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Title

Leaching Behavior of Rare Earth Elements in Fort Union Lignite Coals of North America

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Abstract

Fort Union lignite coal samples were subjected to a series of aqueous leaching experiments to understand the extraction behavior of the rare earth elements (REE). This testing was aimed at understanding the modes of occurrence of the REE in the lignite coals, as well as to provide foundational data for development of rare earth extraction processes. In a first series of tests, a sequential leaching process was used to investigate modes of occurrence of the REE of select lignite coals. The tests involved sequential exposure to solvents consisting of water, ammonium acetate and dilute hydrochloric acid (HCl). The results indicated that water and ammonium acetate extracted very little of the REE, indicating the REE are not present as water soluble or ion-exchangeable forms. However, the data shows that a large percentage of the REE were extracted with the hydrochloric acid (80-95wt%), suggesting presence in HCl-soluble mineral forms such as carbonates, and/or presence as organic complexes. A second series of tests was performed involving single-step leaching with dilute acids and various operating parameters, including acid type, acid concentration, acid/coal contact time and coal particle size. For select samples, additional tests were performed to understand the results of leaching, including float-sink density separations and humic acid extraction. The results have shown that the majority of REE in Fort Union lignites appear to be associated weakly with the organic matrix of the coals, most likely as coordination complexes of carboxylic acid groups. The light REE and heavy REE exhibit different behaviors, however. The extractable light REE appear to have association both in acid-soluble mineral forms and as organic complexes, whereas the extractable heavy REE appear to be almost solely associated with the organics. Scandium behavior was notably different than yttrium and the lanthanides, and the data suggests the extractable content is primarily associated as acid-soluble mineral forms.

1. Introduction

Rare earth elements (REE) include a group of elements with atomic numbers from 57-71, making up the lanthanide series of elements consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Yttrium (Y) and scandium (Sc) are often included in the group because of their similar properties, and have been included in this study. Groupings into light REE (LREE) and heavy REE (HREE) are generally accepted according to the molecular weight, with this study defining LREE to include La through Sm and HREE to include Eu through Lu as well as Sc and Y. Pm is radioactive and is not found in natural settings.

REE have sometimes been known as ‘chemical vitamins’ because combining very small amounts with other materials can result in vastly different properties. According to the U.S. Department of Energy National Energy Technology Laboratory [1], the REE provide significant value to U.S. national security, energy independence, environmental future, and economic growth. Due to their unique properties that include magnetic, catalytic, luminescent and electrochemical, the REE make technologies perform with reduced weight, emissions and energy consumption; or give them greater efficiency, performance, miniaturization, speed, durability, and thermal stability [2]. Major market segments that rely on REE-based products or technologies include health care, transportation and vehicles, lighting, renewable energy systems, communications systems, audio equipment, military defense technologies, and modern electronics. In recent years, the markets for rare earths have been shifting from the more mature applications that mainly use LREE, such as catalysts, to newer applications that employ HREE, such as permanent magnets used in wind turbines and hybrid/electric vehicles.

In recent years, due to control of the REE markets by China and new (and growing) demand, especially for the less abundant HREE, alternative sources of REE are being considered. Among these are coal and coal byproducts, which can have REE that are concentrated above crustal averages and are often relatively enriched in the HREE compared to traditional mineral deposits [3, 4, 5, 6, 7, 8]. In this effort, we explore the acid leaching behavior of REEs in Fort Union lignite coals of North America, some of which have been found to have exceptionally high REE content that would be attractive targets for a commercial recovery process (i.e. > 100 ppm coal basis or >1000 ppm ash basis).

The U.S. ranks only behind China in total coal production, at about 900,000 thousand short tons in 2015 [9]. In terms of total reserves, the U.S. leads the world by a significant margin, with over one quarter of the world’s proven reserves [10]. North Dakota by itself hosts the single largest deposit of lignite known in the world at an estimated 351 billion tons, with about 25 billion tons of that being economically mineable [11]. Ackman et al (2012) [12] performed a detailed assessment of the prospects of coal and coal byproducts as alternative resources for REE production in the U.S. and found that ‘unintended production’ of REE associated with coal mining potentially exceeds 40,000 tons annually, of that the HREE may exceed 10,000 tons annually. They estimated that total recoverable reserves of REE in coal may exceed 2 million tons for the major coalbeds and formations in the U.S. In addition to this, the existing coal mines have already absorbed the cost of mining and in many cases also the cost of transportation, crushing, grinding and coal cleaning. Therefore, there may be opportunities for value-added recovery of REE in several locations throughout the coal utilization value chain. Given the above, recovery of rare earth elements from coal and coal by-products has gained tremendous attention from the research community in recent years. For example, the United States Department of Energy has embarked on a large program to identify promising coal related REE resources and develop methods to recover and concentrate the REE [1]. Seredin and Dai (2012) [7], and Dai and Finkelman (2017) [8] provide excellent reviews on the current progress of REE from coal.

This paper describes the use of acidic leaching experiments both to examine the modes of occurrence of the REE in Forth Union lignites, as well as to examine the ability to extract and recover REE from selected coals. The efficacy of various acid types and acid concentrations is analyzed along with other parameters such as acid/coal contact time and coal particle size. Kinetics evaluations are also discussed. The testing and results shed new light on the modes of occurrence of REE in low-rank coals as well as provide foundational data for REE recovery process development efforts.

2. Occurrence of Rare Earth Elements in Coal

Development of REE recovery processes must be accompanied by a thorough understanding of the modes of occurrence of the REE in the materials. A number of studies [13, 5, 14, 15, 16, 17, 18, 19, 20, 21], [6, 4, 22, 23, 24, 25] have shown that REE in coal can be present in the following general groupings:

- syngenetic clastic and pyroclastic minerals or minerals of terrigenous and tuffaceous origin,
- diagenetic and epigenetic minerals of authigenic origin, and
- organic compounds.

Seredin and Dai (2012) [7] have concluded that the large majority of REE-bearing minerals in coals are authigenic in origin. However, the modes of occurrence of the REE is highly dependent on a number of factors, including the coal rank. For example, Finkelman et al (1990, 2017) [26, 27] attempted to quantify the REE modes of occurrence in various coals through a sequential leaching approach, and identified that the leaching behavior of REE in low-rank coals (LRC) is significantly different than in high-rank coals. In each of these studies, it was found that a high percentage of the REE in LRCs were extractable with dilute hydrochloric acid (HCl), whereas in the high-rank coals the extraction with HCl was much lower. Finkelman et al (1990) surmised that the difference may be due to the presence of REE in organic chelate compounds in LRCs, while Finkelman et al (2017) surmised that the difference may be due to the presence of REE in strong ion-exchangeable forms in the clay minerals in the LRCs.

It is important to note, however, in each of the above Finkelman et al studies only one lignite sample was analyzed and it had fairly low initial REE content not typical of a REE-rich coal that would (presumably) be targeted for a commercial extraction technology. For example, the lignite coal would have fallen well below the 1000 ppm rare earth oxide (REO) concentration (ash basis) proposed as the economic cutoff by Seredin and Dai (2012) [7]. The modes of occurrence of REE in a typical lignite compared to a metalliferous [28] lignite may be different. Additionally, the full suite of REE was not analyzed in the studies, and thus full trends by molecular weight may not be discernable. This paper will show that there are significant differences in the modes of occurrence of the LREE and HREE that are important to understand.

As summarized by Seredin and Dai (2012) [7], organically associated REE, especially in LRCs, have been identified in many other studies. A number of inferred organic associations have been observed by methods such as inverse correlation of REE concentration with ash yield and enrichment of REE in the light specific gravity fractions [13, 5, 14, 18, 19, 4, 22, 25]. These types of indirect methods are validated by experimental work evaluating the sorption characteristics of REE by peat, coals, and humic acids [30, 31]. Further evidence of organic associations can be inferred by the detection of LREE-bearing minerals and non-detection of HREE-bearing minerals by SEM methods in coals that also exhibit enrichment in the HREE, suggesting that the HREE are enriched in the organic fraction and not visible by SEM methods [32]. Direct evidence of organic associations is also available in the literature. For example, Seredin and Shpirt (1999) [33] have shown that about 50% of the REE content of two Russian coals was contained within the humic fraction and was easily extracted by dilute alkaline leaching. Their testing also showed that the humic fraction is slightly enriched in the medium-weight REE, compared to the lightest

and heaviest REE, and they note that the REE concentration in the humic fraction is several times higher than the raw coal. Wang et al (2008) [34] concluded that REE can be present in the organic fraction and probably adsorbed by hydrogen-containing functional groups and the HREE may be directly bound to carbon. Finkelman (1981a, 1981b) and Finkelman et al (2017) [35, 36, 27] also suggest that REE can be bound strongly to the carbon matrix in the coal. In another leaching method approach, Wei and Rimmer (2017) [37] reached the same conclusion as Finkelman et al (1990) [26], that many trace metals, including REE, in two Chinese LRCs were weakly bound in chelate groups within the organic fraction of the coals. Eskenazy (1999) [30] found that Na^+ , K^+ , Ca^{2+} , and Mg^{2+} bound to $-\text{COOH}$ and $-\text{OH}$ were replaced by REE cations. Aide and Aide (2012) [38] showed that HREE-organic complexes are more stable than LREE-organic complexes. Finkelman (1981c) [39] also found that the HREE preferentially complexed over the LREE with the organic components. Eskenazy (1987a, 1987b) [19, 40] found that loosely bound REE can also be sorbed onto the humic components.

