

## Rare earth elements from coal and coal discard – A review

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### ABSTRACT

Given the geographical imbalance distribution and supply shortage of rare earth elements (REEs) in renewable energy processes, magnets, many high-tech technologies, etc., researchers are increasingly seeking to recover REEs from unconventional sources such as coal and coal by-products. This article provides a brief overview of the REEs mode of occurrence and its association in coal. It also discusses existing and potential beneficiation strategies for enriching REEs from coal and coal discard. Furthermore, the hydrometallurgical leaching of REEs from coal and coal discard is reviewed and a summary of recent outcomes on REEs recovery from the coal source is presented. The review validated the technical feasibility of the physical beneficiation of REE minerals from coal without a significant particle size reduction to produce high-grade REE feedstocks for leaching. Although ultrafine milling results in higher REE recovery values, additional milling costs may affect the viability of the process. Overall, the study confirms the abundance of REEs in coal, identifies gaps in knowledge, and highlights future research that must be addressed to advance REEs recovery from these sources.

### 1. Introduction

Rare Earth Elements (REEs) are a group of seventeen chemically similar metallic elements composed of fifteen lanthanide elements as well as scandium and yttrium (Fig. 1). The elements are grouped into light (LREEs) and heavy (HREEs) based on their atomic number, electron arrangement, and chemical properties (OECD, 2015; Reid, 2018; Park et al., 2021). Scandium and yttrium are tagged rare earth elements because their chemical and physical properties are common and similar to the other 15 elements (lanthanide series). REEs are known to possess unique and specialized properties such as electrochemical, optical, nuclear, thermal, magnetic, luminescent, etc. (OECD, 2015). As a result, they endow products with lightweight, low emissions, low energy consumption, improved efficiency, high performance, small size, speed, durability, and thermal stability (OECD, 2015; Ganguli and Cook, 2018). REEs are a ubiquitous ingredient in several high-end technologies and products ranging from permanent magnets, smartphones, lighting, batteries, ceramics, medical laser devices, electric vehicles, electromagnetic motors, high tech electronics, metal catalysts, energy-efficient technologies, aerospace industries, to solid oxide fuel cell technologies (Rozelle et al., 2016; Baron, 2020). Due to their economic importance and supply risk, the United States (Bauer et al. 2010) and the European Union (European Commission, 2020) classify REEs as critical materials. An

exhaustive breakdown of the end-use market application of each REE and their relevance to various industrial sectors can be found in the literature (Norman et al., 2014; OECD, 2015; Ganguli and Cook, 2018).

Traditionally, REEs are mined from ores containing bastnäsite (carbonate-fluoride mineral,  $(La,Ce)FCO_3$ ), monazite (phosphate mineral,  $(Ce,La,Y,Th)PO_4$ ) and xenotime ( $YPO_4$ ), which constitute of the most mined rare-earth minerals worldwide. REEs are also extracted from ion-exchangeable adsorbed clays and apatite mineral ores  $[(Ca,REE,Sr,Na,K)_3Ca_2(PO_4)_3(F,OH)]$  (Suli et al., 2017; Gagarin et al., 2020; Li et al., 2020). Contrary to their name, REEs are comparatively abundant in the Earth's crust. However, the name "rare earth" has been derived because of its unique geochemical properties, so it is unusual to find REEs in exploitable concentrations. Especially when they are locked in traditional mineral ores in very low concentrations, exploiting REEs is deemed uneconomical (Van Gosen et al., 2014; Norman et al. 2014, OECD, 2015). HREEs are typically less produced, are less in demand, but are more expensive than LREEs that are more abundant (Ganguli and Cook, 2018). China produces the majority of the REEs, are the global leader in rare earth processing technology, owns about 50% of global reserves, and controls the REE supply chain of mining, separation, refining, and manufacturing (Van Gosen et al., 2014; Gupta et al., 2017; Lin et al., 2017a; Hussain and Luo, 2019; Park et al., 2021). As a result of this geographically imbalanced distribution of REEs and the surge in

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demand for REEs in numerous high-end technology applications, there is a rapid depletion of traditional rare earth ore deposits. Due to the growing importance, scientific communities and governments are exploring alternative or non-traditional sources of REEs.

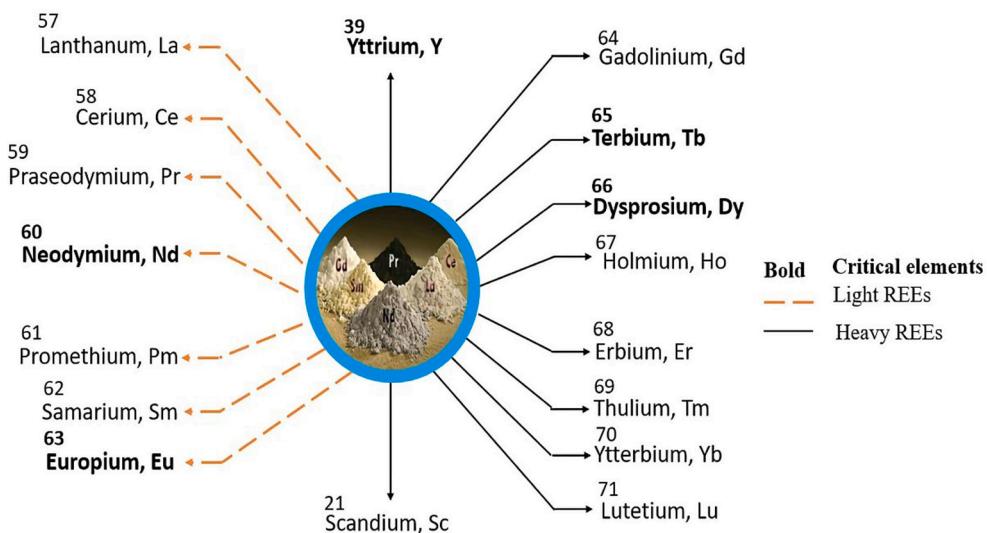
According to the literature (Zhang et al., 2015; Honaker et al., 2016; Ganguli and Cook, 2018; Kuppusamy et al., 2019), coal and coal byproducts are substantially enhanced with trace metals and have been proposed as a promising source of REEs. The vast abundance of coal and coal byproducts combined with the fact that the coal has already been mined, milled, and partially prepared (washed or combusted) (Hodgkinson and Grigorescu, 2020) drives the research of REEs from these sources. This merit potentially increases the economic value of extracting REEs from coal sources compared to the conventional technique that requires environmentally costly mining or extraction. It is understood that the deposition of REEs in and around coal-bearing strata is an outcome of different occurrences. Seredin and Dai, (2012) reported that the deployment or accumulation of REEs within a coal deposit is of four genetic types: 1) Tuffaceous, which is related to the passing of natural acid leachates and alkaline volcanic ash; 2) hydrothermal, linked with thermal mineral water and heated fluids; 3) infiltration or meteorite aquifer water-driven; 4) terrigenous, associated with the deployment of REEs via surface waters. Furthermore, some of these REE occurrences are a result of sedimentation mechanisms. This includes chemical and physical rock weathering, the deployment of REEs with humic matter during coalification and diagenesis, source rock materials hosting high concentrations, etc. (Bank et al., 2017). From the literature, the average REE abundance in coals around the world is about 69 ppm. However, some coal deposits have registered values exceeding 300 ppm (Seredin and Dai, 2012; Zhang et al., 2015) compared to 1000 and 5000 ppm obtainable in traditional mining scenarios. Mastalerz et al. (2020), recently reported REY concentrations of 200 ppm to more than 3000 ppm (ash basis) in Pennsylvanian coals and shales. This value is above the cut-off grade of 1000 ppm (ash basis) for coal-hosted REE deposits and could be considered sufficient for commercial recovery (Dai and Finkelman, 2018).

The potential deposits of REEs recovery opportunities from coal and coal byproducts across the coal utilization and processing value chain are presented in Fig. 2. Zhang et al. (2015) reported that the tailings from a coal preparation plant and the ash from a coal power plant are considered the primary repository for REEs recovery. Laudal et al. (2018b) stated that coal sources are often relatively enriched in the HREEs compared to traditional mineral deposits. Also, Zhang and Honaker (2018) and Zhang et al. (2020) reported that coal-based

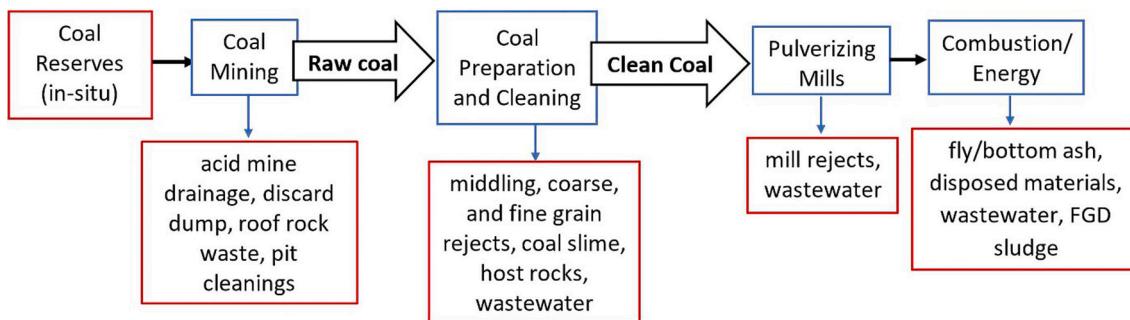
materials are typically rich in HREEs and critical REEs (CREEs) relative to LREEs. There is also well-documented research on the recovery of REEs from coal mine drainage (CMD) sites, and precipitates from CMD treatment systems (Hedin et al., 2019; Moraes et al., 2020; Zhang and Honaker, 2020; Vaziri Hassas et al., 2020; Royer-Lavallée et al., 2020; León et al., 2021; Song et al., 2021; Costis et al., 2021). Numerous studies have also confirmed the presence of REEs in coal fly ash (Blissett et al., 2014; Honaker et al., 2016; Hood et al. 2017; Lanzerstorfer, 2018; Wang et al., 2019; Sorokin et al., 2019; Wen et al., 2020; Hower et al., 2020; Anand Rao et al., 2020).

Over the past decades, the volume of publications on REEs from coal in the open-source literature has increased. The trend of publication of peer-reviewed articles in scientific journals was extracted from a Scopus search by inputting the criteria words like "coal, rare earth elements" according to the format recently reported by Yoro et al. (2021). The visualization (Fig. 3) indicates the growing interest in the recovery and application of REEs from coal and its byproducts. From 1990 till date and during the first half of 2021, a total of 3147 articles and approximately 406 articles have been published respectively. Zhang et al. (2015) reviewed the occurrence and upcoming recovery methods for beneficiating REEs from coal and coal byproducts. Zhang et al. (2020a) reported a systematic review of REEs from coal and coal byproducts with a focus on testing outcomes and separation mechanisms. Peiravi et al. (2020) reviewed REE extraction from nonconventional sources including coal and coal byproducts. The information in this review complements the study of these researchers and is based on research papers and other internet sources associated with the processing of rare earths from coal.

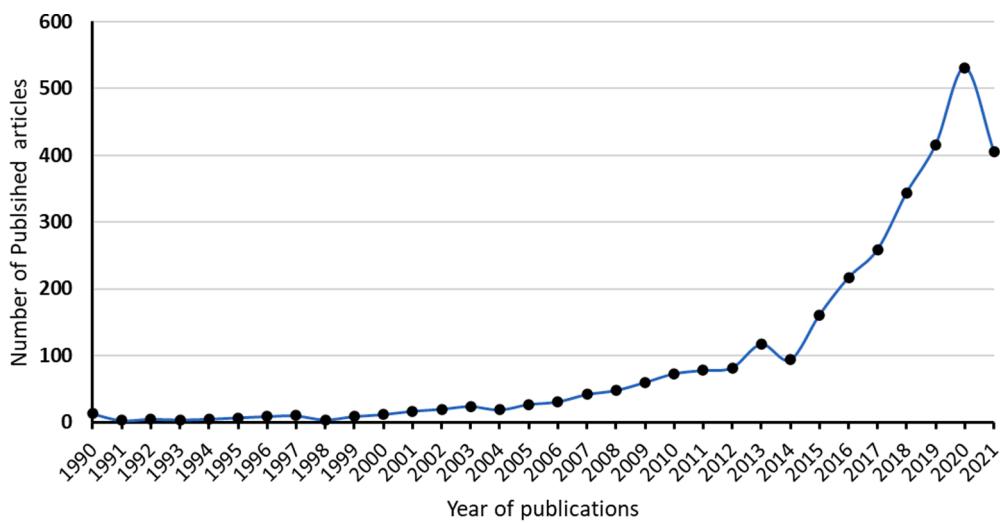
Due to the considerable volume of literature in the field, the scope of this review article is limited to REEs from coal (run-of-mine), over/under-burden/sandstone/clay materials, and coal discard. It does not address REEs from acid mine drainage (AMD) or the precipitates resulting from AMD treatment and coal combustion byproducts (fly ash and residue ash). The article begins with an overview of the mode of occurrence and abundance of REEs in coal. Detailed discussions on the physical enrichment strategies and hydrometallurgical leaching processes for the recovery of REEs from coal and coal discard are presented. Published REEs studies were reviewed to identify the knowledge gaps and future research required to advance the field was provided. Finally, the main research results on the recovery of REEs from coal and coal discard and various (conventional and emerging) REE separation techniques are summarized.



**Fig. 1.** The rare earth elements displaying their atomic number.



**Fig. 2.** Schematic representation of potential value stream of REEs from coal (Adapted and modified from <https://www.energy.gov/sites/prod/files/2018/01/f47/EXEC-2014-000442%20-%20for%20Conrad%20Regis%202.2.17.pdf>).



**Fig. 3.** Published articles on REEs from coal-based materials from 1990 - August 2021.

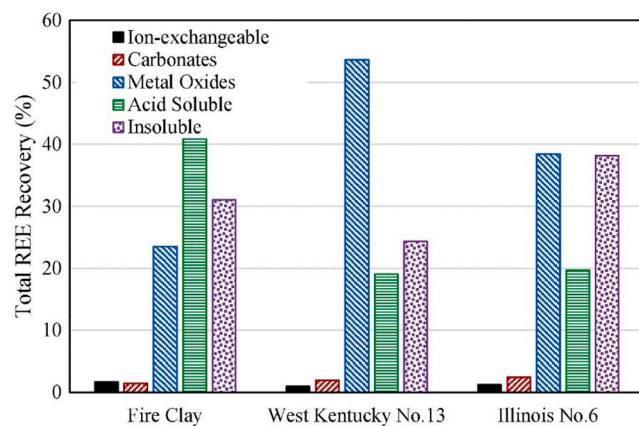
## 2. Modes of occurrence, abundance, and association of rare earth in coal

The modes of occurrence of rare earth elements (REEs) are also referred to as the forms or species of REEs. This needs to be clearly understood to develop technologies that can adequately concentrate, separate, extract REEs from coal and coal byproducts economically. According to [Finkelman \(1993\)](#), the form of occurrence of REEs dictates the leaching and other chemical reactions essential to recover REEs from coal. To begin with, REEs in coal may occur or be present in the form of micro-dispersed minerals, ion exchangeable adsorbed onto the clay surfaces or inner layers, or could be chemically bound with functional groups such as carboxyls and carbonyls, etc. within the organic matrix or host minerals ([Jordens et al., 2013](#); [Zhang et al., 2017](#); [Finkelman et al., 2018](#)).

