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ABSTRACT

The recovery of rare earth elements (REEs) from secondary resources, particularly coal-based materials, has recently received attention due to supply and demand imbalance. Research reported to date indicates that a high REE recovery can be realized when treating bituminous coal sources using strong acid solutions of approximately100 g/L or higher. This study introduces an approach to enhance the total rare earth recovery (TREE), especially for heavy rare earth elements (HREEs), from these coal sources at significantly lower acid concentrations. Based on the presence of REE minerals like monazite and xenotime, a detailed investigation was undertaken to quantify three pre-leach treatment methods, i.e., 1) roasting, 2) direct acid baking, and 3) acid baking after roasting. Roasting tests at 600 °C revealed that the recovery of light REEs (LREEs) was enhanced while the recovery of HREEs remained relatively unaffected. LREE and HREE recovery values of 38.3% and 21.3%, respectively, were achieved using a 50 g/L (0.5 M) sulfuric acid solution at 5% solid concentration and a solution temperature of 75 °C for 2 h. Comparatively, direct acid baking at 250 °C provided substantial increases in LREE and HREE recovery values to approximately 49.4% and 53.0%, respectively, using an equivalent acid dosage. Recoveries were maximized to 77.0% and 79.6% for LREE and HREE, respectively, by roasting followed by acid baking. Similar results were obtained from the treatment of a second bituminous coal source. Due to strong correlations between REE and Al recovery values, tests were performed on kaolinite and illite, which were prominent clay minerals within the source coals. These experiments revealed that the REE recovery improvements were likely a result of dehydroxylation of clays and subsequent release and decomposition of REE-bearing minerals such as monazite, xenotime and zircon.

1. Introduction

Rare earth elements (REE) are a group of 17 elements, including 15 lanthanides from lanthanum to lutetium as well as scandium and yttrium (Tyler, 2004), which have been found in approximately 200 minerals. So far, only minerals such as bastnaesite, monazite, xenotime, and REE-containing clays have been used to economically extract rare earth elements (REEs) (Kanazawa and Kamitani, 2006). The treatment of these REE-bearing minerals using pyrometallurgical processes is a common practice to obtain high REE extraction efficiency. For instance, bastnaesite, which is a rare earth fluorocarbonate mineral ((REE)FCO$_3$), is calcined between 400 and 500 °C to produce rare earth oxides, which can be leached conveniently using sulfuric acid (García et al., May 2020; Zou et al., Dec. 2018). REE-bearing minerals such as monazite and xenotime, which are primarily phosphate-based REEs (REE(PO$_4$)), are thermally and chemically stable in the form of crystalline phosphate

minerals (Kumari et al., 2015). Therefore, dephosphorization of monazite and xenotime is essential for the effective extraction of rare earth elements from both monazite and xenotime (Kumari et al., 2015). Several researchers have reported the decomposition of these REE-bearing minerals by treating them with chemicals such as sulfuric acid and sodium hydroxide at elevated temperatures (Demol et al., 2018; Demol et al., 2019).

Due to the increasing demand for REEs, various researchers have extensively investigated REE extraction from coal-based sources through similar metallurgical extraction processes (Sarswat, 2020; Dai, 2017; Honaker et al., 2017). Zhang and Honaker investigated REE leaching recovery from coarse refuse of Pocahontas No. 3 coal seam and reported only 14% total rare earth element (TREE) recovery using 120 g/L hydrochloric acid (HCl) (1.20 M) (Zhang and Honaker, 2019). The same researchers also performed a detailed study on the leaching behavior of plant feed material from western Kentucky No. 13 (WK No.

13), Illinois No. 6, and Fire Clay coal seams using 120 g/L HCl (1.20 M) and reported low TREE recovery from the untreated material. It was indicated that the low REE recovery from the untreated coal might be due to the finely disseminated REE-bearing minerals in coal, and thermal treatment, also referred to as calcination or blank roasting, is required to liberate those minerals (Zhang and Honaker, 2019; Honaker et al., 2019; Zhang and Honaker, 2020).

Yang et al. investigated the impact of thermal treatment on the thickener underflow of western Kentucky (WK) No. 13 seam material by blank roasting (thermal treatment without chemical addition) at 750 °C for 2 hrs. The LREE recovery obtained was approximately 74% using 120 g/L sulfuric acid (H_2SO_4). This corresponds to an improvement of 43 absolute percentage points in LREE recovery compared to non-thermally treated feedstock using 120 g/L sulfuric acid (1.2 M) (Yang et al., 2019). Furthermore, Zhang and Honaker reported an increase in LREE recovery (80–90%) by using 120 g/L HCl (1.20 M) for Pocahontas No. 3 coal source calcined at 600℃ compared to untreated coal (Zhang and Honaker, 2019). Similarly, Gupta also revealed a significant increase in the TREE recovery by using 120 g/L H_2SO_4 (1.20 M) after thermal treatment of different density fractions of both WK No. 13 coarse refuse (WK13-CR) and Fire Clay coarse refuse (FC-CR) (Gupta, 2021). It can be concluded that a thermal treatment step is essential to increase overall REE recovery from coal (Zhang and Honaker, 2019; Ji et al., 2020). This additional step converts the REEs to a more soluble form and/or liberates the REE-bearing minerals contained in the mineral matter (Zhang and Honaker, 2020).

Interestingly, all the work described previously reported a very low HREE recovery compared to LREEs. This signifies that HREEs are mainly associated with minerals that are difficult to leach (Zhang and Honaker, 2019; Yang et al., Mar. 2019; Gupta, 2021; Yang and Honaker, 2020). In an attempt to explain this leaching behavior of HREEs, Gupta showed indirect evidence of the association of HREEs present in heavy density fractions of both WK13-CR and FC-CR with clay minerals such as illite and kaolinite. They suggested a thermal treatment of coal with additives to extract HREEs from hard-to-leach minerals (Gupta, 2021). Numerous other researchers have also demonstrated a need for thermal pretreatment with a chemical additive to convert the RE minerals to a soluble form (Jha et al., 2016; Kumari et al., 2015; Merritt, 1990). The most common chemicals used in the thermal treatment are concentrated sulfuric acid, sodium hydroxide, and ammonium chloride (Zhang et al., 2015).

So far, high REE recoveries, particularly HREEs, reported in the literature from the chemical treatment of coal byproducts has only been achieved at significantly higher concentration of acids (Liu et al., 2015; Peiravi, 2017). In this study, a novel roasting technique using sulfuric acid is introduced to achieve high REE recovery from coal byproducts at significantly lower chemical dosages. The REE recoveries obtained from sulfuric acid baking are correlated with major contaminant Al to better comprehend the mode of occurrence of HREEs in coals, especially FC-CR. Furthermore, the novel acid baking technique is applied to a different coal source to ascertain the applicability of the method to other coal sources.

2. Materials and methods

2.1. Materials

The primary feedstock used in this investigation was acquired from the Leatherwood, an operating preparation plant treating Fire Clay (FC) seam coal in Perry Country, Kentucky, USA. The Fire Clay source is a high volatile, bituminous coal that occurs within the Central Appalachian coal basin. The plant utilizes dense media separation to reject out of seam dilutions into a coarse reject stream. A representative sample from the coarse refuse belts was collected every 20 min using inline sweep belt sweep samplers. The collected samples were stored in 200-liter barrels and sent to a commercial laboratory for density

fractionation using organic liquids. The weight percent distribution of coarse refuse samples in each density fraction and the ash and total REE contents on a dry basis are provided in Table 1. The material in each fraction was further processed through a jaw crusher and hammer mill to reduce the top particle size to 1 mm. Representative samples from the ground material of each density fraction were collected using rifflers and subsequently passed through a coal pulverizer to achieve a product with top particle size of 80 mesh (177 μm microns). Given the elevated REE contents on a dry ash basis in the lighter density fractions, the 2.2 float density fraction was reconstructed utilizing the %weight distribution data shown in Table 1 for the leaching experiments and used in the study.

The experiments were also performed on a second coal refuse sample produced from the cleaning of Baker (Western Kentucky No. 13) seam coal samples to evaluate the applicability of the novel acid baking technique on a different coal source. The Baker (WK No. 13) seam coal is a high volatile C bituminous coal that occurs within the Illinois coal basin. The sample was collected from the reject stream of a dense medium cyclone that cleaned the 75 × 1 mm size fraction of the run-of-mine material in a coal preparation plant. Upon receiving the sample, the material was density fractionated in the coal preparation lab of the University of Kentucky. The material was subsequently subjected to the same grinding and sampling stages as the FC Fire Clay coal samples, and representative samples were collected for testing. The coal characteristics weight distribution by density as well as ash and REE concentrations for WK#13 are also shown in Table 1.

Given the potential association of the REEs with clay minerals within the coal, the kaolinite and illite clay samples used in the study were purchased from Fisher scientific as a means of developing correlations with the REE modes of occurrence and leachability characteristics with respect to the finding from the leaching studies performed on the coal sources. The illite clay samples were also crushed using a jaw crusher, hammer mill, and finely ground with a pulverizer to produce a product with 80 mesh top size finer than 177 μm. The percentage distribution of REEs in the reconstructed coal feeds, and clay samples are shown in Fig. 1. A comparison of the REE distributions associated with the coal and clay sources indicates very similar values between the coal and clay sources. The concentrations of major contaminants in the different feedstocks used in this study are shown in Table 2. The XRF results indicated that silica and aluminum oxide accounted for more than 75% of the overall concentration in each sample used in this study (Table 2).

