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Project No. 81935

Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts

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FY2003 EMSP Principal Investigator Workshop
Pacific Northwest National Laboratory
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***Site Principal Investigator. ORNL is lead institution.**

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The purpose of this project is to explore new liquid-liquid extraction approaches to the separation of sodium hydroxide and sodium nitrate from alkaline tank waste.

Objectives:

- **Refine understanding of pseudo hydroxide extraction**
  - Develop new weakly acidic cation exchangers for NaOH separation
  - Probe extraction mechanism
- **Explore systems involving macrocyclic extractants**
  - Develop concept of synergistic pseudo hydroxide extraction
  - Determine efficacy of ionizable lariat ethers
  - Establish feasibility of NaOH and $NaNO_3$ co-extraction

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Sodium separation from LAW yields potential savings

Possible benefits:

Reduced low-activity-waste (LAW) glass production

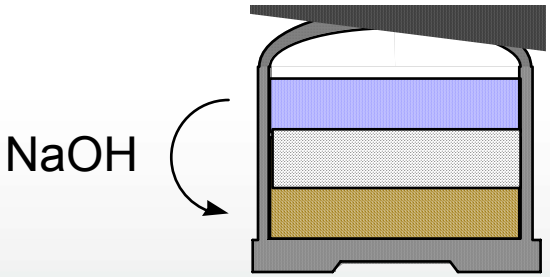
- Divert sodium to alternative waste form, such as grout
- Accelerated waste processing (mission acceleration)

NaOH recycle for enhanced sludge washing

- Reduces or eliminates addition of NaOH
- Reduced retrieval risk

Avoidance of new tank construction

- Waste debulking on skid-mounted units



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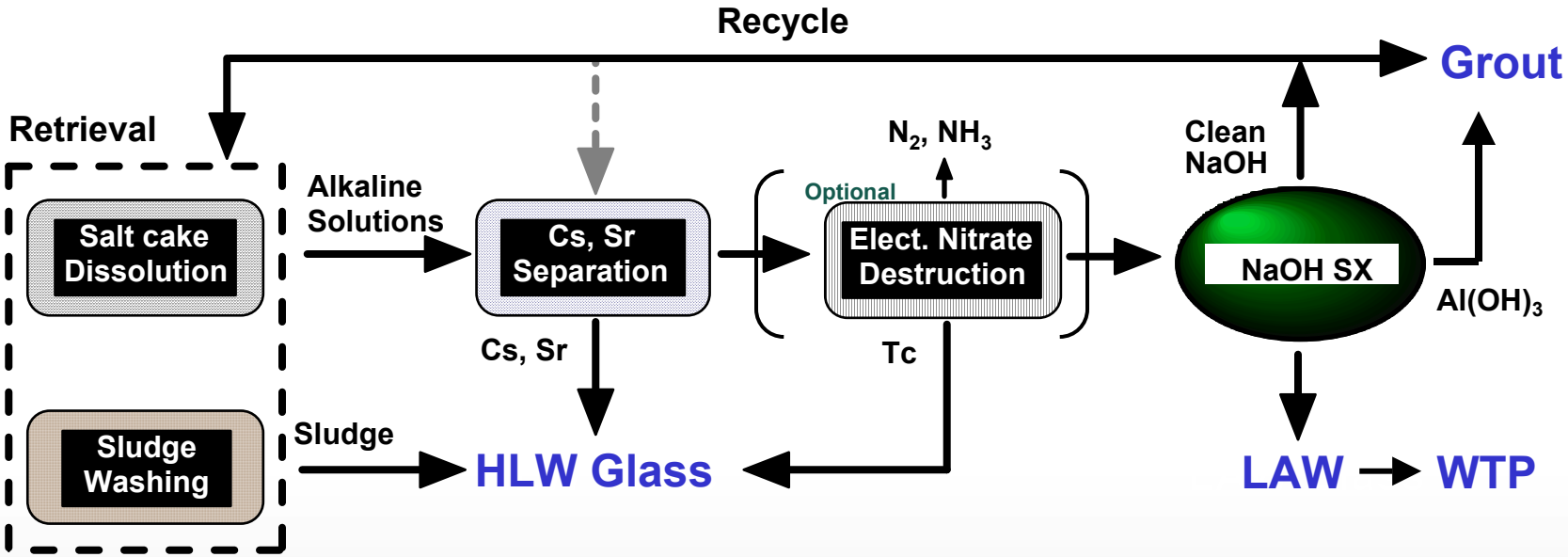
Clean sodium concept using NaOH solvent extraction (SX)



Note! This is a speculative flowsheet for discussion.