In-depth studies that provide an understanding of the modes of occurrence and association of REEs in coals have been reported by various researchers ([Finkelman et al., 2018](#); [Laudal et al., 2018a, 2018b](#)). The sequential extraction procedure is widely used by many scholars to quantify and determine the mode of occurrence of REEs and other trace metals in coal-based sources. [Finkelman et al. \(2018\)](#) applied this technique to show that REEs in bituminous coal were predominantly associated with the monazite and xenotime phosphate minerals (70% LREEs and 50% HREEs). The authors also reported that about 50 – 60% of REEs were primarily associated with clay minerals from low-rank coals. [Laudal et al. \(2018a, 2018b\)](#) sampled and characterized REEs in North Dakota lignite coal and lignite-related materials. Experimental data revealed that a significant quantity of certain elements (including

REEs) in the lignite coals appeared to be associated weakly with the organic portion of coal. The authors reported that the REEs were most likely complexes of carboxylic acid groups and to a lesser extent ion-exchangeable cations or water-soluble minerals. Their findings were attributed to the oxygen functional groups which are naturally present in lignite to make available binding sites for inorganic cations such as REEs. Based on their observations, it was expected that low-rank coals such as lignite and sub-bituminous coals would anchor a high percentage of organically associated REEs compared to high-rank coals due to the presence of a high percentage of carboxylic acid groups in low-rank coals. The same group of researchers conducted studies on low-ash coal samples and observed that the HREEs had a stronger affinity for the organic fraction of coal. Additional analysis using the sequential leaching method showed that about 80 to 95 wt% of REEs were leached by the acid, indicating that the REEs present in the lignite coal samples were acid-soluble. This was presumably due to the strong complexation ability of HREE with the humic acids present in coal during coalification ([Honaker et al., 2019](#)).

[Zhang and Honaker, \(2019a\)](#) utilized the sequential leaching technique to recover minute amounts of REEs in the ion-exchangeable and carbonate forms after calcination. More significant amounts of approximately 54% and 40% of the REEs were recovered as oxides and in acid-soluble forms respectively ([Fig. 4](#)). The results achieved by [Zhang and Honaker \(2019a\)](#) revealed that minute amounts of REEs in their bituminous coal samples are in ion-exchangeable forms. Nonetheless, a combined 50–80% of REEs existed in acid-soluble and metal oxide forms due to the coal samples being calcined before sequential extraction. It was further noted that insoluble silicates represent a minor segment of



**Fig. 4.** Sequential extraction test results on coal calcined at 600 °C (Zhang and Honaker, (2019a), Adapted with permission from Elsevier).

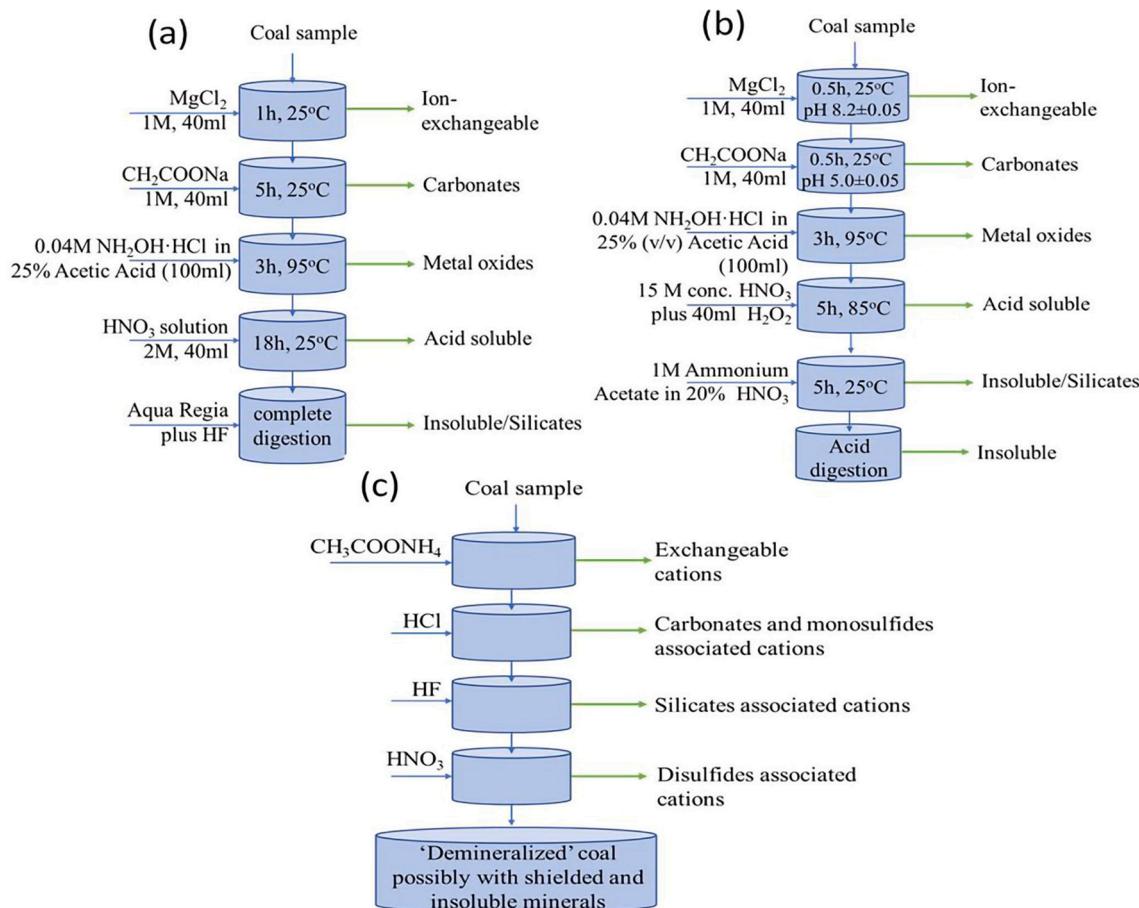
REEs present in the calcined coal samples compared to the original non-calcined coal sample. The sequential extraction procedures used by various researchers demonstrating the targeted phases are presented in Fig. 5.

Yang et al. (2019) assessed REEs distribution in geological core coal and found the coal-rich (organic) segments to have the lowest REEs content because the organic material from the coal-rich segment tended to dilute the REE content. However, REEs with higher concentrations were obtained in the strata below and above the coal seams. The run of mine coal from the Late Permian coal from Hongfa coal mine studied by Cheng et al. (2018) indicated that the inorganic matter in the coal hosted

more REEs than the organic matter. Lin et al. (2017b) also confirmed the presence and association of REEs to the inorganic minerals of coal based on the positive relationship between REE concentrations in the clean coal and coal discard via density separation. The results revealed that the organic portion of the coal was significantly rich in HREEs compared to its inorganic content. Zhang et al. (2015) and Hower et al. (2016) reported that in general, HREEs prefer bonding with coal organic matter, while LREEs are more copious in raw coal but have a greater bonding with the mineral matter in coal.

Mastalerz et al. (2020) investigated the abundance and association of REEs in Pennsylvania coals and shales on an ash basis. The author stated that a positive relationship between REEs and ash yield of the coal could provide indirect evidence of the association of REEs with mineral matter. However, their result did not show such correlation for the coals tested, rather the results revealed that generally HREEs decreased as the ash yield of the samples increased. The author also observed that high ash yield coal samples used in the study reported low REEs and suggested that the major mode of occurrence of REEs in their coal samples may be organically associated. This was supported by the fact that higher REE concentrations were present in the washed coal than in the raw coal. Due to their unexpected finding, the authors advised that the sequential leaching technique and the scanning electron microscopy analysis would be necessary to determine the major associations of the REEs in their coal source.

According to a report by Reid (2018), about 75% of REEs in coal are anticipated to be linked to the mineral matter removed at the coal preparation plant, rather than the organic fraction of coal. This statement infers that coal rejects or waste by-products such as coal tailings, acid mine waste fluids, etc., and some lignite resources could be attractive REE-rich sources. Ash correlation results generated from REE



**Fig. 5.** Sequential extraction schemes showing targeted phase (a) Zhang and Honaker (2019a), (b) Zhang and Honaker (2020) (c) Finkelman et al. (2018).

concentrations in process streams of twenty coal preparation plants located in the Eastern USA, Luttrell et al. (2019) showed that REEs in the streams were hosted by inorganic mineral matter (high ash content products). This conclusion was based on the increase in TREE concentration within the ash content on a whole sample basis. On the contrary, on an ash residue basis, the authors observed that significantly higher TREE concentrations are contained in the residual ash of the medium-ash middling products and low-ash clean coal. Therefore, the authors suggested that REEs are more enriched in the minerals dispersed within the organic portions of the coal seams than the minerals retained within the discarded products. Likewise, other researchers (Honaker et al., 2017; Zhang et al., 2017) have reported that more REEs were hosted in the high density (high ash content) fraction of the coal. On the other hand, Seredin and Dai (2012), reported that many low-ash and low-rank coals are rich in REEs and could be linked to organic matter, rather than minerals and in some cases can occur in both. A review by Zhang et al. (2015) cited works of literature with strong evidence of the existence of REEs (particularly HREEs) that are organically associated with coal.

The key question is whether the organic or inorganic association of REEs in coal and coal byproducts is accurately known. According to the literature, there is no unanimous agreement that REEs are linked organically or to the mineral content of coal. However, the trend from the literature surveyed suggests that a considerable portion of REEs in coal is associated with the inorganic phase. The trend also suggests that HREEs are more likely enriched in low ash and low-density coal fractions. The inconsistency in the results of the association of REEs in coal reflects the heterogeneous nature of coal and that its constituents vary across regions. Even in the same region, coalfield or coal seam, it is likely to find coal with varying properties. The complex mineralogy of REEs and affinity mechanisms in coal may also contribute to the aforementioned observation. More investigations and an in-depth understanding of the form and association of REEs in a particular coal source could pave the way for the development of a robust recovery process of REE from coal efficiently. Eventually, the best or most economical method selected to extract REEs from any coal source will depend on the distribution of REEs in the inorganic and organic content of the coal (Reid, 2018; Yang et al., 2019). In addition, establishing models using statistical software to predict the dominant mode of occurrence of REEs in coal and coal byproducts could provide useful guidance for the enrichment and subsequent extraction of coal.

### 3. Overview of rare earth element processing

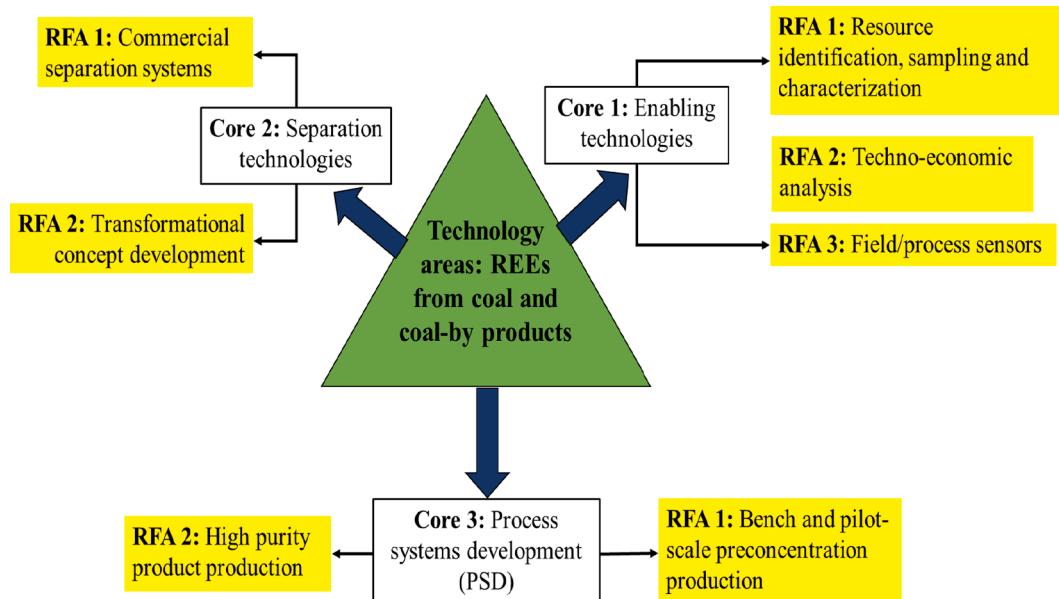
The value of REEs in any coal source depends greatly on the concentration of REEs in the coal source. The concentration of REEs varies from source to source depending on the geological and geochemical conditions of coal formation. The first step in the economic recovery of REEs from coal sources is to identify coal sources with the highest REE levels and accessibility before extraction and recovery. This step is important to avoid the tedious, expensive, and multiple extraction steps involved in REE extraction. Reid (2018) reported that it is economically unattractive to recover REEs from some coal sources or individual sites of coal reserves containing an average level of 35 ppm. The cut-off grade for commercial extraction of REEs varies with the geological characteristics of the coal and coal byproducts. Seredin and Dai, (2012) reported that coal sources with rare earth oxides (REOs) concentration greater than 100 ppm (whole coal basis) or 1000 ppm (0.1%) (ash basis) with the subsequent concentration of REEs to levels greater than or equal to 2% by weight is a sufficient basis for commercial recovery.

To overcome the critical supply of REEs, the U.S. Department of Energy National Energy Technology Laboratory (DOE NETL) summarized three core technology areas and research focus areas (RFA) to address the feasibility of separating and extracting REEs from coal and coal by-products (Fig. 6).

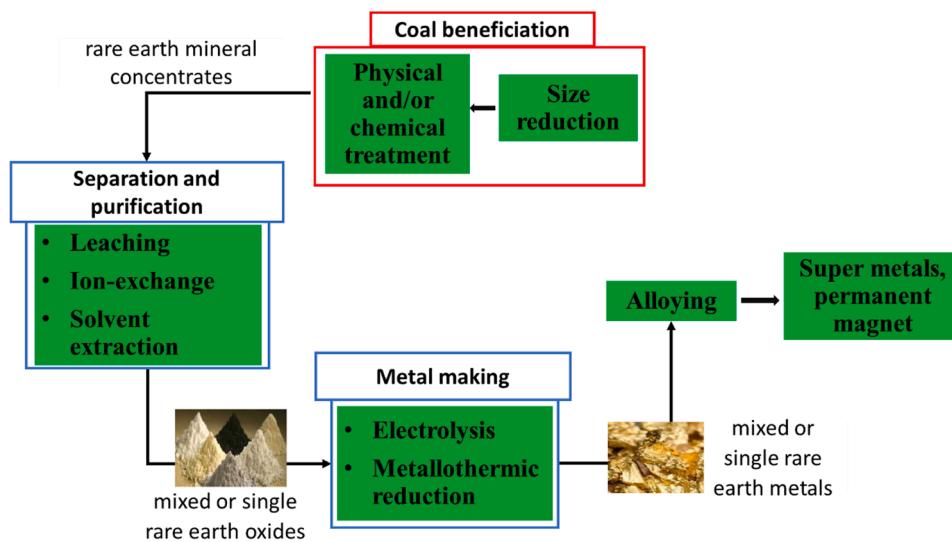
The stages of extracting pure REEs from coal and coal byproducts to produce super metals are summarized in Fig. 7. Coal is first prepared by crushing and milling to liberate the coal organic from its inorganic minerals to produce fine concentrates. The concentrates undergo further beneficiation processing via physical and chemical (leaching) separation, and thereafter purification to extract the REEs into their pure oxide form, i.e., rare earth oxides (REOs) of individual elements. The REOs produced in this stage can occur free-standing, usable, and sellable. However, the refining stage, using an electrolysis or a metallothermic reduction process, is critical for converting REOs into high-purity rare earth metals. These metals may then be alloyed with other elements to make them harder and stronger for the end-use market.

### 4. Characterization techniques of REEs in coal and coal discard

There are various techniques in the literature utilized in characterizing and evaluating the content of REEs in coal and coal byproducts. Laudal et al. (2018) reported the optical emission spectrometry (ICP-



**Fig. 6.** REE from coal: Core technology areas (Adapted and modified from <https://www.netl.doe.gov/sites/default/files/2019-04/2019-REE-Project-Portfolio.pdf>).



**Fig. 7.** A schematic of REE processing stages from coal and coal discard (Adapted and modified from <https://www.energy.gov/sites/prod/files/2018/01/f47/EX-EC-2014-000442%20-%20for%20Conrad%20Regis%202.2.17.pdf>).