2.2. Methods

2.2.1. Experimental apparatus

A laboratory muffle furnace from Thermo scientific was used for thermal treatment of the samples prior to the leaching experiments. The ceramic crucibles utilized in calcination were purchased from Fisher scientific. The samples were calcined in ceramic crucibles with and

Table 1
Weight distribution by specific gravity (SG) as well as the dry-based ash content and total REE content on a dry ash basis for the Fire Clay and Western Kentucky coarse refuse samples.

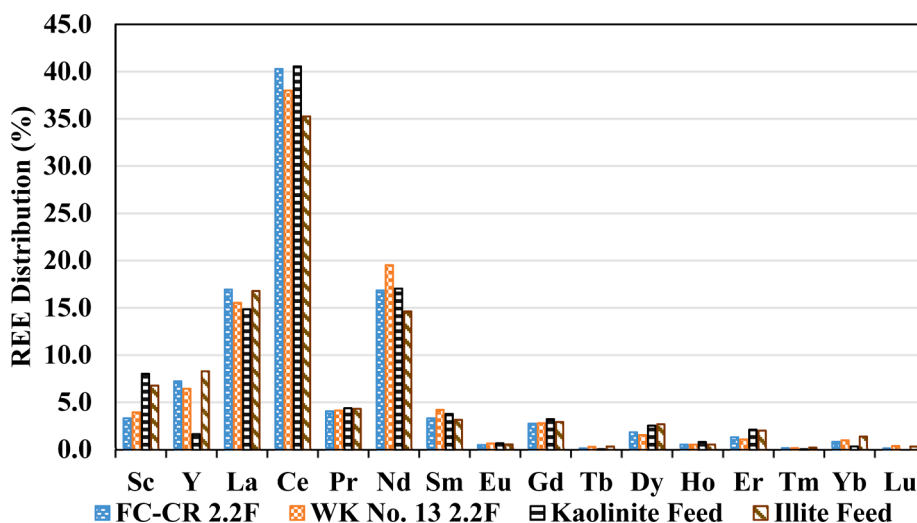| Density Specific Gravity Fraction	Weight (%)	Dry Ash (%, ad)	TREE Concentration (ppm, ad)
Fire Clay			
1.60 Float	3.0	28.3	949
1.60 × 1.80	2.9	43.1	711
1.80 × 2.00	2.3	59.9	667
2.00 × 2.20	4.2	72.9	614
2.20 Sink	87.5	90.5	314
Western Kentucky			
1.80 Float	1.1	22.3	522
1.80 × 2.00	1.0	56.3	621
2.00 × 2.20	2.9	66.1	518
2.20 Sink	95.1	91.0	316

Fig. 1. Percentage relative REE distribution in different coals and clay samples used in the study.

Table 2

Distribution of major and minor phases as detected by XRF in the different feedstocks used in this study (Illite LOI = 5.82%, Kaolinite LOI = 14.14%).

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	BaO (%)	SrO (%)	SO_3 (%)
FC-CR 2.2F (dry ash basis)	66.3	26.47	2.95	0.65	0.73	0.01	<LOD	2.58	0.11	1.65	0.08
WK No. 13 2.2F (dry ash basis)	52.36	26.2	13.19	0.86	0.93	0.02	<LOD	2.87	0.34	1.16	0.06
Illite Feed (whole mass basis)	62.01	18.38	4.59	1.01	2.51	0.04	0.27	5.97	0.1	–	–
Kaolinite Feed (whole rock basis)	43.25	40.85	0.44	0.12	0.02	0	0.1	0.17	0.03	–	–

without the chemical addition of a chemical in static atmospheric conditions. For blank roasting tests, the coal sample was added to each crucible for roasting without any chemical additives. For acid baking tests performed on coal and clay samples, the samples were thoroughly mixed with a fixed concentration of 98% trace metal grade (TMG) sulfuric acid and thermally treated at the required temperature. The furnace was allowed to cool down to room temperature prior to sample extraction.

Leaching experiments were conducted in a three-neck round bottom flask with a total reflux condenser to minimize volume loss. A water bath was used to control the leaching temperature. A constant stirring speed of 500 rpm was used for solid suspension in the solution. The samples collected at the end of each test were cooled down to room temperature and subsequently centrifuged for 10 min at 4000-rpm for solid–liquid separation. The leachate was then filtered using a 0.45 μm PVDF membrane filter. The solution pH was measured using the Orion™ Versa Star Pro™ pH meter from Thermo Scientific. The residual slurry solids were filtered using 5 μm pore size filter paper under vacuum, and the solids residue from the tests was washed thoroughly with deionized water to remove any residue leachate. The filter cakes were then dried in an OMS180 Heratherm oven at 60 °C for 12 h. Afterward, the dry solids were weighed and the values were recorded. Each test was duplicated to establish repeatability.

2.2.2. Experimental procedure

Leaching experiments were performed on un-calcined samples to establish a baseline leaching recovery performance. For the acid baking tests, a 100 ml volume of 50 g/L H_2SO_4 (0.5 M) was preheated to 75 °C. Next, a 5-gram coal sample was added into the lixiviant and leached at 75 °C for 2 h. As previously defined, the reference to blank roasting refers to the thermal treatment of coal without any chemical addition. The temperature range of 100–1000 °C for blank roasting was selected to evaluate the association of REE recovery with major mineral decomposition within this temperature range. The calcinated samples were then leached under standard conditions using 100 ml of 50 g/L

H_2SO_4 (0.5 M) with 5 g of solid at 75 °C for 2 h. This sulfuric acid concentration was selected to provide a direct comparison between blank roasting and acid baking tests.

For the direct acid baking tests, 5 g of raw coal was mixed with 5 g of 98% trace metal grade sulfuric acid in a crucible and roasted in the muffle furnace at various temperatures for 2 h. The temperature range of 100–300 °C as well as the values for coal-to-acid ratio, calcination temperature, and time were selected based on previously reported acid baking studies conducted on monazite (Demol et al., 2018; Berry et al., 2018). Subsequently, the acid-baked material was leached with 100 ml of deionized water at 75 °C for 2hrs. The reference to 2nd stage acid baking refers to the acid baking performed on a pre-calcinated coal feed at 600 °C. This temperature was selected based on the optimal leaching performance achieved in the blank roasting tests and previously reported findings (Gupta, 2021). Standard leaching conditions were maintained throughout the study which included constant values for sulfuric acid dosage, temperature, solid-to-liquid ratio, and time to allow a direct comparison of the results obtained from no acid baking treatment (blank roasting), direct acid baking, and 2nd stage acid baking.

2.2.3. ICP -OES analysis

The pregnant leachate solution obtained from each test was analyzed using an Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES). In preparation for the analysis, solid samples were ashed using a LECO TGA-701 thermogravimetric analyzer followed by digestion. The ash content was recorded and utilized to calculate the elemental concentration in solid samples on a whole mass basis. The digestion was performed using aqua regia and hydrofluoric acids following a modified ASTM D6357-11 method. The concentration values for REEs, Al, Fe, Ca, Th, Li, and Si were used to calculate elemental leaching recovery values (%) using the following formula:

$$LeachingRecovery(\%) = \frac{c_L * V_L}{c_L * V_L + c_{SR} * m_{SR}} * 100$$

where c_L (in mg/L) and c_{SR} (in mg/kg) are elemental concentrations

in the leachate solution as received and solid residue on a whole mass basis, respectively; V_L (in ml) is the volume of pregnant leachate solution used; and m_{SR} (in grams) is the weight of solid residue on a whole mass basis.

2.2.4. TGA-DSC analysis

Thermogravimetric and differential scanning calorimetry (TGA-DSC) analyses were performed on the clay samples using LINSEIS TGA-DSC Simultaneous Thermal Analyzer (STA) to better understand the impact of calcination temperature on the mineralogy transformation. A sample weighing approximately 50 mg was placed in a tared alumina crucible and mounted on the platinum–rhodium thermocouple. An identical empty crucible was put in the reference position of the DSC thermocouple. The chamber was vacuumed and refilled with an inert gas (N_2). Subsequently, the furnace was then heated to 1000 °C at a rate of 10 °C/min under oxidizing conditions while continuously measuring the weight loss and heat flow at 1-sec intervals. The LINSEIS data evaluation software was used to calibrate and evaluate the data.

