Advanced Characterization of Rare Earth Elements in Coal Utilization Byproducts

Circe Verba[1] (circe.verba@netl.doe.gov), Scott Montross[1,2], Matthew Dieterich[3,4], James Poston[3], and Keith Collins[1]
[1] Research and Innovation Center, National Energy Laboratory, Albany, OR, USA [2] ORISE, National Energy Technology Laboratory, Albany, OR, USA [3] Research and Innovation Center, National Energy Laboratory, Morgantown, WV, USA
[4.] ORISE, National Energy Technology Laboratory, Morgantown, WV, USA

Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

Introduction

Rare earth elements (REE) in various forms (e.g., crystalline mineral phases; adsorbed/absorbed state on and into organic macerals, neoformed glass from fly or bottom ash) from domestic coal feedstocks and coal utilization byproducts (CUB) have the potential to reduce foreign REE dependence and increase domestic resource security. Characterization is critical for understanding environmental risks related to their fate and transport as well as determining the most practical and economical techniques for concentrating the REE and converting them into chemical stocks for manufacturing.

Several complementary micro-analytical techniques (e.g., SEM-EDS, EPMA-WDS, FIB-SEM, cathodoluminescence, and XRD) and post image processing techniques were used to understand REE transition from source coal to CUB. Sites of interest were imaged using BSE and respective elemental X-ray maps were acquired and montaged. Pixel classification and object classification of SEM imagers was used to quantify the distribution of REE mineral phases in the sample. Quantitative elemental analysis of phases were completed using EMPA-WDS followed by FIB-SEM. The FIB-SEM results were reconstructed into 3D volumes and features of interest (e.g. monazite) were analyzed to determine the structure and volumetric estimation of REEs and thus predict detrital REE phases present and relate to resource calculations using bulk ICP-MS results.

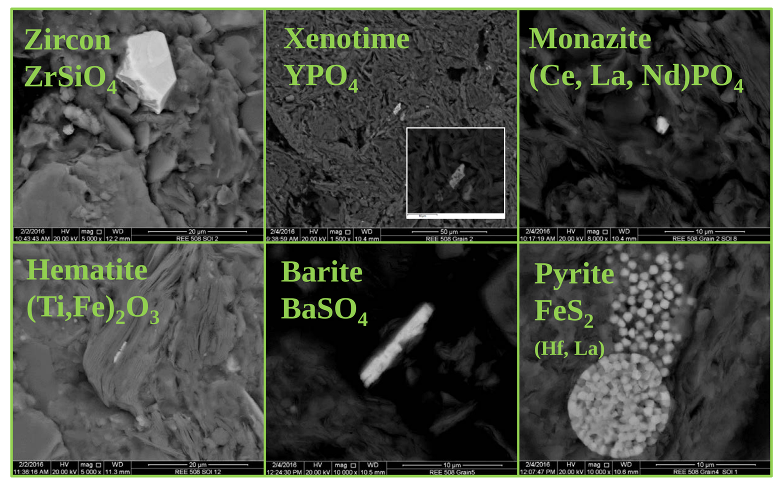


Figure 1: Heavy media cyclone reject (coal). Trace minerals were identified as pyrite, zircon, REE-phosphates' (monazite, xenotime), and barite within the coal tailings.

Amorphous aluminosilicate glass, cenospheres, and particles composed of iron or calcium oxide are present in all CUB samples. Monazite appears to be unaltered by the combustion process in these samples.

Characterization Results

Table 1: Concentrations (µg/g) of REE in CUB determined by ICP-MS.

	57 La	58 Ce	59 Pr	60 Nd	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	TOTAL REEs+Y (ppm)
Coal Reject 508	65	126	28	49	12	1	5	4	4	1	1	2	4	4	312
Coal 443	44	91	32	65	15	5	9	9	10	40	10	7	5	5	372
Fly Ash 251	104	202	62	88	17	5	98	24	16	6	14	7	10	7	761
Fly Ash 339	48	113	48	39	22	3	9	22	13	1	8	12	1	3	390
Fly Ash 345	17	134	33	45	20	4	1	6	17	1	10	2	19	4	383
Bottom Ash 357	560	397	32	49	20	5	1	7	18	97	9	1	20	5	1,286

