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

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

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09-16-20

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NNSA National Nuclear Security Administration

LA-UR-20-27222

LANL Project Team

- Hakim Boukhalfa, biogeochemistry
- Kevin Boland, analytical chemistry
- Janelle Droessler, inorganic chemistry
- George S. Goff, chemical engineering
- George Guthrie, mineralogy and geochemistry, *coordination with LIBS analysis project*
- Nicholas Hubley, 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 for purification of Pu, low-temperature electrochemical recovery of Pu metal 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

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)
  - ***Be integrated*** into 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 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1s	1 H hydrogen 1.008 ±1																	2 He helium 4.003
2	2s / 2p	3 ★ Li lithium 6.968 +1	4 Be beryllium 9.012 +2											5 B boron 10.81 +3	6 C carbon 12.01 −4	7 N nitrogen 14.01 −3	8 O oxygen 16.00 −2	9 F fluorine 19.00 −1	10 Ne neon 20.18
3	3s / 3p	11 Na sodium 22.99 +1	12 Mg magnesium 24.31 +2											13 Al aluminum 26.98 +3	14 Si silicon 28.09 −4	15 P phosphorus 30.97 −3	16 S sulfur 32.07 −2	17 Cl chlorine 35.45 −1	18 Ar argon 39.95
4	4s / 3d / 4p	19 K potassium 39.10 +1	20 Ca calcium 40.08 +2	21 Sc scandium 44.96 +3	22 Ti titanium 47.87 +4,3,2	23 V vanadium 50.94 +5,2,3,4	24 Cr chromium 52.00 +3,2,6	25 ★ Mn manganese 54.94 +3,4,6,7	26 Fe iron 55.85 +3,2	27 ★ Co cobalt 58.93 +2,3	28 ★ Ni nickel 58.69 +2,3	29 Cu copper 63.55 +2,1	30 Zn zinc 65.38 +2	31 ★ Ga gallium 69.72 +3	32 Ge germanium 72.63 +4,2	33 As arsenic 74.92 −3	34 Se selenium 78.97 −2	35 Br bromine 79.90 −1	36 Kr krypton 83.80
5	5s / 4d / 5p	37 Rb rubidium 85.47 +1	38 Sr strontium 87.62 +2	39 ★ Y yttrium 88.91 +3	40 Zr zirconium 91.22 +4	41 Nb niobium 92.91 +5,3	42 Mo molybdenum 95.95 +6,3,5	43 Tc technetium 98 +7,4,6	44 Ru ruthenium 101.1 +4,3,6,8	45 Rh rhodium 102.9 +3,4,6	46 Pd palladium 106.4 +2,4	47 Ag silver 107.9 +1	48 Cd cadmium 112.4 +2	49 ★ In indium 114.8 +3	50 Sn tin 118.7 +4,2	51 Sb antimony 121.8 +3,5	52 ★ Te tellurium 127.6 −2	53 I iodine 126.9 −1	54 Xe xenon 131.3
6	6s / † 5d / 6p	55 Cs cesium 132.9 +1	56 Ba barium 137.3 +2		72 Hf hafnium 178.5 +4	73 Ta tantalum 180.9 +5	74 W tungsten 183.8 +6,4	75 Re rhenium 186.2 +7,4,6	76 Os osmium 190.2 +4,6,8	77 Ir iridium 192.2 +4,3,6	78 Pt platinum 195.1 +4,2	79 Au gold 197.0 +3,1	80 Hg mercury 200.6 +2,1	81 Tl thallium 204.4 +1,3	82 Pb lead 207.2 +2,4	83 Bi bismuth 209.0 +3,5	84 Po polonium 209 +4,2	85 At astatine 210	86 Rn radon 222
7	7s / ‡ 6d / 7p	87 Fr francium 223 +1	88 Ra radium 226 +2		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

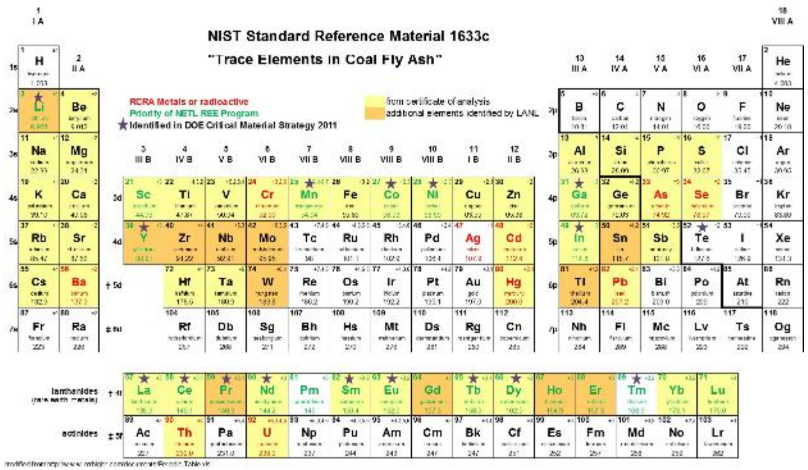
lanthanides (rare earth metals)	† 4f	57 ★ La lanthanum 138.9 +3	58 ★ Ce cerium 140.1 +3,4	59 ★ Pr praseodymium 140.9 +3,4	60 ★ Nd neodymium 144.2 +3	61 Pm promethium 145 +3	62 ★ Sm samarium 150.4 +3,2	63 ★ Eu europium 152.0 +3,2	64 Gd gadolinium 157.3 +3	65 ★ Tb terbium 158.9 +3,4	66 ★ Dy dysprosium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

