Chemical extraction of rare earth elements from coal ash

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Abstract

The overall goal of this study is to develop a suitable flow sheet to extract rare earth elements (REEs) from coal ash. A total of 14 coal samples of different ranks were examined for REE concentration, and an anthracite coal sample with the highest REE concentration of more than 700 ppm in the coal ash was selected for REE extraction tests. This paper reports on the results of the experimental program completed in the first part of the study, which included high-temperature leaching with nitric acid followed by solvent extraction tests using various organic extractants, namely, tributyl phosphate, Cyanex 572, di-(2-ethylhexyl)phosphoric acid (D2EHPA) and their combinations. A 4×2×2 experimental design was used to conduct a total of 32 high-temperature leaching tests by varying acid molarity at four levels, solids content at two levels and leaching time at two levels. The highest recovery rates of 90 percent for light rare earth elements (LREEs) and 94 percent for heavy rare earth elements (HREEs) were obtained from the optimum leaching test conditions while maintaining impurity recovery to the leachate at less than 40 percent. D2EHPA was found to be the best extractant in this solvent extraction test series, providing an REE recovery rate of nearly 99 percent.

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Introduction

Global demand for rare earth elements (REEs) and other strategic metals is increasing rapidly due to their use in a variety of advanced technological applications, with more than 100 kt of rare earth oxides used worldwide on an annual basis. The United States has less than 10 percent of the world reserves of REE mineral deposits, and in 2013 imported more than 60 percent of its rare earth oxides from other countries, mainly China (United States Geological Survey, 2017). China's institution of export quotas has significantly reduced supply to the United States, raising the urgency of finding new ways of producing REEs and/or substitutes. Coal combustion byproducts, which are usually discarded as waste materials, are known to contain REEs in low concentrations that could be extracted with a suitable process flow sheet. This may be a worthwhile route to pursue, considering the short supply of rare earth minerals and the abundance of coal ash in thousands of ash ponds in the United States. More than 110 Mt of coal combustion byproducts are produced annually in the process of satisfying the country's need for electricity (American Coal Ash Association, 2016), and less than 50 percent of these byproducts are being successfully used in various applications, with the remainder dumped as waste materials in landfills and ash ponds.

REE characterization. Nearly 200 rare earth minerals have been identified. Among them, bastnaesite ($(La,Ce)FCO_3$), monazite ($(Ce,La,Y,Th)PO_4$) and xenotime (YPO_4) are the main commercially targeted minerals. Several studies have shown the occurrence of REEs in coal and coal byproducts, including coal ash. Although the concentration of REEs in coal fly ash on an average global basis is estimated at 445 ppm (Ketris and Yudovich, 2009), many regions have coal with higher concentrations of REEs than this average, such as Western Siberia, Inner Mongolia, and the Fire Clay coal bed in eastern Kentucky in the United States. In a recent study conducted by Zhang, Groppo and Honaker (2015), REE concentrations as high as 2,000 ppm were reported in coal seams and coal preparation rejects. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was used to identify monazite, xe-

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notime and bastnaesite as the REE-bearing minerals in coal, and the size of the REE minerals ranged from 1 to 10 µm. In another study conducted by Hower et al. (2013), several coal fly-ash samples were collected from different power plants, and total REE concentrations were found to be in the range of 187 to 600 ppm. Blissett, Smalley and Rowson (2014) used inductively coupled plasma-mass spectrometry (ICP-MS) to subject six different coal ashes — three each from the United Kingdom and Poland — to elemental analysis and found the total rare earth oxide concentrations to be in the range of 297 to 579 ppm for the U.K. coal ash samples and 371 to 432 ppm for the Polish samples. In a more comprehensive study conducted by Seredin and Dai (2012), the widespread accumulation of lanthanides and yttrium in many coal deposits was studied worldwide. They found high concentrations, greater than 10,000 ppm, in the coal samples and coal ashes as well as in the basement rocks of coal basins, and discovered that REEs are present in fine-grained authigenic minerals, such as aluminum phosphates, sulfates of the alunite supergroup, and carbonates. They also indicated that the Haerwusu and Heidaigou mines in Jungar Coalfield in China, which produces 44 Mt/a of coal, have average rare earth oxide contents of 0.12 to 0.16 percent in ash. According to their estimate, the total rare earth oxide content in Jungar Coalfield can be as high as 5 Mt.

Leaching. REEs need to be in ionic form to be extracted from their associated minerals. Leaching is the chemical process used to release REEs from the REE-bearing rocks and minerals.

