

Distributions and Extraction of Rare Earth Elements from Coal and Coal By-Products

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ABSTRACT

NETL is leading a research effort to investigate, characterize, and extract rare earth elements (REE) from coal and coal by-products, including coal ash. Characterization of geologic core samples, coal mine wastes, and coal ash has led to interesting findings on the mode of occurrence and fate of rare earth minerals, such as monazite, in coal-based materials. Mineral associations and elemental distributions have been investigated and results indicate that Th is associated with light rare earth elements (LREE), possibly as monazite, and Zr is associated with heavy rare earth elements (HREE), possibly as zircon. Preliminary extractions of REE from coal ash using 2M hydrochloric acid (HCl) and sodium hydroxide (NaOH) hydrothermal pretreatment have been investigated. Sodium hydroxide solution pretreatment followed by an acid digestion was shown to increase extraction of REE to nearly 90% for coal ash.

INTRODUCTION:

Despite the recent downturn in coal production in the U.S., coal continues to be a tremendous resource with approximately one billion tons of coal mined annually in the U.S. between 1990 and 2014, and ~740 million tons produced in 2016.¹ Renewed interest in the extraction of valuable and critical materials and elements from coal and coal by-products has the potential to shift coal research from pollutant control to economic recovery of critical elements and metals.² Recent studies on rare earth elements and yttrium (REY) in coal and coal ash have focused on REY enrichment and distribution in coals³⁻⁵, REY size dependent variations in fly ash⁶, anomalous REY behavior in coal⁷, and extraction of REY from fly ash.⁸ The National Energy Technology Laboratory (NETL) has created an open access website with REY concentrations in field samples from coal mining to coal combustion processes.⁹ This study focuses on a

pulverized coal fly ash sample from Ohio. Bulk REY concentrations in particle size-separated samples are measured using inductively coupled plasma mass spectrometry (ICP-MS) and discussed. Concentrations and distributions of the REY are also analyzed using laser ablation ICP-MS. Results from preliminary studies of REE extractions using both 2M hydrochloric acid (HCl) leaching and 5M sodium hydroxide (NaOH) hydrothermal pretreatment followed by 2M HCl leaching are presented.

Experimental Procedure:

The fly ash sample used in this study was collected from LTI and is described on the NETL EDX website (<https://edx.netl.doe.gov/ree/>). A GilSonic UltraSiever, model GA-8, with ASTM E-11 stainless steel woven wire cloth sieves was used for particle size separation experiments. A Nexion 300D ICP-MS (Perkin Elmer) with universal cell technology was used for bulk elemental analysis of the samples. Data were collected in kinetic energy discrimination (KED) mode using He as the collision gas. To prepare the samples for analysis, the samples were dried for one hour under nitrogen at 107°C and ashed for five hours under air at 550°C using a LECO Thermogravimetric Analyzer (TGA 701). The dried, ashed samples were fused with lithium metaborate at 1050°C for five minutes and then digested in warm 5% nitric acid and then further diluted in 2% nitric acid before ICP-MS analysis. A detail report on the digestion procedure has been reported.¹⁰ For the laser ablation studies, 100-200mg of fly ash was placed into a ½” (1.27cm) mold and filled with Buehler Epo-Kwick epoxy. After the epoxy cured the mold was slightly polished to expose the fly ash particles. A GeoLas Pro 193nm ArF excimer laser with an energy density of 7-10 J/cm², repetition rate of 5 Hz, and with a circular spot size that varied from 44-120 microns was used to ablate the sample. The ablated sample was then carried by He gas and analyzed by an Agilent 7500ce Q-ICP-MS. The sample was ablated for approximately 60 seconds per spot. The system was calibrated using a standard reference glass NIST SRM 610, and internal standardization was performed by normalizing to 100% oxides. Data were processed using the Analysis Management System (AMS) software. Batch extraction experiments were completed using 2M HCl and a 10:1 liquid to solid ratio by weight. The HCl leaching solution was analyzed using ICP-MS to determine element concentrations and to calculate REE recovery by the extractant. Sodium hydroxide pretreatment was accomplished using 5M NaOH solution with a 10:1 liquid to solid ratio, heated to ~93°C for the desired duration. The solid sample was washed three times with water, dried, and then leached with 2M HCl solution. The recovery of REE in the extractant solution was measured by ICP-MS.

