

# Development of a GANEX Process

Emma Aneheim and Christian Ekberg



Waste is what is left when imagination fails

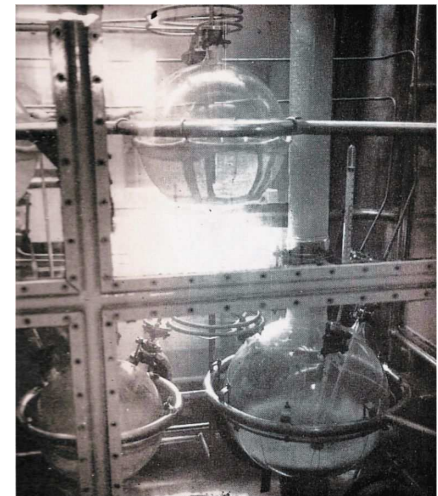
# Nuclear Waste Handling

- The used nuclear fuel contains excess uranium, FP and trans uranic elements (TRUs)
- Highly radiotoxic
  - short term mostly due to FP
  - long term mostly due to TRUs
- Needs to decay for >100 000 years to equal uranium
- The amount of used nuclear fuel in the world is 350 000 tons
- Different strategies for handling the radioactive waste:
  - Once through option
  - Wait and see – no decisions made
  - Reprocessing

# Nuclear Waste handling

## Reprocessing

- Recycling of parts of the used fuel
- $< 2\%$  of the energy is utilized in the once through fuel cycle
- U and Pu are separated (PUREX process) to make new fuel
- Increases the energy utilisation with 25% ( $\rightarrow 2.5\%$ )
- 100 000 tons of spent fuel has been reprocessed  
The capacity is ca 4800 tHM/year



# Nuclear Waste handling

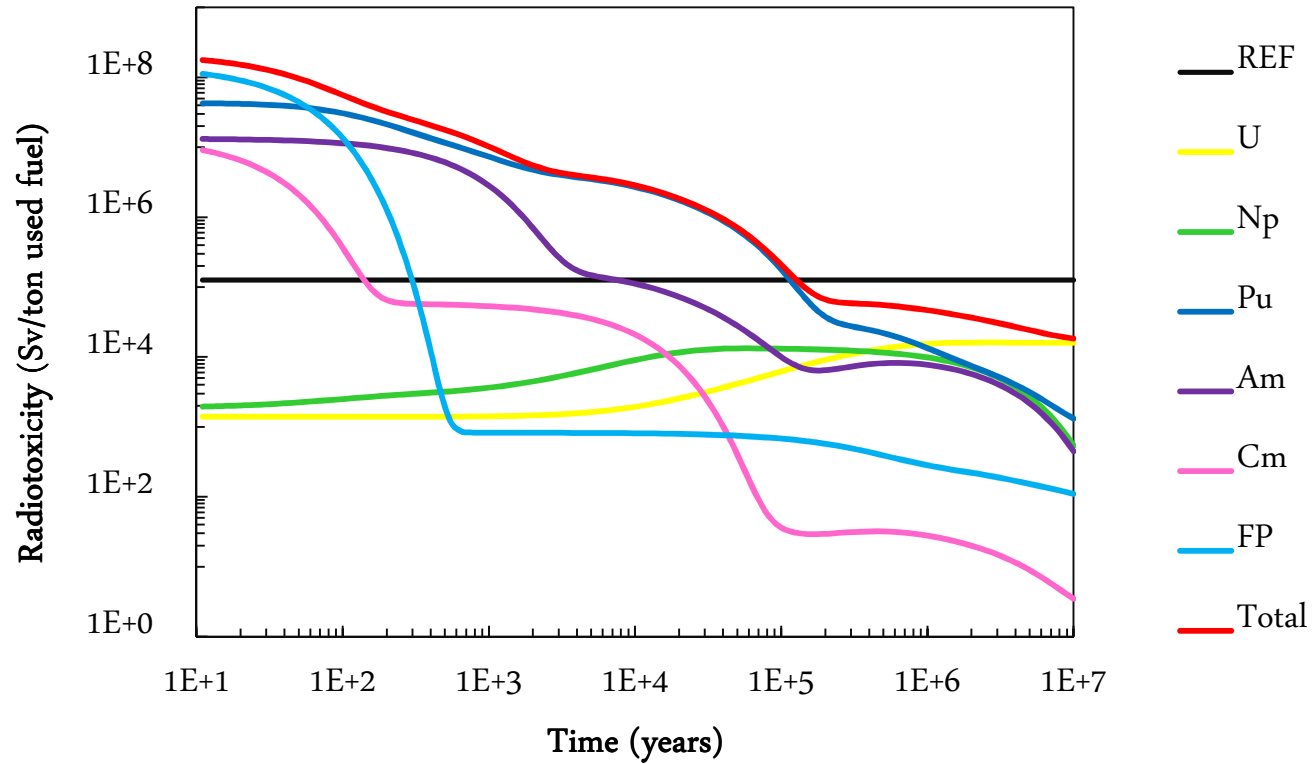
Country	Facility	App. Capacity (tonnes per year)
France	La Hague	1700
United Kingdom	Sellafield (THORP, Magnox)	1500+900
Russia	Ozersk (Mayak)	400
India	Kalpakkam, Trombay, Tarapur	275
(Japan	Rokkasho	800)

- More expensive to reprocess than to use fresh fuel
- Proliferation resistance
- Long storage time needed for the reprocessing waste

