



The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part 1—Initial Survey of the Northern Appalachian Coal Basin

Christopher R. Vass¹ · Aaron Noble² · Paul F. Ziemkiewicz¹

Received: 25 February 2019 / Accepted: 6 June 2019 / Published online: 25 June 2019
© Society for Mining, Metallurgy & Exploration Inc. 2019

Abstract

The conventional rare earth element (REE) industry has historically sought to develop ore deposits where geologic processes have produced mineralized zones with commercially attractive REE concentrations. These deposits are extremely uncommon, particularly in the USA. Given the criticality of these materials and the need for sustainable domestic supply, the current research seeks to leverage other autogenous processes that lead to concentrated REE resources. One such process is the generation of acid mine drainage (AMD). AMD is very common in many coal mining districts and results from the exposure and oxidation of pyrite during mining. During the generation and migration of AMD, liberated sulfuric acid mobilizes several metal ions including REEs. Treatment of AMD is required under U.S.C §1251, the Clean Water Act, and often consists of neutralization, oxidation, and metal hydroxide precipitation. To investigate the deportment of REEs during this process, a field sampling campaign was undertaken, whereby the concentration of REEs in AMD and AMD precipitates was measured directly. In the nine sites evaluated in this study, the REE concentrations of the precipitates varied from 29 to 1286 ppm with an average of 517 ppm among the sampled sites. The individual elements were enriched compared with the associated bulk Northern Appalachian (NAPP) coal material by factors ranging from 3 to 15. Furthermore, the distribution of REEs in all precipitate samples favored the heavy REEs (HREEs) when compared with traditional REE ores. This research represents the first part of multi-part research endeavor to characterize, classify, and determine the practicality of refining REEs from AMD and its by-products.

Keywords Acid mine drainage · Rare earth elements · Coal by-products

1 Introduction

Rare earth elements (REEs) occur in a wide variety of geologic formations; however, these occurrences rarely meet the necessary minimum cutoff limits to facilitate profitable extraction and refining. In cases where the ores do meet cutoff grade limits, the mineralization often contains significant concentrations of the actinides thorium and uranium. The mining and processing of these deposits often entail detrimental environmental consequences and higher operating costs owing to waste disposal and handling [1]. Given the scarcity of

geologic settings that lead to enriched REE deposits, more than 90% of REE production occurs in one country: China [2]. This near-monopoly creates a potential impairment for the USA and other countries where REEs are not readily produced. For example, during 2010 to 2012 rare earth crisis, China imposed reduced export quotas during a period of increased demand. This constrained market caused prices for many REEs to increase more than 100-fold, leading to shortages in downstream markets [3]. As the demand peaked during this period, almost \$6,000,000,000 of investment capital was raised by junior mining companies to secure additional REE resources outside of China. Unfortunately, by 2015, many of these companies entered bankruptcy or lost interest in REEs due to the lower prices. This event indicates the overall importance of REE supply on a local and global basis as well as the need to consider alternative resources [4].

Despite the increased investment, only two REE mines recently started production outside of China [5]. The Mount Weld deposit in Australia began production in 2013. The ore from Mt. Weld is processed in Malaysia by Lynas

✉ Christopher R. Vass
chris.vass@gmail.com

¹ West Virginia Water Research Institute, PO Box 6064,
Morgantown, WV 26506, USA

² Virginia Tech Mining and Minerals Engineering, Holden Hall 100,
Virginia Tech, 445 Old Turner Street, Blacksburg, VA 24061, USA

Corporation, whose operating permit has recently come under controversy concerning the disposal of radioactive waste [6]. The second operation, Mountain Pass located in the USA, has experienced instability in reaching full-scale production due to lower REE prices and the high distribution of light REEs (LREE) in the orebody [7].

Many industrial processes rely on REEs for their products including catalysts, metallurgy, petroleum refining, catalytic converters, ceramics, phosphors, magnets, and electronics. Currently, the USA consumes approximately 12,000 metric tons of REEs per year [8]. Of that, the Department of Defense uses less than 5%, or approximately 600 metric tons [9]. Future demand for individual REEs is difficult to predict due to the number of elements involved and variety of uses; however, given the increasing forecasted demand for green technologies and electronic devices, many researchers believe that demand for REEs will also increase [10, 11]. Specifically, supply concerns regarding the heavy REEs (HREE) are of primary concern because identifying economically feasible HREE-enriched deposits outside of China has been unsuccessful [12].

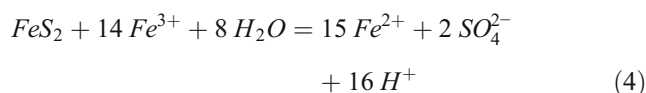
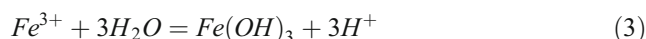
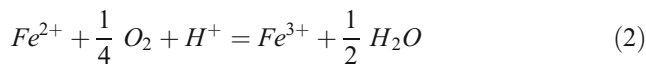
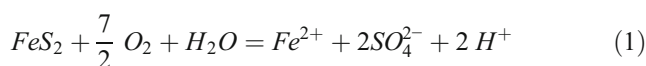
Given the disparity between current REE supply and future REE demand, many stakeholders including researchers, national governments, and private companies have attempted to identify alternative and unconventional REE resources. For example, by-products of phosphoric acid production have been identified as a potential alternative source of REE production [13–16]. Also, there has been an increased interest in recycling of REEs, further indicating the need for alternative REE supplies [17]. While the overall production volume of REEs may alleviate some criticality concerns of the REE supply, it will not successfully compensate for the projected increase in demand over the next several years [18].

The presence of REEs in coal has long been established by many researchers [19–22]. More recently, the classification of REEs as critical minerals by the USA has brought an increased interest in the availability of a domestic REE supply. Since 2014, the US Department of Energy has analyzed the economic feasibility of recovering rare earth elements from coal and coal by-products [23]. Most initial studies focused on the recovery of REEs from coal tailings (refuse) and coal fly ash [24].

In June 2015, researchers at West Virginia University found significant concentrations of REE in precipitates formed during acid mine drainage (AMD) treatment [25]. These findings formed the basis for a detailed study of REE occurrence in the northern (NAPP) and central (CAPP) Appalachian Coal Basin AMD and its by-products. Consequently, this research was developed to identify the grade and potential recovery of REEs from AMD and its by-products.

In the Appalachian Coal Basin, AMD constitutes one of the most significant and widespread water quality challenges.

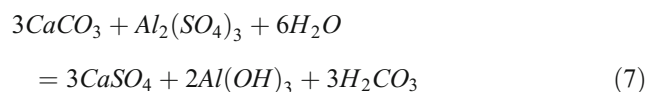
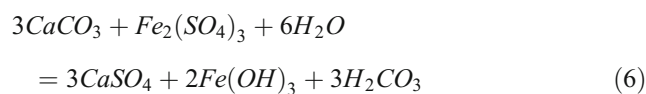
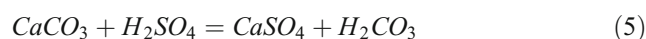
AMD occurs when pyrite-bearing mine spoil oxidizes after mining. It consists of acidity and a varied suite of metals such as iron, aluminum, and manganese as well as the dominant anion, sulfate. Mining exposes these sulfide minerals to weathering, and the increased mineral surface area then leads to elevated oxidation and leaching, resulting in AMD formation as follows [26]:



The detrimental effects of AMD are well-documented and include adverse impacts on nearby streams [27–30]. Over the last 50 years, researchers have extensively studied the factors controlling AMD and developed methods that predict the severity and extent of AMD based on mining practices and geological properties [28, 31].

Per Section 402 of the Clean Water Act, mine operators are obliged to treat AMD prior to discharge. This treatment often incorporates alkaline addition and oxidation to increase the pH and remove metal ions from solution [26, 30, 32, 33]. This method of treatment can be incorporated through the use of different processing systems, both active and passive, to maximize treatment efficiency, minimize cost, and ensure environmental compliance [29, 34].

