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Separation of Americium alone from a Concentrated Raffinate by Liquid-Liquid Extraction (EXAm)

Christian Sorel, Jean-Marc Adnet, Marie-Christine Charbonnel

CEA Marcoule / Nuclear Energy Division, RadioChemistry & Processes Department Separation Process Chemistry and Modeling Service
INTRODUCTION

- **Recycling Am alone**
  - waste lifetime and radiotoxicity
  - long term waste heat power → save repository resource

- **Am and Cm chemistry**
  - Hard acids (HSAB theory)
  - Ionic radius: Am 1.106 Å / Cm 1.094 Å
  - Redox: Am(III) → Am(IV), (V), (VI)

- **Options**
  - Oxidation to Am(VI) and extraction (difficult to stabilize)
    Ex.: SESAME (CEA), NaBiO₃ (B. Mincher et al. INL)
  - Without redox chemistry - With selective lipophilic or hydrophilic system
    Processes tested by CEA: DIAMEX 2 → DMDOHEMA (48 stages!)
    EXAm → DMDOHEMA + HDEHP / TEDGA
    TODGA / TPAEN

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**INTRODUCTION**

- **HLW: 160 ha**
- **HLW: 1200 ha**
- **Am recycling**
- **Deep Geological Repository**

**factor 7 to 8**


**PUREX + New process**

**Final waste**

FP, Cm

**Heterogeneous recycling**

U Pu

**IEMPT 2016, October 18-20, 2016**
Selective Recovery of Americium alone from a PUREX raffinate in 1-cycle

- Feed solution already cleared from U, Pu and Np
- Extractants alone → very low Am/Cm selectivity (SF Am/Cm = 1.6)
- with TEDGA → SF Am/Cm = 2.5 (32 stages)

Complexed chemistry (example with Ln)

- **In the organic phase:** Ln\(^{3+}\)(DEHP)\(_x\) and Ln\(^{3+}\)(NO\(_3\))\(_3\)(DMDOHEMA)\(_y\)
  but also Ln\(^{3+}\)(NO\(_3\))\(_x\)(HDEHP)\(_y\)(DEHP)\(_{3-x}\)(DMDOHEMA)\(_z\), LnNO\(_3\)\(_3\) (TEDGA)\(_n\)(DMDOHEMA)\(_y\)
- **In the aqueous phase:** Ln(TEDGA)\(_n\)\(^{3+}\) (n=1,2 and 3)

Demonstration of the feasibility with a first hot test in ATALANTE facility in 2010

⇒ Am recovery ≈ 98.5% with $DF_{\text{Am/Cm}} = 500$

Improvement suggested: increase the compactness of the process (to reduce industrial contactors size and quantity of side streams)

Next step: Hot Test on genuine PUREX raffinate after concentration
EXAM integral experience

Spent Fuel

- Dissolution / Clarification
  - U, Pu, Np, Am, Cm, FP

- U/Pu Separation
  - Extraction Raffinate
    - FP, Am, Cm

- Concentration
  - Concentrated Raffinates x6
    - FP, Am, Cm

- Selective Am Extraction (EXAM)

- Concentration
  - Am

- Co-conversion
  - Oxalic Co-précipitation
  - Calcination

- (U-Am)O₂

- CBP Concentration

- CBP Spent Fuel Extraction Raffinate (FP, Am, Cm)

Cold and spiked tests

Hot test

Oxalic co-conversion and U-Am oxide fabrication
Overview of the CBP Shielded Process Line

Solvent extraction

Dissolution and clarification

SNF reception
EXAM – Process Development

Preparation of the raffinate for next EXAM test (concentrated) → 25 L of feed solution

Cold tests (G1 facility – PROUST platform):
- Optimization of the concentration factor
- Optimization of scrubbings (Mo and TEDGA)

Concentration by steam distillation
- Validation of the process and optimisation of conditions
- Test with genuine solution

