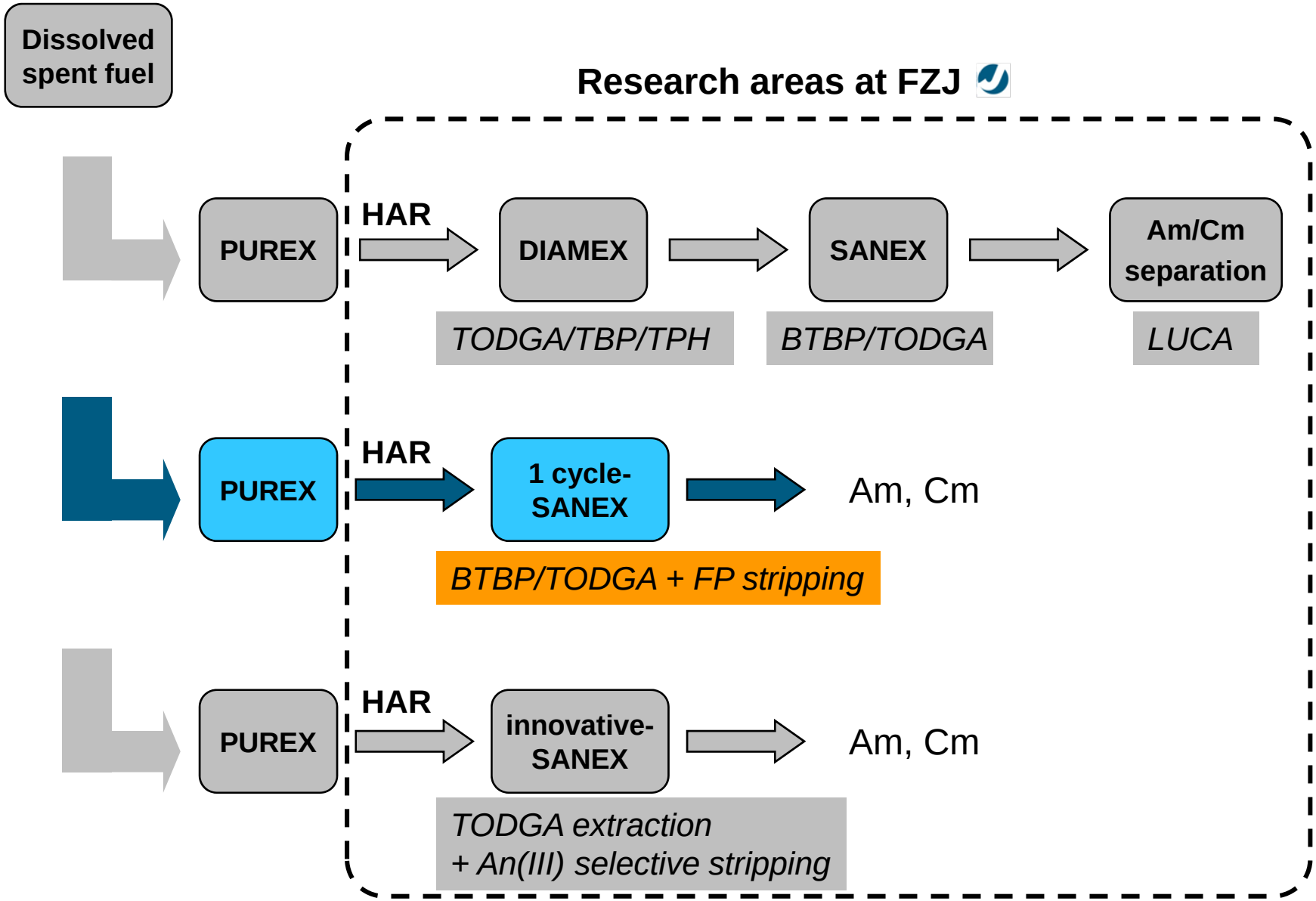
^{241}Am > 99.9 %
^{244}Cm ~ 99.7 %
^{252}Cf > 99.9 %
Ln(III) < 0.1 %
^{152}Eu ~ 0.8 %
Y(III) ~ 3.2 %

Strip
Glycolic acid 0.5 M
set to pH 4
10 mL/h

Is it possible to directly extract An(III) from a PUREX raffinate?

[2]Modolo, G. et al., Tenth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mito, Japan, **2008**.

Overview of the processes



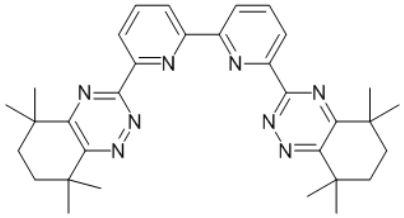
1-cycle SANEX – preliminary tests[3]

+ High selectivity of the extractant ($CyMe_4BTBP$) for An(III) over Ln(III) and most FP from HAR at 3 M HNO_3
+ Hydrolytic- / radiolytic stability
– Slow kinetics
• TODGA is used as phase transfer reagent

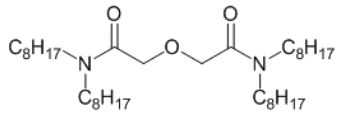
– Coextraction of some fission products (Zr, Mo, Pd, Y, Cu, Ag, Cd, Ni)
+ Oxalic acid works for Zr, Mo
– HEDTA (used in the DIAMEX process) does not work for Pd

Task:

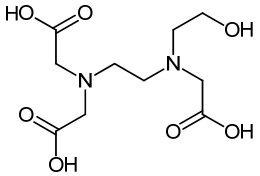
Find a selective masking agent for Pd



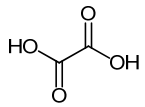
$CyMe_4BTBP$



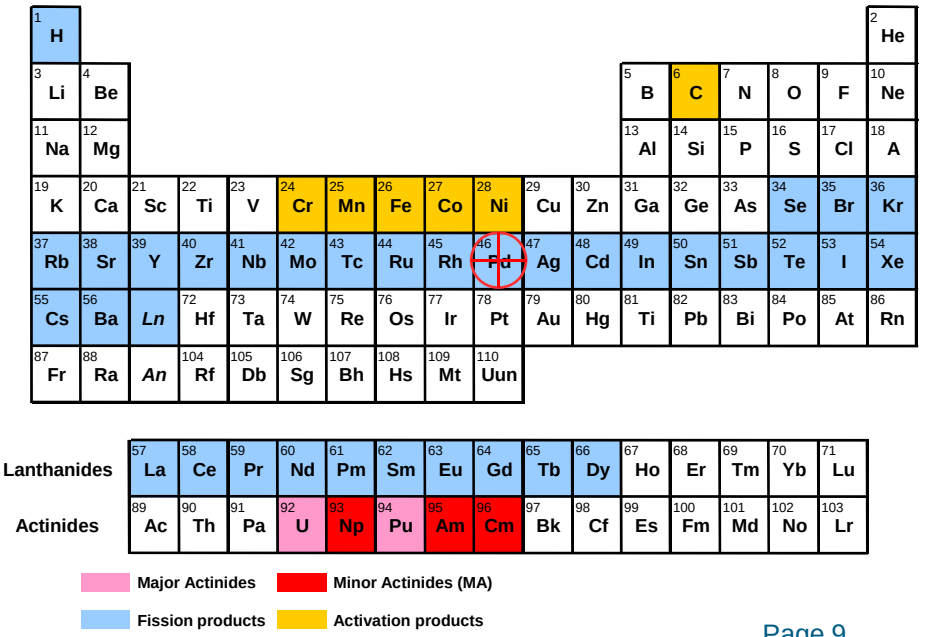
TODGA



HEDTA

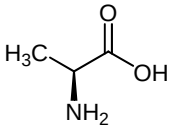


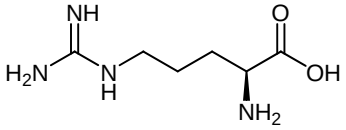
Oxalic acid

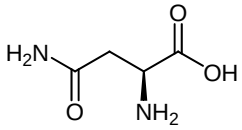


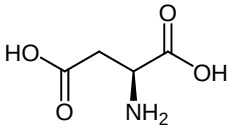
[3] Wilden et al. Solv. Extr. Ion Exch. accepted.

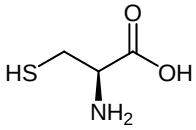
Screening of amino acids and derivatives
- Overview of the tested substances -

