The Application of Current Mineral Processing and Extractive Metallurgy Technologies to Potential Rare Earth Ores in the U.S. Coal Measures: Near-Term Opportunities to Fill Out the U.S. Value Chain

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Executive Summary

Rare earths are critical minerals that are indispensable to the nation's modern economy and national defense. They underpin every aspect of modern society, from clean energy to consumer electronics, missile guidance systems to the catalysts that allow us to refine oil into transportation fuels.

The United States was the leading global producer of rare earths until the 1990s, when a confluence of events resulted in the decline and effective end of domestic production. In the ensuing decades, the U.S. dependence on rare earths imports, – both in the form of raw materials and those embedded in imported goods, – has been recognized as a cause of concern for national security and U.S. competitiveness, particularly as manufacturing with U.S. intellectual property moves offshore. These concerns were underscored in a 2013 Congressional Research Service Report which stated that the U.S. is almost entirely lacking in "*the refining, fabricating, metal-making, alloying, and magnet manufacturing capacity to process rare earths*".

Coal-associated mineral products present a unique opportunity to restore the domestic rare earth value chain lost decades ago. Sampling and analysis have demonstrated concentrations in coal-bearing strata approaching 1,000 ppm and higher. While lower in concentration than traditional rare earth ores that are being developed, these anomalous concentrations of rare earths in coal related rocks offer opportunities for the production of rare earth products in the U.S. Indeed, sampling has found coal measures to be relatively enriched in heavier rare earths compared to other domestic and some international deposits, representing an opportunity for domestic dominance in the market.

Investigations conducted by Department of Energy's (DOE) Office of Fossil Energy, the National Energy Technology Laboratory (NETL), and others over the past decade have established a growing knowledge base regarding rare earths associated with coal measures. This initial work indicates the potential upside for further activities toward the understanding of the potential resource, inclusive of understanding where areas of high rare earth prospectivity might exist. However, substantial and focused action must be taken if timely results are desirable. This type of research is best accomplished through close collaboration of the geosciences, mining, mineral processing, extractive metallurgy, and financial modeling disciplines. While this approach has been used for centuries, it has more recently been given the name Geometallurgy, which is "which geological data, mining data, and processing data are co-analysed to generate useful information and knowledge to optimize resource profitability" (David, 2019).

This report is intended to provide the background on domestic rare earth production and provide potential opportunities for the near-term restoration of the rare earth value chain in the U.S. Background and contextual material is provided on the domestic rare earth industry, as is an overview of the economics of processing rare earth ores through the value chain, including a deeper assessment of different mineral processing pathways and opportunities. This is followed by a discussion on knowledge gaps and key research areas that can address them in developing rare earth production in the near term.

Key takeaways from the report include:

- Results to date have shown that some coal-associated mineral products clear a cutoff grade as a rare earth resource based on historic cost levels of physical concentration and hydrometallurgy. This justifies further geologic exploration work as well as mineral processing and extractive metallurgy research to evaluate the projected performances of these materials in available process technologies.
- There is not a complete domestic value chain for rare earths, but options may exist to leverage idled or underutilized extractive metallurgy facilities and equipment. The innovative repurposing of these assets could rapidly establish a reliable rare earth value chain, establishing near term production at the demonstration- or commercial-scale. These facilities could then perform mineral concentration, chemical extraction, and separation needed to produce rare earth material for the

remaining downstream end users (metal, alloy, and magnet manufacturers) once again in the United States.

- The dearth of existing domestic rare earth separation processing facilities may turn into a competitive advantage, allowing accelerated commercialization of new technologies with cost and performance advantages compared with solvent extraction.
- The effect of transportation costs is reduced dramatically as the rare earth content of coal related materials increases. Therefore, to guard against negative economic effects of transportation on a newly established value chain, geologic exploration of higher assay material will be an ongoing high-priority because a rare earth content even in the 1,000 ppm range cannot be shipped very far without significant adverse impacts on overall process economics.
- Past Federal Government intervention in the U.S. rare earths industry, including in the wake of embargos by producing countries, had long reaching positive impacts. Investments and initiatives in geologic exploration, adaptation of existing production technologies, repurposing of production facilities, and operation of facilities under Federal sponsorship were all among the building blocks of the U.S. rare earth industry of the day. The significance of Federal-sponsored geology work cannot be understated; few items will compete with raw material rare earth content as an economic driver.
- Mineral processing is less expensive than extractive metallurgy, with a historic five-fold cost differential reported here. Therefore, all mineral processing options should be exhausted to improve the existing feedstock assay prior to pursuing extractive metallurgy. This is key to reducing costs associated with tailings, enabling permitting, and minimizing costs.

1. Introduction

1.1. Overview

This report will consider the potential for currently available mineral processing and extractive metallurgy technologies to produce separated rare earth compounds from U.S. coal and coal byproducts. Implementation of production as such would require restoration of elements of the rare earth value chain that have recently been absent in the U.S., notably for chemical extraction of rare earth compounds from the mineral form (i.e. hydrometallurgical extraction).

A variety of existing technologies are available for use in both mineral processing and extractive metallurgy applied to RE production in the U.S. As will be discussed, once a mineral concentrate is produced, the contained rare earth value can be large compared with transportation costs, and the sections of the value chain dealing with chemical extraction (the largest cost) and separation into individual rare earth compounds can be remotely located. Also, as will be discussed, this has been the rule rather than exception in the history of the rare earth industry in the U.S.

A strategy, possibly to include repurposing of existing metallurgical processing facilities, will be presented for near-term production, using a decentralized set of facilities.

Also presented will be research results from the Office of Fossil Energy (FE) and the National Energy Technology Laboratory (NETL), within the U.S. Department of Energy, relevant to economic feasibility of rare earth production, notably from the standpoint of establishing which materials are capable of providing economic production. Simple methodologies are presented for both establishment of cutoff grades and economic evaluation of a process.

The goal of this report is to present an overview of methods and pathways that will result in “the achievement of near-term rare earth production, using currently available technologies to produce a mixed, chemical extracted rare earth concentrate, and existing and new facilities to produce separated rare earths that can “plug in” to the metals and magnet production facilities.” A set of recommendations appears at the end of this work, involving both research and project development activities which will enable the achievement of this noble goal. A set of recommendations appears at the end of this work, involving both research and project development activities.

1.2. Terms of Reference

The scope and boundaries for this report are as follows:

- Technologies that are currently available in the rare earth value chain from ore to metal.
- Logistical considerations: whether the steps in the value chain need to be co-located.
- Special focus on potential production of rare earth elements used in magnets.
- Optimum coal-associated feedstocks, which have been ranked according to contained rare earth value per ton.
- Tonnage requirements along the value chain for 1,000 metric tons per year of rare earth production.
- Addressing resource assessment needs.
- With respect to prospects for near-term production: consideration of the availability and use of existing facilities.
- Locations in the value chain where different coal byproducts would “plug in”.
- Elements of process costs are discussed.
- For this report, the discussion is limited to rare earth (La through Lu) production only. Economic improvements and technical constraints associated with polymetallic production can be considered subsequently.
- A brief history of the rare earths industry in the U.S. and past U.S. Federal Government involvement.

2. Rare Earth Geology

2.1. Overview

Over the past decade, rare earth element deposit types have received significant attention in the geological literature. Much of that research has been conducted by the U.S. Geological Survey (USGS), culminating in three seminal publications on deposits types (Long et al., 2010b, Van Gosen et al., 2017, Van Gosen et al., 2019). According to the USGS, rare earth elements are relatively common in the Earth's crust, however, "economic concentrations" of these elements are not commonplace. Also, rare earths tend to occur in a variety of relatively uncommon igneous and sedimentary rock types.

Those uncommon rock types that host the most well-known rare earth mineral deposits in the U.S. include:

1. Carbonatites,
2. Alkaline igneous rocks,
3. Sedimentary phosphate-rich rocks,
4. Rare earth-rich veins,
5. Iron oxide deposits containing rare earth-bearing apatite,
6. Monazite-xenotime-bearing heavy mineral sands and placer deposits, and
7. Ion-adsorption clay deposits.

Among the most important of these rare earth deposit types are the carbonatites, alkaline igneous rocks, and ion-adsorption clays.

This Section provides a brief description of the nature of major rare earth deposit types and their minerals and chemical composition. A discussion of possible rare earth deposits, associated with coal measures in coal basins, will then be presented. Also presented will be microscopy results from the National Energy Technology Laboratory, showing images of individual rare earth-bearing mineral grains in Appalachian coal-associated rocks, and also yielding information regarding their mineralogy.

2.2. The Nature of Conventional Rare Earth Element Ore Deposits

2.2.1. Igneous and Sedimentary Rare Earth Deposits

Carbonatites

Carbonatite rare earth deposits are hosted in carbonate-rich igneous intrusives such as stocks, tabular lenses, dikes, irregular-shaped masses, and veins. These are often composed of 50 percent or more carbonate minerals, mainly calcite and dolomite, reflecting carbonate-rich source magmas. Bastnaesite is the primary rare earth ore mineral in most carbonatites and may be accompanied by other rare earth-bearing minerals including monazite, apatite, and secondary xenotime that form in weathered ore (Long et al., 2017).

Carbonatites tend to have the highest total rare earth concentrations of any igneous rocks. While the extraordinarily large carbonatite deposits are proven producers and large enough such that a single deposit can produce much of the world's light rare earths demand (LREE, Lanthanum through Gadolinium), they are typically depleted in heavy rare earths (HREE, Terbium through Lutetium). The best example is the world-class Mountain Pass carbonatite deposit in southeastern California—the largest known rare earth deposit in the U.S. which has produced most of the rare earths mined in the U.S. since the late 1960's (Bradley et al., 2019).

Other rare earth-rich carbonatites in the United States include the Bear Lodge deposit in northeastern Wyoming, and the Elk Creek deposit in southeastern Nebraska (Bradley et al., 2019). The Bear Lodge carbonatite complex has been thoroughly drilled with proven plus probable resources of 15.6 million metric tons of ore averaging 2.78 percent total rare earth oxides.

The Elk Creek deposit is a rare earth- and niobium-rich carbonatite that lies about 600 ft below the surface that was discovered in 1970 by a regional airborne geophysical survey.

Alkaline Igneous Rocks

Alkaline igneous rocks are the other major type of igneous-hosted rare earth deposit. These are geochemically characterized by depletion in silica relative to sodium, potassium, and calcium in comparison to “typical,” more silica-rich igneous rocks. Deposits in alkaline igneous rocks have been relatively small contributors to the global rare earth supply, but alkaline-hosted deposits have become important exploration targets, because they tend to be more enriched in the HREEs than carbonatites and most other rare earth deposit types (Long et al., 2017)

One example of an alkaline igneous-related rare earth deposit in the U.S. occurs at Bokan Mountain in a southern part of Prince of Wales Island in southeastern Alaska. The deposit consists of vein-like intrusions (thin igneous dikes) containing elevated concentrations of rare earths (Bradley et al., 2019).

The principal vein-dike system extends for at least 1.6 miles in length and is composed of numerous, subparallel, thin dikes that are 4.8 ft or less in width, forming a zone of about 160 ft in total width. The rare earth mineralogy in these vein dikes is complex and fine-grained, with more than two dozen distinct rare earth minerals, including oxide, silicate, phosphate, and carbonate minerals (Bradley et al., 2019).

Monazite and Xenotime-Bearing Sands

Monazite and xenotime-bearing beach sands and silts are carried by rivers and streams to coastal environments. In these clastic quartz-rich placer-type sediments, monazite occurs in close association with other heavy minerals, most commonly ilmenite, leucoxene, rutile, and zircon. These heavy minerals are considered as indicator minerals of potentially economic quantities of rare earth-bearing monazite and xenotime mineral “deposits”. Economic “black sand” deposits in coastal settings (ancient and modern) typically contain five percent or greater heavy-mineral content (Long et al., 2017).

Some modern and ancient coastal deposits can host large undeveloped, poorly studied deposits of monazite. Coastal deposits offer an advantage in that the deposits are usually unconsolidated and easy to excavate. Also, these deposits are relatively easy to process in order to separate out valuable heavy minerals such as ilmenite and rutile (for titanium and titanium dioxide), zircon (for refractories), and garnet (for abrasives)—in addition to monazite and xenotime rare earth minerals.

Examples of large undeveloped monazite occurrences in coastal sediments, ranging in age from Cretaceous to Recent, occur in coastal southeastern U.S. extending from Virginia to Florida. Many sand and silt units in this coastal plain region contain abundant monazite that originated up gradient from the erosion of igneous and metamorphic source rocks along the Blue Ridge province (Bradley et al., 2019).

Beach placer sandstones were once heavy mineral-rich zones where fluid actions (waves, current, winds) resulted in concentrations of heavy mineral sands (McLemore, 2010)). These deposits include titanium minerals, zircon, and monazite, similar to modern beach placers, and can be cemented by hematite and carbonates. By 1961, prospectors and the U.S. Atomic Energy Commission had discovered numerous deposits of this type in Utah, New Mexico, Colorado, and Wyoming (Dow and Batty, 1961).

Phosphate Rocks

HREE-bearing sedimentary phosphate-rich (phosphorite) deposits exposed over large areas of the midcontinent of the U.S. and in Florida have also been extensively researched by the USGS and others. Many of these phosphorites are enriched in readily extractable HREEs and as such are a potentially large undeveloped rare earth resource (Long et al., 2017).

One of the best examples of sedimentary phosphates is the relatively high rare earth content of central Florida phosphate deposits of the Hawthorne Formation. These are the subject of extensive geochemical analyses by USGS and others, in which the mineral francolite (a carbonate-rich apatite mineral), common to most sedimentary phosphate-rich rocks is highly enriched in HREEs. A continent-scale assessment has identified several unmined HREE-bearing phosphorites in the U.S. that are exposed over large areas such as those in Arkansas (Long et al., 2017, Bradley et al., 2019).

This research has also demonstrated that phosphate-bearing rare earth concentrations vary as a result of oceanic chemical transitions during specific geologic time periods. Formation of phosphorites with anomalous rare earth values appears to be highest within late Mississippian, Devonian, and Ordovician.

Ionic-Adsorption Clays

Rare earth-bearing clay deposits derived from heavily-weathered granitic rocks are the world's primary sources of the HREEs, and are referred to as "south China clay rare earth deposits", or more formally known as rare earth ion-adsorption clay deposits. These appear to have formed through the intensive weathering of rare earth-bearing granites in regions that experienced warm climates with moderate to intensive rainfall.

Ionic-adsorption clay deposits are concentrated when intensive weathering of the decomposed granite bedrock formed thick clay-rich zones of soils or "laterites" atop the weathered granites. Rare earths leached by groundwater from rare earth-bearing granite bedrock were mobilized and became weakly attached or (ion) adsorbed onto the clays to form the rare earth deposit (Long et al., 2017).

A recent USGS study identified rare earth-bearing clay deposits overlying weathered granite plutons in southeastern U.S. as having several important characteristics in common with the southern China rare earth-bearing clay deposits. Comparisons showed similarities in mineralogy, inferred processes of formation, and rare earth concentrations (Bradley et al., 2019).

2.3. Rare Earths in the U.S. Coal Measures

2.3.1. Geologic Setting

Important factors for introducing rare earths into coal measures are the:

1. Provenance of sediments pouring into coal basins
2. Local environment of deposition of rare earth-bearing sediments, and
3. Local tectonic controls that control rare earth concentration.

Primary sources or provenance of rare earths into typical coal basins depend on the regional tectonics and geologic processes surrounding and affecting the basin. For example, areas of active tectonism may result in volcanics or igneous intrusives being emplaced in or near a preexisting coal basin.

Rare Earths in coal basins could be sourced from volcanic eruptions that produce ash flows, or ash clouds resulting in discrete layers of volcanic ash (known as "tonsteins") raining into layers of peat forming in a coal basin.

Another possible rare earth source could be from erosion of an igneous intrusion (a sill, dike, larger pluton), or possibly an exposed lava flow, transporting those igneous-derived sediments into the nearest sedimentary basin pre- or post-coal formation.

As discussed above, rare earths are geochemically incompatible in "basic" or "felsic" intrusive or volcanic rocks, and are preferentially fractionated and incorporated in the more "acidic" igneous rocks (granitic or lighter pegmatitic magmas) or lighter volcanic rocks (rhyolites or ash flows).

In other words, rare earths are compatible with the lightest of igneous products left over at the end of magmatic or volcanic differentiation and cooling, incorporated into those "left over" types of igneous (intrusive or volcanic) minerals that can pair up with or "accept" the uniqueness of rare earth geochemistry.

Rare earth-bearing minerals such as volcanic glass and its products or high- temperature feldspars (sanidine) appear to have been introduced into coal basins in the U.S. via erupted volcanic ash ("tonsteins"). As a result, considerable amounts of rare earths can broadly accumulate in the peat that is forming real-time and/or perhaps be incorporated via surface or groundwater directly into lignite or more mature formed coals.

More likely as a result of local igneous activity, particularly during the emplacement of a major intrusive, associated hydrothermal fluids are able to introduce mobilized rare earth material into developing coal basins. Hydrothermal fluids can mobilize rare earths and keep them in solution until they find a suitable geochemical receptor.

With increasing time, and as weathering breaks down residual volcanic ash layers or lava flows, further rare earth enrichment will likely occur if those sediments are transported and preferentially concentrated in a basin or relatively tectonically stable area, and not dispersed all together. For example, local development of heavy minerals and beach placer type sands and deposits is usually caused by preferential erosion and concentration of heavy resistant minerals (black sands), which are thought to be incorporated into sediments associated with evolving coal basins.

Although coal swamps are low-energy environments not prone to heavy detrital input, cyclical rise in sea level and geologic marine transgression landward would tend to introduce sediments into a developing coal basin. Marine regression, or the gradual lowering of sea level, is an efficient mechanism of sifting and sorting heavy minerals across a coastal or beach environment that may later become incorporated into an evolving coal basin.

Similarly, rare earth-bearing minerals can also be eroded from sedimentary rock layers, metasediments, or high-grade metamorphic rock units, and transported as sediments that consist of rare earth-bearing minerals. These sediments, like the igneous-derived rare earth-bearing minerals are preferentially "sorted" and concentrated in fluvial, deltaic, and beach environments as heavy mineral layers.

Black sand heavy mineral placers range in size from local fluvial channels, to miles of river delta, to broad beach or landward dune-type settings, and are eventually incorporated along with other sediments associated with the sandstone-silt-shale-coal sequences, into a newly-developing or existing coal basins.

In summary, concentrations of rare earth-bearing minerals in coal-related sedimentary rocks have occurred via one or some combination of the processes described above. ***Anomalous levels of rare earths have been demonstrated much more so in the coal underclays, coal rock overburden, and associated acid mine drainage sludges, than in the organic portion of coal seams.***

2.3.2. Provenance of Rare Earth-Bearing Strata in the Coal Measures

If granitic materials are source rocks for rare earth-bearing minerals, especially anomalous rare earth deposits, those source areas must be in a state of deep weathering and may actually be regarded as "laterites". Laterites are actually soils formed from deeply decomposed rocks that are relatively rich in iron and aluminum and are thought to have formed in highly humid tropical environments. They develop by intensive and prolonged weathering of the underlying parent rock, in this case, the granitoid bedrock materials rich in rare earth-bearing minerals (Long et al., 2017).

Worldwide, laterites are best known in tropical environments, however, during Pennsylvanian time, parts of the Appalachian Basin were probably in low latitude or equatorial tropical areas. Therefore, perhaps the heavily-weathered source rocks providing sediments being transported into some coal basins are correctly regarded as laterites (Bradley et al., 2019).

For example, certain granitic source rocks in the southern Appalachian Basin appear to be deeply weathered enough to have formed rare earth-enriched laterite deposits. A rare earth-enriched regolith that contains roughly 2900 ppm of rare earths, weathered from mildly peralkaline rocks in the Robertson River Batholith, a granitic intrusive in central Virginia. These rare earth laterites are derived from enriched source material (from the granite batholith in this case), created by sustained chemical weathering conditions (Long et al., 2017).

Detailed analyses of thorium to potassium (Th/K) ratios is an indicator of the formation of deep weathering or lateritic deposits especially when Th/K > 17. This ratio number, and even greater, is indicative of heavy leaching and K depletion. In addition, for heavily leached laterite field samples, analyses indicate that the titanium to aluminum ratio (Ti/Al) can be used as a good indication of erosion rate, because as the rate of granitic erosion increases, the Ti/Al ratio increases proportionately. Some early work involving Ti/Al ratios, under the U.S. Department of Energy's rare earth research program involving the Office of Fossil Energy (FE) and the National Energy Technology Laboratory (NETL), has been reported by Bank et al. (2016), including correlations with rare earth content, by depth, involving Appalachian coal sequences.

These data strongly suggest that rare earths were not introduced as dissolved, soluble chemical species, but were probably transported as intact insoluble and non-reactive rare earth-bearing mineral grains. Therefore, considering an Alleghenian granitic source or provenance for nearby coal basin sediments, it might be expected that weathering of those granites would cause preferential concentration of rare earth-bearing minerals in sediments transported into coal-forming basins.

