Effect of Extractive Agent and Ca Content on Extractability of Rare Earth Minerals from Ca-Rich Coal Ash

Ward Burgess[1,2], Megan Macala[1,2], Catherine Spencer[1], Bret Howard[1], Murphy Keller[1], Ken Ladwig,[3] Evan Granite[1]

[1]National Energy Technology Laboratory
[2]Leidos Research Support Team
[3]Electric Power Research Institute

Pittsburgh Coal Conference
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Solutions for Today | Options for Tomorrow

Outline

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

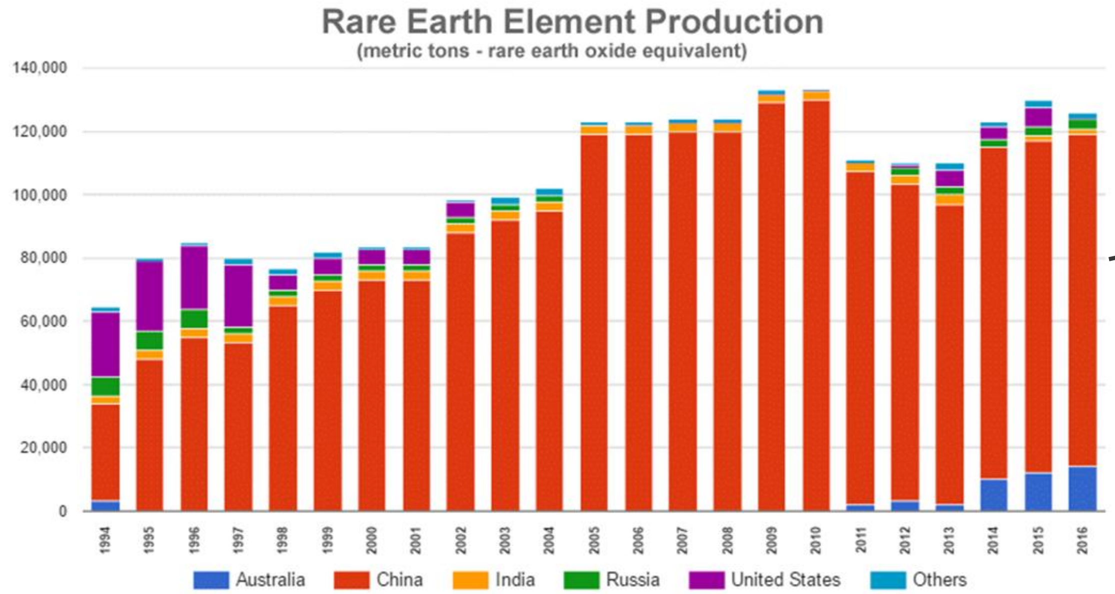
Introduction – Need for Domestic Rare Earth Element (REE) Sources

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



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

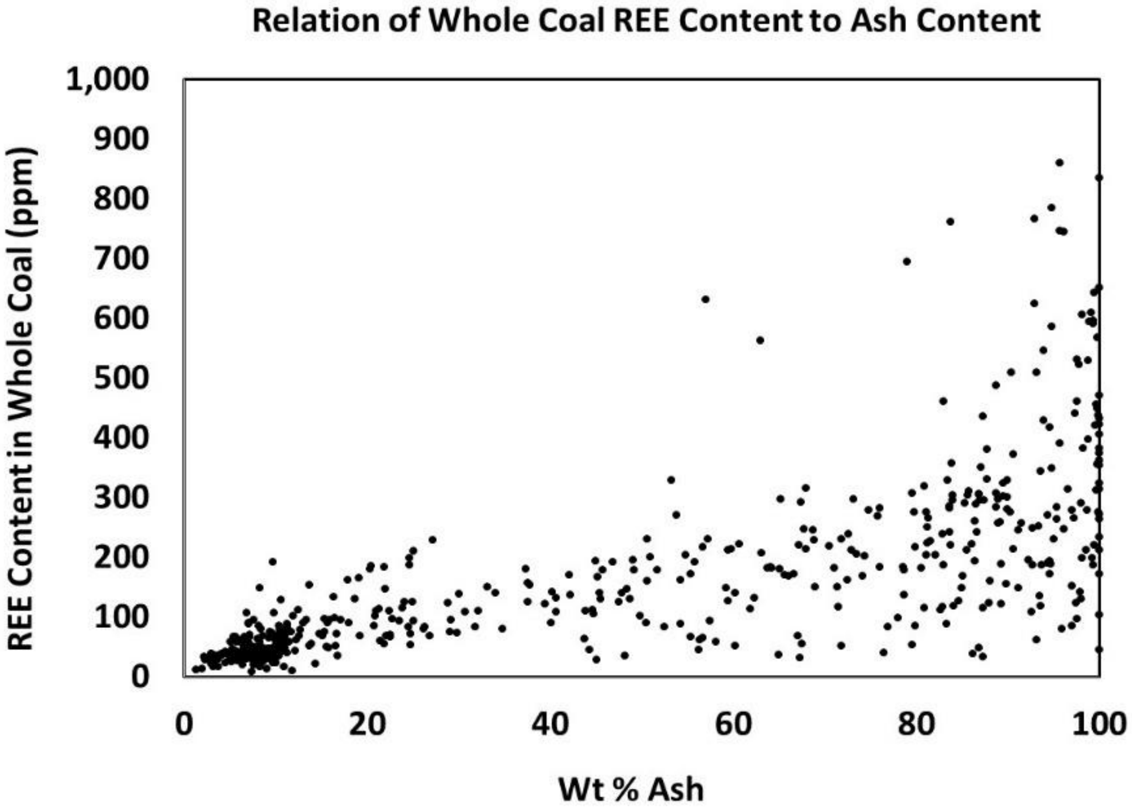
In 2016, the <u>US imported 100% of our REEs (16,000 metric tons mostly from China)</u>

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

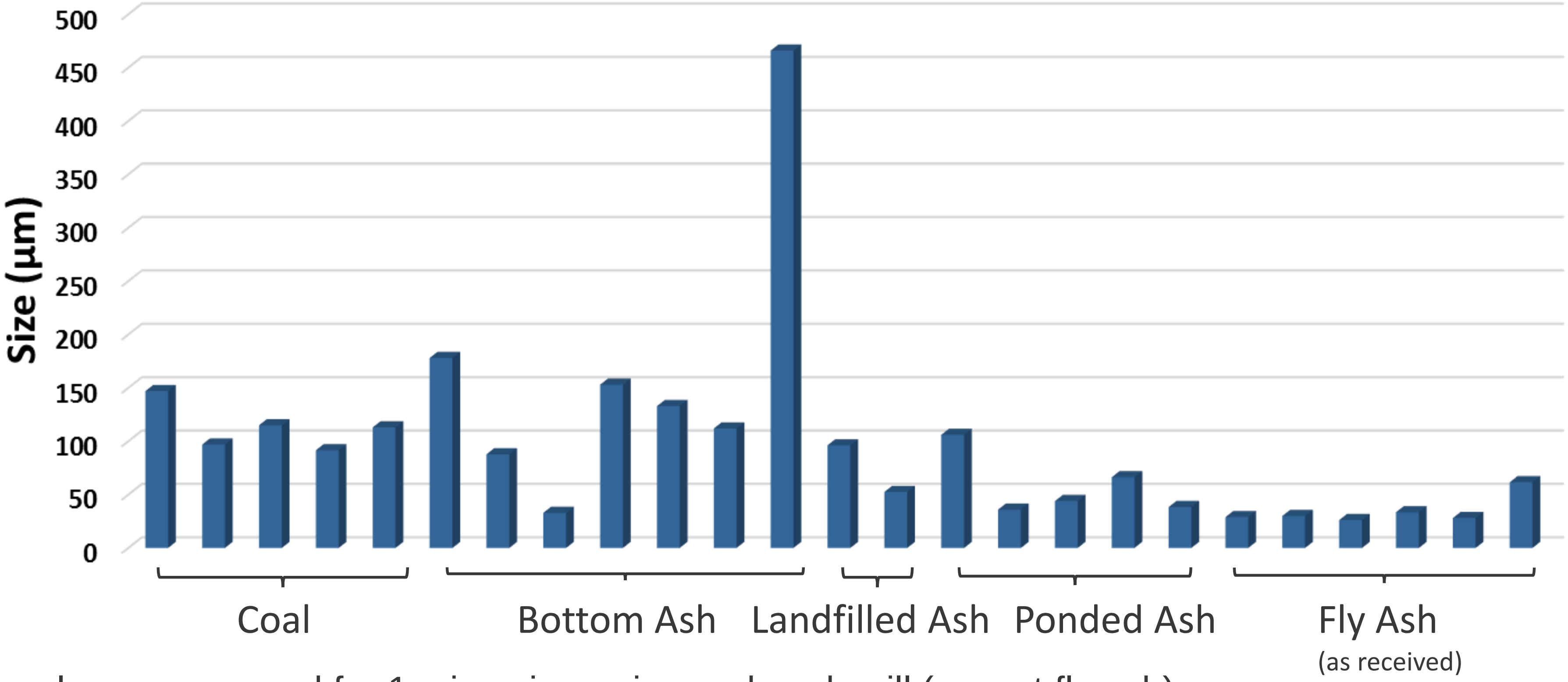


Feedstock materials

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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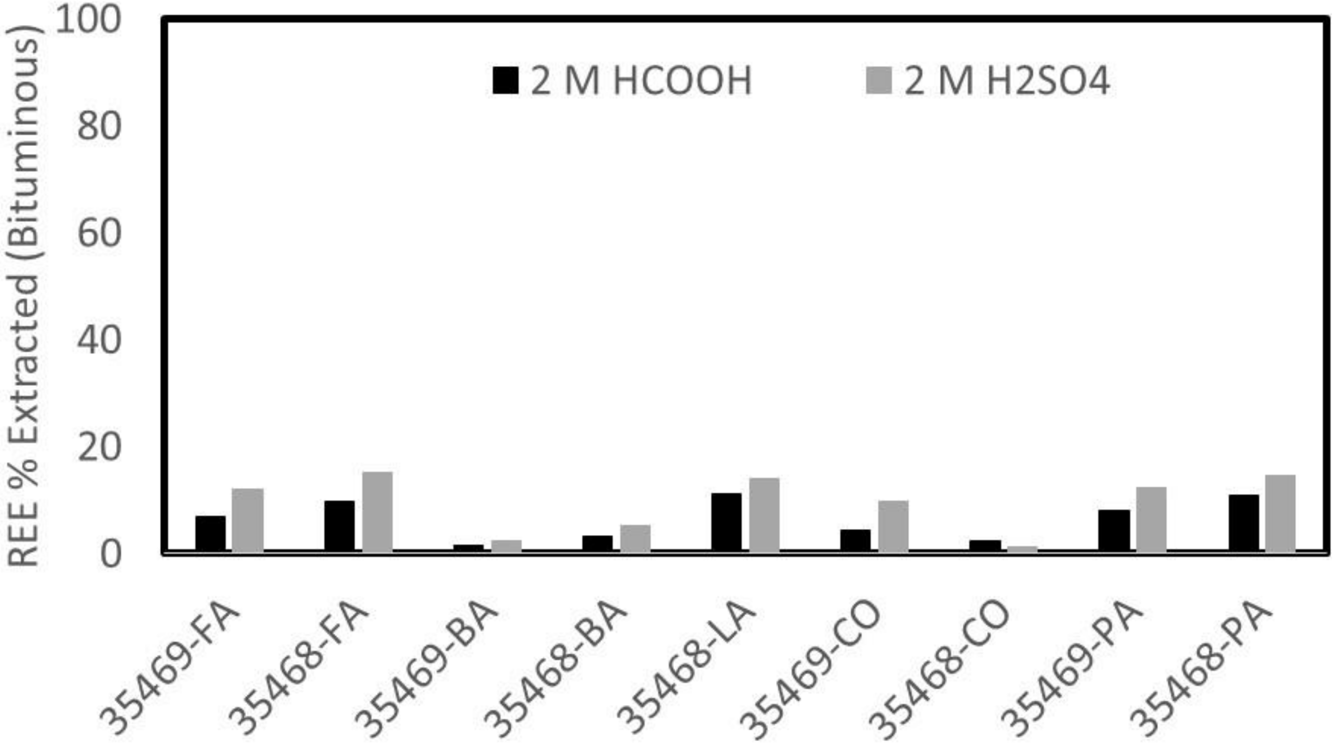
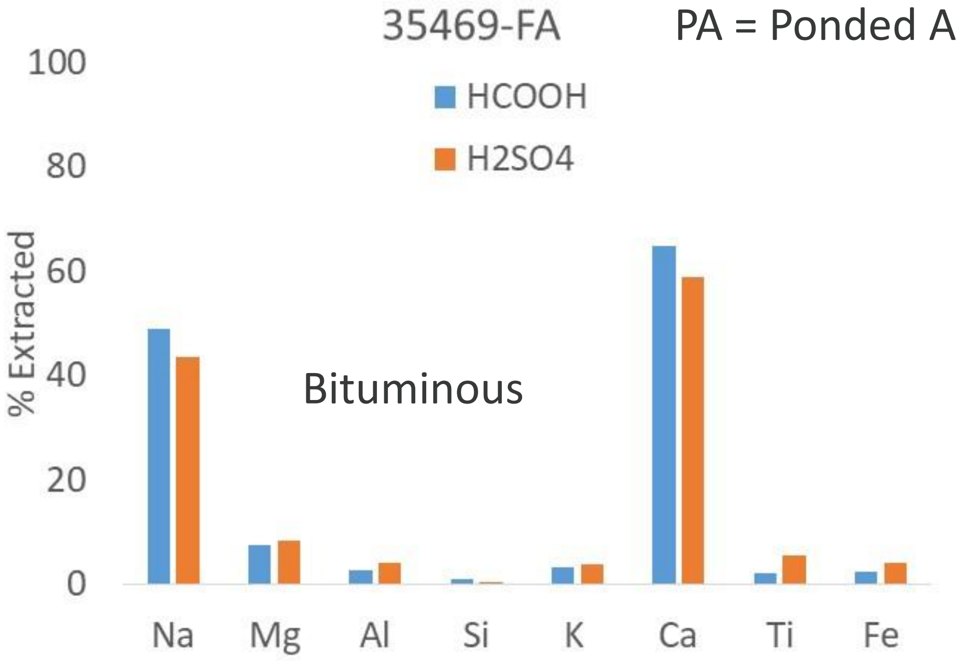
Minimal Recovery of REE from Bituminous Coals, Ash

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.