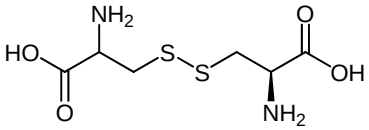

L-Alanine (Ala)
1

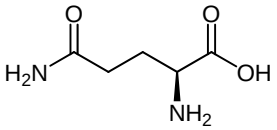

L-Arginine (Arg)
2

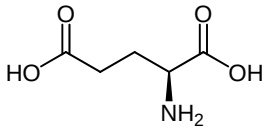

L-Asparagine (Asn)
3

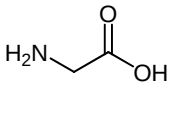

L-Aspartic acid (Asp)
4

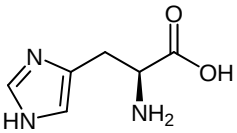

L-Cysteine (Cys)
5

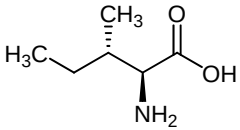

L-Cystine
6

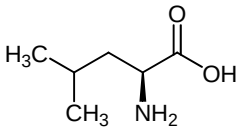

L-Glutamine (Gln)
7

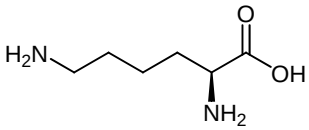

L-Glutamic acid (Glu)
8

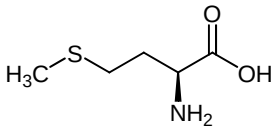

L-Glycine (Gly)
9

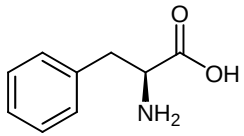

L-Histidine (His)
10

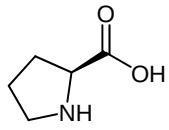

L-Isoleucine (Ile)
11

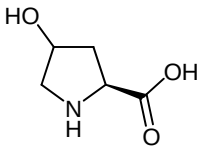

L-Leucine (Leu)
12

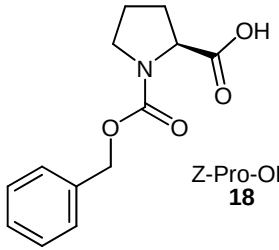

L-Lysine (Lys)
13

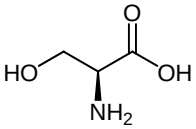

L-Methionine (Met)
14

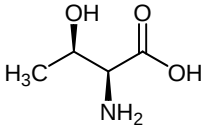

L-Phenylalanine (Phe)
15

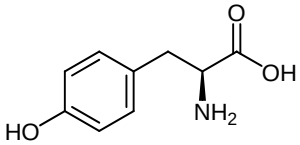

L-Proline (Pro)
16

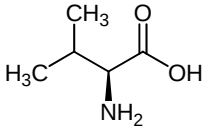

L-4-Hydroxy-proline
17


Z-Pro-OH
18

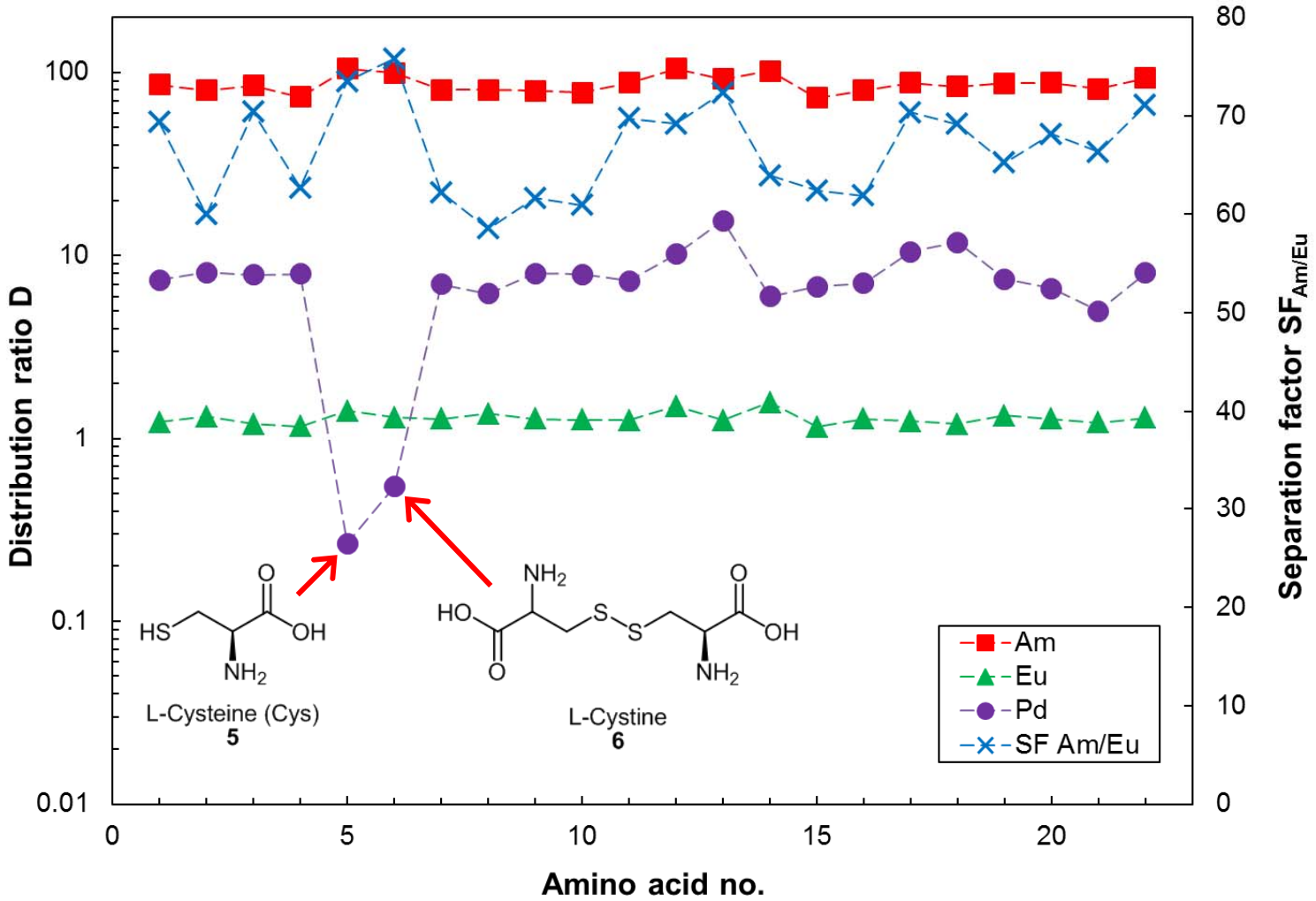

L-Serine (Ser)
19


L-Threonine (Thr)
20


L-Tyrosine (Tyr)
21


L-Valine (Val)
22

Screening of amino acids and derivatives
- Results of the screening tests -



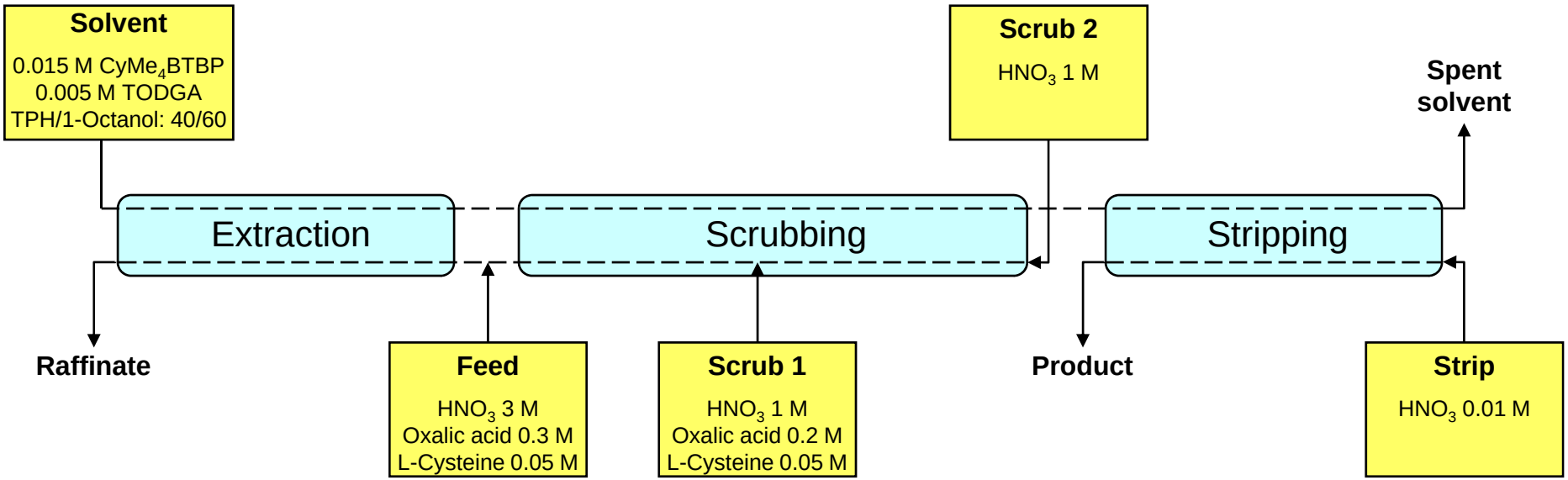
$$D = \frac{c_{org}(M)}{c_{aq}(M)}$$

$$SF = \frac{D(M_1)}{D(M_2)}$$

org. phase: 0.015 M $CyMe_4BTBP$, 0.005 M TODGA in TPH/1-Octanol (40/60)

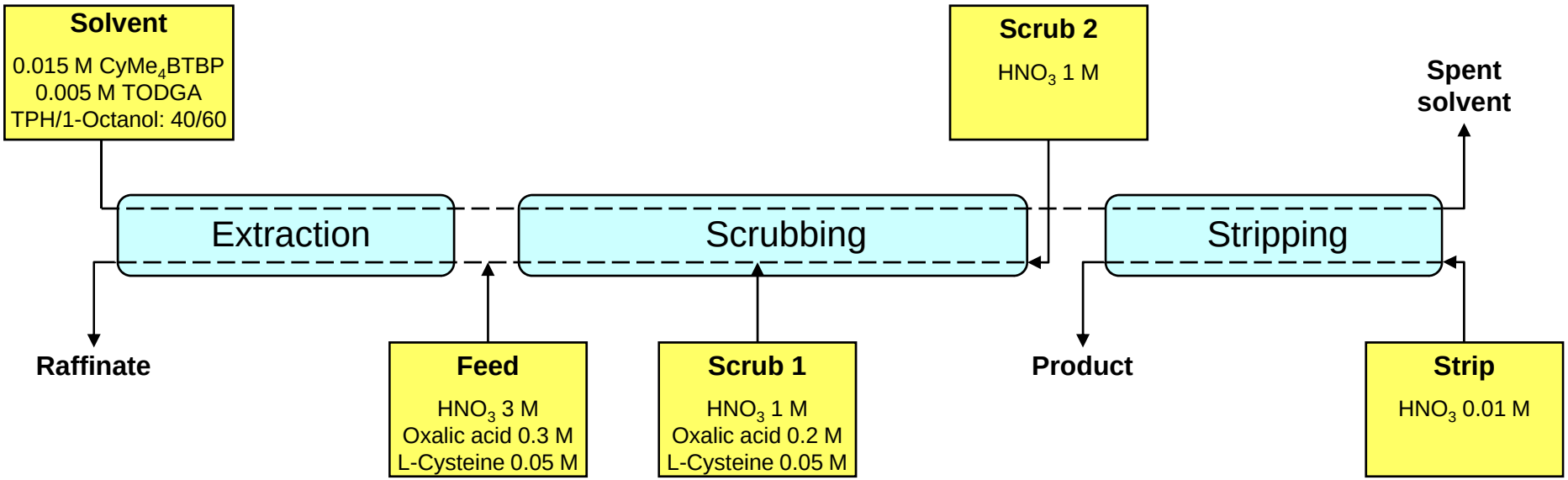
aq. phase: 3 M HNO_3, 150 mg/L Pd (0.0015 M), 0.1 M amino acid + radiotracer, 15 min., 22°C