Results and Discussion:

Particle size, density, and magnetic separations using this fly ash sample and other coal by-product samples were previously conducted using a mechanical sieve.¹¹ In this study, the fly ash sample was separated into eleven size fractions using an ultrasiever, and a modest increase REE concentration with decreasing particle size was observed (Table 1). The increasing REE concentration with decreasing particle size was previously reported in literature and may coincide with increasing glass content in the finer size fraction.^{6,12} REY can be divided into three groups, light (LREY – La, Ce, Pr,

Nd, and Sm), medium (MREY – Eu, Gd, Tb, Dy, and Y), and heavy (HREY – Ho, Er, Tm, Yb, and Lu). The results in Table 2 and Figure 1 show a heavy and medium rare earth enrichment ($L_{AN}/L_{UN} < 1$, $L_{AN}/S_{mN} < 1$) using rare earth concentrations normalized to the upper continental crust (UCC).^{3,7,13} The heavy and medium REY enrichment of the fly ash is most likely due to the feed coal and not the combustion conditions. The Ce and Eu anomalies were calculated using Equations (1) and (2), respectively, where N indicates the REE concentration normalized to concentrations in the UCC.⁷ To avoid Gd anomalies affecting the Eu anomaly calculation, the Eu anomaly was also calculated using Equation(3).⁷ The anomalous behavior of Ce and Eu is consistent for the particle size separated samples and indicates that no fractionation of Ce and Eu is occurring with decreasing particle size. Based on the paper by Seredin et al.³, the REY were separated into critical (Y, Nd, Eu, Tb, Dy, Er), uncritical (La, Pr, Sm, Gd), and excessive REY (Ce, Ho, Tm, Yb, and Lu). The outlook was calculated as the ratio of critical to excessive REY and is reported in Table 2. The REY concentration of this fly ash is comparable to the average world ash concentration of 404 ppm.¹⁴ With an outlook greater than one and the percent critical REY approximately 37-40%, the fly ash studied would be considered promising as a rare earth source, although it is not highly elevated in total REY compared to the world coal ash, and does not meet the 800-1000ppm concentration recommended by Seredin and Dai.³

$$Ce/Ce^* = C_{eN}/((0.5L_{AN}) + (0.5Pr_N)) \quad (1)$$

$$Eu/Eu^* = E_{uN}/((0.5S_{mN}) + (0.5Gd_N)) \quad (2)$$

$$Eu/Eu^{**} = E_{uN}/((0.67S_{mN}) + (0.33Tb_N)) \quad (3)$$

Table 1: Fly ash particle size fractions and REE concentrations on a dry mass basis

Sample	Wt% of each size fraction	REE (ppm)	REY (ppm)
Original Fly Ash		358	431
(+) 100 mesh	1.3	275	328
100-140 mesh	2.2	256	300
140-200 mesh	5.5	304	358
200-230 mesh	3.8	320	379
230-270 mesh	3.9	336	398
270-325 mesh	4.9	336	398
325-400 mesh	5.8	342	407
400-450 mesh	4.5	359	426
450-500 mesh	6.4	356	423
500-635 mesh	10.4	366	438
(-) 635 mesh	51.4	378	457

Table 2: Upper continental crust normalized enrichment indicators, anomalous Ce and Eu behavior and critical, uncritical, and excessive REY. The fly ash sample is enriched in the HREY and MREY, the fly ash has little to no anomalous Ce or Eu behavior and has more critical REY than excessive REY.

