RESEARCH ARTICLE

Asia-Pacific Journal of
Chemical Engineering · Curtin University · WILEY

Rare earth element stripping from kaolin sands via mild acid treatment

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Abstract

Due to their chemical and physical properties, rare earth elements (REEs) are essential in modern applications such as energy conversion or IT technology. The increasing demand for these elements leads to strong incentives for REE recovery and induces the exploration of new, alternative sources for REEs. Accessing REEs from clay minerals, in our case kaolinite, by an elution process is a promising method. The present study investigates the potential application of REE recovery through elution with different mineral acids (HNO_3, H_2SO_4, and HCl) in a microwave process. The material used in this study—residues from an industrial kaolin production process—contained 2.47 g/kg REEs which is a significant amount for REE recovery. The ability of various mineral acids to solubilize metals was studied to assess the REE content of this residual resource. Around 1.87 g/kg of REEs was eluted from industrial kaolinite residues in hydrochloric acid, 1.71 g/kg in sulfuric acid, and 1.13 g/kg in nitric acid.

KEYWORDS
elution, extraction, process data, kaolinite, rare earth element recovery, rare earth elements

1 | INTRODUCTION

Rare earth elements (REEs) are essential materials in today's energy production and IT technology. Due to their wide range of applications, such as permanent magnets, lenses, catalysts, luminescent substances, light emitting diodes, and many others, the demand for REEs is forecast to keep growing in the near future.[1–4] REEs are usually accessed and extracted under harsh conditions.[5] China is the leading producer of rare earth oxides, with an annual production of 210.000 t out of 300.000 t worldwide (2022).[6] The technological importance of REEs leads to an economical supply dependency of industrialized nations on a few producers, which is also a geopolitical factor. New, more environmentally friendly and viable sources/processes to access or recover REEs are being intensely investigated.

The mineral kaolinite, $Al_2(OH)_4Si_2O_5$, belongs to the phyllosilicate group. In nature, this mineral is most abundant within kaolinite group. Kaolinite is a layered mineral that consists of an octahedral alumina layer and a silica layer of tetrahedrally coordinated Si atoms (1:1 ratio), which share a common plane of oxygen atoms.[7,8]

Kaolinite is extensively used in the ceramics production,[9] papermaking,[10] cosmetics,[11] and pigment

industry.[12] Furthermore, it appears to be an excellent ion-adsorbent for various cations. Bear et al. first discussed the cation exchange capacity (CEC) of kaolinite, describing the mineral's ability to exchange cations and retain nutrients in soil.[8,13,14] Due to the influence of abiotic factors (e.g., weathering), valuable metal ions readily accumulate between the layers, including REEs.

Recently, such ion-absorbing clays are becoming more and more important REE resources in the REE mining industry.[15,16] The REEs are not chemically bound to the clays but are rather physisorbed.[17] On the surface, most of the lanthanides are adsorbed in the acidic environment as simple or hydrated cations, such as "clay-REE" or "clay-REE(H_2O)$_n$" types.[17] According to Jun,[18] the ion adsorption in clays is divided into three categories due to the various weathering conditions: colloid phase, exchangeable phase, and mineral phase.[17,18] The REEs are deposited in the colloid phase as insoluble oxides and hydroxides in organometallic compounds. These occur only in small amounts in ores and can be recovered only by acid leaching. In the exchangeable phase, the REEs are present as free soluble cations on clays or in between the layers. These species form most of the total content of adsorbed REEs obtained by ion exchange leaching. The lanthanides are firmly attached in the mineral phase as fine solid particles in the crystal structure and can only be obtained by very elaborate and aggressive methods.[17] Unlike in ores, in the clay minerals, REEs can be easily obtained by ion exchange, described in detail by Hendricks et al.[16,19] REEs from kaolinite are accessible via acids or salts and can be classified in the first or second category, respectively.[1,15,20]

In the leaching process, concentrated salt solutions or weak acids are most often used as leachants to obtain REEs. Accordingly, the cation of the leachant can exchange the REE cations attached between the aforementioned layers.[15]

The aim of this paper is to investigate an energy-friendly process and elucidate the influence of different media on extracting REEs from kaolinite samples. For this study, we used residues from the kaolin refinement process at the production site Amberger Kaolinwerke (AKW, Hirschau, Germany). We investigated the refined residues instead of bare kaolinite because we expected an enrichment of REEs in such residues after the industrial purification process.

