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Rare earth elements and critical minerals in coal and coal byproducts

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What are Critical Minerals (CMs)?

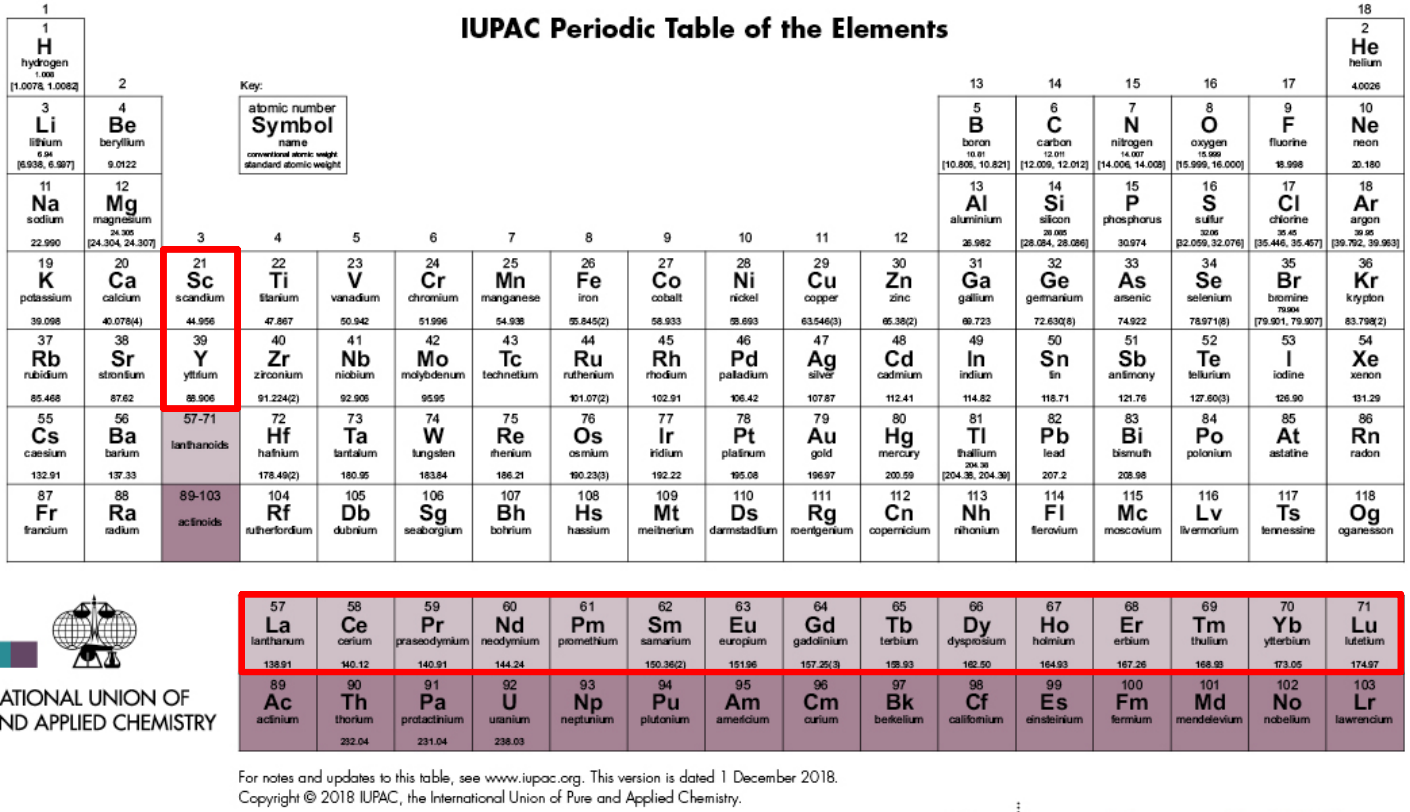
- Under U.S. Presidential Executive, and Interior Secretarial Orders, the USGS Director was asked to produce a list of mineral substances critical to the U.S. economy or national security, that are vulnerable to disruption in supply.
- These 50 “critical minerals” include elements, minerals, and rare earth elements (REEs):

Aluminum, antimony, arsenic, barite, beryllium, bismuth, cerium, cesium, chromium, cobalt, dysprosium, erbium, europium, fluorspar, gadolinium, gallium, germanium, graphite, hafnium, holmium, indium, iridium, lanthanum, lithium, lutetium, magnesium, manganese, neodymium, nickel, niobium, palladium, platinum, praseodymium, rhodium, rubidium, ruthenium, samarium, scandium, tantalum, tellurium, terbium, thulium, tin, titanium, tungsten, vanadium, ytterbium, yttrium, zinc, and zirconium.