As AMD is treated by alkaline addition, the dissolved metal ions precipitate as hydroxides (denoted AMD sludge, AMD precipitate, or AMDp) while clean water is discharged into the receiving stream as follows (when using $CaCO_3$ as the neutralizing agent) [35]:



The chemical and morphological characteristics of AMDp are unique to each treatment site and are a function of the composition of the AMD, type of neutralization chemical used, the amount of aeration, the extent of carbon dioxide release, and the configuration of the treatment system incorporated [26, 36]. Typically, AMDp is composed of an iron-rich sludge that can contain other metals and vary from granular to gelatinous in consistency [36]. Moreover, the AMDp

can contain fine to amorphous flocs that are greatly dependent on the treatment chemical used [37]. As a result, the AMDp from each mine site will vary as to the exact makeup of hydroxides, carbonates, and composition of metals. Lastly, this bulky and often moisture-rich sludge is difficult to handle and dispose of effectively. Alternative applications for this material could prove beneficial to the public and private entities liable for the treatment and disposal of AMD [38].

AMD chemistry represents the integration of reactions that occur on much smaller scales such as the pore water surrounding pyritic versus non-pyritic rock grains and localized oxidizing versus reducing environments. This integration occurs over the scale of mines that range in extent from hundreds of acres to 20 square miles or more as is the case of large, underground mines. AMD precipitate further integrates these variations in discharge chemistry by aggregating the dissolved metal loads over periods of months or years. The volume of mine drainage, either derived from surface or underground sources, changes seasonally according to the volume of infiltrating water; but, ionic composition fluctuates within narrow bounds at a given source. Thus, loads and concentrations vary inversely between the wet winter months and the dry late-summer to fall seasons.

While several prior studies have evaluated the partitioning and concentration of major AMD metals such as iron, aluminum, and manganese, few studies to date have evaluated the quality and quantity of REEs in AMD and AMD treatment by-products. Moreover, the lack of technical data on REEs in AMD limits the ability to answer key questions on the prospectivity (a predictive tool for choosing the location for further exploration efforts) of a potential REE resource derived from AMD. These questions include but are not limited to:

- What are the typical REE concentrations in AMD and what factors influence those concentrations?
- What is the size of the REE resource that can be realized from AMD in the Appalachian coal basin?
- What is the contained value of REEs in AMD and AMDp, and is this contained value sufficient to merit further study?
- What is the conceptual framework for the extraction and processing of these resources?
- What environmental, social, legal, and other intangible considerations must be resolved prior to resource development?

The objective of this manuscript is to evaluate the prospectivity of AMDp as an alternative source of REEs. The current technical literature lacks data from systemic studies that describe the content and quality of REEs in AMD and AMDp, and, as a result, few researchers have critically analyzed the value chain that can be derived from this current

waste stream. This manuscript will describe a prospecting study where nine AMD treatment sites were extensively sampled and analyzed to determine the variation among and within sites as well as the partitioning of REEs among the AMD, AMDp, and treated water streams. Following this initial characterization, a regional production model was developed and used to estimate the resource size and potential value of REEs from AMD. Lastly, the paper investigates the technical, environmental, and civil considerations that would accompany REE extraction from AMD.

2 Materials and Methods

To assist in assessing the prospectivity of REEs in AMD, nine Northern Appalachian coal mine sites with AMD outflows were chosen for detailed sampling that encompassed a variety of coal seams and mine types. Each of these sites employs active chemical treatment of the AMD to meet effluent limits. As a result, both AMD and AMDp were available for sampling. Figure 1 shows the location of these sites within the NAPP basin on a county level, while Table 1 shows the unique characteristics of each site.

Several classes of AMD were represented in the population of sampling sites. The two primary mine categories included underground and surface. The surface category included refuse storage areas and impoundments. Next, the mines were classified as either above or below drainage (a.k.a. flooded). Flooded mines that are located below drainage typically contained net-alkaline water in contrast to the net-acidic water commonly associated with AMD [39, 40]. This difference is caused by the restriction of pyrite oxidation under anoxic, flooded conditions and the gradual accumulation of the alkaline, bicarbonate ion buffer [41]. Under unflooded, oxidizing conditions, pyrite oxidation is unrestricted and acid generation may be controlled by either neutralizing minerals in the spoil or the eventual exhaustion of pyrite [42, 43]. This distinction is significant as the extent of acid generation is anticipated to influence REE loading.

Both aqueous AMD and solid AMDp samples were collected over periods of between four and 17 months, depending on the sampling site. Typically, both the influent and effluent aqueous streams were collected at the AMD treatment plant. Additionally, three AMDp samples were collected at the site during each visit.

The sampling interval was chosen based on the inherent variability, quality, or quantity of the AMDp produced at each site. For example, site AMD_7 was sampled frequently even though it had a low REE concentration in the AMDp because it had a high flux of AMD and was therefore a potentially high-volume producer of REEs. Likewise, site AMD_3 had the highest concentration of total rare earth elements (TREEs) in the population and was therefore intensively sampled.

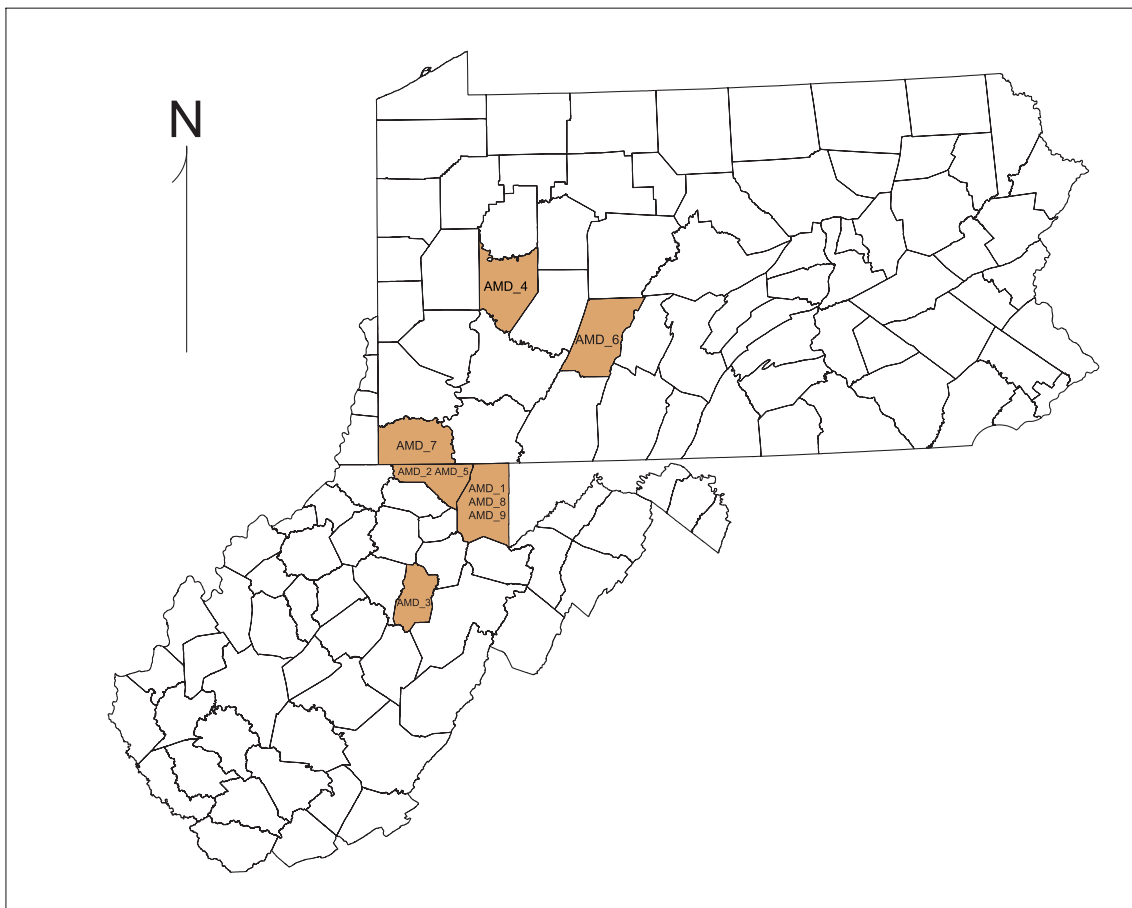


Fig. 1 County level location of the AMD sites evaluated

The collected aqueous and precipitate samples were then analyzed using ICP-MS for the REEs by TestAmerica Laboratories, Inc. and SGS Canada Inc., respectively. Both

laboratories are certified by their respective state/provincial agencies to undertake both aqueous and solid REE analysis. Additionally, West Virginia University's National Research