Hot test in Atalane facility (CBP)
- EXAM scheme with concentrated feed
- 32 stages extraction-scrubbing,
- 4 stages TEDGA scrubbing
- 8 (12) stages Mo, Pd, Ru stripping,
- 8 stages Am stripping,
- 8 stages Ln, Fe stripping

Final step in Atalante facility (C9)
- Co-conversion UAmO$_2$
- Fabrication of pellets

Spiked test in Atalante facility (C17)
- Validation of the new scheme with a surrogate feed

Hot test in Atalane facility (CBP)
- 32 stages extraction-scrubbing,
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Tests at laboratory scale

Modelling
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Tests at laboratory scale

Modelling
Spent fuel dissolution

- **3 dissolution batches**
  - Dissolution of 3 kg of UOX and 1.6 kg of MOX fuel

- **Total volume**: 22 L

- **Main characteristics of the dissolution solution**
  - $C_{\text{HNO}_3} = 4.3\text{M}$, 
  - $c_U = 160 \text{ g/L}$, 
  - $c_{\text{Pu}} = 4.4 \text{ g/L}$, 
  - $c_{\text{Np}} = 49 \text{ mg/L}$, 
  - $c_{\text{Am}} = 160 \text{ mg/L}$ 
  - $c_{\text{Cm}} = 50 \text{ mg/L}$ 
  - Total $\beta\gamma$ activity: $1.9 \times 10^{12} \text{ Bq/L (02/2011)}$, 
  - $^{106}\text{Ru}$ activity: $1.35 \times 10^{11} \text{ Bq/L (02/2011)}$. 

**EXAM – Process Development**

**Cold tests (G1 facility – PROUST platform)**
- Hydraulic tests
  - Optimization of the concentration factor
  - Optimization of scrubbings (Mo and TEDGA)

**Preparation of the raffinate for next EXAM test** (concentrated)
→ 25 L of feed solution

**Spiked test (Atalante facility – C17)**
Validation of the new scheme with a surrogate feed

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**Tests at laboratory scale**

**Modelling**

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Nuclear Energy Division - Marcoule
RadioChemistry & Processes Department

*IEMPT 2016, October 18-20, 2016*
EXAM (Concentrated flowsheet) 
Which concentration factor?

- **Keep a good Am/Cm separation factor**

<table>
<thead>
<tr>
<th>UOx3 (PUREX raffinate)</th>
<th>5x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ Ln (mM)</td>
<td>25</td>
</tr>
<tr>
<td>Σ Cations (mM)</td>
<td>52</td>
</tr>
</tbody>
</table>

- **Main modifications**
  - Increase of $c_{Ln}^{aq}$ $\rightarrow$ **increase** $c_{TEDGA}$
  - But $c_{TEDGA}^{org}$ $\uparrow$ and then the loading capacity $\downarrow$
  - Avoid 3rd phase formation $\rightarrow$ **increase** $c_{HDEHP}$

- **Highest Concentration Factor reasonably achievable is 3.5**

Influence of Ln total concentration on SF(Am/Cm)}
EXAM (concentrated flowsheet) Which influence on stripping steps?

2 main issues with a concentrated flowsheet:

- $c_{TEDGA}$ in the organic phase increases
  - Leak of Am during Mo scrubbing
  - Competition with DTPA during the Am stripping
- pH stabilization in Mo scrubbing steps more difficult
  Study of others buffering/complexing molecules

Additional TEDGA scrubbing to maintain $c_{TEDGA}^{org} < 10$ mM

Citric acid (instead glycolic acid) in Mo scrubbing test
Preparation of the raffinate for next EXAM test (concentrated) → 25 L of feed solution

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- Fabrication of pellets

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Tests at laboratory scale

Modelling
Addition of HEDTA as Pd masking agent (limit the saturation)

