Coal and Coal Byproducts as Potential Sources of Rare Earth Elements (REE) in Indiana

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ABSTRACT

The purpose of this study is to evaluate coal and coal byproducts (coal waste, coal ash, and acid mine drainage) in Indiana as potential sources of rare earth elements (REE). On a whole-rock basis, most Indiana coal samples have REE content below 100 ppm, and only some samples of the Brazil and Staunton Formations (Lower and Upper Block and Viking B coals) reach 100 ppm. Because REE concentrations vary between locations and within individual coal beds, and the correlations of coals within the Brazil and Staunton Formations are often uncertain, a better understanding of the stratigraphy of these formations is needed to identify the most promising REE horizons.

Owing to a long history of coal mining, Indiana has numerous coal preparation plants and associated coarse-and fine-grained coal refuse (known, respectively, as gobs and slurry ponds). This paper reviews the available data on locations and volumes of these deposits. The total extent of slurry pond deposits was estimated at 2,765 acres, and the total volume estimates ranged from 94,000,000 to 136,000,000 cubic yards. No estimates are available for gob deposits in Indiana. To our knowledge, no REE data are available for coal preparation plant waste in Indiana, except for minimal data from coal slurry in Warrick County. Water streams from abandoned coal mines and coal processing (acid mine drainage, AMD) could also be a source of REE or other critical minerals; we review available data from AMD sites.

Indiana, having many coal-fired power plants, has accumulated a large quantity of coal ash during its mining history. Our estimates indicate that coal ash deposits occupy $\sim 2,184$ acres, storing $\sim 52,566,153$ m³ of ash. Volume estimates for individual coal ash sites come from various sources and present our best estimates at this time. To our knowledge, no REE data are available on coal ash in Indiana. Such data would be of great value because coal ash deposits could be an important resource for REE, other critical minerals, or other high-value carbon products.

INTRODUCTION

Recent increasing demand for rare earth elements (REE) due to their use in many modern technologies has intensified the search for new sources. Traditional sources of REE are alkaline igneous or carbonate-rich igneous rocks that crystallized at high temperatures deep within the earth (Dostal, 2017). As these conventional ores become progressively depleted and recovery more difficult, the possibility of recovering REE from sedimentary rocks has gained both technical and economic appeal (Cullers and others, 1979; Condie, 1991; Moldoveanu and Papangelakis, 2016; Emsbo and others, 2015; Laurino and others, 2019).

Extensive research has been conducted worldwide on REE in coal (Goldschmidt and Peters, 1933; Seredin and Dai, 2012; Hower and others, 2016) and coal combustion byproducts (Hower and others, 2016; Kolker and others, 2017; Dai and Finkelman, 2018). Coal ash, in particular, has received much attention; it was even suggested that REE-rich coal ash could match the economic viability of conventional types of ores such as carbonatites, alkaline granites, or weathering crusts (Seredin and Dai, 2012; Seredin and others, 2013). In addition to the REE concentrations, economically viable REE recovery is another critical issue for coal and coal byproducts. Over the past decade, a lot of effort has been put into recovering REE from coal ash and several approaches have been researched and developed. These approaches include membrane-based REE separation (Hendren and others, 2017), extraction by ion exchange (Rozelle and others, 2016), selective chelation for capture of REE from solution on solid substrates (Karamalidis and others, 2017), or bacterial separation (Bonificio and Clarke, 2016). Several smallscale bench projects sponsored by the United States Department of Energy (DOE) validated that REE in coal and coal byproducts could be upgraded to the level of purity normally achieved from conventional



Figure 1. Classification of REE into: A) heavy and light, (source: NETL, 2020); B) light, medium and heavy; and critical, uncritical, and excessive (modified from Seredin, 2010). The concentration of the elements in the upper continental crust after Rudnick and Gao, 2003.

ores, initially exceeding the DOE requirement of 2% concentration, and then proceeding to reach as high as 99 wt. % purity (U.S. DOE, 2022). Those projects involved a combination of standard and novel technologies and integrated physical and chemical separation processes. Subsequent small-scale pilot projects also achieved high-purity REE concentrates, demonstrating the technical feasibility of the process. However, as of 2022, a large-scale successful and economically feasible technique to extract REE from coal ash is not yet available.

The purpose of this study was to evaluate coal and coal byproducts (coal waste, coal ash, and acid mine drainage) in Indiana as potential sources of REE. In this paper, under REE designation, we include 15 elements of the lanthanide series plus yttrium (Fig. 1). We review available data, summarize the availability of coal and coal byproducts, and discuss implications with regard to REE potential.

REE CONCENTRATIONS IN INDIANA COALS

Three publicly available datasets contain REE data on Indiana coals. The samples for these datasets were collected at different times, were analyzed using different techniques, and were obtained on different bases (whole-rock or ash basis). These datasets are summarized below, and in this paper, they are referred to as: a) *whole-rock basis NCRDS dataset*; b) *ash basis EC dataset*; and c) *whole rock-basis Earth MRI dataset*.

The *whole-rock basis NCRDS dataset* is part of the National Coal Resource Dataset (NCRDS) (Oman and others, 1992). The samples were collected by Indiana Geological Survey researchers before 1990. REE analyses were carried out by neutron activation and optical emission spectrographic techniques at the U.S. Geological Survey (USGS) and the data are presented on a whole-rock basis. These data also can be found in the Indiana coal quality database (Drobniak and others, 2018). Full-channel coal samples for which the entire suite of REE is available have a range of REE from 25.4 ppm in the Mariah Hill Coal of the Mansfield Formation to 101.2 ppm in the Lower Block Coal Member of the Brazil Formation (Table 1).

In the whole-rock basis NCRDS dataset, the largest number of full-channel analyses is available on the Springfield Coal Member of the Petersburg Formation

	_			Light REE [ppm]			Heavy REE [ppm]		Average
Formation	Coal bed	N	Minimum	Maximum	Average	SD	Minimum	Maximum	Average	SD	total REE [ppm]
Dugger	Danville	13	20.8	65.7	37.5	14.2	7.0	16.3	11.5	2.8	48.9
	Hymera	11	15.1	87.1	40.7	25.3	4.0	24.7	11.8	6.3	52.5
	Bucktown	3	24.9	26.9	25.9	1.0	11.4	14.6	13.3	1.7	39.2
	Springfield	31	18.4	77.5	32.8	15.6	6.2	22.5	10.4	3.1	43.3
Petersburg	Houchin Creek	3	15.7	19.1	17.7	1.8	8.1	15.9	11.1	4.2	28.7
Linton	Survant	6	29.9	65.5	54.7	13.3	10.7	16.0	13.0	2.0	67.7
	Colchester	2	18.5	19.1	18.8	0.4	7.1	7.4	7.3	0.2	26.1
	Seelyville	5	11.5	87.6	31.7	29.2	6.1	22.5	9.5	6.5	41.1
	Buffaloville	6	12.5	42.5	30.5	13.9	4.9	15.4	10.5	4.4	40.9
	Upper Block	10	31.3	106.9	55.8	21.3	5.1	20.3	11.5	5.1	67.3
Brazil	Lower Block	2	74.6	85.9	80.2	7.9	16.8	25.3	21.0	6.1	101.2
	Unnamed Brazil	13	13.1	144.1	53.2	42.8	5.1	24.2	13.0	5.6	66.2
	Mariah Hill	3	10.7	30.4	17.5	11.1	7.5	8.6	7.9	0.6	25.4
Mansfield	Blue Creek	2	27.5	30.1	28.8	1.8	5.4	5.7	5.5	0.2	34.3
munsheru	Unnamed Mansfield	6	17.5	42.9	29.6	11.0	3.7	10.9	7.3	2.7	36.9

Table 1. Summary of REE data on Indiana coals (full-channel raw samples, whole-rock basis) for the whole-rock basis NCRDS dataset. Only samples that have the entire suite of REE data are included in this table. SD – standard deviation. Light REE (La+Ce+Pr+Nd+Pm+Sm+Eu), heavy REE (Gd+Tb+Dy+Ho+Er+Tm+Yb+Lu+Y).

(31), followed by undifferentiated Brazil Formation coals (13), and the Danville and Hymera Coal Members (13 and 11, respectively) of the Dugger Formation. This brief summary of REE data on full-channel samples and on a whole-rock basis for Indiana coal (Table 1) indicates that REE concentrations are similar to those found in world coals (average 68.5 ppm; Ketris and Yudovich, 2009) and in U.S. coals (62.1 ppm; Finkelman, 1993). These data also show that some coals (e.g., coals of the Brazil Formation) consistently have higher REE concentrations compared to other coals. We note that in this dataset, in addition to the coal samples that have the entire REE suite, there are also numerous coal samples for which complete sets of REE data are





unavailable, with the number of analyses ranging from 234 for yttrium (Y) to 120 for samarium (Sm).