FA = Fly Ash
BA = Bottom Ash
CO = Coal
LA = Landfilled Ash
PA = Ponded Ash

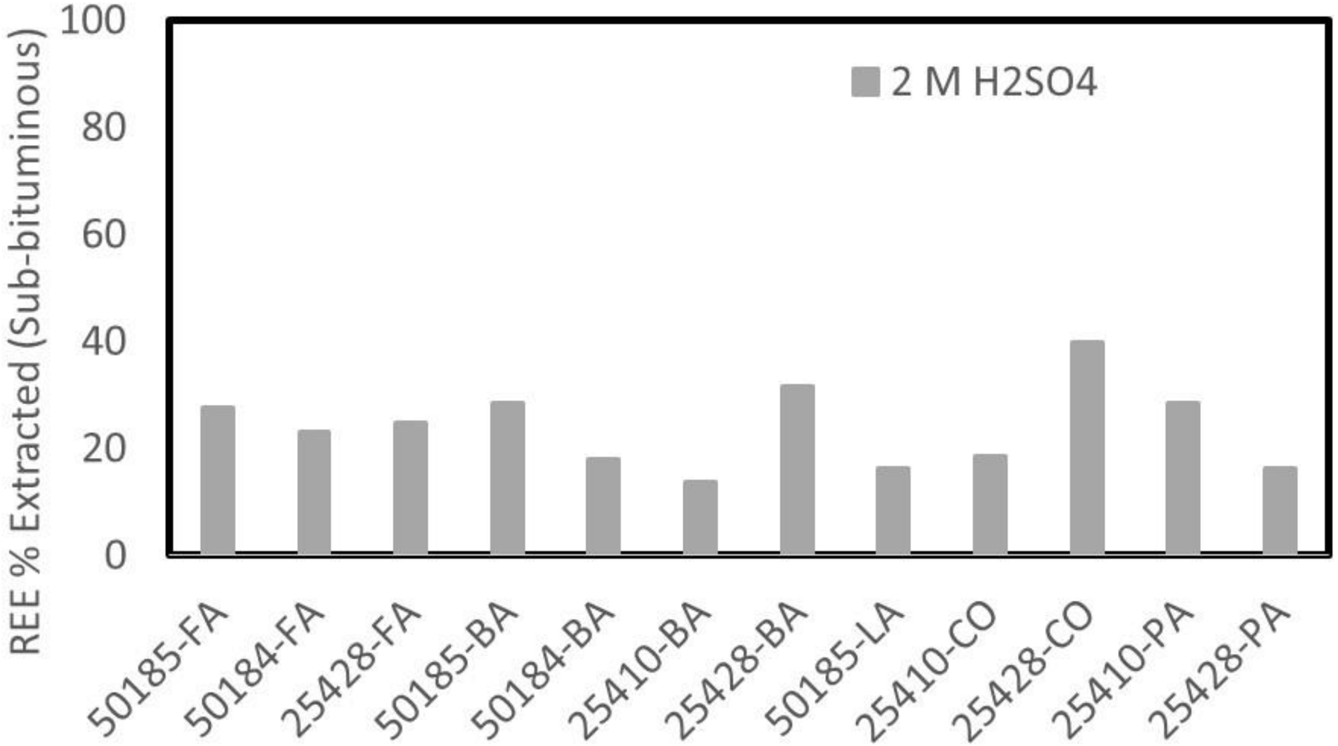




Modest REE recovery from sub-bit coal with H_2SO_4

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.



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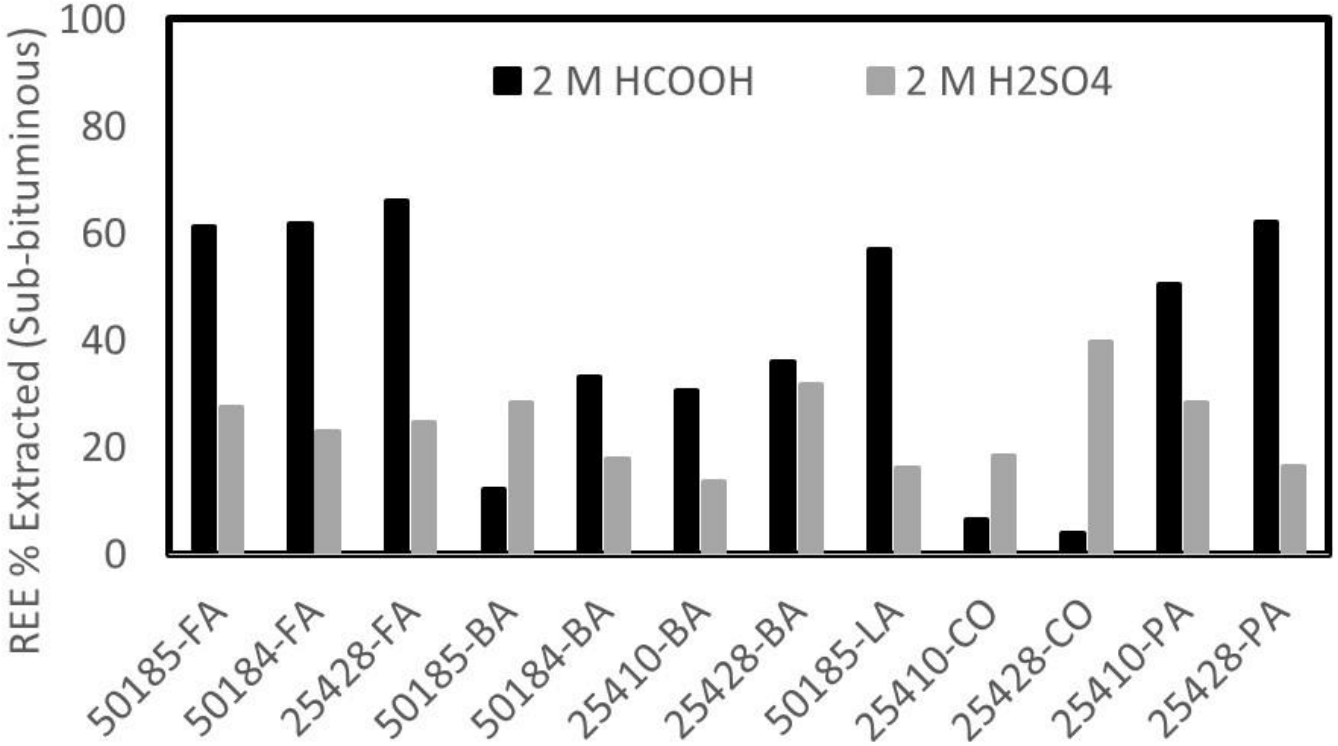
Up to 66% REE recovery from sub-bit coal with HCOOH

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.



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

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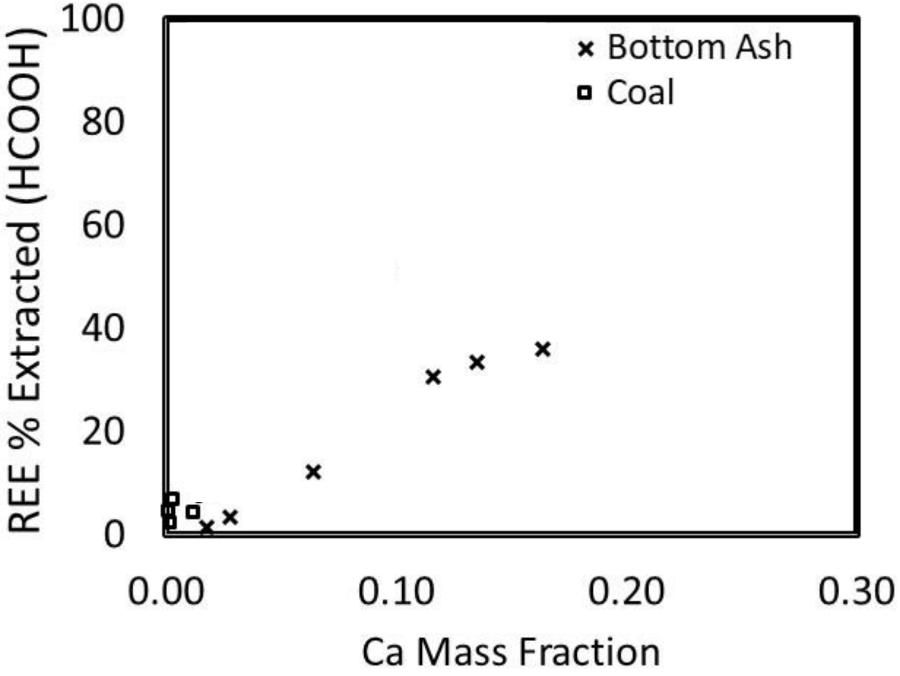
Taggart et al. (2016) used 15 M HNO_3 to recover 50-90 wt% REE from fly ash derived from sub-bituminous PRB coals.

HCOOH extraction – Ca content rough proxy for REE extractability from sub-bituminous-derived and bituminous-derived bottom ash.

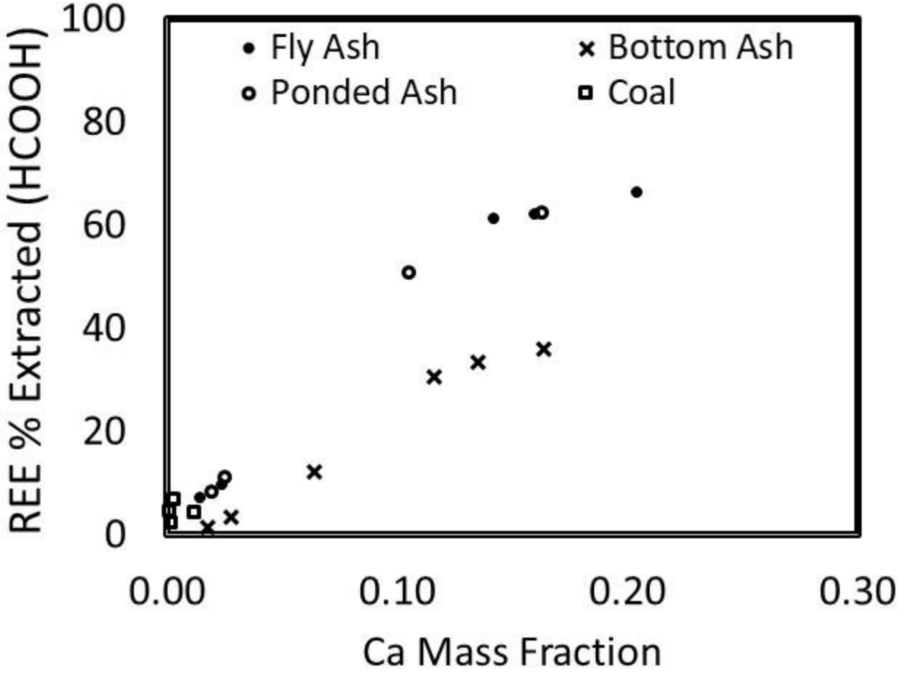
Kolker et al (2016) note that sub-bituminous PRB coal contains REE-associating Ca- and Fe-bearing aluminosilicates that may be more extractable than unsubstituted Al-Si.



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

HCOOH extraction – Ca content rough proxy for REE extractability, but extraction from ponded ash and fly ash (most particles < 50 microns) likely quicker than extraction from bottom ash (most particles < 100 microns).

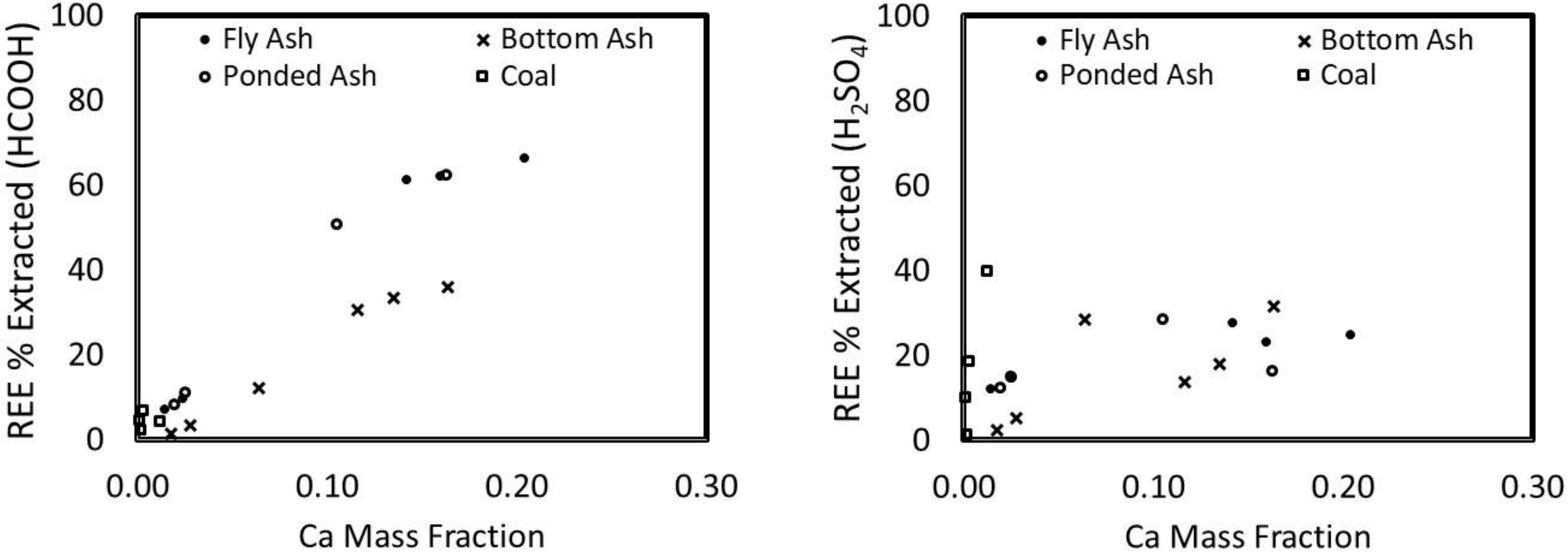
Kolker et al (2016) note that sub-bituminous PRB coal contains REE-associating Ca- and Fe-bearing aluminosilicates that may be more extractable than unsubstituted Al-Si.