Table 1 AMD site topographic settings and characteristics

Site ID	State	County	Influent pH	Treatment chemical	Seam	Mine type	Flooded/above drainage
AMD_1	WV	Preston	2.73	Lime	Freeport	UG	Above drainage
AMD_2	WV	Monongahela	6.91	Lime	Pittsburgh	UG	Flooded
AMD_3	WV	Upshur	3.46	NaOH	Kittanning	SM	Above drainage
AMD_4	PA	Armstrong	3.17	Lime	Kittanning	SM/UG	Above drainage
AMD_5	WV	Monongahela	2.88	Lime	Freeport	UG	Above drainage
AMD_6	PA	Cambria	5.38	Lime	Kittanning	UG	Flooded
AMD_7	PA	Greene	6.58	Lime	Pittsburgh	UG	Flooded
AMD_8	WV	Preston	2.69	Ammonia	Freeport	UG	Above drainage
AMD_9	WV	Preston	2.70	Lime	Freeport	UG	Above drainage

UG, underground mine; SM, surface mine

Center for Coal and Energy Analytical Laboratory (NRCCE) used an ICP-OES to analyze the other major ions. AMDp was digested using a sodium peroxide (Na_2O_2) fusion and re-dissolved in hydrochloric acid. This method appears to be comparable with the United States Environmental Protection Agency's total digestion method 3052 for REEs. Method detection limits (MDL) for the aqueous rare earths were typically in the 0.02 ppb range, while the solid REE analysis had MDL ranging from 5 to 0.5 ppm. Major metal ions were measured in aqueous samples with MDL similar to those of the aqueous REEs.

Aqueous samples were collected in a clean 1000-mL HDPE sample bottle. Next, this sample was then split into two separate containers (one preserved and one raw) for further analysis. Dilute nitric acid (2%) was added to the preserved sample bottle to prevent precipitation or adsorption of the target analytes during shipping. Afterwards, the raw water samples were stored at 4 °C, until it was ultimately delivered to the NRCCE laboratory for major ion analysis. Finally, the aqueous REE samples were shipped to the TestAmerica laboratory in their preserved state.

Precipitates were collected by hand using a shovel or post-hole digger at or near the edge of the drying cell. These samples were placed in new 1-gallon HDPE sample buckets. Later, the AMDp samples were split into 50-mL representative aliquots for the ICP analysis in a laboratory setting. These sub-samples were then placed in 50-mL digestion tubes for transport to SGS Canada Inc. for analysis.

Representative samples of entire AMDp cells were often difficult to impossible to safely obtain due to the depth and semi-liquid consistency of the precipitate. Therefore, many of the collected samples were located near the edge of drying cell ponds. Due to this sampling procedure, bias may have been introduced into some of the results. For example, the AMDp may stratify within the settling pond with varying qualities dependent upon depth. Alternatively, where allowed, various AMDp samples were collected at differing depths across a drying cell for select sites. Figure 2 shows a typical AMDp drying cell where representative samples were difficult to obtain. Finally, at sites that pump an AMDp product to abandoned underground mine works, the samples were collected from the clarifier underflow.

Several authors, including Seredin and Dai [44], Moldoveanu [45], and Gupta [46], have used different classifications methods to assist in analyzing potential REE resources. These classifications can be based on supply-demand relationships (critical REE versus excessive REE) or simple atomic number (heavy REE vs. light REE). For this paper, the following classifications will be observed:

- Heavy REEs (HREE): Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
- Light REEs (LREE): La, Ce, Pr, Nd, Sm, Eu



Fig. 2 Typical AMDp drying pond found in NAPP

- Total REEs (TREE): HREE + LREE
- Critical REEs (CREE): Y, Nd, Eu, Tb, Dy

3 Results and Discussion

The data from the field sampling campaign was used to assess the prospectivity of the REE resource in AMD. Key questions include the concentration of REEs in AMD and the factors that influence concentration, the overall size of the potential resource, the market value, conceptual framework for extraction and processing, and environmental and civil considerations. Each question is addressed in further detail below.

3.1 Concentration of REEs in AMD and AMDp

Tables 2 and 3 show the analytical results of the sampling campaign for AMD and AMDp respectively. TREE concentration averaged 258 $\mu\text{g/L}$ for the aqueous AMD influent. This low REE concentration may seem to preclude AMD as a viable REE feedstock; however, the high enrichment factor after treatment of AMD is significant. Of the samples tested, the average concentration of REEs in AMDp was 517 g/t: a concentration factor of 2000 times, with individual REE concentration factors varying from 1300 to 8400 times. These data show that the process of AMD migration through coal strata and the subsequent treatment of AMD produce a net enrichment, because the average TREE concentration in AMDp (517 ppm) is considerably higher than that of US coal (66 ppm) or the crustal abundance (206 ppm) [19, 47]. Also, REE concentrations in AMD treatment plant effluent was extremely low, often below detection limits, indicating the REEs exited the treatment plant as a precipitate.

Table 2 Average REE concentrations for aqueous AMD influent at nine treatment facilities in PA and WV

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9	Mean	% TREE
Mine type	(txt)	UG	UG	SM	UG	UG	UG	UG	UG	UG	–	–
Horizon	(txt)	AD	BD	AD	AD	AD	BD	BD	AD	AD	–	–
Seam(s)	(txt)	UFP	PITT	KITT	KITT	UFP	KITT	PITT	UFP	UFP	–	–
AMD samples	(#)	4	12	17	4	17	4	13	6	4	9	–
Sc	(ug/L)	2.63	0.83	6.11	38.70	46.50	3.16	3.82	8.05	11.38	13.46	5.2%
Y	(ug/L)	18.38	2.15	41.51	355.03	72.84	16.70	13.27	42.42	66.78	69.90	27.1%
La	(ug/L)	10.48	0.42	11.55	34.65	12.75	2.53	0.32	10.08	20.08	11.43	4.4%
Ce	(ug/L)	31.23	1.41	35.69	137.60	48.81	7.73	1.49	37.33	72.88	41.57	16.1%
Pr	(ug/L)	4.83	0.22	4.34	27.18	7.86	1.07	0.35	6.08	11.40	7.04	2.7%
Nd	(ug/L)	23.00	1.14	20.06	172.15	40.39	5.70	2.55	31.10	56.35	39.16	15.2%
Sm	(ug/L)	6.35	0.27	5.34	72.05	12.27	1.73	0.92	9.25	16.98	13.90	5.4%
Eu	(ug/L)	1.40	0.06	1.40	19.78	3.22	2.83	0.29	2.27	4.15	3.93	1.5%
Gd	(ug/L)	6.98	0.43	7.72	103.08	17.80	3.13	1.83	11.60	20.90	19.27	7.5%
Tb	(ug/L)	0.96	0.05	1.31	15.80	3.35	0.51	0.28	1.80	3.25	3.03	1.2%
Dy	(ug/L)	5.05	0.36	7.95	82.30	20.82	3.15	1.78	10.32	17.40	16.57	6.4%
Ho	(ug/L)	0.86	0.05	1.51	14.40	4.04	0.61	0.42	1.82	3.08	2.98	1.2%
Er	(ug/L)	2.18	0.20	4.26	34.95	11.79	1.60	1.21	4.95	8.15	7.70	3.0%
Tm	(ug/L)	0.28	0.01	0.53	4.33	1.49	2.64	0.15	0.62	1.03	1.23	0.5%
Yb	(ug/L)	1.58	0.13	3.12	23.53	9.14	1.05	0.81	3.88	6.50	5.52	2.1%
Lu	(ug/L)	0.23	0.01	0.45	3.43	1.30	2.62	0.13	0.55	0.88	1.06	0.4%
pH	(pH)	2.73	6.91	3.46	3.17	2.88	5.38	6.71	3.92	2.70	4.20	–
TREE	(ug/L)	116	8	153	1139	314	57	30	182	321	258	100.0%
HREE	(ug/L)	39	4	74	676	189	35	24	86	139	141	54.6%
LREE	(ug/L)	77	4	78	463	125	22	6	96	182	117	45.4%
CREE	(ug/L)	49	4	72	645	141	29	18	88	148	133	51.4%

SM, surface mine; UG, underground mine; AD, above drainage; BD, below drainage; UFP, Upper Freeport; KITT, Kittanning; PITT, Pittsburgh

3.1.1 TREE in Pre and Post Water Treatment

Further evaluation of the influent and effluent streams at each site confirmed that the bulk of the REEs were recovered into the AMDp. Figure 3 compared these influent and effluent streams from the nine sites. From these data, it was shown that the AMD treatment process reduced the REEs in the effluent by an average of 78%. Likewise, the major polluting metals (Al, Fe, Mn, Mg) were also reduced by an average of 57%. As a result, an economic method for recovering REEs from AMDp could further incentivize operators to meet or even exceed the governing effluent limits.

