



U.S. DEPARTMENT OF  
**ENERGY**

**Nuclear Energy**

Fuel Cycle R&D Program

## Status of the ALSEP Concept

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**First SACSESS International Workshop**

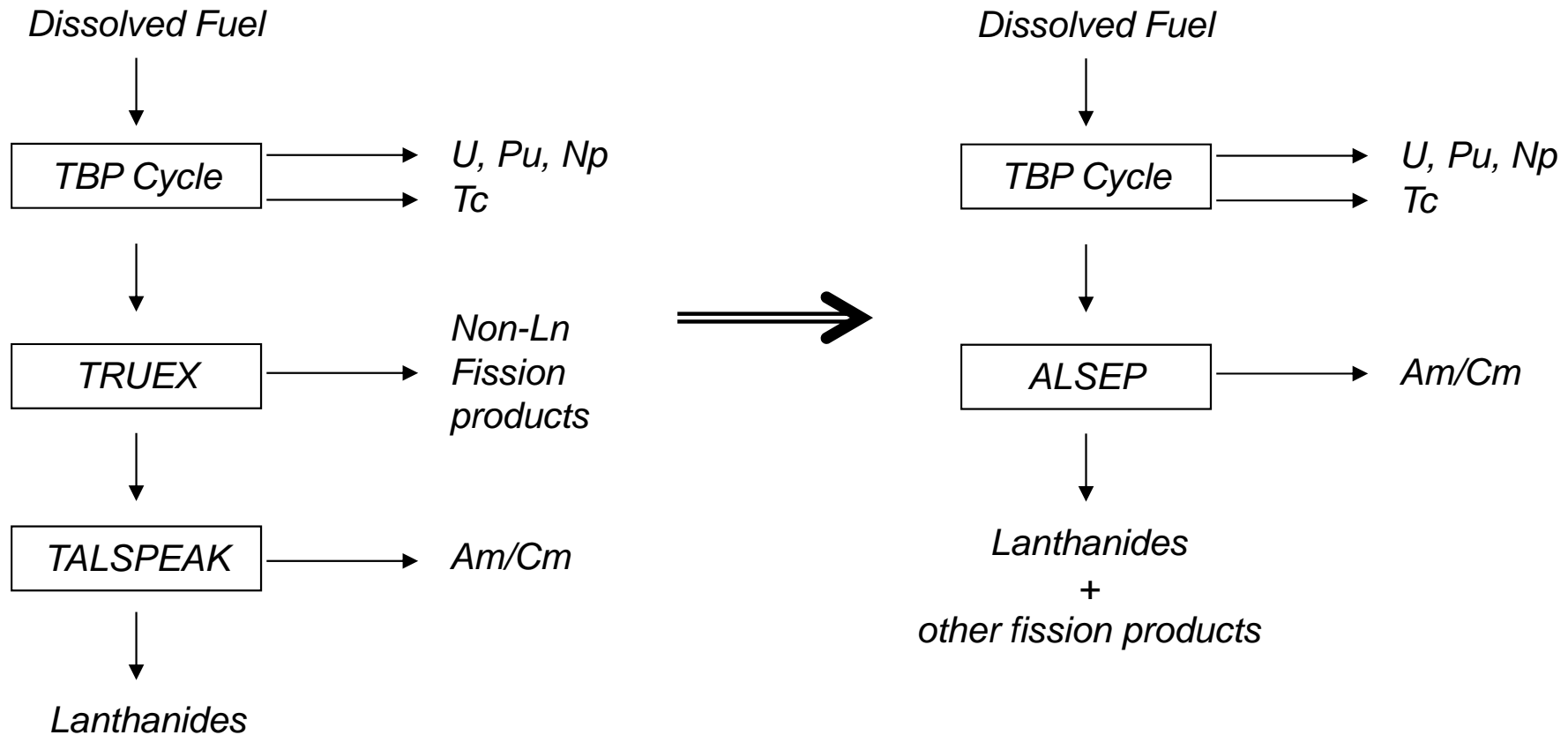
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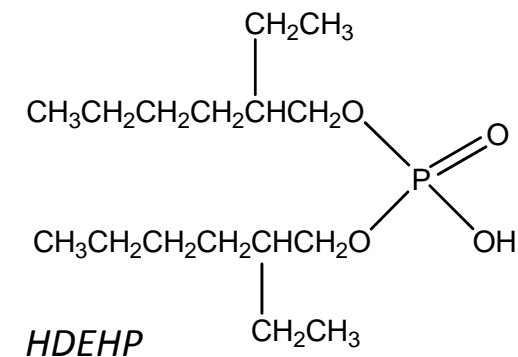
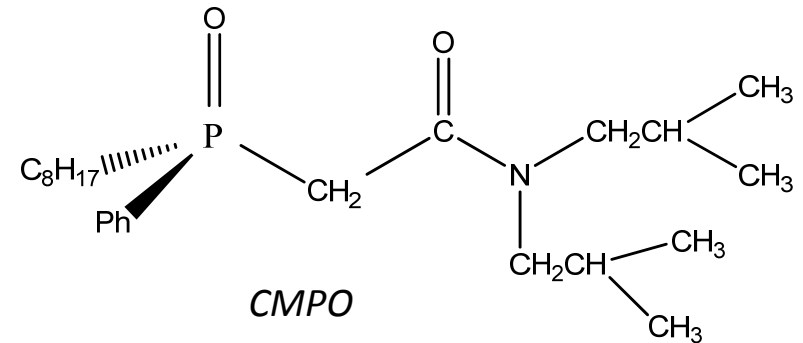