# Partitioning & Transmutation (Gen IV systems)

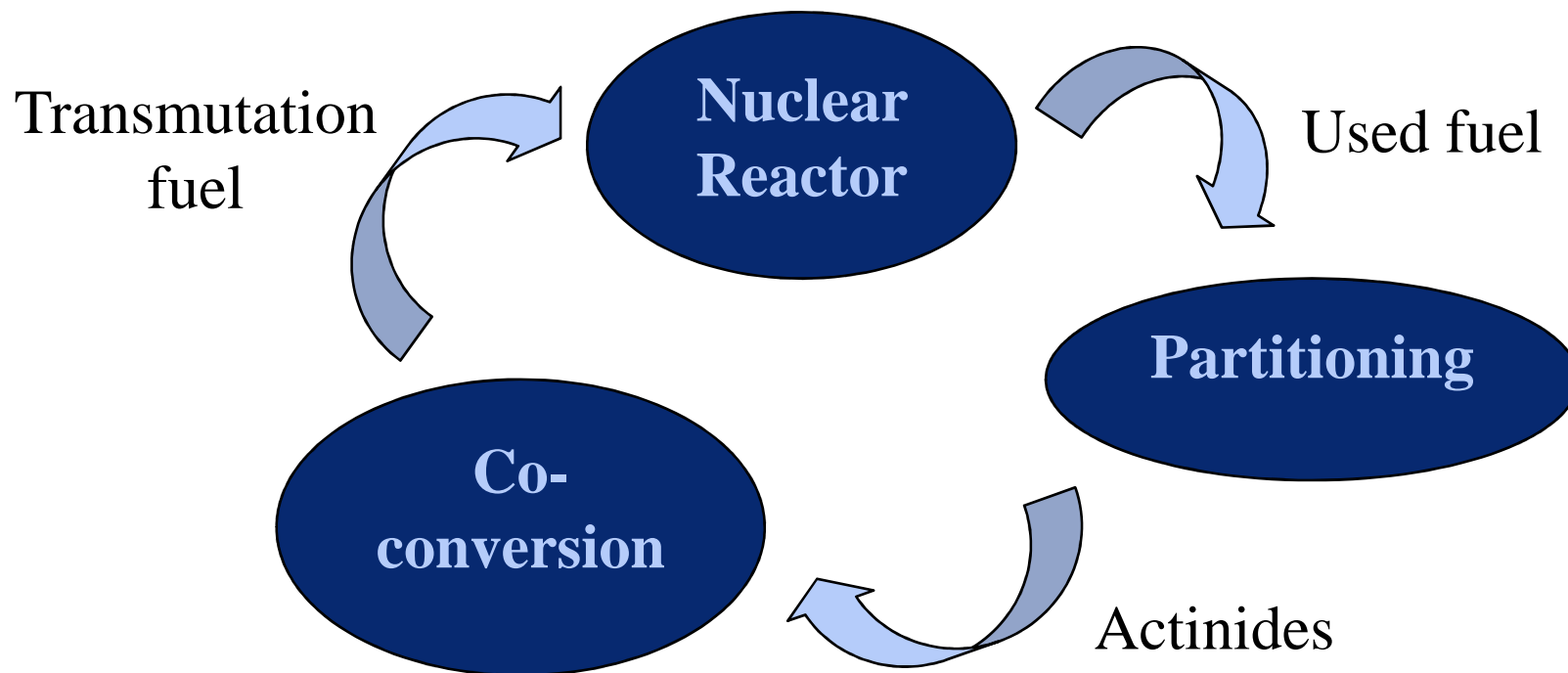
- Advanced version of reprocessing called:  
Partitioning and Transmutation (P&T)
- Separation of all the actinides from the fission products
- Radiotoxicity of the used nuclear fuel is mostly due to the transuranic elements Pu, Am and Cm

# Partitioning & Transmutation



# Partitioning & Transmutation

- P&T, a prerequisite for closing the fuel cycle...



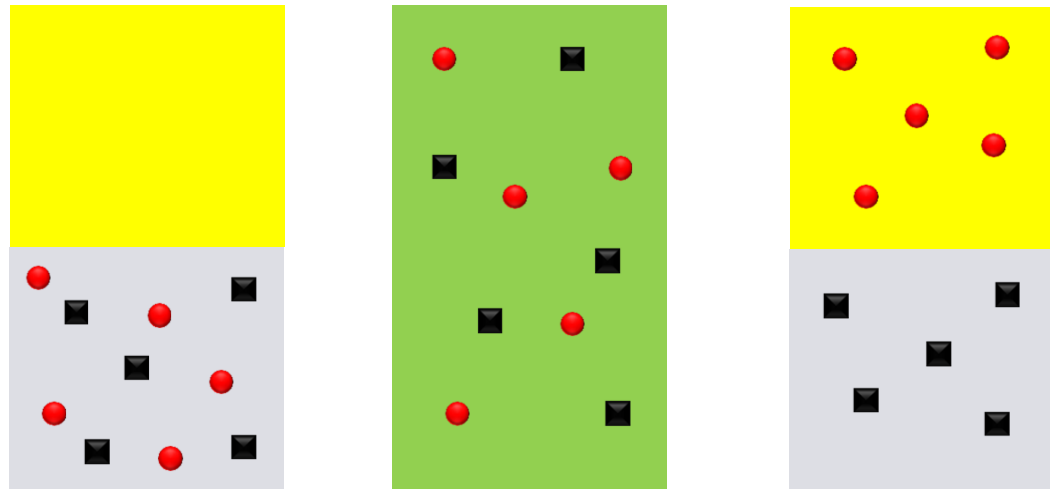
# Partitioning & Transmutation

- Why is separation of the actinides necessary?
  - E.g. Fission Products with high neutron capture cross section
  - Avoid build-up of new long-lived elements
- Method of choice to achieve the separation: Solvent extraction
  - Already existing technology (PUREX)
  - High purity
- Alternative Method to achieve the separation: Pyro processing
  - Proliferation safety



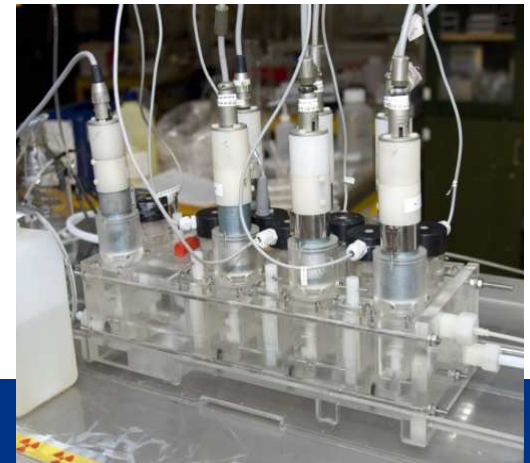
# Solvent Extraction

- Distribution of a solute between two immiscible liquid phases
- Solutes can partition differently between the two phases (organic and aqueous) => Separation
- Molecules that form complexes with the solutes can be employed to enhance the affinity of either phase