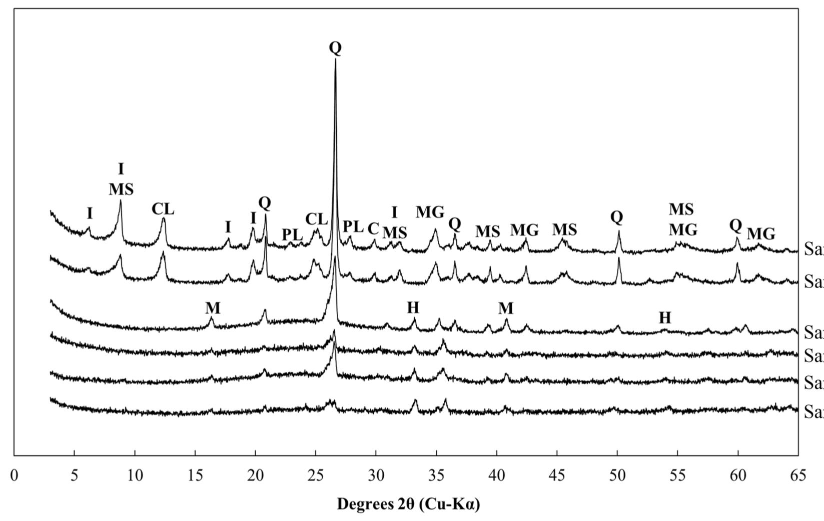


Figure 2: X-ray diffraction patterns for CUB samples. Q= quartz, I= illite, MS= muscovite, MG= magnetite, M= mullite, H= hematite.

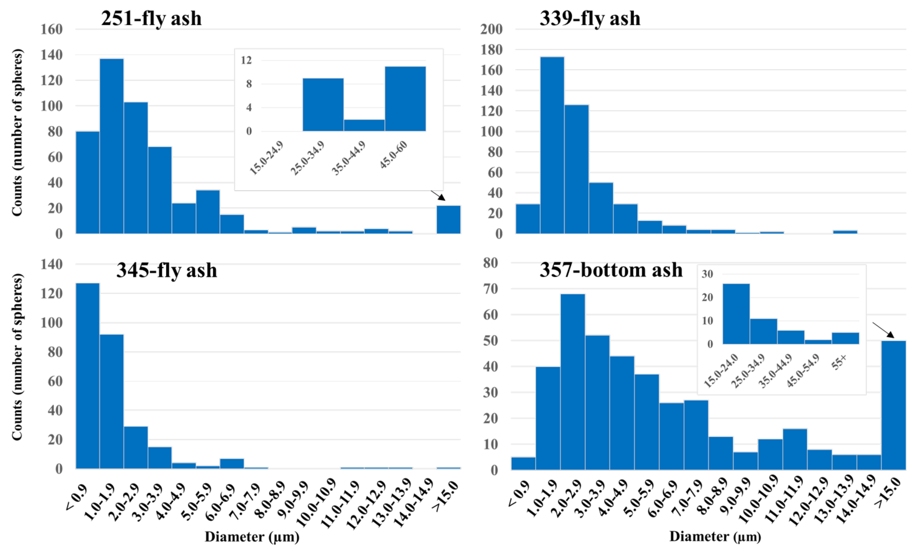
Table 2: Semi-Quantitative XRD Analysis in wt %.

	Quartz	Muscovite	Hematite (Fe/Ti)	Clinochlore	Mullite
Coal Reject 508	42.7	41.8	-	15.5	-
Coal 443	41.4	40.7	-	17.9	-
Fly Ash 251	40.2	10	2.3	-	47.5
Fly Ash 339	24.5	50	8.8	-	16.7
Fly Ash 345	20	58.4	11.7	-	9.9
Bottom Ash 357	19.8	36.4	26	-	17.8

Table 3: Particle analysis by SEM

Sample number	Al/Si-rich spheres	Fe/O-Al/Si-rich spheres	Fe/Ti/O-rich spheres	Ca-rich spheres and particles	Al/Si slag	Unburnt carbon	Crystalline minerals	Agglomerated particles
FA 251	M	Min	T	T	T	T	ND	T
FA 339	M	Min	Med	T	Min	Min	T	T
FA 345	M	T	T	Min	T	T	T	Min
BA 357	Med	T	Min	Min	Med	T	Min	Min

M-Med-Min-T-ND = major (>50%), medium (25-50%), minor (5-25%), trace (<5%), none detected



- Largest diameter spheres in bottom ash (up to 102 µm)
- Inversely the smallest diameter spheres were in sample # 251and 339 at approximately 0.4 µm.
- Agglomerated particles, masses of smaller particles joined together by glass, slag, or mineral floc are most abundant and had the largest diameter in the bottom ash sample (357). The largest agglomerated particle measured was 288 µm in sample #357.

