

Research Article

Open Access



Alkali pretreatment effects on acid leaching recovery of rare earth elements from coal waste of the Western Kentucky No. 13 and Fire Clay seams

Qi Li, Bin Ji, Zhongqing Xiao, Wencai Zhang

Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA.

Correspondence to: Dr. Wencai Zhang, Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Holden Hall, Room 391, 410 Old Turner Street, Blacksburg, VA 24061, USA. E-mail: wencaizhang@vt.edu

How to cite this article: Li Q, Ji B, Xiao Z, Zhang W. Alkali pretreatment effects on acid leaching recovery of rare earth elements from coal waste of the Western Kentucky No. 13 and Fire Clay seams. *Miner Miner Mater* 2022;1:7. <https://dx.doi.org/10.20517/mmm.2022.05>

Received: 17 Mar 2022 **First Decision:** 14 Apr 2022 **Revised:** 21 Apr 2022 **Accepted:** 27 Apr 2022 **Published:** 12 May 2022

Academic Editor: Feifei Jia **Copy Editor:** Fangling Lan **Production Editor:** Fangling Lan

Abstract

The recovery of rare earth elements (REEs) from the Western Kentucky No. 13 and Fire Clay coal wastes was enhanced by alkali pretreatment with concentrated NaOH solutions. The enhancements in the recovery of light REEs (LREEs) are more significant than those of heavy REEs (HREEs). For example, after treating with 5 M NaOH at 90 °C, the recovery of LREEs from the Western Kentucky No. 13 coal waste increased from 26% to 71%, while the recovery of HREEs only increased from 29% to 41%. Based on mineralogical studies through scanning electron microscopy-energy dispersive X-ray spectroscopy and X-ray diffraction analyses, two mechanisms were proposed to explain the positive effect of alkali pretreatment: (1) decomposition of rare earth minerals (primarily crandallite-group minerals) during the alkali pretreatment, and (2) liberation of encapsulated REE-bearing particles due to the enhanced dissolution of clay minerals. The more significant enhancements in the recovery of LREEs were explained by the fact that the REEs comprised in the crandallite-group minerals were mainly LREEs. Compared with zircon, monazite, and xenotime, alkali pretreatment with 5 M NaOH led to a more significant decomposition of crandallite-group minerals. In order to further increase the recovery of REEs, particularly HREEs, harsher alkali treatment conditions are required.

Keywords: Rare earth elements, recovery, alkali pretreatment, acid leaching, coal waste



© The Author(s) 2022. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



INTRODUCTION

Coal-based materials, including coal, coal waste, coal combustion ash, and acid coal mine drainage, have been documented as promising sources of rare earth elements (REEs)^[1-5]. Many studies have been conducted in recent years to recover REEs from coal-based materials due to the supply risk and criticality of REEs to the clean energy industry^[6-13]. During the coal preparation process, a large amount of coal waste is generated and stored in refuse piles and tailings ponds. As reported by Luttrell *et al.*^[14], the amount of REEs in coarse and fine coal wastes accounted for 72.5% and 11.8% of the total REEs (TREEs) in run-of-mine coals, respectively. In addition, when reported on a whole sample basis, the REE content gradually increased with the increase in ash content^[15]. Therefore, satisfactory recovery of REEs from coal waste is required to maximize the recovery from run-of-mine coals.

Several studies have been conducted to recover REEs from coal waste^[16]. Due to the ultrafine particle size of REE-bearing particles in coal waste, physical separations are inefficient to beneficiate and recover the rare earth minerals. For example, a concentrate with 0.47% REEs was obtained from a fine coal waste by froth flotation; however, the recovery was less than 5%^[17]. To achieve satisfactory recovery, hydrometallurgical approaches, such as acid leaching, have been employed, and calcination pretreatment without adding any additives has been used to improve the leachability of REEs^[18]. During the calcination process, certain REE-bearing minerals, such as crandallite-group minerals, were decomposed and converted into easy-to-leach forms, and as such, the recovery of REEs was notably enhanced^[19].

In a recent study by Ji *et al.*^[19], it was found that the REEs in the coal waste of the Western Kentucky No. 13 and Fire Clay seams primarily existed in apatite, zircon, xenotime, monazite, and crandallite-group minerals. As reported in the literature, most rare earth minerals can be decomposed to varying degrees in alkaline solutions^[20-24]. Therefore, alkali pretreatment is a potential method to enhance the acid leaching recovery of REEs from coal waste. Many studies have been carried out to improve the recovery of REEs from coal fly ash using alkali pretreatment^[13,25,26]. A large amount of REEs are dispersed in the amorphous structure of fly ash^[13,27], while alkali pretreatment under proper conditions can destroy the amorphous structure, thus increasing the recovery of REEs from fly ash. Although the recovery of REEs from coal waste is likely improved through alkali pretreatment, little research has been conducted in this area^[28].

In the present study, the effect of alkali pretreatment on the recovery of REEs from the Western Kentucky No. 13 and Fire Clay coal wastes was evaluated. Mechanisms explaining the effect of alkali pretreatment on the recovery were proposed based on mineralogical investigations. The experimental results and findings of the study will contribute to the recovery of REEs from coal waste.

EXPERIMENTAL

Material and methods

Materials

The Western Kentucky No. 13 and Fire Clay coals were collected from two coal preparation plants located in Kentucky, USA, respectively. The samples were air-dried and then dry sieved using a sieve with an aperture of 10 mm. The fractions coarser than 10 mm were subjected to float-sink tests using a dense medium bath of 2.2 specific gravity (SG), which was prepared by mixing magnetite powder finer than 48 μm with tap water. During the tests, air was introduced into the dense medium to generate air bubbles, which helped the medium to remain stable. Around 1 kg of solids were added into the medium each time, followed by stirring for 1 min to disperse the solids in the medium. After that, the slurry was allowed to stand for 5 min, and the solids floating on top of the medium were collected. Then, more solids were added to the medium to repeat the process. The density of the medium was routinely checked during the tests

using a hydrometer, and additional magnetite was added as needed to keep the density at 2.2 SG. After the float-sink separation, the sink materials were rinsed with tap water to remove the entrained magnetite particles, and then air-dried at room temperature and finally pulverized to a top particle size of 0.18 mm using a jaw crusher and a hammer mill. Proximate analysis showed that the pulverized materials had an ash content of 88.47% (Western Kentucky No. 13) and 92.08% (Fire Clay), respectively. The materials were used as feeds for alkali pretreatment and acid leaching tests.

The chemical reagents used in this study include hydrochloric acid (HCl, 34-37 wt.%, trace metal grade), sulfuric acid (H₂SO₄, 98 wt.%, trace metal grade), hydrofluoric acid (HF, 48-51 wt.% trace metal grade), and sodium hydroxide (NaOH, certified ACS grade). All the reagents were purchased from Thermo Fisher Scientific, USA. NaOH and HCl were used for the alkali pretreatment and acid leaching tests, respectively, while HCl, along with the other acids, was used to digest solids.

