Selective extraction of rare earth elements from red mud using oxalic and sulfuric acids

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ARTICLE INFO

ABSTRACT

Red mud is an alkaline industrial solid waste discharged from alumina production via the Bayer process and can be considered a kind of potential resource of rare earth elements (REEs). Many valuable metals such as iron, aluminum, and titanium also exist in red mud. A multi-stage extraction method was proposed in this study by taking full account of the REEs' occurrence in red mud. Firstly, the pretreatments of oxalic acid leaching, roasting, and dilute hydrochloric acid leaching were employed to recover iron and enrich REEs in the residue. Subsequently, sulfuric acid leaching was used to selectively dissolve REEs into the leaching solution. Finally, the effects of sulfuric acid concentration, liquid-solid ratio, reaction temperature, and reaction time on the leaching efficiency of REEs were then investigated. The results show that the maximum extraction of the REEs reached 80 % and less than 4 % of Fe, Na, Ca, Ti and Al were extracted under the experimental conditions of 1 mol/L H_2SO_4, 3 h, 95 °C, and the liquid-solid ratio of 5:1 mL/g. The practicable approach by multi-stage extraction of acid leaching and roasting can split iron and REEs from red mud.

1. Introduction

Red mud (or bauxite residue) is a byproduct of alumina production from the Bayer process. Globally, approximately 200 million tons of red mud are discharged annually for stockpiling as waste [1]. The stockpiled red mud poses a serious environmental threat because of its high alkali and heavy metal contents [2]. Comprehensive utilization or zero-waste valorization of red mud remains a huge challenge for the alumina industry. The compositions of red mud samples vary in extremely broad ranges depending upon the raw bauxite ore and the extraction process [3], and generally, it comprises 6–8 main components and more than 50 trace elements [4,5]. In addition to its main components of iron, aluminum, sodium, and titanium, the valuable metals with low contents like gallium, vanadium, and rare earth elements (REEs) in red mud can also be recovered as resources [6-8].

It is estimated that quantities of REEs could be produced from red mud due to the large discharged volumes as well as the rapid increase in the demand for these critical metals [9,10]. Recovery of REEs from red mud is becoming an increasingly important issue accompanied by the emergence of a variety of leaching and extraction approaches. For

example, direct leaching methods using mineral acids, such as sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid, as the leaching agents can obtain higher leaching efficiencies [4,11], while the major elements like iron, aluminum, and calcium in red mud will be co-extracted in the leachate as impurities which are not conducive to subsequent separation and purification of REEs. There also have been many other studies on the selective recovery of REEs from red mud involving EDTA-enhanced selective leaching [12], acid-roasting followed by water leaching [13-16], and high-temperature smelting followed by acid leaching [17,18]. In terms of the rare earth elements leached into the solution, various techniques including chemical precipitation, ion exchange, solvent extraction, membrane separation, and adsorption, are used to separate and recover them [19-22]. However, the major elements are concentrated in the leaching residue after REEs are selectively extracted from the above methods. Viewed from one perspective, major metals in red mud like iron and aluminum are wasted in the residue. Additionally, concentrated acid is inevitably used to require one-stage acid leaching of REEs from red mud, and this will cause no selectivity. Its subsequent separation and purification with solvent extraction for iron removal will also refer to a complex process

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and economical cost. Therefore, developing a multi-stage extraction method to recover metals in an integrated way with enhanced selectivity is required.

Previous literatures suggest that scandium in red mud mainly substitutes Fe^{3+} in hematite and goethite minerals [23,24], while major lanthanides-bearing phases are ferrotitanates and minor phases are identified as carbonate and phosphate minerals [25]. The modes of REEs have also been demonstrated in the hydrometallurgical process. For example, it is reported that iron and calcium can be leached in the hydrochloric acid solution while REEs can be leached together [11,26]. Therefore, iron and calcium must be removed in advance to enhance the selective extraction of REEs from red mud [18].

Meanwhile, oxalic acid was proposed and applied for selective recovery of iron from red mud in previous literatures [27-30]. In these cases, the famous leaching efficiency of iron was achieved and the iron-containing product was effectively separated by precipitation in the form of $FeC_2O_4 \cdot 2H_2O$. Actually, oxalic acid could dissolve a large number of other main metals such as aluminum and sodium into the leach solutions [31-33,29]. Moreover, REEs would remain in the leaching residue due to the low solubility of rare earth oxalates. Since most of the iron, aluminum, etc. in red mud could be removed by oxalic acid, the oxalic acid-leaching residue would enrich REEs, which would be selectively extracted using mineral acid.

With this in mind, the current work proposes a type of multi-stage extraction method including oxalic acid leaching to isolate iron and aluminum, dilute hydrochloric acid leaching to remove calcium, and sulfuric acid leaching to obtain REEs. Sulfuric acid concentration, reaction temperature, reaction time, and liquid-solid ratio were investigated as key factors to determine the optimum leaching condition. This method was featured by high REEs leaching efficiency and can comprehensively recover the main metals like iron.

2. Material and methods

2.1. Materials and reagents

The red mud used in this study was provided by an alumina refinery located in Qingzhen, Guizhou province, China. The fresh red mud usually contains approximately 30 % water and the sample is in the form of small lumps after natural drying. Before analytical tests and leaching experiments, red mud was dried at 60 °C until a constant weight was achieved. And then, the dried red mud was crushed, ground, and screened to less than 150 μm to obtain a uniform distribution of particle size.

In this study, analytical reagent grade oxalic acid (≥99.5 wt. %, Tianjin Yongda Chemical Industrial Co., Ltd), analytical reagent grade sulfuric acid (95.0–98.0 wt/v %, Sinopharm Chemical Reagent Co., Ltd), and guaranteed reagent grade hydrochloric acid(36.0–38.0 wt/v %, Sinopharm Chemical Reagent Co., Ltd) were used for the follow-up leaching experiments. All solutions involved in this study were prepared with deionized water.

2.2. Experimental procedure

The experimental procedure proposed in this study is depicted in Fig. 1. The experimental procedure is composed of (1) oxalic acid leaching of red mud to separate iron and aluminum, (2) roasting the oxalic acid-leaching residue followed by dilute hydrochloric acid leaching to remove calcium, and (3) sulfuric acid leaching of the hydrochloric acid-leaching residue to dissolve REEs into leachate.