2.2.5. XRD analysis

X-ray diffraction (XRD) analysis was performed using a Bruker Advance D8 instrument. Coal-based minerals from the collected samples as well as the clay samples were compressed into a disc pellet. The scanning was performed from 10-degree to 70-degree at a scanning speed of 1.5-degree/min. The XRD spectra were analyzed using DIFFRAC software to determine the major mineral composition.
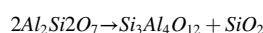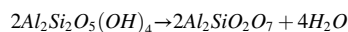
3. Results and discussion

3.1. Blank roasting

The leaching recoveries of total, light, and heavy REEs along with major contaminants are shown in Fig. 2 when treating the 2.2 SG float fraction of the Fire Clay coarse refuse. The light REEs (LREE) refer to Sc, La, Ce, Pr, Nd, Sm, Eu and Gd, and the heavy REEs (HREE) refer to Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Scandium was considered a light REE due to its molecular weight relative to other REEs. However, since scandium has an ionic radius similar to HREEs, it may contribute towards its somewhat similar physio-chemical properties as heavy REEs. The results in Fig. 2 indicate a positive impact of calcination on the recovery of rare earth elements. The overall recovery increased from 18.6% to 36.3% when the temperature was increased from 100 to 600 °C. This was probably due to the oxidation of REEs into a more soluble rare earth

oxide (REO) at the current leaching condition (Gupta, 2021). The recovery of individual elements shown in Fig. 3 indicates that LREEs respond better to thermal treatment than HREEs. The recovery of several heavy rare earth elements, namely Y, Dy, Er, Yb, slightly increased in the 100–600 °C temperature range, but Gd and Ho were unaffected by thermal treatment. This indicates that HREEs are likely associated with minerals that are either very difficult to leach and/or not liberated by simple thermal treatment. Therefore, more rigorous conditions such as acid baking were required to extract the HREEs. Interestingly, the increase and decrease of REE recovery correlate well with the Al recoveries over a range of thermal treatment temperatures, especially for the HREEs, which indicated a possible association between HREEs and clay minerals. A significant rise in the scandium recovery was also noted with an increase in the Al recovery. Zhang et. al. has reported the presence of scandium in the Al-O octahedrons of kaolinite (Zhang, et al., 2017). Additionally, Arbuzov et al. found that the amounts of scandium associated with the minerals resistant to an acid attack were comparable to the minerals decomposed in the acids (Arbuzov and Maslov, 2015). Therefore, it is probable that a portion of Sc along with HREEs were entrained within the clay structure, which were released through the dehydroxylation of clays such as kaolinite and illite.

The thermal treatment of coal up to 300 °C did not impact either REEs or Al recovery, likely owing to the high stability of kaolinite towards acids. The recovery of REEs gradually increased from 21% to 36% while increasing the roasting temperature from 400 °C to 600 °C. Kaolinite typically converts to its meta kaolinite form at a temperature of 500–600 °C, which has been found to dissolve relatively easily compared to its parent kaolinite (Gao et al., 2016). The results indicate that approximately 21% of the REEs are likely not associated with clay minerals, whereas about 16% of REEs were released due to clay decomposition after calcination.

A sharp decrease in the Al recovery was observed above 900 °C, which was likely due to the sintering of clays through the conversion of *meta*-kaolinite to mullite. Edomwonyi et al. proposed the following series of reactions for the conversion of kaolinite to *meta*-kaolinite and eventually mullite (Edomwonyi-Otu et al., 2013):

$$2Al_2Si_2O_5(OH)_4 \rightarrow 2Al_2SiO_2O_7 + 4H_2O$$

$$2Al_2Si2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2$$

$$Si_3Al_4O_{12} \rightarrow 2Si_2Al_6O_{13} + 5SiO_2$$

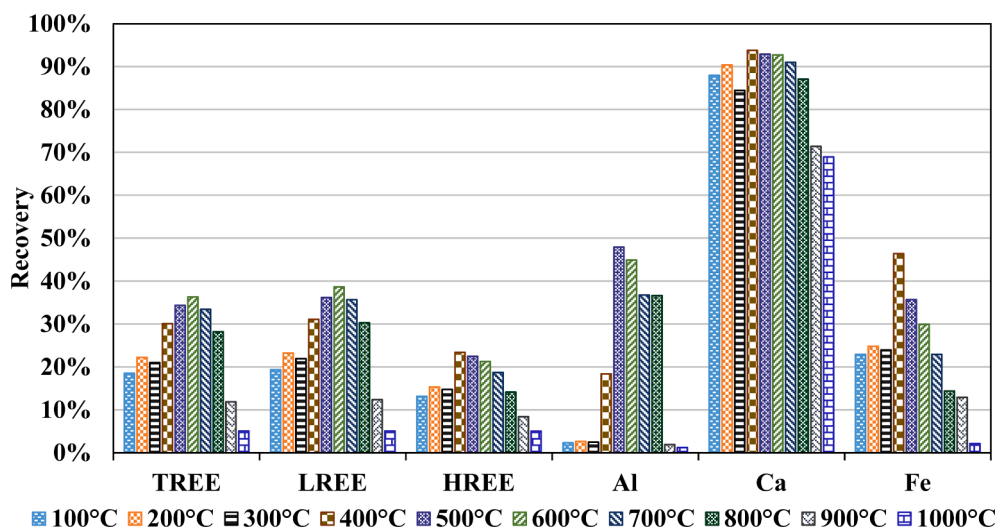Mullite is highly stable in strong acid solutions (Gupta, 2021; Liu

Fig. 2. Leaching recovery of REEs and major contaminants obtained from the thermal treatment of Fire Clay S.G. 2.2 float material from 100 to 1000 °C followed by leaching with 50 g/L H_2SO_4 at S/L of 1/20 and 75 °C for 2hr.
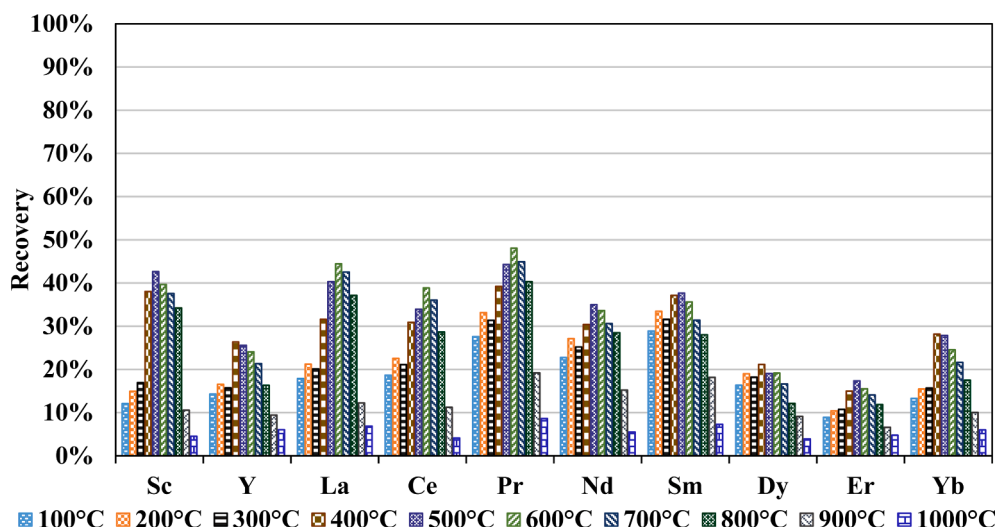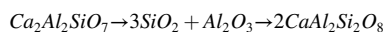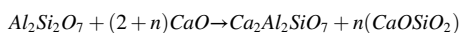
Fig. 3. Leaching recovery of individual REEs from the thermal treatment of fireclay S.G. 2.2F material from 100 to 1000 °C followed by leaching with 50 g/L H_2SO_4 at S/L of 1/20 and 75 °C for 2hr (Gd and Ho were excluded because of insignificant recovery).

et al., 2015). Calcium recovery was high and remained unaffected by an elevation in calcination temperature up to 800 °C. The primary source of Ca ions in the pregnant leachate solution was calcite which was naturally present in the coal and readily soluble in acid (Sanders and Gallagher, 2002; Dash et al., 2000). The calcite has been reported to decompose between 600 and 800 °C into calcium oxide and carbon dioxide through following reaction (Rodriguez-Navarro et al., 2009):

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$
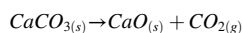
Various researchers have reported the formation of new *meta*-stable phases through the interaction between the calcium oxide resulting from the decomposition of the calcite and clays. The new phases were reported to be wollastonite, anorthite, and gehlenite (Rodriguez-Navarro et al., Apr. 2009; Ghosh; Lenarda et al., 2007; Allegretta et al., 2016). The formation of these new aluminosilicate phases might be the reason for a drastic decrease in the Ca recovery observed above 800 °C. Traore reported the following reactions for the formation of anorthite and gehlenite (Traoré et al., 2003):

$$Al_2Si_2O_7 + (2+n)CaO \rightarrow Ca_2Al_2SiO_7 + n(CaOSiO_2)$$

$$Ca_2Al_2SiO_7 + 3SiO_2 + Al_2O_3 \rightarrow 2CaAl_2Si_2O_8$$

The Fe contamination in the pregnant leach solution (PLS) increased in the 400–500 °C range due to the decomposition of pyrite into an intermediate iron oxide product that is highly soluble. At higher temperatures, the intermediate iron oxide transforms to α-hematite, which has lower solubility under the current leaching condition, thereby resulting in a decrease in recovery (Gupta, 2021; Mitchell, 2002). The Spearmen's correlation coefficient values for the REEs and major contaminants with temperature are shown in Table 3. The data has been divided into two parts based on the impact of calcination temperature on the recovery of REEs. The correlation coefficient with temperature in the 100–600 °C range shows a strong positive correlation. A strong positive correlation coefficient of LREEs with temperature compared to HREEs reiterates the conclusion drawn earlier that thermal treatment primarily impacts the LREEs. A strong negative correlation observed for both REE groups and

the contaminants shows the adverse impact of clay sintering in this temperature range.

