The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA

1858-30

School on Physics, Technology and Applications of Accelerator Driven Systems (ADS)

19 - 30 November 2007

Partitioning. Part I

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EUROPEAN COMMISSION

Partitioning 1

Jean-Paul Glatz

School on Physics, Technology and Applications of Accelerator Driven Systems

November 19th -30th 2007

Trieste, Italy

Outline 1

- introduction
- some historical background
- basic principles and data

break

- process developments
- international networks and collaborations
- outlook

Fuel Cycle Back-End

spent nuclear fuel

spent fuel storage

interim

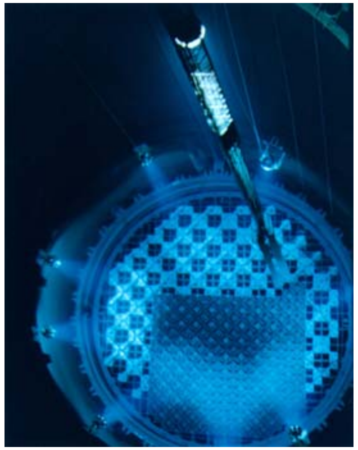
short - term

long - term

final

non-retrievable

retrievable



reprocessing

aqueous (PUREX + advanced)

pyro (IFR /RIAR + advanced)

metallic

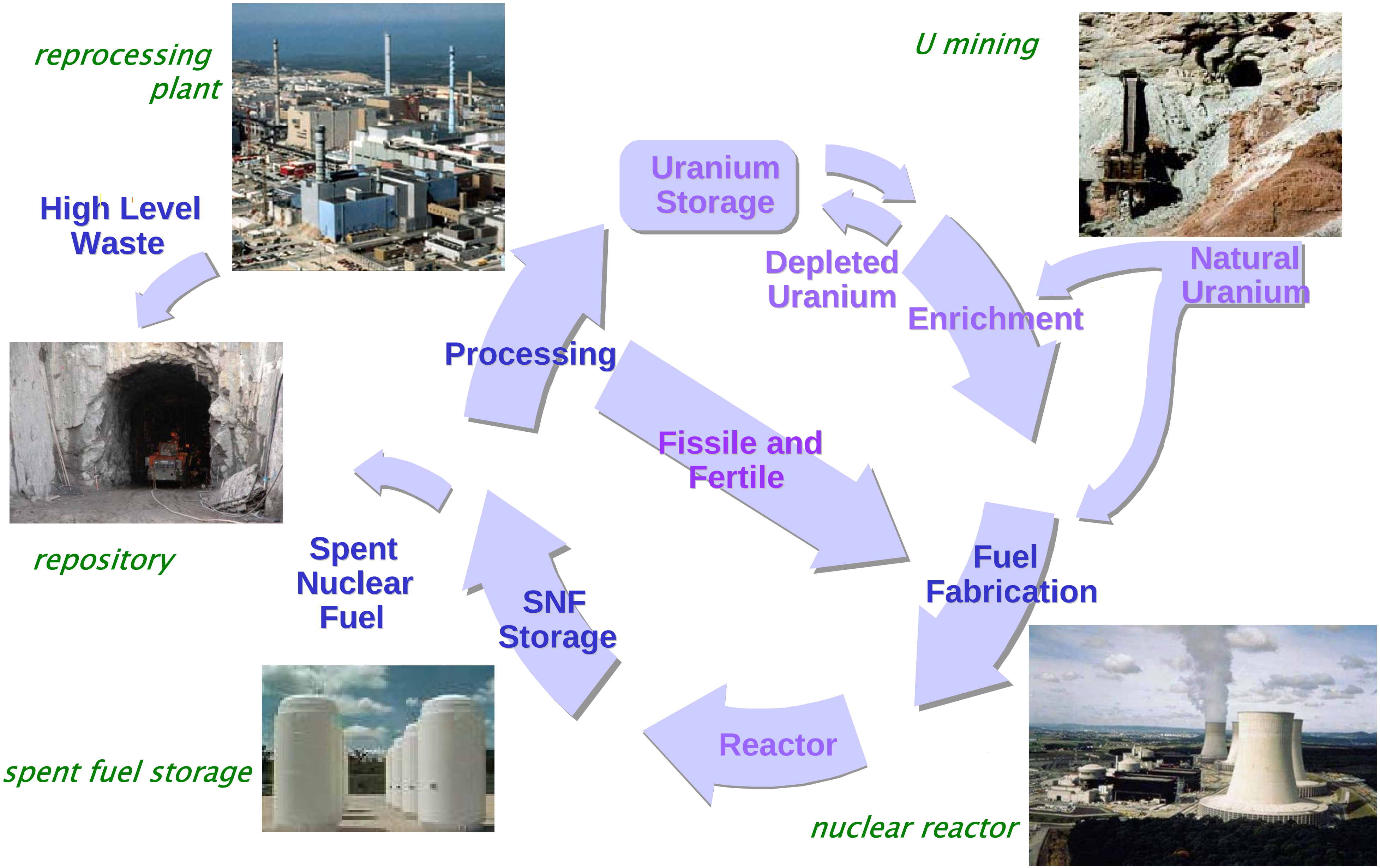
oxide

separated radiotoxic elements

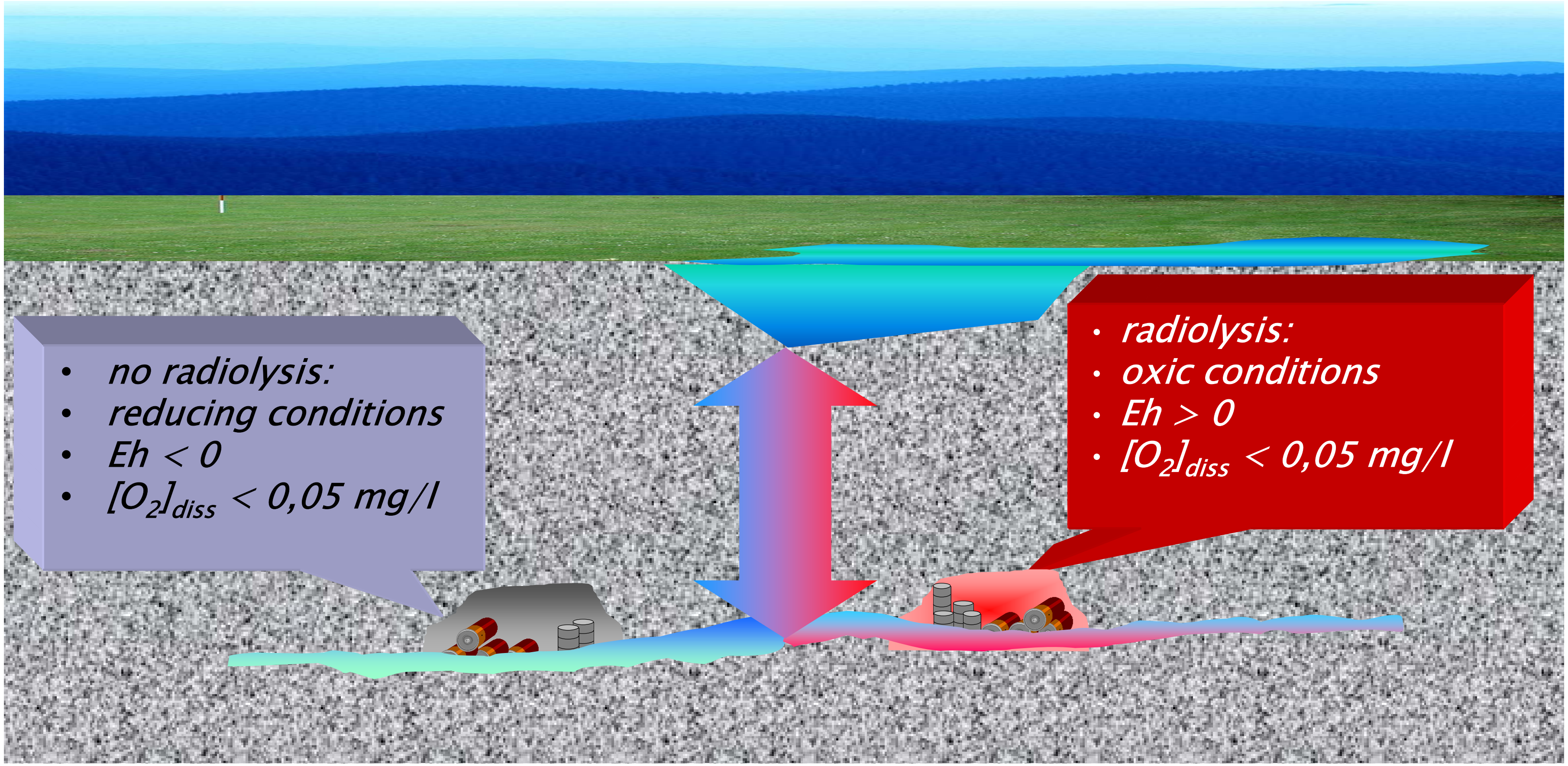
solidification

transmutation

The Nuclear Waste Management Options



Long-Term Storage of Spent Fuel



spent fuel corrosion in water depends on redox conditions that are established in the repository by combined geochemical and radiolysis effects

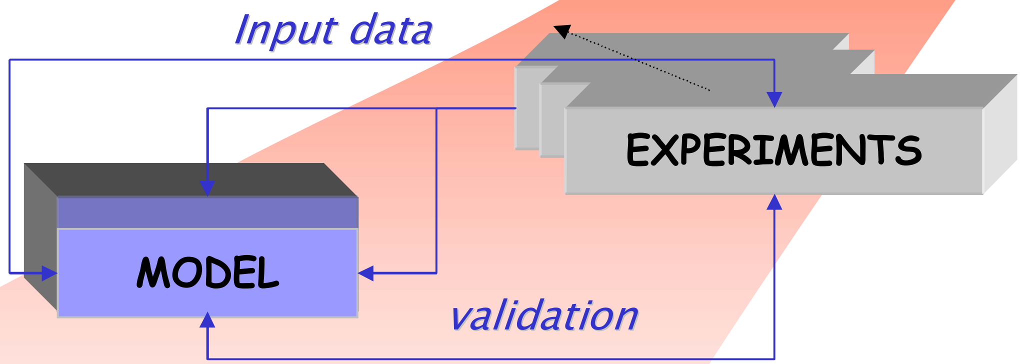
Nuclear Waste Disposal

European repository concept

Strategy

public acceptance of spent fuel (waste) repository depends on reliable assessment therefore assessment procedures (models) need reliable source-term data under realistic conditions (redox, genuine fuel)

investigates key processess affecting the barrier performance of the near-field environment



quantitative assessement of the long-term behaviour of the overall near-field system

European programs:

Spent fuel Stability SFS

Near Field NF PRO

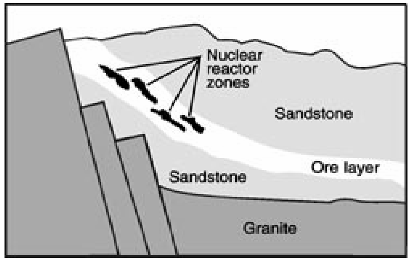
MICADO RECOSY

SEVENTH FRAMEWORK PROGRAMME

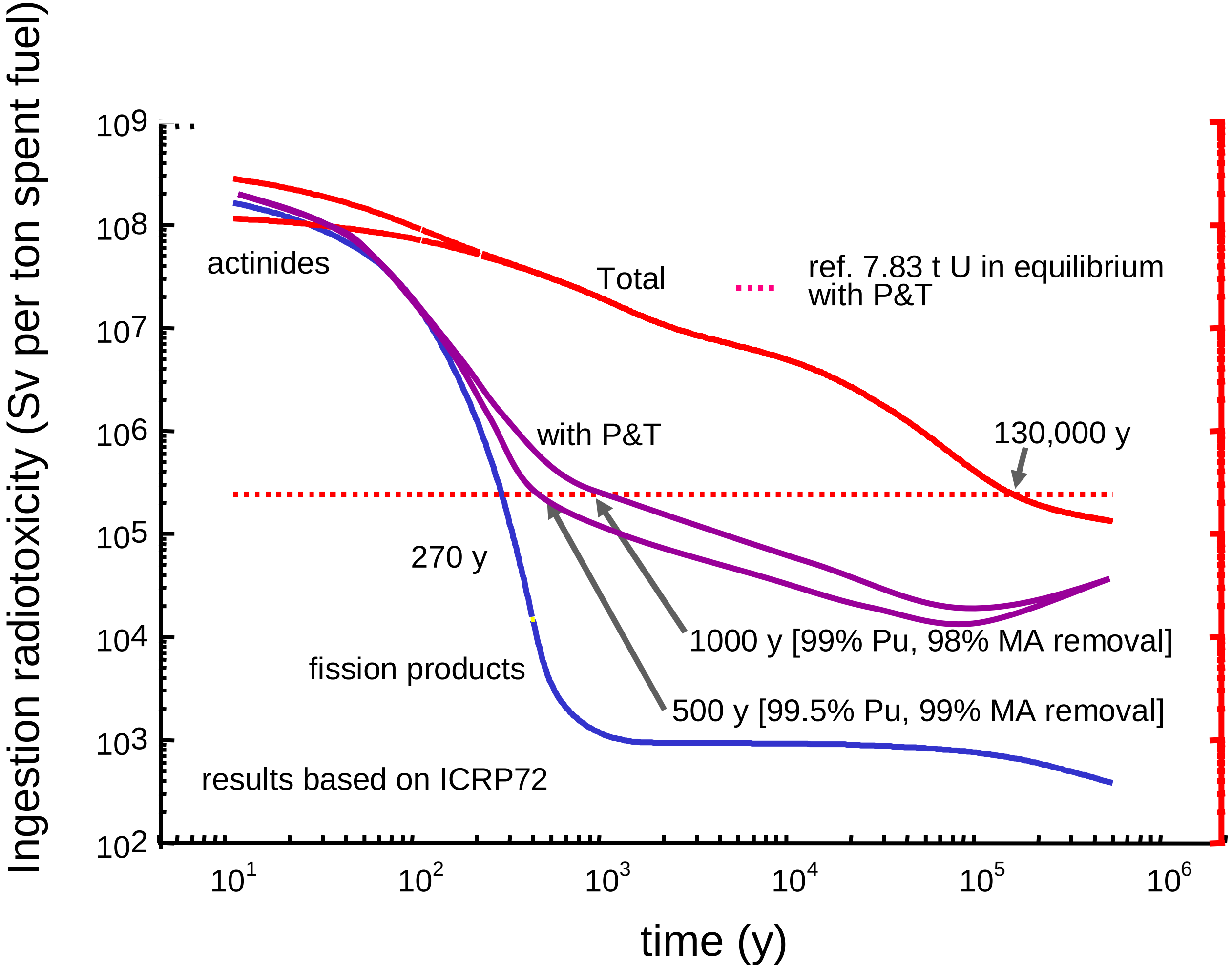
Waste Radiotoxicity
natural & societal analogues

Dunarobba forest

Oklo reactors



The Needle's Eye

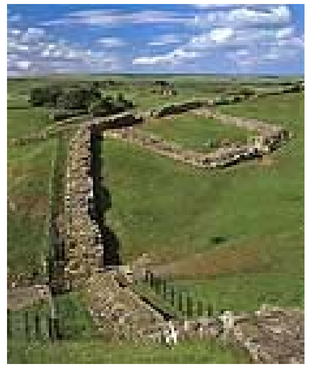


Evolution of radiotoxicity as a function of time: evaluation by CEA, FZK and ITU

Inchtuthil Roman nails

Kronan cannon.

Hadrian's Wall



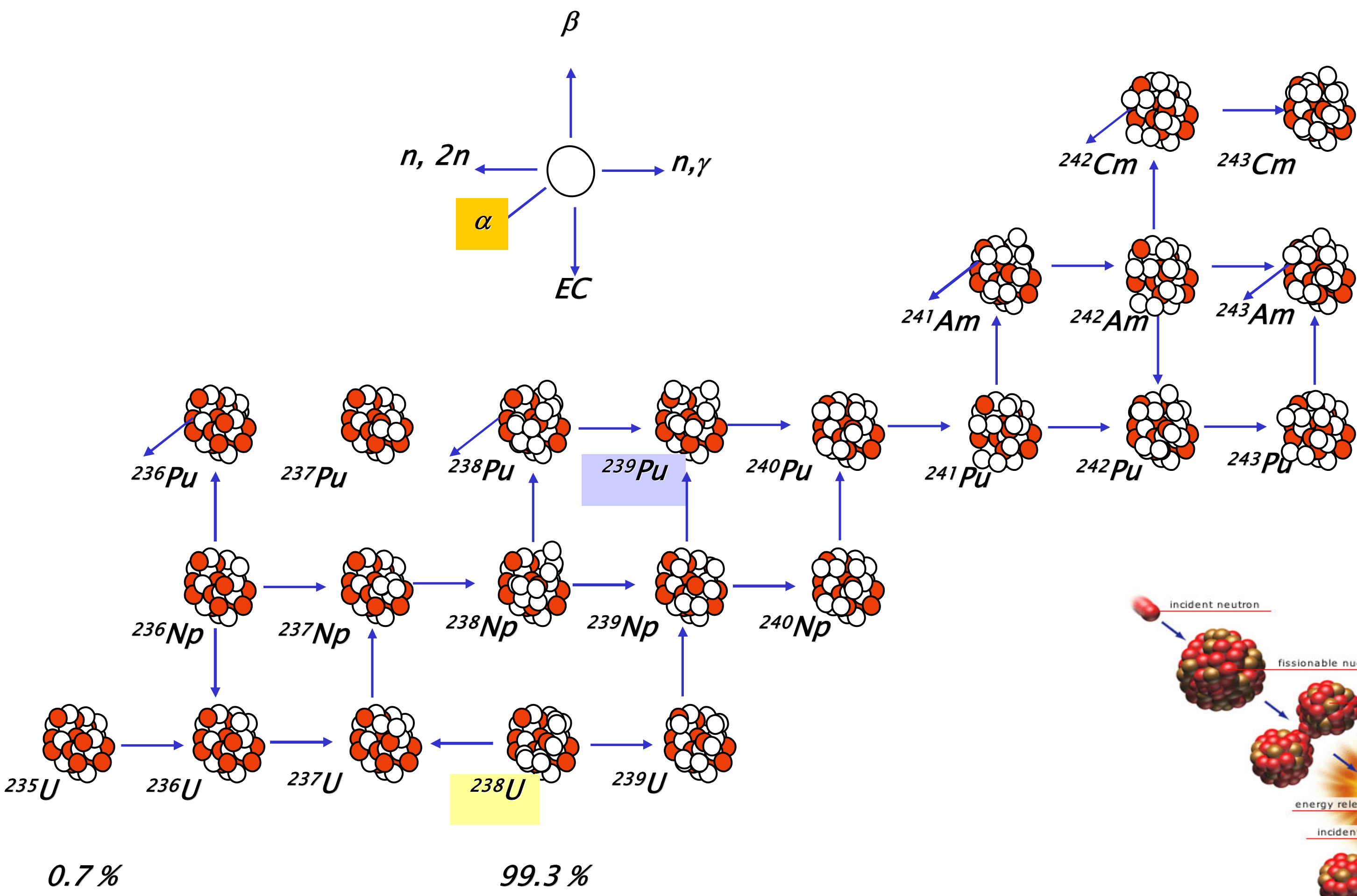
Reprocessing: main requirements

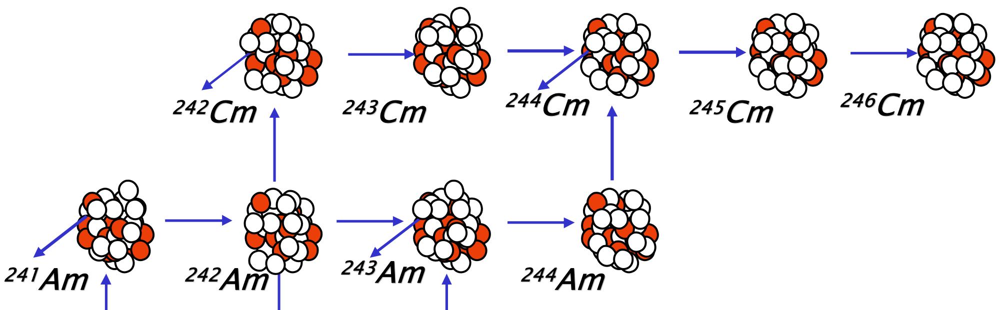
- *Safety*
  - Environmental impact : liquid and gas release waste forms performance
  - Irradiation, criticality
- *Safeguards*
  - Accurate fissile material monitoring
- *Reliability*
  - Chemical, radiolytical long-term effects
- *Economics; costs*

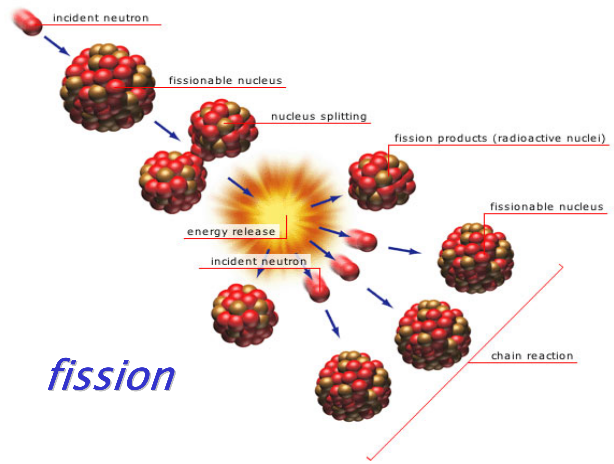
Composition of irradiated fuels

FUEL TYPE		LWR-UOX			LWR-MOX
AVERAGE BURN-UP (GWd/t)		33	45	60	45
COMPOSITION	Pu (g/tU)	9 740	11 370	12 990	48 850
	Np (g/tU)	433	611	887	161
	Am (g/tU)	325	521	765	4 480
	Cm (g/tU)	23	92	213	810
	Zr (g/tU)	3 580	4 740	6 280	3 440
	Tc (g/tU)	814	1 085	1 403	977
	Ru (g/tU)	2 165	3 068	4 156	3 924

Actinide built-up by neutron capture







Spent Fuel Characteristics

- *Extreme diversity*
  - Physico-chemical composition : gas - solids (oxides, metals)
  - Radioactive characteristics : short-lived and very long-lived nuclides
- *Minor Actinides (main contribution to long-term radiotoxicity)*
  - Neptunium, Americium, Curium
- *Fission Products*

  (more « mobile » in repository conditions)
  - Iodine (^{129}I), Cesium (^{135}Cs), Technetium (^{99}Tc)