- **Combine a neutral donor extractant with an acidic extractant to yield a hybrid solvent system for separating minor actinides (MA) from acidic HLW**
  - Neutral extractant co-extracts MA & Ln from HNO<sub>3</sub>
  - Acidic extractant operates in “reverse TALSPEAK” mode—selective stripping of MA with polyaminocarboxylate ligand



### ■ First combination

- CMPO (neutral extractant)
- HDEHP (acidic extractant)
  - *MA and Ln D values decreased with increasing  $[HNO_3]$*
  - *Synergic extraction behavior of Am in the MA stripping regime limited the separation factor*
  - *MA stripping highly pH dependent*
    - Slope of  $\log D$  vs pH is approximately  $-2$





### ■ Second combination

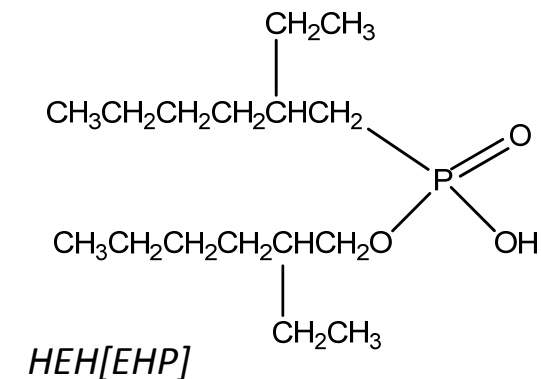
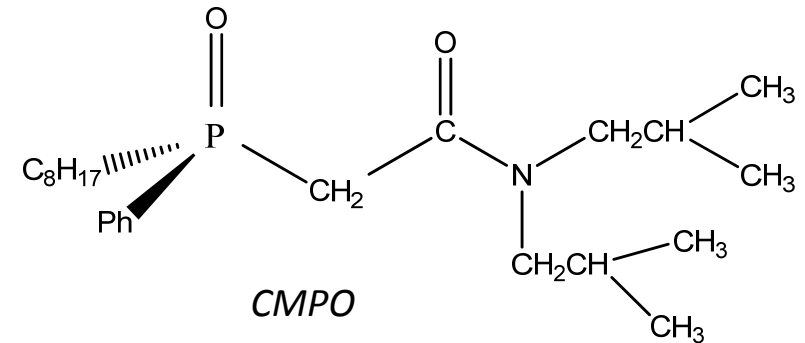
- CMPO (neutral extractant)
- HEH[EHP] (acidic extractant)

#### ■ An improvement

- MA and Ln extraction from  $\text{HNO}_3$  improved
- Less synergism in the distribution behavior of Am in the MA stripping regime
- Less dependence on the pH

#### ■ But...

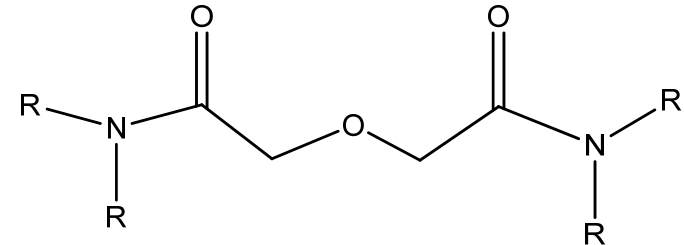
- MA and Ln  $D$  values for extraction from  $\text{HNO}_3$  are modest ( $< 10$ )
- $D$  values decrease at  $[\text{HNO}_3] > 2 \text{ mol/L}$