Batch-tests with simulated HAR-solution

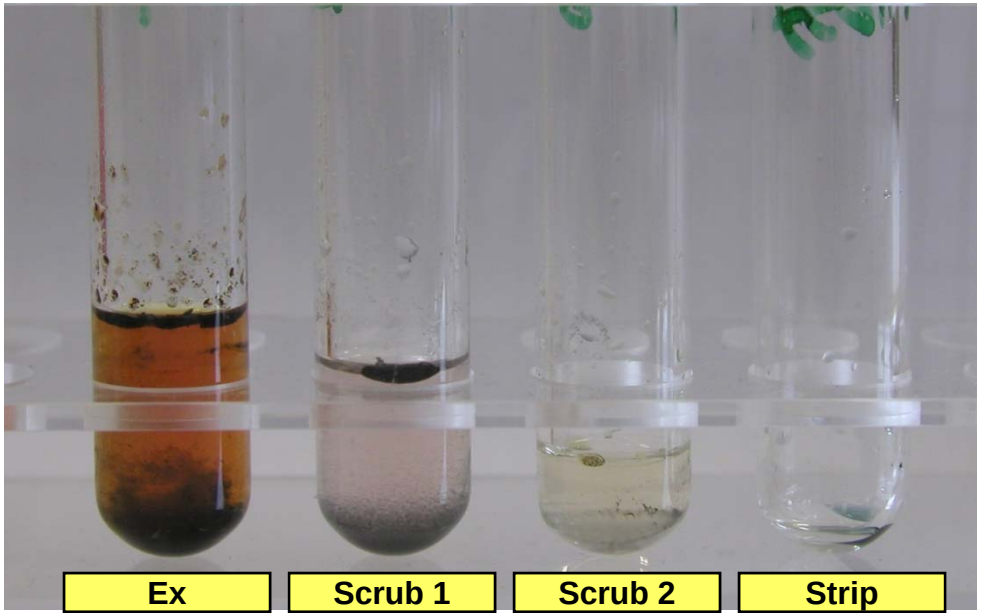


Element	Conc. [mg/L]	Element	Conc. [mg/L]	Element	Conc. [mg/L]
Fe	1900	Mo	678	Ni	40
Zr	1071	Cs	542	Cu	19
Na	1600	Ru	356	Cd	15
Nd	718	Ba	259	Ag	12
Ce	567	Sr	177	Sn	11
La	239	Pd	168	Se	10
Pr	223	Te	165	Sb	4.6
Sm	149	Cr	93	Al	2
Gd	51	Y	90	^{241}Am	trace amounts
Eu	34	Rh	73	^{244}Cm	trace amounts
^{152}Eu	trace amounts	Rb	63		

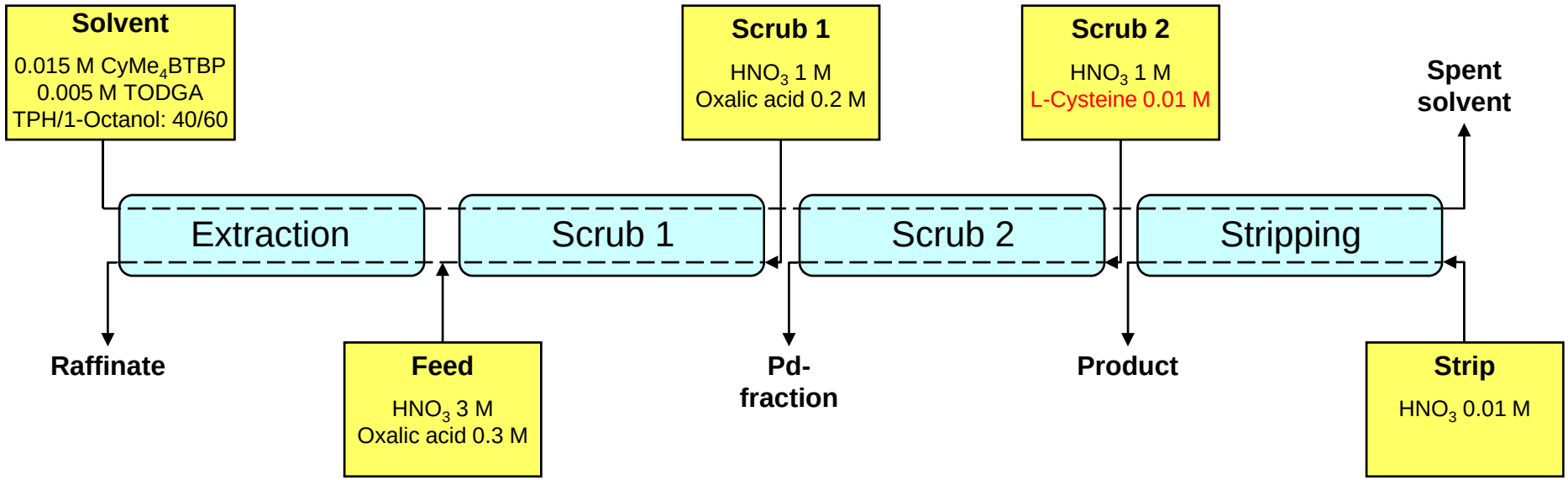
Batch-tests with simulated HAR-solution



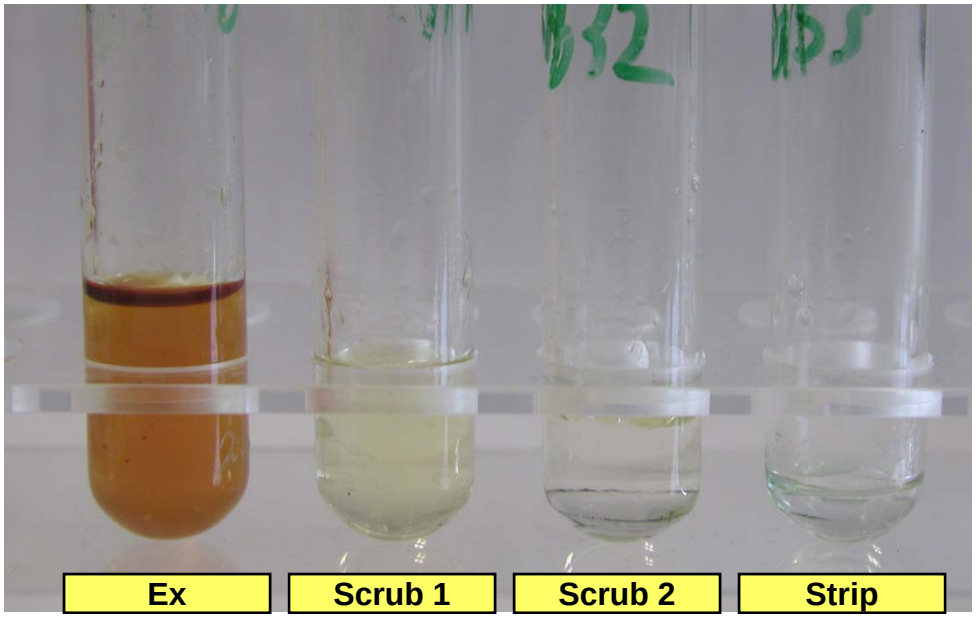
- Voluminous Precipitation during the extraction with L-Cysteine
- Precipitation should be avoided!