Sample	La _N /Lu _N	La _N /Sm _N	Ce/Ce*	Eu/Eu*	Eu/Eu**	Critical	Uncritical	Excessive	Outlook
Original Fly Ash	0.68	0.65	0.95	1.00	1.08	170	112	149	1.1
(+) 100 mesh	0.72	0.66	0.94	0.97	1.04	126	87	115	1.1
100-140 mesh	0.82	0.72	0.95	1.00	1.10	112	81	108	1.0
140-200 mesh	0.77	0.70	0.95	1.00	1.10	134	96	128	1.0
200-230 mesh	0.76	0.69	0.95	1.00	1.09	144	101	135	1.1
230-270 mesh	0.76	0.69	0.95	0.99	1.07	150	106	142	1.1
270-325 mesh	0.76	0.68	1.00	0.96	1.04	149	104	146	1.0
325-400 mesh	0.74	0.70	0.93	0.97	1.06	156	109	143	1.1
400-450 mesh	0.68	0.68	0.94	1.01	1.11	162	113	150	1.1
450-500 mesh	0.70	0.69	0.94	1.01	1.08	162	113	149	1.1
500-635 mesh	0.66	0.66	0.95	0.99	1.08	169	115	154	1.1
(-) 635 mesh	0.61	0.64	0.95	1.00	1.08	183	118	156	1.2