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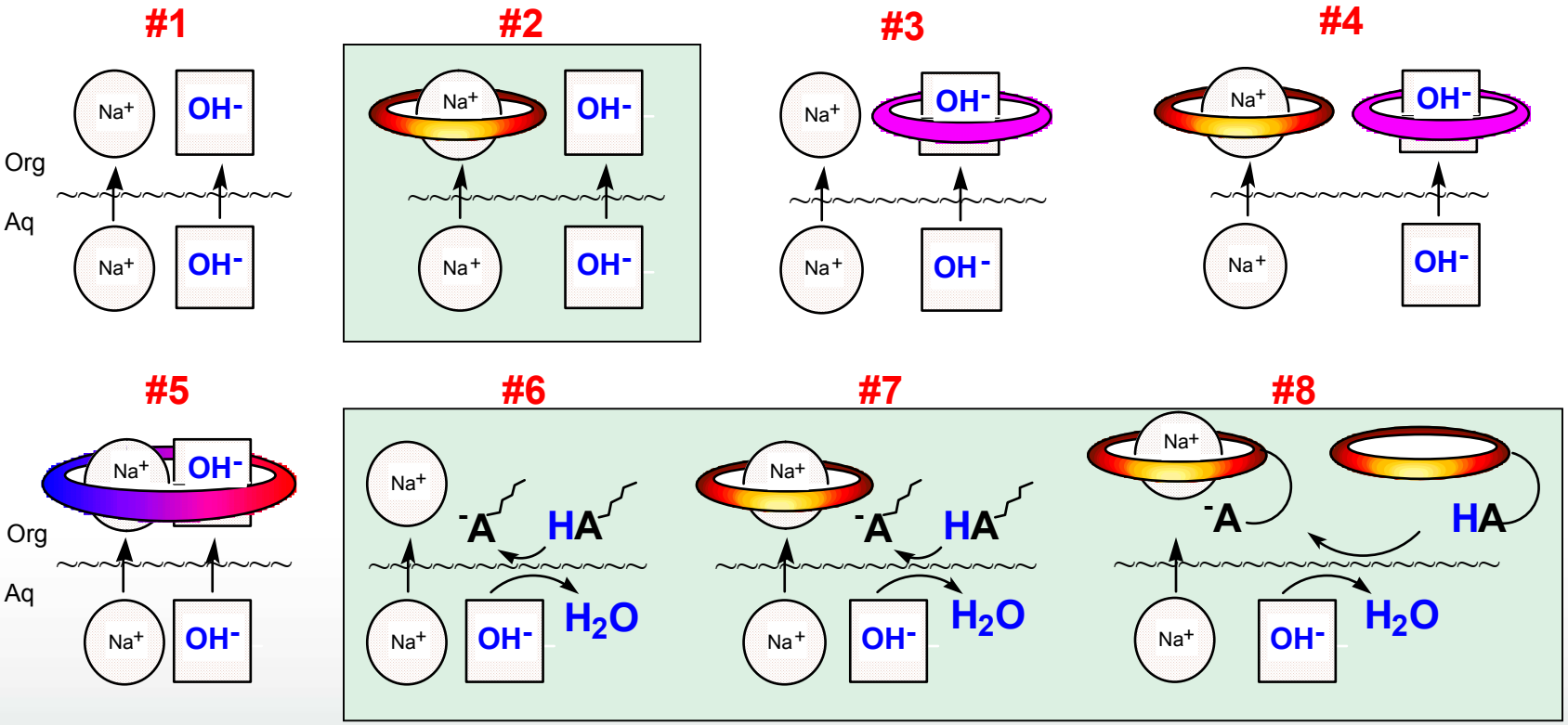
Four of eight SX approaches are being investigated



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B. A. Moyer, P. V. Bonnesen, C. K. Chambliss, T. J. Haverlock, A. P. Marchand, H-S. Chong, A. S. McKim, K. Krishnudu, K. S. Ravikumar, V. S. Kumar, and M. Takhi, in *Nuclear Site Remediation: First Accomplishments of the Environmental Science Program*, ACS Symposium Series, Vol. 778, P. G. Eller and W. R. Heineman, Eds., American Chemical Society, Washington, DC, 2001.

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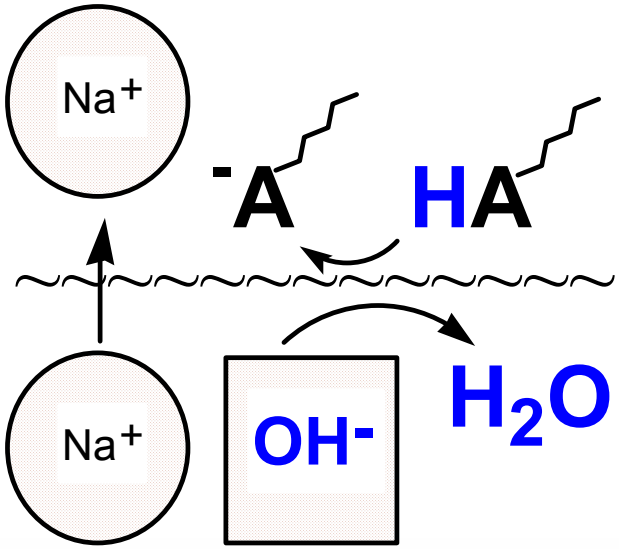
Approach #6: "Pseudo hydroxide extraction"



Weakly acidic, lipophilic proton-ionizable extractant
HA exchanges H^+ for Na^+

- **phenols**
- **fluorinated alcohols**

Hydroxide equivalents transfer via cation exchange

Extraction is specific to hydroxide anion!
Sodium hydroxide regenerated on back-extraction with water

B. A. Moyer, P. V. Bonnesen, C. K. Chambliss, T. J. Haverlock, A. P. Marchand, H-S. Chong, A. S. McKim, K. Krishnudu, K. S. Ravikumar, V. S. Kumar, and M. Takhi, in *Nuclear Site Remediation: First Accomplishments of the Environmental Science Program*, ACS Symposium Series, Vol. 778, P. G. Eller and W. R. Heineman, Eds., American Chemical Society, Washington, DC, 2001.

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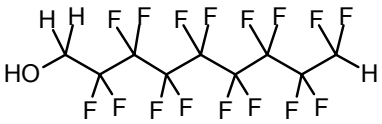
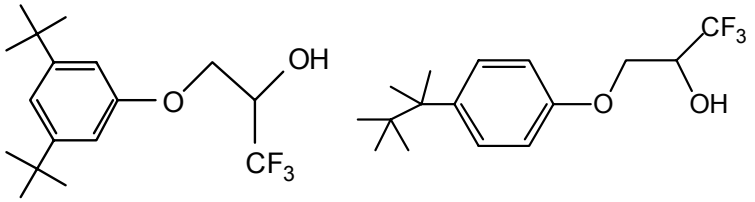
Weakly acidic cation exchangers studied

Linear fluorinated alkanols

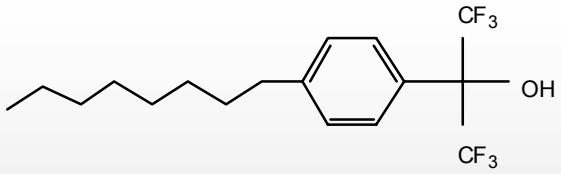


Alkyl phenoxy ethanols



Alkyl phenols

Alkyl benzyl alcohols



Emerging model based on simple cation exchange

$$Na^+ + OH^- \rightleftharpoons \overline{Na^+OH^-}$$

$$Na^+ + OH^- \rightleftharpoons \overline{Na^+} + \overline{OH^-}$$

Detectable with 1-octanol alone

$$Na^+ + OH^- + \overline{HA} \rightleftharpoons \overline{Na^+A^-} + H_2O$$

$$Na^+ + OH^- + \overline{HA} \rightleftharpoons \overline{Na^+} + \overline{A^-} + H_2O$$

Conversion to phenoxide or alkoxide confirmed by FTIR and Raman spectroscopy.

