



# Leaching behavior of rare earth elements in fort union lignite coals of North America

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## A B S T R A C T

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 (80–95 wt%), 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 to 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 \(2017\)](#), 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 ([Economics and Statistics Department - American Chemistry Council, 2014](#)). Major market segments that rely on REE-based products or technologies include health care, transportation and vehicles, lighting, renewable energy systems, communications systems, audio

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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 (Dai et al., 2016a; Seredin, 1996; Arbruzov et al., 2000; Hower et al., 1999; Seredin and Dai, 2012; Dai and Finkelman, 2018). 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 (U.S. Energy Information Administration, 2016). 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 (Countries With the Biggest Coal Reserves, 2013). 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 (Murphy, 2018). Ackman et al. (2012) 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 (U.S. Department of Energy National Energy Technology Laboratory, 2017). Seredin and Dai (2012) (Seredin and Dai, 2012), and Dai and Finkelman (2018) 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 Fort 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 (Arbruzov et al., 2000; Arbruzov and Ershov, 2007; Dai et al., 2008, 2010, 2011; Dill, 2001; Ershov, 1961; Eskenazy, 1987a, 1995; Finkelman, 1993; Seredin, 1996; Hower et al., 1999; Seredin, 2004; Seredin and Shpirt, 1999a; Ward, 1978; Zubovic et al., 1961) 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) 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, 2018) 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. (2018) 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). The modes of occurrence of REE in a typical lignite compared to a metalliferous (Seredin and Shpirt, 1995) 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), 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 (Seredin, 1996; Arbruzov et al., 2000; Arbruzov and Ershov, 2007; Dai et al., 2008; Ershov, 1961; Eskenazy, 1987a; Seredin, 2004; Zubovic et al., 1961). These types of indirect methods are validated by experimental work evaluating the sorption characteristics of REE by peat, coals, and humic acids (Eskenazy, 1999; Szalay, 1964). 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 (Dai et al., 2016b). Direct evidence of organic associations is also available in the literature. For example, Seredin and Shpirt, 1999b 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) 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. (2018) also suggest that REE can be bound strongly to the carbon matrix in the coal. In another leaching method approach, Wei and Rimmer (2017) reached the same conclusion as Finkelman et al. (1990), 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) found that Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> bound to -COOH and -OH were replaced by REE cations. Aide and Aide (2012) showed that HREE-organic complexes are more stable

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