Methods

Alkali Pretreatment Test

The coal wastes were pretreated in NaOH solutions at a high temperature to improve the acid leaching recovery of REEs. For each pretreatment test, 2.0 g solid and 50 mL NaOH solution of a predetermined concentration were added to a polypropylene flask with a maximum volumetric capacity of 100 mL. The flask was then placed in a shaking oil bath that had reached a predetermined temperature of 90 °C. The solid and liquid in the flask were mixed by shaking in the oil bath for 2 h. After that, the slurry was transferred to centrifuge tubes and centrifuged at 4000 rpm for 5 min. The supernatant in the tubes was decanted, and then, the residual solid was rinsed three times by mixing with deionized water, followed by centrifuging. A portion of the supernatant and rinsing solution was collected and subjected to elemental concentration analysis using inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS results were used to calculate the alkali leaching recovery of REEs and other elements from the raw coal wastes. Several residual solids were obtained by pretreating the coal wastes with NaOH solutions of different concentrations (i.e., 0 M, 0.1 M, 0.5 M, 1 M, 2.5 M, and 5 M). Three duplicates were conducted under selected conditions, and standard variances in the leaching recoveries were calculated and represented as error bars in the figures.

Acid Leaching Test

Acid leaching tests were performed on the residual solids generated from the alkali pretreatment process. The acid leaching tests were conducted using similar experimental apparatus and methods as the alkali pretreatment tests. For each test, 1.0 g solid was mixed with 50 mL 1.2 M HCl solution in a polypropylene flask using the shaking oil bath. Being consistent with the alkali pretreatment, the reaction temperature was fixed at 90 °C. After 2 h of reaction, the solid and liquid were separated through centrifuging at 4000 rpm for 5 min. The liquid samples were diluted with 5% HNO₃ and then directly subjected to ICP-MS analysis, while the solid samples were completely digested first, and the digestion solutions were analyzed using ICP-MS. A comprehensive description of the digestion procedures can be found in a previous study^[18]. The ICP-MS analysis results were used to calculate the acid leaching recovery of REEs and major elements from the alkali-pretreated coal wastes. Three duplicates were conducted under selected conditions, and standard variances in the leaching recoveries were calculated and represented as error bars in the figures.

Sample Characterization

The mineralogy of REEs existing in the alkali-pretreated coal wastes and the alkali-pretreated, acid-leached coal wastes was systematically characterized using scanning electron microscopy and energy dispersive X-

ray spectroscopy (SEM-EDS). SEM specimens were prepared by sprinkling the solid particles onto double-sided carbon tape mounted on an SEM stub. The SEM specimens were coated with a layer of Pt/Pd of 5 nm thickness using a desktop sputter coater (Leica EM ACE600, Leica Microsystems, IL, USA). The characterization was performed using a JSM-IT500HR SEM (JEOL, MA, USA) equipped with an Ultim Max EDS detector (Oxford Instruments, Abingdon, UK). The characterization procedures have been published in previous studies by Ji et al.^[19,29] and are reprinted in the [Supplementary Material](#).

The raw, alkali-pretreated, and alkali-pretreated, acid-leached coal wastes were subjected to X-ray diffraction (XRD) analysis to evaluate changes in the mineralogy of major minerals. A Bruker D8 Advance Twin diffractometer manufactured by Bruker Corporation was used for the analysis along with a copper X-ray source (40 kV and 40 mA). Scans were conducted at room temperature from 10° to 70° with a step size of 0.02° 2 θ and a step time of 0.05 s. Data were recorded digitally and analyzed using MDI Jade 6 software. Elemental concentrations in liquid samples were analyzed using a Thermo Electron iCAP-RQ ICP-MS instrument (Thermo Fisher Scientific, USA). The ICP-MS unit was calibrated using five standards prepared at the following concentrations: 0 ppb, 0.1 ppb, 1 ppb, 10 ppb, and 100 ppb. The calibration was verified by three independently sourced check standards, including continuing calibration verifications of 50 ppb and 100 ppb, as well as continuing calibration blank of 0 ppb, every ten samples.

RESULTS AND DISCUSSION

Leaching recovery results

Both the Western Kentucky No. 13 and Fire Clay coal wastes were subjected to alkali pretreatment with NaOH solutions of different concentrations. [Figure 1](#) shows the recovery values of TREEs, light REEs (LREEs; Sc, La, Ce, Pr, Nd, and Sm), and heavy REEs (HREEs; Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu) obtained from the alkali pretreatment of the coal wastes. For the coal waste of both the Western Kentucky No. 13 and Fire Clay seams, the recovery of TREEs and LREEs gradually increased with increases in the NaOH concentration, while the recovery of HREEs remained negligible. After reacting with 5 M NaOH, around 1.3% and 1.4% of TREEs and 1.5% and 1.6% of LREEs were leached from the coal waste of the two different seams, respectively. As [Figure 2](#) shows, the recovery of TREEs and LREEs was primarily attributable to the leaching of Sc, because the recovery of Sc from the two different seams by reacting with 5 M NaOH was around 10.3% and 14.5%, respectively, while the recovery of other REEs was less than 1%.

The Eh-pH diagrams of La-H₂O, Y-H₂O, and Sc-H₂O systems were constructed using HSC Chemistry software. As [Figure 3](#) shows, La and Y exist in solid forms under alkaline conditions; however, Sc transforms from a solid form to an aqueous species when the pH is above around 12. These phenomena suggested that, unlike the other REEs, Sc can be dissolved in alkaline solutions as long as the alkalinity is strong enough. This finding is consistent with previous studies^[30,31] and can explain the much higher recovery values of Sc obtained from the alkali pretreatment process [[Figure 2](#)]. During the alkali pretreatment process, the bearing minerals of all the REEs likely underwent varying degrees of decomposition, whereas a noticeable recovery was only obtained for Sc since the other REEs were insoluble in the alkaline solutions.

After the alkali pretreatment, the coal wastes were subjected to acid leaching with 1.2 M HCl at 90 °C. [Figure 4](#) shows the acid leaching recoveries of TREEs, LREEs, and HREEs from the alkali-pretreated coal wastes. Around 26% and 45% of TREEs were leached from the Western Kentucky No. 13 and Fire Clay coal wastes treated with 0 M NaOH, respectively. As the NaOH concentration increased to 1 M, the TREE recovery remained almost unchanged. However, after being treated with 2.5 M and 5 M NaOH, the TREE

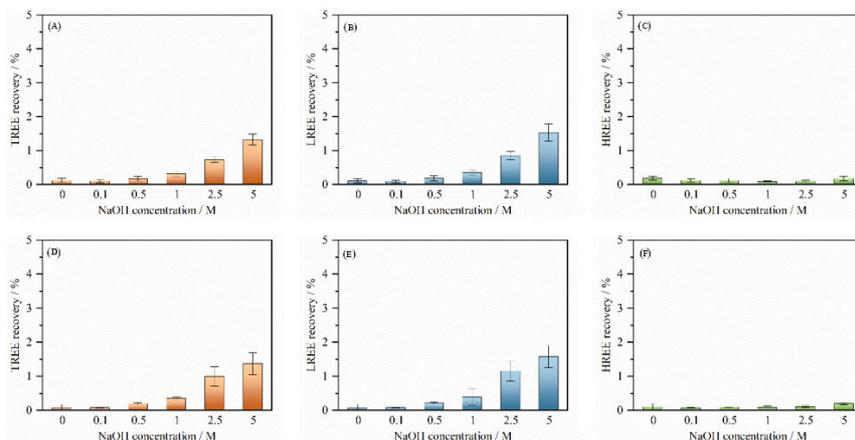


Figure 1. Leaching recoveries of TREEs, HREEs, and LREEs obtained from the alkali pretreatment of the (A-C) Western Kentucky No. 13 and (D-F) Fire Clay coal wastes with NaOH solutions of different concentrations. TREEs: Total rare earth elements; HREEs: heavy rare earth elements; LREEs: light rare earth elements.