2.2.1. Oxalic acid leaching

Original red mud was added to a three-neck flask with 1 mol/L oxalic acid solution at the liquid-solid ratio of 15:1 mL/g. The flask was set into a thermostatic water bath at 75 °C and was stirred mechanically at a
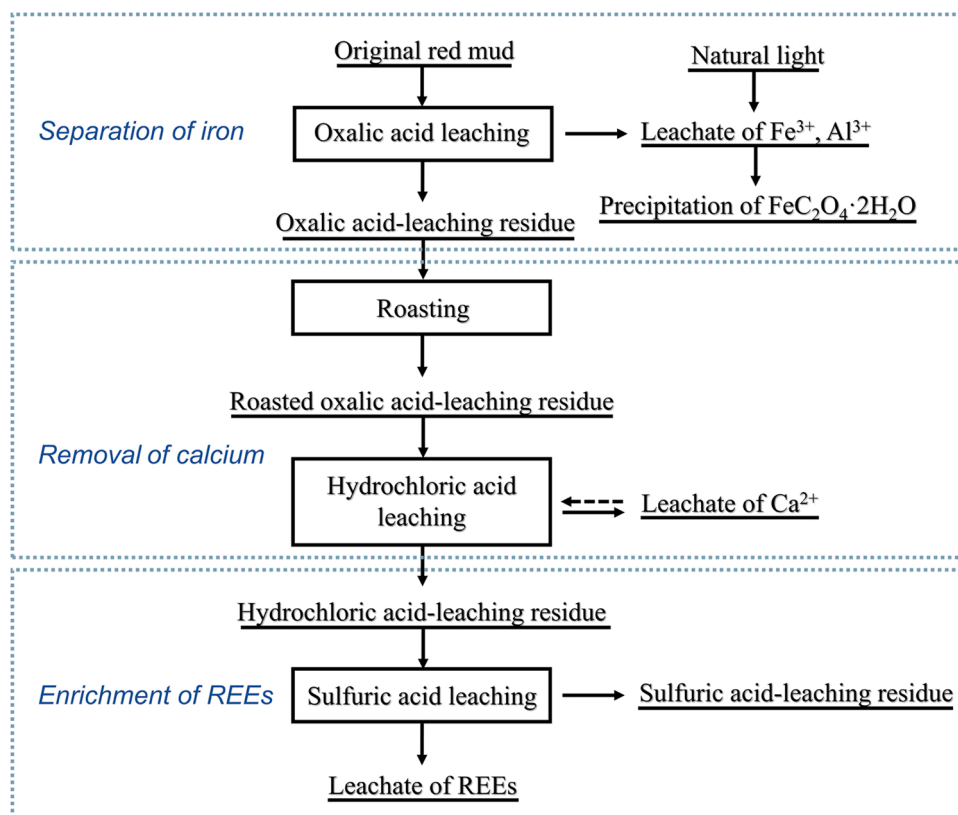

Fig. 1. Experimental flow sheet for REEs extraction from red mud.

speed of 200 rpm for 2 h. Subsequently, the oxalic acid-leaching residue was obtained after filtering, washing, drying, and weighing. The above leaching steps were repeated to obtain the required mass of oxalic acid-leaching residue, and all the as-obtained oxalic acid-leaching residues were mixed homogeneously for the following trials.

2.2.2. Roasting and hydrochloric acid leaching

The oxalic acid-leaching residue was filled in a ceramic crucible, which was then placed into a muffle furnace at a set temperature of 520 °C for 1 h. The roasted oxalic acid-leaching residue was then leached using 0.05 mol/L hydrochloric acid with the liquid-solid ratio of 100:1 mL/g to remove calcium. The leaching reaction was performed with a continuously stirring at the ambient temperature of 20 °C for 2.5 h. The hydrochloric acid-leaching residue was produced after filtering, drying, and weighing for the following trials.

2.2.3. Sulfuric acid leaching

The as-obtained hydrochloric acid-leaching residue in the current study was then treated through batch leaching trials to investigate experimental conditions of sulfuric acid concentration, liquid-to-solid ratio, reaction temperature, and reaction time. Sulfuric acid concentration trials were performed at 95 °C for 3.0 h, and 1.0, 1.5, 2.0, 3.0, and 4.0 mol/L of sulfuric acid concentration were investigated. In the liquid-solid ratio trials, leaching reactions using different liquid-solid ratios (5:1 and 10:1 mL/g) were carried out for 3.0 h at 95 °C. Temperature trials were leached with 2.0 mol/L sulfuric acid in a liquid-to-solid ratio of 5:1 mL/g at different temperatures of 25, 40, 60, 80, and 95 °C for 3.0 h. In addition, reaction time was controlled for 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 h by using 1.0 mol/L sulfuric acid leaching at 95 °C. Each trial of sulfuric acid leaching was conducted twice to obtain the average results of metal leaching efficiencies.

In this study, each of the leaching efficiency of element i (η_i, %) in the leaching solution was calculated according to Eq. (1) as follows:

$$\eta_i = \frac{c_i \bullet V}{0.001 \bullet c_{0i} \bullet m_0} \times 100\% \tag{1}$$

where c_i (mg/L) is the concentration of the element i in the leaching solution, V (L) is the volume of the leaching solution, and c_{0i} (µg/g) and m_0 (g) are the content of the element i in the original red mud and the mass of the original red mud, respectively.

2.3. Characterization methods

Chemical analyses of the major elements in solid samples, such as iron, calcium, aluminum, and sodium of red mud were determined by X-ray fluorescence spectroscopy (XRF, PANalytical PW2424, Netherlands). The REEs in solid samples were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110, USA) and inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900, USA). The phase compositions of the original red mud and the leached residues were characterized by an X-ray diffractometer (XRD, PANalytical Empyrean, Netherlands) equipped with Cu Kα radiation at the 2θ range of 5° − 70°. The element concentrations in leaching solutions were analyzed with ICP-OES or ICP-MS to calculate the leaching efficiency. The thermal stability and the microstructure of the oxalic acid-leaching residue were characterized by thermogravimetric analysis/differential scanning calorimetry (TG/DSC, NETZSCH STA449F3 Jupiter system, Germany) and scanning electron microscopy (SEM, JSM-7800 F, Japan), respectively.

3. Results and discussion

3.1. Oxalic acid leaching

As previously reported, Al_2O_3 (24.97 %), SiO_2 (18.33 %), Fe_2O_3

(16.67 %), TiO_2 (3.90 %), CaO (14.45 %), Na_2O (4.58 %), K_2O (1.77 %), MgO (1.38 %), and SO_2 (1.16 %) occurred as the main components in the red mud. The mineral composition of the original red mud was characterized by XRD as shown in Fig. 2. By combining with the main chemical composition, it can be concluded that the main minerals in the original red mud included diaspore (AlOOH), hematite (Fe_2O_3), cancrinite ($Na_6(Al_6Si_6O_{24})(CaCO_3)(H_2O)_2$), perovskite ($CaTiO_3$), etc. Iron in red mud was mainly in the form of hematite. The contents of REEs in the original red mud obtained from ICP-MS are listed in Table 1, which provides bases to calculate REEs' leaching efficiencies. The red mud sample used in this study contained as high as 1570.16 µg/g of the total REEs.