In addition, chemical leaching could be expected to have created regionally minor deposits similar to the ion-adsorbed clay deposits in China, where there is a demonstrated high Th/K ratio, but with no associated correlation of Ti/Al ratio as for the mineral transport scenario. Example analyses involving the Appalachian coal measures have been offered by Bank et al. (2016).

2.3.3. Review of Rare Earth Minerals in the Coal Measures

With respect to establishing the feasibility of recovering rare earths from U.S. coal and coal byproducts, the importance of understanding the nature and abundance of the rare earth-bearing minerals in the U.S. coal measures cannot be understated.

The nature of the rare earth-bearing minerals is important as physical properties (grain size and density as examples) will influence the suitability of mineral processing technologies for their concentration, and chemical constitution (mineral composition) will dictate the requirements for their extractive metallurgy.

Overall abundance (i.e. assay or ore grade) of the rare earth-bearing minerals is also of the highest importance, as this parameter dominates the economics of rare earth production. Simply put: higher ore grades mean lower production costs.

Rare earth-bearing minerals in coal may be present in both primary and authigenic forms, and REEs may also be bound to clay surfaces (Schatzel and Stewart, 2003). Work by Finkleman (1980) demonstrated rare earth occurrences as phosphates in coal (monazite and xenotime).

Finkleman later (1988) noted the "exceedingly fine-grained" nature of trace element-containing minerals associated with bituminous coal, and had previously (Finkleman, 1979) found an accessory mineral grain size of about 5 microns.

Similarly, Vassilev and Vassileva (1996) commented that the grain sizes of accessory minerals in coal (from 35 locations including 8 in the U.S.), were generally less than 1 micron. Their work also presents grain sizes found for several accessory minerals, with the sizes found for monazite being in the range of one micron and less.

At the outset of the FE/NETL Rare Earths Program, the literature had suggested that very fine grain sizes of rare earth-bearing minerals were to be found in U.S. coal. This, along with the low rare earth concentrations typical of U.S. coal did not bode well for the establishment of an economic feasibility of recovering rare earths from these materials, because very fine grinding would be required to liberate very small uneconomic quantities of rare earth-bearing minerals.

However, early work involving both literature data and results, the latter from the FE/NETL Rare Earths Program, suggested that the rock associated with coal beds in the U.S. measures can contain anomalously high rare earth concentrations. An early finding from the research under the Rare Earths Program was that

Rare earths tend to concentrate in higher ash content sediments associated with coal seams (U.S. Department of Energy, 2017). Data from the USGS and others were available in the literature that reported stratigraphic variations of rare earth content through coal and associated rock strata. This work involved stratigraphic plots of both rare earth content and ash content through coal-bearing zones. An example plot appears in Figure 1. This result involved the Lower Kittanning coal bed in Clarion County, Pennsylvania. Two items are apparent:

1. The rare earth concentration in the rock is significantly higher than in the coal.
2. The rare earth concentration of the Lower Kittanning underclay was sufficiently high to merit further investigation of it and other Allegheny age underclays.

Subsequent results of this work, involving both the in-house FE/NETL sampling and analysis program and other work carried out by contractors has found even higher rare earth concentrations in the Lower Kittanning underclay in the Northern Appalachian region. This led to further investigations of underclays, roof rocks, and partings associated with coal beds of that geologic age in the Northern Appalachian Region.

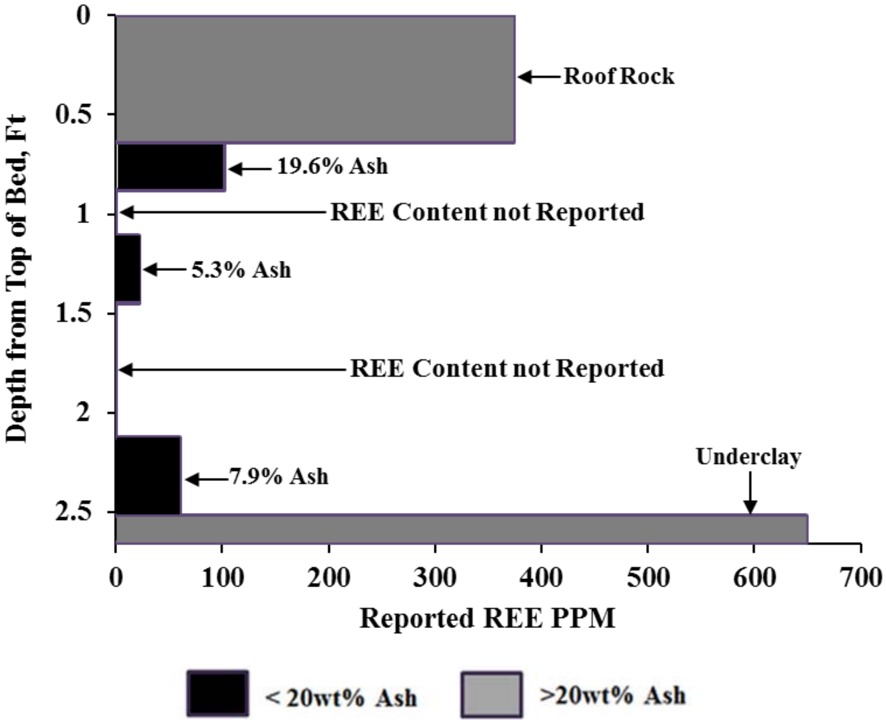


Figure 1: Stratigraphic Distribution of Rare Earth Content, Lower Kittanning Bed, Clarion County, Pennsylvania. Data from Schatzel and Stewart (2003).

The trend where the rock zones associated with coal beds have significantly higher rare earth concentrations is not limited to the Appalachian coal field. More discussion involving the highest rare earth assays appear later in this report.

The rocks associated with coal measures, where anomalous high rare earth concentrations have been found, include roof rock, partings, binders, and underclays. The first three are typically byproducts of coal production, being lost as spoil in the case of surface mining, or where they are included with a run-of-mine product to be washed, rejected to coarse refuse or tailings by the preparation process. The last of these can be produced as a separate product, notably in a surface mine operation involving relatively flat strata.

In addition to finding high rare earth concentrations, in-house work at NETL involving scanning electron microscopy (SEM) techniques applied to these coal-associated rocks, has produced some surprising results: rare earth-bearing minerals were found to have significantly larger grain sizes compared with those suggested by the previously cited literature. A range of grain sizes of rare earth-bearing minerals found in these rocks, is shown in Figures 2 through 7. ***These images indicate significantly larger grain sizes than would have been expected based on the previous investigations cited earlier in this section***. In fact, some of these grain sizes appear to approach mineral grains found in commercial rare earth ores (tens of microns). While it is not clear how representative these grain sizes are in the rocks examined, this discovery merits further examination of the rocks where these grain sizes have been found and their response to mineral processing separations.

Early in the FE/NETL Rare Earths Program, the literature had suggested that the coal and coal byproducts might present significant challenges to any application of mineral processing technology in an effort to improve the rare earth concentrations of coal and coal byproducts (low concentrations and small mineral grain sizes). However, subsequent work on coal byproducts through the sampling and analysis efforts by DOE/NETL and contractors, including in-house microscopy work by NETL, has discovered significantly higher rare earth concentrations in coal-bearing strata in the U.S. (approaching 1,000 ppm), and mineral grain sizes that are significantly larger from the mineral processing standpoint.

Previous mineral processing work in the Program had attempted laboratory mineral processing separations on coal and coal byproducts (Akdogan and Ghosh, 2014, Honaker et al., 2014, Soundarrajan, 2014, Miscovic, 2014), but at much coarser particle size distributions than those that would be expected to liberate even the largest grain sizes found in Figures 2 through 7. Those tests used laboratory flotation, table, magnetic separation, and electrostatic separation systems. However, particle topsizes used for those tests ranged from 150 to 1,000 microns. Figures 2 through 7 do not indicate the possibility of sufficient rare earth-bearing mineral liberation at those topsizes.

These early physical separation and flotation tests achieved, at best, modest rare earth assay upgrades. This preliminary work typically focused on single step processes. Producing a concentrate with a significant rare earth content will require the determination of optimum particle sizes for rare earth mineral liberation, and more focus on multiple-step laboratory tests (for examples, see flowsheets found in Section 3.4.).

The larger grain sizes seen here, along with the higher rare earth concentrations found in subsequent sampling and analysis work, will justify further work of this nature.

As will be discussed in the following Sections of this Report, rare earth concentrations have been found in the U.S. coal measures of sufficient value to cover the operating cost of the application of currently available mineral processing technologies for their beneficiation. Also to be discussed, successful application as such can significantly reduce the required throughput of the most expensive step, chemical extracting the rare earths from the mineral concentrate.

In order to assess the compatibility of any of the potential rare earth resources identified under the Program, with existing technologies, mineral processing research will be required. For identification of near-term production options, this research will also need to be oriented toward flowsheets achievable with:

1. ***Repurposed plant equipment, and***
2. ***Plant equipment available for use under a tolling arrangement.***

The rare earth minerals found in the coal measures thus far (examples being phosphates such as monazite and xenotime) are not unlike those that have been used to commercially produce rare earths.

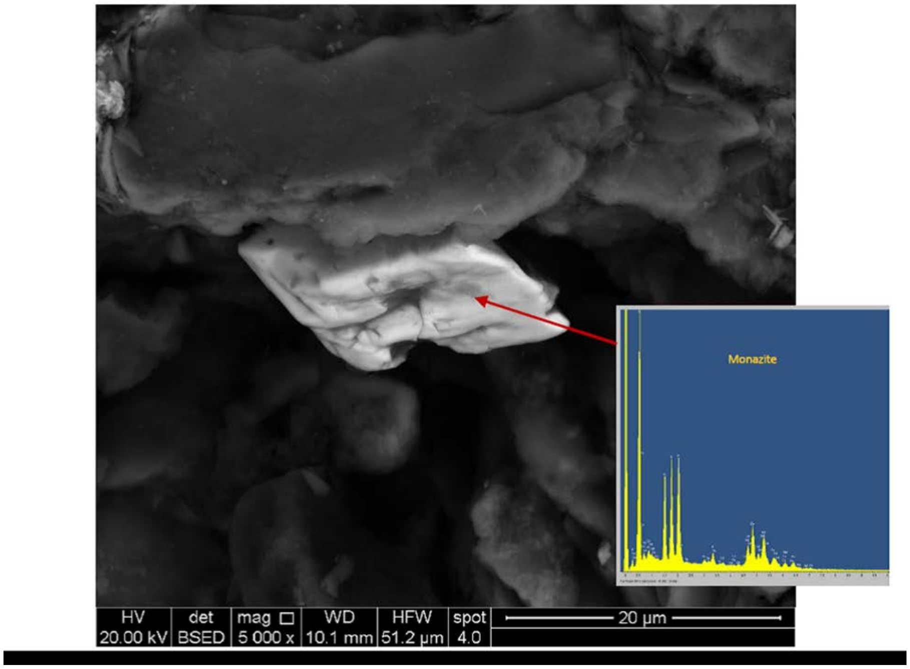


Figure 2: Rare Earth-Bearing Phosphate (Monazite) Grain in Appalachian Coal-Associated Rock (NETL data)

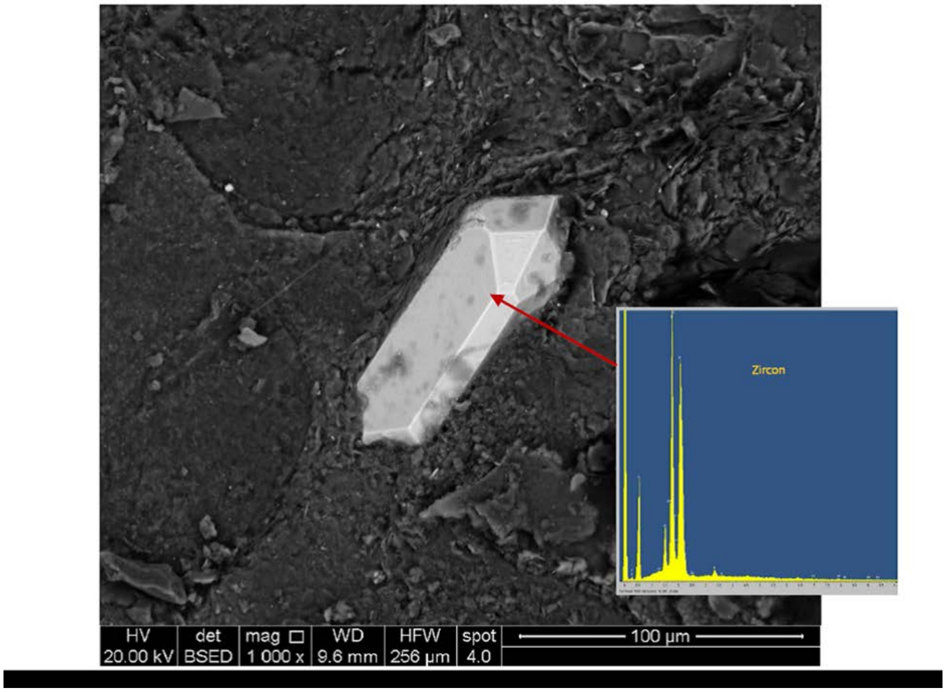


Figure 3: Rare Earth-Bearing Silicate (Zircon) Grain in Appalachian Coal-Associated Rock (NETL data)

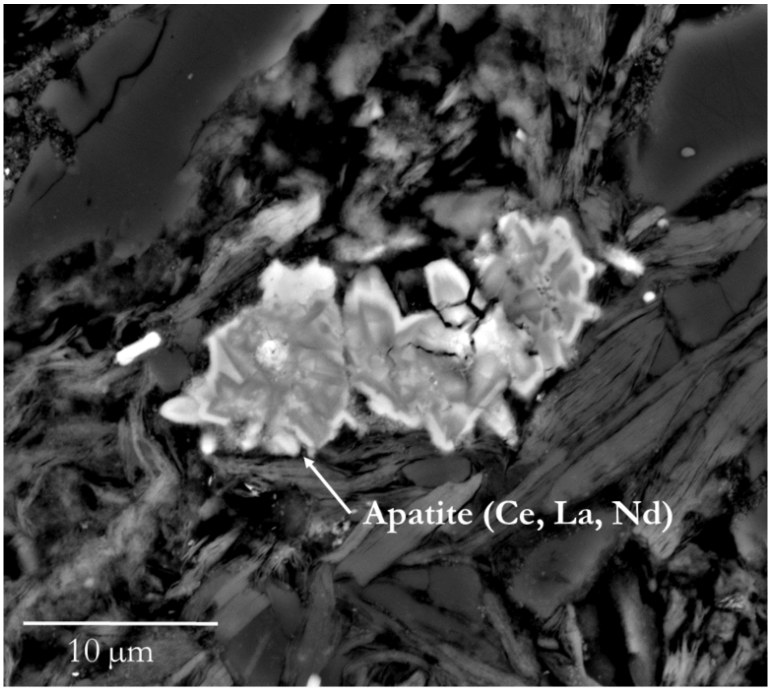


Figure 4: Rare Earth-Bearing Phosphate (Apatite) Grain in Appalachian Coal-Associated Rock (NETL data)

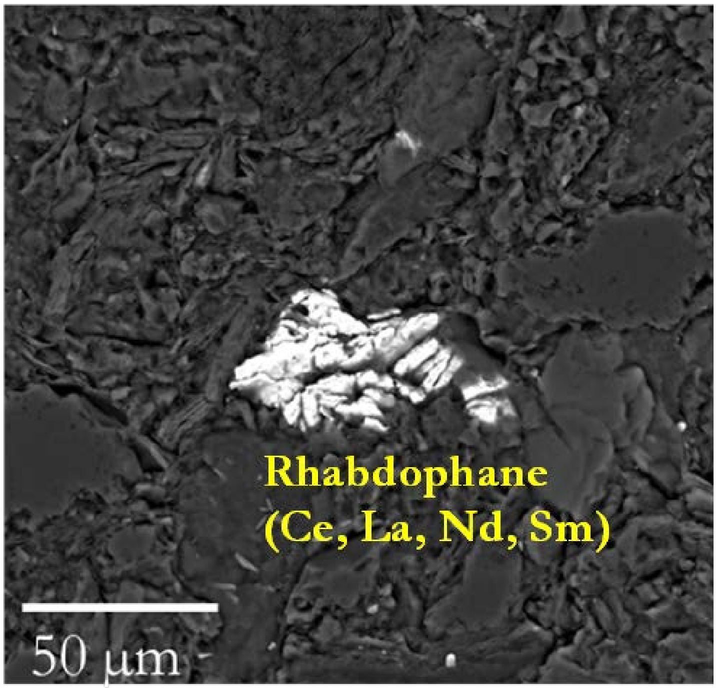


Figure 5: Rare Earth-Bearing Phosphate (Rhabdophane) Grain(s) in Appalachian Coal-Associated Rock (NETL data)

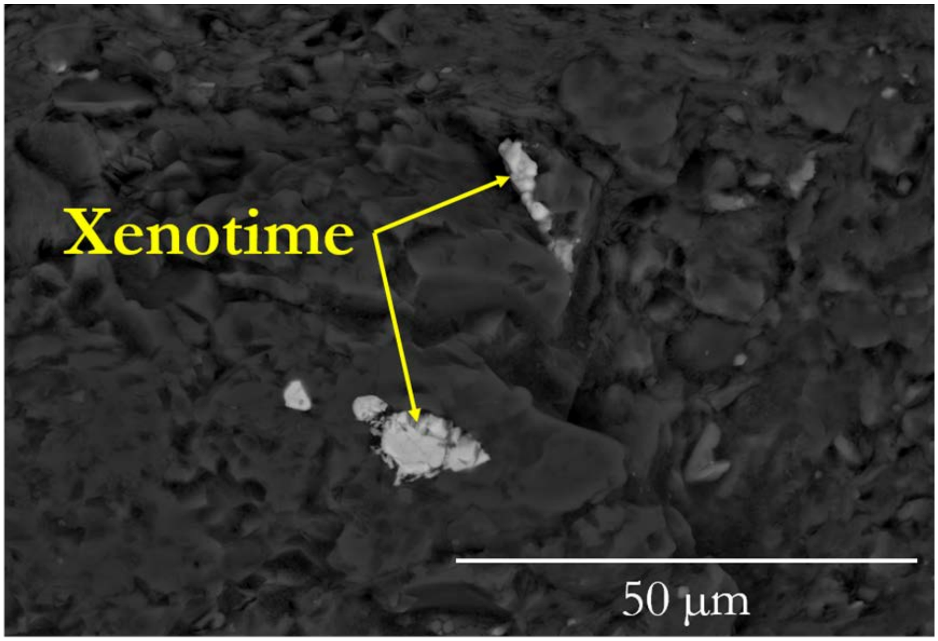


Figure 6: Rare Earth-Bearing Phosphate (Xenotime) Grain in Appalachian Coal-Associated Rock (NETL data)

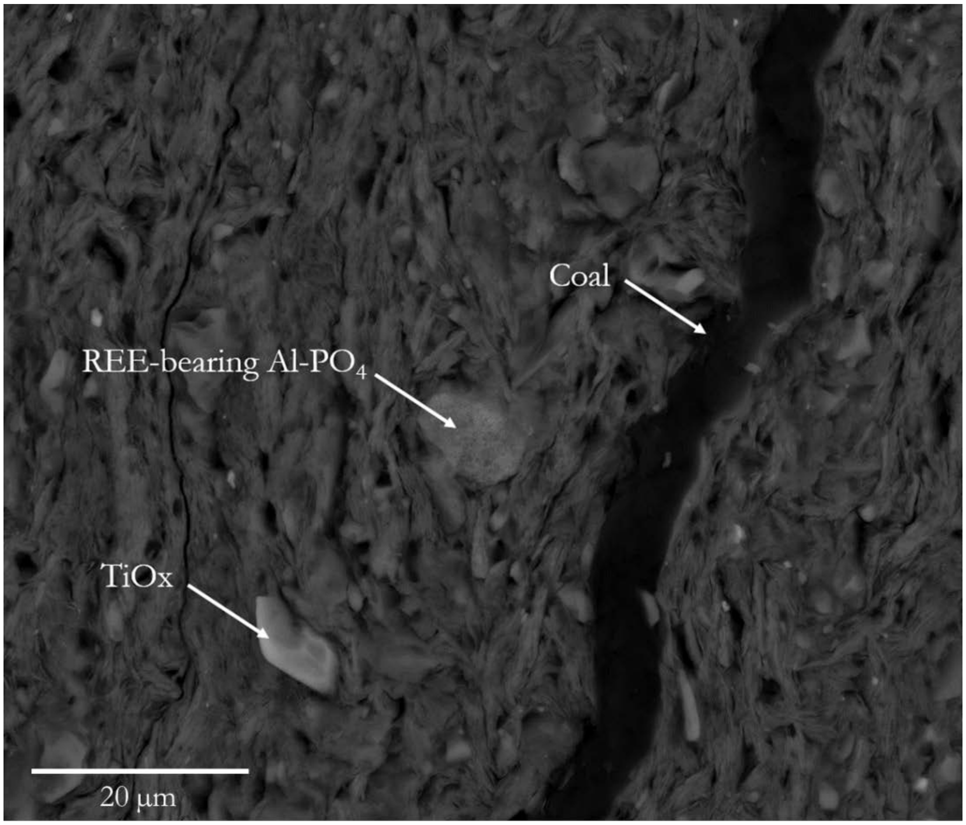


Figure 7: Rare Earth-Bearing Phosphate Grain in Appalachian Coal-Associated Rock (NETL data)

3. Rare Earth Production

3.1. Mineral Processing and Extractive Metallurgy Basics

Broadly, steps involved in the value chain for the production of useful rare earth materials from ores can require the following:

(1) liberation of rare earth minerals or particles from the host material,
(2) enrichment of the rare earth minerals to higher concentrations,
(3) separation or partitioning of rare earths into individual elements or groups of elements, and
(4) reduction of rare earth compounds to pure metals or alloys.