OES) and inductively coupled plasma mass spectrometry (ICP-MS) as the two-standard approach used to determine the abundance of REEs in coal and coal byproducts. Balaram (2019) also reported on the use of instrumental neutron activation analysis (INAA) for determining REEs in a range of materials because of their multi-element functionality, ease of operation, and high sensitivity. A new technique like the luminescence-based sensor technique for detecting REEs is gaining attraction due to its sensitivity, low concentration detection, simpler operation, low cost, and the capability to manufacture handheld systems for field deployment. An extensive review of this technique is given by Crawford et al. (2020). Meanwhile, the Tescan Integrated Mineralogy Analyzer (TIMA) is considered a revolutionary and multifunctional automated mineralogy solution introduced in 2012 (Schulz et al., 2020). This piece of equipment encapsulates Energy Dispersive X-ray (EDX) with Back-scattered Electron (BSE) signals to assist with determining grain-by-grain quantitative and qualitative measurements of mineral phases, grind size, liberation, and elemental composition (Gottlieb et al., 2015; Hrstka et al., 2018). In addition, the equipment can detect minimal amounts of REEs, their mineral association, and distribution (Gottlieb et al., 2015). Also, extensive research and demonstration on the use of sensor technology based on laser-induced breakdown spectroscopy (LIBS) for quantitatively determining REEs in geological samples like soils and rocks have been reported (Harmon et al., 2013; Senesi, 2014; Martin et al., 2015; Labutin et al., 2016; Bhatt et al., 2018). Based on the sensitivity and low-cost attributes of LIBS to provide real-time on-site data, research using this technique to quantitatively determine REEs in coal-related materials is expected to increase (Bhatt et al., 2018; Thompson et al., 2018; Wainner et al., 2018). A thorough grasp of the analytical potential of the above-mentioned techniques is essential for optimum capturing of results. A summary of the commonly reported analytical methods used in analyzing REEs in the literature is presented in Table 1.

## 5. Extraction strategies for the recovery and enrichment of REEs

### 5.1. Physical separation and physico-chemical separation methods to enrich REEs from coal and coal discard

This section discusses the physical and physico-chemical techniques used to produce concentrated REE minerals from coal and coal-based products for potential REE extraction. It should be noted that these techniques may be implemented individually or in combination.

**Table 1**

Major analytical techniques used to determine REE occurrence and composition (Adapted and modified from Laudal et al., 2018b).

Analytical technique	Characterization	Purpose
ASTM standards (ASTM D3172)	Bulk chemical composition	Proximate; ultimate; ash composition
X-ray fluorescence spectrometry (ASTM D4326 – 13)	Bulk chemistry; minor, major, and trace elements	
Inductively coupled plasma mass spectrometry/ optical emission spectrometry (ASTM D 6357–19)	Abundance or amount of trace elements including REEs	
Laser-induced breakdown spectroscopy (LIBS)	Elemental constituents	Detect/identify REEs
Scanning electron microscopy with energy dispersive x-ray spectrometry, transmission electron microscopy (TEM)	Modes or forms of occurrence	Morphological imaging and chemical composition of minerals
Computer-controlled SEM		
Chemical fractionation		Size, chemical composition, and associations (included or excluded relative to coal particles)
		Quantitatively diagnose the modes of occurrence of the inorganic elements

#### 5.1.1. Gravity/density separation

Gravity separation techniques have been employed considerably in the past and present to process coal and other minerals. These techniques exploit the differences in the densities of various compounds (mineral matter and organic matter) within the coal or ores to enrich and recover the target mineral or species. A range of different techniques and methods that utilize the aspect of density separation are discussed:

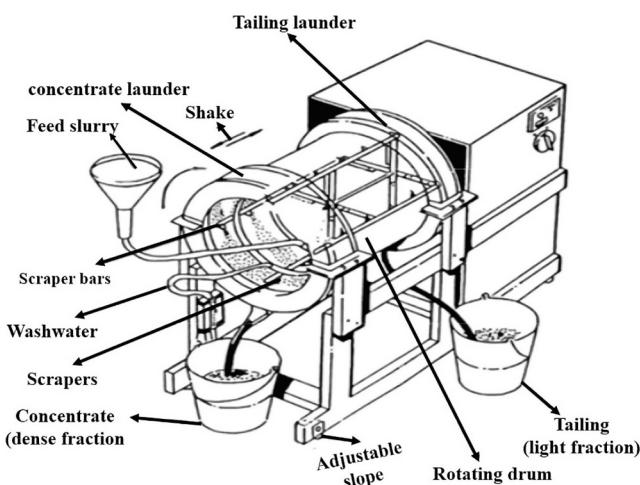
The multi-gravity separator (MGS) was originally manufactured by Richard Mozley Limited, U.K (Kiser et al., 2015). The MGS primarily consists of a shaking table mechanism placed inside a rotating drum, which assists the separation of particles of different densities. The MGS operates on an incline angle and utilizes gravity (freefall) for the downhill movement of the medium to transport the particles into the drum (i.e., water) and less dense particles. The particles inside the drum experience an acceleration greater than that of gravity. Acceleration and

rotation of the drum results in higher density particles moving to the outer wall of the drum, while the less dense particles transferred down the length of the drum together with wash water and thus exiting at the bottom of the drum. An illustration of the MGS is presented in Fig. 8, where higher density particles are seen exiting the drum uphill at the front of the MGS. A study conducted by Kiser et al. (2015) on the Eagle seam, Fire Clay seam, and Fire Clay Rider seam utilized the MGS. The study indicated that the MGS was effective in enriching REEs in the medium to high specific gravity (SG) fraction. The high SG products correlated to an increase in ash content and exhibited a total REE enrichment of 12% to 17% for the samples. However, none of the products manifested an increase in REE concentration of greater than 20% relative to the feed. The study also reveals that REE enrichment in the high SG fraction was due to REEs being distributed within the mineral matter owing to the high ash content in these U.S coal samples.

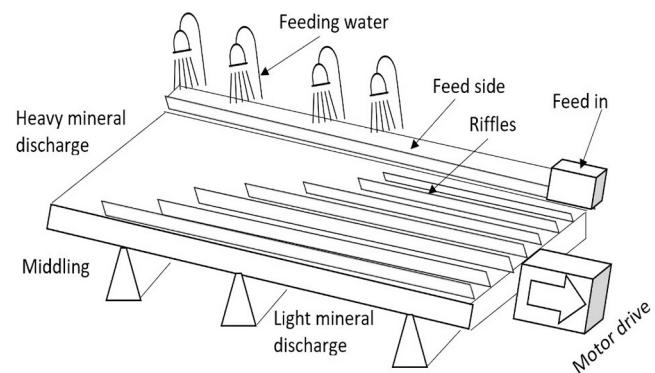
A shaking table, which is also a gravity separation technique was utilized in the enrichment of REEs from coal. A shaking table is essentially a device designed with or without riffles to reduce a sample of coal or ore to half its original size. A schematic depiction of the arrangement of a riffled table with the feed input at the top right corner of the table is shown in Fig. 9. Honaker et al. (2016) utilized a riffled table to separate different coals, and five product streams were produced from each coal. The results obtained showed an increase in ash content from product one to five, with the light fraction reporting to product one and heavy material to product five. A maximum positive REE enrichment of 8.2%, 5.4%, and 12% occurred in product stream two for all three coal samples (Fire Clay seam, Fire Clay rider, and Eagle Seam). Product stream two illustrated that REEs were enriched in the middle-density fraction.

The float-sink method was utilized by Lin et al. (2017a) to benefit coal for REE recovery. The author demonstrated a high-density fraction (high ash content) product relatively enriched in LREEs and a low-density fraction (low ash content) enriched in HREEs. Another study conducted on the freeport coal seam in Pennsylvania also employed the float sink method, and the researchers noticed that REEs were fairly enriched in the lighter SG fraction and scandium was relatively enriched in the light to intermediate SG (Finkelman, 1981). The data from this study was in correlation with the results obtained from the petrography and SEM analyses which noted REE-bearing minerals (xenotime) to be finely dispersed within the coal organic matrix. Honaker et al. (2016) also utilized the same technique to benefit a coarse coal discard from a coal preparation plant, and the results obtained showed a maximum REE concentration reported in the medium density fraction.

Another investigation by Laudal et al. (2018a) on a high-ash coal sample showed that REEs were concentrated in each specific gravity



**Fig. 8.** Details and cross-section of a multi gravity separator (Source: Rao et al. 2017).



**Fig. 9.** Schematic illustration of the arrangement of a riffle table.

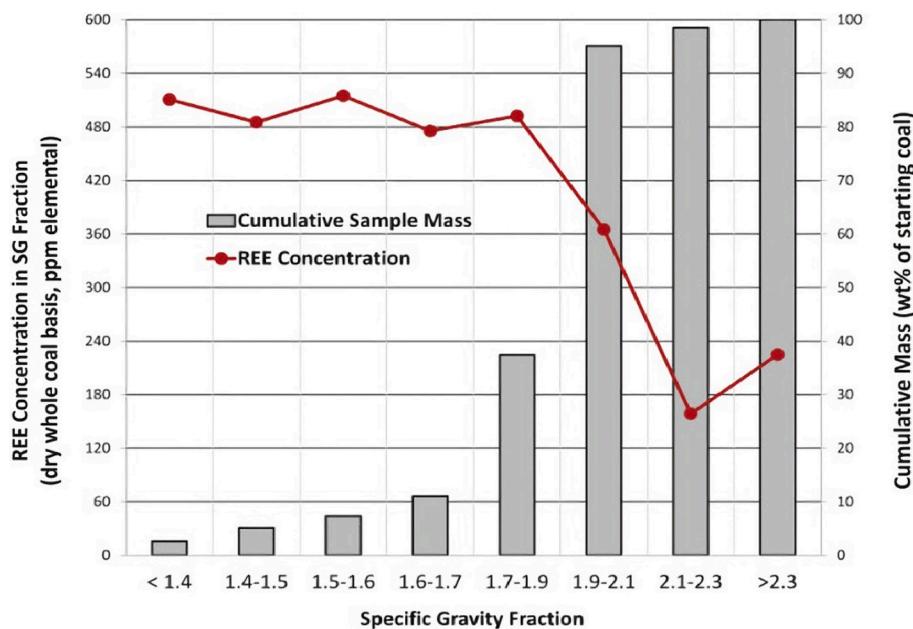
fraction obtained from the sink and float test, as seen in Fig. 10. From the same figure, it could be seen that the REEs were mostly concentrated in the light to intermediate specific gravity fractions. The authors remarked that the ash formed by combusting coals from these fractions may contain elevated REE concentrations but might be difficult to leach because the REEs are fused with the silicates and phosphates in the fly ash (alumina-silicate glass matrices). According to Zhang et al. (2015), when the float-sink method is used alongside fine grinding to liberate REE mineral grains, a relatively high REE concentrate may be obtained. It is worth highlighting that depending on the goal, the separation density of the liquid could be adjusted to much lower levels to magnify the enrichment of the elements of interest.

Gravity separation is a reasonably stable technique for the upstream processing of REE minerals in coal before leaching. Nevertheless, it results in a low enrichment and low grade of REE products with significant amounts of gangue minerals in the concentrate. Another limitation is that significant amounts of REEs are removed in the undesirable density fractions. Additionally, the techniques involve a large degree of milling for effective separation, leading to an energy-intensive liberation stage for the fine processing of the coal source (Kiser et al., 2015; Zhang et al., 2015; Honaker et al., 2016).

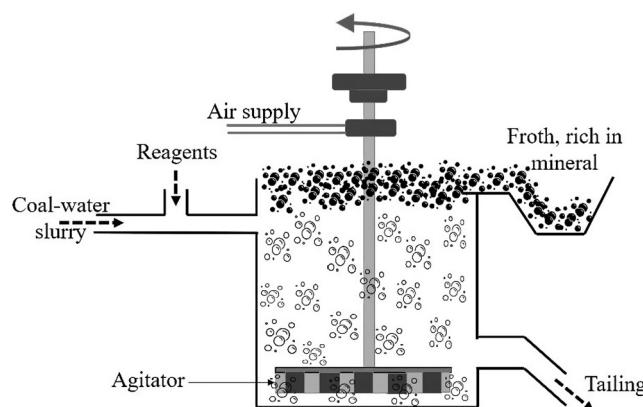
#### 5.1.2. Froth floatation

Froth floatation exploits the difference in coal or other mineral surface properties and can process a wide range of ores with particle sizes ranging between 50  $\mu\text{m}$  and 400  $\mu\text{m}$  (Sinott and Towler, 2020). A typical floatation cell used to separate inorganic mineral content from coal with the aid of a reagent and air bubbles to attract and bind the ultra-fine hydrophobic carbonaceous particles from inorganic minerals (Gupta et al., 2019) is shown in Fig. 11.

A study conducted by Zhang et al. (2017) utilizes this approach in the beneficiation of rare earth oxide from fine discard coal using methyl isobutyl carbinol and diesel as the frother and collector, respectively. The authors used both HCl and NaOH as pH controlling agents, and a clean coal product with 10% ash and 85% combustible material was achieved. Thus, signaling a substantial economic potential for recovering clean coal before REE concentration. In addition, the authors observed low ash products contained a low concentrated amount of REEs on a dry whole mass basis and typically comprised of high REE contents on a dry ash basis with increased amounts of valuable HREEs. The reason being that HREEs tend to fill in cracks and cleats within the organic matrix thus reporting to the low ash products. For the REE release floatation tests, sodium oleate was utilized as the collector for both the conventional batch floatation and continuous floatation column tests. The continuous floatation column exhibited recovery of 20% TREEs, producing a concentrate of 4700 ppm from an initial feed content of 431 ppm resulting in an enrichment ratio of 10:1 at an optimum grind size of 2.76  $\mu\text{m}$ . With increased recovery values above 30%, both floatation cells manifested extremely low REE concentrates below 1000 ppm. Continuous column floatation was found to be more effective as it



**Fig. 10.** Float-sink separation data for the high ash Harmon-Hanson sample 6A-1 (carbonaceous clay) (Laudal et al., (2018a), Adapted with permission from Elsevier).



**Fig. 11.** A simple froth floatation cell.

provided twice as much REE content than the batch floatation cell.

An alternate study was also reported on a batch froth floatation of Alaskan coal ( $<75 \mu\text{m}$ ), using Aerofoam-88 (2-Ethylhexanol, specific gravity = 0.83) as the frother and fuel oil (SG = 0.83) as the collector (Gupta et al., 2019). The froth floatation process was optimized using the Box-Behnken method to enrich REEs in the coal. At optimal reagent dosages, a maximum REE concentration of 506 ppm with 77.3% of total REE recovery was reported. In the floatation test conducted by Honaker et al. (2016) on three coal seams (Fire Clay, Fire Clay rider, Eagle Seam). Three fatty acid collectors, namely Talon 9400, sodium oleate, and oleic acid, were utilized with a slurry pH of 9.5 to maximize the recovery of monazite contained in the coal samples. High total REE recovery values of 65%–70% were observed when utilizing Talon 9400 and sodium oleate collectors. However, these collectors produced concentrates with low total REE contents. For oleic acid, a substantially rich REE concentrate of 380 ppm with low recovery values not exceeding 50% was achieved. The study concluded with an optimized combination of a floatation rougher-cleaner-recleaner and REE concentrate of 1182 ppm was achieved.

