Ac-225 Project Progress: Chemistry, Th Debulking and Automation

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Current separation and problems

• General method
  
  MP1 \rightarrow \text{AG50 Cation column} \rightarrow \text{BDGA}

  • Issues with volume and time when scaling up to 50-500 gram Th target
  
  • Large thorium target masses: formation of the insoluble Th(Cit)$_2$ species requires high volumes

• Debulking goals
  
  • Remove >80% of Th prior to cation column
  
  • Retain as much Ac-225 as possible
# Scale up to 100 g Th targets

<table>
<thead>
<tr>
<th>Method</th>
<th>Problems related to processing 100 gram target</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCST ion exchanger</td>
<td>Capacity 5mg of Th / 1gram of PCST, Need 10L PCST column</td>
<td>Fitzsimmons et al. Submitted to Scie. Rep.</td>
</tr>
<tr>
<td>Cation column/organic acids</td>
<td>Solubility of Th citrate species is poor, Load solution 3.7 L</td>
<td>Fitzsimmons et al. TriLab studies. Submitted to Molecules</td>
</tr>
<tr>
<td>POMS</td>
<td>Need &gt;1000 g of POMS &amp; solubility issues of POMS</td>
<td>Francesconi et al</td>
</tr>
<tr>
<td>Chelex 100 pH&gt;4.0</td>
<td>Precipitation of Th during scale up. Scale up tested by Trilab – (Need 10L)</td>
<td>Radiochim. Acta. 2012, 100, 7, p. 439-444</td>
</tr>
<tr>
<td>HOPO approach</td>
<td>Need &gt;300 g of HOPO ligand per target, solubility issues, synthesis issues</td>
<td>Rebecca Abergel</td>
</tr>
<tr>
<td>Solvent extraction TBP in organic solvent</td>
<td>Regulatory issues with the toxicity of solvent (FDA toluene is class 3 toxin)</td>
<td>Solvent Extraction and Ion Exchange, 32: 468–477, 2014.</td>
</tr>
</tbody>
</table>

**Capacity**

**Solubility**
Testing various solvents for extraction

Used ~0.5 grams of Th and 100 μg of La per experiment, (100 g Th/1L)
Aqueous 6 M nitric acid, Organic ~40% TBP in the organic solvent

% Thorium extracted into organic solvent
1 to 1 volume ratio (n=3)

- Greater than 90% of La in aqueous layer

organic solvent used with ~40% TBP
### Summary of Large scale Thorium experiments

**Goal** remove >80% of Th, retain >85% Ac-225

<table>
<thead>
<tr>
<th></th>
<th>50 g Thorium</th>
<th>100 g Thorium</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thorium dissolved in</strong></td>
<td>6 M nitric acid</td>
<td>6 M nitric acid</td>
</tr>
<tr>
<td><strong>TBP concentration</strong></td>
<td>40% TBP in MEK</td>
<td>40% TBP in MEK</td>
</tr>
<tr>
<td><strong>Recovery of Ac-225</strong></td>
<td>95.1%</td>
<td>quantitative</td>
</tr>
<tr>
<td><strong>Total Th extracted</strong></td>
<td>91.6%</td>
<td>92%</td>
</tr>
<tr>
<td><strong>Mass Thorium in aqueous</strong></td>
<td>4.26 g</td>
<td>8 g</td>
</tr>
<tr>
<td><strong>(after extraction)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Steps</strong></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Amount of organic solvent</strong></td>
<td>300 ml</td>
<td>400 ml</td>
</tr>
<tr>
<td><strong>Cation/citrate step</strong></td>
<td>3000 ml</td>
<td>6000 ml</td>
</tr>
</tbody>
</table>

**ORNL:** Fire suppression system needed in hot cells when greater than 100 ml of a flammable organic solvent is used.

TBP does not have a hazard: Remove the organic solvent? (MEK)
Summary of Large scale Thorium experiments

<table>
<thead>
<tr>
<th>Density of TBP=0.97 g/ml</th>
<th>100 g Thorium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 M nitric acid with NaNO₃</td>
</tr>
<tr>
<td>TBP concentration</td>
<td>100% TBP (300, 70 ml)</td>
</tr>
<tr>
<td>Recovery of Ac-225</td>
<td>98.7%/ quantitative</td>
</tr>
<tr>
<td>Total Th extracted</td>
<td>84g in 1 step/95g in step 1&amp;2</td>
</tr>
<tr>
<td>Mass Thorium in aqueous / volume</td>
<td>4.8 grams / 246mL</td>
</tr>
<tr>
<td>Steps</td>
<td>2</td>
</tr>
<tr>
<td>comments</td>
<td>TBP bottom layer water top layer</td>
</tr>
</tbody>
</table>

Emulsion

- 15 g NaNO₃
- Sudan Black B
1) Process flow sheet 100 g Thorium Target

Dissolved in 100 gram Th target in 200 mls of 6 M nitric acid
Add HF

Organic extraction:
  TBP
  1) (300 ml)
  2) 70 ml
  3) ICP or gamma For Th Conc.

Evaporate

Use current method

Perform columns
  1) Cation
  2) MP1/HCl
  3) BDGA
2) Process flow sheet 100 g Thorium Target

Dissolved in 100 gram Th target in 10 M HCl add HF

MP1 Column to remove Transition metals and reduce dose

Evaporate

Evaporate
Perform Cation column and other columns

Evaporate

Organic extraction: TBP
1) (300 ml)
2) 70 ml

MP1 Column to remove Transition metals and reduce dose
Disposable Hollow fiber contactor


- The liquid membrane is trapped in hydrophobic micropore and this liquid membrane separates the feed and stripping solutions.

- Microporous hollow fibers made of polypropylene

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Like catalysis for solvent extraction

Target Solution: 6 M nitric acid (feed)

Liquid Membrane organic (40% TBP)

Th +4HNO₃

4H⁺ +Th(NO₃)₄

4H⁺

Th(NO₃)₄ .2TBP

WATER or
Dilute nitric acid (Strip solution)
Disposable Hollow fiber contactor (Model G884)

Feed solution (Target solution)

Small foot print for hot cells
- 1.1 inch square
- 1.9 inch including fittings

Disposable (<$200)
Flow rate up to 30 ml/min

Striping solution (water)

Membrane: 40% TBP in MEK
Feed: 6 M nitric acid
0.5 g of Thorium, 100 µg of La
Strip: 2% nitric acid

Extraction of Th with Contactor

Extraction was slow, had extraction of La at 4 ml/min
Moving to larger contactors
ANI touch screen

SIMATIC S7-1500 main controller

SIEMENS automation system fully set up (HW & SW)

Simple controlling program is tested.
- click/touch ① then ② on.
- 5 secs later ② off

• The system can control any DC/AD powered devices
• Fully or semi automatic
• Any analog input can be monitored and controlled
  radiation
  temperature
  flow

Totally Integrated Automation Portal (TIA Portal) Professional V13 SP2
Schematic of automation of Ac-225 processing

Green: columns
Light purple: reaction vessels
Dark purple: pumps

Slide Prepared By: Theresa C. Grimaldi
Summary

• Solvent extraction with TBP and 6 M nitric acid
  • >95% recovery of Ac-225
  • >90% removal of Thorium
  • Approach works to remove bulk thorium for stage 3 targets (100 g)

• Future studies
  • Solvent extraction for 500 grams of Th (multi stack)
  • Examine large solvent contactors
  • Setting up the process at BNL (Rick and Theresa)
  • Automation of process