

Analysis of rare earth elements in coal fly ash using laser ablation inductively coupled plasma mass spectrometry and scanning electron microscopy

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ABSTRACT

Reference standard NIST SRM 1633b and FA 345, a fly ash sample from an eastern U.S. coal power plant, were analyzed to determine and quantify the mineralogical association of rare earth elements (REE). These analyses were completed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and a scanning electron microscope, equipped with an energy-dispersive X-ray spectrometer (SEM-EDS). Internal standardization was avoided by quantifying elemental concentrations by normalizing to 100% oxides. Mineral grains containing elevated REE concentrations were found in diverse chemical environments, but were most commonly found in regions where Al and Si were predominant. Dividing the spot analyses into time segments yielded plots that showed the REE content changing over time as individual mineral grains were being ablated. SEM-EDS images of FA 345 confirmed the trends that were found in the LA-ICP-MS results. Small grains of apatite, monazite, or zircon were frequently observed as free mineral grains or embedded in amorphous aluminosilicate glass and were not associated with ferrous particles. This finding is consistent with previous reports that magnetic enrichment may be an effective way of concentrating non-magnetic REE phases. Furthermore, aggressive mechanical and chemical-based separation schemes will be required to separate and recover REE from aluminosilicate glass.

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1. Introduction

Coal is an important domestic and international economic resource. The United States generates nearly 30% of its electricity through coal combustion and possesses substantial coal reserves. According to the U.S. Energy Information Administration's 2017 Monthly Energy Review, approximately 1 Gt of coal has been mined annually in the United States over the past 25 years; however, the 2015 total was 896 million tons and 2016 total was 728 million tons [1]. The recent decline in domestic coal production is due to the availability of abundant and inexpensive natural gas, regulatory uncertainty with regard to CO₂ emissions from coal combustion, and the retirement of older coal-fired power plants [2].

Rare earth elements (REE), which comprise the 14 naturally occurring lanthanide elements plus scandium and yttrium, are abundant in coal and coal byproducts. Most of the common inorganic lanthanide compounds found in coal, such as phosphates, have high melting, boiling, and thermal decomposition temperatures, which allows them to become concentrated in combustion and gasification byproducts.

REE are commercially produced from ion-exchangeable clays and ores enriched in minerals such as bastnäsite and monazite. REE are also found in coal and combustion byproducts such as ash, coal preparation residues, gasification slags, mining waste, and the strata above and below some coal seams. Some coals and coal byproducts have elevated concentrations of heavy rare earth elements (HREE) [3] which makes these sources economically attractive as HREE are lowest in supply, rank high in criticality and price, and are projected to increase in demand.

The National Energy Technology Laboratory's (NETL) Rare Earth EDX Database [4] is a resource for rare earth element information related to coal and byproducts. The NETL Research and Innovation Center (NETL-RIC) recently initiated research to support the quantification and identification of REE compounds, as well as recovery of REE from abundant domestic coal byproducts [5]. Many other research organizations have also initiated efforts for the analytical characterization and recovery of rare earths from unconventional sources such as coal byproducts.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is an analytical technique which can directly analyze solid samples with spatial resolution down to the μm scale. While the spatial resolution of LA-ICP-MS is not as fine as that of electron

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microscopy, the detection limits for REE are superior. There is limited literature available that utilizes LA-ICP-MS for the study of coal fly ash; no studies where REEs were emphasized were found. LA-ICP-MS was successfully used in the analysis of epoxy-mounted coal fly ash samples from a British power plant, as reported by Spears, [6,7] in which the elemental correlations of analytes including Hg, S, and As were quantified. Another study by Piispanen et al. [8] stated LA-ICP-MS results of NIST SRM 2691 fly ash and four power plant fly ash samples were in agreement with accompanying SEM analyses. LA-ICP-MS analysis reported by Stankova et al. [9] explored the effect of binder on NIST 1633b and power plant fly ashes in the form of pressed powder pellets. Finally, laser induced breakdown spectroscopy (LIBS) was recently used to analyze sub-bituminous coal ash for trace elements, including REE [10].

This study focuses on the concentrations of 36 different elements, with an emphasis on REE in two samples: NIST SRM 1633b, a certified reference coal fly ash and FA 345, a fly ash from an unidentified coal seam collected from a pulverized coal power plant using LA-ICP-MS and compared with bulk analyses performed by ICP-MS on digested samples. The approach to combine LA-ICP-MS results with electron microscopy and x-ray microanalysis data provides elemental correlations between certain major and minor components to REE phases. It is expected that the results from this study will ultimately be useful in locating ways of separating the REE minerals from coal fly ash.

2. Experimental methods

2.1. Fly ash samples

Two different fly ash samples were analyzed in this work: NIST SRM 1633b, a bituminous coal fly ash [11] and FA 345, a dry fly ash from an unidentified coal seam collected from a pulverized coal power plant in Ohio, USA [4].

2.2. Bulk and trace analyses

Particle size determination of FA 345 was performed using a Malvern Mastersizer 3000 with the fly ash dispersed in water. The particle size analysis results for FA 345 is shown in Fig. 1, which shows a bimodal distribution in volume density with a smaller particle size maximum at 0.872 μm and a larger maximum at 24.1 μm . The particle size in number density shows that the $D_n(90)$ value for FA 345 is 1.31 μm , meaning on a number density basis that nearly all fly ash particles are smaller than 1.31 μm in diameter.