The same set of whole-rock REE data was used by Chatterjee and others (2022) to identify REE potential in Indiana coal using a machine learning and augmentation approach. In that study, the REE potential was



expressed as the outlook coefficient — the ratio of critical (Nd, Eu, Tb, Dy, Er, and Y) to uncritical (La, Pr, Sm, Gd) and excessive (Ce, Ho, Tm, Yb, Lu) elements, a parameter based on market trends (Seredin, 2010; Seredin and Dai, 2012). Out of several coal parameters considered as having potential for REE screening, the analysis revealed that ash yield and aluminum oxide (Al₂O₄) content were the two most important ones. The model developed in this study can successfully and with high confidence classify coal samples into promising and unpromising with regard to REE potential (Fig. 2).



 Table 2. Light (LREE) and heavy (HREE +Y) rare earth element content in coal samples (bench and full-channel, ash basis) from Antioch Mine, Shamrock Mine, and grab samples from various coals in the Bear Run, Oaktown, and Francisco mines in Indiana. These data are part of the ash basis CE dataset.

MINE	Sample	LREE [ppm, ash basis]	HREE [ppm, ash basis]	Total REE [ppm, ash basis]
	Unnamed Staunton 1 (upper bench 0-25 cm)	111.2	74.3	185.5
	Unnamed Staunton 1 (lower bench 25-47 cm)	99.5	117.1	216.7
	Unnamed Staunton 1 (full channel 0-47 cm)	105.7	94.4	200.1
	Unnamed Staunton 2 (upper bench 0-33 cm)	1041.6	426.8	1468.3
ш	Unnamed Staunton 2 (lower bench 33-59 cm)	927.1	165.9	1093.0
MIN	Unnamed Staunton 2 (full channel 0-59 cm)	991.1	311.8	1302.9
СН	Buffaloville (upper bench 0-8 cm)	192.1	62.5	254.6
ATIC	Buffaloville (lower bench 8-16 cm)	99.4	49.3	148.7
AI	Buffaloville (full channel 0-16 cm)	145.7	55.9	201.7
	Lower Block (upper bench 0-15 cm)	168.5	150.3	318.8
	Lower Block (middle bench 15-23 cm)	191.5	85.3	276.8
	Lower Block (lower bench (23-35 cm)	308.2	85.8	394.0
	Lower Block (full channel 0-35 cm)	221.6	113.3	335.0
	Unnamed Staunton (upper bench 0-14 cm)	1199.8	107.8	1307.6
	Unnamed Staunton (middle bench 14-23 cm)	177.8	280.1	457.9
	Unnamed Staunton (bottom bench 27-42 cm)	1207.6	352.0	1559.6
(MINE	Unnamed Staunton (full channel 0-42 cm)	960.8	245.0	1205.8
	Buffaloville (upper bench 0-17 cm)	111.1	66.8	177.9
	Buffaloville (lower bench 17-43 cm)	184.9	51.4	236.3
	Buffaloville (full channel 0-43 cm)	155.7	57.5	213.2
CK	Upper Block (upper bench 0-8 cm)	173.3	170.7	344.0
ARO	Upper Block (middle top bench 8-12 cm)	147.6	94.4	242.0
HAN	Upper Block (middle lower bench 12-15 cm)	706.1	117.6	823.7
0	Upper Block (bottom bench 15-27 cm)	344.4	119.4	463.8
	Upper Block (full channel 0-27 cm)	304.7	130.7	435.4
	Lower Block (upper bench 0-20 cm)	261.8	124.2	386.0
	Lower Block (middle bench 20-44 cm)	520.6	138.4	658.9
	Lower Block (lower bench 44-66 cm)	856.4	147.2	1003.6
	Lower Block (full channel 0-66 cm)	538.3	132.8	671.1
	Danville (Bear Run Mine grab)	214.2	59.1	273.3
	Washed Danville (Bear Run Mine grab)	309.8	76.6	386.5
	Hymera (Bear Run Mine grab)	196.2	54.1	250.3
E E	Bucktown (Bear Run Mine grab)	184.0	82.7	266.8
APL	Springfield (Bear Run Mine grab)	349.4	110.6	460.0
US I SAN	Three coals blend (Bear Run Mine grab)	387.3	82.3	469.6
RIO RAB	Springfield 1 (Oaktown Mine grab)	240.4	73.3	313.6
GI K	Washed Springfield 1 (Oaktown Mine grab)	206.1	72.3	278.3
	Springfield 2 (Oaktown Mine grab)	121.2	42.7	163.9
	Washed Springfield 2 (Oaktown Mine grab)	438.6	130.0	568.5
	Washed Springfield (Francisco Mine grab)	381.5	94.3	475.8

The *ash basis CE dataset* includes 69 coal samples from several boreholes and coal mines in Indiana (Fig. 3; Mastalerz and others, 2020). These coal samples were collected in 2017-2019 and the analyses were carried out at the Kentucky Geological Survey by inductively coupled plasma optical emission spectroscopy (ICP-OES) after multi-acid digestion of the coal ash. In this dataset, REE concentrations are presented on the ash basis. Because not all coal samples in this dataset have ash yield determined, it was not possible to recalculate these data into the whole-rock basis and compare to other datasets.

These analyses on an ash basis provide important information about the variation of REE between individual coalbeds as well as within individual coal beds. Selected data on REE concentrations for this dataset are presented in Table 2. Overall, the concentrations of REE on an ash basis in the coals vary from less than 200 ppm to more than 3,000 ppm (Mastalerz and others, 2020). The Lower Block and the Upper Block Coal Members of the Brazil Formation and some coal seams of the Staunton Formation contain the highest REE concentrations and, considering market trends, have the best commercial REE potential. Experimental data related to REE extraction from coal combustion waste of Russian low-rank coals suggest that combined REE oxide content above 1,000 ppm (on ash basis) could be considered the threshold for beneficial recovery of the metals (Seredin, 2004). Seredin and Dai (2012) suggested that this cut-off value could be lowered to 800 to 900 ppm, especially if the coal seam having high REE content is thick. Considering this threshold, several of the Indiana coal beds have such potential, specifically, the Staunton Formation coals in the Antioch and Shamrock mines. Some Brazil Formation coals also would qualify (Table 2). Therefore, the ash of these coals could be viable sources of REE. Concentrations of REE in the most economically important coals, such as the Springfield Coal Member and the Danville Coal Member, are lower and fall below the 800 to 900 ppm threshold (Table 2). Comparison of individual REE concentrations in the unnamed Staunton Formation coal to other known sources of REE is shown in Fig. 4.

The whole-rock NCRDS dataset and the ash basis CE dataset were generated using either neutron activation and optical emission spectrographic analysis or inductively coupled plasma optical emission spectroscopy (ICP-OES). These techniques yield reliable REE concentrations on elements that occur in relatively large quantities. However, for elements that have low concentrations, such as terbium (Tb), holmium



Figure 4. Shale-normalized REE line and area plot of major deposits (after Emsbo and others, 2015). The unnamed Staunton Coal and Veale Shale are added for comparison (after Mastalerz and others, 2020).

(Ho), thulium (Tm), and lutetium (Lu) in Pennsylvanian coals (Mastalerz and others, 2020), these techniques may result in erroneous data. Therefore, for REE analysis, it is important to use techniques that have lower detection limits, for example, inductively coupled plasma-optical emission spectrometry – mass spectroscopy (ICP-OES-MS). This technique has been used recently to analyze 29 coal samples from 11 core locations in Indiana, and these data (referred here as the *whole-rock Earth MRI dataset*) are presented on a whole-rock basis (Table 3).

For this dataset, samples were collected in 2021 from archived cores, and analyses were conducted as part of USGS Earth MRI Program. Most coal samples have REE content less than 100 ppm, and only some samples of the Brazil and Staunton Formation (Lower and Upper Block, and Viking B Coal) reach 100 ppm (Table 3). There is one anomalous sample of the Seelyville Coal of the Linton Formation in location 14Q13-3 with REE as high as 608.3 ppm.

All the above REE data on Indiana coals show that the Indiana coals represent low-grade source material, and that the Staunton Formation and Brazil Formation coals are generally richer in REE than the coals of the Linton, Petersburg, or Dugger Formations (Tables 1, 2, 3). Data from the *ash basis CE dataset* point to the Staunton and Brazil Formation coals and their byproducts as the highest potential source of REE. Because REE concentrations vary both between locations and within individual coal beds, and the correlations of coals within the Brazil and Staunton Formations are often uncertain (Mastalerz and others, 2018, 2019), a better understanding of the stratigraphy of these formations is needed to identify and target the most promising REE horizons (Mastalerz and others, 2020). Moreover, we note that to better understand REE potential of Indiana coals, more high-quality data collected using modern, sensitive techniques are needed on REE concentration and REE associations.