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PUREX PROCESS

Plutonium Uranium Refining by EXtraction

Recovering and Purifying

URANIUM

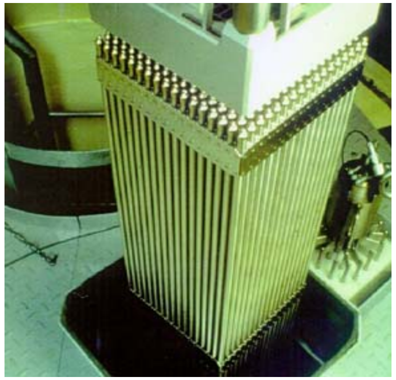
PLUTONIUM

SPENT FUEL

PUREX

WASTE

Confining and Concentrating



SAFETY

RELIABILITY

FLEXIBILITY

COSTS

PUREX PROCESS

Plutonium Uranium Refining by EXtraction

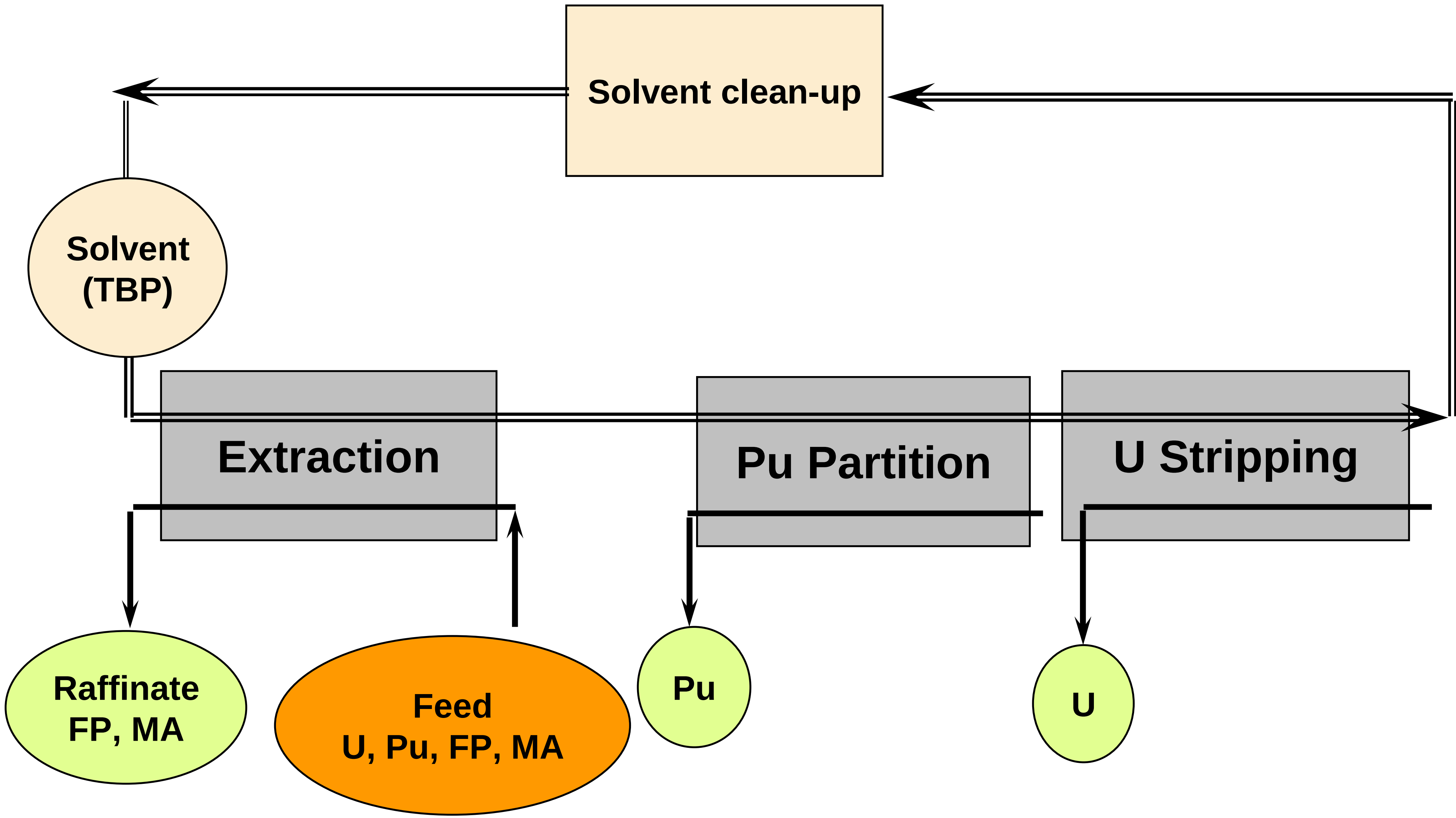
1950s Savannah, Hanford

1953 Windscale

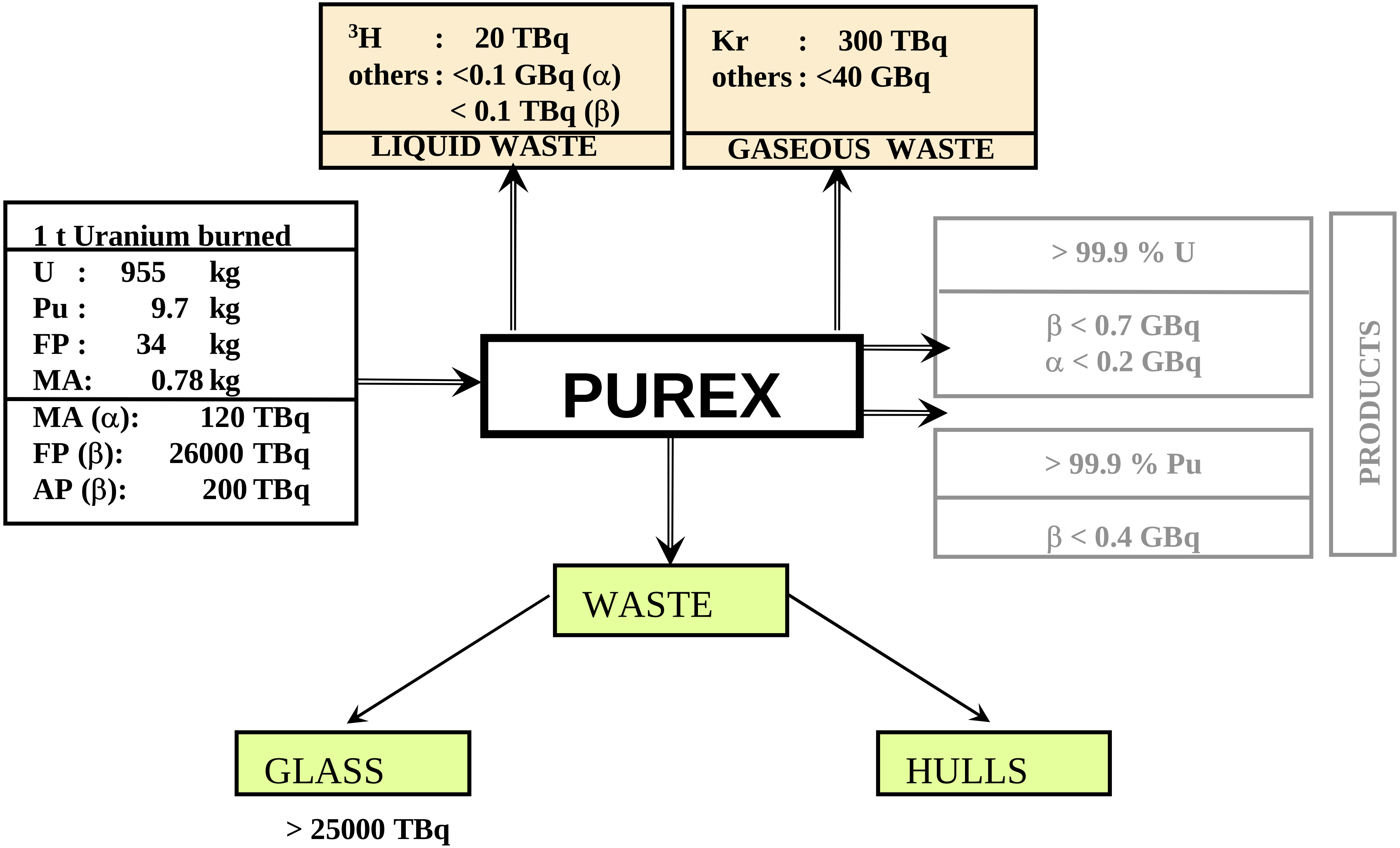
1994 Sellafield

1958 Marcoule, UP1
1967 La Hague, UP2
1976 La Hague, UP2-HAO
1989 La Hague, UP3
1994 La Hague, UP2-800

PUREX process: extraction cycles



Performances of PUREX process



PUREX PROCESS

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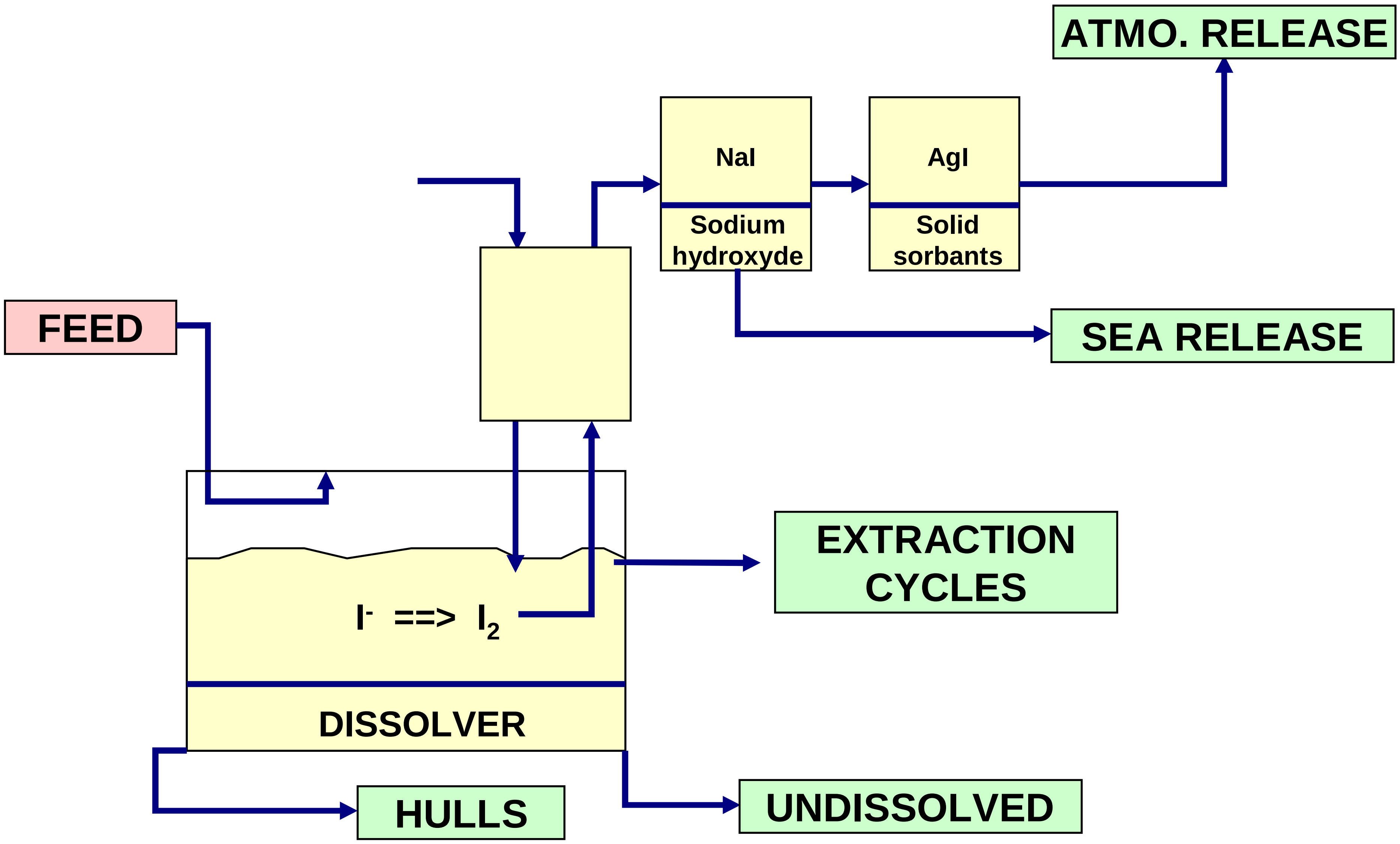
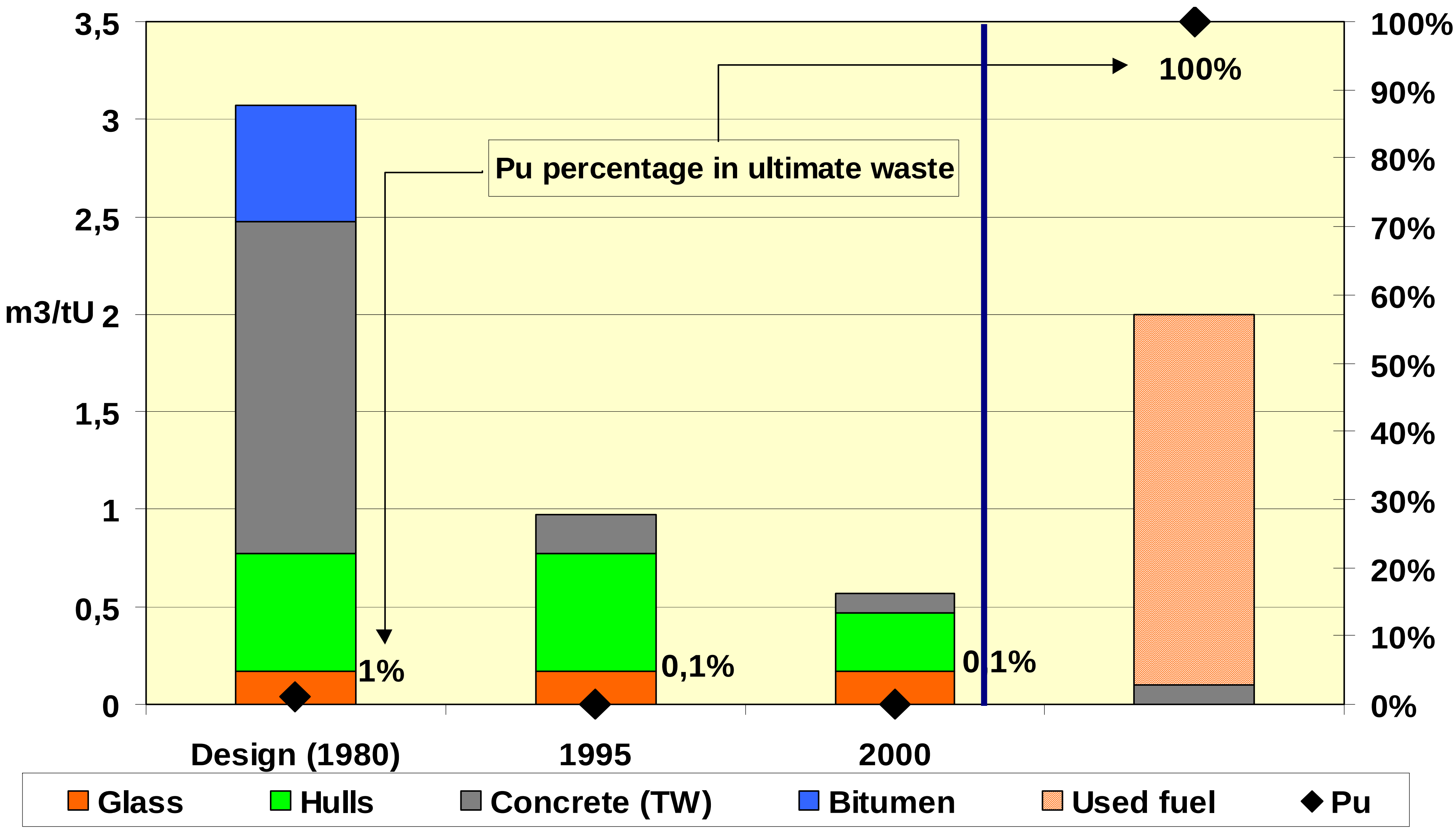


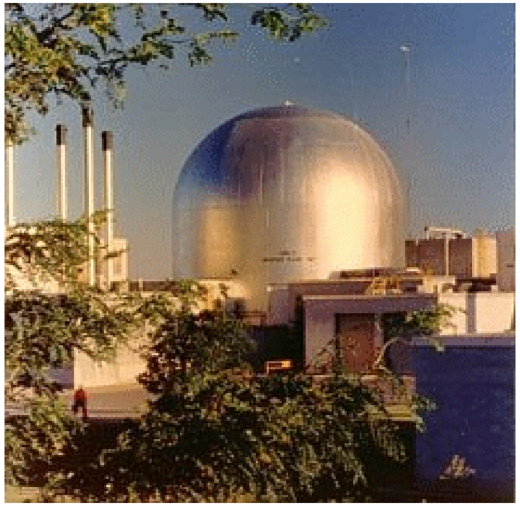
Waste volumes



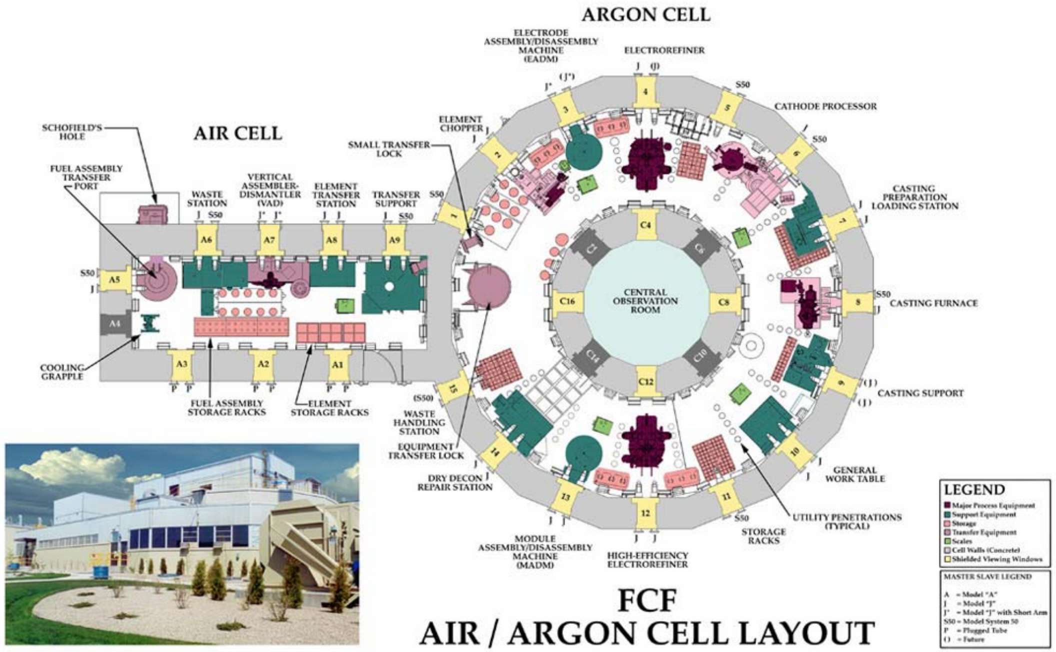
Integral Fast Reactor (IFR) in ANL-W

reactor and Fuel Conditioning Facility (FCF)

- remotely-operated integrated reprocessing and refabrication facility
- demonstrate fuel reprocessing for EBR-II fuel (100 Kg scale)
- road-map issued by DOE, which describes R&D steps necessary to develop a waste transmuter based on the metallic fuel cycle concept



1959: integral nuclear power plant



Research Institute of Atomic Reactors (RIAR)

- research focussed on electrochemical processes for the production of U, Pu oxide granulates (VIPAC) and for the reprocessing of irradiated fuel
- oxide pyrochemical process operated in air atmosphere
- several kg's of irradiated fuels reprocessed in DOVITA (Dry Oxide Vibropac Integral Transmutation of Actinides) process (minor actinides not included)

RIAR in Dimitrovgrad

Nuclear Fuel Cycle Strategy

double strata concept

commercial reactor
EPR, Olkiluoto, Finland

spent fuel

fresh fuel (MOX)

reprocessing plant
La Hague, France

PUREX & advanced aqueous

Integral fast reactor or ADS

Monju, Japan

INL, US

long-lived MA, Tc, I

pyro

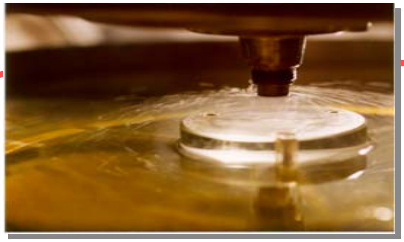
short lived fp

short lived waste

waste repository
SFR, Forsmark, Sweden

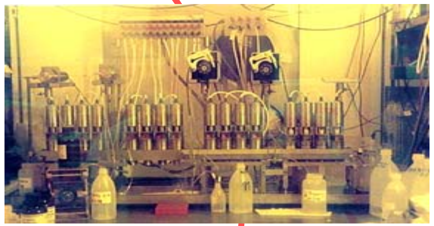
CEA- ITU MA burning experiment (1990)

fuel characterization



fuel fabrication

separated actinides (Np, Am, Cm)



reprocessing

SUPERFACT EXPERIMENT

(U,Pu,Np,Am)O_2
Np: 2-45%
Am: 2-20%

irradiation (PHENIX)
360 EFPD

post irradiation examination

transmutation rate ~ 30%

ITU competences: P&T

Aqueous partitioning

- *demonstrate minor actinide separation schemes in view of an industrial implementation*

Pyrometallurgical reprocessing

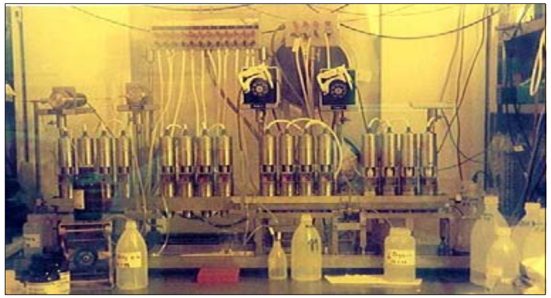
- *reprocessing of new types of fuels (e.g. metallic U,Pu,Zr,MA) and HLW*
- *electroreduction of oxide fuels*