Results from this characterization of REEs in AMD by-products indicated that on average, AMDp contained 517 ppm of REEs on a dry weight basis, as seen in Table 3. In addition, Table 4 shows the 95% upper and lower confidence intervals for repeat samples taken from the same site. In many cases, samples from a given site showed very little variability with respect to REE concentration and distribution. This finding is likely due to the large time scales and spatial scales that govern AMD production and migration. Thus, the

concentration of REEs in AMD represents the integration over several decades and large volumes of rock.

3.1.2 Factors Controlling REE in AMD and AMDp

Each coal mine has unique geochemical features even among those that are in relatively close geographic proximity and coal seam. Furthermore, the elevation of the mine works, whether above or below drainage, also has a clear effect on the quantity of REEs in the aqueous AMD discharging from the mine. Treatment chemistry further influences the REE concentration in AMDp based on the type of treatment required at the mine. As shown in Tables 2 and 3, the sites AMD_2, AMD_6, and AMD_7 have significantly lower TREE concentrations, in both the AMD and AMDp, than the other mines. These three mines are all below-drainage flooded mine complexes. The water chemistry of these flooded AMD mines differs significantly from above-drainage mines. Typically, the pH of AMD discharged from these mines are of higher value (as seen in Table 2) since the oxidizing conditions that produce AMD are not present.

Table 3 Average REE concentrations for AMDp at nine treatment facilities in PA and WV

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9	Mean	% TREE
Mine type	(txt)	UG	UG	UG	UG	SM	UG	UG	UG	UG	–	–
Horizon	(txt)	AD	AD	AD	AD	AD	AD	BD	BD	BD	–	–
Seam(s)	(txt)	KITT	UFP	UFP	UFP	KITT	UFP	KITT	PITT	PITT	–	–
AMDp samples	(#)	14	12	52	12	52	12	13	40	36	27	–
Sc	(g/t)	13.25	14.54	54.87	14.54	15.56	13.71	9.85	3.88	1.32	15.72	3.0%
Y	(g/t)	198.21	141.42	98.33	129.01	396.74	96.37	52.40	8.31	6.67	125.27	24.2%
La	(g/t)	44.94	94.03	20.39	126.75	110.31	149.96	8.85	2.98	3.11	62.37	12.1%
Ce	(g/t)	138.14	127.42	72.07	130.31	296.27	169.00	24.60	8.13	7.22	108.13	20.9%
Pr	(g/t)	21.72	20.05	11.43	19.89	37.21	23.28	3.71	1.16	0.90	15.48	3.0%
Nd	(g/t)	114.07	96.42	55.58	95.92	163.92	111.92	17.38	5.48	4.36	73.89	14.3%
Sm	(g/t)	37.48	29.29	16.74	28.38	41.36	30.18	4.73	1.93	0.82	21.21	4.1%
Eu	(g/t)	9.40	7.35	4.28	7.08	10.84	7.21	1.25	0.64	0.30	5.37	1.0%
Gd	(g/t)	49.36	35.69	24.17	34.98	61.18	35.33	8.52	2.25	1.18	28.07	5.4%
Tb	(g/t)	6.92	5.80	4.43	5.62	10.22	5.53	1.43	0.55	0.30	4.53	0.9%
Dy	(g/t)	37.10	31.15	26.11	32.47	61.72	31.13	8.05	1.94	0.78	25.61	5.0%
Ho	(g/t)	6.86	5.96	5.18	6.25	12.64	6.04	1.84	0.46	0.20	5.05	1.0%
Er	(g/t)	17.38	15.48	14.01	16.45	34.18	16.05	4.72	1.07	0.46	13.31	2.6%
Tm	(g/t)	2.12	2.16	1.95	2.21	4.48	2.06	0.68	0.47	0.40	1.83	0.4%
Yb	(g/t)	11.72	12.12	11.15	12.54	25.38	11.61	3.19	0.70	0.37	9.87	1.9%
Lu	(g/t)	1.76	1.80	1.68	1.86	3.70	1.72	0.57	0.35	0.30	1.53	0.3%
U	(g/t)	7.41	6.83	5.38	8.19	5.22	4.83	0.58	0.75	0.94	4.46	0.9%
Th	(g/t)	4.91	14.37	9.64	7.39	3.96	8.98	0.38	0.82	0.64	5.67	1.1%
TREE	(g/t)	710	641	422	664	1286	711	152	40	29	517	100.0%
HREE	(g/t)	345	266	242	256	626	220	91	20	12	231	44.6%
LREE	(g/t)	366	375	180	408	660	492	61	20	17	286	55.4%
CREE	(g/t)	366	282	189	270	643	252	81	17	12	235	45.4%
TREE Enrichment	(–)	624	1995	1344	3647	8412	6111	2675	1360	3712	2007	–

SM, surface mine; UG, underground mine; AD, above drainage; BD, below drainage; UFP, Upper Freeport; KITT, Kittanning; PITT, Pittsburgh

The current data generally shows that increased pH in raw AMD corresponds to a lower TREE concentration. The quantity of free hydrogen ions available for leaching is a major factor in liberating REEs from the surrounding strata. A correlation of influent water pH and TREE concentration in AMD was derived from the dataset. Figure 4 shows this relationship. Of interest is the lack of data between the pH values 4 and 5 labeled as an “un-buffered zone,” where Fe and Al buffering in AMD results in areas of pH stability in the regions above and below the pH range of 4 to 5, respectively. This bimodal behavior is likely due to the carbonate buffering in the upper pH range and pyrite oxidation at the lower pH range as described by Cravotta et al. [48]. Indeed, this bimodal distribution is a result of the differences in geochemistry between the flooded underground and above-drainage mines. This differentiation may indicate that different processing paths will be required for the different influent geochemistry profiles.

When compared with the average crustal abundance and the average content of REEs in coal, the AMDp contained a

significantly higher abundance of REEs as shown in Fig. 5. Except for Sc, all the REEs in AMDp were found in higher concentrations than in those of either the crustal abundance or native coal material. On average, the REEs in AMDp were 3.5 times more concentrated than the crustal abundance and more than 10 times more concentrated than typical REEs found in coal [19, 47]. More important is the interaction between AMD and the mineralogy of the coal seam. AMD typically seeps through not just the coal seam but the surrounding strata as well. As indicated by Zhang et al. [49], the REEs typically are associated with the gangue materials within the coal seam and not the coal itself.

3.2 Basin Production Estimate

The results from the sampling campaign are analogous to an initial prospecting survey and may be used to approximate the overall regional production at a high level. Unfortunately, comprehensive AMD flowrate datasets are practically

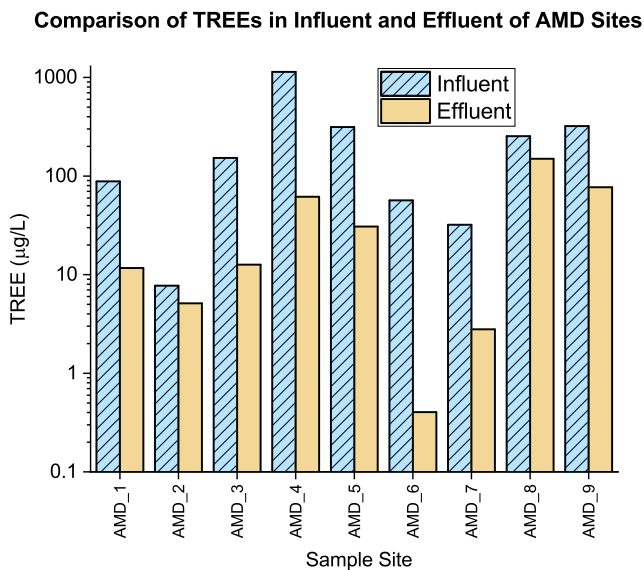


Fig. 3 Difference in the influent and effluent TREE values for nine NAPP AMD sites

nonexistent due to the complexity of flow interactions, large seasonal variations, and the temporal nature of the effluent constituents. As a result, multiple AMD outfall datasets were compiled to estimate the regional AMD flow rate estimate by the authors. These data are composed of projects completed by the West Virginia Water Research Institute, Pennsylvania Abandoned Mine Land Department, West Virginia Department of Environmental Protection, and various studies from others [50–52].

