Evaluation of Novel Strategies and Processes for Separation of Rare Earth Elements for Coal-Related Materials (Project FE-810-17-FY17)

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DOE-NETL's 2020 FE R&D Virtual Project Review Meeting:
Rare Earth Elements and Critical Materials, 05/25/21

LANL Project Team

- Hakim Boukhalfa, biogeochemistry
- Kevin Boland, analytical chemistry
- Janelle Droessler, inorganic chemistry
- Mateusz Dembowski (PD), inorganic chemistry, separations
- George S. Goff, chemical engineering
- George Guthrie, mineralogy and geochemistry, *coordination with LIBS analysis project*
- Nicholas Hubley (PD), inorganic chemistry
- Christopher Leibman, inorganic chemistry
- Iain May, inorganic chemistry
- Artas Migdissov, hydrothermal geology
- Michael Rearick, analytical chemistry
- Kirk Weisbrod, chemical engineering
- Giday WoldeGabriel, geology
- Laura Wolfsberg, solids characterization
- Steven Yarbro, chemical engineering

Project Overview and Objectives

Overall Goal: Evaluate emerging separations technologies for REE separation

- Conduct a preliminary evaluation of these innovative (lower TRL) processes
- *May* include limited experimental evaluation to demonstrate proof-of-concept
- Analysis will include a consideration of gaps and limitations that need to be overcome for commercialization

- Leverage existing LANL expertise in chemistry and separations of *f*-elements
  - Extensive expertise in radiochemistry (quantitative analysis of actinide containing samples), special nuclear material purification and production (oxides and metals), nuclear fuel cycles, & fundamental science.
  - Common separations techniques include solvent extraction, ion exchange, and precipitation

Initial work focused on three thrusts:

1. Hydrothermal methods for extraction and separation
2. Supercritical CO_2 and soluble ligands for simple and effective separation
3. Ionic liquids and process intensification for novel separations
   - Examples of on-going LANL related research using ionic liquids:
     - *Process intensification* of solvent extraction separations, low-temperature electrochemical recovery of metals from waste residues
     - Nuclear fuel cycle: actinide/lanthanide separations for fuel recycling
     - Fundamental science: electrochemical separations in ionic liquids, electrodeposition

Program review in March 2019 resulted in down-select to focus on Thrust 3 and added a task on novel dissolution/leaching chemistry using ABF

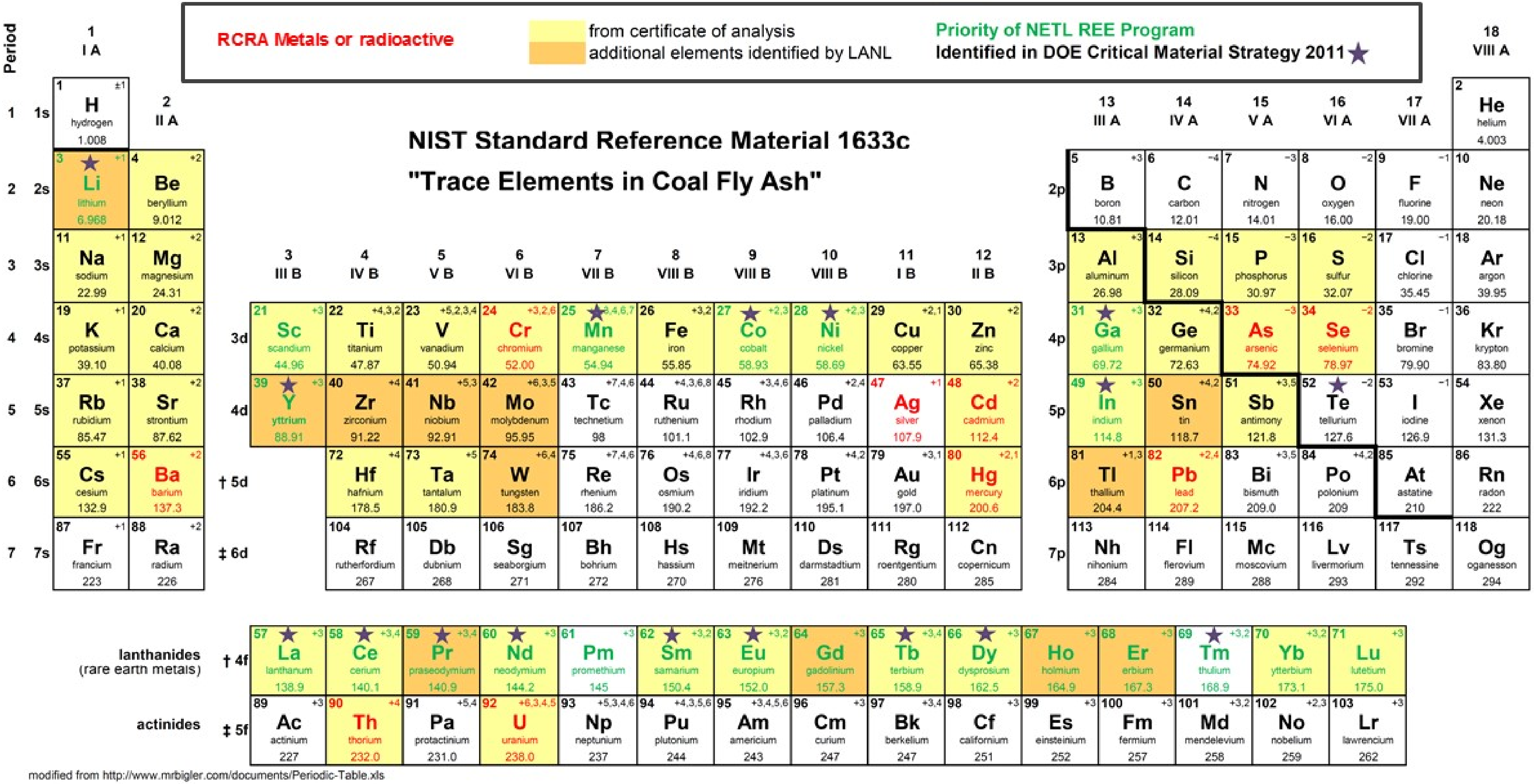
Ammonium Bifluoride Dissolution Process Development

This material is based upon work supported by the Department of Energy Award Number FE-810-17-FY17

Motivation

- Fly ash is an inhomogeneous solid with both organic and inorganic phases
  - Class C fly ash is high in Calcium, Class F is low in Calcium
  - Organic fraction is primarily unburned carbon
  - Inorganic fraction is primarily amorphous glass, contains Al, Si and Fe oxides
  - REEs believed to segregate into the aluminosilicate phases
- Novel selective dissolution chemistry could:
  - ***Reduce*** amount of harsh chemicals and reaction conditions (*e.g.* safer and cheaper)
    - Concentrated acids, HF/HNO_3, alkali fusion, etc.
  - ***Simplify*** downstream separations via selective dissolution
    - Avoid heavily corrosive chemicals (HCl)
  - ***Integrate*** with existing flowsheets to replace conventional leaching/dissolution steps, or serve as the basis for a novel process flowsheet.