As noted in a recent study by Lin et al (2017) [41], the quantification of the distribution of REE in organic and inorganic phases is still a challenging task. The approach developed in the Lin et al study to determine the mass fraction of organically bound REE in high-rank coals used a combination of particle size and density separations and mathematical modeling, and found that 25% of the REE content in one coal sample was organically associated and that the HREE were enriched in the organic fraction of the coal.

As noted above, several studies have undertaken the task of determining the modes of occurrence of REE in LRCs. However, a general consensus is difficult to ascertain. While some previous studies have investigated the REE modes of occurrence in Fort Union lignite coals [26, 27, 42, 43], the study presented here is more comprehensive and also provides foundational research data necessary for development of effective REE extraction technologies. This paper describes the use of aqueous leaching methods to determine the modes of occurrence of REE and to recover REE associated with lignite coals from the Fort Union formation of North America.

3. Methods

The following sections detail the analytical and experimental methods used in this study.

3.1 Analytical Methods

All REE abundance determinations were completed using inductively coupled plasma mass spectrometry (ICP-MS), which has been detailed by Bank et al (2016) [44]. Methods used in this study followed the Bank et al procedures. All REE concentrations were determined on both a dry whole sample basis and ash basis. This was done by first determining moisture content of the analysis sample and then ashing the samples via ASTM D3174 [45] to determine ash yield. Once the REE concentration was measured by ICP-MS (on the ash basis), the dry whole sample basis could be back-calculated. All data reported in this paper are on a dry whole sample basis, with the exception of the comparison provided later in **Table 1**. The coal ash composition data were determined by x-ray fluorescence and follows the ASTM D4326 [46] procedure. Each method carries varying degrees of analytical uncertainty. For the ICP-MS, the methods have been accompanied by standard reference materials (SRMs) to ensure acceptable precision. A number of SRMs were used throughout the study, including several coals and coal ashes of varying rank, soils, river sediments, rock, basalt, shale and carbonatite ore. Each of the testing procedures described in the following sections were mostly run in single experiments, and thus experimental error is difficult to quantify. However, standard sampling and sample preparation procedures were followed according to ASTM D2013 [47], to minimize sampling bias.

3.2 Sequential Leaching Procedure

The sequential extractions (Section 5) used a procedure modified after that developed by Benson and Holm (1985) [48], which was termed chemical fractionation. Chemical fractionation is a method developed to quantitatively determine the modes of occurrence of major, minor, and trace elements in LRCs based on the extractability of the elements in solutions of water, 1 molar ammonium acetate, and 1 molar hydrochloric acid. This type of analysis is especially important for LRCs that can have significant quantities of organically associated elements which are ionically dispersed within the organic matrix of the fuel and are essentially invisible to scanning electron microscopy (SEM) equipped with x-ray analysis capabilities or x-ray diffraction (XRD).

A 75-gram sample of $-45\ \mu\text{m}$ (-325 -mesh) dried coal is stirred with 160 mL of deionized water to extract water-soluble minerals such as sodium chloride or sodium sulfate. After being stirred for 24 hours at room temperature, the water-coal mixture is filtered. The filtered coal is dried, and a portion is removed to be tested by ICP-MS to determine the concentration of each element remaining. The mass of sample removed is such that at least one gram of ash can be produced after igniting the sample. The residues are then mixed with 160 mL of 1 molar ammonium acetate and stirred at 70°C for 24 hours to extract the elements associated with the coal as ion-exchangeable cations present primarily as the salts of organic acids. Ammonium acetate has also been reported to extract some carbonate mineral forms [27, 49, 50]. The ammonium acetate extractions are performed two more times to effect complete removal of the ion-exchangeable cations. After the third ammonium acetate extraction, a sample of the dried residue is analyzed by ICP-MS. The remaining residue after the ammonium acetate extractions is then stirred with 1 molar HCl at 70°C for 24 hours to remove the elements held in coordination complexes (chelates) within the organic structure of the coal, as well as acid-soluble minerals such as carbonates, oxides and sulfates. The hydrochloric acid extraction is repeated once. The residue is then analyzed by ICP-MS. The non-extractable elements are associated in the sample as silicates, aluminosilicates, sulfides, insoluble oxides and other non-HCl soluble forms. As noted by Finkelman et al (2017) [27] the residual REE content may also represent REE strongly bound to the carbon matrix of the coal.

The mass balances for the REE in these experiments (and subsequently in the single-step experiments described in Section 3.3) were determined by analyzing the REE concentration in the starting and leached coals. Combined with the mass loss during the leaching, the percentage extraction of the REE was calculated. The supernatant fluid was not analyzed.

3.3 Single-step Acid Leaching Procedure

The single acid extractions testing was completed in a similar procedure as the chemical fractionation. The dried coal (ground to various particle sizes) was contacted with the acid at 40°C for the desired contact time (1 to 48 hours in this study). All tests with the exception of the 48 hour tests involved a single contact period. The 48 hour tests were completed with two 24 hour periods, with each period using a fresh batch of acid. For all of the tests, the ratio of coal to acid solution was 60 grams (dry mass) to 125 mL. Upon completion of the extractions, the slurry was filtered and the solid residue recovered for analysis by ICP-MS. The percentage extraction of the REE was determined in the same fashion as described previously for the sequential extractions.

3.4 Float-sink Separations Procedure

This paper also includes multi-specific gravity float-sink separations data for one sample (Section 6.5). This testing was completed according to ASTM D4371 [51]. The ground (50 x 100 mesh) coal sample was separated into multiple specific gravity fractions (< 1.4 through > 2.3), and ICP-MS analysis for REE content was performed separately for each of the specific gravity fractions. For this testing,

approximately 2 kg of coal was used for the separations, which ensured both a representative sample and sufficient mass in each specific gravity fraction for the required analysis/testing.

3.5 Humic Acid Extraction Procedure

Finally, one set of data involving extraction of humic acid from a coal sample is provided (Section 7). The humic acid was extracted via the acetone-H₂O-HCl method, in an approach modified from Youngs and Frost (1963) [52]. For this testing, the humic acid extract and the residual material were both analyzed by ICP-MS for REE content. 60 grams of coal (dry mass) was contacted with 480 mL of acetone, 120 mL of water and 20 mL of HCl for about 6 hours at room temperature. The residual coal fraction was recovered by centrifugation and filtering, and the humic acid fraction was recovered by evaporating the liquids.

4. Samples

Table 1 presents the sample information and starting REE concentration for the samples that were used in this study. **Table 2** presents the concentration of the individual REE for each of the samples. **Table 3** presents the ash composition data (presented as oxides, normalized to 100wt%) for four of the samples. **Figure 1** displays the normalized REE distribution for the four Hagel samples and the Leonardite sample. **Figure 2** displays the normalized REE distribution for the three Harmon-Hanson samples. The upper continental crust (UCC) averages have been used for the normalization [53]. The REE distributions shown in Figures 1 and 2 are generally M-type and H-type as classified by Seredin and Dai (2012) [7], as seen by their relative enrichments in the medium (M-type) and heavy (H-type) molecular weight REE.

The United States Geological Survey has compiled a report that details the geology and stratigraphy of Fort Union coals, which are of Paleocene age [54]. More details regarding the Fort Union coal zones and various beds can be found in that report. The Hagel samples were taken from an active mine in North Dakota from various stratigraphic sections, and the Harmon-Hanson samples were collected during an extensive study by Kruger et al (2017) of the North Dakota Geological Survey from exposed outcroppings in the southwestern portion of North Dakota [55]. The three Harmon-Hanson samples (6A, 6A-1 and 6A-2) were collected from the H-Bed [56] from the same site, but in different stratigraphic layers, and thus have significantly different ash yields. The 6A and 6A-2 samples represent coal portions of the seam, while the 6A-1 was taken at the interface of the coal and roof, and contains a high proportion of what is presumably a carbonaceous clay. The E2B1 sample is rich in alkaline earth metals, while the Harmon-Hanson samples are rich in aluminosilicates and iron.

Based on the sampling and characterization by the authors to date, the Hagel coal samples represent fairly typical REE concentrations for the existing North Dakota mines. Thus, they were chosen for this study for comparative purposes. The Harmon-Hanson samples, however, represent exceptionally high concentrations, exceeding the economic threshold of 1000 ppm (ash basis) proposed by Seredin and Dai (2012) [7], and thus could offer economic potential for REE recovery. Additionally, the work presented herein is part of a larger effort, in which these authors are developing a novel technology to extract and concentrate REE from North Dakota lignite coals [57], efforts that will be reported subsequently. The samples chosen for this study were those that were examined in most detail during the larger effort. Only four of the samples were evaluated for ash composition (Table 3) because these were the samples that were the focus of REE extraction efforts in the larger effort. Finally, scandium was not analyzed in all samples studied as it was not initially a focus of the larger technical effort.

Table 1. Sample information for North Dakota lignites and carbonaceous clay evaluated in this study

Sample ID	Coal Zone	Bed	Ash Yield (wt%)	Total REE (dry sample basis, ppm)	Total REE (ash basis, ppm)
16040	Hagel	Hagel A	12.7	61.2 *	482*
16050	Hagel	Hagel B	12.7	59.2 *	466*
16060	Hagel	Hagel B	11.5	43.8 *	381*
E2B1	Hagel	Hagel B	7.2	42.0	583*
6A	Harmon-Hanson	H-Bed	25.6	551	2152
6A-1	Harmon-Hanson	H-Bed	75.7	450	594
6A-2	Harmon-Hanson	H-Bed	36.6	634	1732
Leonardite **			21.5	76.8	356

* Does not include scandium

** Sample procured from commercial vendor (Leonardite Products LLC)

Table 2. Concentration of individual REE for samples listed in Table 1.