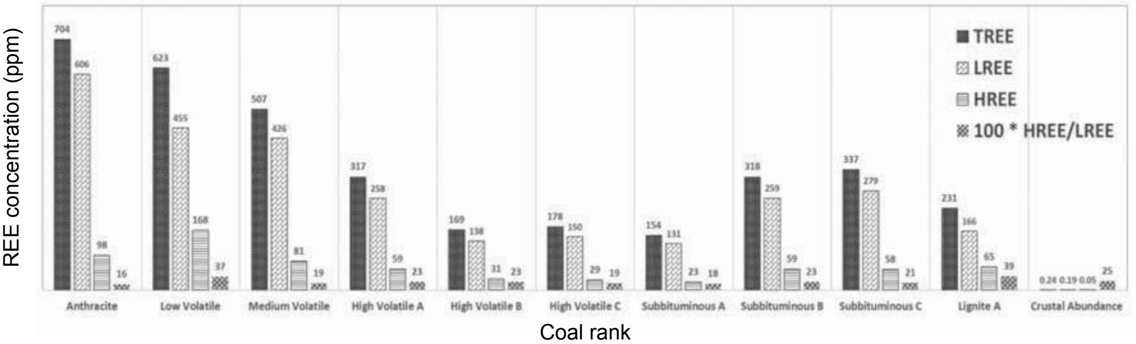


Figure 1 — Rare earth element (REE) concentrations of various coal ranks.

Table 1 — Basic characterization data for the coal samples.

Coal rank	LREE, dry basis (ppm)	HREE, dry basis (ppm)	TREE, dry basis (ppm)	Ash, dry basis (%)	Sulfur, dry basis (%)	Carbon, dmmf basis (%)	Hydrogen, dmmf basis (%)	Volatile matter, dmmf basis (%)	Vitrinite, dmmf basis (%)	Vitrinite reflectance (%)
Anthracite	606	98	704	11.2	0.5	91.5	4.1	3.9	87	5.19
Low volatile	455	168	623	4.6	0.74	90.6	4.9	18.7	89	1.71
Medium volatile	426	81	507	3.9	0.79	88.5	5.4	30.9	77	1.16
Medium volatile	642	108	750	4.2	0.62	88.8	5	25.7	77	1.35
Medium volatile	197	49	247	5.4	0.65	88.1	5.9	28.2	94	1.28
High volatile A*	258	59	317	9.4	3.87	84.6	5.8	42.3	79	0.73
High volatile B	138	31	169	12.3	4.21	82.2	6	45.6	86	0.56
High volatile C	150	29	178	16.2	4.52	81.8	5.7	43.8	87	0.52
Subbituminous A	131	23	154	13.9	0.72	79.2	5.4	40.6	74	0.46
Subbituminous B	259	59	318	7.6	0.43	76.2	6.2	48.1	86	0.29
Lignite A	166	65	231	9.6	0.74	74.1	4.5	61.6	74	0.35
Subbituminous C	359	79	438	13.8	0.73	75.8	5.3	51.8	79	0.37
Subbituminous C	200	36	236	15.8	0.99	75.9	5.8	55.5	78	0.36

* Average of two samples.

Some techniques commercially used for REE leaching from conventional resources are:

- *Sulfuric acid baking and leaching, also called concentrated sulfuric acid leaching*: This method is performed in the temperature range of 200 to 500 °C. Sulfuric acid produces sulfide oxide gases during the process, and this must be efficiently treated for environmental reasons (Lucas et al., 2015).
- *Roast-hydrochloric acid leach process.* This technique was developed to recover REEs from the Mountain Pass Mine in California, where the main REE-bearing mineral is bastnaesite. This process has some drawbacks: the impure cerium still contains some radioactive thorium, and this process is not able to extract the REE fluorides (Lucas et al., 2015).
- *Caustic soda leaching*: This was developed by Kruesi and Duker (1965) for REE extraction from bastnaesite ore. This type of leaching is carried out in the temperature range of 120 to 130 °C. There are several advantages to this process: radioactive impurities like thorium and radium are effectively removed. solid waste production is minimized, and gaseous hydrofluoric acid is not produced, hence there is no need for a complex process

Table 2 — Leaching test conditions and results.