Source: USGS, 2022

What are Rare Earth Elements (REEs?)

- REEs include the lanthanides (57-71) plus Y (39) and Sc (21).
- Yttrium occurs together with the lanthanides, Sc mostly does not.
- But Sc is very important, due to its high value among the REEs.



INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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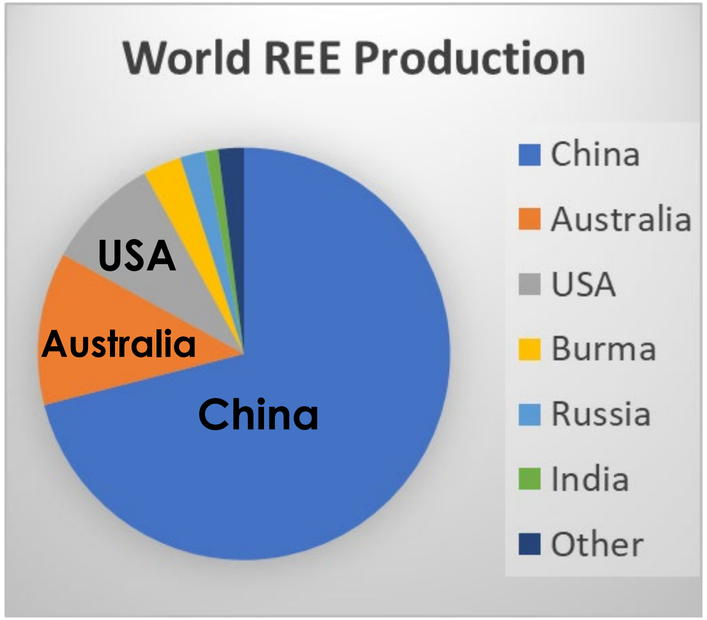
Source: International Union of Pure and Applied Chemistry (IUPAC), 2022.

REE Applications and Sources

- REEs are needed in aerospace, defense, energy, electronics, transportation, medical uses, and many other modern applications.
- China dominates current world REE production.
- New sources of domestic REE production are needed for current and projected uses.



Source: J. Gambogi, 2019, USGS

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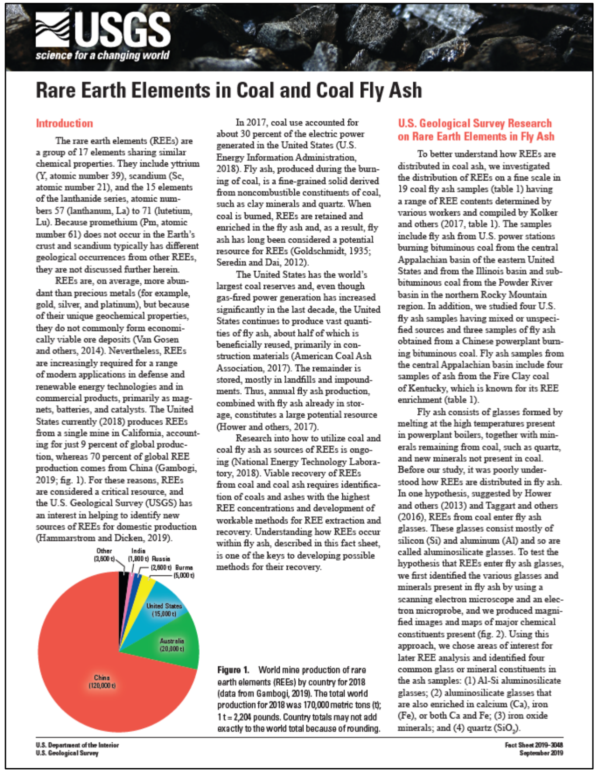
REEs in Coal and Coal Fly Ash

