Effect of Ca on Extractability of Rare Earth Minerals from Fly Ash

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Solutions for Today | Options for Tomorrow

Outline

- Introduction – Coal Ash as Low Grade Feedstock for Rare Earths
- Extractability of Rare Earths
  - From Bituminous Coal
  - From Sub-Bituminous Coal
- Correlation of Extractability and Elemental Composition
- REE-bearing Minerals

Introduction – Need for Domestic Rare Earth Element (REE) Sources

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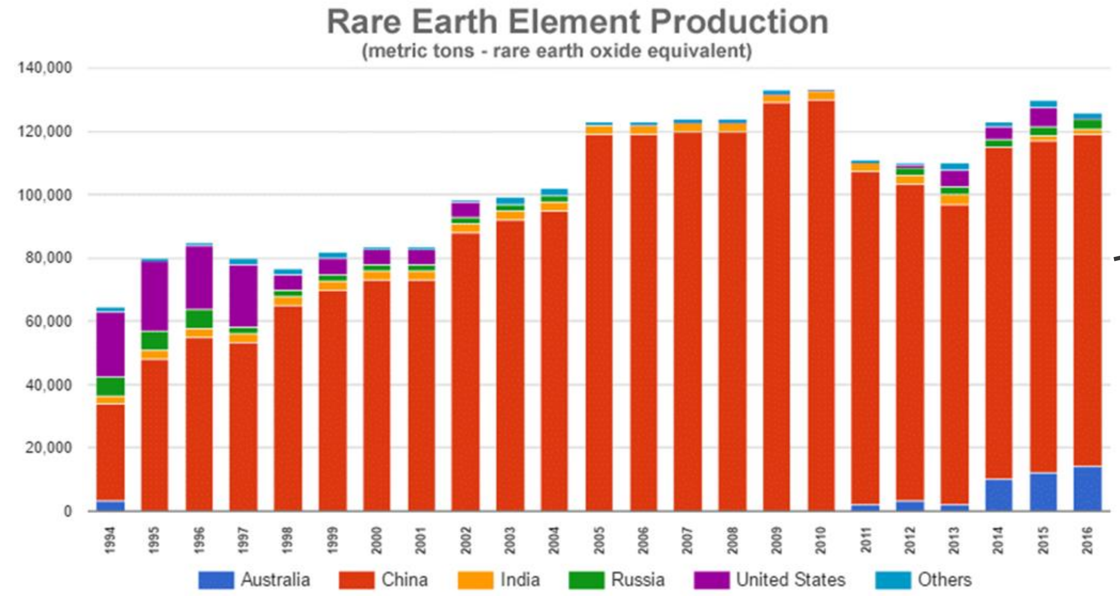
A domestic supply of REEs is needed for national security and economic gains

In 2010, DOE identified Y, Nd, Eu, Tb and Dy as critical REEs crucial for military applications, green energy, electronic industries

REEs are typically not found in concentrated ores and are difficult to extract and separate

~100 million tons of coal ash was generated in 2018 which contains > 2x current U.S. consumption of REEs



In 2016, the US imported 100% of our REEs (16,000 metric tons mostly from China)

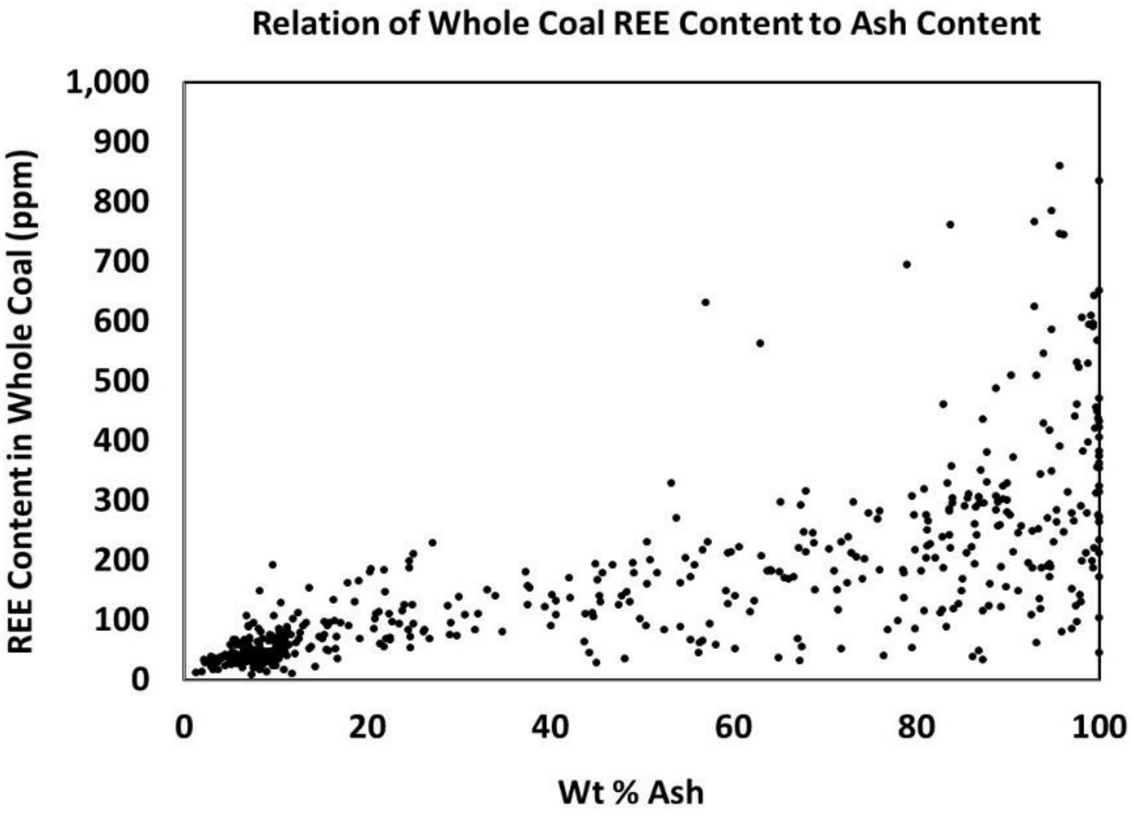
Geology News and Information. REE – Rare Earth Element and their Uses http://geology.com/articles/rare-earth-elements/ (accessed November 30th, 2017)

Introduction – Why Coal Ash?

REEs have previously been leached from lignite coal (Laudal 2018) and coal refuse (Honaker 2018).

But REE concentrations are typically higher in ash than in coal and refuse (https://edx.netl.doe.gov/ree/?p=875)

Incentive for further investigation of REE extraction from coal ash

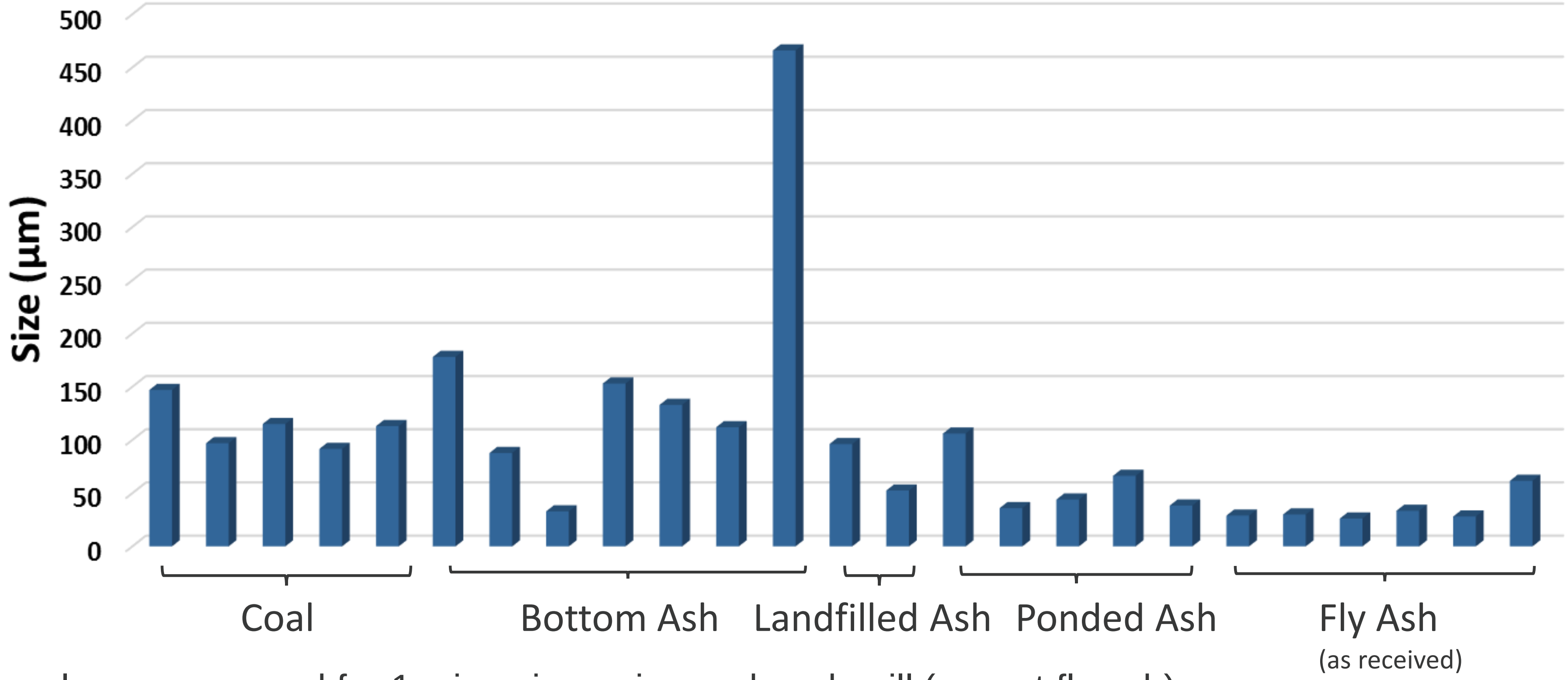


Feedstock materials

Partnership with Electric Power Research Institute (EPRI)

Coal, bottom ash, landfilled ash, ponded ash, fly ash samples obtained.

Fly ash particles are smallest



- Samples were ground for 1 min using a ring and puck mill (except fly ash)
- Average of three trials for each sample
- Instrument: Malvern, Mastersizer 3000 and Malvern, AEROS (wet cell)

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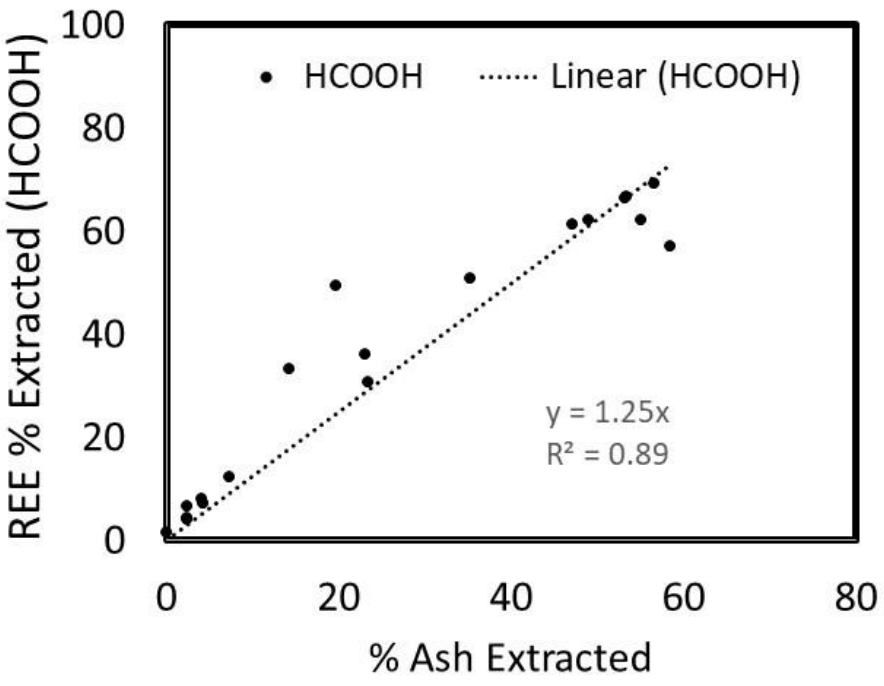
Correlation between % Ash and % REE Extracted

We considered 19 fly ash, ponded ash, landfilled ash, bottom ash derived from sub-bituminous and bituminous coals, as well as the parent coals

Formic acid extraction tests reveal that REE % extracted is correlated with overall ash % extracted.

Matrix minerals in which the REE are trapped must be solubilized in order to solubilize the REE.

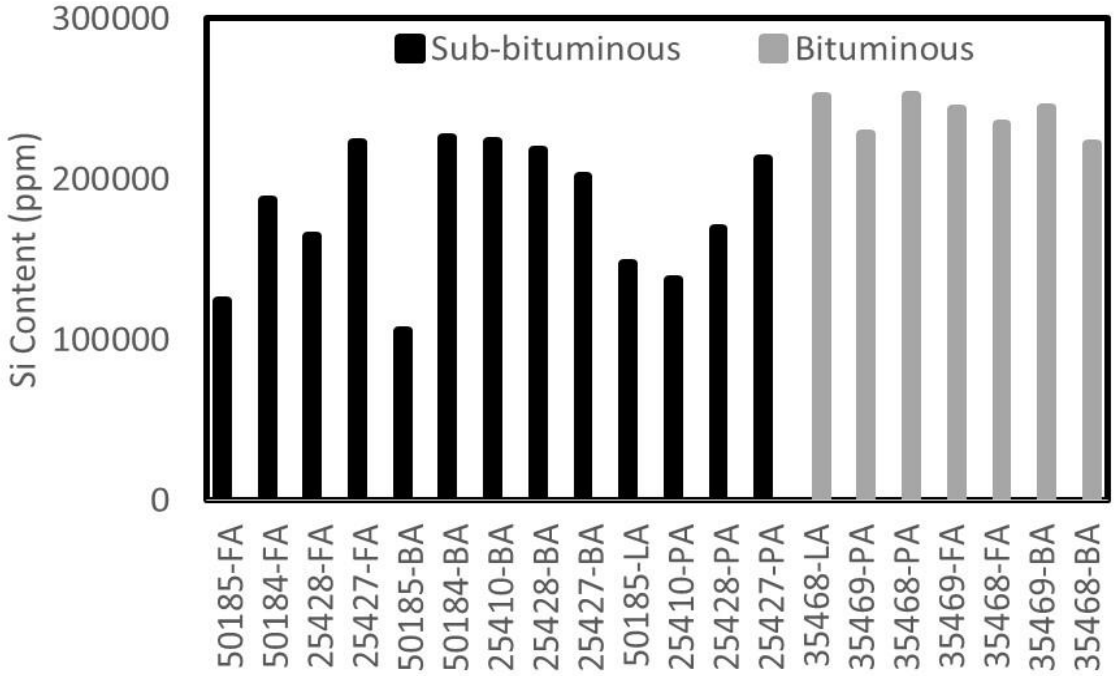
Does coal type (bituminous vs. sub-bituminous) matter?

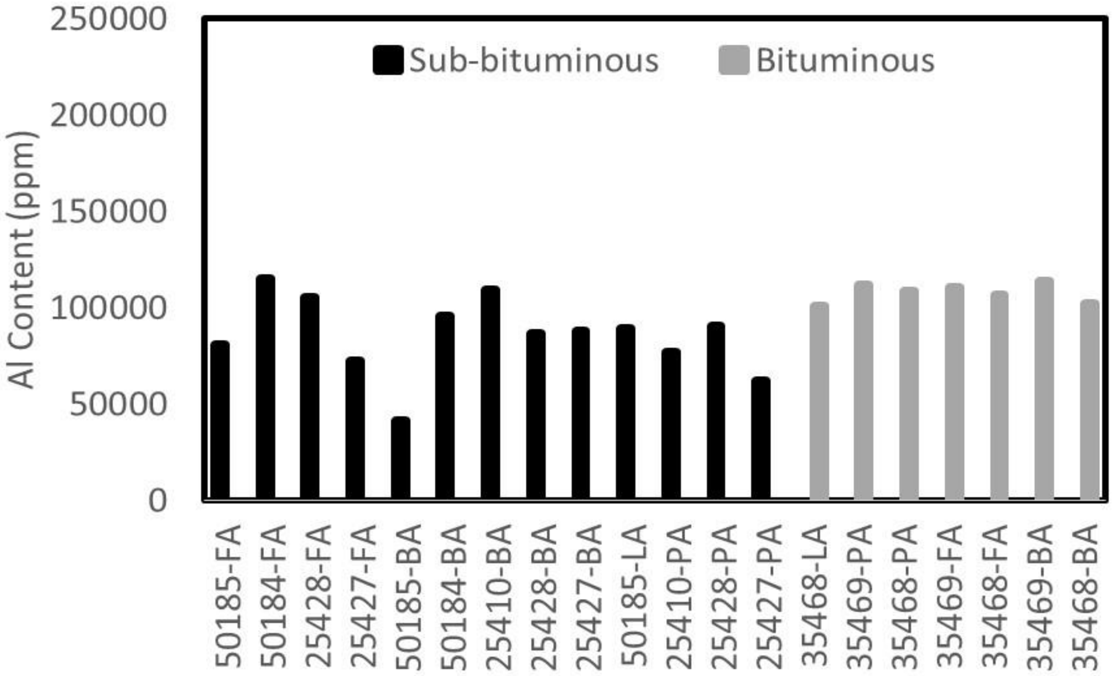


Primary matrix minerals present – Sub-bituminous vs. Bituminous Ash

Al, Si oxides often comprise more than 80% of bituminous ash (ref Dai 2014, Taggart 2016, Hower 2004 and Lin 2017) but only around 60% of sub-bituminous ash (ref Taggart 2016).