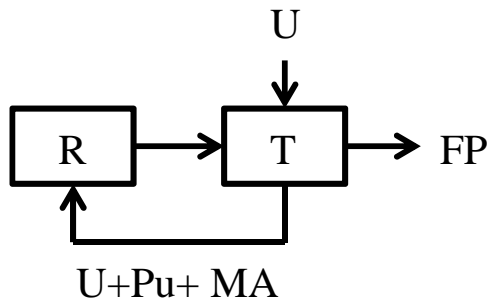


# The GANEX Concept

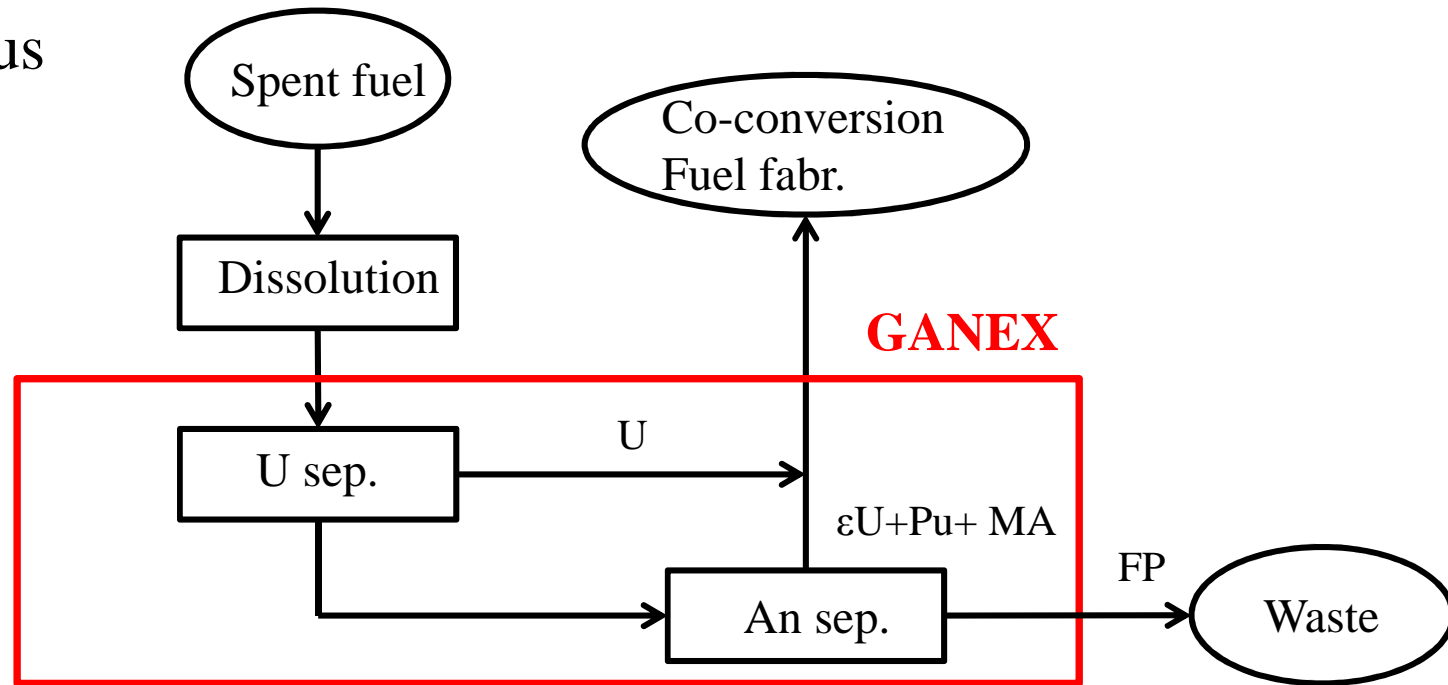
- GANEX= Group ActiNide Extraction (GANEX)
- A solvent extraction process aimed at P&T
- Previous P&T processes designed to come after PUREX
  - SANEX/DIAMEX, TALSPEAK (Heterogenous)
- GANEX - aimed at replacing PUREX, more proliferation safe
  - no pure plutonium stream (Homogenous)
- Extract all the actinides as a group directly from dissolved used fuel, with the removal of bulk U



# The GANEX Concept



Homogenous recycling



Several different GANEX processes are under development

# The Chalmers GANEX Solvent

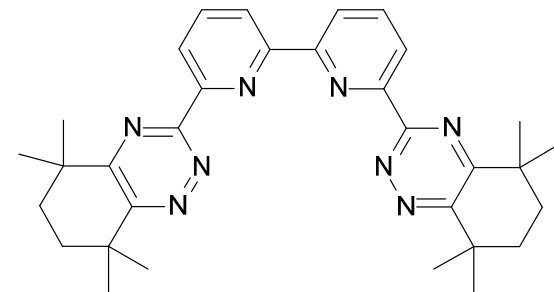
Combine two well known extractants with different properties:

## 1. *bi*-Terpyridine *bis*-Pyridine or **BTBP**

Known to: Extract trivalent actinides and separate them from the trivalent lanthanides. Extract pentavalent actinides.

Due to strong acid and irradiation, a stable BTBP is needed:

CyMe<sub>4</sub>-BTBP

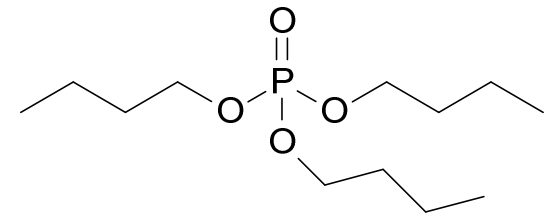


# The Chalmers GANEX Solvent

## 2. *tri*-butyl phosphate or TBP

Known to: Extract tetra- and hexavalent actinides (PUREX process)

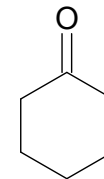
1+2 => No need for redox control



The extractants (BTBP+TBP) should be combined into one solvent  
"the GANEX solvent"