In all, this regional estimate encompasses over 1100 unique AMD outlets, predominately in the NAPP region and indicated that the regional AMD flow rate is approximately 94,700 L/s. Consequently, this estimate may be considered conservative in relation to the actual flow rate. Previously, Stewart et al. provided a regional flow estimate of 417,448 L/s [53]. By comparison, the methods used by Stewart could lead to overestimation of the true quantity of AMD due to the incorrect assumption that all coal mining leads to the generation of AMD and neglecting the spatial reduction of multi-seam extraction, which is common in Central Appalachia (CAPP). Given these complexities, an accurate and precise determination of AMD flowrate for the Appalachian basin would require a more extensive study well beyond the scope of this research. Nevertheless, for the

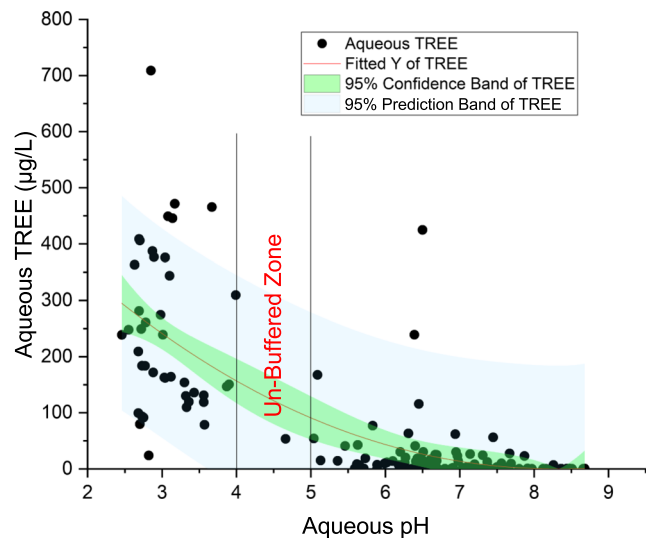


Fig. 4 Relationship between pH and aqueous TREE concentrations

purpose of the current study, both Stewart’s methodology and the authors’ methodology were used to estimate the high and low AMD flow rate values, respectively. In addition, the REE content of this AMD was assumed to be the average for the NAPP values shown in Table 5. Given these inputs, the estimated REE production from AMD was determined to be between 771 to 3400 t of REEs per year. The high variance in the two estimated production rates indicates that further exploration of the resource is required to identify an economically feasible process to extract REEs from AMD.

3.3 Valuation

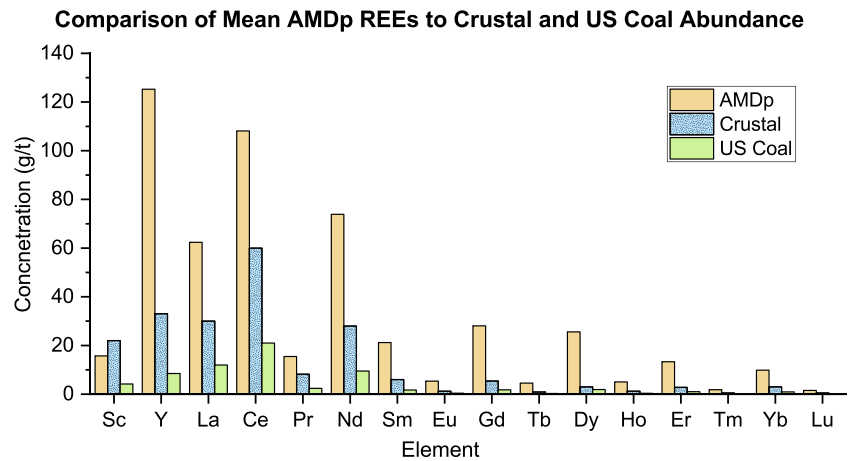
To estimate the contained value of REEs in AMD, an average price deck for the REEs was compiled for the lanthanide series plus yttrium from 2008 through 2015 using the USGS Mineral Yearbooks [54–61]. These 8 years contain the global REE peak prices observed during 2011 as well as the preceding and post market minimums. A similar process for economic valuation has been used in similar coal-based REE deposits [62, 63]. Scandium was not included in this analysis, as the unit high price tends to grossly distort the final values. Additionally, the current global production of scandium is very small, and a large influx of Sc to the market could drastically change the supply and demand relationship [64].

Table 4 AMDp 95% upper and lower confidence intervals for mean TREE values

Site	(txt)	AMD_1	AMD_2	AMD_3	AMD_4	AMD_5	AMD_6	AMD_7	AMD_8	AMD_9
Mean TREE	(g/t)	711	29	1286	710	422	152	40	664	641
95% UCL	(g/t)	507	24	1202	585	406	131	17	504	575
95% LCL	(g/t)	916	33	1369	836	439	173	64	825	707

UCL, upper confidence level; LCL, lower confidence level

Fig. 5 Comparison of mean AMDp REE concentrations to that of crustal and US coal abundance values [19, 47]



The referenced prices were provided on an oxide basis and were averaged across the 8-year span for the present data. Next, the oxide prices were converted to metal equivalents using standard metal to oxide ratios. Table 6 shows the price deck used for this preliminary valuation.

From these prices, two different economic indicators were evaluated for the mean AMDp REE concentration (minus Sc). First, the basket price was determined by weighting the elemental price by the elemental distribution within the AMDp. This indicator was representative of a what 1 kg of final REE metal product would command on the open market, assuming a representative distribution of REEs were produced from the mean AMDp values. This could also be viewed as the gross average selling price for the AMDp product before fixed and variable mining costs are deducted. Additional assumptions in the generation of this metric assume that all elements have demand in the market and all were equally recoverable in the refining process. Overall, the basket price would be a poor indicator when choosing between two projects; however, it does provide a good comparison of an ore’s potential value when identical elemental prices were used between projects.

The second indicator evaluated was the in situ price. This value represents the unitized value of 1 t of the resource in the ground. In relation to AMDp, this metric would correspond to

1 t of AMDp, on a dry weight basis, located in a storage pond. This price was also exclusive of mining, processing, and milling costs; therefore, it was not an indicator of economic viability. Furthermore, this price assumed all elements were fully recovered and salable. Nevertheless, this benchmark may be used to compare the gross unitized value of reserves and resources between multiple projects. When the in situ price of \$89.08/kg TREE was applied to the REE production models

Table 5 Low and high regional flow rate estimates

Regional AMD flow estimate	Units	Low ¹	High ²
PA	(L/s)	51,401	–
WV	(L/s)	24,095	–
OH	(L/s)	18,900	–
MD	(L/s)	317	–
Total	(L/s)	94,712	417,448
TREE concentration (mg/L)	(mg/L)	0.258	0.258
TREE load	(t/year)	771	3400

¹ Regional flow estimates based on proprietary AMD studies

² Regional flow estimate by Stewart et al. [53]

Table 6 Price deck used for economic evaluation consisting of average pricing from USGS Mineral Yearbooks (2008–2015)

Element (txt)	Mean Concentration (g/t)	% TREE (%)	Elemental Value (\$/kg)	Basket Price (\$/kg)	In situ Price (\$/ton)
Sc*	15.72	–	\$5628.83	–	–
Y	125.27	25.0%	\$85.53	\$21.36	\$10.72
La	62.37	12.4%	\$32.73	\$4.07	\$2.04
Ce	108.13	21.6%	\$35.23	\$7.60	\$3.81
Pr	15.48	3.1%	\$123.96	\$3.83	\$1.92
Nd	73.89	14.7%	\$109.10	\$16.07	\$8.06
Sm	21.21	4.2%	\$158.86	\$6.72	\$3.37
Eu	5.37	1.1%	\$1817.44	\$19.47	\$9.77
Gd	28.07	5.6%	\$183.49	\$10.27	\$5.15
Tb	4.53	0.9%	\$1438.75	\$13.00	\$6.52
Dy	25.61	5.1%	\$681.84	\$34.81	\$17.46
Ho	5.05	1.0%	\$859.11	\$8.65	\$4.34
Er	13.31	2.7%	\$195.83	\$5.20	\$2.61
Tm	1.83	0.4%	\$2093.80	\$7.66	\$3.84
Yb	9.87	2.0%	\$455.48	\$8.96	\$4.49
Lu	1.53	0.3%	\$3269.27	\$9.95	\$4.99
TREE	502	100.0%	–	\$177.62	\$89.08
HREE	215	44.6%	–	\$119.87	\$60.12
LREE	286	55.4%	–	\$57.76	\$28.97
CREE	235	45.4%	–	\$104.73	\$52.52

*Sc Excluded from evaluation due to the inherent volatility

in Table 5 at the mean aqueous inflow concentration, a value of approximately \$69M/year to \$303M/year was observed.