PIE of innovative fuels

- *CERMET, inert matrices, metallic fuels, ThO_2, nitrides, carbides etc.*

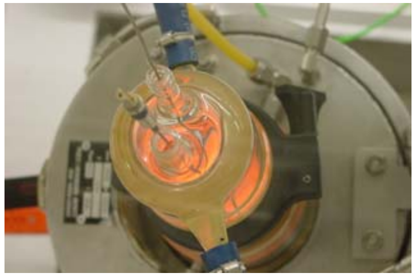
Minor Actinide Laboratory

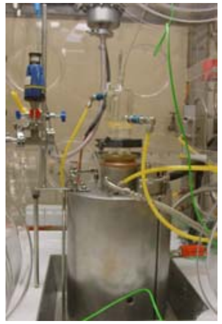
- *fabrication of minor actinide containing fuels and targets for transmutation*



New Centrifugal Contactor equipment

Chlorination equipment





Hot Cell Laboratory

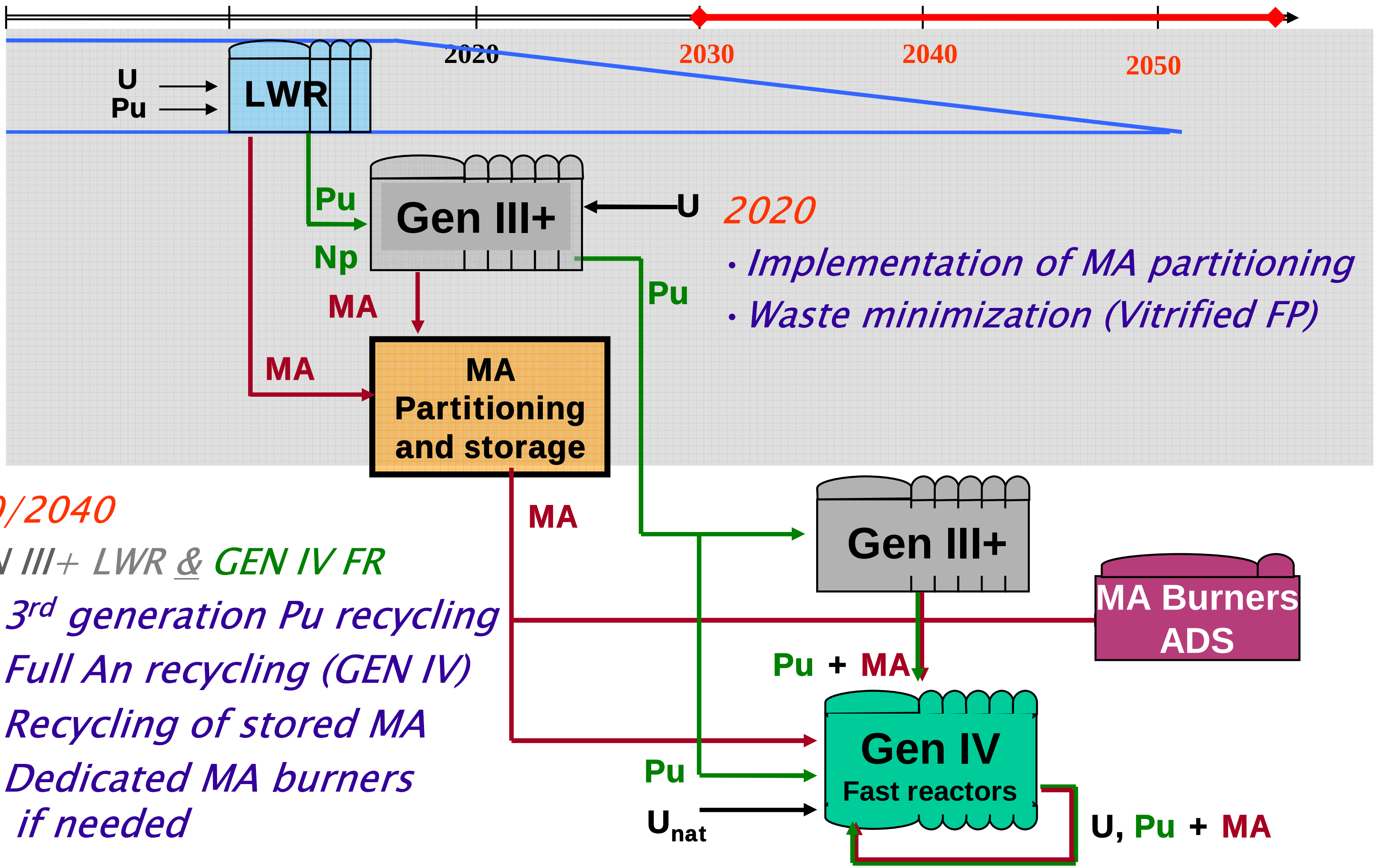
Minor Actinide Laboratory active operation started

Pilot facility for pyrometallurgical reprocessing

Advantages of a P&T Strategy

- Improve long-term public safety (reduce radio-toxicity and future doses to man)
- Provide benefits for repository (reduce repository heat, mass and possibility of criticality)
- Reduce the proliferation risk of plutonium in spent fuel
- Improve the prospects of nuclear power (public acceptance, sustainability)

Global Actinide Management



2020

- *Implementation of MA partitioning*
- *Waste minimization (Vitrified FP)*

2030/2040

- *GEN III+ LWR & GEN IV FR*
  - *3rd generation Pu recycling*
  - *Full An recycling (GEN IV)*
  - *Recycling of stored MA*
  - *Dedicated MA burners if needed*

reprocessing in the second strata fuel cycle

reasons for selecting pyro-techniques

compact process

Integrated Fast Reactor concept, ANL
lower costs, reduced number of transports

faster recycling

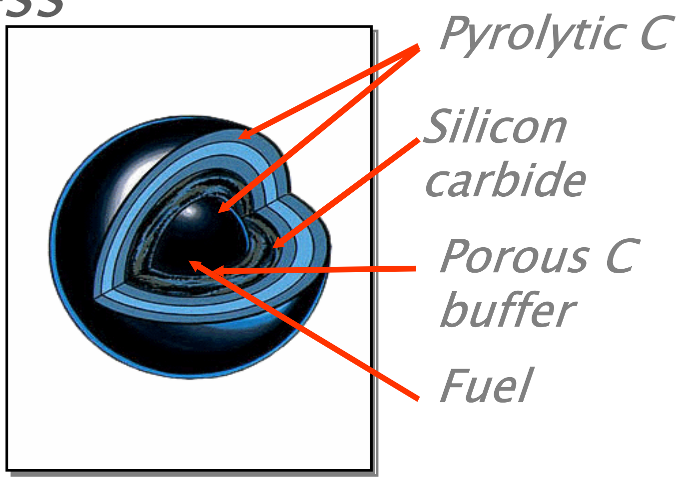
salt more radiation resistant => short fuel cooling-times

"impure" product fractions

more "proliferation-resistant" process

fuel composition

- *Metallic fuels, CERMET*
- *Inert Matrix (MgO, ZrO_2) fuels*
- *Th – MOX*
- *Nitrides eventually carbides*
- *Coated HTR, kernels, various geometries*



P&T requirements

1) Overall P&T efficiency, 99.9%

2) Transmutation efficiency, 10% - 20%

→ multi-recycling required

→ Partitioning efficiency > 99.9%

< 0.1% losses

Decontamination factor > 1 000

losses upon multiple recycling of Pu & MA´s.

total losses during multiple recycling

Losses per cycle (Refabrication and reprocessing)	L	0.10%
Burn up (% of PU+MA)	A	50.00%
Enrichment of fuel (Pu+MA)/(U+Pu+MA)	E	15.00%
Classical Burn Up (% heavy metal)	Aclassical	3.00%
(1-L)*(1-A)=q	q	0.7992
Total Losses	Ltotal	0.20%
Mass entering the system	M	100 kg
Losses in the first fabrication step	Lfirst	0.05%

0	Lfirst*M
1	L*M*(1-Lfirst)*(1-a)
2	L*M*(1-Lfirst)*(1-a)*(1-L)
3	L*M*(1-Lfirst)*(1-a)^2*(1-L)^2
	etc.

Cycle Nr	Mass entering Reactor	Mass leaving Reactor	Losses in Fuel cycle	Remaining mass	Total Losses
1	99,95	49,95	0,05	49,90	0,15%
2	49,90	24,95	0,02	24,93	0,17%
3	24,93	12,46	0,01	12,45	0,19%
4	12,45	6,23	0,01	6,22	0,19%
5	6,22	3,11	0,00	3,11	0,20%
6	3,11	1,55	0,00	1,55	0,20%
7	1,55	0,78	0,00	0,78	0,20%
8	0,78	0,39	0,00	0,39	0,20%
9	0,39	0,19	0,00	0,19	0,20%
10	0,19	0,10	0,00	0,10	0,20%
11	0,10	0,05	0,00	0,05	0,20%
12	0,05	0,02	0,00	0,02	0,20%
13	0,02	0,01	0,00	0,01	0,20%
14	0,01	0,01	0,00	0,01	0,20%
15	0,01	0,00	0,00	0,00	0,20%
16	0,00	0,00	0,00	0,00	0,20%

Advanced reprocessing: Main Objectives

The main objectives of this technology are,:

- Selective extraction of the actinides for subsequent recycling; the extracted product must, therefore, meet specifications for purity with respect to the remaining non-extracted products.

- Minimization of losses of the relevant elements in the various process steps.

- Generation of process waste (not extracted elements in liquid, salt or metallic form and technological waste) compatible with a suitable treatment process.

Major Research topics

Performed in close international collaborations, the research work should focus on the following major topics:

- *Establishing a thermodynamic database on actinide containing fuels for molten salt systems*
- *Testing and evaluating advanced reprocessing techniques*
- *Installing new facilities for large scale reprocessing*
- *Developing supporting analytical techniques*

On Actinide compounds: *ions and molecules*

close	Interactions around actinide core	far

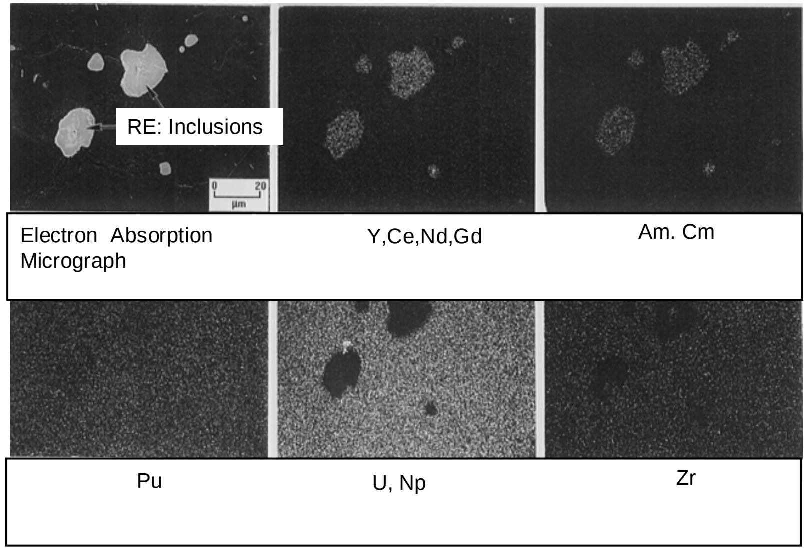
Higher Energy… …Lower Energy

Basic An + Elements Strong An dependent	An + Media An and media dependent	An building + supramolecular level + interface Less An dependent

Compound chemistry	*Solution chemistry*	*Heterogeneous chemistry*
– Solid state	*– Aqueous*	*– liquid-liquid*
– Bonding around An	*– Non aqueous*	*– solid-liquid*
– Solution (non intrusive)	*– HT liquids (Molten salts and metals)*	*– colloids…*
– Basic thermodynamics	*– RT ionic liquids*	

reasons for Ln/An separation

- *material burden: in spent LWR fuels, the Ln content is up to 50 times that of Am/Cm*
- *neutron poisoning: Ln (esp. Sm, Gd, Eu) have very high neutron capture cross sections, e.g. > 250 000 barn for Gd-157*
- *segregation at fuel fabrication: upon fabrication, Ln tend to form separate phases, which grow under thermal treatment; An concentrate in these phases*

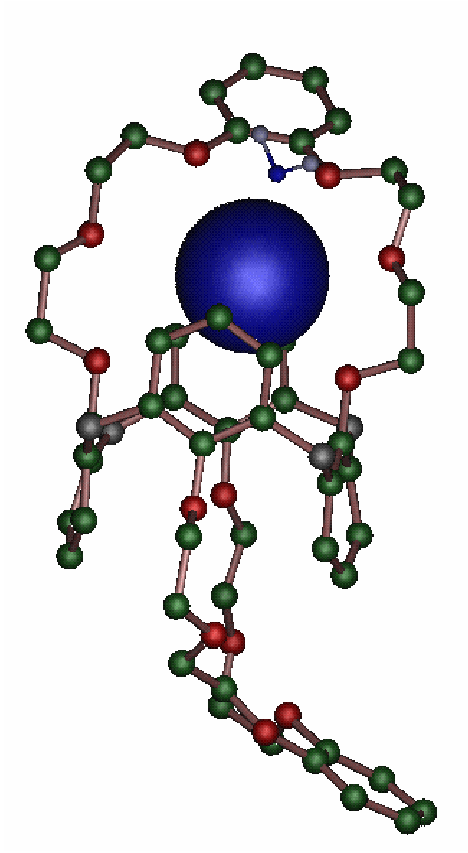


electron micrographs of an UPuZrMA5RE5 alloy

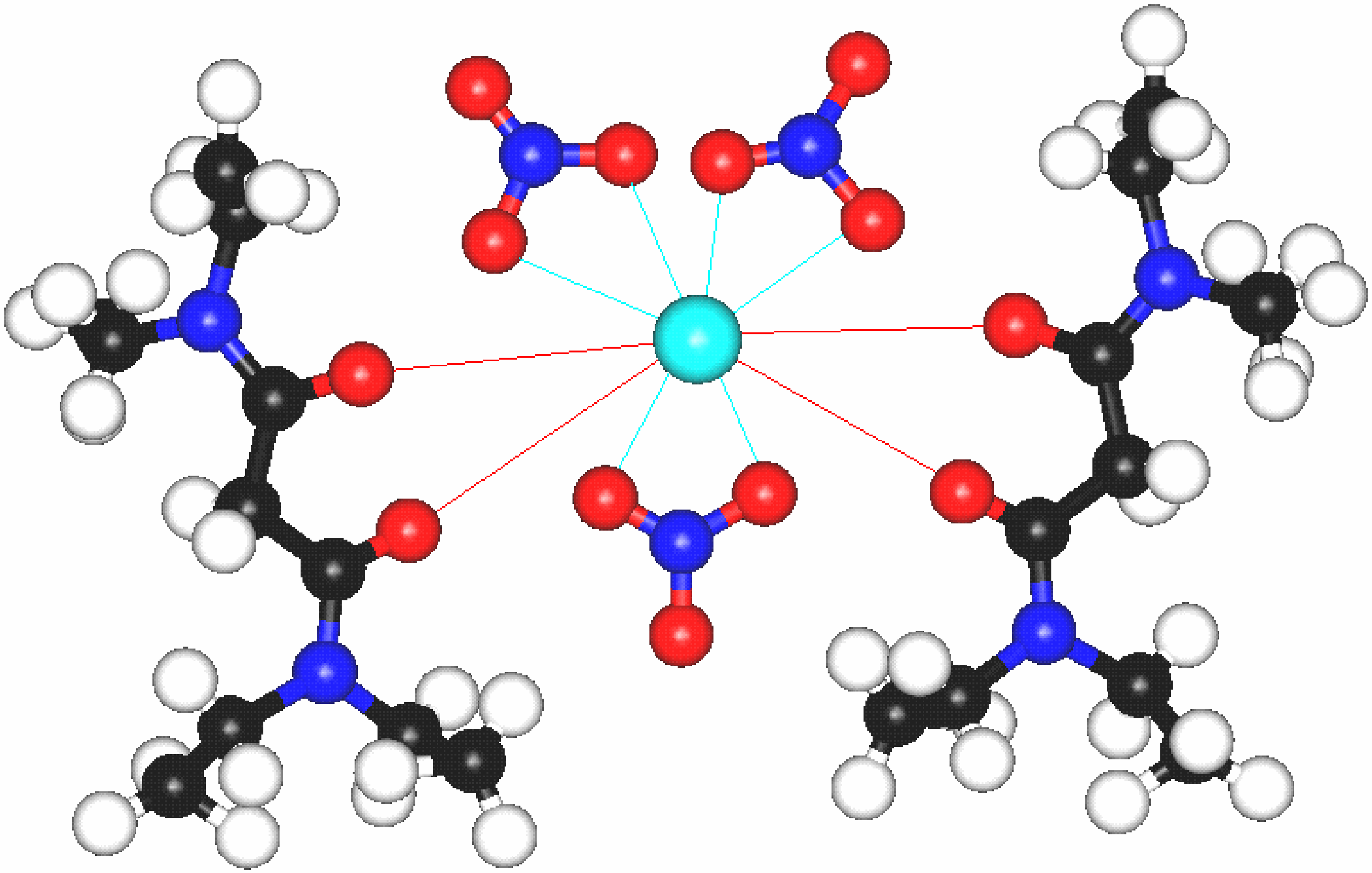
⇒ *consequence: non-uniform heat distribution in the fuel under irradiation*

Design of new extractants : main criteria

- Ability to separate
  - Affinity
  - Selectivity
  - Reversibility
- Medium effects
  - Solubility
  - Stability / hydrolysis, radiolysis
- Industrialization
  - Kinetics
  - Physical properties
  - Ability to regeneration
- Secondary waste minimization
  - Incinerability (C, H, O, N)

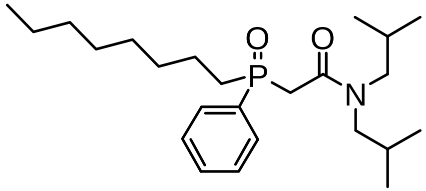


Actinide extraction by diamide (principle)



$$(An^{3+})_{aq} + 3\ (NO_3^-)_{aq} + 2\ (\text{diamide})_{org} \rightleftharpoons (An(NO_3)_2\ ,\ 2\ \text{diamide})_{org}$$

DIAMEX process: diamide optimisation



CMPO

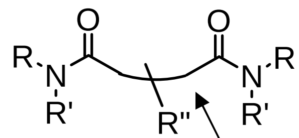
Selective of group 3 elements *vs* main transition elements (TRUEX process)

Process criteria

affinity, selectivity, solubility, stability, etc.

"CHON" principle

Molecular criteria

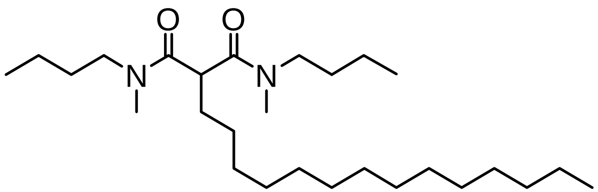


electronic properties

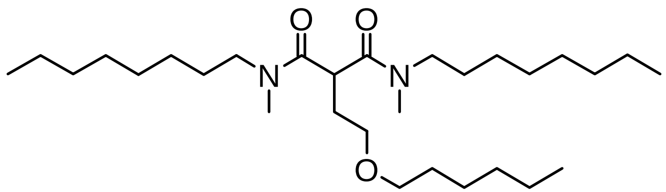
steric hindrance

lipophily

chelation

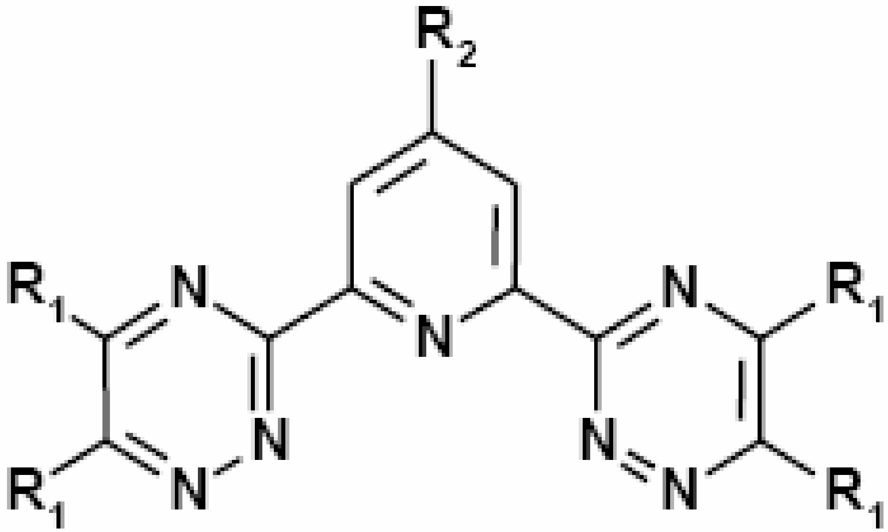


DMDBTDMA



DMDOHEMA

Discovered by Dr. Z. KOLARIK (FZK) in 1998 (NEWPART project) :