Periodic Table of Fly Ash



RCRA Metals or radioactive

🟨 from certificate of analysis
🟧 additional elements identified by LANL

Priority of NETL REE Program
Identified in DOE Critical Material Strategy 2011 ★

NIST Standard Reference Material 1633c
"Trace Elements in Coal Fly Ash"

Period	1 I A	2 II A	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII B	9 VIII B	10 VIII B	11 I B	12 II B	13 III A	14 IV A	15 V A	16 VI A	17 VII A	18 VIII A
1 1s	1 ±1 H hydrogen 1.008																	2 He helium 4.003
2 2s 2p	🟧 3 ★ +1 Li lithium 6.968	🟨 4 +2 Be beryllium 9.012											5 +3 B boron 10.81	6 −4 C carbon 12.01	7 −3 N nitrogen 14.01	8 −2 O oxygen 16.00	9 −1 F fluorine 19.00	10 Ne neon 20.18
3 3s 3p	🟨 11 +1 Na sodium 22.99	🟨 12 +2 Mg magnesium 24.31											🟨 13 +3 Al aluminum 26.98	🟨 14 −4 Si silicon 28.09	🟨 15 −3 P phosphorus 30.97	🟨 16 −2 S sulfur 32.07	17 −1 Cl chlorine 35.45	18 Ar argon 39.95
4 4s 3d 4p	🟨 19 +1 K potassium 39.10	🟨 20 +2 Ca calcium 40.08	🟨 21 +3 Sc scandium 44.96	🟨 22 +4,3,2 Ti titanium 47.87	🟨 23 +5,2,3,4 V vanadium 50.94	🟨 24 +3,2,6 Cr chromium 52.00	🟨 25 ★ 3,4,6,7 Mn manganese 54.94	🟨 26 +3,2 Fe iron 55.85	🟨 27 ★ +2,3 Co cobalt 58.93	🟨 28 ★ +2,3 Ni nickel 58.69	🟨 29 +2,1 Cu copper 63.55	🟨 30 +2 Zn zinc 65.38	🟨 31 ★ +3 Ga gallium 69.72	🟨 32 +4,2 Ge germanium 72.63	🟨 33 −3 As arsenic 74.92	🟨 34 −2 Se selenium 78.97	35 −1 Br bromine 79.90	36 Kr krypton 83.80
5 5s 4d 5p	🟨 37 +1 Rb rubidium 85.47	🟨 38 +2 Sr strontium 87.62	🟧 39 ★ +3 Y yttrium 88.91	🟧 40 +4 Zr zirconium 91.22	🟧 41 +5,3 Nb niobium 92.91	🟧 42 +6,3,5 Mo molybdenum 95.95	43 +7,4,6 Tc technetium 98	44 +4,3,6,8 Ru ruthenium 101.1	45 +3,4,6 Rh rhodium 102.9	46 +2,4 Pd palladium 106.4	47 +1 Ag silver 107.9	🟨 48 +2 Cd cadmium 112.4	🟨 49 ★ +3 In indium 114.8	🟧 50 +4,2 Sn tin 118.7	🟨 51 +3,5 Sb antimony 121.8	52 ★ −2 Te tellurium 127.6	53 −1 I iodine 126.9	54 Xe xenon 131.3
6 6s † 5d 6p	🟨 55 +1 Cs cesium 132.9	🟨 56 +2 Ba barium 137.3		🟨 72 +4 Hf hafnium 178.5	🟨 73 +5 Ta tantalum 180.9	🟧 74 +6,4 W tungsten 183.8	75 +7,4,6 Re rhenium 186.2	76 +4,6,8 Os osmium 190.2	77 +4,3,6 Ir iridium 192.2	78 +4,2 Pt platinum 195.1	79 +3,1 Au gold 197.0	🟨 80 +2,1 Hg mercury 200.6	🟧 81 +1,3 Tl thallium 204.4	🟨 82 +2,4 Pb lead 207.2	83 +3,5 Bi bismuth 209.0	84 +4,2 Po polonium 209	85 At astatine 210	86 Rn radon 222
7 7s ‡ 6d 7p	87 +1 Fr francium 223	88 +2 Ra radium 226		104 Rf rutherfordium 267	105 Db dubnium 268	106 Sg seaborgium 271	107 Bh bohrium 272	108 Hs hassium 270	109 Mt meitnerium 276	110 Ds darmstadtium 281	111 Rg roentgentium 280	112 Cn copernicum 285	113 Nh nihonium 284	114 Fl flerovium 289	115 Mc moscovium 288	116 Lv livermorium 293	117 Ts tennessine 292	118 Og oganesson 294

lanthanides (rare earth metals) † 4f	🟨 57 ★ +3 La lanthanum 138.9	🟨 58 ★ +3,4 Ce cerium 140.1	🟧 59 ★ +3,4 Pr praseodymium 140.9	🟨 60 ★ +3 Nd neodymium 144.2	61 +3 Pm promethium 145	🟨 62 ★ +3,2 Sm samarium 150.4	🟨 63 ★ +3,2 Eu europium 152.0	🟧 64 +3 Gd gadolinium 157.3	🟨 65 ★ +3,4 Tb terbium 158.9	🟨 66 ★ +3 Dy dysprosium 162.5	🟧 67 +3 Ho holmium 164.9	🟧 68 +3 Er erbium 167.3	69 ★ +3,2 Tm thulium 168.9	70 +3,2 Yb ytterbium 173.1	71 +3 Lu lutetium 175.0
actinides ‡ 5f	89 +3 Ac actinium 227	🟨 90 +4 Th thorium 232.0	91 +5,4 Pa protactinium 231.0	🟨 92 +6,3,4,5 U uranium 238.0	93 +5,3,4,6 Np neptunium 237	94 +4,3,5,6 Pu plutonium 244	95 +3,4,5,6 Am americium 243	96 +3 Cm curium 247	97 +3,4 Bk berkelium 247	98 +3 Cf californium 251	99 +3 Es einsteinium 252	100 +3 Fm fermium 257	101 +3,2 Md mendelevium 258	102 +2,3 No nobelium 259	103 +3 Lr lawrencium 262

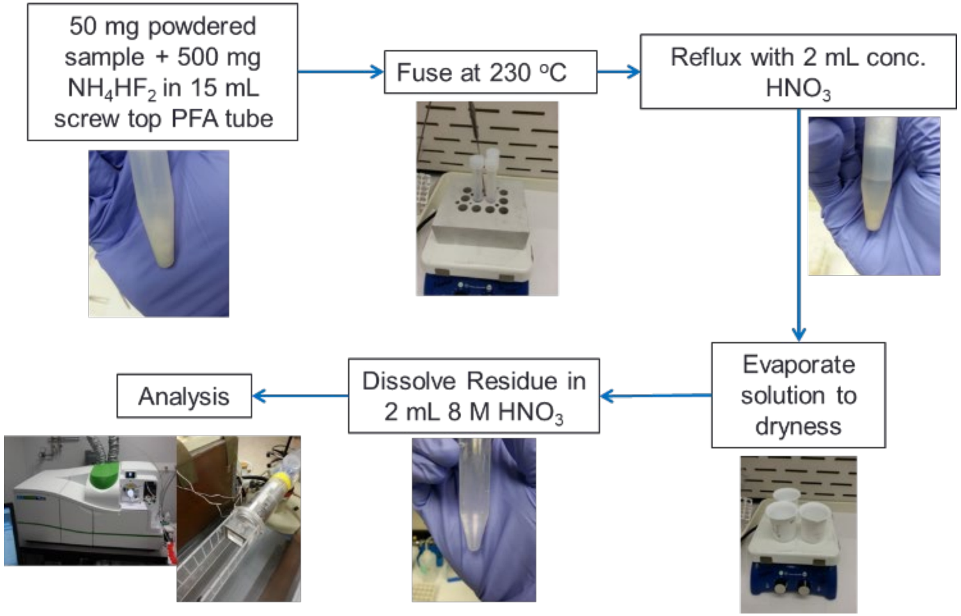
modified from http://www.mrbigler.com/documents/Periodic-Table.xls

Why Ammonium Bifluoride (ABF, NH_4HF_2)?

ABF was studied as an alternative for processing the refractory phases such as silicate based glass phases formed within post-det debris

- Used as a fluorinating agent
- Fusion with ABF has been used for analytical nuclear forensics sample dissolution (Nick Hubley & Chris Leibman)
  - Variety of sample types including post-det debris total dissolution, and quantitative recoveries
  - U. Missouri, LANL, others
- Developed as an analytical-scale method for quantitative analysis

Trinitite sample

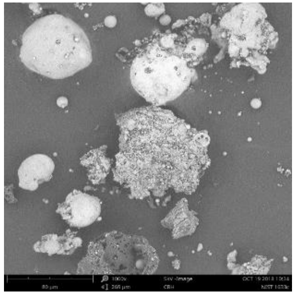


50 mg powdered sample + 500 mg NH_4HF_2 in 15 mL screw top PFA tube → Fuse at 230 °C → Reflux with 2 mL conc. HNO_3 → Evaporate solution to dryness → Dissolve Residue in 2 mL 8 M HNO_3 → Analysis

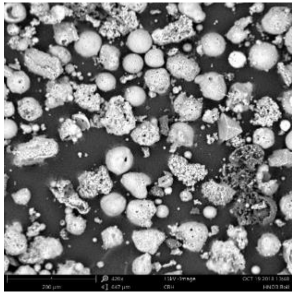
ABF Fusion of NIST 1633c Coal Fly Ash

Does the ABF fusion translate to coal fly ash?