To compare the viability of AMDp as a reasonable REE feedstock, the two aforementioned price indexes were applied to 58 different REE resources. The assays for these projects were compiled from NI 43–101, JORC, or SAMREC statements [65]. As a means of comparison, the in situ price for each resource was plotted against that resource’s basket price, as shown in Fig. 6.

The AMDp ranks reasonably well among the other resources, indicating that it has a moderate potential as a feasible resource. While AMDp does have a lower in situ price than many other reserves, it also has several unique qualities that are more amenable to processing than traditional hard-rock ores. For example, AMDp does not rely on traditional extraction, comminution, or physical separation as part of the processing flowsheet. AMDp processing to recover REEs would likely occur on brownfield sites that are already permitted for waste disposal. Furthermore, AMDp possesses a significant basket price when compared to other resources.

While this research shows that the production potential of REEs through AMD is below that of the current US demand, AMD is still significant as a steady and reliable domestic source. AMD typically loses acidity over time; however, new mining works are constantly being added that could create the oxidizing environment necessary for future AMD production. Additionally, the generation of REEs through AMD flows is stable over long periods of time; as a result, this resource could be used to supplement other US-based REE sources.

Lastly, AMDp is viewed by the industry as an impediment and the treatment, storage, and removal are conducted in a manner that minimizes cost. As a result, many of the AMDp resources are currently pumped underground or disposed of in impoundments. These practices do not allow for the recovery of REEs from the AMD treatment waste streams. Furthermore, there are many potential positive environmental impacts that could be achieved with the beneficiation of AMDp.

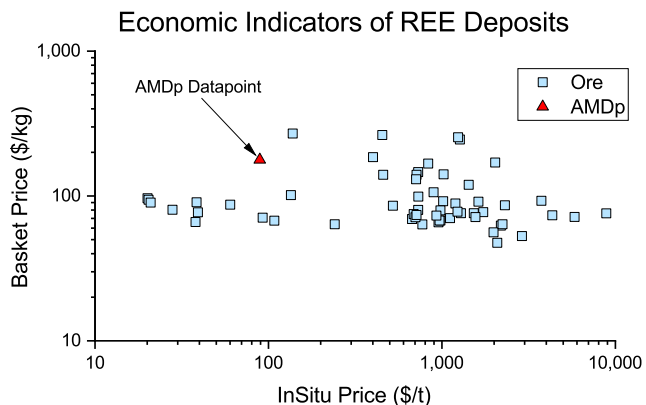


Fig. 6 Comparison of the basket and in situ price index for NAPP AMDp and 58 other REE resources. Ore-based project data after Lifton [65]

3.4 Conceptual Framework for Extraction and Processing

Currently, REEs are processed from a large variety of feedstocks that utilize a multitude of mineral processing and hydrometallurgical technologies [66]. By emulating these proven mining and hydrometallurgical processes in the REE industry, a high-level conceptual framework can be applied to AMDp. Figure 7 shows this theoretical flowsheet that could be used in the production of REEs from AMDp.

Initially, the AMDp would need to be extracted from the current in situ location. This material handling process could involve several mining practices from loading and hauling to pumping to transporting the feedstock to a processing facility. Once at the facility, several costly steps that are used in hard-rock ore processing could be bypassed due to the amorphous consistency of the precipitate. For example, extensive sizing processes like crushing and grinding as well as physical concentration such as flotation would not be necessary to classify and concentrate the feed material.

Next, the hydrometallurgical process used in the REE industry typically requires the REEs to be in an aqueous form. Likewise, the AMDp would need to be converted from the current oxide form into a soluble feedstock. Multiple leaching routes are available to accomplish this solubilization.

Separation of the REEs from other gangue metals in the AMDp could be accomplished using a variety of techniques. Currently, ion exchange, solvent extraction, or selective precipitation are used to recover REEs in an oxide form. Once separated, the REE oxides could be packaged and transported

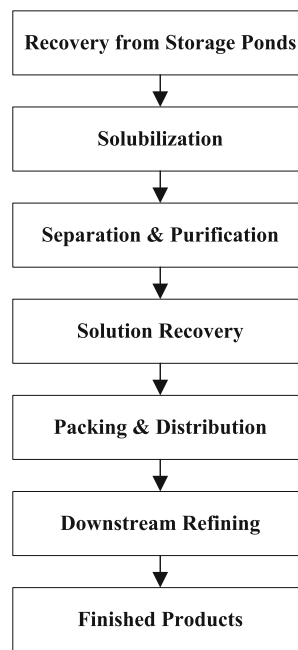


Fig. 7 Conceptual framework for extraction and recovery of REEs from AMDp

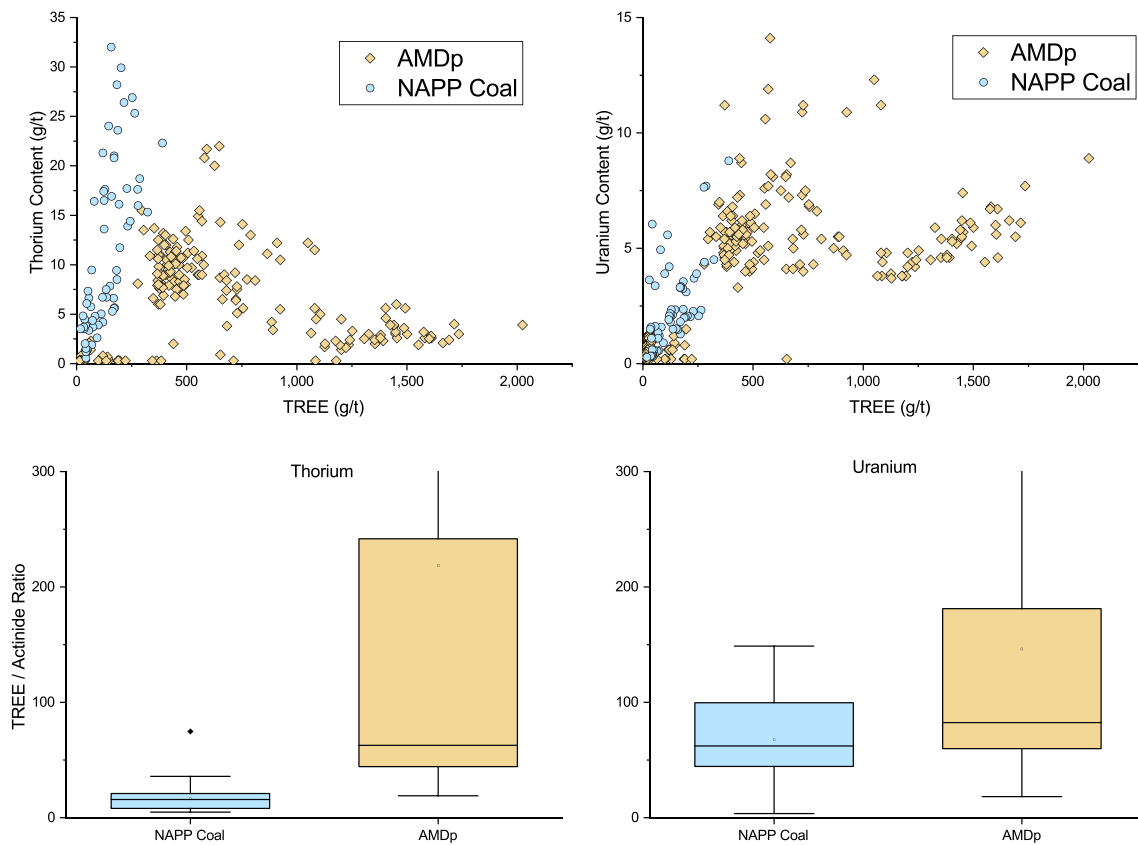


Fig. 8 Comparison of U and Th between NAPP coal and AMDp

to a toll refiner with advanced capabilities to turn the oxides into metal. Typically, these processes utilize a type of smelting or electrolysis to isolate REE metals. Finally, these metals would constitute a finished product that can be sold on the open market.