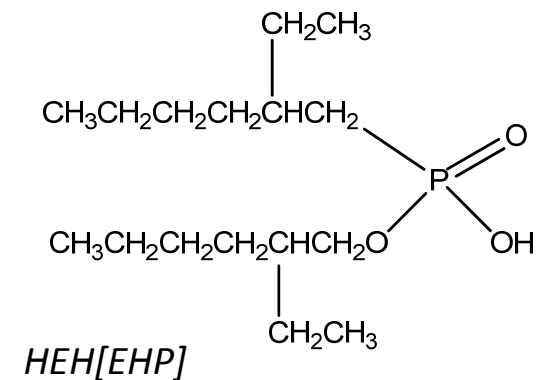
### ■ Third combination

- T2EHDGA (neutral extractant)<sup>(a)</sup>
- HEH[EHP] (acidic extractant)



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

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

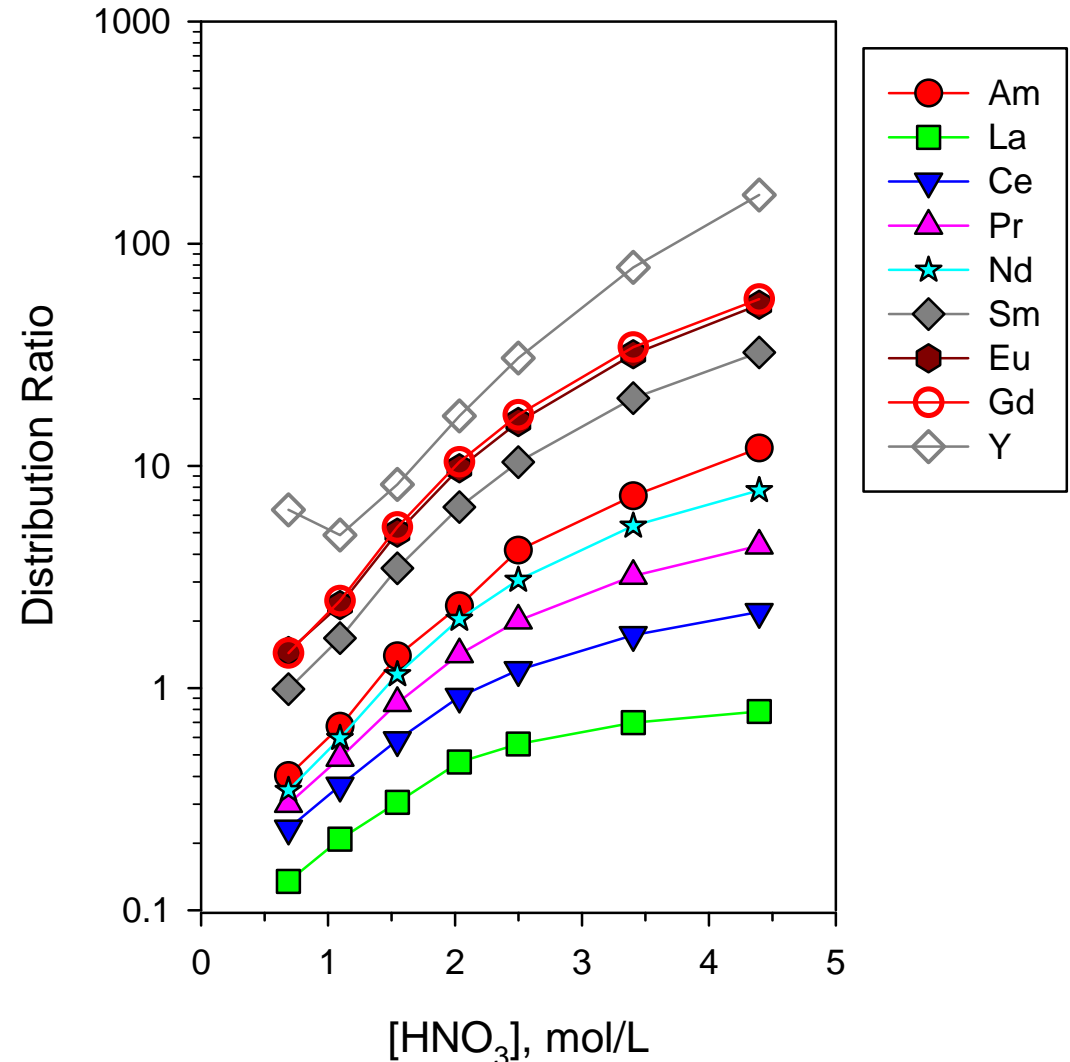


(a) TODGA can also be considered



# “Reference” ALSEP solvent: 0.05 M T2EHDGA + 0.75 M HEH[EHP]

- Am reasonably extracted at  $\geq 2$  M  $\text{HNO}_3$
- 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