Moisture and ash determinations were performed using a Leco TGA 701. Combustion analyses of the fly ash was performed using a Perkin

Elmer 2400 Combustion Analyzer. The moisture (as received, determined at 107 °C in N_2), ash content (dry basis, determined at 550 °C in air), and combustible carbon and sulfur content of the samples analyzed in this work are listed in Table 1. Both samples had 3% or less combustible carbon and no detectable combustible sulfur.

Powder X-ray diffraction (XRD) analysis of the bulk mineral composition of both fly ashes was carried out using a PANalytical X'Pert PRO diffractometer equipped with a Cu anode operated at 45 kV and 40 mA. Phase identification was verified by comparison to the International Centre for Diffraction Data (ICDD) inorganic compound data base. Results from XRD analysis are summarized in Table 2.

Bulk ICP-MS measurements were carried out on dried, ashed sample aliquots (0.05 g), which were mixed with lithium metaborate (0.4 g) in Pt crucibles, then fused in a furnace at 1100 °C. The resulting sample glasses were dissolved in 5% nitric acid and brought to volume (100 mL). Further dilutions, when needed, were performed using 2% nitric acid as diluent.

Bulk measurements of element concentrations were conducted using a Perkin Elmer Nexion 300D ICP-MS in kinetic energy discrimination (KED) mode using ultra high purity He as the collision gas. The flow rate of He was optimized and set to 2 mL/min for the all elements. The system uses a Perkin Elmer quartz cyclonic spray chamber and a Glass Expansion Seaspray nebulizer and Pt cones. An in-line internal standard of 50 $\mu\text{g/L}$ In was used for the normalization of all bulk measurements. Prior to data collection, a daily performance test was completed to maximize signal intensity, while minimizing the oxide formation to <2.5% CeO^+/Ce^+ and minimizing the doubly charged ions to <1% $\text{Ce}^{++}/\text{Ce}^+$. No correction equations were employed for any of the element analyses reported.

LA-ICP-MS samples were ablated using a GeoLas Pro 193 nm ArF excimer laser, connected to an Agilent 7500ce quadrupole ICP-MS by way of flexible tubing. Circular laser spots varying from 32 to 60 μm in diameter were used for sample ablation and He was used as the sweep gas in the sample cell [12]. The position of the laser on the sample surface was monitored using a camera attached to a video monitor. The operating conditions for both the laser and the ICP-MS are listed in Table 3. All the LA-ICP-MS instrumentation used in this study is located at the Virginia Tech Geosciences Department.

Laser ablation samples must be immobilized prior to analysis on a relatively flat surface to provide clear microscope images and efficient delivery of sample. A variety of mounting techniques were attempted, but were found to be inadequate for acceptable results. These methods included pressing fly ash particles into molding clay, double-sided adhesive tape, and semi-hardened epoxy; these attempts failed to provide a useful sample. The method used for preparing samples for LA-ICP-MS analysis in this work was adopted from that reported previously for similar analyses by both Spears [6], Hower, et al. [13], in which a layer of fly ash (as received) was spread on the bottom of a 0.5 in cylindrical mold, then was backfilled with Buehler Epo-Kwick epoxy (5:1 resin to hardener ratio) and allowed to cure for 24 h. When the epoxy had cured, the mold was cut away and the resulting mount was polished by hand to expose a layer of immobilized fly ash particles. This procedure provided a densely-packed sample of fly ash which provided a flat surface and permitted convenient handling of the sample within the ablation cell. In addition to the two samples prepared in house, SRM 1633b was mounted professionally by Spectrum Petrographics (Vancouver, WA), in which the fly ash was embedded using EPOTEK 301, and mounted on a glass slide using Loctite Impruv. Fig. 2 shows camera images of the surfaces of all three samples after polishing taken by a petrographic microscope.

All LA-ICP-MS data were reduced using AMS LA-ICP-MS Data Reduction Software [14,15], a freely available software package for LA-ICP-MS analysis of a wide variety of geologic materials developed by the Virginia Tech Geosciences department. This software was used to quantify element concentration for entire spot analyses and for time segments of those spots. Samples were blank subtracted using a 1 min. Segment at

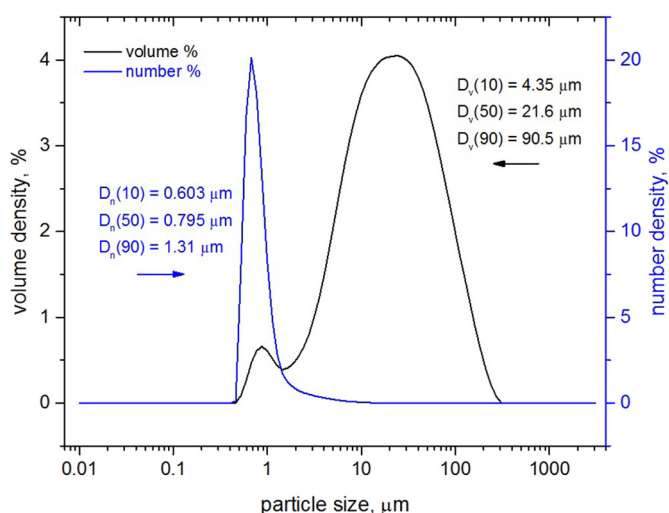


Fig. 1. Particle size analysis of FA 345 by both volume and number density.

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