It has been reported that scandium and iron have a close relationship on account of the similarities in ionic radius [34], and that separation of scandium from iron in the leaching solution from red mud is a particular challenge because of their similar physicochemical properties [12]. Yttrium and the lanthanides were reported in the form of ferrotitanates, carbonate, and phosphate minerals in red mud, and these mineral phases can be dissolved in hot oxalic acid solution. As stated, oxalic acid was also applied for selective recovery of iron from red mud [28,30]. Accordingly, 1 mol/L oxalic acid was used to separate iron from red mud and 68.59 % iron was dissolved during the process in this study. The iron leaching efficiency was not as high as reported by Yu et al. [30] which might be due to the variety of red mud. Sodium was also removed by oxalic acid leaching, and only 0.32 % sodium remained in the oxalic acid-leaching residue. Moreover, the contents of REEs in the oxalic acid-leaching residue were enriched from the results as shown in Table 1. And in the oxalic acid leachate, as shown in Table 2, the concentrations of rare earth elements (except scandium) were below the detection limit (< 0.01 mg/L). Based on the yield of the oxalic acid-leaching residue (64.43 % weight of the raw red mud) and the contents of the element in Table 1 and Table 2, it can be calculated that the losses of REEs were negligible. Thus, it is believed that REEs that participated in a reaction with oxalic acid would be transformed into REEs oxalates, and that the new-generated REEs oxalates can make for subsequent extraction using sulfuric acid. In addition, the separated $FeC_2O_4 \cdot 2H_2O$ from red mud can be a kind of raw material for other iron-containing products [27,29].

The composition and morphology of oxalic acid-leaching residue was analyzed, and the SEM image and EDS analysis results are shown in Fig. 3a. The EDS analysis revealed that lanthanum, cerium, and neodymium appeared with carbon, oxygen, silicon, aluminum, calcium, and titanium, etc. These major elements were the main components of the leaching residue. Therefore, it can be inferred that the newly-generated REEs oxalates were unevenly attached on the residue surfaces.
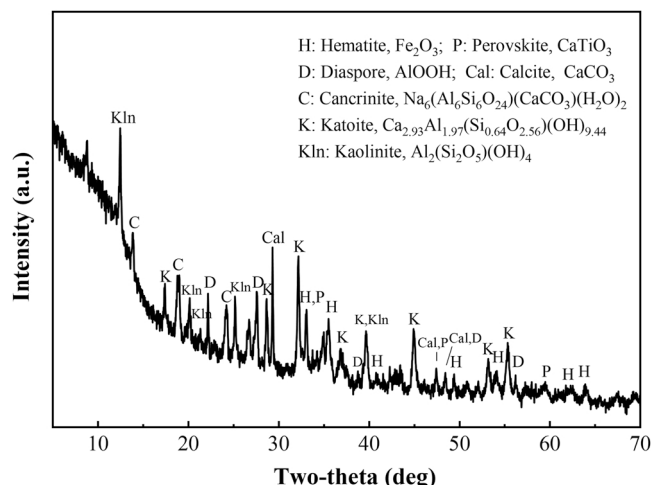

Fig. 2. XRD pattern of the original red mud.

Table 1

Contents of REEs in original red mud and the oxalic acid-leaching residue (μg/g).

REEs	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
Original red mud	72.4	179.5	281	565	64.5	227	45.5	8.44
Oxalic acid-leaching residue	106.0	284	433	888	107.0	369	72.7	12.95
REEs	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Original red mud	37.9	5.84	33.8	6.78	19.00	2.94	17.85	2.71
Oxalic acid-leaching residue	58.5	4.60	53.2	10.60	29.1	4.60	27.9	4.32

Table 2

Concentrations of major elements and REEs in the oxalic acid leachate (mg/L).

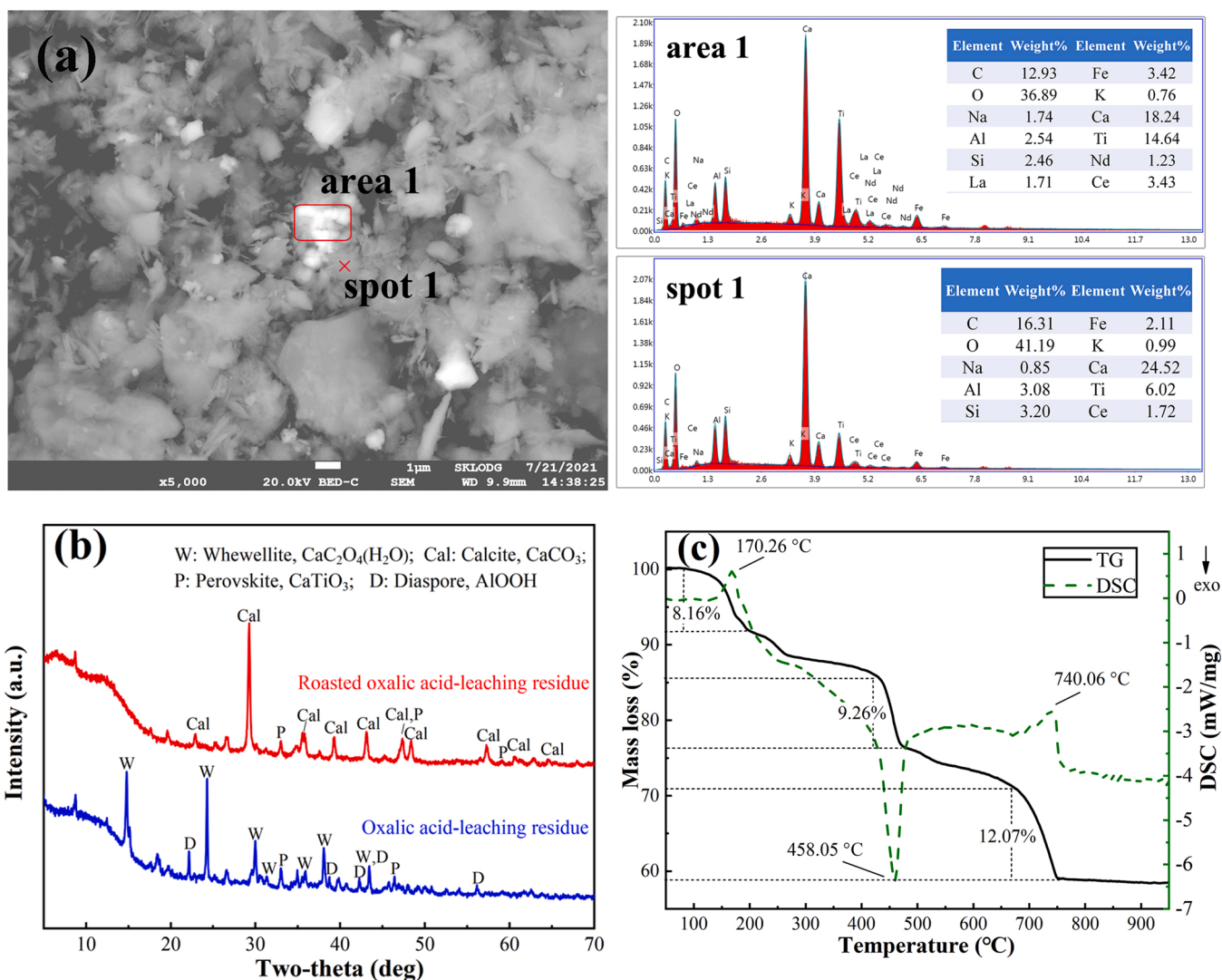| Element	Al	Ca	Fe	Ti	Na	K	Mg	Sc	REEs
Concentration	3830	120	145	801	1595	306	278	0.518	<0.01