The diluent used for this (so far) is cyclohexanone

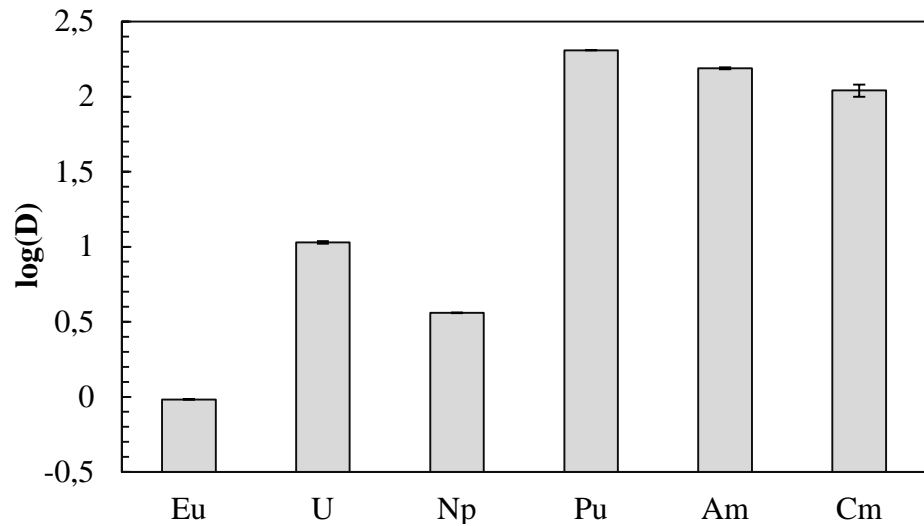
- solubility
- kinetics



# The Development Process

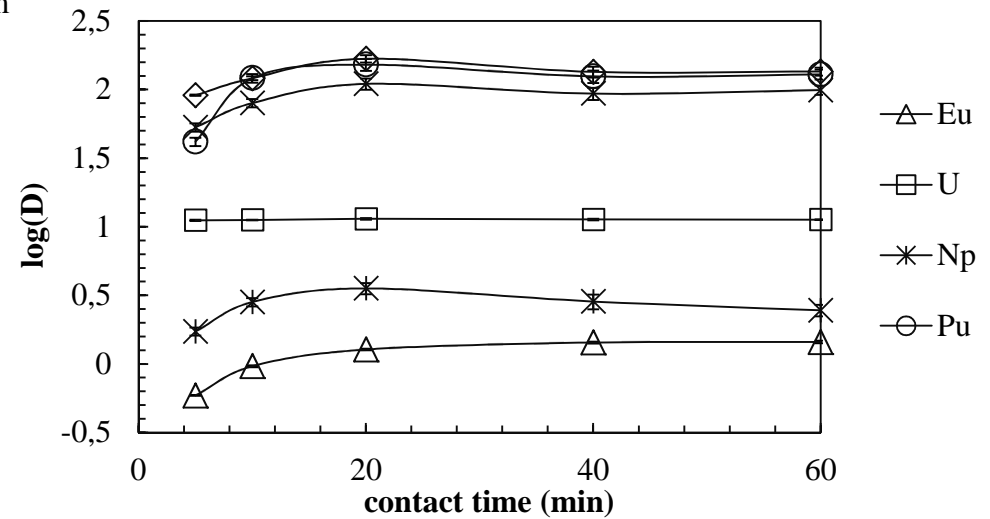
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  - An extraction, kinetics, An/Ln separation
  - Extractant behaviour – e.g. synergistic/antagonistic effects
- Stability
  - Hydrolytic
  - Radiolytic
  - Temperature
- Fission and Corrosion Product Handling
  - Extractions
  - Action plan- solutions
- Towards Process Implementation
  - FP Loading
  - Batch process test
  - Continuous tests

# Screening of the Extraction Behaviour



$$SF_{Am/Eu} = 160$$

Fast kinetics (< 20 min)