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

Used Nuclear Fuel vs Fly Ash

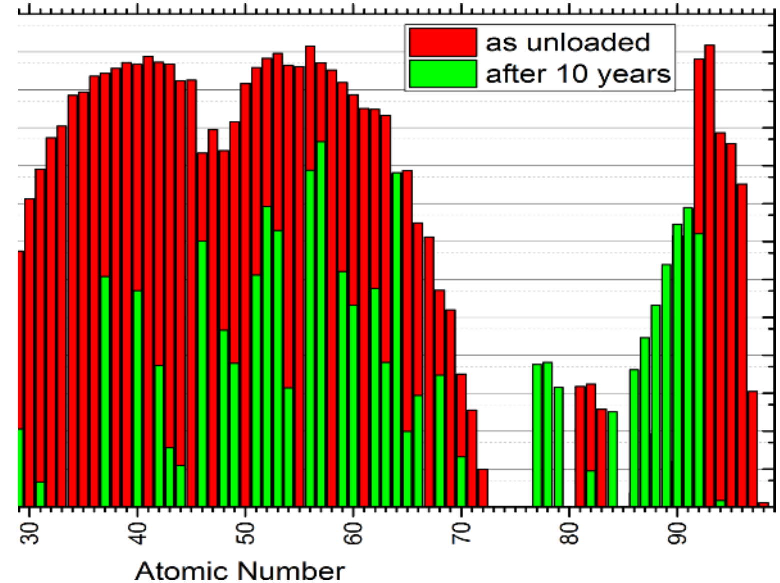
- Complicated, hard to dissolve matrices (typically oxide based)
- Large distribution of trace elements
- Minor actinides (*e.g.*, Am, Cm) behave like lanthanides (predominantly +III)

EX: elemental composition of reference fly ash



Rare Earth Elements play a key role: valuable products in fly ash, unwanted neutron poison in nuclear fuel

EX: Distribution of radioactive elements in used fuel from a molten-salt fast reactor



Lanthanides: Z# 57-71, Actinides: Z#89-103

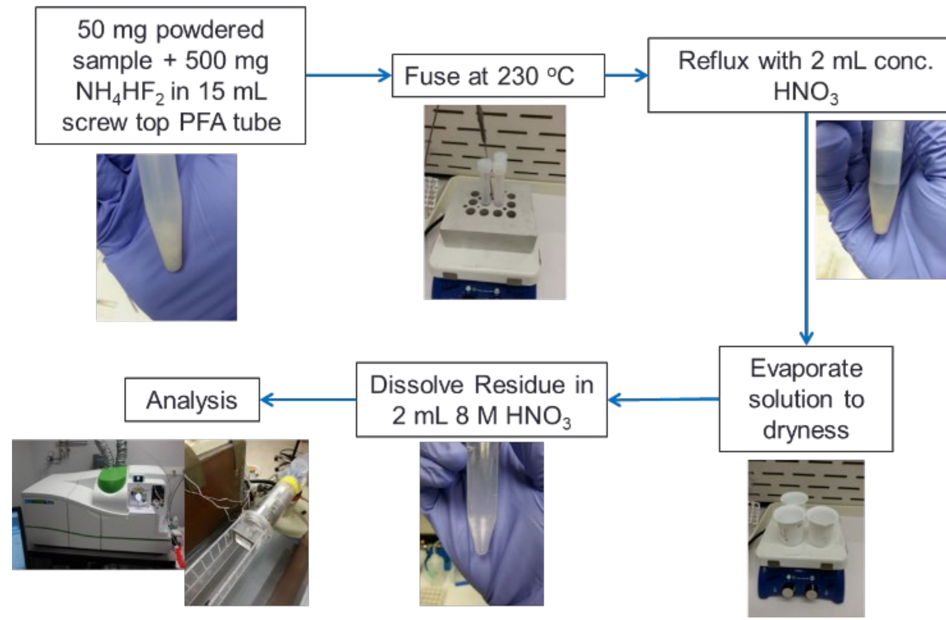
https://doi.org/10.1371/journal.pone.0192020

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

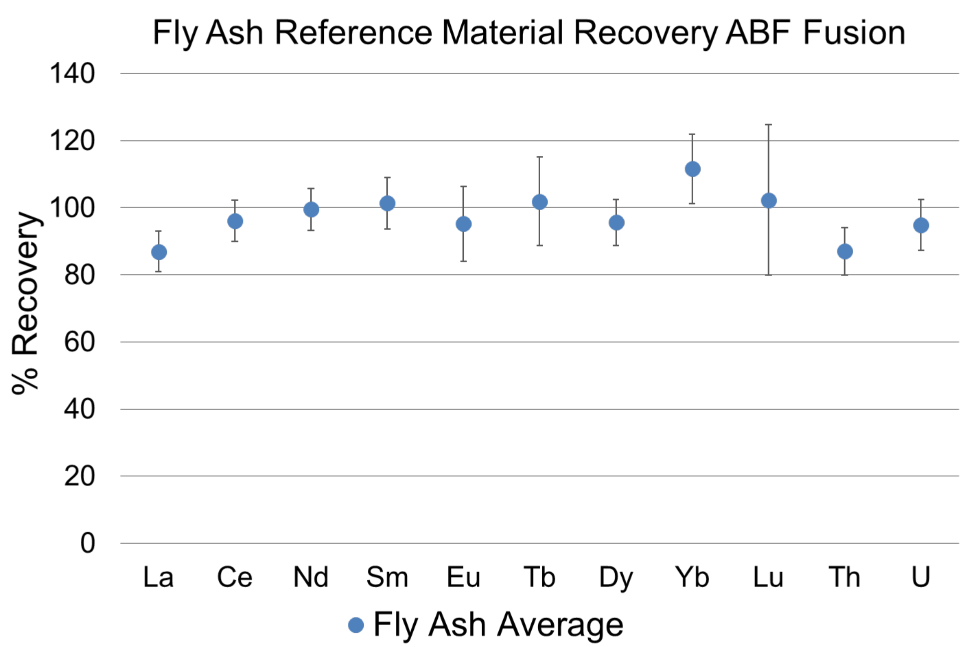


ABF Fusion of NIST 1633c Coal Fly Ash

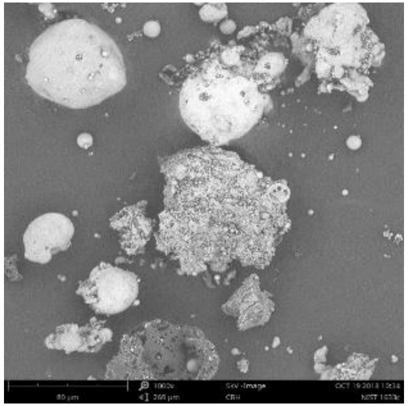
Does the ABF fusion translate to coal fly ash?

