Development status on the pyrochemistry R&D program at CEA

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Introduction

Outlines

- Several spent fuel pyrochemical processes studied worldwide:
  - Electrorefining/Electrolysis in molten chloride melts → most studied technique
  - Precipitation/Electrolysis assessed
  - Reductive extraction in molten chlorides also investigated
    *mainly as a step of the electrorefining complete process*

- Reference route developed by CEA: **Reductive liquid/liquid extraction in fluoride media**
  - France: only country currently considering this alternative route for fuel reprocessing

LiF-AlF₃ solvent at 830°C
- Al both solvent and reductor
  \[ \text{AnF}_3(\text{salt}) + \text{Al} \leftrightarrow \text{An}_{(\text{Al})} + \text{AlF}_3 \]
Liquid/liquid extraction core of process demonstration
Liquid/liquid extraction core of process demonstration 1/3

Experimental conditions

- LiF-AlF$_3$ (20g) / Al-Cu (20g) system at 830 °C
- Chosen salt compositions:
  E1 (85-15% mol. LiF-AlF$_3$), C (75-25) and E2 (65-35)
- U: 200mg, Pu: 25mg, Am: 100mg and Nd: 50mg
- Liquid/liquid extraction reaction:
  \[ \text{AnF}_3(\text{salt}) + \text{Al}_{(\text{met})} \rightleftharpoons \text{An}_{(\text{met})} + \text{AlF}_3(\text{salt}) \]
- Distribution coefficient:
  \[ D = \frac{x_{\text{An}_{(\text{Al})}}}{x_{\text{AnF}_3(\text{salt})}} \]
- Salt composition (LiF-AlF$_3$) modifies the distribution coefficients
  \[ D_{\text{An}} = K \cdot \frac{\gamma_{\text{AnF}_3}}{\gamma_{\text{An}_{(\text{Al})}}} \cdot \frac{1}{a_{\text{AlF}_3}} \]
- Excellent An/Ln separation factors: >100 for a single liquid/liquid extraction step
- Good agreement with previous studies

After experiment in E1 → stripping step using pure LiF-AlF$_3$ (C)
An oxidative liquid/liquid back-extraction step:
In chloride media, using oxidizing reagent → AlCl₃

\[ \text{An}^{(\text{met})} + \text{AlCl}_3^{(\text{salt})} \rightleftharpoons \text{AnCl}_3^{(\text{salt})} + \text{Al}^{(\text{met})} \]

From previous studies, optimal operating conditions:
- LiCl-CaCl₂ (30-70 mol.%) at 700°C (4h experiment)
- Reagent NaAlCl₄, overstoechiometry: 7 (stabilisation of AlCl₃)
- Crucible filled inside tightened container (prevent AlCl₃ volatilisation during experiment)
- Al-Cu ingots coming from reductive extraction step (ingot from run E1 coming from stripping step)

Back-extraction efficiency:
- Pu, Am: >99%
- U: 87 to 95% → as expected, most difficult actinide to be back-extracted (redox potential U³⁺/U⁰ close to Al³⁺/Al⁰)
- Nd: 86 to 92%
- No An/Ln selectivity during back-extraction step (as expected)

⇒ Importance of the selectivity during reductive extraction step
### Results for a one-stage experiment promising

- **E1 and C**: more than 96% global recovery of Pu and Am. U: 73% with 2% of Nd (after stripping)
- **E2**: worse results than expected (mainly due to metal drops transferred into the salt during experiment → distortion of the results)
- **U behaviour**: no quantitative recovery could be achieved in a one-stage experiment. Could be due to a possible precipitation of U during reductive extraction step
- **Advantages of implementing run E1 with stripping step**: Nd back-extraction 92%
  - If no stripping implemented: 25% of initial Nd together with An.
  - Stripping: only 1.8% of the initial Nd in the chloride salt.