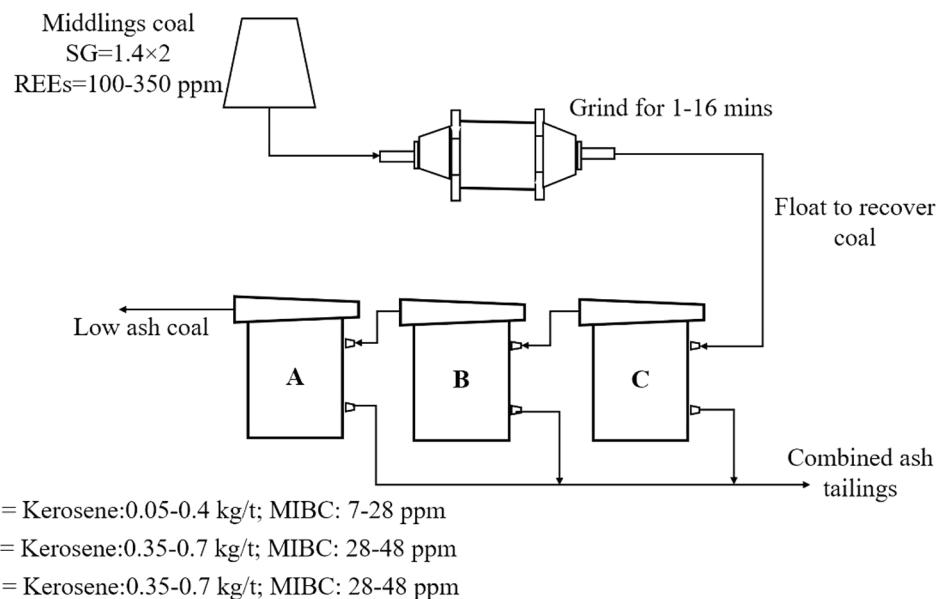
From most of the literature in the public domain, REE floatation processes employ fatty acid as the collector of choice because it is readily

available and of low cost (Anderson et al., 2016). The authors reported that hydroxamates as chelating collectors are ideal for the floatation of rare earth minerals due to increased selectivity over fatty acids. The increase in selectivity is attributed to the ability of hydroxamates to easily form chelates with rare-earth ions rather than the associated gangue. It should be noted that despite the good attributes of hydroxamates, low recovery could still be achieved depending on the solubility of the rare earth minerals. Hence, there is a significant opportunity for research to produce a higher selectivity and high recovery of REE-bearing minerals using hydroxamates as the collector for coal and its byproducts. Furthermore, increasing the collector's temperature has been reported to increase both the grade and recovery of bastnasite floatation, which in turn increases both the grade and recovery of rare earth oxides by using fatty acid collectors (Anderson et al., 2016). To the best of our knowledge, no similar investigations have been reported for coal or coal byproducts using this approach.

Huang et al. (2018) utilized froth floatation to beneficiate coal middlings and discards from three coal preparation plants with different particle sizes. 4-methyl-2-pentanol (MIBC) and Kerosene were used as the collector and frother, respectively. The floatation is comprised of one initial stage and two cleaning stages for the effective removal of the gangue minerals. The results indicated that at smaller particle sizes of  $< 20 \mu\text{m}$ , the REE contents of the floatation tailings increased with an increase in ash content, as well as in tailings. The Fire Clay coal sample exhibited high REE contents of 700 ppm after undergoing floatation in the process represented in Fig. 12.

An innovative ground-breaking technique for froth floatation known as the hydrophobic hydrophilic separator (HHS) was developed by Gupta and Li (2016). The HHS technique provided an enhanced recovery and concentration of ultrafine micron size particles, while also delivering a dewatered product. In this novel technique, hydrocarbon oil is employed to agglomerate hydrophobic particles and to recover the small particles by separating the phases. Octylhydroxamate was utilized as a collector during the HHS test. A REE concentrate of 17,428 ppm from Fire Clay decarbonized thickener underflow and an REE enrichment ratio of 53:1 was achieved.

Floatation is a beneficial technique for producing an REE-rich pre-concentrate which thereafter requires hydrometallurgical treatment. However, its main drawback is the requirement of an extremely fine



**Fig. 12.** REE release test protocol of a combined milling and floatation circuit (Adapted from Huang et al., 2018).

particle as a feed to achieve a substantial REE enrichment. This subsequently leads to energy and cost-intensive process (Jordens et al., 2013; Zhang et al., 2015; Honaker et al., 2016). More so, flotation results in the recovery of surplus undesirable minerals, thus increasing downstream purification costs.

#### 5.1.3. Magnetic separation

The magnetic separation technique is quite popular in the beneficiation of rare earth minerals and it is employed to concentrate the desired paramagnetic REE-bearing minerals (Jordens et al., 2013). In this technique, the magnetically susceptible mineral is extracted from a slurry using a magnetic force, as explained in the article published by Honaker et al. (2016) and Gupta et al. (2017). Using this method may be advantageous as it minimizes the risk of contaminating the extraction leaching process with iron. A depiction of a magnetic separator is shown in Fig. 13.

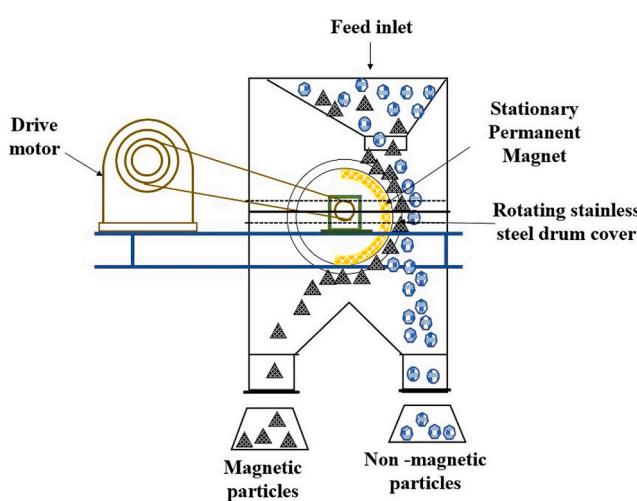
Magnetic separation tests were performed on three coal samples using a wet high-intensity magnetic separator (WHIMS) and employing 4 different magnetic field strengths of 1.5 T, 0.4 T, 0.75 T, and 1.1 T (Honaker et al., 2016). The study indicated that at ultrafine particle sizes, magnetic separation was highly efficient in recovering the

paramagnetic REE-bearing minerals notably monazite and xenotime. Nonetheless, it was noted that REE recovery was low (<2%), owing to small mass recovery and mainly due to small particle size limitations, together with the WHIMS equipment being relatively small. A study conducted by Lin et al. (2017a) made use of magnetic separation on coal and coal by-products. The results obtained reflect that the recovered REEs mainly reported to the nonmagnetic fraction, implying that the REEs in the coal utilized are likely associated with non-iron minerals. In the study conducted at the University of Utah, a wet high-intensity magnetic separator (WHIMS) was used to explore the possibility of concentrating REE + Y + Sc from coal (Miskovic, 2015). The study indicated that only a minute amount of REEs can be recovered in the magnetic fraction of the coal, which is only comprised of a 2% mass yield, denoting limited amounts of minerals in this coal sample are paramagnetic. It was further indicated that most of the REEs in the sample reported to the nonmagnetic fraction owing to the increased recovery of REEs in this fraction. The authors concluded that the only downside of the WHIMS is that it fails to concentrate the elements, even though the nonmagnetic fraction recovered 98–99% of REEs.

A significant study was conducted at the University of Pennsylvania on a roof rock sample of a coal seam (Soundarajan et al., 2015). A low-intensity ferromagnetic separator was passed over a thinly spread sample to eliminate any loose ferromagnetic material present. Thereafter, a cross-belt electromagnetic separator was utilized to separate the sample into its magnetic and nonmagnetic fractions. The study illustrated that almost equal amounts of REEs were contained in both fractions, with the nonmagnetic fraction exhibiting a slightly higher enrichment of REEs. Magnetic separation alone can only assist in removing contaminant elements (particularly Fe), but it does require a large degree of liberation to recover and concentrate REEs. As a result, this suggests that it may be more advantageous when applied in combination with other physical separation techniques to produce a high REE recovery. The main limitation with magnetic separation is that it can only be applied to minute particle sizes of 10  $\mu$ m and a small mass of sample at any given period. Therefore, making the large-scale implementation non-feasible (Gao and Chen, 2010; Soundarajan et al., 2015; Honaker et al., 2016).

#### 5.1.4. Electrostatic separation

Principally, electrostatic separation is used when the above-mentioned physical separation techniques are not significantly



**Fig. 13.** Schematic of a magnetic separator.

effective for the recovery of REEs (Zhang et al., 2015). Electrostatic separation is a technique that assists in the separation of mineral matter as well as coal organics from inorganic matter based on the differences in the particles' conductivity (Bada et al., 2010; Jordens et al., 2013). Many studies have employed this technique to recover REEs from iron mine waste (Moghise et al., 2016), bastnaesite ores, and other secondary sources. On the other hand, very few researchers have subjected coal to electrostatic separation for REE recovery. A schematic of an electrostatic separator separation process is shown in Fig. 14.

Roof rocks (containing coal) occurring on the horizon of a coal seam were subjected to electrostatic separation at the Pennsylvania State University (Soundarajan et al., 2015). High tension electrodes were utilized to create a localized electric (corona) discharge, together with coal particles falling over a rotating drum. The rotating drum provided different currents or trajectories to separate conducting and insulating particles. From the initial feed, equal amounts (40% wt. for each) of the sample were separated into the conducting and nonconducting fractions with the remaining non-responsive coal falling to the middlings section. A small amount of REE enrichment (355 ppm) was collected in the conducting fraction from the coal sample, while substantial REE amounts were still present in the nonconducting fraction (312 ppm). To understand which fractions were enriched in REEs, the study further utilized a discard coal sample and the results indicated that REEs were enriched in the conducting fraction with a concentrate of 313 ppm, while the insulating fraction exhibited a concentrate of 142.65 ppm.

Electrostatic separation is an effective technique when integrated with other physical separation techniques, thereby leading to excess processing costs. Furthermore, the technique entails the usage of extremely fine coal particles ( $<37 \mu\text{m}$ ), which involves the aeration of the particles before being fed into the separator. Apart from the conventional ion-adsorbed clay ores, all alternative REE-bearing ores require some degree of fine liberation. Thus, leads to an escalation in energy costs related to milling and is not feasible for large-scale practical applications (Jordens et al., 2013).

#### 5.1.5. Sensor-based sorting

The sensor-based sorting technique is used in mineral processing to produce valuable minerals from a given ore resource. As the name implies, the technique detects single or multiple properties of single particles by employing a sensor without coming in contact with it, followed by classification using an external force (Knapp et al., 2014). The technique is predominantly applied to reject waste from coarse particles ranging from 10 to 100 mm to reduce downstream processing costs (Kern et al., 2019). A complete range of detection systems for sensor-based sorters with their mineral application is listed in a recent study by Robben and Wotruba (2019). Unlike the other techniques, sensor-

based sorting consumes less energy, water, and reagents (Knapp et al., 2014). The major challenge with this technique is the associated cost of washing, drying, and pre-sizing the feed, and the ore sorting process (Kiser, 2015). In addition, a lot of modification and optimization is required especially on the type of sensor that suits the objective of classification. Veras et al. (2020) effectively used the dual-energy X-ray transmission (XRT) sensors-based sorting technology to sort ores rich in REEs and composed primarily of xenotime minerals. However, the use of a more representative sample and the cost of the equipment were required to further access the use of this technique for industrial-scale operations.

Akdogan et al. (2019) applied a two-stage XRT demonstration sorting plant to characterize REE contents in a coal seam situated in the Witbank coalfield, South Africa. The results from this investigation revealed TREE occurrence up to 280 ppm (ash basis) with HREEs associated strongly with the inorganics. Likewise, Sarswat et al. (2020) noted that the dual-scan x-ray ore sorter can successfully distinguish coal, rock, and pyrite materials but is not capable of detecting the dilute REE components. The schematic of a sensor-based sorting process is shown in Fig. 15.

The dual x-ray transmission sorting was also utilized by Honaker et al. (2020) to achieve the specific gravity of a coal fraction needed to preconcentrate the HREE fraction in coal before grinding (1 mm top size) with results indicating enhanced REE recovery after leaching. From the review of the literature on sensor-based sorting, many sensor-based sorting studies are limited to mineral applications that are not inclusive of coal. Hence, there is a need to increase the volume of investigations, optimize existing, or develop new detection systems relevant for REE concentration from coal sources.

Rare earth minerals existing in ion-absorbed forms require little or no direct physical treatment, rather it makes direct use of hydrometallurgy techniques (Zhang et al., 2015). The physical beneficiation techniques discussed in this review can be employed to recover REE-bearing minerals and to substantially concentrate REEs from coal and coal discard. However, the recovery values obtained may be too low to develop an economically viable physical separation process. The main reason is that REEs occur in ultrafine particles associated with minerals that fill cracks and cleats within the organic matrix (Zhang et al., 2017). SEM characterization of coal and coal discard has illustrated that REEs occur in fine particles of  $< 10 \mu\text{m}$  (Huang et al., 2018) and are partially or fully enveloped by the major minerals present in coal (Zhang and Honaker, 2020). To achieve a high degree of liberation, extensive grinding and milling would be required to attain ultra-dispersive and fine particle forms of REEs from coal sources. This renders the process economically non-viable due to the high amount of energy and high operating costs that will be required (Zhang et al., 2015). Though particle size is a limiting factor in physical beneficiation, the techniques reviewed can be employed without a hefty particle size reduction to produce a high-grade feedstock, but it would require further downstream processes to recover and concentrate the REEs.

Based on this review, the difference in physical properties of coal can be exploited to liberate a significant amount of REEs using some of the physical separation techniques described. However, the selection of any suitable physical technique or the combination thereof will depend on the concentration of REEs in the coal and the grain size for the liberation of REEs from coal. Meanwhile, a good geological knowledge, characteristics, and mineralogy of coal and the fundamental mechanisms involved in producing acceptable REE concentrates from coal and coal byproducts is imperative. Given the low recovery and excessive liberation costs using physical separation techniques, fine-tuning the process to obtain the optimum parameters is necessary to realize a significant economic and time-saving liberation of REEs present in coal and coal discard. Nevertheless, physical beneficiation assists significantly in the enrichment of the fraction of REEs within their ore state. In addition, the hydrometallurgy process could be integrated with the above techniques leading to effective recovery of native elemental ions to produce REE-

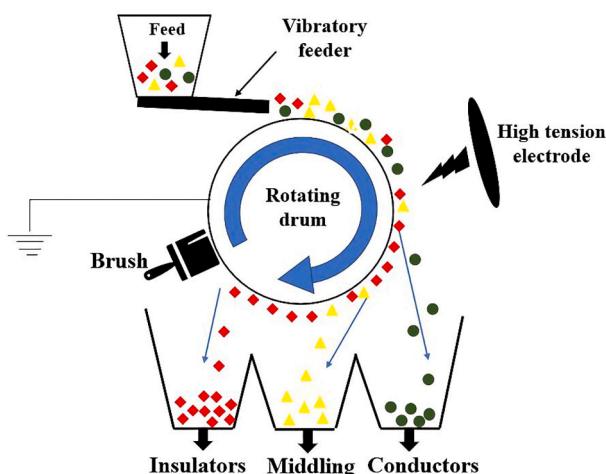
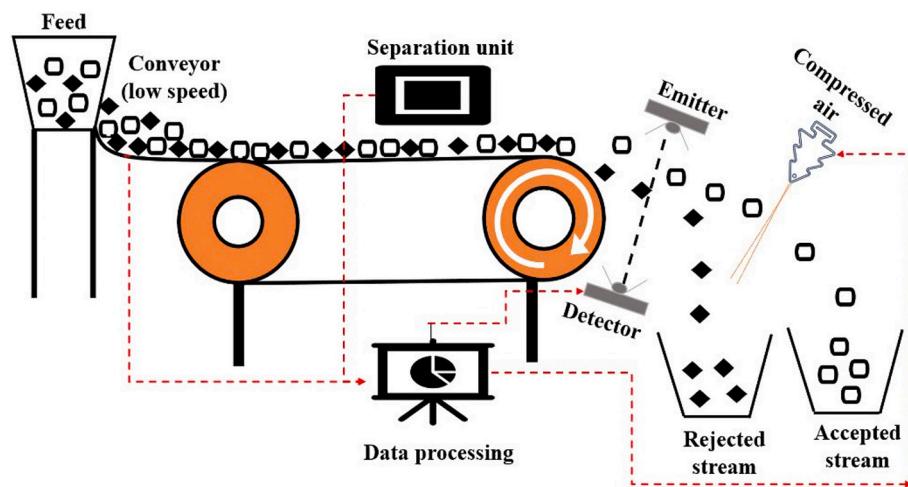


Fig. 14. Schematic of a high-tension electrostatic separator.



**Fig. 15.** Schematic of the sensor-based sorting process.

rich preconcentrate.