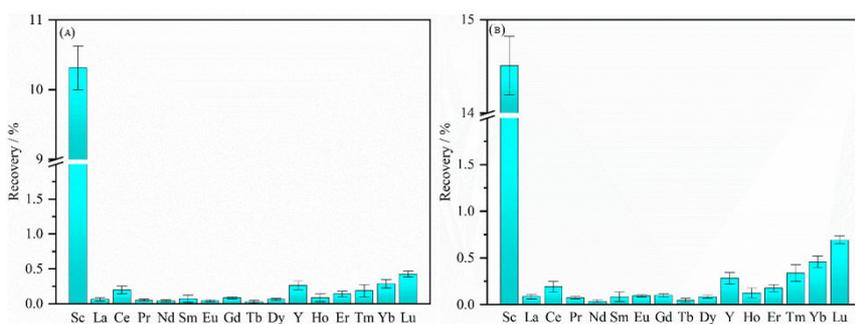


Figure 2. Leaching recoveries of individual REEs obtained from the alkali pretreatment of the (A) Western Kentucky No. 13 and (B) Fire Clay coal wastes with 5 M NaOH. REEs: Rare earth elements.

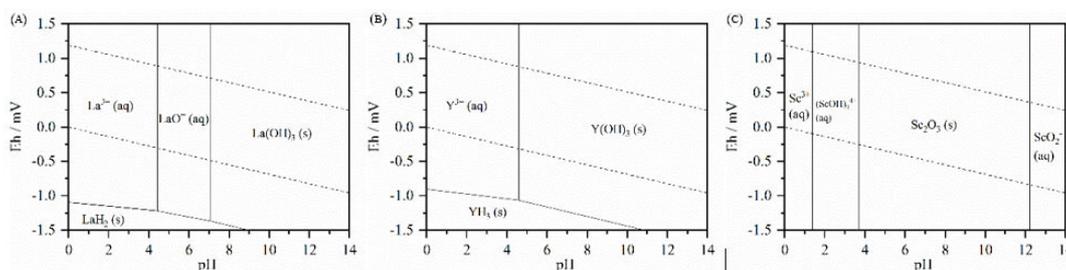


Figure 3. The Eh-pH diagrams of (A) La-H₂O, (B) Y-H₂O, and (C) Sc-H₂O systems at 90 °C under atmospheric pressure with 5×10^{-6} M of REEs. (Note: The REE concentration was estimated based on the REE contents of the coal wastes). REEs: Rare earth elements.

recovery was considerably enhanced; for example, around 66% and 61% of TREEs were leached from the 5 M NaOH-treated Western Kentucky No. 13 and Fire Clay coal wastes, respectively. Comparisons among the recovery of LREEs and HREEs showed that the increases in the NaOH concentration led to more significant enhancements in the recovery of LREEs than HREEs. For example, when the NaOH concentration was increased from 0 M to 5 M, the recovery of LREEs from the Western Kentucky No. 13 coal waste increased from 26% to 71%, while the recovery of HREEs only increased from 29% to 41%. Similarly, the recovery of LREEs from the Fire Clay coal waste increased from 48% to 66%, while the

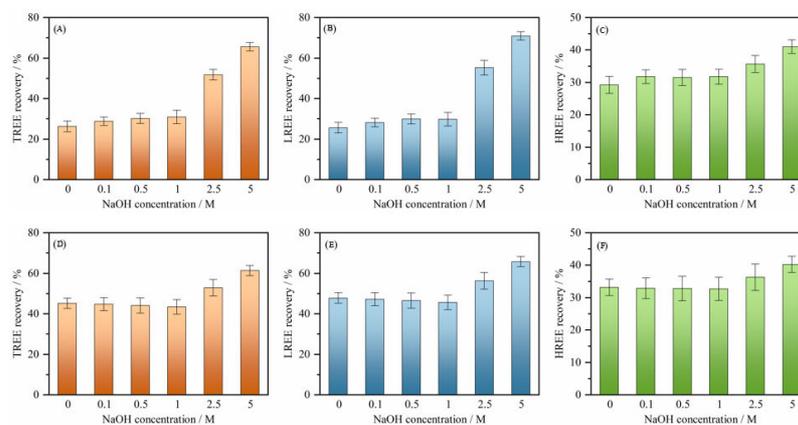


Figure 4. Acid leaching recoveries of TREEs, HREEs, and LREEs from the (A-C) Western Kentucky No. 13 and (D-F) Fire Clay coal wastes pretreated with NaOH solutions of different concentrations. TREEs: Total rare earth elements; HREEs: heavy rare earth elements; LREEs: light rare earth elements.

recovery of HREEs only increased by seven absolute percentage points (33% to 40%). Therefore, the alkali pretreatment posed a more significant positive effect on the recovery of LREEs than HREEs.

Mineralogy characterization

Distinguishing between monazite and crandallite-group minerals

Ji *et al.*^[19] found that apatite, zircon, monazite, xenotime, and crandallite-group minerals (e.g., florencite, crandallite, goyazite, and gorceixite) are the major REE-bearing minerals in the coal waste of the Western Kentucky No. 13 and Fire Clay seams. Apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$], zircon (ZrSiO_4), and xenotime (YPO_4) are characterized by high Ca and P, Zr and Si, as well as Y and P contents, respectively; whereas, monazite (REEPO_4) and crandallite-group minerals are rich in LREEs and P. Therefore, based on the elemental composition data obtained through EDS analysis, apatite, zircon, and xenotime can be easily distinguished from monazite and crandallite-group minerals; however, it is challenging to distinguish monazite from crandallite-group minerals since they are both rich in LREEs and P.

By analyzing the EDS elemental composition data of many REE-rich particles, Ji *et al.*^[19] developed a method to distinguish the two different types of minerals based on the ratio of total REE to P content (TREE/P): particles with TREE/P less than 2.0 are crandallite-group minerals, while particles with TREE/P greater than 2.0 are monazite. The authors have successfully used this criterion to investigate the occurrence modes of REEs in the Western Kentucky No. 13 and Fire Clay coal wastes. In the present study, florencite, a typical crandallite-group mineral, was synthesized and subjected to SEM-EDS analysis to verify this criterion. A hydrothermal method modified from a previous study by Schwab *et al.*^[32] was employed for the synthesis. The synthesis procedures are presented in the [Supplementary Material](#).