	Sample ID, REE concentration (dry whole sample basis, ppm)							
	16040	16050	16060	E2B1	6A	6A-1	6A-2	Leonardite
Sc	n/a	n/a	n/a	2.0	35.4	19.5	27.2	5.1
La	16.1	15.6	4.2	7.3	62.5	81.3	103.2	11.6
Ce	21.2	20.5	8.9	9.7	176.0	161.4	228.3	22.4
Pr	2.0	1.9	1.2	1.0	26.0	19.0	28.3	2.8
Nd	6.7	6.5	5.0	4.1	118.4	75.1	112.9	11.1
Sm	1.3	1.3	1.3	1.0	28.5	15.5	24.0	2.4
Eu	0.3	0.3	0.4	0.3	6.3	3.4	5.3	0.7
Gd	1.4	1.4	1.7	1.2	21.6	13.6	20.2	2.5
Tb	0.2	0.2	0.3	0.2	2.9	1.9	2.8	0.4
Dy	1.3	1.3	2.2	1.3	14.4	9.6	13.9	2.3
Y	8.7	8.4	14.5	11.8	43.6	38.9	53.6	12.5
Ho	0.3	0.3	0.5	0.3	2.4	1.7	2.4	0.4
Er	0.8	0.8	1.6	0.9	6.2	4.2	6.0	1.3
Tm	0.1	0.1	0.2	0.1	0.8	0.6	0.8	0.2
Yb	0.7	0.7	1.5	0.8	5.3	3.5	4.5	1.1
Lu	0.1	0.1	0.2	0.1	0.7	0.5	0.6	0.2
Total	61.2	59.2	43.8	42	551	450	634	76.8

Table 3. Ash composition data for four of the samples detailed in Table 1.

Oxide	Sample ID, wt% (ash basis) normalized to 100%			
	E2B1	6A	6A-1	6A-2
SiO ₂	19.61	42.84	63.88	45.25
TiO ₂	0.36	1.37	0.82	0.68
Al ₂ O ₃	12.84	22.62	25.39	20.34
Fe ₂ O ₃	5.04	26.64	4.14	16.85
MgO	8.74	0.36	1.06	0.76

CaO	35.84	2.68	0.91	7.09
MnO	0.13	0.02	n/a	0.09
Na ₂ O	1.47	0.37	0.60	0.99
K ₂ O	0.32	0.61	1.60	1.43
P ₂ O ₅	0.24	0.36	0.42	0.15
SO ₃	13.91	1.59	1.19	6.18
SrO	0.56	0.07	n/a	0.10
BaO	0.92	0.47	n/a	0.08
LOI*	92.80	74.40	24.30	63.40

* loss on ignition (dry whole sample basis)

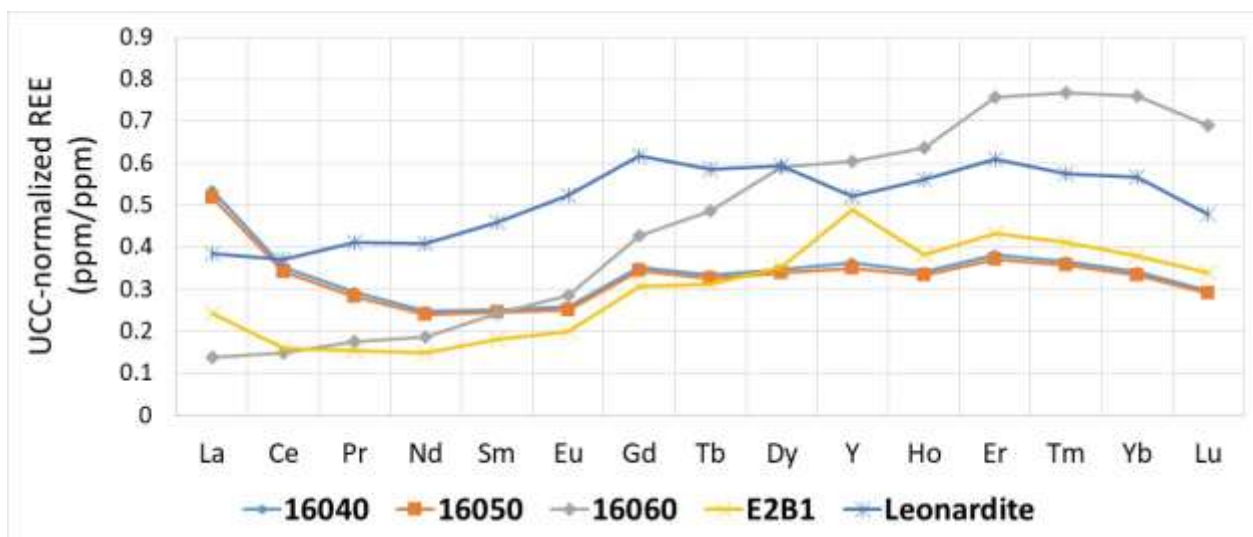


Figure 1. Upper continental crust (UCC)-normalized REE distribution of four samples detailed in Table 1 – Hagel and Leonardite.

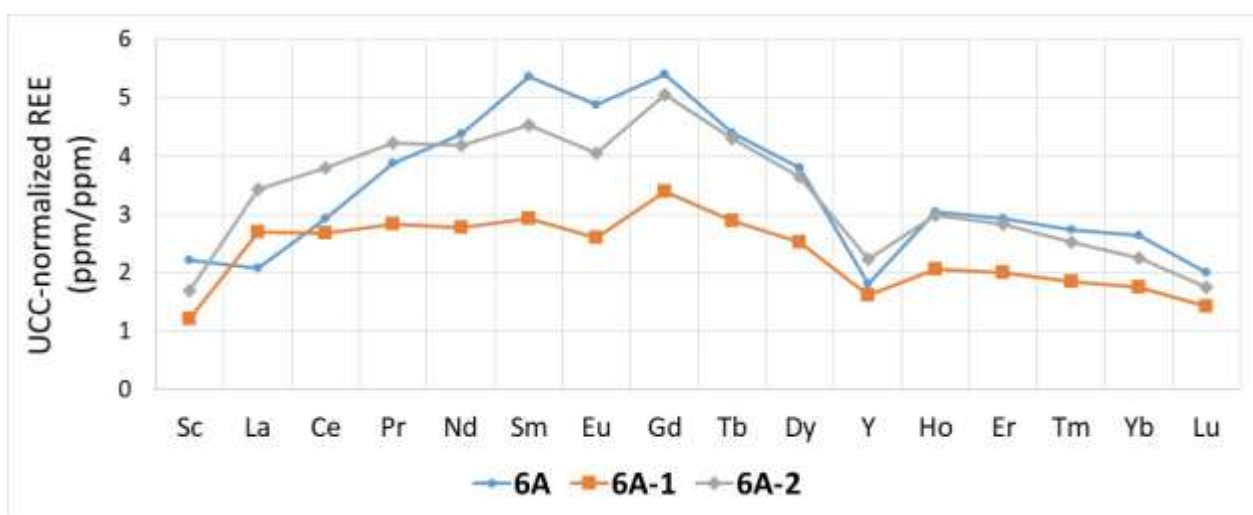


Figure 2. UCC-normalized REE distribution of three samples detailed in Table 1 – Harmon-Hanson

5. Sequential Solvent Extraction Results and Discussion

The results of the sequential solvent extraction for four of the samples shown previously in Table 1 (16040, 16050, 16060, 6A) are provided in the supplementary data files. In the event that very large differences in results between samples were observed, additional samples would have been tested via this approach. However, results were quite consistent between samples, and thus no additional samples were evaluated. In general, the results are consistent with the previous work by Finkelman et al (1990, 2017) [26, 27]. A very small amount (or none) of the REE were leached either by water or ammonium acetate, indicating negligible REE association in water soluble or ion-exchangeable forms. However, a large fraction of the REE were leached by the HCl (80 to 95wt%), indicating REE association as acid-soluble minerals (i.e. carbonates, sulfates and some oxides), in non-mineral inorganic forms such as organic complexes (chelate compounds) or as suggested by Finkelman et al (2017) [27] in some type of strong ion-exchangeable form associated with clay minerals that is resistant to ammonium acetate leaching.

In general, REE extraction with HCl decreases with increasing molecular weight, with the notable exception of scandium for sample 6A (only sample where Sc was measured). For this sample, there is clearly a very different mode of occurrence as compared to the rest of the REE. In general, this would be expected given scandium's lack of f-orbital electrons.

Although the sequential solvent extraction method cannot directly distinguish the modes of occurrence of the HCl-soluble phases, the data, combined with previous studies in the literature and the experience of these authors, can provide some useful insight. Unlike high-rank coals, LRCs have high levels of oxygen associated with the organic matrix. The oxygen is in the form of chemical functional groups (i.e., carboxylic acid groups - COOH) that can be bonding sites for inorganic elements such as alkali and alkaline earth metals and multivalent metal ions via cation exchange and coordination complexes [48, 49]. The extreme differences in LRC's compared to other coals is shown in **Table 4**, which indicates that LRCs, and especially lignites, have a high percentage of carboxylic acid groups which are not present in higher rank coals.