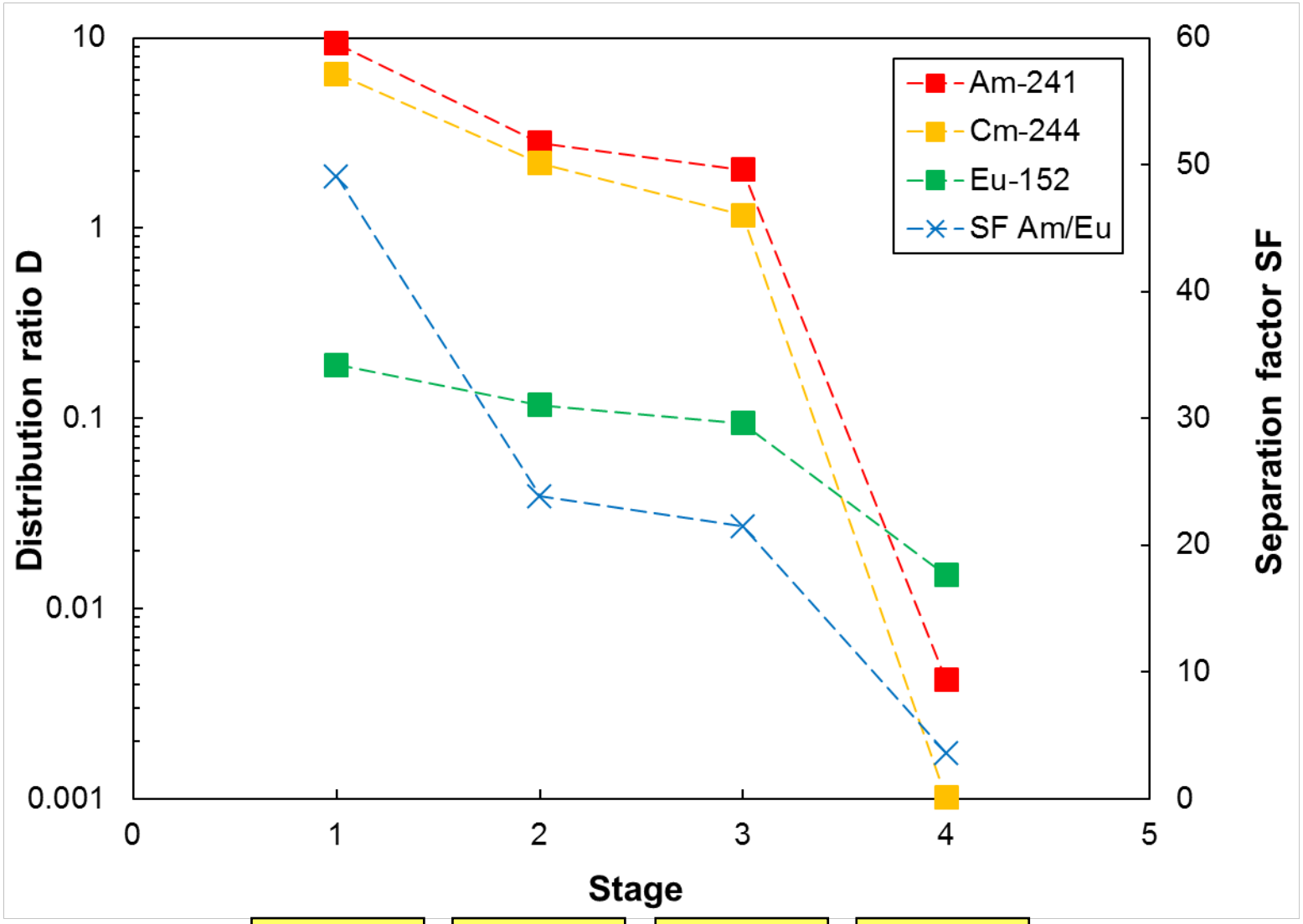
Batch-tests with simulated HAR-solution



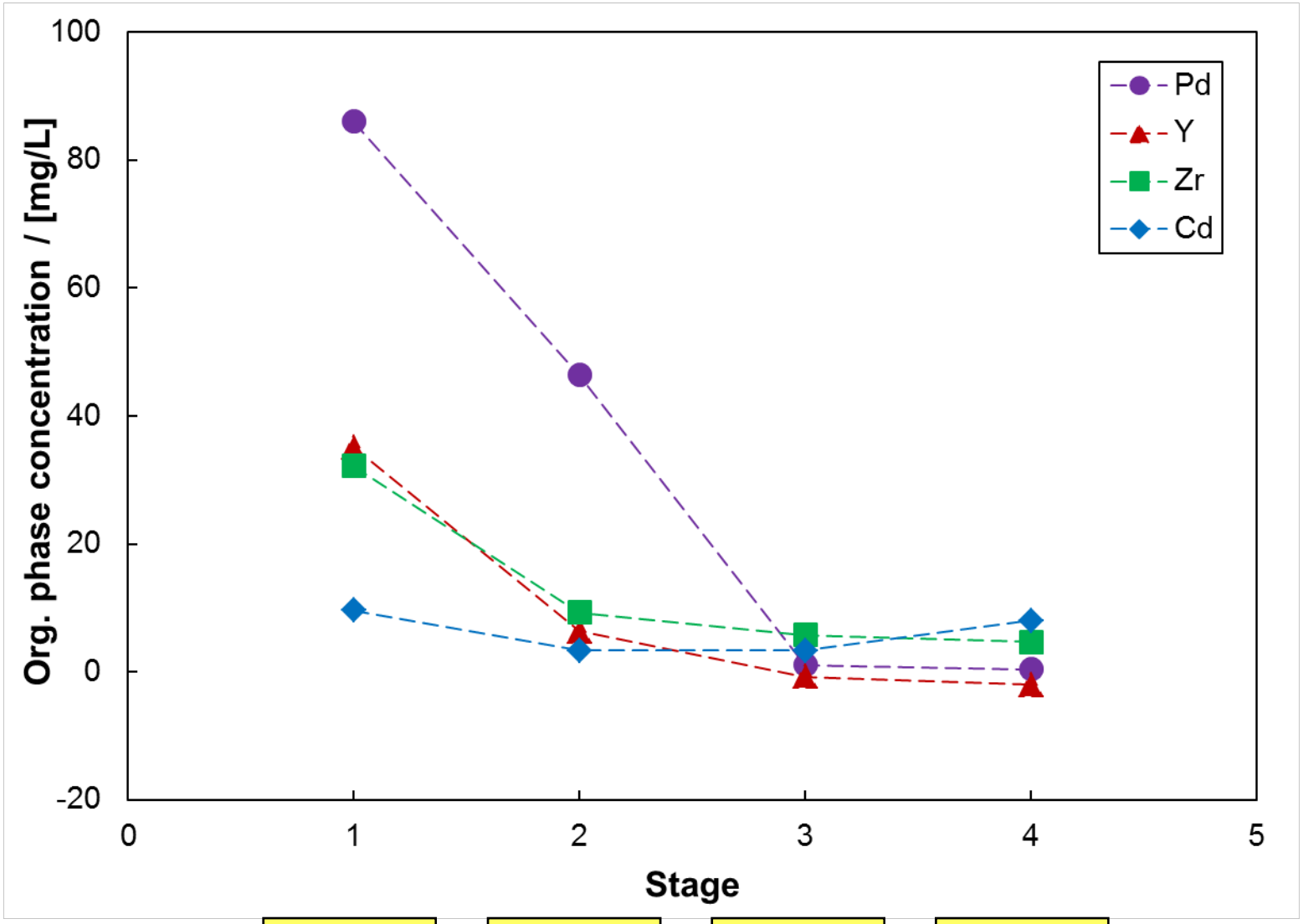
\+ No Precipitation!