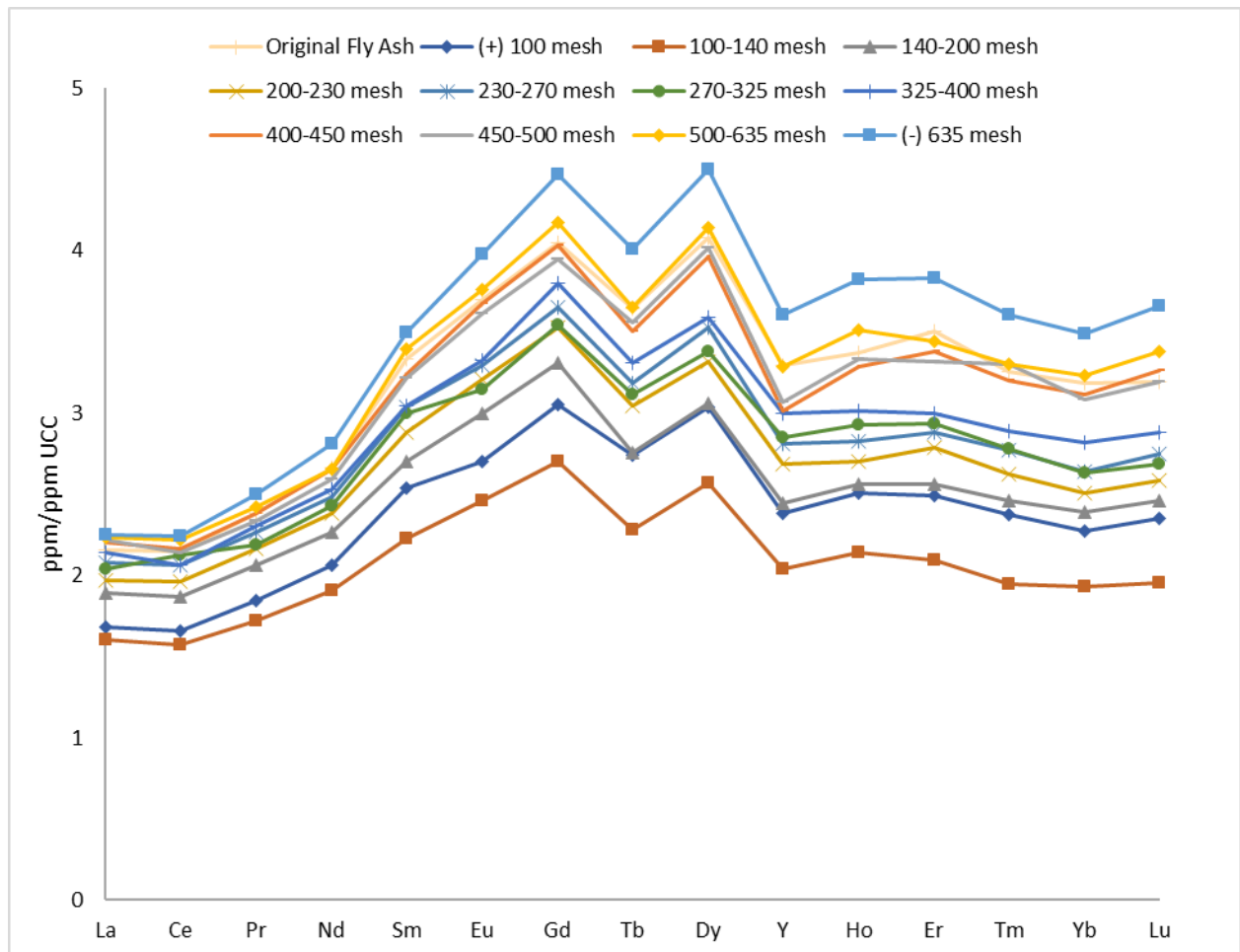


Figure 1: UCC-normalized REY distribution showing a medium and heavy REY enrichment pattern.

To investigate the heterogeneity of the fly ash and to compare REY distribution patterns of different particles, laser ablation studies were conducted at Virginia Tech on fly ash samples mounted in epoxy. Laser spot sizes ranging from 44 to 120 microns were used. The REY distribution patterns normalized to the bulk ICP-MS data are shown in Figure 2. Results indicate that spot 3 is enriched in the HREY elements and depleted in the LREY compared to the bulk ICP-MS analysis. Hf, Yb, and La concentrations are plotted against Zr concentrations for each laser ablation spot in Figure 3, and results illustrate that Yb and Hf correlate with Zr. These data may indicate that zircon is a source of HREY in fly ash. By comparing the La and Ce concentrations with Th (Figure 4), it appears that LREY are associated with minerals containing Th, such as monazite.

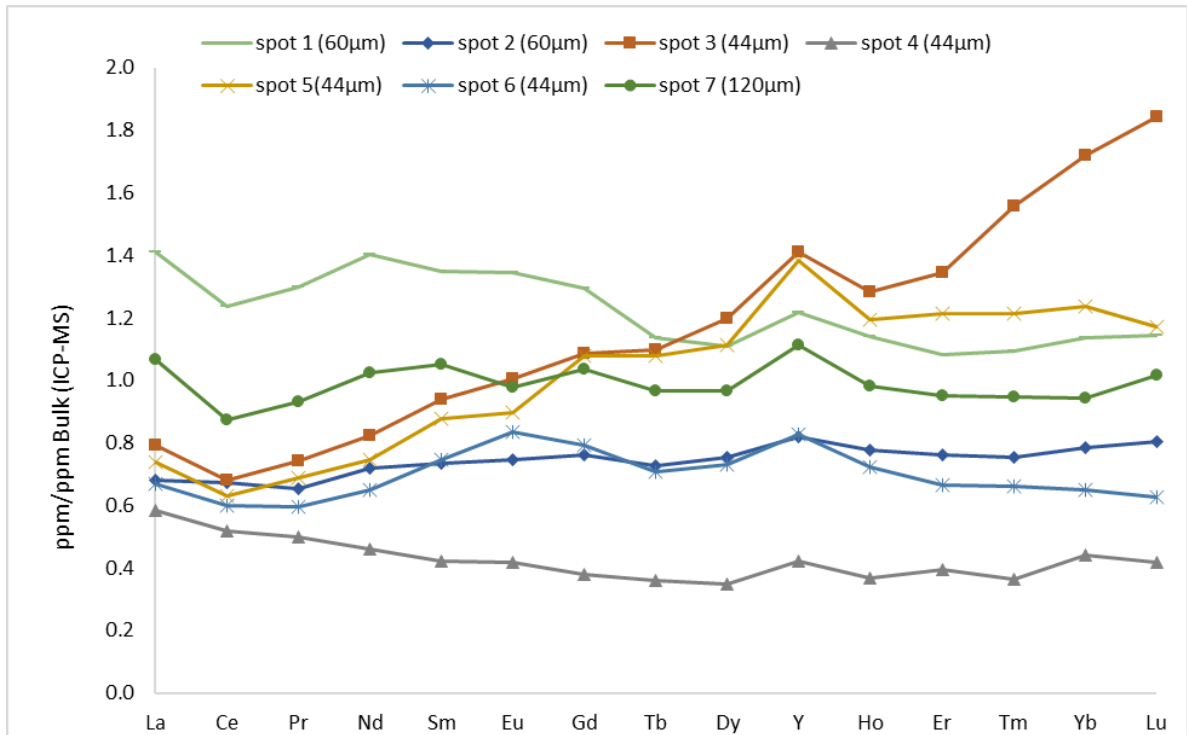


Figure 2: Laser Ablation REY distributions normalized to bulk ICP-MS data. Spot 3 and spot 5 are depleted in the LREY and enriched in the HREY.