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

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.



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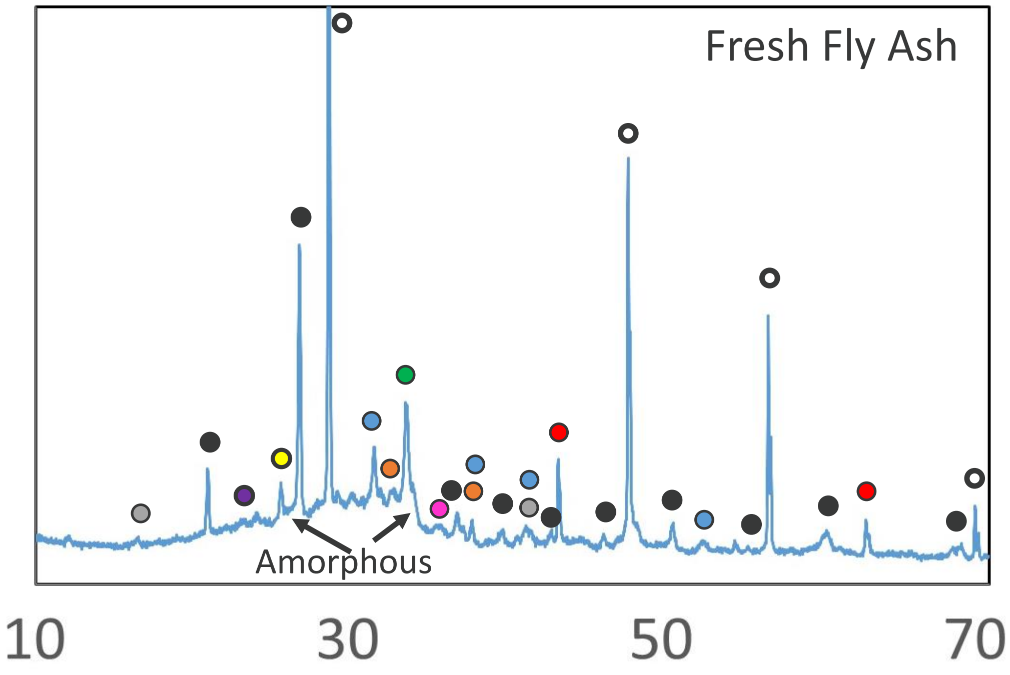
XRD – Fresh Fly Ash

- Several Ca-rich crystalline minerals are detected by XRD.
- An amorphous phase of unknown composition (indicated by the raised baseline) is also detected.



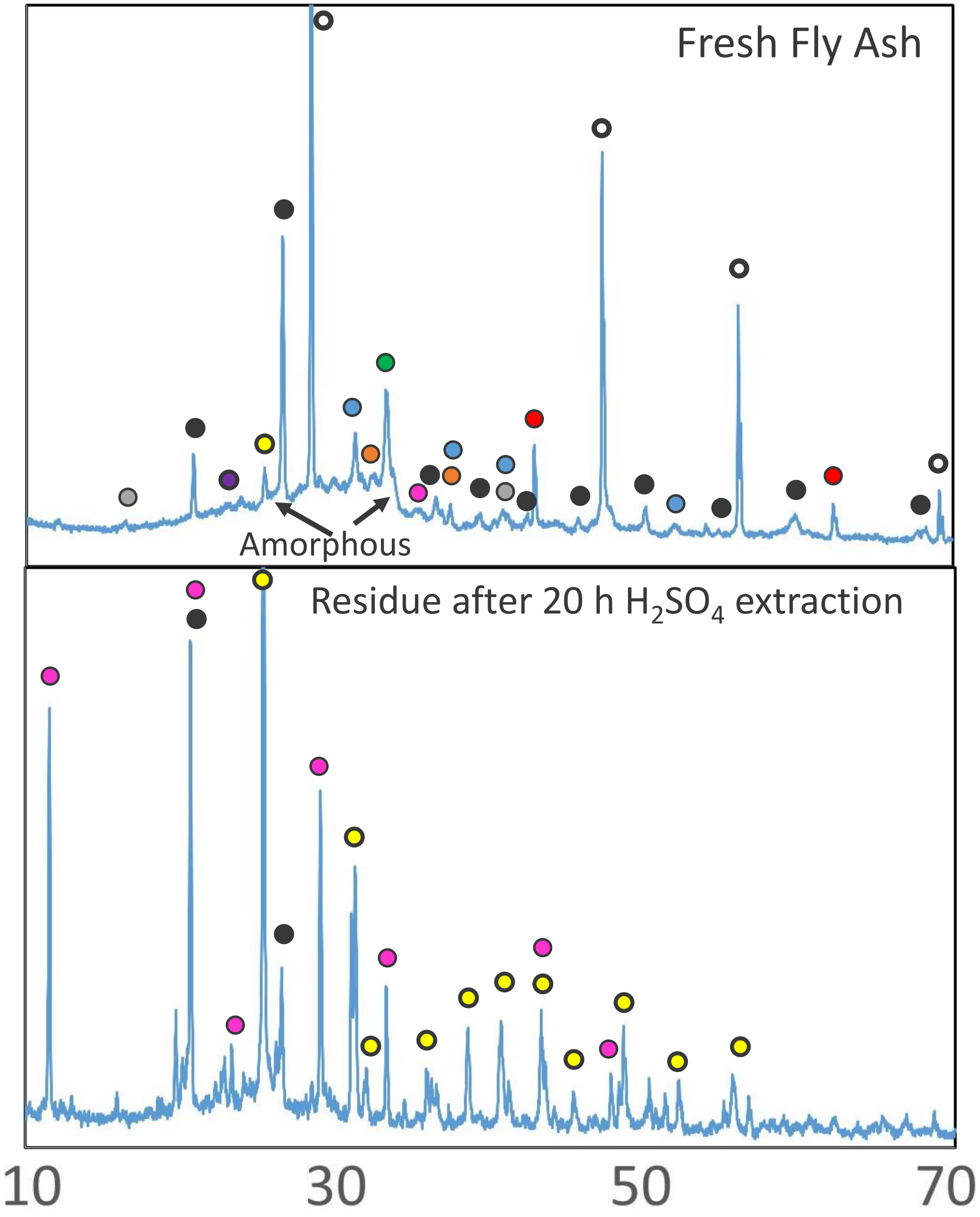
- ● Quartz – SiO_2
- ● Periclase – MgO
- ● Lime – CaO
- ● Merwinite – $Ca_3Mg(SiO_4)_2$
- ○ Silicon standard
- ● Gehlenite – $Ca_2Al(AlSiO_7)$
- ● Anhydrite – $CaSO_4$
- ● Mullite – $3Al_2O_3*2SiO_2$
- ● Diopside – $MgCaSi_2O_6$

Raised baseline signifies presence of amorphous phase.

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 surface of fly ash particles.

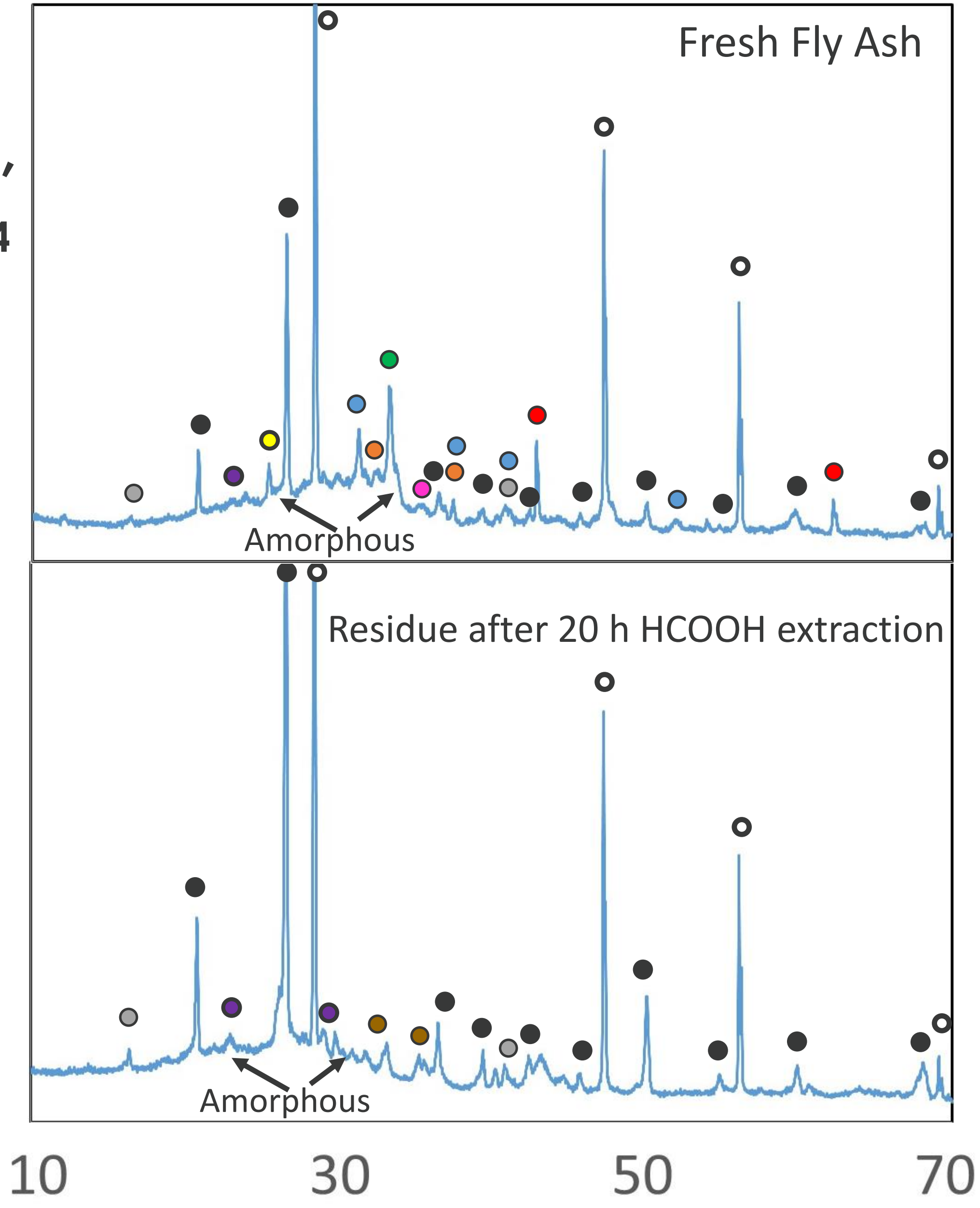
This behavior prevents further REE extraction and is why there is no strong dependence between REE extraction, Ca content when H_2SO_4 is extractive agent.



Raised baseline signifies presence of amorphous phase.

XRD – Fresh Fly Ash

- MgO, CaO, $Ca_3Mg(SiO_4)_2$, $Ca_2Al(AlSiO_7)$, and $CaSO_4$ are extracted using HCOOH.
- It is concluded that the bulk of the Fe (and HREE) is in the amorphous phase (Feed ash 3.4% Fe).



● Quartz – SiO_2
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● Anhydrite – $CaSO_4$
● Mullite – $3Al_2O_3*2SiO_2$
● Ba-Sr sulfate – $BaSr(SO_4)_2$
● Gypsum – $CaSO_4*2H_2O$
● Diopside – $MgCaSi_2O_6$

Raised baseline signifies presence of amorphous phase.