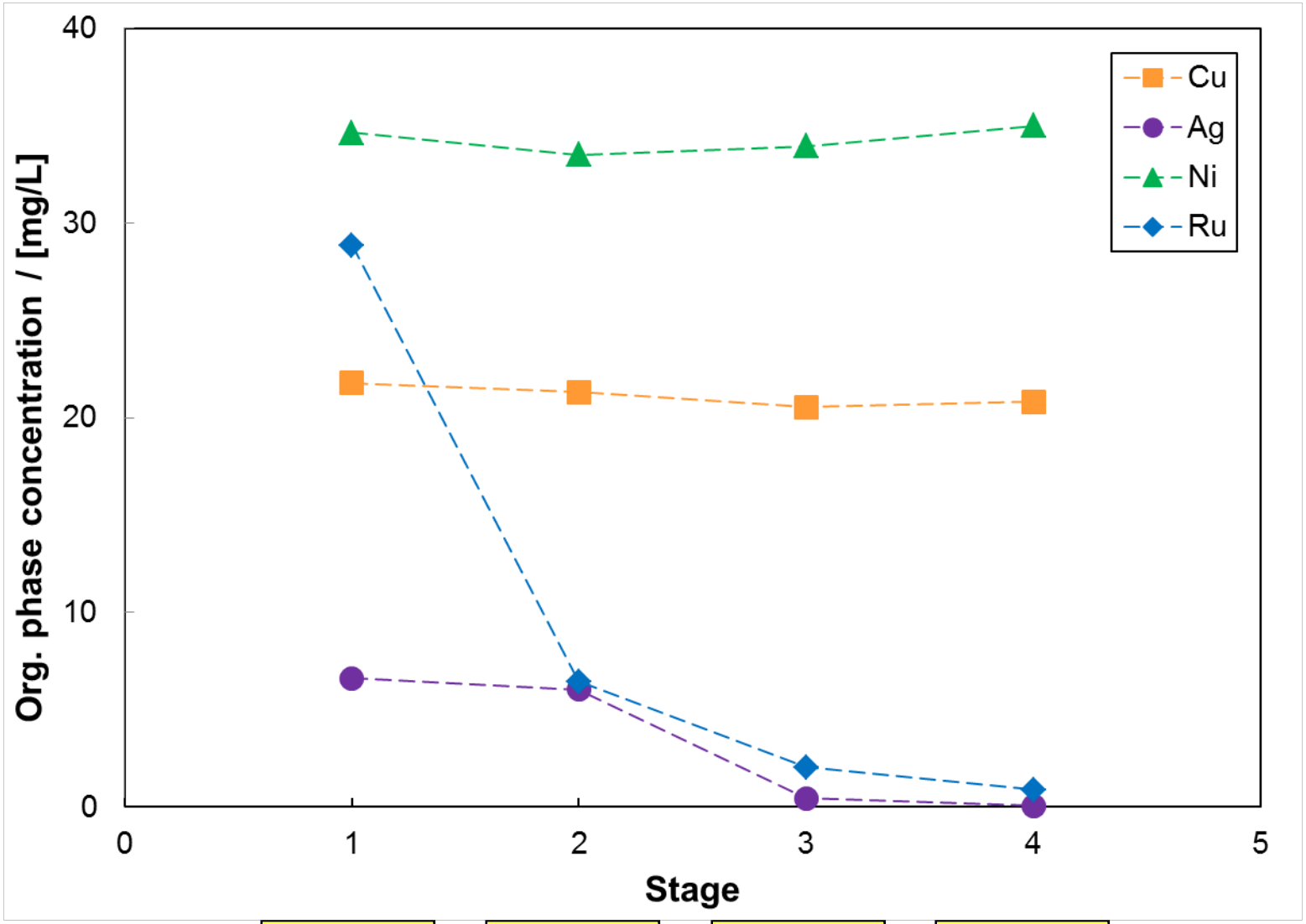
Batch-tests with simulated HAR-solution



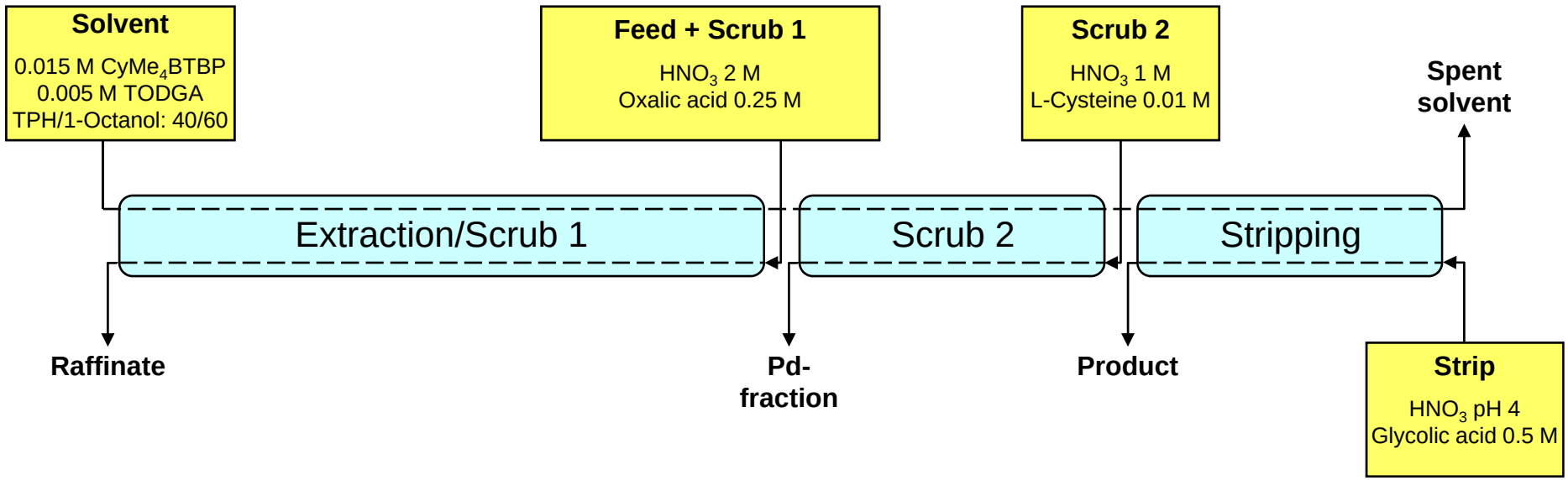
Batch-tests with simulated HAR-solution



Batch-tests with simulated HAR-solution

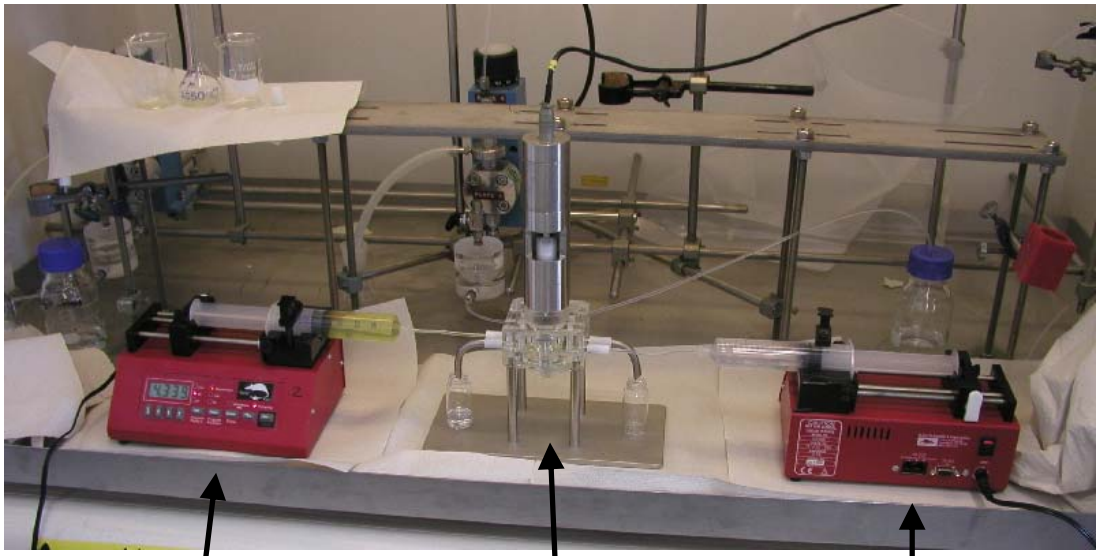


Single centrifuge tests



- Feed solution a 1:1 mixture of HAR-element (3 M HNO_3 + 0.3 M oxalic acid) solution and Scrub 1 solution (1 M HNO_3 + 0.2 M oxalic acid)
- Extraction test at different flow rates
- Stripping with:
  - pH 4 + 0.5 M glycolic acid