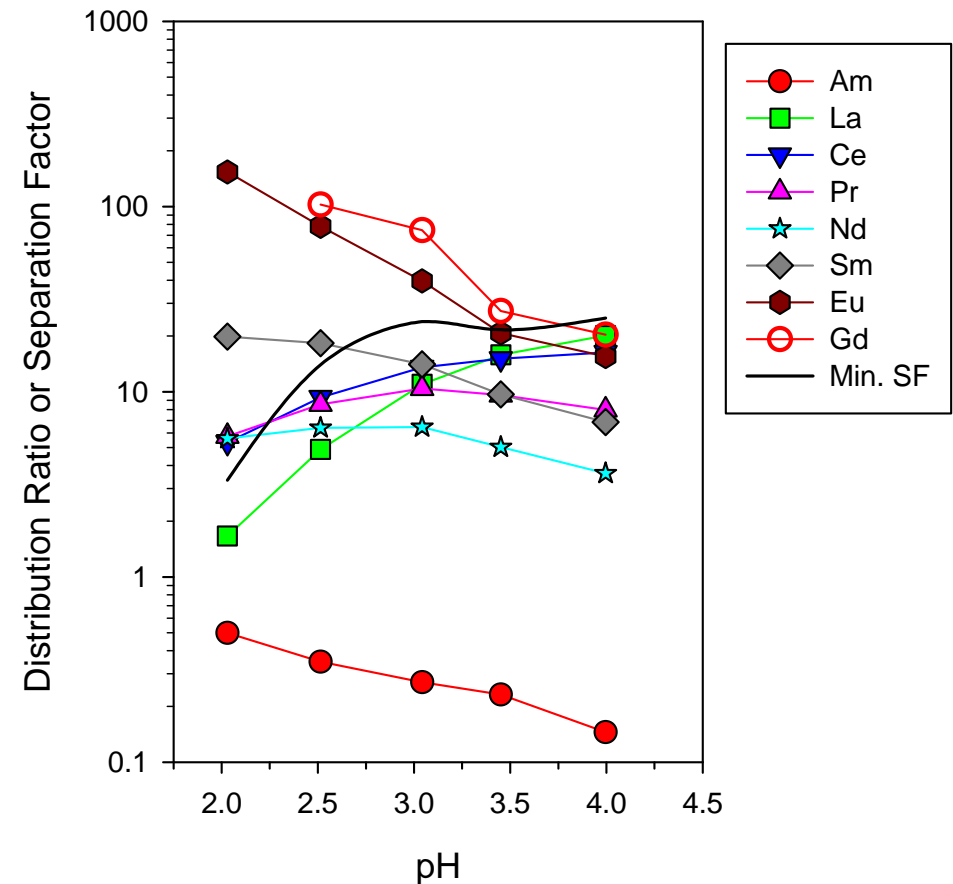
## ■ The Am *D* values

- 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 ~ 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*

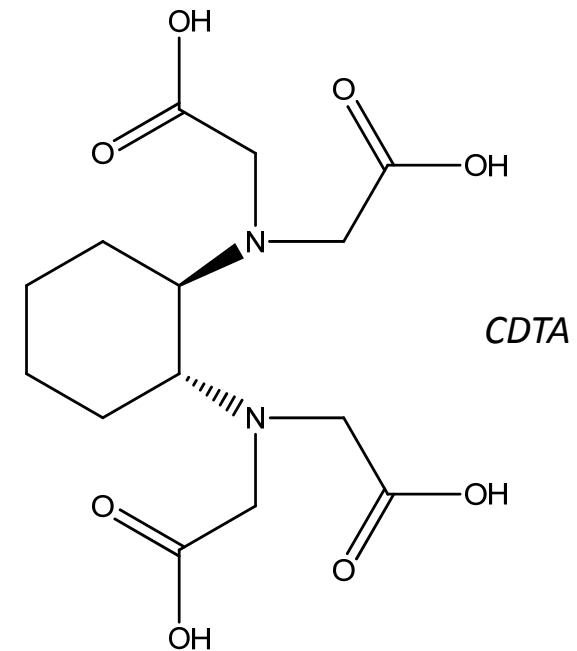






# Zirconium management in ALSEP

- **Zr(IV) strongly extracted by the ALSEP solvent**
- **Addition of CDTA to the feed completely suppresses Zr extraction**





