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RESEARCH

Extractability and mineralogical evaluation of rare earth elements from Waterberg Coalfield run-of-mine and discard coal

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Abstract

This study explores the extraction of rare earth elements (REEs) from high-ash run-of-mine and discard coal sourced from the Waterberg Coalfield. Three distinct methods were employed: (1) ultrasonic-assisted caustic digestion; (2) direct acid leaching; and (3) ultrasonic-assisted caustic-acid leaching. Inductively coupled plasma mass spectrometry was utilized to quantify REEs in both the coals and resultant leachates. Leaching the coals with 40% NaOH at 80 °C, along with 40 kHz sonication, yielded a total rare earth element (TREE) recovery of less than 2%. Notable enrichment of REEs was observed in the run-of-mine and discard coal by 17% and 19%, respectively. Upon employing 7.5% HCl, a recovery of less than 11.0% for TREE was achieved in both coal samples. However, leaching the caustic digested coal samples with 7.5% HCl significantly enhanced the TREE recovery to 88.8% and 80.0% for run-of-mine and discard coal, respectively. X-ray diffraction analysis identified kaolinite and quartz as the predominant minerals. Scanning electron microscopy-energy dispersive microanalysis revealed monazite and xenotime as the REE-bearing minerals within the coal samples. These minerals were found either liberated, attached to, or encapsulated by the clay-quartz matrices. Further mineralogical assessments highlighted the increased REE concentrations in coals post-caustic digestion and subsequent recovery during acid leaching. This increase was attributed to the partial dissolution of kaolinite encapsulating the RE-phosphates and the digestion of REE-bearing minerals. Notably, undissolved REE-bearing elements in the caustic-acid-leached coal indicated the necessity of harsh leaching conditions to augment REE recovery from these coal samples.

Keywords Acid leaching · Caustic · Mineralogical · Pre-digestion · REE recovery · Ultrasonic

1 Introduction

Rare earth elements (REEs) are pivotal components crucial for the advancement of green energy technologies, military applications, and the production of smart electronic devices (Whitworth et al. 2022; Golroudbary et al. 2022). Anticipated estimations from Roskil indicate a projected surge of 41% in REE demand by 2030 (Gielen and Lyons 2022). Commercially, REEs are conventionally extracted from bastnasite, monazite, loparite, ion-adsorbed clays, and xenotime (Gielen and Lyons 2022). A pressing concern arises from the fact that deposits bearing REE minerals are often found in limited quantities, rendering economic mineral development challenging and localized to select countries (Barakos et al. 2020). Consequently, these elements have been deemed critical materials by several institutions (Riesgo García et al. 2017; Liu et al. 2019; Blengini et al. 2020). Geopolitical concerns and potential supply risks linked to REEs have been highlighted in various studies (Jellicoe 2019; Seaman 2019), prompting a wave of research aimed at discovering alternative sources and developing efficient recovery methods (Jepson 2012; Binnemans et al. 2013; Dutta et al. 2016; Costis et al. 2019; Dushyantha et al. 2020; Eterigho-Ikelegbe et al. 2021).

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Considerable attention has been drawn to coal and its by-products as promising secondary sources of REEs (Eterigho-Ikelegbe et al. 2021; Seredin and Dai 2012; Dai et al. 2016, 2020; Lin et al. 2017a, b; Finkelman et al. 2018, 2019; Dai and Finkelman 2018; Wagner and Matiane 2018; Zhang et al. 2020; Harrar et al. 2022). Diverse methodologies for extracting REEs from these materials have been explored (Zhang et al. 2015, 2018; Lin et al. 2017a, b; Yang 2019; Yang and Honaker 2020; Li et al. 2022; Hamza et al. 2022). Notably, studies have reported REE concentrations in South African coals ranging from 95 ppm to 280 ppm, with a significant portion associated with the mineral components (Wagner and Matiane 2018; Harrar et al. 2022; Akinyemi and Akinlua 2012; Akdogan et al. 2022).

Total rare earth element (TREE) concentrations in coal are generally comparatively low compared to traditional ores (Okeme et al. 2022). Furthermore, extracting REEs from coal hinges on factors such as the type and crystallinity of REE-bearing minerals, their distribution, and their associations with other coal minerals (Li et al. 2022; Yang et al. 2021). The micron-sized particle nature of REE occurrence in coal limits the efficacy of physical beneficiation methods, resulting in relatively low recovery rates (Zhang et al. 2020). Nonetheless, these methods have been advocated for concentrating REEs in coal prior to chemical leaching (Zhang et al. 2020), even though fine grinding has been deemed economically impractical (Zhang and Honaker 2019). On the other hand, direct acid leaching yields modest REE recoveries due to the presence of REEs in acid-insoluble phosphate minerals and ion adsorption clays, partially soluble in acid (Yang et al. 2021; Zhang and Honaker 2019, 2020; Gupta and Krishnamurthy 1992; Eze et al. 2012; Honaker et al. 2019; Kuppusamy 2022). Consequently, scholars have explored thermal or alkali treatments of coal and coal-related materials before acid leaching (Li et al. 2022; Hamza et al. 2022; Yang et al. 2019, 2021; Zhang and Honaker 2019). These studies indicated that thermal treatment decomposed clay minerals, releasing REEs adsorbed on their surfaces, whereas the RE phosphates were converted into acid-soluble RE oxides and hydroxides (Li et al. 2022; Hamza et al. 2022; Yang et al. 2021; Zhang and Honaker 2019).

This investigation delves into the leachability of REEs from run-of-mine and discard coal obtained from the Waterberg coalfield, employing direct leaching with hydrochloric acid (HCl), caustic soda (NaOH) solution, and predigestion by the NaOH solution followed by acid leaching. We particularly examine the association of REE-bearing minerals with gangue minerals by comparing the recovery of gangue elements (aluminum (Al) and iron (Fe) with the REEs. This comparative analysis serves to evaluate the potential contamination of the REE-pregnant leachate by gangue elements. Remarkably, the coals under scrutiny contain REE-bearing minerals - monazite and xenotime and are more thermally and chemically stable than those previously studied using the alkali-acid leaching method (Li et al. 2022; Yang et al. 2019). These aspects remain relatively unexplored in South Africa. Hence, our study aims to assess lixiviants' impact on coal minerals and their REE recovery potential, contributing valuable insights to the existing literature.