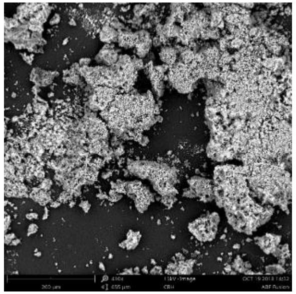
- Achieved high/quantitative recovery of the REEs
- Large amount of residue left after the procedure
  - Total dissolution not achieved
  - ABF appears to target the aluminosilicate phase



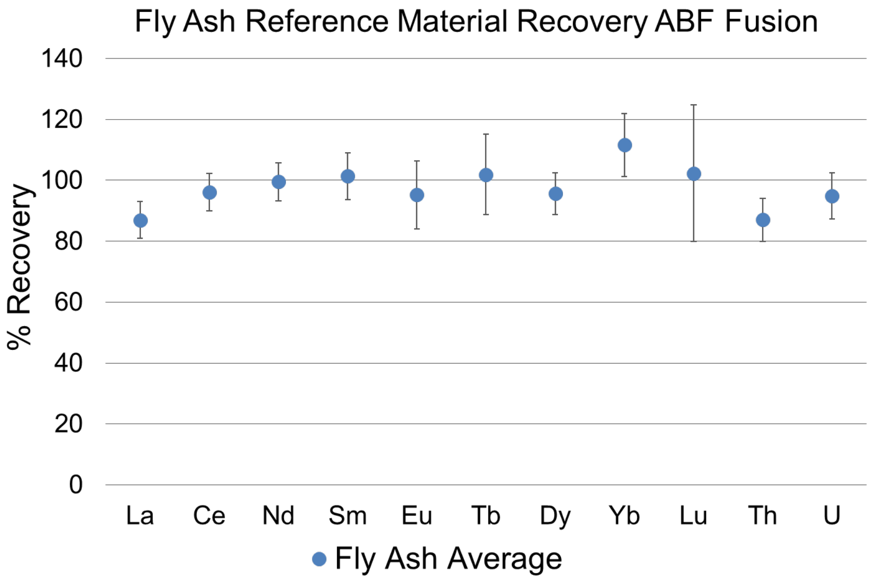
NIST 1633c



boiled in HNO_3



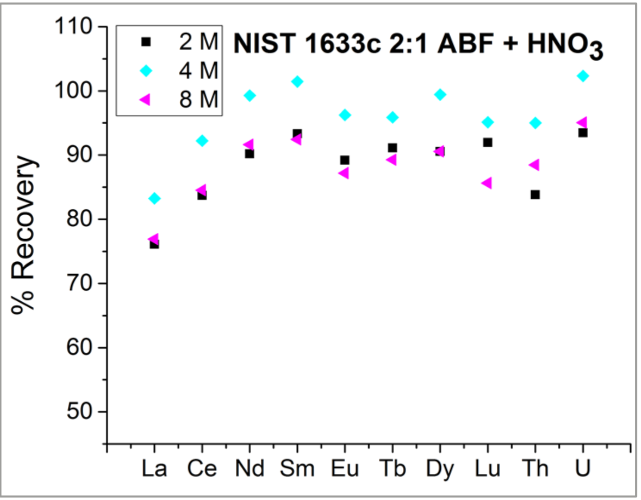
ABF fusion



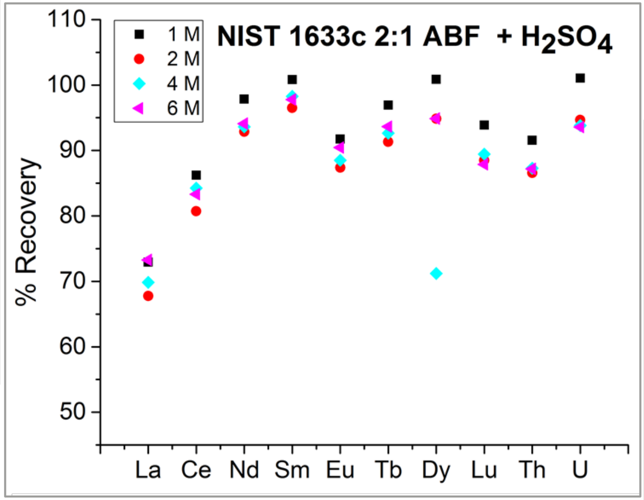
ABF targets the silicate phase within fly ash allowing REE recovery, more effective than boiling concentrated HNO_3

METHOD EMBODIMENTS FOR EXTRACTING ELEMENTS FROM COAL COMBUSTION PRODUCTS, U.S. Provisional Patent App. No. 62/989,497

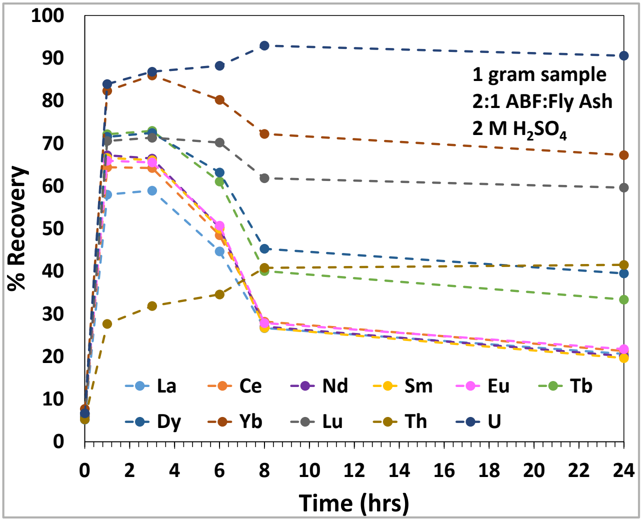
Summary of Dissolution Optimizations with NIST 1633c



Optimization of HNO_3 concentrations



Optimization of H_2SO_4 concentrations



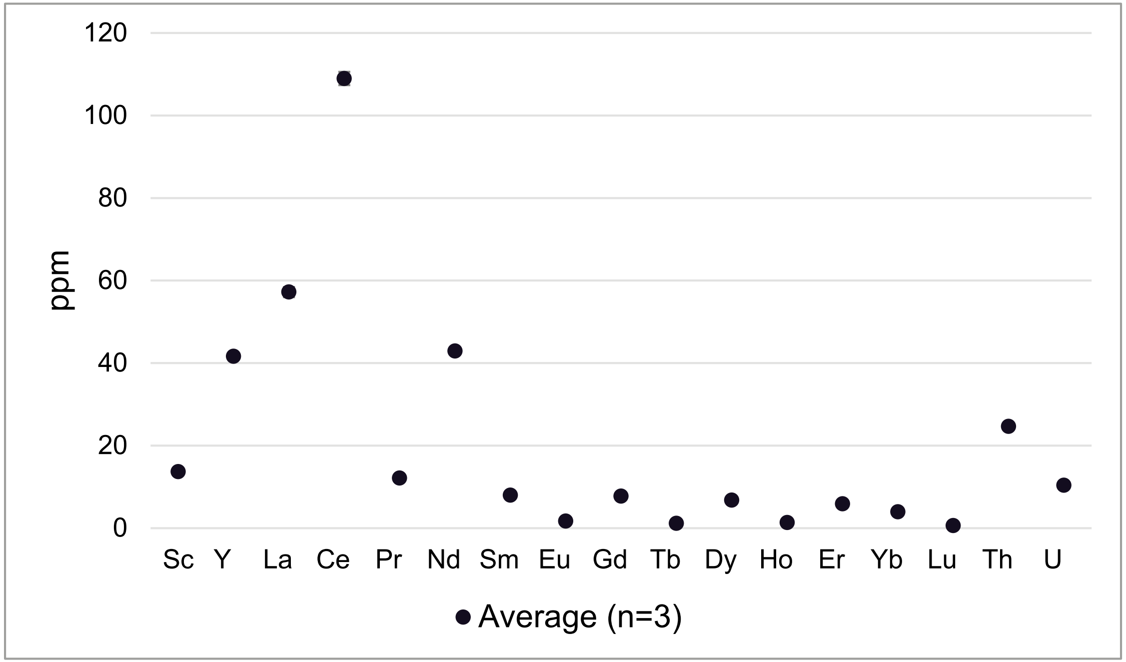
Optimization of dissolution time

San Juan Fly Ash (NM) Analysis: Fusion method

San Juan Generating Station (847 MW)
https://www.enchantenergy.com/san-juan-generating-station/