L. Maya, B. A. Moyer, and M. J. Lance *Appl. Spectrosc.* (In press).

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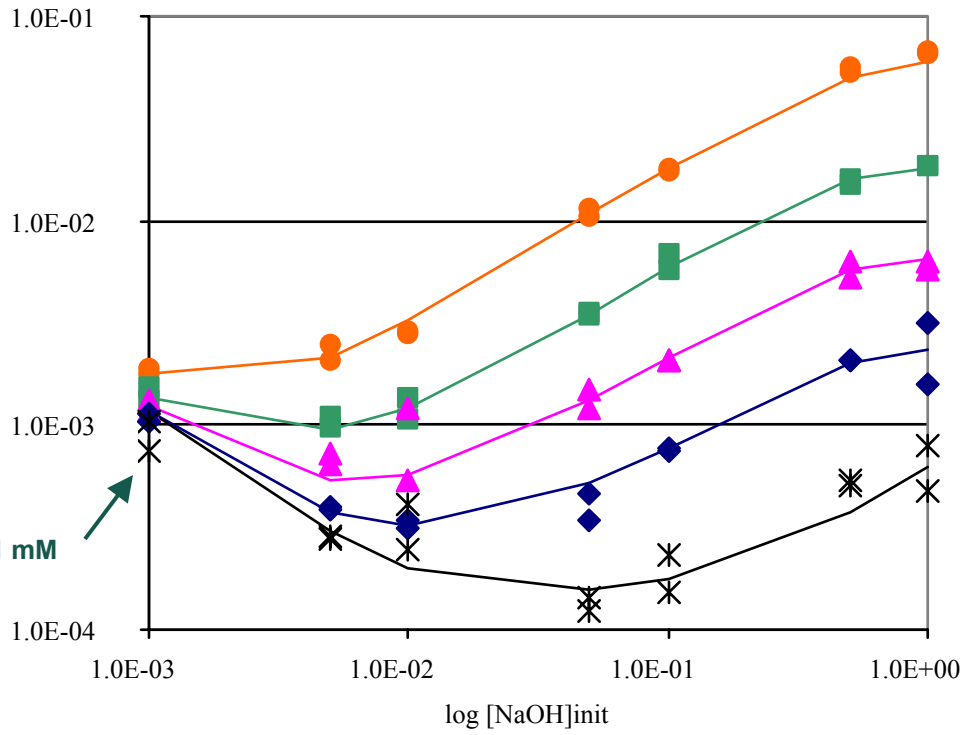
Cation-exchange model fits data



Model assumes 1 mM anionic impurity

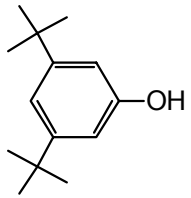
0.1 M

0.03 M

0.01 M

0.003 M

1-octanol alone



NaOH extraction isotherms @ 25 °C

H.-A. Kang, P. V. Bonnesen, L. H. Delmau, N. L. Engle, T. J. Haverlock, and, B. A. Moyer (Unpublished results).

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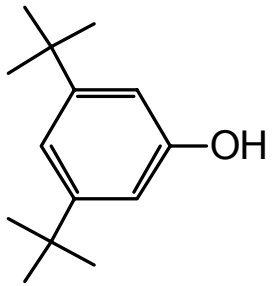
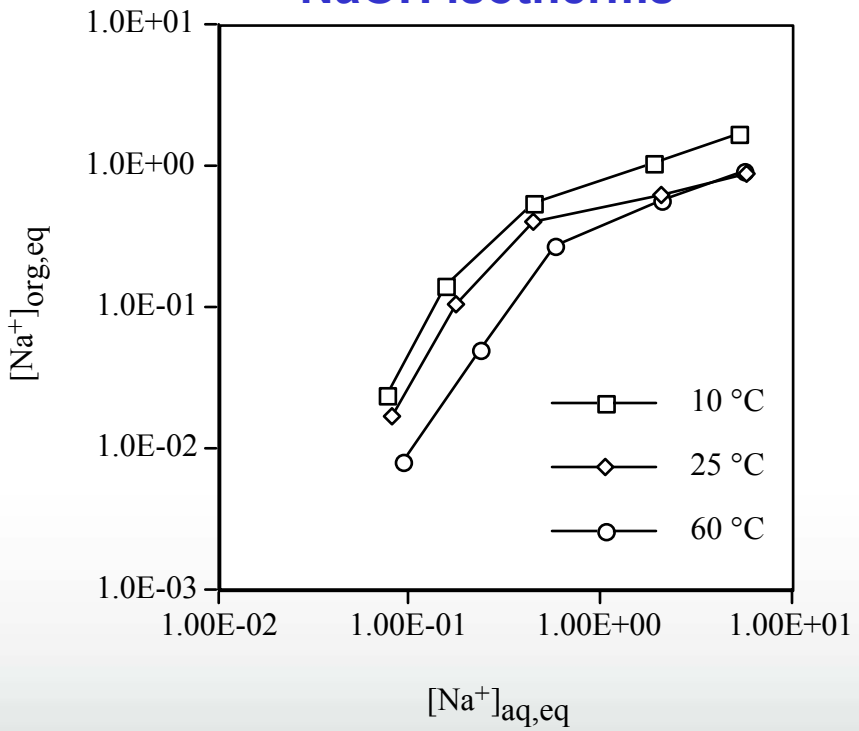
High loadings can be achieved over range of T