2 Materials and methods

2.1 Materials

This study employed coal sourced from South Africa's Waterberg coalfield, encompassing both run-of-mine (RCW) coal and its discard (DCW) fraction derived through gravity separation of RCW. The coal specimens underwent sun-drying to eliminate excess moisture, followed by subdivision using a rotary splitter to produce representative samples for subsequent analysis. After initial crushing and screening to obtain −1 mm representative samples, further processing involved milling, screening, and splitting to obtain −212 and −106 micrometer (µm) particle size representative samples. Analytical-grade sodium hydroxide (NaOH) pellets and 37% hydrochloric acid (HCl) were utilized, with deionized water employed for solution preparation and washing of the leached coal solids.

2.2 Leaching tests

2.2.1 Ultrasonic-assisted caustic digestion tests

A 20 g coal feed sample comprising −106 µm particles from both RCW and DCW was individually mixed with a 500 ml NaOH solution, resulting in a slurry with a solid-to-liquid ratio of 1:25. The slurry was transferred into volumetric flasks and subjected to ultrasound-assisted caustic leaching within a tank-type sonicator. The caustic leaching process occurred in a 25-liter Scientech Ultrasonic cleaner filled with tap water. The leaching conditions, determined through response surface methodology (Modiga et al. 2023), involved utilizing a 40% NaOH solution at 80°C under sonication at 40 kHz for 106 min. Subsequently, the caustic-leached coal slurry underwent filtration to isolate the rare earth elements (REE) leachate, which was then analyzed using ICP-MS for quantifying REE, Al, and Fe. The remaining solids underwent triple washing with deionized water, followed by filtration, air-drying for 48 h, and weighing, then the dried samples were further characterized.

2.2.2 Direct acid leaching of the run-of-mine and discard coal samples

To assess the impact of direct acid leaching on REE recovery, run-of-mine (RCW) and discard (DCW) coals underwent leaching with HCl using an adapted method from Kuppusamy et al. (Kuppusamy et al. 2019). A 20 g coal feed sample was blended with a 7.5% HCl solution in a glass beaker, resulting in a slurry with a solid-to-liquid ratio of 1:8. The beaker was sealed to prevent evaporation and placed on a hot plate magnetic stirrer, maintaining a temperature of 50 °C for 30 min. Stirring by the magnetic stirrer occurred at 600 rpm. Following acid leaching, the coal slurry was filtered to isolate the REE pregnant leachate, and subsequently analyzed using ICP-MS for quantification of REEs, Al, and Fe. The remaining solids underwent a triple wash with deionized water, followed by filtration, air-drying for 48 h, and weighing, then the dried samples were further analyzed.

2.2.3 Ultrasonic-assisted caustic pre-digestion and acid leaching tests

The recovery of REEs via ultrasonic-assisted caustic pre-digestion followed by acid leaching followed the methodologies outlined in Sects. 2.2.1 and 2.2.2. Nevertheless, a modification was introduced during the acid leaching phase, wherein the caustic pre-digested coal samples underwent leaching with 160 mL of 7.5% HCl.

2.3 Characterization

The quantification of REEs, aluminum (Al), and iron (Fe) in the feed samples, chemically treated coals, and leachates was carried out using inductively coupled plasma mass spectrometry (ICP-MS) at the University of Johannesburg. A slurry composed of 0.1 g coal and 2 mL of 65% nitric acid (HNO_3) was subjected to microwave digestion. The temperature of the slurry was gradually increased by 1 °C per minute for 20 min until it reached 200 °C. The mixture was then kept at 200 °C for another 10 min to complete the digestion process. Following filtration of the digested slurry, the obtained filtrate underwent a two-fold dilution (from 500 µL to 10 mL with 2% HNO_3). For liquid samples, REE-rich solutions underwent filtration to remove suspended particles. The resulting filtrate was then diluted by a factor of 200 (from 50 µL to 10 mL with 1% HNO_3) for REE quantification using ICP-MS. To validate the ICP-MS results, the South African Reference Material (SARM) 18 standard was employed. The recovery of these elements was calculated using Eq. (1).

$$\%\text{REE recovery} = \frac{C_L \times V_L}{C_{FC} \times M_{FC}} \times 100 \quad (1)$$

The concentration of total rare earth elements (TREEs) is denoted as C_L (µg/L). V_L represents the volume (L) of the leaching solution. Conversely, the concentration of rare earth elements (REEs) in the alkali-leached fractions of run-of-mine (RCW) and its discard (DCW) is represented by C_{FC} (µg/g). Meanwhile, M_{FC} stands for the mass (g) of the alkali-leached fractions of RCW and DCW.

Proximate analysis, following the American Society for Testing and Materials (ASTM D-5142) standard, was conducted to determine the ash content of the coals. This analysis was carried out using a thermographic analyzer, the Leco TGA 701. X-ray diffraction (XRD) analysis was performed to identify the mineral phases in the feed samples (RCW and DCW) and chemically treated coal samples. The analysis utilized a Malvern Panalytical Aeris diffractometer equipped with a PIXcel detector and fixed slits, with Fe-filtered Co-Kα radiation. The observed peaks were matched to known minerals or compounds with the assistance of X'Pert HighScore Plus software. Further investigation into the bright mineral particles on selected grains containing REEs in both feed and chemically treated coals was conducted using a Zeiss Supra55 VP field emission scanning electron microscope (SEM). The microscope is equipped with an Oxford Inca microanalysis system, employing energy dispersive spectroscopy (EDS). These analyses shed light on the distinctive composition of REE-bearing minerals in the studied coals and provided insights into the association of the REE-containing particles with other coal components, the liberation, and the relative grain sizes of the REE mineral phases.

3 Results and discussion

3.1 Characterization of coal samples

The quantification of REEs in the coal samples via ICP-MS revealed that the run-of-mine coal (RCW), characterized by a higher fixed carbon content, exhibited a lower total rare earth element (TREE) concentration (225 ppm) compared to discard coal (DCW) (245.5 ppm) on a whole mass basis. This aligns with previous studies attributing lower REE concentrations in coal to dilution by higher organic matter (Yang et al. 2019). REEs are categorized into light rare earth elements (LREEs) and heavy rare earth elements (HREEs) based on their atomic weights (Gupta and Krishnamurthy 1992). LREEs include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), and europium (Eu). HREEs include

gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Yttrium (Y) is categorized as an HREE due to its ionic radius matching that of Ho (Seredin and Dai 2012). Analyzing the LREE/HREE ratio for RCW and DCW (6.2 and 7.4, respectively) indicated that the coal samples had a higher enrichment of LREEs than HREEs. HREEs constituted 14% and 12% of the TREEs in RCW and DCW, respectively. The observed high total LREE content in DCW compared to RCW could be attributed to the higher affinity of LREEs to the mineral matter within the coal, which was higher in DCW (Dai et al. 2020; Dai and Finkelman 2018; Yang 2019; Finkelman 1981). Conversely, the higher concentration of HREEs in RCW relative to DCW suggested a greater affinity of HREEs to the coal's organic matter than LREEs (Lin et al. 2017a, b; Zhang et al. 2018).