	Test conditions				Leachate REE concentration			Leaching recovery (%)		
Test #	Acid Conc. (mol/L)	Solids Conc. (g/L)	Time (min)	Temp. (°C)	LREE (ppm)	HREE (ppm)	TREE (ppm)	LREE	HREE	TREE
1	0.3	30	20	85	8.14	1.48	9.61	45.86	54.72	47.03
2	0.3	100	20	85	25.69	4.75	30.43	41.85	50.81	43.04
3	1	30	20	85	10.52	1.73	12.25	59.69	64.38	60.31
4	1	100	20	85	30.8	5.28	36.08	49.56	55.81	50.39
5	3	30	20	85	12.24	2.01	14.25	70	75.63	70.74
6	3	100	20	85	35	5.6	40.6	56.21	59.14	56.6
7	6	30	20	85	12.27	1.81	14.08	68.93	66.75	68.64
8	6	100	20	85	39.59	5.99	45.59	65.54	65.21	65.5
9	0.3	30	60	85	10.88	1.89	12.77	59.81	68.19	60.92
10	0.3	100	60	85	28.03	5.18	33.22	41.99	51.02	43.18
11	1	30	60	85	12.68	2.22	14.9	71.03	81.65	72.43
12	1	100	60	85	36.74	5.98	42.72	59.86	64	60.41
13	3	30	60	85	13.83	2.12	15.95	77.14	77.74	77.21
14	3	100	60	85	40.45	6.42	46.87	64.97	67.78	65.34
15	6	30	60	85	16	2.36	18.36	90.86	88.19	90.5
16	6	100	60	85	44.43	6.65	51.08	71.04	69.81	70.88
17	0.3	30	20	85	7.9	1.55	9.45	44.25	57.23	45.96
18	0.3	100	20	85	19.74	4.13	23.87	31.11	42.75	32.65
19	1	30	20	85	10.69	1.92	12.61	60.91	71.92	62.37
20	1	100	20	85	31.57	5.59	37.17	50.09	58.32	51.17
21	3	30	20	85	12.47	2.1	14.57	69.1	76.37	70.06
22	3	100	20	85	34.75	5.68	40.43	56.13	60.23	56.67
23	6	30	20	85	13	2	15	72.89	73.69	73
24	6	100	20	85	37.37	5.71	43.08	59.77	59.98	59.8
25	0.3	30	60	85	10.34	1.96	12.3	55.78	69.3	57.57
26	0.3	100	60	85	29.38	5.29	34.67	48.62	57.49	49.79
27	1	30	60	85	11.53	1.97	13.51	64.88	72.98	65.95
28	1	100	60	85	29.65	5.1	34.75	47.7	53.93	48.53
29	3	30	60	85	16	2.59	18.59	88.66	94.19	89.39
30	3	100	60	85	34.35	5.31	39.65	59.86	60.78	59.98
31	6	30	60	85	15.16	2.29	17.45	84.7	83.88	84.59
32	6	100	60	85	43.31	6.35	49.67	73.22	70.56	72.87

to capture the hydrofluoric acid. Fluorine is removed as sodium fluoride (NaF) in aqueous solution (Lucas et al., 2015; Peelman et al., 2014).

There is as yet no commercially available leaching technique to leach REEs from coal ash, though several laboratory investigations have been reported in recent years. Kashiwakura et al. (2013) used dilute sulfuric acid (H_2SO_4) to dissolve REEs from coal fly ash. Two different coal ash samples collected from an electrical power company in Soma, Japan, were leached at temperatures of 30 to 80 °C for 120 minutes. The overall results were not promising, with the highest leaching recovery rate at 45 percent and the lowest around 8 percent. Another laboratory-scale study performed by Peramaki (2014) investigated the recovery of REEs from industrial biomass and peat fly ash. Joshi et al. (2013) patented a process to recover REEs from coal ash in which hot nitric acid at 90 °C was used in two stages to leach REEs from coal ash, and the REEs were extracted from the aqueous leachates by solvent extraction using a mixture of tributyl phosphate and kerosene. Other than acid leaching, alkali and ammonium carbonate leaching can also be used for REE leaching. Vasconcellos et al. (2006) used ammonium carbonate to enrich yttrium from a monazite sand concentrate and then applied a 200-g/L solution of ammonium carbonate at room temperature to leach yttrium from the sand concentrate. After 10 to 30 minutes of contact time, a rich yttrium solution was obtained with 60.3 percent Y_2O_3 content. Other REEs were also dissolved in the ammonium carbonate, but the goal was to concentrate yttrium from an REE mixture. In the next stage, the yttrium solution was treated with an excess of hydrogen peroxide to separate cerium, praseodymium and neodymium peroxides as precipitates.