As [Figure 5](#) shows, the synthesized material occurred as rhombohedral crystals, agreeing with the geometry of naturally formed florencite^[33]. Sharp diffraction peaks corresponding to florencite (PDF#43-0673) appeared in the XRD pattern of the synthesized material, and no other minerals were identified [[Figure 6A](#)]. The SEM images and XRD results confirmed that the synthesized material was pure florencite with high crystallinity. According to the elemental compositions shown in [Figure 6B](#), the TREE/P of the synthesized florencite was calculated to be around 2.1, which is close to the criterion of 2.0. Crandallite-group minerals have a general chemical formula of $\text{RAl}_3(\text{PO}_4)(\text{OH})_5$, where R is REEs, Ca, Sr, and Ba for florencite, crandallite, goyazite, and gorceixite, respectively^[34]. The TREE/P of florencite should be greater

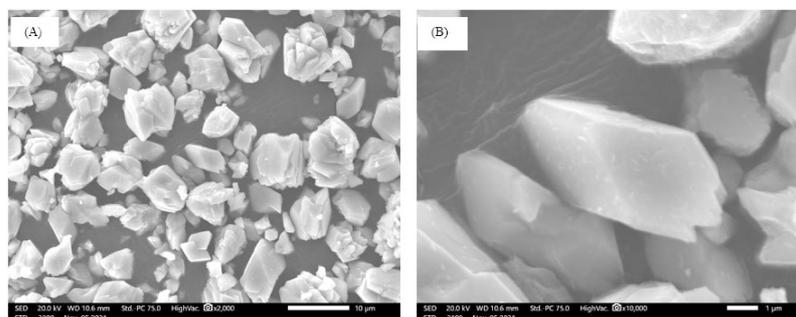


Figure 5. SEM images of the synthesized florencite under different magnifications (A) 2000x (B) 10,000x. SEM: Scanning electron microscopy.

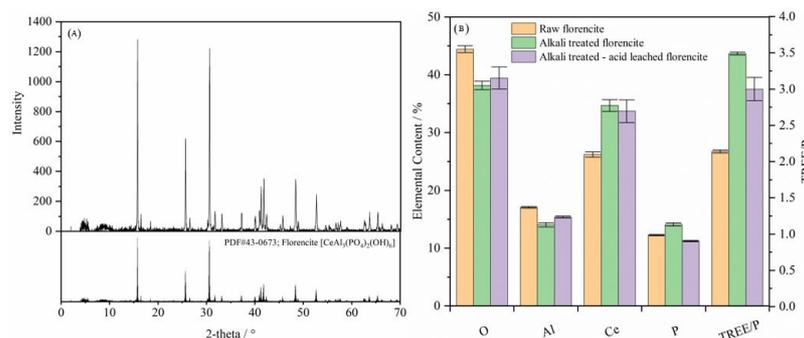


Figure 6. (A) XRD pattern of the florencite and (B) elemental composition and TREE/P of the raw and alkali-treated florencite. XRD: X-ray diffraction; TREE/P: total REE to P content.

than that of the other REE-bearing crandallite-group minerals because *R* in the other crandallite-group minerals is primarily Ca, Sr, Ba, etc. Therefore, the TREE/P of REE-bearing crandallite-group minerals should be no greater than 2.1, and the method developed by Ji *et al.*^[19] for distinguishing the monazite and crandallite-group minerals present in coal waste is reasonable.

After alkali treatment using 5 M NaOH at 90 °C, the TREE/P of the synthesized florencite increased from 2.1 to 3.5, because of the preferential dissolution of P relative to REEs [Figure 6B]. This finding suggested that after the alkali treatment, the TREE/P of the crandallite-group minerals existing in the Western Kentucky No. 13 and Fire Clay coal wastes increased but should be no greater than 3.5. As reported in the literature^[20-22], monazite can be dissolved to certain degrees in concentrated NaOH solutions, with REE hydroxides and sodium phosphate being generated. REE hydroxides except scandium hydroxide are insoluble, while sodium phosphate is soluble in strong alkaline solutions; therefore, after the alkali treatment using 5 M NaOH at 90 °C, the TREE/P of the monazite existing in the Western Kentucky No. 13 and Fire Clay coal wastes also increased. The degree of increase depended on the degree of dissolution of the monazite.

Based on the above discussion, for the coal wastes treated with 5 M NaOH at 90 °C, the following method can be used to determine whether an REE-bearing particle originated from monazite or crandallite-group minerals: particles with TREE/P less than 2.0 originated from crandallite-group minerals, particles with TREE/P greater than 3.5 originated from monazite, and particles with TREE/P between 2.0 and 3.5 originated from either monazite or crandallite-group minerals. Using a TREE/P of 2.0 instead of 2.1 is consistent with the method used for the raw coal wastes. As Figure 6B shows, after being leached with 1.2 M

HCl at 90 °C, the TREE/P of the alkali-treated florencite decreased from 3.5 to 3.0, suggesting the preferential leaching of REEs relative to P. Therefore, for the alkali-pretreated, acid-leached coal wastes, the TREE/P of 3.5 should be replaced with 3.0 in the method for judging whether an REE-bearing particle originated from monazite or crandallite-group minerals.

REE mineralogy in the alkali-pretreated coal wastes

REE mineralogy and association characteristics in the coal wastes treated with 5 M NaOH at 90 °C were investigated through SEM-EDS analysis. A total of 49 REE-bearing particles were found from the alkali-pretreated coal waste of the Western Kentucky No. 13 and Fire Clay seams, respectively, which were referred to as WAL 1-49 and FAL 1-49. Elemental compositions and SEM images of all the particles are presented in the [Supplementary Material](#). Based on the elemental compositions and the method developed in the prior section, it can be inferred that among the REE-bearing particles found in the Western Kentucky No. 13 material, there were eight zircon, three apatite, five xenotime, twelve monazite, and fifteen crandallite-group mineral particles. One of the remaining six particles, particle WAL 44, was identified as a crandallite-group mineral due to the existence of Sr in the particle. A summary of the REE-bearing particles is presented in [Table 1](#). It is worth mentioning that some of the REE-bearing particles might have been decomposed during the alkali pretreatment process; therefore, it is more reasonable to call them zircon-, apatite-, xenotime-, monazite-, and crandallite group-derived particles. However, it is difficult to tell which particles were decomposed and to what extent, and as such, the REE-bearing particles were collectively referred to as zircon, apatite, xenotime, monazite, and crandallite-group mineral particles.

As the SEM images in the [Supplementary Material](#) show, most of the zircon, xenotime, monazite, and crandallite-group particles had a particle size of 1-5 µm, while a few particles had a particle size of hundreds of nanometers. Compared with the other REE-bearing particles, apatite particles had a coarser size of 5-10 µm. Based on the physical association characteristics with the dominant minerals, the REE-bearing particles can be divided into three categories: liberated, partially encapsulated, and completely encapsulated. [Figure 7](#) shows the backscattered electron (BSE) images of three REE-bearing particles: WAL 14, WAL 15, and WAL 20. Two BSE images were taken for each particle with an accelerating voltage of 20 kV and 10 kV, respectively. The region corresponding to particle WAL 15 was bright when using 20 kV [[Figure 7C](#)]; however, when the voltage decreased to 10 kV, no notable difference in brightness was observed between the region and the overall image [[Figure 7F](#)]. The difference observed between 10 kV and 20 kV was likely due to the reduction in penetration depth and interaction volume of electrons as accelerating voltage decreases. This phenomenon indirectly proved that particle WAL 15 was completely encapsulated by the dominant mineral. Unlike particle WAL 15, the entire particle WAL 20 and a portion of the particle WAL 14 remained brighter than the overall images when the accelerating voltage decreased from 20 kV to 10 kV, suggesting that the particles were liberated and partially encapsulated, respectively.

