

DISTRIBUTION AND SPECIATION OF RARE EARTH ELEMENTS IN COAL COMBUSTION BYPRODUCTS

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Keywords: Rare Earth Elements; μ -XANES and XRF; Sequential Extraction; Fly Ash; Coal

Introduction

Coal and coal combustion by-products (CCBs) are being explored as potential resource to recover rare earth elements in the United States, due to their relatively abundant REE content, low-to-no-cost availability as waste products, and enrichment with critical REEs. However, there is limited information on the fate and transformations of REEs at different stages (e.g., raw coal, fly ash, bottom ash, coal rejects) of coal processing and combustion. This study investigated speciation and distribution of REEs in different CCBs using sequential extraction and synchrotron-based technologies. Our results will help to develop more effective extraction of REEs from CCBs.

Methods

Nineteen CCBs were collected from various power plants and coal mines from KY, OH, and PA, USA. These 19 samples include samples of different fly ash, bottom ash, coal reject, landfilled ash and clay roof rock materials. Selected samples were subjected to mineral phase analysis by XRD and 7-step sequential extraction described by Jegadeesan et al. (2008), in order to identify REE distribution in different solid fractions. All CCB samples together with Ce reference materials were further prepared into powder and polished thin-sections (30 μ m thick) for synchrotron analysis at the Stanford Synchrotron Radiation Lightsource (SSRL). Bulk X-ray absorption spectroscopy (XAFS) was collected at the Ce LIII edge for the powdered CCBs. Ce was studied due to its different oxidation states (3+ and 4+) and as a proxy for other light REEs. Micro-X-ray fluorescence (μ -XRF) elemental maps with 50 μ m and 2 μ m beam size were used to identify regions of interest and Ce hotspots on thin section samples. Micro-X-ray absorption near edge structure (μ -XANES) was collected on identified Ce hotspots. Linear combination fitting (LCF) of the Ce LIII edge XANES spectra against Ce reference materials was used to characterize Ce speciation and the coordination environments in different samples or regions of interest on thin sections.

Results

Preliminary 7-step sequential extractions in three types of CCBs (A003 as bottom ash, K37 as coal reject, and RE443 as clay roof rock materials, see Figure 1) showed REEs were bonded to different phases. REEs were mostly extracted by the sulfide extraction step (REE extracted: 20% for A003, 38% for K37 and 52% for RE443). Other REE-extractable phases include carbonates (up to 1.8% in A003), amorphous Fe/Mn oxides (up to 5.3% for A003) and crystalline Fe oxides (up to 3.1% for RE443). Further sequential extractions are in progress on additional samples in order to better characterize REE associated phases in different types of CCBs.

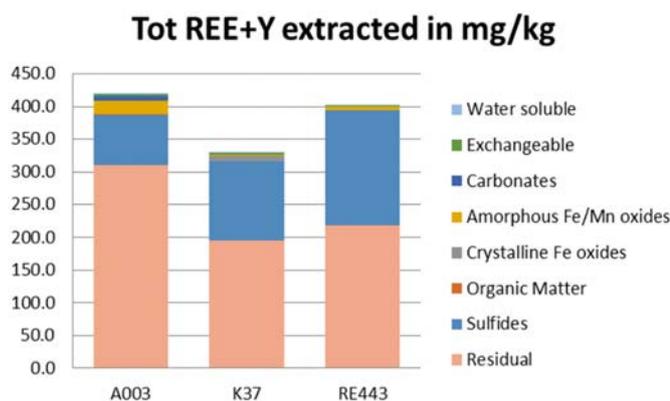


Figure 5. Extracted and non-extractable residuals of total REE+Y from 7-step sequential extraction (mg/kg)

Synchrotron-based bulk XAFS demonstrated that Ce-III was the dominant oxidation state for all samples, with some Ce-IV signatures present in 5% of the 19 samples studied to date. Fractionation of cerium (Ce) speciation and oxidation states were observed in the studied bottom ash and fly ash samples, where μ -XRF and μ -XANES further resolved the presence of REE phosphates (Ce-III), oxides (Ce-IV) and sulfates (Ce-III) in CCB samples (Lopano et al., 2015) (Figure 2).

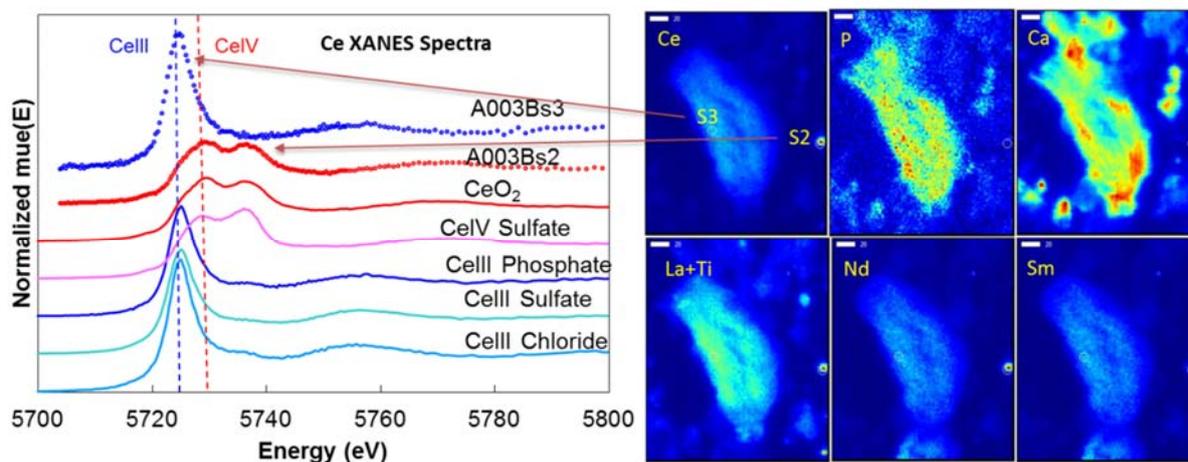


Figure 2. Synchrotron μ -XANES spectra at Ce LIII edge for Ce hotspots (A003Bs3 and A003Bs2) in bottom ash sample A003 and for reference materials CeO_2 , $\text{Ce}(\text{SO}_4)_2$, CePO_4 , $\text{Ce}_2(\text{SO}_4)_3$, and CeCl_3 (Left panel); and synchrotron μ -XRF maps (Right panel) for light REEs, P and Ca distributions for 30 μm thick thin-section of bottom ash samples A003. Scale bar is 20 μm . The maps were collected at 7000eV, with 2 μm step size and 100msec dwell time. Red and yellow colors in maps indicate high intensity fluorescence signal and high elemental concentrations. From LCF, micro-XANES in left panel for A003Bs2 (red dot) is consistent with CeO_2 (in red), while micro-XANES for A003Bs3 (blue dot) is consistent with CePO_4 (in blue).

Conclusion

Analysis of results from a 7-step sequential extraction protocol performed on a small subsample of CCBs to date revealed various REE-associated phases, including but not limited to: exchangeable clays, and different iron and sulfide phases. Additional characterization via synchrotron techniques on a larger subset of CCBs implies that cerium exists as sulfates, oxides and phosphates in various phases in CCB samples. These results, while still preliminary, may inform and potentially aid in the simplification of the processes for separation and extraction of REE from CCBs.

References

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