Both RCW and DCW exhibited high ash contents of 50.90% and 68.30%, respectively (see Table 1). This significant finding is further supported by the semi-quantitative X-ray diffraction (XRD) results. Specifically, the discard coal, DCW, displayed a higher mineral content, as illustrated in Table 1 and Fig. 1.

Quartz and clay minerals (kaolinite and illite) emerged as the dominant minerals in the coal samples, with higher concentrations observed in DCW. Additionally, trace amounts of anatase, dolomite, calcite, and siderite were identified in the samples, with the latter three minerals notably absent in DCW.

The semi-quantitative XRD results illustrated in Fig. 2, depict a gradual increase in organic carbon content following the digestion of both DCW and RCW with a caustic solution. This increase persists even after acid leaching post-caustic digestion. The increase in organic carbon can be attributed to the marginal decline of kaolinite, a result of its solubilization by the caustic solution. This effect is evident in the reduction of kaolinite peaks at 2θ equal to 14° and 29° in the XRD spectra, as represented in Fig. 1. Conversely, the decrease in kaolinite is notably insignificant after acid leaching of the caustically digested samples, indicating its low solubility in HCl (Li et al. 2022). This was also observed by minimal to no change in the remaining kaolinite peaks after the acid leaching of caustic-pre-digested RCW and DCW, as shown in Fig. 1. These observations align with findings in the literature, confirming the consistent behavior of kaolinite across all chemical stages (Li et al. 2022; Kuppusamy et al. 2019).

Table 1 Composition of run-of-mine (RCW) and discard (DCW) coal samples

Analysis	Sample	RCW	DCW
Proximate analysis (mass %)	Ash	50.9	68.3
	Fixed carbon	27.2	15.0
X-ray diffraction (mass %)	Quartz	13.6	26.1
	Kaolinite	34.9	40.5
	Pyrite	1.1	0.8
	Illite	2.0	3.3
	Anatase	0.4	0.4
	Dolomite	1.5	0.0
	Calcite	1.3	0.0
	Siderite	0.2	0.0
REEs (ppm)	TREEs	225.0	245.5
	LREEs	194.0	216.4
	HREEs	31.3	29.1
	LREE/HREE	6.2	7.4

Interestingly, quartz exhibited an increase following the caustic digestion of coal samples and was particularly significant in the caustic-digested DCW (Fig. 2). This rise in quartz concentration suggests the potential re-precipitation of quartz initially dissolved by the caustic solution, forming an amorphous quartz phase insoluble in acids (Fan et al. 2023). A subtle increase in pyrite content was also noted, possibly attributed to its inherent insolubility in HCl (Dhawan and Sharma 2019). While pyrite exhibits solubility in caustic solutions, this depends on various factors such as temperature, pH, mineral characteristics, the type and concentration of oxidants, particle size, and surface area (King 2015). Another contributing factor to the increased presence of quartz and pyrite in the coal samples might be the consumption of caustic solution by highly soluble kaolinite, leading to their enrichment. Caustic digestion removed all carbonate minerals in RCW, while illite experienced partial solubilization, leaving trace quantities (less than 1%) in both RCW and DCW. Notably, anatase in both coal samples appeared unreactive throughout all stages of the leaching process.

The SEM images provided in Fig. 3a-d offer a detailed view of the grains of the REE-bearing minerals within RCW and DCW. The phases identified as RE phosphate minerals, monazite ($REEPO_4$), and xenotime (YPO_4) were found to be liberated, attached to, and encapsulated by the clay-quartz matrices. This signified two distinct modes of occurrence for monazite and xenotime: authigenic and detrital (Wang et al. 2008). The observed grain sizes of the RE phosphate minerals were less than 10 μm in diameter, and notably, no REE-bearing carbonate minerals were identified.

Further insights on the REE-bearing minerals gained through SEM-EDS analysis (Table 2) indicated that xenotime emerged as the predominant RE phosphate mineral in RCW, accompanied by minor phases of monazite. Conversely, in DCW, monazite appeared to be prevalent, with small quantities of xenotime also present.

A slight increase in monazite particles was noted in caustic-digested RCW (Table 3), although xenotime remained the predominant REE-bearing mineral. Conversely, in caustic-digested DCW, fewer monazite particles were observed than in DCW, suggesting the particles potentially