# Screening of the Extraction Behaviour



The extractants doesn't react with each other

Neither affect the extraction behaviour of each other

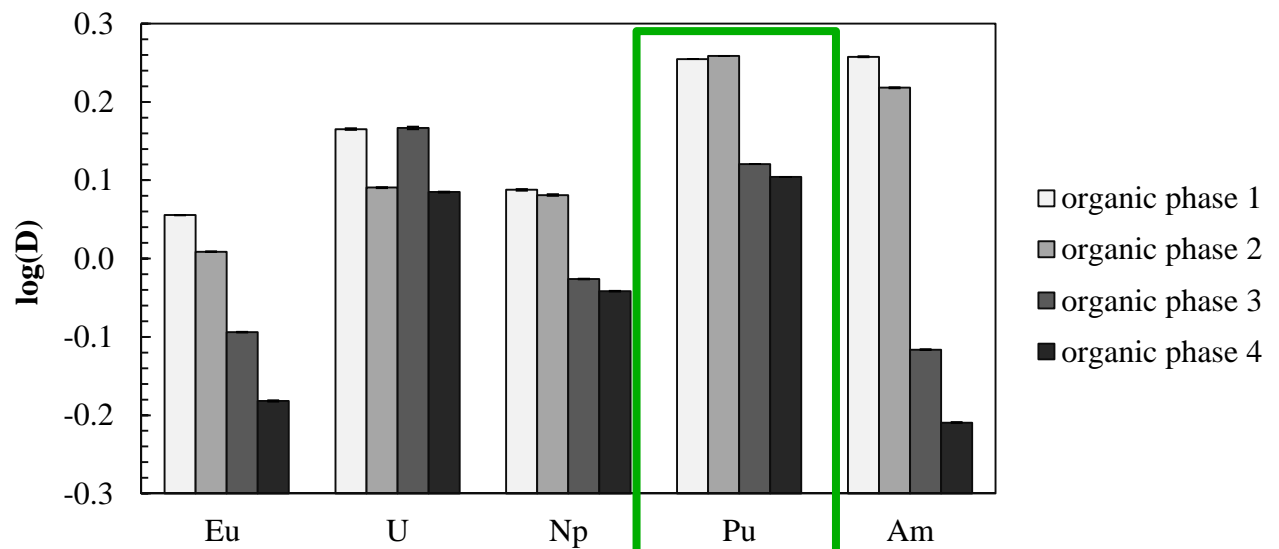
1=BTBP+TBP

2=BTBP

3=TBP

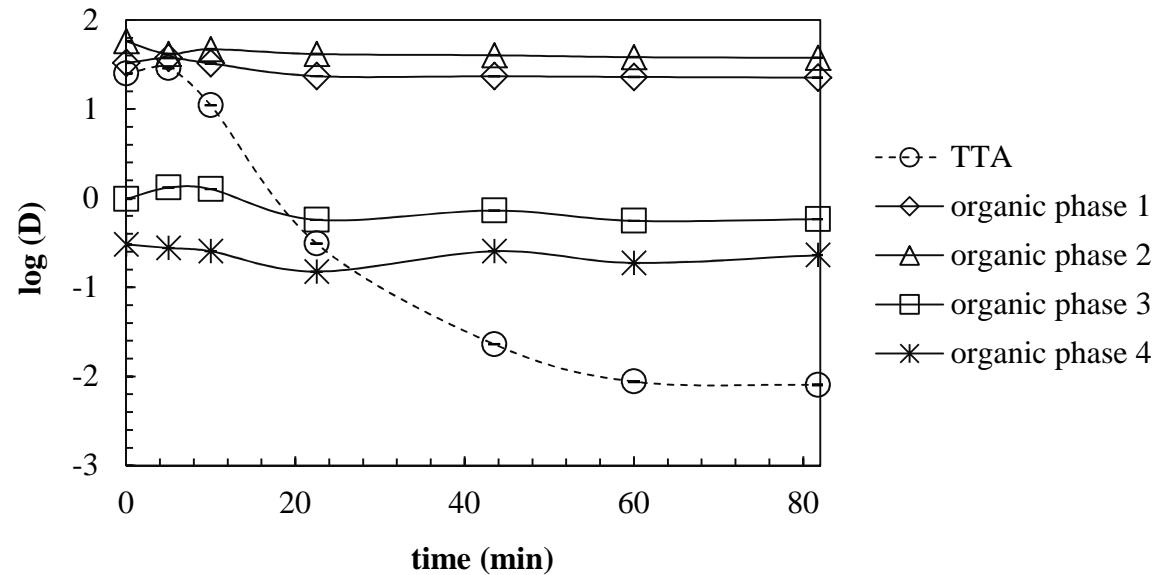
4=cyclohexanone

1M HNO<sub>3</sub>+3M NaNO<sub>3</sub>





# Screening of the Extraction Behaviour

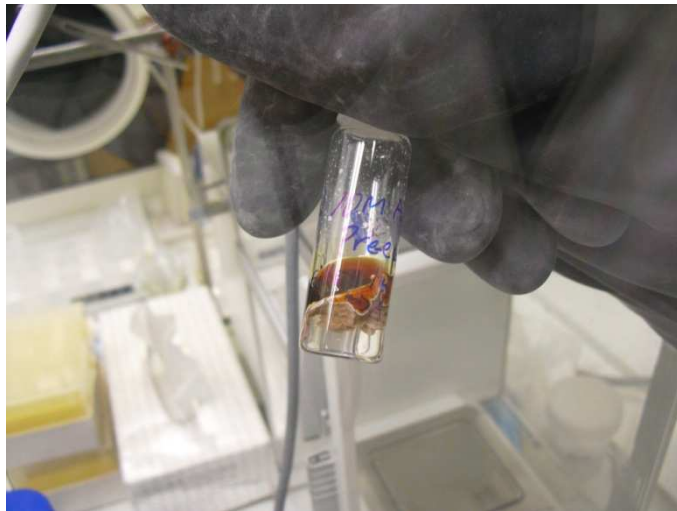


Plutonium extracted by BTBP in this solvent!

Important to consider in the context of Plutonium loading...

# Pu loading

Original stock, 4.5 g Pu in HCL, add AgNO<sub>3</sub>, precipitation of AgCl



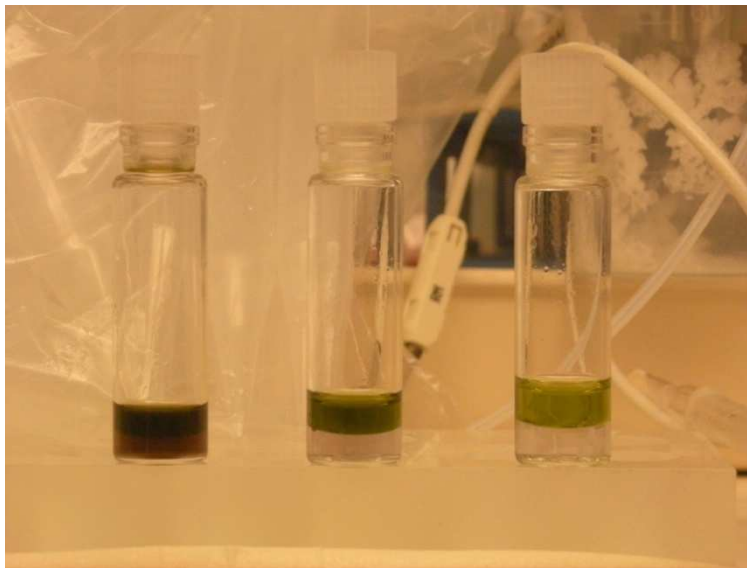
# Pu loading

Three concentrations extracted (pure organic solvent to the left)



# Pu loading

## Three concentrations extracted



**To the left: The solution directly from the precipitation! 37 mM 8.8 g/l**

**In the middle: 9.5 mM 2.2 g/l**

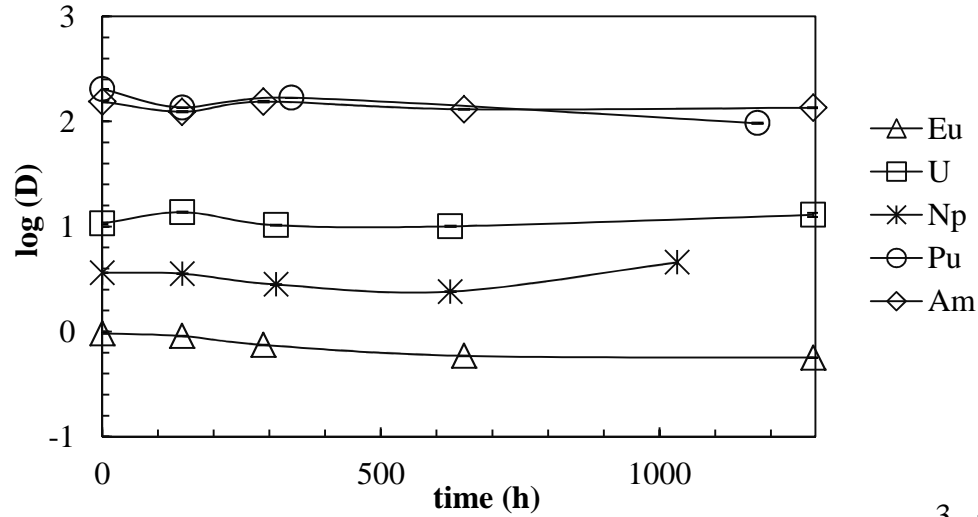
**To the right: 3,7 mM 0.88 g/l**

# The Development Process

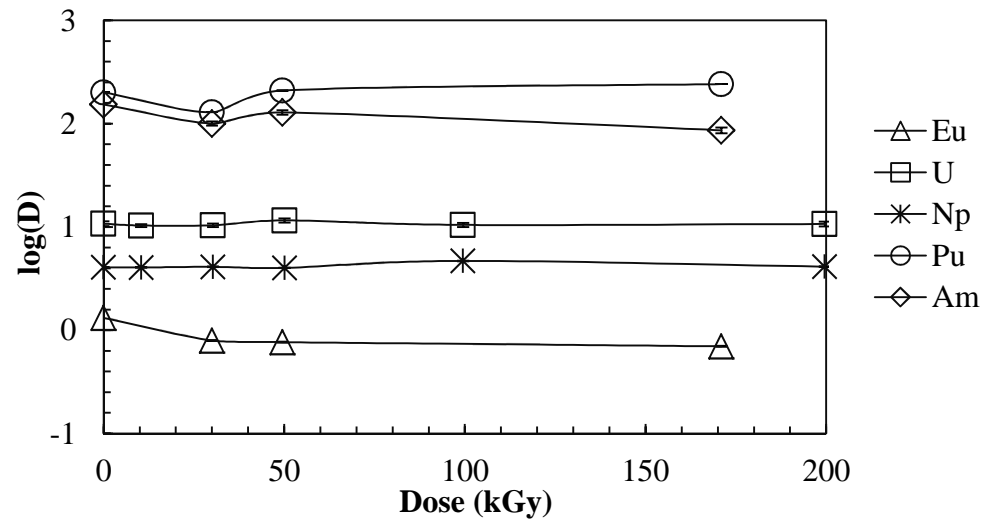
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# Stability