TEDGA Scrubbing

pH control, online spectrophotometry

Solvent recycled by batch (after analysis c and re-adjustment)
Main results

- Very good adequation between data calculated and measurements

Performances

<table>
<thead>
<tr>
<th>Step</th>
<th>Am Recovery</th>
<th>Decontamination factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am Extraction</td>
<td>~ 98.4%</td>
<td>DF(Am/Cm) ~ 40</td>
</tr>
<tr>
<td>Cm Scrubbing</td>
<td></td>
<td>Efficient TEDGA scrubbing (c_{TEDGA_{org}} &lt; 10\text{mM})</td>
</tr>
<tr>
<td>Mo Scrubbing</td>
<td>(c_{Am_{raffinat}} &lt; 0.1%)</td>
<td>Quantitative recovery of Mo (&lt; 0.1%)</td>
</tr>
<tr>
<td>Am Stripping</td>
<td>&gt; 99.87%</td>
<td>DF(Am/Nd) = 100</td>
</tr>
</tbody>
</table>

Technical problems

Equilibrium not reached

pH well controlled
EXAM – Process Development

Hot test in Atalane facility (CBP)
- 32 stages extraction-scrubbing,
- 8 stages Mo, Pd, Ru stripping,
- 20 stages Am stripping,
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Spiked test (Atalante facility – C17)
Optimization of the concentration factor
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Preparation of the raffinate for next EXAM test (concentrated)
→ 25 L of feed solution

Cold tests (G1 facility – PROUST platform):
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Final step in Atalante facility (C9)
- Co-conversion UAmO_2 (C10)
- Fabrication of pellets

Tests at laboratory scale

Modelling

Nuclear Energy Division - Marcoule
RadioChemistry & Processes Department

IEMPT 2016, October 18-20, 2016
Concentration of PUREX raffinate

- **Choice of steam distillation instead of classical formic denitration**
  - Safety regulation at Atalante facility
  - Acidity very high

- **Goals of the steam distillation**
  - Increase the salts concentrations by a factor of 6
  - Maintaining the nitric acid concentration around 8 M

- **Preliminary optimization of operational conditions: (C17 cell)**
  - Low acidity of the feed solution: $[H^+]_{\text{feed}} = 3.4$ M
  - High acidity in the reactor: $8$ M $\Rightarrow [H^+]_{\text{distillate}} = 1.8$ M
  - Minimization of effluent volumes
  - Absence of precipitates (only RuO$_2$ and small quantity of Zr/phosphates)

- **Concentration of the active solution (CBP)**
  - Test of the cooling system, determination of the maximum heating power and of the optimum flowrates
  - Concentration in two batches of 11 L (duration of 3 shifts)
## Composition of PUREX raffinates

<table>
<thead>
<tr>
<th>Elements</th>
<th>Before concentration</th>
<th>After concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$ (mol/L)</td>
<td>3.4</td>
<td>8.2</td>
</tr>
<tr>
<td>Am (mg/L)</td>
<td>155</td>
<td>1197</td>
</tr>
<tr>
<td>Cm (mg/L)</td>
<td>-</td>
<td>323</td>
</tr>
<tr>
<td>Nd (mg/L)</td>
<td>740</td>
<td>3269</td>
</tr>
<tr>
<td>Ce (mg/L)</td>
<td>440</td>
<td>2169</td>
</tr>
<tr>
<td>Pr (mg/L)</td>
<td>200</td>
<td>956</td>
</tr>
<tr>
<td>La (mg/L)</td>
<td>240</td>
<td>1245</td>
</tr>
<tr>
<td>Sm (mg/L)</td>
<td>156</td>
<td>917</td>
</tr>
<tr>
<td>Eu (mg/L)</td>
<td>29</td>
<td>151</td>
</tr>
<tr>
<td>Gd (mg/L)</td>
<td>38</td>
<td>376</td>
</tr>
<tr>
<td>Zr (mg/L)</td>
<td>276</td>
<td>900</td>
</tr>
<tr>
<td>Mo (mg/L)</td>
<td>405</td>
<td>1186</td>
</tr>
<tr>
<td>Pd (mg/L)</td>
<td>138</td>
<td>617</td>
</tr>
</tbody>
</table>
Preparation of the raffinate for next EXAM test (concentrated) → 25 L of feed solution