Solvent
1 M 3,5-di-*t*-butylphenol in 1-octanol



$\Delta H = -29\ kJ^{-1}\ mol^{-1}$
$\Delta S = -85\ J\ K^{-1}\ mol^{-1}$

NaOH isotherms



T. J. Haverlock, P.V. Bonnesen, and B.A. Moyer *SX&IX* (In press).

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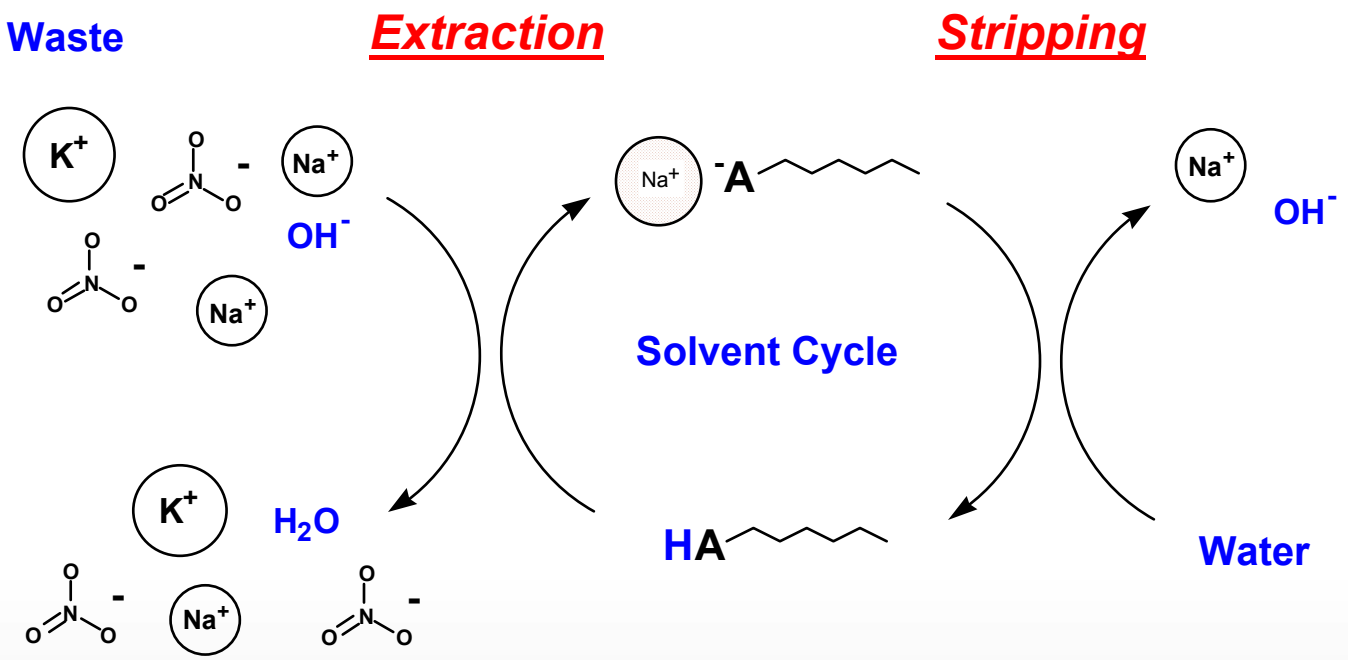
Pseudo hydroxide extraction cycle



B. A. Moyer, C. K. Chambliss, P. V. Bonnesen, and T. J. Keever, **Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures,** U.S. Patent 6,322,702, Nov. 27, 2001.

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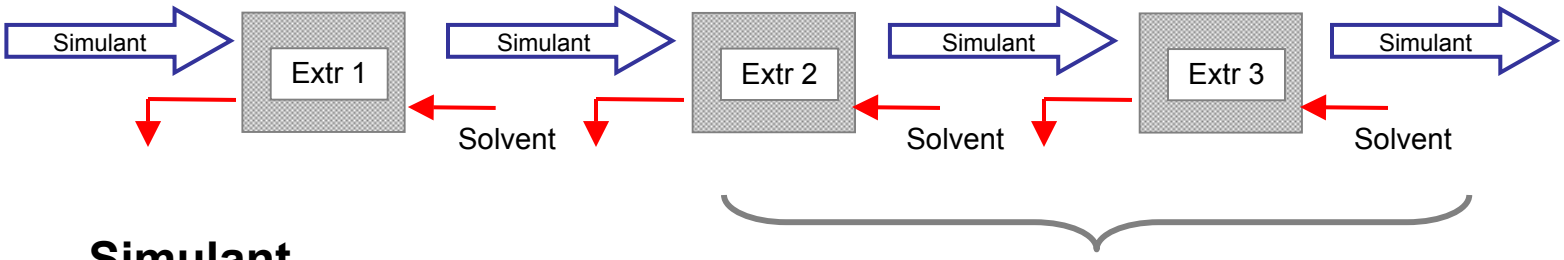
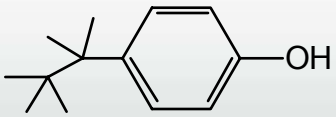
Efficient and selective NaOH removal from simulant



Simulant
1.88 M free NaOH
0.70 M $NaAl(OH)_4$
3.5 M $NaNO_3$

Solvent
1 M 4-*t*-octylphenol in 1-octanol



$Al(OH)_3$ (Bayerite) precipitates
$Al(OH)_4^- \rightleftharpoons Al(OH)_3(s) + OH^-$
More hydroxide is generated

After 3 extractions with fresh solvent @ 60 °C
107% removal of free NaOH
32% removal of Na
Avg. strip: **1.15** Na : **1** OH^-: **0.007** Al

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T. J. Haverlock, P.V. Bonnesen, and B.A. Moyer *SX&IX* (In press).