3.2. Acid baking

The thermal treatment of REE-bearing minerals has been universally applied to extract REEs (Kumari et al., 2015). However, simple thermal treatment has been reported to be insufficient for some REE-containing minerals. Monazite and xenotime, in particular, have a significantly higher decomposition temperature (>1000 °C) (Xue, 2010). Therefore, the thermal treatment of monazite/xenotime with a chemical is commonly used to transform REEs into a soluble form (Kumari et al., 2015).

It has been reported that one of the primary rare earth minerals in the Fire Clay coal source is monazite (Yang, 2019), which may explain the relatively low REE leaching recovery values obtained after calcination and leaching using a 120 g/L (1.2 M) H_2SO_4 solution. As such, acid baking tests were performed on the 2.2 SG float fraction of a Fire Clay coarse refuse sample to assess the potential for improving REE recovery. As per literature following reaction takes place between REE-phosphates and sulfuric acid to form water-soluble REE-sulfates (Nazari and Krysa, 2013; Habashi, 2013):

$$2REPO_4 + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 2H_3PO_4$$
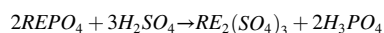
3.2.1. Direct acid baking

The initial acid baking experiments performed on the un-calcined 2.2 SG float material were performed over a range of treatment temperatures from 100 °C to 300 °C with the knowledge of 250 °C being an optimum for the treatment of monazite (Safatle and de Oliveira, 2020). Fig. 4 shows that the recovery values for both LREEs and HREEs were maximized at 150 °C. Compared to blank roasting (no chemical treatment), which results in a TREE recovery of 36.3% (Fig. 2), direct acid baking without a pre-roast step increased recovery to 64.5% TREEs at a baking temperature of 150 °C using the same quantity of H_2SO_4, i.e., 50 g, which is equivalent to 50 g/L (0.5 M) concentration used in the leaching of blank roasted material. Even though both LREEs and HREEs show an increase in recovery, the absolute percentage point increase in HREE recovery was considerably higher than LREEs. The HREE recovery increased from 21.3% after calcination at 600 °C to 64.0% following the acid baking treatment at 150 °C. This reiterates the conclusion drawn earlier that HREEs in the Fire Clay coal high specific gravity fractions are associated with minerals that require thermal treatment with chemicals to decompose as opposed to high-temperature calcination only. It is

Table 3
Correlation coefficients for the blank roasted samples with temperature.
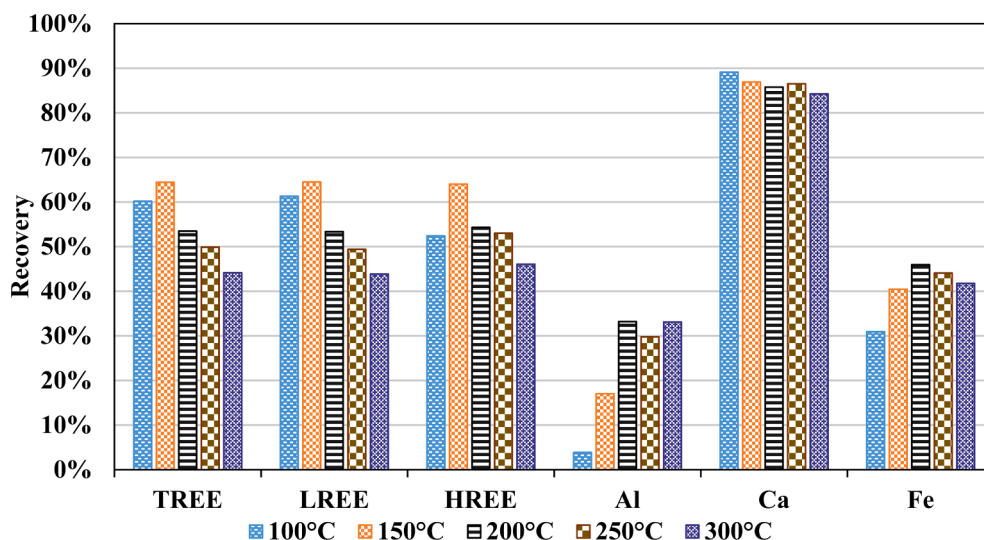
	LREE	HREE	Al	Ca	Fe
Temperature (100–600 °C)	0.953	0.790	0.901	0.628	0.742
Temperature (700–1000 °C)	−0.976	−0.975	−0.955	−0.975	−0.982

Fig. 4. Recovery of REEs and major contaminants obtained by direct acid baking of raw coal feed from 100 to 300 °C at 1:1 coal to acid ratio followed by leaching with 100 ml DI water at 5% S/L, 75 °C for 2hrs.

noted that the recovery values for individual rare-earth elements like gadolinium and dysprosium, which were not significantly improved by calcination at 600 °C, were substantially elevated to values of approximately 64.2% and 74.5%, respectively, from acid baking treatment at 150 °C.Fig. 5.

An additional positive outcome of direct acid baking treatment is the reduction of Al recovery under the optimum conditions for REE extraction relative to the recovery value realized from blank roasting. Total REE recovery is about 28 percentage points higher relative to the values realized by roasting at 600 °C while Al recovery is 28 percentage points lower. This finding implies that complete decomposition of the clays is not necessary to effectively leach most of the LREEs and HREEs from the associated minerals. As per literature, the calcination of kaolinite with sulfuric acid results in the formation of aluminum sulfate complexes, whereas the calcination of muscovite/illite with sulfuric acid produces potassium aluminum sulfate through dehydroxylation and subsequent decomposition of the respective clays (Colina et al., 2002; Han, 2020). This indicates that Al recovered at higher temperatures in the direct acid baking may primarily be due to the decomposition of illite/muscovite and some kaolinite. The increase in REE recovery using

direct acid baking is likely reflective of the amount of rare earth-bearing minerals that are either liberated or sufficiently exposed to the high-strength acid and decomposed under the given baking temperatures.

As previously mentioned, the maximum REE recovery occurs at an acid baking temperature of 150 °C. At 100 °C, total REE recovery is 5% lower while heavy REE recovery is 12% lower. The lower recovery values of REEs, as well as Fe and Al, occur despite the lowest pH solution at a pH value of 0.8 and a maximum weight loss of around 59%, as shown in Fig. 6. As the acid baking temperature was raised above 150 °C, the acidity of the final solution reduced significantly, reaching an equilibrium pH value of 2.4 partly due to evaporation of the H_2SO_4, which reduced mass loss to approximately 30% (Kim and Osseo-Asare, 2012). Han and Kim studied the rare earth stability in sulfate and phosphate systems and concluded that REEs precipitate as REE-phosphates in solutions having a pH between 1 and 3 in the presence of sulfate and phosphate anions. Since the increase in pH in this study was from 0.85 to 2.40, it is likely that this increase in the pH caused the REEs to precipitate as REE-PO_4, which is one possible contributing factor to the decrease observed in the REE recovery (Han and Kim, 2021; Tang et al., 2017).
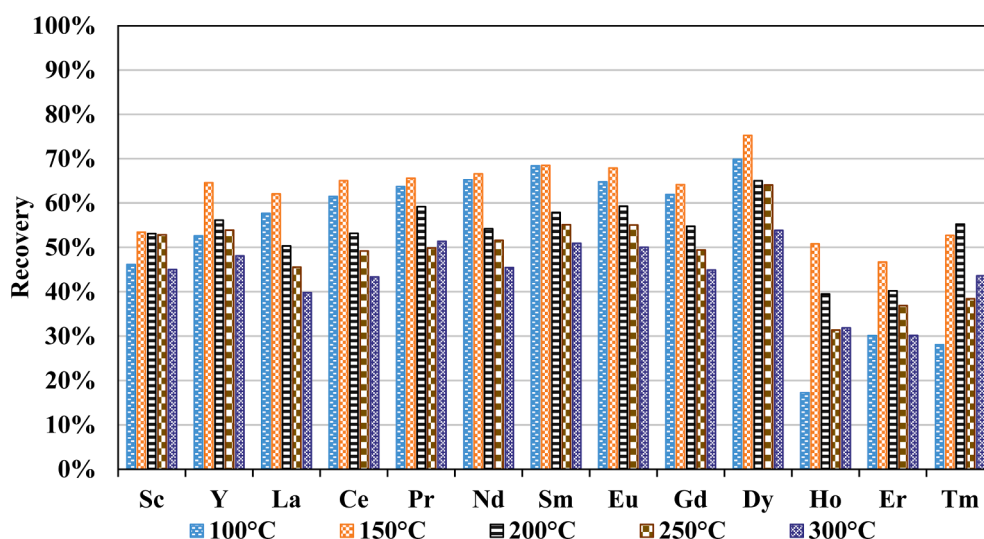