Solvent extraction. After leaching, the next stage is to extract the REEs from the aqueous leachate solution. The three conventional extraction methods include solvent extraction, ion exchange and precipitation, among which solvent extraction is the most widely used in the world. Almost all of the REE plants in countries like China, the United States and Malaysia are based on solvent extraction (Lucas et al., 2015; Peppard et al., 1953; Sherrington, 1983). Solvent extraction conditions and the type of organic extractants used depend on the technical requirements, such as efficiency, selectivity and environmental factors, as well as cost considerations. The main extractants used in REE separation processes are tributyl phosphate (TBP), tricaprylylmethyl ammonium chloride, Versatic acid (Hexion Inc., Columbus, OH), di-(2-ethylhexyl) phosphoric acid (D2EHPA) and mono-2-ethylhexyl ester. The chemical reaction involved in the extraction process determines the extraction mechanism, which in turn determines the energy consumption (Lucas et al., 2015; Xie et al., 2014).

Research has been scarce on the extraction or precipitation of REEs from coal ash. In a recent study, Peramaki (2014) tried solvent extraction to extract REEs from leachate of industrial fly ash, using D2EHPA mixed in kerosene in varying proportions as extractant. Heavy rare earth elements (HREEs) were efficiently extracted with 5 percent D2EHPA in kerosene, but a higher percentage was needed for the extraction of light rare earth elements (LREEs). The pH environment was found to be a critical factor in the REE extraction. Raising pH to above 1.5 was found to significantly decrease extraction recovery because of REE precipitation, so a pH of 1 or slightly higher was recommended for optimum results. Aqueous to organic ratios (A/O) ranging from 10:1 to 1:5 were also studied. An A/O of 10:1 was found to be more favorable for HREE extraction, whereas LREE extraction required a higher proportion of D2EHPA, resulting in an optimum A/O of 1:5. Mixing times of five to 40 minutes were investigated without any significant increase in REE extraction by longer duration of mixing.

In light of the above, the present study aims to identify a coal source having reasonably high REE concentration, greater than 500 ppm, for use as the feedstock for REE extraction, with an overall goal of developing a suitable chemical process flow sheet for extracting rare earth oxides from coal ash. This paper presents the results from the first part of the study, which concentrated on the leaching and solvent extraction steps. The results from the second part of the study, focusing on subsequent process steps such as scrubbing, stripping and precipitation, will be presented in a future paper.

Materials and methods

A total of 14 coal samples of different ranks, from lignite to anthracite, were obtained. They were originally collected from different regions of the United States and preserved in the U.S. Department of Energy's (DOE) Penn State Coal Sample Bank, maintained at Pennsylvania State University. The coal samples were burned in a furnace at 750 °C to produce ash samples for each coal type. The ash samples were analyzed for REEs by BV Minerals in Canada using ICP-MS. Lanthanum (La), scandium (Sc), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu) and gadolinium (Gd) are generally referred to as the LREEs, while yttrium (Y), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium

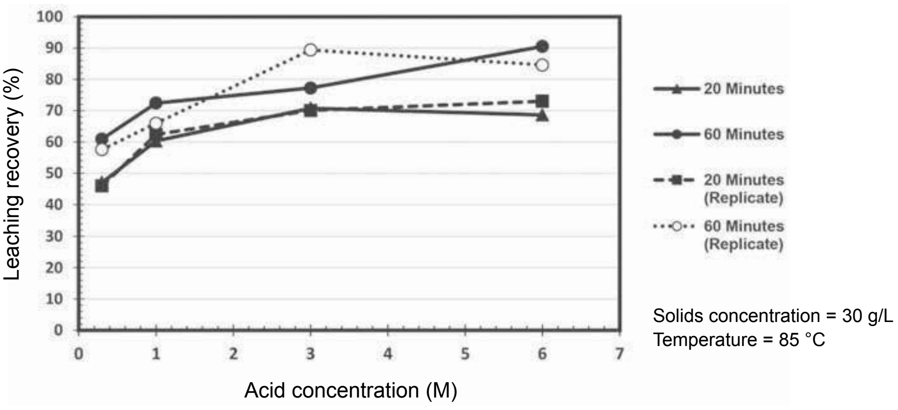


Figure 2 — TREE leaching recovery versus acid concentration.

(Tm), ytterbium (Yb) and lutetium (Lu) are considered to be in the category of the more valuable HREEs.