- Coal, especially coal ash, has long been considered a potential source of REEs and other valuable elements (Goldschmidt, 1935).
- REEs are strongly retained in solids remaining after coal is burned (fly ash, bottom ash).
- REEs are next most abundant in waste coal.
- USGS role: understand how REEs occur, to help engineers develop extraction methods.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Rare Earth Elements in Coal and Coal Fly Ash

Introduction

The rare earth elements (REEs) are a group of 17 elements sharing similar chemical properties. They include yttrium (Y, atomic number 39), scandium (Sc, atomic number 21), and the 15 elements of the lanthanide series, atomic numbers 57 (lanthanum, La) to 71 (lutetium, Lu). Because promethium (Pm, atomic number 61) does not occur in the Earth's crust and scandium typically has different geological occurrences from other REEs, they are not discussed further herein.

REEs are, on average, more abundant than precious metals (for example, gold, silver, and platinum), but because of their unique geochemical properties, they do not commonly form economically viable ore deposits (Van Gosen and others, 2014). Nevertheless, REEs are increasingly required for a range of modern applications in defense and renewable energy technologies and in commercial products, primarily as magnets, batteries, and catalysts. The United States currently (2018) produces REEs from a single mine in California, accounting for just 9 percent of global production, whereas 70 percent of global REE production comes from China (Gambogi, 2019; fig. 1). For these reasons, REEs are considered a critical resource, and the U.S. Geological Survey (USGS) has an interest in helping to identify new sources of REEs for domestic production (Hammarstrom and Dicken, 2019).

Figure 1. World mine production of rare earth elements (REEs) by country for 2018 (data from Gambogi, 2019). The total world production for 2018 was 170,000 metric tons (t); 1 t = 2,204 pounds. Country totals may not add exactly to the world total because of rounding.

In 2017, coal use accounted for about 30 percent of the electric power generated in the United States (U.S. Energy Information Administration, 2018). Fly ash, produced during the burning of coal, is a fine-grained solid derived from noncombustible constituents of coal, such as clay minerals and quartz. When coal is burned, REEs are retained and enriched in the fly ash and, as a result, fly ash has long been considered a potential resource for REEs (Goldschmidt, 1935; Seredin and Dai, 2012).

The United States has the world's largest coal reserves and, even though gas-fired power generation has increased significantly in the last decade, the United States continues to produce vast quantities of fly ash, about half of which is beneficially reused, primarily in construction materials (American Coal Ash Association, 2017). The remainder is stored, mostly in landfills and impoundments. Thus, annual fly ash production, combined with fly ash already in storage, constitutes a large potential resource (Hower and others, 2017).

Research into how to utilize coal and coal fly ash as sources of REEs is ongoing (National Energy Technology Laboratory, 2018). Viable recovery of REEs from coal and coal ash requires identification of coals and ashes with the highest REE concentrations and development of workable methods for REE extraction and recovery. Understanding how REEs occur within fly ash, described in this fact sheet, is one of the keys to developing possible methods for their recovery.

U.S. Geological Survey Research on Rare Earth Elements in Fly Ash

To better understand how REEs are distributed in coal ash, we investigated the distribution of REEs on a fine scale in 19 coal fly ash samples (table 1) having a range of REE contents determined by various workers and compiled by Kolker and others (2017, table 1). The samples include fly ash from U.S. power stations burning bituminous coal from the central Appalachian basin of the eastern United States and from the Illinois basin and subbituminous coal from the Powder River basin in the northern Rocky Mountain region. In addition, we studied four U.S. fly ash samples having mixed or unspecified sources and three samples of fly ash obtained from a Chinese powerplant burning bituminous coal. Fly ash samples from the central Appalachian basin include four samples of ash from the Fire Clay coal of Kentucky, which is known for its REE enrichment (table 1).