<table>
<thead>
<tr>
<th>Run</th>
<th>Efficiency (%)</th>
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<tbody>
<tr>
<td></td>
<td>Extraction</td>
</tr>
<tr>
<td></td>
<td>Scrubbing</td>
</tr>
<tr>
<td>E1</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>Pu</td>
</tr>
<tr>
<td></td>
<td>Am</td>
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<tr>
<td></td>
<td>Nd</td>
</tr>
<tr>
<td></td>
<td>U</td>
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<tr>
<td></td>
<td>Pu</td>
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<tr>
<td></td>
<td>Am</td>
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<tr>
<td></td>
<td>Nd</td>
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<tr>
<td>E2</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>Pu</td>
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<tr>
<td></td>
<td>Am</td>
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<tr>
<td></td>
<td>Nd</td>
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</table>
Conversion to oxide step
After Back-extraction step: An(III) in molten chlorides must be converted into oxide form.

For nuclear fuel re-fabrication:
- Quantitative
- Oxide form AnO₂
- Solid solution (U,Pu,MA)O₂

Reference routes: precipitation with carbonates

\[ \text{Li}_2\text{CO}_3 \rightarrow 2\text{Li}^+ + \text{CO}_2\text{(g)} + \text{O}^2- \]

Leads to increase of salt volume

Chosen route: precipitation using a process gas
⇒ Wet Argon sparging

\[ \text{H}_2\text{O}_\text{(g)} \rightarrow \text{O}^2-_{\text{(salt)}} + 2\text{HCl}_\text{(g)} \]

Studied systems:
- Nd – Ce (inactive study) and U – Pu
Conversion into oxides

\[ \text{LiCl-CaCl}_2 \rightarrow \text{LiCl-CaCl}_2 \text{ (salt)} + 2H_2O(g) \rightarrow \text{UO}_2(ppt) + 3\text{HCl}(g) + \frac{1}{2}\text{H}_2 \]

\[ a = 5.470(1) \]

**Images:**
- **LiCl-CaCl\_2** 700°C
- **Precipitate**
- **SEM**
- **XRD**
- **Uranium**
- **Plutonium**
Conversion of Nd(III) – Ce(III)

\[ X_{Nd} = \frac{Nd}{Ce+Nd} \rightarrow 0; 0.25; 0.5; 0.75 \text{ and } 1 \]

\[
\text{NdCl}_3(\text{salt}) + H_2O(g) \rightarrow \text{NdOCl(ppt)} + 2\text{HCl(g)}
\]
Conversion into oxides

Conversion of Nd(III) – Ce(III)  
\[ X_{Nd} = \frac{Nd}{Ce+Nd} \rightarrow 0; 0.25; 0.5; 0.75 \text{ and } 1 \]

ICP analysis: 99.9%  

CeCl₃(salt) + H₂O(𝑔) → CeOCl₁(𝑝p𝑡) + 2HCl(𝑔)  
80%

Nd-Ce Solid solution formation  

CeOCl₁(ppt) + 2HCl(𝑔) → CeO₂(ppt) + 3HCl(𝑔) + \( \frac{1}{2} \)H₂  
20%

Intensity (a. u.)

\( 2\theta (°) \)

CeCl₃(salt)

CeOCl₁(ppt)

CeO₂(ppt)

CeOCl

CeO₂

Nd-Ce Solid solution formation

ICP analysis: 99.9%
Conversion of U(III) – Pu(III)

\[ \text{UO}_2 \times \text{Pu} = \text{PuO}_2 \times 0.20; \times \text{Pu} = \text{PuO}_2 \times 0.50; \times \text{Pu} = \text{PuO}_2 \times 0.75 \]

Uranium volatilization observed (10-15%)

ICP analysis: conversion rate > 99.9%

Intermediate sample

<table>
<thead>
<tr>
<th>( X_{\text{Pu}} )</th>
<th>( \text{U}^{3+} )</th>
<th>( \text{Pu}^{3+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>&lt; 1%</td>
<td>70%</td>
</tr>
<tr>
<td>0.5</td>
<td>&lt; 1%</td>
<td>76%</td>
</tr>
<tr>
<td>0.2</td>
<td>&lt; 1%</td>
<td>61%</td>
</tr>
</tbody>
</table>
Nd(III)-Ce(III) precipitation:

Partially oxidative method

1 - Quantitative → OK
2 - Oxide Form \( \text{LnO}_2 \) → OK calcination
3 - Solid solution → OK