Cold tests (G1 facility – PROUST platform):
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- Co-conversion UAmO₂ (C10)
- Fabrication of pellets

Tests at laboratory scale

Modelling

Nuclear Energy Division - Marcoule
RadioChemistry & Processes Department
Flowsheet of the EXAm process

Am Extraction
- Feed solution
- TEDGA 0.5M
- HEDTA 0.15M
- TEDGA 0.5M
- HNO₃ 10M
- Ln scrub.
- Am, Ln, Mo, Fe, Ru, (TEDGA)
- NaOH 2M
- Citric acid 0.5M
- pH 3.2
- Am extraction
- Stage 1
- Mo scrubbing
- pH
- NaOH 2M
- Citric acid 0.5M
- pH 3.2
- pH
- Mo
- Ln, Fe stripping
- Ln, Fe stripping
- Stage 1
- TEDGA 0.2M
- Oxal. 0.5M
- HNO₃ 0.1M
- HNO₃ 3M
- HA
- HB
- HAA
- HEDTA 0.15M
- HNO₃ 7M
- DTPA 0.03M
- Malonic acid 0.3M
- pH 2.6
- Am
- Ln
- Fe
- online monitoring with 12 optic fibers
- cₐm and c₉d
- Am + most FP (heavy Ln, Zr, Pd)
- TEDGA Scrubbing
- HNO₃ 4M
- Am stripping
- Oxal. 0.5M
- HNO₃ 1M
- HEDTA 0.15M
- HNO₃ 7M
- Am
- NaOH 2.6M
- HEDTA 0.1M
- HNO₃ 0.1M
- HA
- HAA
- HEDTA 0.15M
- HNO₃ 7M
- Am
- DTPA 0.03M
- Malonic acid 0.3M
- pH 2.6
**EXAM – Process Development**

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- Co-conversion UAmO$_2$
- Fabrication of pellets

**Tests at laboratory scale**

**Modeling**

Nuclear Energy Division - Marcoule
RadioChemistry & Processes Department

*IEMPT 2016, October 18-20, 2016*
High capacity of the PAREX code

- **Before the test**
  - design the entire flowsheet according the required performances,
  - carry out sensitivity studies towards operating parameters,
  - identify relevant status parameters for process monitoring,
  - propose a flowsheet correction procedure,

- **During the test**
  - help experimenters to modify flowsheet (flows, stage…),
  - simulate all operating condition changes by transient calculations,

- **After the test**
  - compare the calculated and measured concentrations to assess the accuracy of the model.

- ① Thermodynamic of acid and metals extraction
- ② Mass transfer kinetic
- ③ Hydrodynamic in contactors
Development of the model with laboratory data

- **Extraction step (high acidity)**
  - 15 extractable elements **taken into account** (HNO₃, Am, Cm, rare earths, Fe, Mo, Pd, Zr)
  - Ln and An(III)
    - \[
      \frac{M(\text{NO}_3)_3(\text{HNO}_3)_3(\text{DMDOHEMA})_3}{M(\text{DEHP})_3(\text{DMDOHEMA})_2} \frac{M(\text{NO}_3)_3(\text{TEDGA})_n(\text{DMDOHEMA})}{}
    \]
  - Pd and Ru → extraction by DMDOHEMA (1:1 complexes)
  - Fe and Mo → Quantitatively extracted by HDEHP (D>30)
  - Zr → 1:3 non-extractable complex with TEDGA