Fig. 5. Recovery of individual REEs obtained by direct acid baking of raw coal feed from 100 to 300 °C at 1:1 coal to acid ratio followed by leaching with 100 ml DI water at 5% S/L, 75 °C for 2hrs.
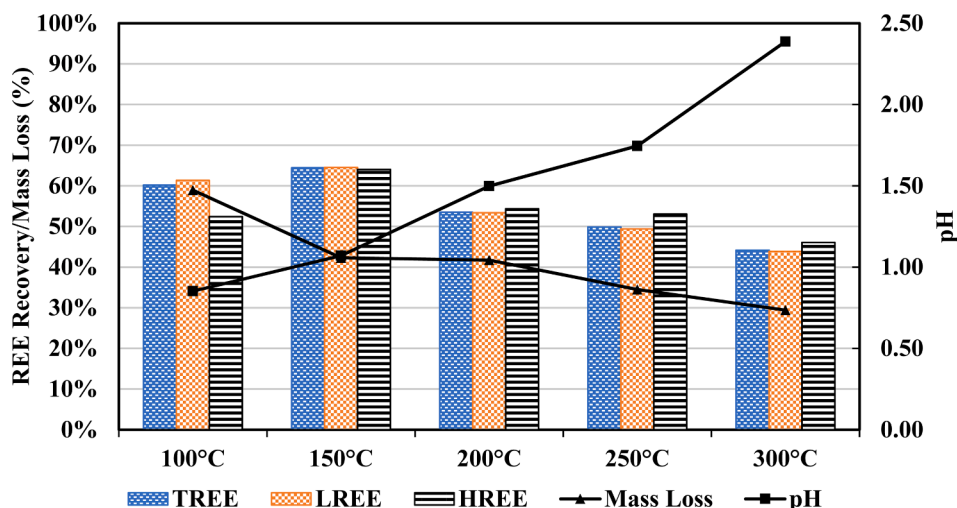
Fig. 6. REE recovery, mass loss, and pH at various temperatures observed in the leaching of direct acid baked product at 1:1 coal to acid ratio for 2 hrs with 100 ml DI water at 5% S/L, 75 °C for 2hrs.

An increase in Al recovery with the elevated baking temperature may be due to the acid activation of clays present in the coal. Various researchers have reported the delamination of clay particles, mineral impurity removal, and destruction of the external layer by acid treatment of clays. As a result, an increase in the surface area, pore volume, and surface activity is reported (Yang, 2017; Scott et al., 2017). Scott et al. discovered REE phosphate minerals within the interparticle pore space of the underclays of a coal seam (Ji et al., 2022). Based on XRD evidence presented later in this publication, acid activation of clays may involve the dissolution of aluminum through the reaction of aluminum with sulfuric acid under elevated baking temperatures to produce potassium aluminum sulfate.

The Spearmen's correlation coefficient shown in Table 4 also shows a strong positive correlation between aluminum and REEs recovery with baking temperature. On the other hand, LREE recovery has a strong negative correlation with temperature, whereas the HREEs appear to have a relatively weaker negative correlation coefficient with temperature. This finding agrees with the general observations previously presented and discussed in this manuscript.

3.2.2. 2nd stage acid baking

As mentioned previously, the 2nd stage acid baking treatment involves pre-calcination of the material at 600 °C followed by acid baking with sulfuric acid at a given temperature. The hypothesis for this treatment approach is that the pre-calcination step will liberate clay particles from carbon material and dehydroxylation of the clays resulting in exposure of unliberated REE mineral particles thereby allowing better exposure to the acid during the acid baking treatment.

As shown in Fig. 7, the TREE recovery increased from a value of 36.3% with pre-calcination treatment only to 64.5% using direct acid baking and 83.1% after acid baking the pre-calcination product. Similar to direct acid baking, a rise in the baking temperature caused evaporation of the sulfuric acid which increased the pH of the leach solution. As a result, a slight decrease in light REE recovery occurred as shown in Fig. 7 which may be explained by the precipitation of the light REEs as RE-PO$_4$ (Han and Kim, 2021). However, HREE recovery was increased

from 45.7% under 100°C to a maximum value of 79.6% at the highest temperature tested. The HREE recovery increase with baking temperature seems to correlate well with aluminum recovery which implies that the HREE recovery gain may be linked to the breakdown of the aluminum silicates and dissolution of the aluminum. This observation provides support for the hypothesis pertaining to the role of clay dehydroxylation and the subsequent exposure of REE-containing minerals. The incremental recovery gain from 64.0% obtained from direct acid baking to 79.6% achieved from acid baking the pre-calcination product likely is associated with minerals like xenotime and zircon that are locked in the aluminum–silicate inner layers (He et al., 1995).

As expected, Al recovery obtained from 2nd stage acid baking is significantly higher than the direct acid baking treatment (Fig. 8). As referenced previously, calcination at 600 °C converted kaolinite to metakaolinite. Subsequently, the decomposed aluminum silicate compounds react with sulfuric acid during acid baking to form aluminum sulfate, which is easier to dissolve in solution during leaching. In both direct acid baking and 2nd stage acid baking scenarios, Ca recovery remains unaffected by a rise in temperature, probably owing to the high solubility of calcite. In regards to iron, recovery increased by about 10 percentage points when using 2nd stage acid baking and was elevated by about 5 percentage points when increasing the acid baking temperature. This finding may be a result of improved liberation of the naturally occurring, finely disseminated pyrite and improved dissolution at elevated temperatures.

Fig. 9 provides the element-by-element recovery as a function of the acid baking temperature. It is interesting to note the trends from La through Yb including Sc and Y. Starting from La, there is a significant recovery decrease with an elevation in baking temperature and the delta recovery change approaches zero through Sm. Starting with Gd and including Y, recovery increases by varying amounts with an elevation in baking temperature. This suggests multiple mechanisms are occurring. In regards to the recovery decline observed for the LREEs, a possible explanation could be the substitution of the REEs for calcium during the formation of gypsum, which has been previously reported (Arbuzov and Maslov, 2015; Meinhold et al., 1992). This substitution occurs due to similar ionic radii between the LREEs and Ca with an exception to Sc. Regarding the increased recovery of the HREEs, acidity is higher and solids loss is greater under the elevated baking temperatures relative to the direct acid baking results. The lower pH values relative to direct acid baking may be explained by the consumption of the sulfuric acid by the dehydroxylation of the clays. By roasting the material prior to acid baking, the clays are dehydroxylated, and decomposition occurs without the use of acid. As such, acid is more effectively utilized for the

Table 4
Spearman's correlation coefficients for direct acid baking and 2nd stage acid baking with temperature.

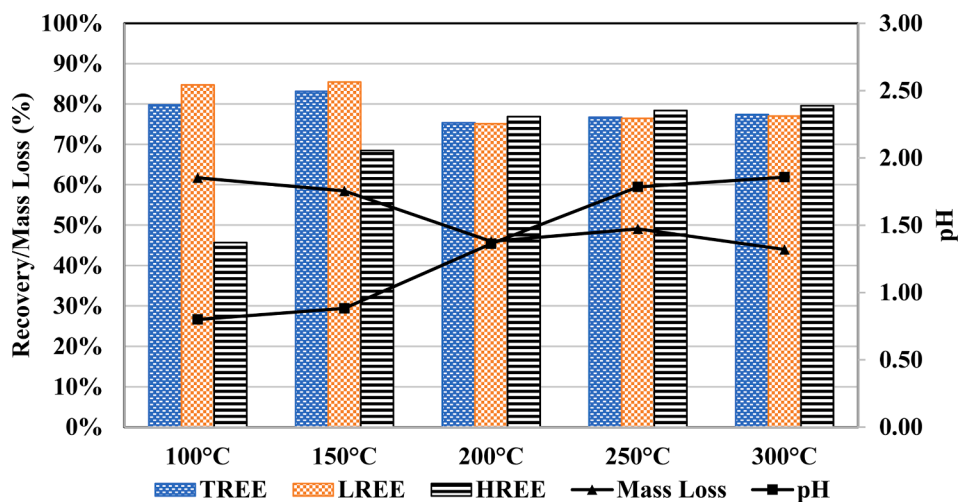|	LREE	HREE	Al	Ca	Fe
Direct Acid Baking	−0.9	−0.4	0.7	−0.9	0.6
2nd Stage Acid Baking	−0.6	0.9	1	−0.7	0.2

Fig. 7. REE recovery, mass loss, and pH at various temperatures observed in the leaching of 2nd stage acid baked product at a 1:1 coal to acid ratio for 2 hrs with 100 ml DI water at 5% S/L, 75 °C for 2hrs.
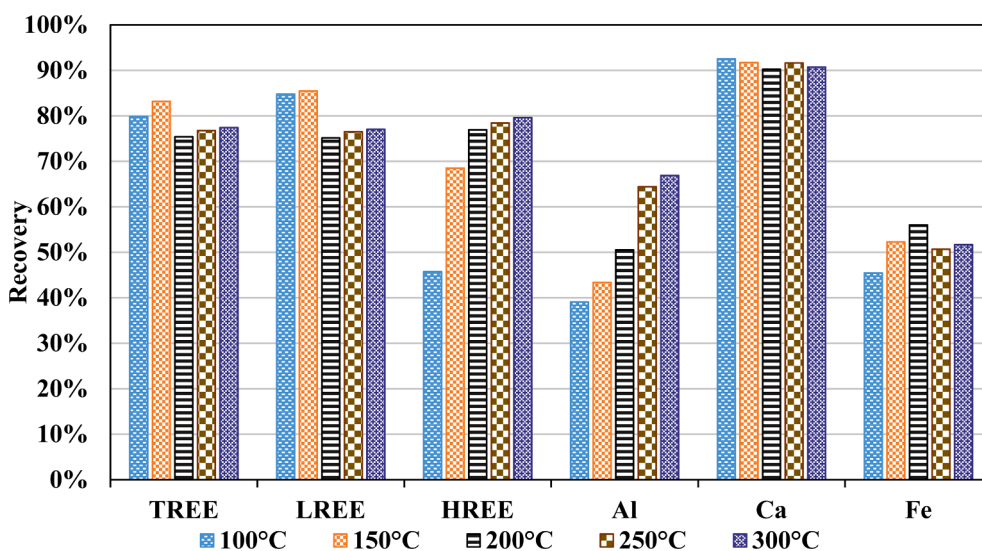