One example of REE recycling of dissolved REE ions in aqueous solution was recently reported, and the potential of cyanobacteria for the adsorption and enrichment of REEs was tested.[21] REEs were coordinated effectively to functional groups at the surface of these cyanobacteria at pH values between 5 and 6. With this study, we intend to illustrate an effective way to access REEs from mineral residues capable to be utilized in modern REE recycling processes.

2 | EXPERIMENTAL

2.1 | Materials and methods

The residual materials were obtained from different production steps of the kaolin refinement from AKW. This company provided various deposited samples (RK 1 to RK 15) from different steps in the kaolin production/refinement that could be considered a possible raw material for the subsequent extraction of REEs. These samples were characterized in detail, and their elemental composition was investigated with regard to REEs and other metals. In this study, the REE content of the residual material streams produced at AKW was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES). Various acids with different concentrations were used to extract REEs from these samples. Elution and digestion of REEs from residues of kaolin production were processed using microwave-assisted elution. All used chemicals are listed in Table 1. The phase analysis of all samples was performed by powder X-ray diffraction (XRD).

2.1.1 | Elution and digestion of REEs using microwave

The extraction experiments from kaolinite clay minerals residues were performed by *ETHOS One* Microwave Laboratory solutions of the company MLS GmbH. For this purpose, 0.5 g of each sample and 9 mL of a mineral acid (aqueous) were added to Teflon vessels. The acids were concentrated nitric acid (65%), hydrochloric acid (30%), sulfuric acid (96%), hydrofluoric acid (47–51%), diluted nitric acid (15%), hydrochloric acid (5%), and sulfuric acid (19%). The Teflon vessels were heated to 65°C for 1 h in a microwave oven at 400 W power during continuous stirring. The heating and cooling phases were set to 25 and 30 min, respectively. This entire protocol defines

TABLE 1 List of chemicals used in the elution process, manufacturer of the chemicals, and purity (analytical quality).

Substance	Manufacturer	Quality
Nitric acid (HNO_3)	VWR-Chemicals	67%, Ultrapure NORMATOM®
Hydrochloric acid (HCl)	VWR-Chemicals	30%, Ultrapure NORMATOM®
Sulfuric acid (H_2SO_4)	Merck	96%, Suprapur®
Ultrapure water	-	deionized, specific resistance according to Direct-Q® 3 UV: 18.2 MΩ.cm

one elution process step in the following study. Multiple elution steps, as stated later on in the manuscript, means that the protocol was performed several times. In this case, the previous residue from an elution step was filtered off of the elution solvent without further drying or workup, 9 mL of fresh elution acid was refilled, and the elution process was started again.

2.2 | Characterization methods

2.2.1 | Powder X-ray diffraction (XRD)

Powder XRD data were collected on a STOE STADI P powder diffractometer (Cu-K$_{\alpha1}$ radiation ($\lambda = 1.54051$ Å, Ge-monochromator) equipped with a *DECTRIS Mythen 1 K* detector. The powder XRD data were derived from a 14-h measurement in a *Hilgenberg* glass capillary with 80-mm length, 0.5-mm outside diameter, and 0.01-mm wall thickness. The program package *STOE WinXPOW* was used to process the raw data for phase analysis performed in *Jana2006*.[22,23] Literature data for kaolinite,[24] quartz,[25] orthoclase feldspar,[26] muscovite,[27] and gorceixite[28] were used to identify the most probable phases occurring in RK1 and RK2. This selection of phases is based on the knowledge provided by AKW. We used the published structure models without refining of atomic coordinates or displacement parameters. Isotropic displacement parameters were set uniformly to a standard value of 0.02 Å^2 for all non-hydrogen sites and 0.04 Å^2 for hydrogen sites. In order to allow a certain deviation from the published lattice parameters for each phase due to substitutions and impurities in natural minerals, we allowed the refinement of the lattice parameters of each component. We found a maximum deviation of 0.21% for the lattice parameters in our refinements compared with literature values. A detailed summary of the lattice parameters is given in Table S2. We refined the fractions of the five different phases neglecting the occurrence of additional phases which might be present in our samples. As a final outcome of such a rudimentary refinement, we estimated the overall composition of the samples based on these five components.