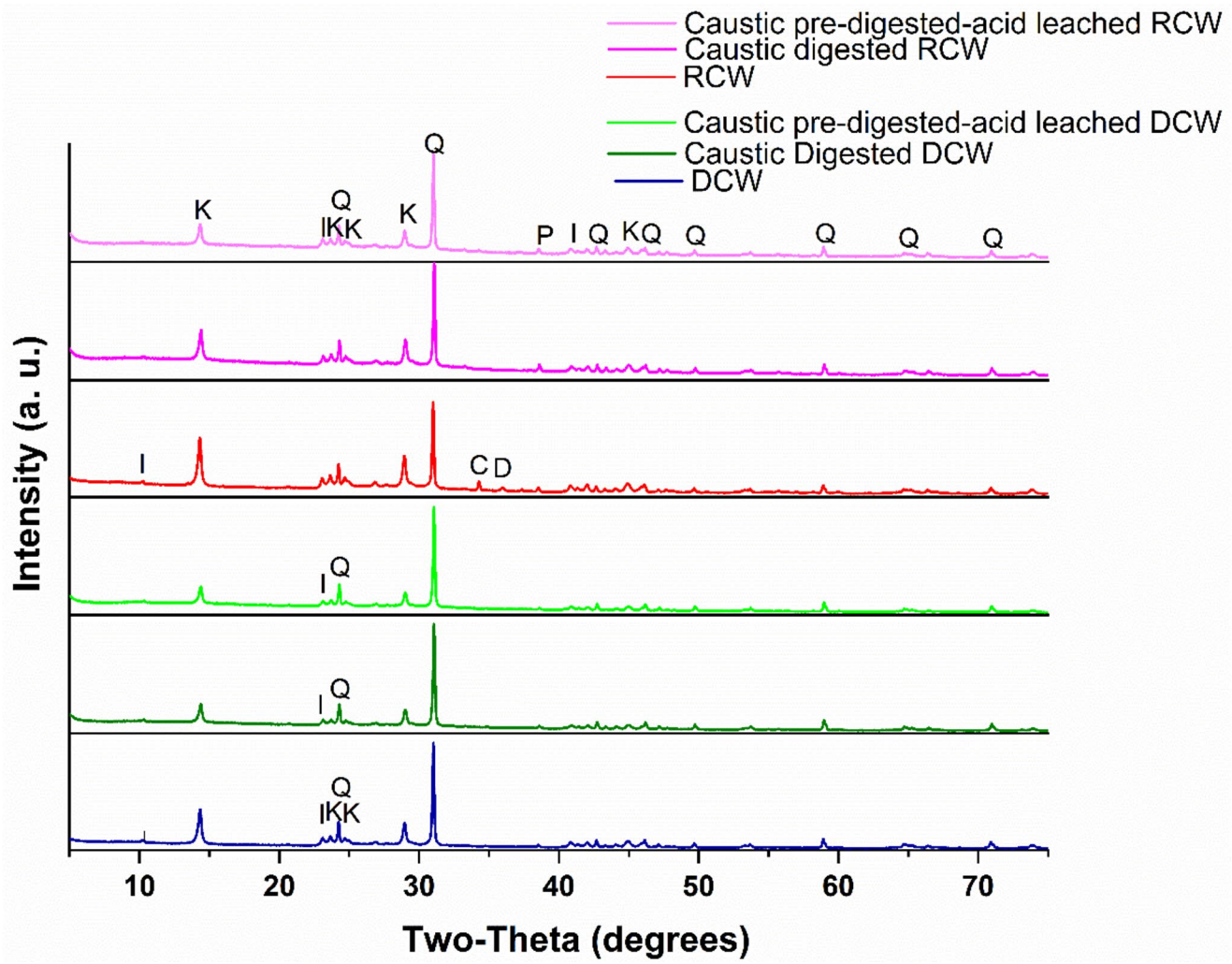

Fig. 1 XRD spectra of the feed, caustic-digested and caustic digested-acid leached coal (C: Calcite, D: Dolomite, I: Illite, K: Kaolinite, P: Pyrite, Q: Quartz)

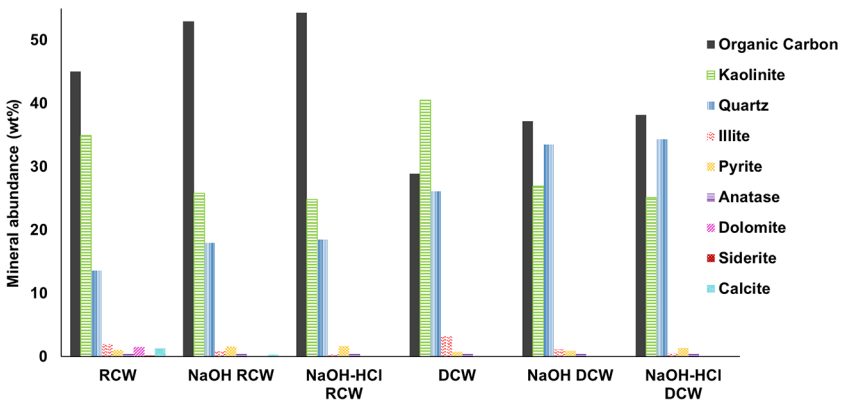

Fig. 2 Semi-quantitative XRD results for the feed, caustic-digested (NaOH) and caustic-digested-acid leached (NaOH-HCl) run-of-mine (RCW) and discard (DCW) coal samples

decomposed during caustic digestion (Li et al. 2022). The fraction of xenotime particles in caustic-digested DCW increased, though still lower than the monazite fraction. The increase in REE-bearing particles in caustic-digested RCW and DCW is attributed to their liberation after the dissolution of kaolinite by the caustic solution, as supported by the decrease in kaolinite content (Fig. 2).

Monazite and xenotime grain sizes observed in the two caustic-digested coal samples (RCW and DCW) ranged from 1 to 9 µm, averaging around 4 µm, with SEM images

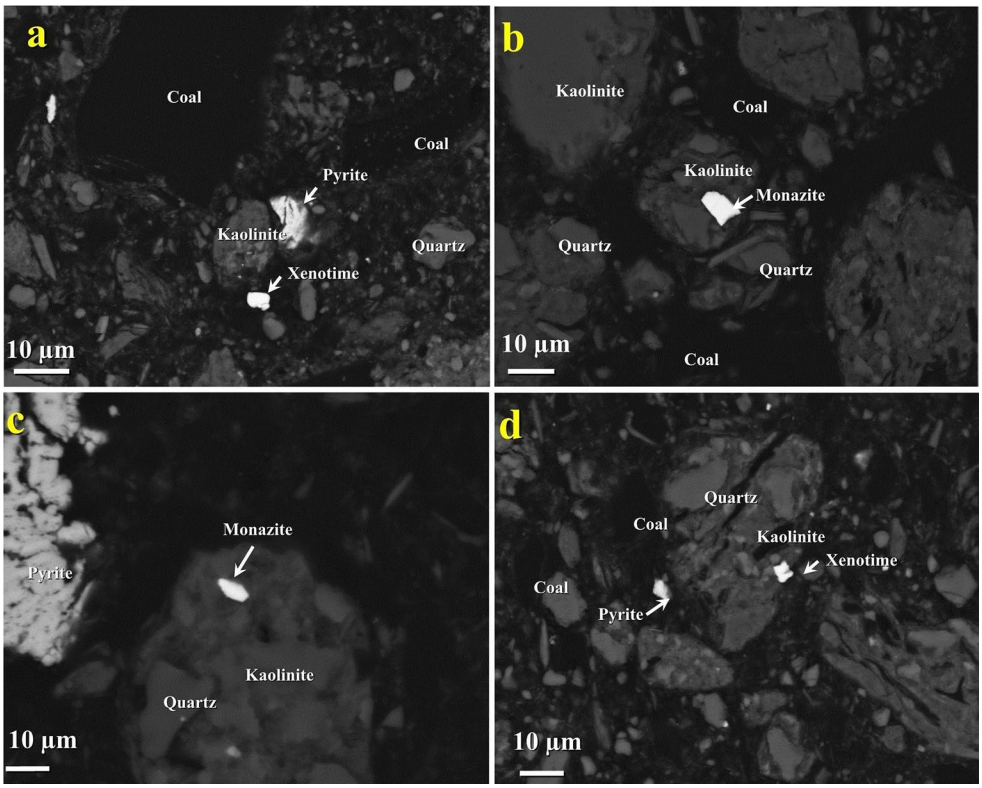

Fig. 3 SEM images of run-of-mine (RCW) **a** and **b** and discard (DCW) **c** and **d** Coal samples