- Mo(VI) strongly extracted from  $\text{HNO}_3$
- 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

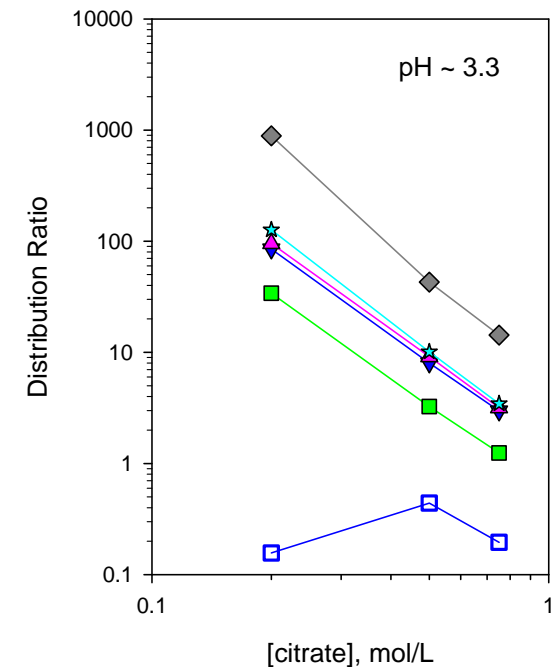
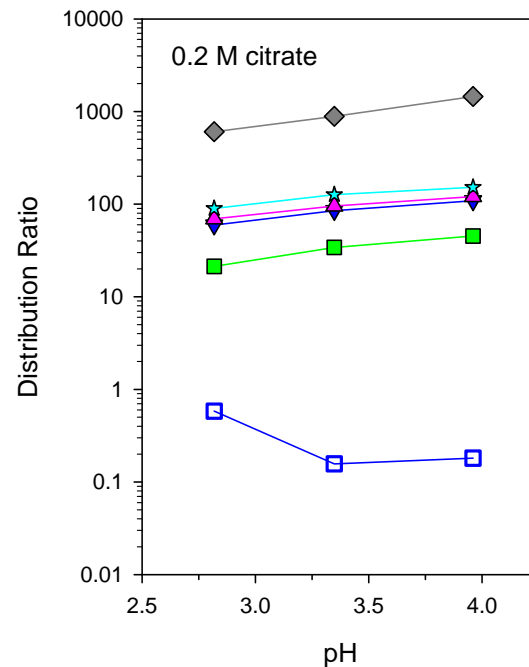
- Removes Mo
- Conditions solvent for subsequent MA stripping step
  - Residual acid in the solvent is removed

- 0.2 M citrate is adequate—no advantage to higher concentrations

- pH independent at  $\text{pH} > 3.3$

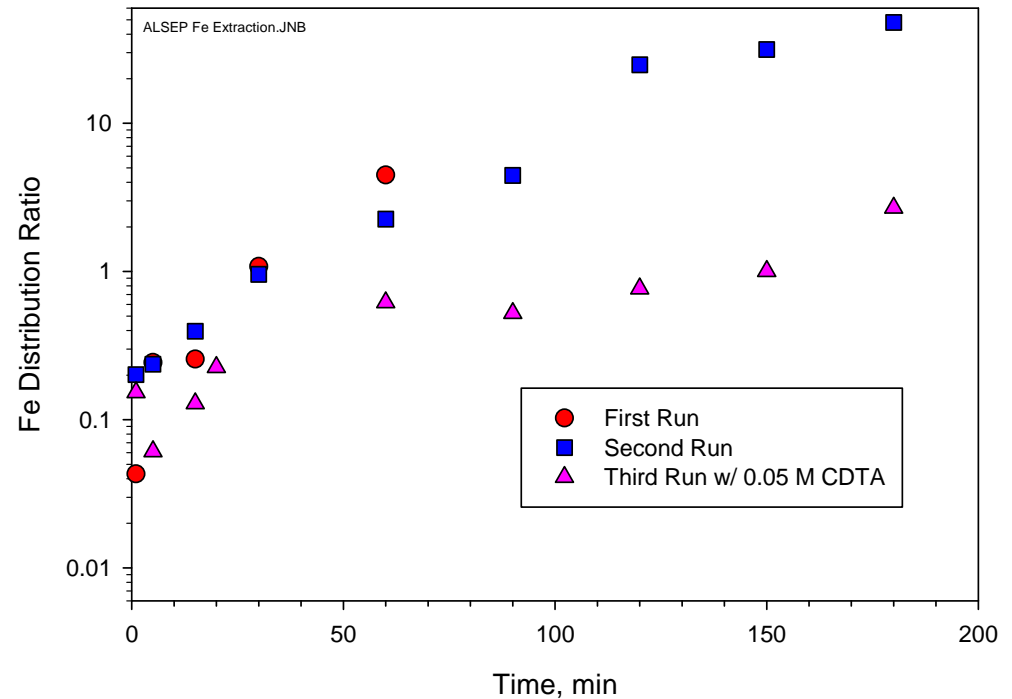
- But must account for initial drop in pH caused by neutralization of residual  $\text{HNO}_3$  in the solvent