Process steps used to produce salable rare earth-bearing commodities from an ore fall under two disciplines: Mineral Processing and Extractive Metallurgy. Useful definitions for these are found in the 2019 SME Mineral Processing and Extractive Metallurgy Handbook (Das and Young, 2019):

- Mineral Processing "is the field of engineering concerned with the separation of valuable minerals from ores into concentrates usually without chemical change"
- Extractive Metallurgy "is the field of engineering concerned with the extraction of valuable metals from ores or concentrates usually with chemical change"

Extractive Metallurgy involves inducing chemical changes to ores and then recovering the metal value. Within Extractive Metallurgy (Das and Young, 2019):

- Hydrometallurgy is used in the presence of liquid water, the primary property being exploited to accomplish extraction is solubility.
- Pyrometallurgy is used in the absence of liquid water, the primary property being exploited to accomplish phase extraction is phase change.

Mineral Processing systems involve technologies that reduce rock particle size (crushing and grinding), separate particles according to particle size and mineral properties, and can also include dewatering and drying components. With respect to conventional rare earth element production, a mineral processing system is fed ore and produces a mineral concentrate that is enriched in rare earth content.

Mineral processing components that separate particles according to mineral properties include both physical separation- and flotation technologies. Broken solids produced from ore deposits vary in mineral composition and particle size, and in turn will vary in mineral properties such as specific gravity, magnetic properties, electrical properties, and hydrophobicity. As such, these are distributive properties. A basic mathematical relationship describing the summation of particle property increments and their response to a physical separation stimulus appears in Rozelle et al. (2018), which also includes elements of the historical evolution of some of these technologies as applied to coal production.

Mineral processing is used commercially in rare earth production. Some physical properties of rare earth minerals, along with those of gangue minerals found in the coal measures, appear in Table 1. As a rule (excepting pyrite), the specific gravities of the rare earth-bearing minerals significantly exceed those of the gangue minerals. There are also differences in magnetic properties.

Physical separations technologies separate particles by size, specific gravity, magnetic properties and electrical properties. Examples are as follows:

Dense Medium Systems include static bath vessels and cyclones (separate by specific gravity)

Water Only Systems include **jigs, concentrating tables, spirals, and cyclones** (separate by specific gravity and possibly particle size).

Magnetic Separators (separate by magnetic properties)

Electrostatic Separators, also referred to as Tribo-Electric Separators (separate by electrical properties)

Table 1: Mineral Processing Properties of Example Target and Gangue Minerals found in the U.S. Coal Measures

Mineral	Specific Gravity	Magnetic Property	Electrostatic Property	Naturally Hydrophobic
Target Minerals				
Bastnaesite	5.0	Paramagnetic	Insulator	No
Monazite	4.9-5.5	Paramagnetic	Insulator	No
Xenotime	4.4- 5.1	Paramagnetic	Insulator	No
Zircon	4.7	Diamagnetic	Insulator	No
Gangue Minerals				
Kaolinite	2.6	Diamagnetic	Insulator	No
Muscovite	2.8-3.0	Diamagnetic	Insulator	No
Pyrite	5.0	Diamagnetic	Conductor	Weak
Quartz	2.7	Diamagnetic	Insulator	No

In addition to physical separation processes, **froth flotation** is also a mineral processing technology. Froth flotation systems separate by particle hydrophobicity, a surface property. Mineral-specific collectors may be added to render non-hydrophobic minerals hydrophobic.

Where minerals to be separated are present in the rock as fine grains, liberation is required. Where the particle size of the rock is coarser than the size of the mineral grains, particle size reduction, or comminution is required. Mineral liberation has been defined as “the extent to which the particles are made of discrete mineral grains” (Bradshaw et al., 2019).

Comminution in mineral processing and extractive metallurgy reduces the particle size of an ore. In the case of mineral processing systems, the resultant particle size distribution should exhibit a degree of mineral liberation that allows for particles to be separated according to mineral properties, as discussed in the preceding Section.

Crushing systems found in mineral processing plants include jaw, gyratory, cone and roll crushers, as well as impactors. Grinding systems are sometimes classified by mill speed, including high medium and low speed mills. The last of these categories includes semi-autogenous grinding (SAG) mills, ball mills, and rod mills.

Hydrometallurgy, within the context of rare earth production, involves the conversion of rare earth compounds from insoluble mineral phases such as phosphates and fluorocarbonates to soluble phases. Other hydrometallurgy process steps can include those used to remove gangue elements from leach solutions, and separation of the mixed rare earth product to produce individual rare earth element compounds.

The requirements for converting rare earth minerals into soluble species are governed by mineral specific thermodynamics. While reacting with sulfuric acid at elevated temperatures, followed by leaching (acid bake/water leach) is a common practice for solubilizing rare earth minerals, a range of other options is reviewed by Verbaan et al. (2014), covering applications envisioned for projects under development. These applications include leaching with HCl, HNO_3, and H_2SO_4, and H_2SO_4 acid baking. Caustic (NaOH) digestion of monazite has also been a commercial practice for solubilizing rare earths, converting the phosphates to hydroxides (Krishnamurthy and Gupta, 2016).

Once solubilized and present in the leach solution, precipitation and solid-liquid separations may be used to remove gangue elements from the leach solution.

For production of a solid, mixed rare earth filter cake, an oxalate or carbonate may be added to the purified leach solution to precipitate rare earth oxalates or carbonates. This, like precipitation of impurities from the leach solution, will also involve solid-liquid separation steps, where thickener and filter press equipment may be employed.

With respect to separating rare earth elements from each other, solvent extraction has been referred to as "generally accepted as the most appropriate commercial technology for separating rare earths due to the need to be able to handle larger volumes of dilute pregnant liquors" (Xie, 2014). The application of solvent extraction to rare earth recovery, as a commercial practice, dates back to its use in Canada in the 1960's (Goode, 2013).

3.2. Rare Earth Reduction to Metal

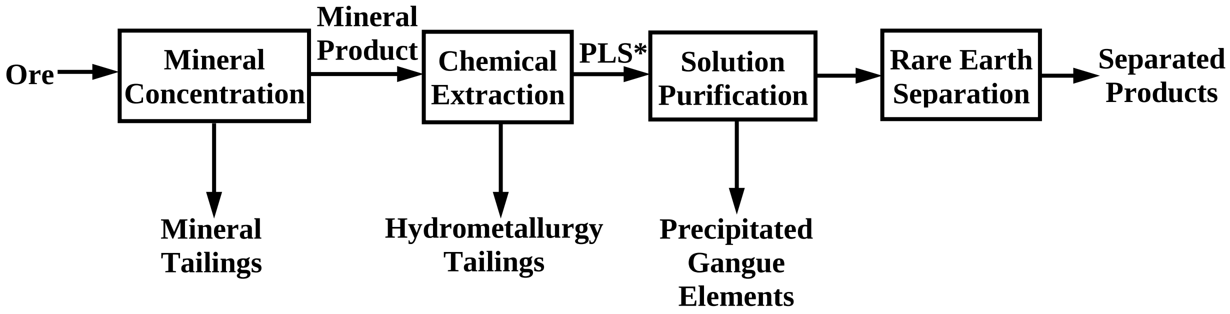
The production of metal from a rare earth compound is typically a pyrometallurgical operation, and involves reduction. As is the case with hydrometallurgy, it is governed by thermodynamics, which dictate process conditions and reductant choices. The choice of reductant is a matter of free energies of formation associated with reactants and products, and influenced by the type of rare earth compound (oxide, chloride, fluoride) to be reduced (Krishnamurthy and Gupta, 2016).

Reactor conditions used to produce metals from rare earth compounds can involve thermophysical and thermochemical properties relevant to solid, liquid, and vapor phases, these in turn involving the reactants and products associated with both reductant and the compounds of fourteen different rare earth elements. Reductants themselves can be other metals (i.e. the process is a metallothermic reduction). These include calcium, lithium, potassium and sodium (Krishnamurthy and Gupta, 2016).

Given the complexity involved with the possible rare earth feedstock compounds and their reductants, a detailed discussion of rare earth reduction technologies is outside the scope of this report.

3.3. Generic Rare Earth Process Steps

A generic set of process steps for the production of separated rare earth compounds from an ore is shown in Figure 8. The ore is fed to a concentrator (mineral processing system) that produces a mineral concentrate to be fed to the chemical extraction step. As stated by Verbaan et al. (2014), "Most processing costs are incurred in the hydrometallurgical plant, where rare earths are chemically extracted using an acid or alkaline reagent or a combination thereof. Operating costs are usually directly related to material throughput, therefore a reduction in mass recovery (or equivalent increase in concentrate grade), even at the expense of some rare earth recovery, is usually worth considering." The mineral processing system represents a lower cost option for removing some gangue elements ahead of the more expensive chemical extraction step.



***PLS = Pregnant Leach Solution**

Chemical Extraction is "most of the cost"- Verbaan et al., 2014

Figure 8: Generic Rare Earth Value Chain, Adapted from Verbaan et al. (2014)

The degree to which mineral processing can concentrate rare earth elements will depend on mineralogy considerations and how these mineral will respond to grinding and the separation stimuli associated with mineral processing separations. However, given the lower costs associated with a mineral processing system, as well as the potential for reduced environmental costs associated with mineral processing tailings (compared with hydrometallurgy tailings), mineral processing research is justified. As stated by Hazen and Robertson in the 2019 SME Mineral Processing and Extractive Metallurgy Handbook, "***Exhaust the options for physical separation before accepting the result that you must treat the whole ore. A difficult physical separation is almost always cheaper than a chemical separation***."

The chemical extraction step chemically reacts the concentrate and leaches it into the pregnant leach solution, a hydrometallurgical process, with further hydrometallurgical processing including impurity (gangue element) removal from the solution and separation of individual rare earth compounds.

The distinctions between a feedstock derived from the U.S. coal measures and a conventional rare ore, in the flowsheet shown in Figure 8, are diminished as the process moves from left to right. Coal byproducts can be expected to differ in mineralogy and exhibit lower assays as ores (left side of flowsheet). If they can be concentrated through mineral processing, the concentrates will differ from those of conventional ores ("mineral product" in the flowsheet). Once the mineral concentrate has been leached and the solution is purified, that product will need to have similar characteristics to those required for the separation step (i.e. solvent extraction or equivalent). Any consideration of differences between U.S. coal byproducts and conventional rare earth ores in the value chain must first begin with their mineralogical differences from mineral processing and extractive metallurgy standpoints, and include the locations in the value chain in Figure 8 where they would be suitable as inputs. This in turn must be preceded by a discussion of commercial rare earth mineral processing and extractive metallurgy practices.

3.4. Commercial Rare earth Ore Concentration Processes

The U.S. Geological Survey (USGS) has divided global rare earth production into three historical periods (USGS, 2002). The first, through the mid-1950's is called the "Monazite-Placer Era", where rare earth production was gained from monazite-bearing placers and veins. The second period is the ""Mountain Pass Era" beginning in the mid-1950's, with the Mountain Pass operation in California grew to dominate rare earth production. The third period is the "Chinese Era", which continues today, dominated by production from the Bayan Obo operation in Inner Mongolia.

The Monazite-placer Era in the U.S. began with initial placer production in 1886 (Overstreet et al., 1959, Aplan, 1989). With respect to monazite recovery from placer sand deposits, Aplan (1989) presented multiple flowsheets. Plants described in that work used gravity concentration (jigs, wet tables, and air tables), magnetic separation, and electrostatic separation. Reported feed and product topsizes were in the millimeter size range. A generalized flowsheet for a placer monazite concentration operation appears in Figure 9. This type of system takes advantage of key differences in physical properties among the minerals to be separated, including density and magnetic and electrical properties.

The placer and beach sand operations discussed in the Aplan work produced multiple products. In addition to monazite, these plants produced columbite-euxenite, garnet, ilmenite, leucoxene, and zircon. ***An operation that produces a rare earth concentrate as one of several products may be less vulnerable to reductions in market prices for the material as compared with an operation that produces only the concentrate.***

Aplan (1989) also presented a discussion of the system at Climax, Colorado, at the time operated by AMAX. The plant was installed to recover monazite and other products from molybdenite flotation tailings. The topsize fed to the byproducts recovery plant was in the range of -1 mm, and cassiterite, monazite, and wolframite were recovered. Separation units included spirals, flotation, tables, and magnetic separations.

In the U.S., the mineral processing requirements changes as the Monazite Placer Era transitioned to the Mountain Pass Era. An ore from a hard rock mine, such as Mountain Pass, will be delivered to the concentrator at a larger particle size than that fed through a placer operation, dictating comminution. The topsize required for a separation circuit will be dictated by that required to yield acceptable liberation of the mineral to be separated. This in turn will be influenced by the grain size of the mineral in the deposit.

Bastnaesite grain sizes reported for the Mountain Pass deposits are in the 87-300 micron range (Castor, 2008). Liberation in this case will require grinding, and as seen in that presented by Aplan (1989) for bastnaesite concentration at Mountain Pass, the flowsheet includes grinding of the ore to a 150 micron topsize followed by multiple stage (rougher/cleaner/scavenger) flotation. This is shown in Figure 10.

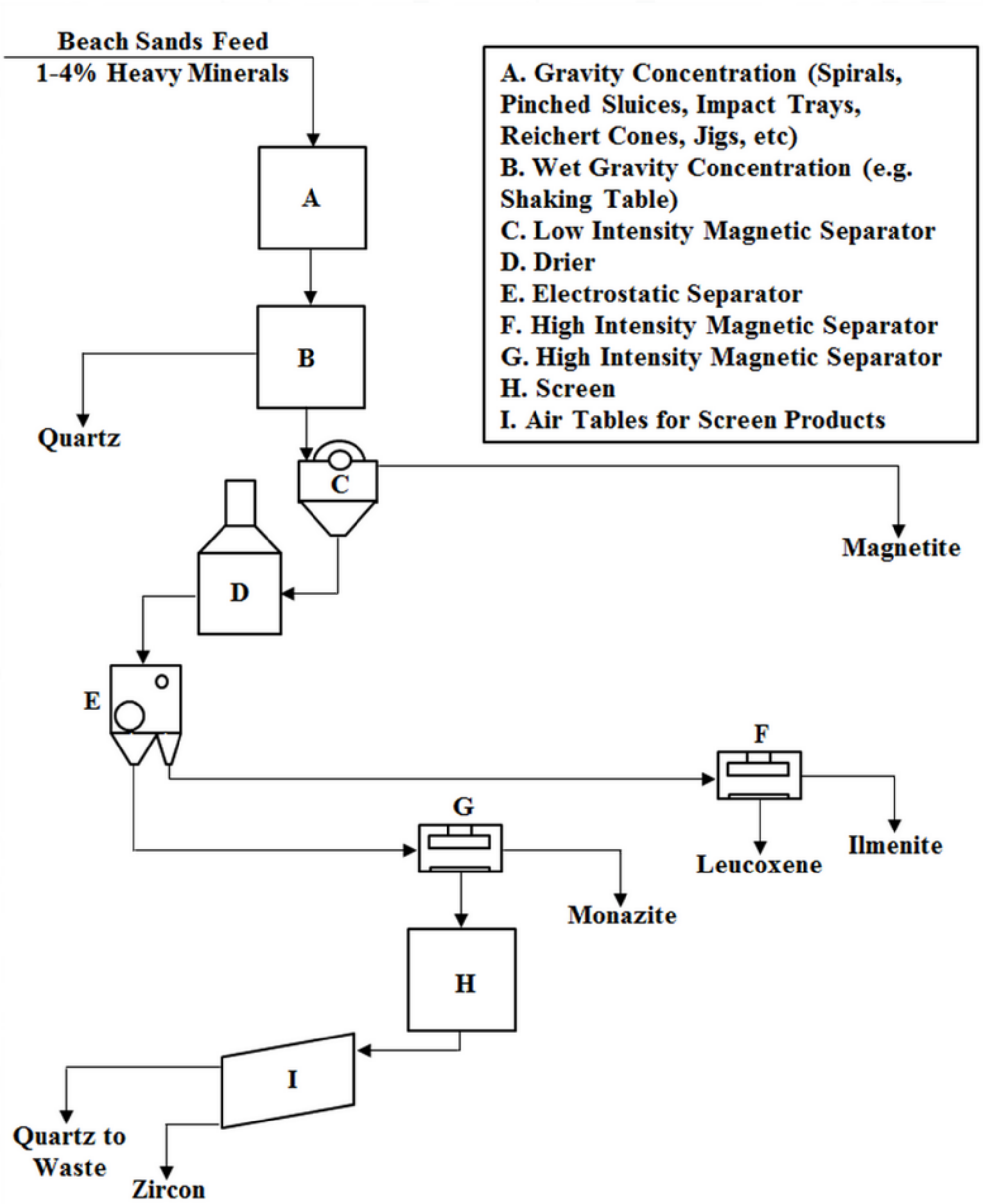


Figure 9: Generalized Placer Processing Flowsheet, from Aplan (1989)

In addition to grinding and flotation, the flowsheet includes steam addition (heating) to the conditioning step ahead of the flotation system. A discussion of the effect of temperature on flotation considerations, involving the Mountain Pass ore, appears elsewhere (Jordens et al., 2013).

The transition from the Mountain Pass Era to the Chinese Era has been influenced by the development of rare earth production at Bayan Obo, which in turn owes its roots to the discovery of an iron ore deposit there by Professor Ding Daoheng in 1927. In addition to an average iron ore grade of 35 wt% Fe, the deposit (Li and Yang, 2014) also contains niobium (average grade 0.13 wt%) and rare earths (average grade 6 wt%). The principal rare earth ores present are bastnaesite with lesser quantities of monazite, and the iron ores include both magnetite and hematite (Li and Yang, 2014). The grain sizes of the rare earth minerals in the deposit is in the 74 micron to 10 micron size range, with 70-80 wt% in the range of 40 microns and finer. This grain size is reflected in the feed size to the system (90-95 wt% passing 74 microns). A set of flowsheets yielding multiple products is presented in Figures 11 and 12.

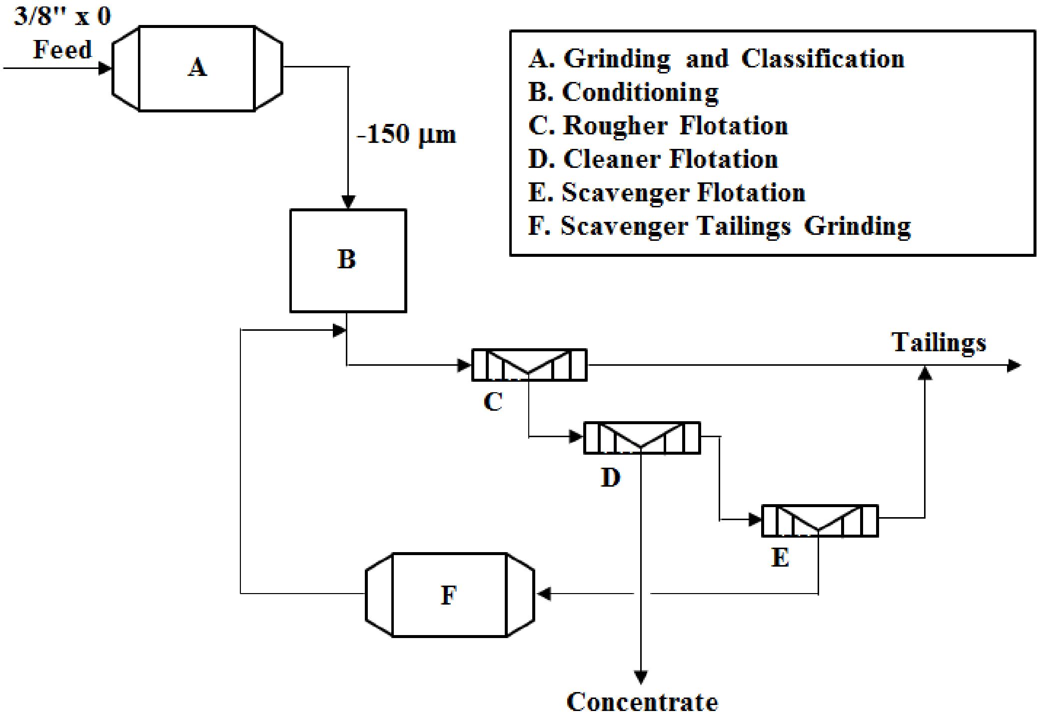


Figure 10: Mountain Pass Concentrator Flowsheet, from Aplan (1989)

The Mt. Weld operation in Australia produces a concentrate from a monazite-bearing ore in Australia. Ore is first crushed to a topsize of 0.8”, and then fed to a grinding system with an output topsize of 38 microns (Lynas Corporation, 2015), followed by rougher/cleaner/scavenger flotation to produce the concentrate.

