Recent progresses in advanced Actinide recycling processes

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Advanced processes for Actinide recycling:
French recent experiments and results

December 30, 1991 and June 28, 2006

OUTLINE


2 – (2006-2012) Recycling R and D program, in the frame of the 2006 Act

3 – Recent and on going R and D results for MAs recycling

4 – Industrial potentiality

5 – Conclusion
Radiotoxicity of waste, to be disposed

Spent fuel

Uranium (ore)

Time after unloading (years)

250 000 years
Radiotoxicity of waste, to be disposed

- **Uranium (ore)**
- **Spent fuel**
- **Glasses FP+MA**

- 10,000 years
- 250,000 years

**Time after unloading (years)**

Radiotoxicity relative

- Samples: Glasses FP+MA
- Time: 0, 1, 10, 100, 1000, 10000, 100000, 1000000
Radiotoxicity of waste, to be disposed

Time after unloading (years)

- Glasses without MAs (only FPs) 300 years
- Glasses FPs+MAs 10,000 years
- Spent fuel 250,000 years
- Uranium (ore) 250,000 years

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Radiotoxicity of waste, to be disposed

- Glasses without MA (FPs only)
- Glasses Pu multirecycling
- Spent fuel
- Uranium (ore)

Time after unloading (years)

- Radiotoxicity relative
- Spent fuel
LLRN Recycling for waste management

1st contributor: Pu
2nd contributor: Minor Actinides Np, Am, Cm
3rd contributor: Long-Lived Fission Products (LLFP)

Potential radiotoxicity

Processing and Recycling should minimize both the needed repository space and environmental impact

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Needed waste repository space, versus strategy

Due to interim storage time
Due to Am partitioning
Due to Cm partitioning

Interim storage time

<table>
<thead>
<tr>
<th>Interim Storage Time</th>
<th>Reduction of Necessary Repository Space</th>
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<tbody>
<tr>
<td>70 years</td>
<td>1</td>
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<tr>
<td>90 years</td>
<td>10</td>
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<tr>
<td>120 years</td>
<td>10</td>
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Actinide recycling: what fuel cycle option?

- **U and Pu recycled, **
  - **PUREX**

- **U and Pu recycled together, **
  - **COEX**

- **MA heterogeneous recycling**

- **MA homogenous recycling**
  - **MA: Np, Am, Cm**

- **FP&MA**

- **FP**

- **R → T**
The enhanced Partitioning 2005 results

- **A true challenge**: a sophisticated partitioning chemistry under highly radioactive conditions; fundamental and applied research:
  - exploration: new extracting molecules and systems
  - fundamentals: in-depth study of mechanisms at work

- **Applied research**:
  - process design
  - lab experiments on actual spent fuel material
  - “demonstration” experiments: integration, representativeness, long-lasting performance, secondary waste

- **Neptunium**: recovery ratio up to 99%, with modified La Hague PUREX
- **Americium and Curium**: recovery ratio up to 99.9%, with new DIAMEX-SANEX process
- **Technetium**: recovery ratio from 45 to 90%
- **Iodine**:
  - recovery ratio > 97% with PUREX
  - additional recovery up to ~ 99% possible
- **Cesium**:
  - recovery ratio > 99.8%, with the use of the calixarene extractant

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DIAMEX demonstrative hot run, November 2005

DIAMEX Production Am, Cm, Ln

0.65 M DMDOHEMA/TPH

4 m high Pulsed columns

PUREX raffinate 15 kg genuine fuel

extraction An+ Ln (CP)

extraction An+ Ln (CP)

Back-extraction An-Ln (MS)

Am ~ 0.015%
Cm < 0.002%

Am, Cm, Ln > 99.9%

Am ~ 150 mg/L
Cm ~ 15 mg/L
Ln ~ 2.5 g/L
V ~ 1 L/h
Future fuel cycle options in the 2006 Act: the 2012 milestone

1. 2005 conclusions:
   - Transmutation of Fission Products (I, Cs, Tc) is either not feasible or unrealistic; it should be abandoned
   - MAs transmutation is not realistic in LWR; on the contrary, for FR, transmutation calculations and experiments at pin scale have been carried out for americium and neptunium in a power reactor, such as Phénix, which demonstrates the feasibility of their transmutation in SFR