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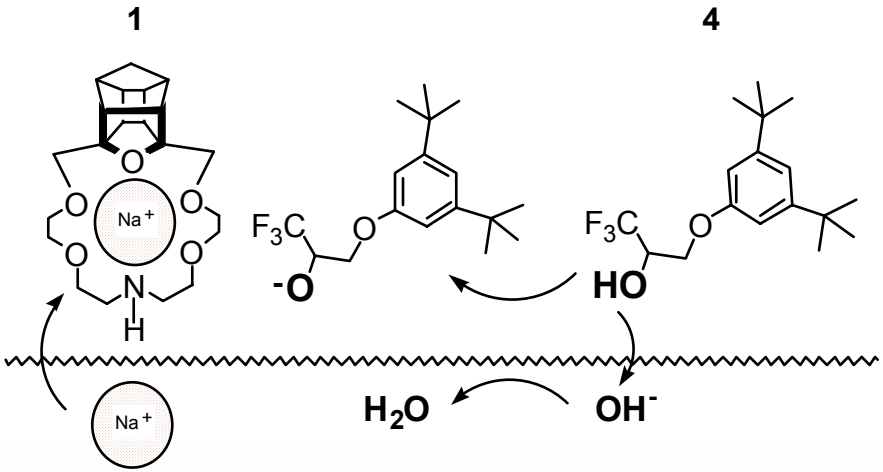
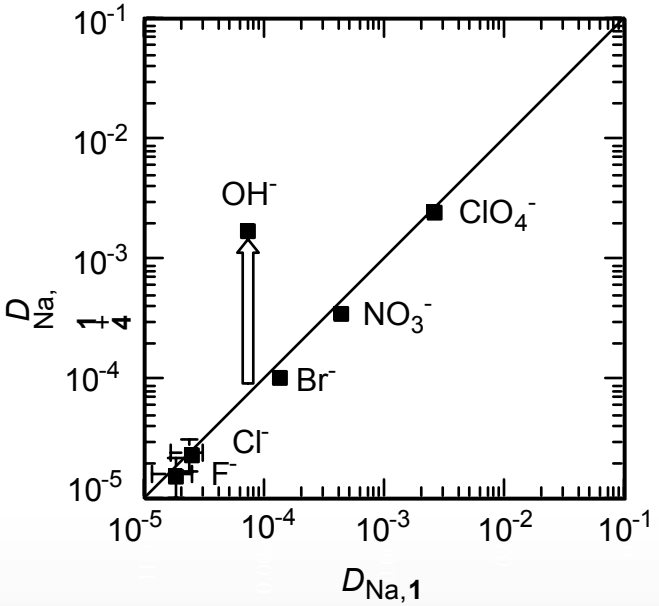
Concept of synergistic pseudo hydroxide extraction demonstrated to give selectively enhanced OH^- separation

(Approach #7)





T. G. Levitskaia, B. A. Moyer, P. V. Bonnesen, A. P. Marchand, K. Krishnudu, Z. Chen, Z. Huang, H. G. Kruger, and A. S. McKim *J. Am. Chem. Soc.* (2001).

22 mM crown + 0 or 44 mM ROH in nitrobenzene; 1 M NaX in aq phase 25 °C, O/A = 1

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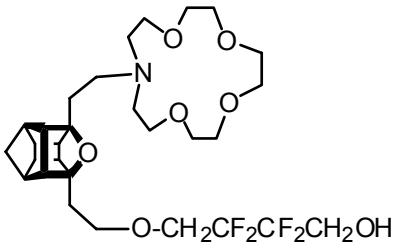
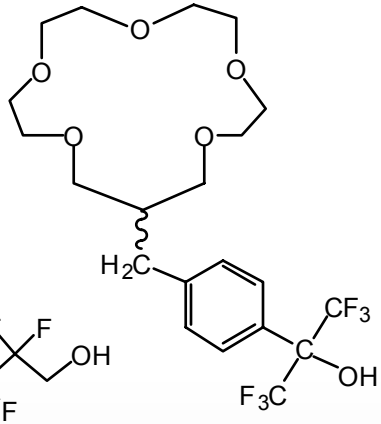
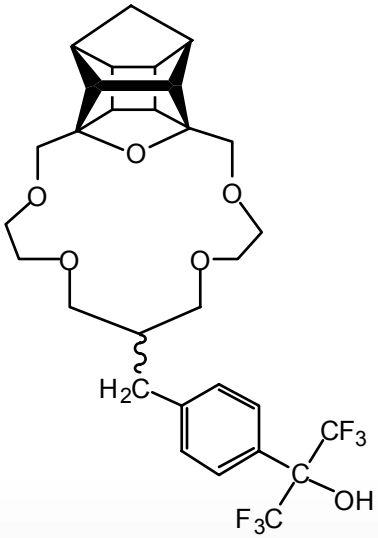
Ditopic NaOH pseudo hydroxide extractants will provide insight into intra-molecular cooperativity (Approach #8)

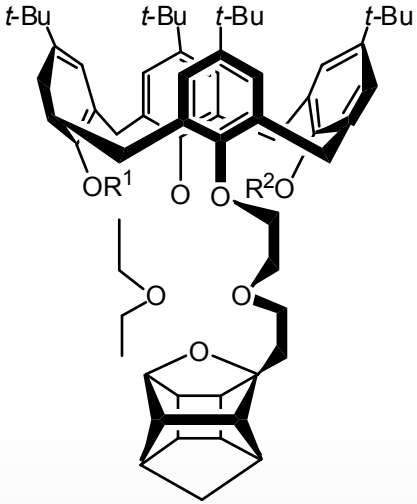
Synthesis by Alan P. Marchand and co-workers, Univ. of N. Texas

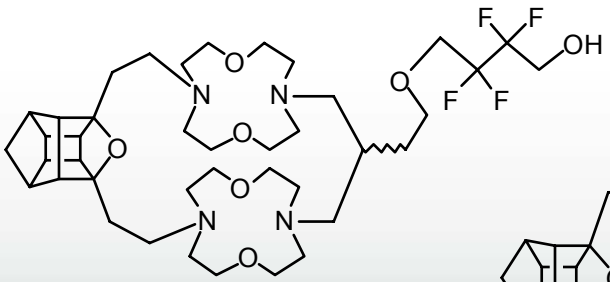
Lariat compounds being examined:

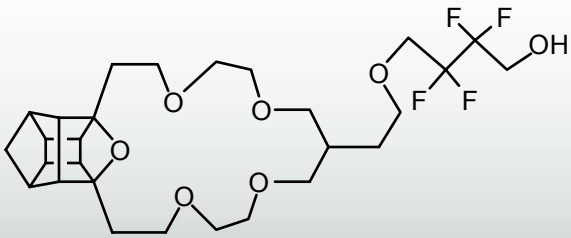












TP-I-66 ($R^1 = R^2 = CH_2CH_2\text{-}O\text{-}CH_2CF_2CF_2CH_2OH$)
TP-1-68 ($R^1 = CH_3$; $R^2 = CH_2CH_2\text{-}O\text{-}CH_2CF_2CF_2CH_2OH$)

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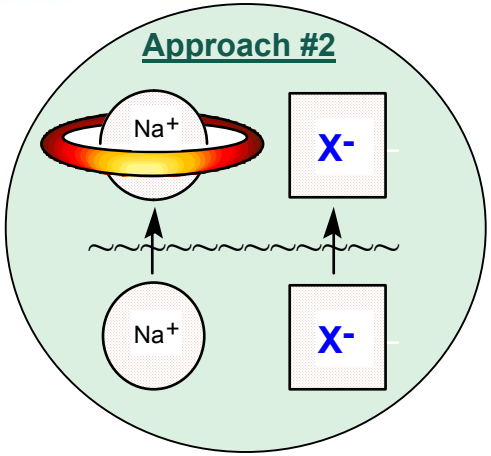
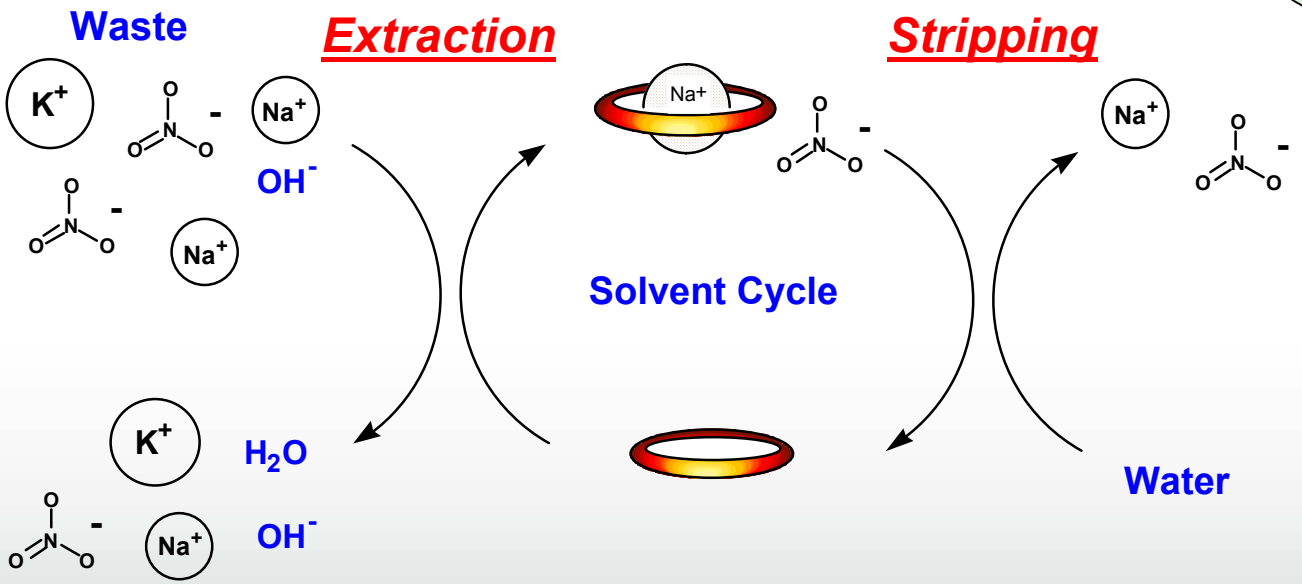
Sodium nitrate extraction may provide greater sodium removal



Approach #2 relies on a crown ether to effect extraction.



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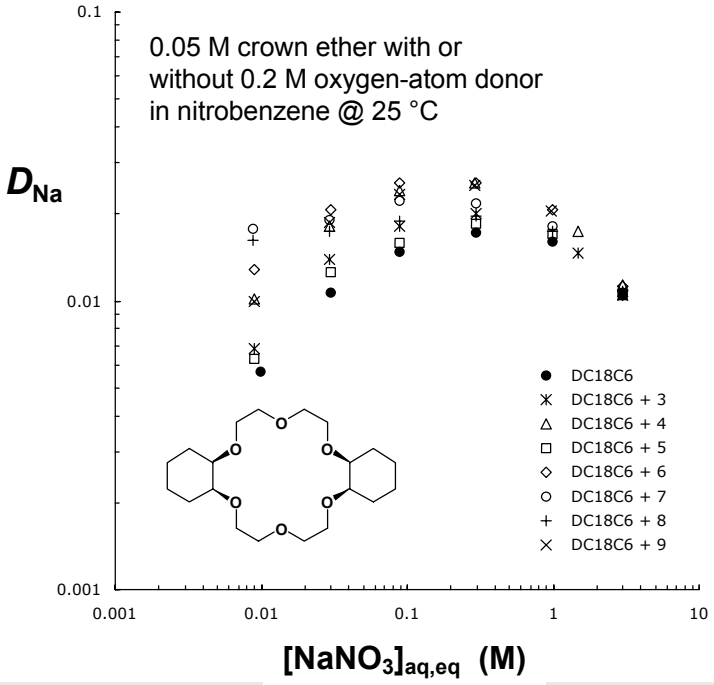
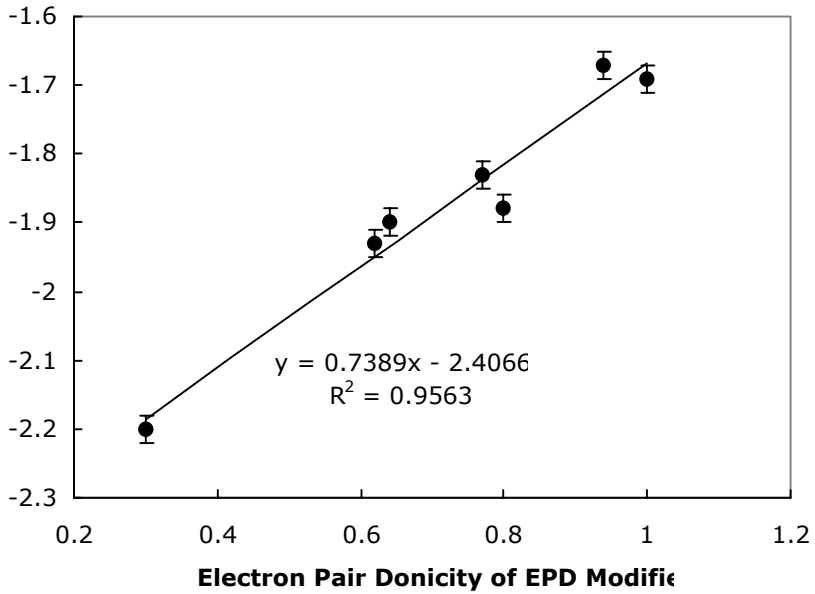
Crown ether extracts $NaNO_3$ with simple 1:1 mechanism that correlates with electron-pair donicity of solvent matrix