0.05 M T2EHDGA + 0.75 M HEH[EHP]





- 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

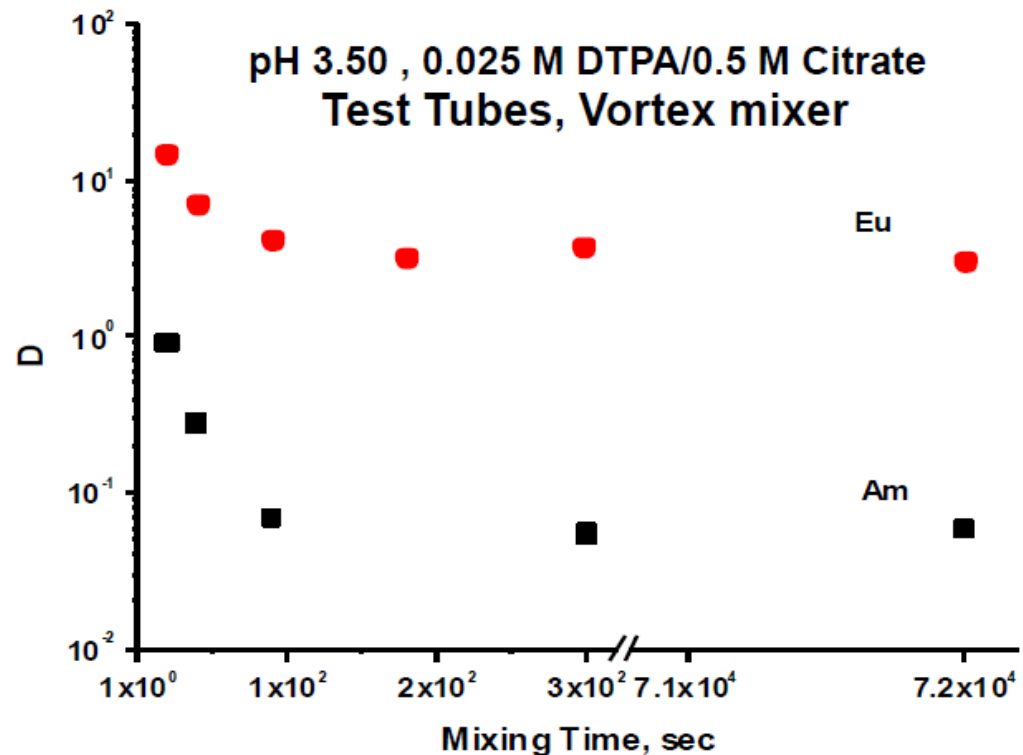


*Iron(III) distribution ratios as a function of time for extraction from 2 mol/L HNO<sub>3</sub> into 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in n-dodecane.*