The flowsheets shown in Figures 9 through 12 have the same requirement, common for mineral processing systems: in order to take advantage of differences in physical properties among minerals, the mineral mixture to be fed to the system must be at a particle size where the minerals to be separated are liberated. This is in turn dictated by the grain sizes of the minerals in the host rock. In the case of monazite recovery from a placer deposit, individual grains of monazite (and other heavy minerals) may be present, removing any crushing and grinding requirement. In the case of hard rock deposits, such as at Mountain Pass or Bayan Obo, there is a significant difference between the size consist of the run-of-mine material, expected to range in topsize to several inches, and the grain size of the rare earth minerals present, which in the cases of these operations have been reported to largely exist in the range of tens of microns.

Significantly, none of these flowsheets presented uses a single separation step. They use combinations individual separation units. Even where flotation is the only technology used for a separation, a single step is not used. The Mountain Pass, Bayan Obo and Mt. Weld flowsheets presented here use multiple recirculating flotation units, in rougher/cleaner/scavenger circuits.

Also of significance is the degree of enrichment achieved by the Mountain Pass and Bayan Obo systems. These are presented in Table 2. The concentrator designs for both operations have production capabilities to concentrate feed in the range of 10 Wt% rare earths reported as oxides (REO) to the range of 60 Wt% REO.

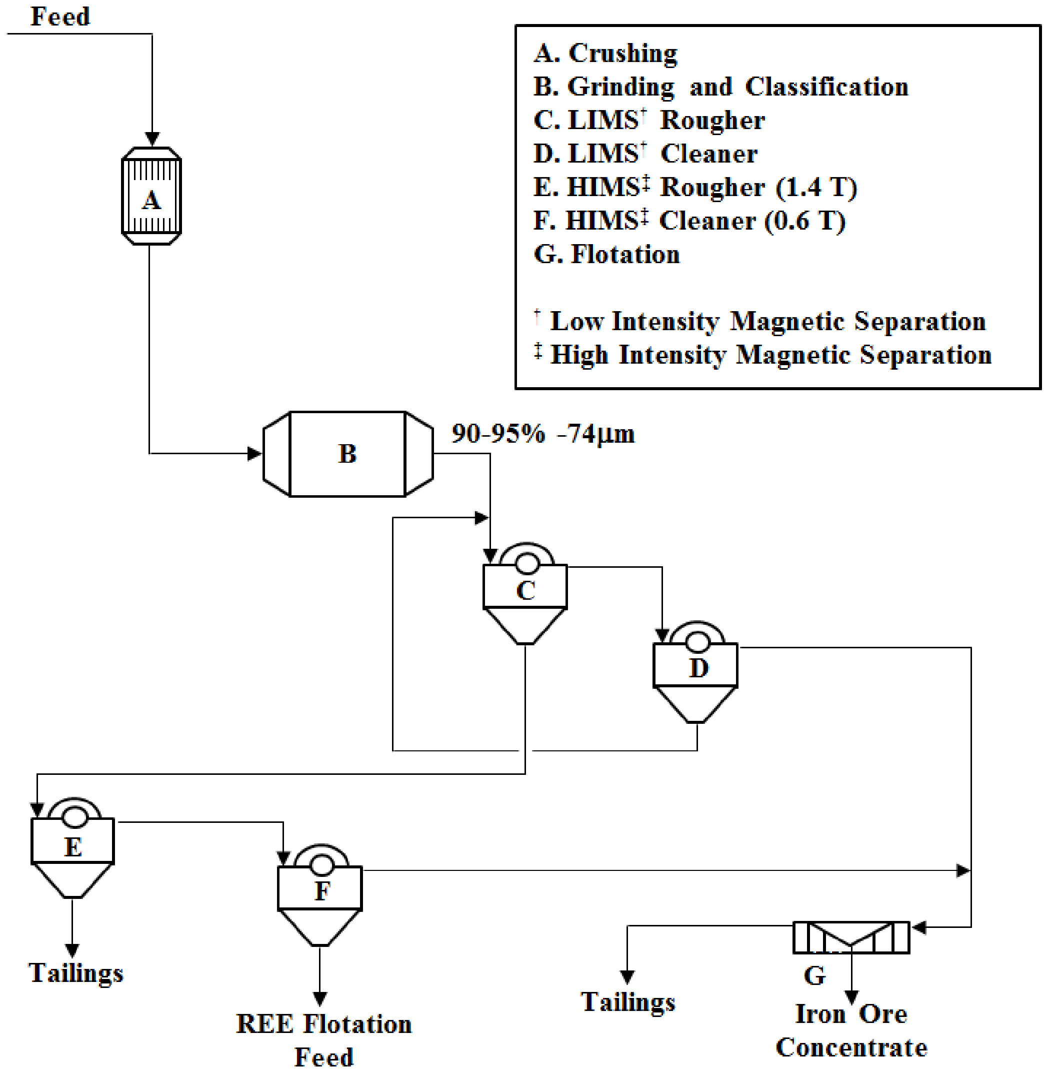


Figure 11: Bayan Obo Iron Ore Concentration Flowsheet from Li and Yang (2014)

3.5. Hydrometallurgy- Rare Earth Extraction

Unlike the application of mineral processing technologies to produce a mineral concentrate, the chemical extraction of rare earth ores, through hydrometallurgy, effects chemical changes to the feedstock. This requires the addition of chemical reagents to the ores, may require elevated temperatures to “crack” the rare earth-bearing minerals, and requires handling of solid, liquid and gaseous byproducts of the process.

As mentioned previously, the conditions and reagents required to convert rare earths in ores from insoluble minerals to soluble compounds are dictated by the thermodynamics involved. The feasibility of accomplishing the solubilization as such will be dictated by the process costs associated with the reaction (including reagents), as well as the costs of downstream purification of the leach solution, where gangue elements that have reported to the leach solution must be removed. The latter consideration also argues for maximizing the rare earth grade of the feed to the extraction step, in turn justifying the use of mineral processing ahead of the hydrometallurgy process.

Table 2: Feed and Concentrate Grades for the Mountain Pass and Bayan Obo Concentration Plants

Plant	Feed Assay	Concentrate Assay
Mountain Pass	7.7-8.4 Wt% REO	58.0-63 Wt% REO
Bayan Obo (Rare Earth Flotation Circuit)	9.8-12 Wt % REO	>60 Wt% REO† >30 Wt% REO‡

†Flotation Cleaner 1 Product

‡Flotation Cleaner 2 Tailings

Multiple acid and alkaline reagents have been the subject of commercial use for the extraction of rare earths, and more have been examined in the laboratory. A good review of both appears in Krishnamurthy and Gupta (2016).

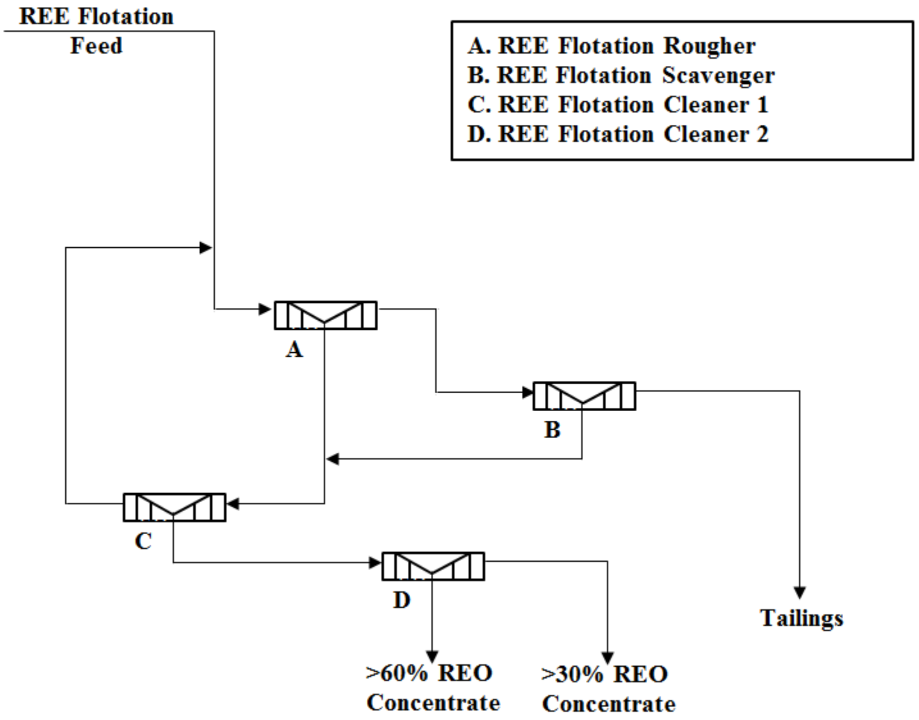


Figure 12: Bayan Obo Rare Earth Concentration Flowsheet, from Li and Yang (2014).

Rather than reviewing all of the laboratory work on possible hydrometallurgical reagents and process conditions available, existing hydrometallurgy practice that may be applicable to coal byproducts will be presented within the context of commercial practices.

Fluorocarbonates:

Bastnaesite is a rare earth fluorocarbonate mineral, and acid leaching can be complicated by the propensities for formation of insoluble rare earth fluorides (Goode, 2019). One previous flowsheet (pre-2010) at Mountain Pass included roasting the mineral concentrate at 1200 F to decompose bastnasite, oxidize cerium, and volatilize the resultant fluorine species. The calcine was then leached with dilute HCl to dissolve rare earths, excepting cerium which had been oxidized to Ce^{+4}. Following the 2010 restart of operations, the extraction system used leaching with concentrated HCl, with the rare earth fluoride reaction products in the leach residue being reacted with NaOH and re-leached to the pregnant leach solution (Goode, 2019).

The mineral concentrate produced at the Bayan Obo operation in Inner Mongolia contains both monazite and bastnasite (Demol, 2019). Rare earths in both minerals can be converted to sulfates in the H_2SO_4 acid baking process (Goode, 2019). The mineral concentrate produced at Bayan Obo is extracted using this process at temperatures exceeding 570 F, followed by water leaching of the resultant solids.

Phosphates:

As discussed above, the H_2SO_4 acid baking process, followed by leaching, is used for rare earth extraction of both bastnasite and monazite at the Bayan Obo operation. A monazite concentrate is produced at the Mt. Weld mine in Australia, and is currently processed at a plant in Malaysia (Lynas, 2015), using an H_2SO_4 acid baking system (Goode, 2019).

Reaction with NaOH (caustic cracking) has also been used to break down monazite ores, converting phosphates to hydroxides which can then be leached. Example installations have included Indian Rare Earths Ltd at Alwaye, India, Rhone Poulence in La Rochelle, France and Freeport, Texas, Asian Rare Earths in Malaysia (Krishnamurthy and Gupta, 2016). Required conditions have included temperatures in the 280-300 F range, and very fine grinding of the feed ore, in the range of -37 microns. Caustic cracking processes can include fusion with pure alkali in the absence of water, or reaction at high temperatures with concentrated caustic solutions.

Oxides:

The Solikamsk Magnesium Works in Russia has used a carbochlorination process for the recovery of rare earths from a loparite concentrate (Goode, 2019), utilizing conditions that are not unlike those used for titanium or zirconium production, including distillation-like product recovery.

Broadly, processes discussed for these minerals are:

1. Rare earth fluorocarbonate calcining followed by HCl leaching.
2. HCl leaching of rare earth fluorocarbonate followed by cracking of the rare earth fluoride precipitate and leaching the cracked product.
3. H_2SO_4 Baking of rare earth phosphate or rare earth fluorocarbonate followed by leaching
4. Caustic cracking of rare earth phosphate
5. Carbochlorination of rare earth-bearing oxide.

In addition to these processes, HCl pressure leaching of alumina from clays is a process originally developed by the U.S. Bureau of Mines as an alternative source of smelter-grade alumina to imported bauxite products. Recent results that have included pressure leaching of aluminous shale materials have indicated significant recoveries of rare earths to the leach solution and further extraction processing (Boudreault et al., 2016).

3.6. Purification of Rare Earth Leach Solutions

The chemical extraction of rare earths from rock results in a leach solution that contains, in addition to rare earth values, gangue elements that have also been leached. The degree to which the leach solution contains species other than rare earths will be influenced by the hydrometallurgy conditions applied, as well as the thermodynamic response of gangue element-containing minerals to these conditions.

The feed to the rare earth separation step shown in Figure 8 can require low concentrations of gangue elements such as Al, Fe, Ca, Th, and sulfates (Goode, 2019). Where hydrometallurgical processing has entrained these species into the leach solution in objectionable quantities, their removal is required, especially where a process with inherent complications such as solvent extraction is used for the separation into individual rare earth compounds.

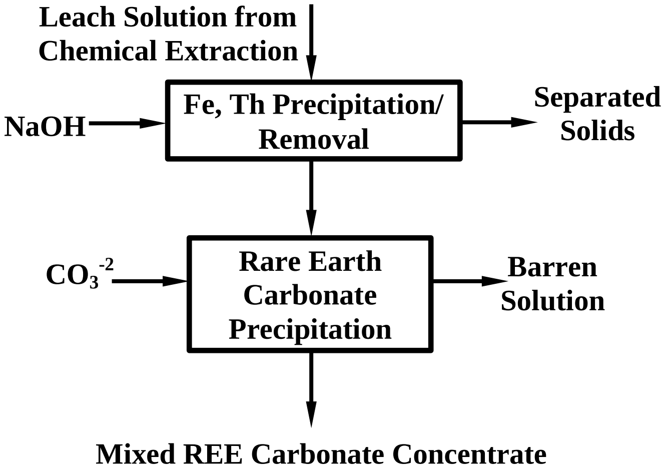


Figure 13: Simple Leach Solution Purification System, from Gagnon et al. (2015)

Process steps for removal of these impurities from the leach solution include precipitation and solid-liquid separations. A relatively simple example flowsheet, from a rare earths production project under development, appears in Figure 13.

Verbaan et al. (2014) have offered a generic flowsheet based on the evaluation of flowsheet selections for numerous rare earth production facilities at various stages of development. The system presented there includes a primary impurity removal step (example: pH adjustment to precipitate gangue elements), crude rare earth compound precipitation (example: as oxalates), re-leaching and secondary impurity removal (example" through precipitation), and purified rare earth recovery (example: as precipitated oxalate).

Each of the steps involved in impurity removal from the leach solution will also remove some rare earth compounds. Each step can also involve reagent additions, solid-liquid separation equipment, and their associated costs. These detrimental effects on rare earth recovery and capital and operating costs can be minimized through suppressing the presence of the impurities in the leach solution. This need has driven a significant amount of research into the elemental selectivity of hydrometallurgy processes for extracting rare earths from ore minerals, as well as leach solution processing. A detailed review of this body of research is outside the scope of this report.

However, one strategy for keeping gangue elements out of the leach solution is to minimize their relative presence in the mineral concentrate to be treated. This, in addition to its beneficial effect on the cost of chemical extraction, is an argument for the mineral processing step to produce a mineral concentrate ahead of the chemical extraction process.

Equipment required for solution purification as discussed here includes that for storage, handling, and feeding of reagents, reaction tanks, and solid-liquid separation components such as thickeners and filter presses.

3.7. Separation of a Mixed, Water Soluble Rare Earth Stream into Individual Compounds

The separation of a mixture of rare earth compounds into those of the individual elements is not a trivial task, but small differences in basicity, arising from a decrease in ionic radius across the series (lanthanum through lutetium), allow for process opportunities for separation These differences impact the relative solubilities of rare earth species, as well as properties involving ion hydrolysis and formation of complexes (Krishnamurthy and Gupta, 2016). These differences in turn allow for separation through processes such as fractional crystallization, fractional precipitation, ion exchange, and solvent extraction.

As has been mentioned, solvent extraction has been referred to as “generally accepted as the most appropriate commercial technology for separating rare earths”. The technology has been in commercial use for rare earth production since the 1960’s (Goode, 2013).

Solvent extraction (SX) involves an aqueous phase and a non-aqueous (such as an organic) phase (Krishnamurthy and Gupta, 2016). Additional reagents are added to promote transfer of ions between phases. Required equipment includes that required to mix and separate two liquid phases, for removal of the target species from the feed solution (the extraction step). An additional set of similar equipment can then strip the ions of interest from the system (the stripping step). A simple flowsheet for recovering a rare earth and scandium concentrates, from a barren uranium solution at an early pilot operation in Australia, is shown in Figure 14. In this system, the organic phase was a solution of di-(2-ethylhexyl) phosphoric acid (DEHPA) in kerosene.

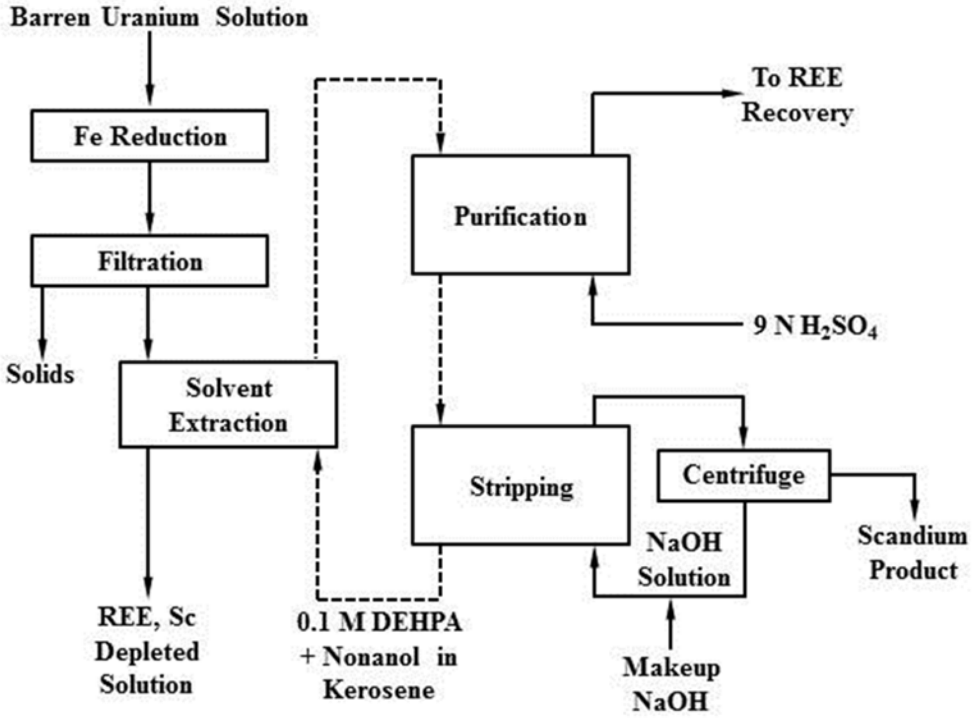


Figure 14: Early Flowsheet for Rare Earth Element (REE) Recovery from Barren Uranium Leach Solution, from Canning (1961)

This system was relatively simple, as it produced a mixed rare earth product and a scandium product. Solvent extraction (SX) for the production of multiple rare earth products, including those that produce the entire series separately, are considerably more complicated.

As stated by Goode (2019). “A typical SX-based production plant separating all the REE will include up to 1,500 mixer-settlers, extensive product precipitation, liquid–solid separation and washing systems, and calcining equipment. Such plants are expensive to build and operate.”

While the Molycorp operation dominated U.S. rare earths production for decades in the late 20th Century, Rhone-Poulenc (later Rhodia) operated a solvent extraction-based separation facility in Freeport, Texas until the company announced plans to close the facility in 1998 (Hedrick, 1999). Rare earth production at that facility began with caustic cracking of monazite followed by HNO_3 leaching (Gupta and Krishnamurthy, 2005). The Rhone-Poulenc process was designed for the recovery of the entire series of rare earths as separated compounds (Xie, 2013), and a flowsheet for the solvent extraction process appears in Figure 15.