  - pH 3 without complexant
  - pH 2 without complexant

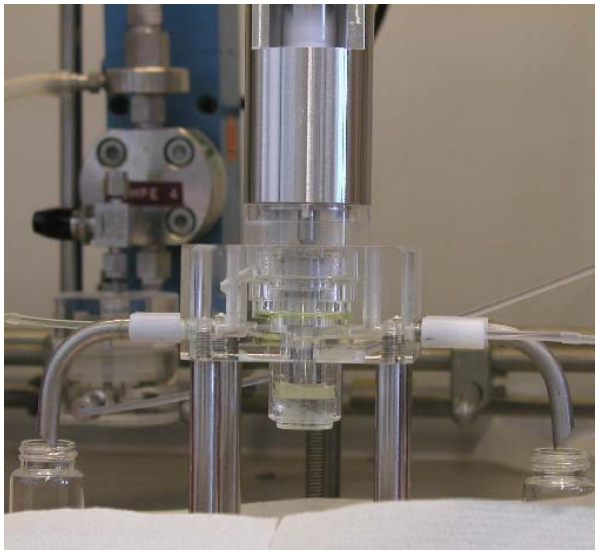
Experimental setup



Syringe pump
org. phase

Single centrifuge

Syringe pump
aq. phase

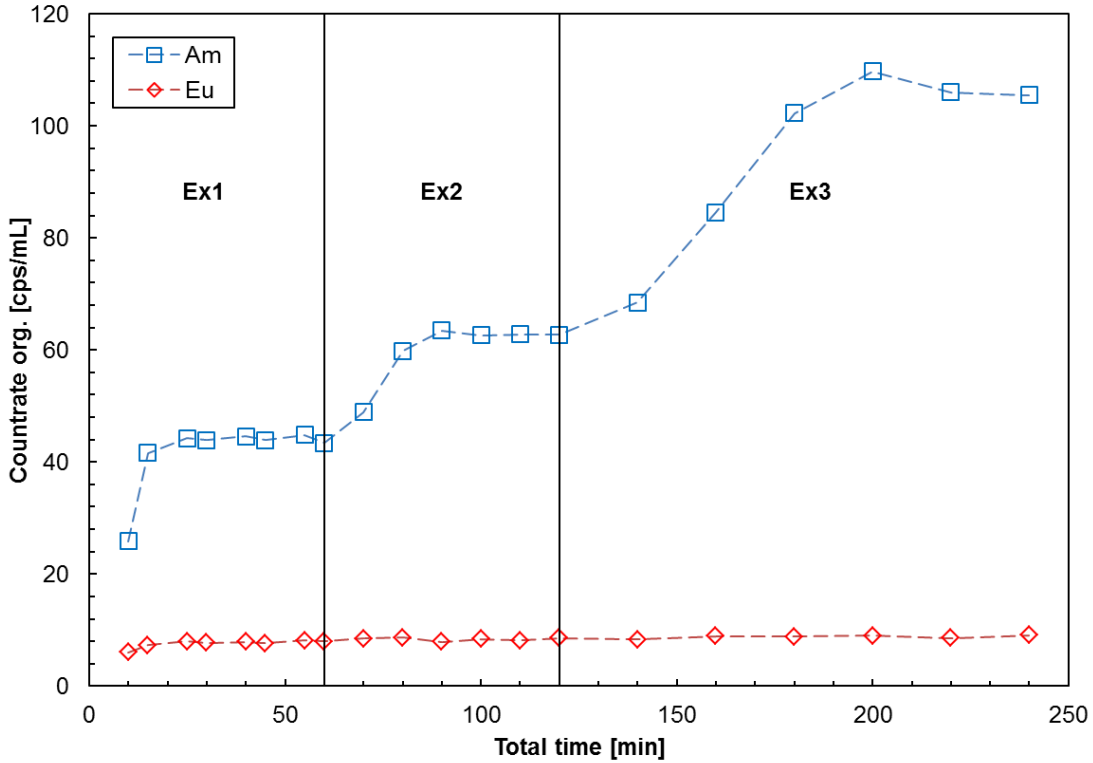


Acrylic glass mixing chamber
and housing
Stainless steel rotor

- Test at different flow rates
- Mixing chamber volume approx. 5.5 mL

Extraction test

	Flow rate org. [mL/h]	Flow rate aq. [mL/h]	Experiment time [min]	Total time [min]
Ex1	20	40	60	60
Ex2	10	20	60	120
Ex3	5	10	120	240