- Achieved high/quantitative recovery of the REEs
- Large amount of residue left after the procedure
  - Total dissolution not achieved

Believed most REEs associated with aluminosilicate phase

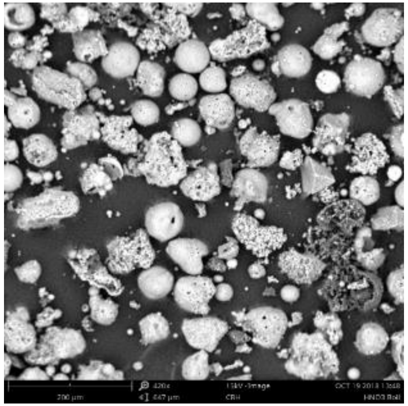


SEM/EDS analysis of fly ash residue



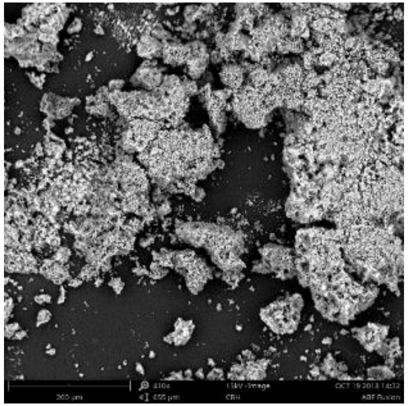
NIST 1633c unreacted

Element Symbol	Atomic Conc.	Weight Conc.	Stoich. wt Conc.
O	71.64	57.82	
Si	10.97	15.54	36.84
Al	7.42	10.10	23.96
C	4.79	2.90	6.88
Fe	3.97	11.19	26.53
K	1.06	2.09	4.96



NIST 1633c boiled in HNO_3

Element Symbol	Atomic Conc.	Weight Conc.	Stoich. wt Conc.
O	60.29	54.43	
C	24.48	16.59	36.40
Si	7.38	11.70	25.68
Al	5.88	8.95	19.64
Fe	1.27	3.99	8.77



NIST 1633c ABF fusion

Element Symbol	Atomic Conc.	Weight Conc.	Stoich. wt Conc.
F	73.68	69.36	69.36
Al	11.31	15.12	15.12
N	11.11	7.71	7.71
Fe	2.41	6.66	6.66
C	1.45	0.86	0.86

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

ABF Leaching of Fly Ash

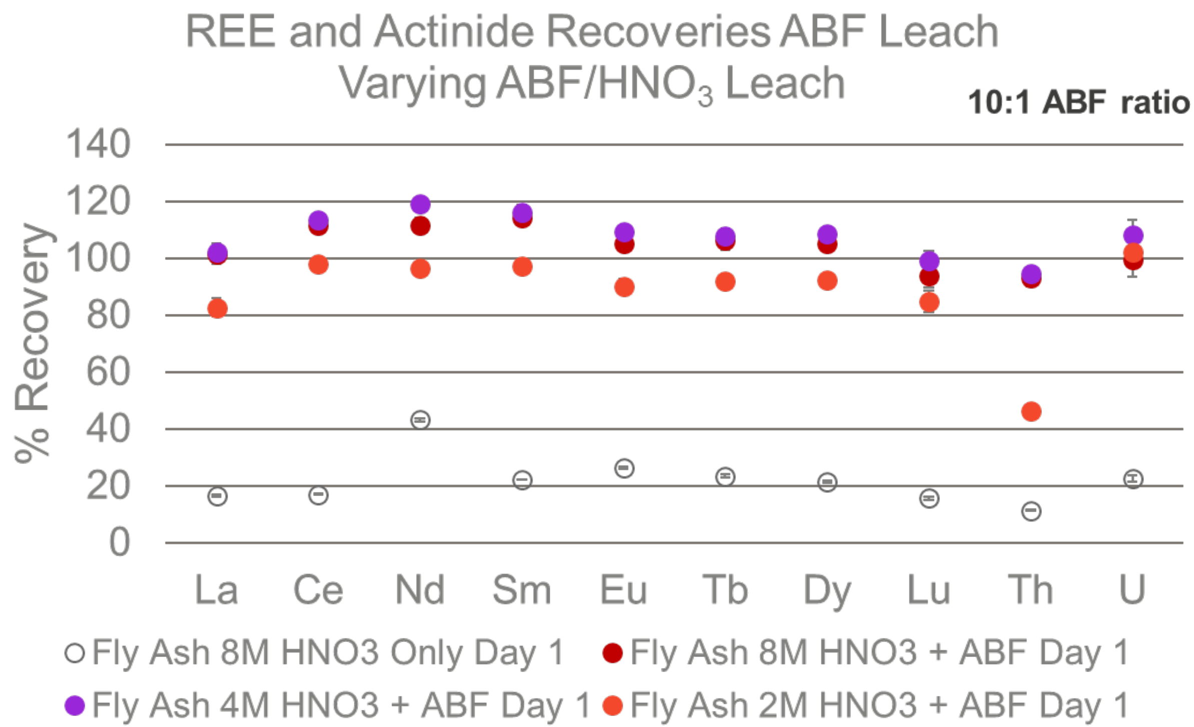
Assessment of efficacy of ABF leach as a targeted chemistry for REE recovery from fly ash

