Sequential Extraction of Coal-Related Feedstocks: Rare Earth Element Targetable Fractions and Extractability

Sophia Bauer[1,2], Jonathan Yang[1,2], Mengling Stuckman[3,4], R. Burt Thomas[1], Circe Verba[1]

[1]U.S. Department of Energy, National Energy Technology Laboratory, Albany OR; [2]NETL Support Contractor, Albany OR; [3]U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh PA; [4]NETL Support Contractor, Pittsburgh PA **Contact at sophia.bauer@netl.doe.gov Paper ID: 3641346**

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Introduction

Abstract

The global economy relies on rare earth elements (REE) for numerous modern industries. The increase in demand and uncertainty related to the REE supply chain has pushed the U.S. to find stable domestic resources and evaluate non-conventional sources. REE modes of occurrence are critical to the evaluation of non-conventional resources, along with an understanding of the mineralogy and subsequent REE distribution. Understanding REE fractionation across these modes can lead to more direct and efficient extraction techniques.

A seven-step sequential extraction was conducted on four coal-related samples associated with the Middle and Lower Kittanning coal seams in the Appalachian Basin (U.S.). These seven steps are operationally defined as accessing the water soluble, exchangeable, acid soluble, mildly reducible, moderately reducible, strongly reducible, and oxidizable fractions. In a West Virginia Middle Kittanning underclay **21%** of total REE was extracted. For the West Virginia Middle Kittanning coarse coal refuse, **1.8%** of total REE was extracted. For the central Pennsylvania Lower Kittanning underclay, **1.5%** of total REE was extracted. Lastly, in the central Pennsylvania Middle Kittanning underclay, **5.5%** of total REE was extracted. All samples showed a middle REE and heavy REE enrichment. These results illuminate the high variability of extractability and fractionation of REE from Lower and Middle Kittanning coal-related samples and can inform future extraction efforts.

Research Questions

- Will the extractability of REE vary between sample types due to the adsorbed state/bond of REE in each sample?
- Will the total extractability and the fractionation of extracted REE be similar for the two Middle Kittanning underclay samples?
- Will critical elements of interest or gangue elements be co-extracted?
- Will the REE extracted be enriched in either LREE, MREE, or HREE?

Methods

- Four coal-related samples underwent a seven-step sequential extraction to determine the fractionation of extractable REE.
- During each step the samples were reacted with a reagent in a rotator at 40 rpm, centrifuged, then the solids and liquids were separated .

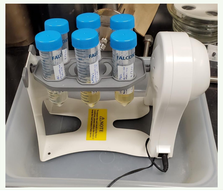

Table 1: Sequential extraction procedure modified from Lin et al., 2018 and Ruttenberg 1992.

Step #	Targeted Fraction	Reagents	L:S ratio	Temp (°C)	Duration (h)	pH
1	Water-Soluble	MilliQ Water	20:1	25	24	4.9
2	Exchangeable	1.0 M Ammonium Acetate	20:1	25	24	6.0
3	Acid Soluble	1.0 M Sodium-Acetate Trihydrate	25:1	25	24	4.0
4	Mildly Reducible	0.1 M Hydroxylamine Hydrochloride	20:1	25	0.5	3.5
5	Moderately Reducible	0.2 M Ammonium Oxalate + 0.2 M Oxalic Acid in Dark	20:1	25	4 in dark	3.0
6	Strongly Reducible	0.2 M Ammonium Oxalate + 0.2 M Oxalic Acid + 0.1 M Ascorbic Acid	20:1	80	0.5	2.3
7	Oxidizable	1) Acidified 30% H_2O_2	10:1	25/85	1 + 1	2-3
		2) Acidified 30% H_2O_2	10:1	85	1	2-3
		3) 1.0 M Ammonium Acetate	50:1	25	16	2.0
8	Residual	$LiBO_2$ Digestion	-	-	-	-

Results and Discussion

Primary fractions of extracted REE:

A)
- **Exchangeable** (40%)
- **Oxidizable** (36%)

B)
- **Acid soluble** (39%)
- **Moderately reducible** (25%)
- **Oxidizable** (16%)

C)
- **Strongly reducible** (23%)
- **Moderately reducible**[3] (23%)
- **Oxidizable** (23%)
- **Acid soluble** (23%)

D)
- **Oxidizable** (71%)
- **Acid soluble** (22%)

- The **acid soluble** fraction primarily includes **amorphous calcium phosphates**; the **mildly reducible** fraction primarily includes **Mn oxides**; the **moderately reducible** fraction primarily includes **amorphous Fe oxides**; the **strongly reducible** fraction primarily includes **crystalline Fe oxides**; and the **oxidizable** fraction primarily includes **organics and sulfides**.