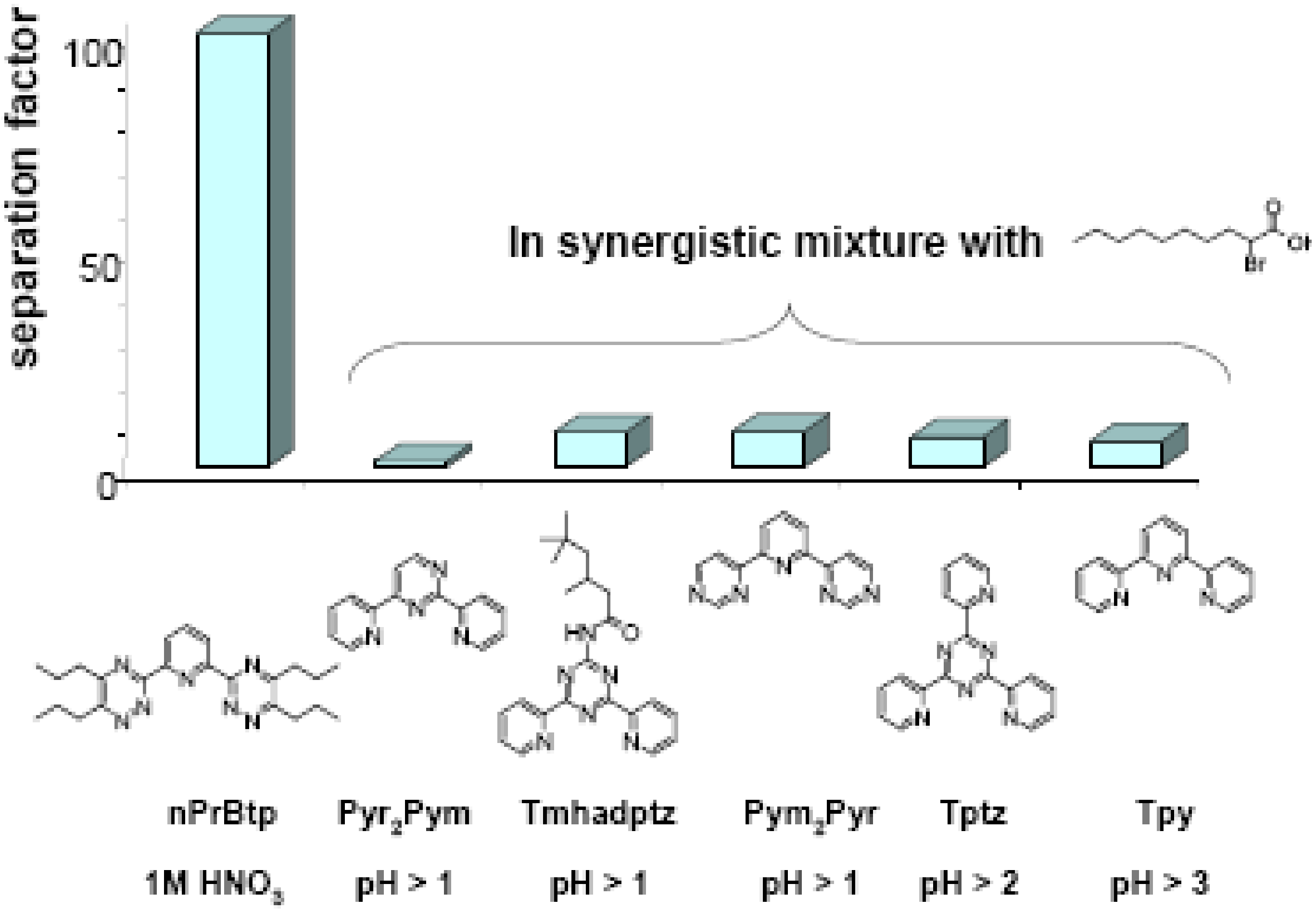


R_1 = H, Me, *n*-Propyl, *i*-Pr, *n*-Butyl, *i*-Bu, (1-Me)Pr, *neo*-Pe, *i*-Pe, ϕ, ϕ-OMe, Phen, Pyr

R_2 = H, *i*-Nonyl

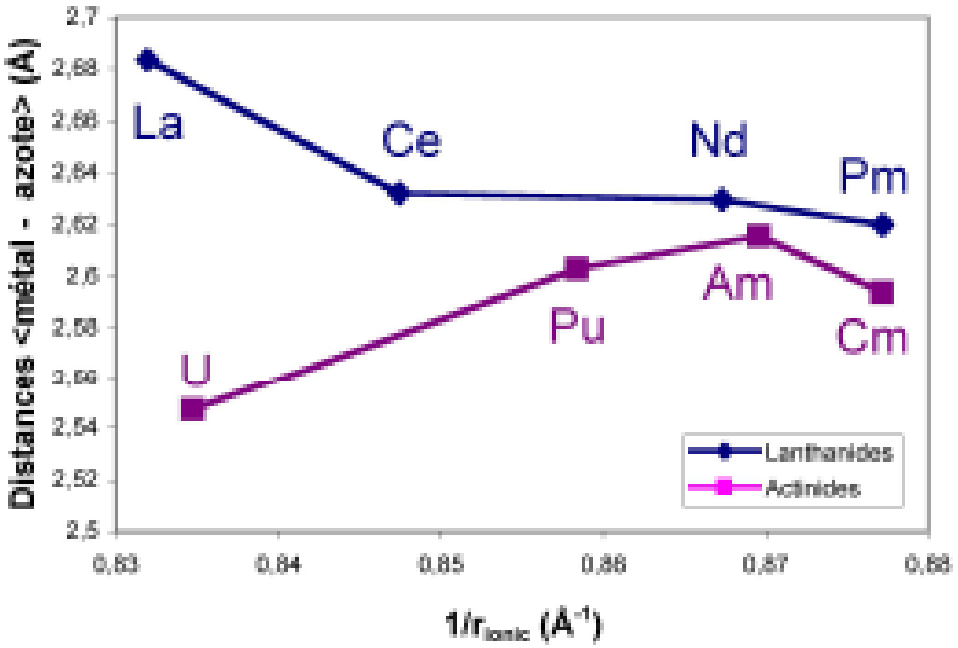
Actinide / Lanthanide separation

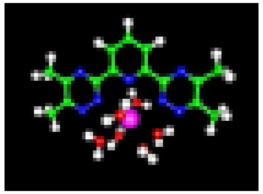
Bis-Triazinyl-Pyridines (BTPs)



Actinide / Lanthanide separation

Bis-Triazinyl-Pyridines (BTPs)





BTP

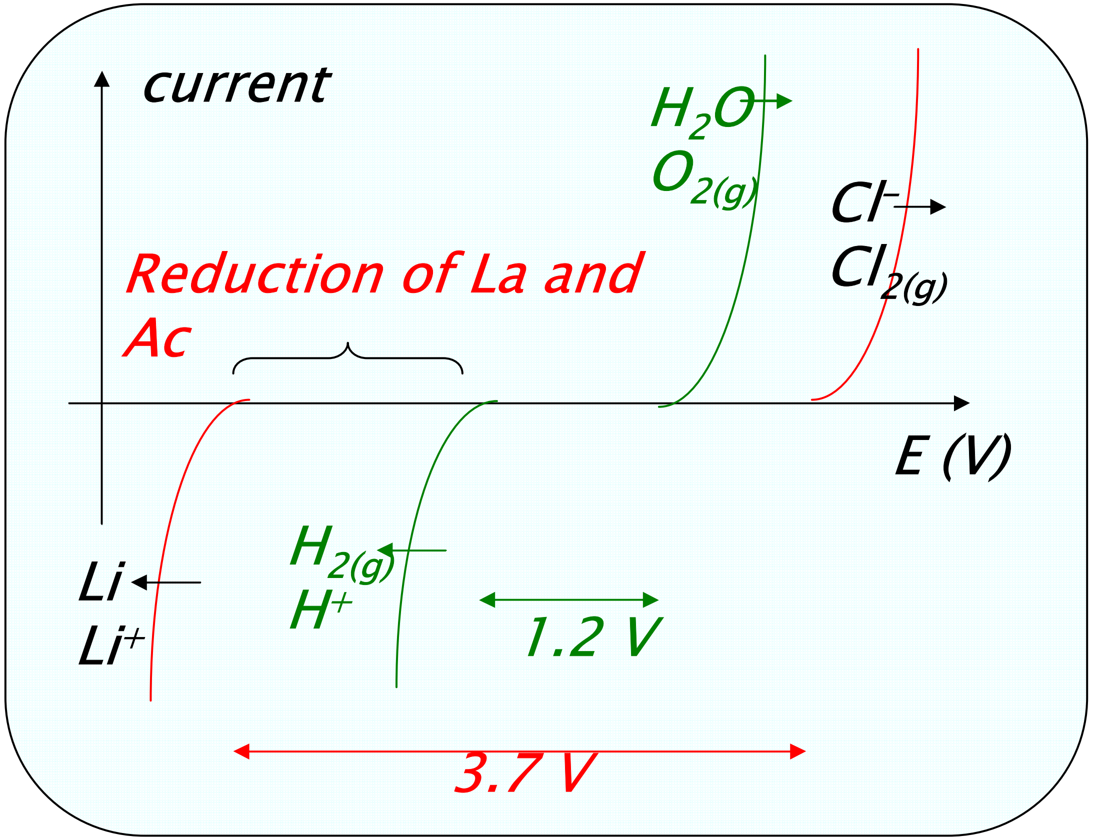
- For equivalent ionic radius : An(III), N <u>shorter than</u> Ln(III), N
- *Indication of an <u>« enthalpic »</u> selectivity ?*

Theoretical approach Guillaumont et al. 2006

Why molten salts ?

- Large 'electrochemical window'
- High conductivity
- Resistant to radiolysis
- High temperatures (400-800°C)
- ⇒ kinetics are fast

- Salts are hygroscopic and An
- metal oxidize easily
- pure atmosphere required (< 10 ppm for O_2 and H_2O)
- Salts are corrosive



Electrochemical windows: LiCl-KCl compared to water

Fundamental Data.

A large number of fundamental data are still missing to develop pyroprocessing technology. Basic thermodynamic and electrochemical data to be investigated

- *Vapour pressure of actinides and fission product in chloride salts, especially with high potential volatility such as Cd, Am, I*
- *Solubility of actinide ionic compounds (oxides, chlorides, and fluorides) in molten salts*
- *Activity coefficients of actinide elements in molten salts*
- *Modeling of thermodynamic mixing of molten salts or alloys to calculate the phase diagrams and the distribution coefficient of the elements between the various phases*
- *Mass transfer in molten salt/liquid metal reactions or in the vicinity of an electrode.*

Electrochemical An & Ln behaviour
investigated in molten chloride salt

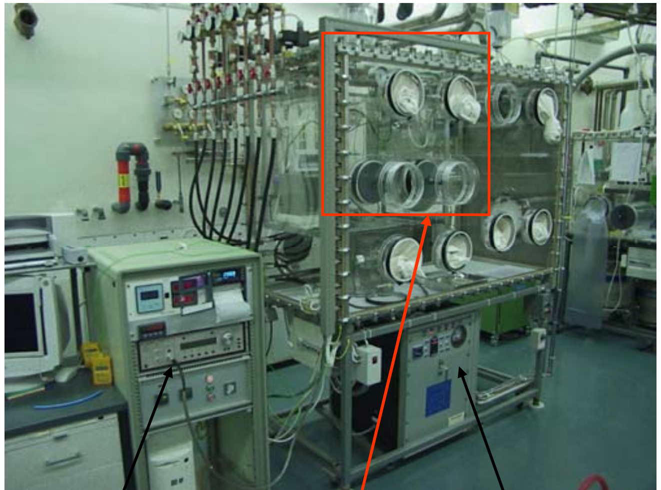
Basic thermodynamic and kinetic data to assess electrochemical separation paths in molten LiCl-KCl salt for U, Pu, Np, Am, Cm, La, Pr, Ce, Nd, Y, Zr

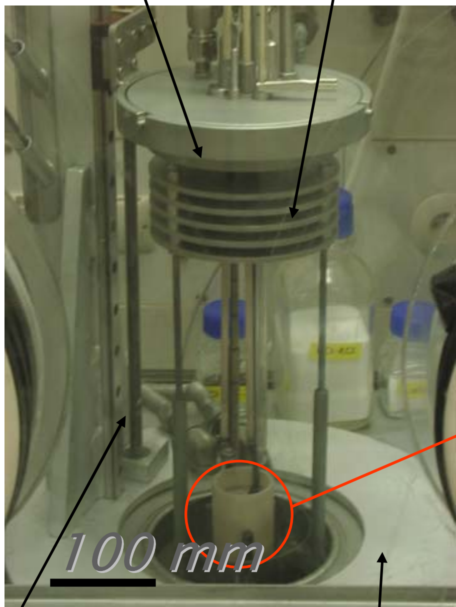
- *Thermodynamic properties*
  - *Standard potentials, activity coefficient, ΔG ΔH, ΔS of formation*
- *Electrochemical behaviour on*
  - *Solid cathodes (W, Mo, Ni, Al)*
  - *Liquid cathodes (Cd, Bi, Al)*
- *Kinetic parameters*
  - *Diffusion coefficients*
  - *Nucleation and crystal growth*

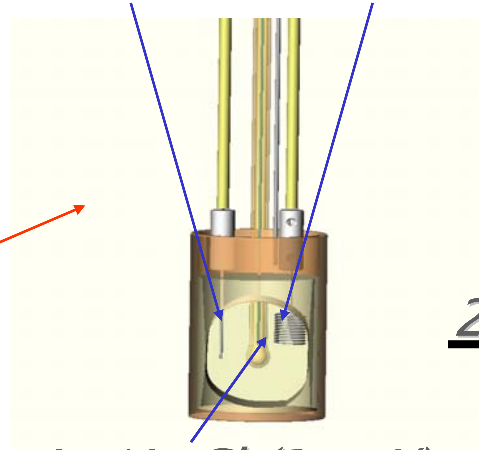
Facilities and equipment

Double glove-box with electrochemical set-up

- inner box purified Ar (1 ppm H_2O and O_2)
- outer box N_2





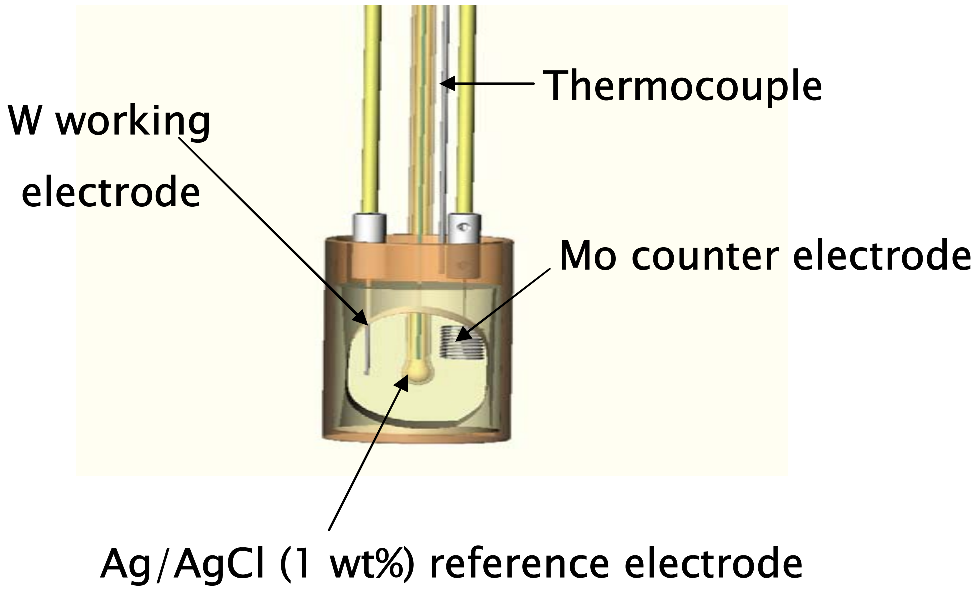


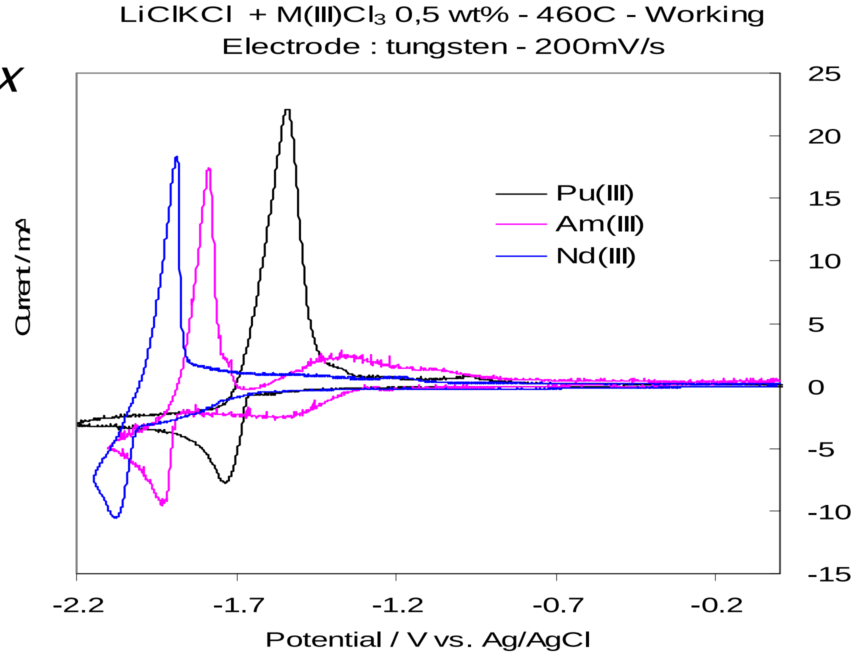
Basic electrochemical data

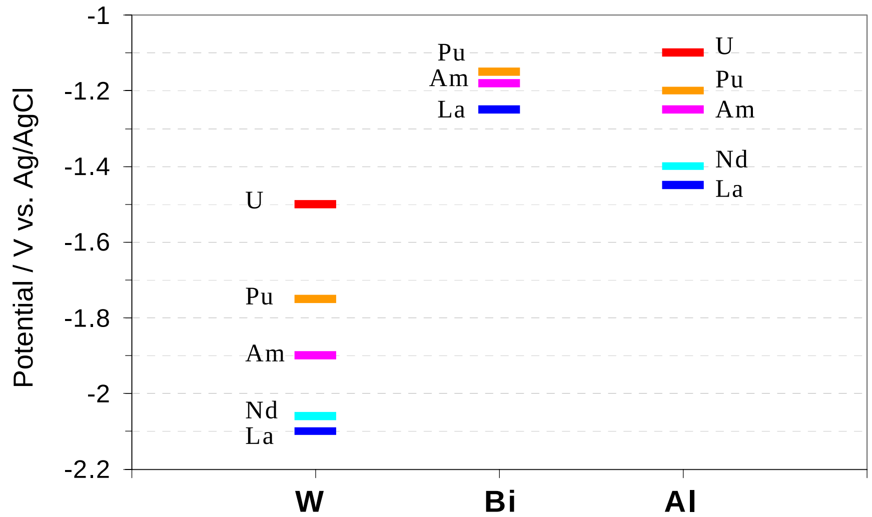
Installation of electrochemical cell in glove box to measure:

relevant potentials (free energy of halide formation)
activity coefficient in the salt and in metals
diffusion coefficient in the salt phase

Cyclic voltammetry







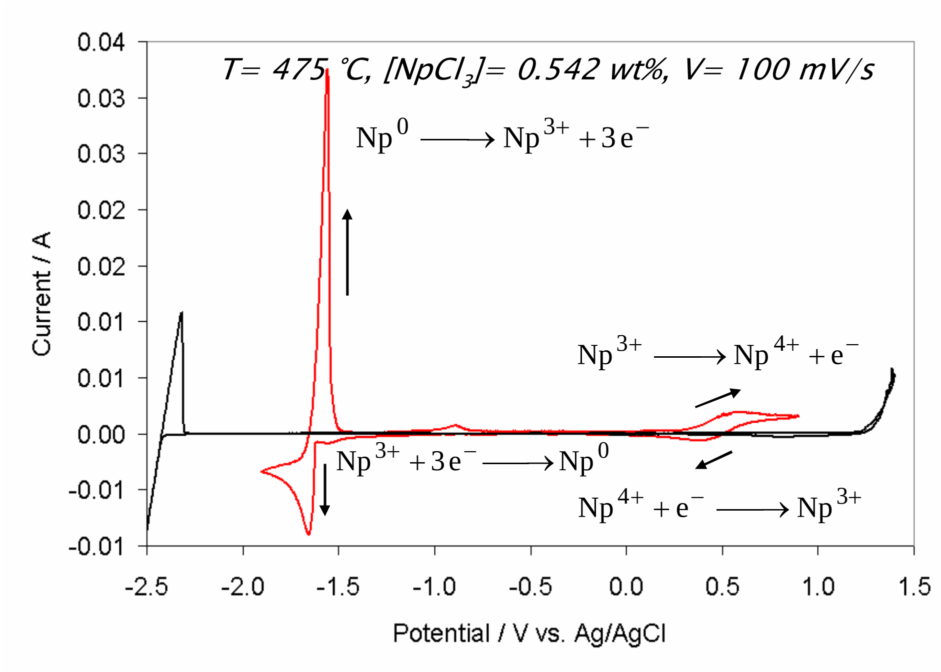
Neptunium electrochemical behavior

- *Neptunium-based solution preparation in the LiCl-KCl eutectic*

$$NpCl_4 + 4Li\text{-}Bi \longrightarrow 4Li^{+}_{salt-phase} + Np^{0}_{metallic-phase} + Bi^{0}_{metallic-phase}$$

$$Np^{0}_{metallic-phase} + Bi^{3+}_{salt-phase} \longrightarrow Bi^{0}_{metallic-phase} + Np^{3+}_{salt-phase}$$

- *Electrochemical behavior*



- *$NpCl_4$ and $NpCl_3$ used as starting material for the the electrochemical measurements*

◊ *similar electrochemical behavior*

◊ *$[NpCl_3]$= 0.542 ± 0.01 wt%*

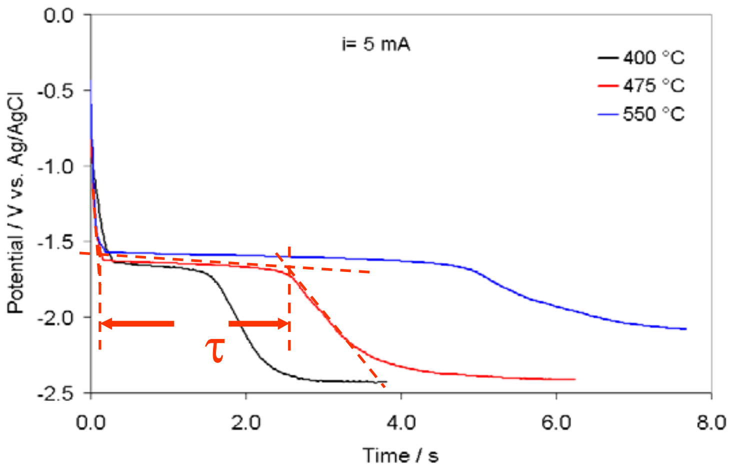
◊ *3+ state stable in the LiCl-KCl eutectic*