2.3 | Analytical methods

2.3.1 | Inductively coupled plasma optical emission spectrometry (ICP-OES)

The resulting samples were analyzed with an *Agilent 725* (ICP-OES) spectrometer with radially viewed plasma to determine the amount of REEs and other metals. The ICP-OES equipment includes a *VistaChip II CCD* detector that provides a complete wavelength range from 167 to 785 nm. Additionally, the ICP-OES system is equipped with an *Agilent SP3* auto-sampler, which allows automatic measurement. The operating conditions are shown in Table S1. Five points were measured for the calibration line (50, 10, 1, 0.1 mg/L, and blank). The resulting samples were diluted in the ratio 19:1 and then measured. The measurement data was processed using the software *Agilent ICP Expert II*. The ICP standards used are listed in Table 2.

2.3.2 | X-ray fluorescence (XRF)

XRF data were recorded on a *S8 LION* X-ray spectrometer from Bruker AXS. The dried sample was reduced to the required amount by a sample divider. Then the sample was ground in the analytical mill for 12 min. The sample material is homogenized in a Turbula mixer for 5 min after the addition of two *Widia* balls. After removal of the balls, the homogenized powder is pressed into a tablet using a press and pressing tools. In a drying cabinet (2 h) or microwave (2 min), the ground sample was dried. The dried sample was then mixed with the flux agent lithium tetraborate, melted in a muffle furnace at 1150°C for 15 min, poured onto a platinum-gold mold, and then rapidly cooled with compressed air. This was followed by the measurement. The measurement data were processed using the software *SpectraPlus*. Each sample was measured for 60 s.

2.3.3 | Scanning electron microscopy (SEM)

The samples were prepared on a steel holder with a double-sided conductive adhesive tape from Plano GmbH. Scanning electron microscope (SEM) images were collected by a Jeol JSM-IT200 InTouchScope™ electron microscope, and the acceleration voltage was set to 10 kV.

TABLE 2 ICP standards used for quantitative analyses.

Substance	Manufacturer	Quality
Rare earth element mix for ICP	Merck	50 mg/L: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu in 2% nitric acid
ICP multi-element standard solution IV	Merck	1000 mg/L: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn

Note: ICP, inductively coupled plasma.

3 | RESULTS AND DISCUSSION

It has been shown that some natural sources of alumino-silicate minerals, such as kaolinite or feldspar, may contain up to 0.2 wt.% REEs.[29] REEs are often only physically adsorbed in the minerals or, in the case of kaolinite, intercalated between the mineral layers. These physisorbed ions are therefore rather easy to recover. The adsorption of cations in alumina-based minerals like kaolinite is enabled by the isomorphous substitution in the cation substructure of, that is, Si^{4+} against Al^{3+}, which induces a permanent negative charge in the aluminosilicates.[29] Unfortunately, the REE content in natural minerals is too low to be interesting for industrial REE recovery, and an enrichment of the REE content to significant levels > 2% is needed. Our intention with this study is to verify if accessible deposited industrial kaolinite residues are in principle suitable for REE recovery, and if a process can be developed to enable a more environmentally friendly REE recovery process than to entirely rely on the hazardous state-of-the-art production process.[30–32]

In the following paragraphs, we will illustrate that kaolinite residues, which are annually generated on a multi-ten-thousand-ton scale worldwide as a discarded side product, are suitable source for REE production. In our study, we concentrated our interest on residues from AKW, Germany. For this study, the kaolinite samples from AKW were eluted in various inorganic acids, and the amount of REEs was determined by ICP-OES in the obtained elution media.