(Approach #2)

$$Na^+ + NO_3^- + \overline{CE} \rightleftharpoons \overline{NaCE^+} + \overline{NO_3^-}$$





T. G. Levitskaia, G. J. Lumetta, and B. A. Moyer (Unpublished results).

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Future work

Establish mechanism for pseudo hydroxide extraction

Characterize $NaNO_3$ extraction by crown ether

Explore combined NaOH and $NaNO_3$ extraction

Synthesis and testing of new ditopic extractants

Examine extraction of real-waste sample (in hand)

No sample-availability issues identified. However, would welcome opportunities to pursue technology development with partner.

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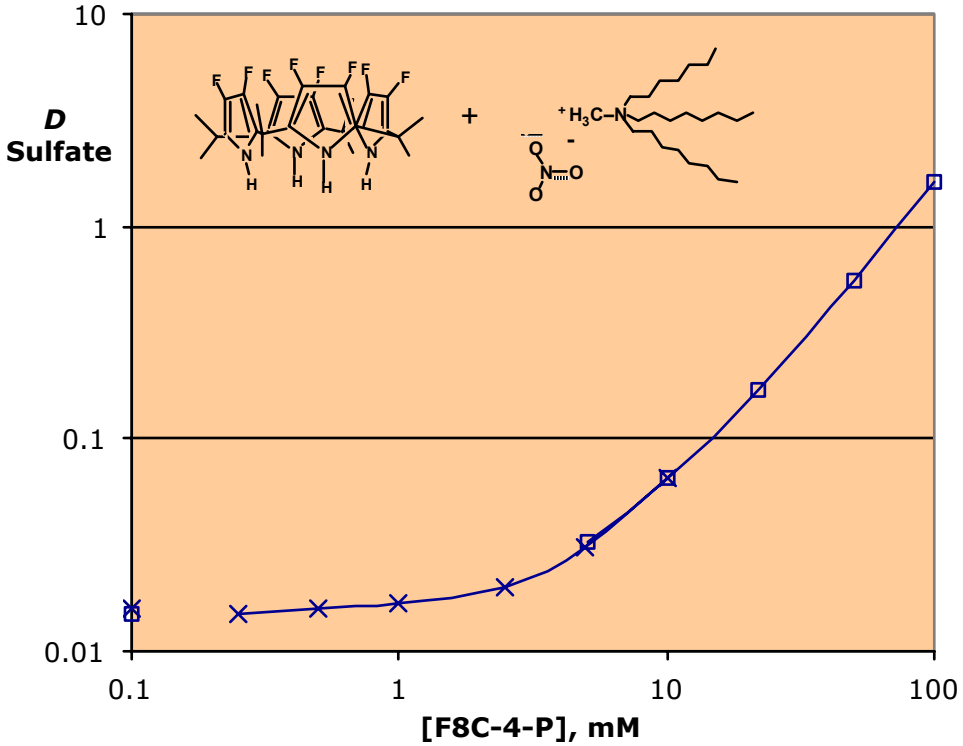
Highlight
Project No. 74019

Fluorinated calix[4]pyrrole markedly enhances extraction of sulfate by novel anion exchange process



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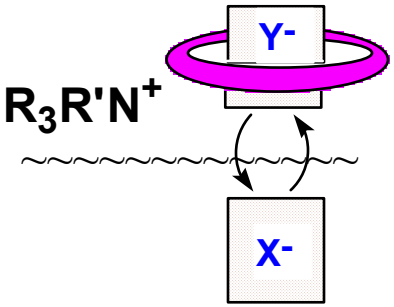

Chris Fowler, Alexandre Ruas, Lætitia Delmau, Bruce Moyer, Manuel Marquez, James Shriver, and Jonathan Sessler, in preparation.

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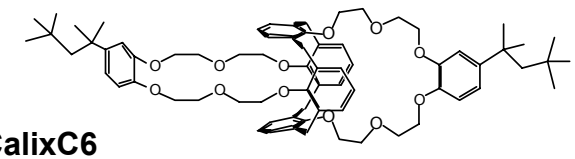
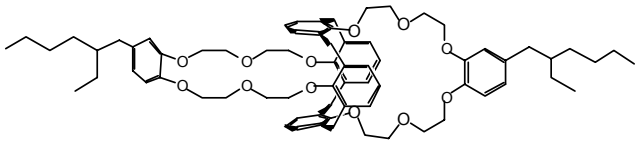
Highlight
Project No. 73803

New calixcrowns with high solubility and good Cs extraction strength have been synthesized