◊ *2 redox systems observed as with U*

◊ *Np^{4+}/Np^{3+}: Ep,c ~ -1.69 V vs. Ag/AgCl*

◊ *Np^{3+}/Np^{0}: Ep,c ~ + 0.4 V vs. Ag/AgCl*

Electrochemical characterisation of Np

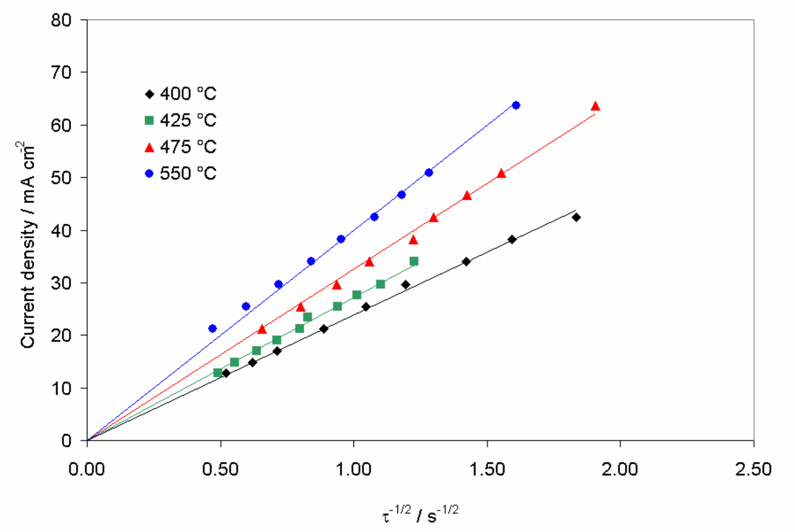


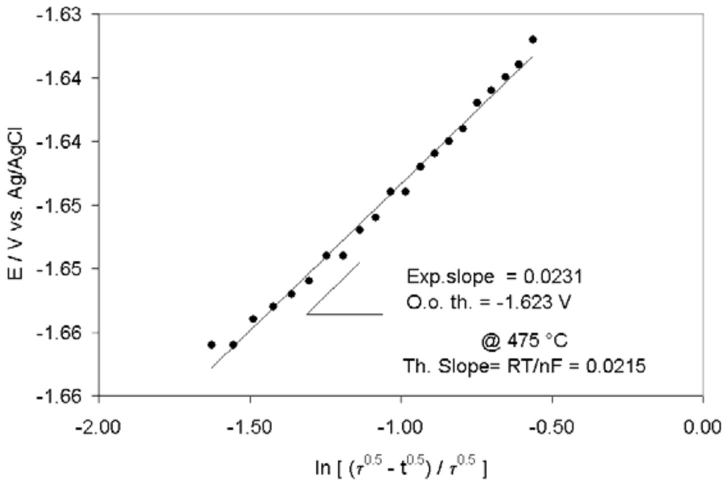
Chronopotentiometry experiments

◊ determination of transition time t

Sand´s law verified : **i =k(T)** $\tau^{1/2}$

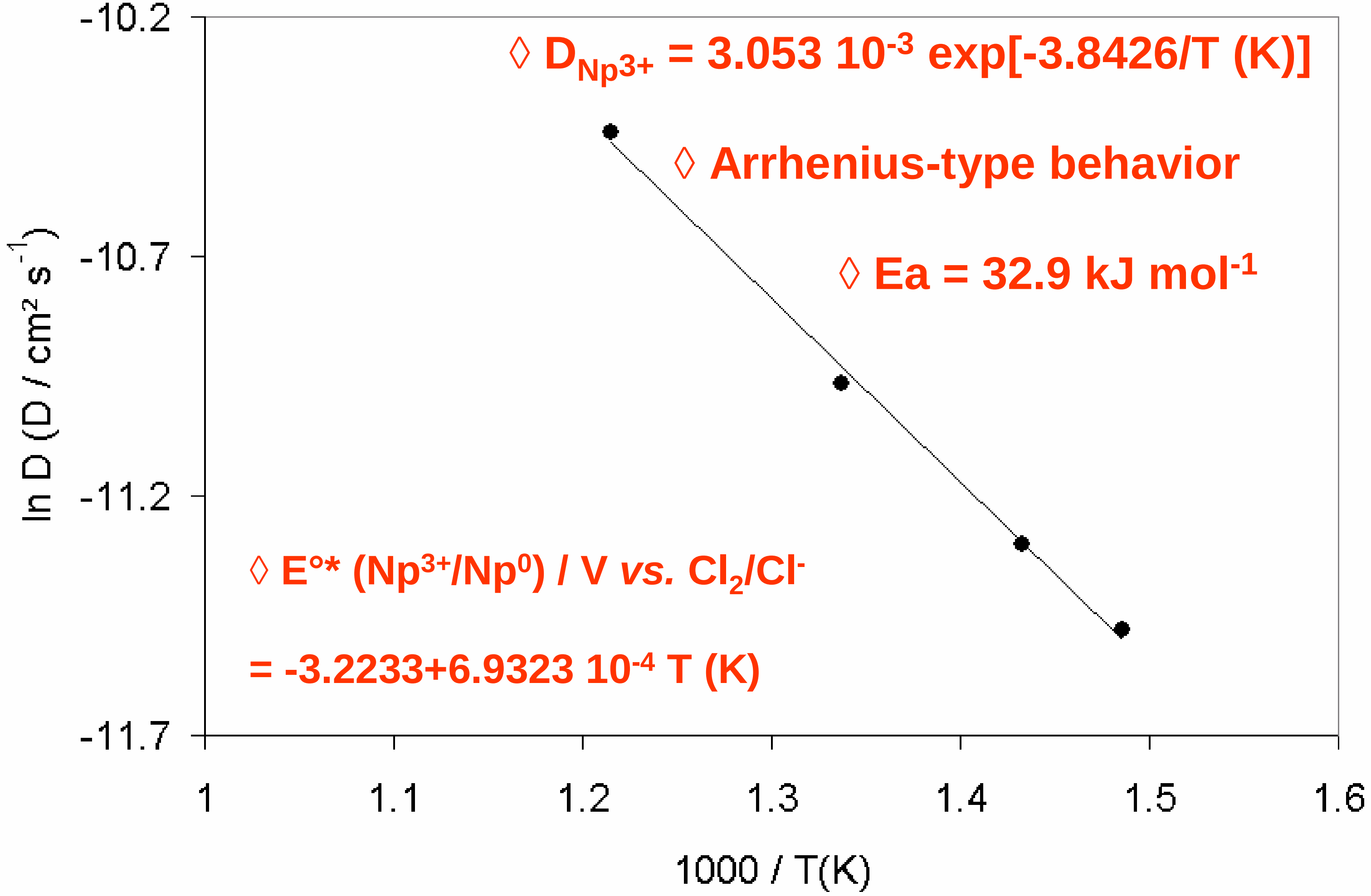
$$i\sqrt{\tau} = 0.5\, n\, F\, C_{Np^{3+}}\, S \sqrt{\tau D_{Np^{3+}}}$$



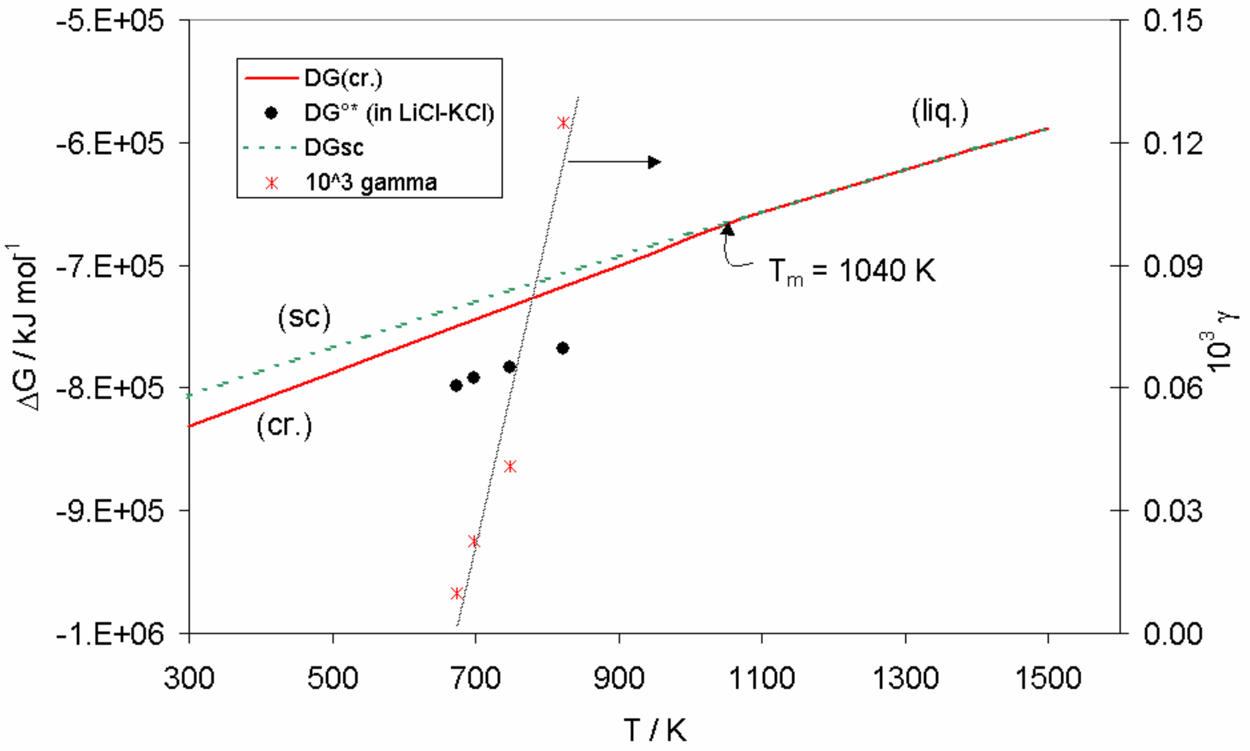


$$E = E^{0*}_{Np^{3+}/Np^{0}} + \frac{RT}{nF}\cdot\ln\left(X_{Np^{3+}}\right) + \frac{RT}{nF}\cdot\ln\left(\frac{\tau^{1/2} - t^{1/2}}{\tau^{1/2}}\right)$$

Diffusion coefficient and apparent standard potential



Thermochemical properties of $NpCl_3$



$$\Delta G^{\infty}_{MCl_n} = -\,nFE^{*0}_{M^{n+}/M^0}$$

$$\ln \gamma_{MCl_x} = \frac{\Delta G^{\infty}_{MCl_x} - \Delta G^{0}_{MCl_x,sc}}{R\,T}$$

Conditions

◊ super-cooled state: liquid phase taken as reference state

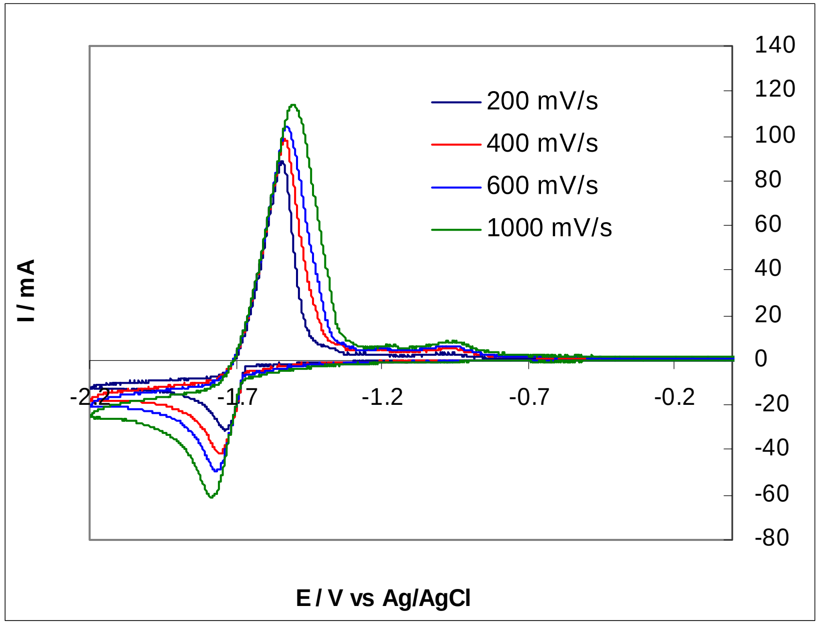
◊ ΔG_{sc}: extrapolation of the $\Delta G_{(liq.)}$ curve

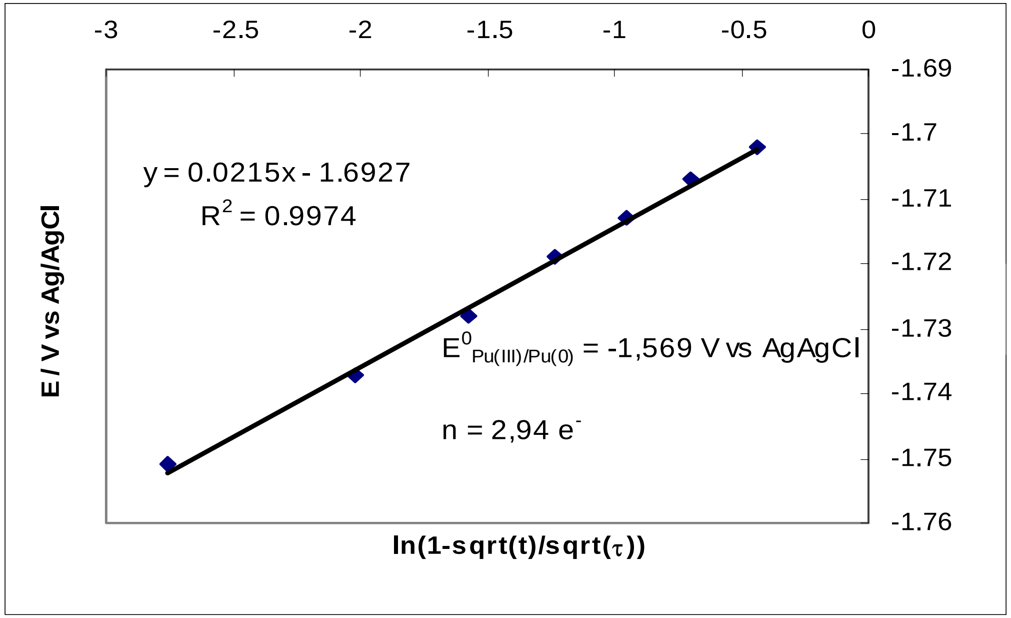
◊ $\Delta G°^{*}$ = nF (- 3.2233 + 6.9323 10^{-4} T (K))

◊$10^3\,\gamma$ ($NpCl_3$) = - 5.09 10^{-4} + 7.594 10^{-7} T (K)

Electrochemical behavior of $Pu(III)Cl_3$

$LiCl/KCl$ eutectic at T = 460°C





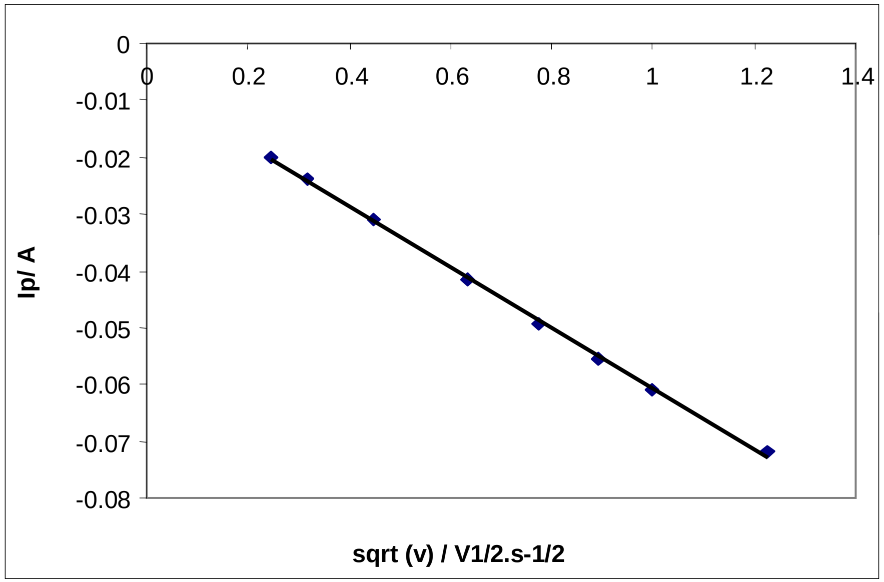
Cyclic voltammetry:

$$Ip = 0,61.(nF)^{3/2}.(RT)^{-1/2}.SC_{Pu}.(vD)^{1/2}$$

Chronopotentiometry:

$$I.t^{1/2} = 0,5nFSC_{Pu}(pD)^{1/2}$$

$$E = E'^{0}_{Pu(III)/Pu(0)} + RT/nF.lnC_{Pu} + RT/nF.ln(1-t^{1/2}/\tau^{1/2})$$



Electrochemical behaviour of $Pu(III)Cl_3$

LiCl/KCl eutectic at T = 460°C

C_{Pu} wt %	Method	n	$10^5.D_{Pu(III)}$	$E'^0_{Pu(III)/Pu(0)}$	$E'^0_{Pu(III)/Pu(0)}$
1,275	CP	3,2	1,8	-1,567	Sakamura (2001) -1,592
	CV	Less than 2	1,5	-	
	Convolution	3,1	1,4	-1,512	
2,15	CP	3,1	1,9	-1,562	
	CV	Less than 2	1,3	-	
	Convolution	3,05	1,5	-1,510	

Chronopotentiometry (CP) gives reproducible results for n and E'^0. Value of D seems to be overestimated (measurement of transition time?).

Cyclic voltammetry difficult to analyze in case of quasi-reversible system (low scan rates).

Convolution gives reproducible results for E'^0 but lower than for CP.