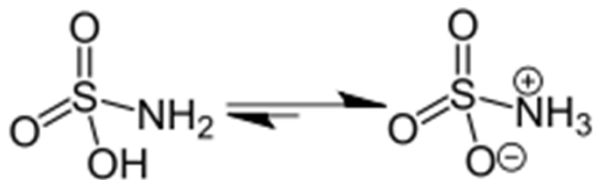
- Hydrolytic



- Radiolytic



- Temperature

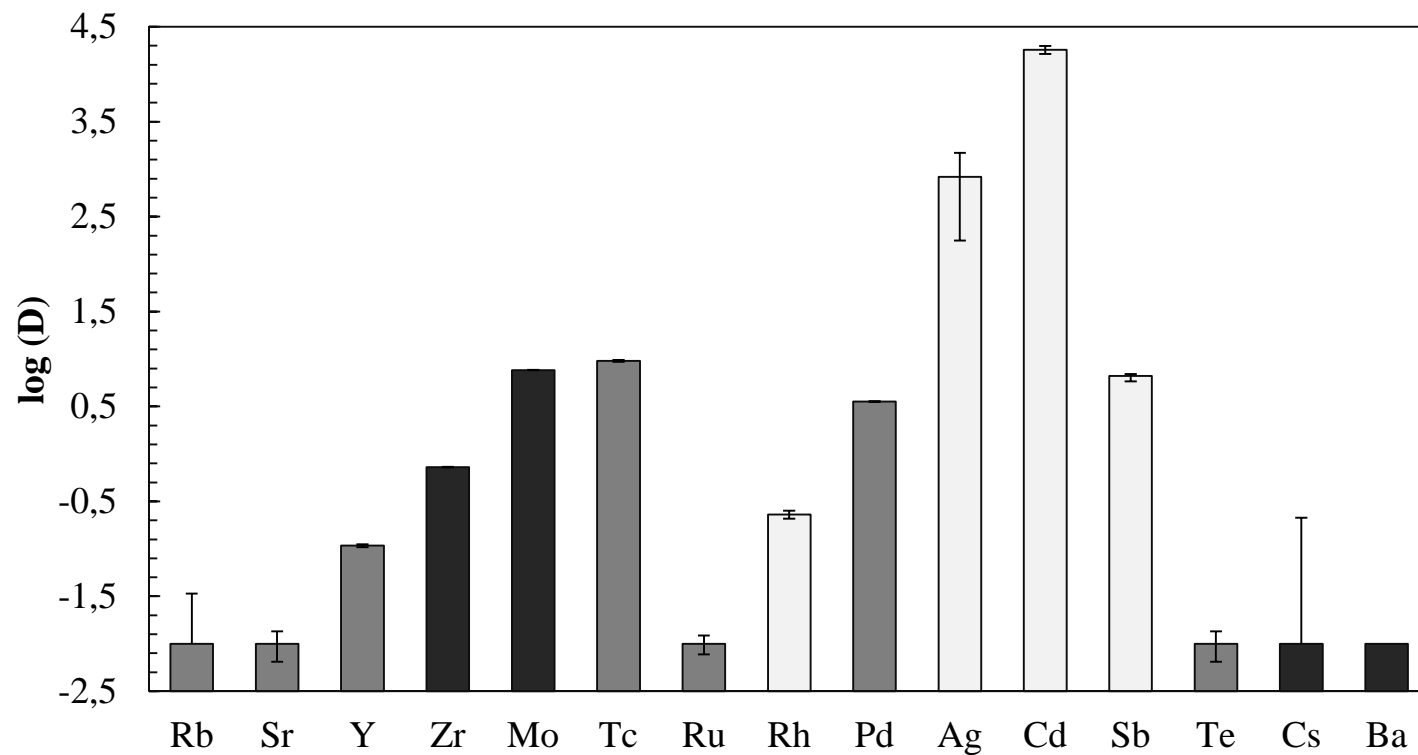


Stable after nitrous acid scavenger addition

# The Development Process

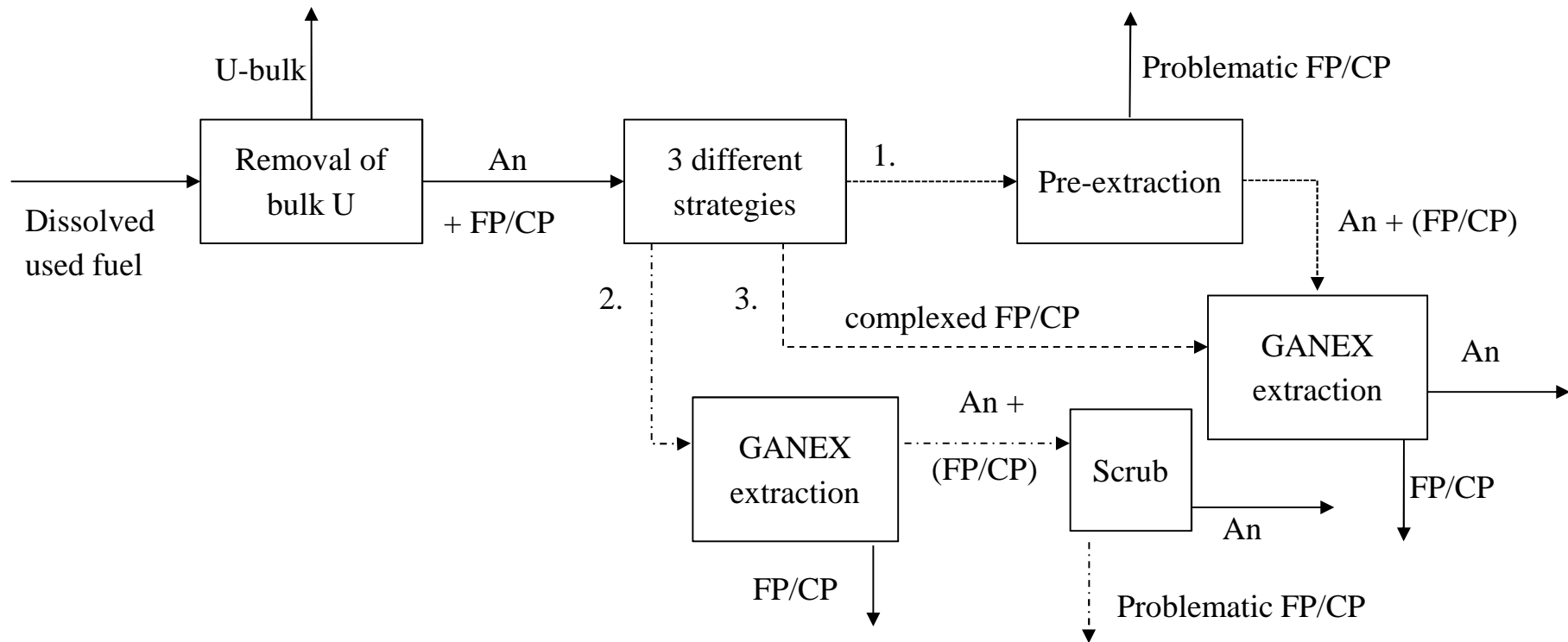
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# Fission and Corrosion Product Handling