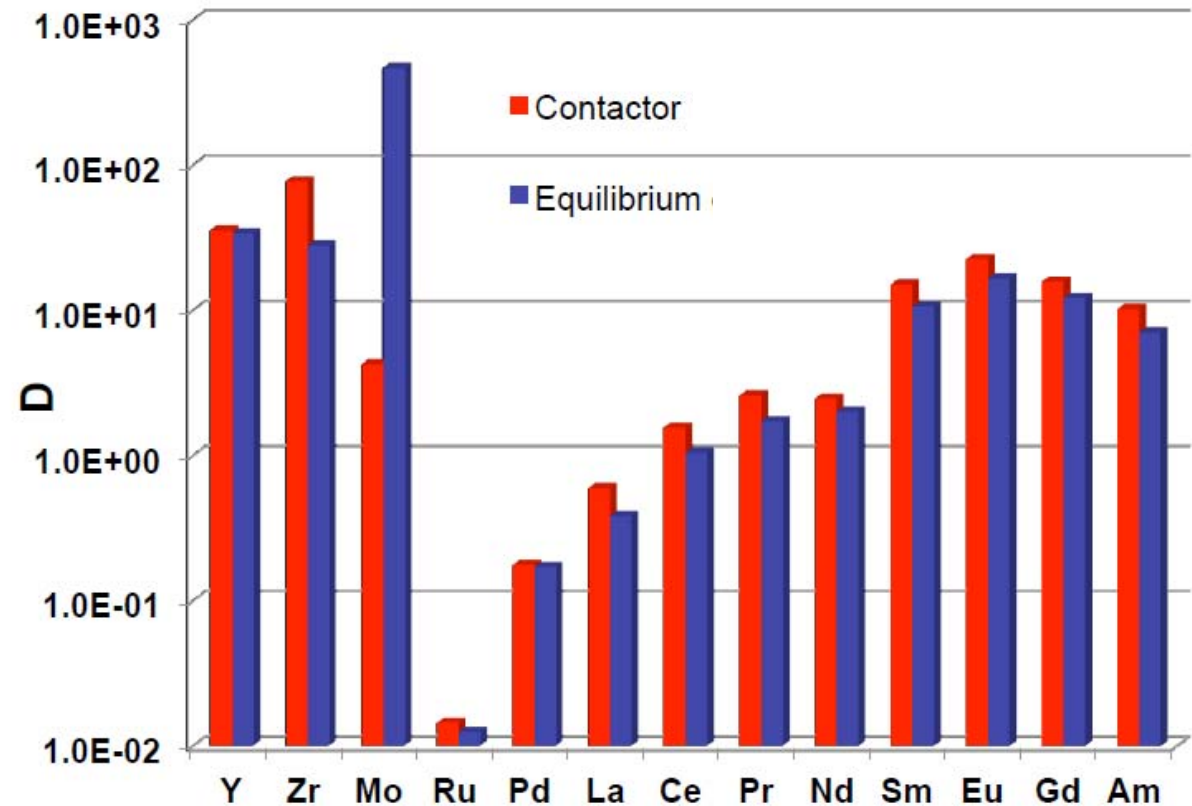
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- Forward extraction kinetics from 3M HNO<sub>3</sub> appears to be fast
  - Less than 1 min shaking on Vortex mixer @ 3200rpm is sufficient
- Back extraction kinetics of Am from 0.05M TODGA/0.75M HEH[EHP] with 0.025 M DTPA takes somewhat longer
  - SF ~ 60 in 90 sec, might be an issue for centrifugal contactors with short residence times



## 2-cm ANL Centrifugal Contactor Test – Forward Extraction at 3 M HNO<sub>3</sub>

- Forward extraction kinetics with ALSEP solvent from 3M HNO<sub>3</sub> PUREX raffinate is fast
- Only Mo extraction is slow
  - OK since it is desired that Mo remain in the ALSEP raffinate





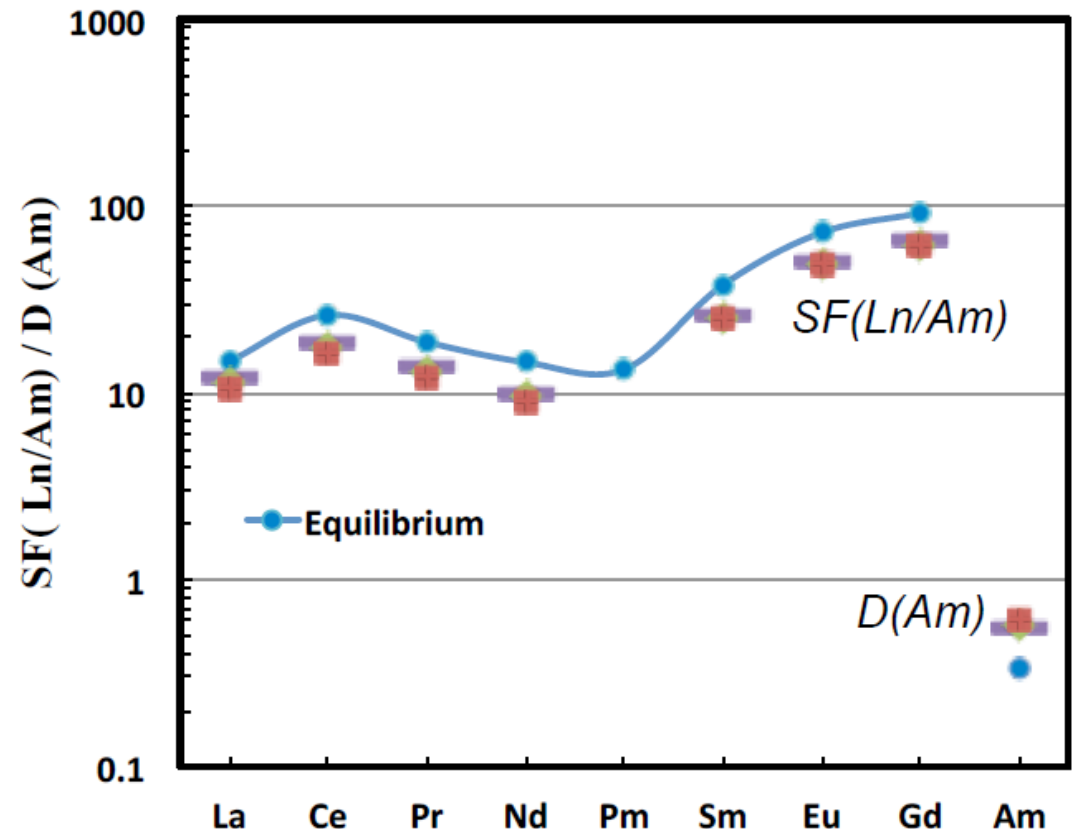
## 2-cm ANL Centrifugal Contactor Test – Back-Extraction with DTPA