Table 4. Oxygen content of coals of various rank. Lignite and subbituminous have oxygen contained within the organic matrix in the form of carboxylic acid groups which can be bonding sites for inorganic elements. Data from Given (1984) [58].

	<i>Lignite</i>	Subbitu- minous	High volatile bituminous			Bituminous		Anthracite
			C	B	A	Medium volatile	Low volatile	
% C (min. matter free)	65-72	72-76	76-78	78-80	80-87	89	90	93
% H	4.5	5-4	5.5	5.5	5.5	4.5	3.5	2.5
% O	30	18	13	10	10-4	4-3	3	2
% O as COOH	13-10	5-2	0	0	0	0	0	0
% O as OH	15-10	12-10	9	?	7-3	2-1	1-0	0
Aromatic C atoms % of total C	50	65	?	?	75	80-85	85-90	90-95
Avg. no. benzene rings/layer	1-2	?	←————— 2-3 —————→				5?	>25?
Volatile matter (%)	40-50	35-50	35-45	?	31-40	31-20	20-10	<10

Reflectance (%) of vitrinite	0.2-0.3	0.3-0.4	0.5	0.6	0.6- 1.0	1.4	1.8	4
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LRCs contain high levels of natural organic ligands, such as humic acids, that naturally complex (or chelate) multivalent metals such as REE. To confirm the presence of metals bound by these natural ligands, previous studies have used various organic solvents to extract targeted compounds of the organic fraction in the coals and evaluate the partitioning of the metals to determine their modes of occurrence. Wang et al (2014) [59] evaluated multiple organic solvents on a high volatile bituminous coal and found that, in general, the content of inorganic elements in the coal extracts were lower than the residual coal. However, they also note that some elements that occur in organic phases in the parent coal were relatively enriched in the extracts. Bonnett et al (1981) [60] contend that some metals in coal are extractable by organic solvents, and used sequential Soxhlet extraction on multiple coal types with several organic solvents to examine the distribution of the metallic elements in the various extract fractions generated. The authors state that metals enrichment in coals can occur in various ways, but diagenetic formation of compounds such as humic acids results in the presence of functional groups that behave as powerful organic ligands. The authors used acid-modified organic solvents to provide sufficient “chemical energy” to allow the liberation of the organometallic complexes (from the non-soluble coal fraction) to the organic solvent phase.

In efforts not detailed in this paper [61], we have attempted to identify REE-bearing minerals such as monazite and xenotime in lignite coal samples using SEM with energy dispersive spectroscopy (SEM-EDS), which have been identified in higher-rank coals in numerous other studies [13, 21, 62, 63, 64, 65]. Despite extensive efforts, no REE-bearing minerals were detected in the Fort Union lignite coals. In our judgement, and combined with the M-type and H-type enrichments observed in Figures 1 and 2 and the results of sequential extraction testing, this lack of REE-bearing mineral detection provides evidence of an organic REE association, but could also suggest that the REE-bearing minerals are present in particle sizes too small to be detected by SEM-EDS.

A possible organic form could be organometallic complexes associated with carboxylic acid groups in the lignites. Humic acids also have a suite of other naturally occurring functional groups such as amines, thiols, phosphines and phenols that can also provide inorganic element binding sites. However, because the HCl-leaching can attack some mineral forms (i.e. carbonates), we cannot rule out acid-soluble REE bearing minerals being a significant component.

6. Acid Extraction Results and Discussion

The results for the sequential extraction tests clearly demonstrate that the majority of REE in the lignite coals were leachable with dilute HCl. Additional evaluations with single-step acid leaching were undertaken to understand the impact of various parameters. The data are presented and discussed in the following sections. This information provides foundational data for subsequent REE extraction process development (efforts by these authors currently ongoing), as well as sheds additional light on the REE modes of occurrence in the lignite coals.

6.1 Acid Type

Two of the samples listed previously in Table 1 – E2B1 (Hagel B) and 6A-1 (high ash Harmon-Hanson) – were leached with three types of acids (hydrochloric, sulfuric and phosphoric) in two concentrations each. These samples were chosen based on the availability at the time the tests were performed, as well as on the large difference in REE concentration and ash yields between the two,

allowing testing of two ends of the spectrum. The mineral acids were chosen based on their common use in mineral processing and relatively low cost, which could enable an economically viable process. The results for the E2B1 coal are presented in **Figure 3**, and for the 6A-1 carbonaceous clay in **Figure 4**. Each of these tests was completed using a 48-hour contact time, with acid replenishment at 24 hours, as described previously in Section 3. With excess fresh acid at relatively high liquid-to-solid ratio (125 mL acid solution to 60 g dry coal) and a long contact time, the data can be considered near-equilibrium extraction.

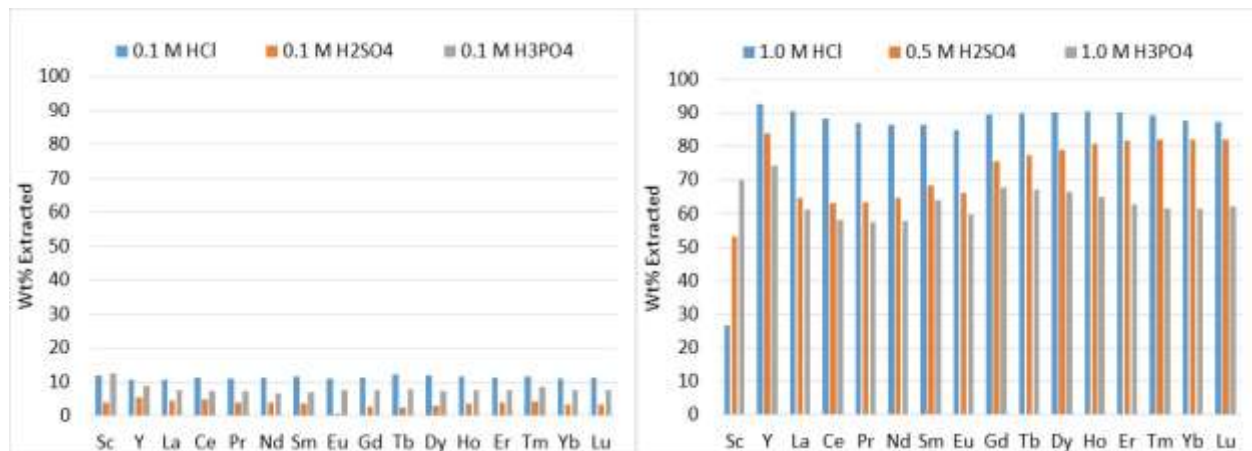


Figure 3. Results of acid screening tests for sample E2B1 (Hagel B coal, Table 1).

The key results from the data in Figure 3 and Figure 4 are that moderate acid concentrations (0.5-1M) were needed to provide good extraction efficiencies and HCl was the most effective acid for each of the REE with the exception of scandium.

For the E2B1 sample (Hagel B coal), the low acid concentration tests resulted in fairly low extraction of the REE, ranging from less than 1 wt% to about 12 wt%. The HCl provided the highest extraction, with the H_2SO_4 providing the lowest extraction. The exception is scandium, which was best extracted using the H_3PO_4 . In fact, for the low concentration tests, the highest overall extraction of any element was scandium using the H_3PO_4 , an interesting result given the very low extraction achieved during the chemical fractionation tests discussed previously in Section 5. At the low concentrations, the extraction efficiencies are uniformly low and there does not appear to be any obvious trends for molecular weight.

For the higher acid concentrations for the E2B1 sample, as expected, much higher overall extraction resulted. For the 1M HCl, the results shown in **Figure 3** are very similar to the previous chemical fractionation results for the other Hagel coal samples. This would suggest that pre-leaching of the lignite with water and ammonium acetate did not significantly alter the modes of occurrence of the REE, resulting in similar HCl leaching behavior. Overall for the E2B1 sample, the HCl provided the highest extraction, with the exception of scandium. The 0.5M H_2SO_4 was slightly more effective than the 1M H_3PO_4 , most notably for the HREE. The H_2SO_4 actually shows a strong trend of increasing extraction with molecular weight. However, again, scandium behaves differently than the other REE. The H_3PO_4 was fairly consistent between the various elements, but interestingly produced a very high degree of scandium extraction at about 70wt%, significantly higher than either of the other acids.