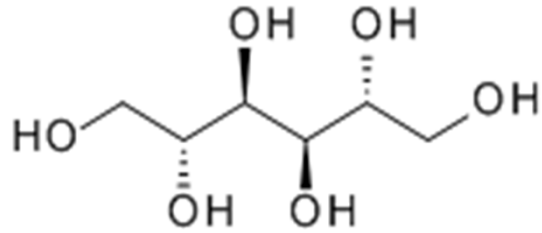




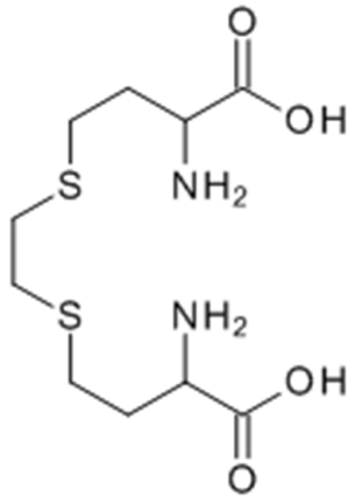
# Fission and Corrosion Product Handling



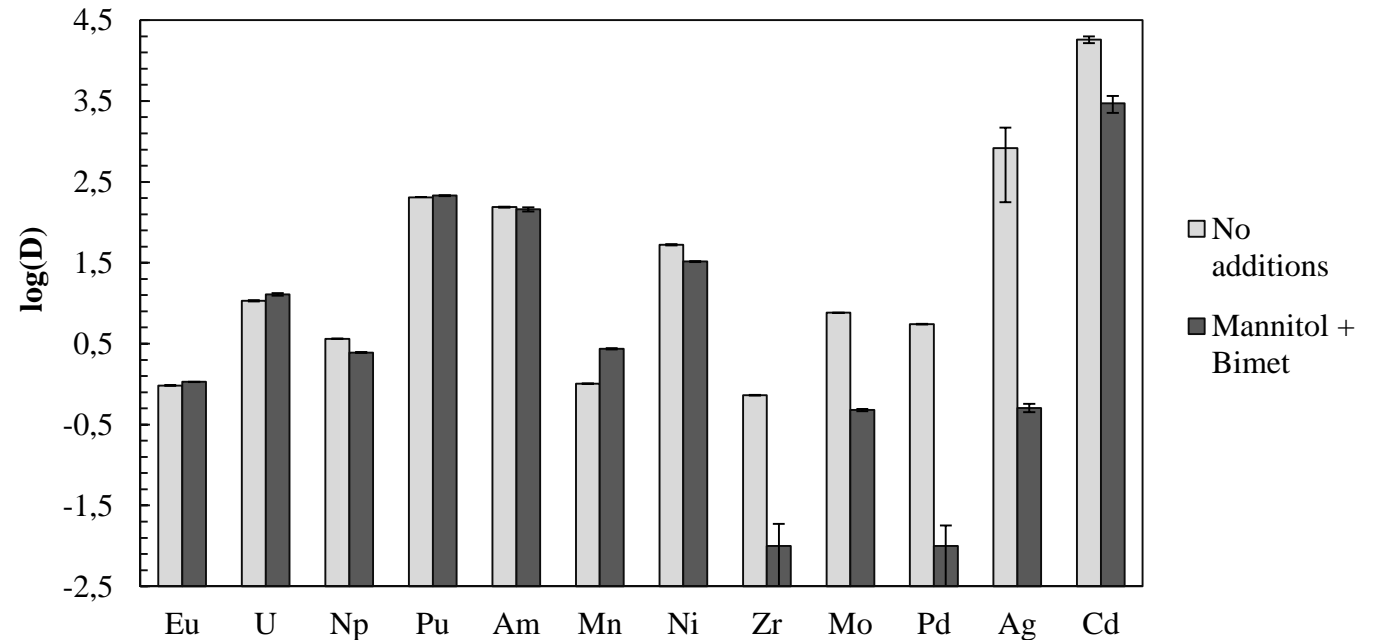
# Fission and Corrosion Product Handling