Table 3. Light (LREE) and heavy (HREE +Y) rare earth element content in coal samples from the whole-rock basis Earth MRI dataset.

Well and sample	Coal member	LREE [ppm, whole-rock	HREE [ppm, whole-	Total REE [ppm, whole-
SDH-4-4	Danville Coal	10.6	4 2	14.8
SDH-259-4	Danville Coal	19.1	6.2	25.3
SDH-366-1	Danville Coal	14.2	8.1	22.2
SDH-347-2	Danville Coal	45.0	10.7	55.7
SDH-259-9	Hymera Coal	11.3	5.6	16.9
SDH-300-3	Hymera Coal	40.4	7.9	48.3
SDH-347-6	Hymera Coal	22.4	6.8	29.2
SDH-366-5	Hymera Coal	54.7	19.7	74.5
SDH-259-11	Herrin Coal	6.5	6.7	13.2
SDH-347-11	Springfield Coal	39.0	10.5	49.5
SDH-366-7	Springfield Coal	42.3	11.9	54.2
SDH-259a-2	Springfield Coal	32.7	12.1	44.9
SDH-300-8	Springfield Coal	12.3	3.7	16.0
SDH-259a-5	Houchin Creek Coal	14.9	8.7	23.6
SDH-366-11	Houchin Creek Coal	25.7	11.5	37.1
SDH-379-3	Houchin Creek Coal	9.5	8.1	17.6
SDH-300-13	Houchin Creek Coal	7.0	8.8	15.8
SDH-379-9	Colchester Coal	9.0	7.9	17.0
14Q13-2	Colchester Coal	8.5	12.2	20.7
SDH-259a-12	Upper Seelyville Coal	15.7	10.1	25.8
14Q13-3	Upper Seelyville Coal	238.8	369.6	608.4
14Q13-6	Lower Seelyville Coal	5.8	10.3	16.0
SDH-259a-19	Viking A Coal	25.7	6.7	32.4
14Q13-10	Viking A Coal	18.5	5.6	24.1
14Q13-13	Viking B Coal	89.7	11.7	101.5
SDH-217-2	Minshall Coal	53.8	21.7	75.6
14Q13-16	Upper Block Coal	16.1	13.5	29.6
SDH-217-6	Upper Block Coal	106.0	13.7	119.7
SDH-217-10	Lower Block Coal	94.1	12.8	106.9



Figure 5. Aerial photograph of a coal slurry pond, Switz City, Indiana.

COAL PREPARATION PLANT WASTE

Indiana has a long history of coal mining (~150 years) and is still a major coal producer (17,871,402 tons in 2021). Due to the high sulfur contents of most Indiana coals (e.g., Mastalerz and others, 2009), the vast majority of the coal has been washed in coal preparation facilities to meet coal quality specifications. Consequently, in addition to the clean coal product, these preparation plants generate coal waste-rejects from the coal cleaning process. Rejects can be broadly classified as coarse-grained refuse (also called "gob") and finegrained refuse (also known as coal tailings or slurry; see Fig. 5 as an example). This coal waste material is typically deposited close to the coal preparation facilities. Because coal waste often contains large amounts of pyrite exposed to both water and atmospheric oxygen, the soil becomes acidic, and unreclaimed waste deposits typically remain without vegetation for many years until pyrite becomes completely oxidized. After passage of the Surface Mining Control and Reclamation Act (SMCRA) in 1977, coal mine operators were required to reclaim their coal waste after mining terminated, and the Abandoned Mine Lands (AML) program was instituted to reclaim abandoned coal waste deposits (Harper and others, 2009). Most of the deposits have since been revegetated after being covered by a cap of soil, synthetic soil, or spoil, or after the application of large quantities of agricultural limestone.

Indiana has numerous coal preparation plants and associated coarse- and fine-grained coal refuse (Fig. 6), and several studies attempted to map Indiana's coal waste deposits. In the early 1970s, color-infrared Earth Resources Technology Satellite imagery was used to map these deposits, and their area was estimated at 1,631 acres (Wobber and others, 1974 and 1975). Weismiller and Mroczynski (1978) provided maps of both slurry ponds as well as gobs. Eggert (1979) generated a map showing the locations of 44 slurry deposits and active preparation plants. More recently, Harper and others (2009) conducted a comprehensive study of coal slurry deposits. In that study, maps, reports, and historical aerial photographs were georeferenced, slurry deposits were identified, and their extent and volumes were estimated. Shapefiles with accompanying preparation plant information are available from the Indiana Geological and Water Survey (Figs. 7-10). The intent of these maps is to provide a quick reference as to where in Indiana the most slurry pond sediments are available. The total extent of the slurry pond deposits identified in Harper and others (2009) was estimated at 2,765 acres, and the total volume estimate ranged from 94,000,000 to 136,000,000 cubic yards. Taking into account mineability considerations, they estimated that potentially mineable raw slurry would be in the range of 74,000,000 to 171,000,000 tons.



1-Sunspot	40-American No. 2
2-Universal	41-Sycamore
3-Otter Creek	42-Julian
4-unknown	43-Apraw
5-Rio Grande	44-White Ash
6-Talleydale	45-Standard No. 2
7-Green Walley-Wabash	46-Air Quality
8-Saxton No. 1	47-Monroe City
9-Lone Star	48-Viking
10-Old Chinook	49-Cannelburh
11-Victory	50-Corning
12-Chinook	51-Pride
13-Dresser	52-Prides Creek
14-Springhill	53-Old Ben No. 2
15-Mt. Pleasant	54-Black Foot No. 5
16-Chieftain No. 20	55-Wick
17-Chieftain No. 20	56-Oatsville
18-Black Hawk	57-Patoka River
19-Farmersburg	58-Gibson County
20-Thunderbird	59-Kings Station
21-Jonay	60-Francisco
22-Little Betty	61-Columbia
23-Latta	62-Augusta
24-unknown	63-Black Foot No. 2
25-Ax	64-Black Foot No. 2
26-Fourth Vein	65-Old Ben No. 1
27-New Hope-Friar Tuck	66-Somerville North
28-Pandora	67-Somerville Central
29-Regent	68-Enterprise
30-Miller Creek	69-Buckskin
31-Switz City	70-Deer Ridge
32-Airline	71-Tecumseh Nos. 3-4
33-Allendale	72-Buckskin-Tecumseh No. 2
34-Hawthorn	73-Lynville
35-Freelandville No. 1	74-Lynville South
36-Freelandville No. 2	75-Vanderrick
37-Shasta	76-Ayrshirs
38-Maid Marian	77-Squaw Creek
39-Enoco	78-Sunlight

Figure 6. Map showing the locations of coal preparation plants and coal slurry ponds in Indiana after Harper and others (2009). See Figures 7-10 for more detailed locations, area, and volume of the ponds.



Figure 7. Map showing coal slurry pond areas and table of volumes in Vermillion, Vigo, and Clay Counties. Note that the size of the ponds on the map is not to scale.

ID-IGS-PLY	Area [acres]	Volume [m ³]
A2_1	16.6	205,105
A2_2	10.8	132,855
A2_5	23.7	292,334
A2_7	69.3	6,407,198
B1_1	2.7	16,403
B1_2	0.4	2,239
B4_1	3.2	78,758
B4_2	9.8	121,151
B4_3	4.9	120,111
B4_4	10.6	261,819
B4_5	6.3	156,015
B5_1	4.4	272,132
B5_2	80.5	496,784
B5_3	6.9	42,702
B9_1	15.7	582,211
B9_2	2.5	91,363
B9_3	2.8	23,959
B9_4	42.2	364,227
B9_5	4.7	40,340
B9_6	4.8	41,369
B9_7	1.7	21,478
B9_8	1.7	21,234
B9_9	0.3	11,293
B9_10	0.9	33,317
C1_1	36.4	1,257,460
C1_2	11.0	813,994
C1_3	35.6	1,754,269
C1_5	21.1	1,041,386
C2_1	6.4	631,532
C2_2	0.7	65,218
C2_3	3.5	300,952
C2_6	5.6	381,494
C2_7	15.9	1,079,261
C2_13	9.0	939,085
C2_15	10.1	1,558,519
C2_16	2.0	208,507



ID-IGS-PLY	Area [acres]	Volume [m ³]
D1_1	53.8	994,999
D1_3	15.1	280,208
D3_1	43.3	1,068,815
D3_2	6.8	83,555
D3_3	2.3	86,816
D3_4	2.8	24,019
D3_5	9.2	79,363
D3_6	9.0	77,314
D3_7	4.7	175,091
D3_8	5.8	213,960
D3_9	16.3	241,545
D3_10	7.8	106,001
D3_11	25.1	185,847
D3_12	2.5	18,310
D3_13	2.0	12,240
D3_14	15.6	827,315

Figure 8. Map showing coal slurry pond areas and tables of volumes in Sullivan and Greene Counties. Note that the size of the ponds on the map is not to scale.

