Fuel Cycle R&D Program

Status of the ALSEP Concept

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Purpose: Reduce Complexity

Dissolved Fuel

TBP Cycle

TRUEX

TALSPEAK

Lanthanides

U, Pu, Np, Tc

Non-Ln Fission products

Am/Cm

Dissolved Fuel

TBP Cycle

ALSEP

Lanthanides + other fission products

Am/Cm

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Combine a neutral donor extractant with an acidic extractant to yield a hybrid solvent system for separating minor actinides (MA) from acidic HLW

- Neutral extractant co-extracts MA & Ln from HNO₃
- Acidic extractant operates in “reverse TALSPEAK” mode—selective stripping of MA with polyaminocarboxylate ligand
First combination

- CMPO (neutral extractant)
- HDEHP (acidic extractant)

  - MA and Ln D values decreased with increasing [HNO₃]
  - Synergic extraction behavior of Am in the MA stripping regime limited the separation factor
  - MA stripping highly pH dependent

    - Slope of logD vs pH is approximately −2
Second combination
- CMPO (neutral extractant)
- HEH[EHP] (acidic extractant)

An improvement
- MA and Ln extraction from HNO₃ improved
- Less synergism in the distribution behavior of Am in the MA stripping regime
- Less dependence on the pH

But...
- MA and Ln $D$ values for extraction from HNO₃ are modest (< 10)
- $D$ values decrease at [HNO₃] > 2 mol/L
Third combination

- T2EHDGA (neutral extractant)\(^{(a)}\)
- HEH[EHP] (acidic extractant)

\[ \text{T2EHDGA; } R = \text{CH}_2\text{CH}([\text{CH}_2\text{CH}_3])\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

\[ \text{TODGA; } R = n-(\text{CH}_2)_7\text{CH}_3 \]

\[ \text{HEH[EHP]} \]

\(^{(a)}\) TODGA can also be considered
Am reasonably extracted at $\geq 2$ M HNO$_3$.

Lanthanide $D$ values increase with increasing Z, up to Eu and Gd (which are nearly the same).

La $D$ values are less than 1.
  - Can separate La from the MA in the extraction stages.
### Ln $D$ values
- La and Ce increase with increasing pH
- Pr and Nd go through maxima
- Sm, Eu, Gd decrease with increasing pH

### The Am $D$ values
- Decrease as the pH increases from 2 to 4
- Slope $-0.26$

### Above pH 2.9, the minimum separation factor depends little on pH
- SF $\approx$ 21 to 25
- Defined by Nd/Am couple

0.05 M T2EHDGA + 0.75 M HEH[EHP]
0.125 M HEDTA + 0.2 M citrate
- Zr(IV) strongly extracted by the ALSEP solvent
- Addition of CDTA to the feed completely suppresses Zr extraction
Mo scrubbing

- Mo(VI) strongly extracted from HNO$_3$
- Mo must be removed from the solvent before MA stripping so that the MA product is not contaminated with Mo
- Scrubbing with a citrate buffer is the preferred method
  - Removes Mo
  - Conditions solvent for subsequent MA stripping step
    - Residual acid in the solvent is removed
- 0.2 M citrate is adequate—no advantage to higher concentrations
- pH independent at pH > 3.3
  - But must account for initial drop in pH caused by neutralization of residual HNO$_3$ in the solvent

**0.05 M T2EHDA + 0.75 M HEH[EHP]**

- **0.2 M citrate**
- **pH ~ 3.3**
- **[citrate], mol/L**

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Fe(III) behavior

- In the absence of CDTA, the Fe $D$ values increased with increasing time and do not appear to reach equilibrium even after 3 h.
- When CDTA present, the $D$ values do level off some after 50 min (but eventually creep up again at longer contact times).
- Potential explanation: slow precipitation of Fe from the system.

Iron(III) distribution ratios as a function of time for extraction from 2 mol/L HNO$_3$ into 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in n-dodecane.
Kinetics poses some challenges

- Forward extraction kinetics from 3M HNO₃ appears to be fast
  - Less than 1 min shaking on Vortex mixer@3200rpm is sufficient

- Back extraction kinetics of Am from 0.05M TODGA/0.75M HEH[EHP] with 0.025 M DTPA takes somewhat longer
  - SF ~ 60 in 90 sec, might be an issue for centrifugal contactors with short residence times
Forward extraction kinetics with ALSEP solvent from 3M HNO₃ PUREX raffinate is fast

Only Mo extraction is slow

- OK since it is desired that Mo remain in the ALSEP raffinate
Am back extraction with DTPA/citrate following a citrate wash step

La and Ce $D$ values are independent of the flow rate, but Am $D$ value increases with increasing flow...lower separation factors at desired flow rates

Elevated temperature helps, but SF (Nd/Am) is lower than 10
- ALSEP solvent back-extracted with HEDTA/citrate solution
- SF for Nd, Pm and La are the worse case, but value of 10 is accomplished
- D(Ln) are lower than equilibrium D despite back-extraction regime
- Total flow rates are lower than desired
- Also tested HEDTA/Citrate pH 3.2 (ambient T) and pH 2.4 at elevated temperature without particular success
Modified compositions—
0.04M T2EHDGA/0.6M HEHEHP
12 mM DTPA/0.8M Malonate

- Decreased both HEHEHP and DGA conc.
- Decreased [DTPA], lowered pH and switched to malonate buffer to minimize Am-buffer complex formation
- Co-extraction step from 3 M HNO₃
  - D's are sufficient: Am-4.1, Pm-6.5, Eu-15, La-0.5
- Back extraction – test tube results:

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**Summary**

- ALSEP is a promising method for recovering minor actinides from acidic HLW in a single solvent extraction process cycle.
- The basic aspects of the process chemistry have been established:
  - Extraction from nitric acid
  - Scrubbing of Mo
  - MA stripping
  - Ln stripping
  - Zr suppression/stripping
- Minor actinide stripping kinetics present some challenges to implementing ALSEP with centrifugal contactors, but progress is being made to resolve this issue:
  - Use of HEDTA as stripping agent with citrate buffer at pH ~2.7
  - Use of DTPA as stripping agent with malonate buffer at pH ~2.7 and 40 to 45 °C
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