Fig. 8. Impact of 2nd stage acid baking temperature on leaching recovery of REE and major contaminants.
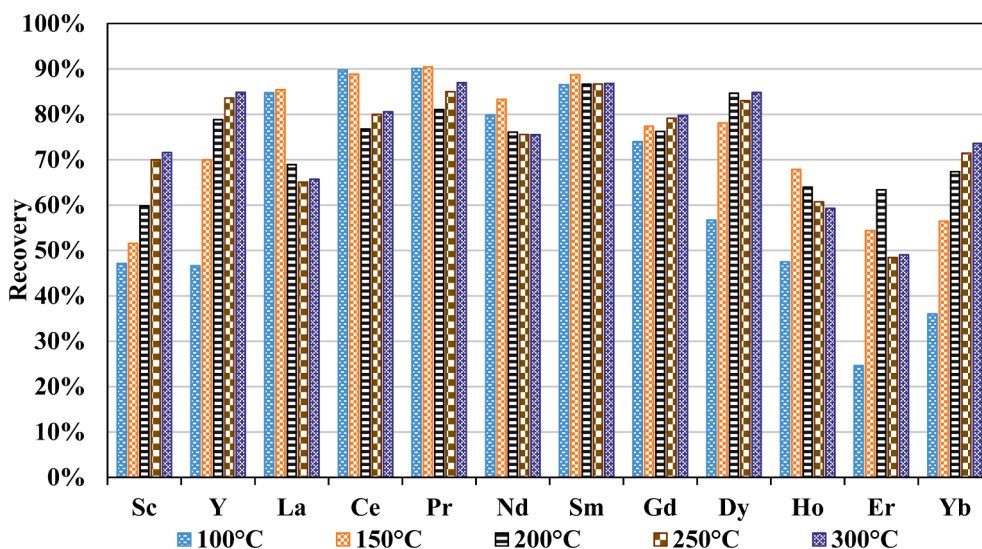

Fig. 9. Impact of 2nd stage acid baking temperature on leaching recovery of individual REEs.

extraction of REEs from the associated minerals. The improved REE recovery with acid baking temperature is likely due to higher sulfuric activity and subsequent decomposition of the HREE minerals such as xenotime (Demol et al., Aug. 2018). Interestingly, Sc recovery followed a similar trend as the HREEs, which may be due to the association of Sc with minerals like zircon as previously reported (He et al., 1995).

3.3. Clay mineral testing

The correlations between REE and Al recovery from the acid baking treatment tests suggested that REE minerals containing heavy REEs, in particular, may be locked within the clay minerals. Common clay minerals in coal-based material are kaolinite and illite, as indicated in the XRD findings in Fig. 10. In an effort to study the acid baking effect on this mode of occurrence, tests were performed using clay samples of both mineral types. Direct leaching of the clay samples without pre-treatment resulted in statistically insignificant REE recovery from the kaolinite sample, as shown in Fig. 11. On the other hand, 10% of the light REEs and 20% of the heavy REEs were extracted from the illite sample under the same conditions (Fig. 12). Very similar results were obtained for Al.

After calcining at 600 °C, the TREE recovery for kaolinite increased from 2.81% to 84.93%, which was primarily due to the light REE recovery (Fig. 11). Heavy REE recovery was only 28.5%. The near 90% recovery of the light REEs corresponds to an increase in Al recovery of 52 percentage points, which seems to indicate that the thermal treatment enhanced the ability to decompose both the kaolinite and the light REE containing minerals under the standard leach conditions. Evidence provided by XRD data shown in Fig. 13 indicates that de-hydroxylation of the kaolinite to form metakaolinite occurred when calcined at 600 °C as the kaolinite peak is absent from the XRD graph.

Conversely, the illite crystal structure was not destroyed during 600 °C roasting treatment, as shown in Fig. 14, which aligns with the findings from other studies (Belver et al., 2002). As a result, Al recovery remained low at around 10%. Interestingly, heavy REE recovery remained relatively unchanged at 24%, while the light REE recovery increased from 10.51% to 59.54% (Fig. 12). This finding suggests that the majority of the light REEs have a different mode of occurrence relative to the heavy REEs and that the heavy REEs potentially have an association with the illite.

The thermal behavior of both kaolinite and illite clays is shown in Figs. 15 and 16, respectively. There are two characteristic exothermic peaks observed at 545 °C and 992 °C from the calcination of the kaolinite sample. The first endothermic peak may be due to the de-hydroxylation of kaolinite to its metakaolin form, which has been reported to occur between 450 and 650 °C(Gupta, 2021; Ilić et al., 2010; Earnest, 1991) and can be represented by the following reaction (Colina et al., 2006);

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O$$
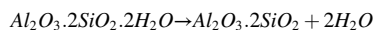
The second exothermic peak at 992 °C corresponds to the conversion of metakaolinite to mullite (Ilić et al., 2010; Murat and Driouche, 1988). The reactions resulting in the formation of these new phases have been described previously in the Section 3.1. In the case of illite, TGA-DSC results revealed two reaction peaks at 580 °C and 815 °C. Earnest, in an investigation on illite clay, found that the first peak corresponds to the de-hydroxylation process (Colina et al., 2001). According to Gupta, the second peak observed at 820 °C was likely due to the destruction of the illite structure (Gupta, 2021). He et al. also indicated that illite is more stable towards thermal treatment compared to kaolinite (Belver et al., 2002). The XRD analysis performed on the 600 °C calcined coal and illite samples shows the illite/muscovite peaks, which implies that de-hydroxylation did not destroy the crystal structure of illite, reaffirming the findings of previous researchers (Gupta, 2021; Belver et al., 2002). Interestingly, the de-hydroxylation temperature ranges of kaolinite and illite samples correspond to an increase in the recovery of REEs and Al in the same temperature range as the Fire Clay coal samples shown in Fig. 2. Since both clay mineral types have been detected in Fire Clay seam coal by XRD analysis (Fig. 10), this points towards a potential association between REEs and Al.

A comparison of the direct and 2nd stage acid baking treatment on both clay mineral types indicates that acid baking treatment primarily impacts the HREE recovery (Figs. 11 and 12). Furthermore, the heavy REE recovery improvements can be directly correlated with Al recovery. These findings are very similar to the results obtained from acid baking of the Fire Clay coal sample after roasting at 600 °C (Fig. 7). A comparison of the recovery trends between heavy REEs and Al shows better similarities between the coal-based material and kaolinite in which roasting to dehydroxylate the clays followed by acid baking provides the highest recovery values.

As previously discussed, the impact of 2nd stage acid baking on HREE seems more profound on kaolinite samples compared to illite. This finding may be due to the transformation of kaolinite into metakaolinite, which is more susceptible to acid attack, resulting in an increase in both
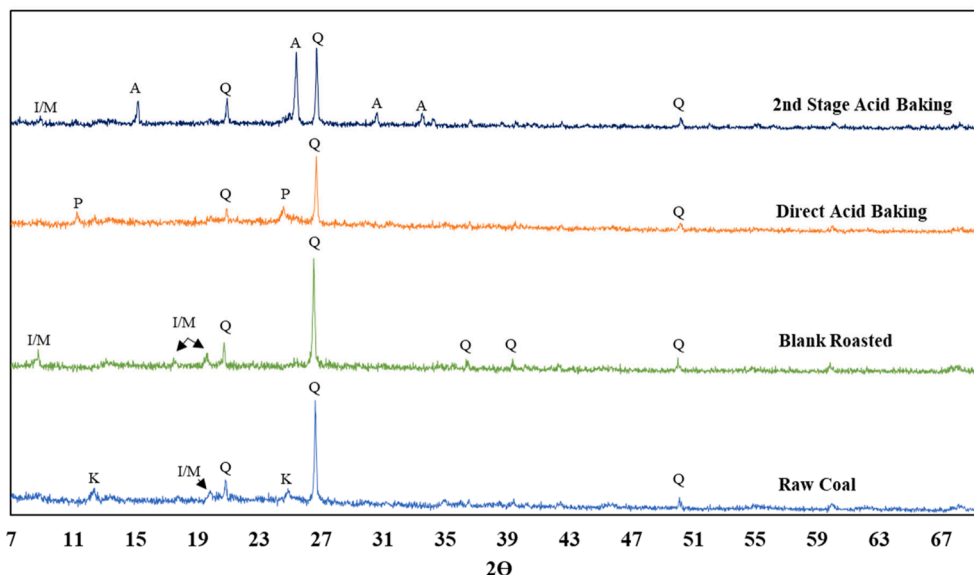