ID-IGS-PLY	Area [acres]	Volume [m ³]
D4_1	9.1	335,677
D4_2	1.0	8,953
D4_3	2.0	63,210
D4_4	0.5	14,805
D4_5	0.9	27,215
D4_6	17.3	256,574
D4_7	6.1	90,617
D4_8	38.6	524,154
D4_9	47.5	760,954
D5_1	1.7	20,619
D5_2	2.9	35,489
D5_3	32.8	405,181
D6_4	19.4	479,728
D6_5	14.4	177,016
D6_7	4.5	27,687
D7_2	22.2	547,431
D8_1	12.0	1,179,700
D8_2	3.2	275,928
D8_4	6.6	81,964
D8_5	15.6	1,349,282
D8_9	10.4	1,537,590
D8_11	23.7	1,313,303
E1_1	32.6	321,952
E1_2	17.8	175,639
E1_3	35.5	350,203
E1_4	10.7	105,861
E1_5	15.0	148,115
E3_1	47.8	3,241,587
E3_4	18.7	1,130,501
E4_2	55.3	2,184,282
E4_5	15.7	965,317
E4_7	2.8	172,358
E4_8	2.7	201,998
E4_9	20.2	1,991,769
E4_15	28.1	2,255,909
E4_16	20.4	2,641,711
E5_1	2.4	29,921
E5_2	3.9	33,504
E5_8	4.0	34,318
E5 9	11.4	98.621



Figure 9. Map showing coal slurry pond areas and table of volumes in Knox and Daviess Counties. Note that the size of the ponds on the map is not to scale.

ID-IGS-PLY	Area [acres]	Volume [m ³]
F1_1	0.8	63,702
F1_3	4.1	50,754
F1_4	2.0	24,787
F1_5	6.6	81,826
F1_6	11.7	144,854
F1_7	2.9	231,777
F4_1	13.1	404,154
F4_2	1.5	9,419
F9_1	2.1	91,066
F9_3	4.4	270,297
F11_1	35.3	261,009
F13_1	4.3	26,756
F13_2	13.8	255,666
G1_1	7.3	447,649
G1_2	1.2	73,600
G3_4	7.6	560,600
G3_5	12.4	613,379



ID-IGS-PLY	Area [acres]	Volume [m ³]
H2_1	4.5	55,286
H5_1	2.1	25,547
H5_2	1.4	8,332
J1_10	9.9	791,154
J12_3	5.6	479,466
J12_4	3.1	271,035
J14_3	12.2	1,882,926
J14_5	2.2	332,036
J14_6	15.9	1,857,794
J3_2	0.3	4,186
J3_3	10.2	125,463
J4_1	5.8	107,670
J4_2	1.6	29,292
J4_4	2.7	33,802
H2_1	4.5	55,286
H5_1	2.1	25,547

Figure 10. Map showing coal slurry pond areas and tables of volumes in Gibson, Pike and Warrick Counties. Note that the size of the ponds on the map is not to scale.

ID-IGS-PLY	Area [acres]	Volume [m ³]
J5_1	12.2	120,858
J5_11	1.1	52,169
J5_12	33.1	327,019
J5_13	1.4	13,500
J5_2	20.2	124,313
J5_4	3.6	199,330
J5_5	0.4	22,394
J5_8	1.0	53,820
J5_9	5.2	287,326
J6_4	11.8	145,233
J6_5	4.7	40,909
J7_1	11.4	98,702
J7_2	3.7	32,068
J7_3	37.5	324,118
J8_1	2.7	133,866
J8_2	1.1	47,897
J9_1	7.7	190,527
K1_2	117.6	4,350,487
K1_3	85.2	3,677,096
K1_6	26.1	1,222,514
K1_7	99.9	12,932,762
K1_8	25.9	2,880,578
K2_1	3.8	93,626
K2_3	31.7	2,108,742
K2_4	3.2	77,759
K2_9	11.0	204,005
K2_12	16.8	727,009
K2_13	3.9	166,260
K2_14	5.3	227,664
K2_17	3.3	101,846
K2_19	0.6	17,619
K2_21	1.7	30,549
K3_1	14.0	277,273
K4_7	8.9	749,097
K4_8	9.9	828,761
K4_9	10.5	881,364
K4_12	3.8	322,011
K4_13	13.4	1,122,466
K5_2	33.9	1,255,800
K5_3	16.9	625,248
K5_5	4.0	197,048
K5_6	9.1	558,710
K5_7	8.9	441,338
K5_8	50.3	3,101,959
K8_1	12.9	1,756,885
K8_3	11.4	1,547,857

Slurry deposits contain fine-grained refuse and, as such, are composed of coal fines mixed dominantly with clay minerals. The average ash and sulfur contents (as received) of 454 slurry samples from Indiana are 31.4 %, and 4.1 %,

respectively. Heating values (as received) average 7,689 Btu/lb, and on moisture ash-free basis, 12,972 Btu/lb, testifying to large proportions of coaly material. Statistical values for individual sites are listed in Table 4.

Table 4. Ash yield, sulfur content, and heating value of slurry deposits in Indiana. Abbreviated ar - as received; maf -	- mois-
ture ash free basis (from Harper and others, 2009).	

Mine	ID-IGS	No. of drill holes	No. of samples	Ash (ar, wt. %)	Sulfur (ar, wt. %)	Btu/lb (ar)	Btu/lb (maf)
Airline	E3	11	99	42.4	4.4	7,143	12,657
Buckskin	K3	7	17	29.0	2.7	8,589	12,873
Chinook	C1	14	81	30.5	3.2	5,577	13,310
Friar Tuck	D4	9	37	28.1	2.1	8,092	13,663
Green Valley	B4	9	23	20.9	5.1	9,780	13,305
Hawthorn	E4	11	55	45.2	5.8	6,608	11,920
Lynnville	K1	6	36	35.0	4.3	8,150	13,344
Minnehaha	D3	18	74	20.2	2.2	6,893	13,680
Otter Creek	B1	4	4	26.7	2.6	8,893	13,025
Tecumseh	K2	4	28	35.9	8.9	7,168	11,942
Sum		93	454				
Average				31.4	4.1	7,689	12,972

While the locations, extents and volumes of coal slurry deposits are relatively well documented, it is difficult to evaluate their REE potential because of the absence of REE data. To our knowledge, the only available REE data come from Ayrshire coal tailings in Chandler, Warrick County, Indiana (Xie and others, 2022). The tailings come from the preparation plant that dominantly handled the Springfield Coal and Hymera Coal. In that slurry pond, samples were collected at five sites. The ash content of the sediments ranged from 31.60 to 58.35 % and sulfur content from 4.06 to 7.75 %, a similar range to other slurry ponds in Indiana summarized in Table 4. At the Ayrshire pond, the total REE+Y+Sc on ash basis ranged from 245 to 285 ppm, and on whole-sample basis from 93 to 166 ppm. The ratio between LREE and HREE ranged from 7.53 to 8.49 (Xie and others, 2022) (Table 5). Although the concentrations of REE are below what is normally considered an economic grade (1,000 ppm on ash basis, Seredin and Dai, 2012), other factors such as ease of obtaining the sediment, proximity to highways, rails, etc., favor further investigation of these types of material. Even though the authors of the study caution about drawing conclusions based on only five sites, it is important to note that there are strong correlations between REE and ash yield, Al_2O_3 , and SiO_2 , providing a strong motivation to test these relationships in other locations. If these relationships are confirmed, these parameters, and ash yield in particular, could be valuable proxies to delineate most REE-potential zones within slurry ponds.

While the slurry pond deposits in Indiana are relatively well mapped by Harper and others (2009), the delineation of coarser-grained refuse (gobs) is not well known and an estimation of their volume in Indiana has not been attempted. These deposits, typically occurring in close proximity to slurry ponds, are composed of rock fragments from coal seam partings, roof or floor clastic sediments, or coal portions rich in mineral matter. Although currently, no data

Table 5. Concentrations of individual elements from Ayrshire coal tailings in Chandler, Indiana (after Xie and others, 2022). Summations in blue.