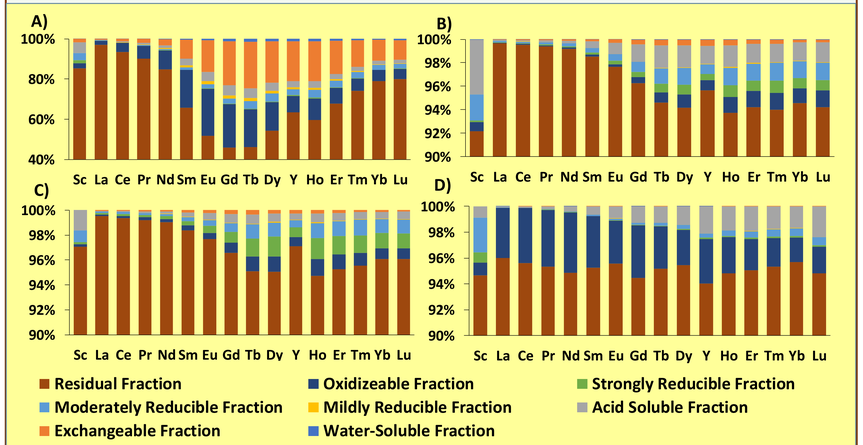

Figure 1: Normalized distribution of extracted REE in seven fractions as well as the residual. A) Normalized distribution of REE in West Virginia Middle Kittanning underclay. B) Normalized distribution of REE in in West Virginia Middle Kittanning coarse coal refuse. C) Normalized distribution of REE in central Pennsylvania Lower Kittanning underclay. D) Normalized distribution of REE in central Pennsylvania Middle Kittanning underclay

Table 2: Concentrations and percentages of extracted: total REE, critical elements (Co, Ni, Cu, and Zn), and gangue elements (Al, Ca, and Fe).

	Total REE Extracted		Total Co Extracted		Total Ni Extracted		Total Cu Extracted		Total Zn Extracted		Total Al Extracted		Total Ca Extracted		Total Fe Extracted	
Sample	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
West Virginia Middle Kittanning Underclay	62	21	49	88	68	70	39	63	107	69	1048	1.7	2503	60	3408	26
West Virginia Middle Kittanning Coarse Coal Refuse	6	1.8	7	51	12	29	21	37	35	36	1556	1.3	1186	50	1542	9.2
Central Pennsylvania Lower Kittanning Underclay	3	1.5	4	54	8	26	10	60	46	44	648	0.7	878	64	181	2.0
Central Pennsylvania Middle Kittanning Underclay	40	5.5	13	64	37	44	39	50	91	35	1585	2.0	19655	22	4363	16

- Critical metals of interest (Co, Ni, Cu, and Zn) and gangue elements (Al, Ca, and Fe) were extracted
- All four coal-related samples showed a MREE and HREE enrichment

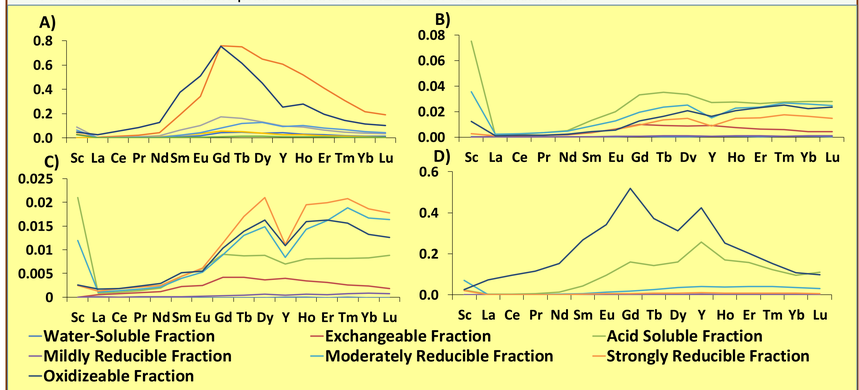

Figure 2: Distribution of REE concentrations by elemental weight normalized to upper continental crust concentrations. A) West Virginia Middle Kittanning underclay. B) West Virginia Middle Kittanning coarse coal refuse. C) Central Pennsylvania Lower Kittanning underclay. D) Central Pennsylvania Middle Kittanning underclay

Conclusion

This study assessed the extractability and fractionation of REE in coal-related strata from the Central Appalachian Basin. Variability was observed in the extractability of REE from varying fractions. The coal-related material with the highest total REE concentration had a total extractability rate an order of magnitude below the highest extractability rate. Phases hosting REE are suggested to be the: exchangeable fraction (e.g., clays), oxidizable fraction (e.g., organics and sulfides), and moderately to strongly reducible fractions (e.g., Fe oxides). In all coal-related materials in this study, the REE distribution shows a MREE and HREE enrichment which agrees with the REE distribution patterns of previous work conducted at NETL on coal-related products.

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