- Room temperature reaction of fly ash with a solution of ABF and HNO_3 or H_2SO_4
- Varied ABF to fly ash mass ratio (10:1, 2:1, 1:1, 0.5:1)
- Varied acid concentration
- Fly ash and ABF/acid solution stirred
- Studied reaction time
  - Quantitative recovery of REEs within one day, high recovery within hours
- Used NIST 1633c fly ash to evaluate REE recoveries
- Provisional Patent filed in March, 2020:

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

ABF Leaching of Fly Ash: analytical scale

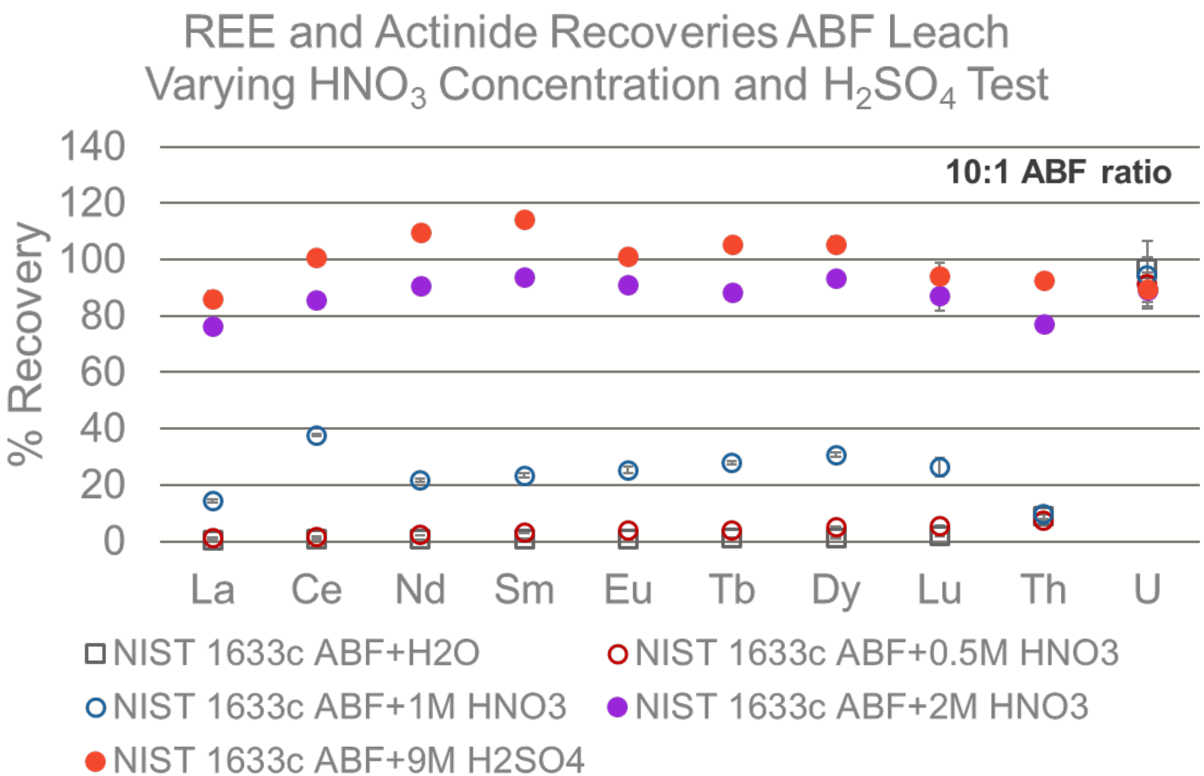
20 mg
NIST 1633c



ABF increases recovery to near quantitative recovery of REEs from coal fly ash at room temperature leaching compared to high HNO_3