Fly ash consists of glasses formed by melting at the high temperatures present in powerplant boilers, together with minerals remaining from coal, such as quartz, and new minerals not present in coal. Before our study, it was poorly understood how REEs are distributed in fly ash. In one hypothesis, suggested by Hower and others (2013) and Taggart and others (2016), REEs from coal enter fly ash glasses. These glasses consist mostly of silicon (Si) and aluminum (Al) and so are called aluminosilicate glasses. To test the hypothesis that REEs enter fly ash glasses, we first identified the various glasses and minerals present in fly ash by using a scanning electron microscope and an electron microprobe, and we produced magnified images and maps of major chemical constituents present (fig. 2). Using this approach, we chose areas of interest for later REE analysis and identified four common glass or mineral constituents in the ash samples: (1) Al-Si aluminosilicate glasses; (2) aluminosilicate glasses that are also enriched in calcium (Ca), iron (Fe), or both Ca and Fe; (3) iron oxide minerals; and (4) quartz (SiO_2).

U.S. Department of the Interior
U.S. Geological Survey

Fact Sheet 2019–3048
September 2019

Source: Scott and Kolker, 2019

REEs in Coal and Coal Byproducts

More

Less

Material

- Fly Ash
- ***Coal Waste***
- Raw Coal
- Acid Mine Drainage (AMD)

Progress

Pilot-scale projects are underway to recover REEs from each coal material.

Advantages

- REEs from coal are strongly retained in a smaller mass.
- *Non-coal material is REE-enriched relative to coal itself.*
- Abundant and well understood.
- REEs already in solution or in a colloidal form. Precipitates from AMD concentrate REEs.

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Source: U.S. Dept. of Energy National Energy Technology Laboratory, 2022

Coal Preparation

- Coal preparation minimizes mineral matter, thereby increasing thermal energy.
- Material removed during coal preparation is a waste.
- Coal waste includes rock material, underclays, coal overburden, and some discarded coal.

Source: A. Kolker, USGS

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Pilot Scale REE Extraction from Waste Coal

- Multistage process developed at Univ. of Kentucky, using calcination (pre-heating) to increase REE mobility.
- High level of concentration of REEs from U.S. Illinois Basin waste coal from Kentucky.
- Set-up is modular and can be moved to waste sites.

Source: University of Kentucky

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REEs and Critical Elements from Waste Coal

- Waste from coal mining and preparation requires no new mining. Extraction of REEs could help reduce the impact of this waste.
- <u>Good news</u>: Coal waste shows relative enrichment in REEs and other lithophile elements such as Li, Al, Ti, Sc, Rb, Y, Zr, Cs, Ba.
- <u>Bad news</u>: Coal waste is also enriched in harmful chalcophile elements, such as Hg, As, Sb, and Pb, as pyrite is concentrated in waste from coal preparation.
- Nonetheless, recovery of REEs from waste coal is one of the more promising approaches to REE recovery, at the pilot scale.

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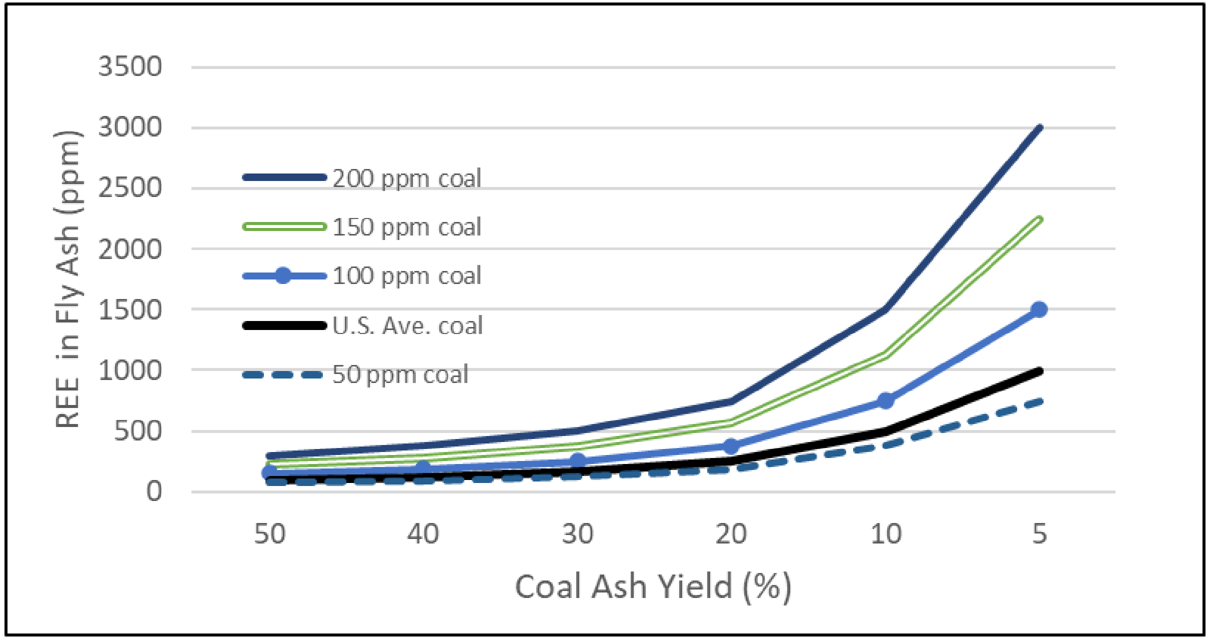
Source: U.S. Dept. of Energy National Energy Technology Laboratory, 2022