Using the same judgment methods as the Western Kentucky No.13 material, it was concluded that among the 49 REE-bearing particles found in the alkali-pretreated coal waste of the Fire Clay seam, there were six zircon, eight xenotime, seventeen monazite, and thirteen crandallite-group mineral particles. The mineralogy of the remaining five particles was difficult to determine based on their elemental compositions and TREE/P values. A summary of the REE-bearing particles is presented in [Table 2](#). Similar to the particles found in the Western Kentucky No. 13 material, most of the REE-bearing particles in the Fire Clay material had a particle size of 1-5 µm, while a few particles had a particle size of hundreds of nanometers. In addition, as [Figure 8](#) shows, the three physical association characteristics, i.e., liberated, partially encapsulated, and completely encapsulated, also occurred for the REE-bearing particles found in the Fire Clay material.

Table 1. REE-bearing particles found from the alkali-pretreated Western Kentucky No. 13 coal waste through SEM-EDS analysis

Particle number	Mineral	Quantity	Proportion/%
WAL 1-8	zircon	8	16.33
WAL 9-11	apatite	3	6.12
WAL 12-16	xenotime	5	10.20
WAL 17-28	monazite	12	24.49
WAL 29-44	crandallite-group	16	32.65
WAL 45-49	NA	5	10.20

REE: Rare earth element; SEM-EDS: scanning electron microscopy and energy dispersive X-ray spectroscopy.

Table 2. REE-bearing particles found from the alkali-pretreated Fire Clay coal waste through SEM-EDS analysis

Particle number	Mineral	Quantity	Proportion/%
FAL 1-6	zircon	6	12.24
FAL 7-14	xenotime	8	16.33
FAL 15-31	monazite	17	34.69
FAL 32-44	crandallite-group	13	26.53
FAL 45-49	NA	5	10.20

REE: Rare earth element; SEM-EDS: scanning electron microscopy and energy dispersive X-ray spectroscopy.

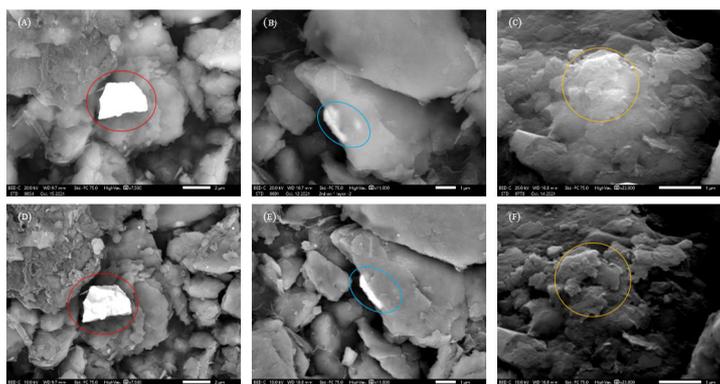


Figure 7. BSE images of a liberated ((A and D), WAL 20), a partially encapsulated ((B and E), WAL 14), and a completely encapsulated ((C and F), WAL 15) REE-bearing particle found in the Western Kentucky No. 13 material. ((A-C) and (D-F) were taken with an accelerating voltage of 20 kV and 10 kV, respectively). BSE: Backscattered electron; REE: rare earth element.

As the SEM images in the [Supplementary Material](#) show, the REE-bearing particles found in both the Western Kentucky No. 13 and Fire Clay seams had irregular shapes, and it is difficult to justify whether the particles were decomposed during the alkali pretreatment process based on their shapes. However, many pores and cracks appeared in a few particles, such as WAL 41 and FAL 34 shown in [Figure 9](#), suggesting that a portion of the particles was dissolved during the alkali pretreatment. Coincidentally, based on their TREE/P ratios, both WAL 41 and FAL 34 were identified as crandallite-group particles; therefore, crandallite-group minerals existing in the coal wastes were partially decomposed by treating with 5 M NaOH at 90 °C.

REE mineralogy in the alkali-pretreated, acid-leached coal wastes

REE mineralogy in the acid leaching solid residue of the alkali-pretreated coal wastes was investigated using the same method as the alkali-pretreated coal wastes. A total of 45 and 46 REE-bearing particles were found

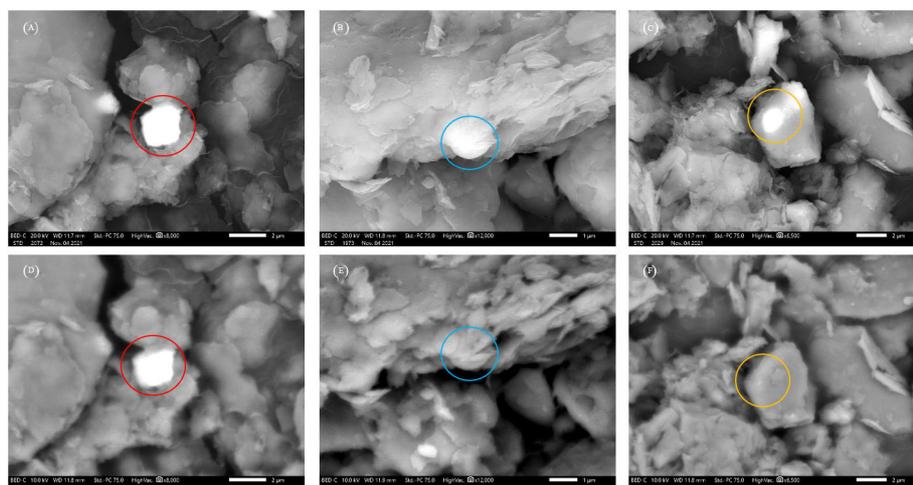


Figure 8. BSE images of a liberated ((A and D), FAL 23), a partially encapsulated ((B and E), FAL 19), and a completely encapsulated ((C and F), FAL 10) REE-bearing particle found in the Fire Clay material. ((A-C) and (D-F) were taken with an accelerating voltage of 20 kV and 10 kV, respectively). BSE: Backscattered electron; REE: rare earth element.

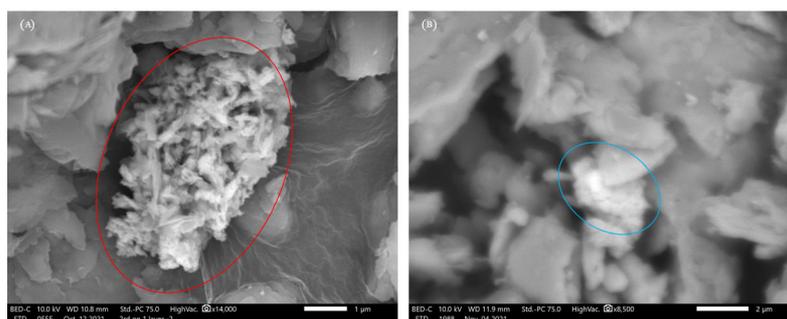


Figure 9. BSE images of (A) WAL 41 and (B) FAL 34 particles. BSE: Backscattered electron.

in the Western Kentucky No. 13 and Fire Clay materials, respectively. A summary of the REE-bearing particles found in the two materials is presented in [Table 3](#) and [Table 4](#), respectively. The SEM images and EDS elemental composition data of the particles are presented in the [Supplementary Material](#). Most of the particles had a particle size of 1-5 μm , which is similar to the size of the particles found in the alkali-pretreated coal wastes. However, as compared with the alkali-pretreated coal wastes, the proportion of crandallite-group mineral particles was notably reduced. For example, with similar total numbers of REE-bearing particles (49 vs. 45), the number of crandallite-group particles found in the alkali-pretreated coal waste of the Western Kentucky No. 13 seam reduced from 15 to 6 [[Table 1](#) vs. [Table 3](#)]. This phenomenon indicated that a large portion of the crandallite-group mineral particles existing in the alkali-pretreated coal wastes was dissolved by leaching with 1.2 M HCl at 90 °C, leading to the enhancements in the recovery of REEs after the alkali pretreatment. As mentioned in the prior section, pores and cracks were observed in some crandallite-group particles. Therefore, it can be concluded that crandallite-group minerals were partially decomposed during the alkali pretreatment, and the decomposed products were relatively easy to leach under the leaching conditions used in the present study. In addition, because the REEs existing in crandallite-group minerals were primarily LREEs, it can be concluded that the more significant positive effect of alkali pretreatment on the recovery of LREEs than HREEs was mainly due to the decomposition of crandallite-group minerals.