Fig. 3. (a) The SEM image and EDS analysis of oxalic acid-leaching residue, (b) the XRD pattern of the oxalic acid-leaching residue before and after roasting, and (c) TG and DSC curves of oxalic acid-leaching residue.

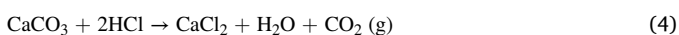### 3.2. Roasting and hydrochloric acid leaching

From the XRD pattern of oxalic acid-leaching residue in Fig. 3b, the as-obtained oxalic acid-leaching residue contains a large amount of whewellite ($CaC_2O_4 \cdot H_2O$), which will be converted into sulfates if the oxalic acid-leaching residue were directly leached using sulfuric acid. The newly generated calcium sulfate is slightly soluble and might cover on the residue surface to hinder the extraction of REEs. Hence, calcium removal from the oxalic acid-leaching residue is necessitated.

As reported, $CaC_2O_4 \cdot H_2O$ dissolution needs concentrated hydrochloric acid [35,36], but its decomposition product $CaCO_3$ is relatively easy to be dissolved by dilute hydrochloric acid [37]. And REEs could probably be dissolved by concentrated hydrochloric acid. In the process of removing the calcium oxalate, compared with the use of concentrated

acid which generates a large amount of waste liquid and dissolves REEs, intermediate temperature roasting and minimizing the use of hydrochloric acid were more appropriate choices.

The thermal decomposition behavior of the oxalic acid-leaching residue was studied by the TG/DSC analysis as given in Fig. 3c. It is found that three main weight losses can be observed from the TG curve. The first weight decline (8.16 %) at 128–181 °C was attributed to the dehydration of $CaC_2O_4 \cdot H_2O$. The latter two stages of weight loss (9.26 % and 12.07 %) from 429 to 478°C, and from 689 to 754°C were correspondingly ascribed to the decomposition of CaC_2O_4 with the formation of $CaCO_3$ and the decomposition of $CaCO_3$. As shown in the DSC curve, two endothermic peaks (170.26 and 740.06 °C) were associated with the decomposition reaction of the thermal decomposition process. The exothermal peak at 458.05 °C was attributed to the decomposition of CaC_2O_4 and the consequent oxidation of CO in the air atmosphere [38]. Therefore, before the sulfuric acid leaching process, $CaC_2O_4 \cdot H_2O$ in the oxalic acid-leaching residue could be removed by dilute hydrochloric acid leaching after the thermal decomposition reaction. The calcium removal process was performed as described in Reactions (2)-(4).

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \qquad (2)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \text{ (g)} \qquad (3)$$

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \text{ (g)} \qquad (4)$$

Through considering synthetically with the above factors, 520 °C was selected as the appropriate roasting temperature. The XRD pattern of mineral phases after the roasting process is shown in Fig. 3b, which confirmed that whewellite in the oxalic acid-leaching residue transformed to calcite after roasting at 520 °C. Meanwhile, the newly-formed REEs oxalates could have been decomposed into oxides more easily than CaC_2O_4 decomposition into $CaCO_3$ when subjected to the roasting treatment. Actually, REEs were considered to be oxides before the roasting temperature reached 480 °C as shown in Reaction (5) [39]. In addition, the difference of solubility in dilute hydrochloric acid between $CaCO_3$ and rare earth oxides was also instrumental in $CaCO_3$ removed from the roasted oxalic acid-leaching residue.

$$REE_2(C_2O_4)_3 + nO_2 \rightarrow 2REEO_n + 6CO_2 \qquad (5)$$

Since $CaCO_3$ was the main calcium-containing phase in the roasted oxalic acid-leaching residue, 0.05 mol/L of dilute hydrochloric acid was used to remove calcium. The leaching efficiency of elements in the hydrochloric acid leaching process is presented in Table 3. It is found that 70.51 % calcium was removed, while the effect of hydrochloric acid on the rare earth metals was less than 1 %. The pH of the hydrochloric acid leachate was close to neutral, and the concentrations of elements in the leachate compared to calcium were negligible. Therefore, the leachate could be recycled for the preparation of dilute hydrochloric acid for cyclic utilization. After hydrochloric acid leaching, the weight yield of the hydrochloric acid-leaching residue was approximately 31.89 % compared with the original red mud used. The REEs contents in the hydrochloric acid-leaching residue are presented in Table 4. Owing to the decomposition of oxalates and the separation of calcium, the REEs were further enriched in the hydrochloric acid-leaching residue. Compared with the original red mud, the concentration of the REEs in the hydrochloric acid-leaching residue was around tripled. Accordingly,

REEs were enriched in the hydrochloric acid-leaching residue with a total content of REEs up to 4791.06 μg/g. The higher contents of REEs in the hydrochloric acid-leaching residue would be beneficial for subsequent extraction using sulfuric acid solution.