Table 2 REE-bearing minerals identified in the run-of-mine (RCW) and discard (DCW) coals from SEM-EDS analysis

Sample	Mineral	Quantity	Fraction (%)
RCW	Monazite	2	28.6
	Xenotime	5	71.4
DCW	Monazite	21	91.3
	Xenotime	2	8.7

Table 3 REE-bearing minerals identified in the caustic-digested run-of-mine (RCW) and discard (DCW) coals from SEM-EDS analysis

Sample	Mineral	Quantity	Fraction (%)
RCW	Monazite	3	37.5
	Xenotime	5	62.5
DCW	Monazite	7	58.3
	Xenotime	5	41.7

(Fig. 4) confirming a similar mode of occurrence in both samples.

Xenotime particles were prevalent in the caustic-digested-acid leached RCW, while monazite was the dominant REE-bearing mineral in the caustic-digested-acid leached DCW (Table 4).

The grain size of REE-bearing minerals in both samples was relatively smaller, ranging between 0.5 and 3 µm, with an average size of around 1.5 µm (Fig. 5). Similar to caustic-digested samples, the grains were generally liberated, with some attached to or included in the coal's clay. This indicates incomplete dissolution of silicate minerals and decomposition of REE-bearing minerals. These findings align with those reported by Li et al. (Li et al. 2022), underscoring the high stability of xenotime and monazite during chemical treatment and the necessity for severe process conditions.

3.2 The behaviour of major and rare earth elements during chemical treatment

3.2.1 Ultrasonic-assisted caustic digestion

The application of ultrasound-assisted caustic digestion to RCW and DCW led to the enrichment of REEs in the coal samples as illustrated in Fig. 6.

The TREE concentration in the as-received coals increased from 225 ppm in RCW to 270 ppm in caustic-digested RCW, and from 245.5 ppm in DCW to 301.5 ppm in caustic-digested DCW. This observation aligns with the findings of Kuppusamy et al. (Kuppusamy et al. 2019) and Zhang et al. (Zhang et al. 2020), suggesting that REEs in samples treated with a caustic solution remained within the solid matrices. The enrichment of REEs in the coal samples was attributed to the dissolution of kaolinite, as evidenced by XRD results (Figs. 1 and 2), as per Eq. (2) (Kuppusamy et al. 2019)

$$Al_2Si_2O_5(OH)_{4(s)} + 6NaOH_{(aq)} \rightarrow 2Na_2SiO_{3(aq)} + 2NaAlO_{2(aq)} + H_2O_{(aq)} \quad (2)$$

The SEM-EDS analysis revealed a strong association between REE-bearing minerals in the studied coals and

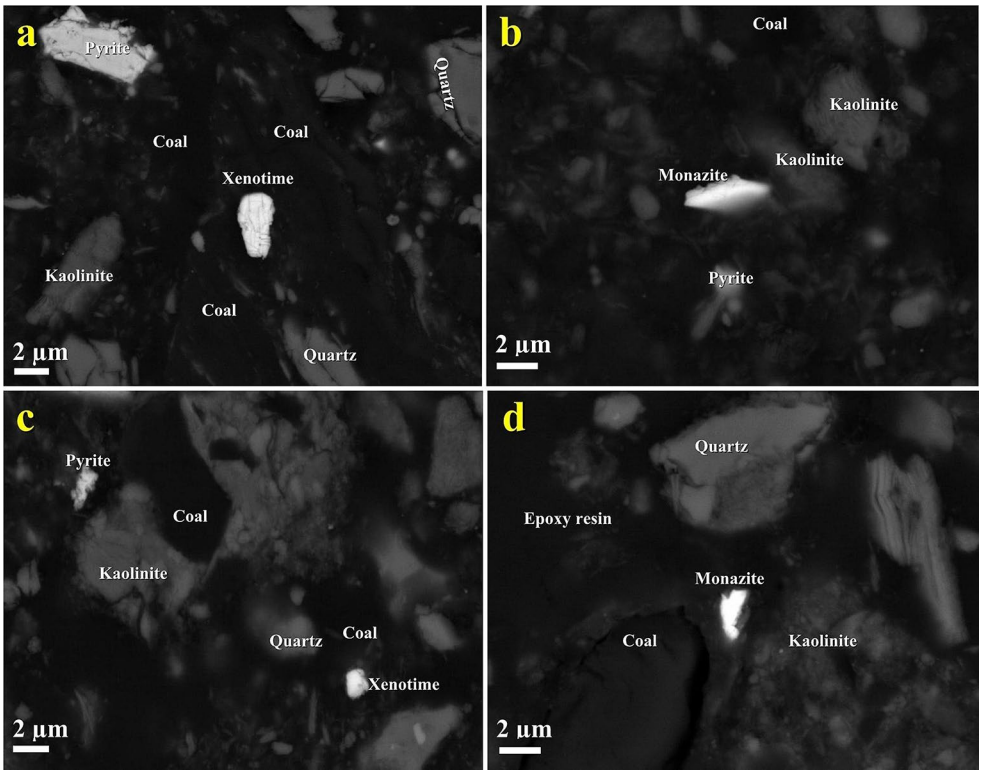

Fig. 4 SEM images of REE-bearing particles found in the caustic-digested run-of-mine (RCW) **a** and **b** and discard (DCW) **c** and **d** Coal samples

Table 4 REE-bearing minerals identified in the caustic-digested-acid leached run-of-mine (RCW) and discard (DCW) coals from SEM-EDS analysis