REE in ashes derived from bituminous coals are primarily trapped within Al-Si glass matrix (Dai 2014, Mengling 2018, Montross TRS, LA-ICP-MS paper)

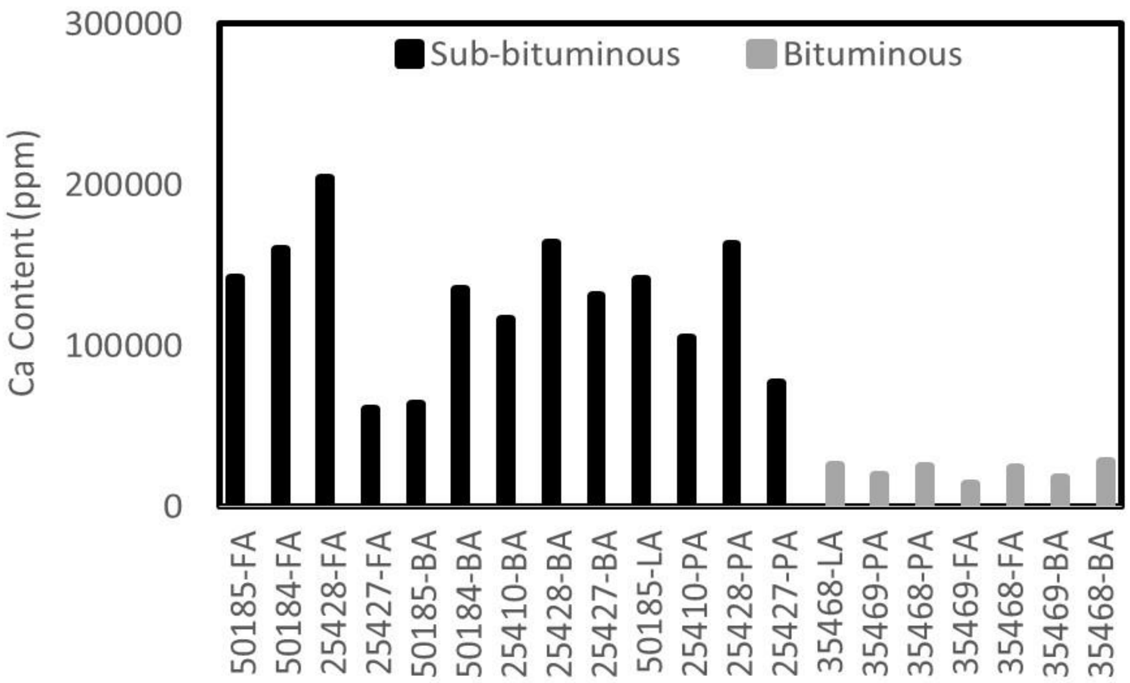


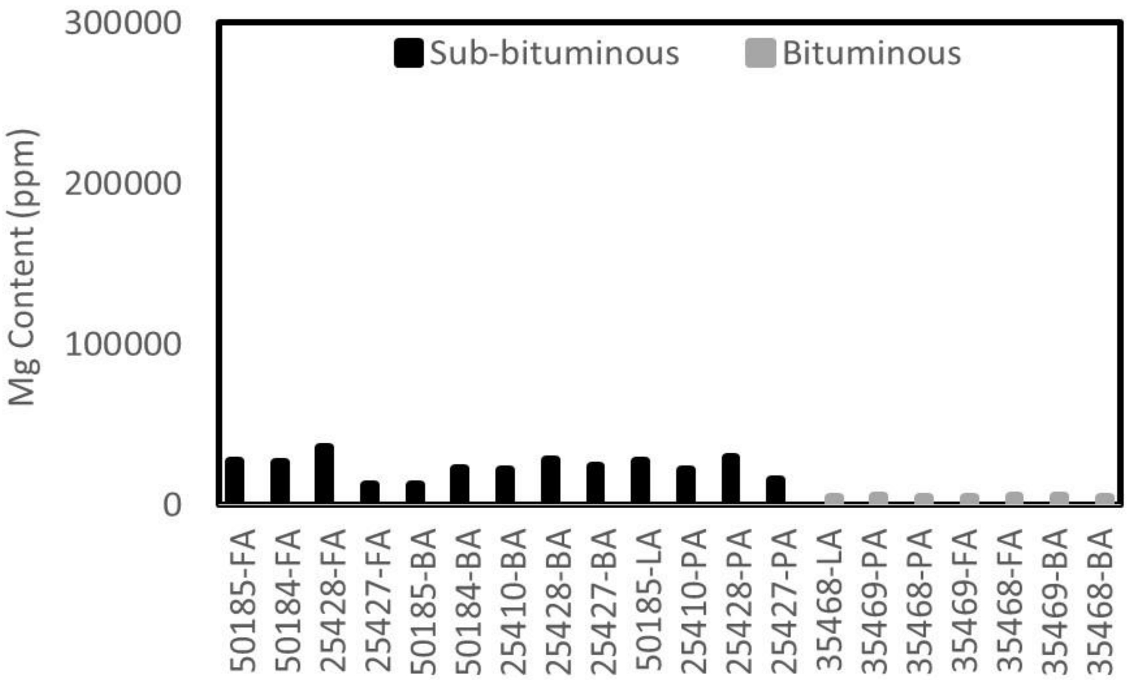


Primary matrix minerals present – Sub-bituminous vs. Bituminous Ash

However, Group 2 Ca and Mg compositions are considerably higher in sub-bituminous than bituminous ash (ref agreement with Taggart 2016).

REEs in sub-bituminous coal may be trapped in either Al-Si or Ca matrix (Mengling 2018)





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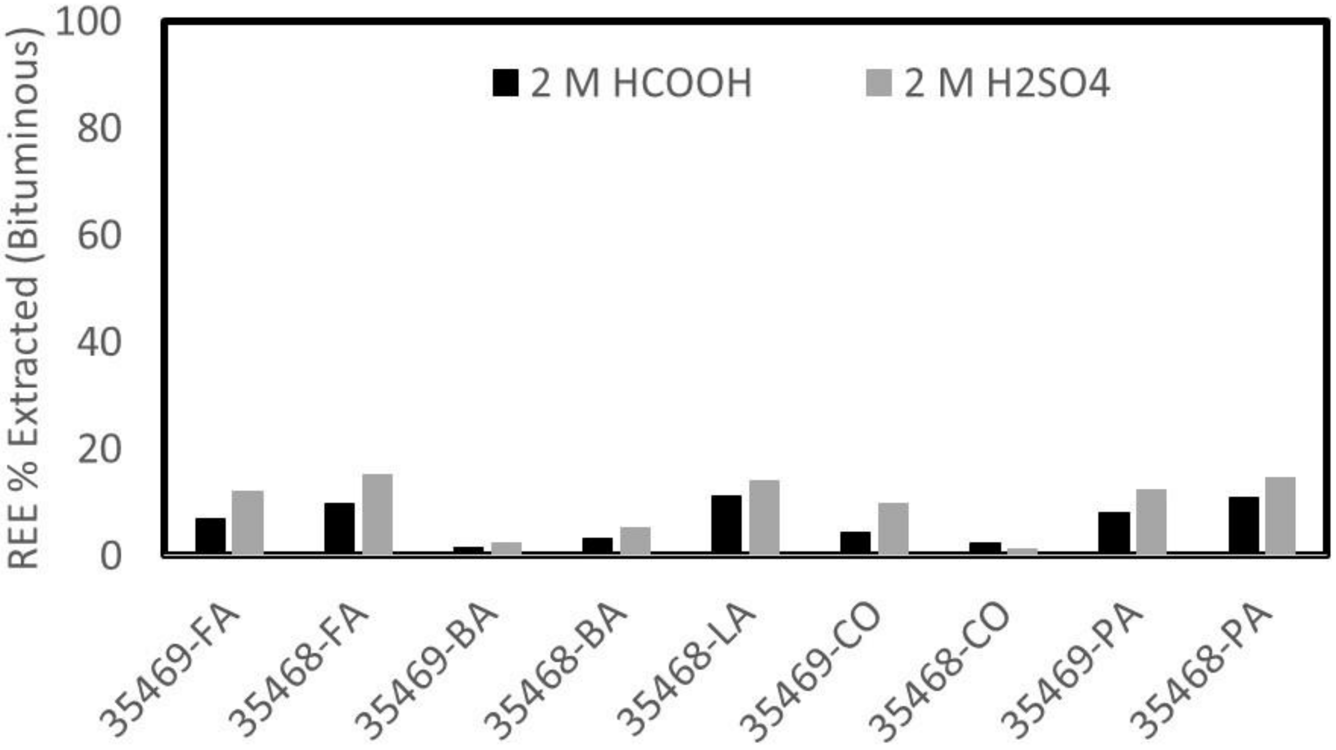
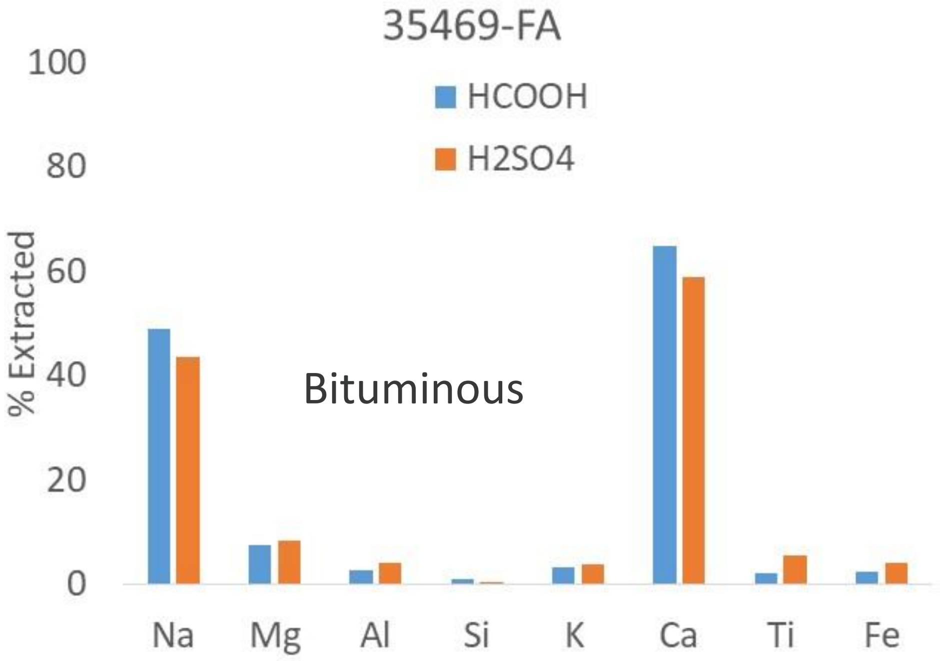
Minimal Recovery of REE from Bituminous Coals, Ash

Taggart et al. (2016) only obtained 15-45 wt% REE extracted from fly ash derived from bituminous Illinois and Appalachian coals using concentrated 15 M HNO_3.

In this work, REE recovery from all bituminous coals is low (ranging from 1-15%) using less concentrated 2 M HCOOH or 2 M H_2SO_4.





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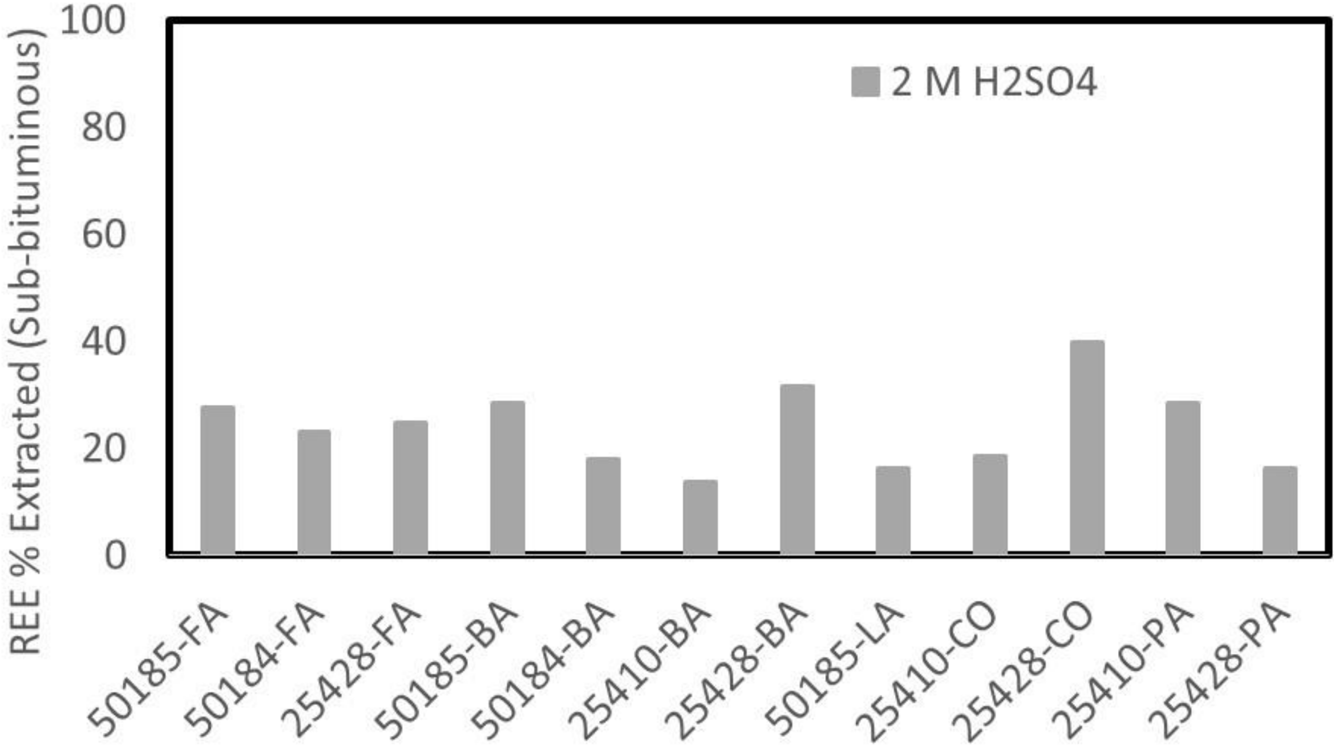
Modest REE recovery from sub-bit coal with H_2SO_4

REE recovery from sub-bituminous coal and its ash byproducts ranged from 14-40% (vs 1-15% for bit coals) when using 2 M H_2SO_4 as extraction agent.

Taggart et al. (2016) used 15 M HNO_3 to recover 50-90 wt% REE from fly ash derived from sub-bituminous PRB coals.



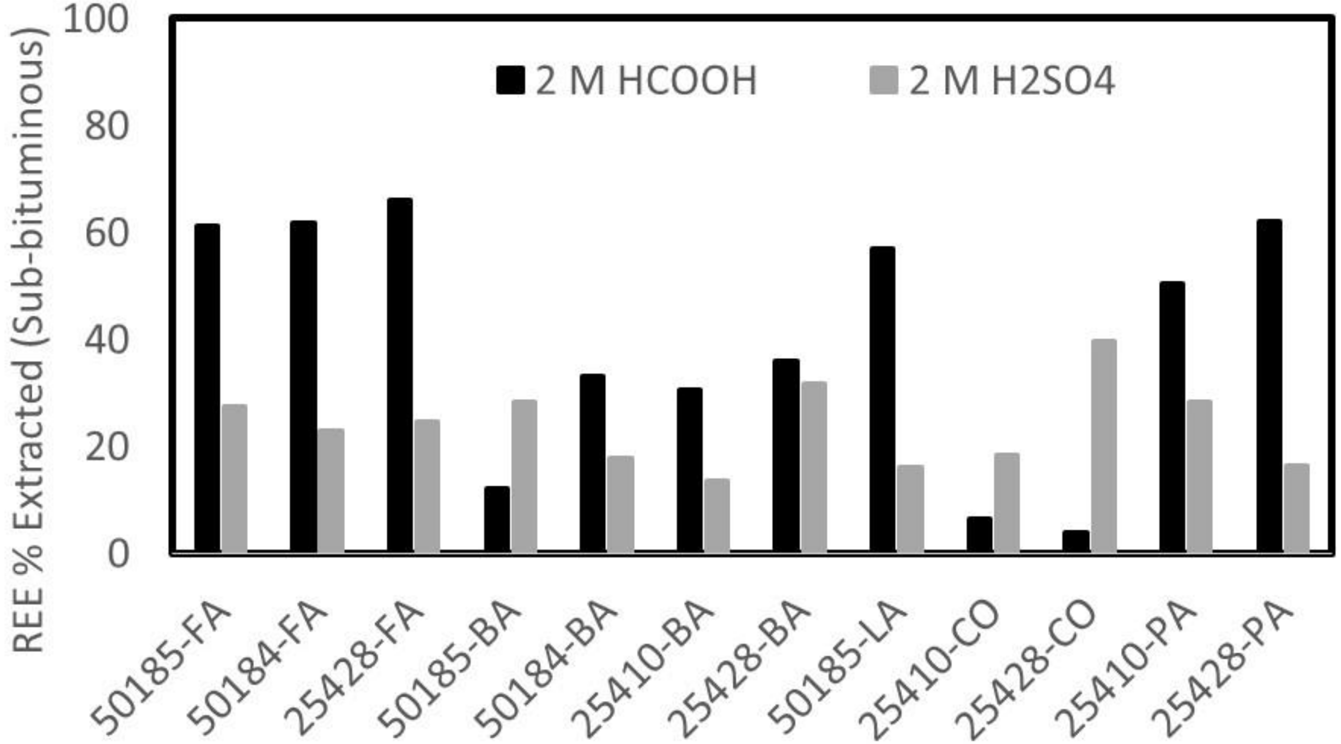
Up to 66% REE recovery from sub-bit coal with HCOOH

REE recovery from sub-bit fly ash jumps to 61-66% when using 2 M HCOOH as extraction agent (comparable to Taggart results with much more concentrated 15 M HNO_3).