3.3. Sulfuric acid leaching process

3.3.1. Effect of sulfuric acid amount

Sulfuric acid was performed to leach REEs from the obtained hydrochloric acid-leaching residue. The effects of sulfuric acid concentration on REEs leaching efficiency were firstly investigated under the condition of the liquid-solid ratio of 5:1 mL/g at 95 °C for 3 h. The results are shown in Fig. 4a. For the sake of concise, the concentrations of scandium, yttrium, lanthanum, and cerium were selected to show in the leaching efficiency figures. An obvious gap in leaching efficiency was observed between the major metals and REEs, and the REEs' leaching efficiencies were much higher than the leaching efficiency of major elements such as iron and titanium. This was proposed to be due to interactions between REEs and sulfuric acid, and it was summarized as the Reaction (6).

$$REEO_n + nH_2SO_4 \rightarrow REE(SO_4)_n + nH_2O \qquad (6)$$
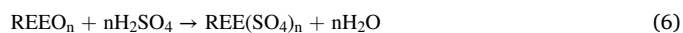
The leaching efficiency of REEs presented an increasing tendency with an increase in sulfuric acid concentration. The extraction of scandium reached nearly 100 % when the sulfuric acid concentration was at 3 mol/L. However, as the sulfuric acid concentration changed from 3 to 4 mol/L, the leaching efficiencies of yttrium, lanthanum, and cerium did not increase distinctly. Increasing sulfuric acid concentration from 1.0 to 4.0 mol/L, the leaching efficiencies of iron and titanium increased gradually from 3.40 % to 31.02 % and from 1.63 % to 27.94 %, respectively. Hematite in red mud has been subjected to oxalic acid dissolution and the residual hematite can be eluted in the high concentration sulfuric acid solution [40]. Titanium-bearing phases such as perovskite and anatase are insoluble under the condition of low concentration of acid at room temperature, but they can dissolve at high temperature and using high concentration of acid [41]. Due to these reasons, the residual iron and titanium were further leached into the leaching solution with sulfuric acid concentration increasing.

When 1 mol/L sulfuric acid was used, the leaching efficiency of scandium reached 80.02 % and the leaching efficiencies of all major elements were less than 4 %. According to previous reports in the literature, sulfuric acid would reveal more excellent leaching ability for scandium in comparison with other mineral acids [42]. Therefore, it seems that low concentration sulfuric acid had better selectivity for REEs dissolution. For controlling the dissolution of major metals, 1 mol/L was chosen as a suitable sulfuric acid concentration.

However, the leaching efficiency of lanthanum and cerium was around 60 % under the condition of 1 mol/L sulfuric acid with the liquid-to-solid ratio of 5:1 mL/g. To pursue higher REEs leaching efficiency, 1 mol/L sulfuric acid with a liquid-to-solid ratio of 10:1 mL/g was carried out as a contrast in this study. These samples prepared for liquid-to-solid ratio experiments were leaching for 3 h at the constant temperature of 95 °C. Fig. 4b shows the extraction of REEs and major elements in the leaching solution with the liquid-solid ratios of 5:1 and 10:1 mL/g, respectively. The leaching efficiencies of REEs with the liquid-solid ratio of 10:1 mL/g were above 80 % (88.39 % for scandium), and were obviously higher than those with the liquid-solid ratio of 5:1 mL/g. Nonetheless, the leaching efficiency of iron was close to 17 %, and the leaching efficiencies of aluminum and titanium were approximately 7 % with the liquid-solid ratio of 10:1 mL/g. Herein, the option of liquid-solid ratio will result in significant differences in concentrations of iron and REEs in the sulfuric acid leaching solution, and the concentrations of iron and REEs depend on leaching efficiency as well as the contents in the original red mud samples. When the iron content in the original red mud is not high, the liquid-solid ratio of 10:1 mL/g can

Table 3
Metals leaching efficiency during the hydrochloric acid leaching process (wt. %).

Element	Al	Ca	Fe	Ti	Na	K	Mg	
Extraction	0.02	70.51 ± 0.76	0.00	0.00	1.80	1.49	0.60	
Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Extraction	0.34	0.065	0.10	0.08	0.00	0.00	0.17	0.00
Element	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y
Extraction	0.19	0.00	0.33	0.00	0.35	0.00	0.52	0.42

Table 4

REEs Contents in the hydrochloric acid-leaching residue (µg/g).

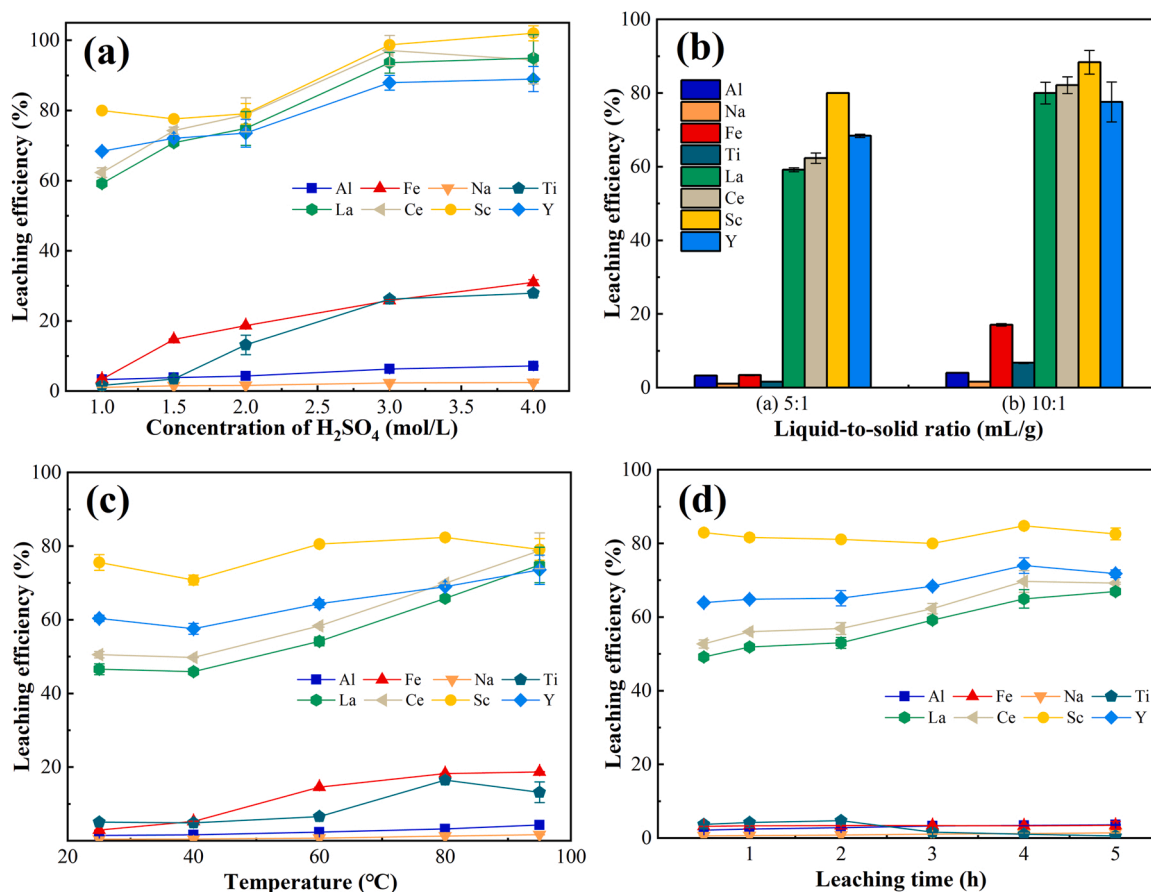| REEs	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
Hydrochloric acid-leaching residue	141.5	550	844	1720	203	758	148.5	26.8
REEs	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Hydrochloric acid-leaching residue	117.5	17.9	106	20.8	61.2	8.96	58.1	8.80