Ash leaching tests. About 5 kg of a desired coal sample was obtained from the DOE's Penn State Coal Sample Bank. The coal sample was burned in a muffle furnace at 750 °C to generate fine ash material to serve as the feedstock for the leaching experiments. Based on our literature survey, 70 percent nitric acid (HNO_3) was used for the leaching tests. An experimental program was designed to vary three process parameters — acid concentration at four levels, solids content at two levels and leaching time at two levels — and temperature was kept constant for all of the experiments. With two replicates for each test, a total of 32 experiments were conducted using a 4×2×2 factorial design. Exactly 100 mL of nitric acid, at the respective molar concentration, was used for each test. A PolyScience (Niles, IL) high-temperature water bath, set at 85 °C, was placed on a New Brunswick Scientific (Edison, NJ) shaker going at a speed of 100 rpm to provide a suitable mixing and contacting environment inside the Erlenmeyer flask. Filtration of the leached fly ash was performed right after the leaching tests to prevent any unwanted leaching time. For the elemental analysis, samples were filtered with Whatman No.2 filter paper and sent to the University of Nebraska-Lincoln spectroscopy core facility, which is equipped with an Agilent 7500cs ICP-MS system (Agilent Technologies, Santa Clara, CA) and an ESI SC-4 high-throughput autosampler (Elemental Scientific, Omaha, NE). Ga was used as an internal standard.

Table 3 — Leaching results for some other elements.

Test #	Leaching recovery (%) Impurities	Thorium	Uranium
1	18.04	13.02	55.39
2	14.75	17.78	53.96
3	20.01	42.00	63.35
4	14.85	37.97	55.02
5	22.91	79.00	70.08
6	15.70	61.81	56.51
7	21.12	98.56	60.73
8	19.29	80.67	59.68
9	41.81	49.80	61.35
10	25.32	20.54	50.34
11	40.27	64.40	71.09
12	28.44	63.81	58.13
13	35.47	82.26	65.66
14	23.71	73.72	58.79
15	40.20	–	70.95
16	30.82	80.04	58.00
17	16.87	19.32	50.82
18	10.28	15.17	39.33
19	18.20	48.56	58.96
20	13.92	41.57	49.36
21	19.25	78.91	60.61
22	12.97	61.41	49.16
23	20.52	87.42	58.09
24	14.54	66.12	47.59
25	30.41	28.69	55.95
26	21.73	34.50	47.74
27	31.64	56.39	57.50
28	21.22	37.57	43.90
29	37.60	99.9	67.75
30	23.44	61.46	46.40
31	40.08	90.53	59.55
32	38.14	73.59	52.89

Solvent extraction experiments. Although high REE recovery is immensely desirable, it was decided to focus on REE grade in the first series of our tests. Using the leaching conditions that resulted in the maximum concentration of 51.1 ppm of REEs in the leachate, more than one liter of leachate solution was prepared to serve as the feed for the solvent extraction experiments. A 2^3 experimental program was carried out by varying the three important factors — pH, the organic to aqueous ratio (O/A), and the solvent concentration in kerosene — each at two levels. Using two replicates for each test condition, a total of 16 solvent extraction tests were conducted. A 1:1 mixture of TBP and Cyanex 572 (Cytec Industries Inc., Woodland Park, NJ) was used as the organic extractant. A mixing time of 10 minutes was kept constant for all of the solvent extraction tests. After calculating the extraction percentages, another series of tests was designed using a more promising extractant, D2EHPA, to improve the REE extraction percentage. Using two replicates for each test, a total of 12 tests were conducted by varying the pH from 1 to 1.5, and the TBP to D2EHPA ratio from 0:1 to 1:1 to 1:0.

Results and discussion

Characterization. Table 1 shows the basic properties of the coal samples that were predetermined by the Penn State Coal Sample Bank along with the REE data generated by this study. Although no specific correlation was obvious, a careful examination of the data indicates that the total REE contents in the coal samples were more related to the volatile matter content than any other parameters, including vitrinite reflectance.

From the REE data, it can be inferred that the REE contents of the higher-rank coals, such as anthracite and low volatile bituminous coal, are generally higher than the lower-rank coals, such as lignite and high volatile C bituminous coal. The bar chart in Fig. 1 shows a similar trend with a few anomalies.

By examining the data in Table 1 for the same-rank coals with different origins, it can also be inferred that there are other nonrank-related factors that significantly affect the REE concentrations of coal. For example, for medium volatile coal, the analysis of three samples originating from Colorado, West Virginia and Virginia showed 247, 507 and 750 ppm REEs in their ashes, respectively. Clearly, this much of a variance cannot be attributed to chance. Other factors not related to coal rank may be behind this difference in REE concentration.