Concentration of REEs in Fly Ash (Calculated)

- REEs from coal are strongly retained in a smaller mass in coal ash.
- High REEs in coal and low ash yield lead to highest REE contents in coal ash.
- REE contents are still below those in primary REE ores.



Calculation assumes100% retention of REEs from coal in coal ash and a 75:25 proportion of fly ash to bottom ash.

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Source: Kolker and others, in press.

REEs and Critical Elements from Fly Ash

- Fly ash has long been considered a source of valuable constituents because certain elements, including REEs, are strongly retained during coal combustion.
- Good news: Of coal-related sources, fly ash shows the greatest REE enrichment because REEs from coal are retained in a smaller mass.
- Bad news: Extraction can be difficult because a significant fraction of REEs in fly ash is contained in aluminosilicate glasses.
- Chemical and physical pretreatment approaches currently being tested may help improve the extractability of REEs from coal ash.

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REEs and Critical Minerals from Raw Coal

- On average, lanthanide REEs in U.S. coal are <40% of the average upper continental crust (UCC).
- Good news: Coals can become unusually REE-enriched by interaction with REE-bearing fluids, or volcanic activity concurrent with coal deposition. Within-bed REE enrichment occurs mostly at the top or bottom (underclays) of coal beds.
- Bad news: Within-bed REE enrichment requires detailed sampling to delineate the most enriched zones, and selective mining to extract.
- Ongoing DOE CORE-CM Initiative seeks to identify the most promising REE and CM sources within U.S. coal basins.

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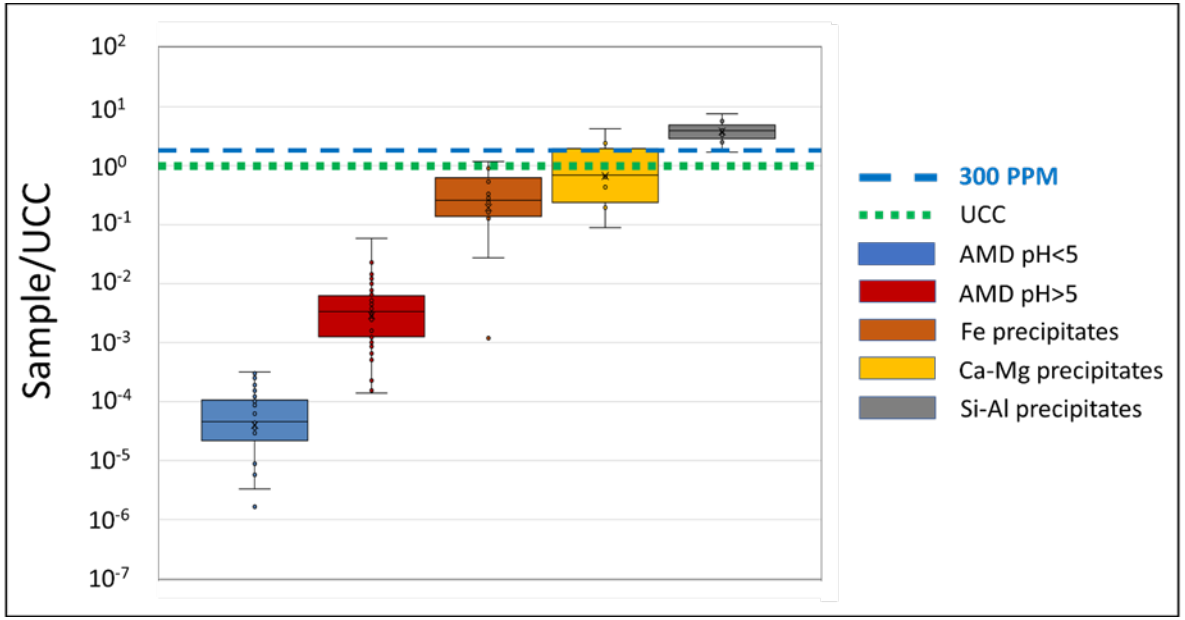
REEs and Critical Minerals from Coal Mine AMD