ABF Leaching of Fly Ash: analytical scale

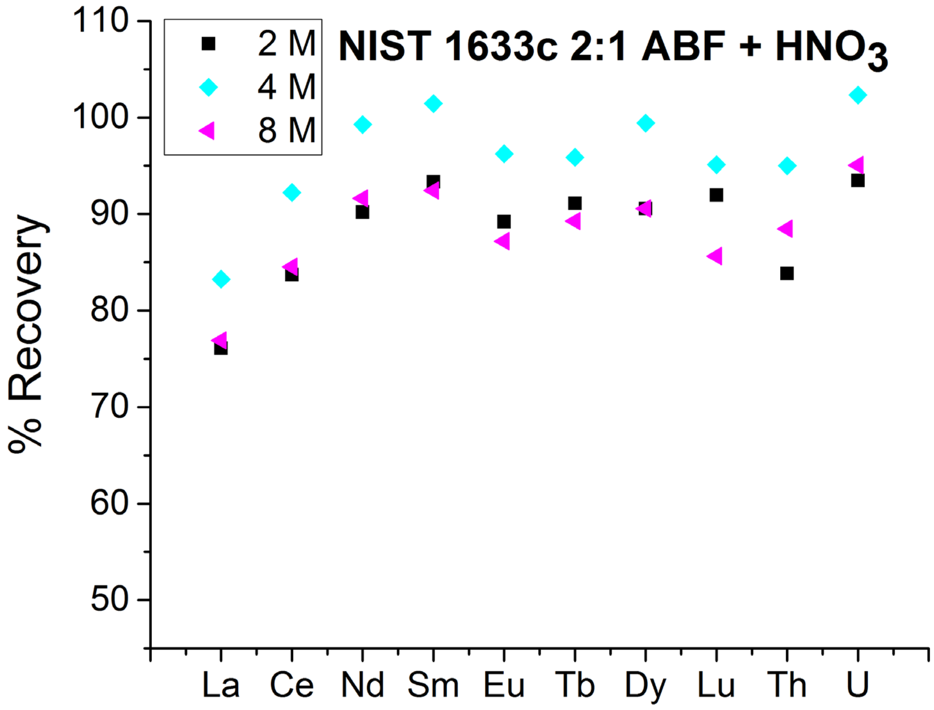
20 mg
NIST 1633c

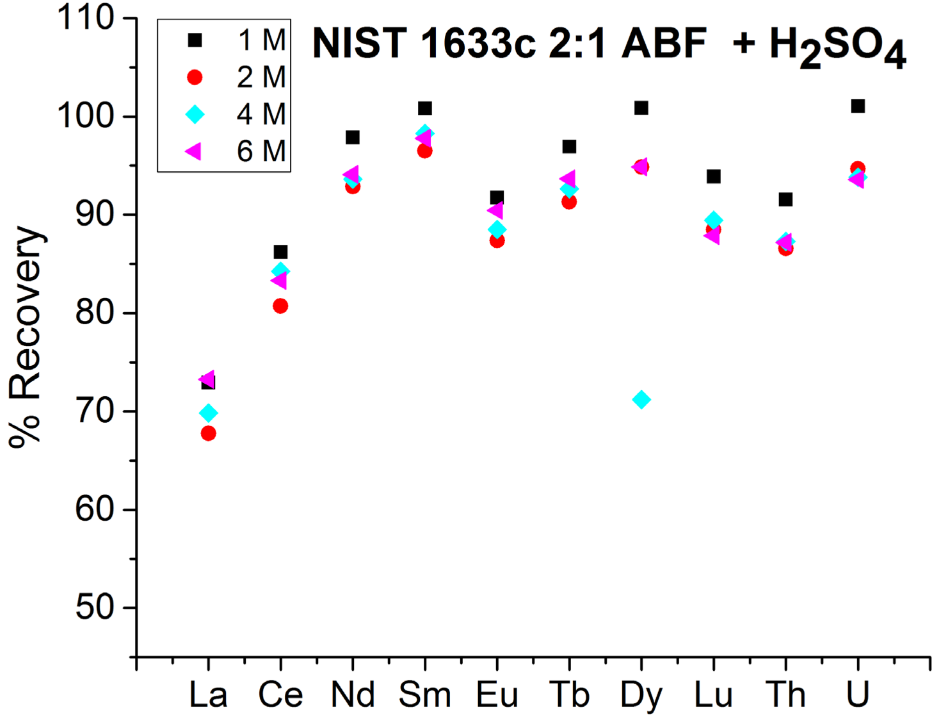


High recovery of REEs using ABF with 2 M HNO_3

Leaching of Fly Ash: Reducing reagent

20 mg
NIST 1633c

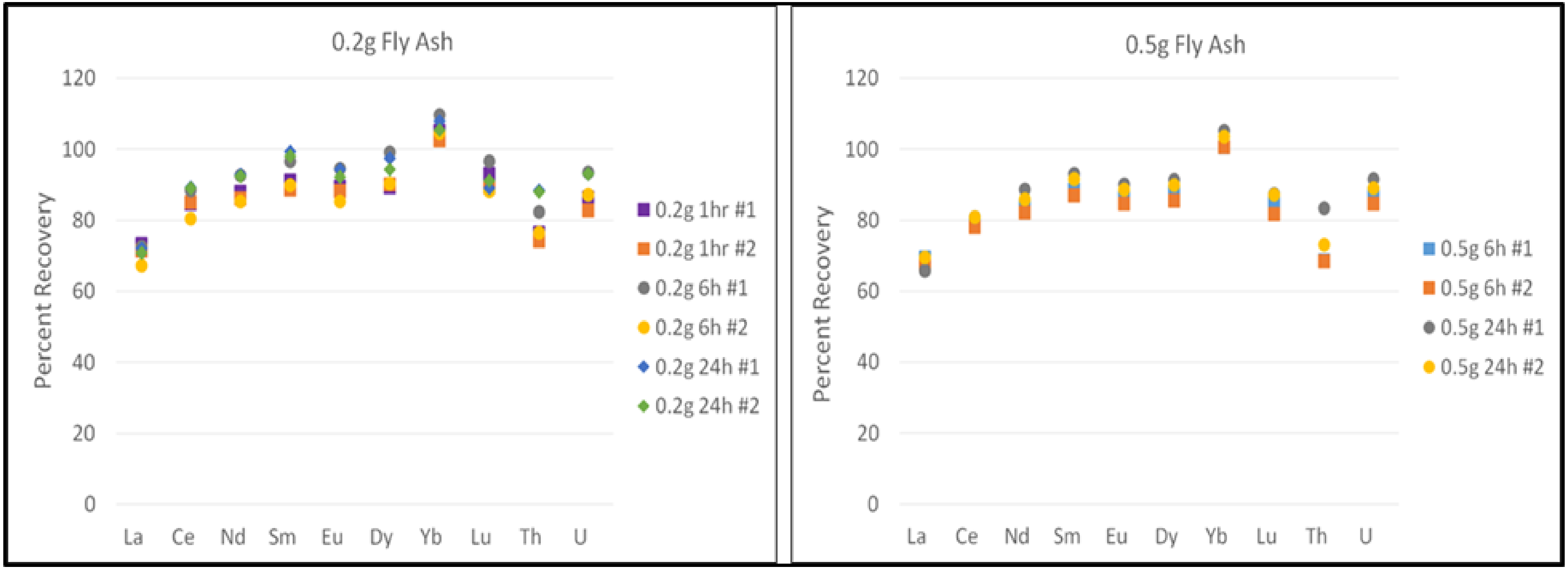




Lowering ABF and acid able to still recovery high percentage of REEs.
Proof of concept of the chemistry confirmed for fly ash leaching at the analytical scale.