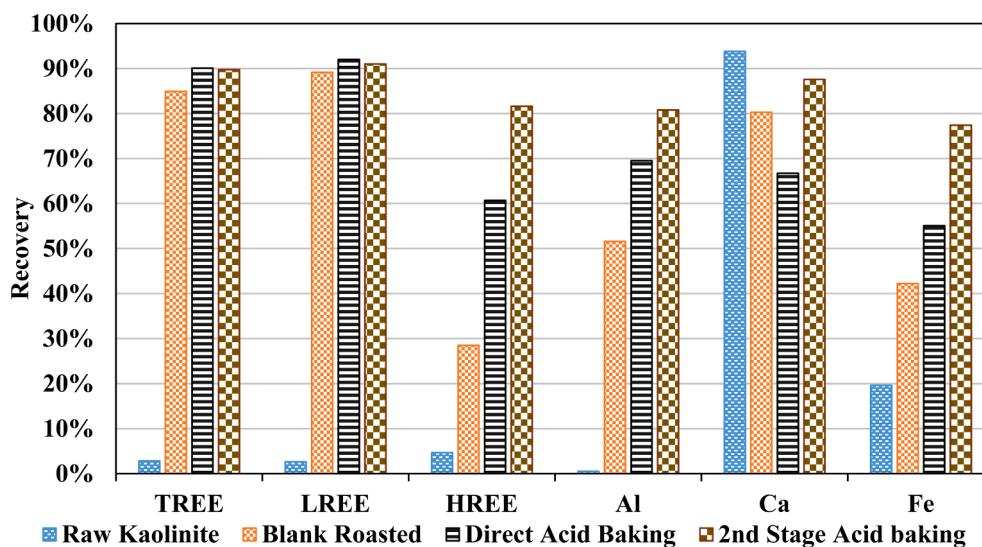**Fig. 10.** XRD patterns of treated and untreated coal.

Fig. 11. REE and contaminants recovery from kaolinite treated under different conditions.
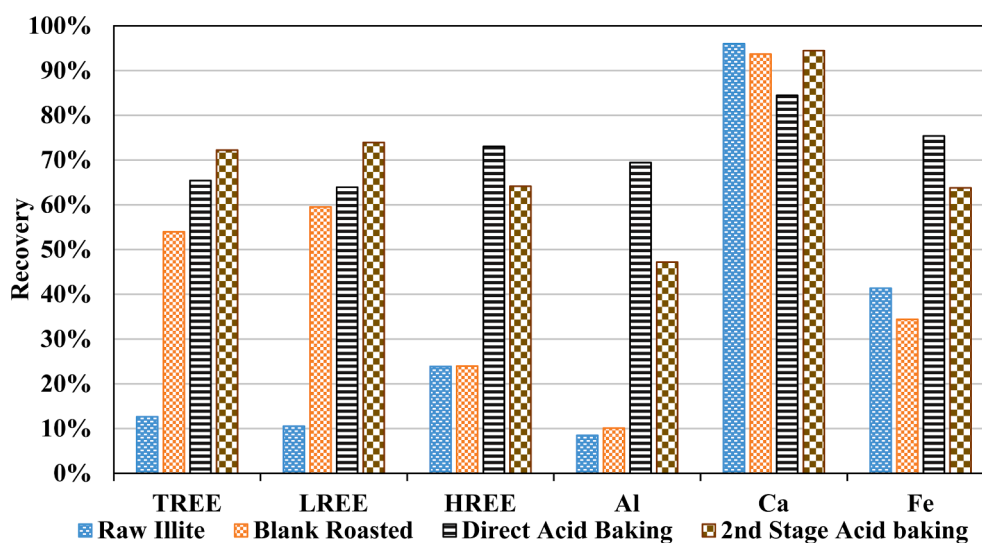

Fig. 12. REE and contaminant recovery from illite treated under different conditions.

heavy REE and Al recoveries. Since acid baking of kaolinite has been reported to decrease the dehydroxylation temperature of kaolinite (Han, 2020; Zhang et al., 2020; Colina et al., 2001) it is possible that either the acid quantity used in the direct acid baking of kaolinite was not sufficient or/and the dehydroxylation of the clays was not complete at 250 °C. Since the decomposition of kaolinite was incomplete in direct acid baking, as shown in Fig. 13, this might explain a relatively lower HREE recovery compared to 2nd stage acid baking. The Al recovery in the 2nd stage acid baking of illite samples decreases significantly compared to direct acid baking. The XRD analyses for both kaolinite and illite samples showed the formation of aluminum sulfate compounds after acid baking, which indicates that the majority of the clay minerals are converted to aluminum sulfate. Most of the aluminum sulfate was likely dissolved in solution, which contributed to the elevated Al recovery. A portion remained in solid form either due to saturation in liquid under current leaching conditions or incomplete decomposition.

Comparing the XRD data for direct and 2nd stage acid baking of the illite sample, it is evident that the direct acid baking of illite produced both aluminum sulfate and potassium aluminum sulfate peaks, whereas 2nd stage acid baking only provided aluminum sulfate peak. This observation reiterates the conclusion drawn earlier that illite/muscovite

decomposition might be the primary source of potassium aluminum sulfate observed in direct acid baking of coal samples. Both potassium aluminum sulfate and aluminum sulfate are highly soluble at elevated temperatures which may explain the higher Al recovery values realized from the direct acid baking of illite as compared to the results obtained from 2nd stage acid baking. Based on these findings, it can be concluded that the improved REE recovery, particularly HREE, from the coal samples was, in fact, partially due to the decomposition of clays observed in both types of acid baking. This would indicate that some HREEs in Fire Clay coarse refuse are entrapped within the clay structure and rigorous environments such as acid baking are crucial for their extraction. A mineralogical characterization performed by another researcher on the FC-CR found HREEs entrapped within the clay particles (He et al., 1995).

3.4. Application on a second coal source

The primary focus of the acid baking studies involved the processing of the Fire Clay coal seam source located in the Central Appalachian coalfields USA. This was primarily due to the high REE concentrations within the source as described by many publications and the significant
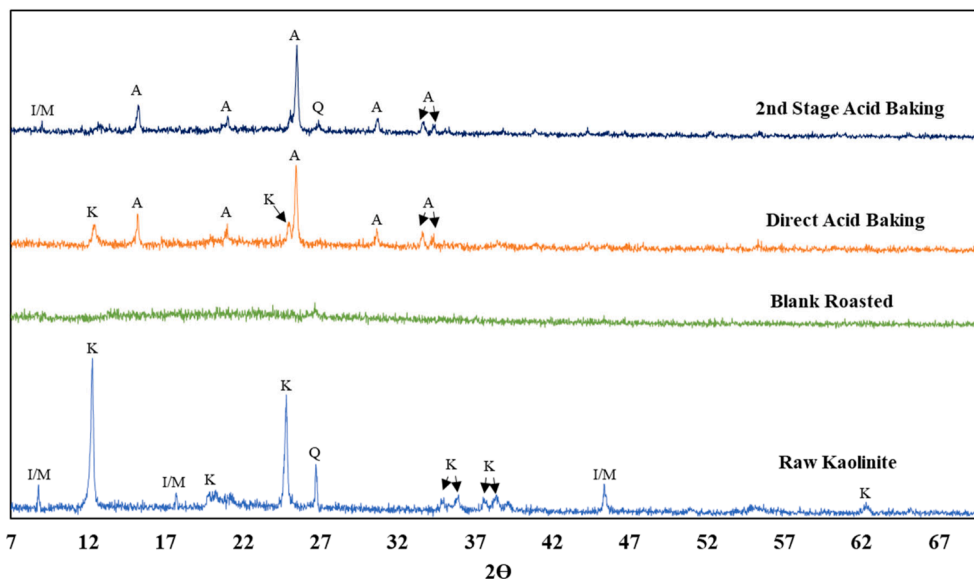
Fig. 13. XRD patterns of untreated and treated kaolinite (Q = Quartz, A = Aluminum Sulfate I/M = Illite/Muscovite, K = Kaolinite).
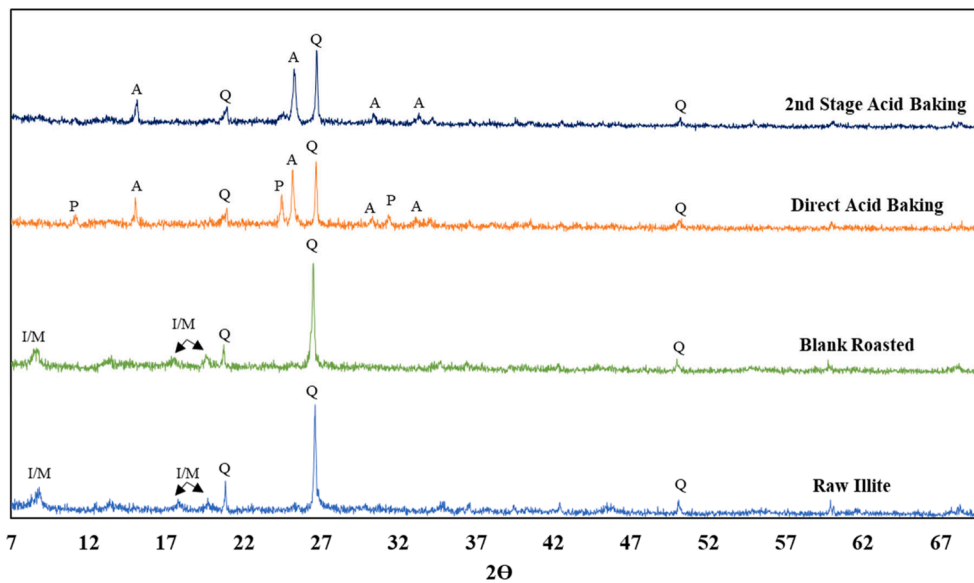