Table 3. REE-bearing particles found from the alkali-pretreated, acid-leached Western Kentucky No. 13 coal waste through SEM-EDS analysis

Particle number	Mineral	Quantity	Proportion/%
WALAL 1-16	zircon	16	35.56
WALAL 17-26	xenotime	10	22.22
WALAL 27-39	monazite	13	28.89
WALAL 40-45	crandallite-group	6	13.33

REE: Rare earth element; SEM-EDS: scanning electron microscopy and energy dispersive X-ray spectroscopy.

Table 4. REE-bearing particles found from the alkali-pretreated, acid-leached Fire Clay coal waste through SEM-EDS analysis

Particle number	Mineral	Quantity	Proportion/%
FALAL 1-17	zircon	17	36.96
FALAL 18-23	xenotime	6	13.04
FALAL 24-38	monazite	15	32.61
FALAL 39-46	crandallite-group	8	17.39

REE: Rare earth element; SEM-EDS: scanning electron microscopy and energy dispersive X-ray spectroscopy.

As shown in the Table 3 and Table 4, with similar total numbers of REE-bearing particles, more zircon and xenotime/monazite particles were found from the alkali-pretreated, acid-leached coal wastes than the alkali-pretreated coal wastes. This phenomenon suggested that zircon, xenotime, and monazite were less likely decomposed than crandallite-group minerals by reacting with 5 M NaOH at 90 °C. To further improve the recovery of REEs, particularly HREEs, from the coal wastes, harsher treatment conditions with higher NaOH concentrations and higher reaction temperatures are required.

XRD patterns of the raw, alkali-pretreated, and alkali-pretreated, acid-leached coal wastes are presented in Figure 10. The diffraction peaks corresponding to clay minerals, particularly kaolinite, disappeared from the pattern of the alkali-pretreated, acid-leached coal wastes. This phenomenon suggested that clay minerals were notably dissolved during the alkali pretreatment - acid leaching process, agreeing with the findings reported in the literature^[35,36]. It has been proved by Ji *et al.*^[19] that a portion of REE-bearing particles in the raw coal wastes was completely encapsulated within clay minerals. This conclusion can be corroborated by the fact that some REE-bearing particles were also completely encapsulated within the major minerals in the alkali-pretreated coal wastes [Figure 7 and Figure 8]. In addition, in a recent study by Xie *et al.*^[37], it was also concluded that REE-bearing minerals in coal waste were likely physically associated with clay minerals. Because clay minerals were dissolved during the alkali pretreatment - acid leaching process, the completely encapsulated REE-bearing particles were likely liberated, leading to improvements in the leaching recovery of REEs. As reported in the literature, clay minerals are difficult to dissolve in most mineral acids (e.g., HCl, HNO₃, and H₂SO₄), while alkali pretreatment can convert kaolinite into soluble silicate and aluminate and/or aluminosilicate precipitates that are easy to dissolve in acid solutions^[36,38,39]. As Figure 11 shows, the leaching recovery of Al in the alkali pretreatment step was largely enhanced with increases in the NaOH concentration. Greater than 40% of Al was leached from the raw coal wastes by treating with 5 M NaOH. Therefore, in the alkali pretreatment - acid leaching process, alkali pretreatment played a significant role in the dissolution of clay minerals and thereby was the major contributor to the liberation of REE-bearing particles.

In this study, the presence of Zr was used to determine whether an REE-bearing particle is a zircon; however, this method of judgment is not entirely correct. The ratio of Zr to total REE content (Zr/TREE) of

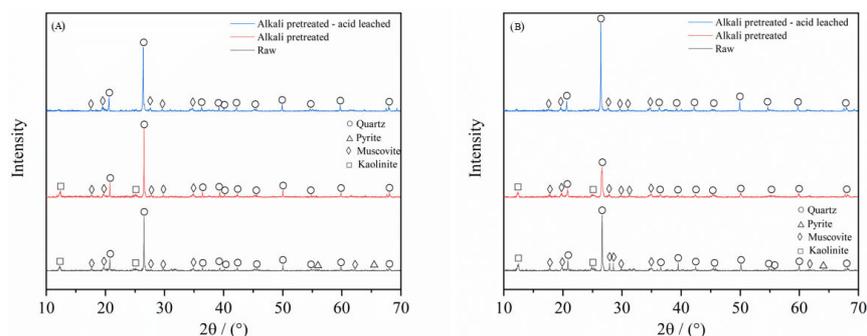


Figure 10. XRD patterns of the raw, alkali-pretreated, and alkali-pretreated, acid-leached coal wastes of the (A) Western Kentucky No. 13 and (B) Fire Clay seams. (Alkali pretreatment conditions: 5 M NaOH at 90 °C; acid leaching conditions: 1.2 M HCl at 90 °C). XRD: X-ray diffraction.

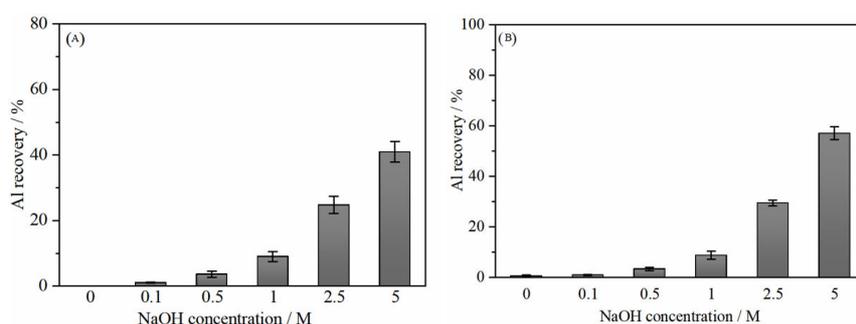


Figure 11. Leaching recoveries of Al obtained from the alkali pretreatment of the (A) Western Kentucky No. 13 and (B) Fire Clay coal wastes with NaOH solutions of different concentrations.

the zircon particles found in the alkali-pretreated and alkali-pretreated, acid-leached coal wastes was plotted against the TREE content. As [Figure 12](#) shows, for most of the zircon particles, Zr/TREE decreased with increases in the TREE content, agreeing with the fact that the substitution of Zr by REEs reduces the content of Zr in zircon. The particles with a decreasing trend of Zr/TREE content *vs.* TREE content are circled in [Figure 12](#). Several particles fall outside the circle, and as such, instead of existing in the crystal structure of zircon, the REEs likely existed as rare earth minerals that were physically associated with zircon in the particles. As [Figure 13](#) shows, different areas in particle WAL 1 have different elemental compositions. In selected areas (e.g., spectrum 1319), Zr existed, but REEs were not detected. This phenomenon supported the inference that REE minerals were physically associated with zircon in certain particles. This type of association only accounted for a small portion of the total number of zircon particles shown in [Figure 12](#), and additionally, only HREEs and Sc were detected in the zircon particles. Therefore, although the judgment method is not entirely correct, the major conclusions relevant to the positive effect of alkali pretreatment on the acid leaching recovery of REEs from the coal wastes remain valid.