REE recovery from sub-bit ponded, landfilled, and fly ashes are comparable.

Interestingly, HCOOH yields higher recovery from sub-bit ash than H_2SO_4.

On the other hand, REE recovery from sub-bit coal (HCOOH extraction) is much less than that obtained using H_2SO_4 as extractive agent.



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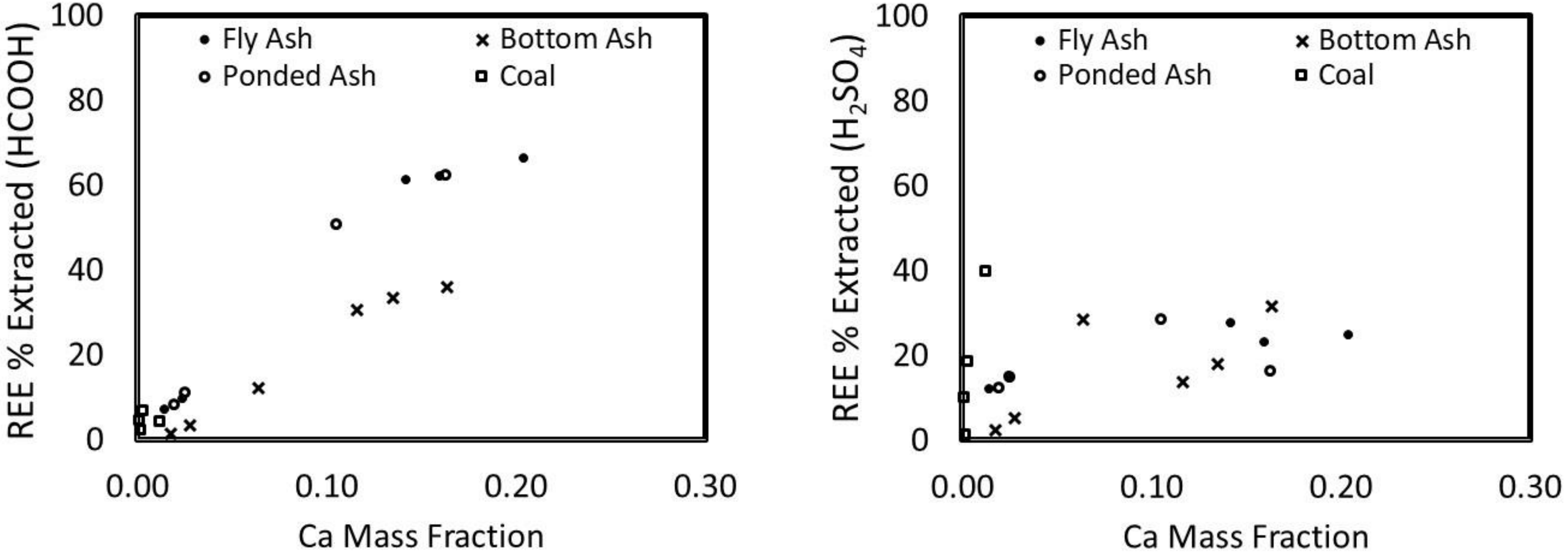
Ca content as a proxy for REE Extractability from Coal and Coal Ash

HCOOH extraction – Ca content rough proxy for REE extractability, but may require longer extraction time to recover REE from relatively larger bottom ash particles.

H_2SO_4 extraction – REE extractability has weak correlation to Ca content.

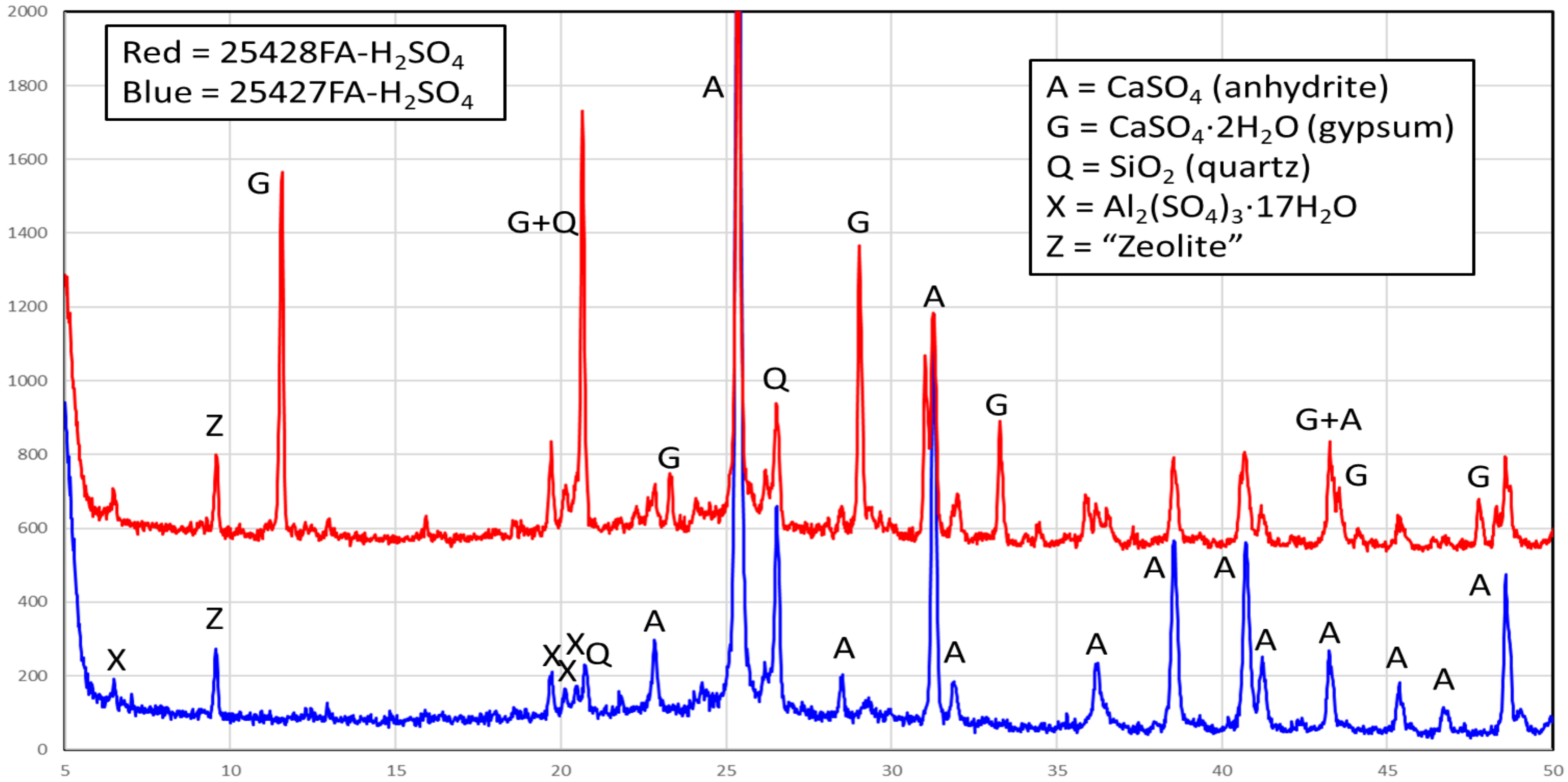
Kolker et al (2016) note that sub-bituminous PRB coal contains REE-associating Ca- and Fe-bearing aluminosilicates that may be more extractable than unsubstituted Al-Si.



Ca content as a proxy for REE Extractability from Coal and Coal Ash

XRD results suggest that the result of H_2SO_4 extraction is the deposition of a layer of $CaSO_4$ or $CaSO_4$*$2H_2O$ (gypsum) on the surface of the fly ash particles.

This behavior limits Ca extraction by H_2SO_4, and ultimately REE extraction.



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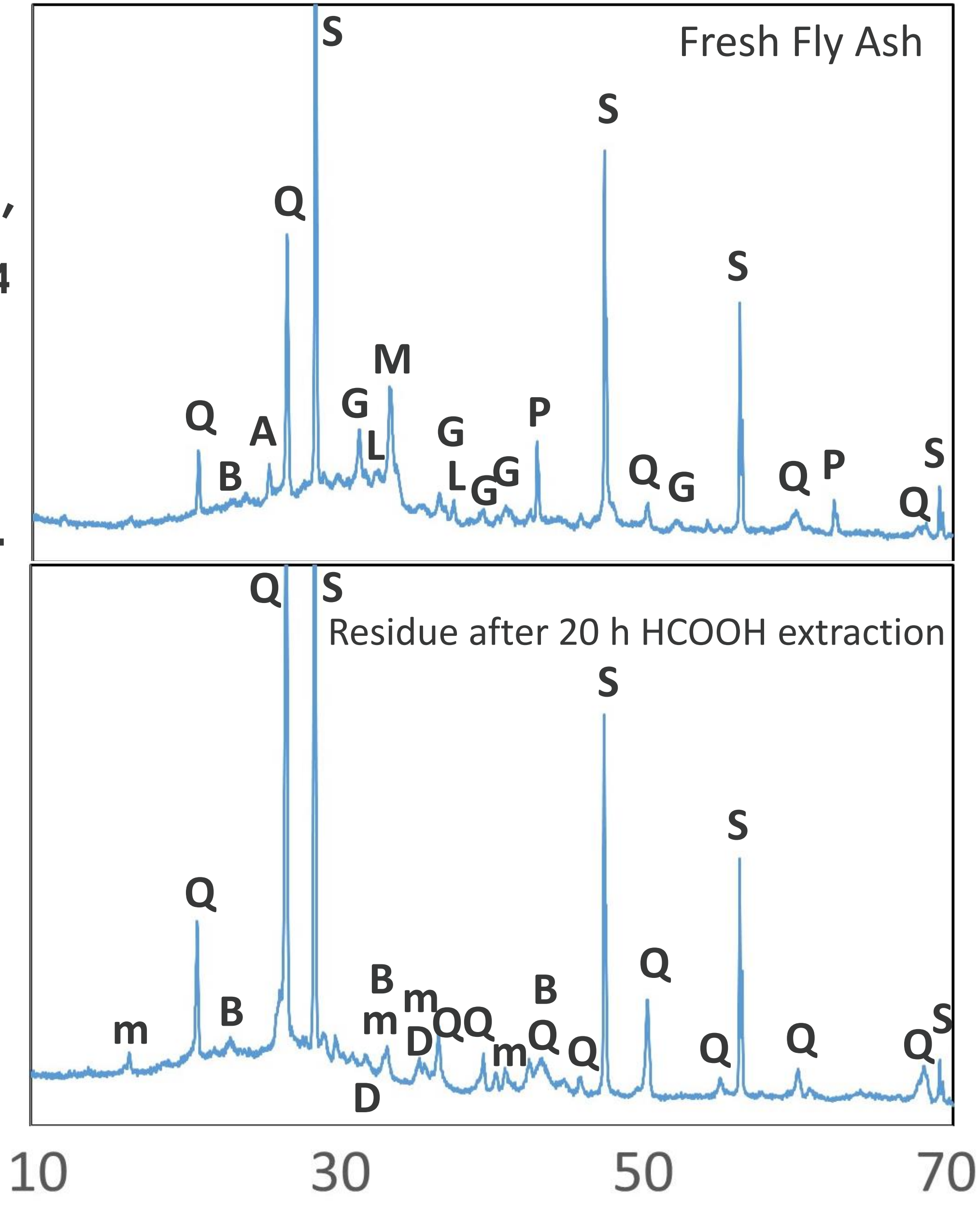
XRD – Fly Ash

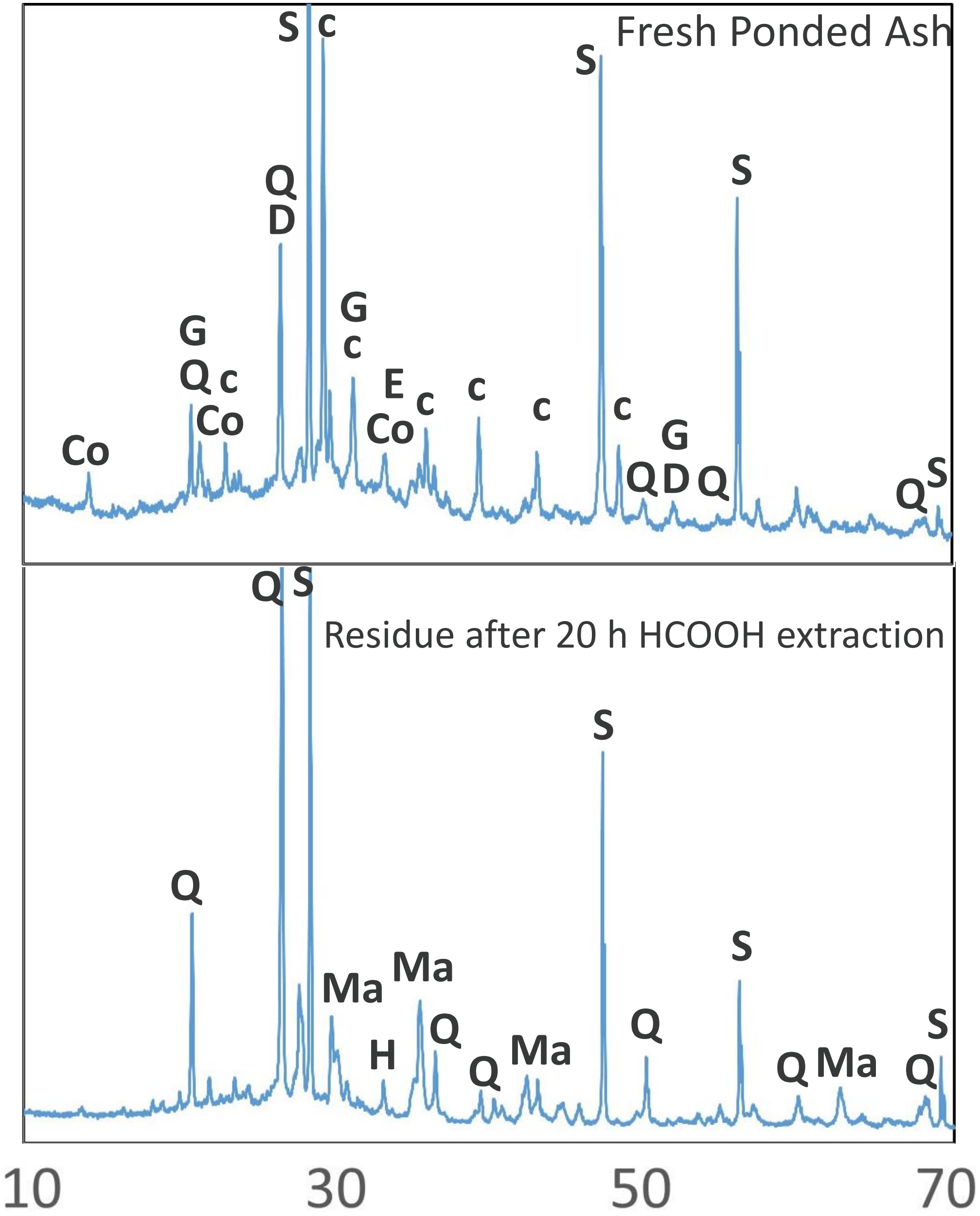
- MgO, CaO, $Ca_3Mg(SiO_4)_2$, $Ca_2Al(AlSiO_7)$, and $CaSO_4$ are extracted using HCOOH.
- Quartz, mullite, diopside, and BaSr disulfate are not extracted.
- It is concluded that the bulk of the Fe is in the amorphous phase.