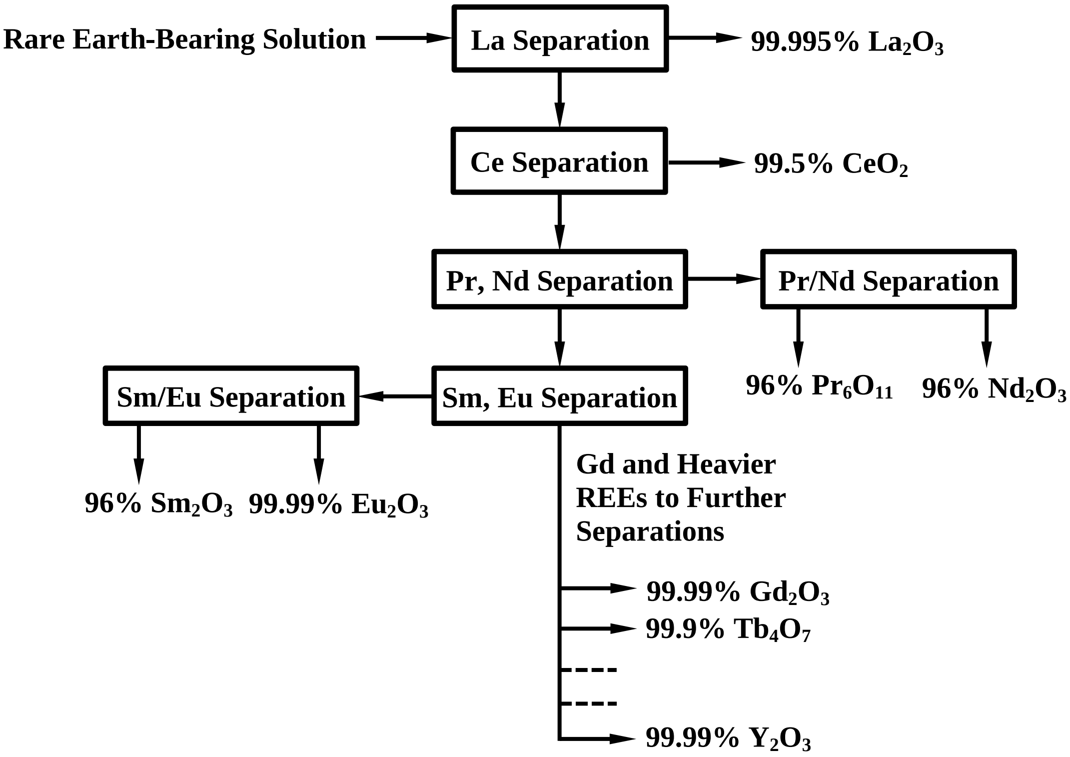


Figure 15: Rhone Poulenc Solvent Extraction Process for Rare Earth Separation, from Gupta and Krishnamurthy, 2005.

While this particular flowsheet has been referred to as “the standard for all industrial producers” (Gupta and Krishnamurthy, 2005), a “variety of chemical extractants” is required for the multiple separation steps, including “acidic and neutral organophosphorus compounds, amines, and carboxylic acids”, and “

The solvent extraction separation of each REE was carried out in multistage batteries of mixer–settlers. At least 50 mixture settler stages per stream are needed to obtain a product with 99.99 to 99.9999% purity.” (Krishnamurthy and Gupta, 2016).

In addition to costs and dealing with numerous separations of water and organics such as diesel fuel, the complication of solvent extraction processes offer incentives for the development of alternative technologies. A discussion of alternative technologies under development will be presented in a subsequent section. Closures of solvent extraction facilities, while eliminating U.S. capacity for producing separated rare earth compounds, have offered opportunities for newer, possibly less complicated technologies as this separation step in the rare earth value chain is rebuilt in the U.S.

3.8. The Rise and Fall of the U.S. Rare Earth Value Chain: A Synopsis

In 1994 (25 years ago), two operations in the U.S. produced rare earth ores. Molycorp's Mountain Pass operation continued as the largest U.S. producer, producing 20,664 metric tons of rare earth oxides as a bastnasite concentrate. The other producer, RGC (USA) Minerals, Inc., produced monazite as a byproduct of a dredging operation targeting titanium and zirconium ores in Florida. RGC Minerals was a subsidiary of an Australian firm (Hedrick, 1994).

Also in that year, there were three companies producing refined lanthanides: Molycorp at Mountain Pass, Rhone-Poulenc in Freeport, Texas, and Grace-Davison, a division of W.R. Grace, in Chattanooga, Tennessee (Hedrick 1994).

Rare earth production in the U.S. had begun a little over a century earlier, with monazite recovery from placer operations in the Carolinas (Overstreet et al., 1959). An early driver for the market resulted from the invention of a gas light mantle by Auer von Welsbach in the 1880's (Greinacher, 1981).

Rare earth extraction from monazite ore began in the U.S. following the incorporation of the Welsbach Incandescent Light Company. A set of Philadelphia, Pennsylvania business interests that had acquired the rights to the Thaddeus Lowe's water gas generator (a coal gasification system), and formed the United Gas Improvement Company in 1882. In addition to marketing the Lowe gasification system, the company also entered into the manufactured gas business. In 1887, the company acquired the U.S. rights for the Welsbach gas mantle, and formed the Welsbach Incandescent Light Company to produce the mantles (UGI Corporation, 1982). These products used thorium and cerium compounds in their manufacture, the former being required in much larger quantities.

The Welsbach production operation was located in Gloucester, New Jersey. The primary product from the extraction of monazite was thorium nitrate, and the company was involved in rare earth research in an effort to develop markets for the co-produced rare earths. In 1891, Dr. Waldron Shapleigh from the Welsbach Incandescent Light Company displayed separated rare earth compounds at the September Meeting of the Franklin Institute, including those of lanthanum, praseodymium, neodymium and erbium. In some cases, this was the first time that the compounds had been displayed in the U.S. In others, it was the first time that they had been prepared anywhere (Wahl, 1891).

The early market for monazite concentrates derived from their thorium content, with the recovered thorium and some cerium used to manufacture the mantles (Overstreet et al., 1959). From 1911 to 1948 there was no domestic monazite production, as this had been supplanted by imports from Brazil and India (Parker and Baroch, 1971),

Although not having a significant impact on the U.S. rare earths industry for another thirty years, an important event in the history of the industry was the incorporation of the Molybdenum Corporation of America, headquartered in the Empire Building in Pittsburgh, Pennsylvania (Anonymous, 1920). At the time of this development, the company was involved in the development of a molybdenum property in New Mexico, and was affiliated with the Electric Reduction Company in the Pittsburgh region (Voynick, 1996). Nearly thirty years later, the firm acquired the Mountain Pass property.

Toward the end of this period in rare earth history, thorium was envisioned as fuel for nuclear (breeder) reactors. This would have expanded the demand for monazite. However, India in 1946 and Brazil in 1951 restricted exports of the mineral (Allardice and Baroch, 1959). The U.S. "domestic thorium and rare earth industries appeared to be in a critical condition" (quoting from Allardice and Baroch), and the U.S. Bureau of Mines and the USGS, through agreement with the U.S. Atomic Energy Commission, began a series of explorations for monazite in Idaho and the Southeastern States.

While these events demonstrate an earlier issue with domestic rare earth availability in the U.S., other exploration for newly marketable radioactive ores led to Mountain Pass discovery.

In 1949, an engineer named Marty Hess was in Goodsprings, Nevada to give a talk on the search for uranium, sponsored and financed by Donald Cameron of the Nevada Department of Education (Olson et al., 1954). A local engineer (Herbert Woodward) was present for the talk, in which Hess mentioned an association of uranium and cobalt (known to occur in the Goodsprings District). Following the presentation, Woodward discussed the possibility, with local miners, of using a Geiger Counter to search for uranium in areas known to contain cobalt minerals. P.A. Simon, owner of a regional gas station and motor court, offered to purchase a Geiger Counter for an interest in the enterprise (Olson et al., 1954).

After finding nothing in multiple mine dumps, Woodward was invited to test rocks collected by Fred Piehl, at Piehl's cabin. Lead and gold ores from Sulphide Queen Hill, a previously worked gold property, were found to be radioactive. Following this find, Woodward, accompanied by Mrs. Woodward, "quickly proceeded to the Sulfide Queen mine, a mile or two northeast of Mountain Pass, and soon found much of the material on the Sulphide Queen mine dump and hill nearby was radioactive." (Olson et al., 1954).

The Sulphide Queen area was covered by Piehl claims, and Woodward searched the area a mile or more northwest. With an additional partner, Clarence Watkins of Goodsprings, "the partners found intense radioactivity along the outcrop of a vein, about 4,000 feet northwest of the Sulphide Queen shaft, located the Birthday Claim, named for its discovery on Woodward's birthday anniversary. A shallow pit showed the presence of about 6 feet of vein which contained a large amount of a light brown heavy mineral. Not recognizing it and not having the facilities to determine its identity, they submitted a specimen to E.T. Schenk, at the Boulder City Station of the U.S. Bureau of Mines. A spectroscopic test showed the presence of considerable rare-earth oxides, fluorine, and carbon dioxide and indicated that the mineral was bastnasite," (Olson et al., 1954). In February 1950, the Birthday group of claims was sold to the Molybdenum Corporation of America, and in May of that year the work was begun to sink the Birthday Shaft. Production began in 1952 (Long et al., 2010).

Also during that time, intermittent production of monazite from placers in the Carolina, Florida and Idaho had resumed (Parker and Baroch, 1971).

Meanwhile, Congress, through the Atomic Energy Acts of 1946 and 1954, had declared thorium to be a source of material for atomic energy (Parker and Baroch, 1971), and monazite was a source of Thorium. From 1955 to 1959, thorium was produced from a euxenite concentrate, along with rare earths, by Mallinckrodt Chemical Works, at St. Louis, Missouri, under contract to the Atomic Energy Commission (AEC). Another AEC contractor was the Lindsay Chemical Company, which was to become part of American Potash and Chemical Corp.

Lindsay Chemical was a pioneer in the U.S. rare earths industry and had been producing thorium gas mantles since 1902 (Parker and Baroch, 1971). Lindsay Chemical had built a plant in West Chicago, Illinois, with a capacity, by 1954, to process 9,000 tons/year of monazite for thorium production (including under contract to the AEC). This plant used H_2SO_4 to extract rare earths and thorium from monazite, and added an ion-exchange system to produce high purity rare earths in 1955. By the late 1960's (following merger with American Potash) this was the largest U.S. producer of rare earth products (Parker and Baroch, 1971). In 1968, American Potash in turn became part of Kerr McGee Corporation.

In 1956, Crane Minerals and Vitro Corporation of America announced a joint operation to produce thorium and rare earths from monazite sands and other materials (The Wall Street Journal, 1956). The partnership also included an ilmenite/rutile/zircon/monazite mining operation near Aiken, South Carolina. The monazite extraction at that plant used caustic leaching (Enderlin, 1978), and the facility operated until 1983 (Rehmann, 2000).

In New Jersey, the Maywood Chemical Works had processed monazite from 1916 to 1957 to produce thorium (Cerilli, 1983), and Between 1948 and 1956, Rare Earths, Inc. processed monazite to recover rare earths, as well as thorium for the AEC (Frame, 1983), near Pompton Plains, New Jersey. In 1956, the U.S. Bureau of Mines listed the Lindsey Chemical operation in Illinois and the Maywood and Rare Earths, Inc. operations in New Jersey as the principal domestic processors of monazite (Kaufmann and Baber, 1956).

The W.R. Grace Company, Davison Chemical Division absorbed Rare Earths, Inc. in 1956, and also operated a monazite extraction plant near Baltimore, Maryland under contract to the AEC, in 1956-1957 (Parker and Baroch, 1971). In 1965, the company acquired the Vitro operation in Chattanooga (Parker and Baroch, 1971).

The Michigan Chemical Company, with a facility in St. Louis, Michigan, announced in 1959 that it had the largest heavy rare earth production facility in the world. The company used ion-exchange columns for production (Barron's National Business and Financial Weekly, 1959). Solvent extraction and reduction facilities for metal production were also available by 1971. In 1966, the company acquired an operation in Idaho to supply ore (Parker and Baroch, 1971).

The Mountain Pass operation had been mining and producing concentrate since 1952, and the concentrator capacity was expanded to 25,000 short tons/year of product capacity by the end of 1966. Molycorp also operated a solvent extraction plant in Louviers, Colorado, producing high purity oxides of lanthanum, praseodymium, gadolinium, and yttrium (Parker, 1968), as well as rare earth chloride plant in York, Pennsylvania that was originally the destination for much of the concentrate produced at Mountain Pass..

By 1966, Mountain Pass had become the paramount rare earth source, supplying over half of global production and rendering the U.S. largely self-sufficient with respect to rare earth requirements through the mid-1980's. This was fortunate, as the commercialization of the color television had increased domestic rare earth demand (notably europium for the red phosphor), supporting development of the Mountain Pass operation (USGS, 2002).

When the Molycorp acquired rights to the Mountain Pass rare earth deposit, the company also acquired a concentrating plant, previously installed for gold recovery (Baroch, 1958). ***Following several unsuccessful attempts, the existing concentrator was successfully adapted to accommodate the challenge of bastnaesite concentration, and repurposed as the first processing step in in Molycorp's value chain in 1952 (Baroch, 1958)***. Most of the Mountain Pass concentrate prior to 1965 was shipped to the company's York plant (Anonymous, 1965), following acid leaching to remove calcium. The concentrate sent to York where the residual minerals comprising the rare earth concentrate were attacked with HCl, to produce a soluble, mixed rare earth chloride product (Kruesi and Duker, 1965). The hydrometallurgical extraction system at Mountain Pass evolved over the years, and has been discussed in Section 3.5.

Molycorp sponsored research at academic institutions, including a multi-year program at Penn State University in the late 1950's and early 1960's (Anonymous, 1963). One topic under this program was the use of organic phosphates for the extraction of rare earths (lanthanum, cerium, praseodymium and neodymium) from leach solutions (Maneval, 1961). With the advent of the color television and associated europium demand, Molycorp in 1964 retained the Colorado School of Mines Research Foundation to develop a solvent extraction technology to recover europium at Mountain Pass. The plant was built by Bechtel, and the organic phosphate-based solvent extraction system built on results that had been developed under AEC sponsorship and Ames and other laboratories (Anonymous, 1965).

The period in that marked the rise of production at Mountain Pass was accompanied by declines of other producers. In 1973, Kerr-McGee and Michigan Chemical had closed the West Chicago, Illinois and St. Louis Michigan facilities and were dismantling them (Jolly, 1973).

The closure of the Kerr-McGee and Michigan Chemical facilities in 1973 had left Molycorp and W.R. Grace as the only significant rare earth processors in 1973 (Jolly, 1973), and monazite extraction ceased at the Grace plant in Chattanooga in 1983 (Rehmann, 2000). However, in 1981, Rhone-Poulenc had begun rare earth production at their new facility in Freeport, Texas, with a 4,000 metric tons/year capacity (Hedrick, 1981). Feedstock was monazite, and a flowsheet of the Rhone-Poulenc system, downstream of caustic cracking of the monazite, was shown in Figure 15. The plant capacity was doubled to 8,000 metric tons/year (Jackson and Christianson, 1993).

Back to 1994, Molycorp, Rhone-Poulenc, and W.R. Grace were the three firms producing refined lanthanides in the U.S., and monazite extraction had ceased at the Grace plant in 1983, leaving Molycorp and Rhone-Poulenc as the remaining companies with U.S. chemical extraction and separation capabilities.

By 1996, Molycorp had closed both the Louviers, Colorado and York, Pa. plants (ENSR, 1996). In 1998, Molycorp ceased production of refined lanthanides at Mountain Pass, due to a blocked wastewater pipe underlying lands that were administered by several State and Federal Government jurisdictions (Hedrick, 1998).

In 1999, Rhodia (formerly Rhone-Poulenc) announced the closure of the Freeport, Texas separation plant, in conjunction with its plan to build a facility in China near the Bayan Obo operation (Hedrick, 1999).

After a restart and bankruptcy (2010-2015) and restart, the Mountain Pass operation is currently shipping mineral concentrate to China.

While the previous availabilities of mineral processing, chemical extraction, and separation facilities in the U.S. has been the primary focus of this Section, reduction facilities producing metal also bear mention. In 1990, the Ronson plant in Newark, NJ, a mischmetal producer (for lighter flints) closed (Hedrick, 1990), leaving the Reactive Metals and Alloys plant in Western Pa. as the sole U.S. mischmetal producer. As of 2012, the sole U.S. producer of high purity rare earth metals and alloys was the Santoku America, Inc. plant in Phoenix, Arizona, which at that time had been acquired by Molycorp (USEPA, 2012).

Mineral processing practices in the U.S., applied to the rare earth value chain, have included those used for concentrating monazite from placer deposits, as well as grinding and flotation for the production of a bastnasite concentrate. Extraction of rare earths from mineral concentrates have included both acid and caustic extraction of monazite, and the extraction processes used at Mountain Pass for bastnasite concentrate. Both ion exchange and solvent extraction have been used over the last 70 years for separation processing.

Re-establishment of the rare earth value chain in the U.S. will require extractive metallurgy facilities and those that can separate a mixed rare earth stream into individual compounds. These facilities have existed previously in the U.S., including extraction operations capable of processing significant tonnages (Molycorp, Rhone-Poulenc, Lindsay/American Potash/Kerr-McGee).

It is also instructive to consider the historical role of the U.S. Federal Government in the development of this now largely vanished rare earth value chain. Among the Federal Government actions were:

- Tariffs on imported rare earth-bearing ores (monazite), and rare earth compounds and alloys (Parker and Baroch, 1971).
- Following the decline of the thorium market, due to electric lighting replacing gas lighting, Atomic Energy Commission purchases of thorium from monazite extraction operations (Parker and Baroch, 1971); this effectively converted a disposal cost for the operations into a revenue source.
- The establishment of the Defense Minerals Administration (DMA) in 1950, which designated cerium and rare earth ores as scarce materials (Parker and Baroch, 1971). The DMA and its successors offered Federal cost shares for geologic exploration activities, and no-cost assaying of samples. An example was the aforementioned U.S. Bureau of Mines assaying work involved in

the discovery of Mountain Pass. Additionally, the deposit was subsequently mapped by the U.S. Geological Survey (Olsen et al., 1954).
- Research on processing technologies. Much of the actual technology development work that was done focused on separation of rare earths from each other (ion exchange, solvent extraction. The U.S. Bureau of Mines maintained a substantial program in mineral processing and extractive metallurgy associated with rare earth ores. However, this work was more focused on the adaption of existing technologies to these ores rather than the development of new technologies.

3.9. Rare Earth Production Summary

The rare earth value chain in the U.S. began with recovery of monazite from placer operation in southeastern states. Monazite extraction provided, in addition to rare earths, thorium for mantles and later for the Atomic Energy Commission.

Monazite recovery from placer operations typically requires physical separations (mineral processing), and commercial practice for the chemical extraction of rare earths from the resultant mineral concentrates, in the U.S., has been accomplished through the use of either acid or caustic (NaOH) treatments.

Bastnasite concentration in the U.S. has been accomplished through grinding to liberate mineral grains, followed by flotation. Chemical extraction of rare earths from the mineral concentrate has involved leaching with HCl, either alone or preceded by calcining.

Solvent extraction has been used in rare earth production in the U.S. for decades, producing separated rare earth compounds.

Re-establishing the rare earth value chain in the U.S., for production from ores, will require re-establishing the steps shown in Figure 8, including mineral processing and extractive metallurgy technologies. As the flowsheet shown in that figure proceeds to the right, any distinctions between rare earth derived from conventional ores and those derived from coal byproducts will be minimized. The largest differences (grade, gangue minerals, etc.) will be at the beginning of the process.

Constraints in the availability of imported rare-earth bearing minerals, after World War II, led to significant Federal Government involvement in the development of rare earth production and processing in the U.S. Installations that had produced thorium under contract to the AEC were repurposed as rare earth extraction facilities. The Federal Government also provided cost shares for geologic exploration activities.

A variety of existing technologies are available for use in both mineral processing and extractive metallurgy applied to rare earth production in the U.S. Past practice in the U.S. has shown that the individual steps in the process do not need to be co-located. Monazite concentrate from Idaho has been processed in the Midwest, as an example. As the process proceeds from left to right (Figure 8), the value of the concentrate increases significantly, and the influence of shipping costs within the U.S. overall production costs is minimized.

4. The Current Knowledge Base Applicable to Coal and Coal Byproducts in the U.S.

4.1. The Effect of Feed Ore Grade on Rare Earth Production Costs

The cost of producing a concentrate from a feedstock to a concentration, extraction, or separation system, will include the following:

- Feedstock cost delivered to the plant
- Capital and operating costs per ton of feedstock
- Yield at the required product grade
- Refuse (or tailings) disposal costs.

Production cost per ton of product will be a function of yield, which in turn will be a function of the feed assay (head grade to the process). For a fixed set of costs per ton of feed, production cost per ton of product will be a function of the inverse of the yield. Less product at a fixed set of costs, per ton of feedstock, means higher production cost per ton of product. This is compounded by the fact that the refuse disposal requirement also increases as yield is decreased.

Evaluating production costs on a per ton of feed basis allows for examinations of the effect of product yield, in turn a function of assay. An example set of production costs, for a range of feedstock head grades, appears in Figure 16. Feedstock, capital, operating, and refuse costs are fixed, as is rare earth recovery to the product (85% recovery, 50% rare earth product grade). It must be noted that with all costs held constant (i.e. a given process), feedstock rare earth content strongly affects production cost.