3.5 Environmental and Civil Considerations

AMD treatment within the coal industry currently focuses on simply meeting effluent limits. In meeting these limits, the AMD treatment process does not maximize the removal of metals and REEs. This compliance-based practice thus creates opportunities to increase treatment of the influent to further remove metals before the effluent is discharged into the environment. Should REEs become a revenue stream for AMD plant operators, the overall process could incentivize private or governmental organizations to purchase and treat additional AMD streams that are currently polluting waterways.

Incidentally, the REE revenue could even change mining practices within the Appalachian region. Currently, AMD-producing material is separated using specific material handling plans that result in this material being stored in non-oxidizing conditions or acid-producing overburden is mitigated with alkaline amendments. Alternatively, lined, spoil containment areas could be created in the form of heap-leaching

structures. These leach beds would intentionally channel AMD to treatment plants where processing would subsequently follow. As a result, the pyritic AMD-producing spoil would not have an opportunity to adversely affect external waterways.

For most hard-rock REE deposits, uranium and thorium are common contaminants that require specialized handling and disposal during the treatment process. Notably, AMDp has very low concentrations of these elements relative to similar grade REE deposits. This decreased occurrence of the actinides is common among coal and coal byproduct REEs feedstocks; however, AMDp is also significantly lower in these actinides than NAPP coal sources, as shown in Fig. 8 [67].

Thermodynamic considerations (e.g., pH–EH diagrams) show that uranium and thorium typically do not mobilize in solution at pH values greater than 1 [68]. Since typical AMD does not reach these low pH values, AMDp samples often contain very low concentrations. The AMDp samples in this study exhibited an average uranium and thorium concentration of 4.46 and 5.67 g/t, respectively. Conversely, monazite (a typical REE-bearing mineral) ores routinely contain 4 to 12% thorium along with uranium [69]. REE deposits with high concentrations of these actinides need to be evaluated with particular attention to these elements as demonstrated by the 2002 closure of the Mountain Pass mine [5].

4 Conclusions

In all, nine AMD sites were evaluated for REE content in both raw water and AMDp. This research has verified that REEs concentrate in the by-products of AMD treatment. These concentrated REEs in AMDp may also possess the qualities needed to justify their use as a viable feedstock resulting in a US-based REE supply. Additionally, a conceptual framework was presented to show different unit operations that could be implemented for the beneficiation of REEs from AMD. Finally, by utilizing these precipitates to refine the REEs, certain environmental incentives may mitigate additional AMD pollution.

The following key findings were developed during this research:

- Data from 81 samples showed that the REE concentration in AMD inflows was a strong function of pH.
- For AMD influent samples with a pH < 4, the average TREE concentration was 371 µg/L.
- For AMD influent samples with a pH > 4, the average TREE concentration was 88 µg/L.
- Typically, the data showed that net-alkaline flooded underground mines had significantly lower TREE flux than net-acidic aboveground and surface mines.
- Traditional AMD treatment captured approximately 78% of the TREES, leaving a precipitate with an average concentration of 517 g/t.
- A regional flow rate estimate showed that the total amount of REEs produced from AMD can vary between 771 and 3400 t per annum.
- The AMDp data indicated that the precipitate contains concentrations of thorium and uranium that are less than 6 g/t.

Acknowledgments This material is based upon work supported by the U.S. Department of Energy under Award Number DE-FE0026927.

Compliance with Ethical Standards

Disclaimer This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the US Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the US Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the US Government or any agency thereof.

Conflict of Interest The authors declare that they have no conflict of interest.

References

1. Fernandez V (2017) Rare-earth elements market: a historical and financial perspective. *Resour Policy* 53:26–45. <https://doi.org/10.1016/j.resourpol.2017.05.010>
2. Schulz KJ, DeYoung JH, Seal RR, Bradley DC (2017) Critical mineral resources of the United States - economic and environmental geology and prospects for future supply Professional Paper 1802
3. Jordens A, Cheng YP, Waters KE (2013) A review of the beneficiation of rare earth element bearing minerals. *Miner Eng* 41:97–114. <https://doi.org/10.1016/j.mineng.2012.10.017>
4. Cox C, Kynicky J (2018) The rapid evolution of speculative investment in the REE market before, during, and after the rare earth crisis of 2010–2012. *Extr Ind Soc* 5:8–17. <https://doi.org/10.1016/j.exis.2017.09.002>
5. Hellman PL, Duncan RK (2014) Evaluation of rare earth element deposits. *Appl Earth Sci* 123:107–117. <https://doi.org/10.1179/1743275814Y.0000000054>
6. Smyth J (2018) Lynas eyes legal action after Malaysia rare-earths blow. *Financ Times London* 18
7. Imholte DD, Nguyen RT, Vedantam A, Brown M, Iyer A, Smith BJ, Collins JW, Anderson CG, O’Kelley B (2018) An assessment of U.S. rare earth availability for supporting U.S. wind energy growth targets. *Energy Policy* 113:294–305. <https://doi.org/10.1016/j.enpol.2017.11.001>
8. U.S. Geological Survey (2018) Mineral Commodity Summaries 2018: US Geological Survey
9. Humphries M (2012) Rare earth elements: the global supply chain
10. Campbell GA (2014) Rare earth metals: a strategic concern. *Miner Econ* 27:21–31. <https://doi.org/10.1007/s13563-014-0043-y>
11. Goodenough KM, Wall F, Merriman D (2017) The rare earth elements: demand, global resources, and challenges for resourcing future generations. *Nat Resour Res* 27:1–16. <https://doi.org/10.1007/s11053-017-9336-5>
12. Van Gosen B, Verplanck PL, Emsbo P (2019) Rare earth element mineral deposits in the United States
13. Preston JS, Cole PM, Craig WM, Feather AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41:1–19. [https://doi.org/10.1016/0304-386X\(95\)00051-H](https://doi.org/10.1016/0304-386X(95)00051-H)
14. Preston JS, Cole PM, Du Preez AC, Fox MH, Fleming AM (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 2: the preparation of high-purity cerium dioxide and recovery of a heavy rare earth oxide concentrate. *Hydrometallurgy* 41:21–44. [https://doi.org/10.1016/0304-386X\(95\)00067-Q](https://doi.org/10.1016/0304-386X(95)00067-Q)
15. Preston JS, Du Preez AC, Cole PM, Fox MH (1996) The recovery of rare earth oxides from a phosphoric acid by-product. Part 3. The separation of the middle and light rare earth fractions and the preparation of pure europium oxide. *Hydrometallurgy* 42:131–149. [https://doi.org/10.1016/0304-386X\(95\)00079-V](https://doi.org/10.1016/0304-386X(95)00079-V)
16. Preston JS (1996) The recovery of rare earth oxides from a phosphoric acid byproduct. Part 4. The preparation of magnet-grade neodymium oxide from the light rare earth fraction. *Hydrometallurgy* 42:151–167. [https://doi.org/10.1016/0304-386X\(95\)00082-R](https://doi.org/10.1016/0304-386X(95)00082-R)
17. Binnemans K, Jones PT, Blanpain B, Van Gerven T, Yang Y, Walton A et al (2013) Recycling of rare earths: a critical review. *J Clean Prod* 51:1–22. <https://doi.org/10.1016/j.jclepro.2012.12.037>
18. Rademaker JH, Kleijn R, Yang Y (2013) Recycling as a strategy against rare earth element criticality: a systemic evaluation of the potential yield of NdFeB magnet recycling. *Environ Sci Technol* 47:10129–10136. <https://doi.org/10.1021/es305007w>
19. Finkleman RB (1993) Trace and minor elements in coal. In: Engel MH, Macko SA (eds) *Org. Geochem.* Springer, Boston, p 594