Fig. 4. Leaching efficiency of major elements and REEs from the hydrochloric acid-leaching residue (a) using different sulfuric acid concentrations at 95 °C for 3 h with a liquid-solid ratio of 5:1 mL/g, (b) with the liquid-solid ratio of 5:1 and 10:1 mL/g under the condition of 1 mol/L H_2SO_4 at 95 °C for 3 h, (c) at different leaching temperatures using 2 mol/L H_2SO_4 for 3 h with a liquid-solid ratio of 5:1 mL/g, and (d) for different reaction times using 1 mol/L H_2SO_4 at 95 °C with a liquid-solid ratio of 5:1 mL/g.

be acceptable. The previous literatures reported less than 5 % iron extraction as good selectivity for REEs [11,14], but their red mud samples contain higher iron contents. Therefore, it is proposed that 1 mol/L sulfuric acid with the liquid-to-solid ratio of 5:1 and 10:1 mL/g can meet the requirements depending on the different iron contents of red mud samples.

The series of pretreatment processes were proved to be efficient for selective extraction of major and rare earth elements from red mud. Compared with previous studies such as the method of roasting with concentrated sulfuric acid and leaching [15,43], the current leaching process can obtain gratifying REEs leaching efficiencies under the condition of maintaining low leaching efficiency of iron, sodium, etc. The one-stage acid leaching and solvent extraction process involved several procedures and concentrated acid leaching was poorly selective, although significant rare earth recoveries were obtained using concentrated acids and high temperatures [44-46]. In addition, both acid consumption and roasting temperature were reduced in this study.

3.3.2. Effect of reaction temperature

In this section, the effects of reaction temperature on REEs leaching

efficiency were investigated under the condition of 2 mol/L of H_2SO_4 for 3 h with the liquid-solid ratio of 5:1 mL/g. The results are shown in Fig. 4c. The element leaching efficiencies showed an increasing trend basically with the increase of reaction temperature. The results revealed that temperature in this period was a determinant factor affecting extraction. At room temperature of 25 °C, the leaching efficiency of iron and cerium were 2.94 % and 50.57 %, whereas they respectively reached 18.70 % and 78.79 % at 95 °C. The results indicated that higher temperature was in favor of the leaching reaction activity. The particles were diffused into the leaching agent more rapidly as the temperature increased, and the interfacial reaction rate between mineral particles and the leaching reagent increased, resulting in the promotion of the particles' dissolution [47]. The increase in leaching temperature was beneficial for REEs dissolved in the solution. Significantly, the leaching efficiency of iron and titanium raised with the growth of reaction temperature under the condition of 2 mol/L H_2SO_4. As discussed, the leaching efficiency of iron and titanium was steady below 4 % when using 1 mol/L H_2SO_4 at 95 °C. Consequently, the leaching temperature of 95 °C was conceived as a suitable temperature condition to use in other condition experiments.

3.3.3. Effect of reaction time

[Fig. 4](#)d presents the impact of leaching efficiency on reaction time under conditions using 1 mol/L of H_2SO_4 at 95 °C with a liquid-solid ratio of 5:1 mL/g. As reaction time increased from 0.5 to 5 h, the leaching efficiencies of lanthanum, and cerium increased respectively from 49.18 % to 66.96 %, and from 52.73 % to 69.24 %. The results shown in [Fig. 4](#)d proved that reaction time was not the main factor affecting the leaching efficiency of REEs. With the increase in reaction time, the leaching efficiency of all elements was still relatively untouched. The leaching efficiency of major elements was maintained below 4 % throughout the increase in reaction time. Although the highest points of REEs leaching efficiency were mainly focused on 4 h, the leaching time of 3 h was used as the suitable reaction time in other effect factor trials in this study. It was on the grounds of the no-significant growth in leaching efficiency and energy conservation.

4. Conclusions

In this work, a multi-stage extraction process was used to selectively extract REEs from red mud, which included oxalic acid leaching to dissolve iron and to release REEs, dilute hydrochloric acid leaching to remove calcium, and sulfuric acid selectively leaching REEs. Firstly, sodium, iron, and aluminum were dissolved in the oxalic acid solution, while REEs were enriched in the oxalic acid-leaching residue due to the divergences of solubility of the major metals and REEs oxalates. Furthermore, the treatment of roasting was demonstrated to be beneficial for calcium removal and obtaining REEs oxides. Subsequently, REEs oxides were selectively dissolved into the sulfuric acid solution. Elements of iron, aluminum, and calcium extracted at each stage can be further recovered.

High selectivity and low energy consumption are deemed as significant advantages of multi-stage extraction in this study. Calcium and iron in red mud are effectively separated in the pre-treatment process. The concentration of sulfuric acid used for selectively leaching REEs was determined as 1 mol/L H_2SO_4 at the temperature of 95 °C. With the liquid-solid ratio of 10:1 mL/g, all the REEs leaching efficiencies were more than 80 % (88.39 % for scandium) with 17 % iron co-extracted. When the liquid-solid ratio was 5:1 mL/g, the REEs leaching efficiencies were approximately 60 % (80.02 % for scandium) with less than 4 % iron dissolved. A new insight is provided into the recovery and full utilization of valuable metals from red mud in this work.

CRediT authorship contribution statement

Wanyan Li: Investigation, Resources, Data curation, Writing - original draft. **Zehai Li:** Investigation, Data curation. **Ning Wang:** Conceptualization, Resources, Supervision. **Hannian Gu:** Writing - review & editing, Conceptualization, Validation, Resources, Methodology, Supervision, Funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgments

References

[1] S. Xue, Y. Wu, Y. Li, X. Kong, F. Zhu, H. William, X. Li, Y. Ye, Industrial wastes applications for alkalinity regulation in bauxite residue: a comprehensive review, J. Cent. South Univ. 26 (2019) 268–288, https://doi.org/10.1007/s11771-019-4000-3.

[2] Z. Li, H. Gu, B. Hong, N. Wang, M. Chen, An innovative process for dealkalization of red mud using leachate from Mn-containing waste, J. Environ. Chem. Eng. 10 (2022), 107222, https://doi.org/10.1016/j.jece.2022.107222.