Coal Source: San Juan Mine
6.4 Million tons annual production

Class F Fly Ash

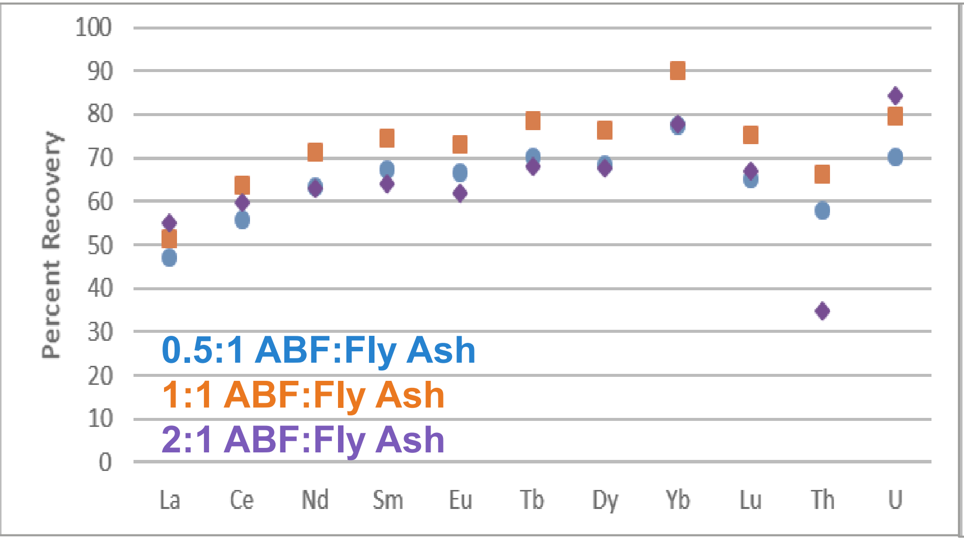


Total REEs + Sc + Y = 313 ppm

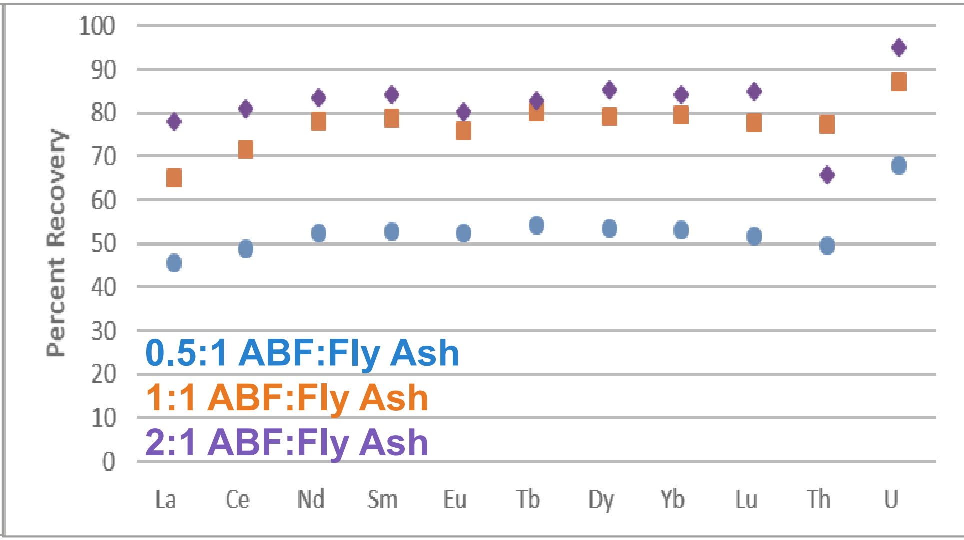
Analytical determination of REEs from NM sourced fly ash, for use in REE leach scale up demo. Ran in parallel to NIST 1633c for verification of method.

Comparison of NIST 1663c and San Juan Fly Ash Dissolutions

NIST 1633c



San Juan



1 gram fly ash samples
6 hour contact time
2 M H_2SO_4

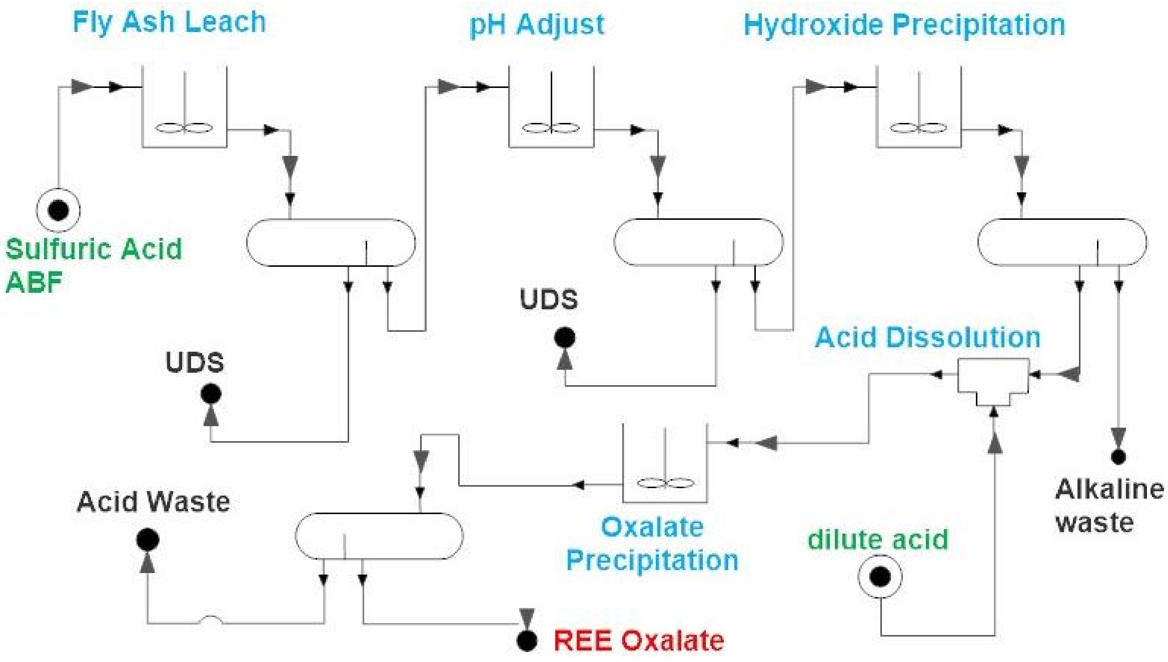
Lower ABF can also be effective for REE recovery.

At lower ABF, the San Juan Fly Ash exhibits lower recoveries than NIST, while at higher ABF the recovery is equivalent.

Flowsheet concept and Scale-up testing

- Scale-up testing performed Q4 of FY20
- Leach tests performed 5 gram batches of San Juan Fly Ash.
  - Recall San Juan contains high Ca/Mg and is dilute in REE
- Testing based on conceptual flowsheet at right
- Dissolution tests examined contact times of 2 or 6 hours
- Also examined multi-contact dissolutions (fly ash contacted multiple times with leach solution combined before subsequent processing

Conceptual flowsheet for scale-up testing



Scale-up tests were inconclusive, likely due to the increased concentration of Ca and Mg in San Juan Fly Ash (e.g. possible formation of CaF_2)