Figure 3: Size distribution of spherical ash particles. Average diameter for ash spheres was 8.4, 4.3, 4.1, and 2.4 µm for samples #s 357, 251, 345, and 339 respectively. 80% of the glass spheres in the samples are < 7 µm.

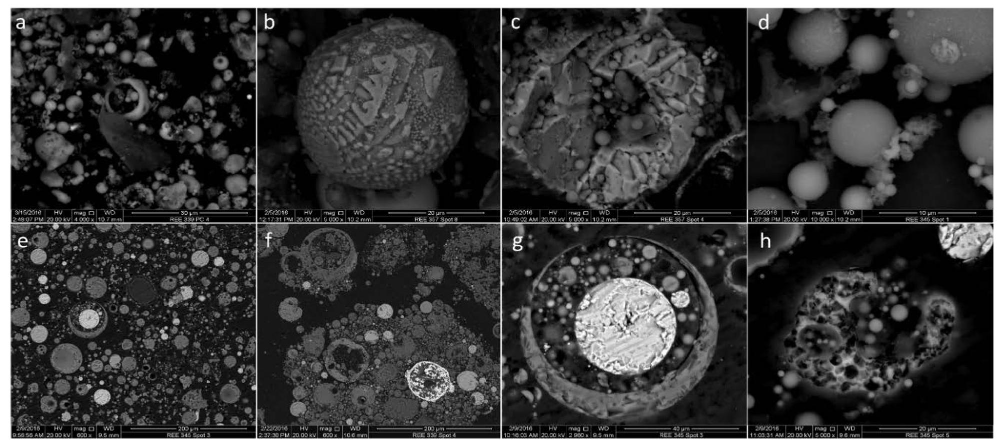


Figure 4: SEM-BSE images. Fly ash samples containing Si-Al cenospheres (a-h), Fe/Ti oxide spheres (b-c; e-h), solid Si-Al spheres (e-g), Al-Si slag and agglomerated particles (e-h), REE mineral grains (a; e-f) and Ca-Si-Al oxides (h).