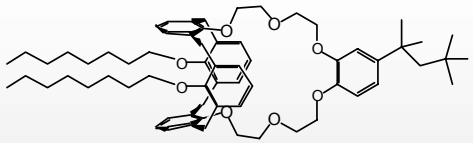


BOBCalixC6

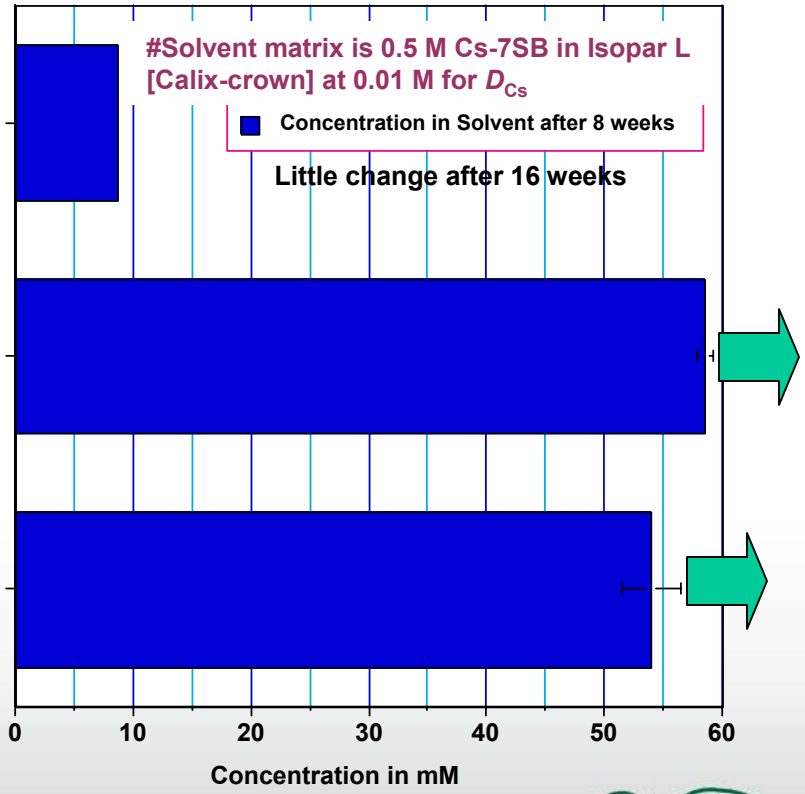
D_{Cs} = 13.5 ± 0.2



D_{Cs} = 13.1 ± 0.5



D_{Cs} = 12.0 ± 0.1



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P. V. Bonnesen, N. L. Engle, T. J. Haverlock, and B. A. Moyer (Unpublished

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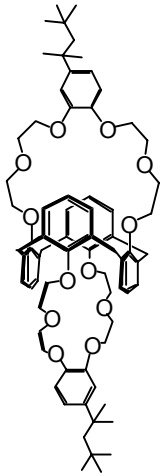
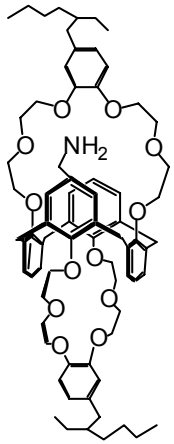
Highlight
Project No. 73803

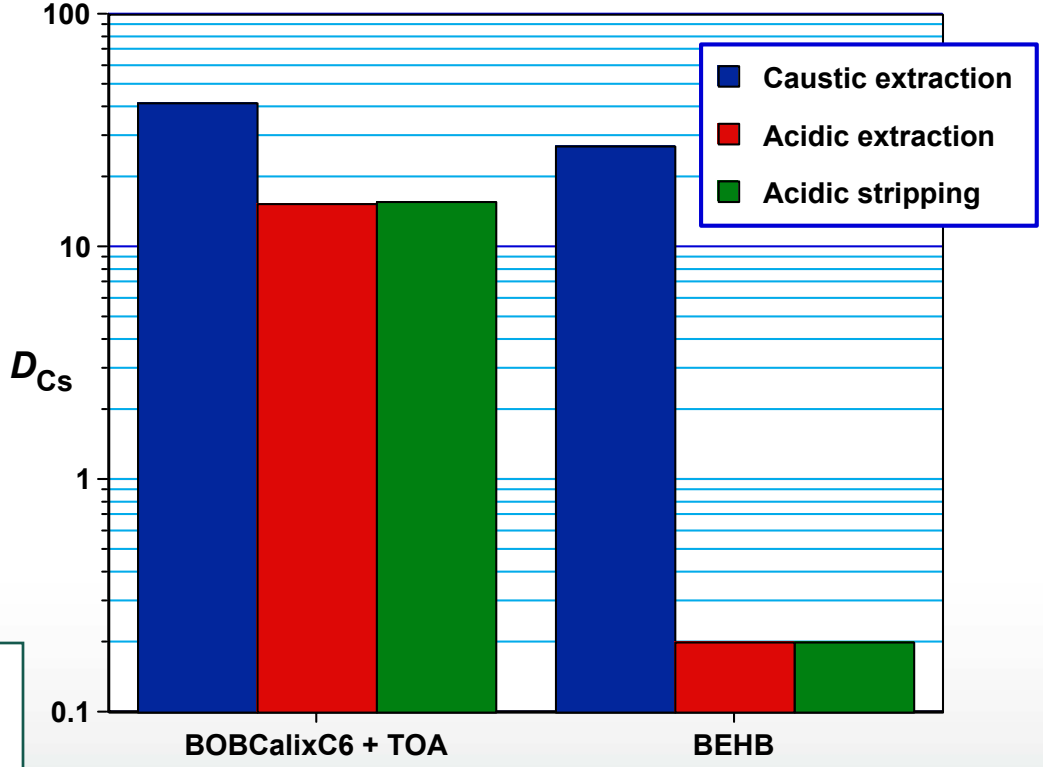
New aminated calixcrowns offer improved stripping of cesium for CSSX application



BOBCalixC6



BEHB



Caustic Extraction: 1 M $NaNO_3$, 0.05 M NaOH, 10^{-4} M $CsNO_3$
Acidic Extraction: 0.95 M $NaNO_3$, 0.05 M HNO_3, 10^{-4} M $CsNO_3$
Acidic Stripping: 0.95 M $NaNO_3$, 0.05 M HNO_3, No $CsNO_3$

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M. G. Gorbunova, P. V. Bonnesen, N. L. Engle, E. Bazelaire, L. H. Delmau, and B. A. Moyer, *Tetrahedron Lett.* (Submitted).

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U.S. Department of Energy

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