Q = Quartz – SiO_2
P = Periclase – MgO
L = Lime – CaO
M = Merwinite – $Ca_3Mg(SiO_4)_2$
S = Silicon standard
G = Gehlenite – $Ca_2Al(AlSiO_7)$
A = Anhydrite – $CaSO_4$
m = Mullite – $3Al_2O_3*2SiO_2$
B = Ba Sr disulfate – $BaSr(SO_4)_2$
D = Diopside – $MgCaSi_2O_6$

XRD – Ponded Ash

- $CaCO_3$, coalingite, ettringite, $Ca_2Al(AlSiO_7)$, and $CaSO_4$ are extracted using HCOOH.
- Quartz, magnetite, hematite are not extracted.
- It again appears that most of the extractable Fe is in the amorphous phase.



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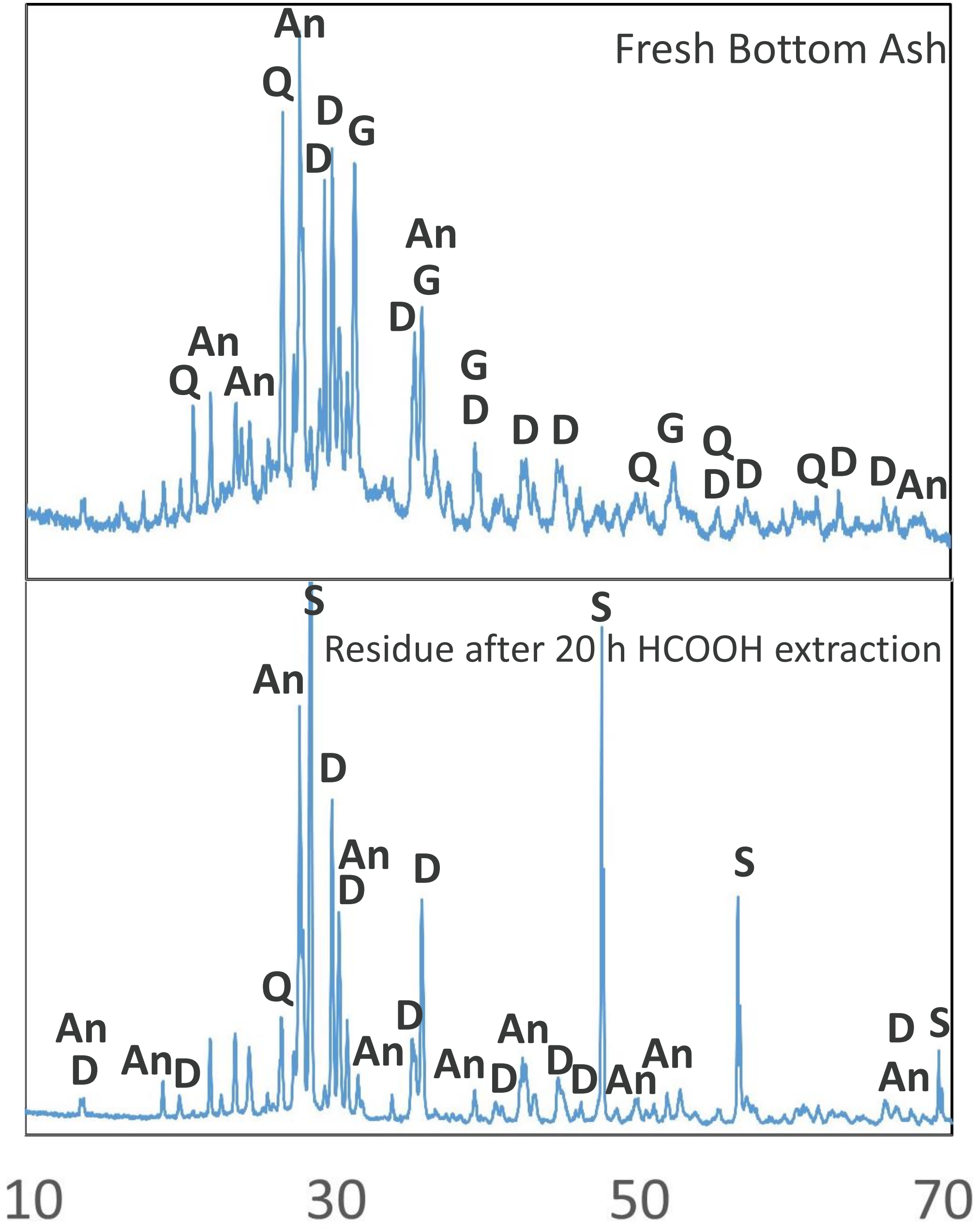
Q = Quartz – SiO_2
c = Calcite – $CaCO_3$
Co = Coalingite – $Mg_{10}Fe_2CO_3$(
S = Silicon standard
G = Gehlenite – $Ca_2Al(AlSiO_7)$
E = Ettringite – $Ca_6Al_2(SO_4)_3$(O
Ma = Magnetite – Fe_3O_4
H = Hematite– Fe_2O_3
D = Diopside – $MgCaSi_2O_6$

XRD – Bottom Ash

- $Ca_2Al(AlSiO_7)$ is extracted using HCOOH.
- Diopside, quartz, anorthite are not extracted.
- It again appears that most of the extractable Fe is in the amorphous phase.



Q = Quartz – SiO_2
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Ma = Magnetite – Fe_3O_4
H = Hematite– Fe_2O_3
D = Diopside – $MgCaSi_2O_6$

Extraction from Fly Ash – LREE vs. HREE

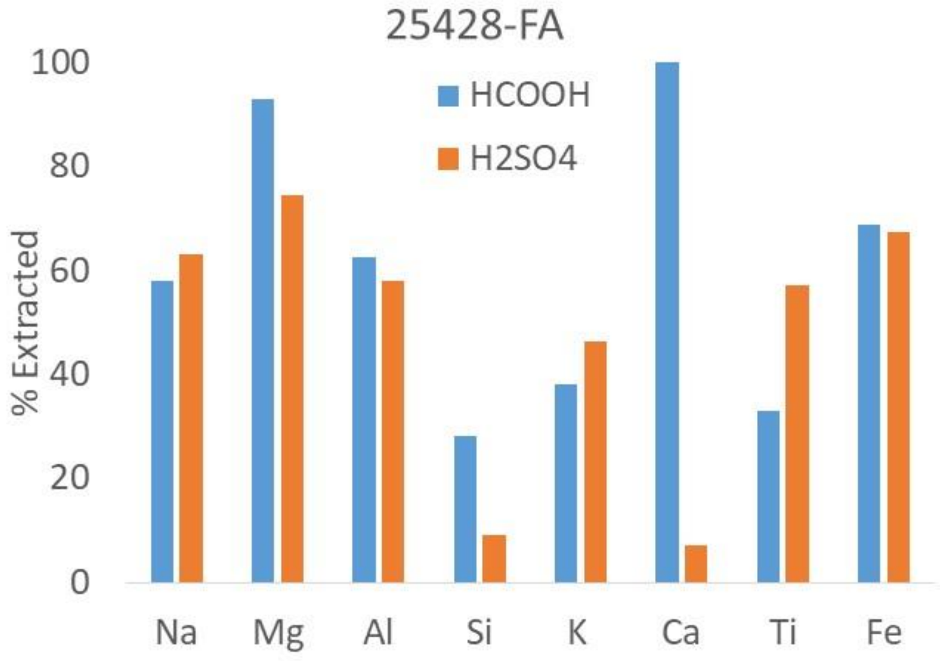
Sub-bituminous fly ash – HCOOH and H_2SO_4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

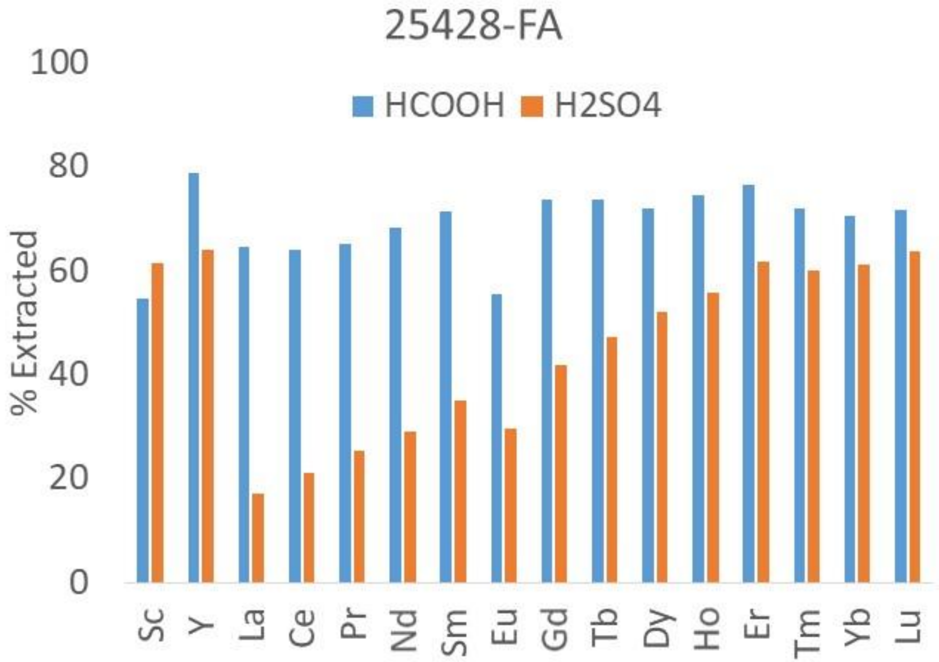
However, Ca extractability is much greater in HCOOH than H_2SO_4.

Extractability of Fe, Al is similar to that of Y, HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu).

Results are consistent with conclusion (Stuckman 2018) that the HREE are more likely to be found in Fe-rich aluminosilicates, while LREE are found in Ca-rich aluminosilicates.

HREE may primarily be associated with amorphous phase.





Extraction from Ponded Ash – LREE vs. HREE

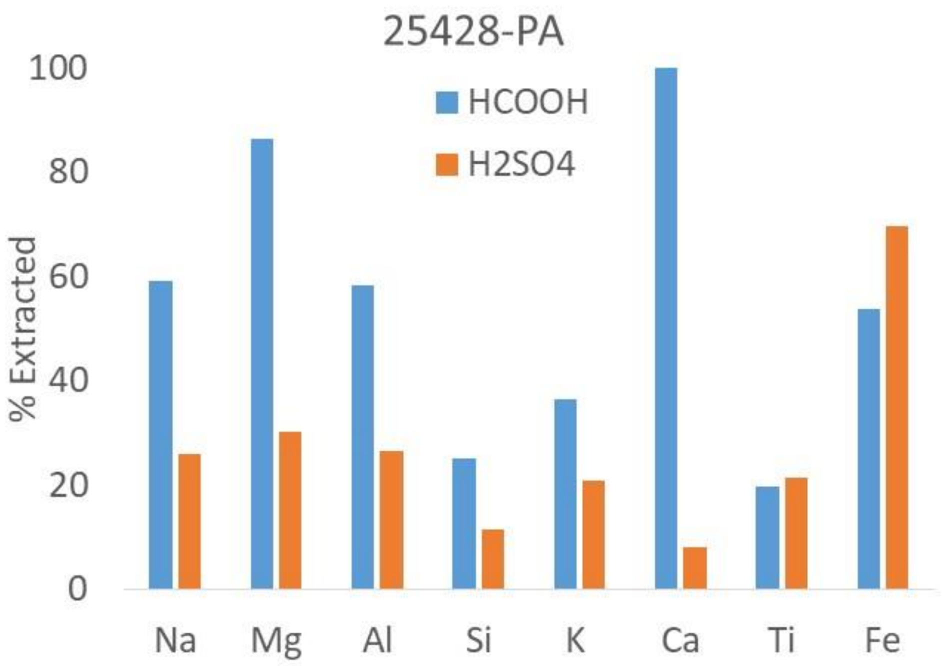
Sub-bituminous fly ash – HCOOH and H2SO4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

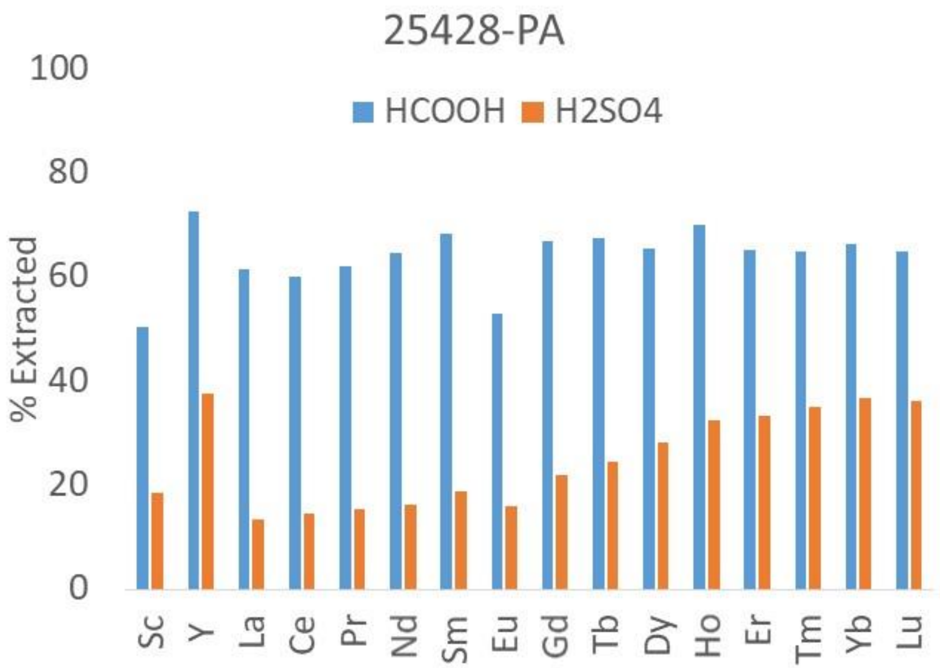
However, Ca solubility is much greater in HCOOH than H2SO4.

Extractability of Fe, Al is similar to that of Y, HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu).

Results are consistent with conclusion (Stuckman 2018) that the HREE are more likely to be found in Fe-rich aluminosilicates, while LREE are found in Ca-rich aluminosilicates.

HREE may primarily be associated with amorphous phase.





Extraction from Bottom Ash – LREE vs. HREE

Sub-bituminous fly ash – Ca solubility is much greater in HCOOH than H_2SO_4.

Extractability of Fe, Al is similar to that of Y, HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu).

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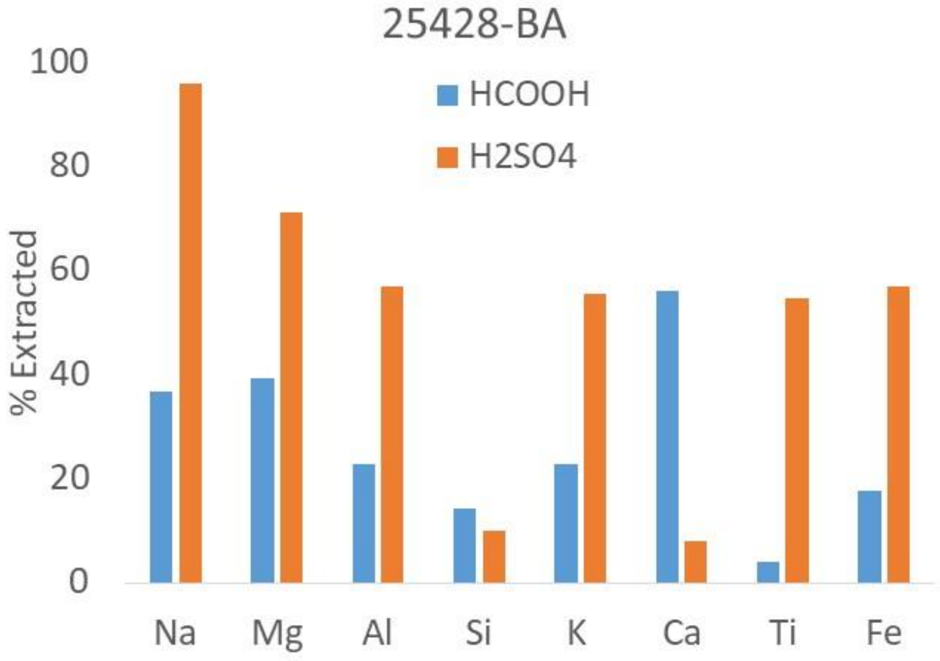