3.1 | Phase analysis of kaolinite residues

The aim of this study is to evaluate the efficiency of elution processes for REE recovery from kaolinite residues that emerge after industrial kaolinite refinement. We used various forms of residues from AKW that were separated from the main products and deposited after the refinement process (RK1 and RK2) as well as samples (RK3 to RK15) taken at different steps in the separation and purification process. Natural kaolinite sources usually contain kaolinite as a major phase and also several other side phases. For raw material from AKW, the most likely ones are α-quartz, orthoclase feldspar, muscovite, and gorceixite.[25–28] Multiple separation steps are required to separate the different phases and to purify the single phases prior to the usage. The raw material at AKW is treated in a magnetic separation process, whereby the purer stream is separated from the magnetic impure side stream. Usually, kaolin and all other minerals that contain magnetic cations like Fe^{3+} are colored and are therefore separated from the white residues by a refinement process using strong magnets. This magnetic side fraction was concentrated in this process and formed the RK2 residue. RK1 resulted from another separation process step during the kaolin production that did not use magnetic separation. RK1 and RK2 are major residues that are produced on a multi-thousand-ton-scale annually at AKW and are deposited after the refinement process. On the other hand, RK3–RK15 are side residues in lower amounts, which occur during the refinement process at different stages within the industrial workup process of kaolin. Due to the overall low amount of REEs in RK3 to RK15 (see later on in the elution chapter of this study), we decided to perform a phase analysis for RK1 and RK2 only, because they are relevant for REE recovery due to their availability and the REE content. In addition, RK1 had a higher weight percentage of rare earth metals compared to samples RK3–RK15, which most likely resulted from abiotic environmental factors, for example, water (pH), light, atmosphere, temperature, and salinity.[33]

The powder diffraction pattern of the residue samples (RK1 and RK2) are shown in Figure 1. Beside $Al_2Si_2O_5[OH]_4$ (kaolinite)[24] itself, major expected side phases like SiO_2 (α-quartz),[25] $KAlSi_3O_8$ (orthoclase feldspar),[26] and $KAl_2(AlSi_3O_{10})(F,OH)_2$ (muscovite)[27] are denoted. Due to an XRF analysis provided by AKW (see Tables S3–S6) that contained Ba and phosphate as minor components we added $BaAl_3(PO_4)(PO_3OH)(OH)_6$ (gorceixite)[28] as an additional and most-probable phase in the XRD phase analysis. Calculated reflection intensities based on published structure data of those compounds are drawn with negative intensity for better visibility and comparison. The main reflections in the powder diffractograms belong to kaolinite, and they are denoted with stars in Figures 1 and 2. According to the Rietveld refinement of RK1 and RK2, in total, five phases were identified and used for phase analysis: kaolinite (k), quartz (q), feldspar (f), muscovite (m), and gorceixite (g). The refinement for RK1 ensued following phase ratios (k/q/f/m/g): 80.3/5.1/11.2/3.1/0.3 atomic ratio, and for RK2 the 80.1/5.0/11.2/3.4/0.3 atomic ratio.