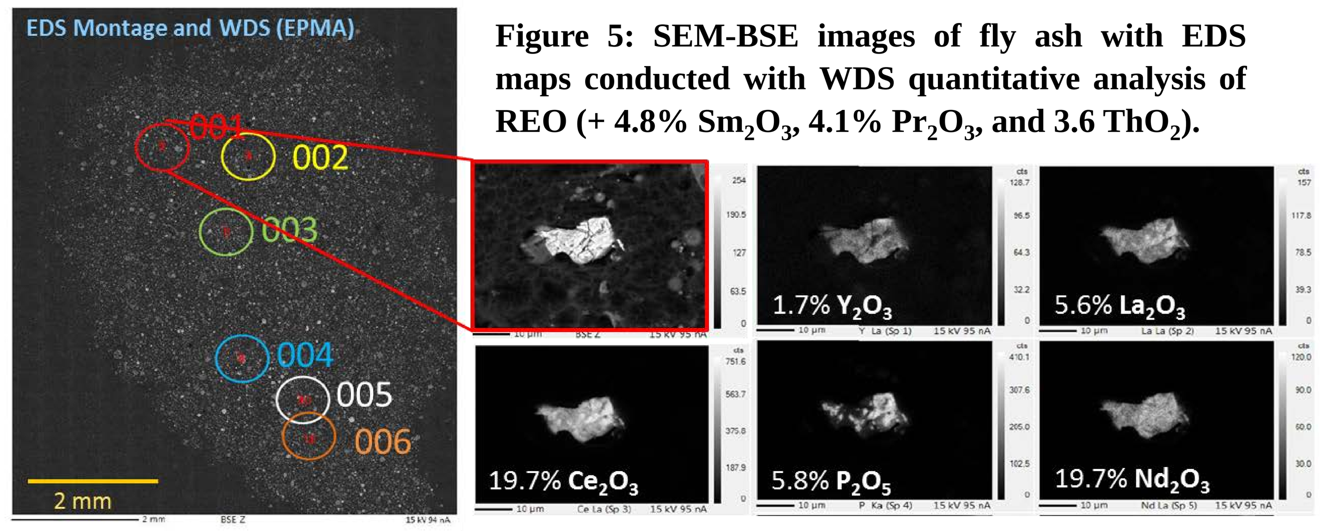


Figure 5: SEM-BSE images of fly ash with EDS maps conducted with WDS quantitative analysis of REO (+ 4.8% Sm_2O_3, 4.1% Pr_2O_3, and 3.6 ThO_2).

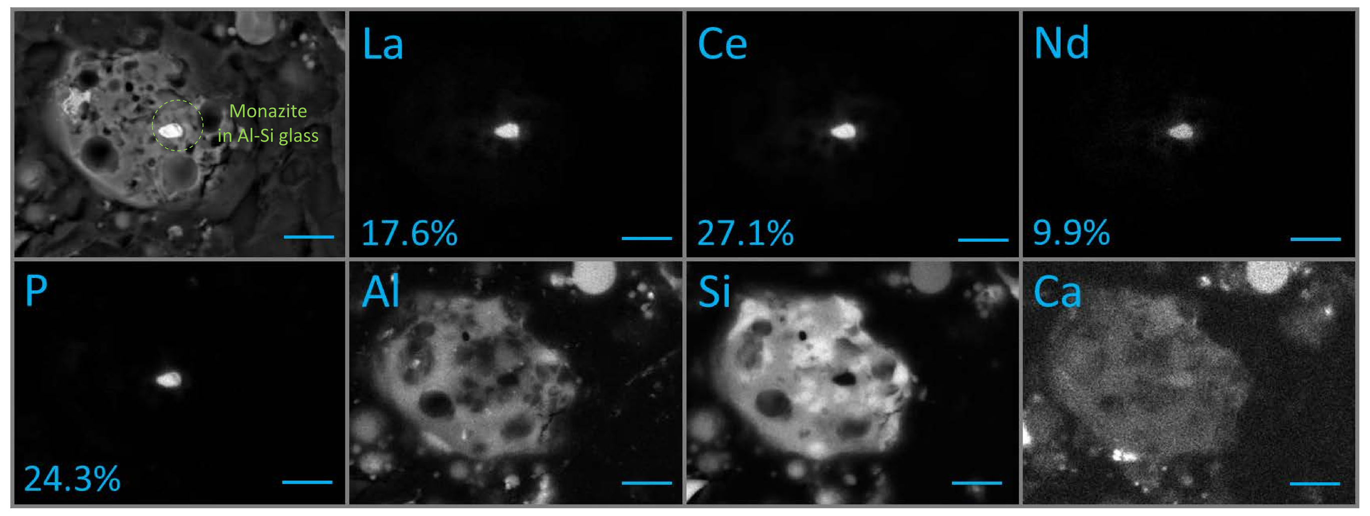


Figure 6: EMPA image of fly ash with BSE. EMPA-WDS quant of elements in weight percent (oxide) collected at 15 kV and 95 nA with 25 ms dwell time. Scale bar is 10 µm.