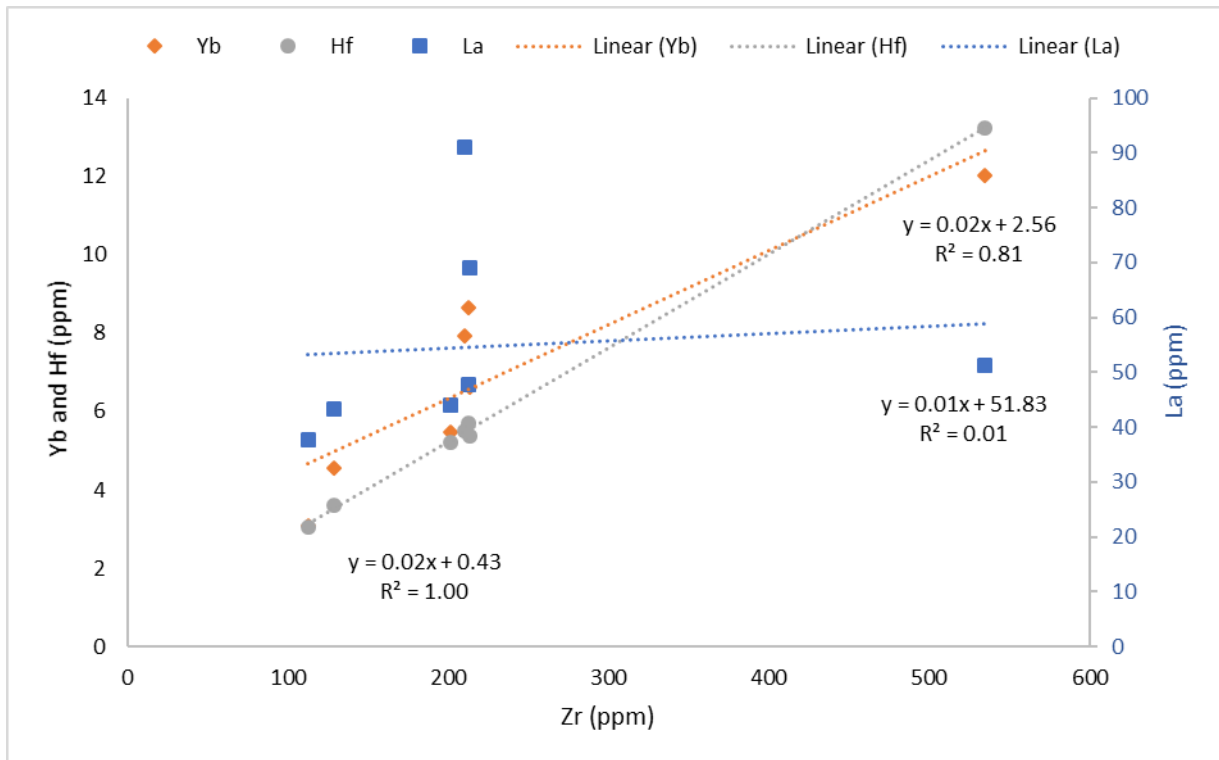


Figure 3: Laser Ablation ICP-MS data. The strong positive correlation of Zr and Hf, the high R^2 value for Yb and Zr, and no correlation of La and Zr indicate that zircon may be a source of HREY, such as Yb, in fly ash.