Leaching of Fly Ash: Increasing sample size/various contact times

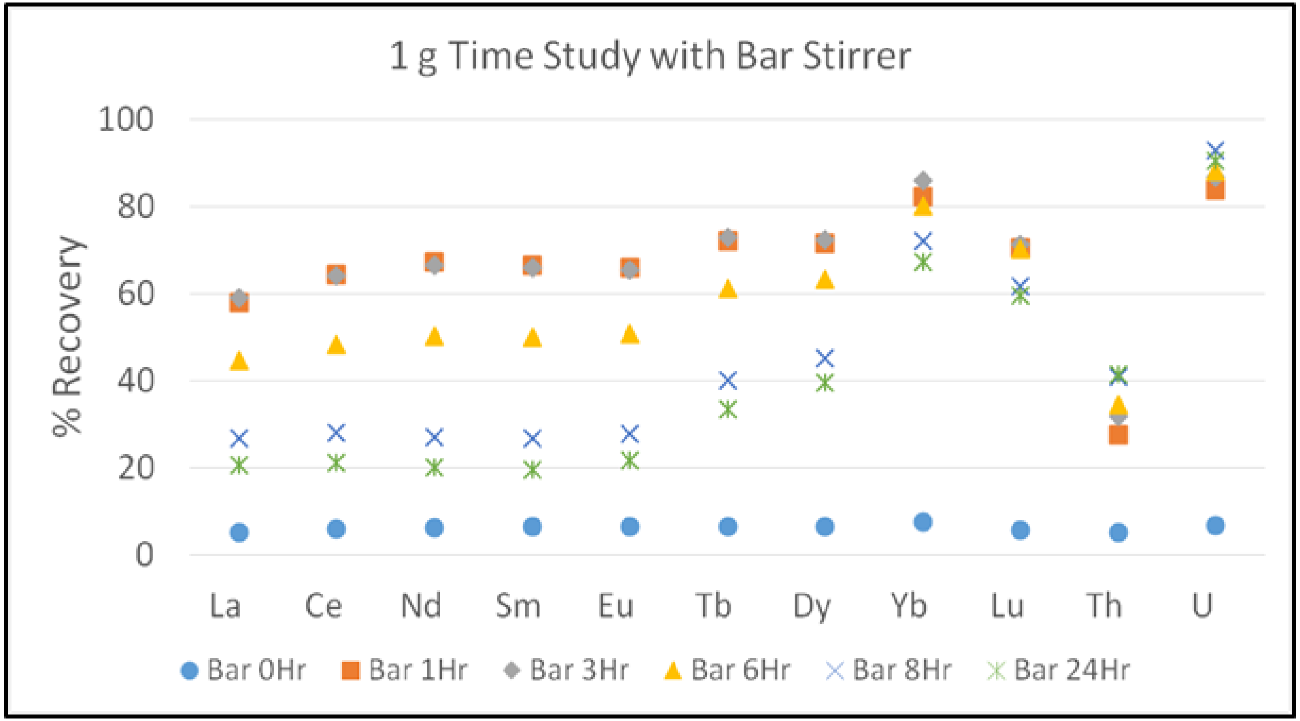
2:1 mass ratio of ABF : NIST 1633c fly ash



High percentage of recovered REEs occur within 6 hours.
Initial proof of principle to start scaling up from analytical size samples.

Leaching of Fly Ash: 1 g sampled over time

2:1 mass ratio of ABF : NIST 1633c fly ash



High percentage of recovered REEs occur within 1-3 hours.
Possible REE fluoride or oxyfluoride precipitation at longer times.

NIST Standard Reference Material 1633c

"Trace Elements in Coal Fly Ash"

RCRA Metals or radioactive

from certificate of analysis
additional elements identified by LANL

Priority of NETL REE Program
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3 3s / 3p	11 Na sodium 22.99 +1	12 Mg magnesium 24.31 +2											13 Al aluminum 26.98 +3	14 Si silicon 28.09 −4	15 P phosphorus 30.97 −3	16 S sulfur 32.07 −2	17 Cl chlorine 35.45 −1	18 Ar argon 39.95
4 4s / 3d / 4p	19 K potassium 39.10 +1	20 Ca calcium 40.08 +2	21 Sc scandium 44.96 +3	22 Ti titanium 47.87 +4,3,2	23 V vanadium 50.94 +5,2,3,4	24 Cr chromium 52.00 +3,2,6	25 ★ Mn manganese 54.94 +2,3,4,6,7	26 Fe iron 55.85 +3,2	27 ★ Co cobalt 58.93 +2,3	28 ★ Ni nickel 58.69 +2,3	29 Cu copper 63.55 +2,1	30 Zn zinc 65.38 +2	31 ★ Ga gallium 69.72 +3	32 Ge germanium 72.63 +4,2	33 As arsenic 74.92 −3	34 Se selenium 78.97 −2	35 Br bromine 79.90 −1	36 Kr krypton 83.80
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6 6s / † 5d / 6p	55 Cs cesium 132.9 +1	56 Ba barium 137.3 +2		72 Hf hafnium 178.5 +4	73 Ta tantalum 180.9 +5	74 W tungsten 183.8 +6,4	75 Re rhenium 186.2 +7,4,6	76 Os osmium 190.2 +4,6,8	77 Ir iridium 192.2 +4,3,6	78 Pt platinum 195.1 +4,2	79 Au gold 197.0 +3,1	80 Hg mercury 200.6 +2,1	81 Tl thallium 204.4 +1,3	82 Pb lead 207.2 +2,4	83 Bi bismuth 209.0 +3,5	84 Po polonium 209 +4,2	85 At astatine 210	86 Rn radon 222
7 7s / ‡ 6d / 7p	87 Fr francium 223 +1	88 Ra radium 226 +2		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 roentgenium 280	112 Cn copernicium 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