Another observation from the data in Table 1 is that the majority of the REEs present in coal ash are LREEs. The highest percentage for the more valuable HREEs was 27 percent, found in the low volatile bituminous coal sample.

Leaching. Table 2 shows the results of the leaching tests. The highest recovery rates of 90.5 percent for TREEs and 90.9 percent for LREEs were obtained from Test 15, whose experimental conditions included a 6-M acid solution, 30 g of ash per liter of acid solution and 60 min of leaching time.

Table 4 — Conditions of solvent extraction tests with TBP and Cyanex 572.

Test #	Solvent concentration (%)	TBP to Cyanex 572 ratio	pH	Organic to aqueous ratio (O/A)	Time (min)	Kerosene (mL)	TBP (mL)	Cyanex 572 (mL)
33	30	1:1	0.5	1:4	10	14	3	3
34	30	1:1	0.5	4:1	10	56	12	12
35	30	1:1	1.2	1:4	10	14	3	3
36	30	1:1	1.2	4:1	10	56	12	12
37	50	1:1	0.5	1:4	10	10	5	5
38	50	1:1	0.5	4:1	10	40	20	20
39	50	1:1	1.2	1:4	10	10	5	5
40	50	1:1	1.2	4:1	10	40	20	20
41	30	1:1	0.5	1:4	10	14	3	3
42	30	1:1	0.5	4:1	10	56	12	12
43	30	1:1	1.2	1:4	10	14	3	3
44	30	1:1	1.2	4:1	10	56	12	12
45	50	1:1	0.5	1:4	10	10	5	5
46	50	1:1	0.5	4:1	10	40	20	20
47	50	1:1	1.2	1:4	10	10	5	5
48	50	1:1	1.2	4:1	10	40	20	20

Clearly, higher molarity, lower solids content and longer retention time resulted in higher recovery of LREEs (Fig. 2). But the highest molarity did not produce the highest recovery rate for HREEs. Instead, an intermediate molarity, 3 M, resulted in the highest HREE recovery rate of 94.2 percent in Test 29.

Leaching recovery percentages were also calculated for thorium (Th), uranium (U) and the sum of other elements collectively termed impurities, namely, mercury (Hg), sulfur (S), potassium (K), sodium (Na), aluminum (Al), barium (Ba), magnesium (Mg), chromium (Cr), phosphorus (P), calcium (Ca), cadmium (Cd), arsenic (As), iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), lead (Pb), copper (Cu) and molybdenum (Mo). Table 3 shows the results.

Solvent extraction. Tables 4 and 5 list the experimental conditions and results, respectively, for the first series of solvent extraction tests conducted using TBP and Cyanex 572 as extractants. Tables 6 and 7 present the experimental conditions and results with a more effective extractant, D2EHPA, and with D2EHPA combined with TBP. The distribution coefficient, D_M, separation factor, β, and extraction percentage, %E, were calculated using the equations:

Table 5 — Results of of solvent extraction tests with TBP and Cyanex 572.

Test #	Concentration in organic phase at equilibrium (ppm)			Concentration in aqueous phase at equilibrium (ppm)			Distribution coefficient, *D*		Separation factor, β (LREE/HREE)	Extraction percentage, *E*		
	LREE	HREE	TREE	LREE	HREE	TREE	LREE	HREE		LREE	HREE	TREE
33	7.56	3.13	10.69	28.96	4.72	33.68	0.26	0.66	0.39	4.7	11.2	5.7
34	4.19	1.06	5.25	15.15	1.68	16.83	0.28	0.63	0.44	44.9	65.0	47.9
35	18.42	14.29	32.71	27.28	2.76	30.05	0.67	5.17	0.13	10.9	48.3	16.5
36	8.22	1.12	9.34	7.44	2.20	9.63	1.11	0.51	2.17	75.8	59.1	73.3
37	10.15	6.78	16.93	29.06	4.10	33.16	0.35	1.65	0.21	6.4	24.5	9.1
38	6.21	0.84	7.06	9.94	2.51	12.45	0.63	0.34	1.86	66.4	51.5	64.2
39	13.90	3.19	17.09	28.94	4.90	33.84	0.48	0.65	0.74	9.1	11.9	9.5
40	7.52	0.93	8.46	8.67	2.58	11.25	0.87	0.36	2.40	70.8	50.3	67.8
41	4.29	5.95	10.23	27.51	3.98	31.49	0.16	1.50	0.10	2.4	19.3	4.9
42	3.88	0.86	4.74	20.40	3.05	23.45	0.19	0.28	0.67	34.7	44.1	36.1
43	17.93	15.61	33.54	25.39	2.84	28.23	0.71	5.50	0.13	8.3	41.4	13.2
44	6.73	1.01	7.75	15.31	3.13	18.44	0.44	0.32	1.36	55.3	47.7	54.2
45	11.13	7.25	18.38	28.60	3.96	32.56	0.39	1.83	0.21	7.1	26.4	10.0
46	7.97	1.22	9.18	7.81	1.80	9.61	1.02	0.68	1.51	71.4	62.4	70.0
47	34.74	13.26	47.99	23.86	3.23	27.09	1.46	4.10	0.35	16.0	34.9	18.8
48	8.33	0.80	9.13	5.70	2.88	8.59	1.46	0.28	5.25	80.8	44.5	75.4