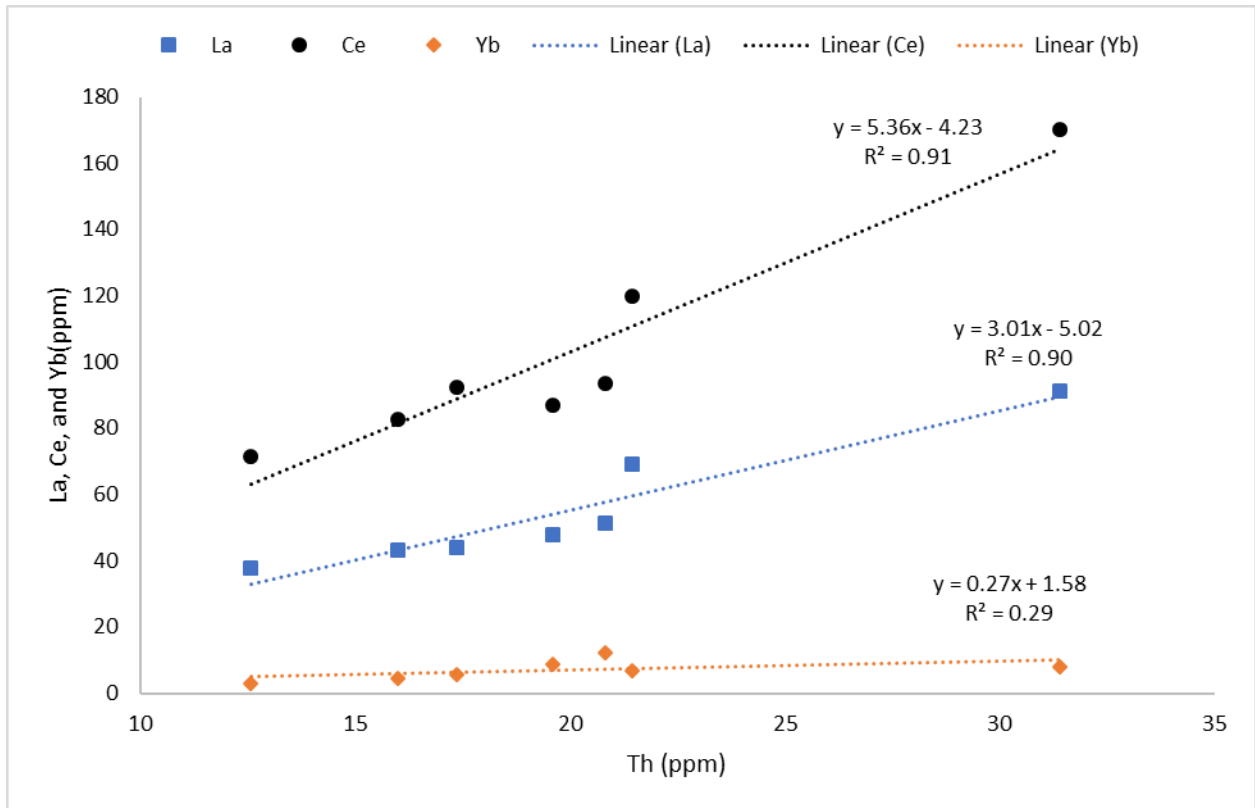


Figure 4: Laser Ablation concentration data. The high R^2 value for La and Ce vs. Th indicate that LREY are associated with minerals containing Th, possibly monazite.

Preliminary extraction studies were performed on the original fly ash. The percent extracted from the solid was calculated using Equation (4).

$$\% \text{ Extraction} = \frac{\text{Mass in HCl solution}}{\text{Mass in original solid}} \times 100 \quad (4)$$

The preliminary extraction results are shown in Figure 5. Less than 6% of the REE was extracted from the solid using 2M HCl. The results suggest that 2M HCl was not sufficient by itself to dissolve the REE-containing minerals and/or glassy fraction that possibly encapsulated the REE bearing minerals. Applying a 5M sodium hydroxide pretreatment to attack the glassy fraction of the fly ash prior to the HCl extraction produced significantly different results. The NaOH pretreatment may have dissolved the glassy fraction of the fly ash and converted rare earth phosphates into rare earth hydroxides. The NaOH pretreatment caused a significant increase in the REE extracted from the fly ash in 2M HCl solution. Increasing the time of the NaOH pretreatment to 8 hours was sufficient to achieve ~90% extraction of the REE in the subsequent HCl leaching. The sodium hydroxide pretreatment may be beneficial to the cost of REE extraction from fly ash, due to the potential formation of valuable products, such as zeolites.^{15,16} It is noted that the extraction results are preliminary and need to be further investigated.