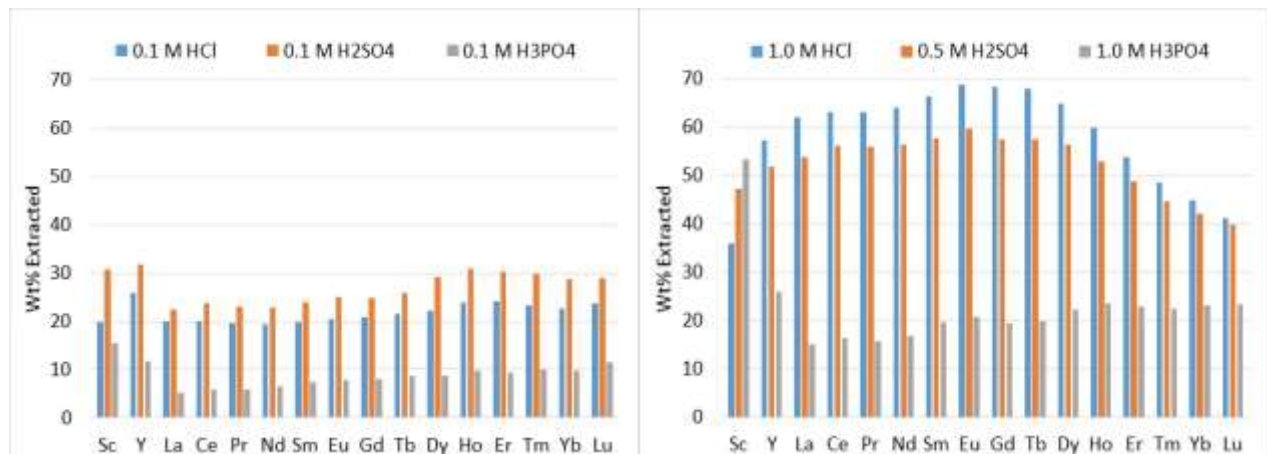


Figure 4. Results of acid screening tests for sample 6A-1 (Harmon-Hanson carbonaceous clay, Table 1)

For the 6A-1 sample (Harmon-Hanson carbonaceous clay), the results are considerably different than the E2B1 sample (shown in Figure 3). This is most evident for the low acid concentration tests and for both concentrations of the H_3PO_4 . At the low concentration, the H_2SO_4 provided the best overall REE extraction, ranging from about 22 to 32wt%, significantly higher than for the E2B1 sample. The HCl extraction results were similar, albeit slightly lower for all the REE. The H_3PO_4 resulted in dramatically lower extraction ranging from about 5 to 15wt%. However, as with the E2B1 coal, the H_3PO_4 was most effective for scandium. For the higher concentration acids, extraction efficiency improved, similar to the general trends observed in the E2B1 sample, but with lower overall extraction efficiency. As with the low concentration, the H_3PO_4 resulted in dramatically lower overall extraction than the other two acid types, but again with the exception of scandium.

The data in Figures 3 and 4 clearly show extraction efficiencies are generally impacted by the type of acid, the concentration of the acid (higher clearly better), and the type of coal. It must be noted that for Figures 3 and 4 at the higher acid concentrations, 1M HCl and H_3PO_4 were compared to 0.5M H_2SO_4 . HCl and H_2SO_4 can be seen to typically be the best acid for REE extraction. H_2SO_4 has the advantage of being the most cost effective acid for any future extraction process. With a few exceptions, H_3PO_4 exhibited poorer leaching performance compared to HCl and H_2SO_4 , especially for the Harmon-Hanson (6A-1) sample that was high in REEs. The difference is likely due to a combination of reduced acidity (higher pH) and solubility. 1M HCl and H_2SO_4 each deprotonate to provide a pH 0 acidic solution while 1M H_3PO_4 is only partially deprotonated resulting in pH of ~ 1.1 . The lower solution acidity provided by H_3PO_4 (for equivalent HCl and H_2SO_4 molarity) likely negatively impacts extraction efficacy. Another factor likely impacting the effectiveness of H_3PO_4 leaching is the solubility of REE phosphates, which are products of the dissolution process with phosphoric acid. While phosphates have strong affinity for the REE, the REE-phosphate complexes have very low solubility in aqueous solutions [66, 67]. So, the addition of H_3PO_4 to REE containing materials can result in poor extraction/leaching efficiency due to the formation of REE phosphate solids that immediately precipitate upon extraction of the REE from the coal matrix. The differing solubility of scandium phosphate and the other REE can also explain the higher extraction of scandium. The solubility theory is supported by comparing the performance of the 1M phosphoric acid on the leaching from the E2B1 sample (Hagel B coal, Fig. 3) to 6A-1 (Harmon-Hanson carbonaceous clay, Fig 4.). The Harmon-Hanson sample 6A-1 has $\sim 10\times$ higher concentration of REE (see Table 1) and the relative extraction efficiencies for H_3PO_4 can be observed to be much lower – possibly the result of solubility limits being reached due to higher REE concentration in the 6A-1 sample.

Scandium and yttrium can be observed to have some different chemical reactivity trends in figures 3 and 4 as well as elsewhere in this effort. Yttrium, and to a lesser extent scandium, have many similarities with lanthanides such as matched electron configuration to lanthanum (2s and 1d electron) and they are commonly found as trivalent cations and have similar ionic radii. These similarities result in scandium and yttrium typically being found, and recovered with lanthanides from mineral deposits in nature. However, scandium and yttrium do not have f-block electrons and this can result in different chemical behaviors and divergent trends from lanthanides (as observed in Figures 3-5, 7,10,13,14).

In summary, the acid screening leaching tests have provided valuable information regarding the types of acidic leaching solutions that are effective in extracting REE from various Fort Union lignites. Each of the acid types and acid concentrations resulted in markedly different REE leaching behaviors. While pH of the acid solution plays an important role, the chemistry of the solution also dictates the REE extraction behavior. Solubility of extraction products as well as the type of anion(s) associated with the REE in the coal also likely play significant roles in the leaching behavior with a specific acid solution.

6.2 Sulfuric Acid Extraction Kinetics

The testing described previously in Section 6.1 can be considered near-equilibrium extraction. Kinetics evaluations were also performed by controlling the contact time between the acid solution and the lignite coal. Data for three coal samples are presented in this section. Each of the test series used 0.5M H₂SO₄ as the solvent. **Figure 5** shows the results for contact time ranging from 1 hour to 48 hours for sample E2B1 (Hagel B coal). The results show, as one would expect, an increasing trend of extraction with contact time. However, this trend is more pronounced for the LREE and scandium. With one hour of contact time about 50wt% of the HREE are extracted, compared to about 20% for the LREE. At short contact time, a HREE-selective leach is produced. Overall, there appears to be a performance plateau after about 14 hours. Although there is a small increase in extraction between 24 and 48 hours, this is not likely kinetics-related, but rather due to the addition of a fresh batch of acid for the final 24-hour period, as previously noted in Section 3.

The data also show a significant jump in LREE extraction between 8 and 14 hours of contact time. This suggests association of a fraction of the LREE content in a mineral form that only became solubilized after 8 hours. For this data set, when looking at the step change for lanthanum and cerium observed between 8 and 14 hours, it appears that about 20-30wt% of the LREE are associated as acid-soluble mineral forms, with the remaining 20-30wt% of the extractable LREE likely associated in weaker bonding forms such as organic complexes. On the contrary, this data suggests that the extractable HREE are almost entirely associated in these weaker bonding forms as indicated by their high extractability under short contact times with the 0.5 M H₂SO₄.

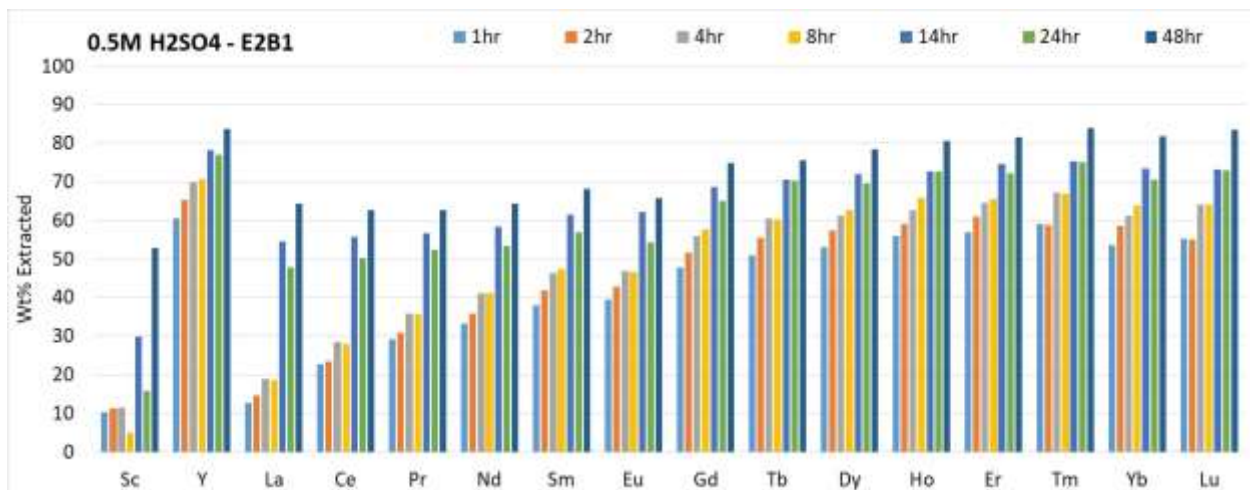


Figure 5. REE extraction results as a function of coal/acid contact time (increasing contact time left to right) for sample E2B1 (Hagel B, Table 1) using 0.5M H₂SO₄.

Figure 6 shows data for sample 6A (low-ash Harmon-Hanson coal) for three contact times ranging from 2 to 48 hours. Similarly to the E2B1 sample in Figure 5, there does appear to be a trend of higher extraction of the HREE, albeit less pronounced. There is also a larger increase in extraction at the near-equilibrium (48 hr) condition over the 14 hour contact time. This is possibly due to the significantly higher total REE content of the 6A sample that would result in a higher concentration of REE in the solution. Overall, the extraction rate for sample 6A is significantly higher than for the E2B1 sample, especially for the LREE. Further, the step change in extraction that was observed between 8 and 14 hours for E2B1 was not observed for the 6A sample. This would presumably suggest that the LREE are not associated in acid-soluble minerals in this sample. The data also show that the overall extractability of the REE, and particularly the LREE and scandium, is higher in the 6A sample.