Zr, Mo suppression



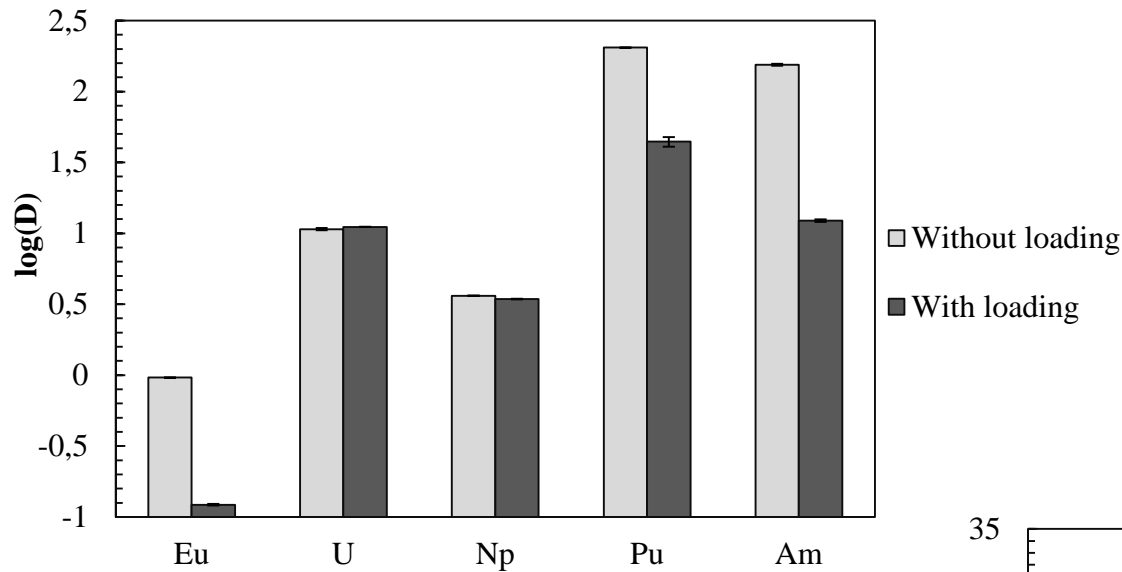
Pd, Ag, Zr suppression



# The Development Process

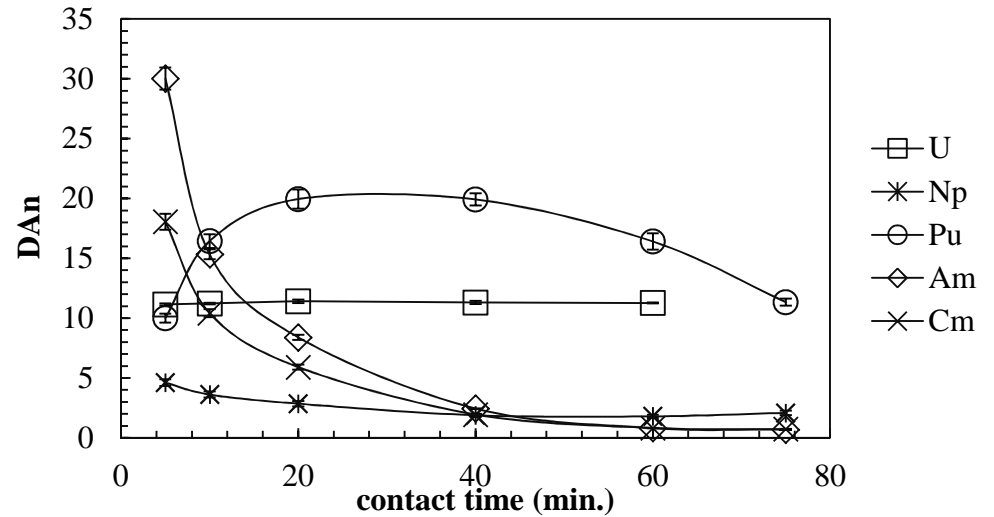
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# Towards Process Implementation



FP Loading at Chalmers = OK

FP Loading in Jülich = affecting An extraction!  
-Large Iron content



# Towards Process Implementation



Centrifugal contactor test

HAR diluted 1:10, increased aq phase density

# Towards Process Implementation

Element	% of initial in aqueous strip
Eu	0.32
U	93.5
Np	99.8
Pu	99.6
Am	99.8

## Centrifugal contactor data

$$\Theta=0.6$$

15 extraction steps

3 acid scrub steps

1 strip step

## Batch Process data

$$\Theta=0.6$$

7 extraction steps

6 acid scrub 1 steps

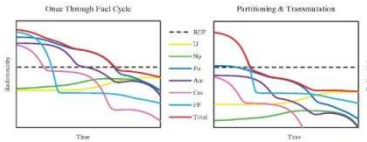
6 acid scrub 2 steps

1 strip step

Element	% of initial extracted	% of initial in aqueous strip
Eu	11	9.1
U	100.0	95
Np	100.0	96
Pu	100.0	58
Am	100.0	25



# ELECTRA-CHALMEX



Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel

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Kärnkraften står i mål för knappt hälften av hela Sveriges elproduktion och är ett av de alternativ som ger oss låga kol-dioxidutsläpp per minnt bidrag till den så kallade vättnings-faktorn. I dag används endast en väldigt liten del av energin i kärnbränslet och dessutom måste avfallet slutförvaras under en mycket lång tidspenod (över 100 000 år) för att anses säkert för människor och miljö. Varje år producerar svenska kärnkraftverk 150-200 ton kärnavfall som i framtiden skall slutförvaras 50 meter ner i utbyggt stannor Forsmark i Upland. Att endast använda en liten del av energinnehållet i bränslet för att sedan slutförvara det gör dock kärnkraften till ett vack-samt energialternativ ur hållbarhetsperspektiv. Om de farligaste ämnena (de långlivade aktiniderna) som finns i det använda kärnbränslet kunde separeras ut och användas som nytt bränsle (transmuteras) så skulle energifaktorn öka, samtidigt som lagringstiden i det planerade slutförvaret skulle kunna kortas ner till mer greppbara 1000-års fr. Konceptet, som heter separation och transmutation, skulle kunna göra kärnkraften mer hållbar.

Separationen av aktiniderna kan utföras med en metod som kallas vättske-vätske extraktion. Vättske-vätske extraktion utnyttjar det faktum att många organiska lösningsmedel inte är blandbara med vatten. Genom att lösa upp det utbrända kärnbränslet i lösnings-medel och använda specialdesignade organiska extraktionsmedel och lösningsmedel kan aktiniderna sedan selektivt extraheras från vattenfasen till den organiska fasen och på så sätt separeras från de övriga ämnena i det använda bränslet.

I det här arbetet har ett innovativt vättskeextraktionssystem (enligt GANEX-modellen) för återvinning av använt kärnbränsle utvecklats och analyserats. GANEX (Group Acti-Nide EXtraction)-modellen innebär att aktiniderna separeras tillsammans som en grupp från de resterande ämnena i det använda bränslet. Det här är fördelaktigt ur icke-spred-ningsperspektiv då man sålgt släpper en ren plattinamateria. Den här extraktionen är dock inte så enkel att genomföra. I det applicera bränslet återfinns nämligen en mängd olika metaller (fissionsproduktier) vars vassa extraheras med samma molekyler som kan användas för att extrahera aktiniderna. Ökta metaller måste därför utvecklas för att för-hindra den önskade molekylstraktion som t.ex. att tillåta vattenlösliga molekyler som håller kvar metallerna i vattenfasen. Dessutom så måste den organiska fasen vara stabil både mot den starka syran samt mot den bestrålning som kommer från de radioaktiva ämnena i bränslet. För att utvärdera om extraktionssystemet är lämpligt för mer storskalig användning måste även frägesällningar rörande vättskeextraktionssystemet tas i beakt-ande och experiment i densamma utföras.

- A GANEX process based on well known reagents and diluents (TBP, CyMe4-BTBP and cyclohexanone)
- Process parameters developed and tested within EU FP7 project ACSEPT
- Equipment will be AKUFVE centrifuges run in SISAK mode
- Very high throughput but small dead volume = no criticality risk
- Optimal storage tanks eliminating criticality issues
- Small and flexible unit where different extraction processes can be tested and optimised
- Based on a thesis by Emma Aneheim at Chalmers (co funded by the EC and SKB)

# Conclusion

- Many aspects are needed to be investigated and understood before any separation process can be used practically
- Experiments are needed. Computer exercises are far from adequate for systems development or even proof of principle
- Proof of concept of a true **Group Actinide Extraction** system has been made, now...
- Further solvent improvements – performance, safety etc.
  - New diluent ?
  - New extractant ?
  - Development now part of EU project SACCESS