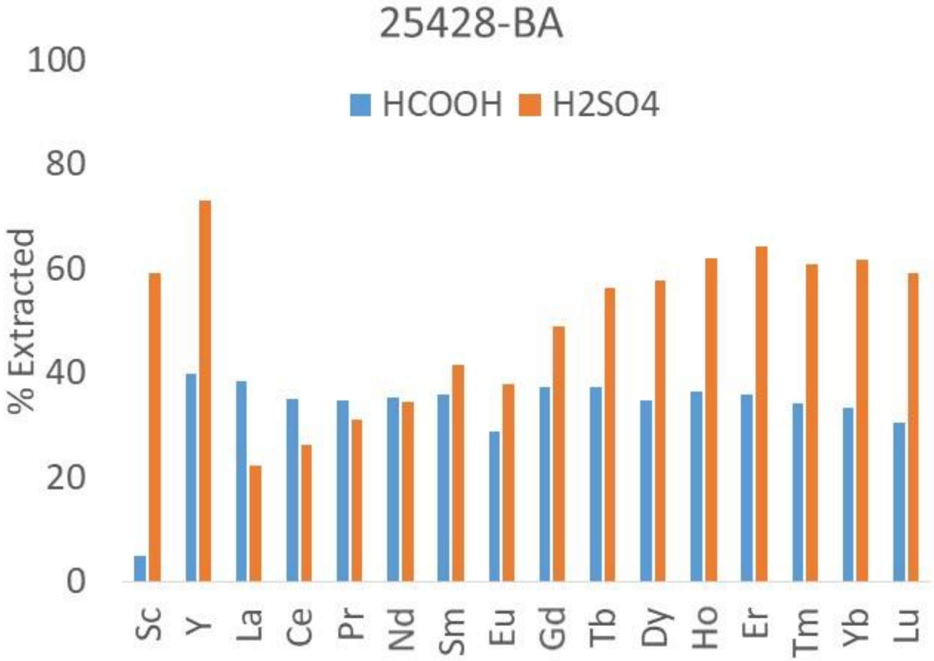

Conclusions and Future Work

- High-Ca,Mg ash derived from sub-bituminous coal is much more extractable than low-Ca,Mg ash derived from bituminous coals.
- Organic acid extraction shows promising results at mild pH.
- XRD suggests REE associate with Ca-bearing minerals
- Kinetic studies to model extraction rate are a must

Acknowledgments

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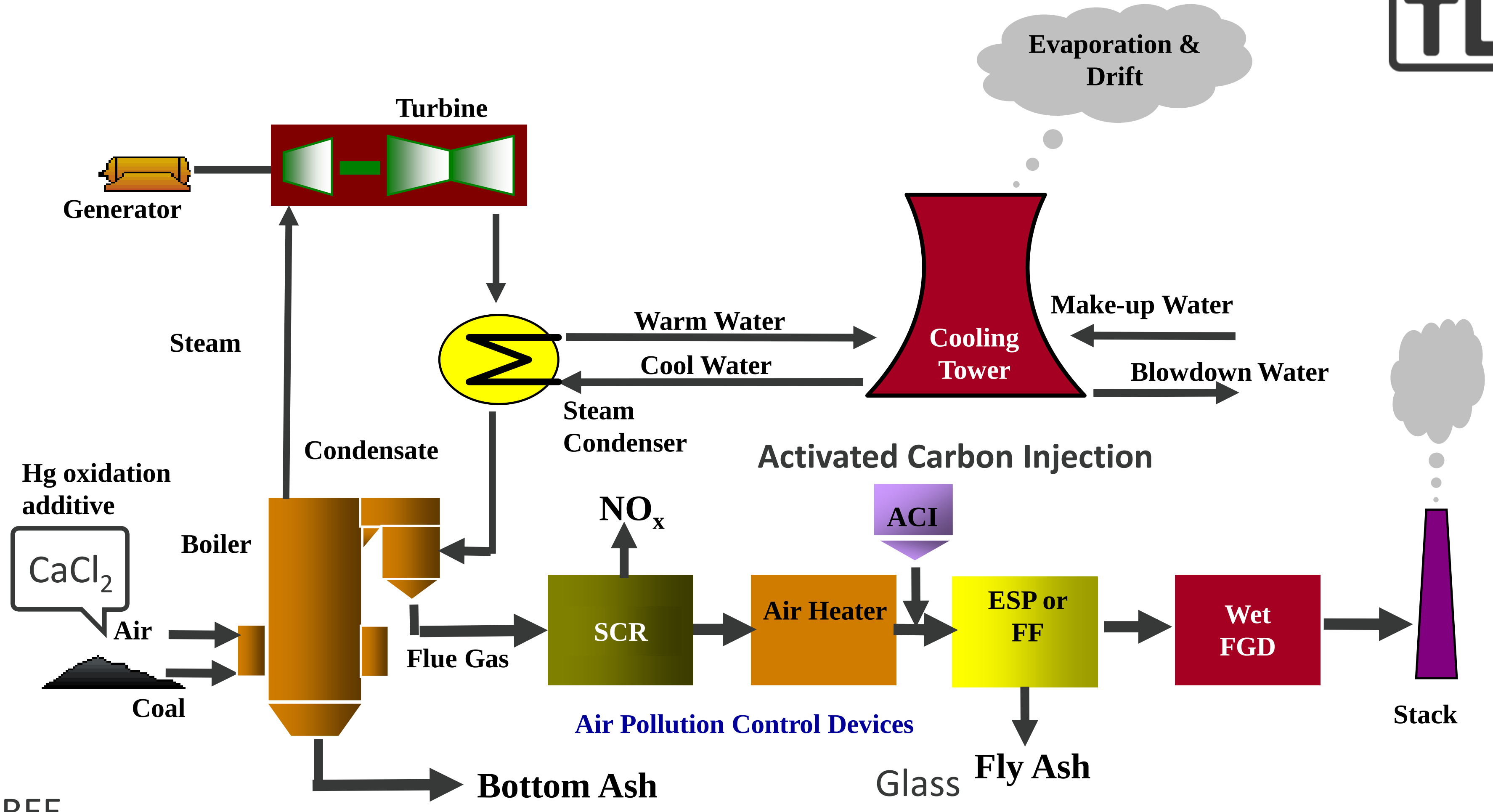
Disclaimer

Coal-Fired Power Plant Process Schematic

REE compounds are non-volatile and they concentrate in the ash.



Quartz
Kaolinite
Calcite
30-50 ppm REE

108-283 ppm REE

Glass
CaO (lime)
Ca perovskites ($CaTiO_3$)
Gehlenite ($Ca_2Al(Al,Si)O_7$)
Bit of quartz; apatite, mullite, MgO, $CaSO_4$
210-306 ppm REE

What reactions happen during combustion?

$CaCO_3 \rightarrow CaO + CO_2$

Quartz + Kaolinite → Glass

$3CaO + MgO + 2SiO_2 \rightarrow Ca_3MgSi_2O_8$
(Merwinite)

Feedstock materials

Partnership with Electric Power Research Institute (EPRI)

Coal, bottom ash, landfilled ash, ponded ash, fly ash samples were obtained.

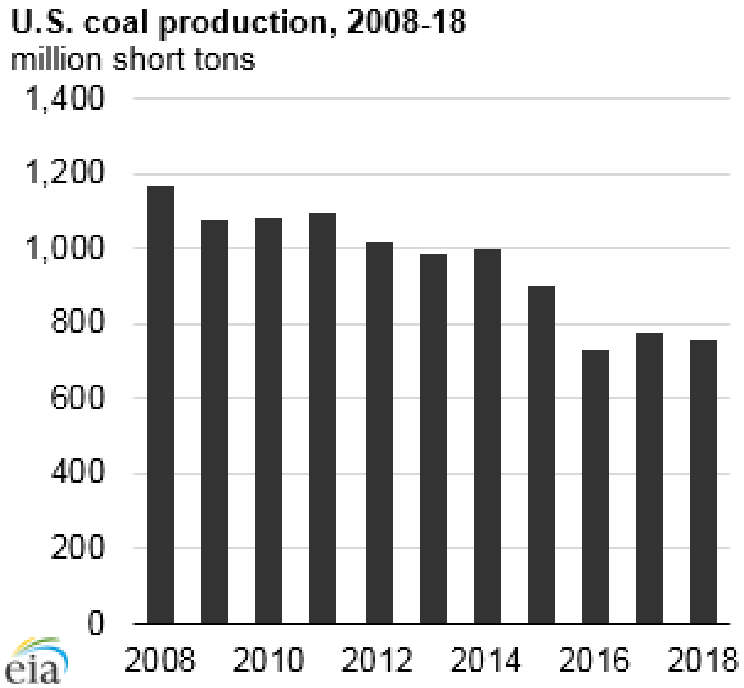
Sub-bituminous and bituminous parent coals

Sample ID	Type of Parent Coal	Origin of Parent Coal	d_{90} (μm)	REE	REY	REY+Sc
50185-FA	Sub-bituminous	PRB	26.2	210	243	265
50184-FA	Sub-bituminous	PRB	30.0	306	355	384
25428-FA	Sub-bituminous	PRB	28.1	262	301	327
50185-BA	Sub-bituminous	PRB	32.9	108	127	136
50184-BA	Sub-bituminous	PRB	87.8	247	290	313
25428-BA	Sub-bituminous	PRB	112	196	229	250
25428-CO	Sub-bituminous	PRB	91.6	20	24	26
25428-PA	Sub-bituminous	PRB	66.3	223	257	276
50185-LA	Sub-bituminous, bituminous	PRB,	96.2	277	322	345
25410-BA	Sub-bituminous, bituminous	PRB, Illinois Basin	153	238	278	302
25410-CO	Sub-bituminous, bituminous	PRB, Illinois Basin	90.0	18	22	25
25410-PA	Sub-bituminous, bituminous	PRB, Illinois Basin	35.9	213	251	273
35469-FA	Bituminous	Illinois Basin, CAPP, NAPP	33.5	271	325	358
35468-FA	Bituminous	Illinois Basin, CAPP, NAPP	61.6	279	344	379
35469-BA	Bituminous	Illinois Basin, CAPP, NAPP	133	283	333	364
35468-BA	Bituminous	Illinois Basin, CAPP, NAPP	466	265	321	354
35468-LA	Bituminous	Illinois Basin, CAPP, NAPP	52.5	256	313	340
35469-CO	Bituminous	Illinois Basin, CAPP, NAPP	115	30	36	39
35468-CO	Bituminous	Illinois Basin, CAPP, NAPP	113	20	24	26
35469-PA	Bituminous	Illinois Basin, CAPP, NAPP	44.0	281	335	364
35468-PA	Bituminous	Illinois Basin, CAPP, NAPP	38.4	278	342	372

Introduction

- **Typically Burn ~ 1 Billion Tons Coal/Yr Make Electricity (1990-2014)**

755 Million Tons Coal Produced in US in 2018

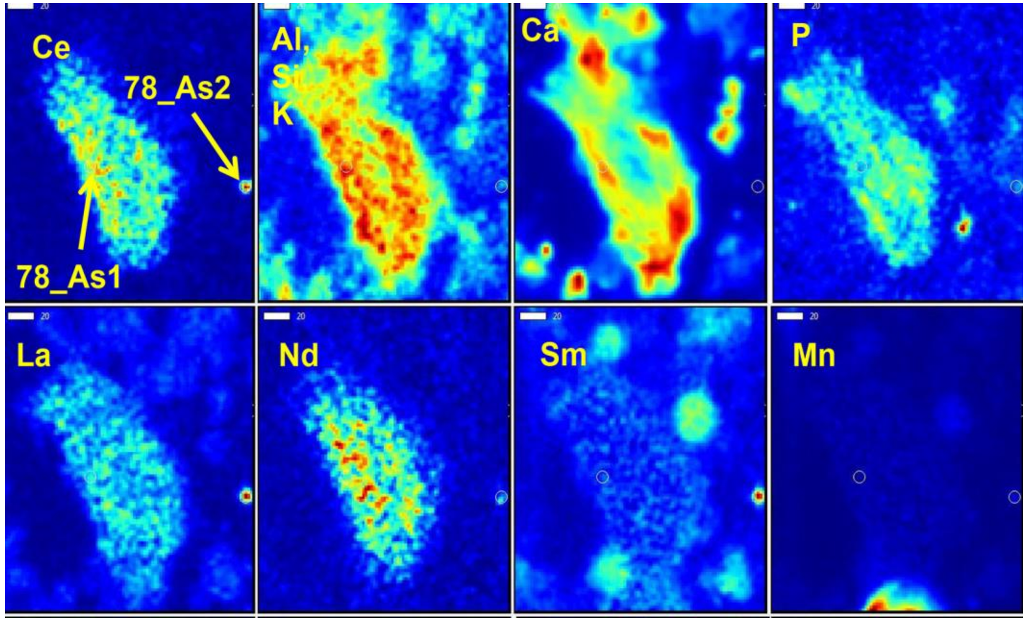


Introduction

Rare earth elements (REEs) present in minerals in ash derived from sub-bituminous coal from Powder River Basin, either as single particles or evenly distributed throughout Al-Si-Ca matrix.

REEs have been successfully recovered from ash derived from sub-bituminous coal from Powder River Basin.

Taggart et al (2016) used strong acid (15 M HNO_3) to recover 50-90% REE from the coal ash samples.



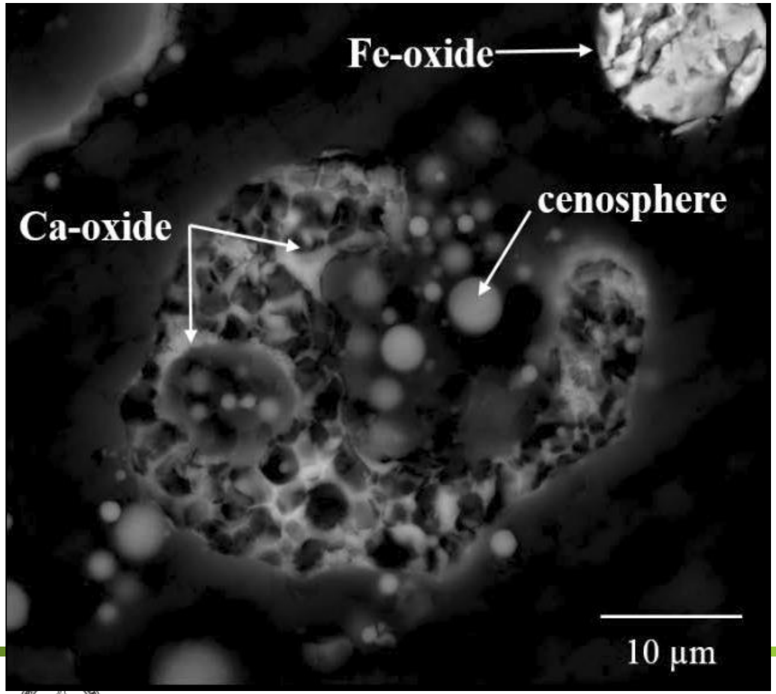
Why is it so hard to recover REE from ash?

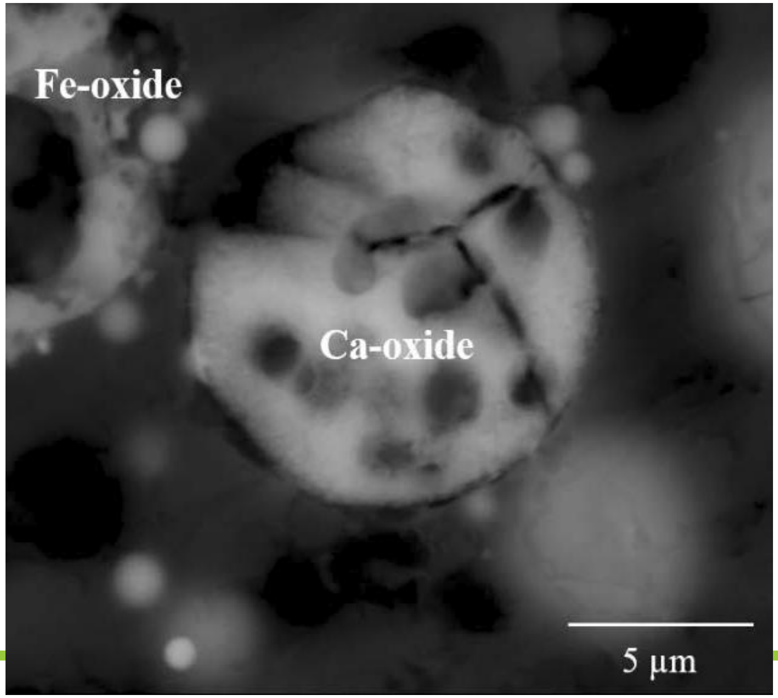
Case study of UN 345 ash (bituminous, low-Ca ash)

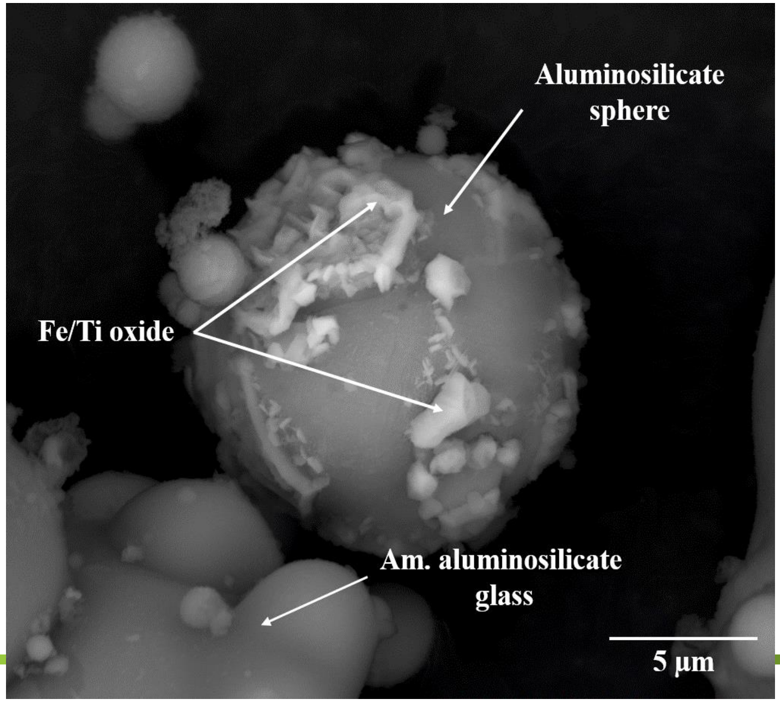
Main species present in UN 345 ash are mullite and quartz, with some hematite and magnetite present (Montross, Ronghong). Amorphous glass phase is 60-70%.