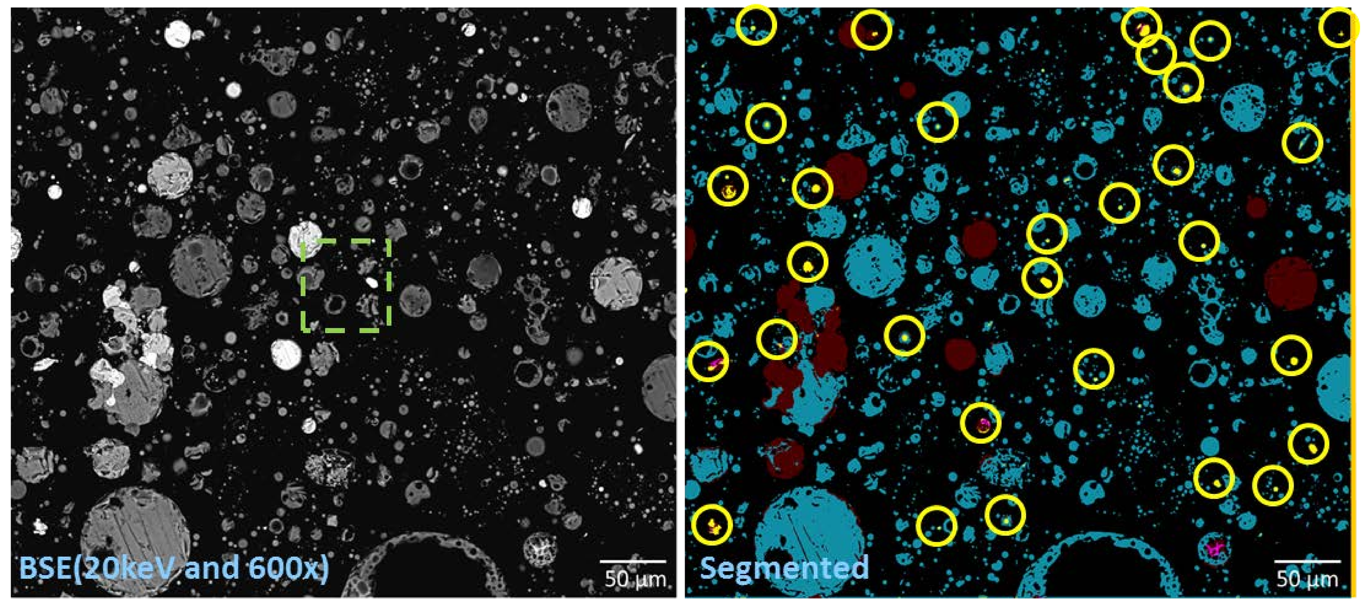


Figure 7: (Left) SEM-BSE image of fly ash. Green box- used for initial pixel/object classification. (Right) Mineral phases of fly ash (segmented image) are Al-Si oxide (blue), Fe oxide (red), Monazite (yellow), and Ca-Al-Si oxide (pink).

- Pixel and object classification on montaged SEM-BSE images (up to 1024 fields of view) of coal ash particles collected at 4000x magnification.
- Allows for identification and mapping of the distribution of REE minerals and other mineral phases in CUB samples over a 1x1" area of the sample.