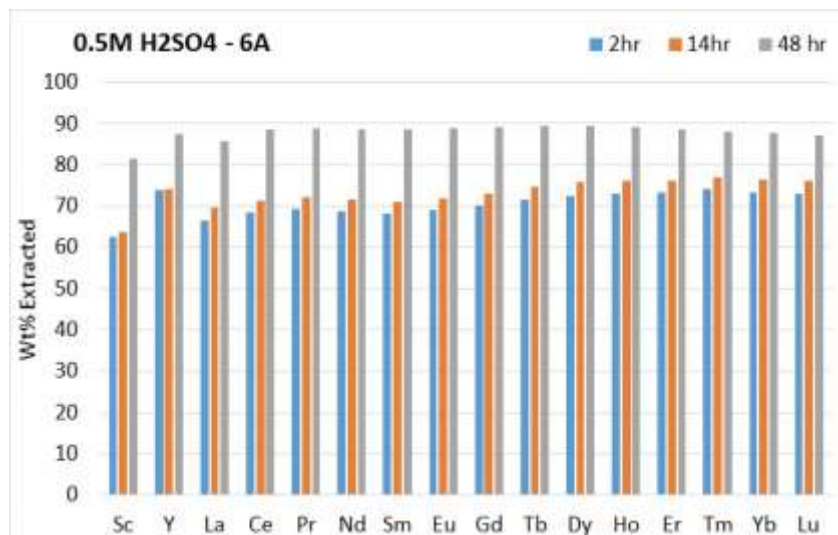


Figure 6. REE extraction results as a function of coal/acid contact time (increasing contact time left to right) for sample 6A (low ash Harmon-Hanson coal, Table 1) using 0.5M H₂SO₄.

Figure 7 shows data for four contact times ranging from 1 to 14 hours for the mid-ash Harmon-Hanson coal, sample 6A-2. Longer durations were not used for this sample due to the performance plateau that was previously observed for sample E2B1 (Figure 5), and due to the desire to limit the

contact time for economic reasons (i.e. for REE recovery process development). Overall, for this sample there appears to be minimal impact of contact time up to 14 hours. However, there is a significant increasing trend of extraction with molecular weight that was not evident with the low-ash 6A sample shown in Figure 6. This could be due to presence of a higher proportion of inorganic materials (i.e. roof clays) in this sample, in which primarily non-acid soluble LREE-bearing minerals would be present.

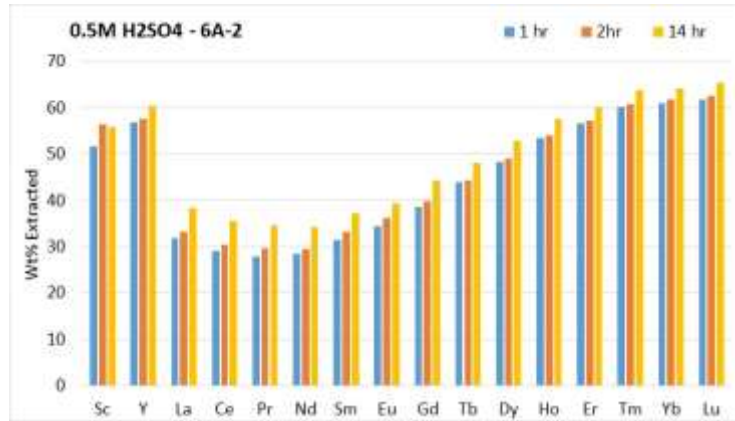


Figure 7. REE extraction results as a function of coal/acid contact time (increasing contact time left to right) for sample 6A-2 (mid ash Harmon-Hanson coal, Table 1) using 0.5M H₂SO₄.

The extraction kinetics are especially important for any process development efforts since they determine process throughputs and/or equipment sizes. This data is currently being used by these authors in an ongoing effort to develop an REE extraction process for lignite coals. However, as has been noted in this section, this type of analysis also provides additional information regarding REE modes of occurrence that is not observable at equilibrium conditions.

6.3 Sulfuric Acid Concentration

All of the tests detailed in Section 6.2 were performed with 0.5M concentration sulfuric acid. To determine the impact of acid concentration, additional tests were completed with 0.25M, 0.75M and 1.0M and compared to the existing data for 0.5M. Four contact times ranging from 1 to 14 hours were used. The testing was done using only the E2B1 sample (Hagel B coal). The data shown in **Figure 8** have been grouped into total REE and clearly shows that minimal increase in total REE extraction is observed at concentration above 0.5M, but that a significant drop in extraction occurs with the 0.25M acid. Therefore, a performance plateau likely exists at a concentration between 0.25M and 0.5M. Although limited increase in total REE extraction is observed beyond 0.5M, this is not the case for scandium. As shown in Figure 9, the difference in scandium extraction between 0.5M and 1.0M concentration for each of the contact times is significant, with more than twofold increase in extraction at the shorter contact times. Again, this is more evidence of a different mode of occurrence for scandium compared to the other REE. For all of the REE with the exception of scandium, there appears to be a minimum “chemical energy” under these contact times that is needed to solvate the REE in the lignite coal, beyond which limited increase in extraction occurs.

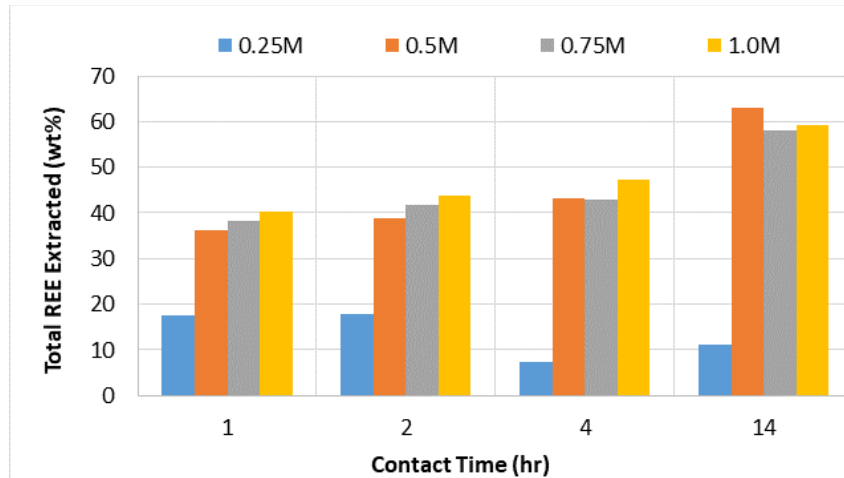


Figure 8. Total REE extracted for a range of sulfuric acid concentrations at four contact times for sample E2B1 (Hagel B coal, Table 1).

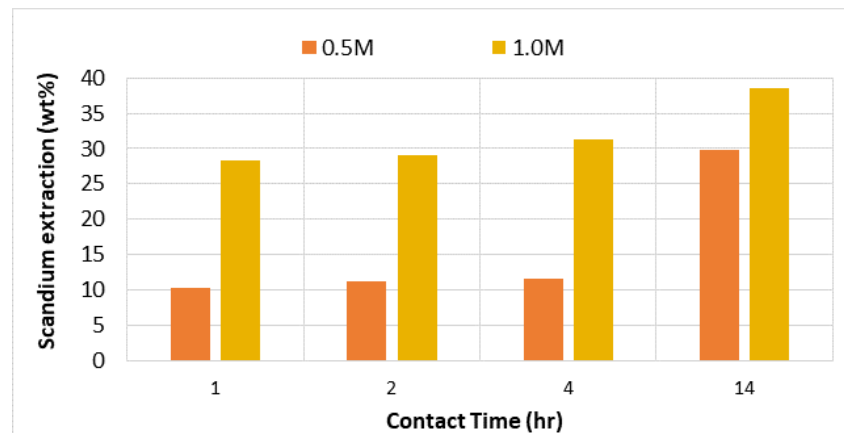


Figure 9. Difference in scandium extraction between 0.5M and 1.0M sulfuric acid concentration for sample E2B1 (Hagel B coal, Table 1). Scandium is the only of the REE that exhibited any significant difference in extraction beyond 0.5M.

6.4 Impact of Coal Particle Size

Each of the tests described in Sections 6.1 – 6.3 for the E2B1 sample (Hagel B coal) were performed with a relatively coarse particle size of -4 mesh. To investigate the impact of coal particle size on REE extraction, an additional set of tests was performed at a particle size of -100 mesh for contact times ranging from 1 to 4 hours. The tests were all run using 0.5M sulfuric acid as the solvent. **Figure 10** provides the data in comparison to the -4 mesh that was previously shown in Figure 5. The data show that there is limited/no change in REE extraction at the finer particle size, with the exception of scandium which resulted in about a twofold increase in extraction at the finer size. This is more evidence of a different mode of occurrence for scandium, and would seemingly suggest an acid-soluble mineral form association that was better liberated (from the coal particles) with the finer grind size.