Table 6 — Conditions of additional solvent extraction tests with D2EHPA and TBP.

Test #	Solvent extraction test conditions								
	Solvent concentration (%)	TBP to D2EHPA ratio	pH	Organic to aqueous ratio (O/A)	Time (min)	Kerosene (mL)	TBP (mL)	D2EHPA (mL)	Leachate
70	50	1:1	1	1:4	10	5	2.5	2.5	40
71	50	0:1	1	1:4	10	5	0	5	40
72	50	1:0	1	1:4	10	5	5	0	40
73	50	1:1	1.5	1:4	10	5	2.5	2.5	40
74	50	0:1	1.5	1:4	10	5	0	5	40
75	50	1:0	1.5	1:4	10	5	5	0	40
76	50	1:1	1	1:4	10	5	2.5	2.5	40
77	50	0:1	1	1:4	10	5	0	5	40
78	50	1:0	1	1:4	10	5	5	0	40
79	50	1:1	1.5	1:4	10	5	2.5	2.5	40
80	50	0:1	1.5	1:4	10	5	0	5	40
81	50	1:0	1.5	1:4	10	5	5	0	40

$$D_M = C_O / C_A \quad (1)$$

$$\beta = D_{M1} / D_{M2} \quad (2)$$

$$\%E = 100D / (D + (V_A / V_O)) \quad (3)$$

where $M1$ and $M2$ are metal 1 and metal 2, C_O and C_A are the concentrations of each element in the organic phase and aqueous phase, respectively, and V_O and V_A are the volumes of the organic phase and aqueous phase, respectively, at equilibrium.

From Tables 4 and 5, a higher O/A of 4:1 resulted in higher extraction rate, and a pH increase from 0.5 to 1.2 also resulted in higher extraction rates. From Table 5, the highest extraction rate of 80.8 percent was obtained with Cyanex 572 and TBP mixed in a 1:1 ratio for Test 48. Figure 3 shows the effect of pH on the extraction rates.

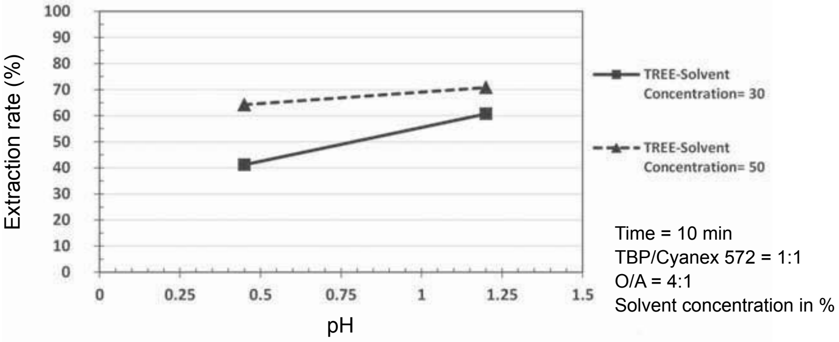
To improve the REE extraction rates, a second series of tests was conducted with D2EHPA and TBP mixed in different ratios. As shown in Tables 6 and 7, almost all of the REEs were extracted from the leachate solution when D2EHPA alone was used, at both pH 1 and pH 1.5. In addition, a mixture of D2EHPA and TBP resulted in a TREE extraction rate of 98.72 percent at pH 1.5 for Test 73. Figure 4 compares the extraction rates obtained using TBP, D2EHPA and a combination of the two. D2EHPA was found to be the most effective organic extractant for both the LREEs and HREEs present in the anthracite coal ash studied in this investigation.