Sample	Mineral	Quantity	Fraction (%)
RCW	Monazite	2	33.3
	Xenotime	4	66.7
DCW	Monazite	8	80.0
	Xenotime	2	20.0

some of the dominant minerals. Elements like Al and Fe, while potentially complicating REE leaching and subsequent processes, offer insights into the mineral phases that regulate leaching kinetics (Balinski et al. 2020; Zhang and Noble 2020). To understand these trends, we examined the leaching kinetics of these elements. The recovery of REEs, Al and Fe during caustic digestion is illustrated in Fig. 7. Digestion of RCW and DCW in caustic solution, resulted in very low TREE recoveries of 0.8% and 1.9%, respectively. Notably, higher recovery percentages were observed for HREEs and Sc, with DCW showing superior recoveries (7.5% and 22.6%) compared to RCW (1.3% and 10.8%). Interestingly, Al recovery significantly exceeded Fe recovery in both coal samples, with DCW leachates exhibiting comparatively higher concentrations. These findings shed light on the intricate interplay between REEs, Al and Fe during caustic digestion.

The notable recovery of Al aligns with the dissolution of kaolinite, as indicated by Eq. (2), and is evident in Fig. 2. This observation concurs with previous studies (Finkelman et al. 2018; Li et al. 2022; Zhang and Honaker 2020; Ohki et al. 2004). Consequently, the ion-adsorbed REEs were released, and some of the REE-bearing minerals encapsulated by clay minerals were exposed to the caustic solution and decomposed according to Eq. (3) (Kuppusamy et al. 2019).

$$\mathrm{REEPO}_{4(s)} + 3\mathrm{NaOH}_{(aq)} \rightarrow \mathrm{REE}\,(\mathrm{OH})_{3(s)} + \mathrm{Na}_3\mathrm{PO}_{4(aq)} \quad (3)$$

The liberated REEs from these reactions might have transformed into RE hydroxides, known to be insoluble in an alkaline medium (Li et al. 2022; Yang et al. 2021; Kuppusamy et al. 2019). However, the solubility of REEs in alkaline media increases with higher atomic numbers, a phenomenon referred to as basicity (Gupta and Krishnamurthy 2015). Scandium (Sc) is noted as the least basic among REEs, making it more soluble than others. Thus, the decrease in basicity, as reported by Gupta and Krishnamurthy (Gupta and Krishnamurthy 2015), follows the order: $La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Y^{3+}\ Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+} > Sc^{3+}$. This elucidates why HREEs and Sc leached into the solution during caustic digestion, while the recovery of LREEs was lower for both RCW (0.7%) and DCW (1.2%). The substantial recovery of Sc was the primary factor that influenced the observed levels of LREE recovery.

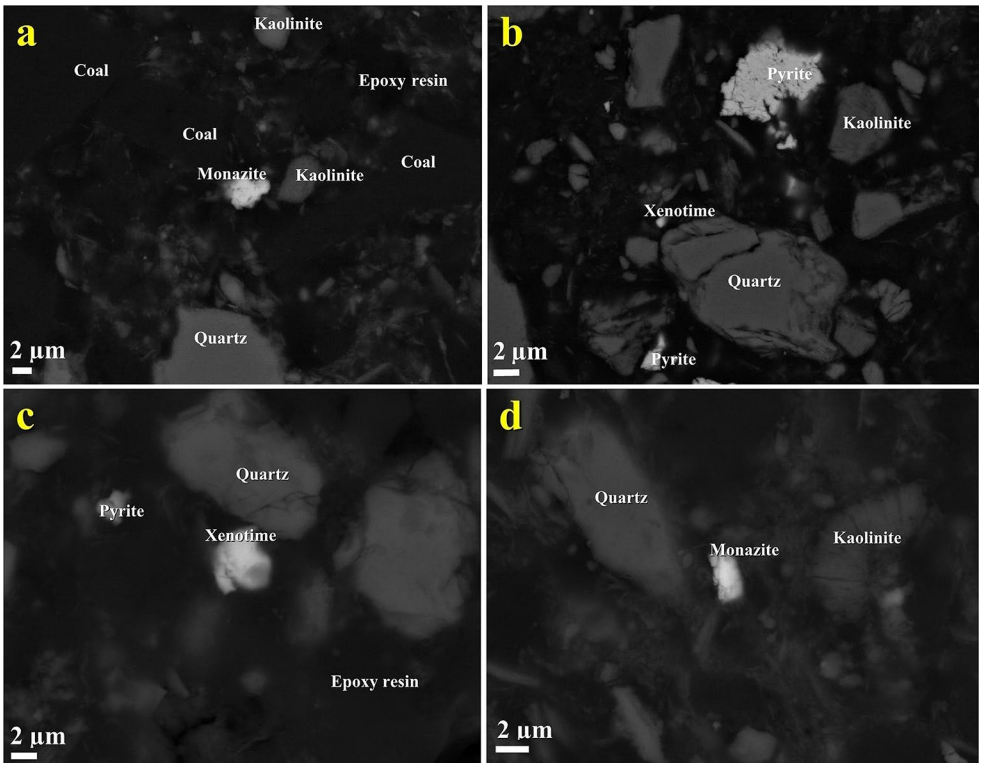

Fig. 5 SEM images of REE-bearing particles found in the caustic-digested- acid-leached run-of-mine (RCW) **a** and **b** and discard (DCW) **c** and **d** Coal samples

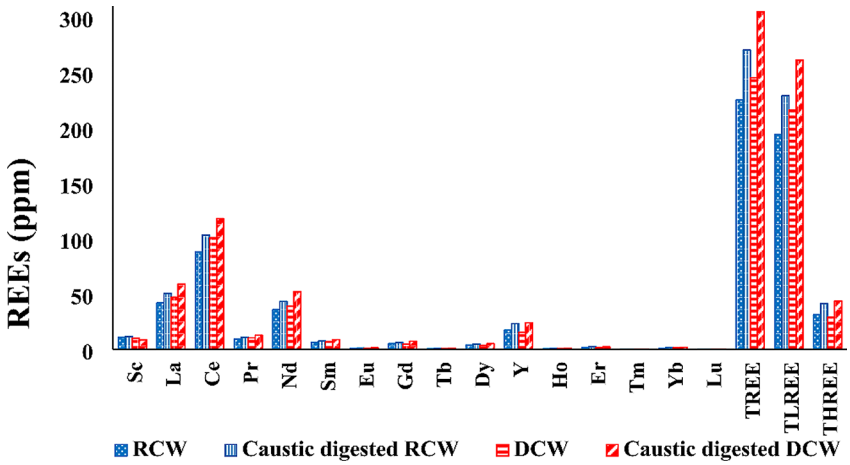

Fig. 6 Enrichment of the REEs in run-of-mine (RCW) and discard (DCW) coal samples after ultrasound-assisted caustic digestion