3.2 | Utilization of various kaolinite residues for REE recovery

3.2.1 | General aspects

In the first step, 15 local kaolinite clay mineral residues (RK1–RK15) were collected from different deposition spots and process steps during the kaolinite refinement at AKW to identify the most valuable samples for REE
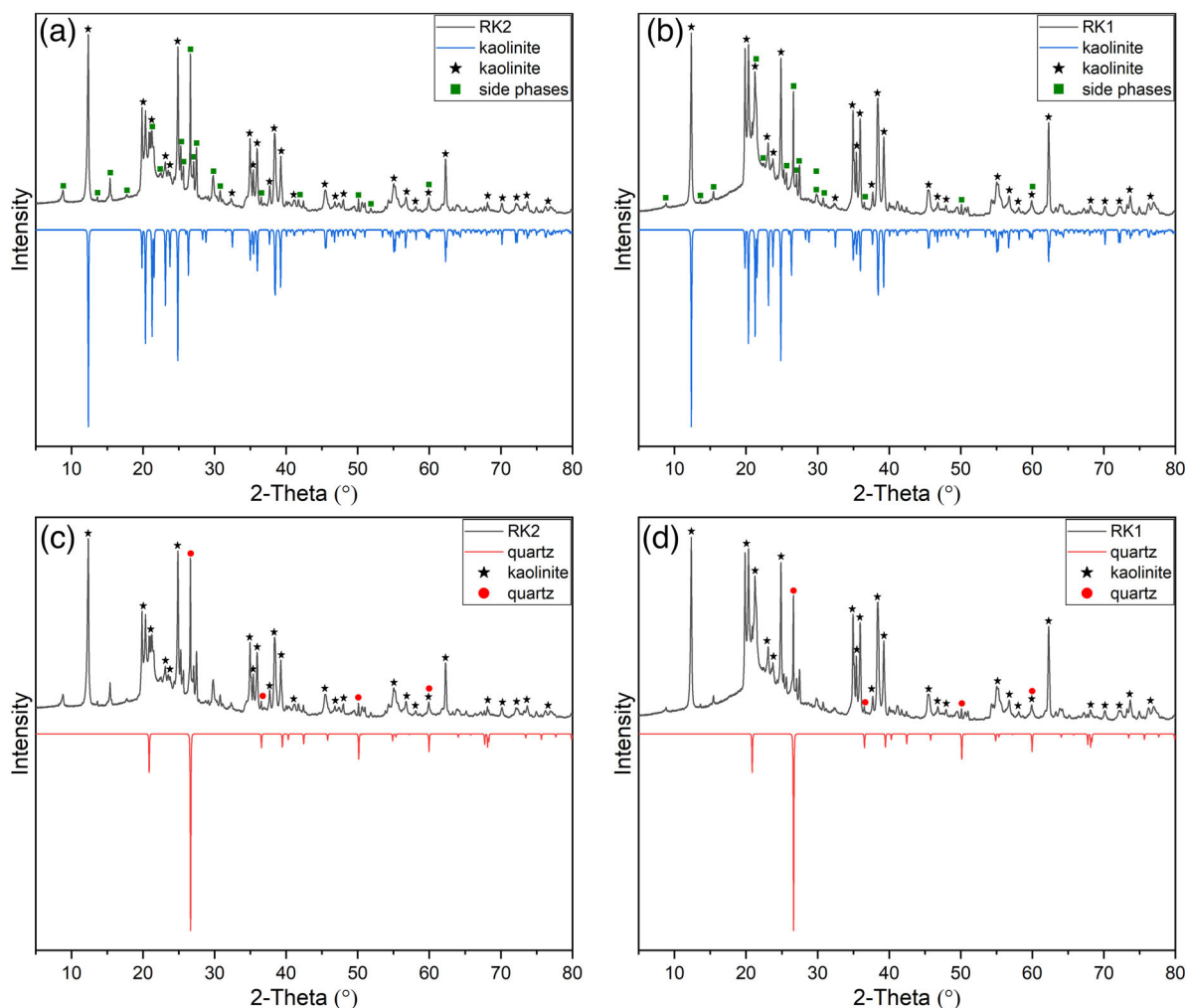
FIGURE 1 X-ray diffraction (XRD) data of RK1 (right) and RK2 (left) derived from a 14-h measurement in a capillary. Calculated diffractograms based on structure data of kaolinite[24] and quartz[25] are drawn with negative intensities. The main phase, kaolinite (star), and all side phase reflections (square) are denoted for the (a) RK2 and (b) RK1 samples; non-overlapping reflections of the minor phase, quartz (circle) are illustrated in the (c and d) diffractograms.

extraction. In a cation exchange elution process, we intend to extract as much REEs as possible rather than to perform a complete dissolution of the kaolinite matrix or to delaminate kaolinite into smaller fragments.