### 5.2. Hydrometallurgy processing of REEs from coal

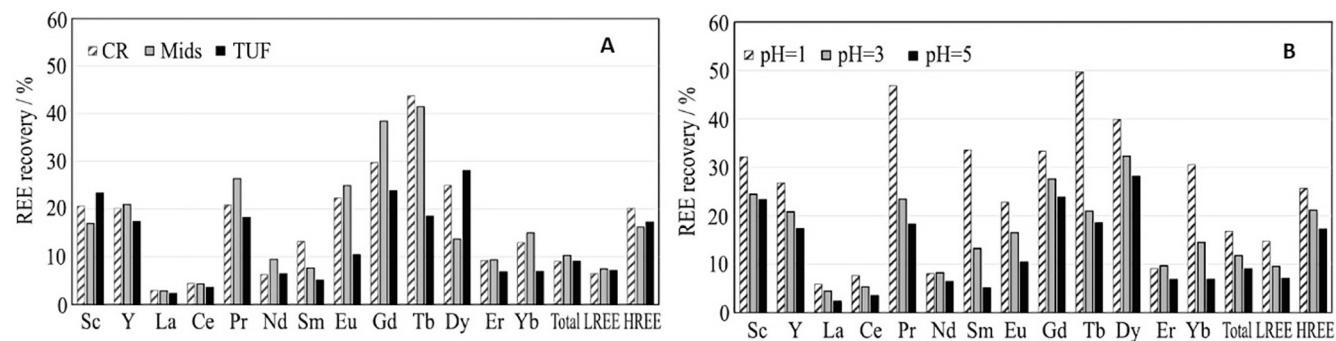
Hydrometallurgy is considered an attractive technique to process minerals because it consumes low energy and can produce products of high purity (Zhang et al., 2016). The hydrometallurgical process involves the decomposition of REE-bearing minerals and the leaching of REEs into solutions. Generally, during leaching, the coal feedstock is contacted with a suitable leaching reagent (water, acid, or salt) at a certain temperature for the desired contact time to dissolve REEs into a pregnant leach solution (Laudal et al., 2018a; Honaker et al., 2019; Yang et al., 2019; Ji et al., 2020). The effectiveness of the technique depends on the ability of the leaching reagent to extract rare earth from other unwanted components by altering the feed pH and molarity. Once the leaching is completed, the slurry is filtered and the solid residue is collected for analysis. The most common acids used in REE leaching from conventional sources are sulfuric acid ( $H_2SO_4$ ), hydrochloric acid (HCl), nitric acid ( $HNO_3$ ), or their combinations (Peiravi et al., 2020).

Yang et al. (2019) accessed the REE potential of each core segment of an Illinois coal basin and discard coal samples from a dense medium cyclone. The middlings obtained from float and sink SG 1.8 were pulverized to improve the mineral liberation. A two-stage floatation was subsequently employed due to a large amount of acid-consuming minerals like calcite, dolomite, and alkali materials present in the coal. The upgraded REE mineral concentrate was then used as feed for the leaching experiments. Acid leaching was done using sulphuric acid solution maintained at 75 °C while ion-exchange leaching (0.1 M/L ammonium sulfate salt) was used to leach the clay absorbed and ion exchangeable REEs present primarily as the salts of organic acids. Acid leaching of the West Kentucky No. 13 coal discard sample recorded low REE contents alongside a relatively large amount of iron in the leachate. The iron was attributed to the notorious high pyrite content in the coal basin. According to the author, such occurrence of a high amount of iron in a low REE leachate can pose problems during the downstream REE refining processing. The author further recommended that coal discard containing a high amount of pyrite should be subjected to proper temperature and oxidation in the natural environment to oxidize the pyrite in coal to produce sulphuric acid for self-leaching action. On the other hand, acid leaching of REEs from different segments of the core samples registered TREEs between 161.2 and 1144 ppm on a dry ash basis equivalent to 143.3 and 928.9 ppm on a whole mass basis. It is worth noting that a high amount of REEs in any particular core segment did not translate to high recovery values due to the preferential leaching behavior of REEs. Furthermore, based on particle size, a total REE

recovery of 50% for the  $-10 \mu\text{m}$  coal middlings was recorded for a 24-h retention time. Yang et al. (2019) further explored how changing the pH of the solution by adding nitric acid improves REE recovery via ion exchange leaching. The results presented in Fig. 16 showed that there was a significant improvement in REE recovery by decreasing the pH of the solution, though noticeable for only a few elements. From Fig. 16a, it can be observed that the total recovery of REEs via ion exchange in the coal samples was between 9 and 10%, with HREEs doubling this amount.

Laudal et al. (2018a) studied the effect of adjusting operating parameters in a single step leaching of coal samples (60 g) using dilute acids (125 mL; 40 °C; 1–48 h). Of the acids tested, namely, sulphuric, hydrochloric, and phosphoric in two concentrations each, the extraction efficiency of moderate concentration of acids (0.5–1 M) was more effective than 0.1 M. Concerning the effect of contact time on the extraction kinetics of 0.5 M  $H_2SO_4$ , the results clearly showed that the longer the contact time, the more REEs were extracted especially the LREEs and scandium. However, for a short contact time of 1 h, HREEs were selectively leached in about 50%. In summary, the study confirmed that for a specific solution, the pH of the leaching solution, the chemistry of the solution, the solubility of extracted products, and contact time influenced REE extraction and leaching behavior. Likewise, the type of anion(s) associated with the REEs in coal strongly affects the leaching pattern. To maximize REE recovery from a specific coal source requires a thorough understanding of the relationship between these parameters and leaching efficiency.

Middleton et al. (2020) subjected coal discard from the South-Western U.S to 1 M HCl acid leaching to study the extractability of REE. The pulp density (solids to liquid ratio) was investigated at a threshold of 70 g/l–80 g/l pulp density and the results obtained show approximately 80% of REEs recovered from the sample. Additionally, the authors noted that at low pH values, REE-bearing minerals tend to exhibit a positive surface charge, thus inhibiting the sorption of positive charge REEs onto clay minerals. Nevertheless, at high pH values above 4.5, deprotonation of the mineral surface led to hydroxyl mineral groups receiving a negative charge, thus causing sorption of REE cations, and resulting in fewer REEs being recovered in the lixiviate solution. The Fire Clay coal sample obtained from the secondary dense medium vessel and consisted of coal in the SG fraction of  $1.4 \times 1.6$  was investigated by Yang and Honaker (2020). The coal samples were reduced to a top size of 80 mesh (177  $\mu\text{m}$ ), further milled to reduce the particle size, and then subjected to froth floatation. Tailings collected from this recovery circuit were further subjected to the second stage to remove acid-consuming materials such as calcite and subsequently utilized as feed for the leaching experiments. Various parameters such as lixiviant type, acid

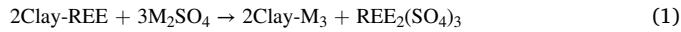


**Fig. 16.** (a) Ion exchangeable REEs recovery in plant samples at an initial pH of 5. (CR - Coarse discard; Mids - Middling; TUF - Thickener underflow) (b) Effect of adjusting pH using nitric acid on REE recovery from TUF fine discard samples (Yang et al. (2019), Adapted with permission from Elsevier).

concentration, solid to liquid ratio, temperature, stirring speed, were investigated to determine the optimum leaching recovery and reaction kinetics. HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> at 1 M were employed as lixiviant with REE recovery of 80%, 76%, and 74% for each lixiviant, respectively. HCl and HNO<sub>3</sub> exhibited fast leaching recovery rates within the first 5–10 min, whereas sulfuric acid was the least effective as indicated by its slow leaching rate. The optimum REE recovery in this study was obtained at a stirring speed of 530 rpm, 1 M acid concentration, 75 °C, and a solid/liquid ratio of 10 g/l was established to improve REE recovery.

A sequential leaching procedure was also used to quantify the amount and analyze the association of available REEs in water-soluble, ion-exchange, acidic leaching, etc. In this regard, coal samples were mixed with deionized water and stirred for 24 h, then the residue was subjected to a 1 M ammonium acetate ion-exchange test (Laudal et al., 2018a). The test results showed that small amounts of REEs were recovered in the ion-exchange test, indicating that the REEs present in this sample in the form of ion exchange or water-soluble are negligible. Subsequently, 1 M HCl leaching improved REE recovery by 80–95%, illustrating the association of REEs as acid-soluble minerals. Based on this, the study then used 1 M HCl and H<sub>3</sub>PO<sub>4</sub> acids and compared the results to 0.5 M H<sub>2</sub>SO<sub>4</sub>. HCl at 1 M and H<sub>2</sub>SO<sub>4</sub> at 0.5 M exhibited a low acidic pH of 0, whereas 1 M of H<sub>3</sub>PO<sub>4</sub> resulted in a pH of approximately 1.1, and with 1 M HCl reflecting the highest extraction efficiency of REEs. A low concentration of 0.5 M H<sub>2</sub>SO<sub>4</sub> reflected a higher REE recovery of 22–32%, while phosphoric acid at 1 M reflected the lowest REE recovery ranging from 5–15% but was seen to be effective for high scandium recovery. The reasons for the low recovery of phosphoric acid were because of reduced acidic conditions of the solution, partial deprotonation as depicted by a pH of 1.1, and the low solubility of REE phosphates that are the product of phosphoric acid dissolution.

The ion exchange technique is another hydrometallurgical technique used to leach REEs from mineral ores into solutions. It is reported that the bulk of the commercial REE extraction in China is sourced from ion-exchangeable clay deposits (Borst et al., 2020) and is recovered using the ion exchange technique. Sodium chloride was used as a lixiviant in the early 1970s, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for batch and heap leaching in the early 1980s, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for in situ leaching from 2011 upward (Papangelakis and Moldoveanu, 2014). The authors also reported that typical inorganic monovalent cation salt solutions can be used to leach the ore. By so doing, the monovalent ions and physisorbed or weakly adsorbed REEs are substituted easily on the substrate, then the REEs transfer into solution as soluble sulfates or chlorides, following a 3:1 stoichiometry represented in Eq. (1) (Papangelakis and Moldoveanu, 2014).



It is important to state that beneficiation is not needed for ion-exchangeable REE clay deposits (Wall et al., 2017). According to Rozelle et al. (2016), if a significant amount of REEs in coal and coal byproducts is in the ion adsorbed associated form, the coal may not need

physical beneficiation.

To determine the concentration and extractability of the ion exchange technique, Rozelle et al. (2016) used an ionic liquid (1-butyl-3-methylimidazolium chloride), a deep eutectic, and ammonium sulfate solvent as lixiviant to examine REE ion extraction from clays associated with two U.S. coals (samples A and B) from a surface mine. A 595 by 150 μm size fraction of both samples was magnetically stirred in 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at a solid: solution mass ratio of 1: 2 starting with 5 g at room temperature for 1 h. After the test, the solids were recovered and dried at 20 °C under vacuum for 12 h to calculate the residual solids and REE recoveries as weight fractions. Extraction of REEs using the ion solvent and the deep eutectic solvent was performed under similar conditions to compare whether these solvents improved the recovery of REEs. It was reported that sample B had higher starting clay than sample A. The summary of the results of the investigation is presented in Table 2.

From Table 2, it is evident that the ion exchange technique using ammonium sulfate solution produced the highest level of recovery and the other solvents were in a narrow range. The authors indicated that given the similarities in the results, the use of ammonium sulfate compared to other solvents would be difficult to justify for commercial operations. It was recommended that moderate enrichment of the REE content in the coal i.e., particle size and its relationship to the recovery of REEs are necessary for future studies.

Montross et al. (2020) carried out sequential acid digestion and leaching experiments employing sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and hydrochloric acid (HCl) to investigate REEs in the Central Appalachian Coal Seam Underclays. The ammonium sulfate ion exchange test recovered minimal amounts of REEs with the highest recovery percentage being 7.5% for one of the samples. Subsequently, acid digestion with 1 M HCl resulted in a further 10–30% of REEs being extracted, while a maximum of 20% REEs was recovered when the filtrate sample was subjected to sulfuric acid leaching at 1.2 M. Compared to bench experiments developed using different concentrations of citrate leaching solutions, the citrate leaching agent recovered a higher concentration of 33% TREE. Based on the results, the researchers reported that the citrate leaching agent is more efficient for REEs that are easily liberated or are in ion-exchangeable form. Further investigation by the same author using citrate solutions of pH range 3–6 signified that REEs were relatively leached out equally at all pH levels and contaminant elements (Al, Si, and Fe) were reduced at higher pHs. Conversely, calcium tends to increase in the solutions of higher pH.

All things considered, the hydrometallurgy techniques typically employ an isolated acid or ion-exchanged leaching system which is effective in REE recovery. But, to achieve more improved REE recovery during leaching, some form of prior chemical and thermal activation is required as it could enhance REE leaching efficiency and hydrometallurgy REE recovery while reducing leaching time. Furthermore, prior chemical/thermal activation can also improve the cost feasibility of the process as more REEs are recovered in a shorter time.

**Table 2**

Summary of the investigations of different solvents via ion exchange technique (Rozelle et al., 2016).

Description	Untreated		Ammonium sulfate		Ionic liquid		Deep eutectic solvent	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
Ash, wt.% dry	56.9	89	60.3	89.3	56.4	85	55.4	83.3
Total REE + Y (mg/kg)	131	293	17	90	31	124	40	41
Solid yield (%)	–	–	82	91	84	73	96	83
REE recovery (%)	–	–	89	72	80	69	71	89

### 5.3. Thermal and chemical activation of REEs in coal before leaching

Rare earths and REE-enriched minerals existing within the crystal structure of coal and coal discard may be relatively difficult to leach as a result of REE-mineral dilution with organic matter in coal (Jordens et al., 2013; Zhang et al., 2015). It has also been reported that carbon adsorbs the leaching reagent, lowers leaching efficiency, and hence could be a nuisance to the enrichment procedures. Therefore, to increase the leaching efficiency, pretreatment using chemical activation via strong acid/alkaline, salt, or thermal activation via calcination or roasting may be required.

#### 5.3.1. Thermal pretreatment

Thermal pretreatment assists in the decomposition of REE-bearing minerals and increases the surface area available for interaction with the leachate. A review of the various methods of roasting as an REE enrichment technique was thoroughly discussed by Zhang et al. (2015). According to Honaker et al. (2019b), the roasting or calcination approach permits the removal of unwanted volatiles and advantageously converts contaminant elements such as iron sulfides into less leachable hematite forms. Similarly, Zhang and Honaker (2019 a,b) reported that the technique has the potential to increase REE recovery by employing milder acid conditions. Since acid cost is one of the main challenges in developing an economically feasible REE extraction process, correspondingly, pretreatment by calcination reduces the amount of acid consumption and therefore enhances the feasibility of the process (Zhang et al., 2020).

The benefits of calcination (with or without reactants) as a pretreatment step before a leaching process have been investigated by numerous researchers (Zhang et al., 2015; Zhang and Honaker, 2019a, 2019b, 2020). Yang et al. (2019) pretreated the West Kentucky coal-rich segment seam no. 13 by implementing a low-temperature plasma furnace to decarbonize coal and to liberate the mineral matter within the coal before leaching. From the analysis conducted, the plasma treatment was found to increase both the surface area and pore volume of the coal particles. As a result, the authors were able to achieve a recovery exceeding 60% for some segments of the coal seam. In addition, blank roasting (no chemical additives) of the  $-180\text{ }\mu\text{m}$  middling sample at  $750\text{ }^{\circ}\text{C}$  for 2 h followed by 1.2 M  $\text{H}_2\text{SO}_4$  leaching at  $75\text{ }^{\circ}\text{C}$  was shown to significantly improve the total REE recovery from 31% to 74%. The blank roasting assisted in converting REE-bearing minerals such as silicates and phosphates into REE oxides which are more readily leachable. Congruently, roasting increased the surface area as it breaks down the coal sample into thin flakes, thereby exposing the rare earth oxides/hydroxides, ion exchangeable REEs, and the micro-dispersed mineral matter within the coal in the leachate.