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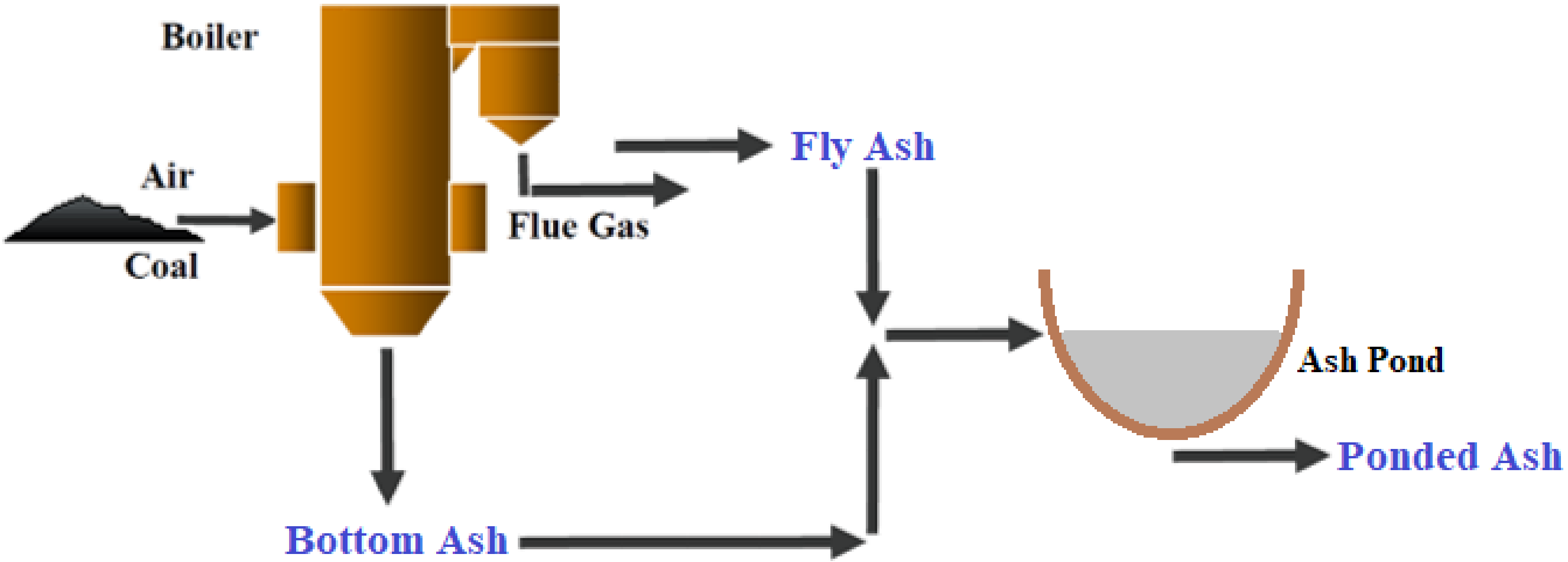
Choice of Ash

Questions to Answer

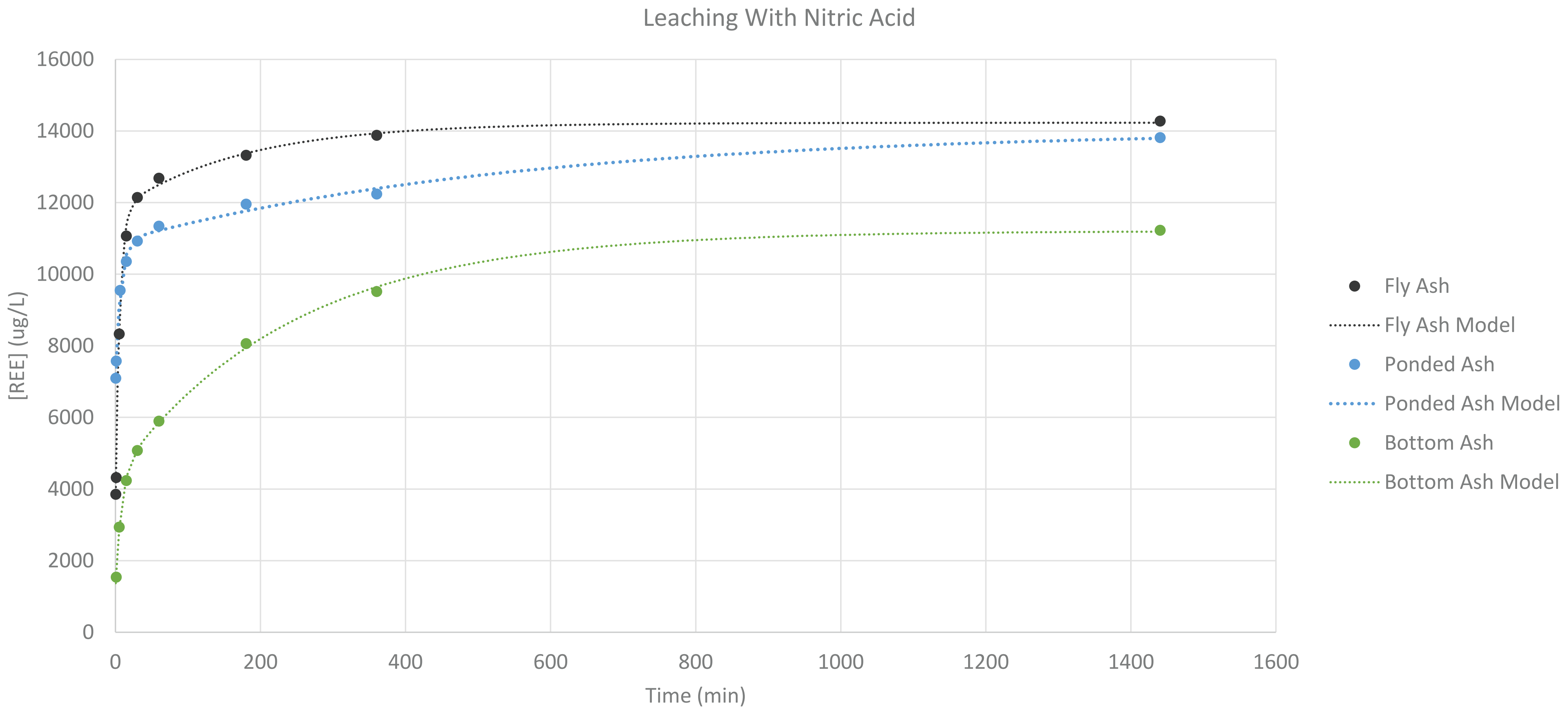
- What type of ash makes for the best feedstock for the acid leaching?
  - Fly Ash, Ponded Ash, Bottom Ash tested



Which type of ash is best feedstock?

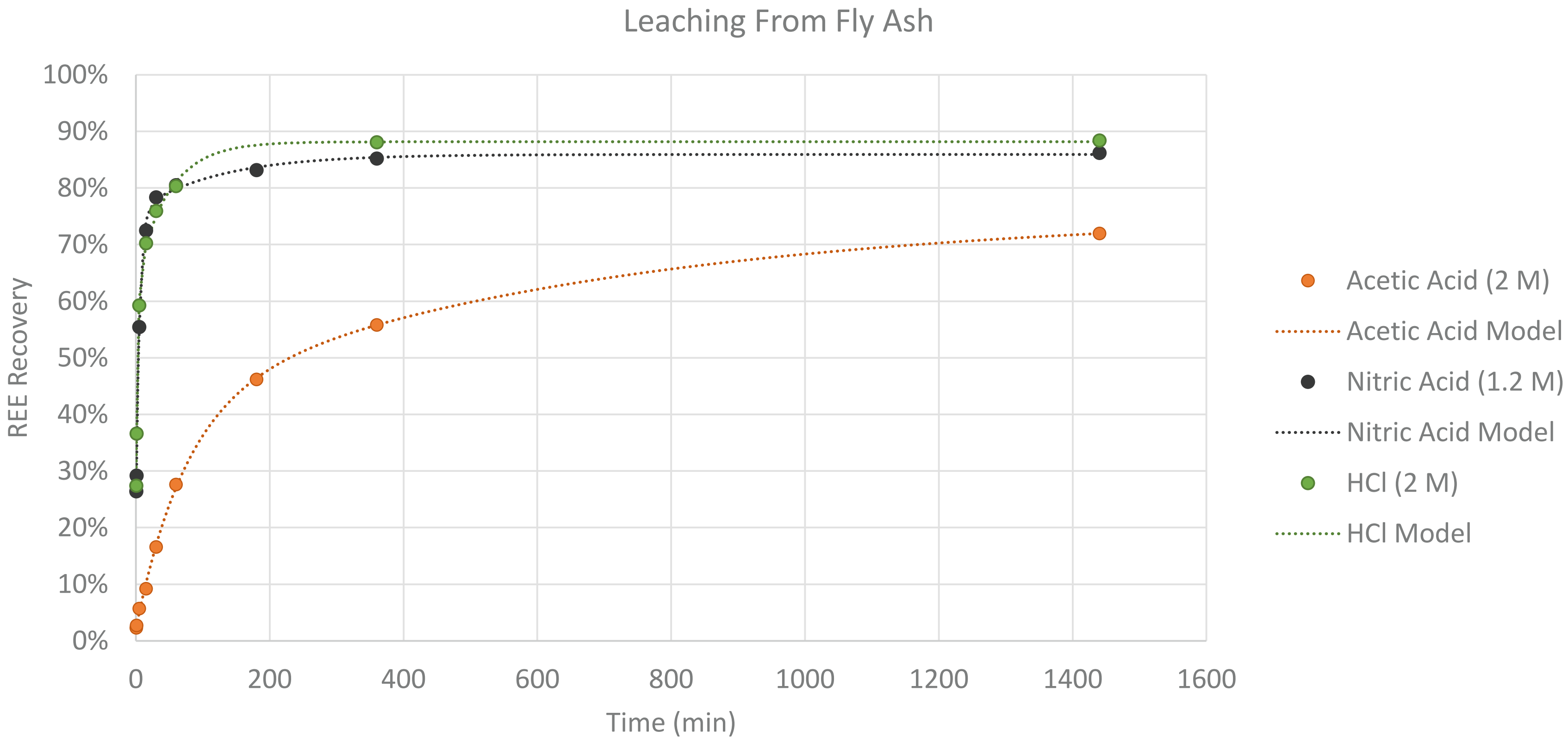
REE extraction from ponded, fly ash quicker than from bottom ash.

Fly ash preferable to ponded ash – it can be used as is, without pre-grinding.



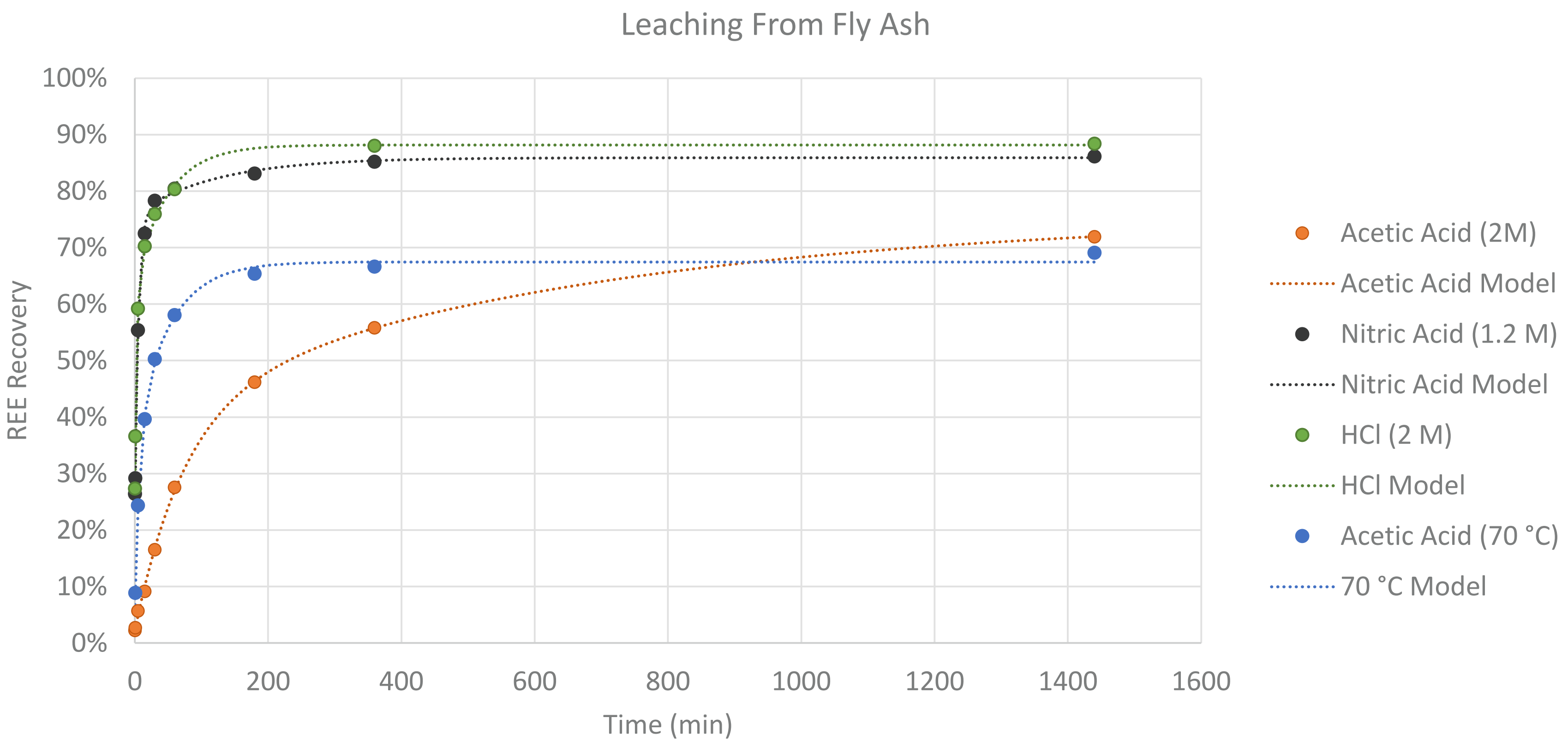
What acid is best suited to extraction of REEs?

Strong acids (HCl, HNO_3) result in higher yield and faster extaction kinetics than weak organic acid (acetic acid).



High-Temperature Acetic Acid vs. Strong Acids

Raising temperature to 70° C accelerates kinetics of acetic acid extraction, but extraction is still faster with strong acids at room temperature.