Grim et al. summarized the difference in the shape of adsorption isotherm for kaolinite and showed a variation depending on the cation-exchange capacity (CEC),[14] which describes the number of how many cations can be ingested between the negatively charged interlayer in the soil. The CEC depends on the size of the cation; the larger the ionic radius, the higher the relative adsorption.[14] The relation of hydration and interlayer expansion of dehydrated and contracted particles along the adsorption isotherms is described in five steps by adsorbing water molecules.[34] The ability to absorb water in the interlayer is proportional to the cation exchange capacity per unit area.[34]

Hendricks et al. discussed the cation exchange of crystalline silicates.[19] In general, silicate structures are determined by the ratios of negative ions (usually oxygen of the silicate units) to positive ions, the ratios of the ionic radii which determine the coordination number of cations, and a principle of microscopic neutrality.[19] The cations are located in the vicinity of the excess negative charge of the silicate framework to conform to the conditions of microscopic neutrality. Typically, the negative position in the lattice structure is caused by the replacement of low by higher charged cations, such as M^{2+} for M^{3+}, often showing a similar radius. The anion framework of kaolinite consists of octahedrally arranged oxide ions around aluminum (Al^{3+}) and tetrahedrally coordinated silicon cations (Si^{4+}), respectively. Due to this structure, the migration of ions through the layers is prevented. The compensation of the excess negative charge
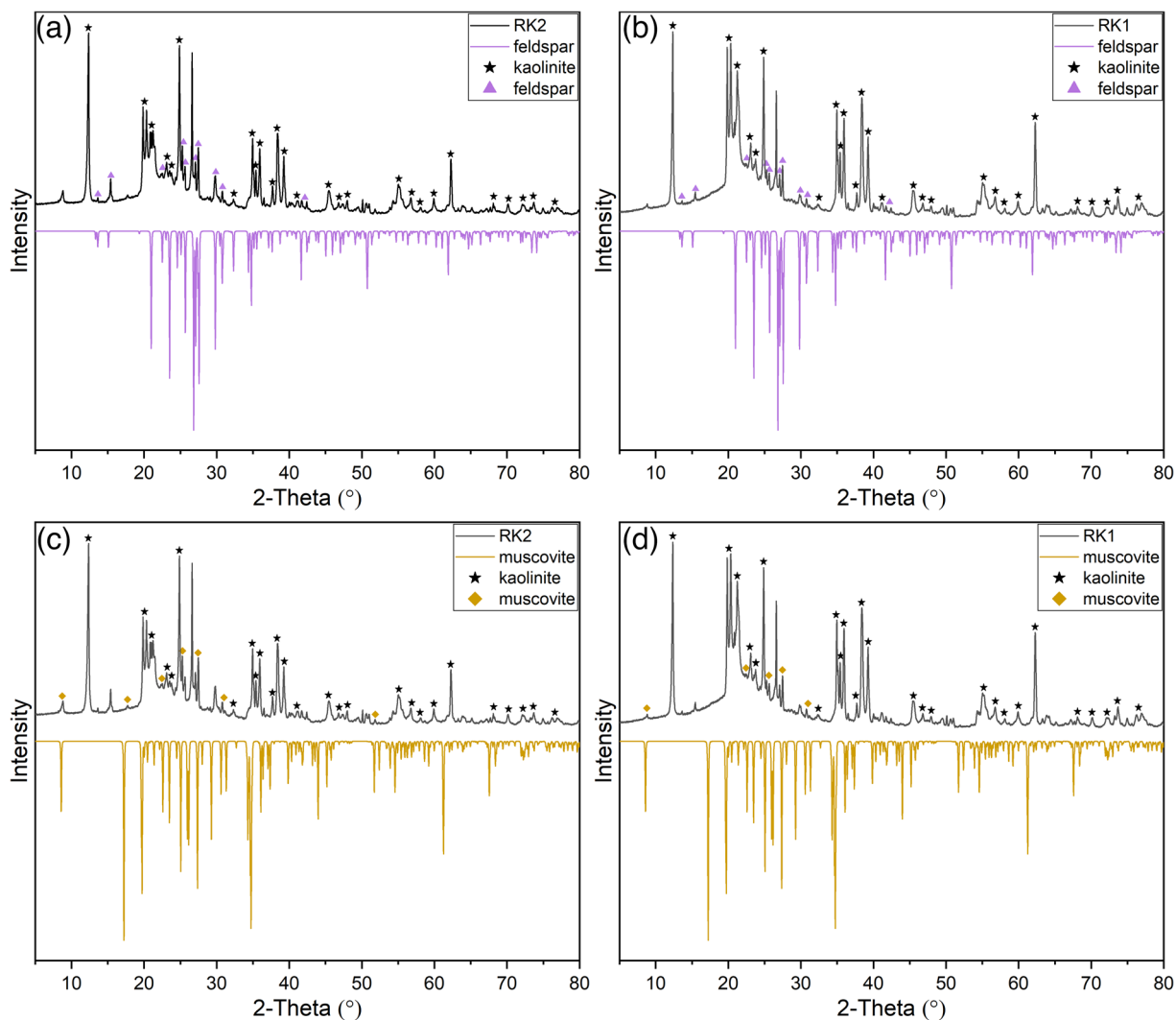
FIGURE 2 X-ray diffraction (XRD) data of RK1 (right) and RK2 (left) derived from a 14-h measurement in a capillary. Calculated diffractograms based on structure data of feldspar[26] and muscovite[27] are drawn with negative intensities. The main phase, kaolinite (star), and non-overlapping reflections of the minor phases, feldspar (triangle) and muscovite (diamond), are marked in the (a–d) diffractograms.