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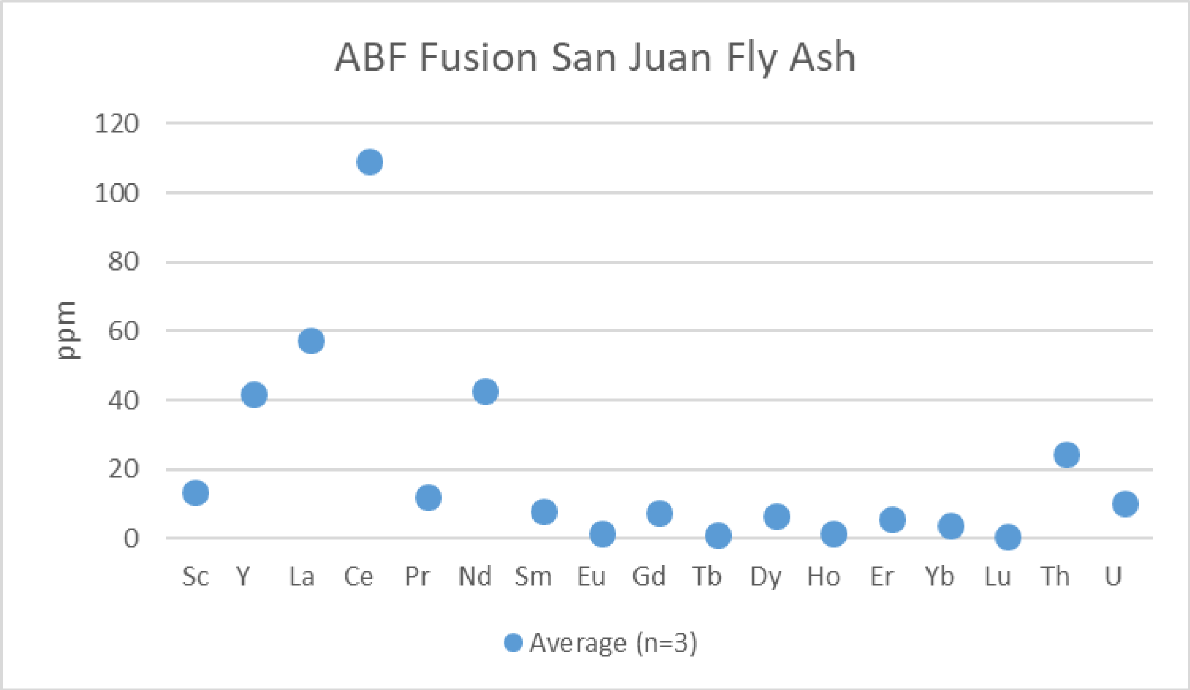
actinides ‡ 5f	89 Ac actinium 227 +3	90 Th thorium 232.0 +4	91 Pa protactinium 231.0 +5,4	92 U uranium 238.0 +6,3,4,5	93 Np neptunium 237 +5,3,4,6	94 Pu plutonium 244 +4,3,5,6	95 Am americium 243 +3,4,5,6	96 Cm curium 247 +3	97 Bk berkelium 247 +3,4	98 Cf californium 251 +3	99 Es einsteinium 252 +3	100 Fm fermium 257 +3	101 Md mendelevium 258 +3,2	102 No nobelium 259 +2,3	103 Lr lawrencium 262 +3