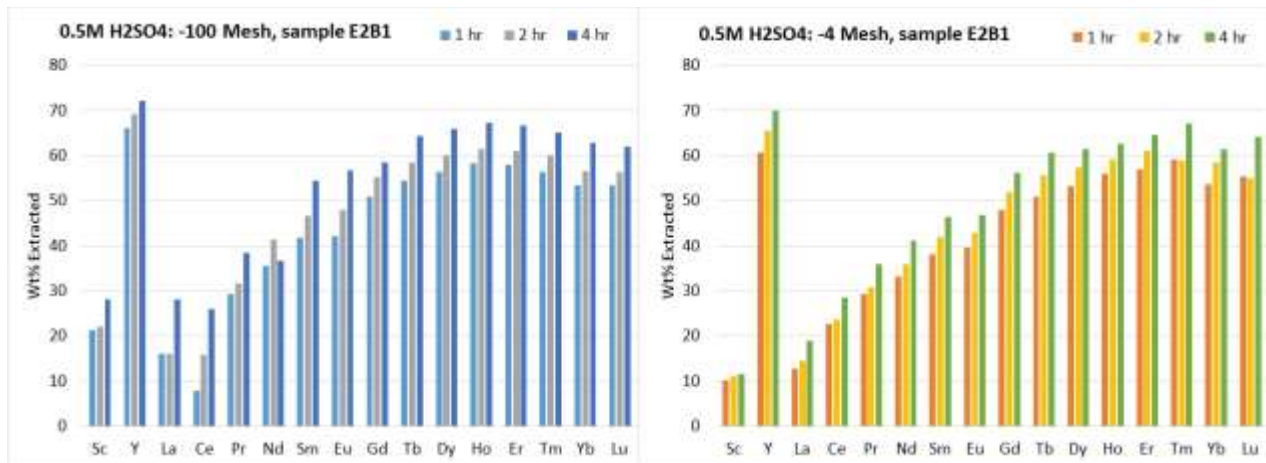


Figure 10. Comparison of REE extraction for sample E2B1 (Hagel B coal, Table 1) for two particle sizes using 0.5M sulfuric acid as the solvent. The data show limited difference in extraction as a function of particle size with the exception of scandium, which has about twofold increase in extraction with the finer particle size.

6.5 Impact of Ash Yield on REE Extraction

As described previously in Section 4 and shown in Table 1, the three Harmon-Hanson samples (6A, 6A-1, 6A-2) were all taken from the same seam at the same sample site, but in different stratigraphic layers. Thus, the coals each have a significantly different ash yield, presumably due to influx of inorganic roof clays/materials in the samples closer to the margin of the seam and at the interface of the roof/coal. **Figure 11** compares the REE extraction at near-equilibrium contact time (48 hours) for the low-ash (6A) and the high-ash (6A-1) sample, and the REE extraction at 14 hour contact time for the low-ash and the mid-ash (6A-2) sample. Each test was performed using 0.5M sulfuric acid as the solvent. The data clearly show that there is decreasing REE extractability with increasing ash yield, suggesting that the extractable REE content is associated with the organics rather than with the inorganic materials.

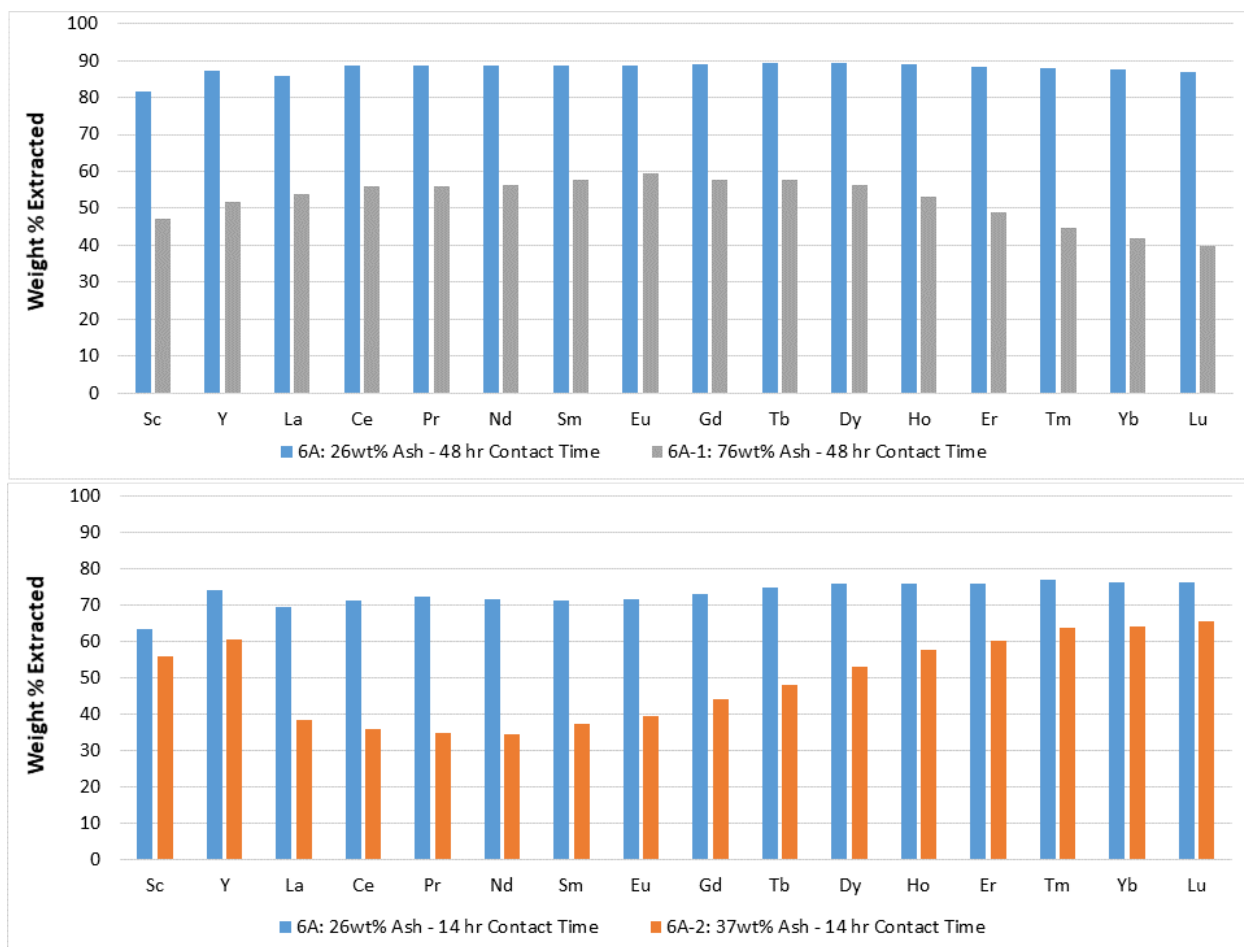


Figure 11. Top – REE extraction with 0.5M sulfuric acid at 48 hour contact time for low-ash and high-ash Harmon-Hanson samples, samples 6A and 6A-2, respectively. Bottom – REE extraction with 0.5M sulfuric acid at 14 hour contact time for low-ash and mid-ash Harmon-Hanson samples, samples 6A and 6A-1, respectively.

The data for the high-ash (76wt% ash yield) sample are particularly interesting. About 40-60% REE extraction resulted, which was unexpectedly high given the high ash yield of the sample and presumably the presence of primarily non-acid-soluble REE-bearing minerals in the inorganic materials (mainly clay minerals) associated with the coal seam. To further investigate this, float-sink separations were performed on the high-ash 6A-1 sample and each of the specific gravity fractions were analyzed for total REE content. The float-sink data are shown in **Figure 12**. The data clearly show that on a dry whole sample basis (each specific gravity fraction before ashing), the REE concentration is significantly higher in the light specific gravity fractions. This data, combined with the unexpected reasonably high extraction of the REE, suggests that the extractable REE content is associated with the organic portion of the coal, rather than with inorganic materials. This is in contrast to the most recent theory by Finkelman et al (2017) that suggests an ion-exchangeable clay association [27], but agrees with an earlier theory of an organic association proposed by Finkelman et al (1990) [26]. The slight increase in REE concentration in the heaviest specific gravity fraction (> 2.3) could possibly be explained by presence of REE-bearing zirconium minerals (i.e. zircon) which have been identified with SEM-EDS in the clays associated with the lignite coal seams in other efforts by these authors [61].

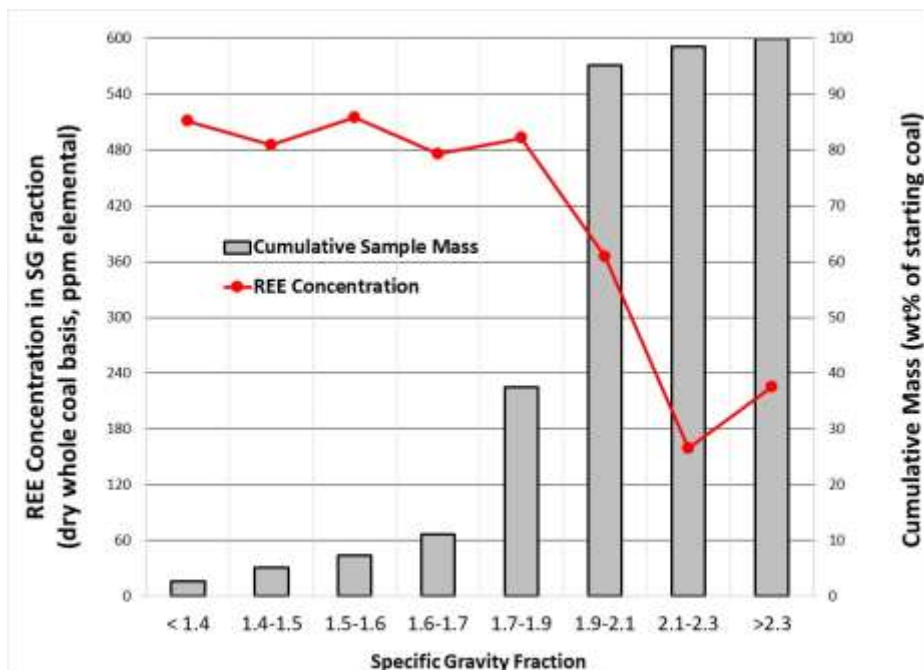


Figure 12. Float-sink separations data for the high ash Harmon-Hanson sample 6A-1 (carbonaceous clay) showing REE concentration in each specific gravity fraction and the cumulative mass of the sample. The REE are most concentrated in the light specific gravity fractions representing coal-rich particles. This suggests an organic REE association.