U(III)-Pu(III) precipitation

1 - Quantitative → OK
2 - Oxide Form \( \text{AnO}_2 \) → OK
3 - Solid solution → OK
Hydrofluorination : in situ HF production
Why in-situ production of HF?
- Conversion of spent fuel into fluoride is needed.
- Few hot cells facilities are equipped with HF gas line

HF produced by dissociation of solid HF-KF at 200-350°C
- Experimental set-up including three eating areas

Study of oxide fluorination: La, Ce, Pr, Nd, Mo, Ru, Rh, Sm, Eu, Pr, Zr, Sr, Ag, Y
- Determination of the best reaction conditions
- Assessing behaviour of oxides under HF gas flow (fluorination rate, final product)
Hydrofluorination by in situ produced HF

Thermodynamic calculations (HSC Chemistry® V.4.1)

- Gibbs free energy of fluoride formation from oxide form, with HF $\rightarrow$ Determination of optimum experimental temperature range.

- Temperature acts in opposite direction
  However, Gas/Solid reaction $\rightarrow$ higher specific surface of the solid and higher temperature should favour kinetic

- Ln oxides: temperatures ranging from 400 to 500°C are favourable.

- ZrO$_2$: favourable temperature rather from 300 to 320°C.
Experimental results

- Fluorination experiments: 6h, 330 °C to 420 °C (depending on oxide to convert), HF excess ~3.5

- Oxides behaviour: *(determined by XRD)*

  Nd₂O₃, CeO₂, SrO, Eu₂O₃, La₂O₃, Y₂O₃, Sm₂O₃, Pr₂O₃ successfully converted into fluorides
  → Pr, La, Eu presence of oxyfluorides could be evidenced

  MoO₃, Rh₂O₃, RuO₂, AgO remained in oxide form
  good agreement with thermodynamic calculations.

- Case of ZrO₂: Several experiments on commercial and nanopowder ZrO₂.
  Commercial ZrO₂ → No fluorination
  Nanopowder (350°C) → 25% of Zr fluorinated
<table>
<thead>
<tr>
<th>Potential routes</th>
<th>Principle</th>
<th>Media</th>
<th>Average working Temp.</th>
<th>Predilection fuels</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrorefining/Electrolysis</td>
<td>Electrorefining Selective electrodeposition</td>
<td>LiCl, LiCl-KCl</td>
<td>450 °C</td>
<td>Metal, (oxide)</td>
<td>The most studied and the most advanced pyro process At pilot scale</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>Selective electrodeposition</td>
<td>NaCl-2CsCl (with Cl$_2$(g)/O$_2$(g))</td>
<td>550-800 °C</td>
<td>Oxide</td>
<td>At semi-pilot scale, coupled with vibrocompact fuel fabrication</td>
</tr>
<tr>
<td>Reductive extraction</td>
<td>Selective extraction in a metal phase (Cd) with reductor (Li)</td>
<td>LiCl-KCl/Cd</td>
<td>450 °C</td>
<td>Oxide, Metal</td>
<td>Laboratory scale</td>
</tr>
<tr>
<td>Reductive extraction</td>
<td>Selective extraction in a metal phase (Al)</td>
<td>LiF- AlF$_3$/Al</td>
<td>830 °C</td>
<td>Oxide Carbide</td>
<td>Laboratory scale, high temp. and corrosive solvents and gases ➔ material issues Very good recovery yields and separation factors</td>
</tr>
</tbody>
</table>
Conclusion

- The core of process is now well assessed at lab scale with encouraging results on a One stage Extraction-Back-extraction experiment
- Conversion step:
  Use of wet Argon → promising method. U(III) and Pu(III) coconversion lead to UO$_2$ and PuO$_2$ mixture
  Still some further investigations are needed
- Hydrofluorination highlighted Zr behaviour (should be studied and simulated in the whole process)
- Analytical techniques are under development.

Perspectives

Reference Route in molten fluorides
- A few steps need to be tested with genuine fuel (thermal treatment, digestion)
- An alternative head of process is under investigation in order to prevent use of HF to convert oxides fuels into fluorides.

Electrorefining process in molten chloride
- CEA is collaborating with JRC-ITU and LGC (Toulouse university, France) to study the salt cleaning step by exhaustive electrolysis.
  Development of a dedicated reactor within the framework of the ACSEPT program.
Thank you for your attention