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

San Juan Fly Ash (NM) analysis: Fusion method

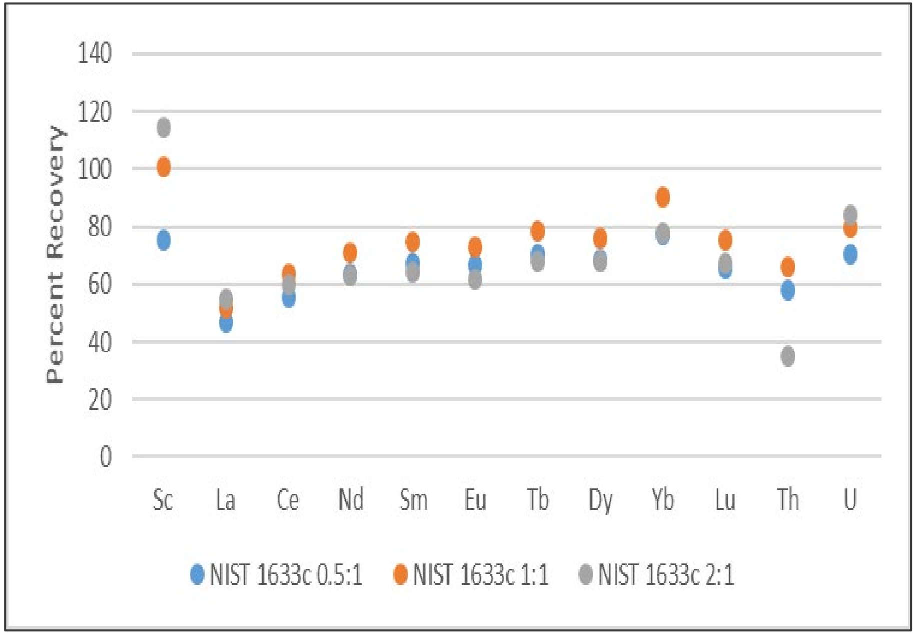


Total REEs + Sc + Y = 313 ppm

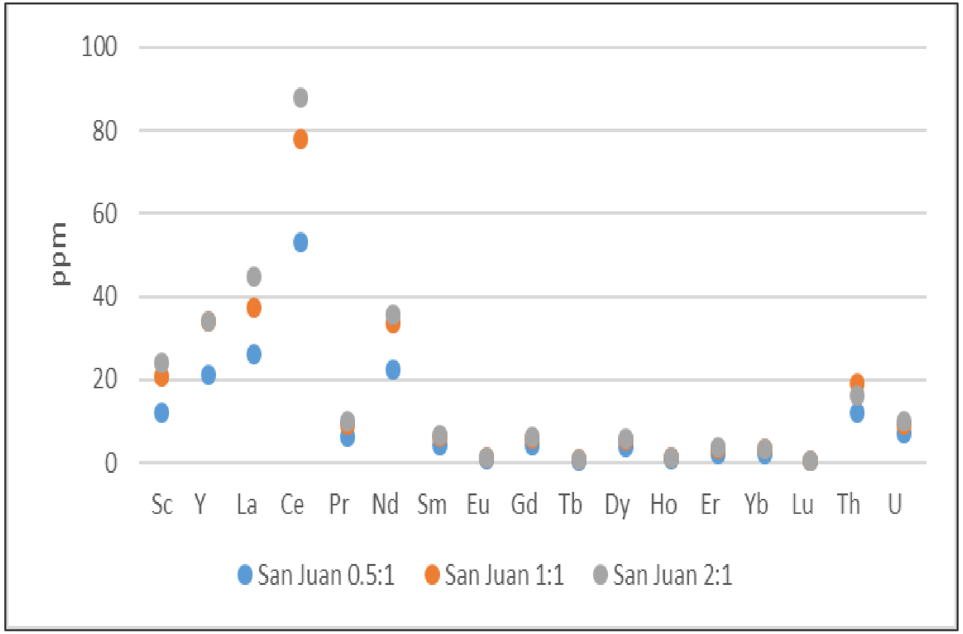
Analytical determination of REEs from NM sourced fly ash, for use in REE leach scale up demo. Ran in parallel to NIST 1633c for verification of method.

San Juan Fly Ash: 1 g, 6 hr Leach comparison

NIST 1633c



San Juan



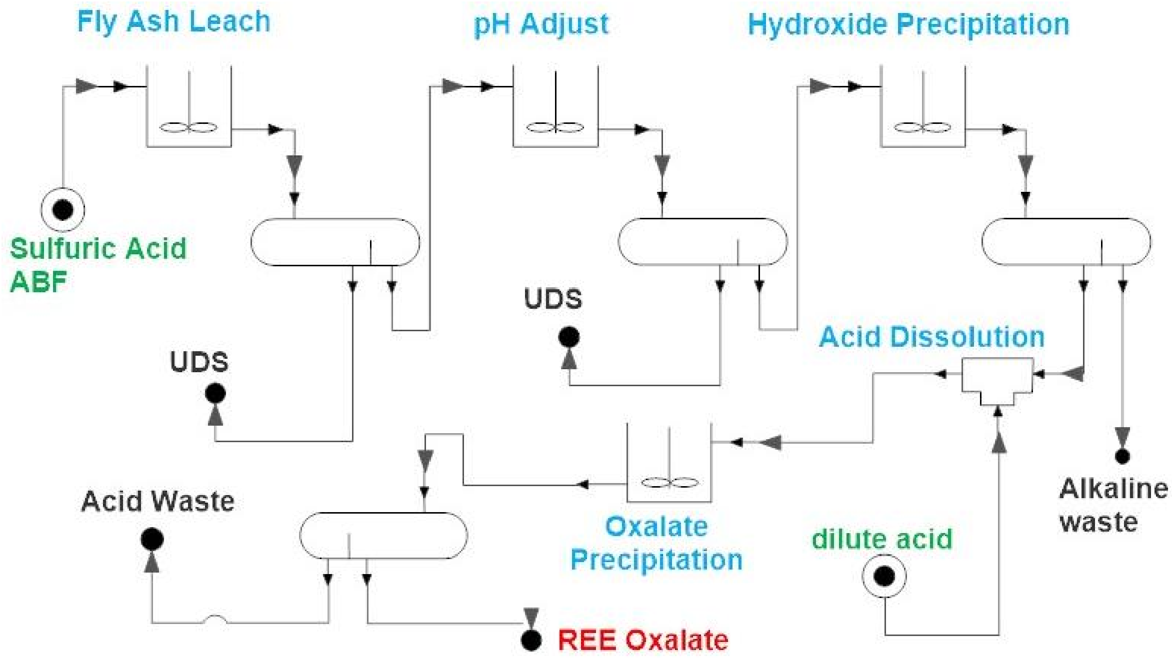
Lower ABF can also be effective for REE recovery. Minimizing reagents and acid will benefit process economics.

San Juan fly ash REE % Recovery
0.5:1 ratio = 51%
1:1 ratio = 76.5%
2:1 ratio = 84.8%

Scale-up Demo

- Scale-up demo currently underway.
- Fly ash leach tests performed using 10-50 grams of fly ash for proof of principal.
- Leach solution is 2 M H_2SO_4 with 0.9 M ABF.
- Dissolution testing with both NIST 1633c and San Juan fly ash (NM).

Conceptual flowsheet for scale-up testing



If successful, this will represent a ~ 1,000X scale-up in ~ 1 year

ABF Leaching of Fly Ash Conclusions

- Able to quantitatively recover REEs and actinides
  - Effective for *targeted recovery* from aluminosilicate fraction
  - Complete dissolution <u>not necessary</u>
  - Novel dissolution chemistry can be integrated into existing process flowsheets or serve as the front end of new process flowsheets
- Acid
  - 2 M HNO_3
  - 1 M H_2SO_4 equally effective for REEs
    - More cost effective acid
    - lowered dissolution of other unwanted metals (Cr, Pb, Ba, and lesser extent Fe and Al)
- Reagent
  - 2:1 ABF ratio most often used
    - Similarly high selective recovery of REEs, some increased
  - recent reduction to 1:1 and 0.5:1
    - 75% recovery of REEs + Sc + Y for 1:1 reagent to fly ash mass ratio

ABF Leaching of Fly Ash Conclusions

- Scale up of sample size
  - 20 mg to 1 g leach (**50x** scale up from analytical scale)
  - REE recovery >70%
- Time
  - Majority of recovered REEs achieved within 2 hours
  - >85% REEs recovered in 6 hours at 0.2 g and 0.5 g sample sizes

- Scale up demo (in process)
  - multi-gram fly ash leach demo as proof of concept of the chemistry towards kg scale
  - Chemistry could fit into similar flow sheet for initial REE recovery from alternative REE resources such as fly ash
  - Characterization of % REE in resulting mixed REE product

Additional options as feed for REE separations based upon novel LANL contactors

Thank you!