7. Partitioning of REE in Leonardite and Humic Acid

The following data and discussion have been included in this paper because it provides additional evidence of organic association of REE in Fort Union lignite coals. Leonardite is a naturally oxidized lignite coal that is typically associated with surface mines. Leonardite is currently mined commercially at two sites in North Dakota, and due to its very high percentage of humates (significantly higher than non-oxidized lignites), has application in industries such as agriculture and oil & gas operations [68]. Extraction of the humic acids from the leonardite is commonly employed using either alkaline solutions or organic solvents such as acetone.

A sample of commercially available leonardite was procured for leaching studies (see Table 1). The sample was exposed to leaching with 0.5M sulfuric acid for a contact time of 24 hours. The results of the extraction are presented as **Figure 13**. When comparing these results to the non-oxidized lignites presented in Section 6, the REE extraction is significantly lower. This is likely attributed to the oxidation process that has occurred with the leonardite that would have transformed the modes of occurrence of the REE. For example, oxidation of pyrite produces sulfuric acid, which could have leached the REE in their natural forms in the lignite and made them available for reaction with other components in the coal, resulting in non-acid soluble forms. As with most of the other data sets described in Sections 5 and 6 previously, scandium behaved very differently than the rest of the REE, with less than 5wt% extracted. Yttrium had the highest overall extraction, and there was a clear trend of higher extraction of the HREE than the LREE. As described previously in Section 2, the HREE are known to form stronger organic complexes (i.e. they could have survived the oxidation process of the coal), which is consistent with this data.

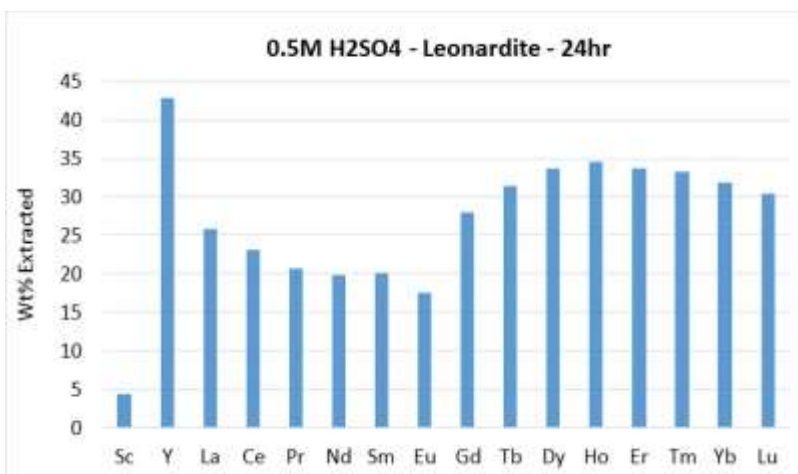


Figure 13. REE extraction results for leonardite (see Table 1) using 0.5M sulfuric acid with contact time of 24 hours.

In addition to the sulfuric acid leaching tests, the starting leonardite was also subjected to humic acid extraction using the acetone-H₂O-HCl method as described in Section 3. The humic acid extract fraction was about 62wt% of the overall dry mass of the starting leonardite, and was analyzed for REE concentration. In total, 37.4wt% of the REE reported to the humic acid fraction, indicating that fraction of the REE was associated with the humates in the parent leonardite. However, as shown in Figure 13 only 25.7wt% of the REE were extractable with sulfuric acid from the parent leonardite, thus suggesting multiple REE organic bonding forms are present. **Figure 14** provides a comparison for each element. The bottom bars represent the percentage of REE that was extracted from the parent leonardite via sulfuric acid leaching. The total (bottom bars plus top bars) represents the percentage mass of REE in the parent leonardite that reported to the humic acid extract. The difference is clearly observable in this figure.

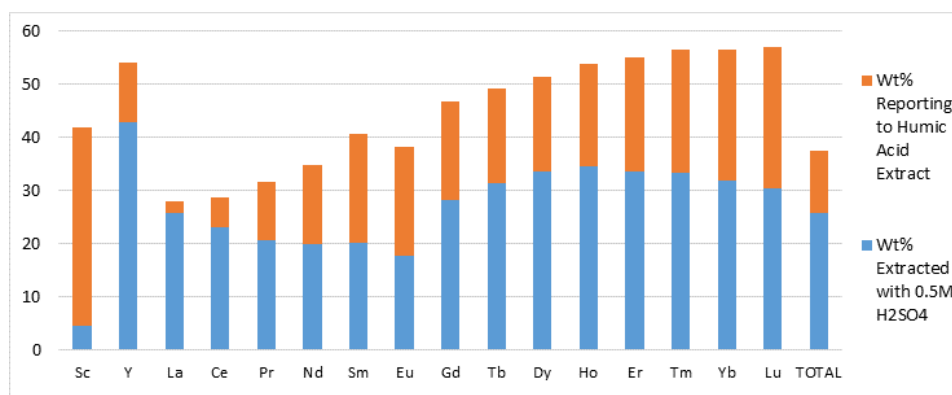


Figure 14. Comparison of REE extracted from starting leonardite (data from Figure 13) and the REE reporting to the humic acid extract fraction. In total, 25.7wt% of the REE were extractable from the starting leonardite via 0.5M sulfuric acid, but 37.4wt% reported to the humic acid extract.

Others [27, 41, 34] have suggested that REE can be tightly bound directly to the carbon matrix in coals, and this could be an explanation for the multiple organic associations that are suggested by this data. The fraction of REE that was extracted by sulfuric acid leaching could represent organic complexes (weak bonding forms), and the remainder could represent strong bonding to the carbon matrix. The differences between the various elements is also interesting. For example, although less than 5wt% of scandium was extracted with the sulfuric acid, over 40wt% reported to the humic acid fraction. There is also a trend of HREE having a higher percentage reporting to the humic acid fraction. For the LREE

reporting to the humic acid fraction, it appears that the primary bonding forms are the weaker forms, as little additional mass (beyond that extracted by sulfuric acid) reported to the humic acid.

While we believe this type of method can provide useful data and supports association of REE in organic complexes, additional testing is needed on more samples, specifically non-oxidized lignites. Targeted organic extractions accompanied by detailed analysis of the organic structure and chemistry of the extracts, combined with inorganic element analysis can be a valuable tool in better understanding the organic associations of the REE and other non-mineral inorganic elements in low-rank coals.

8. Conclusions

A series of leaching experiments have been performed both to provide information to determine the modes of occurrence of REE in Forth Union lignite coals and to identify acidic solvent types and operating parameters that can be effective for extraction and recovery of the REE from the lignites. This foundational research is currently being used in the development of a novel low-cost REE extraction technology that has exhibited promising technical performance to date.

Overall, about 70-90wt% of the REE are extractable with dilute acids at mild temperature when given sufficient contact time. At short contact time, the data suggest that the REE associated in weak bonding forms such as organic complexes are preferentially extracted over acid-soluble (0.5M H₂SO₄) REE-bearing mineral forms. Particle size of the coal does not appear to have any significant impact, with the exception of scandium which has improved extraction at finer particle size. Testing has shown that to extract the REE associated in organic complexes, a minimum acid concentration is needed. With higher concentration, limited increase in extraction results. Scandium is again the exception, which showed significantly improved extraction at higher acid concentration. For one set of REE-rich lignite samples, the REE extractability was shown to be inversely proportional to ash yield. Combined with results of float-sink testing that shows dramatic enrichment of the REE in the light specific gravity fractions, this result indicates the extractable REE are likely associated with the organic fraction of the coals, rather than in ion-exchangeable forms associated with clay minerals in the coal, which has recently been suggested in the literature. The data also show that for an oxidized lignite material, about 37% of the REE were associated with the humates in the coal, while about 26% were extractable with dilute acid. This suggests presence of REE associated in multiple organic forms.

Combined with a review of the literature and these authors experience, we believe the data discussed in this paper strongly point towards the primary mode of occurrence of REE in Fort Union lignites being organic complexes, most likely associated with carboxylic acid functional groups that are uniquely prevalent in low-rank coals. However, the data also suggest that multiple organic bonding types are likely, such as strong bonding directly to the carbon matrix of the lignite coals. Further, the data suggest that for the LREE, there is likely to be up to about 30wt% of the total REE associated in acid-soluble mineral forms (i.e. carbonates, sulfates, some oxides). In contrast, the data suggest that little of the HREE are associated in these acid-soluble mineral forms. The HREE appear to have a larger degree of organic association than the LREE. Scandium behavior was notably different than the other REE, and the extractable fraction appears to have a primarily acid-soluble mineral form.

We recognize that limited samples have been analyzed in this study, as well as the qualitative nature of some of our conclusions. We also recommend that future work employing this type of leaching analysis approach be accompanied by evaluation of the mineralogy of the coals both before and after the leaching to identify changes in the mineral content and forms and apply that information to the behavior of the REE or other elements of interest. This should help to form more quantitative conclusions. Despite these limitations, we feel that the data presented are a valuable contribution and sheds new light on the modes of occurrence of the REE in lignite coals.

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