- 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



# 2-cm ANL Centrifugal Contactor Test – Back-Extraction with HEDTA

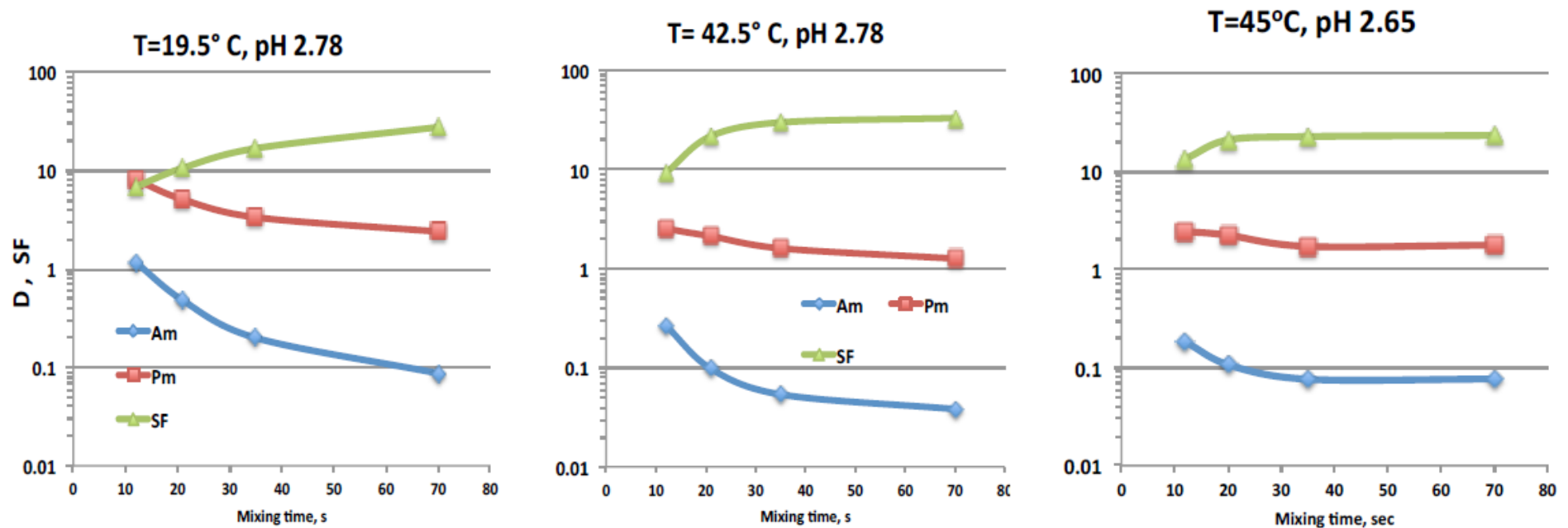
- ALSEP solvent back-extracted with HEDTA/citrate solution
- SF for Nd, Pm and La are the worse case, but value of 10 is accomplished
- $D(\text{Ln})$  are lower than equilibrium  $D$  despite back-extraction regime
- Total flow rates are lower than desired
- Also tested HEDTA/Citrate pH 3.2 (ambient 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 HNO<sub>3</sub>
  - D's are sufficient: Am-4.1, Pm-6.5, Eu-15, La-0.5
- Back extraction – **test tube** results:







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- **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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