can only be achieved by external cation exchange in the interlayers to ensure the neutrality requirement.[19] The cation exchange by H^+ follows this principle, the positively charged cations in the interlayers are exchanged with H^+ in a stepwise manner migrating them out of the kaolinite framework. We took SEM images of selected samples before and after the elution process. Neither a significant change in morphology nor a tendency for degradation/delamination of the materials after the ion exchange could be observed. Selected SEM images are summarized in Figures S1 to S4.

Such an exchange procedure would allow an energy- and resource-effective elution process at low temperatures and with economic usage of elution solvents, most probable in a continuous, resource-efficient, and closed process cycle. Price and availability (even in existing industrial processes at kaolinite manufacturers) were the

primary reasons for the examination of standard acids (HCl, HNO_3, and H_2SO_4) for the elution process. After the elution of REEs from the kaolin residues, the intention is to adsorb the REEs on cyanobacterial biomass from the diluted solutions that are generated by the process to make them accessible for further workup processes. Recently, this process was reported showing the efficiency of REE recovery.[21] Here, the influence of the concentration of REEs, the acidity of the solvent, and the type of REEs on the adsorption capacity of different cyanobacteria was evaluated. Five cyanobacteria (*Nostoc* sp. 20.02, *Synechococcus elongatus* UTEX 2973, *Calothrix brevissima* SAG34.79, *Desmonostoc muscorum* 90.03, and *Komarekiella* sp. 89.12) were identified that are capable to adsorb reasonable amounts of REEs. Dependent on the conditions, these cyanobacteria were able to absorb 84.2–91.5, 69.5–83.4, 68.6–83.5, 44.7–70.6, and 47.2–

67.1 mg g^{-1} (milligram REEs per gram dry biomass), respectively. After drying and burning the biomass, the accumulated REEs can be transferred to their respective oxides in a concentrated form, which are then ready for subsequent separation processes. This represents the first step towards an economic and environment-friendly process for biosorption-based REE recovery.

In the following discussion throughout the paper, the given results always refer to the sample mass and represent only the recovered amount of REEs in the investigated soil sample. Naturally, a certain fraction of REE cations remain physisorbed in the kaolinite residue.

3.2.2 | Elution of kaolinite residues for REE recovery with concentrated acids

A total number of 15 samples from AKW (RK1 to RK15) were analyzed as potential candidates for REE elution. Concentrated nitric acid (67%), sulfuric acid (96%), and concentrated hydrochloric acid (30%) were used as elution media.