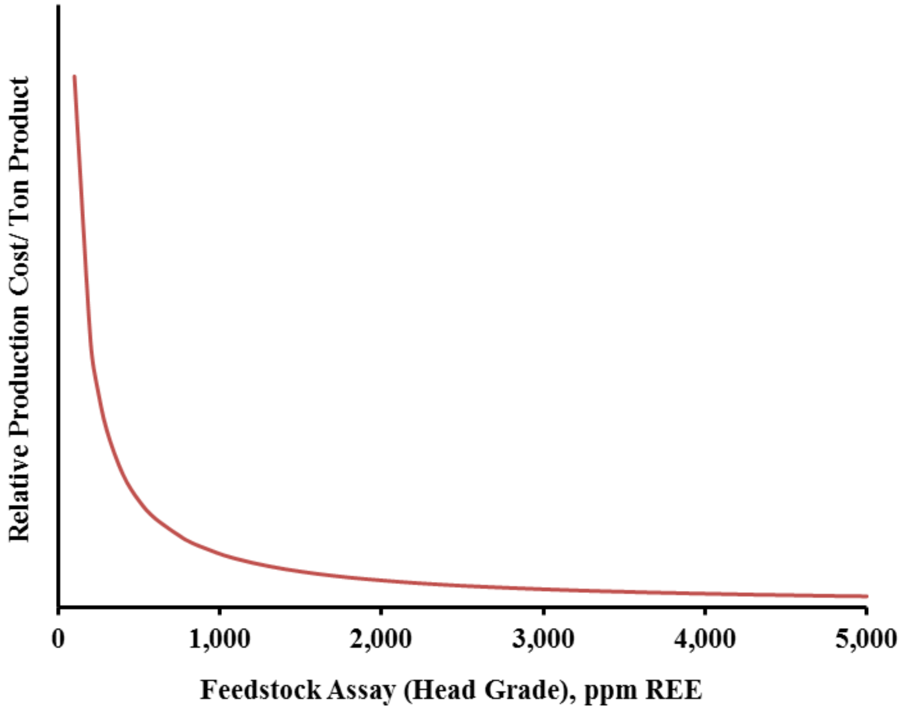


Figure 16: Generic Relationship between Production Cost and Feedstock Assay

Useful equations for producing the type of curve found in Figure 16 are as follows:

$$\boldsymbol{Y = \frac{G_P}{R_P}} \tag{1}$$

Where Y is the yield, G_P is the product grade, and R_P is the product recovery.

$$\boldsymbol{P = Y \cdot F} \tag{2}$$

$$\boldsymbol{T = (1 - Y) \cdot F} \tag{3}$$

Where F is the feed rate to the system (example, tons/hr), P is the product production rate, and T is the refuse production rate.

$$\boldsymbol{C_F = c_F \cdot F} \tag{4}$$

$$C_Z = c_Z \cdot F \tag{5}$$

$$C_R = c_R \cdot T \tag{6}$$

Where C_F is the cost of feedstock per hour, c_f is the feedstock cost per ton, C_Z is the plant capital and operating cost per hour, c_Z is the plant capital and operating cost per ton of feed, C_R is the refuse disposal cost per hour, and c_r is the refuse disposal cost per ton of refuse.

$$C_T = C_F + C_Z + C_R \tag{7}$$

Where C_T is the total cost per hour. The production rate is P, and the production cost per ton of product C_P, is:

$$C_P = \frac{C_T}{P} \tag{8a}$$

Equation 8a can also be written as a function of yield, as such:

$$C_P = \frac{c_F + c_Z}{Y} + \frac{c_R \cdot (1-Y)}{Y} \tag{8b}$$

It is evident that production cost (per ton of product) is a function of yield. As seen in Equation 1, yield is a function of feed assay and recovery.

While this type of analysis can be useful for comparison of feedstocks for a specific system, where the inputs are known, it can also be useful on a more generic basis for comparisons of feedstocks to each other, using rare earth assays and example data for the other inputs. Comparisons of this nature will be presented in Section 4.3.

4.2. Example Process Operating Costs

The options for replacing the domestic rare earth value chain in the near term include new plant construction, repurposing of existing facilities (an opportunity for near term production at reduced cost), and engaging existing facilities to process rare earth-bearing feedstocks on a tolling basis. Of these, the last two, if compatibility can be found between ores and process equipment, would be the most likely options in the near term

In this section, published cost data for mineral processing, ore extraction, and solvent extraction will be presented. This data will be used in conjunction with DOE sampling and analysis results, to establish cutoff grades for coal and coal byproduct materials that have been assayed to date. As the near-term options will vary in capital charges, only operating costs will be used for screening purposes. A potential feedstock, that does not have enough contained rare earth value to cover the operating cost figure, will not clear the cutoff grade.

Using contained rare earth value to establish cutoff grade eliminates the economic influence of variations in rare earth distributions across the suite of available data sets. It also provides a simple comparison criterion (contained rare earth value vs. processing cost).

If mineral processing systems can concentrate rare earths in coal byproducts, with improvements over previous work (see Section 2.3.3), fine grinding to liberate the rare earth-nearing minerals and physical separations or flotation will provide a useful basis for both initial research and an initial examination of processing cost.

National Instrument (NI) 43-101 reports can include both plant capital and operating cost estimates for rare earth production. Some rare earth projects that are under development have reached the stage of publishing plant designs and cost estimates for parts of the value chain shown in Figure 8.

Mineral processing plant data are available for the following:

1. The Ashram Project in Ontario, using fine grinding (ore liberation size is 30 microns) and flotation to beneficiate are consisting of rare earth phosphates and fluorocarbonates (Gagnon et al., 2015).
2. The Strange Lake Project, Quebec, which also has grinding and flotation in the mineral processing plant design, grinding to 80% passing 40 microns to liberate multiple rare earth-bearing minerals).

As might be expected due to fine product topsizes, the power requirement for grinding is significant, as shown in Figure 17 (cost breakdown for the Ashram Project). However, the inclusion of on-site diesel generation in the project scope is an influence here. However, a 49 kWh/metric ton (MT) power requirement for grinding is expected (Gagnon et al., 2015).

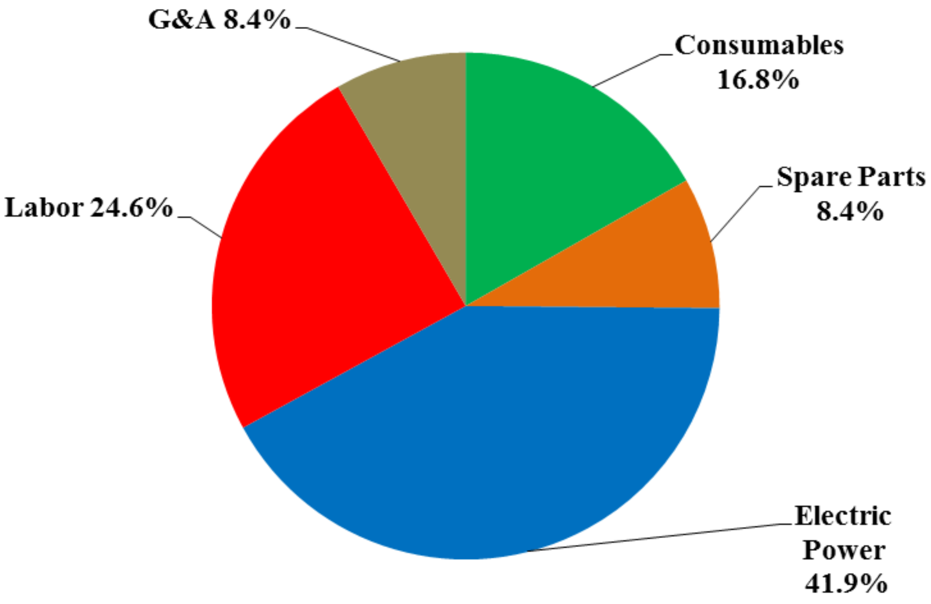


Figure 17: Mineral Processing Operating Cost Breakdown, Ashram Project (from Gagnon et al., 2015)

All cost data presented in this Section have been converted to U.S. dollars, at the end of the year of publication, and have been escalated to 2019 dollars using the Consumer Price Index.

Table 3 presents operating costs per metric ton of feed for the two projects. These costs are expressed in U.S. dollars (2019) per metric ton of feed. They are also not far apart.

With respect to extraction or rare earths from mineral form into solution, both the Ashram and Foxtrot (Masun, 2016) projects have acid baking followed by leaching in their plant designs. These are considerably more expensive to operate (per metric ton of feed), as shown in Table 4. Comparison of Tables 3 and 4 provide arguments for the application of mineral processing ahead of a hydrometallurgy process.

Operating costs are influenced by the choice of process, and that choice in turn is dictated by the thermodynamics of converting insoluble rare earth-bearing minerals into soluble compounds. Leaching thermodynamics are mineral- and reagent-specific, and basic research is required to identify optimum process parameters. Any assumption that a less expensive process would yield an acceptable performance must be validated with laboratory work.

Table 3: Processing of Rare Earth Ores: Example Grinding and Flotation Costs for North American Rare Earth Projects under Development.

Project	Grinding Product Size	Equipment	Operating Cost/Metric Ton of Feed (2019 USD)
Ashram (Gagnon et al., 2015)	**~37 µm**	**Jaw Crusher/SAG Mill/Ball Mill/Flotation**	**$22.99**
Strange Lake (Gowans et al., 2014)	**80% -40 µm**	**Jaw Crusher/SAG Mill/Ball Mill/Flotation**	**$22.50**

Table 4: Processing of Rare Earth Ores: Example Hydrometallurgical Extraction Operating Costs for North American Rare Earth Projects under Development.

Project	Reagent	Equipment	Operating Cost/Metric Ton of Feed (2019 USD)
Ashram (Gagnon et al., 2015)	**H_2SO_4**	**Acid Bake + Leach**	**$131.83**
Foxtrot (Masun et al, 2016)	**H_2SO_4**	**Acid Bake + Leach**	**$112.43**

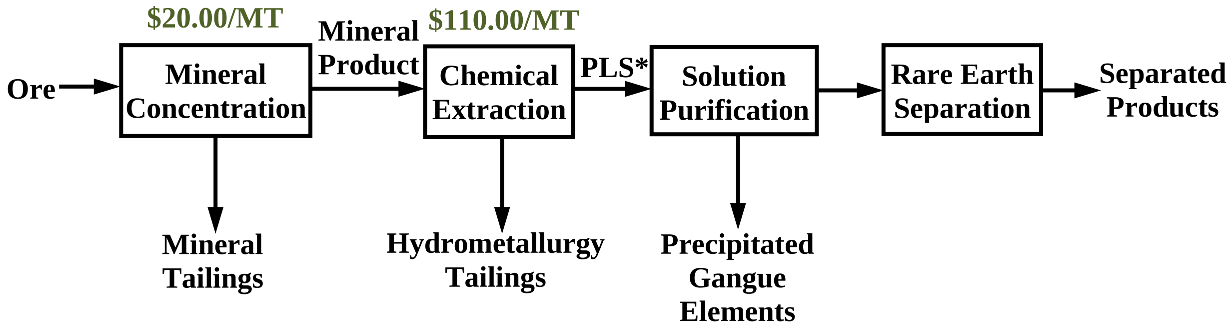
The last step found in Figure 8 is the separation of the purified, mixed rare earth stream into individual rare earth compounds. The current state of the art for addressing this need is solvent extraction. Numerous projects under development have not included this step in their plant designs, the end product is a mixed rare earth filter cake that would be sold to a separation facility for processing into individual compounds. As such, operating cost data for this type of facility are not readily available in NI 43-101 reports. However, two feasibility study reports do have information of this type (Arafura Resources, Limited, 2014, Peak Resources Limited, 2014). Calculation of costs from those works will yield figures for solvent extraction in the thousands of dollars per metric ton of feed (dry basis).

For calculation of cutoff grades in the next section, $20/metric ton will be the assumed operating cost for a mineral processing system. While not to be used here, $110/metric ton can be assumed as an operating cost for an acid baking system for comparison with the mineral processing cost.

These costs are added to Figure 8, as seen in Figure 18.

4.3. Establishment of Cutoff Grades for U.S. Coal Byproducts

Since the inception of the FE/NETL Rare Earth Program in 2014, a substantial amount of sampling and analysis work has been conducted, both in-house and through contracts. Work since 2015 has produced over 2,900 data sets including rare earth analyses for coal and coal byproducts.



***PLS = Pregnant Leach Solution**

Figure 18: Operating Cost per Ton of Feed Estimates for the Conventional Rare Earth Value Chain

These data sets are the result of one set of in-house sampling and analysis work, and five sets of external contractor work. The data will allow calculation of contained rare earth values per metric ton of material (dry basis), however price data for the complete series of rare earths, expressed as oxides, are rare in the public domain. One such public domain source is another NI 43-101 Report, this time from the Lofdal Project (Dodd et al., 2014). That work published prices for oxides as seen in Table 5.

Table 5: Rare Earth Oxide Prices Used to Calculate Contained Rare Earth Values in Coal Byproducts, from Dodd et al. (2014).

Compound	Price/kg
La_2O_3	$ 5.00
CeO_2	$ 4.00
Pr_6O_{11}	$ 95.00
Nd_2O_3	$ 73.00
Sm_2O_3	$ 8.00
Eu_2O_3	$ 750.00
Gd_2O_3	$ 47.00
Tb_4O_7	$ 870.00
Dy_2O_3	$ 530.00
Ho_2O_3	$ 55.00
Er_2O_3	$ 75.00
Tm_2O_3	$ 1,000.00
Yb_2O_3	$ 55.00
Lu_2O_3	$ 1,250.00

The prices in Table 5 are from 2014, no attempt has been made to escalate them. The results presented here are examples of the use of this method for applying an economic cutoff grade. However, application of current prices is not likely to create significant changes in the results to be presented.

Calculations of this type have originally been presented under the FE/NETL Rare Earths program by Noble and Luttrell (2016).

Available data include those from in-house work (NETL, 2016), and contractor-generated data (Tetra Tech, 2018a, Tetra Tech, 2018b, Groppo, 2018, Ziemkiewicz et al., 2018, Uhrin, 2018).

Coal byproducts from those data have been grouped into a “rock” data sets (overburden, underclay, preparation refuse) and a “sludge” data set (acid mine drainage sludge), across all of the cited data sources.

Prior to examination of the values of rare earths contained in the materials analyzed, a view of the data, by set, presented in the assay/cost curve format found in Figure 16 can be instructive. The rock data set is presented as such in Figure 19.

The curve seen here shows that significantly higher assay material has been found in both the coal measures and coal byproducts on the ground, as compared with 300 ppm material. For a given process, the lower cost production can be expected from the higher assay materials. This curve argues for a focus on the higher assay materials, if research toward near-term rare earth production is a goal.

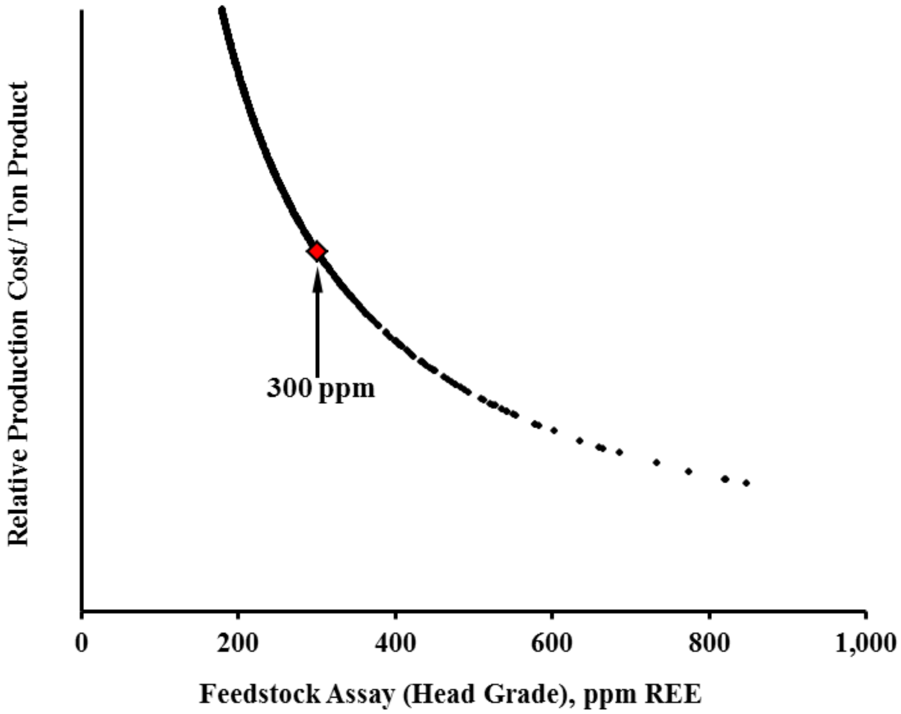
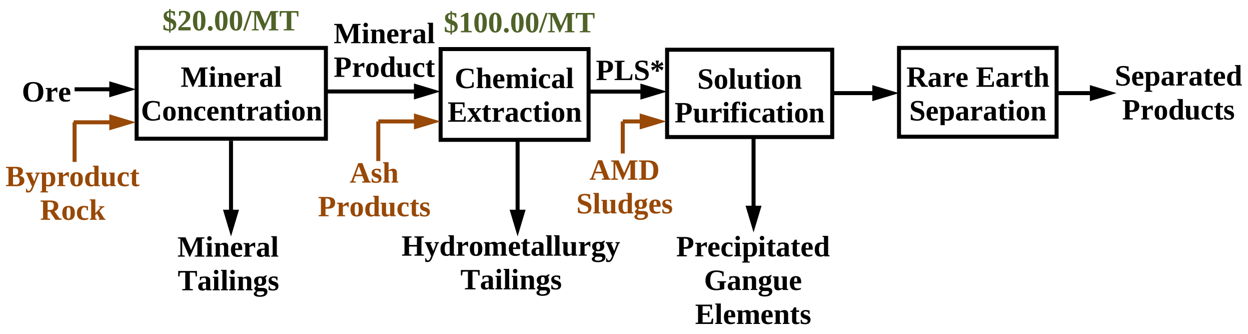


Figure 19: Assay/Relative Production Cost Curve for Coal Byproducts Analyzed

Among three categories of coal byproducts (rock, ash, sludge), Figure 20 shows where they would "plug in" to a conventional rare earth production value chain. Rock products such as mining and preparation byproducts would enter at the mineral processing step, assuming that fine grinding can sufficiently liberate the target rare earth-bearing minerals.



*PLS = Pregnant Leach

Figure 20: Plug in Points for Coal Byproducts in the Conventional Rare Earth Value Chain

Some removal of carbon and magnetics can be accomplished with ash products through mineral processing. However, in Figure 20 it is shown entering the value chain as feed to chemical extraction. Depending on the abilities of mineral processing techniques to significantly improve the contained rare earth value in an ash product, it could also enter at the mineral processing step, noting that a different cost value would be required for that step (starting topsize is much lower corresponding to lower grinding costs).

Acid mine drainage sludges contain rare earth compounds that have precipitated from solution (i.e. they have already been solubilized from their original mineral form). They are also likely of insufficient purity to be compatible with the separation step, and are shown here entering the value chain at the step where a leach solution would be purified.

Using the processing cost per metric ton of feed for mineral concentration step, and the contained rare earth values per metric ton of material (rock data set), the material with contained rare earth values per metric ton that clear the $20/metric cost are those that exceed the cutoff grade.

Out of 1.660+ analyses in the rock data set, 149 (nearly 10%) exceed the $20/metric ton threshold value for contained rare earths. This is shown in Figure 21, where the number of analyses with contained rare earth values, within value increments, is presented.

The materials that have cleared the cutoff grade criteria merit further examination in three areas:

1. Response to conventional mineral processing stimuli, using (1) fine grinding preceded by microscopy to determine mineral grain sizes, and (2) laboratory flotation testing. Fine particle physical separation testing may also be useful.
2. Further geologic exploration work to try to find higher rare earth content materials, within the geologic zones where the materials clearing the cutoff grade have been found.
3. Preliminary estimates of the extent of the resources (for each geologic zone), as well as mineability, the latter should be done in consultation with the mining industry. As these materials are associated with coal deposits, an operation would produce coal as well as a rare earth ore.

The distribution of materials that clear the cutoff grade, by state, is shown in Table 6.

State	**Number of Samples Clearing the Cutoff Grade**
Pennsylvania	71
Kentucky	31
Colorado	21
West Virginia	15
New Mexico	9
Indiana	2

Table 6, Distribution by State of Rock Analyses that Clear the Cutoff Grade

In the Western U.S., several of the materials from Colorado and New Mexico came from the Raton Mesa coal field. In the Eastern U.S., most of the materials from Pennsylvania and about half of those from West Virginia came from the lower Allegheny Group zone in the Appalachian coal field.

While these analyses suggest that these materials may provide useful feedstocks for rare earth production, it must be considered that, as mentioned, mineral processing laboratory work further geologic exploration, and work on mineable resource estimation are required. However, if economically viable near-term production of rare earths is a goal, these activities are justified.

Of specific note for those activities- the goal of mineral processing research should be the production of a mineral concentrate that clears the processing cost of the next step in the value chain- chemical extraction (in Figure 19- $100/metric ton).

4.4. Example Concentrate Grades and Shipping Costs

As seen in the discussion in Section 3.8, co-location of all elements of the U.S. rare earth value chain has not been a requirement. As rare earth-bearing materials proceed through the value chain, their contained value per ton of material can increase to the point that shipping costs, even those involving significant distances, have less of an effect on overall production costs.