Samples	94,021	94,022	94,023	94,024	94,025	94,021	94,022	94,023	94,024	94,025		
Ash (%)	58.35	39.90	31.60	57.36	43.13	58.35	39.90	31.60	57.36	43.13		
Element		in pp	m on ash	basis		in ppm on whole-rock basis						
Sc	14	19	20	19	19	9	8	7	12	9		
Y	28	34	35	36	35	18	14	11	22	16		
La	37	42	45	40	42	24	17	15	25	20		
Ce	85	94	96	89	93	55	37	31	55	43		
Pr	10	11	11	11	11	7	4	4	7	5		
Nd	41	44	44	41	42	27	18	14	25	20		
Sm	8.5	9.4	9.3	9.1	8.9	5.50	3.7	3.0	5.6	4.1		
Eu	1.6	1.9	1.8	1.8	1.8	1.0	0.80	0.60	1.10	0.80		
Gd	6.8	7.9	7.6	7.8	7.8	4.4	3.1	2.5	4.8	3.6		
Tb	0.98	1.1	1.1	1.2	1.1	0.6	0.4	0.4	0.7	0.5		
Dy	5.2	6.1	6.1	6.4	6.0	3.4	2.4	2.0	3.9	2.8		
Но	1.0	1.2	1.2	1.2	1.2	0.6	0.5	0.4	0.7	0.6		
Er	2.7	3.0	3.3	3.2	3.1	1.8	1.3	1.1	2	1.4		
Tm	0.38	0.47	0.48	0.45	0.45	0.25	0.19	0.2	0.28	0.21		
Yb	2.4	2.9	3.0	2.8	2.7	1.6	1.2	1.0	1.7	1.3		
Lu	0.35	0.45	0.45	0.41	0.42	0.23	0.18	0.2	0.25	0.2		
REE ¹	203	226	230.0	215	221	132	90	75.0	132	103		
REY ²	231	260	265.0	251	256	150	103	87.0	154	119		
REYSc ³	245	279	285	270	275	160	111	93.0	166	128		

¹REE – rare earth elements

 $^{2}REY - REE + yttrium$

³*REYSc* – *REE* + *yttrium* + *scandium*

are available on REE concentrations in gobs in Indiana, from our REE data in Indiana coals (Mastalerz and others, 2020) we sugest that the assessment strategy should be to focus on gob piles related to older coal seams such as those of the Staunton and Brazil Formations, which were mined primarily in the more northern counties in Indiana along the basin margin during the early- to mid-20th century. The data also suggest that there are sufficient REE concentrations in the Springfield Coal to warrant evaluation of as many gob piles generated from mining this coal seam as can be discovered. Due to the Springfield's larger distribution and thickness, there are more large gob piles containing this waste rock than the thinner, more discontinuous older coal seams of the Brazil and Staunton Formations.

ACID MINE DRAINAGE

Water streams from abandoned coal mining and coal processing are called abandoned mine drainage or acid mine drainage (AMD). Mine drainage occurs when pyrite (a common mineral in coal) is exposed and reacts with water and air to form sulfuric acid and iron. The acidic runoff also dissolves some heavy metals such as nickel, zinc, or copper. Some of the dissolved iron can precipitate to form red, orange, or yellow sediments in such streams (Fig. 11).

Waste streams from abandoned coal mines and from the processing of Indiana coals are typically characterized by low pH and variably mineralized waters. Sources of these AMDs include coarse refuse piles (gobs), fine refuse slurries and piles (tailings), net acidic piles of overburden rock (spoil ridges), and flooded underground mine voids. The degree of mineralization is closely tied to the presence and amount of sulfide minerals in the coal or coal waste.

Highly mineralized acidic waste streams do not necessarily translate to elevated concentrations of REE. Our preliminary investigations indicate that a more diverse mineralization, usually indicated by the elevated presence of aluminum and magnesium, shows the potential of containing elevated REE. The highest degrees of aluminum- and magnesium-enriched mineralized waters are associated with gob piles containing substantial amounts of clastic rocks entrained in the waste pile during preliminary coal cleaning. The combination of highly acidic water enriched in sulfuric acid generated from the oxidation of abundant sulfide in gob piles, along with diverse mineralogy and substantial organic matter aggressively dissolved by the sulfuric



Figure 11. Photographs of acid mine drainage sample collection at the Midwestern (left) and Friar Tuck (right) sites.

acid, may result in significant concentrations of REE. For the purpose of evaluating the potential for economic deposits of REE in Indiana, it is important to locate and map the extent of abandoned mine land gob piles and evaluate the chemical composition of AMD leaching from them. Both surface and underground mine gob piles qualify for this approach. Such piles can be found from Vigo County in western Indiana down to Warrick County on the Ohio River in southern Indiana (Table 6, Fig. 12).



1-Green Valley B
2-Green Valley A
3-Chinook N Seep
4-Minnehaha Gob
5-Friar Tuck STR4 & STR5
6-Friar Tuck STR2
7-Friar Tuck Seep 108
8-Lacy Bioreactor Outlet
9-Lacy Seep 2
10-Midwestern Seep SP2A
11-Midwestern Bioreactor
12-Midwestern Seep
13-Midwestern Oxidation Pond
14-Midwestern Seep SW9A
15-Blackfoot MOAS Seep
16-Blackfoot SRB Seep
17-Enos Outlet
18-Enos Bioreactor
19-Enos VFP Outlet
20-Enos Acidic Pond
21-Enos Seep
22-Tecumseh Seep

Figure 12. Map showing known acid mine drainage sites in Indiana.

	ELEMENTS (all values in µg/l)														
Sites sampled	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Green Valley A	749.5	58.96	201.3	42.62	200.5	115.7	34.78	138.3	30.71	149.1	31.13	73.91	9.940	52.27	8.400
Green Valley B	674.9	102.4	371.1	61.76	220.1	99.47	30.47	131.3	28.18	137.7	28.51	69.26	9.150	48.10	7.700
Friar Tuck Seep 108	1791	120.4	690.4	138.6	650.6	242.9	72.06	278.7	53.46	244.8	57.59	143.9	17.90	105.1	17.13
Lacy Seep	152.7	9.978	77.09	17.79	86.87	30.40	7.981	30.61	5.396	24.64	5.182	11.49	1.428	6.827	1.050
Lacy Bioreactor Outlet	1.002	0.272	0.740	0.065	0.245	0.077	0.044	0.091	0.013	0.065	0.016	0.035	0.005	0.020	0.004
Midwest Seep	119.2	19.39	82.55	14.18	52.62	17.53	5.137	21.17	4.099	16.15	3.984	8.59	1.112	5.194	0.843
Midwest Bioreactor Outlet	11.17	3.662	8.121	1.081	3.939	0.953	0.250	1.434	0.206	0.896	0.203	0.431	0.047	0.196	0.032
Blackfoot Seep	839.7	54.36	360.8	81.32	393.9	142.1	35.84	158.8	27.93	131.0	26.55	62.42	8.739	41.46	7.002
Enos Seep	27.17	20.11	44.55	7.204	19.76	5.882	1.338	6.318	0.926	4.164	0.907	2.039	0.270	1.292	0.211
Enos Acidic Pond	15.18	7.250	18.63	3.168	11.49	3.272	0.746	3.172	0.486	2.150	0.444	0.997	0.132	0.675	0.109
Enos Bioreactor	0.344	0.129	0.239	0.030	0.105	0.037	0.022	0.034	0.006	0.026	0.006	0.015	0.002	0.010	0.002
Enos VFP Outlet	0.279	0.261	0.836	0.050	0.178	0.053	0.022	0.059	0.008	0.034	0.008	0.020	0.003	0.015	0.003
Enos Outlet	0.111	0.126	2.128	0.026	0.083	0.035	0.026	0.042	0.005	0.017	0.004	0.010	0.002	0.009	0.002
Alcoa Seep	1696	105.6	553.9	119.2	612.5	228.2	61.70	263.3	45.57	229.5	49.51	125.4	16.75	90.06	14.49

Table 6. Rare earth element concentrations from acid mine drainage seeps occurring in Indiana.



Figure 13. Examples of principal component analysis for AMD sites in Indiana.

Preliminary principal component analysis (PCA) of chemical data collected from these sites shows that strong correlation occurs between aluminum, magnesium, zinc, and REE (Fig. 13). This correlation suggests that a larger set of seeps can be evaluated using PCA to identify locations of high REE concentrations utilizing standard (less expensive than REE) metal analyses.