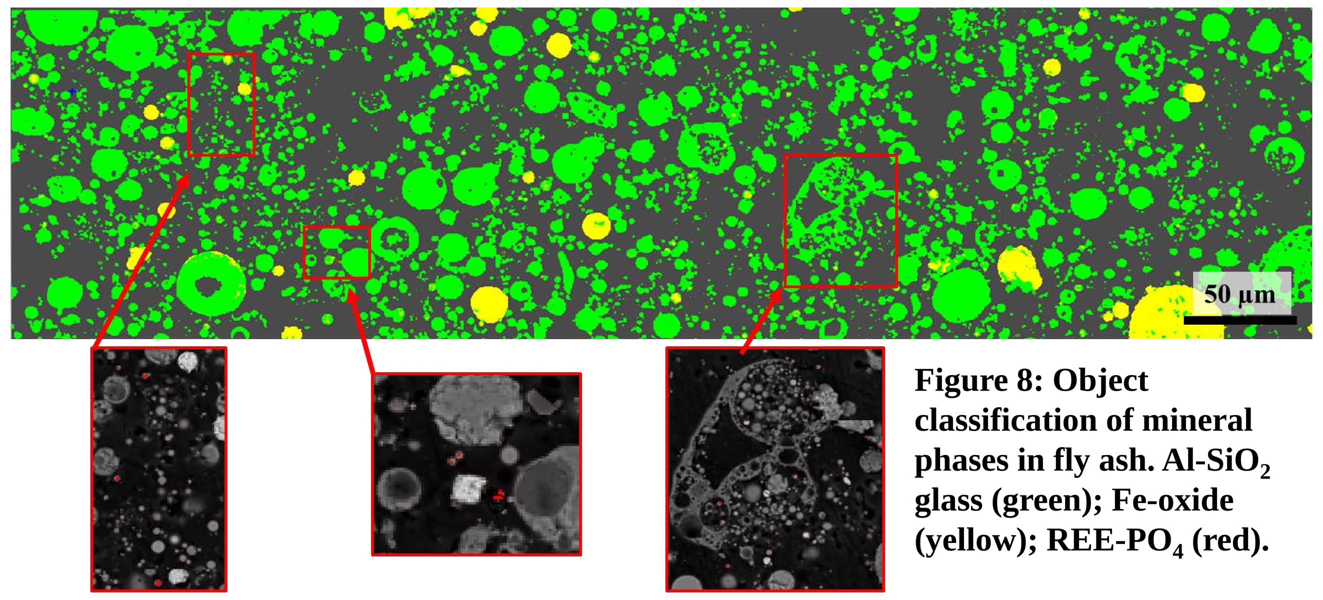


Figure 8: Object classification of mineral phases in fly ash. Al-SiO_2 glass (green); Fe-oxide (yellow); REE-PO_4 (red).

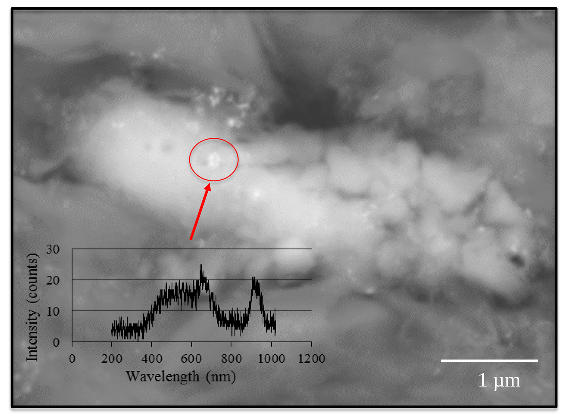


Figure 9: SEM-CL image of mineral embedded in muscovite from coal reject. (Inset) CL spectra for the particle highlighted by the red circle.

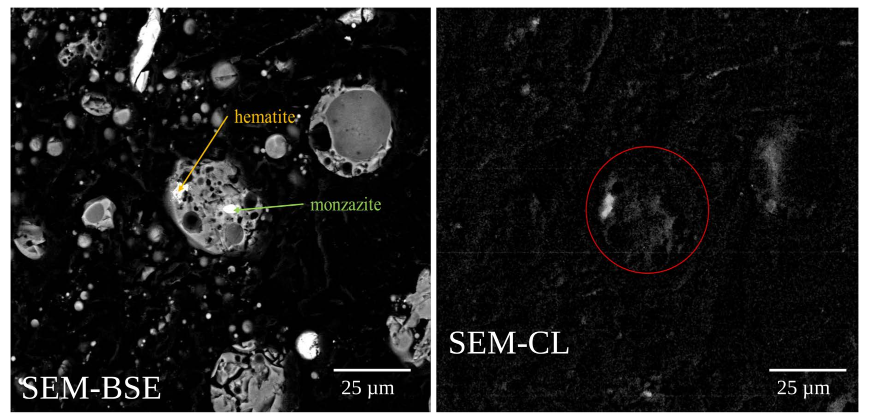


Figure 10: SEM-BSE (left) and SEM-CL (right) of fly ash with EMPA-WDS measured REE concentrations (see Figure 6).

- CL spectra and cathodoluminescence image confirms presence of cerium that are collocated with zircon and in matrix phyllosilicate in coal reject.
- No REE luminescence from monazite; may be quenched in fly ash.
- Additional work required to see REE activators.

- Coupled SEM-EDS and FIB-SEM analysis to quantify to volume and mass of REE in coal refuse.
- Total volume of monazite
    - Coal: 5.392 µm^3
    - Fly ash: 187.09 µm^3
- Composition of monazite (wt %)

	Coal	Fly ash
Ce	8.86%	27.6%
La	4.12%	11.2%
Nd	3.61%	9.9%

- Mass of REE (g)

	Coal	Fly ash
Ce	2.17×10^{-12}	2.66×10^{-10}
La	1.13×10^{-12}	1.08×10^{-10}
Nd	9.91×10^{-13}	9.59×10^{-11}