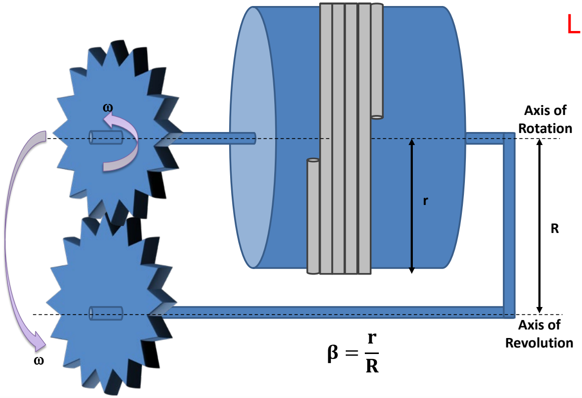
ABF Conclusions and Recommendations

- ABF has been demonstrated as a viable and safer alternative to HF
  - Able to quantitatively recover REEs and actinides
  - Acts through *targeted recovery* from aluminosilicate fraction
  - Complete dissolution not necessary, but can be tuned for partial or total digestion
    - selective dissolution of other unwanted metals (Cr, Pb, Ba, and lesser extent Fe and Al) simplifies purification
  - Effective with either Nitric or Sulfuric acid at relatively low acid concentrations (1-2 M)
  - Scale increased by factor of 50X over course of FWP (20 mg to 1 gram)
  - Typically > 70% recovery of REE with contact times of 2-6 hours
  - Novel dissolution chemistry can be integrated into existing process flowsheets or serve as the front end of new process flowsheets
- Recommendations for future work
  - Expand chemistry to test effectiveness with other fly ash sources
  - Scale-up testing to 10-100 gram scale will require ash source with reasonable REE content
  - Understand the role of Ca and Mg on the dissolution effectiveness
  - Determine solubility limits for REE in ABF/H_2SO_4 solutions

Novel Separations using High Speed Counter-Current Chromatography

High Speed Counter-Current Chromatography (HSCCC)

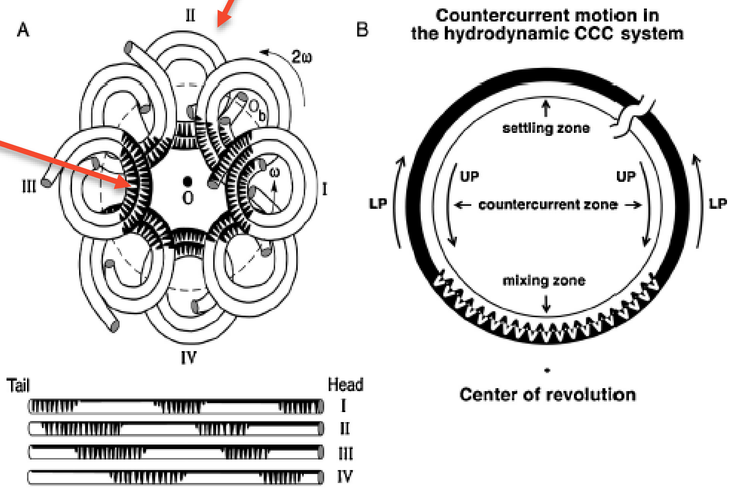
- High Speed Counter-Current Chromatography:
  - Hybrid technique analogous to HPLC with features of a pulsed column
  - HSCCC uses liquid phases with the stationary phase held in place by gravitational forces
  - Liquid stationary phase gives significantly higher column capacity than conventional HPLC
  - Initially developed in the 1970s for bio-separations and purification of natural products
  - Small-scale mixing gives enhanced mass transfer rates
  - Enables many contacts in short time with a small footprint
  - Can be run with both phases mobile (dual-flow)
  - Can be run with solids (S-L-L)



Greater than 100k mixing and settling events per minute!

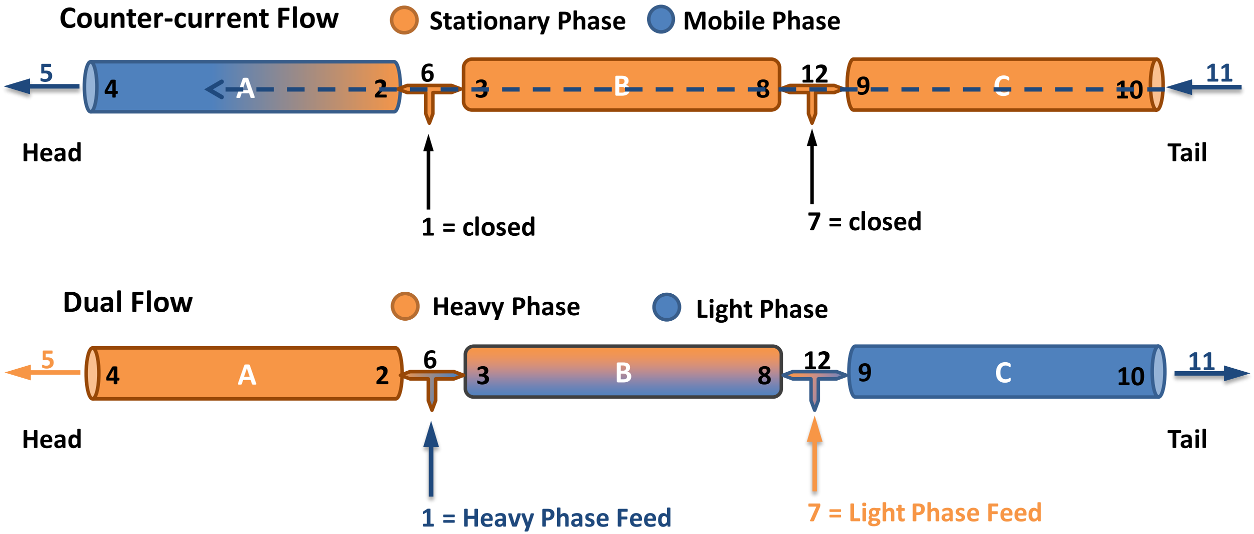
High g-force (100-200g)

Low g-force (30-70g)



J. Chromatogr. A, 1372 (2014), pp. 128-132

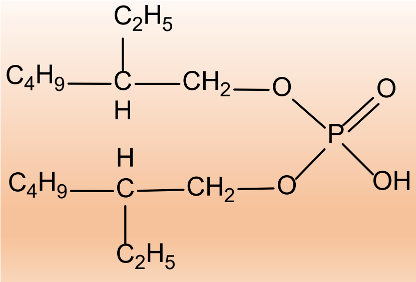
HSCCC Details



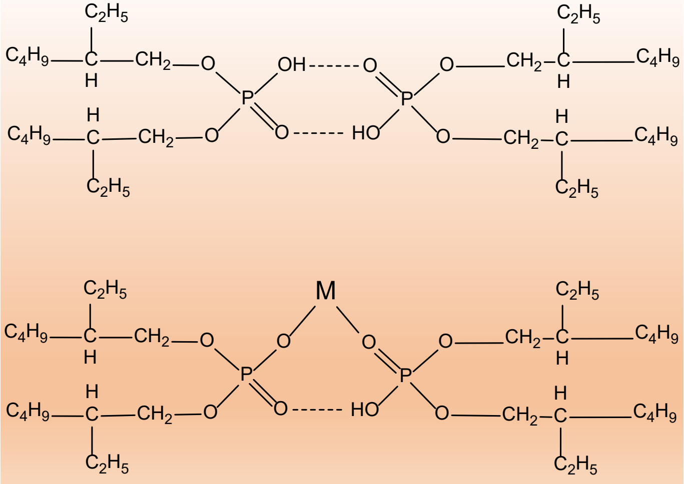
- HSCCC typically used for analytical chromatography separations
- Dual flow applications are much more rare, typically used with batch sample injection
- No domestic commercial source…**LANL has developed in-house fabrication capabilities**
- LANL has been developing HSCC for a variety of applications including REE separations for nuclear forensics and heavy metal waste processing
- Currently funded through LANL LDRD for radiolanthanide separations including ^{161}Tb from ^{91}Y

Solvent Extraction Scheme

- **Di-(2-ethylhexyl)phosphoric acid - HDEHP**



- **Tried and tested extractant for REE separation**
- **Multiple studies in various diluents**
- **D = 1 at low aqueous acidity**
- **Best suited to separation of the lighter lanthanides**
- **Dimeric extraction mechanism with acid dependence**
- **Neutral extractant at high acidities**
  - Currently used for separation of Ce(IV) from REE(III)