Because all REE have a +3 oxidation state, there is a strong likelihood that AMD enriched in REE may result in these elements being sequestered in the aluminum and iron oxide precipitates that result from oxidation and neutralization of AMD in treatment cells (oxidation ponds, wetlands, and bioreactors). These treatment cell precipitates warrant investigation to determine if REE are entrained at elevated concentrations and in which type of treatment cell they are most concentrated, as this would indicate a successful, passive way of concentrating REE from AMD. The preliminary data (Table 6) suggest that bioreactors may be a promising passive method for concentrating REE as shown at the Lacy, Midwest, and Enos sites. Because of the expense and time to have many seeps analyzed for REE, we suggest that a good strategy would be to use the pathfinder elements of aluminum, magnesium, and zinc to locate the most promising gob piles. Analyzing these elements along with calcium, iron, sulfate, and silicon would be more rapid, requiring less expensive instrumentation, and could be sufficiently informative to indicate where elevated REE concentrations could be expected.

COAL COMBUSTION PRODUCTS

Coal is a heterogeneous material with a solid fraction composed of organic and mineral matter. Upon combustion, the organic matter releases a large amount of heat and produces gaseous products, whereas the mineral fraction is turned into solid residue. This solid residue includes fly ash, bottom ash, boiler slag, and gypsum (from limestone-based flue gas desulphurization, FGD). Assuming that on average, coal used in a coal-fired power plant has ~10 % of mineral matter, then ~10 % of the volume of the coal feed used in the boiler remains as coal ash after combustion. This results in large volumes of coal ash produced in states that have coal-fired power plants. For example, in 2018, Indiana coal-fired power plants produced 6,849,800 tons of coal ash (American Coal Ash Association, 2018).

Coal ash storage concerns

Coal combustion residue is disposed of in landfills, surface impoundments built in the proximity of the power plants, or as mine fill. Some is also beneficially reused in concrete or as construction material. Coal combustion residue disposed of in landfills or in impoundments can be a source of water contamination. The environmental risk of improperly disposed coal ash on Indiana's water resources was comprehensively studied by the Hoosier Environmental Council (Frank and Maloney, 2020). Therefore, it is of great importance to have clear and consistent rules regarding coal ash disposal.

In the U.S., prior to 2015, states had the option of adopting their own requirements for safe coal ash disposal. Indiana had rules that applied to coal ash landfills and rules that applied if a coal ash impoundment was closed. No rules existed on ash impoundment site selection, construction, or whether they were monitored for groundwater contamination.

In 2015, the U.S. Environmental Protection Agency (EPA) proposed a rule on coal ash disposal known as the Coal Combustion Residuals Rule, or CCR Rule. It introduced a set of standards for the location and structure of coal ash impoundments to reduce the risk of structural failure or water contamination, and over the years, several revisions to that rule were made. In 2016, Indiana's Environmental Rules Board adopted the federal CCR Rule language on impoundments. This rule is considered by the Indiana Department of Environmental Management (IDEM) to be self-implementing, and not necessarily enforced. In 2015, the EPA issued a companion rule to the CCR Rule regarding the release of water that had been in contact with coal ash titled the "Effluent Limitation Guidelines and Standards for the Steam Electric Power Generating Point Source Category" and known as the ELG Rule. Issued under the Clean Water Act, this rule introduced limits on the coal ash contaminants that could be released into waterways as point source discharges. In 2017, the US Administration tabled the implementation of this rule, and in 2020, finalized a revision of the ELG Rule, which relaxed some of the limits proposed in the original ELG Rule.

As a result of the original CCR and ELG Rules, most Indiana coal-fired power plants stopped disposing of coal ash in impoundments and began using dry handling systems and landfills. Some existing coal ash impoundments have failed the CCR Rule location requirements or violated standards for groundwater protection and will have to close. In January 2022, the EPA released documents that clarify important portions of the federal coal ash rule (CCR Rule). These clarifications are meant to avoid misinterpretations and to contribute to more effective and environmentally sound management of coal ash sites in Indiana.

Quantities of coal ash in Indiana

In total, coal ash deposits occupy $\sim 2,184$ acres, storing $\sim 52,566,153$ m³ of ash (Table 7, Figs. 14-15). The data for individual sites come from various sources (dominantly,

site closure reports of various companies) and present our best estimates at this time. However, the volumes of ash change as a result of the beneficial use or displacement of the material in response to EPA regulations.

Table 7. Compilation of coal ash impoundments, their areas, and the volumes of coal ash available at individual sites. For site locations, see Figure 14.

Coal ash impoundments	Company	Area (acres)	Volumes of ash (m ³)		
1-Mitchell	NiSource	8.3	152,375.9		
2-Bailly	NIPSCO	19.51	76,523.6		
3-Michigan City	NIPSCO	15.0	130,739.0		
4-Shaffer Station	NiSource	116.2	960,468.3		
5-Cayuga	Duke Energy	250.5	8,169,738.1		
6-Wabash	Duke Energy	283.2	5,636,693.1		
7-Harding Street	Indiana Power & Light	102.4	283,691.4		
8-Eagle Valley	Indiana Power & Light	84.2	2,182,410.2		
9-Edwardsport	Duke Energy	12.76	gasification slag		
10-Petersburg	Indiana Power & Light	150.1	4,357,966.4		
11-Frank E. Ratts	Hoosier Energy	57	175,847.8		
12-Gibson	Duke Energy	423	15,742,771.2		
13-A.B. Brown	Vectren	156	4,687,333.0		
14-F.B. Culley	S IN Gas and Electric	43	1,010,222.5		
15-Rockport	American Electric Power	111.1	390,687.9		
16-Gallagher	Duke Energy	158.5	5,828,676.8		
17-Clifty Creek	IN-KY Electric Corporation	115	2,633,561.9		
18-Tanners Creek	Indiana Michigan Power	91.4	246,446.8		







Figure 15. Bar graph showing volumes of coal ash available at individual sites in Indiana. For site locations, see Figure 11.

Coal ash composition

Composition of coal ash has been well researched worldwide, to a large extent because of environmental concerns (e.g., Silva and others, 2012; Saikia and others, 2015. In Indiana, Mastalerz and others (2004) studied relationships between the properties of the low-sulfur Danville Coal and the high-sulfur Spring-field Coal and their corresponding ashes (Table 9). From the baghouse ash collection system, Danville Coal ash yield ranged from 64.4 to 98.1 weight %, and carbon (C) content ranged from 0.84 to 22.73 weight % (Table 8). Sulfur (S) content ranged from 0.19 to 0.29 %. SiO₂ ranged from 54.5 to 63.7 % and Al₂O₃ from 21.7 to 25.8

weight %. Fly ash from the high-sulfur Springfield Coal contained more than 95 % ash and about 3 % C. Sulfur content ranged from 0.66 to 0.80 %, higher than in the Danville ash. SiO₂ ranged from 40.5 to 44.6 and Al₂O₃ ranged from 17 to 19.6 % (Tables 10-11). Mastalerz and others (2004) concluded that the properties of fly ash from these coals reflect the properties of the feed coal, as well as local combustion (e.g., temperature) and post-combustion (e.g., ash collection conditions). Sulfur and spinel content, as well as arsenic (As), lead (Pb), and zinc (Zn) concentrations of the fly ash, are the parameters that most closely reflect the properties of the feed coal.

Table 8. Table showing properties of fly ash from low-sulfur Danville Coal in comparison to pulverized coal and delivered
coal (from Mastalerz and others, 2004). Abbreviated as B-boiler, BH-baghouse, RPH-rear pass hopper, PC-pulverized
coal, nd-not determined, wt-weight.