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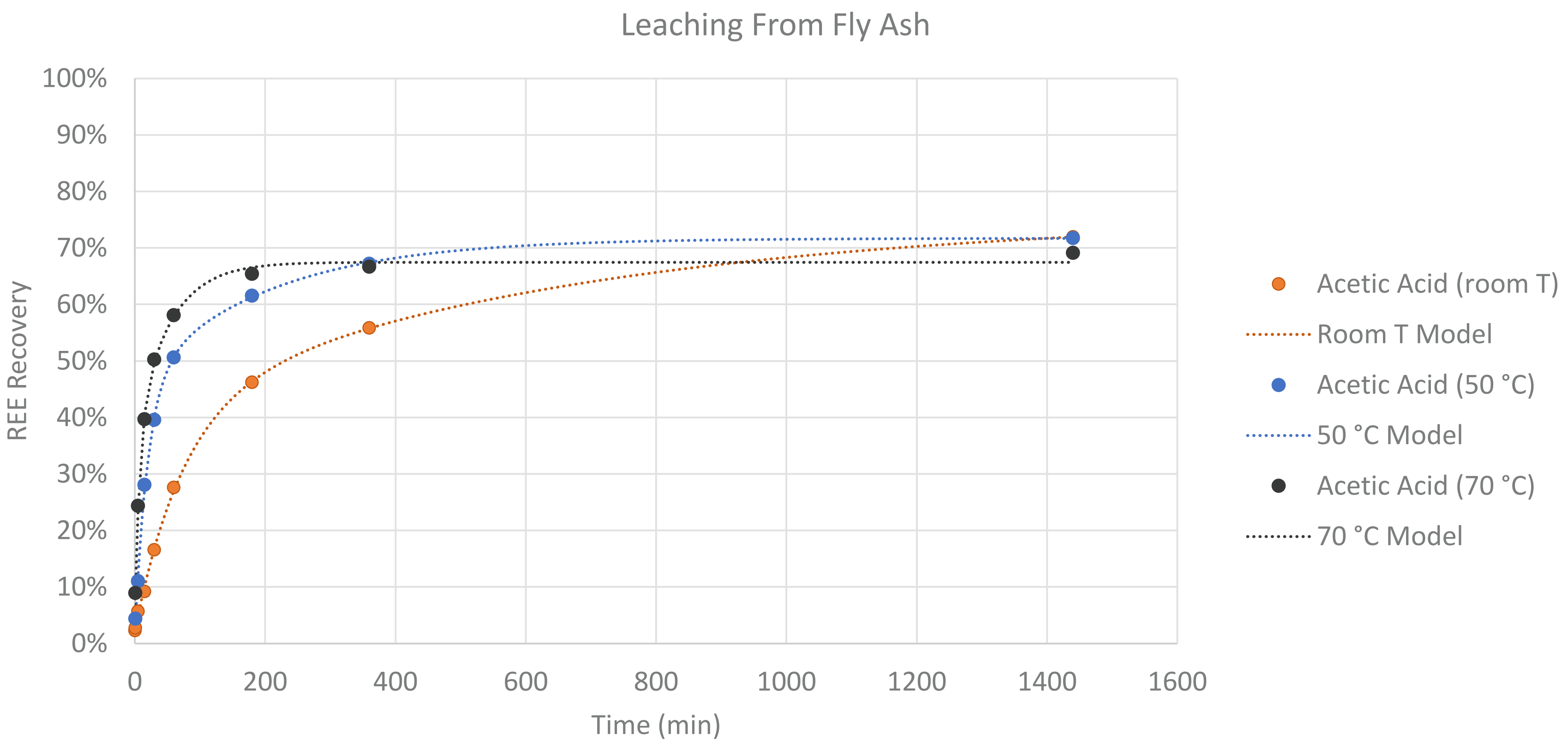
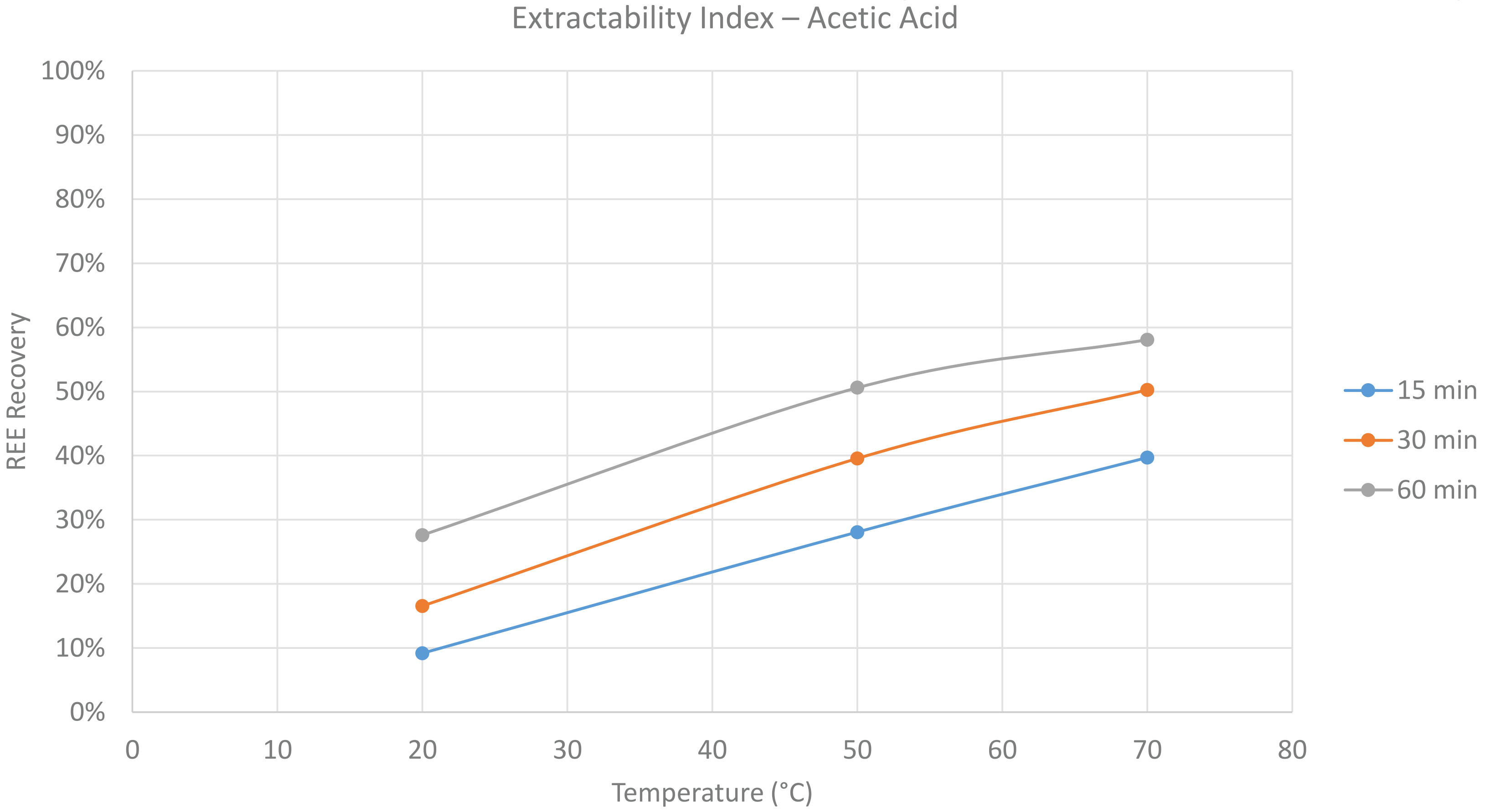


Extractability Index

What is the effect of reaction temperature on recovery?



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 comparable to yield obtained with concentrated HNO_3.
- H_2SO_4 not recommended as extractant for high-Ca content ashes because $CaSO_4$ will precipitate.
- Other strong acids (HNO_3, HCl) provide most rapid extraction kinetics and also the highest REE % yield.
- Approximately 70% REE recovery after 30 minutes achieved when 2M HCl, 1.2 M HNO_3 extraction agent used.
- Use of lower acid concentration (1 M) may increase selectivity for REE during extraction.

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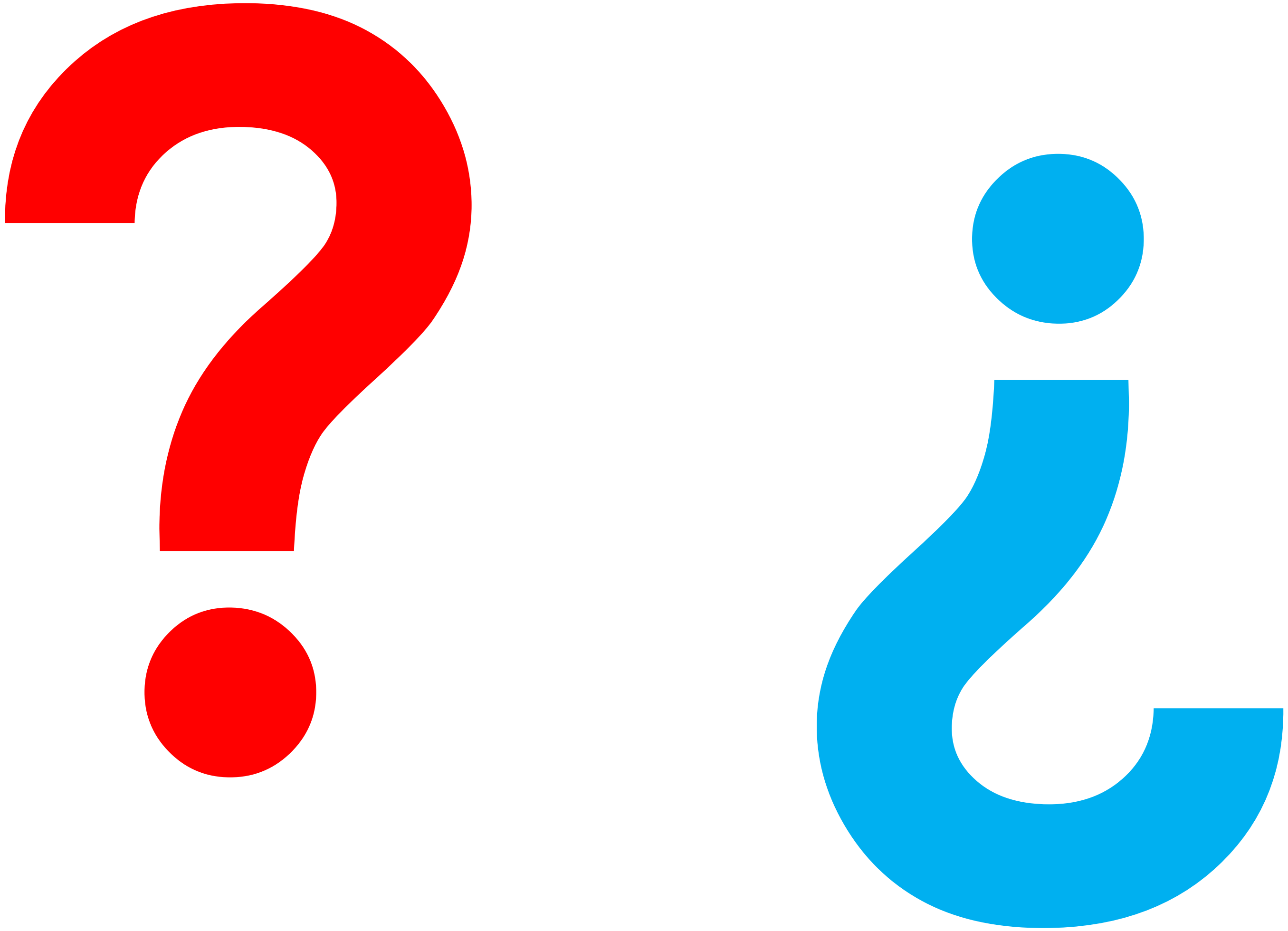
Questions?



Feedstock materials

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

Rare Earth Species in Solid Coal and Coal Byproducts

1. Minerals (most common)
    - Monazite – Rare Earth Phosphate
    - Bastnäsite – Rare Earth Fluorocarbonate
2. Colloidal Rare Earth Oxides/Hydroxides
3. Ion-Adsorbing clays
4. Organically Associated (important in lignite)

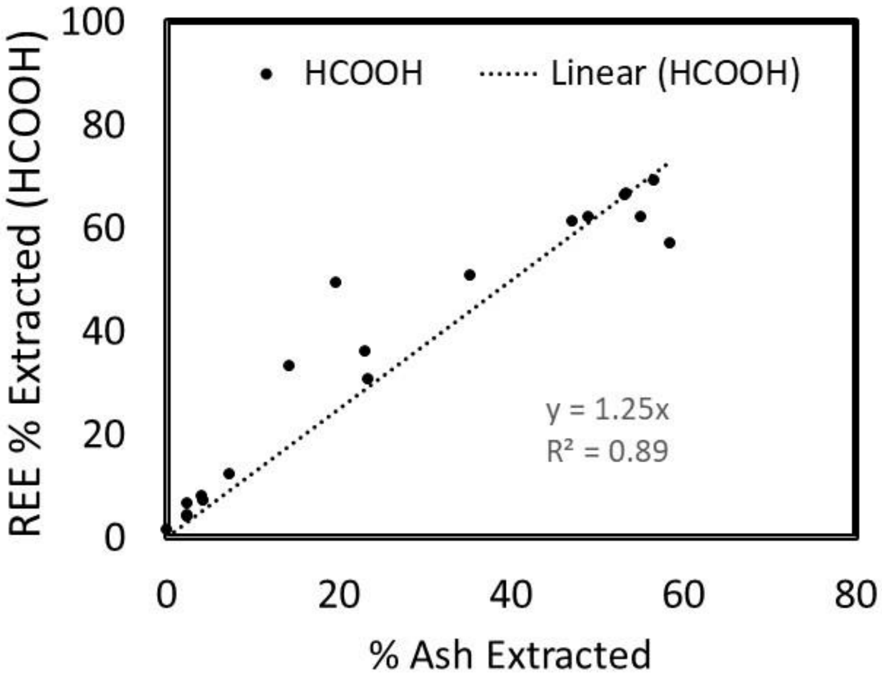
Correlation between % Ash and % REE Extracted

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.