Diffusion coefficients of An and Ln

T = 460 °C

$D_{U^{3+}} = 2.5 \times 10^{-5}$ cm² s

$D_{U^{4+}} = 1.2 \times 10^{-5}$ cm² s

$D_{Pu^{3+}} = 1.6 \times 10^{-5}$ cm²

$D_{Np^{3+}} = 1.7 \times 10^{-5}$ cm²

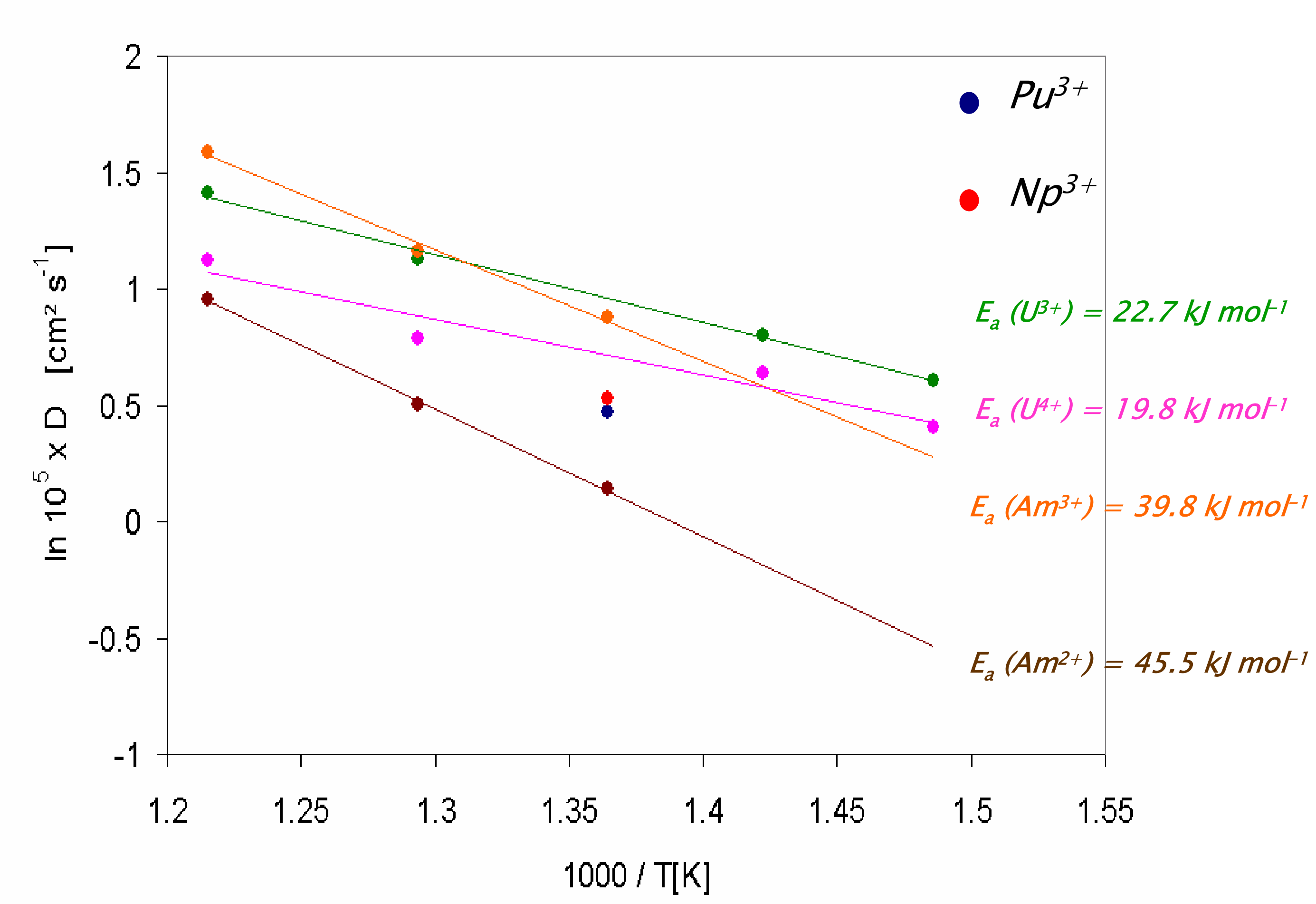
$D_{Am^{3+}} = 2.5 \times 10^{-5}$ cm²

$D_{Am^{2+}} = 1.1 \times 10^{-5}$ cm²

$D_{Nd^{3+}} = 1.1 \times 10^{-5}$ cm²

$D_{Nd^{2+}} = 1.2 \times 10^{-5}$ cm²

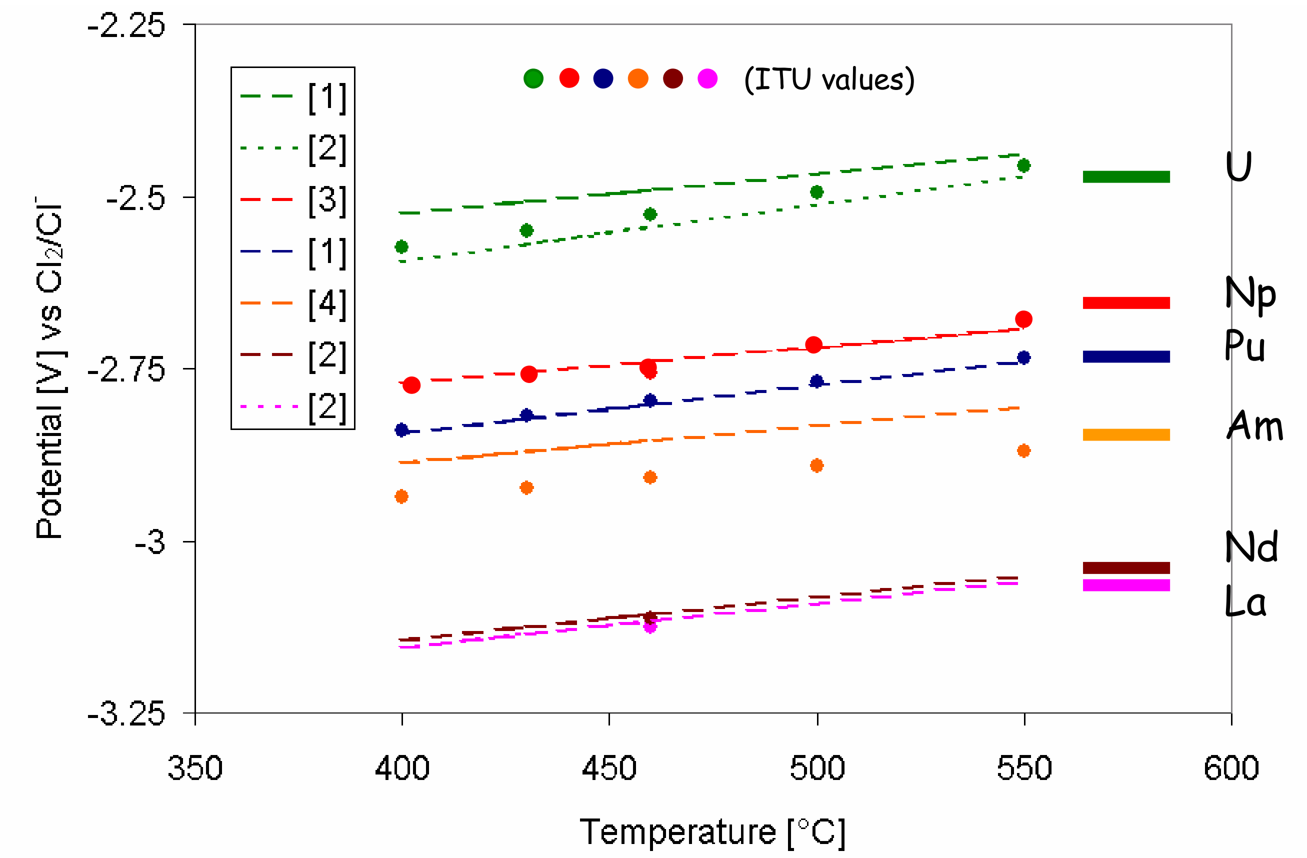
$D_{La^{3+}} = 0.8 \times 10^{-5}$ cm²



Arrhenius-type behaviour

Apparent standard potentials of An and Ln

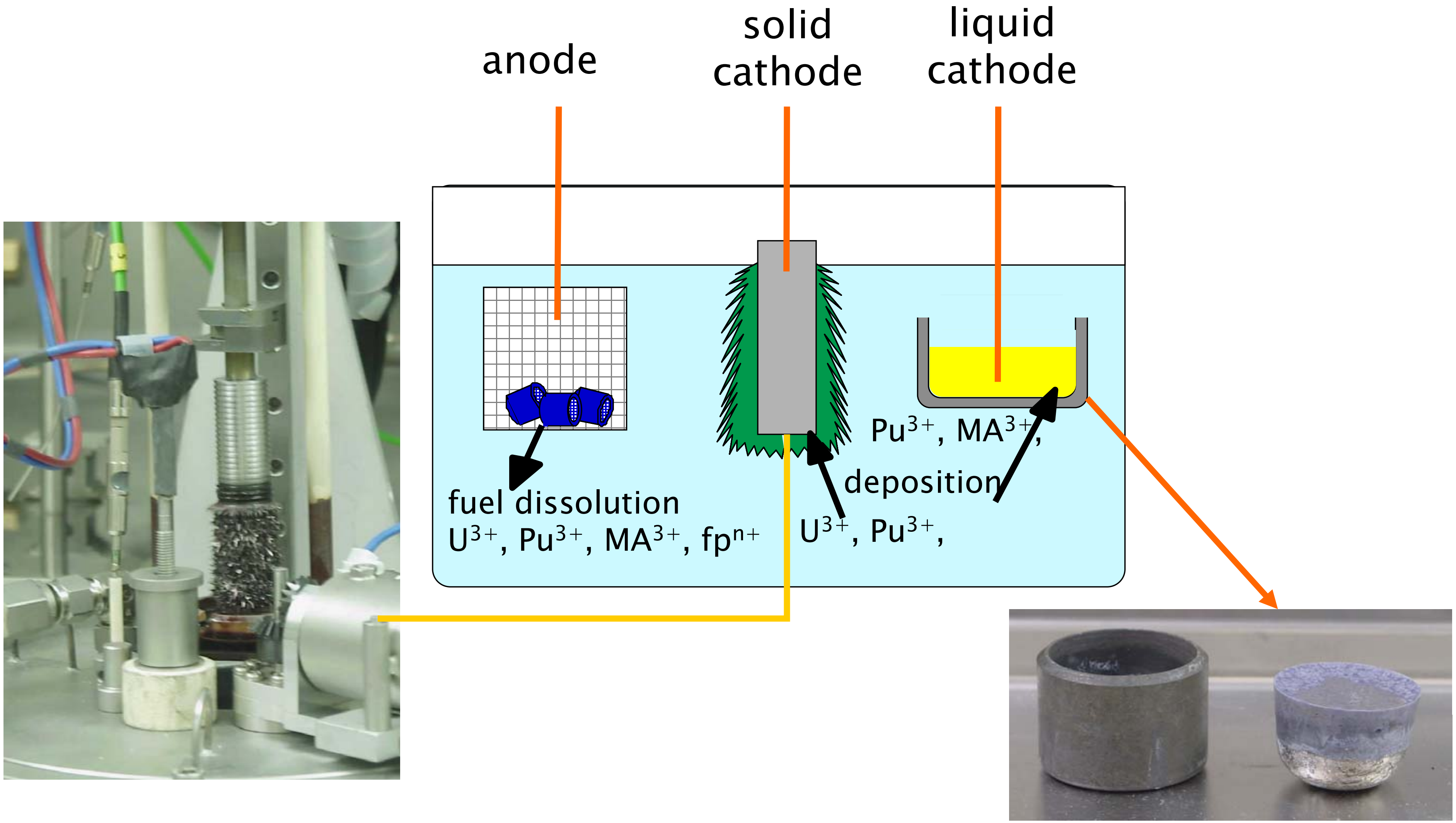
- Good agreement with literature data
- Discrepancies observed for Am (multi valence)



[1] J.J. Roy et al., J. Electrochem. Soc., 143(8) (1996) 2487-2492.
[2] European contract FIKW-CT-2000-00049 project FIS-1999-00199 "Pyrorep" Pyrometallurgical Processing Research Programme Final Scientific Report.
http://www3.sckcen.be/adopt/news/view.aspx?suffix=_PARTITION_PYROREP&tree=7.11
[3] O. Shirai, J. App. Electrochem., 31 (2001) 1055-1060
[4] S.P. Fusselman et al., J. Electrochem. Soc., 146(7) (1999) 2573-2580.

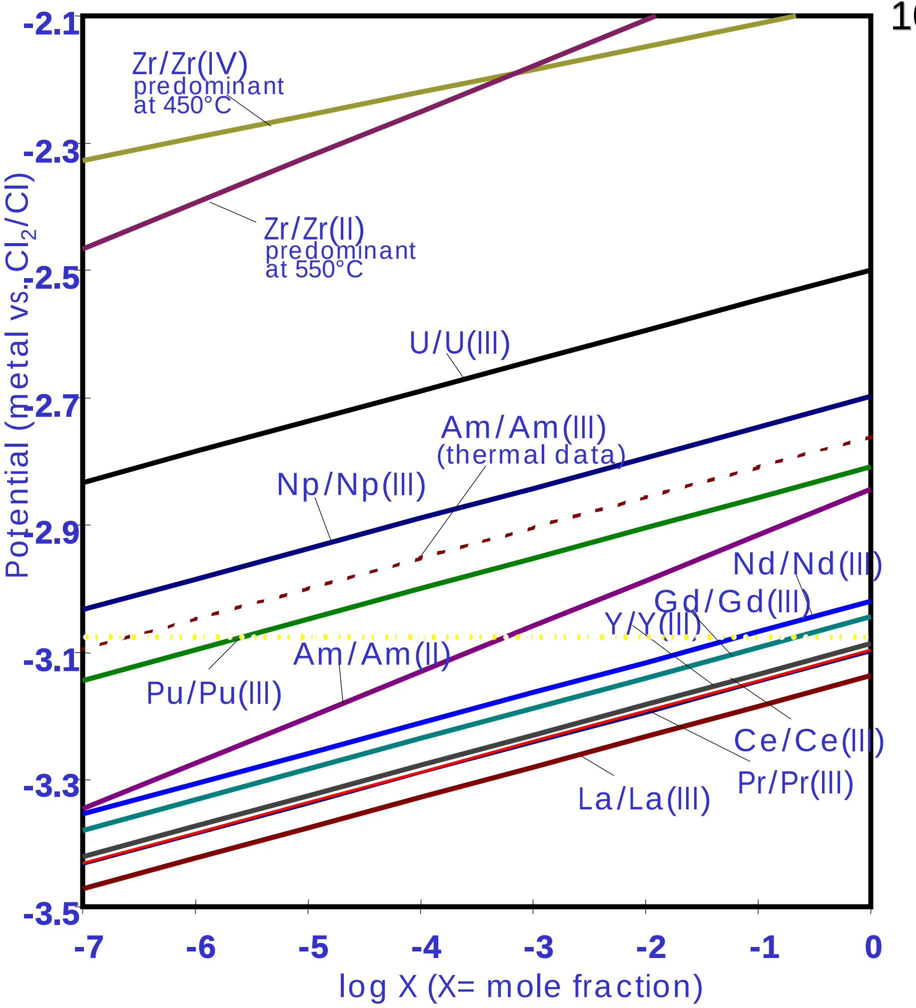
Pyroprocessing of metallic fuels

process scheme and An/Ln behavior

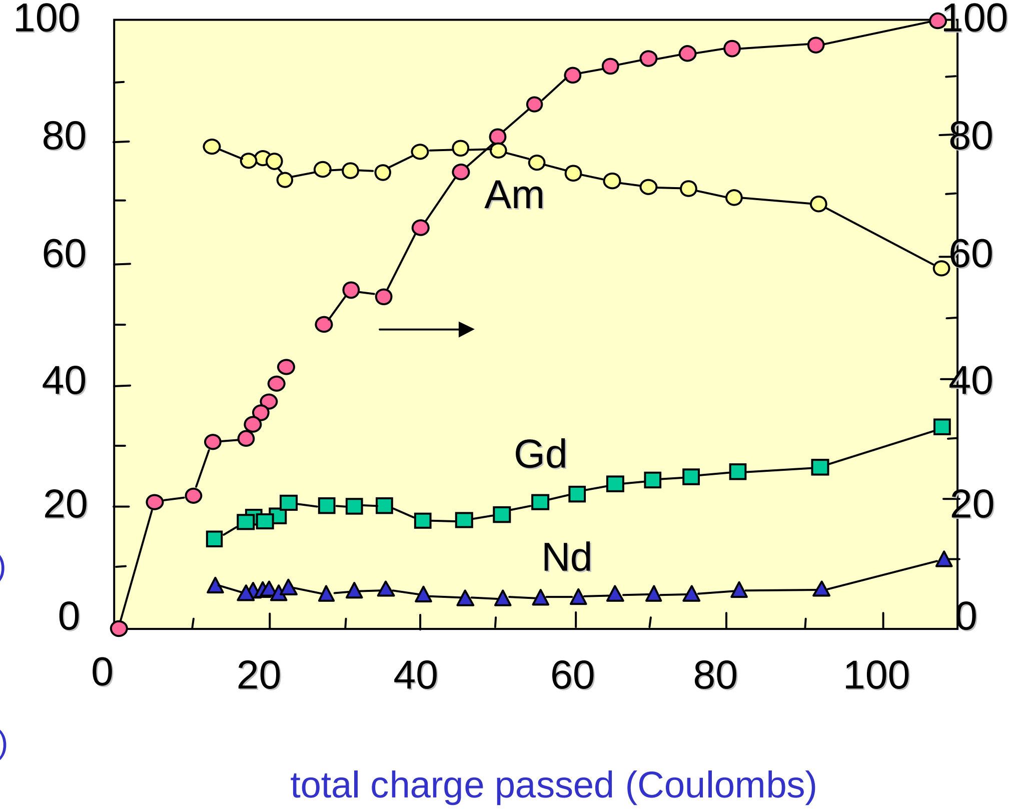


electrorefining of metallic fuels

Pyrometallurgical Processing
Am electrorefining



potentials in molten KCl-LiCl eutectic 450°C
(calculated from electrochemical data)

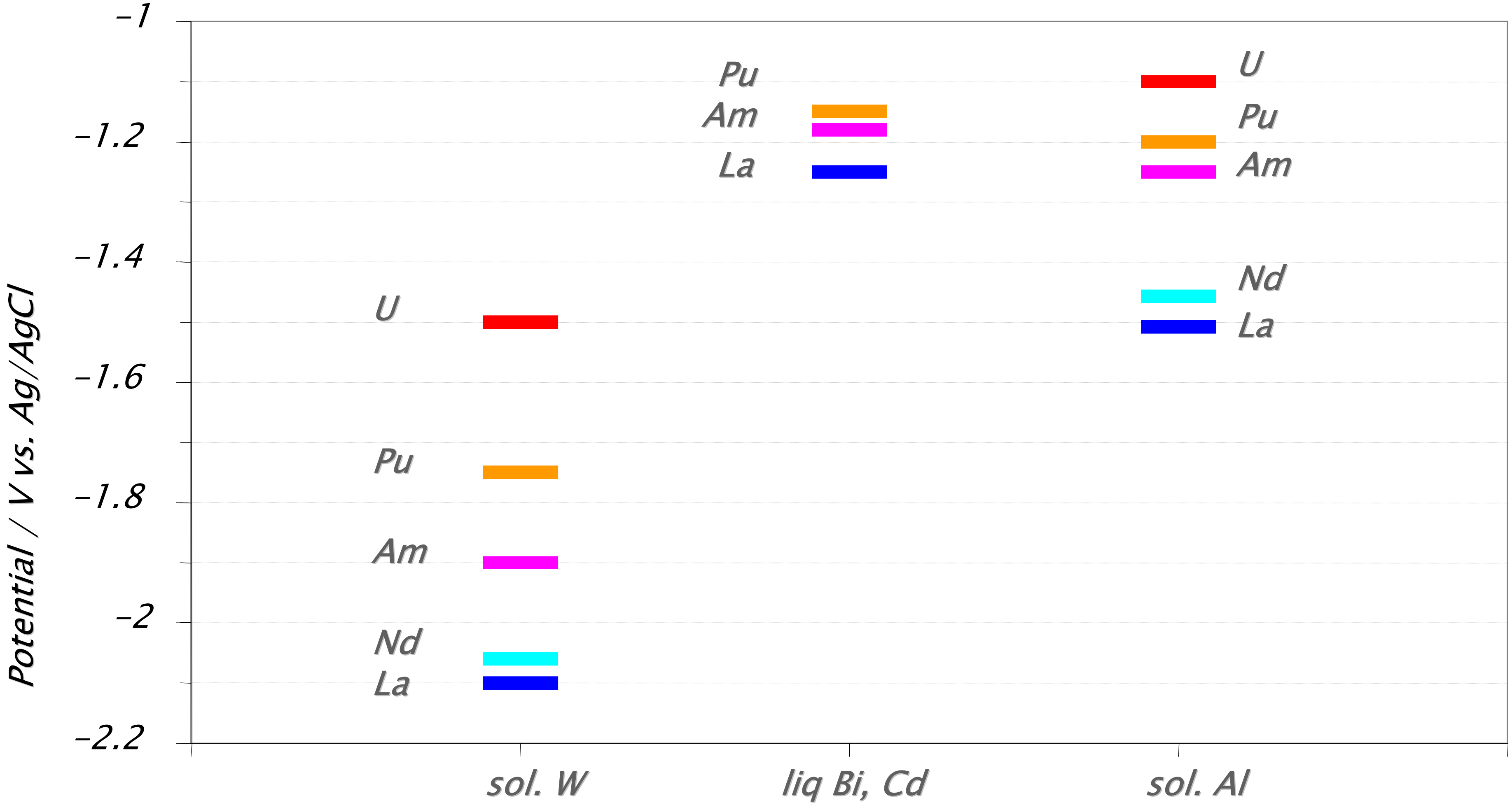


Am separation from Nd and Gd by electrorefining
mg amounts deposited at 450°C on solid cathode

ref.: Y. Sakamura, T. Inoue, T.S. Storvick, L..F. Grantham Proc. Global'95, (1995) 1185

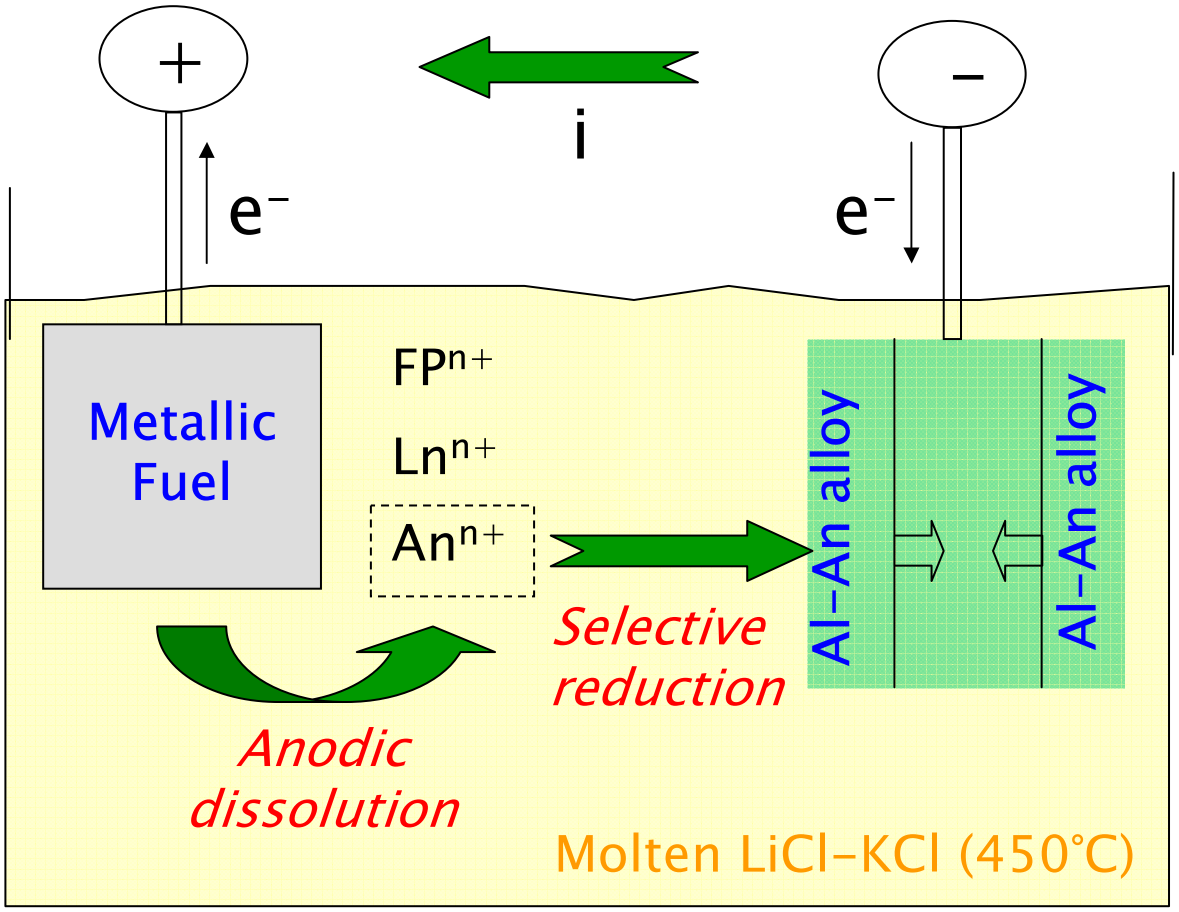
Pyroprocessing of metallic fuels

An reduction potentials on different cathodic materials

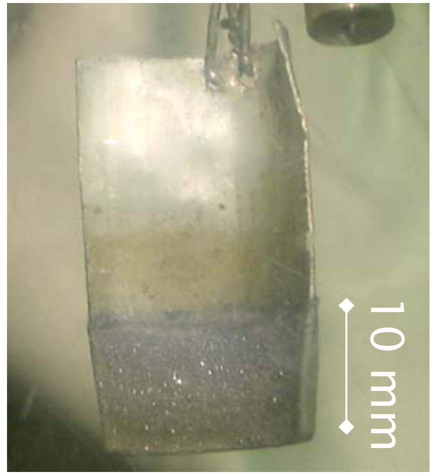


- more efficient An/Ln separation on solid cathodes (W and Al)
- alloying with An stabilizes the deposit (liquid Cd ,Bi and Al)
- Al unifies both advantages

electrorefining on solid aluminium cathode



Principle of the electrorefining



Two main advantages of aluminium:

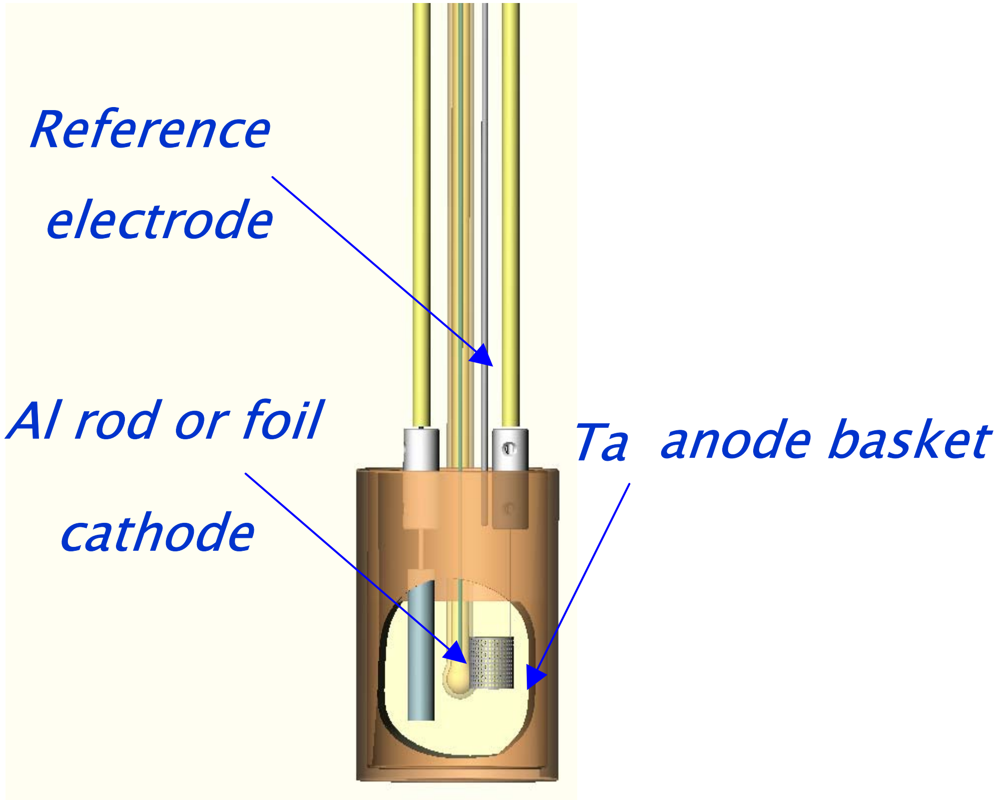
- An can beselectively deposited on the Al cathode