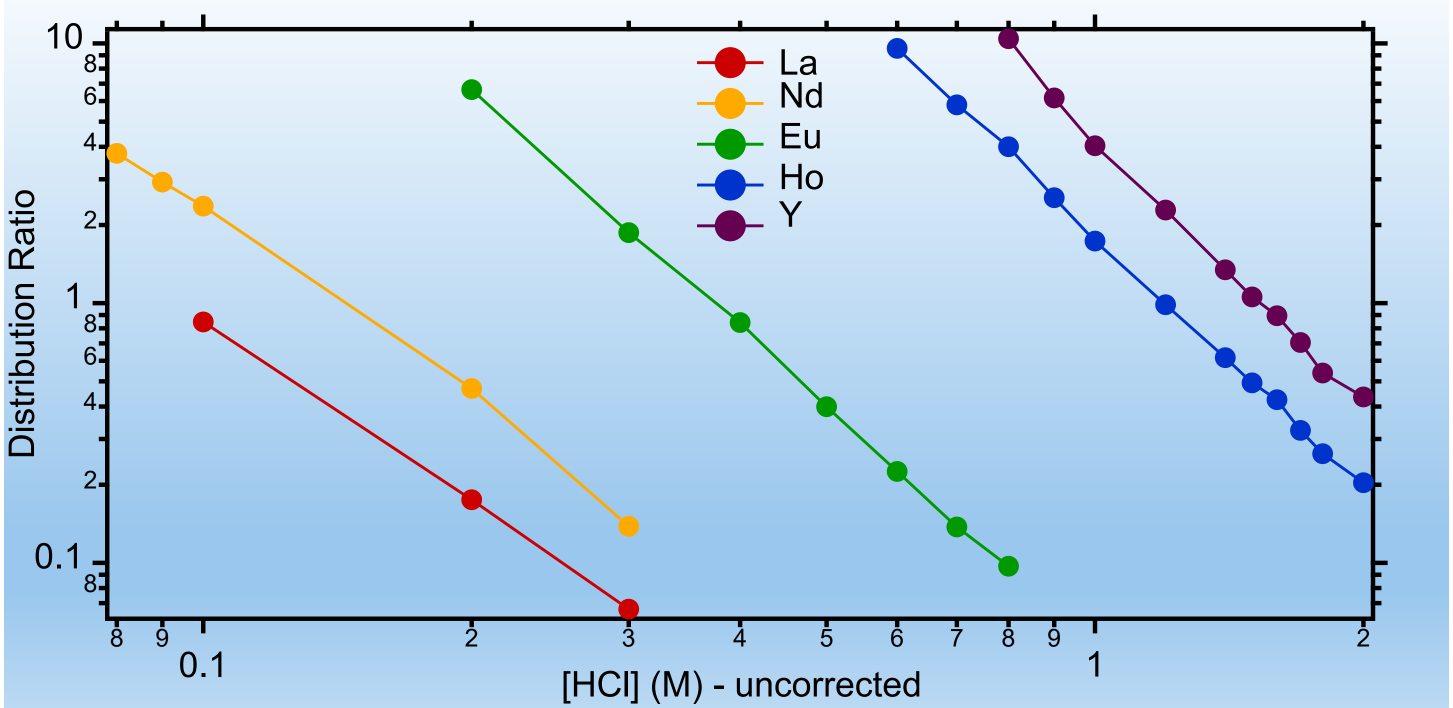


$$REE^{3+}_{aq} + 3(HA)_{2\,(org)} \rightleftharpoons REE(HA_2)_{3\,(org)} + 3H^{+}_{(aq)}$$

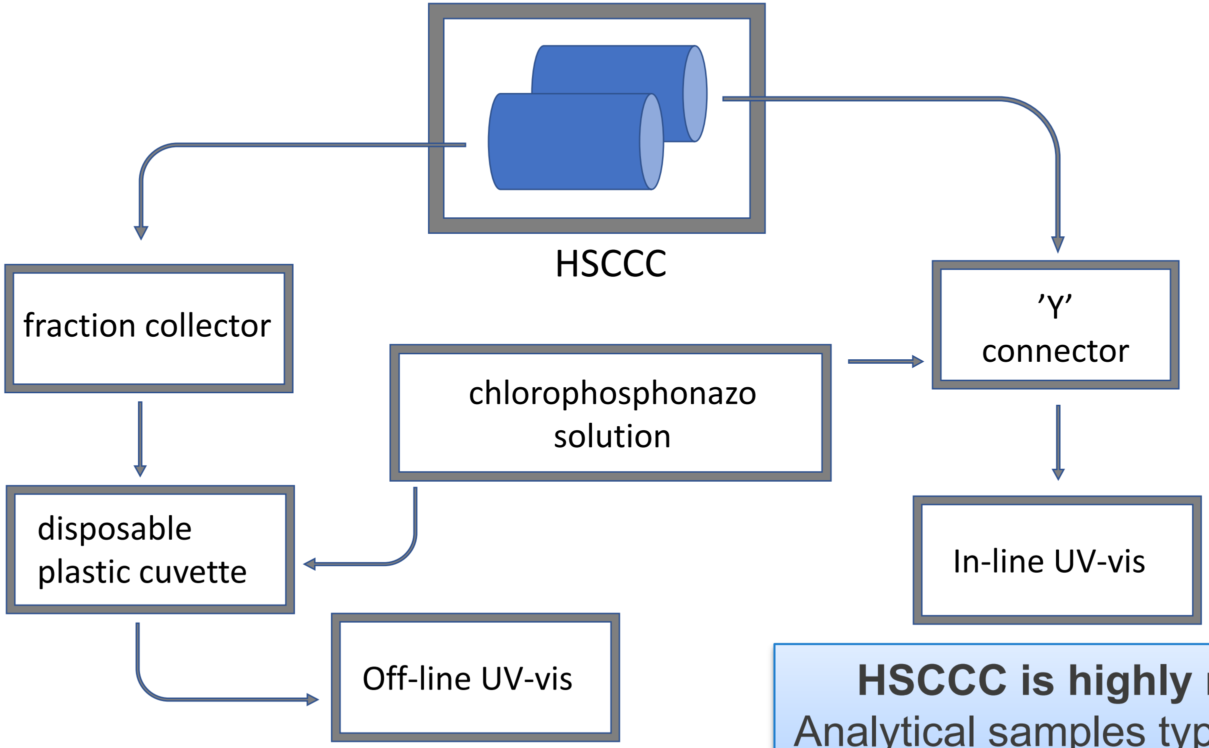
D. Qi, Hydrometallurgy of Rare Earths, Extraction and Separation, Elsevier, 2018

Distribution ratios in HDEHP

- **1 M HDEHP in toluene**
- **Also measured in xylenes, heptane and n-dodecane**
- **Comparable with literature data**