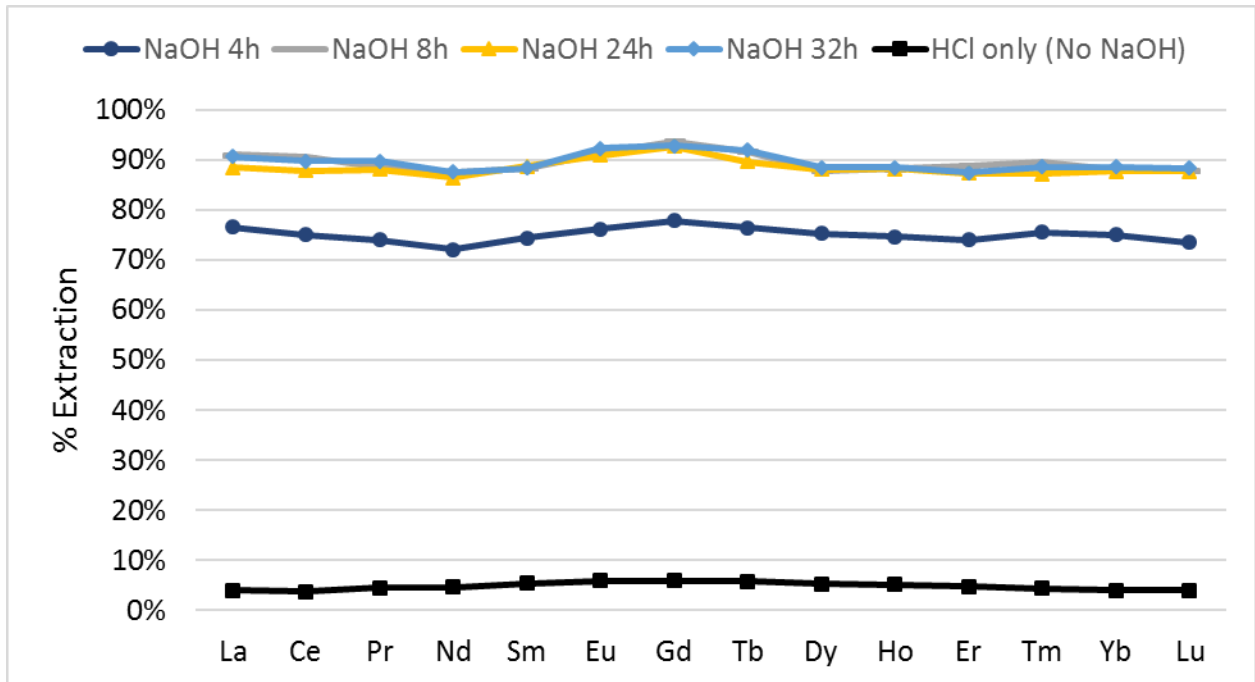


Figure 5: Extraction of the REE (%) using 2M HCl leaching only, and using 5M NaOH pretreatment followed by 2M HCl leaching. The NaOH pretreatment greatly increased the % extraction of REE.

Conclusions:

A particle-size-separated coal fly ash sample with an REE concentration comparable to the average world REE concentration was studied using ICP-MS and laser ablation ICP-MS. The sample has a medium and heavy rare earth enrichment pattern and a slight increase in REE concentration with decreasing particle size. Laser ablation spot analyses suggest that zircon could be a source of HREY in this sample. Extraction of the REE using only 2M HCl was very limited. However, when using a sodium hydroxide pretreatment, REE extraction increased to ~90%. Future work will look at mechanisms for REE extraction and the formation of value-added products, such as zeolites, from fly ash.

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