- **Mo stripping (low acidity)**
  - \[
    (\text{DMDOHEMA})(\text{DEHP}) \ M(\text{DMDOHEMA})(\text{DEHP})_3
  \]
  - Low pH (D₀ increases with pH): \[
    \text{MoO}_2^{2+} + 2\text{HDEHP} \rightleftharpoons (\text{MoO}_2)(\text{DEHP})_2(\text{HDEHP})_2 + 2\text{H}^+
  \]
  - Moderate pH (pH independent): \[
    \text{MoO}_3 + 2\text{HDEHP} \rightleftharpoons (\text{MoO}_3)(\text{HDEHP})_4
  \]
  - High pH (D₀ decreases with pH): \[
    \text{MoO}_4^{2-} + 2\text{HDEHP} + 2\text{H}^+ \rightleftharpoons (\text{MoO}_2)(\text{DEHP})_2(\text{HDEHP})_2
  \]
On-line measurement of Am concentration during an EXAm pilot test

On-line analysis shows a malfunction from the nominal operation

Calculated graphs leading to various performances

Nominal flowsheet

PAREX can rapidly calculate transient curves (live acceleration factor > 100) to correct the flowsheet during a pilot test

The main issue during the test : keep important Am recovery and high DF (TEDGA, agitation, flowrates, …)
Main results
- Operating parameters optimized during three successive tests (acid, surrogate, HA)
- Good hydrodynamic behavior
- Efficient monitoring thanks to online analysis with laboratory support
- Flowsheet optimization during the test

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<td>Mo Scrubbing</td>
<td>$C_{Am}^{raffinate}$ from 0.01 to 0.02% (Target 0.1%)</td>
<td>Quantitative recovery of Mo</td>
</tr>
<tr>
<td>Am Stripping Ln Scubbing</td>
<td></td>
<td>$DF_{Am/Nd} = 2800$ (target value = 400)</td>
</tr>
<tr>
<td>Global</td>
<td>2.46 g of Am (96.5%)</td>
<td>$DF_{Am/Cm} \sim 54$ (target 500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>With Am: less than 1.7% lanthanides, 0.3% Fe, 0.05% Mo, 0.7% Pd and 1.1% Ru</td>
</tr>
</tbody>
</table>
Conclusions

- Demonstration of the feasibility of a concentrated scheme with real raffinate
  - Flowsheet adaptations were implemented and consolidated by successive tests: laboratory scale data, tests on inactive feed solution and spiked test with trace amounts of americium and curium.
  - Production of **2.4 grams of americium** (58.5%$^{241}$Am-40.9%$^{243}$Am-0.5%$^{242}$Am), well decontaminated from lanthanides and molybdenum. But lower DE$_{\text{Am/Cm}}$ than expected may be understood.
  - Reduction of liquid waste volume and improvement of compactness, in parallel first evaluation of feasibility to manage all effluents with classical outlets (study to continue).
  - Ultimate steps of the integral experience will be performed next years
    - Concentration of the 2.7L of Am solution to obtain c$_{\text{Am}}$ 7g/L (Atalante CBP) Mi 2017
    - Co-conversion of Am (Atalante C9), Production of Am pellets
    - Transfer to ATR for irradiation experiments.
Further studies (small effort, mainly laboratory studies)

- EXAM process
  - Complete the study of Cm chemistry (stability constants with TEDGA estimated from extraction tests and from Sm behavior)
  - Recent results from KIT (A. Geist): TRLIFS data, soon published,
  - Extraction tests to perform
  - Modification of the model in progress

  - Design of new ligands with lower partitionning and with higher Am/Cm AND Am/Ln selectivity, following of S. Chapron thesis (SEIE, 2015, 33(3), 236-248)

- TPAEN process
  - Some tests (mixer settlers) with representative solution
  - Design of new ligands (increase the solubility)
Acknowledgments

CBP team
Frédéric Antégnard, Marie-Jordane Bollesteros, Sylvain Costenoble, Marc Montuir,

Modeling team
Vincent Vanel, Vincent Pacary, B. Dinh

Process development
Cécile Marie, Xavier Heres, M. Miguirditchian

Analytical team of CBA
Atalante

Thank you for your attention