As an example, a set of ore grades and contained values is presented in Table 7, along with an example shipping cost (500 miles, rear-dump 24 short ton loads, $0.15/short ton-mile cost). Shipping cost has the effect of increasing the feedstock cost to a process (c_f in the Equations found in Section 4.1). For a fixed processing cost per ton of feed, as shown in Figure 20, the effect of shipping cost (c_S) can be evaluated by subtracting it from the contained rare earth value of the feedstock, for comparison with the processing cost. The difference between the contained rare earth value and the shipping cost is here referred to as the net contained value after shipping, c_F', and is calculated as seen in Equation 9.

$$c_F' = c_F - c_S \tag{9}$$

The rare earth values have been calculated for a set of ore grades based on the rare earth distribution found in Sample N-417 (NETL, 2016), and the ore grade has been varied from 849 ppm to 75 wt% REE.

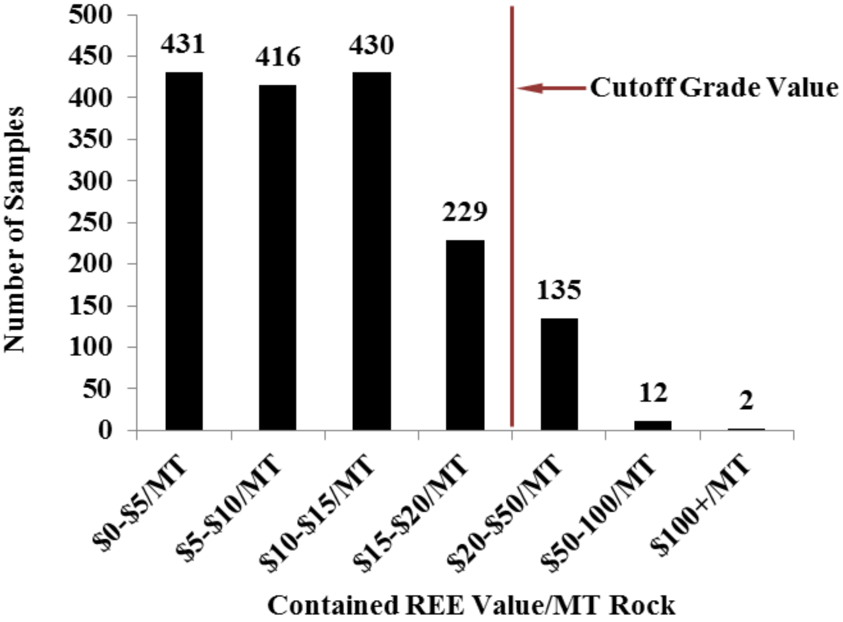


Figure 21: Distribution of Contained Rare Earth Values in Coal Byproducts and Example Cutoff Grade

It can be seen here that as the ore grade increases, the effect of transportation on its value is minimized. It is also apparent that at a low assay (noting that the example used is among the highest found under the program), the transportation cost example renders the material uneconomic.

Type of Product	REE Assay	Contained REE Value/MT	Trucking Cost/MT	Net Contained REE Value/MT
Unprocessed	849 ppm	$32.68	$82.50	-$49.82
Concentrate	1 wt%	$385.36	$82.50	$302.86
Concentrate	2 wt%	$770.73	$82.50	$688.23
Concentrate	5 wt%	$1,926.82	$82.50	$1,844.32
Concentrate	10 wt%	$3,853.63	$82.50	$3,771.13
Concentrate	25 wt%	$9,634.08	$82.50	$9,551.58
Concentrate	50 wt%	$19,268.15	$82.50	$19,185.65
Concentrate	75 wt%	$28,902.23	$82.50	$28,819.73

Table 7: A Range of Rare Earth Assays and the Effects of Transportation Cost on their Net Value

As the rare earth content of the material increases, the effect of shipping cost on its value becomes less important. However, given the rare earth contents that have been found under the current program, unless some beneficiation is accomplished, shipping costs can quickly render the material uneconomic for rare earth production.

Within the context of the example conventional value chain shown in Figure 20, it is apparent that the mineral concentration facility must be very close to the source of the material. However, if mineral processing can economically produce a mineral concentrate with a much higher rare earth content, the next steps in the value chain, chemical extraction through separation, may not need to be in close proximity. In fact, these might be centralized facilities that can process material from multiple mineral processing operations. As the chemical extraction is “most of the cost” (Verbaan), this may be advantageous.

4.5. Near Term Production: Example Tonnage Requirements

An example will be offered here regarding the requirements for producing 1,000 metric tons/year of rare earth, using options that can achieve near term production. The results to be presented will include the scale of raw material production (coal byproducts) required, as a function of assay, as well as the scale of chemical extraction facilities required.

Table 8 shows the raw material tonnages required for the production of 1,000 MT/year, assuming an 80% overall rare earth recovery to separated products.

Raw Material Assay, ppm	Metric Tons per Year of Raw Material Required
300	4,167,000
500	2,500,000
1,000	1,250,000
5,000	250,000

Table 8: A Range of Raw Material Requirements for the Production of Rare Earths from Coal and Coal Byproducts

As would be expected, the tonnage requirement shrinks significantly as the raw material assay increases. This is an argument for expanded geologic exploration activities under the program.

The effect of mineral concentrate grade has a significant impact on the required feed capacity of a chemical extraction plant. This is especially significant, given the costs associated with this type of system.

Example capacity requirements for a chemical extraction system, at a range of feedstock assays are shown in Table 9. Here, the recovery to products is assumed at 88%.

Feedstock REE Assay	**Required Plant Feed Capacity, MTPY**
300 ppm	3,787,900
500 ppm	2,272,700
1,000 ppm	1,136,300
5,000 ppm	227,270
1 wt%	113,640
5 wt%	22,727
10 wt%	11,364
20 wt%	5,682
50 Wt%	2,273

Table 9: The Effect of Feedstock Assay on Chemical Extraction Plant Capacity Requirements for 1,000 Metric Tons/year of Rare Earth Products.

Under these conditions, a 300 ppm feedstock to the chemical extraction process would require a plant that could handle over 3.7 million metric tons of feedstock (noting also that the overwhelming majority of the material fed will be process waste). However, if a 50 wt% concentrate can be produced, the plant capacity requirement is reduced to less than 2,300 metric tons/year. Assuming 7,000 hours per year of operation, this required capacity can be expressed as approximately 700 lbs/hour.

4.6. Contained Rare Earth Value in Power Plant Ash and Acid Mine Drainage Sludges

Where coal combustion byproducts (power plant ash and flue gas desulfurization residues) would enter the value chain shown in Figure 20 is not definitively known. However, the following have led to the entry points shown in the Figure:

1. While power plant ash can exhibit a fine particle size distribution, enhancing the potential for mineral liberation, the use of mineral processing techniques for the beneficiation of rare earth content have yet to show significant improvements in rare earth content (Honaker et al., 2014, Zhang et al., 2015).
2. Sludges produced from the treatment of acid mine drainage would need to be re-dissolved prior to the separation step, and, given the relatively low rare earth contents of most of the sludges, a significant amount of gangue element removal is a likely requirement ahead of that step.

A set of data regarding the rare earth concentrations of power plant ash and flue gas desulfurization residues has been assembled from the NETL-EDX data (Tetra Tech, 2018a), Hood et al. (2017), Fan et al. (2017), and a data set from the NETL Pittsburgh Analytical Laboratory. The distribution of contained rare earth values, calculated from the data set, appears in Figure 22.

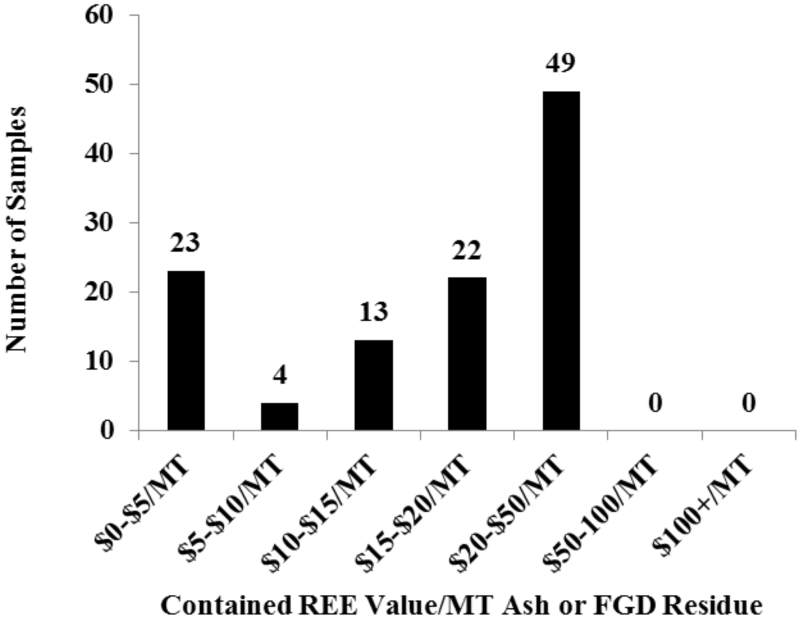


Figure 22: Distribution of Contained Rare Earth Values in Power Plant and Flue Gas Desulfurization Reside Samples

Based on the cost constraints shown in Figure 20, none of the materials analyzed would have sufficient rare earth contents to justify their use in an extraction process that costs $100/metric ton of feed to operate. Options for improving the prospects of power plant ash as a feedstock for rare earth recovery would likely include finding a lower cost hydrometallurgical extraction process, although, as discussed previously, the process itself is dependent on the thermodynamics of the ore minerals. It must be noted that a lower cost process that is capable of solubilizing rare earths from an ore mineral, found in power plant ash, is likely to also solubilize rare earths from the same mineral found in a mineral concentrate, in a higher concentration. The latter scenario could prove more economically feasible. Another option would be to continue research into possible means of physically concentrating ash.

The data set for the distribution of contained rare earth values in acid mine drainage sludges, appearing in Figure 23, was developed from Tetra Tech (2018a) and Ziemkiewicz et al. (2018). A significant number of the analyzed materials have contained rare earth values in excess of $100/metric ton. While the data in Figure 23 use the same groupings of contained rare earth value found in Figures 21 and 22, it bears mention that several of these samples contained over $200/metric ton worth of rare earths, and the contained rare earth value of one sample exceeded $480/metric ton.

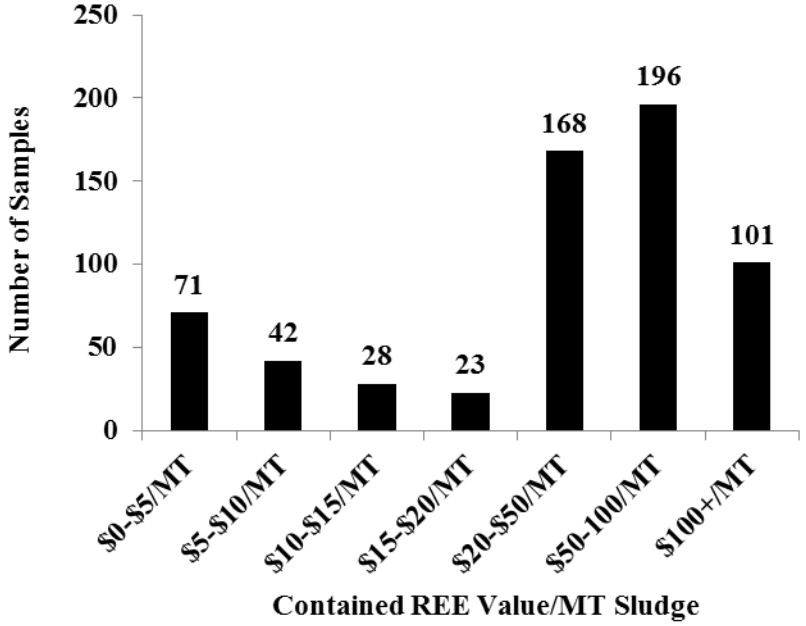


Figure 23: Distribution of Contained Rare Earth Values in Acid Mine Drainage Sludge Samples

Given that contained rare earth values exceed $200/metric ton in some cases, it is also likely that these materials could incur some modest transportation costs without rendering them uneconomic, as these values exceed even the $100/metric ton extraction cost.

4.7. A Perspective on Available Feedstocks and Value Chain Requirements

With respect to near-term production of rare earth products from coal and coal byproducts, the following can be summarized here with respect to tonnage requirements:

1. ***Any beneficiation, near the source of the material (mine site, as an example), will reduce the effects of transportation on product value. Successful achievement requires mineral processing research, and successful implementation of the results may allow for a centralized chemical extraction facility that could process mineral concentrates from multiple sources.***
2. ***The highest raw material assays will minimize the raw material tonnages required for 1,000 metric tons per year of production capacity. This is important with respect to achieving near-term production, development and permitting of smaller production facilities can require less time for development and permitting.***
3. ***The required capacity of a chemical extraction plant shrinks as the rare earth content of its feedstock increases. For a system capable of producing 1,000 metric tons/year of rare earth products, this required capacity can be in the single digit metric tons/hour range if a high enough grade mineral concentrate can be produced.***

4.8. Options to Fill Gaps in the Value Chain

The disappearance of the rare earth value chain in the U.S. was discussed in Section 3.8. One means of re-establishing that value chain would be the replacement of mineral concentration, chemical extraction, and separation facilities to produce material for the remaining downstream end users (metal and magnet facilities, for examples).

Currently available technologies that can be used to re-establish the value chain include mineral processing equipment, hydrometallurgy and solution purification equipment, and separation equipment. With respect to the establishment of near-term production, there are three options available:

1. Adapting any available tolling facilities to beneficiation and chemical extraction of rare earth-bearing materials derived from coal byproducts.
2. Acquiring and repurposing idle facilities with beneficiation and/or chemical extraction equipment.
3. Construction of new facilities (***note: this will be required for the separation step in Figure 8***).

If facilities can be found, the first option would likely result in near-term production, with minimized capital cost requirements. The other two options in order have increased capital cost and lead time requirements.

Additional observations are as follows:

Mineral Concentration

Location near the source of the material will be an economic requirement. A conventional system would require fine grinding, some materials found under the DOE/NETL Rare Earths Program have sufficient contained rare earth value to cover the cost of that type of processing. There is a significant U.S. manufacturing base experienced in the supply of mineral processing equipment, and modular systems have been offered for decades. A modular system is advantageous for this type of operation as a plant can be moved and restarted in less than two months. Smaller mineral processing systems in multiple locations could be used to feed a central chemical extraction system, should mineral processing research find ways to achieve high rare product grades.

Chemical Extraction

This step can be expected to be expensive. However, it has been shown that the required throughput contracts dramatically with feed grade. In the longer term, construction of dedicated facilities is a likely requirement. However, the history of rare earths production in the U.S. has also seen this type of production grow out of repurposed facilities with Federal Government (AEC) involvement (see Section 3.8). Options for this step in the near term would include the engagement of existing facilities on a tolling basis. This will be discussed in the next section. The research requirement here is leaching tests on rare earth-bearing minerals, known to occur in coal, using condition achievable in hydrometallurgy facilities available on a tolling basis.

Another research requirement will be the determination of the ability of solution purification facilities at existing facilities to remove gangue elements from leach solutions produced from coal byproducts.

Separation

Given the inherent complexity of the technology, the installation of a new solvent extraction plant in the near term may be difficult. While this report has largely been focused on current, commercial technologies for replacing the U.S. rare earth value chain, the lead times associated with a new solvent extraction facility at a significant capacity may not be compatible with near-term production. However, a range of new technologies is under development that can replace solvent extraction. These technologies are at different stages of development, and multiple Federal Agencies have been involved. The use of any existing capacity using solvent extraction alternatives, as well as accelerating the scale-up of others, are the preferred alternatives for near-term production capacity.

4.9. Near Term Production- Available Facilities and Options

In the near term, options can include the use of tolling facilities as well as the re-purposing of idle plant equipment. In addition to shorter lead times, the potential exists for achieving near-term production with reduced capital cost requirements.

Facilities are currently available for use on a tolling basis. Examples, from the State of Nevada, are listed in DeMull et al. (2018). Other examples can be found in locations in the U.S. and Canada that host mineral processing and hydrometallurgy facilities associated with the production of base and precious metals.

Examples of available capacity from DeMull et al. include grinding, gravity concentration and flotation machinery among the mineral processing equipment, and leaching, precipitation, and roasting leaching and precipitation steps are included with hydrometallurgy equipment.

In addition to available capacity found in DeMull et al., exclusive to Nevada, tolling capacity exists in other states and Canadian provinces. Additionally, other facilities that have been idled may be available. A comprehensive list of extractive metallurgy facilities, including design processing parameters, would be useful in establishing a range of potential options for near-term production.

Within the available set of processing conditions, hydrometallurgical laboratory work, involving rare earth-bearing minerals found in the U.S. coal measures, would help establish the chemical extraction achievable at existing facilities. This should be done in conjunction with thermodynamic modeling of these minerals under extraction conditions. It must be acknowledged that, depending on the rare-earth mineral, severe conditions may be required to render the rare earths in a soluble form, and that recoveries to solution may not be optimum. However, the goal is near-term production, and quantification of these recoveries, based on thermodynamic and laboratory work, will establish the achievable rare earth extraction and its impact on process economics.

As presented in Tables 7 and 9, the effect of transportation cost on process economics and feed capacity of an extraction system are reduced dramatically as the rare earth assay of the material increases. Further, lower assay material, even in the 1,000 ppm range, cannot be shipped far without significant adverse impacts on overall process economics. As such, moving idle mineral processing capacity to locations near the material sources is likely the optimum option, followed by shipping the mineral concentrate to the chemical extraction system. Another option would be the construction of smaller, modular mineral processing systems near multiple sources, each then shipping a concentrate to the central extraction facility.

Additionally, as seen in Table 9, the required feed capacity of the chemical extraction step drops very significantly as its feed grade increases. From 300 ppm rare earths to 50 wt% rare earths, this requirement drops by over two orders of magnitude. At a sufficient feed grade, the required hydrometallurgy capacity can be less than one ton per hour, in order to achieve a 1,000 short ton per year output.

A concentrate produced by a chemical extraction system will also have a high assay, allowing for shipping over considerable distances without significant adverse impacts on overall economics. This also argues for a central facility for separation of chemical extraction product into individual rare earth compounds. Additionally, as material derived from coal byproducts moves from left to right across the value chain shown in Figure 8, the distinctions between the material and that produced from a conventional rare earth ore are disappearing; in both cases, the feed to the separation step is derived from a purified rare earth solution.

New technologies are at varying stages of development as alternatives to solvent extraction. Development stages range from the laboratory to commercial operations. Given the complexities of a solvent extraction system, engagement of, and possibly expansion of an existing facility with an alternative technology may be the preferred alternative. Additionally, a 1,000 ton/year production capacity, at 7,000 operating hours per year, corresponds to a little over 300 lb/hour of product. At this capacity, scale-up of one or more alternatives to solvent extraction that are under development may be useful alternatives.

Based on the discussion in this section, the following steps could assist in re-establishing the rare earth value chain in the U.S., achieving near term production with currently available technologies:

1. ***Decentralized mineral processing facilities, near the mineral sources. These facilities would be designed to produce a mineral concentrate with an assay sufficient to permit shipping to a centralized extraction facility and minimize that facility's required throughput. Modular designs would allow for moving facilities as local resources are exhausted. Mineral processing research is required, including grinding and liberation studies, laboratory physical separations and flotation work, flowsheet design, and cost estimation. Location of the mineral processing facility near the source also simplifies tailings management, reducing transportation costs and allowing for the use of the tailings in, as an example, in reclaiming past mining operations to environmentally acceptable standards..***
2. ***Centralized chemical extraction and purification facilities, at first possibly involving existing or repurposed equipment. Feasibility is improved through production of the highest mineral concentrate grade achievable (see above). The scope and cost for a new facility is dramatically reduced if a high grade mineral concentrate can be produced.***
3. ***Separation of individual rare earths from a mixed chemical extraction concentrate could be achieved in the near term through (1) contracting with facilities that have alternatives to solvent extraction and (2) scale-up of new technologies under development to a composite 300 lb/hour of product capacity.***

5. National Security and Environmental Discussion

5.1. National Security Policy Drivers and Example Results Presented in this Document

In 2018, the Defense Industrial Base Report of the Defense Department (Department of Defense, 2018) provided a list of rare earth use in major weapons systems, which included lasers, radar, sonar, night vision systems, missile guidance, jet engines and alloys for armored vehicles.

Five Presidential Determinations, Pursuant to Section 303 of the Defense Production Act of 1950, as Amended, were issued by the White House on July 22, 2019 (Trump, 2019a-2019e). These determinations stated that the following domestic production capabilities are essential to the National Defense:

1. Separation and processing of Heavy Rare Earth Elements
2. Separation and processing of Light Rare Earth Elements
3. Rare earth metals and alloys
4. Neodymium Iron Boron Rare Earth Sintered Material and Permanent Magnets
5. Samarium Cobalt Rare Earth Permanent Magnets

Process steps and historical context involving the commercial rare earth value chain have been presented here in Section 3, and those discussions and the generic value chain found in Figure 8 relate to the domestic production capabilities of the first two items above (light rare earths and heavy rare earths). Once separated into individual rare earth compounds (at the end of the value chain in Figure 8), these compounds can be reduced to metal (third item above), as highlighted in Section 3.2.

A 2013 Congressional Research Service Report (Grasso, 2013) found the U.S. almost entirely lacking in "the refining, fabricating, metal-making, alloying, and magnet manufacturing capacity to process rare earths", although some production of magnet alloys was reported. The reference notes the alloy and magnet producers at the time.