CONCLUSIONS

The effect of alkali pretreatment on the acid leaching recovery of REEs from the Western Kentucky No. 13 and Fire Clay coal wastes was investigated in this study. Leaching test results showed that the alkali pretreatment of the coal wastes with concentrated NaOH solutions notably enhanced the acid leaching recovery of REEs. In addition, the enhancements in the recovery of LREEs are greater than the enhancements in the recovery of HREEs. For example, after pretreating with 5 M NaOH at 90 °C, the acid leaching recovery of LREEs from the Western Kentucky No. 13 coal waste increased from 26% to 71%, while the recovery of HREEs only increased from 29% to 41%.

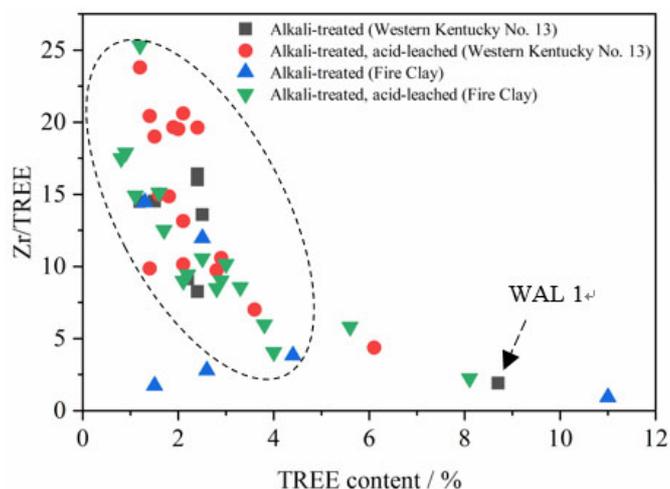


Figure 12. Changes in Zr/TREE as a function of the TREE content for zircon particles found in the alkali-pretreated and alkali-pretreated, acid-leached coal wastes. Zr/TREE: Zr to total REE content.

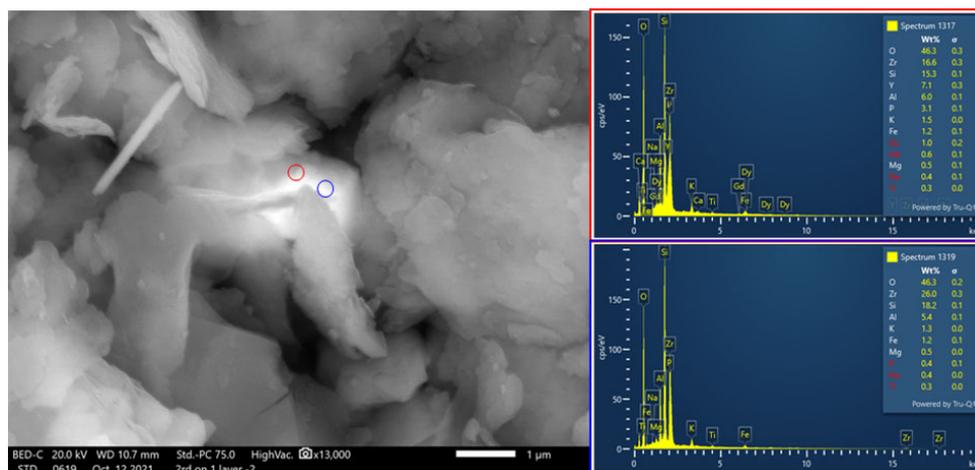


Figure 13. EDS spectra and elemental compositions of the different areas in particle WAL 1. EDS: ENERGY dispersive X-ray spectroscopy.

To understand the positive effect of alkali pretreatment on the recovery of REEs, REE mineralogy in the alkali-pretreated and alkali-pretreated, acid-leached coal wastes was studied through SEM-EDS analysis. Similar to the raw coal wastes, apatite, zircon, xenotime, monazite, and crandallite-group minerals were found in the alkali-pretreated coal wastes; however, apatite is not found in the alkali-pretreated, acid-leached coal wastes, and the proportion of crandallite-group particles was significantly reduced. The disappearance of apatite was expected since it is easy to dissolve under weakly acidic conditions. The reduction in the number of crandallite-group particles suggested that alkali pretreatment led to a more significant decomposition of crandallite-group minerals than zircon, xenotime, and monazite. EDS elemental composition data showed that the REEs comprised in the crandallite-group minerals were primarily LREEs. This finding agreed with the fact that alkali pretreatment posed a more significant positive effect on the recovery of LREEs than HREEs. Moreover, both the present study and the study by Ji *et al.*^[19] confirmed that a portion of the REE-bearing particles existing in the coal wastes was encapsulated in clay minerals. In the alkali treatment - acid leaching process, the clay minerals existing in the coal wastes were

notably dissolved, thus promoting the liberation of REE-bearing particles. This effect also explained the positive effect of alkali pretreatment on the leaching recovery of REEs from the coal wastes.

DECLARATIONS

Acknowledgments

The authors acknowledge use of facilities within the Nanoscale Characterization and Fabrication Laboratory (NCFL) at Virginia Tech.

Authors' contributions

Methodology, Investigation, Writing - Original Draft: Li Q

Investigation: Ji B

Writing - Review & Editing: Xiao Z

Conceptualization, Writing - Review & Editing, Funding acquisition: Zhang W

Availability of data and materials

Not applicable.

Financial support and sponsorship

This material is based upon work supported by the Department of Energy Award Number DE-FE0031827.

Disclaimer: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States 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 represented 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 United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2022.

REFERENCES

1. Seredin VV, Dai S, Sun Y, Chekryzhov IY. Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies. *Appl Geochem* 2013;31:1-11. [DOI](#)
2. Dai S, Finkelman RB. Coal as a promising source of critical elements: Progress and future prospects. *Int J Coal Geol* 2018;186:155-64. [DOI](#)
3. Fu B, Hower JC, Zhang W, Luo G, Hu H, Yao H. A review of rare earth elements and yttrium in coal ash: Content, modes of occurrences, combustion behavior, and extraction methods. *Prog Energy Combust Sci* 2022;88:100954. [DOI](#)
4. Huang Q, Talan D, Restrepo JH, Baena OJR, Kecojevic V, Noble A. Characterization study of rare earths, yttrium, and scandium from