In particular, the leaching of clean coal and middling fractions of low-ash high-rank coals like bituminous coal is envisaged to be a lot harder due to the lack of exposure of the REE-bearing micro-dispersed minerals (Honaker et al., 2018a; Yang et al., 2019). Although grinding could be used to overcome this challenge, the associated high cost is of great concern. Based on previous experiences in which high recovery of REEs was recorded at a calcination temperature of  $750\text{ }^{\circ}\text{C}$ , Honaker et al. (2019) suggested that a fluidized bed combustion (FBC) unit typically operating between  $750\text{ }^{\circ}\text{C}$  and  $900\text{ }^{\circ}\text{C}$  could present products enriched with REEs. To test the hypothesis, experiments were conducted using

calcined and original ROM low ash coals from western Kentucky seam no 13, Fire Clay, and Illinois no 6 seams then compared with ash samples from two FBC boiler units. The content of REEs in all FBC ash samples was found to be lower than the ROM coals, and this was attributed to the reduction effect of lime used to capture sulfur during the combustion process. This observation differs from Ma et al. (2019) where the authors reported that REEs were more enriched in the fly ash from a circulating fluidized bed compared to the feed coal. The difference could be because of the diverse nature of coal and the association of REEs of the two coals with their organic and inorganic contents.

Nonetheless, in the investigation by Honaker et al. (2019), the leaching kinetics of both ash samples and calcined coal samples signaled a quick release within the 5 min of leaching. The effect of different calcination temperatures –  $600\text{ }^{\circ}\text{C}$ ,  $750\text{ }^{\circ}\text{C}$ , and  $900\text{ }^{\circ}\text{C}$  on the coal samples for 120 min was also studied. Thereafter, the calcined coal samples were subjected to 1.2 M HCl acid leaching at a temperature of  $75\text{ }^{\circ}\text{C}$ . XRD performed on the raw coal samples at 1.4 to 1.8 specific gravity (SG), identified kaolinite, quartz, illite, pyrite, and anatase as the dominant mineral phases. The calcined coal samples between  $600\text{ }^{\circ}\text{C}$  and  $900\text{ }^{\circ}\text{C}$  indicated that the kaolinite peaks have been destroyed and the observation was explained by the dehydroxylation of the kaolinite crystal structure. The XRD results also showed that pyrite in the coal sample calcined at  $600\text{ }^{\circ}\text{C}$  and above, transformed into hematite. At a calcination temperature of  $900\text{ }^{\circ}\text{C}$ , the illite structure was partially damaged compared to the samples calcined at  $600\text{ }^{\circ}\text{C}$ . Acid leaching tests indicated that at a calcination temperature of  $600\text{ }^{\circ}\text{C}$  for 2 h, REE recovery increased from a mere 25% (non-calcined coal) to a significantly high recovery above 80% (calcined coal) for the Fire Clay coal and Western Kentucky no 13 coal. On the other hand, REE recovery significantly decreased for coal samples calcined at  $750\text{ }^{\circ}\text{C}$  and  $900\text{ }^{\circ}\text{C}$  owing to the pozzolanic nature of the clays after calcination, which reduced the surface area and shields the associated REEs. In such instances, more aggressive acid conditions would be required to dissolve the minerals and extract the encapsulated REEs. The study confirmed that coal calcinated at low temperatures typically improves REE recovery due to the improved solubility of REE-bearing minerals as they are converted to REE oxides. According to Honaker et al. (2019), two crucial components led to the improved REE recovery via leaching after calcination; 1) The organic and inorganic distribution of REEs are liberated after calcination and REE leachability is increased. Likewise, REEs found in clays such as kaolinite become dehydrated, as a result, the surface area increases considerably, leading to a larger degree of exposure of REEs in the lixiviant. 2) High-temperature calcination at  $600\text{ }^{\circ}\text{C}$  removes all the organic volatile matter leaving behind the non-volatile REEs which are transformed into REE oxides. Thus, improving both REE solubility in the leachate and REE recovery.

In an alternate study conducted by Zhang and Honaker (2019b), calcination of the coal particles was also employed before leaching. Representative samples were collected from coarse coal discard and middlings originating from a coal preparation plant that processes coal from the Pocahontas No. 3 coal seam in America. A dense medium bath was used to process the coarse discard coal sample to obtain the 2.2 SG coal fraction. Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) was utilized for the ion-exchange tests and 1.2 M HCl at  $75\text{ }^{\circ}\text{C}$  was employed for the acid leaching tests. Five temperatures ( $400\text{ }^{\circ}\text{C}$ ,  $500\text{ }^{\circ}\text{C}$ ,  $600\text{ }^{\circ}\text{C}$ ,  $750\text{ }^{\circ}\text{C}$ , and  $900\text{ }^{\circ}\text{C}$ ) were used to calcine the middlings and coarse discard samples.

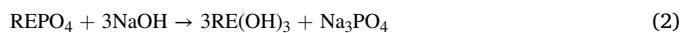
To understand the effects of calcination, XRD was performed on calcined coal and the raw coal samples. It was noted that pyrite experiences thermal decomposition at a temperature of 400 °C and is transformed to hematite. Dehydroxylation of kaolinite, muscovite, and illite occurred at high calcination temperatures and led to the breakage of Al-OH and the subsequent destruction of the crystal structure of kaolinite. The maximum surface area attained was due to an increase in pore size and volume, which occurred at a temperature of 400 °C. On the contrary, the pore size and surface area decreased when temperatures exceeded 600 °C. For the calcined and non-calcined coal samples, a minimal REE recovery was reported in the ion exchange test. Furthermore, approximately 80% of REEs were recovered from the calcined coal samples at 600 °C (consisting of coarse discard and middlings) at a fast rate within the first 15 min using 1.2 M HCl. Thereafter, REE recovery remained fairly constant, illustrating that REEs in the calcined coal samples are exceedingly soluble. At increased calcination temperatures (750 °C–900 °C), the total REE recovery decreased from 80%–72% (see Fig. 17) due to the sintering of the clay minerals.

A study on the calcination of Fire Clay, West Kentucky No. 13, and Illinois No. 6 seams coal before leaching was reported by Zhang and Honaker (2019a). The coal samples were calcined at 600 °C for 2 h, resulting in almost 100% removal of the organic matter before leaching. The researchers noted that minute amounts of REEs were recovered in the ion-exchangeable (<2%) and carbonate forms after calcination. Larger amounts of approximately 54% of REEs were recovered in their oxide forms and 40% of REEs were recovered in their acid-soluble forms when leached with 2 M HNO<sub>3</sub>.

It can be concluded that even though the concentration of REEs by roasting may be an additional cost to the extraction process and may be time-consuming, the process seems to be effective for coals with elevated concentrations of REEs. This is because a greater number of REEs will be oxidized by calcination into easily extractable acid forms. However, for coal sources with a lower concentration of REE, roasting before leaching may render the process economically unsustainable and may not be necessary.

### 5.3.2. Alkaline pretreatment

Alkaline pretreatment is used to break refractory REE-bearing minerals and to convert REE minerals into more soluble REE hydroxides, as depicted in Eq. (2) to enhance the REE leaching recovery from coal and coal byproducts. A review of alkaline roasting as an enrichment technique for REEs in coal is published by Zhang et al. (2015).



To investigate the effect of alkaline pretreatment, Yang et al. (2019) pre-leached discard obtained from thickener underflow utilizing 8 M

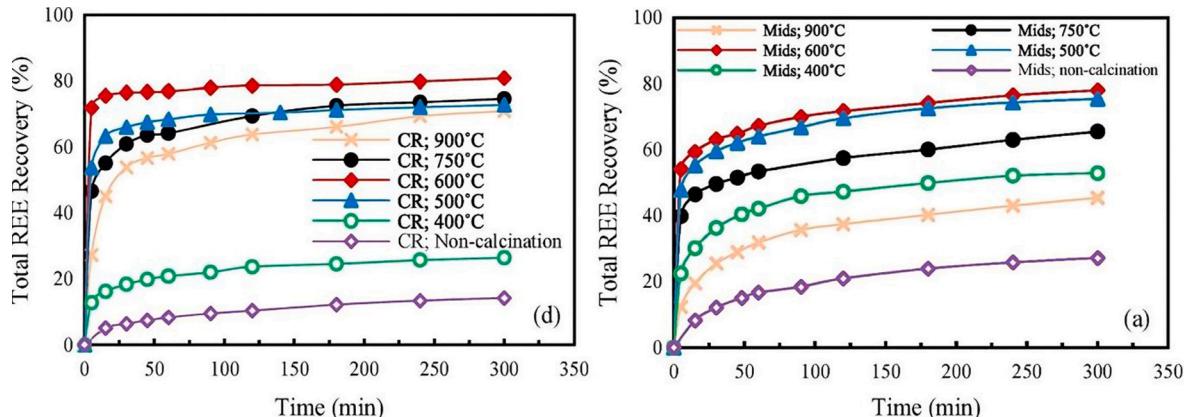
NaOH solution, solid/liquid ratio 1/10 (G/L) at 75 °C for 2 h. The results show an increase in TREE recovery from around 22% for non-treated samples to 75% for alkaline-treated samples. In addition, the treatment was selective to LREEs and showed a slightly better improvement compared to thermal treatment. Kuppusamy et al., (2019) adopted alkaline pretreatment in treating coal tailings obtained from the floatation process. The tailings were treated simultaneously with 7.5 wt% HCl acid leaching. During Alkali leaching, the interactions between NaOH and mineral matter such as clays and silicates resulted in the formation of soluble sodium aluminates and sodium silicates to which REEs are attached. The results of the investigation indicated that coal tailings treated to 20% NaOH at 190 °C for 60 min yielded the highest recovery of REE during acid leaching. It was also reported that the amount of REEs leached in HCl solution was significantly higher than the amount of REEs present in the NaOH solution, with almost 97% of LREEs and 76% HREEs being extracted.

It is worth mentioning that despite the positive effect of alkaline pretreatment before leaching, the process may dissolve unwanted elements alongside REEs which could decrease the selectivity of the leaching agent. Additional studies that establish the effects of thermal and alkaline pretreatment on the REE recovery kinetics need to be documented.

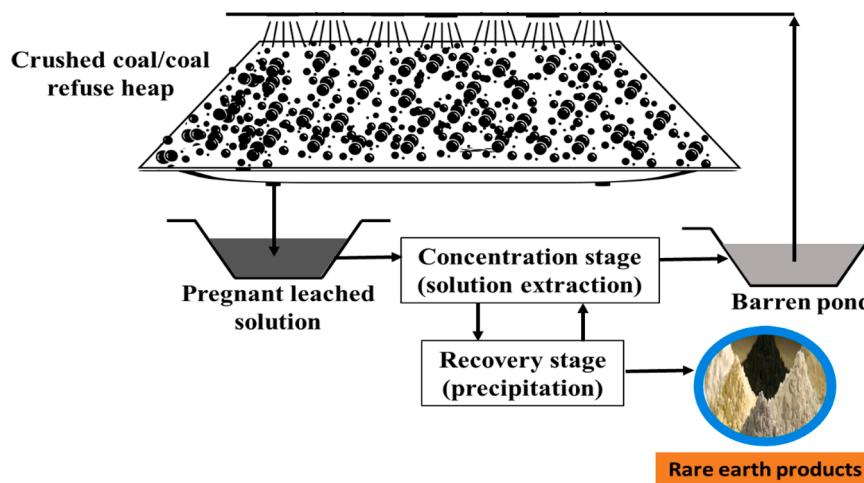
### 5.4. Heap leaching and bioleaching

Heap leaching has been successfully investigated in the past to recover precious metals from their ores (Mwase et al., 2012, 2014; Petersen, 2016; Svetlov et al., 2017; Sarswat et al., 2020). In heap leaching, the lixiviant used to extract precious metals is generated in situ from the dissolution of different minerals from the ore. In the case of coal, acidic leachates are generated from coal discard containing pyrite when exposed to the natural environment. Heap leaching (Fig. 18) is suited for low-grade ores, abandoned tailings, and discard stockpiles that cannot be economically processed via other beneficiation processes (Papangelakis and Moldoveanu, 2014; Petersen, 2016; Svetlov et al., 2017). It is considered a low-cost approach due to minimal chemical and water consumption, environmentally benign, and an effective waste management strategy (Thenepalli et al., 2019; Sarswat et al., 2020).

Biological-based leaching also known as bioleaching or biometallurgy, is an established technique in the mining industry and is considered attractive for its cost-effectiveness and environmental friendliness benefits compared to its chemical counterparts (Auerbach et al., 2019; Jin et al., 2019; Alipanah et al., 2020). In this process, a wide range of microorganisms is used to oxidize the sulfidic minerals in the ore to produce metabolites (acids) for the dissolution and release of metals (Brandl et al., 2016; Hopfe et al., 2018; Fathollahzadeh et al., 2019; Jin et al., 2019). The technique has been successfully applied to



**Fig. 17.** 1.2 M HCl leaching of coarse discard coal (CR) and middlings (Mids) coal as a function of calcination temperature (Zhang and Honaker, 2019b), Adapted with permission from Elsevier.

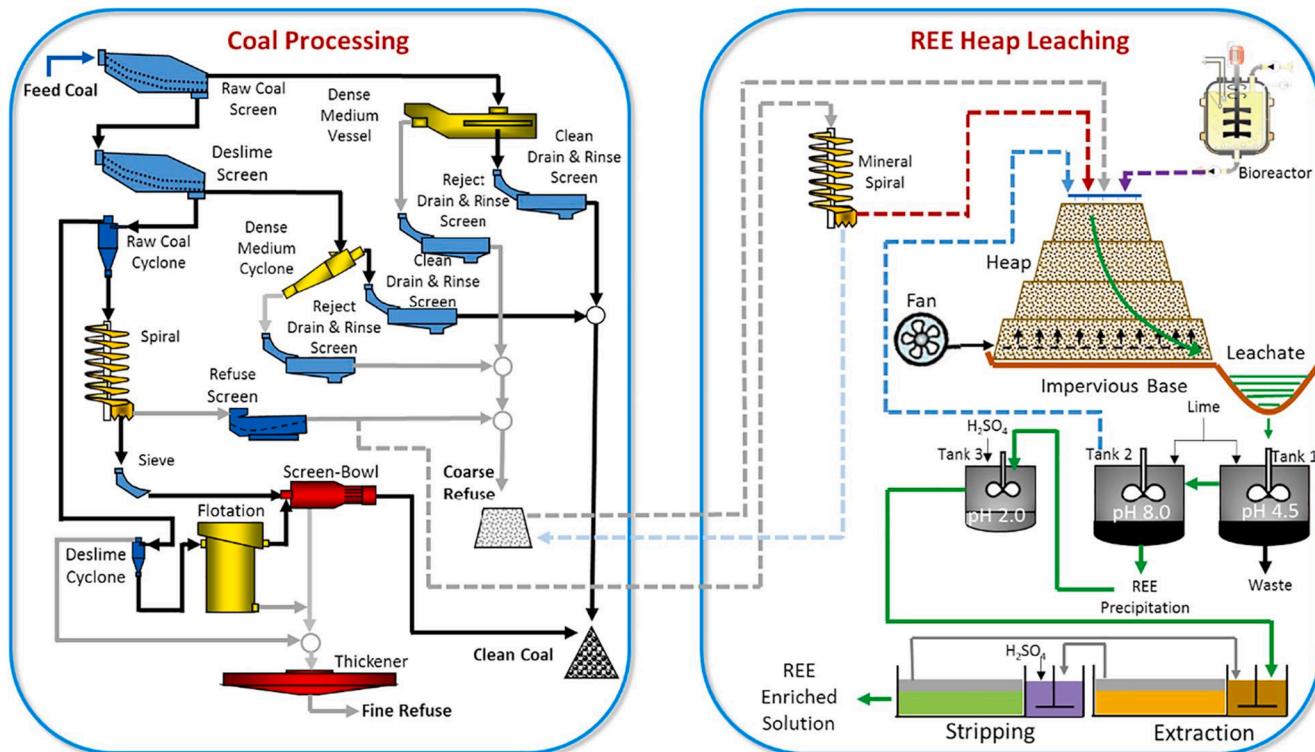


**Fig. 18.** A simple heap leach circuit for the recovery of REE products from coal discard.

leach REEs from discards (Reed et al., 2016; Auerbach et al., 2019; Jin et al., 2019; Alipanah et al., 2020) where microorganisms are employed to solubilize REEs contained in coal or to sorb the REEs from the aqueous solution (biosorption). A review on the recovery and separation of REEs from a variety of sources was published by Rasoulnia et al. (2021) with a focus on the effects of adjusting operational parameters on the REE leaching efficiency. The review noted that leaching yields and the reaction rate are of great concern, while pH and temperature are the main parameters that improve bioleaching recovery. In addition, bioleaching is effective for certain low-grade REE-containing minerals. A review by Dev et al. (2020) suggested that the utilization of genetically modified microbes as microbial growth substrates over pure substrates like glucose, sucrose, etc. could lessen the toxicity of heavy metals and organic wastes such as agricultural residue, sewage sludge, and food wastes. This approach can be further researched to reduce the operation

costs of biological recovery of REEs from coal and coal discard.