[3] T. Guo, H. Yang, Q. Liu, H. Gu, N. Wang, W. Yu, Y. Dai, Adsorptive removal of phosphate from aqueous solutions using different types of red mud, Water Sci. Technol. 2017 (2) (2018) 570–577, https://doi.org/10.2166/wst.2018.182.

[4] Abhilash, S. Sinha, M.K. Sinha, B.D. Pandey, Extraction of lanthanum and cerium from Indian red mud, Int. J. Miner. Process. 127 (2014) 70–73, https://doi.org/10.1016/j.minpro.2013.12.009.

[5] H. Gu, N. Wang, S. Liu, Characterization of Bayer red mud from Guizhou, China, Miner. Metall. Process. 29 (3) (2012) 169–171, https://doi.org/10.1007/BF03402256.

[6] S. Agrawal, N. Dhawan, Evaluation of red mud as a polymetallic source - a review, Miner. Eng. 171 (2021), 107084, https://doi.org/10.1016/j.mineng.2021.107084.

[7] C.R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T.V. Gerven, Recovery of rare earths and other valuable metals from bauxite residue (red mud): a review, J. Sustain. Metall. 2 (2016) 365–386, https://doi.org/10.1007/s40831-016-0068-2.

[8] Z. Liu, H. Li, Metallurgical process for valuable elements recovery from red mud-a review, Hydrometallurgy 155 (2015) 29–43, https://doi.org/10.1016/j.hydromet.2015.03.018.

[9] G. Gaustad, E. Williams, A. Leader, Rare earth metals from secondary sources: Review of potential supply from waste and byproducts, Resour., Conserv. Recycl. 167 (2021), 105213, https://doi.org/10.1016/j.resconrec.2020.105213.

[10] D. Zhang, H. Chen, Z. Nie, J. Xia, E. Li, X. Fan, L. Zheng, Extraction of Al and rare earths (Ce, Gd, Sc, Y) from red mud by aerobic and anaerobic bi-stage bioleaching, Chem. Eng. J. 401 (2020), 125914, https://doi.org/10.1016/j.cej.2020.125914.

[11] C.R. Borra, Y. Pontikes, K. Binnemans, T.V. Gerven, Leaching of rare earths from bauxite residue (red mud, Miner. Eng. 76 (2015) 20–27, https://doi.org/10.1016/j.mineng.2015.01.005.

[12] K. Zhou, C. Teng, X. Zhang, C. Peng, W. Chen, Enhanced selective leaching of scandium from red mud, Hydrometallurgy 182 (2018) 57–63, https://doi.org/10.1016/j.hydromet.2018.10.011.

[13] J. Anawati, G. Azimi, Recovery of scandium from Canadian bauxite residue utilizing acid baking followed by water leaching, Waste Manag. 95 (2019) 549–559, https://doi.org/10.1016/j.wasman.2019.06.044.

[14] F. Meng, X. Li, L. Shi, Y. Li, F. Gao, Y. Wei, Selective extraction of scandium from bauxite residue using ammonium sulfate roasting and leaching process, Miner. Eng. 157 (2020), 106561, https://doi.org/10.1016/j.mineng.2020.106561.

[15] R.P. Narayanan, N.K. Kazantzis, M.H. Emmert, Selective process steps for the recovery of scandium from Jamaican bauxite residue (Red Mud, ACS Sustain. Chem. Eng. 6 (2018) 5333–5341, https://doi.org/10.1021/acssuschemeng.7b03968.

[16] R.M. Rivera, B. Ulenaers, G. Ounoughene, K. Binnemans, T.V. Gerven, Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching, Miner. Eng. 119 (2018) 82–92, https://doi.org/10.1016/j.mineng.2018.01.023.

[17] C.R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T.V. Gerven, Smelting of bauxite residue (red mud) in view of iron and selective rare earths recovery, J. Sustain. Metall. 2 (2016) 28–37, https://doi.org/10.1007/s40831-015-0026-4.

[18] R.M. Rivera, B. Xakalashe, G. Ounoughene, K. Binnemans, B. Friedrich, T. V. Gerven, Selective rare earth element extraction using high-pressure acid leaching of slags arising from the smelting of bauxite residue, Hydrometallurgy 184 (2019) 162–174, https://doi.org/10.1016/j.hydromet.2019.01.005.

[19] Z. Chen, Z. Li, J. Chen, P. Kallem, F. Banat, H. Qiu, Recent advances in selective separation technologies of rare earth elements: a review, J. Environ. Chem. Eng. 10 (1) (2022), 107104, https://doi.org/10.1016/j.jece.2021.107104.

[20] Z. Li, J. Chen, H. Tan, J. Wu, H. Qiu, Selective adsorption of rare earth elements by Zn-BDC MOF/Graphene oxide nanocomposites synthesized via in situ interlayer-confined strategy, Ind. Eng. Chem. Res. 61 (4) (2022) 1841–1849, https://doi.org/10.1021/acs.iecr.1c04180.

[21] J. Lu, K. He, Y. Wang, G. Chen, H. Weng, M. Lin, An effective process for the separation of U(VI), Th(IV) from rare earth elements by using ionic liquid Cyphos IL 104, Chin. Chem. Lett. 33 (7) (2022) 3422–3428, https://doi.org/10.1016/j.cclet.2022.03.089.

[22] J. Xiao, B. Li, R. Qiang, H. Qiu, J. Chen, Highly selective adsorption of rare earth elements by honeycomb-shaped covalent organic frameworks synthesized in deep eutectic solvents, Environ. Res. 214 (4) (2022), 113977, https://doi.org/10.1016/j.envres.2022.113977.

[23] Z. Liu, Y. Zong, H. Li, Z. Zhao, Characterization of scandium and gallium in red mud with Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) and Electron Probe Micro-Analysis (EPMA, Miner. Eng. 119 (2018) 263–273, https://doi.org/10.1016/j.mineng.2018.01.038.

[24] J. Vind, A. Malfliet, C. Bonomi, P. Paiste, I.E. Sajó, B. Blanpain, A.H. Tkaczyk, V. Vassiliadou, D. Panias, Modes of occurrences of scandium in Greek bauxite and bauxite residue, Miner. Eng. 123 (2018) 35–48, https://doi.org/10.1016/j.mineng.2018.04.025.

[25] J. Vind, A. Malfliet, B. Blanpain, P.E. Tsakiridis, A.H. Tkaczyk, V. Vassiliadou, D. Panias, Rare earth element phases in bauxite residue, Minerals 8 (2018) 77, https://doi.org/10.3390/min8020077.