Experimental Setup


HSCCC

fraction collector

’Y’ connector

chlorophosphonazo solution

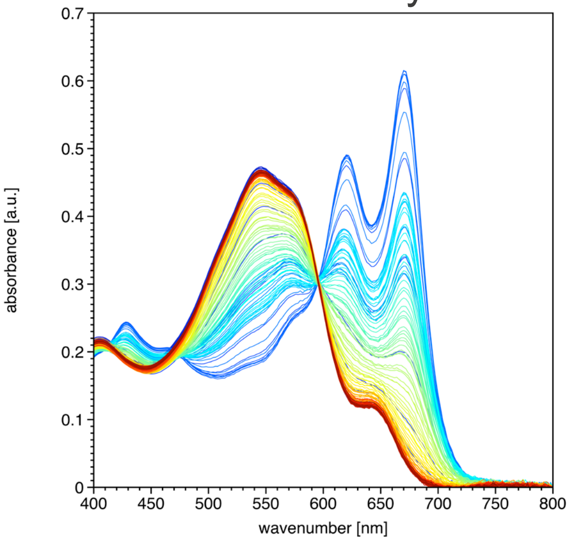
disposable plastic cuvette

In-line UV-vis

Off-line UV-vis

Additional off-line analysis with
ICP-OES and/or ICP-MS

UV-vis analysis



HSCCC is highly reproducible and scalable

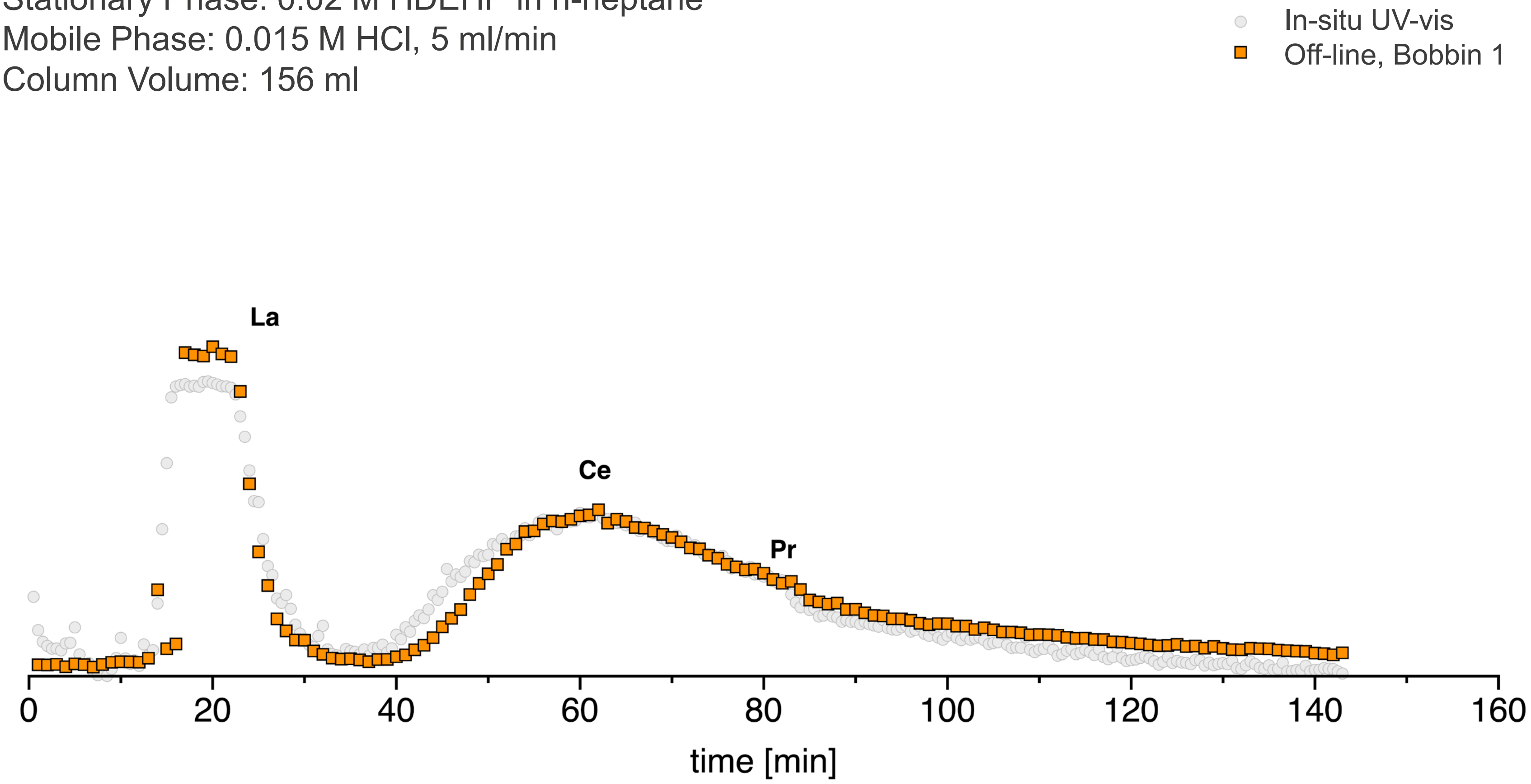
Analytical samples typically mg scale

Have processed samples up to 50 grams (dual flow)

Plans to scale-up to > 1 kg/week of product

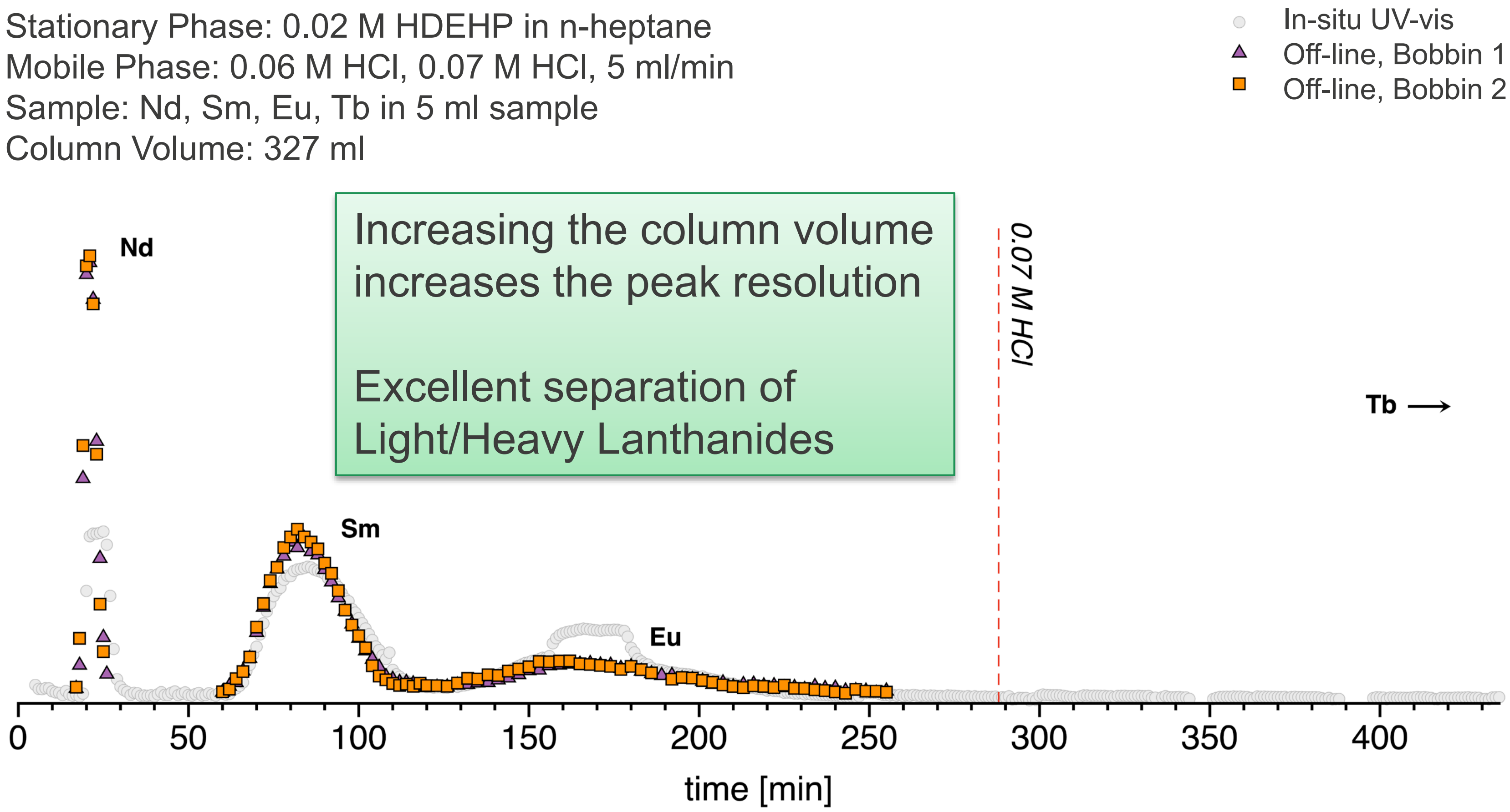
Example of Light Lanthanide Separation

Stationary Phase: 0.02 M HDEHP in n-heptane
Mobile Phase: 0.015 M HCl, 5 ml/min
Column Volume: 156 ml



Improved Light/Heavy Lanthanide Separations with Isocratic Elution

Stationary Phase: 0.02 M HDEHP in n-heptane
Mobile Phase: 0.06 M HCl, 0.07 M HCl, 5 ml/min
Sample: Nd, Sm, Eu, Tb in 5 ml sample
Column Volume: 327 ml