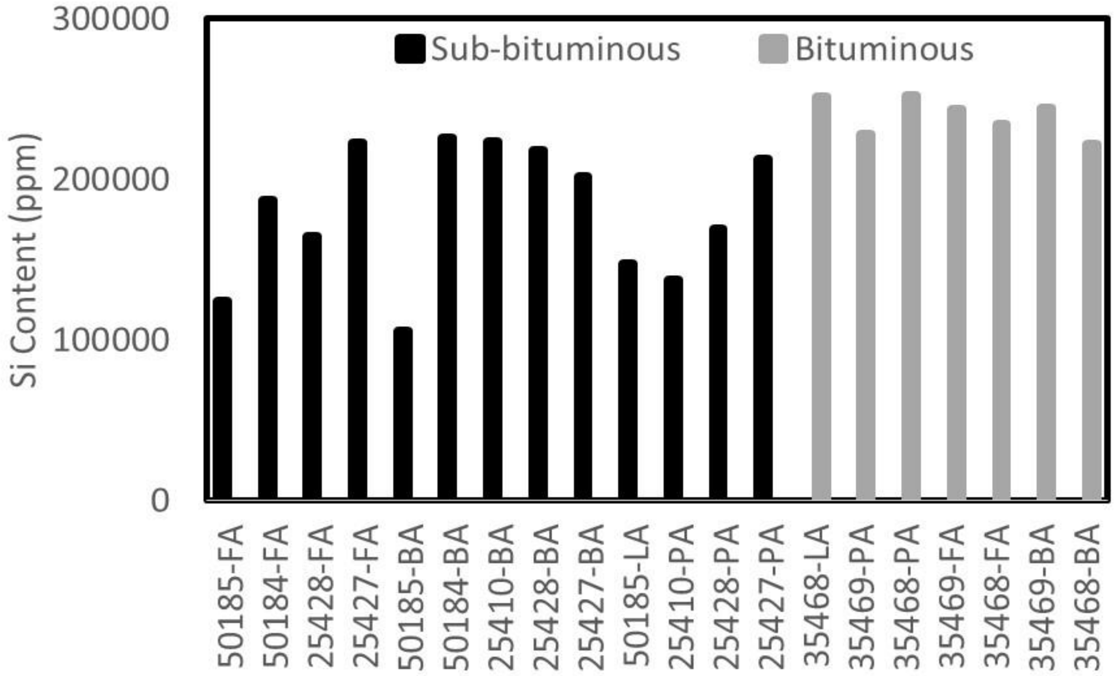
Does coal type (bituminous vs. sub-bituminous) matter?

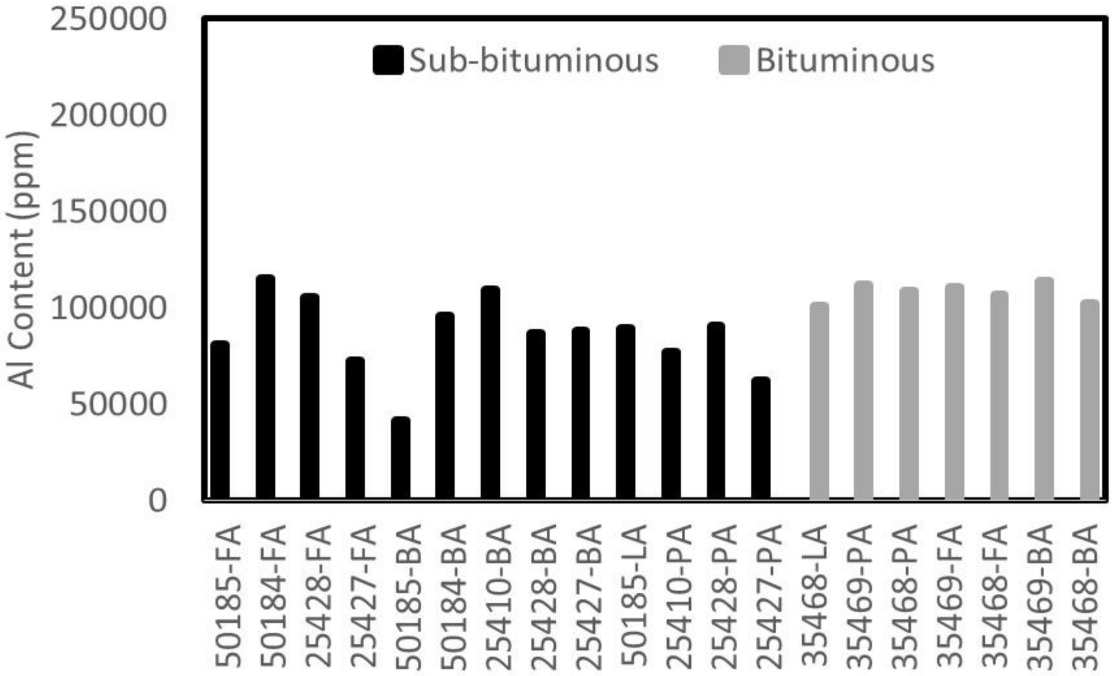


Primary matrix minerals present – Sub-bituminous vs. Bituminous Ash

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 (Stuckman et al., 2018, Thompson et al., 2018)

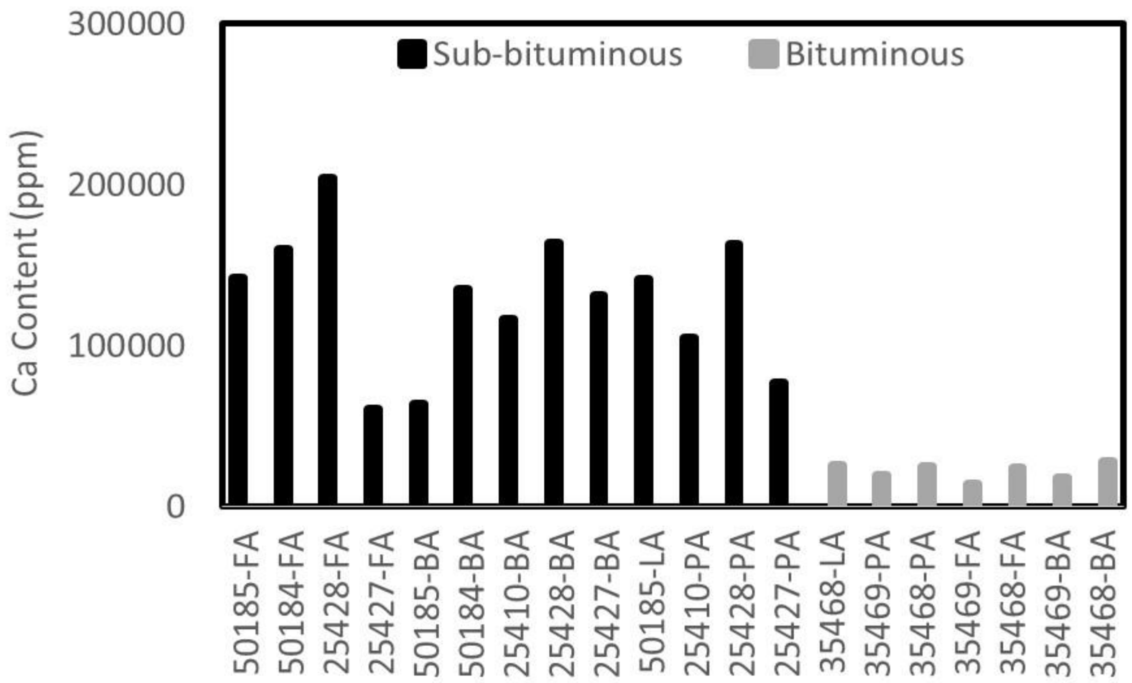


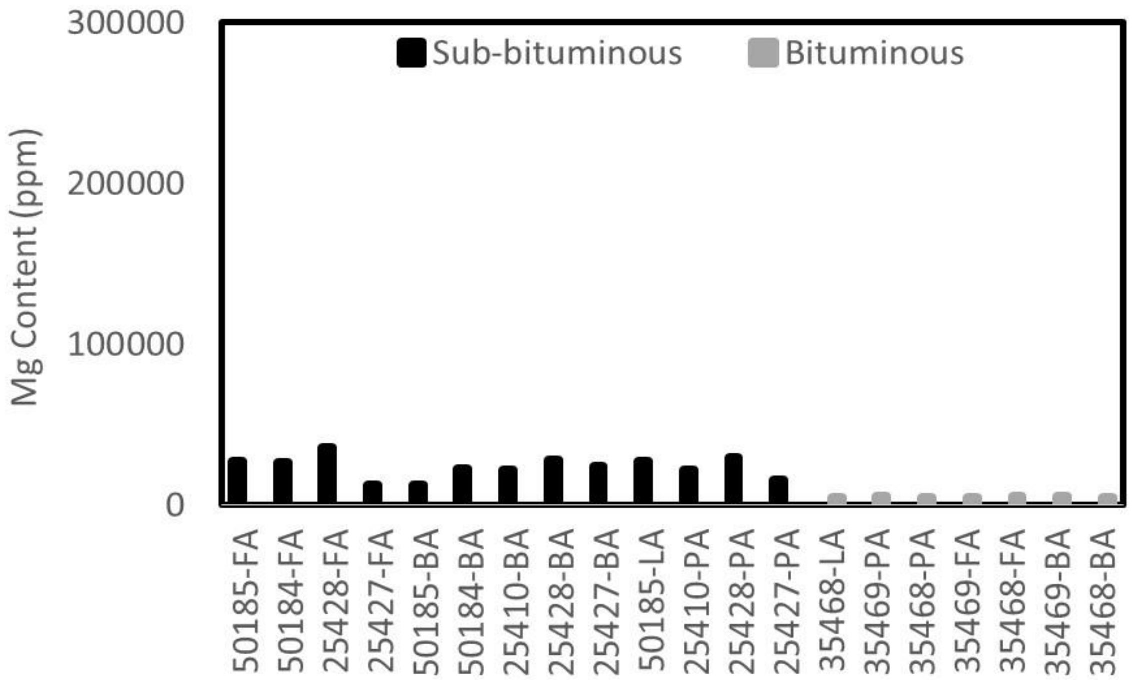


Primary matrix minerals present – Sub-bituminous vs. Bituminous Ash

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 (Stuckman 2018)





Extraction from Fly Ash – LREE vs. HREE

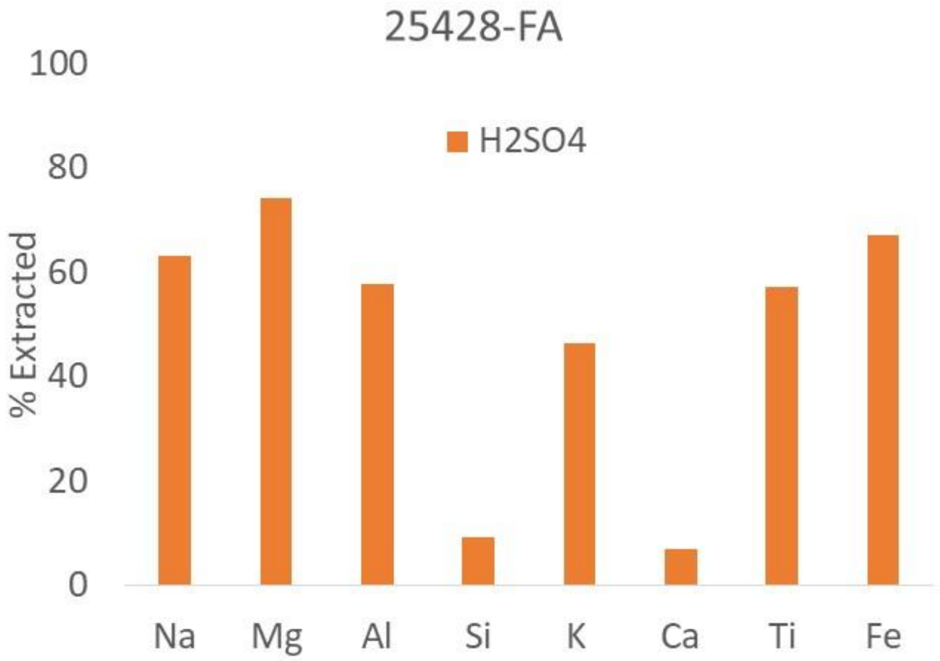
Ca extractability is very weak when H_2SO_4 is extractive agent.

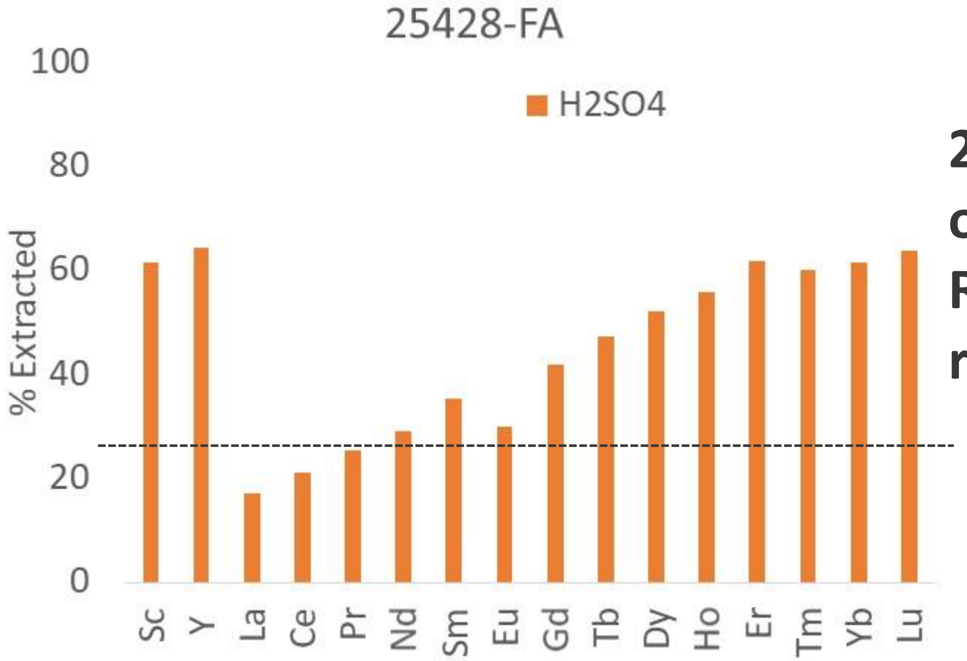
Extractability of Fe, Al is similar to that of Y, HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu).