- Steady-state plateau is reached after ~3-4 exchanges of the mixing chamber volume
- After reaching the plateau the flow rates were changed
- Efficiency increases with decreasing flow rate

Extraction test

	Flow rate org. [mL/h]	Flow rate aq. [mL/h]	Distribution ratio		SF
			Am	Eu	Am/Eu
Ex1	20	40	0.85	0.18	4.7
Ex2	10	20	1.38	0.17	8.1
Ex3	5	10	5.72	0.21	27
Equilibrium value by shaking the content of the mixing chamber after Ex3:			12.3	0.23	54

Distribution ratios D for inactive elements at Ex2 conditions:

Element	D	Element	D	Element	D
Pd	2.46	Ag	0.74	Cu, Ni, Cd	>10
Y	0.39	Mo	0.10	La	0.02
Ce	0.03	Pr	0.04	Nd	0.06
Sm	0.12	Eu	0.16	Gd	0.12
Zr	<0.01	Fe, Ru	<0.10	Rh, Rb, Sr, Ba, Cr, Sn, Sb, Te, Cs	<0.01

Lanthanides follow the trend reported by Geist et al., Solvent Extr. Ion Exch., 2006, 4, 463

Scrubbing with L-Cysteine

- Flow rates for the scrubbing and the stripping tests were set to 10 mL/h for both phases
- Aq. phase was prepared freshly
- All loaded org. phase samples of the extraction test were combined after analysis and used for the scrubbing test

	HNO_3	Complexant	Distribution ratio			
			Am	Eu	Pd	Ag
Sc1	1 mol/L	0.1 M L-Cysteine	8.36	0.65	0.34	0.55
Equilibrium value by shaking the content of the mixing chamber after Sc1:			1.84	0.07	0.03	0.06

- Equilibrium values were not reached in one step, affording a larger number of stages
- Cu, Ni and Cd stayed in the org. phase and were not scrubbed
- Mo, Ru, Y and the Lanthanides were partly back-extracted

Stripping

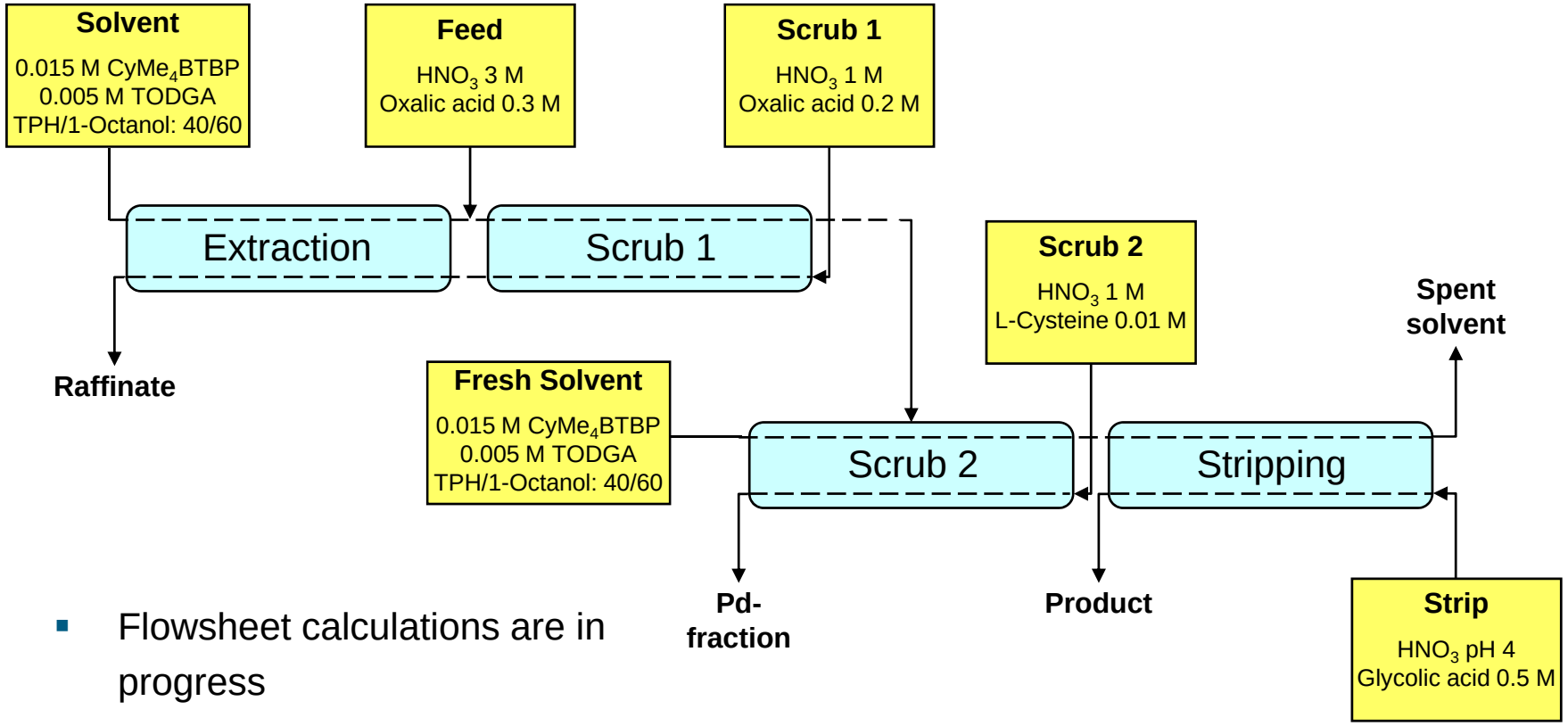
	HNO_3 pH	Complexant	Distribution ratio	
			Am	Eu
St1	4	0.5 M Glycolic acid	0.11	0.08
St2	3	-	0.74	0.15
St3	2	-	0.67	0.13
Equilibrium value by shaking the content of the mixing chamber after St3:			0.01	0.01

Results:

- Cu, Ni and Cd stay in the org. phase, no contamination of the aq. Phase
- Still some Pd, Ru and Mo in both, the org. and aq. phase
- Little contamination of the aq. Phase with Y and lanthanides

- Slow stripping kinetics
- Best results with glycolic acid at pH 4

Flowsheet of a planned spiked counter-current test



- Flowsheet calculations are in progress
- No. of stages for quantitative extraction of Am/Cm
- No. of stages for quantitative scrubbing of Pd without loss of Am/Cm
- No. of stages for a sufficient separation of coextracted fission/corrosion products

Conclusions and outlook

+ It is possible to directly extract An(III) from a PUREX raffinate!
+ No Precipitation during the extraction
+ No 3rd phase formation
+ Am and Cm are selectively extracted and stripping is possible
+ Ag, Y and Ru can be scrubbed in the scrubbing sections
+ Zr and Mo are masked by oxalic acid
+ Pd is scrubbed by L-Cysteine

– Cu, Ni and Cd are nearly completely extracted and remain in the org. phase
– Solvent clean-up is necessary

- Flow sheet design
- Solvent clean-up studies
- Spiked process demonstration test
- Hot process demonstration test

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Thank you for your kind attention!