20. Schofield A, Haskin L (1964) Rare-earth distribution patterns in eight terrestrial materials. *Geochim Cosmochim Acta* 28:437–446. [https://doi.org/10.1016/0016-7037\(64\)90117-6](https://doi.org/10.1016/0016-7037(64)90117-6)
21. Zubovic P, Stadnichenko T, Sheffey NB Distribution of minor elements in coals of the Appalachian region, Washington, D.C, p 1966
22. Cravotta CA (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations 23:166–202. <https://doi.org/10.1016/j.apgeochem.2007.10.011>.
23. United States Department of Energy (2017) Rare earth elements from coal and coal byproducts
24. Hower J, Granite E, Mayfield D, Lewis A, Finkelman R (2016) Notes on contributions to the science of rare earth element enrichment in coal and coal combustion byproducts. *Minerals* 6:32. <https://doi.org/10.3390/min6020032>
25. Ziemkiewicz PF, He T, Noble A, Liu X (2016) Recovery of rare earth elements (REEs) from coal mine drainage. West Virginia Mine Drain. Task Force Symp., Morgantown, WV
26. Skousen JG, Sexstone A, Ziemkiewicz PF (2000) Acid mine drainage control and treatment. *Reclam Drastically Disturb Lands*, pp 1–42
27. Hoehn RC, Sizemore DR (1977) Acid mine drainage (AMD) and its impact on a Virginia stream. *Water Resour Bull* 13:153–160. <https://doi.org/10.1111/j.1752-1688.1977.tb02000.x>
28. Acid Mine Drainage Prediction (1994) Washington, D.C. EPA 530-R-94-036
29. Akcil A, Koldas S (2006) Acid mine drainage (AMD): causes, treatment and case studies. *J Clean Prod* 14:1139–1145. <https://doi.org/10.1016/j.jclepro.2004.09.006>
30. Kalin M, Fyson A, Wheeler WN (2006) The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Sci Total Environ* 366:395–408. <https://doi.org/10.1016/j.scitotenv.2005.11.015>
31. Kleinmann RLP (2001) Prediction of water quality at surface coal mines. *Natl Mine L Reclam Cent Located West Virginia Univ Morgantown, West Virginia* 239:247
32. Hill DW (1969) Neutralization of acid mine drainage. *Ater Pollut Control Fed* 41:1702–15.
33. Ziemkiewicz PF (1998) Steel slag : applications for AMD control. *Proc 1998 Conference Hazard Waste Res*, p 44–62.
34. Gazea B, Adam K, Kontopoulos A (1996) A review of passive systems for the treatment of acid mine drainage. *Miner Eng* 9:23–42. [https://doi.org/10.1016/0892-6875\(95\)00129-8](https://doi.org/10.1016/0892-6875(95)00129-8).
35. USEPA (1983) Design manual: neutralization of acid mine drainage. Cincinnati, OH
36. Ackman TE (1982) Sludge disposal from acid mine drainage treatment. Avondale, MD
37. Payette C, Lam W, Angle C, Mikula R (1991) Evaluation of improved lime neutralization processes. *Proc. Second Int. Conference Abat. Acidic Drain., Monreal, Can*
38. Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. *Sci Total Environ* 338:3–14. <https://doi.org/10.1016/j.scitotenv.2004.09.002>
39. Demchak J, Skousen J, McDonald LM (2013) Longevity of acid discharges from underground mines located above the regional water table. *J Environ Qual* 33:656. <https://doi.org/10.2134/jeq2004.6560>
40. Light DDM, Donovan JJ (2015) Mine-water flow between contiguous flooded underground coal mines with hydraulically compromised barriers. *Environ Eng Geosci* 21:147–164. <https://doi.org/10.2113/gseegeosci.21.2.147>
41. Capo RC, Winters WR, Weaver TJ, Stafford SL, Hedin RS, Stewart BW (2001) Hydrogeologic and geochemical evolution of deep mine discharges, Irwin Syncline, Pennsylvania. *Proc. - West Virginia Surf. Mine Drain. Task Force Symp.*, vol 22, p 144–53
42. Skousen J, Simmons J, McDonald LM, Ziemkiewicz P (2002) Acid-base accounting to predict post-mining drainage quality on surface mines. *J Environ Qual* 31:2034. <https://doi.org/10.2134/jeq2002.2034>
43. Mack B, McDonald LM, Skousen J (2010) Acidity decay of above-drainage underground mines in West Virginia. *J Environ Qual* 39:1043. <https://doi.org/10.2134/jeq2009.0229>
44. Seredin VV, Dai S (2012) Coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol* 94:67–93. <https://doi.org/10.1016/j.coal.2011.11.001>
45. Papangelakis VG, Moldoveanu G. Recovery of rare earth elements from clay minerals. 1st Eur Rare Earth Resour Conf 2014:191–202
46. Gupta T, Ghosh T, Akdogan G, Srivastava VK (2017) Characterizing rare earth elements in Alaskan coal and ash. *Miner Metall Process* 34:138–145. <https://doi.org/10.19150/mmp.7614>
47. Taylor SR (1964) Abundance of elements in the crust: a new table. *Geochim Cosmochim Acta* 28:1273–1285. [https://doi.org/10.1016/0016-7037\(64\)90129-2](https://doi.org/10.1016/0016-7037(64)90129-2)
48. Cravotta CA, Brady KB., Rose AW, Douds JB (1999) Frequency distribution of the pH of coal-mine drainage in Pennsylvania. *US Geol Surv Water-Resources Investig Report* 99-4018A, pp 313–24
49. Zhang W, Rezaee M, Bhagavatula A, Li Y, Groppo J, Honaker R (2015) A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. *Int J Coal Prep Util* 35:295–330. <https://doi.org/10.1080/19392699.2015.1033097>
50. Cravotta CA (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentrations. *Appl Geochem* 23:203–226. <https://doi.org/10.1016/j.apgeochem.2007.10.003>
51. Goode DJ, Cravotta CA, Homberger RJ, Hewitt MA, Hughes RE, Koury DJ, et al (2013) Water budgets and groundwater volumes for abandoned underground mines in the Western Middle Anthracite Coalfield, Schuylkill, Columbia, and Northumberland Counties, Pennsylvania—preliminary estimates with identification of data needs. Reston, VA
52. Denicola TA, Donovan JJ, Leavitt BR, Sharma S (2013) Geochemistry of mine pool discharges in the Pittsburgh Coal Basin Thesis Submitted to: The Eberly College of Arts and Sciences at West Virginia University in partial fulfillment of the requirements for the degree of Masters of Science In Geology Departme
53. Stewart BW, Capo RC, Hedin BC, Hedin RS (2016) Rare earth element resources in coal mine drainage and treatment precipitates in the Appalachian Basin, USA. *Int J Coal Geol* 169:28–39. <https://doi.org/10.1016/j.coal.2016.11.002>
54. Cordier DJ, Hedrick JB (2010) 2008 Minerals yearbook - rare earths
55. Cordier DJ (2011) 2009 Minerals yearbook
56. Gambogi BJ, Cordier DJ (2012) 2010 Minerals yearbook
57. Gambogi J (2013) 2011 Minerals yearbook
58. Gambogi J (2013) 2012 Minerals yearbook - rare earths
59. Gambogi J (2016) 2013 Minerals yearbook - rare earths
60. Gambogi J (2014) 2014 Minerals yearbook - rare earths
61. Gambogi J (2018) 2015 Minerals yearbook
62. Honaker RQ, Groppo J, Yoon R-H, Luttrell GH, Noble A, Herbst JA (2017) Process evaluation and flowsheet development for the recovery of rare earth elements from coal and associated byproducts. *Miner Metall Process* 34:107–115. <https://doi.org/10.19150/mmp.7610>
63. Noble A, Luttrell GH (2016) Micro-pricing: the value of trace rare earth elements in coal and coal byproducts. 2016 SME Annu Conference Expo; Preprint N:1–6
64. Binnemans K, Jones PT, Müller T, Yurramendi L (2018) Rare earths and the balance problem: how to deal with changing markets? *J Sustain Metall* 8:126–146. <https://doi.org/10.1007/s40831-018-0162-8>
65. Lifton J, Hatch G (2016) Technology Metals Research. <http://www.techmetalsresearch.com/metrics-indices/tmr-advanced-rare-earth-projects-index/>. Accessed 10/09/2017

66. Verbaan N, Bradley K, Brown J, Mackie S (2015) A review of hydrometallurgical flowsheets considered in current REE projects
67. National Energy Technology Laboratory UD of E (2018) Rare earth element database. https://edx.netl.doe.gov/ree/?page_id=1587. Accessed 12/14/2018
68. Kim E, Osseo-Asare K (2012) Aqueous stability of thorium and rare earth metals in monazite hydrometallurgy: Eh-pH diagrams for the systems Th-, Ce-, La-, Nd- (PO₄)-(SO₄)-H₂O at 25 °c. *Hydrometallurgy* 113–114:67–78. <https://doi.org/10.1016/j.hydromet.2011.12.007>
69. Gupta CKK, Krishnamurthy N (1992) Extractive metallurgy of rare earths. vol 37. <https://doi.org/10.1179/imr.1992.37.1.197>.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.