2. 2006-2012 objectives
   - Define the several recycling options of interest, which could be successively deployed (heterogeneous, homogeneous, all-actinide, Americium only, ...)
   - Assess benefits / costs ratio for the several recycling options, considering diverse criteria and “densification” of the final storage
   - Design / Optimize separation processes, transmutation fuels and their fabrication processes
   - and gather technical elements for industrial operation evaluation
Fuel cycle, the MA heterogeneous recycling option

- U, Pu, Np by COEX™
- Am (and Cm) separation : simplified DIAMEX-SANEX,…
- Am (and Cm) recycled on dedicated « targets-blankets »
Simplified SANEX-TODGA process

- Co-extraction An (III) and Ln (III) with TODGA, using HNO₃ 4N

- Selective back-extraction of An (III)
  - With polyamino-carboxylic hydrophile complexing agent

- Advantages: simple scheme, TODGA synthesis low cost
- Drawbacks: high sensitivity of the Am-Cm back extraction step to pH and temperature

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Fuel cycle, the MA homogeneous recycling option

The grouped actinide GANEX concept

Spent fuel

DISSOLUTION

1st step
U Extraction

UPuNpAmCm Conversion

 Pu+MA

2nd step
An Stripping

Ln Stripping

F.P.

Ln

WASTE

RECYCLE
The GANEX process

HA spent fuel solution  ~ 4M HNO₃

Monoamide

DEHiBA

HDEHP-DMDOHEMA
HEDTA/citric acid

TRU + FP

TRU

Excellent compromise between complete Uranium extraction, and good U(VI)/Pu(IV) selectivity

Adaptation of the process already demonstrated in 2005

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1st step: U selective extraction

GANEX demonstrative hot runs, 2008

2nd step: Pu-Np-Am-Cm co-recovery (DIAMEX-SANEX diamide-based process)

(performing successfully in November 2008)
Partitioning: concepts and results

- **Enhanced separation:**

  **PUREX / COEX**

  U (Np) (U)Pu(Np)

  **DIAMEX / SANEX**

  Am and Cm

  SF

  FPs.

Chemical structures:

- HEDTA
- Other chemical structures (not clearly visible)

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Partitioning: concepts and results

- **Enhanced separation**

  - PUREX / COEX
    - U (Np)
    - (U)Pu(Np)

  - DIAMEX / SANEX

  or

  - SANEX-TODGA
    - Am and Cm

- **Grouped separation**

  - GANEX-1
    - U

  - GANEX-2
    - Pu Np Am Cm
Partitioning: concepts and results

**Enhanced separation:**

- PUREX / COEX
- DIAMEX / SANEX
- Am(Np) separation
- FP and SF

**Grouped separation:**

- GANEX-1
- GANEX-2
- U, Pu, Np, Am
- FP and SF

**Am only separation:**

- PUREX / COEX
- EXAM
- Am
- FP and SF

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Separation process: towards industrialization

**Extractant synthesis**

**Core of the process demonstrated at lab scale**

- Extr-scrub.
- An stripping
- Ln stripping

**Equipment**
- Implementation, extrapolation

**In situ analysis**
- Cations, pH...

**FP solution adapted to vitrification**
- Concent., Calcination

**Long term effects**
- (solvent treatment)

**Modeling**
- (flowsheet, sensitivity, operation)

**An(III) + Ln(III)**

**FP**
- PUREX or COEX
- Raffinate

**Interface Co-conversion**

- DTPA pH 3-4

- Ln
MA bearing fuels: development of fabrication process

- **Synthesis of MA compound powders**, starting from separated MA nitric solution (interface co-conversion)
- **A promising process**: the oxalic co-precipitation, calcination, then direct-powder or UO$_2$-diluted powder pelletizing

• Characteristics of the powders: physico-chemistry, purity, flowability, sintering properties, ...

• Technology: continuous precipitation apparatus: vortex effect, pulsed column, ...

• Modeling
**Conclusion : towards 2012 milestone**

- **Recycling options**, for sustainable FR systems
- Some **options** still open (what, and how), assess benefits/cost ratio by 2012: a progressive step by step approach (from U and Pu first, Am to MA recycling?)
- A need for **flexible** processes?
- On-going research in the CEA Atalante facility, with international collaboration for optimizing separation process (many process options already explored, optimization, simplification)
- A specific new and important program on **reprocessing modeling**
- **A consolidation program** for industrial potentiality by 2012
- From separated MA solutions to Am and MA-bearing experimental fuels: to be tested at pin scale in the ASTRID SFR after 2020 …