Show how the matrix changes, and Al-Si glass is much harder than kaolinite or another kind of matrix.

REEs are primarily associated with Al-Si glass phase in ash derived from bituminous coals; their low extractability of Al, Si prevents liberation and dissolution of the REEs in acid.

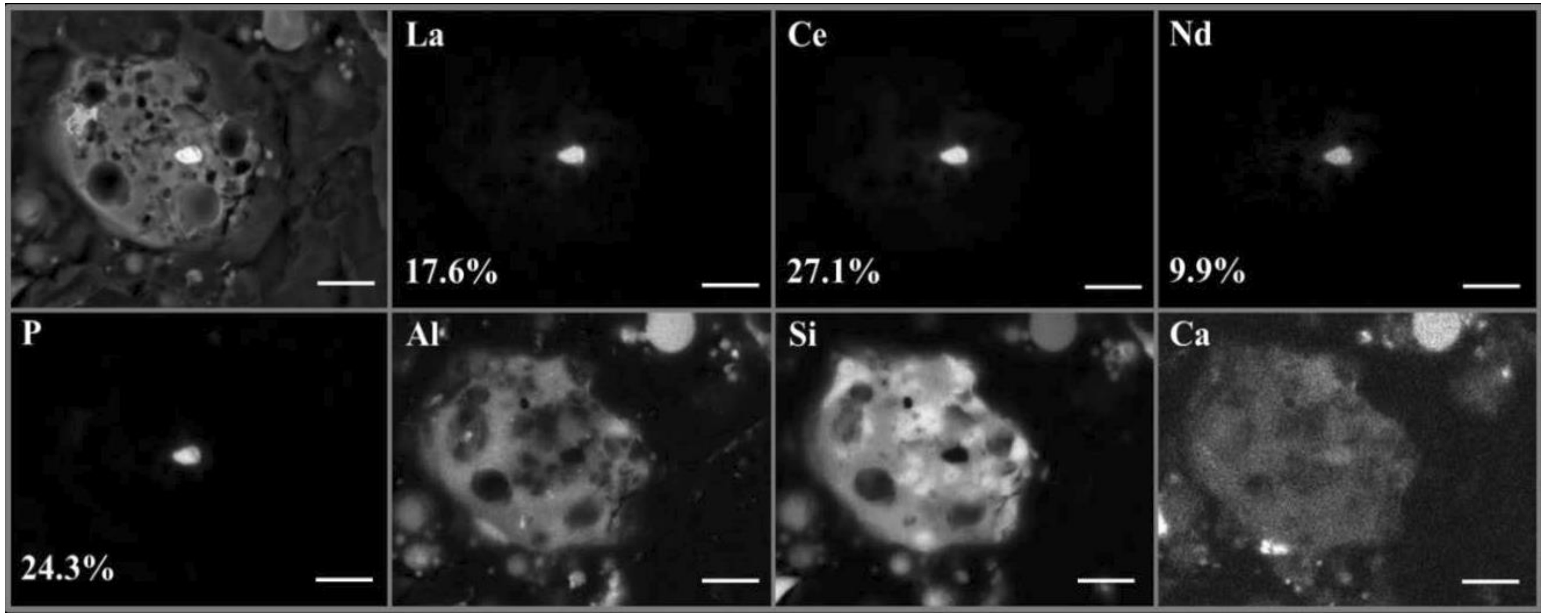






Some matrix minerals dissolve more easily than others

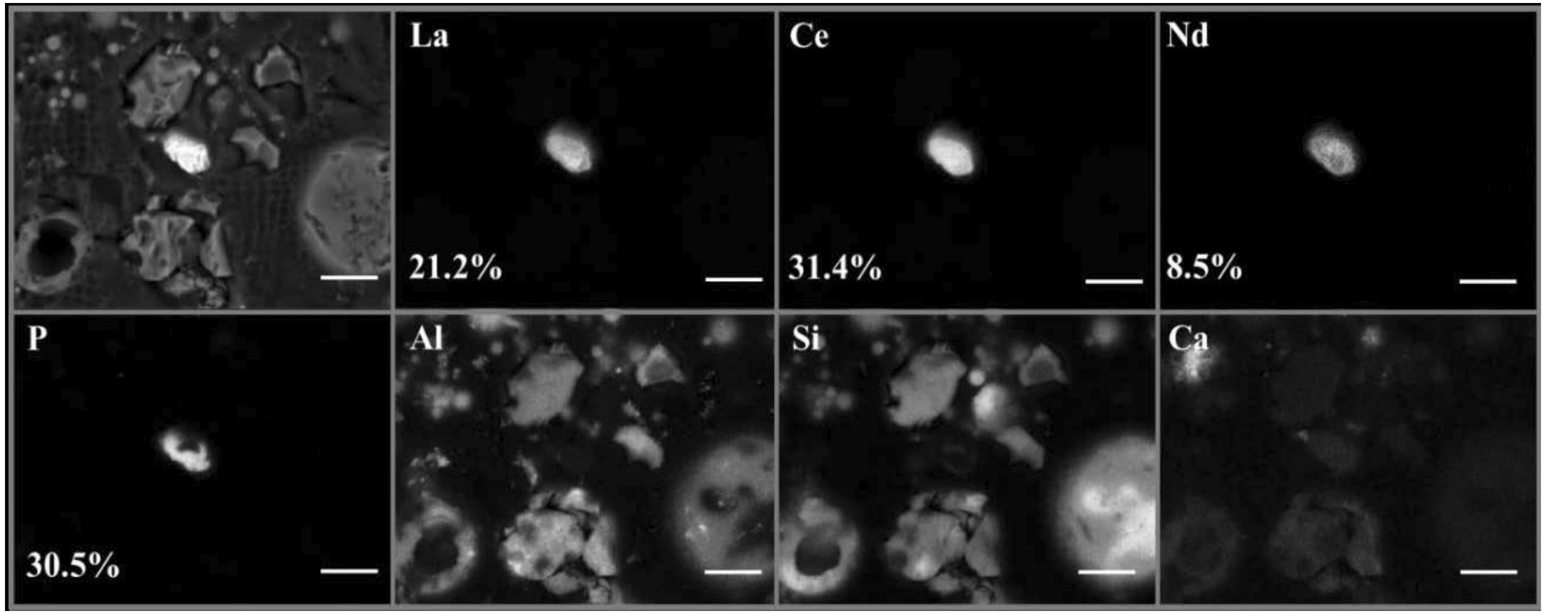
Previous work (Montross 2017, Lin 2018, Stuckman 2018) shows that REE primarily associate with the amorphous Al-Si glass phase in ash derived from bituminous coal.

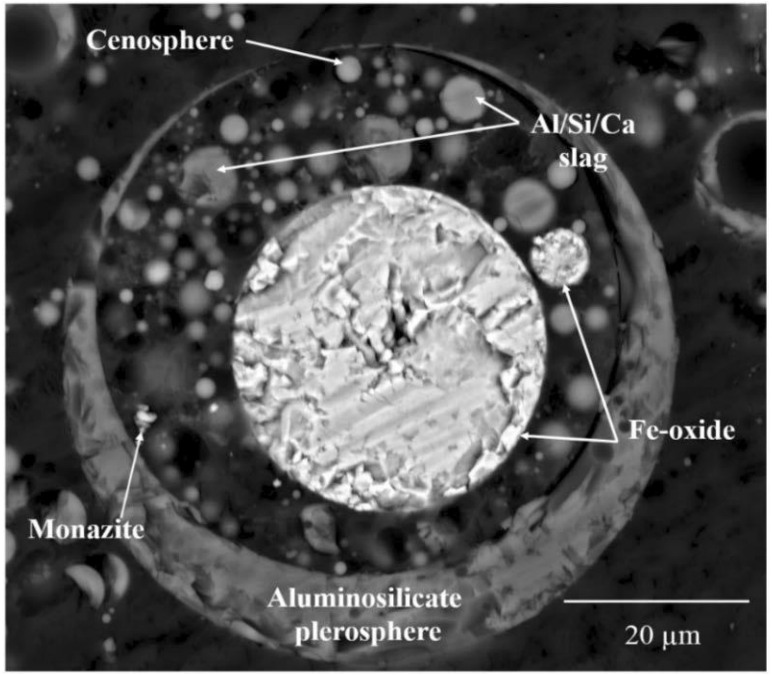


Montross 2017

Some matrix minerals dissolve more easily than others

REEs not encapsulated in the Al-Si phase exist as (La, Ce, Nd)PO_4, monazite, which is not very responsive to the acid.





Free monazite crystal within a bituminous fly ash

Montross, 2017

Introduction

Feedstock	Extractant	RE Recovery	L:S		Reference
Hagel B lignite	1.0 M HCl 0.1 M HCl	85-90% (28% Sc) 10% (10% Sc)	2	40° C, 48 h; REEs in mineral specks or organically associated.	
Hagel B lignite	0.5 M H_2SO_4 0.1 M H_2SO_4	62-82% 1-5%	2	40° C, 48 h; HREE recovery slightly more favored than LREE recovery	
Carbonaceous clay	1.0 M HCl 0.1 M HCl	41-69% 20-25%	2	40° C, 48 h	
Carbonaceous clay	1.0 M H_2SO_4 0.1 M H_2SO_4	40-60% 22-30%	2	40° C, 48 h	
Coarse refuse	~1 mM H_2SO_4 1.2 M H_2SO_4	8-18% 25-70%	8.5	75° C; 1-24 h; Quartz, kaolinite, illite, pyrite, calcite, dolomite dominant	
Fly ash	15 M HNO_3	15-90%	25-125	85-90° C, 4 h; High REE recovery in high-Ca ash of sub-bituminous coal	
Japanese Fly ash	2 M H_2SO_4	11-28%	100	30° C, 2 h; REE recovery rises wrt Ca	
Japanese Fly ash	2 M H_2SO_4	28-45%	100	80° C, 2 h; REE recovery rises wrt Ca	

Some matrix minerals dissolve more easily than others

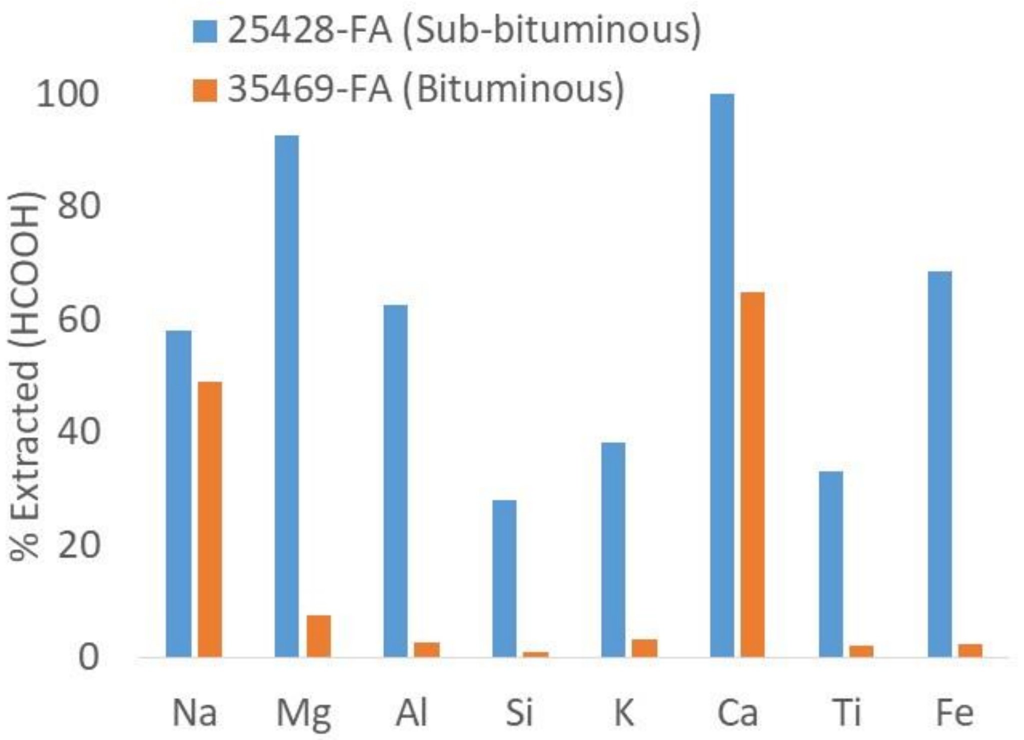
REE in bituminous coal primarily associate with amorphous Al-Si glass, which is resistant to even concentrated acid.

Previous work (2018) shows that REE in sub-bituminous ash associate with $CaTiSiO_5$ and possibly CaO as well as Al-Si.

This result is consistent with hypothesis of Kolker et al (2016), who posited that sub-bituminous PRB coal contains Ca- and Fe-bearing aluminosilicates in which REE may be more numerous AND more extractable than unsubstituted Al-Si.

HCOOH effectively dissolves many sub-bituminous ash matrix minerals, even solubilizing ~ 30 wt% Si.

These results suggest that REE recovery from sub-bituminous coals will be significantly greater than from bituminous coals.



dissolve more easily than others

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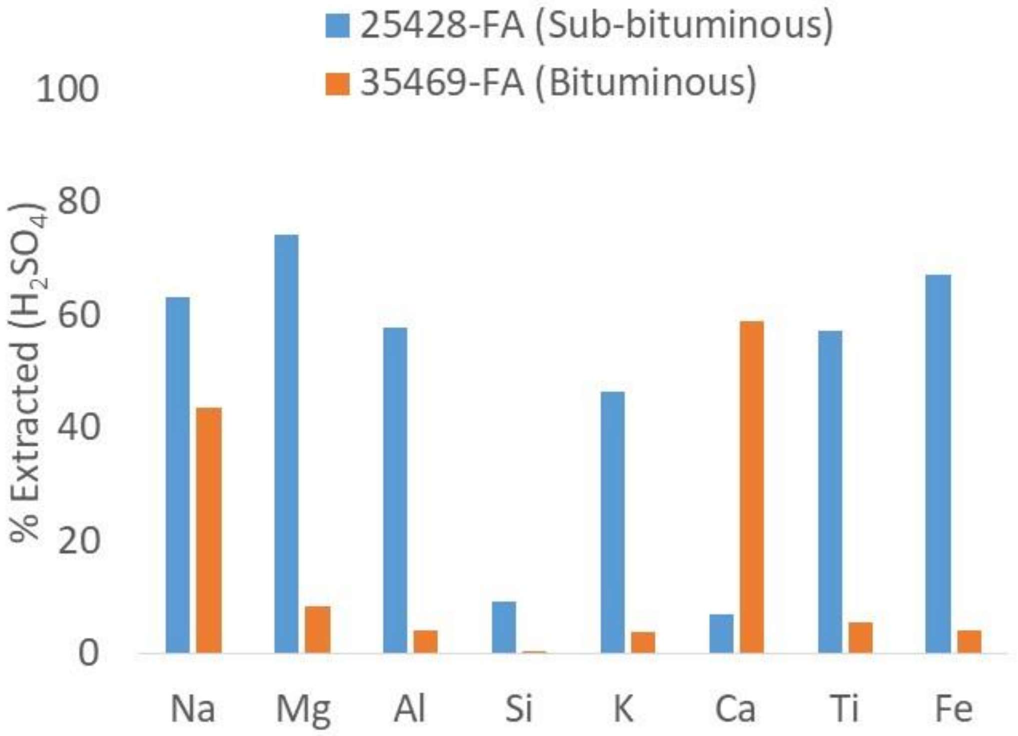
H2SO4 effectively dissolves many sub-bituminous ash matrix minerals, but only 5-10 wt% Si, Ca.

Even so, the greatly increased Al and Fe recovery relative to the bituminous 35469-FA suggest that using H2SO4 to recover REE from sub-bituminous coals will produce significantly greater REE yields than from bituminous coals.