Parameter	Unit	B1 BH1	B1 BH3	B1 BH5	B1 BH7	B1 average	B2 BH2	B2 BH4	B2 BH6	B2 BH8	B2 average	B1 RPH	B1 PC	B2 PC	Mine product washed
Ash	wt%	73.3	74.1	64.4	72.5	71.08	77.3	69.5	76.5	81.5	76.2	98.10	9.94	10.40	9.84
Moisture	wt%	0.85	0.91	1.00	0.88	0.91	0.66	0.71	0.74	0.66	0.69	0.34	3.31	3.30	7.27
VM	wt%	3.65	3.17	3.19	3.03	3.26	1.90	1.89	2.02	2.20	2.00	1.74	32.03	32.30	nd
FC	wt%	21.03	21.23	18.33	23.24	20.96	19.71	17.40	17.82	14.69	17.41	0.01	51.25	52.03	nd
С	wt%	22.71	22.73	17.60	24.20	21.81	20.71	18.31	19.00	15.71	18.43	0.84	69.04	69.78	nd
Н	wt%	0.23	0.20	0.18	0.21	0.21	0.15	0.12	0.14	0.10	0.13	0.07	5.47	5.34	nd
N	wt%	0.36	0.36	0.26	0.38	0.34	0.29	0.26	0.26	0.20	0.25	0.01	1.62	1.65	nd
S _{total}	wt%	0.34	0.35	0.30	0.32	0.33	0.19	0.19	0.23	0.19	0.20	0.29	0.48	0.45	0.508
0	wt%	1.83	1.38	3.82	1.96	2.25	0.85	0.92	0.81	1.23	0.95	0.67	13.87	12.96	nd
Hg	ppm	0.19	0.13	0.12	0.17	0.15	0.20	0.15	0.22	0.21	0.20	0.01	0.02	0.02	< 0.02
CI	%	< 0.02	0.03	0.05	0.03	0.04	0.02	0.02	0.02	0.02	0.02	0.03	0.1	0.10	0.11
SiO ₂	%	63.7	58.8	54.5	57.9	58.7	59.4	58.9	56.1	62.9	59.3	58.0	51.7	54.8	54.1
Al ₂ O ₃	%	25.8	24.0	22.5	23.4	23.9	23.6	22.7	21.7	25.1	23.3	22.6	21.7	22.4	23
Fe ₂ O ₃	%	6.0	5.6	9.6	7.1	7.1	8.8	9.2	9.0	5.5	8.1	11.7	5.8	4.9	5.7
CaO	%	1.7	1.7	6.0	2.6	3.0	2.3	4.0	3.0	1.3	2.7	1.6	1.4	1.3	1.3
MgO	%	1.5	1.4	1.4	1.4	1.4	1.5	1.4	1.4	1.5	1.5	1.3	1.3	1.4	1.4
Na ₂ O	%	1.10	1.00	0.78	1.00	0.97	0.94	0.95	0.96	1.10	0.99	1.00	1.00	1.30	1.20
K ₂ O	%	3.6	3.4	2.9	3.4	3.3	3.3	3.0	2.9	3.5	3.2	3.1	3.0	3.4	3.2
P ₂ O ₅	%	0.12	0.13	0.16	0.12	0.13	0.12	0.14	0.12	0.12	0.13	0.13	0.10	0.12	0.13
TiO ₂	%	1.4	1.3	1.0	1.2	1.2	1.3	1.2	1.2	1.5	1.3	1.4	1.3	1.4	1.3
SO ₃	%	0.29	0.27	0.74	0.52	0.46	0.26	0.65	0.35	0.10	0.34	0.43	0.96	1.00	1.10
Hyd Se	ppm	6.8	7.2	6.9	6.0	6.7	39.6	23.4	12.6	10.3	21.5	3.0	0.6	0.6	0.7

Table 9. Table showing trace elements of fly ash from low-sulfur Danville Coal in comparison to pulverized coal and coal delivered to the plant (mine product), (from Mastalerz and others, 2004). Abbreviated as B-boiler, BH-baghouse, RPH-rear pass hopper, PC-pulverized coal.

Parameter	Unit	B1 BH1	B1 BH3	B1 BH5	B1 BH7	B1 average	B2 BH2	B2 BH4	B2 BH6	B2 BH8	B2 average	B1 RPH	B1 PC	B2 PC	Mine product washed
Ag	ppm	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
As	ppm	17.5	18.8	9.3	16.7	15.6	21.3	15.4	17.4	21.6	18.9	61.6	21.6	18.9	15.9
Au	ppm	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Bi	ppm	0.59	0.61	0.22	0.48	0.48	0.99	0.54	0.51	0.82	0.72	0.50	0.76	0.39	0.46
Cd	ppm	5.2	4.2	10.4	5.6	6.4	4.5	4.6	7.3	5.1	5.4	5.1	6.0	4.1	5.9
Cs	ppm	13.6	13.8	10.3	13.3	12.8	12.1	12.0	12.2	14.1	12.6	12.1	13.6	12.5	14.1
Ga	ppm	35.5	37.7	22.3	34.7	32.6	30.5	26.8	31	38.6	31.7	32.0	43.0	40.9	43.0
Ge	ppm	250	268	111	218	212	200	153	188	275	204	214	207	180	202
Мо	ppm	42.9	43.4	28.8	39.6	38.7	38.5	37.2	42.5	46.2	41.1	39.1	39.3	37.2	43.2
Nb	ppm	18.2	18.6	11.8	16.8	16.4	16.1	15.1	16.3	26.0	18.4	17.7	19.6	32.7	19.3
Pb	ppm	74.2	79.1	36.9	74.3	66.1	63.1	54.1	64.7	84.8	66.7	102.0	103.0	70.0	69.2
Rb	ppm	193	199	153	194	185	176	174	178	201	182	176	186	175	193
Sb	ppm	47.9	51.1	26.8	45.4	42.8	41.4	37.0	41.6	58.4	44.6	42.4	42.1	45.7	42.0
Sn	ppm	10.3	10.5	6.3	9.2	9.1	10	9.0	9.1	19.6	11.9	8.5	13.3	13.1	9.8
Те	ppm	0.35	0.34	0.22	0.28	0.30	0.4	0.3	0.3	6.5	1.9	0.4	0.2	1.8	0.3
TI	ppm	1.6	1.8	0.7	1.5	1.4	1.7	1.1	1.3	2.0	1.5	3.6	2.4	1.6	2.0
U	ppm	11.8	12.2	7.9	11.4	10.8	10.9	10.6	11.2	13.2	11.5	12.4	10.5	10.0	10.5
Ве	ppm	24.6	25.1	14.0	22.3	21.5	20.7	17.5	19.2	24.1	20.4	20.9	25.8	23.1	27.6
Co	ppm	68.7	70.2	43.9	63.9	61.7	60.0	53.1	59.0	71.5	60.9	69.6	82.3	94.1	83.6
Cr	ppm	155	159	113	148	144	144	138	138	145	141	157	172	182	147
Cu	ppm	92.0	87.2	80.3	95.0	88.6	90.5	89.8	100.0	94.9	93.8	90.5	250.0	138.0	114.0
Li	ppm	91.5	93.5	95.0	93.1	93.3	90.9	94.1	88.8	93.8	91.9	94.4	87.0	88.0	90.7
Mn	ppm	399	383	1270	626	670	627	942	951	359	720	466	405	360	427
Ni	ppm	311	318	178	282	272	264	230	254	326	269	296	517	463	342
Sc	ppm	34.8	35.5	27.7	33.4	32.9	32.5	30.7	32.0	35.5	32.7	34.5	39.3	39.2	46.8
Sr	ppm	389	387	393	390	390	356	374	373	381	371	391	408	424	464
Th	ppm	16.4	16.3	13.4	20.1	16.6	16.4	25.8	17.8	18.5	19.6	19.2	20.8	21.0	21.3
V	ppm	278	276	185	260	250	244	229	240	292	251	274	284	352	297
Y	ppm	44.3	44.0	36.1	43.8	42.1	41.4	41.0	42.8	47.1	43.1	47.1	37.3	43.7	39.4
Zn	ppm	507	446	1380	667	750	519	534	718	476	562	475	556	445	658
В	ppm	691	765	632	640	682	780	790	739	814	781	545	1180	1090	1140
Ва	ppm	540	522	457	500	505	510	492	461	544	502	476	470	488	493
Zr	ppm	343	356	262	305	317	327	279	288	351	311	316	331	348	330

Table 10. Table showing properties of fly ash from high-sulfur Springfield Coal in comparison to pulverized coal (from
Mastalerz and others, 2004). Abbreviated as FA-fly ash, PC-pulverized coal, FDG-flue gas desulfurization, nd-not deter-
mined, wt-weight.