- various Colombian coal samples and non-coal lithologies. *Int J Coal Geol* 2019;209:14-26. DOI
5. Franus W, Wiatros-Motyka MM, Wdowin M. Coal fly ash as a resource for rare earth elements. *Environ Sci Pollut Res Int* 2015;22:9464-74. DOI PubMed PMC
 6. Yang X, Honaker RQ. Leaching Kinetics of Rare Earth Elements from Fire Clay Seam Coal. *Minerals* 2020;10:491. DOI
 7. Yang X, Werner J, Honaker R. Leaching of rare Earth elements from an Illinois basin coal source. *J Rare Earths* 2019;37:312-21. DOI
 8. Hassas B, Rezaee M, Pisupati SV. Precipitation of rare earth elements from acid mine drainage by CO₂ mineralization process. *Chem Eng J* 2020;399:125716. DOI
 9. Zhang W, Honaker R. Process development for the recovery of rare earth elements and critical metals from an acid mine leachate. *Miner Eng* 2020;153:106382. DOI
 10. Vass CR, Noble A, Ziemkiewicz PF. The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part I—Initial Survey of the Northern Appalachian Coal Basin. *Mining Metall Explor* 2019;36:903-16. DOI
 11. Pan J, Nie T, Vaziri Hassas B, Rezaee M, Wen Z, Zhou C. Recovery of rare earth elements from coal fly ash by integrated physical separation and acid leaching. *Chemosphere* 2020;248:126112. DOI PubMed
 12. Taggart RK, Hower JC, Hsu-kim H. Effects of roasting additives and leaching parameters on the extraction of rare earth elements from coal fly ash. *Int J Coal Geol* 2018;196:106-14. DOI
 13. Lin R, Stuckman M, Howard BH, et al. Application of sequential extraction and hydrothermal treatment for characterization and enrichment of rare earth elements from coal fly ash. *Fuel* 2018;232:124-33. DOI
 14. Luttrell GH, Kiser MJ, Yoon R, et al. A Field Survey of Rare Earth Element Concentrations in Process Streams Produced by Coal Preparation Plants in the Eastern USA. *Mining Metall Explor* 2019;36:889-902. DOI
 15. Zhang W, Yang X, Honaker RQ. Association characteristic study and preliminary recovery investigation of rare earth elements from Fire Clay seam coal middlings. *Fuel* 2018;215:551-60. DOI
 16. Zhang W, Noble A, Yang X, Honaker R. A Comprehensive Review of Rare Earth Elements Recovery from Coal-Related Materials. *Minerals* 2020;10:451. DOI
 17. Zhang W, Honaker R, Groppo J. Concentration of rare earth minerals from coal by froth flotation. *Miner Metall Process* 2017;34:132-7. DOI
 18. Zhang W, Honaker R. Characterization and recovery of rare earth elements and other critical metals (Co, Cr, Li, Mn, Sr, and V) from the calcination products of a coal refuse sample. *Fuel* 2020;267:117236. DOI
 19. Ji B, Li Q, Zhang W. Rare earth elements (REEs) recovery from coal waste of the Western Kentucky No. 13 and Fire Clay Seams. Part I: Mineralogical characterization using SEM-EDS and TEM-EDS. *Fuel* 2022;307:121854. DOI
 20. Kumari A, Panda R, Jha MK, Kumar JR, Lee JY. Process development to recover rare earth metals from monazite mineral: A review. *Miner Eng* 2015;79:102-15. DOI
 21. Costa Lauria D, Rochedo ER. The legacy of monazite processing in Brazil. *Radiat Prot Dosimetry* 2005;114:546-50. DOI PubMed
 22. Ali A, El-nadi Y, Daoud J, Aly H. Recovery of thorium (IV) from leached monazite solutions using counter-current extraction. *Int J Miner Process* 2007;81:217-23. DOI
 23. Srikanth S, Devi VL, Kumar R. Unfolding the complexities of mechanical activation assisted alkali leaching of zircon (ZrSiO₄). *Hydrometallurgy* 2016;165:125-36. DOI
 24. Kuzmin VI, Flett DS, Kuzmina VN, et al. The composition, chemical properties, and processing of the unique niobium–rare earth ores of the Tomtor deposit. *Chem Pap* 2019;73:1437-46. DOI
 25. Wang Z, Dai S, Zou J, French D, Graham IT. Rare earth elements and yttrium in coal ash from the Luzhou power plant in Sichuan, Southwest China: Concentration, characterization and optimized extraction. *Int J Coal Geol* 2019;203:1-14. DOI
 26. Ma Z, Zhang S, Zhang H, Cheng F. Novel extraction of valuable metals from circulating fluidized bed-derived high-alumina fly ash by acid–alkali–based alternate method. *J Clean Prod* 2019;230:302-13. DOI
 27. Pan J, Zhou C, Tang M, et al. Study on the modes of occurrence of rare earth elements in coal fly ash by statistics and a sequential chemical extraction procedure. *Fuel* 2019;237:555-65. DOI
 28. Kuppusamy VK, Kumar A, Holuszko M. Simultaneous Extraction of Clean Coal and Rare Earth Elements From Coal Tailings Using Alkali-Acid Leaching Process. *J Energy Resour Technol* 2019;141:070708. DOI
 29. Ji B, Li Q, Tang H, Zhang W. Rare earth elements (REEs) recovery from coal waste of the Western Kentucky No. 13 and Fire Clay seams. Part II: Re-investigation on the effect of calcination. *Fuel* 2022;315:123145. DOI
 30. Nikolaychuk PA. The revised potential-pH diagram of Sc-H₂O system, Региональные Геосистемы. 2016. Available from: https://www.researchgate.net/publication/311971416_The_revised_potential_-_pH_diagram_of_Sc_-_H2O_system [Last accessed on 6 May 2022]. DOI
 31. Rizk HE, El-nadi YA, El-hefny NE. Extractive Separation of Scandium from Strongly Alkaline Solution by Quaternary Ammonium Salt. *Solvent Extr Ion Exch* 2020;38:350-63. DOI
 32. Schwab R, Pimpl T, Schukow H, Stolle A, Breiting D. Compounds of the crandallite-type: Synthesis, properties and thermodynamic data of pure crandallite and woodhouseite. *Neues Jahrb Mineral Monatshefte* 2004;2004:385-409. DOI
 33. Mckie D. Goyazite and florencite from two African carbonatites. *Mineral Mag J Mineral Soc* 1962;33:281-97. DOI
 34. Wilson JA. Crandallite group minerals in the Helikian Athabasca Group in Alberta, Canada. *Can J Earth Sci* 1985;22:637-41. DOI
 35. Panagiotopoulou C, Kontori E, Perraki T, Kakali G. Dissolution of aluminosilicate minerals and by-products in alkaline media. *J*

- Mater Sci* 2007;42:2967-73. [DOI](#)
36. Wang H, Feng Q, Liu K. The dissolution behavior and mechanism of kaolinite in alkali-acid leaching process. *Appl Clay Sci* 2016;132-133:273-80. [DOI](#)
 37. Xie P, Liu J, Fu B, Newmaster T, Hower JC. Resources from coal beneficiation waste: Chemistry and petrology of the Ayrshire coal tailings ponds, Chandler, Indiana. *Fuel* 2022;313:123054. [DOI](#)
 38. Aldabsheh I, Houry H, Wastiels J, Rahier H. Dissolution behavior of Jordanian clay-rich materials in alkaline solutions for alkali activation purpose. Part I. *Appl Clay Sci* 2015;115:238-47. [DOI](#)
 39. Bauer A, Berger G. Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80 °C. *Appl Geochem* 1998;13:905-16. [DOI](#)