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

LREE = Light REE

HREE = Heavy REE





22% overall REE recovery

Extraction from Fly Ash – LREE vs. HREE

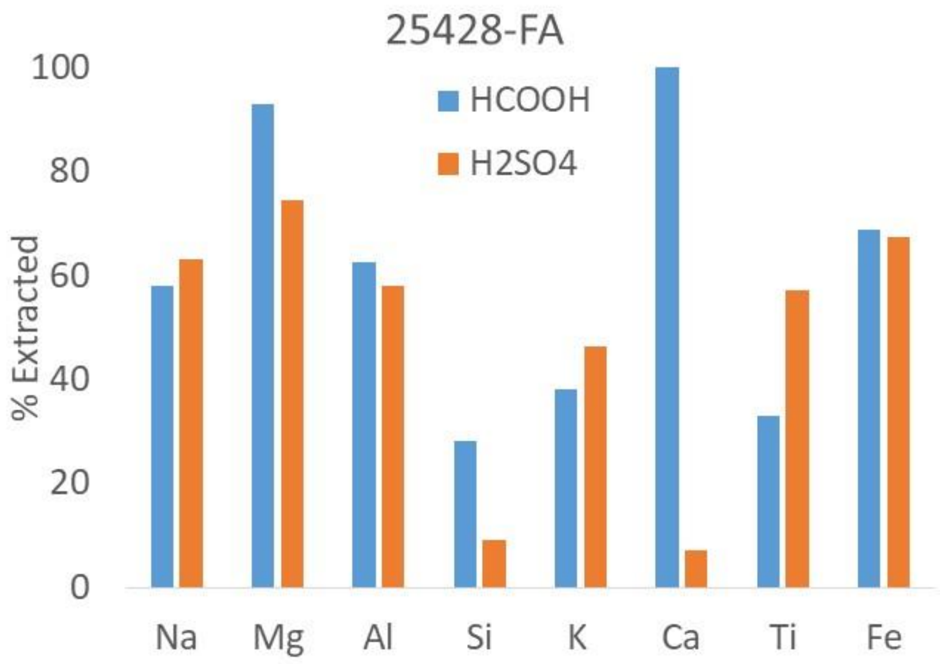
Sub-bituminous fly ash – HCOOH and H_2SO_4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

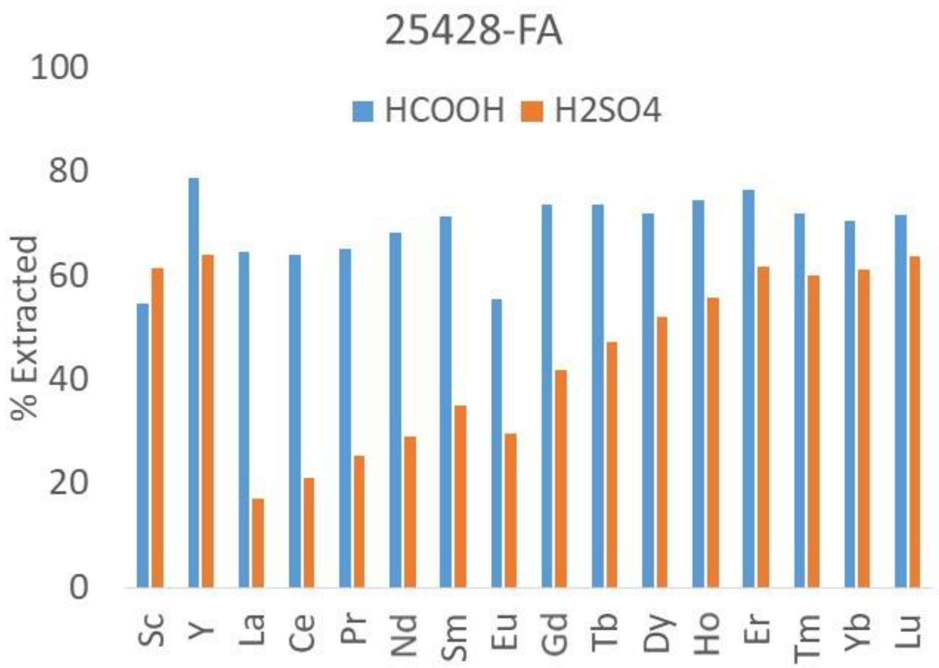
However, Ca extractability is much greater in HCOOH than H_2SO_4.

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

Results are consistent with conclusion (Stuckman et al., 2018) that the HREE are more likely to be found in Fe-rich aluminosilicates, while LREE (La, Ce, Pr, Nd, Sm, Eu, Gd) are found in Ca-rich aluminosilicates.

LREE = Light REE
HREE = Heavy REE





Extraction from Ponded Ash – LREE vs. HREE

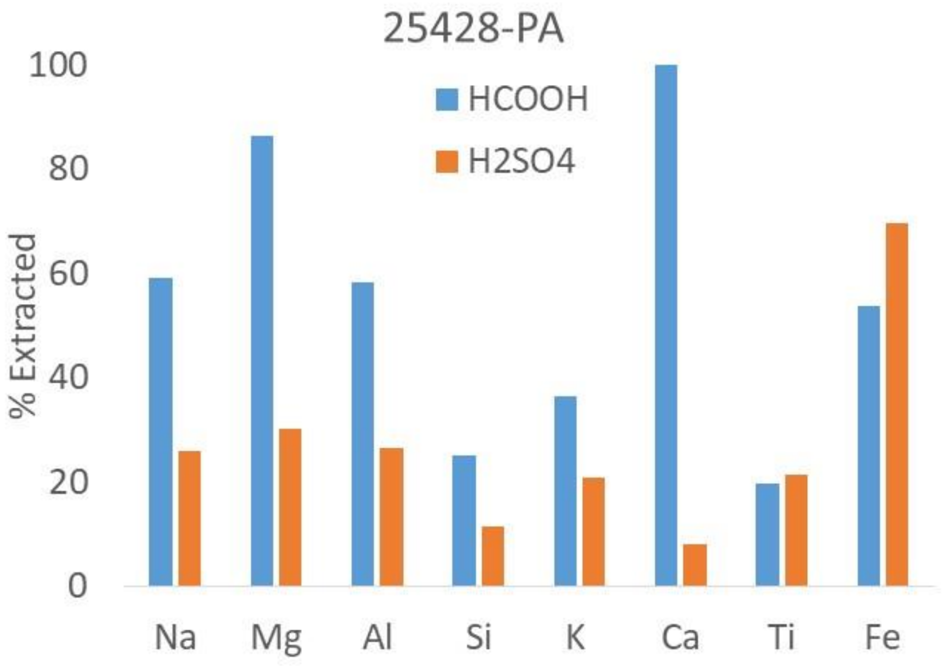
Sub-bituminous fly ash – HCOOH and H2SO4 solubility values are comparable for most major components (Na, Mg, Al, Si, K, Ti, and Fe).

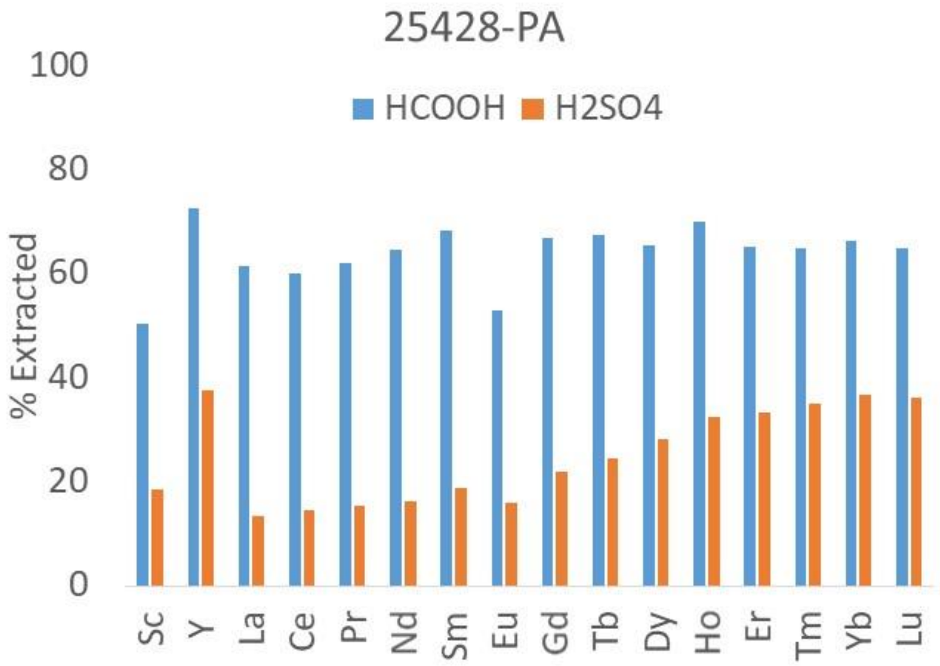
However, Ca solubility is much greater in HCOOH than H2SO4.

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.





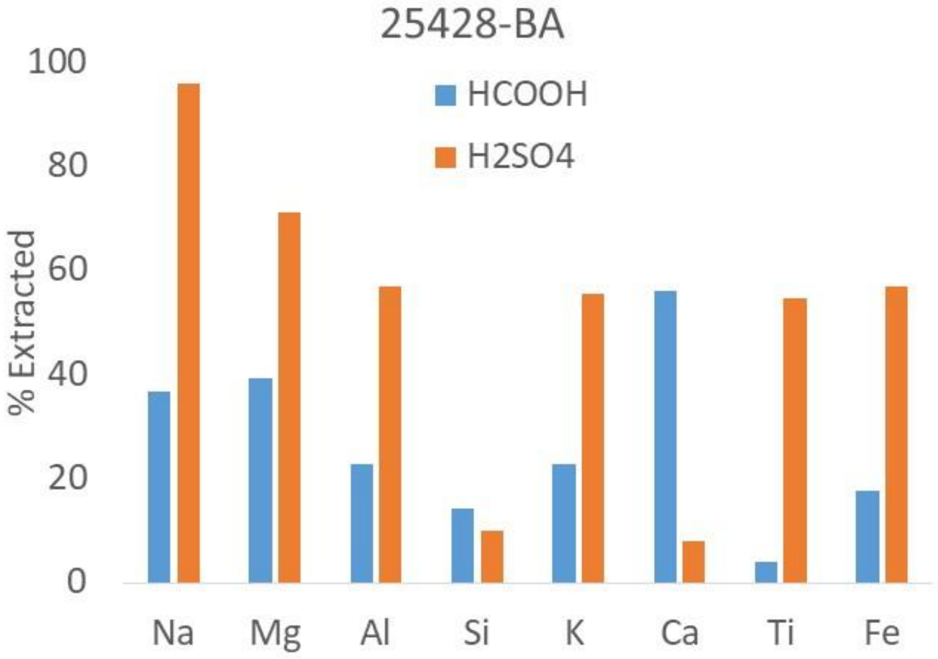
Extraction from Bottom Ash – LREE vs. HREE

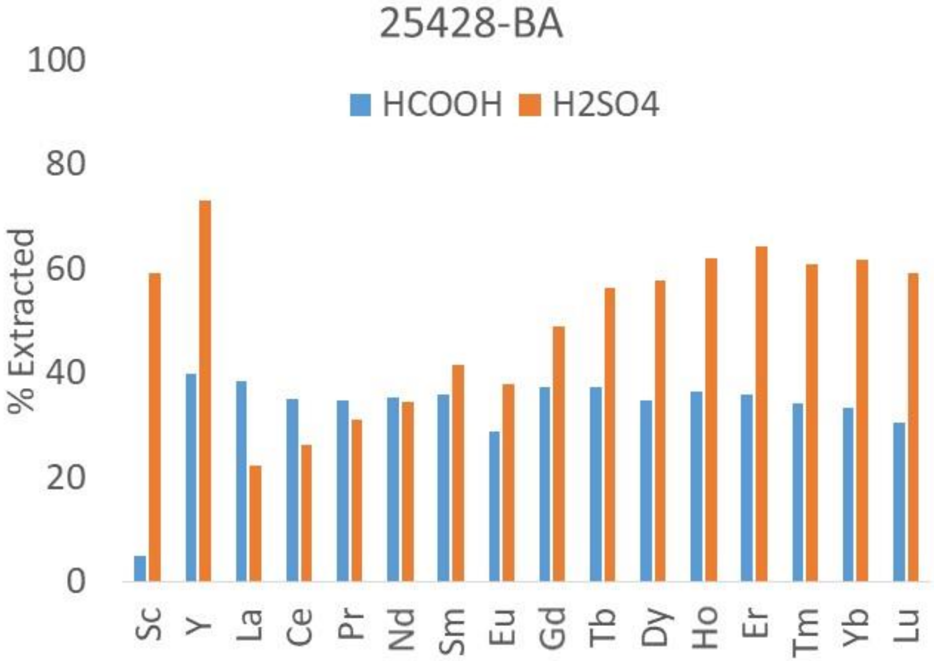
Sub-bituminous fly ash – Ca solubility is much greater in HCOOH than H_2SO_4.

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

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.