Honaker and his colleagues were the first to study the concept of heap leaching to extract REEs with a focus on developing a low-cost recovery circuit from coal discard (Honaker et al., 2018b). The author characterized several natural leachates, solid coal discard samples, conducted laboratory acid leaching, and selective precipitation to produce a REE preconcentrate. Subsequent processing was then carried out to generate rare-earth oxides. The results indicated that high-valued critical REEs (i.e., Dy, Eu, Nd, Y, and Tb) were selectively leached from coarse discard samples in the natural environment by the acidic leachate generated via pyrite oxidation. The authors also found that the dissolved solids from a given leachate sample contained a total REE of 380 ppm, which was higher than the 332 ppm obtained from the coarse discard leachate. Based on the findings from their study, a conceptual heap bio-leaching flow sheet (Fig. 19) was developed that could guide



**Fig. 19.** An integrated heap leaching flowsheet for the extraction of REEs from coal coarse discard (Honaker et al., 2018b), Adapted with permission from Elsevier).

other researchers intended to conduct laboratory, pilot, and industrial studies in the future for recovery REEs from coal sources.

**Fig. 19** shows the proposed process integrating physical separation, heap leaching, pyrite bio-oxidation, solvent extraction, and selective precipitation processes. The natural acid leachate dissolves REEs that are present in the discard arranged in heap leach pads and the pregnant leaching solution (PLS) is collected at the bottom of the coal discard heaps after a certain time. A bioreactor attached to the heap is used for increasing the production of ferric ions to accelerate leaching and to obtain the desired pH. The PLS is then subjected to solvent extraction and precipitation processes to produce a preconcentrate which can then be upgraded to produce rare earth oxides. Despite that this setup is expected to enhance the selectivity of REE recovery and considerably reduce the cost of extracting REEs from coal discard, it is worthy to mention that the process may be time-consuming as the leaching kinetics could be slow. Hence, more research especially on the effects of particle size distribution can be conducted to investigate the rate of REE leaching using this technique. Optimization using computational software and mathematical models may be employed to achieve greater efficiency. More successes recorded in this area could fast-track the scaling up of the heap leaching process in the recovery of REEs from coal and coal discard.

Sarswat et al. (2020) also reported on bioheap leaching as an approach for an effective recovery of REEs from coal discard (**Fig. 20**). From the Figure, the REE-bearing minerals are first crushed to the desired size, followed by the oxidation of pyrite (ferrous ions) by microbial activities under continuous stirring. The influence of bacterial population, bacteria activity, pH, and the presence of impurities at this stage opens up a window for optimization. Ferric ions precipitate in the process as a by-product during solution conditioning and are then used to promote the solubilization and release of REEs from the coal discard heap. It is well known that high sulfur coals cause acid mine drainage (AMD) around coal mines. However, according to the authors, the reaction occurring between the ferric ions, the acid generated, and discard coal removes residual sulfides and prevents the formation of AMD and other environmental hazards around the dump. The pregnant leached solution then undergoes purification by solvent extraction and selective precipitation to selectively concentrate the metals and another precipitation stage to recover the rare earth products of interest from the REE-based salts.

Based on the studies on heap leaching, there is room for research to establish the mechanism of interaction between REEs and the microbes, to increase the recovery of REEs from coal discard, and to limit legacy

contaminants associated with the technique. Novel designs that allow for process integration and modification to an existing design can form the next generation of advanced heap leaching concepts for the extraction of REEs from coal dumps. In addition, the successful modeling of the heap leaching process could also facilitate implementation.

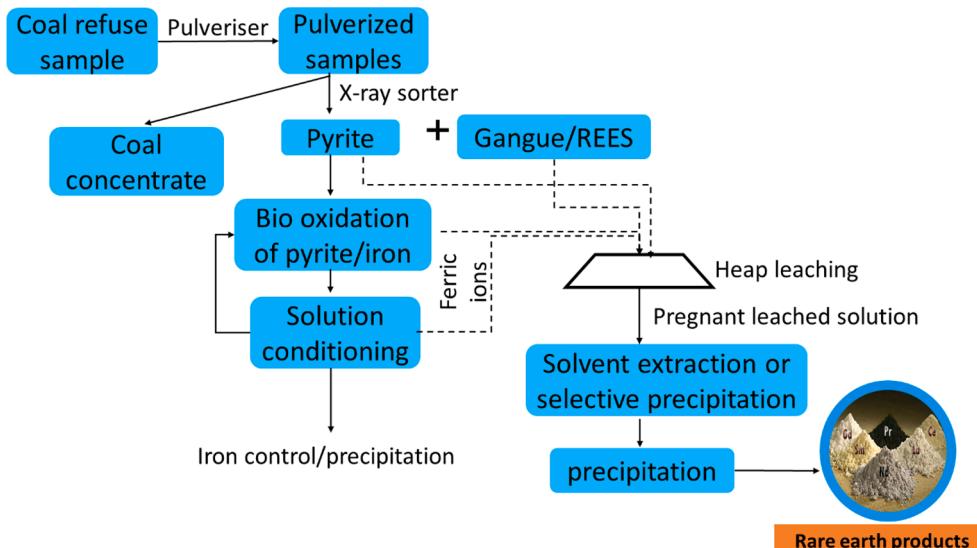
To concentrate REEs after leaching, other downstream processes are required that convert the REE minerals to rare earth oxides of individual elements. Hydrometallurgical techniques such as ion exchange, solvent extraction, precipitation, fractional crystallization, etc. are widely consulted to accomplish this purpose. Nevertheless, other techniques such as biosorption, supercritical CO<sub>2</sub>, electrowinning, reduction, membrane extraction, and liquid membrane are being developed for the extraction/separation of REEs from waste and other pregnant leach solutions (Suli et al., 2017). These techniques may be integrated and applied for extracting REEs from coal and coal discard. A summary of these techniques is presented in **Table 3** and a summary of key findings of REE recovery from coal and coal discard are presented in **Table 4**.

### 5.5. Pilot scale studies on REE recovery from coal and coal discards

The literature reviewed in this paper are studies carried out on laboratory and bench-scale but only one study as can be ascertained has emerged to pilot-scale investigation and demonstration. This suggests that more research is still needed before possible commercialization and implementation using coal as a source for REE recovery. Based on the wealth of experience Honaker and coworkers have gained in this field, the researchers constructed a 0.23 t/h solid feed pilot plant capable of continuously testing different coal-based feedstocks (Honaker et al., 2020). The plant provided an insight into the various techniques involved, its economic viability, and the scaling-up potential. By optimizing the design process flowsheet, the authors established that roasting 1 mm top size Fire Clay coal discard at 600 °C in open air led to the reduction in the acid usage for leaching and solvent extraction. The roasting treatment also resulted in a gain of overall REE recovery values by 40%. Furthermore, the authors reported that the pilot test plant is capable of producing >90% purity level rare earth concentrates from coal-based materials. **Fig. 21** shows a schematic of the flowsheet developed by the authors that could be adopted to recover REEs from coal-based sources commercially.

### Conclusions and prospects of rare earth elements processing/recovery from coal and coal discard

Increasing demand for rare earth elements (REEs), a strategic resource used in modern technologies, combined with the uncertainty in



**Fig. 20.** Bioheap leaching flowsheet for extracting REEs from coal discard (Adapted and modified from Sarswat et al. (2020)).

**Table 3**

Present and emerging techniques for concentrating REEs from a given leachate.

Concentration and/or purification	Type	Mechanism	Process	Reference
Solvent or Liquid-liquid extraction	Hydrometallurgy	Solubility difference, ion exchange, chelating separation	The liquid containing the REEs of interest is contacted with an immiscible solvent that extracts the desired REEs. After the liquids are separated, the REEs separate from the solvent.	Xie et al., 2014; Peiravi et al., 2017; Honaker et al., 2017, 2018a, 2020; Giese, 2020; Sarswat et al., 2020; Talan and Huang, 2020
Ionic liquid	Hydrometallurgy	Chemical affinity	Ionic liquids contact the REE pregnant leach liquor for a certain time to selectively extract REEs.	Wang et al., 2017; Hunter et al., 2018; Huang et al., 2019; Okamura and Hirayama, 2021; Deng et al., 2021; Quijada-Maldonado and Romero, 2021
Precipitation	Hydrometallurgy	pH dependant	The REE leachate is contacted with precipitants at different pH levels to recover the REE precipitates.	Zhang and Honaker, 2018; Avdibegović et al., 2018; Honaker et al., 2018b, 2020; Kumari et al., 2019; Talan and Huang, 2020; Vaziri Hassas et al., 2020; Rozelle et al., 2016; Yang et al., 2019
Ion exchange	Hydrometallurgy	Chemical affinity	The REE ions from the aqueous solution are exchanged with ions held by electrostatic forces on exchange resin OR the exchange resin is contacted with the REE clay minerals to extract REEs physisorbed ions.	Sun et al., 2008; Hidayah and Abidin, 2017; Héres et al., 2018; Dardona and Dittrich, 2019; Hovey et al., 2021
Solid-liquid extraction, Solid-phase (adsorption)	Hydrometallurgy	Ion exchange, adsorption, chelating separation, solubility	The aqueous phase containing the REEs is attracted towards a reactive solid phase or the extractant immobilized on a solid phase to extract the desired REEs.	Parhi et al., 2019; Smith et al., 2019
Liquid membrane	Hydrometallurgy	Facilitated transport, chemical affinity.	Nonaqueous solvents dissolve chelating agents to physically separate the aqueous leachate and acidic stripped phases while simultaneously recovering REEs. The aqueous strippant is either stabilized within an emulsion or the non-aqueous solvent impregnated in a physical membrane.	Park et al., 2017, 2020; Giese and Jordão, 2019; Giese, 2020
Biosorbent extraction	Biometallurgical	Affinity difference, adsorption capacity	REEs from leachates are removed by their passive binding to biosorbent materials either active, dead, or biomass materials in aqueous solutions	M. Izatt et al., 2015; Izatt et al., 2016, 2018
Molecular recognition technique	Green chemistry	Molecular recognition	A pregnant REE leached solution is contacted with a pre-designed ligand chemically bounded by a tether on a solid support.	Sinclair et al., 2017, 2018, 2019; Das et al., 2018; Zhang et al., 2020a; Song et al., 2021
Supercritical extraction using CO <sub>2</sub> (soluble ligands)	hydrometallurgical	Reaction, complexation, and dissolution	The REE-rich solution is contacted with supercritical carbon dioxide as the solvent containing a dissolved extractant to extract REEs.	Brewer et al., 2019; Argumedo et al., 2020; USDOE, 2020
Electrowinning	Electrometallurgy	Electronegativity	Current is generated from an inert anode and passed through the REE leachate. The REE ions are thus oxidized and thereafter undergo reduction at the cathode at which the REEs undergo electrolyzing.	Chen et al., 2017; Momen et al., 2019; Kostanyan et al., 2020; Sanku et al., 2021
Chromatography (ion exchange, affinity, extraction, counter current, column, etc.)	Hydrometallurgical	Various	The pregnant leach solution is brought in contact with different combinations of stationary phase and mobile phase in columns to adsorb the desired elements & separating them using different eluents.	Maes et al., 2017; Couto et al., 2020, 2021
Electrolysis, electrodialysis, electrophoresis	Electrometallurgy	Electric field, electrophoretic mobility	Ionized REE mineral concentrates or in solution are electrodialytically treated in a cell/membrane at different current intensities, treatment periods, and pH to extract REEs.	

supply, has prompted international research to explore REEs from unconventional sources. Consequently, coal-based feedstocks have been identified as potential hosts for REEs, and the abundance of REEs in these materials is well documented. To this end, this review provided a comprehensive update on the progress of research to date and highlighted potential research opportunities in extracting REEs from coal and coal discard. Given the challenge, it is apparent that the recovery process begins with the analysis and acquisition of detailed information on a targeted coal feedstock. This is because the value of REE in any coal feedstock will determine both the selection of suitable separation technology and the cost.

Towards commercial extraction, the nucleus of most research in the field has been on finding methods and pathways to maximize and optimize REE recovery from coal and coal discard. Hence, REE-related research on coal and coal discard is still in the laboratory phase. Depending on the association and abundance of REEs in coal feedstock, physical beneficiation, thermal, and/or chemical pretreatment is/are consulted to liberate and concentrate the REE-bearing minerals for leaching. Based on this review, physical enrichment techniques may be

used to beneficiate coarse coal particles to produce feedstocks for acid leaching. Natively, acid leaching alone can consume elevated amounts of lixivants especially when significant amounts of carbon are present. The integration of physical techniques with thermal or alkaline preprocessing can reduce the quantity and cost of leachate used for REE recovery. This approach could also enhance liquid management and result in a sufficiently high-quality REE concentrate. However, more research is required concerning the removal of impurity elements (i.e., Ca, Fe, Al, Mg, Na, K, etc.) during the leaching of REEs to produce high-quality leachate from coal and coal dicard. Information obtained from this approach could reduce the downstream separation/purification stages and costs to achieve high-quality rare earth metals. However, this can only be confirmed through cost and revenue modeling to evaluate the economic performance of the process.

In terms of the leaching of REEs into solutions, leaching recovery, leaching kinetics, and leaching efficiency are some of the key indicators of an effective leaching process. In addition, the grade of the final REE products depends heavily on the leachate's ability to release contaminants. Therefore, developing a highly selective lixiviate is a prerequisite.

**Table 4**

REE recovery from ROM coal/coal discard: Summary of key findings.