With respect to the last two items listed above, from the July, 2019 Presidential Determinations, they are associated with neodymium iron boron (NdFeB) and samarium cobalt (SmCo) magnets. The use of rare earth elements in these magnets is as follows:

- Praseodymium (NdFeB magnets)
- Neodymium (NdFeB magnets)
- Samarium (SmCo magnets)
- Gadolinium (SmCo magnets)
- Terbium (NdFeB magnets)
- Dysprosium (NdFeB magnets)

To understand the size and scope of a coal-related rare earth production facility, we provide an example of the how one coal-related feedstock, an underclay from the Northern Appalachian Region could be leveraged to address U.S. demand for these materials. This material referenced is one of the samples from the data set discussed in Section 4.3, Sample NA-140 from Tetra Tech (2018a). While the extent of high rare earth concentrations in the geologic zone remains to be fully explored, the reserves of the underclay itself will be extensive, given the nature of underclays, and the tonnage may be in the same order of magnitude as the coal itself (in this case the Lower Kittanning). The distribution of rare earths in this material is shown in the chondrite-normalized curve in Figure 24.

This material is relatively rich in heavy rare earths. With respect to the six magnet-specific rare earths shown in the list above, the production rates of these elements, from an operation with an overall 1,000 metric ton per year production capacity, is shown in Table 10. The operation would produce over 200 metric tons per year of neodymium. Also of note is the projected production of over 57 metric tons per year of dysprosium.

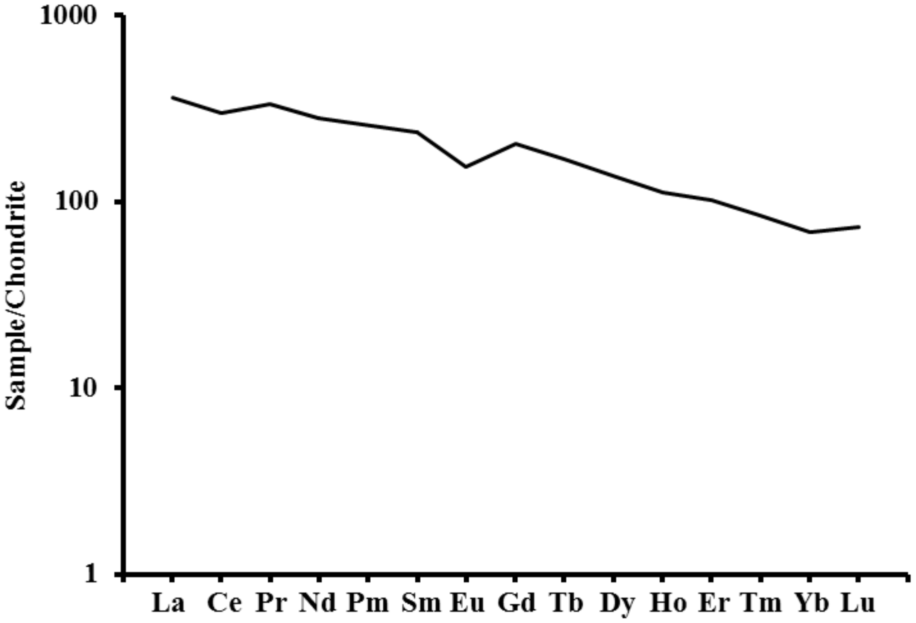


Figure 24: Chondrite-Normalized Rare Earth Distribution, Lower Kittanning Underclay.

Table 10: Example Magnet-Specific Rare Earth Content and Potential Production Rate (1,000 Metric Tons/Year Composite), Lower Kittanning Underclay

Element	Assay in Rock, ppm	Annual Production Rate
Praseodymium	29.6	50.7
Neodymium	127.8	219.0
Samarium	34.9	59.9
Gadolinium	40.3	69.1
Terbium	6.1	10.5
Dysprosium	33.6	57.5

5.2. Environmental Considerations Regarding Processing

Much has been written about the nature of processing byproducts in the rare earths value chain, notably with respect to radioactivity. That which might be considered a conventional rare earth value chain will produce byproducts as seen at each step (Figure 8). There are two items of note with respect to the steps shown in the Figure. The first is permit considerations for the process steps involving emissions and tailings. The second relates to management of any materials where radionuclides have been concentrated.

With respect to permits, a system requiring elevated temperature operation, notably including acid baking, is likely to involve one or more combustion sources, with attendant concerns about acid gas emissions. Potential emissions can include SO_2 in the case of acid baking, as well as gaseous fluoride species such as HF in where fluorocarbonate ores such as bastnasite are involved.

Given the relatively low run-of -mine head-grades involved with rare earth production, tailings management considerations can be very significant, both with respect to tonnage requirements and cost. Tailings production will be a function of ore grade. Referring to Table 8, over 4 million metric tons/year of material is required to produce 1,000 metric tons per year of rare earths if the head grade is 300 ppm. If the head grade is 1,000 ppm, this requirement is 1.25 million metric tons per year. Material that is not rare earths is gangue, and will ultimately report to process tailings. In these cases, the composite gangue production from the 300 ppm feedstock will be over 4 million metric tons per year, and the corresponding figure from the 1,000 ppm feedstock will be reduced by approximately 70%.

The two primary types of tailings produced by the process steps shown in Figure 8 are the concentrator tailings and hydrometallurgy tailings. Concentrator tailings have not been chemically altered. Hydrometallurgy tailings have been subject to chemical extraction and have been chemically altered. There are two tailings management considerations of note here:

- A rare earth ore concentration system would likely qualify as a “beneficiation” process (USEPA, 2000), with the tailings exempt from regulation under the Resource Conservation and Recovery Act (RCRA).
- Bevill determinations may be required for rare earth-specific process streams involving hydrometallurgy (the solids having undergone significant chemical changes). The result of the determination could be RCRA regulation of the materials as a hazardous waste (USEPA, 2012)

Costs associated with tailings management can be significantly higher if they are RCRA listed as hazardous waste. In the extreme, an operation processing 4,000,000 metric tons per year of 300 ppm material to produce 1,000 metric tons/year of rare earths could produce nearly 4,000,000 million metric tons per year of hazardous waste. Given hazardous waste disposal costs, this will not be economic. This is another argument for removing as much of the material as possible ahead of the hydrometallurgy step, using mineral concentration.

With respect to concentration of radioactive species in the process byproducts, this has caused concern in the past, and is likely to be influenced by the step in the value chain where the radioactive species are removed. This is of specific interest with respect to rare earth phosphate minerals, noting that, as discussed in Section 3.8. that monazite has also been used as feedstock for thorium production. Where the radioactive species is separated from the process stream with tailings from the mineral concentration step, little increase in their concentration can be expected.

In the case of the use of a caustic cracking step for a phosphate ore, such as has been used by two significant U.S. producers (W.R. Grace and Rhone-Poulenc), the process inherently produces a concentrated thorium-bearing stream. This would complicate tailings management. One potential solution was the use of uranium tailings sites for disposal. The Conquista uranium mill and tailings impoundment in Texas was permitted to receive byproduct material from the Rhone-Poulenc plant in Freeport (U.S. Nuclear Regulatory Commission, 2018).

6. Analysis

6.1. Summary of the Current Situation

The availability of coal byproducts as feedstocks for the production of rare earth products can offer opportunities for the restoration of key parts of the domestic production value chain that were lost two or more decades ago, notably the chemical extraction and separation steps.

The potential for currently available technologies to produce rare earth products from coal-associated feedstocks has yet to be fully explored. However, if the goal is the development of near-term production of rare earths, the adaption of existing technologies to service with these feedstocks will offer options for restoring key parts of the U.S. value chain that have been lost over the years. The potential for these options to achieve production in the near term at reduced cost is especially notable.

In addition to offering options for the re-establishment of domestic production of rare earth products in the near term, investigation of the application of currently available technologies to coal-associated feedstocks will also aid in the establishment of a technology baseline. Without data on the cost of rare earth production using currently available technologies, R&D investments in new technologies are difficult to justify.

Much of the research required to evaluate the potential application of commercial technologies to rare earth production, from coal-associated feedstocks, is basic in nature. Results are applicable to processes (physical separations, floatation, hydrometallurgy, etc.) that span multiple vendors' offerings, rather than specific to any vendor's technology. As such, laboratory work of this nature is of a broader and likely more significant scope than that which might be considered "technology development".

The use of currently available technologies in the context presented here may require the installation of new equipment, however, useful capacity to perform the required steps may be currently available, either existing plant capacity that might be available on a tolling basis, or existing plant equipment that might be repurposed for rare earth production. The basic research required for evaluation of existing technologies will also be useful in evaluating the adaption of currently available plant equipment for service in rare earth production.

It is worthy of note that similar research is required for both the adaptation of existing technologies and existing plant equipment to coal-associated rare earth feedstocks. This was successful in achieving near-term production at Mountain Pass when the property was first opened. The concept of repurposing existing technologies and equipment to new feedstocks is not unknown in the mining and metallurgy industries; on the contrary, it may be the first option investigated for new projects.

The chemical extraction of rare earths from ore minerals requires chemical transformation of those mineral components to soluble rare earth species. This step involves significant operating costs for reagents, harsh system environments, and can require elevated temperature operation. The reaction requirements are mineral-specific and controlled by thermodynamics. Example costs for this step, presented in Section 4.2, are several times higher than those associated with a mineral processing concentration system. However, it has been shown in Section 4.4 that the use of mineral processing technology (also itself less expensive) can dramatically reduce the scope (i.e. feed capacity) of the required downstream chemical extraction equipment. This in turn can reduce the cost associated with "most of the expense", reduce capital costs and lead times associated with new plant development and construction, and may expand the range of plant equipment that might be engaged for tolling or repurposed for rare earth production.

Some preliminary mineral processing research results, under the FE/NETL Rare Earths program, has shown limited ability for beneficiating coal byproducts as rare earth ores. However, no efforts were reported on the state of mineral liberation at the particle size distributions examined. More recent microscopy results from NETL have shown, in coal byproducts, mineral grain sizes that are not unlike those found in commercial ores, suggesting that they may be liberated at grinding product topsizes used in commercial grinding and flotation plants in operation and under development. Cost data presented show that while the grinding cost is significant, the overall cost of mineral processing along these lines remains a fraction of that required for chemical extraction.

Separation of a mixed, soluble stream of rare earths into individual compounds would require either new solvent extraction facilities, or facilities that can achieve the same results. New technologies have been under development that could provide alternatives to solvent extraction. Accomplishing significant production may require utilization of newer facilities, as well as the inclusion of technologies that are ready for scale-up to small commercial scale. An inventory of these technologies will assist in meeting the requirements for near-term production.

As a rare earth concentrate proceeds along the value chain, the contained rare earth value grows significantly, especially in comparison to shipping costs. This has been the case since the early days of the industry in the U.S., and in the past, mineral concentrates (monazite) produced in the Southeast U.S., Idaho, and overseas have been processed for extraction in New Jersey and the Midwest. Concentrates produced from California ore have been shipped to Colorado for separation, and to Pennsylvania for product manufacture. With the exception of the mineral concentration step, which processes a lower value material, the steps in the value chain do not need to be co-located. The more expensive steps, chemical extraction and separation, may be accomplished at centralized facilities with their own optimum location criteria. Multiple smaller (and modular) mineral processing facilities, located at the mineral sources, may provide an optimum set of feedstocks for centralized chemical extraction facilities.

Restoration of elements of the U.S. rare earth value chain, using coal byproducts as feedstocks, can also have significant alignment with projects to produce from other U.S. sources, such as hard rock deposits. As the value chain seen in Figure 8 moves to the right, the differences between streams produced from coal byproducts and other sources begin to disappear. Restoration of important process steps involving chemical extraction, and, especially separation into individual elements, can, if spare capacity is available, provide outlets for other rare earth projects under development that are not based on coal byproducts.

This document has presented known information with respect to the potential for rare earth production from coal byproducts, involving research results to date, economics, and potential application of currently available technologies. However, significant knowledge gaps remain with respect to the application of today's technologies to the use of these materials in the value chain.

Currently available technologies, including mineral processing and extractive metallurgy systems, are the result of decades of evolution in response to industrial needs, as well as decades of operations experience where they have been proven. The use of these technologies is likely the optimum option for achieving near-term, economic rare earth production from coal and coal byproducts. Further, many of these technologies, such as grinding, flotation, physical separation systems, and hydrometallurgy systems have been available for decades and are available from multiple vendors.

Past Federal government intervention in the U.S. rare earth industry was discussed in Section 3.8, especially events in the wake of embargos by producing countries that affected the availability of rare earth ores in the U.S. following World War II. A notable result of these embargoes was the almost immediate Federal sponsorship of geologic exploration for rare earths. Meanwhile, concurrent technology development relied on adapting existing technologies, such as used in placer beneficiation and flotation of bastnasite, to service rare earth ores.

Additionally, some operations that produced rare earth following World War II were originally producing another product (thorium), under contract to the Federal Government. As such, geologic exploration, the adaptation of existing production technologies, repurposing of production facilities, and operations under Federal sponsorship were all among the building blocks of the U.S. rare earth industry of the day. The significance of Federal-sponsored geology work cannot be understated; as seen in Figure 10, few items will compete with raw material rare earth content as an economic driver.

Many of the remaining knowledge gaps relate to the behavior of coal byproducts and their derivatives in these systems, and basic research is required to address these gaps. This research is of the type used in the development of new mining and metallurgical projects, and can provide information that is specific to a given process (for example, grinding), rather than a specific vendor's offering.

This type of research is best accomplished through close collaboration of the geosciences, mining, mineral processing, extractive metallurgy, and financial modeling disciplines. While this approach has been used for centuries, it has more recently been given the name *Geometallurgy*, which is "which geological data, mining data, and processing data are co-analysed to generate useful information and knowledge to optimize resource profitability" (David, 2019).

6.2. Knowledge Gaps

Knowledge gaps remain in all the disciplines mentioned above. These knowledge gaps are optimally addressed through collaboration of the required disciplines (Geometallurgy), and are grouped by discipline as follows:

1. **Resource Knowledge**: This includes geological, mineralogical, and mineable tonnage considerations. Specific items needed here are the geologic controls governing rare earth contents in the coal measures, controls affecting rare earth mineral grain sizes, resource tonnages (in the ground), and mineable tonnages. For some coal byproducts, such as preparation refuse, acid mine drainage sludges, and power plant ash, these tonnages can be collected from available information (as an example, inventories done by regulatory agencies). The tonnages that clear cutoff grades will be a smaller subset. Underclays will have much higher tonnages, and important collaboration with agencies such as the USGS will facilitate the required development of resource knowledge..
2. **Mining Knowledge**: This is the set of information required to establish the feedstock cost for financial modeling (see Equations 1-8b). For some byproducts (preparation refuse, AMD sludge, and power plant ash), these costs will include excavation and loading costs. For underclays, these will likely be incremental mining costs incurred after the associated coal has been removed.
3. **Mineral Processing Knowledge**: This is the knowledge base required for flowsheet design of a mineral processing system, and includes laboratory work related to mineralogy, grinding and liberation behavior, flotation, and physical separation work. The bulk of this is specific to the unit processes themselves rather than any vendor offerings. Also required here is an inventory of available (tolling or idle) facilities. This topic will also require the construction of a capital and operating cost database for modular, distributed facilities producing the highest feasible mineral concentrate grade. The higher the ore grade, the smaller the facility required in the next (most expensive) step.
4. **Extractive Metallurgy Knowledge**: This begins with identification of the rare earth minerals in the coal byproducts of interest, followed by thermodynamic evaluations of their behavior in

hydrometallurgical systems. An inventory should be developed of available facilities (tolling or idle), and the hydrometallurgical conditions that they are capable of achieving. Specific focus should be given to evaluating these conditions for rare earth extraction in the laboratory, using the types of rare earth minerals that have been identified in the coal byproducts of interest. Additionally, special attention should be paid to the possibility of contracting with new facilities that separate rare earths, for the processing of mixed concentrates produced from the chemical extraction step. New technologies under development, with respect to the separation step, should be inventoried, and considered for scale-up to ton per day capacity. This could both help with scale-up and diversify the available facilities for achieving a composite 1,000 metric ton per year of production capacity.

5. **Financial Modeling Knowledge**: A generic financial model, including coal byproducts as feed, should be constructed to describe the system shown in Figure 8. Without a baseline model, it is difficult to justify any expenditure on the development of “new technology”. The first application of this model would be as a financial evaluation toll for restoring the U.S. rare earths value chain (i.e. near-term production from coal byproducts), options for which have been discussed in this report.

6.3. Research Requirements

Research requirements to fill the remaining knowledge gaps will require both expertise and laboratory facilities in related to the following fields:

- Geosciences
- Mineralogy
- Mining and Mine Environmental Management
- Mineral Processing
- Extractive Metallurgy
- Financial Modeling

7. The Goal and Recommendations

7.1. The Goal

The goal here is the achievement of near-term rare earth production, using currently available technologies to produce a mixed, chemical extracted rare earth concentrate, and existing and new facilities to produce separated rare earths that can “plug in” to the metals and magnet production facilities.

Toward that end, the most likely pathway would include:

- Multiple modular mineral concentration systems producing the highest achievable mineral concentrate grade.
- A hydrometallurgy facility, likely available on a tolling basis or a repurposed facility, with a required capacity rendered as small as possible through production of high mineral concentrate grades in the preceding step.
- Contracting with recently installed facilities for separation, possibly also involving metric ton per day-capacity installations of new technologies, including those developed through funding from other Federal agencies, that can be scaled up to the target aggregate capacity.

7.2. Recommendations

As stated in the 2019 SME Mineral Processing and Extractive Metallurgy Handbook, “Mineral processing and extractive metallurgy are atypical disciplines, requiring a combination of knowledge, experience, and art" (Nelson, 2019). A wealth of these attributes is available within the U.S. mineral industries. There is no substitute for industrial experience if successful near-term rare earth production is the goal, and the largest repository of applicable industrial experience in the U.S. is the industry itself. Industrial experience has successfully helped guide the FE/NETL Turbines Program for decades, helping develop that program's successful track record of producing commercial results with Federal R&D expenditures. Modeling program formulation, associated with rare earths and other critical minerals, after the Turbines Program can help assure success, and will be a requirement if economic, near-term rare earth production is to be achieved.

Specific recommendations toward achievement of near-term rare earth production, from coal byproducts, using currently available technologies, are as follows:

1. Resource Knowledge
    1.1. Additional geologic field work should be conducted in coal-bearing strata that have been found to date to have the highest rare earth assays. This includes the lower Allegheny Group in the Northern Appalachian Region and the Raton Mesa field in Colorado and New Mexico. The result would be geologic models that may help predict the highest rare earth contents and largest rare earth-bearing mineral grain sizes in these resources.
    1.2. Develop preliminary estimates of both in-ground- and mineable tonnages for these resources.
    1.3. Compile publicly available data on current tonnages (on the ground) and annual generation rates for preparation refuse, AMD sludges, and power plant ash, adding ore grades where these are available.
    1.4. Resume sampling and analysis work in the coal measures to find higher assay materials in more locations in the U.S.
2. Mining Knowledge
    2.1. Develop generic mine plans for extracting these resources (i.e. preparation refuse, AMD sludge, power plant ash) including financial models.
    2.2. Develop generic mine plans for two example underclays, including financial models.
    2.3. Develop a database of permit requirements, to include mineral concentrator tailings disposal with the mine plan.
3. Mineral Processing Knowledge
    3.1. Conduct mineralogy, grinding, liberation, and laboratory separation work on example materials from the two areas where the highest rare earth assays have been found (Lower Allegheny in Northern Appalachia, Raton Mesa Field on Colorado and New Mexico). This will lead to preliminary flowsheet design.
    3.2. Commission multiple vendors of mineral processing equipment to develop preliminary plant design and cost data for modular mineral processing plants, based on results from 3.1.
    3.3. Develop an inventory of available (tolling or idle) mineral processing facilities.
4. Extractive Metallurgy Knowledge
    4.1. Develop a database of rare earth minerals found in the coal measures.
    4.2. Develop an inventory of available (tolling or idle) extractive metallurgy facilities, including their capabilities with respect to lixiviant, achievable process conditions, and solution purification capabilities.
    4.3. Begin theoretical and fundamental laboratory work on the hydrometallurgical extraction of the rare earth minerals found in the U.S. coal measures. Priority should be given to lixiviants and achievable process conditions associated with existing facilities.
    4.4. Hydrometallurgy tailings produced in the laboratory should be subjected to the Toxic Characteristic Leaching Procedure (TCLP) test, to determine whether they would be RCRA list able as hazardous waste.
    4.5. An inventory of recently built rare earth separation facilities should be constructed, as well as an additional inventory of technologies that are close to scale able to a metric ton per day capacity

This can result in a set of separation facilities with geographic diversity, in aggregate capable of producing 1,000 metric tons per year of rare earths.

5. Financial Modeling Knowledge
    - 5.1. An initial generic financial model should be constructed to represent the overall rare earth value chain, using currently available technologies, from ore through separated rare earth compounds.
    - 5.2. This model should be used first to guide activities toward near-term rare earth production in the U.S., as described in this report.
    - 5.3. Begin the development activities to achieve near-term rare earth production.

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