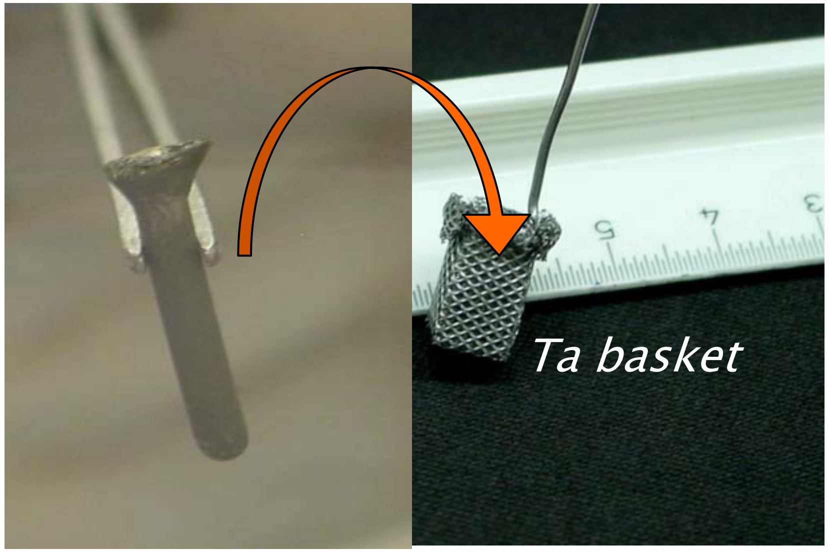
- The An–Al alloy formation prevents from further reoxidation of An

Set-up for An/Ln separation by electrolysis

Electrorefining of metallic actinides under constant current operation

Electrodeposition tests





Anode basket is loaded with Pu metal

Anodic reaction:

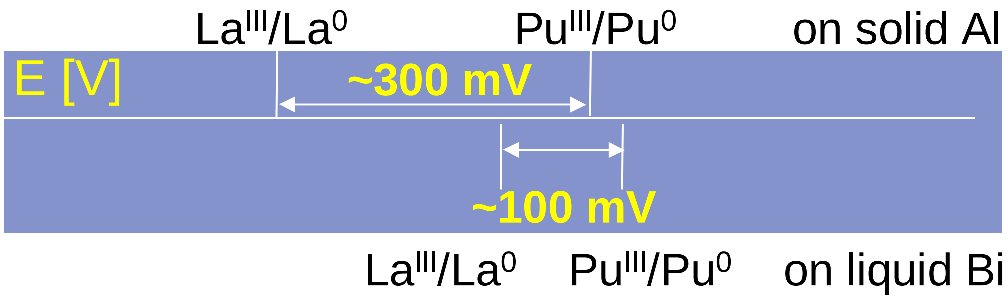
$$Pu^0 \rightarrow Pu^{3+} + 3\ e^-$$

Cathodic reactions

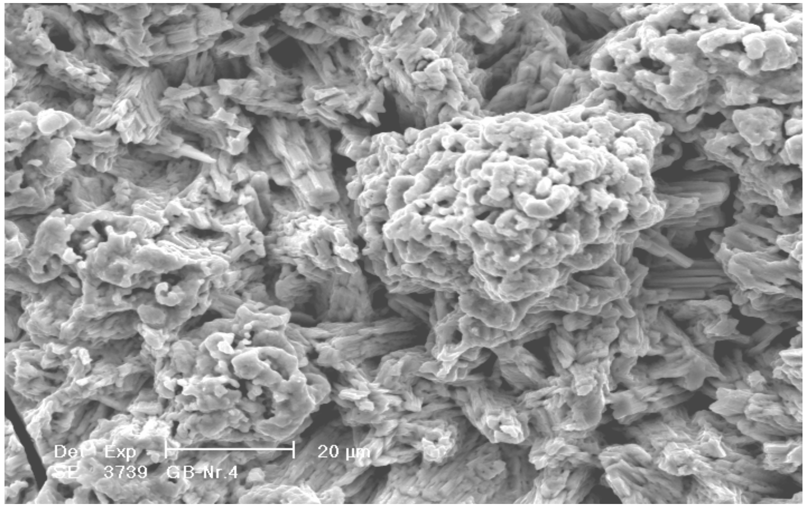
$$Am^{3+} + 3e^- \xrightarrow{Al} Am_xAl_y$$

$$\text{or}\ Pu^{3+} + 3e^- \xrightarrow{Al} PuAl_4$$

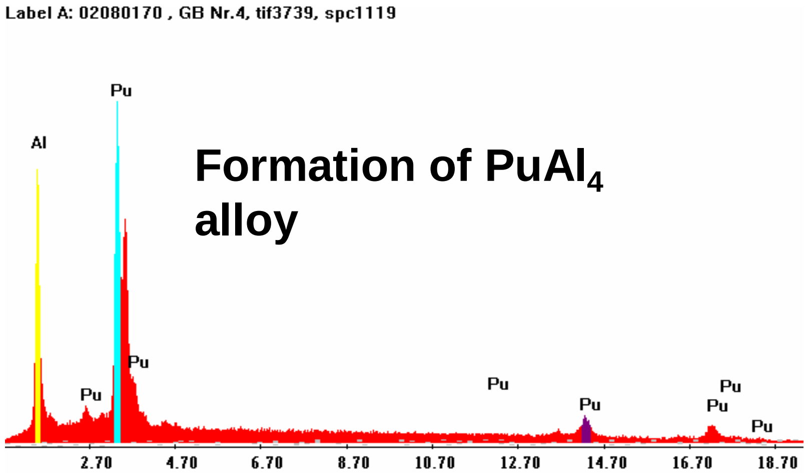
Pu/Ln electroseparation
deposition on solid Al cathode in molten chlorides

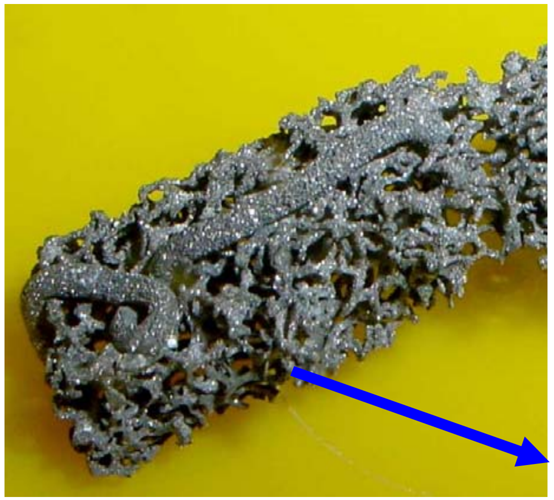


Better separation factors are expected using a solid Al cathode due to bigger difference in reduction potential.



SEM-EDX analysis of cathode surface



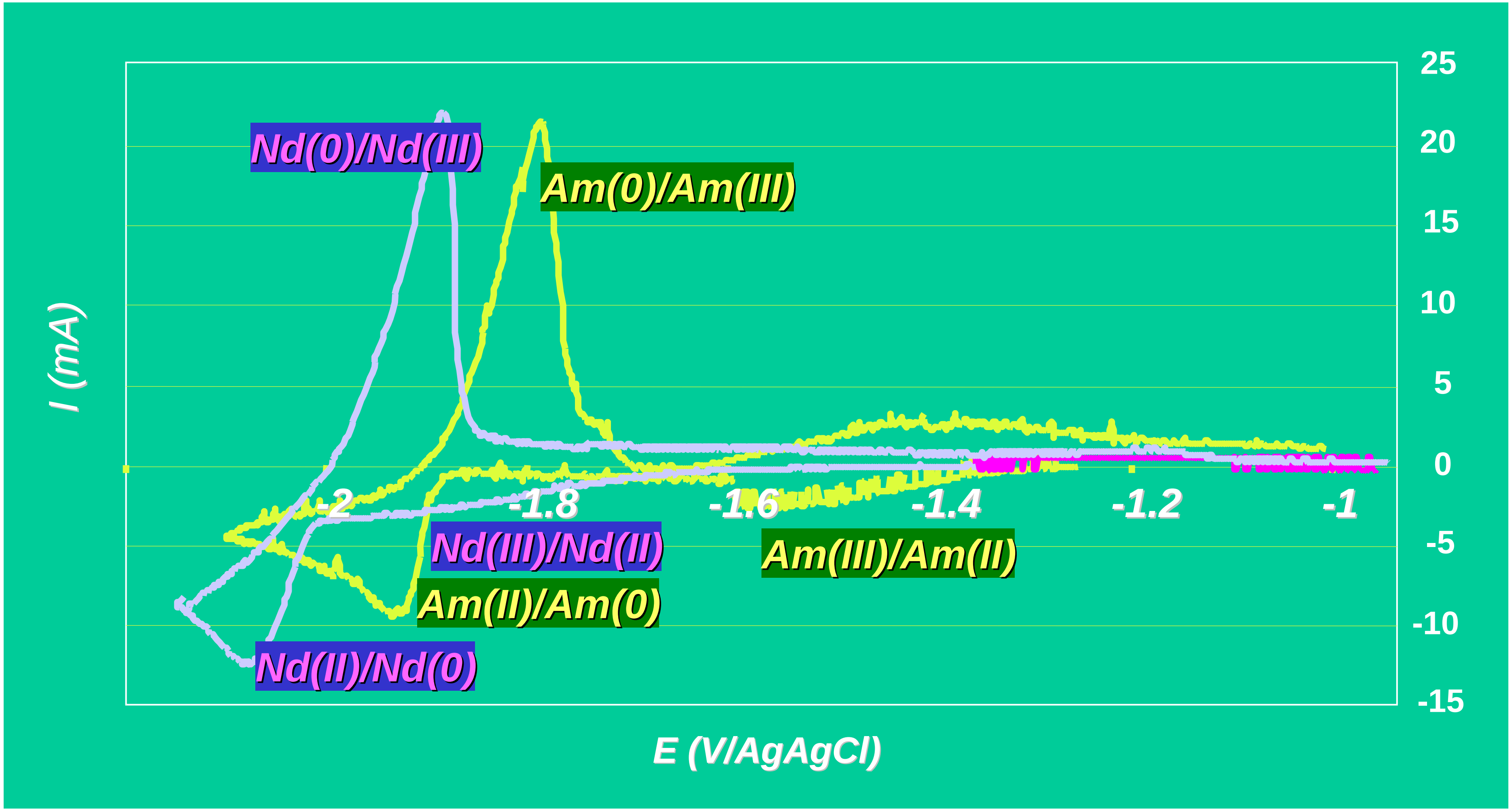


- *Good adherence due to $PuAl_4$ formation*
- *almost 100% faradic yield for Pu recovery onto Al cathode*
- *Excellent separation from Nd.*

Al foam (800 mg) covered by 350 mg of Pu

Pyroprocessing of metallic fuels

Am and Nd valency in molten salt

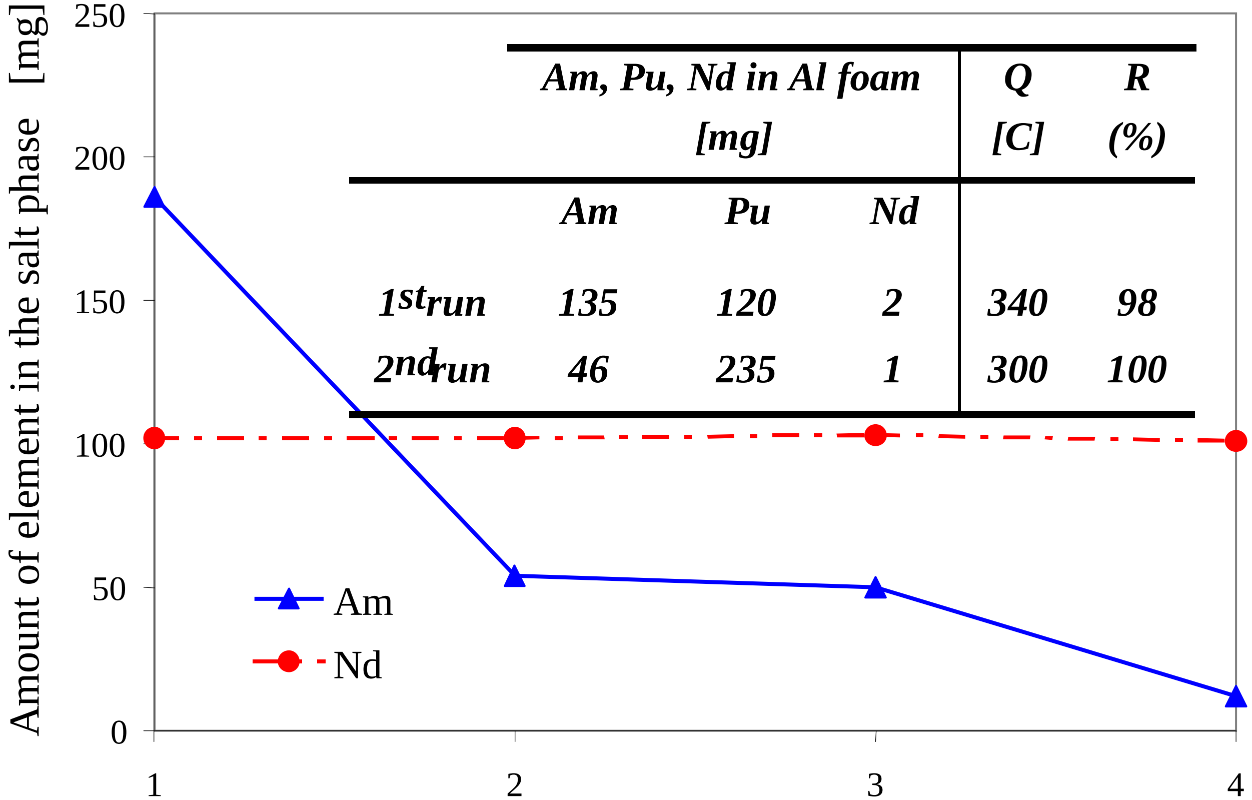


cyclovoltamograms of Nd and Am in liquid Cd

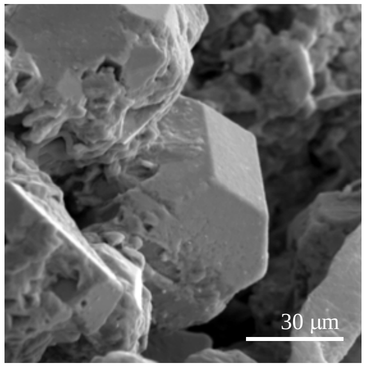
Separation of Am from Nd on solid Al foam

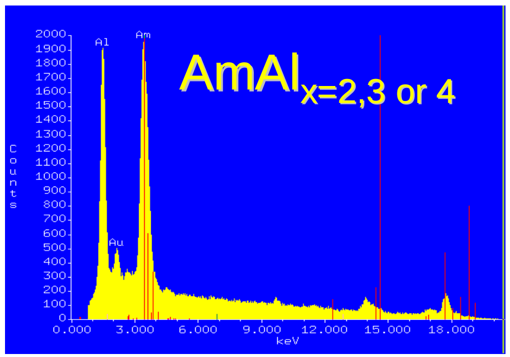
An electrolysis on Al foam performed at a cathodic potential equal or greater than -1.25V (vs. Ag/AgCl 1 wt %) allows only actinides to be recovered because

- ✓ *the difference in reduction potential is high*
- ✓ *the Am alloys with Al and thereby the Am cannot reoxidize to Am(II)*



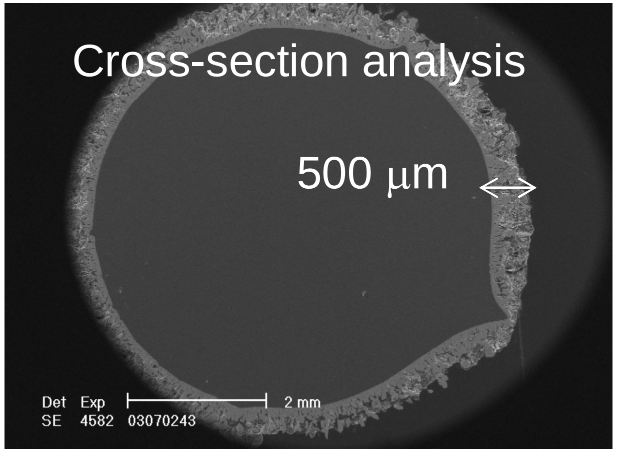
	Am, Pu, Nd in Al foam [mg]			Q [C]	R (%)
	Am	Pu	Nd		
1st run	135	120	2	340	98
2nd run	46	235	1	300	100



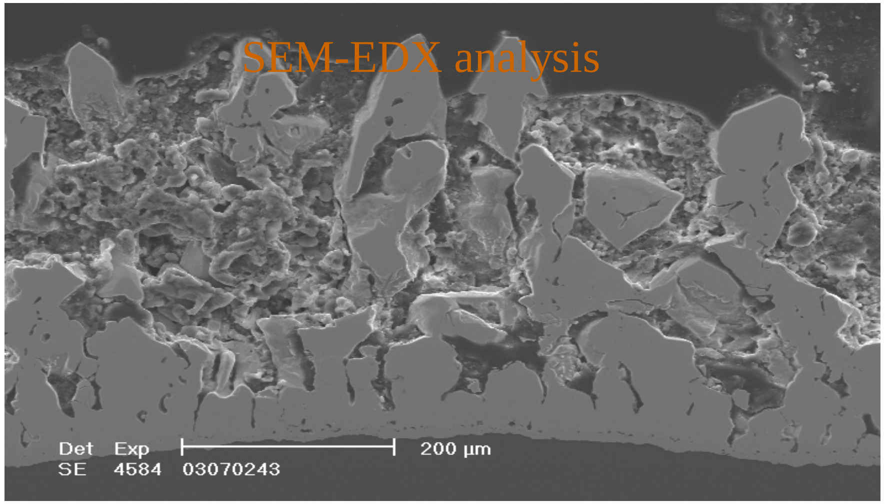


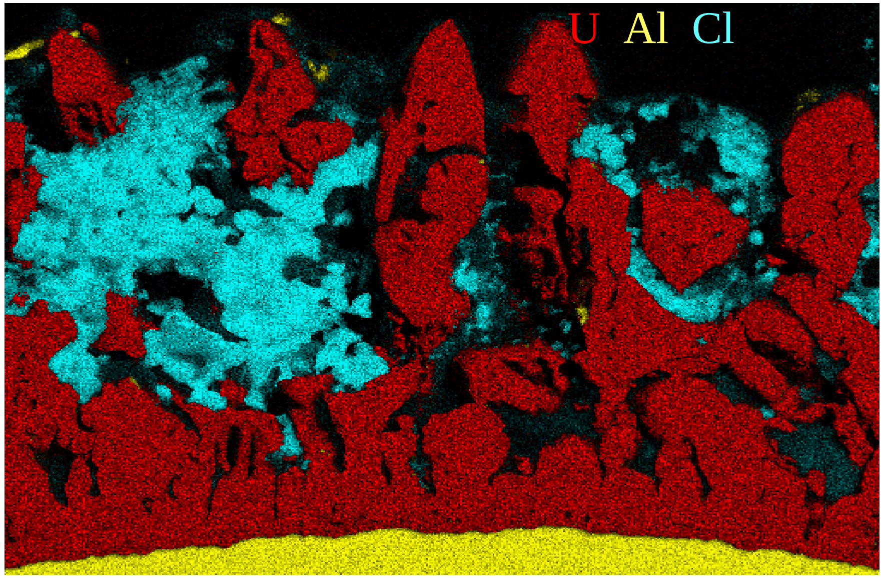
SEM / EDX analysis

Surface characterisation of deposit



- *U deposit after 735 C about 500 mm thick*
- *First 100 mm is a solid, compact UAl alloy without salt inclusions*
- *EDX mapping clearly identifies UAl_4 alloy*

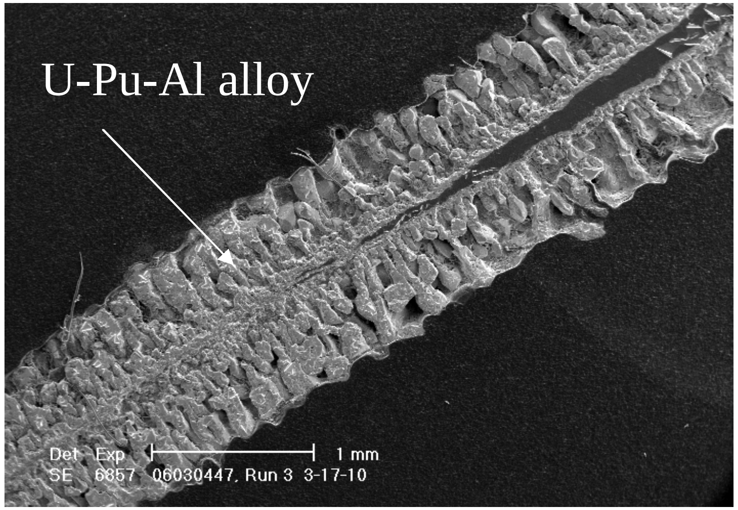




Pyro-reprocessing: in-house support

1. Strongly dependant on the analytical possibilities in ITU :

- ICP-MS : salt and metal samples analysis,
- NDA (g-spec and calorimetry) : development of non destructive techniques for specific samples (U+Pu content in Al cathodes),
- XRD : An-Al alloys characterizations, chlorinated products characterization,
- SEM-EDX : cathodes imaging and analysis.