Fig. 14. XRD patterns of untreated and treated Illite (Q = Quartz, A = Aluminum Sulfate I/M = Illite/Muscovite, K = Kaolinite, P = Potassium Aluminum Sulfate).
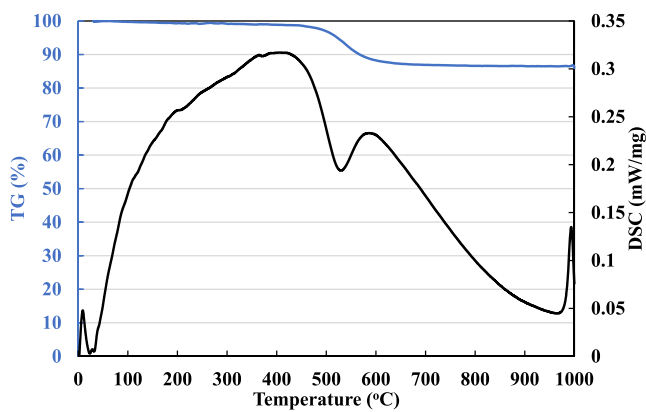

Fig. 15. TGA-DSC curves of kaolinite obtained at the heating rate of 10° C/min and oxidizing condition.
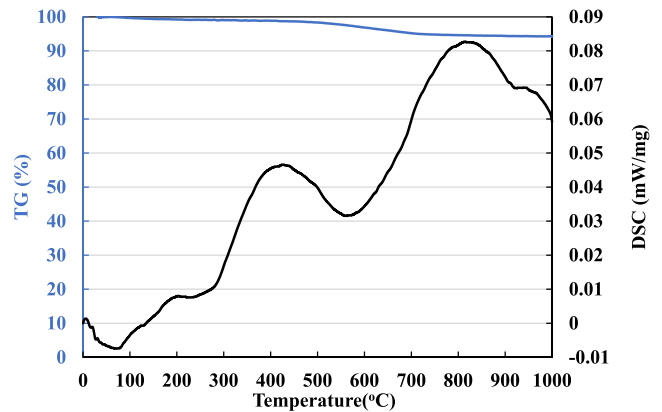

Fig. 16. TGA-DSC curves of mineral illite obtained at the heating rate of 10° C/min under oxidizing conditions.

presence of monazite, which is commonly treated by acid baking to extract the REEs. To assess the application for other sources, tests were performed on coarse refuse generated from the processing of West Kentucky No. 13 (Baker) coal seam, which is found within the Illinois coal basin, USA.

The leaching results for a West Kentucky No. 13 (WK#13) sample that was not pretreated by calcination or acid baking found that 23.79% of the heavy REEs and 16.54% of the light REEs were recovered (Fig. 17). Calcining prior to leaching substantially enhanced the overall REE recovery from 17.43% to 64.66%, which was a more significant impact than the findings associated with the Fire Clay source. Other researchers have also reported similar results and stated that REEs in WK#13 coal are relatively easier to extract compared to Fire Clay coal, likely due to the prominence of crandallite group minerals as opposed to monazite (Zhang and Honaker, 2019; Zhang et al., 2020; Gupta, 2021). The recovery of heavy REEs was slightly increased to 31.21% by the calcination treatment. However, when the sample was acid baked without calcination, heavy REE recovery improved to 45.69% while the recovery of light REEs (49.94%) dropped from a high of 64.66% achieved after calcination and without acid baking. This finding may be due to the presence of a significant amount of carbonaceous shale in the WK#13 sample which is easily decomposed during roasting at 600°C but serves as a host material for RE minerals and resists decomposition during direct acid baking.

When acid baking follows calcination, the recovery of heavy and light REEs are maximum at values of 77.44% and 80.55%, respectively. This finding likely reflects the benefit of roasting to burn off the remaining carbon, dehydroxylating the clays and exposing the REE-containing minerals to the sulfuric acid during the acid baking process. The final results are very similar to the findings observed for the Fire Clay sample.

4. Conclusion

This study focused on pretreatment methods for bituminous coal-based sources for enhancing the leach recovery of rare earth elements, especially heavy REEs. Specifically, a detailed investigation was conducted on the impact of roasting and acid baking on REE recovery. Roasting test results revealed that thermal treatment provides improvement in REE recovery, especially for the light elements. It was established that this rise in the recovery may be due to the dehydroxylation of clays. The thermal characteristic peaks for kaolinite and illite samples showed that both clays undergo de-hydroxylation at 545 °C and 580 °C, respectively. Furthermore, increasing the temperature to 900 °C

was found to cause sintering of clays, which might be the reason for the decrease in the REE recovery. Even though blank roasting increased the light REE recovery, the improvement in the heavy REE recovery was not as significant. It was concluded that more rigorous conditions such as acid baking are required to effectively recover the REEs, specifically heavy REEs.

Direct acid baking without thermal pretreatment resulted in a significant increase in the TREE recovery over simple roasting using the same amount of acid. Even though the recoveries of both light and heavy REEs were improved, the increase in heavy REE recovery was significantly greater. It was found that the REE recovered from direct acid baking at 100 and 150 °C are likely associated with the dissolution of the REE-bearing minerals. Increasing the acid baking temperature from 150 to 300 °C provided an elevation in Al recovery due to transformation of illite into soluble potassium aluminum sulfate, as shown by XRD analysis results. Raising the acid baking temperature slightly decreased the REE recovery, possibly due to a decline in the acid concentration resulting from the consumption during clay dehydroxylation and simple evaporation of the sulfuric acid.

Acid baking of a roasted product provided a significant increase in the REE recovery relative to the results from direct acid baking using the same quantity of acid. It was established that this rise in light REE and heavy REE recovery may be due to the exposure of REE-bearing minerals within the original clay mineral. The REE-bearing minerals released during clay dehydroxylation by calcination were converted into a more soluble form during acid baking.

The correlation coefficients for blank roasting, direct acid baking, and 2nd stage acid baking implied that there is a strong correlation of heavy REEs with Al recovery. Therefore, similar tests were performed on kaolinite and illite samples to understand the REEs association with clay decomposition. The results indicated that higher heavy REE recovery obtained from both direct acid baking and 2nd stage acid baking is, in fact, due to the decomposition of clays. The de-hydroxylation of clays in the pre-calcination stage makes them more susceptible to an acid attack resulting in high Al recovery using acid baking on a calcined product. The XRD analysis of the acid baked clay samples indicated the formation of aluminum sulfate, which also has a high solubility in acidic solutions.

Finally, the novel acid baking concept was applied to a second bituminous coal source found in a different coal basin in the U.S. The results indicated that direct acid baking had a lower light REE recovery than simple roasting while heavy REE recovery improved. Comparatively, the acid baking of the calcinated product provided maximum recovery of heavy and light REEs at or near 80%.
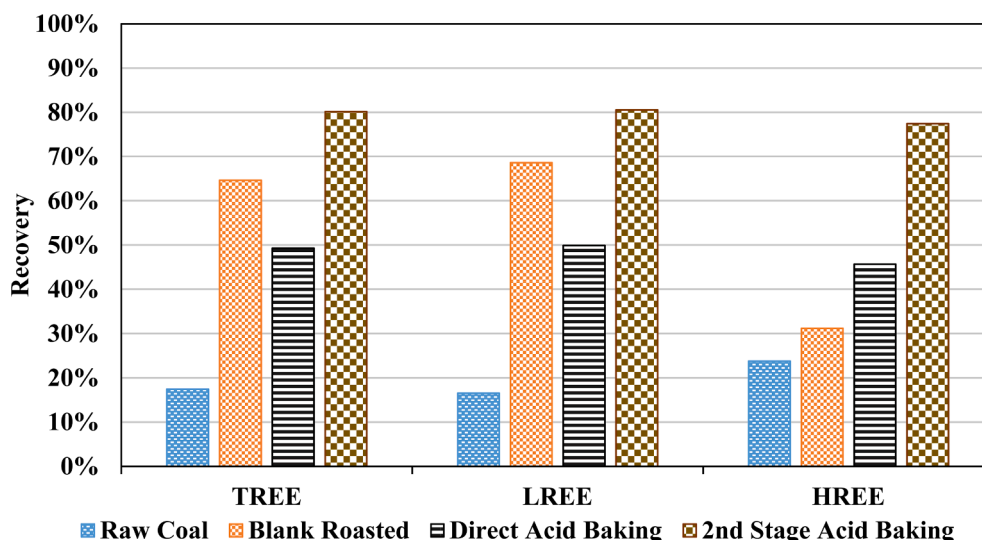

Fig. 17. REE recovery from WK#13 samples treated under different conditions.

CRediT authorship contribution statement

Ahmad Nawab: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **Xinbo Yang:** Validation, Writing – review & editing. **Rick Honaker:** Supervision, Funding acquisition, Project administration, Resources, 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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