Objective/purpose	Pretreatment/beneficiation	Technique	Conditions	Results	Reference
Analysis of segments of core coal samples and samples collected from process waste streams within a coal preparation plant treating...	Low-temperature plasma oxidation	Leaching	1.2 mol/L sulphuric acid; 75 °C	REE recovery > 60% for the claystone parting material, direct float & the micro-dispersed mineral matter.	Yang et al. (2019)
	Thermal activation by roasting or chemical activation by pre-treatment	Leaching by ion-exchange mechanism	0.1 mol/L $(\text{NH}_4)_2\text{SO}_4$ at pH 5	Total REE recovery from coal discard materials increased from 31% to about 80% with considerably higher gains obtained for the LREEs. However, the process may be economically prohibitive.	
Understanding the modes of occurrence of REEs in Fort Union lignite coal samples.	-	Sequential leaching	Water, 1 M ammonium acetate, and 1 M dilute hydrochloric acid (HCl).	The small amount of REEs extracted using water and ammonium acetate indicated REEs are not present as water-soluble or ion-exchangeable forms. 80–95 wt% REE extracted using HCl indicated HCl-soluble mineral forms such as carbonates, and/or presence as organic complexes.	Laudal et al. (2018a)
Measurement of REE concentration in the clean coal, coarse and fine discard from 20 coal preparation plants operating in Kentucky, USA.	Wet screening/sieving and float-sink testing	Ashing followed by ASTM D6357 standard procedure		TREEs in the clean coal products 23–84 ppm; in coarse discard (130–266) ppm; and fine discard (84–224) ppm on a whole sample basis.	Luttrell et al. (2019)
Studied the characterization of North Dakota lignite and lignite-related feedstocks.	Float and sink	Sequential solvent extraction method (chemical fractionation tests)	1 M ammonium acetate was stirred at 70 °C or 24 h (2x), then 1 M hydrochloric acid at 70 °C for 24 h.	REE in North Dakota lignite coals are primarily associated with organic coordination complexes, and to a lesser extent as ion-exchangeable cations or water-soluble minerals.	Laudal et al. (2018b)
To confirm the existence of organically associated REE in Appalachian coal.	Grinding and float-sink density separation	REE concentrations determined by inductively coupled plasma-mass spectrometry	5 g of coal + 40 mL lithium metatungstate, deionized water for the next density level for float-sink density separation.	HREE or LREE in any particle size fraction enriched only to a little degree. REE concentration on whole coal basis and LREE/HREE ratio increased as ash yield increased. Organic matter was relatively enriched in HREEs. 2056.1 ppm total REE (ash basis) at density fractions 1.34 – 1.30 (g/ml), 33.69% weight recovery, organically-associated.	Lin et al. (2017b)
Extraction of REEs from coal processing discard from South Western USA.	-	Acid leaching	1 M HCl, 85 °C, 4 h, and pulp density 40 g/l.	80% TREE recovery.	Middleton et al. (2020)
Extraction of REEs from Fire Clay seam coal products (SG = 1.4–1.6).	Grinding, two prior floatation steps utilizing diesel fuel No. 2 as the collector and 4-methyl-2-pentanol as the frother for the 1st floatation stage and octanohydroxamic acid for the second floatation stage.	Acid leaching of the final tailings material	1.2 M $\text{H}_2\text{SO}_4$ , 75 °C, 5 h Pulp density 10 g/l, P80 particle size = 7.3 μm 1 M $\text{H}_2\text{SO}_4$ , 75 °C, 3 h, pulp density 10 g/l 1 M HCl, 75 °C, 3 h, pulp density 10 g/l 1 M $\text{HNO}_3$ , 75 °C, 3 h, pulp density 10 g/l.	84.3% TREE recovery 74% TREE recovery 80% TREE recovery 76% TREE recovery	Yang and Honaker (2020)
REE recovery from natural leachate containing 6.14 ppm REEs and pH 2.70 from coarse coal discard.	Grinding and riffle splitter	Staged precipitation	The pH of the solution was increased gradually by adding 2 M NaOH solution. pH increase in step by adding 0.5 mL NaOH before each stage.	Precipitate contained about 1.1% total REEs in the pH range of 4.85 – 6.11, 64% considered critical REEs, recovered greater than 80% of the REEs contained in the original leachate.	Zhang and Honaker, (2018)

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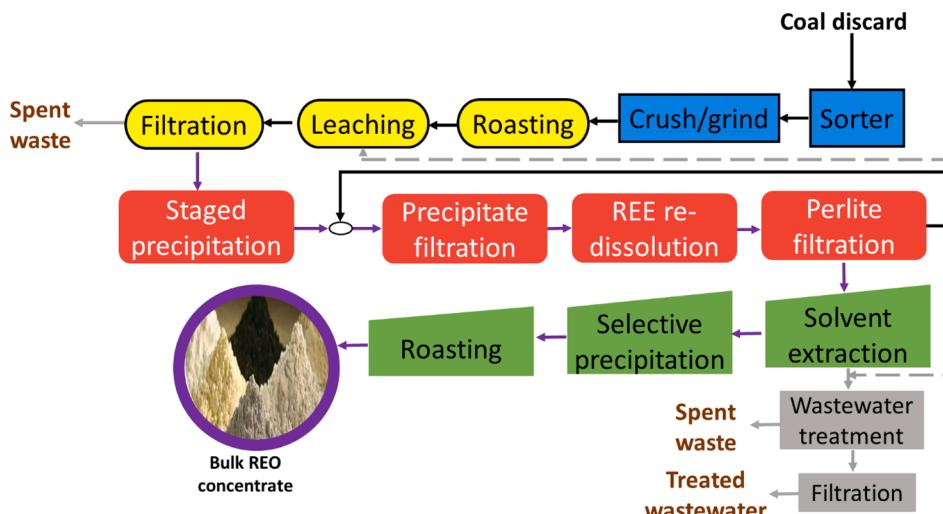
**Table 4 (continued)**

Objective/purpose	Pretreatment/beneficiation	Technique	Conditions	Results	Reference
REE recovery from coarse coal discard and natural leachate.	–	Acid leaching and selective precipitation		The highly valued critical REEs (i.e., Y, Nd, Eu, Tb, and Dy) were selectively leached from natural leachate due to the acid generated by pyrite oxidation. The total REE content in the dissolved solids was 380 ppm compared to 322 ppm (La and Ce accounted for nearly 50%) generated from coarse discard material.	Honaker et al. (2018b)
TREE content of Fire Clay samples collected at a coal preparation plant.	High-intensity magnetic separator followed by treatment in two stages of floatation using a laboratory conventional cell	Leaching	Acid leaching 1.2 M sulphuric acid heated to 75 °C. Nitric acid, 75 °C, atmospheric conditions.	80% of REEs recovered from coarse discard samples and were selective towards HREEs. TREE on ash basis, including yttrium and scandium; Thickener underflow: 360; Middlings: 1,308; Coarse reject: 348. Leaching followed by solvent extraction was reported to be the most effective to recover REEs from coarse middlings (greater than 80 percent).	Honaker et al. (2017)
To determine the content of REEs in hard coal.	Fine grinding	The wet mineralization process was carried out by a microwave mineralizer	Analyzed to the dry matter content.	Y, La, Ce, Nd, Pr greater than 5 ppm (seam 301). Y, Ce, Eu greater than 5 ppm (seam 212). Recommended a classifying hydrocyclone to justify the economic recovery of REE.	Baron (2020)
To determine the REE leachability and mineralogy of roof and floor strata of the coal seam.	Grinding	Leaching	1 M acid concentration, 75 °C leaching temperature, 100/1 (v/w) liquid/solid ratio, 500 rpm mixing speed.	Roof (770 ppm) and floor strata (2087, 1495 ppm) TREEs on a dry whole sample basis. Nearly 60% and 75% recovery at 120 min for the floor strata. HREE recovery from the roof and floor samples was < 25%.	Zhang and Noble, (2020)
Examined the concentration of REEs and extraction potential of materials associated with coal deposits.	Crushing	Ion extraction	Lixivants - ammonium sulfate, ionic liquid, deep eutectic solvent.	Extraction of REEs leached a high amount of REEs to the solution in each case. Ionic liquid and a deep eutectic solvent did not indicate a special advantage over ammonium sulfate as lixivants.	Rozelle et al. (2016)
Feasibility of using acid leaching to recover REEs from coarse discard, middlings, and thickener underflow samples were collected from coal preparation plants.	Thickener underflow - floatation column,Middling - grinding + riffle table	Leaching followed by solvent extraction	1.2 M of sulfuric, 75 °C under atmospheric pressure.	Acid leaching indicated leachability of REEs depends mainly on coal seam, sample type, & particle size. Fire Clay middlings 511,685 REO, Fire clay thickener underflow 34,470 (ppm, dry whole basis). 85% of REEs extracted and simultaneously produce clean coal from coal tailings; no valid relationship was found between the ash reduction in coal (residue after leaching).	Honaker et al. (2018a)
Simultaneous extraction of REEs and clean coal from coal tailings.	Floatation	Tailings from the used as feed for alkali-acid leach	–	Calcination at 600 °C significantly and preferentially improved LREEs recovery to values in the range of 80 – 90%. HREE recovery was lower (40 – 60%) due to differences in the mode of occurrence.	Kuppusamy et al. (2019)
Calcination pretreatment effects on the acid leaching characteristics of REEs from middlings and coarse coal discard.	Calcination at (400, 500, 600, 750, and 900 °C). 25 °C at a rate of 10 °C/min for two hours	Leaching	75 °C, 1% solid concentration by weight, 1.2 M HCl, and 500 rpm magnetic stirring.	Calcination at 600 °C significantly and preferentially improved LREEs recovery to values in the range of 80 – 90%. HREE recovery was lower (40 – 60%) due to differences in the mode of occurrence.	Zhang and Honaker, (2019b)
REE concentration tests.	Froth floatation, wet high-intensity magnetic separation (WHIMS)	Leaching	High ash content in 1 M nitric acid using deionized water and pH value of 0.	7000 ppm (0.7%) of REEs was achieved from a feed containing 500 ppm REEs.	Zhang et al. (2018)
REEs recovery from Fire Clay seam coal middlings.	Sequential grinding and floatation steps			Mineral matter in the organic matrix is more enriched in HREEs; more than 80% of the total REEs recovered except for Sc.	

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**Table 4 (continued)**

Objective/purpose	Pretreatment/beneficiation	Technique	Conditions	Results	Reference
Evaluated separation performance of Th, U, & REEs from a strip solution generated from coal by-products.	Not available	Selective precipitation + Solvent extraction	pH 4.8 (2 M NaOH), KOH, and NH <sub>4</sub> OH (NH <sub>3</sub> /H <sub>2</sub> O); solvent extraction feed pH of 3.5, 50 V % tributyl phosphate (TBP), organic to aqueous (O/A) ratio at 3:1.	Corresponds to an optimum separation performance of 79.6% overall rare earth recovery.	Talan and Huang, (2020)
Preliminary assessment of the leaching of REEs from the coal seam underclays from the Central Appalachian Basin.	Grinding then homogenized using cone and quarter technique	Leaching - Citric acid anion recovery Leaching - Sequential Acid Digestion	Citrate from citric acid but in some cases, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , or NaCl was added to citrate to provide an additional source of ions for ion exchange (22 °C, 24 h, pH 2–6) 0.5 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (22 °C, 4 h, pH 5), 1 M HCl (22 °C, 24 h, pH 1), 1.2 M H <sub>2</sub> SO <sub>4</sub> (70 °C, 1 h, pH 0.86), LiBO <sub>2</sub> - Digestion.	Bench-top leaching and flow-through experimental results indicated citrate is a chemically effective molecule for leaching exchangeable or weakly bound REEs or other elements of interest from clay-rich sedimentary rocks. Lower concentrations of gangue elements compared to sequential digestion using ammonium sulfate and mineral acids.	Montross et al. (2020)
Impacts of calcination on the leaching recovery of REEs and other critical metals from a Baker seam coarse coal discard.	Calcination under 600–750 °C for two hours	Sequential chemical extraction	1 M 40 mL, pH 8.2 ± 0.05, 25 °C, 0.5 h MgCl <sub>2</sub> ; 1 M 40 mL, pH 5 ± 0.05, 25 °C, 0.5 h CH <sub>3</sub> COONa; 0.04 M, NH <sub>2</sub> OH-HCl in 25% (v/v) acetic acid solution (100 mL, 95 °C, 3 h); 15 mL conc. HNO <sub>3</sub> plus 40 mL H <sub>2</sub> O <sub>2</sub> (55 mL, 85 °C, 5 h); 1 M ammonium acetate in 20% HNO <sub>3</sub> (25 mL, 25 °C, 5 h); acid digestion.	Leaching recovery of the REEs, especially the light REEs, increased significantly from around 24% to 80–90%. Sequential chemical extraction tests showed that approximately 75% of the REEs in the raw material were present in an insoluble form. Sequential leaching changed with calcination temperature, suggesting rare earth decomposes to varying degrees of calcination.	Zhang and Honaker, (2020)
Effect of leaching characteristics on West Kentucky No. 13, Illinois No. 6, and Fire Clay coal seam calcined and fluidized bed combustion (FBC) ash samples	Calcined in an oven at 600, 750, and 900 °C in an oxidizing atmosphere at a rate of 10 °C/ Min for 120 min.	Acid leaching	1% solid concentration by weight, 1.2 M HCl at 75 °C, magnetically stirred at 500 rpm. Slurry samples (15 mL) were collected at 5, 15, 30, 45, 60, 90, 120, 180, 240, and 300 min from the onset of the leaching process.	Pre-treatment at 600 °C for 2 h significantly increased REE recovery from a range of 20–40 to ca. 80% for all coal sources. REE recovery decreases significantly when the temperature was elevated to 900 °C. Fast REE leaching kinetics and within the first few minutes of the process. ca. 75% of the REEs of West Kentucky No. 13 coal source leached in the first 15 min from the 1.4–1.8 SG fraction calcined at 600 °C. REE recoveries from FBC ash samples were lower than calcined samples due to higher combustion temperature but were higher than non-calcined coal samples and pulverized coal combustion ash.	Honaker et al. (2019)
Extraction of REE from Thickener underflow, coarse coal discard, and middling samples.	Thickener underflow – floatation Middlings – grinding + riffle table + floatation cell.	Acid leaching by solvent extraction.	1.2 M of sulfuric acid, pH 0 at 1, 3, 5, 10, 24 and 48 h.	Middlings material 1–85% recovery of the REEs. Middlings material 2–60%. Grinding to <10 µm improved REE recovery. Solvent extraction treatment – 50% TREEs from around 300 ppm starting feedstocks	Honaker et al. (2018a)
Determination of REY + Sc concentration in select Main Karoo Basin (South Africa).	None	Samples were digested using a sodium peroxide fusion	Samples mixed with 0.6 g dry Na <sub>2</sub> O <sub>2</sub> , preheated to 450 °C for 30 min then mixed with 10 mL deionized water, 0.25 mL Lu Internal Standard Solution (400 µg/mL Lu) and 10 mL 25% HNO <sub>3</sub> were added to the mixture and thoroughly mixed. 5 mL aliquot diluted with 1% HNO <sub>3</sub> to 10 mL.	REY concentrations in the coal samples ranged from 121 to 150 ppm (excluding Sc).	Wagner and Matiane, (2018)



**Fig. 21.** Pilot-scale flowsheet for the recovering of REEs from coal-related resources (Adapted and modified from Honaker et al., 2020).

It is clear from the literature that several factors such as leachate selection, leachate concentration, pulp density, stirring speed, temperature, retention time, etc. that cannot be controlled simultaneously, play an integral role in REE recovery. It is therefore recommended that a combined multifactorial optimization of these parameters may be used to optimize the hydrometallurgical leaching process. Alternate techniques like ultrasound leaching, microwave leaching, organic leaching, the inclusion of hydrogen peroxide before leaching, or ozone (oxygen) assisted leaching could be considered in the future as possible techniques to develop environmentally benign and efficient REE processing from coal and coal discard.

The recovery and purification steps are essential to concentrate REEs from the leachate or the pregnant leached solution and to produce high-grade pure rare earth products. While the most reported and established technique is the solvent or liquid–liquid extraction in traditional ore settings, adopting it to low REE concentration resources like coal in a manner that reduces costs are vital. In addition, the advancement of new technologies such as liquid membrane separation, molecular recognition technology, supercritical CO<sub>2</sub> extraction, etc. have been investigated to a degree of success and could play a role in the future in extracting REEs from coal and coal byproducts.

While it is acknowledged by the research community and government that REEs can contribute to clean energy transitions and energy conservation, their extraction processes from coal should not avoid environmental monitoring. Therefore, it is necessary to recognize and establish its environmental and social barriers/impacts, their costs, and compare them with competing technologies. There is little research data in these areas concerning the extraction and recovery of REEs from coal and coal discard, so the lack of information hinders judgment. Using tools such as life-cycle assessment and techno-economic analysis (TECA), environmental hotspots, bottlenecks, or process problems can be identified. It should be noted that closed-loop models that encourage recycling and reuse of waste generated and the recovery of spent chemicals are highly recommended. This approach could pave the way for improving the economy and reducing the potential environmental impact of waste, but at the same time may result in additional complications.

In short, the development of a large-scale metallurgical flow sheet for the extraction of REEs from run-of-mine coal and coal discard requires vigorous and holistic process planning. With the advancement in technologies for separating and extracting REEs from coal and other waste, commercial REE exploitation from coal and coal discard is likely in sight. Accomplishing this would address REEs scarcity, create new markets, new job opportunities, and expand the non-energy products of

coal while at the same time reduce the ongoing environmental impact of coal discard.

#### CRediT authorship contribution statement

**Orevaoghene Eterigho-Ikelegbe:** Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Hamza Harrar:** Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Samson Bada:** Funding acquisition, Supervision, Validation, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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