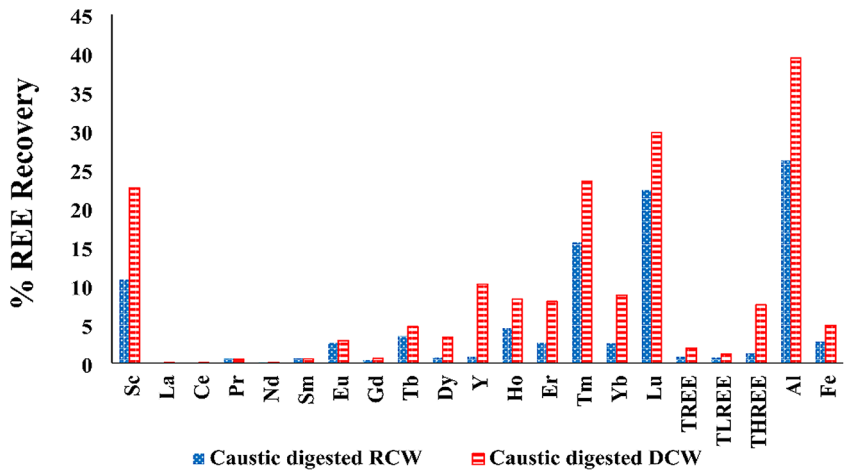

Fig. 7 REE recoveries during the caustic digestion of run-of-mine (RCW) and discard (DCW) coal samples

3.2.2 Direct hydrochloric acid leaching

The comparative investigation of REE recovery, employing only direct HCl leaching on RCW and DCW, is presented in Fig. 8. The recoveries of TREEs from RCW and DCW were notably low, registering at 10.6% and 10.3%, respectively.

Various studies have consistently reported low recoveries of TREEs (Yang et al. 2021; Zhang and Honaker 2019). Zhang and Honaker (Zhang and Honaker 2020) attributed these low recoveries to the occurrence of REEs in acid-insoluble forms.

The significantly low recovery of Al suggests that the dissolution of clays wasn't a major contributor to REE recovery. Ohki et al. (Ohki et al. 2004) and Finkelman et al. (Finkelman et al. 2018) pointed out that acidic solutions can leach very low concentrations of Al, either in organic association or from acid-soluble inorganic minerals. The Al content in the leachate may be due to the partial decomposition of REE-bearing minerals containing Al and the alteration of clay structures through ion exchange (Eze et al. 2012), releasing REEs adsorbed on clay surfaces into the acid solution (Finkelman et al. 2018; Yang et al. 2019). Additionally, HREEs exhibit a higher affinity to clays finely distributed in organic matter than LREEs, and their concentration increases as the coal ash content decreases (Lin et al. 2017a, b). The relatively higher HREE recovery from RCW (42.6%) compared to DCW (25.7%) aligns with this correlation since RCW had a lower ash content and was more enriched in HREEs than DCW.

Less than 10% recovery of LREEs was observed in both coal samples, with RCW showing the lowest recovery (Fig. 8). These findings support the association of LREEs with acid-insoluble phosphates observed using SEM-EDS. High quantities of Fe were recovered from RCW compared to DCW due to the dissolution of acid-soluble siderite observed in RCW using XRD (Ohki et al. 2004; Steel et al. 2001). Additionally, during the alteration of clays, Fe adsorbed onto their surfaces may have been released, similar to HREEs, into the acid solution, contributing to the Fe recovery (Eze et al. 2012). However, pyrite is unlikely to have contributed to the reported Fe, given its insolubility in HCl solutions (Steel et al. 2001).

Examining individual REE recoveries, La, Ce, Pr, and Nd showed very low recoveries relative to other REEs in both samples, suggesting the likelihood of these elements co-occurring in the same mineral configuration (Yang et al. 2019). Scandium (Sc) showed relatively higher recovery in both coal samples, with DCW exhibiting a recovery of more than 35%, confirming its similar mode of occurrence to HREEs. Equations (4–6) describe the possible chemical reactions that took place during direct acid leaching (Pak et al. 2019).

$$REEPO_{4(s)} + 3HCl_{(aq)} \rightarrow REECl_{3(aq)} + H_3PO_{4(aq)} \quad (4)$$

$$FeCO_{3(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + CO_{2(g)} + H_2O_{(aq)} \quad (5)$$

$$Al_2Si_2O_5(OH)_{4(s)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 2SiO_{2(s)} + 5H_2O_{(aq)} \quad (6)$$

3.2.3 Ultrasonic-assisted-caustic-acid leaching

The REE recovery from the acid-leaching of caustic-pre-digested RCW and DCW are depicted in Fig. 9. Notably, acid-leaching of caustic-pre-digested RCW achieved higher recoveries (88.8%) compared to DCW (80%). This finding aligns with Zhang et al. (Zhang et al. 2020), indicating that REE recovery from coal middlings is relatively higher than from coal discards. Zhang et al. (Zhang et al. 2018) further explained that fine particles of kaolinite distributed within the organic fraction of middlings correlate with easily leachable ion adsorbed REEs. In contrast, DCW contains hard-to-leach REE-bearing minerals, as indicated by SEM-EDS. Recoveries for LREEs and HREEs from DCW were 86%