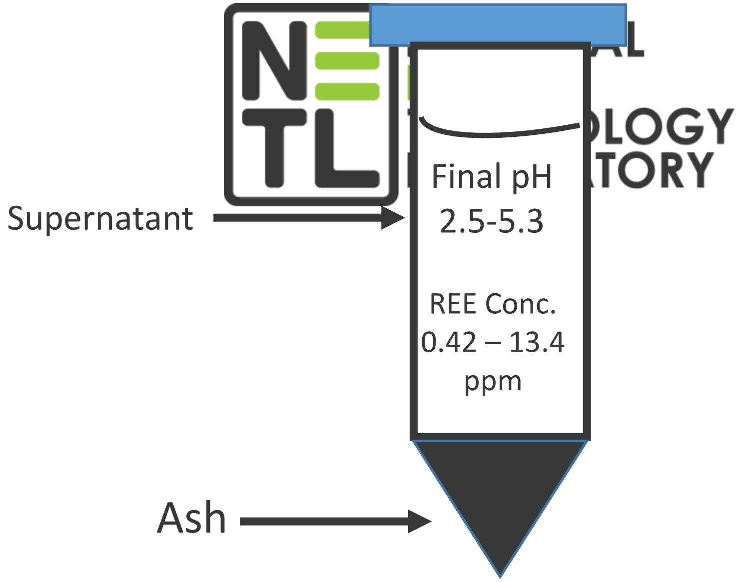
Numbers next to data points represent final equilibrium pH of supernatant

pH must be lower than ~5 to recover appreciable amounts of rare earths

Ideally, the initial amounts of acid and ash present should be 1:1 or there should be an excess of acid.

A final pH in the range 2.5 – 4.5 is desirable because it is easier to process the leachate to produce a rare-earth rich solid.

Previous work by Honaker shows that rare earths precipitate out of solution above pH 5 when sulfates are present.



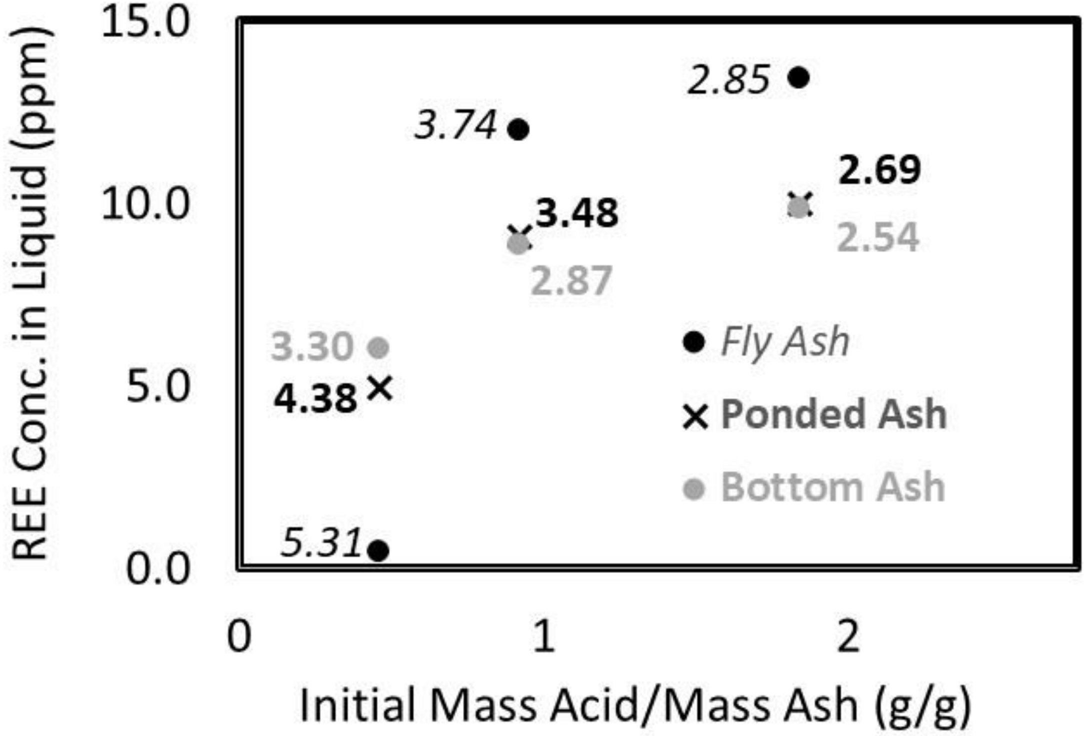
Supernatant

Final pH
2.5-5.3

REE Conc.
0.42 – 13.4
ppm

Ash

Extractions carried out in centrifuge vial, inverted ~ 30x per minute for 20 hours.
Ash and supernatant separated by centrifugation for ~20 minutes.



Extractions carried out in centrifuge vial, inverted ~ 30x per minute for 20 hours.

2 M HCOOH

Ash and supernatant separated by centrifugation for ~20 minutes.

pH must be lower than ~5 to recover appreciable amounts of rare earths

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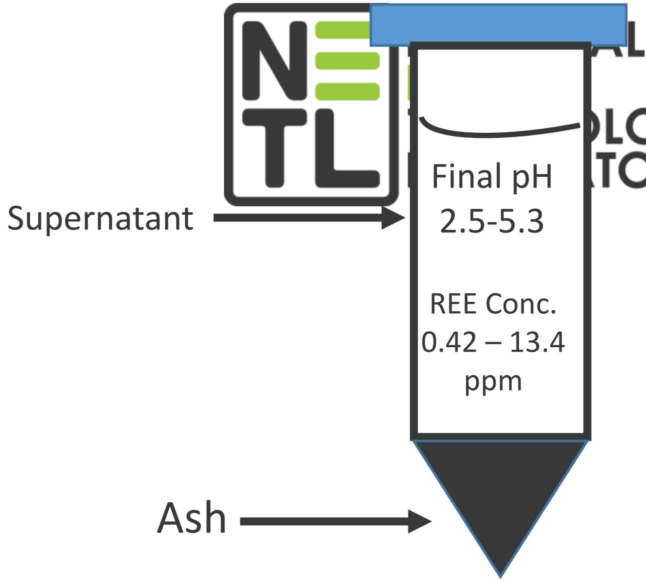
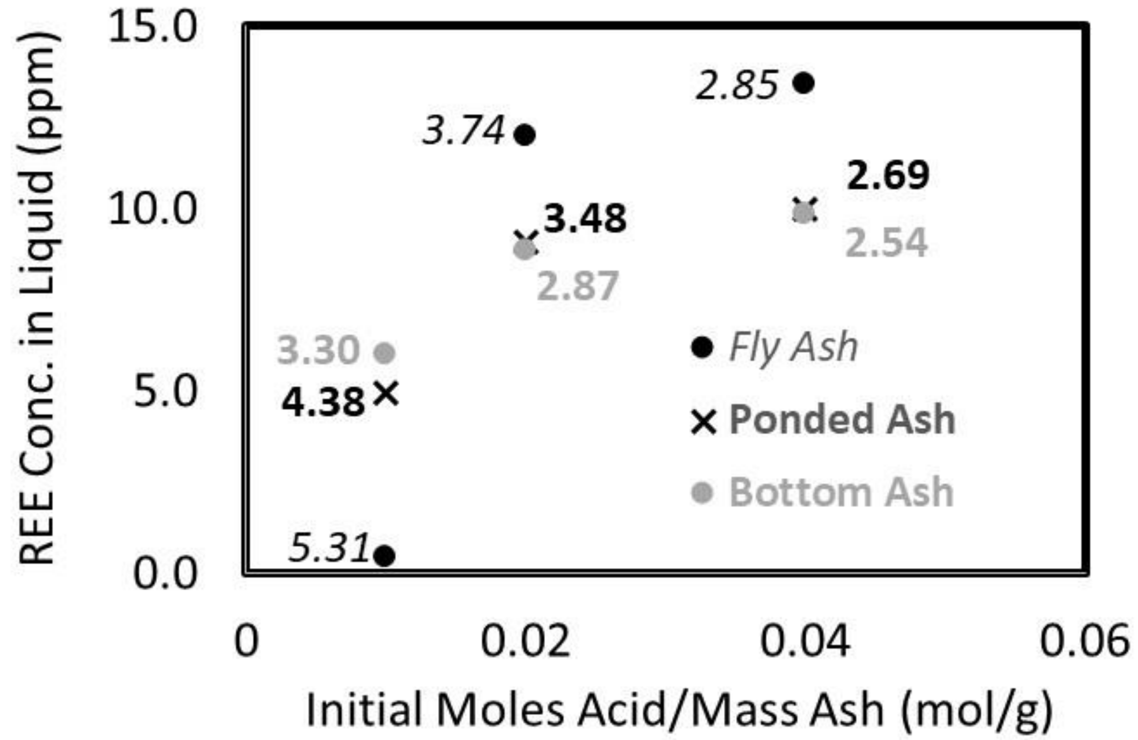

Supernatant

Final pH 2.5-5.3

REE Conc. 0.42 – 13.4 ppm

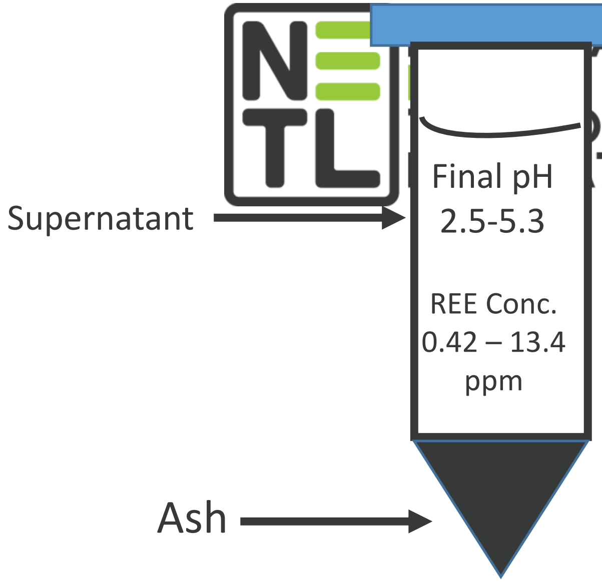
Ash

Final pH of supernatant indicated next to each data point.



Extractions carried out in centrifuge vial, inverted ~ 30x per minute for 20 hours.
Ash and supernatant separated by centrifugation for ~20 minutes.

If 0.02 moles acid/mass ash (corresponds to 1 M HCOOH per 2 grams ash at 20:1 mass ratio), recovery of REE from fly ash, ponded ash, bottom ash similar (62-75%)