SEM : Cross section of an Al cathode after loading with U-Pu

2. Thermochemical calculations (FactSage)

3. Supply of purified An as starting materials (An, AnCl, An alloys, etc…)

pyrometallurgical reprocessing: analyses

HR - ICP-MS
- analysis of bulk-trace elements
- hot cell instrument
- special procedures required

IDMS
- U, Pu, MA concentrations

absorption spectrophotometry
- U, Pu, Am-241 concentration and valency determination on dissolved salt sample
- U, Pu, Am-241 valency determination on solid salt pellet

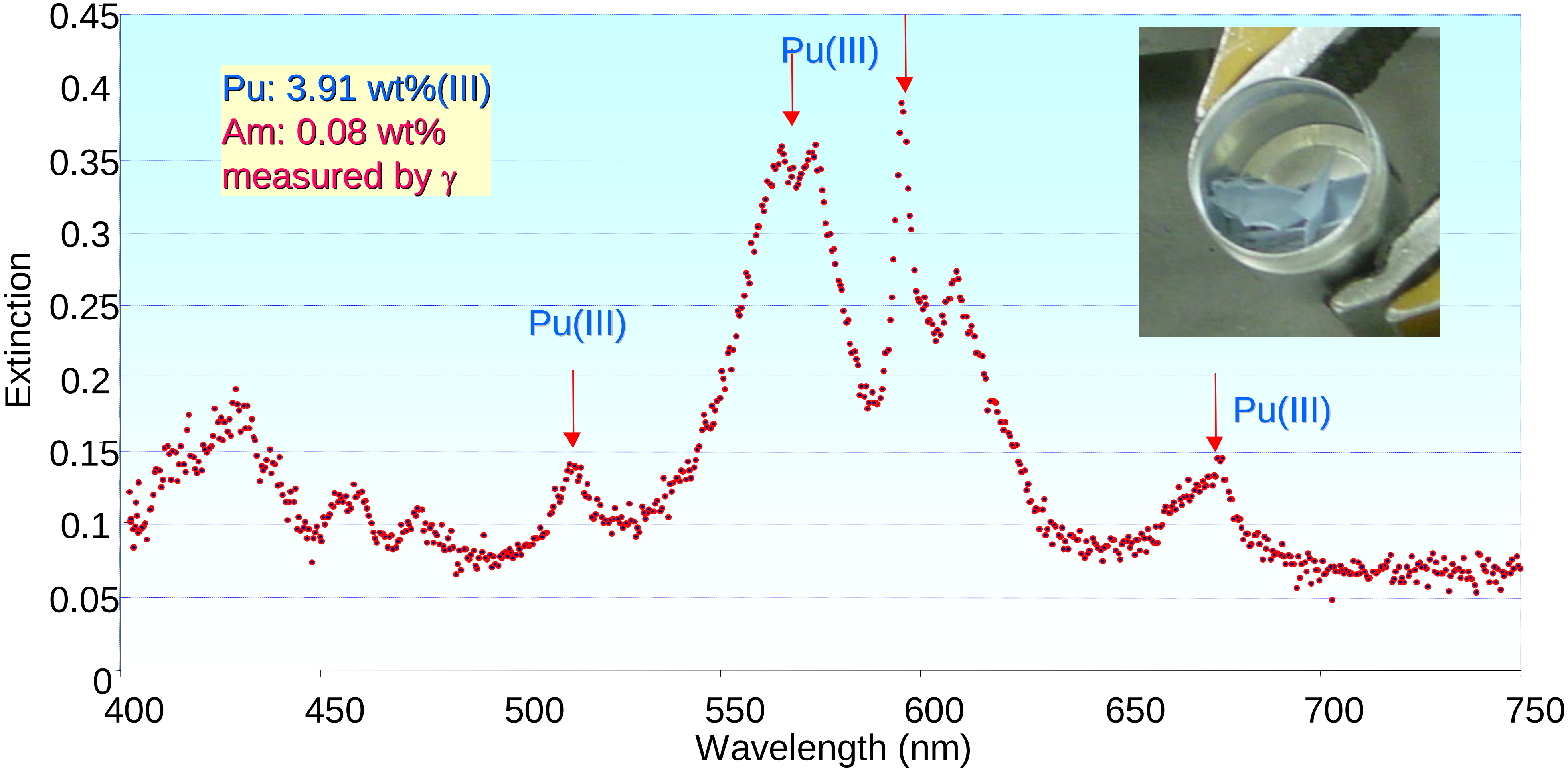
γ spectrophotometry
- Am-241 concentration determination on dissolved and solid salt sample

XRF and gamma counting
- determination of concentration and isotopic composition for TRU's

EUROPEAN COMMISSION

Pyrometallurgical Reprocessing

Spectrophotometric Analyses



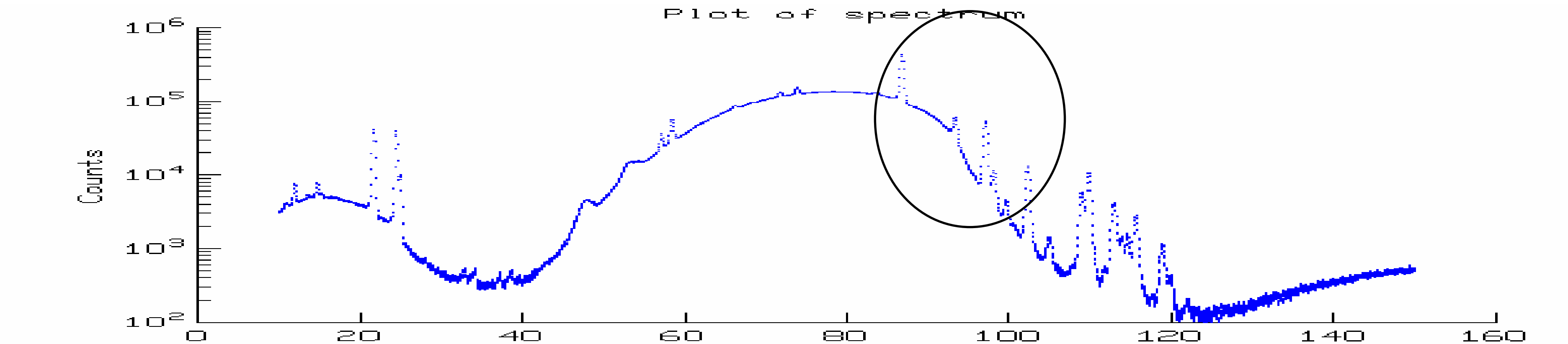
absorption spectrum of LiCl-KCl/KBr pellet

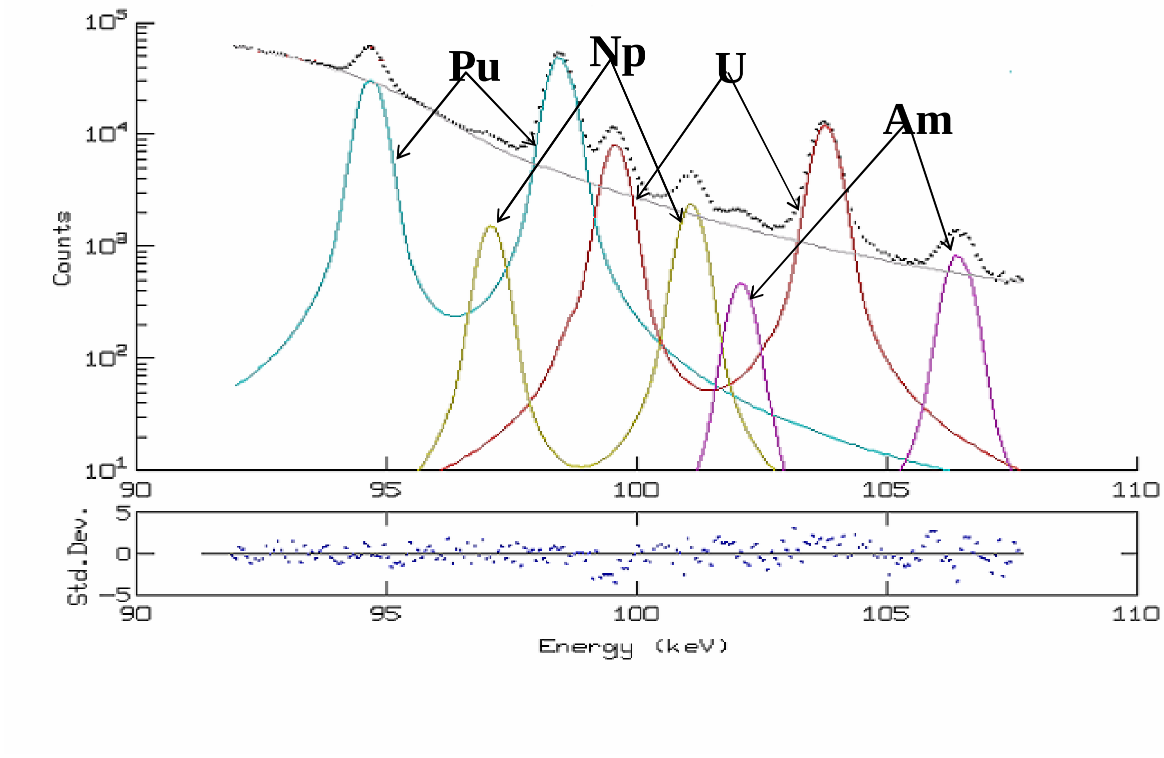
Application of radiometric techniques for MAs

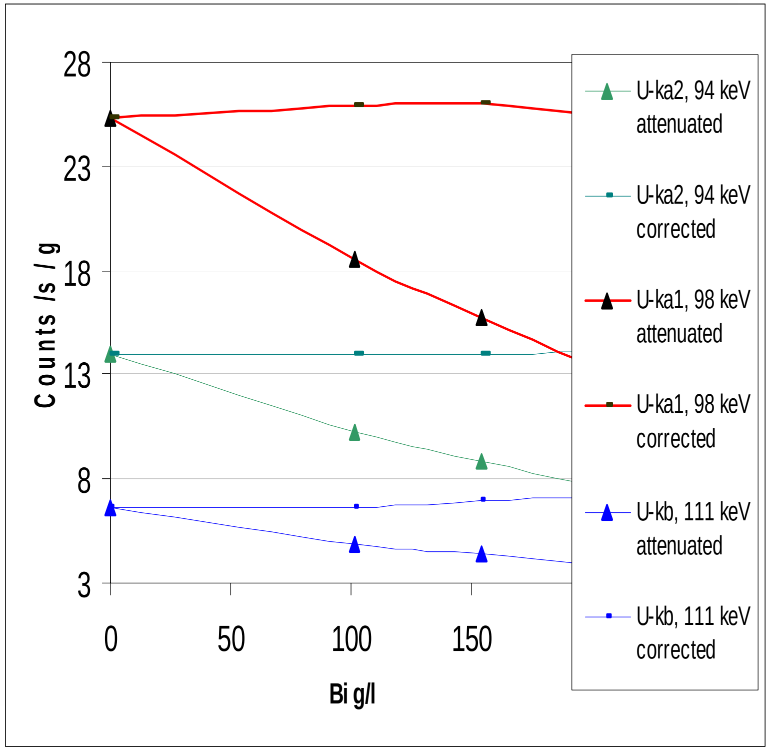
Technique	Element/ isotope measured	Isotope contribution to response*	Minimum amount for assay	Application
K-XRF	Np Am Cm	- - -	50 µg 70 µg 100 µg	Any sample type in liquid form mass fractions of analyte ≥ 0.02 %.
NCC	Cm	^{244}Cm. 90-95% ^{246}Cm: 5-10%	200 ng	For any type of Cm-containing samples (liquid or solid) with Pu/Cm ratios ≤ 1000
HRGS	^{237}Np ^{241}Am ^{243}Am	- - -	500 µg 10 ng 100 ng	Liquid samples for absolute measurements. Low FP content for ^{237}Np assay.
Calorimetry	Am Cm	^{241}Am: 98% ^{243}Am: 2% ^{244}Cm: 99% ^{243}Cm: 1%	5 mg** 200 µg**	Refractory MA fuels for transmutation. Combined with NCC/HRGS for interpretation.

* For typical MA isotopic composition in spent LWR/FBR fuels
** Can be lowered by factor of 10 when using microcalorimeters

XRF spectrum from a molten salt sample.







Electrorefining in Ionic liquids

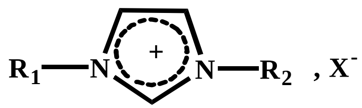
Ionic liquids:
+Low operating temperature
+Large negative electrochemical window

–High viscosity, therefore

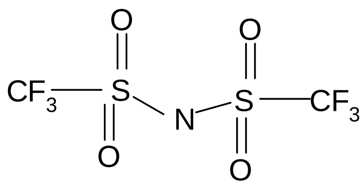
low reaction and diffusion kinetics

weak dissolution of chemicals

Cations:
N-N-dialkylimidazolium
R_1 = methyl ,ethyl or butyl



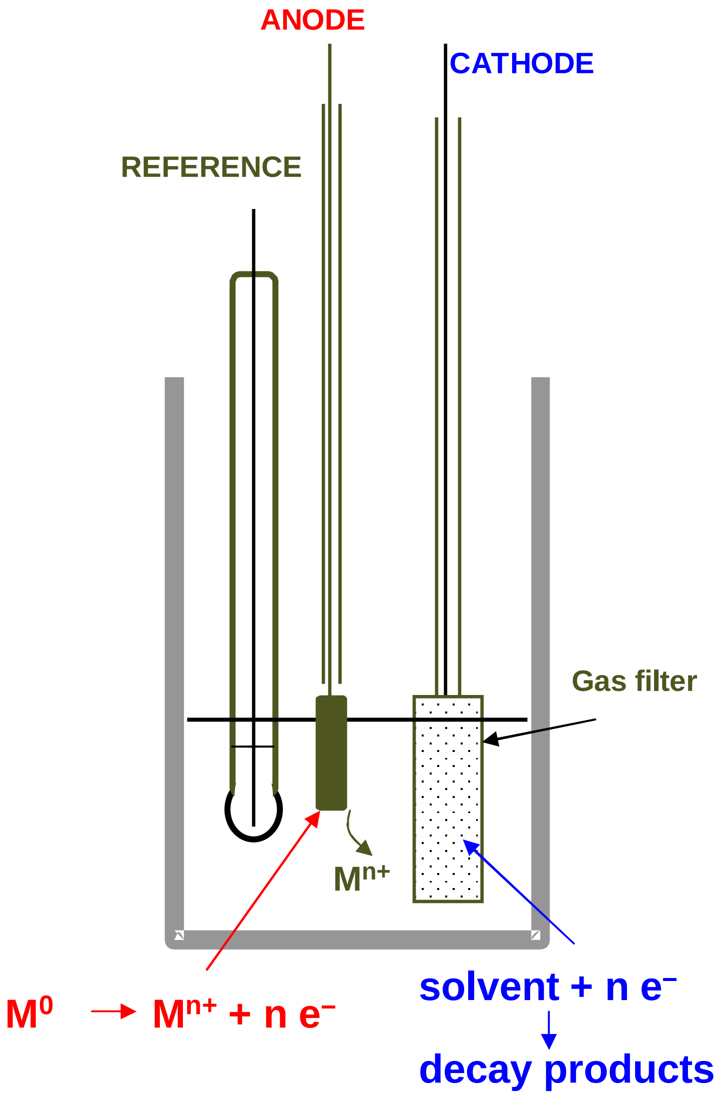
bistriflimide Tf2N- or TFSI



triflate Tf-

$CF_3SO_3^-$

Anions:
BF_4^- or Cl^- or $CF_3SO_3^-$

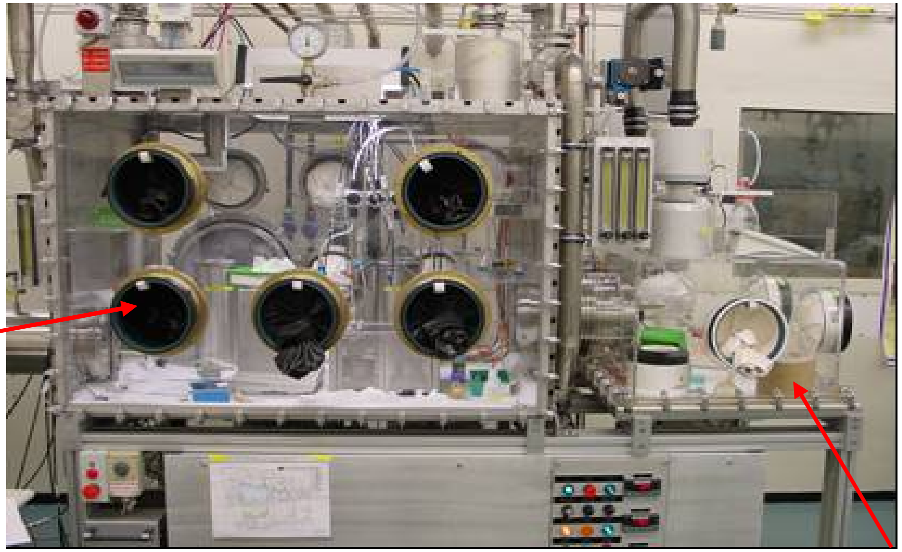


Ionic liquids: experimental set-up

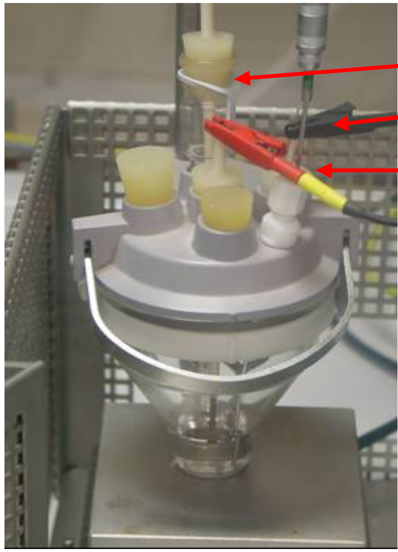
- *purpose-built glove box with purified argon atmosphere (1)*
  - *oxygen and moisture-free conditions (< 10 ppm)*
  - *handling of lanthanides and actinides metals*
  - *experiments from ambient temperature up to 200°C*
  - *UV-Vis spectrophotometer that makes possible in situ analysis*

- *connected smaller box (nitrogen atmosphere) (2) : synthesis of actinide-containing RTILs, vacuum distillation for moisture removal*

(1)

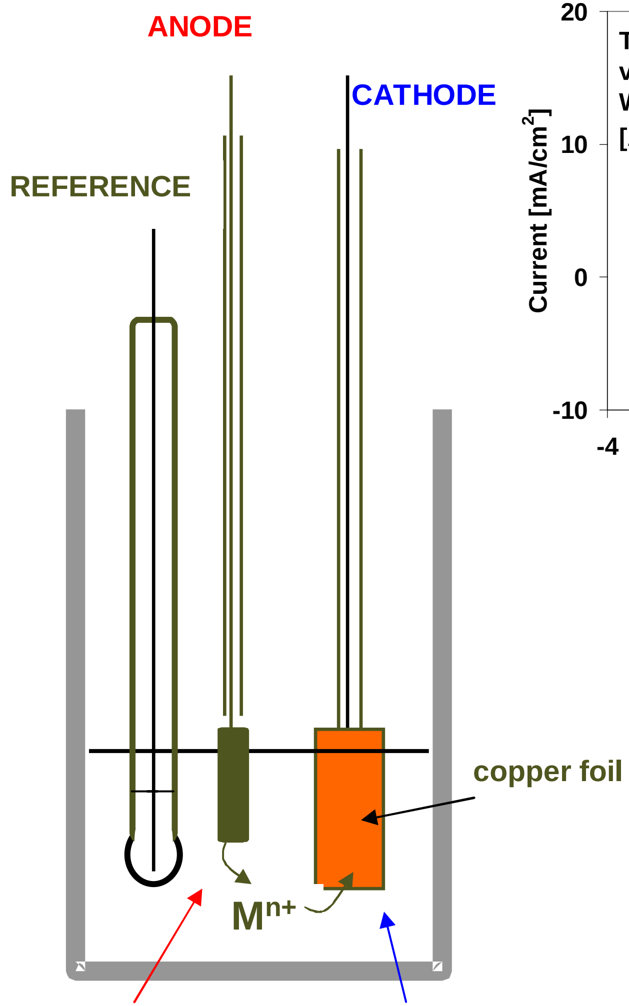


(2)

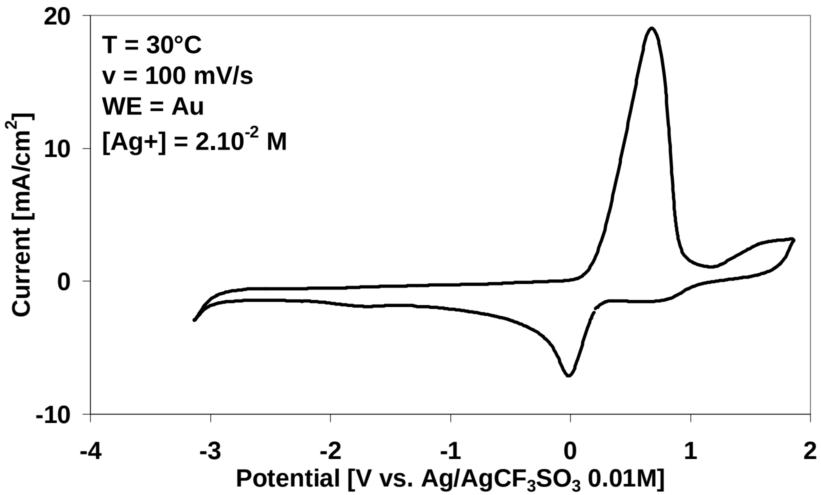


electrochemical cell

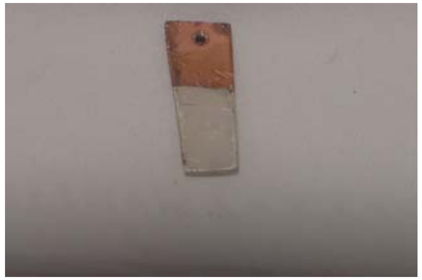
Ionic liquids: experimental set-up



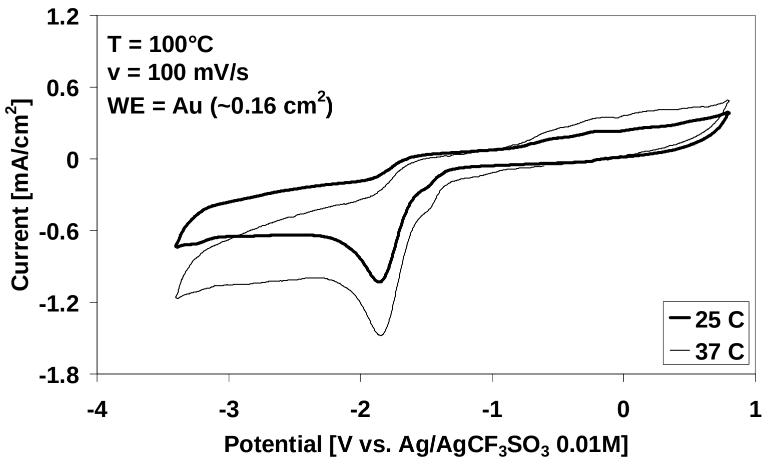
$M^0 \rightarrow M^{n+} + n\,e^-$ $M^{n+} + n\,e^- \rightarrow M^0$



Ag cyclovoltametry



Ag deposit on copper



U cyclovoltametry
not reversible

U deposit on copper

Outline 2

- *introduction*
- *some historical background*
- *basic principles and data*

break

- *process developments*
- *international networks and collaborations*
- *outlook*