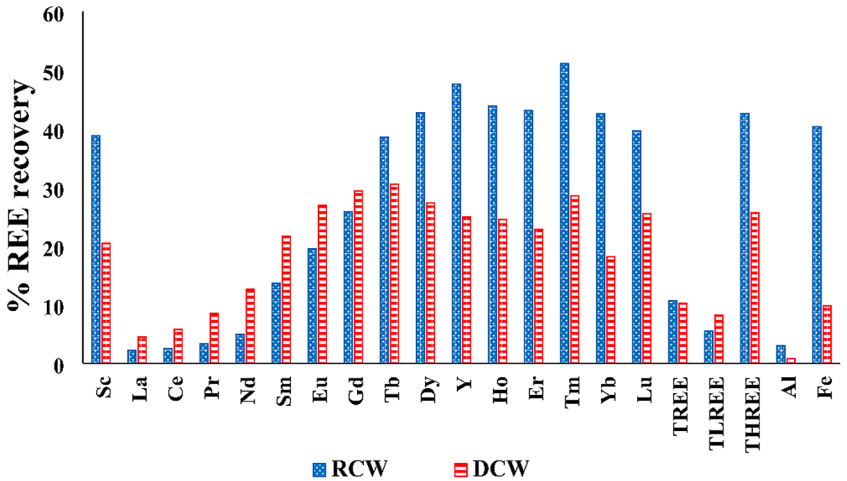

Fig. 8 REEs, aluminium (Al) and iron (Fe) recovery from run-of-mine (RCW) and discard (DCW) coal samples using direct hydrochloric acid leaching

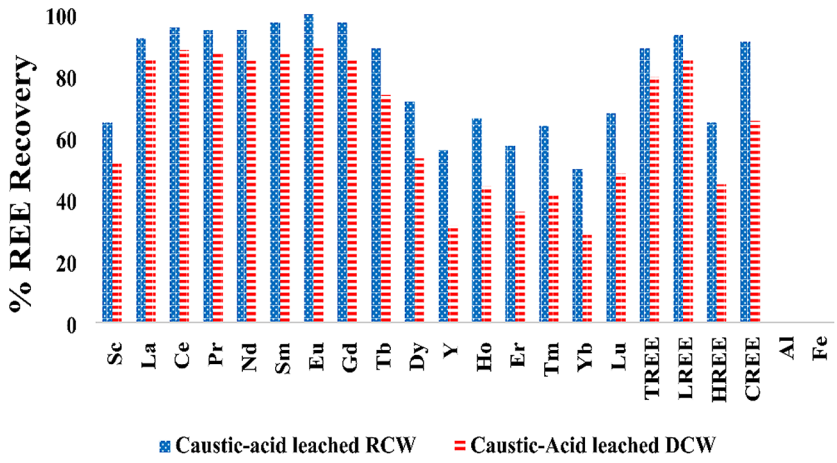

Fig. 9 REE recovery from run-of-mine (RCW) and discard (DCW) coal samples using ultrasound-assisted caustic-acid leaching

and 45%, respectively, with more than 60% recovery for critical rare earth elements (CREEs) such as Nd, Eu, and Tb.

The RE hydroxides formed Eq. (4) were solubilized to RE chlorides by the HCl solution Eq. (7).

$$\mathrm{RE(OH)}_{3(s)} + 3\mathrm{HCl}_{(aq)} \rightarrow \mathrm{RECl}_{3(aq)} + 3\mathrm{H_2O} \quad (7)$$

In contrast, acid-leaching of caustic-pre-digested RCW resulted in slightly higher recovery for LREEs (93.1%) and HREEs (64.9%), with 91% recovery for CREEs. RCW's higher organic matter content contributed to the enhanced extraction of REEs associated with finely dispersed kaolinite particles throughout the coal matrix. A significant discovery was the recovery of more than 90% of CREEs from RCW, attributed to the relatively higher quantities of recovered HREEs. The recovery of Sc from RCW, surpassing that from DCW, is noteworthy, given Sc's high selling price compared to other REEs (Gielen and Lyons 2022).

Similar to Yang et al. (2021), high recoveries of La, Ce, Eu, and Nd (more than 80%) from both coals suggest that LREEs in REE-bearing minerals likely have low crystallinity. Moreover, Gd and Tb recoveries from both RCW and DCW were relatively higher than other HREEs, possibly due to differences in the crystallinity of the minerals hosting the HREEs. The leachates from both coal samples showed trace concentrations of contaminants Al and Fe (less than 0.01% and 0.02%, respectively). Consequently, the difficulty in eliminating them during subsequent downstream processes will be diminished.

4 Conclusions

This study explored the influence of caustic pre-digestion on rare earth element (REE) recovery through hydrochloric acid leaching from run-of-mine (RCW) and discard coals (DCW) from South Africa's Waterberg Coalfield. Both coal samples exhibited high ash content, with a total rare earth element (TREE) concentration exceeding 200 ppm. SEM-EDS analysis revealed particles of Ce- and Nd-monazite and xenotime, liberated and embedded in clay minerals. Caustic digestion resulted in TREE enrichment in the coal samples and facilitated high TREE recovery during subsequent acid leaching. This enrichment was attributed to the dissolution of clay minerals, as indicated by the elevated aluminum content in the leachate. However, limited heavy rare earth elements (HREEs) and Sc were recovered due to their higher solubility in alkaline solutions. Efficient leaching with HCl recovered HREEs from RCW (42.6%) and DCW (25.7%), associated with clays finely distributed in the organic matrix. However, LREE recovery was below 10% for both coal samples, primarily due to their prevalence in acid-insoluble phosphate minerals. This low recovery resulted from the partial alteration of clays, releasing REEs during ion exchange along with trace amounts of Al. Significant Fe release occurred due to its high solubility in HCl solutions. Caustic pre-digestion followed by acid leaching led to the recovery of 86% of LREEs and 45% of HREEs from DCW. Critical elements (Nd, Eu, and Tb) exhibited recovery rates exceeding 60%. LREEs were recovered at 93.1%, HREEs at 64.9% from RCW, and 91% of CREEs. TREE recovery was higher for RCW (88.8%) compared to DCW (80%). The leachate showed very low concentrations of contaminants Fe and Al (less than 0.02%), and consequently, would reduce separation challenges during refining stages. Mineralogical characterization indicated that caustic pre-digestion partially dissolved clay minerals and decomposed REE-bearing minerals in both coals (caustic-digested and caustic-pre-digested-acid-leached). Monazite dominated in caustic-digested and caustic pre-digested-acid-leached DCW, while xenotime prevailed in caustic pre-digested-acid-leached RCW. Kaolinite content significantly decreased during caustic digestion, with increased pyrite and quartz indicating unfavorable leaching conditions for their dissolution. Consequently, Fe contamination in the REE leachate was

minimized. These findings emphasize the importance of coal pre-treatment for effective REE recovery. Finally, further investigation using harsher conditions, such as fine grinding and mechanical stirring during caustic pre-digestion might lead to enhanced REE recovery from these coals.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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