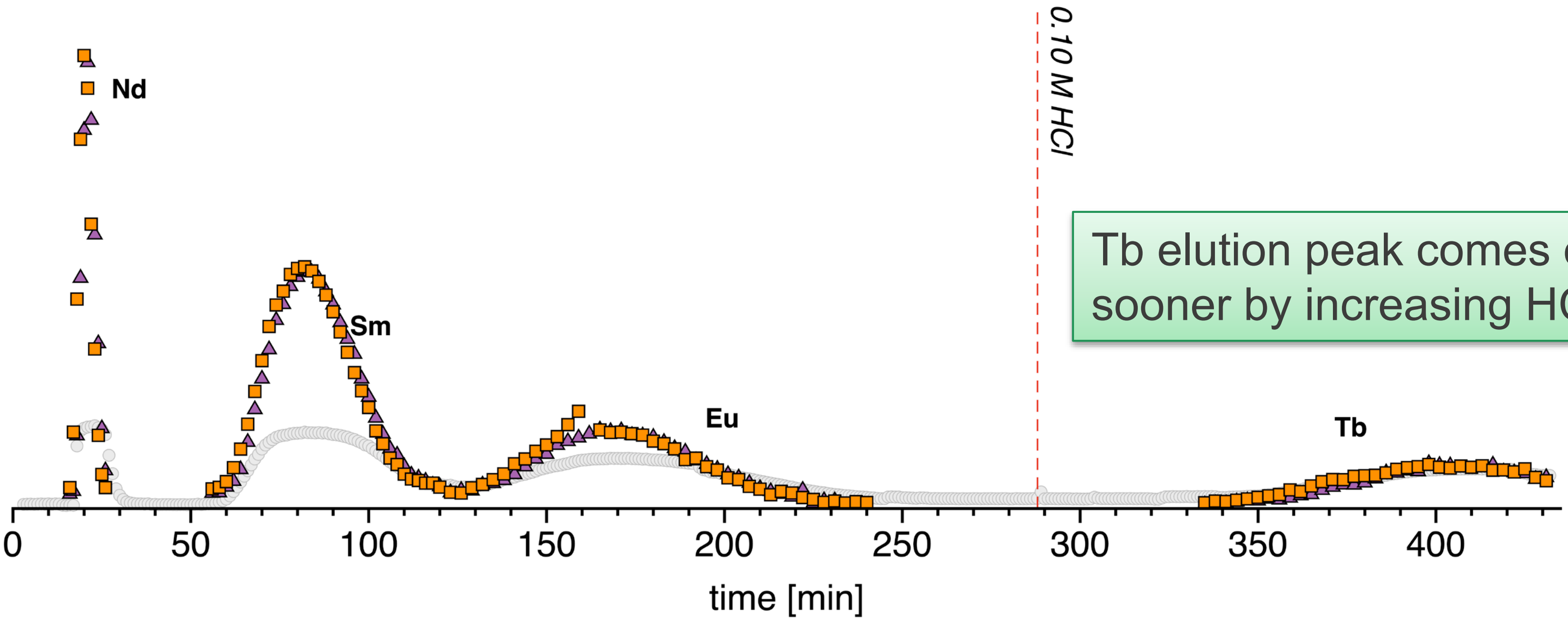
Increasing the column volume increases the peak resolution

Excellent separation of Light/Heavy Lanthanides

Improved Light/Heavy Lanthanide Separations with Step-wise Elution

Stationary Phase: 0.02 M HDEHP in n-heptane
Mobile Phase: 0.06 M HCl, 0.10 M HCl, 5 ml/min
Sample: Nd, Sm, Eu, Tb in 5 ml sample
Column Volume: 327 ml

- ○ In-situ UV-vis
- ▲ Off-line, Bobbin 1
- ■ Off-line, Bobbin 2

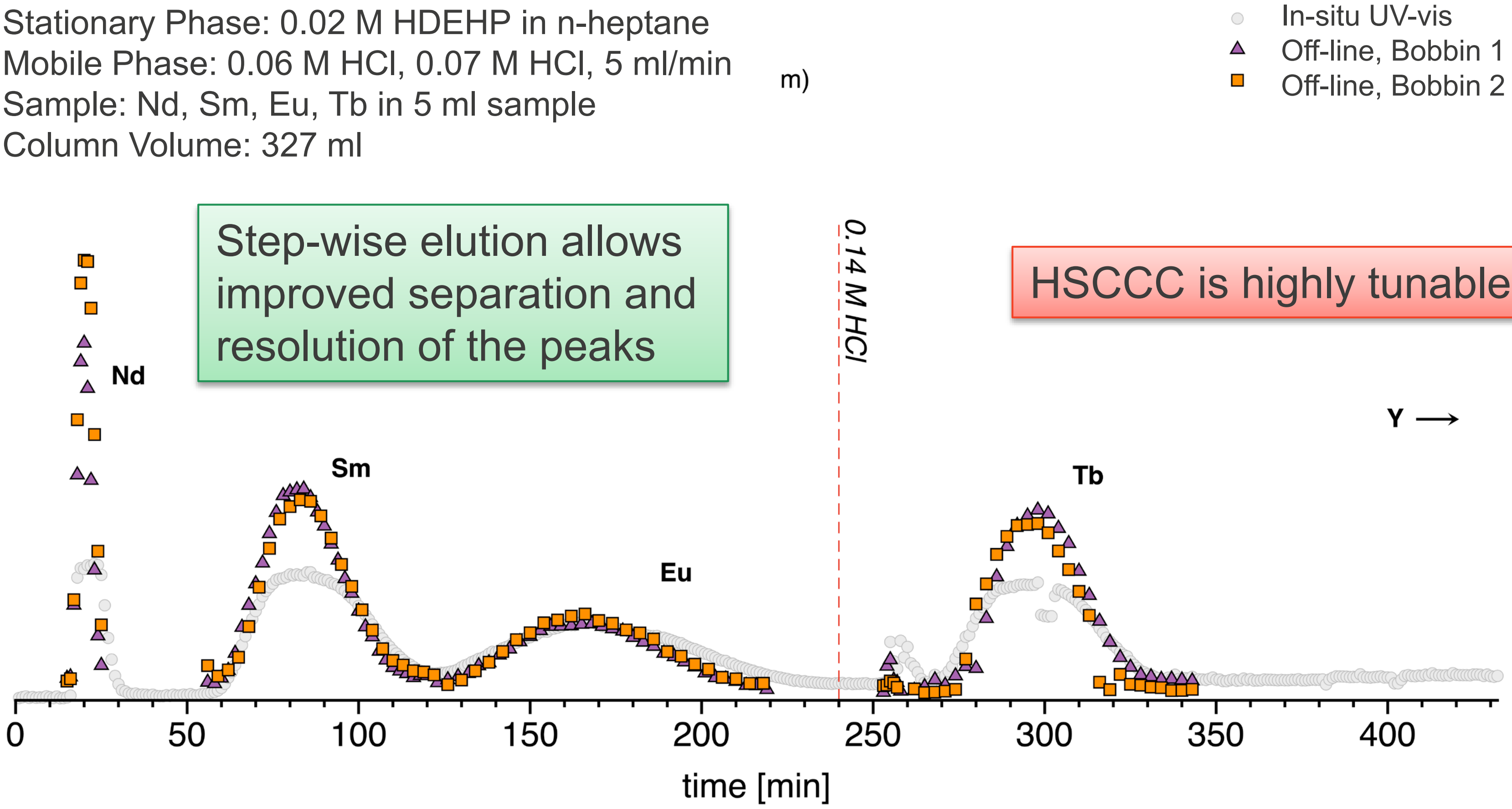


Tb elution peak comes out sooner by increasing HCl

Optimized Separation

Stationary Phase: 0.02 M HDEHP in n-heptane
Mobile Phase: 0.06 M HCl, 0.07 M HCl, 5 ml/min
Sample: Nd, Sm, Eu, Tb in 5 ml sample
Column Volume: 327 ml

m)



Step-wise elution allows improved separation and resolution of the peaks

HSCCC is highly tunable!

HSCCC Conclusions

- HSCCC is a novel separation technique with significant advantages over other conventional separation methods
  - Large number of stages, small footprint
  - Scalable from analytical to industrial scale
  - Bobbins are customizable to accommodate a wide range of process chemistries using either conventional or novel solvent extractants
  - Separation can be easily tuned to achieve required purities
- LANL has developed capability to design and manufacture HSCCC units for a wide range of applications
- Demonstrated tunable separation of REE using HDEHP in n-heptane on the analytical scale
  - Would love to discuss extending methodology to other industrially relevant feed materials (e.g. pure or impure REE mixed oxides)

Thank you!