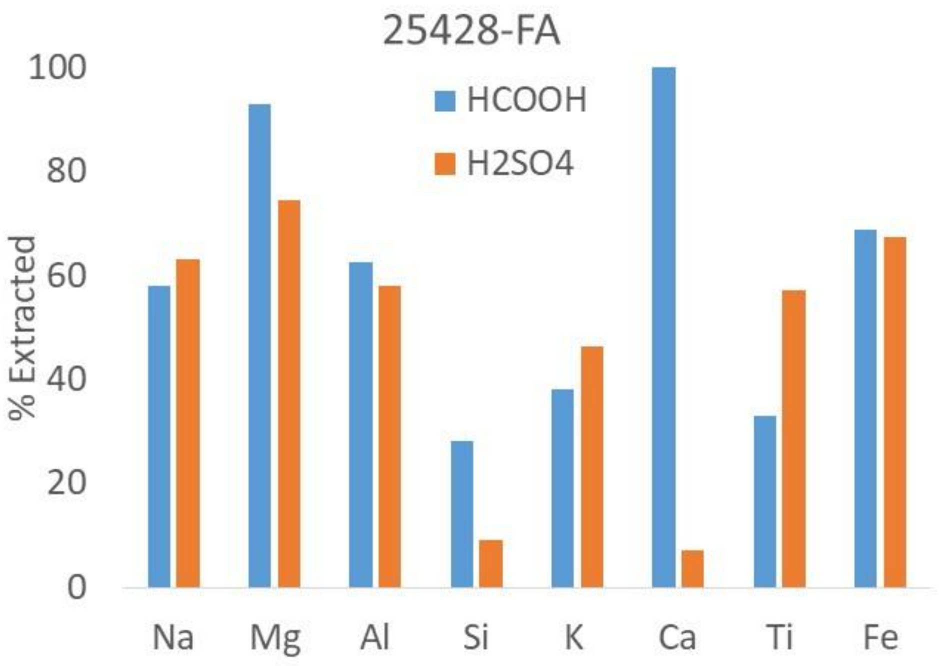


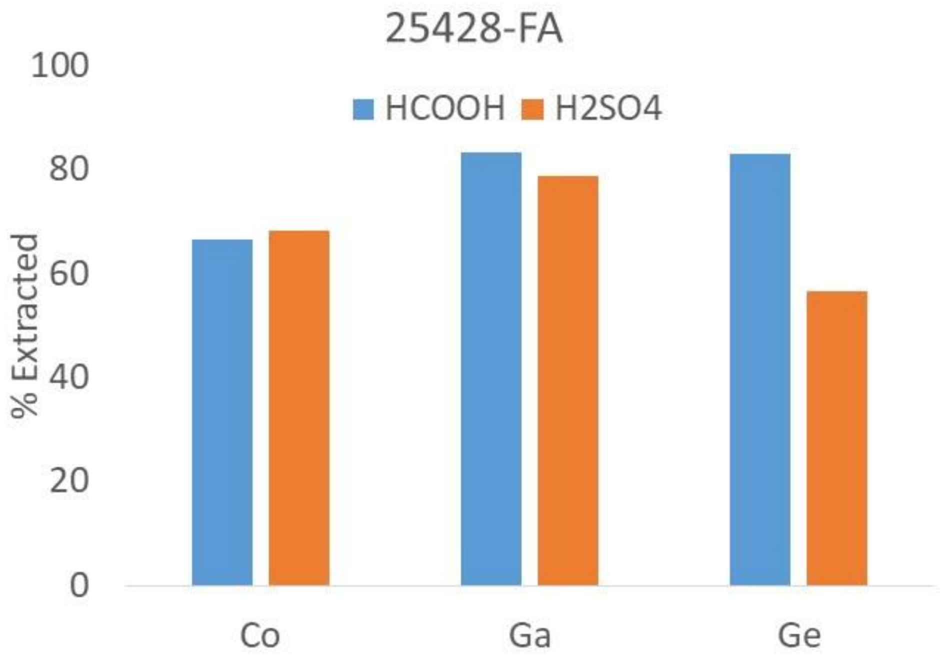
Extraction of Co, Ga, Ge from Fly Ash

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.



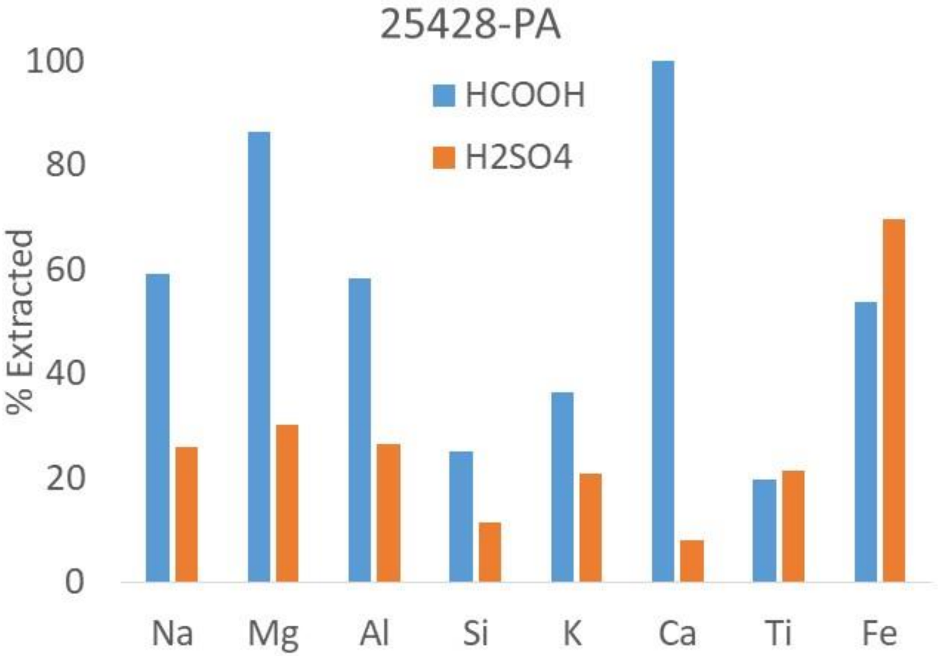


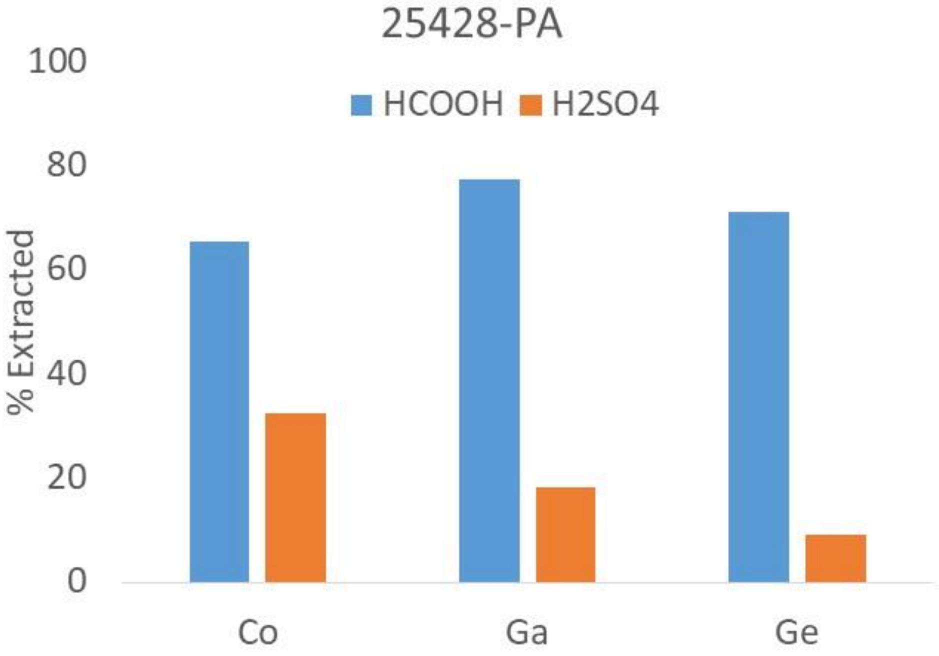
Extraction of Co, Ga, Ge from Ponded Ash

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.



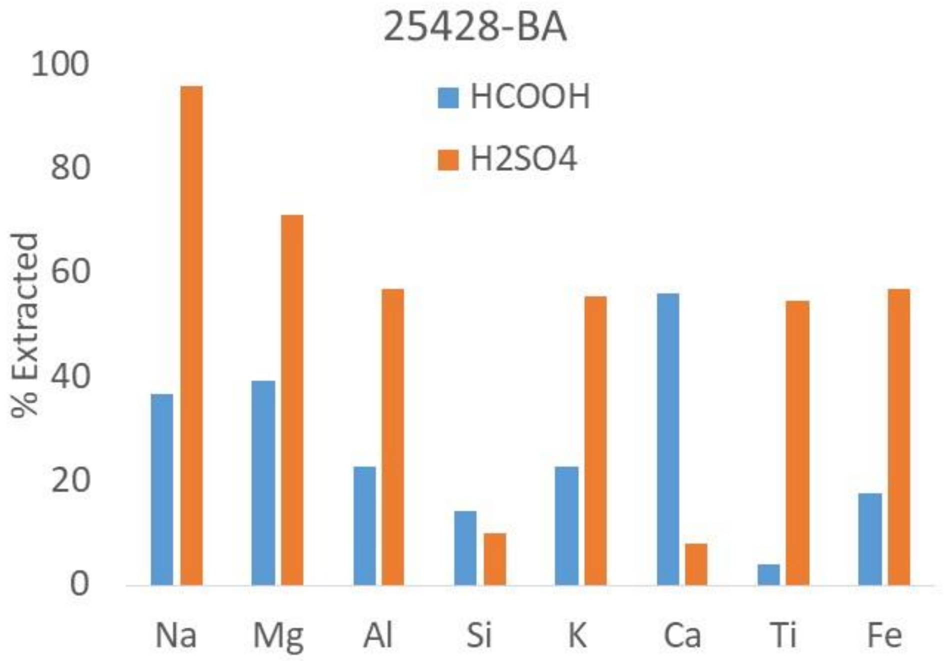


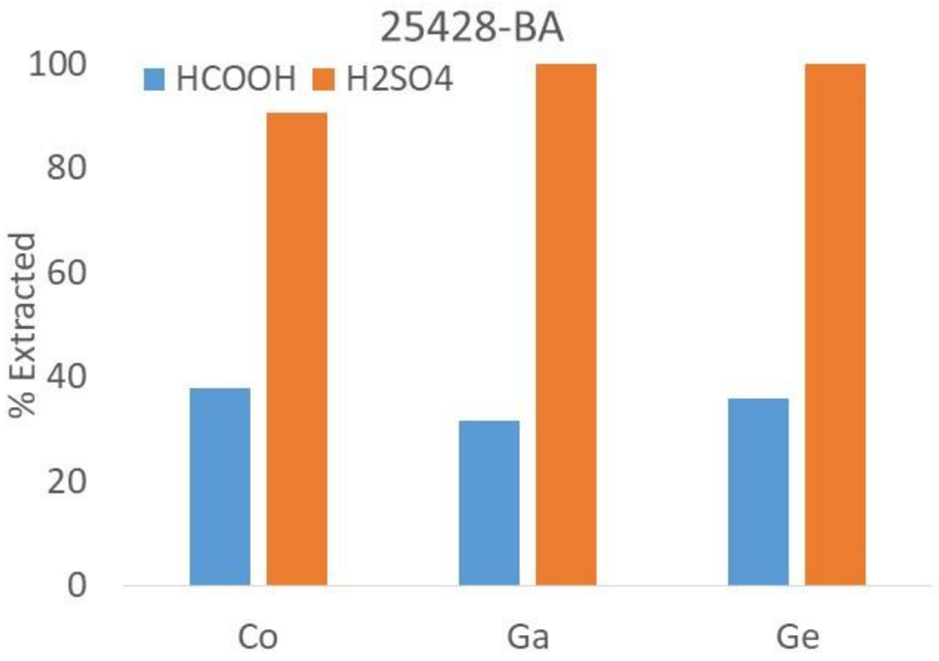
Extraction of Co, Ga, Ge from Bottom Ash

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.

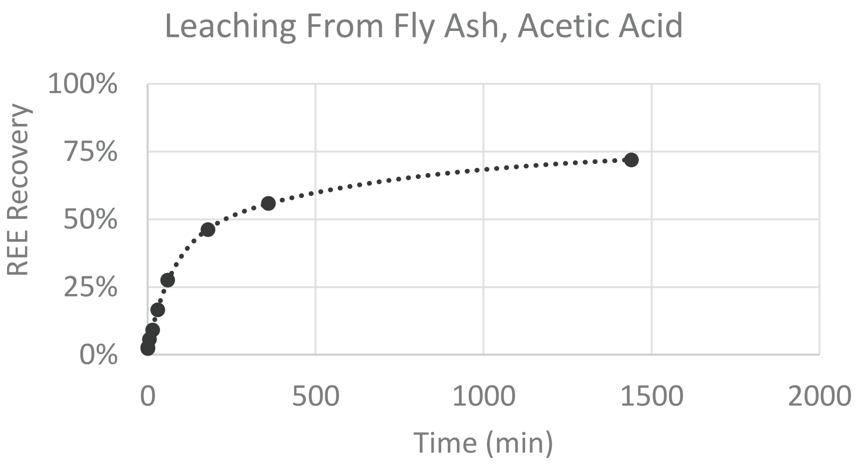
Co, Ga, Ge solubility correlated with solubility of Mg, Al, K – likely they are not associated with the Ca-bearing species in bottom ash.





Kinetic Models For Extraction

- Rare Earth Recovery
- $R_t = R_\infty - \left(A_1 e^{-k_1 t} + A_2 e^{-k_2 t}\right)$
- $[REE]_t = [REE]_\infty - (A_1 e^{-k_1 t} + A_2 e^{-k_2 t})$
    - A_1, A_2- related to initial reactant concentrations
    - k_1, k_2- apparent rate constants (k_1 being larger)
    - $R_\infty/[REE]_\infty$ - theoretical maximum recovery/concentration



Leaching From Fly Ash, Acetic Acid