[26] X. Zhang, K. Zhou, W. Chen, Q. Lei, Y. Huang, C. Peng, Recovery of iron and rare earth elements from red mud through an acid leaching-stepwise extraction approach, J. Cent. South Univ. 26 (2019) 458–466, https://doi.org/10.1007/s11771-019-4018-6.

[27] H. Gu, J.S.J. Hargreaves, J. Jiang, J.L. Rico, Potential routes to obtain value-added iron-containing compounds from red mud, J. Sustain. Metall. 3 (3) (2017) 561–569, https://doi.org/10.1007/s40831-016-0112-2.

[28] Y. Yang, X. Wang, M. Wang, H. Wang, P. Xian, Recovery of iron from red mud by selective leach with oxalic acid, Hydrometallurgy 157 (2015) 239–245, https://doi.org/10.1016/j.hydromet.2015.08.021.

[29] Y. Yang, X. Wang, M. Wang, H. Wang, P. Xian, Iron recovery from the leached solution of red mud through the application of oxalic acid, Int. J. Miner. Process. 157 (2016) 145–151, https://doi.org/10.1016/j.minpro.2016.11.001.

[30] Z. Yu, Z. Shi, Y. Chen, Y. Niu, Y. Wang, P. Wan, Red-mud treatment using oxalic acid by UV irradiation assistance, Trans. Nonferrous Met. Soc. China 22 (2) (2012) 456–460, https://doi.org/10.1016/S1003-6326(11)61198-9.

[31] A.I. Arogundade, P.S.M. Megat-Yusoff, F. Ahmad, A.H. Bhat, L.O. Afolabi, Modification of bauxite residue with oxalic acid for improved performance in intumescent coatings, J. Mater. Res. Technol. 12 (2021) 679–687, https://doi.org/10.1016/j.jmrt.2021.03.010.

[32] H. Gu, W. Li, Z. Li, T. Guo, H. Wen, N. Wang, Leaching behavior of lithium from bauxite residue using acetic acid, Min., Metall. Explor. 37 (2) (2020) 443–451, https://doi.org/10.1007/s42461-020-00181-1.

[33] É. Ujaczki, R. Courtney, P. Cusack, R.K. Chinnam, S. Clifford, T. Curtin, L. O'Donoghue, Recovery of gallium from bauxite residue using combined oxalic acid leaching with adsorption onto zeolite HY, J. Sustain. Metall. 5 (2019) 262–274, https://doi.org/10.1007/s40831-019-00226-w.

[34] Ş. Kaya, Y.A. Topkaya, Extraction behavior of scandium from a refractory nickel laterite ore during the pressure acid leaching process, Rare Earths Ind. 11 (2016) 171–182, https://doi.org/10.1016/B978-0-12-802328-0.00011-5.

[35] D. Hourlier, Thermal decomposition of calcium oxalate: beyond appearances, J. Therm. Anal. Calorim. 136 (2019) 2221–2229, https://doi.org/10.1007/s10973-018-7888-1.

[36] J. Yao, Y. Cao, J. Wang, C. Zhang, W. Wang, W. Bao, L. Chang, Successive calcination-oxalate acid leaching treatment of spent SCR catalyst: a highly efficient and selective method for recycling tungsten element, Hydrometallurgy 201 (2021), 105576, https://doi.org/10.1016/j.hydromet.2021.105576.

[37] X. Zhang, C. Zang, H. Ma, Z. Wang, Study on removing calcium carbonate plug from near wellbore by high-power ultrasonic treatment, Ultrason. Sonochem. 62 (2020), 104515, https://doi.org/10.1016/j.ultsonch.2019.03.006.

[38] R. Svoboda, Z.O. Zmrhalová, G. Duan, D. Brandová, J. Chovanec, Thermal decomposition of mixed calcium oxalate hydrates - kinetic deconvolution of complex heterogeneous processes, Phys. Chem. Chem. Phys. 22 (2020) 8889–8901, https://doi.org/10.1039/C9CP06867H.

[39] N.N. Bushuev, D.S. Zinin, Thermal decomposition features of calcium and rare-earth oxalates, Russ. J. Inorg. Chem. 61 (2) (2016) 161–167, https://doi.org/10.1134/S0036023616020030.

[40] G. Li, F. Gu, J. Luo, B. Deng, Z. Peng, T. Jiang, Recovery of iron-, titanium-bearing constituents from bauxite ore residue via magnetic separation followed by sulfuric acid leaching, Light Met. 2017 (2017) 75–81, https://doi.org/10.1007/978-3-319-51541-0_11.

[41] B. Deng, G. Li, J. Luo, Q. Ye, M. Liu, Z. Peng, T. Jiang, Enrichment of Sc₂O₃ and TiO₂ from bauxite ore residues, J. Hazard. Mater. 331 (2017) 71–80, https://doi.org/10.1016/j.jhazmat.2017.02.022.

[42] G. Alkan, B. Xakalashe, B. Yagmurlu, F. Kaussen, B. Friedrich, Conditioning of red mud for subsequent titanium and scandium recovery - a conceptual design study, World Metall. -ERZMETALL 70 (2) (2017) 84–91.

[43] F. Meng, X. Li, P. Wang, Recovery of scandium from bauxite residue by selective sulfation roasting with concentrated sulfuric acid and leaching, JOM: J. Miner., Met. Mater. Soc. 72 (2) (2020) 816–822, https://doi.org/10.1007/s11837-019-03931-9.

[44] C.R. Borra, J. Mermans, B. Blanpain, Y. Pontikes, K. Binnemans, T.V. Gerven, Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching, Miner. Eng. 92 (2016) 151–159, https://doi.org/10.1016/j.mineng.2016.03.002.

[45] A.B. Botelho Junior, D.C.R. Espinosa, J.A.S. Tenório, Selective separation of Sc(III) and Zr(IV) from the leaching of bauxite residue using trialkylphosphine acids, tertiary amine, tri-butyl phosphate and their mixtures, Sep. Purif. Technol. 279 (2021), 119798, https://doi.org/10.1016/j.seppur.2021.119798.

[46] M. Ochsenkuehn-Petropoulou, L.-A. Tsakanika, T. Lymperopoulou, K.-M. Ochsenkuehn, K. Hatzilyberis, P. Georgiou, C. Stergiopoulos, O. Serifi, F. Tsopelas, Efficiency of sulfuric acid on selective scandium leachability from bauxite residue, Metals 8 (11) (2018) 915, https://doi.org/10.20944/preprints201810.0063.v1.

[47] W. Li, X. Yan, Z. Niu, X. Zhu, Selective recovery of vanadium from red mud by leaching with using oxalic acid and sodium sulfite, J. Environ. Chem. Eng. 9 (1003–1008) (2021), 105669, https://doi.org/10.1016/j.jece.2021.105669.