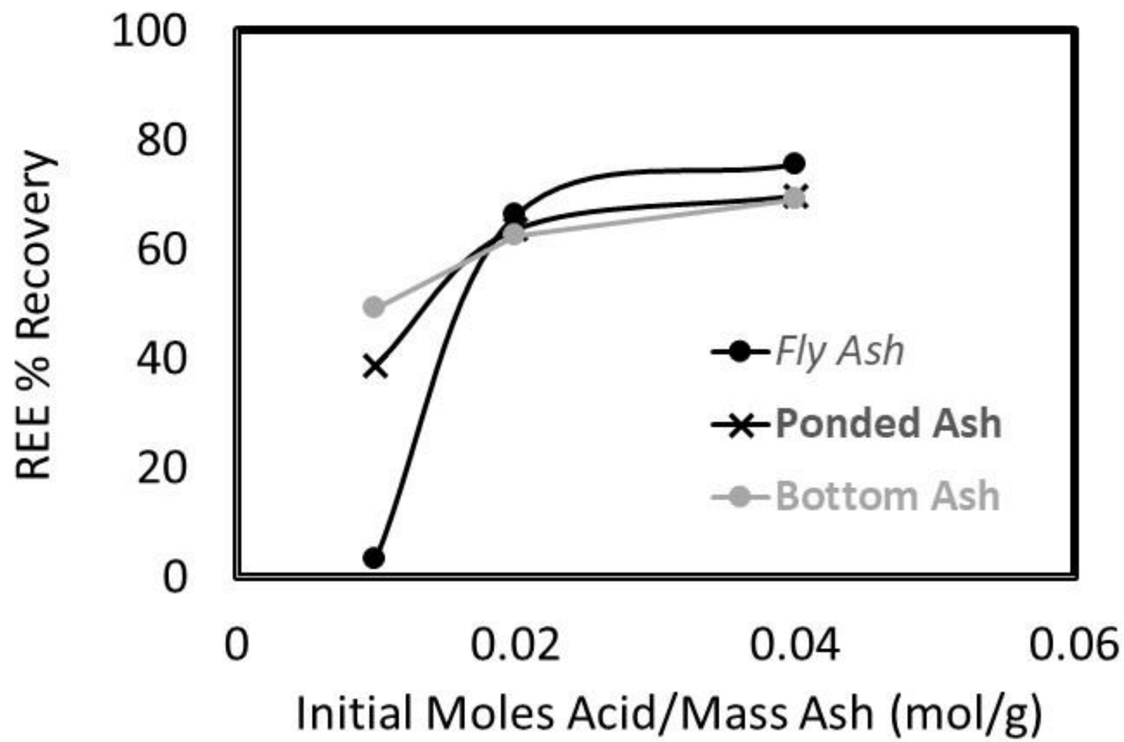


Supernatant

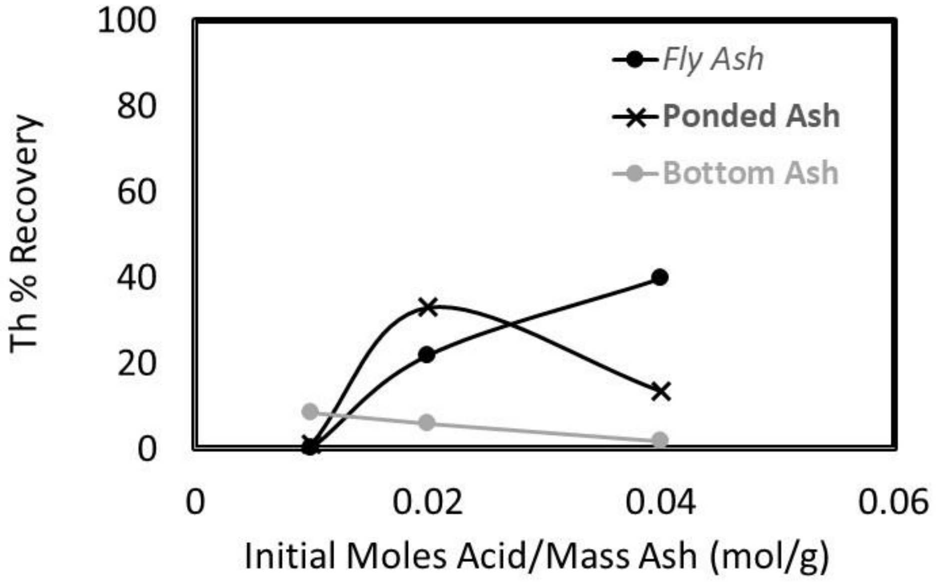
Final pH
2.5-5.3

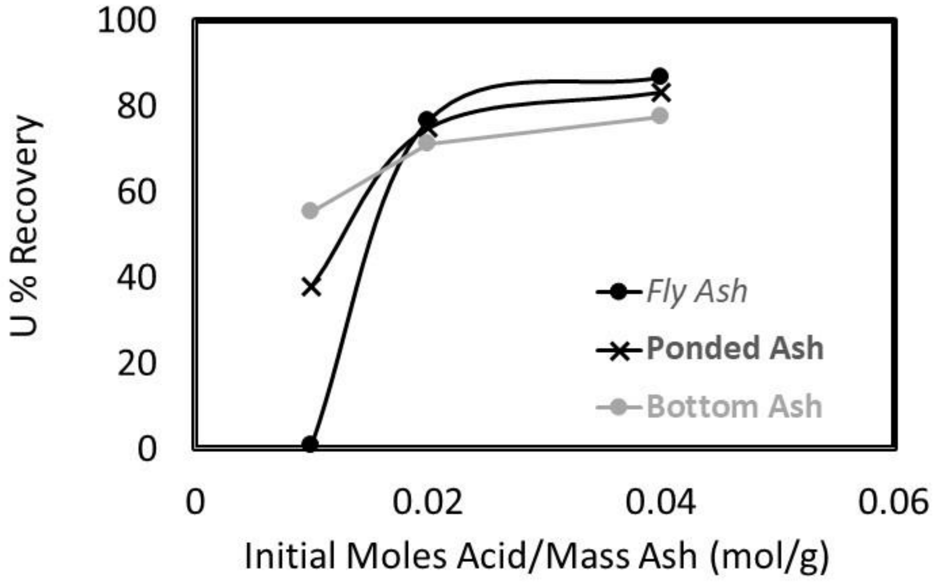
REE Conc.
0.42 – 13.4
ppm

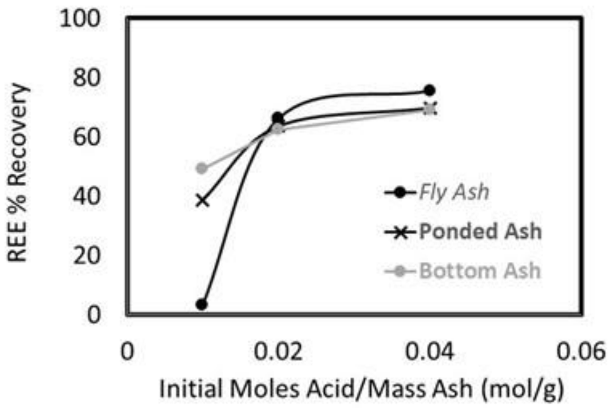
Ash



Th, U Recovery vs REE Recovery





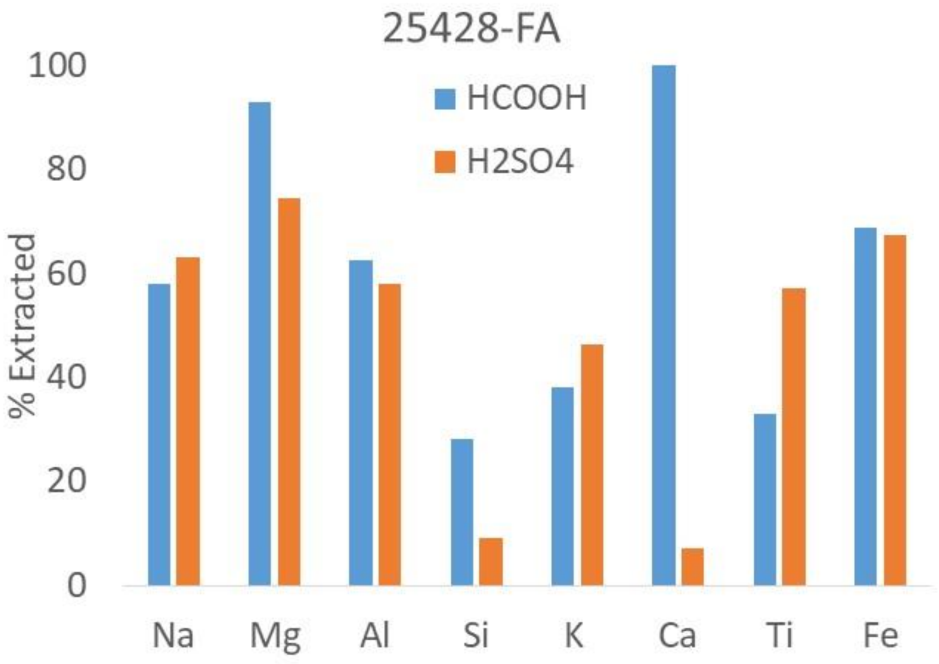


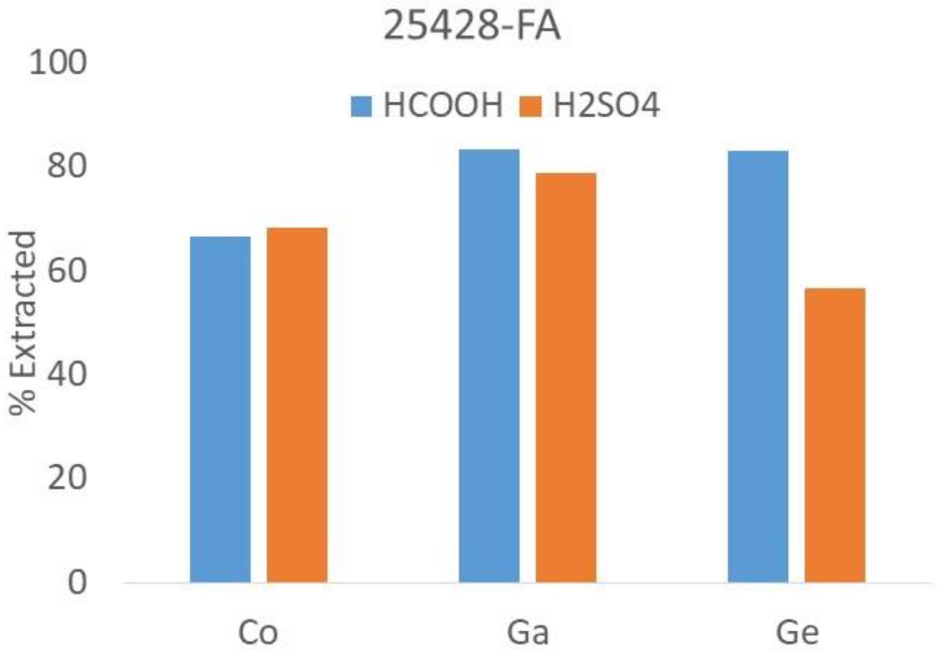
Extraction of Co, Ga, Ge from Fly Ash

Sub-bituminous fly ash – HCOOH and H_2SO_4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

However, Ca solubility is much greater in HCOOH than H2SO4.

Co, Ga, Ge solubility correlated with solubility of Mg, Al, K – likely they are not associated with the Ca-bearing species in fly ash.



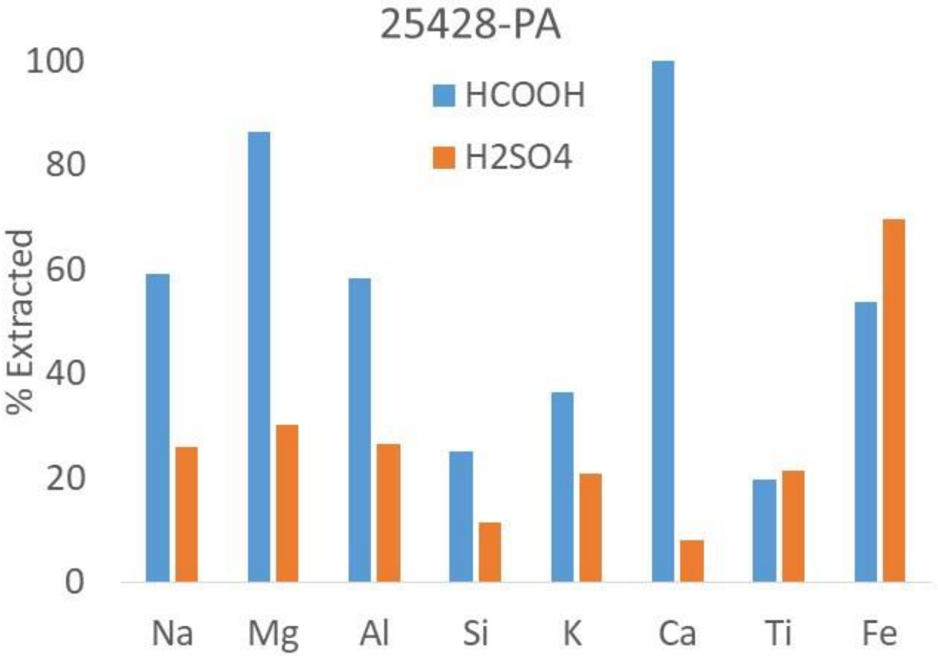


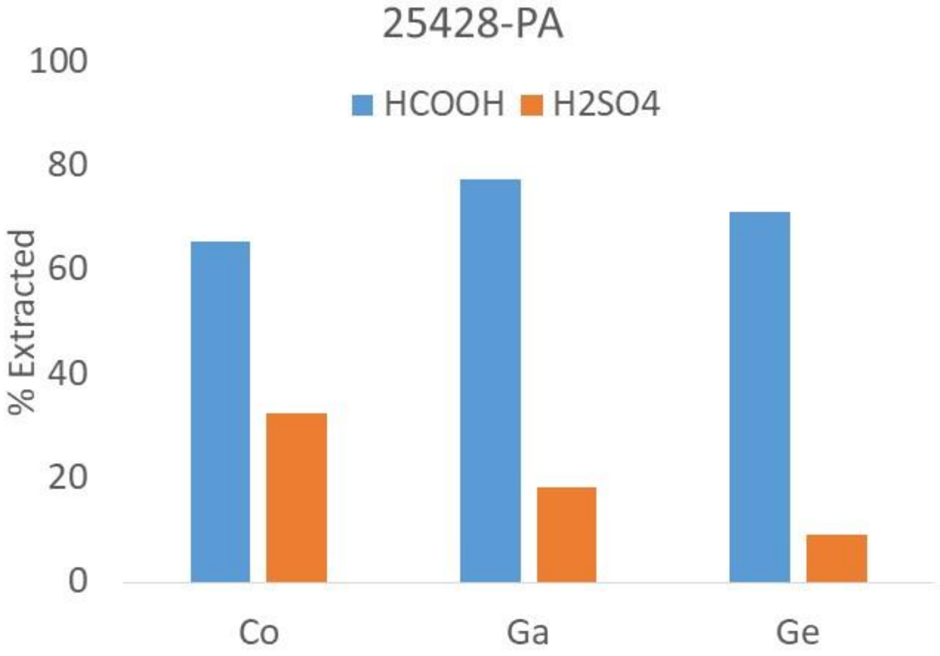
Extraction of Co, Ga, Ge from Ponded Ash

Sub-bituminous fly ash – HCOOH and H_2SO_4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

However, Ca solubility is much greater in HCOOH than H_2SO_4.

Co, Ga, Ge solubility correlated with solubility of Mg, Al, K – likely they are not associated with the Ca-bearing species in ponded ash.



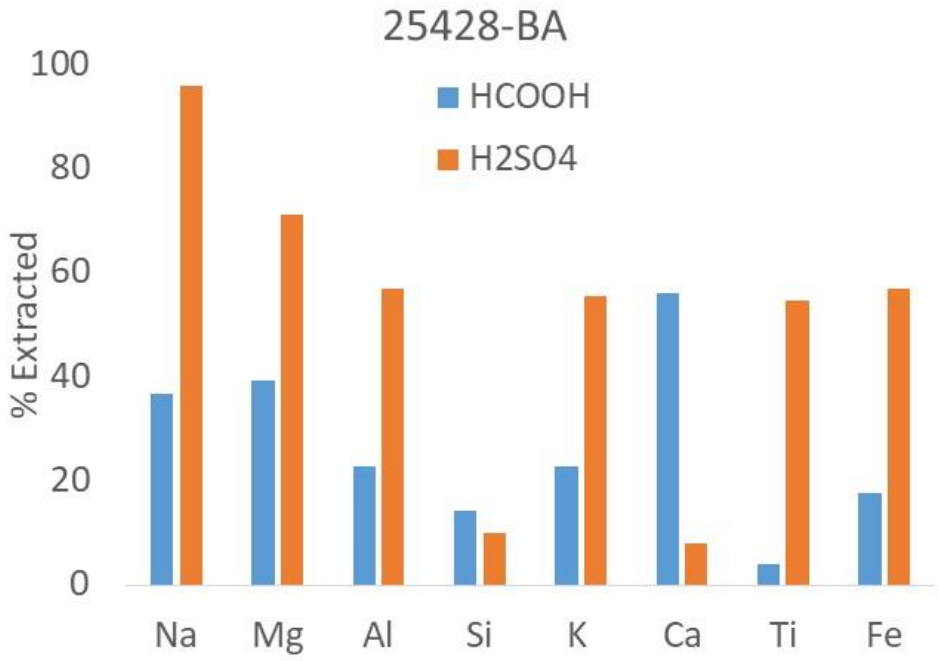


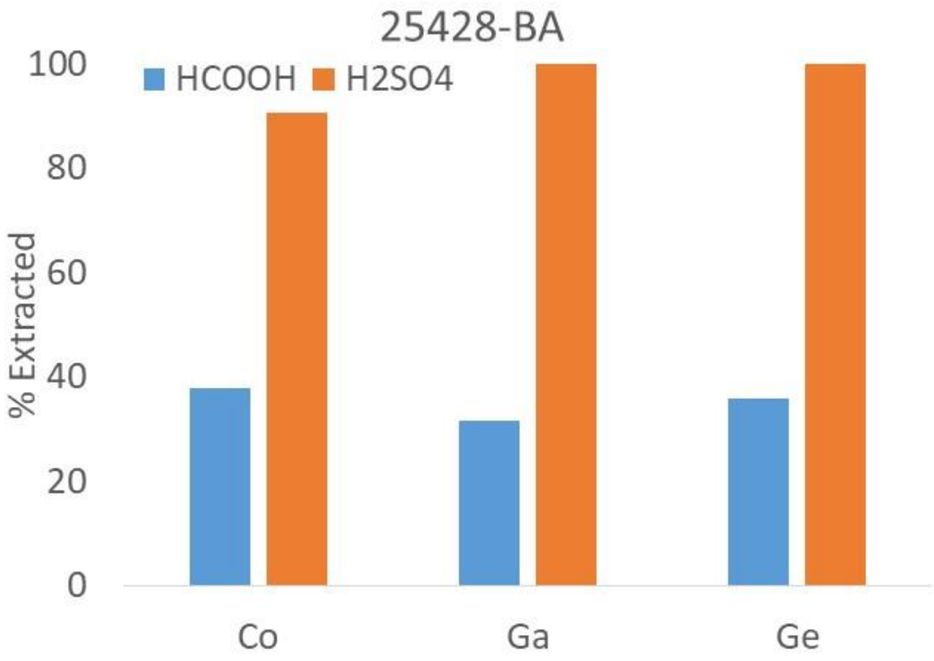
Extraction of Co, Ga, Ge from Bottom Ash

Sub-bituminous fly ash – HCOOH and H_2SO_4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

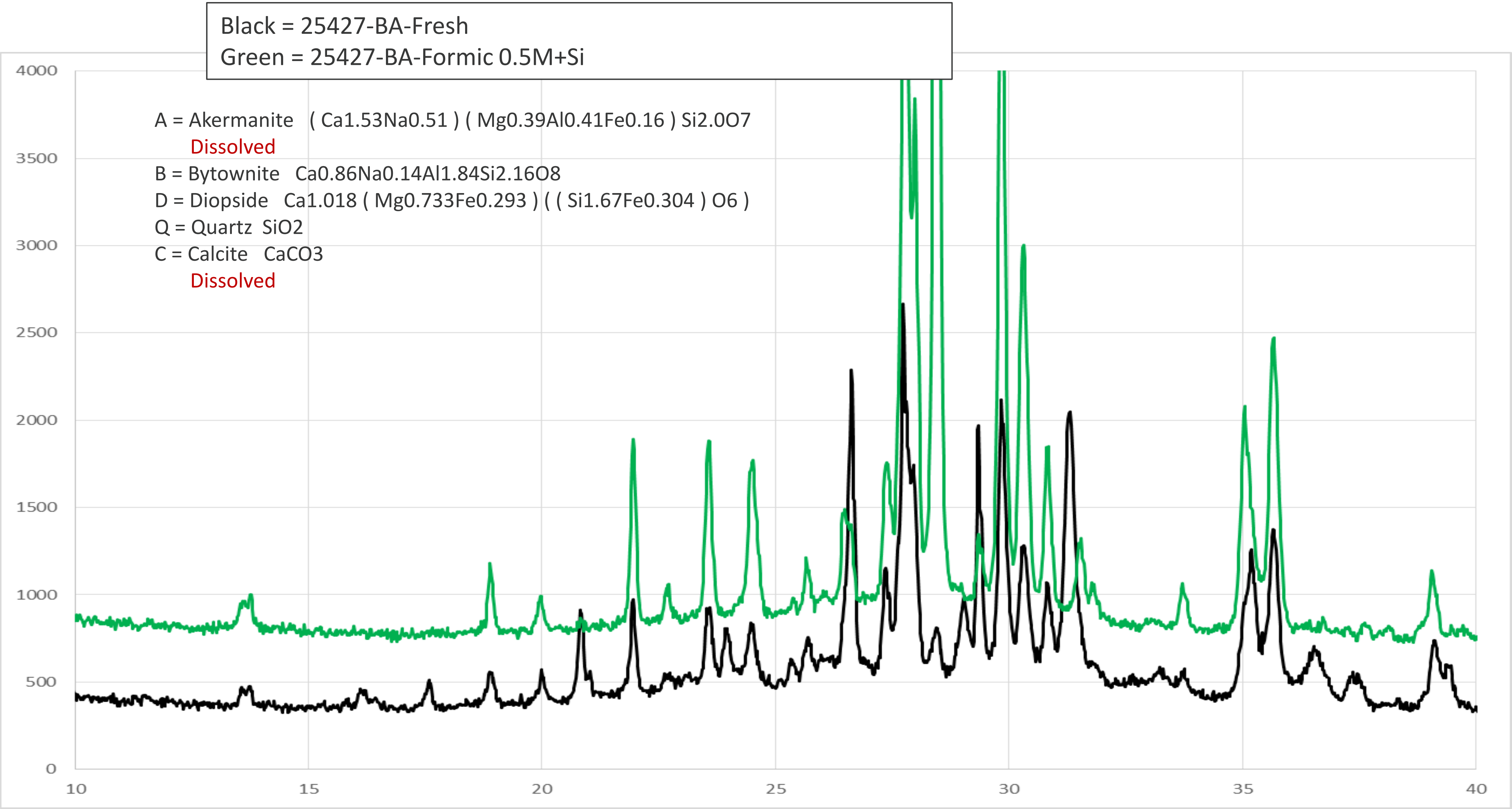
However, Ca solubility is much greater in HCOOH than H2SO4.

Co, Ga, Ge solubility correlated with solubility of Mg, Al, K – likely they are not associated with the Ca-bearing species in bottom ash.





XRD Evidence- High-Ca Silicates Dissolve in 2 M Formic Acid!!!



Black = 25427-BA-Fresh
Green = 25427-BA-Formic 0.5M+Si

A = Akermanite (Ca1.53Na0.51) (Mg0.39Al0.41Fe0.16) Si2.0O7
Dissolved
B = Bytownite Ca0.86Na0.14Al1.84Si2.16O8
D = Diopside Ca1.018 (Mg0.733Fe0.293) ((Si1.67Fe0.304) O6)
Q = Quartz SiO2
C = Calcite CaCO3
Dissolved