- Research in areas of past coal mining shows potential for recovery of REEs and CMs from coal mine acid mine drainage (AMD).
- <u>Good news</u>: REEs occur in a dissolved state or as precipitates. The most REE-enriched precipitates are at or slightly above the DOE 300 ppm interest level.
- <u>Bad news</u>: Dissolved concentrations are much below those in coal-related solids. Coal mine AMD is limited to areas of past mining.
- REEs and CMs from coal mine AMD are waste-derived resources.

REEs and Critical Elements from Coal Mine AMD

- Figure shows REE contents for fluids and precipitates relative to UCC and 300 ppm total REE DOE interest level.
- Enrichment is highly dependent on fluid or precipitate chemistry.



REE concentration values in AMD from U.S. Illinois Basin; and U.S. Appalachian Basin; REE concentration values in Fe, Ca-Mg and Si-Al precipitates from U.S. Appalachian Basin.

Source: Kolker and others, in press.

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Summary

- Critical elements are those that are essential but whose supply is limited or controlled by external sources.
- Potential coal-related sources of critical REEs include fly ash, waste from coal mining and preparation, coal-mine acid mine drainage, and coal itself.
- Each material source has been considered in DOE-supported investigations outside of USGS, and each has advantages and disadvantages, as outlined in this presentation.

Summary

- When coal is burned, REEs are strongly retained in coal combustion fly ash, making it the most REE-enriched coal-related material.
- But fly ash also poses the biggest challenge to REE extraction due to retention of REEs in aluminosilicate glasses.
- Waste coal is next most enriched in REEs, but these too are much below REE contents of primary REE ores.
- Recovery of REEs from each coal-related material has shown promise at the pilot scale, but without commercial development.

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Questions on Critical Minerals from Coal Waste

Provided by the NASEM Panel

- Can we expect the currently developed coal-waste-based critical materials (CMs) extraction technologies to be commercialized in the next 5 years?
  - *This is largely dependent on market forces, and likely, support from agencies outside the USGS. It is not possible for me as a geologist to predict.*
- The pace of coal-fired retirements is being accelerated. Will coal wastes still be targeted as an important CMs (especially REEs) production resource?
  - *There are large portions of these wastes from past coal use that could be targeted even if the rate of new waste generation declined.*

Questions on Critical Minerals from Coal Waste

Provided by the NASEM Panel

- What is the percentage of heavy REEs among the total recoverable REEs in coal wastes in the U.S.?
  - *Coal and coal wastes generally exhibit a crustal distribution of REEs which, by definition, is light rare earth (LREE) enriched. If heavy rare earths (HREEs) are defined as the sum of Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, the percentage of HREEs is typically about 30%, with Y (not a lanthanide) commonly the most abundant HREE.*
  - *Seredin and Dai (2012) introduced a classification based on economic utility, in which "critical" REEs are Y, Nd, Eu, Tb, Dy, and Er. In this classification, some non-critical HREE, such as Ho, Tm, Yb, and Lu are excluded, and Nd, an important LREE, is added. The proportion of "critical" REEs in U.S. coal and coal combustion products is typically 30 to 40%.*

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Questions on Critical Minerals from Coal Waste

Provided by the NASEM Panel

- How do the quantities of critical minerals in coal waste compare to the quantities in other types of mining waste?
  - *This is very dependent on the specific mining waste being compared. Coal waste is potentially a source of some non-REE CMs that include Cr, V (present in illite-smectite); Sb, As (present in pyrite); and Rb, Cs (lithophile elements enriched similarly to REEs).*

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