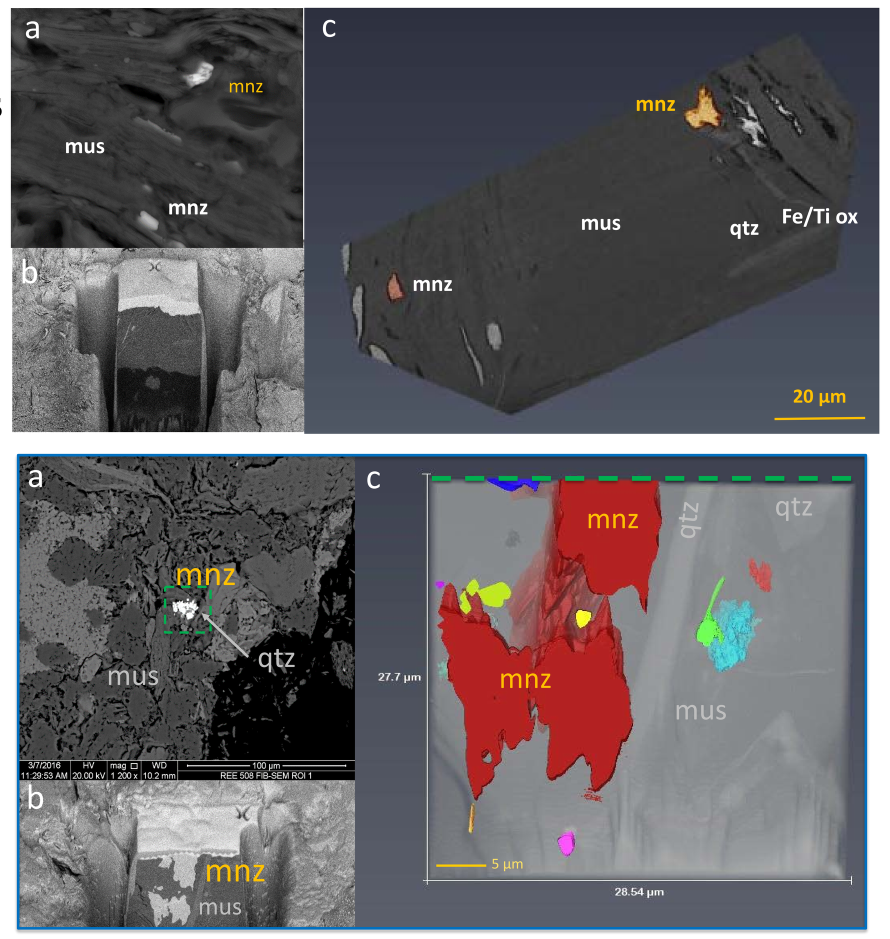


Figure 10. Analysis of coal refuse by field emission SEM coupled with a focused ion beam (FIB-SEM). (a) SEM-BSE image of site of interest for FIB-SEM analysis containing monazite (mnz), muscovite (mus), and quartz (qtz). (b) Z-contrast image of the milled site of interest. (c) Three dimensional reconstruction of FIB-SEM images showing accessory mineral phases in the sample (c).

Summary

- An initial assessment of the mineralogical and elemental composition of coal provides context to the partitioning of elements of interest into minerals formed during combustion. During combustion, a majority of the inorganic mineral phases in the coal become fluidized at combustion temperatures that may exceed 1400°C. Monazite, xenotime, and zircon have relatively high melting points and are unaltered after combustion.
- Monazite (LREE-PO_4) and xenotime (HREE-PO_4) coexist with muscovite, kaolinite, and other phyllosilicates within parent rock and coal refuse samples as isolated crystals or encapsulated by secondary phases in CUB samples. REE-PO_4 crystals are less than 10 µm in size.
- Pixel and object classification allows for the identification and quantification of REE minerals in CUB samples
- Limited REE-PO_4 observed by SEM; high REE in ICP-MS analysis indicates that REE is encapsulated in ash mineral phases or as REE adsorbed to the surfaces of minerals (e.g. phyllosilicates) or phases (e.g., silicate and aluminosilicate amorphous glass, slag, and unburnt carbon).
- FIB-SEM analysis yielded quantitative data on the volume of monazite grains and REE in coal refuse.

ACKNOWLEDGEMENTS: The authors acknowledge the NETL Rare Earth Elements team, specifically Evan Granite and Eliot Roth; Han Chan, Teresa Sawyer at Oregon State University Electron Microscopy Facility for FIB-SEM data collection and reconstructions; Michael Outrequin, Anne-Sophie Robbes, and Dan Jacobson from Cameca/Ametek for EPMA analysis.

U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

Science & Engineering To Power Our Future