Parameter	Unit	Unit 2 econ. east FA	Unit 3 econ. east FA	Unit 3 econ. west FA	Unit 2 + 3 FGD gypsum	Unit 3 Mill C1 PC	Unit 3 Mill B1 PC	Unit 3 Mill E PC	Unit 2 Mill B3 PC	Unit 2 Mill A PC
Ash	wt %	96.10	95.70	95.90	77.30	16.50	14.20	13.30	14.30	15.40
Moisture	wt %	0.43	0.47	0.44	0.69	2.59	2.57	2.74	2.48	2.33
VM	wt %	2.46	3.60	2.45	13.13	nd	36.88	37.54	37.79	37.97
FC	wt %	1.80	1.49	1.51	1.12	nd	43.19	44.46	43.51	43.32
C	wt %	3.32	3.11	3.28	0.09	nd	62.61	65.17	64.51	64.61
Н	wt %	0.03	0.05	0.07	2.43	nd	5.12	5.36	5.14	5.28
N	wt %	0.01	0.01	0.01	0.01	nd	1.29	1.32	1.29	1.26
S _{total}	wt %	0.70	0.80	0.66	20.7	5.35	5.49	5.16	5.52	5.19
S _{pyr}	wt %	nd	nd	nd	nd	nd	2.42	2.20	2.55	2.22
S _{sulf}	wt %	nd	nd	nd	nd	nd	0.31	0.24	0.13	0.19
S _{org}	wt %	nd	nd	nd	nd	nd	2.76	2.72	2.84	2.78
0	wt %	0.41	0.96	0.26	0.01	nd	10.40	10.18	8.64	9.87
Hg	ppm	0.02	0.01	0.02	0.04	0.06	0.08	0.08	0.08	0.07
CI	%	< 0.02	< 0.02	0.02	0.02	0.03	0.02	0.02	0.04	0.04
SiO ₂	%	44.6	41.9	40.5	1.7	35.6	34.8	34.7	32.1	33.1
Al ₂ O ₃	%	19.6	17.6	17.0	0.3	15.7	15.6	14.9	14.5	14.8
Fe ₂ O ₃	%	28.9	27.6	30.7	0.4	25.0	26.3	25.7	22.8	26.6
Ca0	%	8.6	8.5	9.4	45.8	7.0	7.9	7.3	7.6	7.4
MgO	%	1.20	1.00	0.99	0.06	0.92	0.95	0.88	0.84	0.89
Na ₂ O	%	0.59	0.55	0.49	0.01	0.57	0.59	0.51	0.54	0.52
K ₂ O	%	2.8	2.4	2.4	0.1	2.5	2.1	2.0	2.0	2.1
P ₂ O ₅	%	0.17	0.18	0.17	0.02	0.15	0.19	0.18	0.16	0.16
TiO ₂	%	0.88	0.78	0.75	< 0.02	0.7	0.74	0.72	0.66	0.69
SO ₃	%	1.5	1.6	1.4	59.8	4.4	4.4	4.0	3.7	4.0
Se	ppm	7.4	5.3	5.1	0.8	3.8	4.6	3.9	6.1	4.2

Table 11. Table showing trace elements of fly ash from high-sulfur Springfield Coal in comparison to pulverized coal andpetrographic composition of fly ash (from Mastalerz and others, 2004). Abbreviated as FA-fly ash, PC-pulverized coal,FDG-flue gas desulfurization.

Parameter	Unit	Unit 2 econ. east FA	Unit 3 econ. east FA	Unit 3 econ. west FA	Unit 2 + 3 FGD gypsum	Unit 3 Mill C1 PC	Unit 3 Mill B1 PC	Unit 3 Mill E PC	Unit 2 Mill B3 PC	Unit 2 Mill A PC
Ag	ppm	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
As	ppm	66.3	82.8	52.7	< 0.2	72.7	78.0	75.8	56.4	56.4
Au	ppm	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Bi	ppm	0.41	0.37	0.19	< 0.10	0.38	0.38	0.36	0.36	0.32
Cd	ppm	6.2	7.1	4.8	0.1	5.3	7.7	9.6	7.2	5.0
Cs	ppm	9.3	8.4	7.3	< 0.1	7.6	7.3	7.0	7.3	7.2
Ga	ppm	20.5	19.1	14.7	0.3	20.0	20.7	21.1	19.2	19.0
Ge	ppm	19.0	27.2	19.4	0.3	18.0	23.3	27.9	19.7	17.2
Мо	ppm	50.0	53.7	41.6	1.6	43.2	52.4	48.4	46.0	39.2
Nb	ppm	9.9	9.5	8.4	0.1	8.0	8.5	8.8	8.2	8.4
Pb	ppm	31.4	33.4	25.3	< 0.5	26.9	31.9	35.6	27.2	25.4
Rb	ppm	140	131	117	1.6	116	112	108	111	109
Sb	ppm	10.6	8.3	6.2	0.2	5.2	6.6	7.2	7.9	6.8
Sn	ppm	5.8	5.7	4.1	< 3.0	5.8	4.9	4.8	4.4	4.7
Те	ppm	0.35	0.36	0.29	< 0.10	0.29	0.29	0.28	0.28	0.24
TI	ppm	11.9	12.8	9.2	< 0.1	11.4	11.7	12.3	11.9	12.1
U	ppm	24.4	22.6	21.7	0.57	16.7	20.3	19.0	21.1	18.6
Ве	ppm	9.2	9.2	8.2	1.0	8.0	9.0	9.8	8.4	8.2
Со	ppm	27.7	30.0	27.6	2.0	30.3	32.4	32.1	30.0	30.3
Cr	ppm	152	141	140	3	162	138	132	141	143
Cu	ppm	100.0	84.0	85.5	5.8	98.6	103.0	97.9	114.0	102.0
Li	ppm	74.7	77.9	79.0	55.0	79.5	78.6	71.5	64.8	70.6
Mn	ppm	462	530	522	10	434	507	436	494	456
Ni	ppm	91	104	102	4	120	110	112	157	99
Sc	ppm	18.8	18.2	17.1	4.0	25.3	26.5	25.6	23.6	23.8
Sr	ppm	208	216	214	494	244	278	280	252	251
Th	ppm	17.6	13.1	14.4	7.6	17.1	17.1	14.0	14.3	13.9
V	ppm	286	310	295	2.2	280	342	312	305	269
Y	ppm	446.0	45.0	44.7	8.8	44.6	48.4	46.5	42.0	41.5
Zn	ppm	351	318	232	39.2	361	337	372	348	336
В	ppm	1,300	1,160	1,060	< 20	860	1,010	1,040	932	862
Ва	ppm	407	356	354	22	327	322	311	317	323
Zr	ppm	167	162	145	40	125	128	136	124	123

Coal ash has been suggested as one of the more promising sources for REE (e.g., Blissett and others, 2014; Franus and others, 2015; Hower and others, 2020; Pan and others, 2020). Kolker and others (2017) indicated that these elements are concentrated in the glass phase, the most abundant component of coal fly ash, and suggested that this fraction should be targeted for further concentration and extraction.

To our knowledge, no REE data are available on coal ash deposits in Indiana. The association of REE with mineral matter in numerous coals in other areas (e.g., Seredin and Dai, 2012; Dai and others, 2018), and commonly mentioned correlations between Al and REE (Franus and others, 2015; Kolker and others, 2017; Lin and others, 2017; Kolker and others, 2021) point to coal ash deposits as a promising source of REE, especially considering the large volumes of coal ash available in Indiana (Table 6). However, a well-designed geochemical survey that would include REE as well as major, minor, and trace element analyses is necessary to determine REE concentrations and identify the most promising deposits.

CONCLUSIONS

The available REE data on Indiana coals show that these coals represent low-grade source material and that the Staunton Formation and Brazil Formation coals are generally richer in REE than the coals of the Linton, Petersburg, or Dugger Formations. However, we note that to better understand REE potential of Indiana coals, more high-quality data collected using modern sensitive techniques are needed on REE concentrations and REE associations.

Few data are available on coal preparation plant waste from Indiana; the available data come from one slurry pond. Correlations between REE and ash yield, SiO_2 , and Al_2O_3 provide a strong motivation to test these relationships in other locations. If such relationships are confirmed, these commonly available parameters could be valuable proxies to delineate the most REE-potential zones within slurry ponds.

No data are available on REE concentrations in gobs in Indiana, but based on our REE data in Indiana coals, we suggest that the assessment strategy should be to focus on gob piles related to older coal seams such as those of the Staunton and Brazil Formations which were mined primarily in the more northern counties in Indiana along the basin margin. The data on coals also suggest that there is sufficient REE concentration in the Springfield Coal to warrant evaluation of as many gob piles generated from mining this coal seam as can be discovered. In addition to locating and mapping the extent of abandoned mine land gob piles, it is also important to evaluate the chemical composition of AMD leaching from them, both surface and underground. Such piles can be found from Vigo County in western Indiana down to Warrick County on the Ohio River in southern Indiana. Preliminary PCA chemical data collected from AMD sites show that there is a strong correlation between aluminum, magnesium, zinc, and REE. This correlation, although preliminary, strongly suggests that a larger set of seeps can be evaluated using PCA to identify the most potential REE sites.

To our knowledge, no REE data are available on coal ash deposits in Indiana and this type of data are in great demand. The association of REE with mineral matter in numerous coals in other areas, and commonly mentioned correlations between Al and REE, point to coal ash deposits as a very promising source of REE, especially considering the large volumes of coal ash available in Indiana.

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