The AmSel Process – Selective Separation of Americium from PUREX raffinate

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Partitioning and Transmutation:

- Strategy to reduce long term radiotoxicity and heat load of nuclear waste.

- Aim: separation of Pu and minor actinides (Np, Am and Cm) and transmuting them into short-lived or stable nuclides.

Our goal: **selective extraction of Am(III) from PUREX raffinate**

→ separation of Am(III) from Cm(III), Ln(III) & other fission products (FP) and corrosion products (CP)
Why separate americium from curium?

Curium:
- no significant impact on long-term radiotoxicity or heat load of nuclear waste
- High neutron dose rates and decay heat complicate production of new nuclear fuel

→ disposal in high active waste

Separation of Am(III) should be performed early in the process

EXAm process already successfully tested

Strategy

- Co-extraction of Am(III), Cm(III) and Ln(III)
- Selective Am(III) stripping
Strategy

- Co-extraction of Am(III), Cm(III) and Ln(III)
- TODGA
  - Extracts An(III) + Ln(III) from HNO₃
  - Rejects most non-Ln fission products
  - Rejects corrosion products
  - Successfully used in DIAMEX and i-SANEX processes
Strategy

- TODGA prefers Cm(III) over Am(III) \( SF_{\text{Cm(III)/Am(III)}} = 1.6 \)

- Requirement for selective Am(III) stripping:
  - Ligand has to prefer Am(III) over Cm(III)
  - Well soluble in water / nitric acid

- BTBP prefers Am(III) over Cm(III) \( SF_{\text{Am(III)/Cm(III)}} = 1.6 \)
  - Water soluble BTBP? \( SF(\text{TODGA}) \cdot SF(\text{BTBP}) = 2.6? \)
Extraction experiments with TODGA and SO$_3$-Ph-BTBP

Aq. phase: 20 mM SO$_3$-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) in HNO$_3$
Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80

$SF_{\text{Cm(III)/Am(III)}} = 2.5–3$

$\frac{\text{[HNO}_3\text{]}_{\text{ini}} \text{[mol/l]}}{10^0}$

$D(\text{M(III))}$

$10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^0 10^1 10^2 10^3 10^4$

$SF$

$10^{-2} 10^{-1} 10^0 10^1 10^2 10^3 10^4$

$\alpha$ Am(III)  $\gamma$ Am(III)  $\alpha$ Cm(III)  $\gamma$ Eu(III)  $\frac{SF_{\text{Cm(III)/Am(III)}}}{SF_{\text{Eu(III)/Am(III)}}}$
Extraction experiments with TODGA and SO$_3$-Ph-BTBP

Aq. phase: 20 mM SO$_3$-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) and 6 mg/l of each Ln(III), Y(III) and La(III) in HNO$_3$

Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80
Extraction experiments with TODGA and SO$_3$-Ph-BTBP

Formation of 1:1 complex? → TRLFS studies

Aq. phase: SO$_3$-Ph-BTBP, Am(III)-241, Cm(III)-244, Eu(III)-152 (1 kBq/ml each) in 0.51 M HNO$_3$
Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80
Complexation of Cm(III) with SO$_3$-Ph-BTBP

Cm(III) emission spectra with increasing SO$_3$-Ph-BTBP concentration in 0.5 M HNO$_3$

only one complex species
Complexation of Eu(III) with SO$_3$-Ph-BTBP

Eu(III) $^7F_4$ band emission spectra with increasing SO$_3$-Ph-BTBP concentration in 0.5 M HNO$_3$

2 complex species formed, primarily 1:2 complex
Complexation of Cm(III) with SO$_3$-Ph-BTBP

The reaction can be represented as:

$$[\text{M(solv)}]^{3+} + \text{SO}_3\text{-Ph-BTBP}^{4-} \rightleftharpoons [\text{M(SO}_3\text{-Ph-BTBP)}]^+ \rightleftharpoons [\text{M(SO}_3\text{-Ph-BTBP)}]^2]^{5-}$$

where $\text{M(solv)}$ represents the solvent-separated ion pair.

The equilibrium constants are denoted as $\log K_{01}$ and $\log K_{12}$.