Conclusions

The characterization work completed on 14 coal samples of different coal ranks, from lignite to anthracite, originating from all over the country indicated a maximum coal ash REE content of more than 700 ppm for the highest-rank coal (anthracite) sample. The majority of the REEs present in the coal types of all ranks were LREEs. The highest percentage

Table 7 — Results of additional solvent extraction tests with D2EHPA and TBP.

Test #	Concentration in aqueous phase at equilibrium (ppb)			Concentration in organic phase at equilibrium (ppb)			Distribution coefficient, *D*			Separation factor, β (LREE/HREE)	Extraction percentage, *E*		
	LREE	HREE	TREE	LREE	HREE	TREE	LREE	HREE	TREE		LREE	HREE	TREE
70	4312	212	4524	19126	7737	26863	4.44	36.5	5.94	0.12	54.19	90.68	61.29
71	337	11.8	349	33999	8487	42484	101	719	122	0.14	96.32	99.47	96.93
72	6910	1075	7985	6233	3067	9300	0.90	2.85	1.16	0.32	25.61	52.12	30.77
73	137	1.97	139	29501	5569	35070	215	2827	252	0.08	98.51	99.88	98.72
74	60.77	0.97	61.73	34203	6408	40611	563	6606	658	0.09	99.31	99.94	99.41
75	7350	1247	8597	7245	1798	9043	0.99	1.44	1.05	0.68	21.04	28.04	22.14
76	332	34.17	366	34034	8402	42437	102	246	116	0.42	96.43	98.48	96.83
77	283	7.93	291	34248	8503	42751	121	1072	147	0.11	97.03	99.66	97.54
78	6919	1083	8003	8311	4308	12616	1.20	3.98	1.58	0.30	23.55	50.50	28.79
79	998	24.83	1023	29755	6134	35888	29.8	247	35	0.12	88.99	98.53	90.48
80	127	5.87	133	33964	6390	40353	267	1089	303	0.25	98.62	99.66	98.78
81	7015	1210	8225	8485	1935	10420	1.21	1.60	1.27	0.76	24.64	30.18	25.51



Time = 10 min
TBP/Cyanex 572 = 1:1
O/A = 4:1
Solvent concentration in %

Figure 3 — TREE extraction rate versus pH of the leachate and solvent concentration.

for the more valuable HREEs was 27 percent, found in the low volatile bituminous coal sample. It can be inferred that the REE contents of the higher-rank coals, such as anthracite and low volatile bituminous coal, are generally higher than the lower-rank coals, such as lignite and high volatile C bituminous coal.

The nitric acid leaching tests conducted using a 4×2×2 factorial design indicate that the highest rate of LREE recovery is achieved at the highest molarity of the acid solution, lowest solids content and longest retention time. However, the highest rate of HREE recovery needed only an intermediate level of acid molarity.

Solvent extraction tests conducted using three different extractants, namely, TBP, D2EHPA and Cyanex 572, and their combinations showed that D2EHPA was the best extractant for recovering REEs from the nitric acid leachate solution.

Investigation of the scrubbing, stripping and precipitation steps of this study on REE extraction are ongoing, the results of which will be reported in a future paper.

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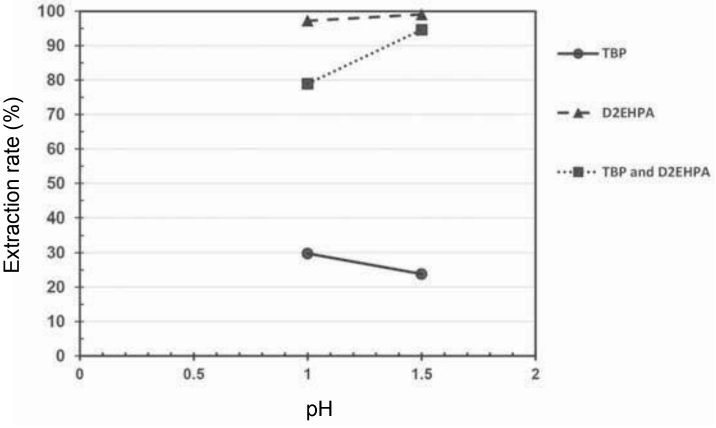

Figure 4 — TREE extraction rates with TBP alone, D2EHPA alone and a combination of TBP and D2EHPA.