The stability constants are given by:

$$\log \beta_{02} = 7.3 \pm 0.3$$

$$\Delta \log \beta_{02} = 1.9$$

**Cm(III) complexation**

**Eu(III) complexation**

$$\log \beta_{02} = 5.4 \pm 0.5$$

$$\log \beta_{02} = 5.4 \pm 0.5$$

$n = 2$

$slope = 1.2 \pm 0.2$

$n = 1$

$slope = 0.9 \pm 0.2$
TRLFS with extraction experiments

2 phase extraction experiments containing Cm(III)/Eu(III) in the aq. Phase

SO$_3$-Ph-BTBP forms 1:2 complexes in extraction experiments

Aq. phase: 20 mM SO$_3$-Ph-BTBP, Cm(III)-248 in 0.5 M HNO$_3$
Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80
Complexation of Cm(III) at pH 3

- TRLFS investigation of Cm(III) with SO$_3$-Ph-BTP showed the formation of intermediate complexes

- studies with SO$_3$-Ph-BTP were performed in water at pH 3

→ investigation of Cm(III) complexation with SO$_3$-Ph-BTBP at pH 3

Complexation of Cm(III) at pH 3

Cm(III) emission spectra with increasing SO$_3$-Ph-BTBP concentration in 10$^{-3}$ M HClO$_4$

$\log \beta_{02} = 10.4 \pm 0.4$

($\log \beta_{02} (0.5$ M HNO$_3$) $= 7.3 \pm 0.3$)

→ large influence of solvent
Complexation of Cm(III) in different media

0.5 M NaClO₄, pH 3

0.5 M NaNO₃, pH 3

0.5 M HClO₄
Influence of medium on conditional stability constant

<table>
<thead>
<tr>
<th>M(III)</th>
<th>Solvens</th>
<th>log$\beta_{01}$</th>
<th>log$K_{12}$</th>
<th>log$\beta_{02}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm</td>
<td>10^{-3} M HClO$_4$</td>
<td>5.3 ± 0.3</td>
<td>5.1 ± 0.3</td>
<td>10.4 ± 0.4</td>
</tr>
<tr>
<td>Cm</td>
<td>0.5 M HNO$_3$</td>
<td>-</td>
<td>-</td>
<td>7.3 ± 0.3</td>
</tr>
<tr>
<td>Cm</td>
<td>0.5 M NaClO$_4$</td>
<td>-</td>
<td>-</td>
<td>9.7 ± 0.3</td>
</tr>
<tr>
<td>Cm</td>
<td>0.5 M NaNO$_3$</td>
<td>-</td>
<td>-</td>
<td>9.4 ± 0.3</td>
</tr>
<tr>
<td>Cm</td>
<td>0.5 M HClO$_4$</td>
<td>-</td>
<td>-</td>
<td>8.5 ± 0.4</td>
</tr>
</tbody>
</table>

Large effect of medium on speciation and conditional stability constant
Influence of ionic strength

Cm-SO$_3$-Ph-BTBP complexation with increasing ionic strength
Conclusion

- The SO$_3$-Ph-BTBP/TODGA system shows good performance for the separation of Am(III)/Cm(III).

- The system does not require buffers, auxiliary ligands or salting out agents.

- SO$_3$-Ph-BTBP forms 1:2 complexes during extraction.

- Formation of the same complexes in monophasic and biphasic experiments.

- The applied medium has a large effect on the speciation and the conditional stability constants of M(III)-SO$_3$-Ph-BTBP complexes.
Outlook

- Extraction experiments at elevated temperatures.
- Investigation of SO$_3$-Ph-BTBP loading with realistic Am(III) concentrations.
- Spectroscopic investigation of Am(III)-SO$_3$-Ph-BTBP complexes.
Thank you for your attention

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Complexation of Cm(III) in the org. phase

TRLFS experiments with organic phase of extraction experiment

No evidence for the formation of mixed complexes → sensitivity too low?

Aq. phase: 20 mM SO$_3$-Ph-BTP, Cm(III)-248 in 0.5 M HNO$_3$
Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80
Fluorimetric measurements with org. Phase

Idea:
Utilizing the energy transfer from ligand to metal to selectively excite the Eu(III) in mixed complexes

Aq. phase: 20 mM SO$_3$-Ph-BTP, 30 mM Eu(NO$_3$)$_3$ in 0.5 M HNO$_3$
Org. phase: 0.2 M TODGA + 5% vol. 1-octanol in Exxsol D80
Schematic flowsheet

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Institute for Nuclear Waste Disposal (INE)

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pKᵦ value of SO₃-Ph-BTBP

The pKᵦ value of SO₃-Ph-BTBP was determined to be pKᵦ = 2.2 ± 0.2.
TRLFS Setup
Spectroscopic properties of Cm(III)

- Identification and quantification of different species
- Large effect of changes in first coordination sphere
- Little effect of changes in second coordination sphere
Spectroscopic properties of Eu(III)

- Small shifts of the emission bands with changes in inner coordination sphere
- Characteristic splitting
- Information on the coordination structure and symmetry