A first series of elution experiments was conducted with concentrated (67%) nitric acid (Figure 3a). The results of this experiment series show that for samples RK3–RK15, only a certain low weight proportion of REEs (between 0.1 and 0.2 g/kg) can be extracted. In contrast, the aforementioned samples, RK1 and RK2, contain high amounts of accessible REEs. Those two samples are discussed in more detail as follows.

Elution in concentrated nitric acid yields a REE weight proportion of 1.13 g/kg for RK2 and 0.79 g/kg for RK1 (Figure 3a), respectively. To verify the elution efficiency, the overall REE content of these two samples by complete dissolution of the samples in HF/H_2SO_4 was determined. Obviously, RK1 adsorbed significantly less REEs than RK2. An overall REE content of 2.48 g/kg for RK2 was determined and 0.93 g/kg for RK1 (see also Figure 3, HF/H_2SO_4 column). Around 45.6% of REEs are recovered in RK2 in one extraction step, while this percentage increases to 84.9% for RK1. The elements Ce, La, Nd, Pr, and Y represent the majority of the retrieved REEs in the systems and belong to the LREEs (light rare earth elements, La-Sm) group in good accordance with the natural abundance.

For this purpose, the REEs were recovered by an ion exchange mechanism in which the adsorbed REEs in the mineral is exchanged by H^+ ions of the acid.[35–37] REE cations are transferred by this simple leaching process into solution with nitrate, chloride, or sulfate as counter ions. There are numerous studies on such a cation exchange reported in the literature.[38–40] Beside

studies on minerals, they also include cation extraction in hyperaccumulator plants, seaweed, and algae.[38,41,42] Ion exchange is based on the chemical equilibrium in which the cations are exchanged and the state of equilibrium is influenced by the substance concentration. Accordingly, the adsorbed ions are displaced by the excess of other ions. Therefore, a higher concentration of acid leads in principle to a higher weight fraction of extracted REEs.

After the promising results for elution with concentrated nitric acid, the behavior of concentrated sulfuric acid (96%) and concentrated hydrochloric acid (30%) as elution media was investigated in order to optimize the elution process (Figure 3b and c). Using concentrated hydrochloric acid, a higher percentage of REEs can be obtained than with the previous method. Amounts of 1.89 g/kg (76% elution rate) for RK2 and 0.90 g/kg (97% elution rate) for RK1 were realized. A set of experiments using concentrated sulfuric acid indicates a slightly higher elution efficiency for RK1 but less efficiency for RK2. For RK2 and RK1, 1.73 g/kg (70%) and 0.95 g/kg (102%) could be recovered, respectively. Evidently, an efficiency of 102% is not possible, and one has to take the experimental errors during elution and elemental analysis into account. Additionally, the results can also be influenced by the inhomogeneity of the clays. It is obvious that the pH value plays a crucial role in the elution process and anions are not affecting the REE elution efficiency. Taking pKs values of the acids into account, the acid strength is $HCl > H_2SO_4 > HNO_3$ with values of -6, -3, and -1.32, respectively. This fits to the trend that HNO_3 shows the less-effective elution tendency followed by H_2SO_4 and HCl for RK2.

From our results, it can be concluded that there is no significant difference in the REE elution efficiency for RK 1 when different concentrated acids are used (see also Figure 4, right column). Concentrated sulfuric acid seems slightly more favorable than concentrated hydrochloric acid, but the elution appears to be almost quantitative for all cases. Nevertheless, all studied processes show a one-step elution efficiency greater than 85%.

Amounts of 0.87 g/kg in concentrated hydrochloric acid, 0.93 g/kg in concentrated sulfuric acid, and 0.79 g/kg in concentrated nitric acid were recovered for RK1 (Figure 4). The total REE content of 0.95 g/kg was determined by hydrofluoric acid dissolution of RK1. This total amount is only marginally higher than the amount of REEs found after a one-step elution process with all concentrated acids. As shown in Figure 4, the dissolving capability of RK1 for each concentrated acid is saturated at over 85%.
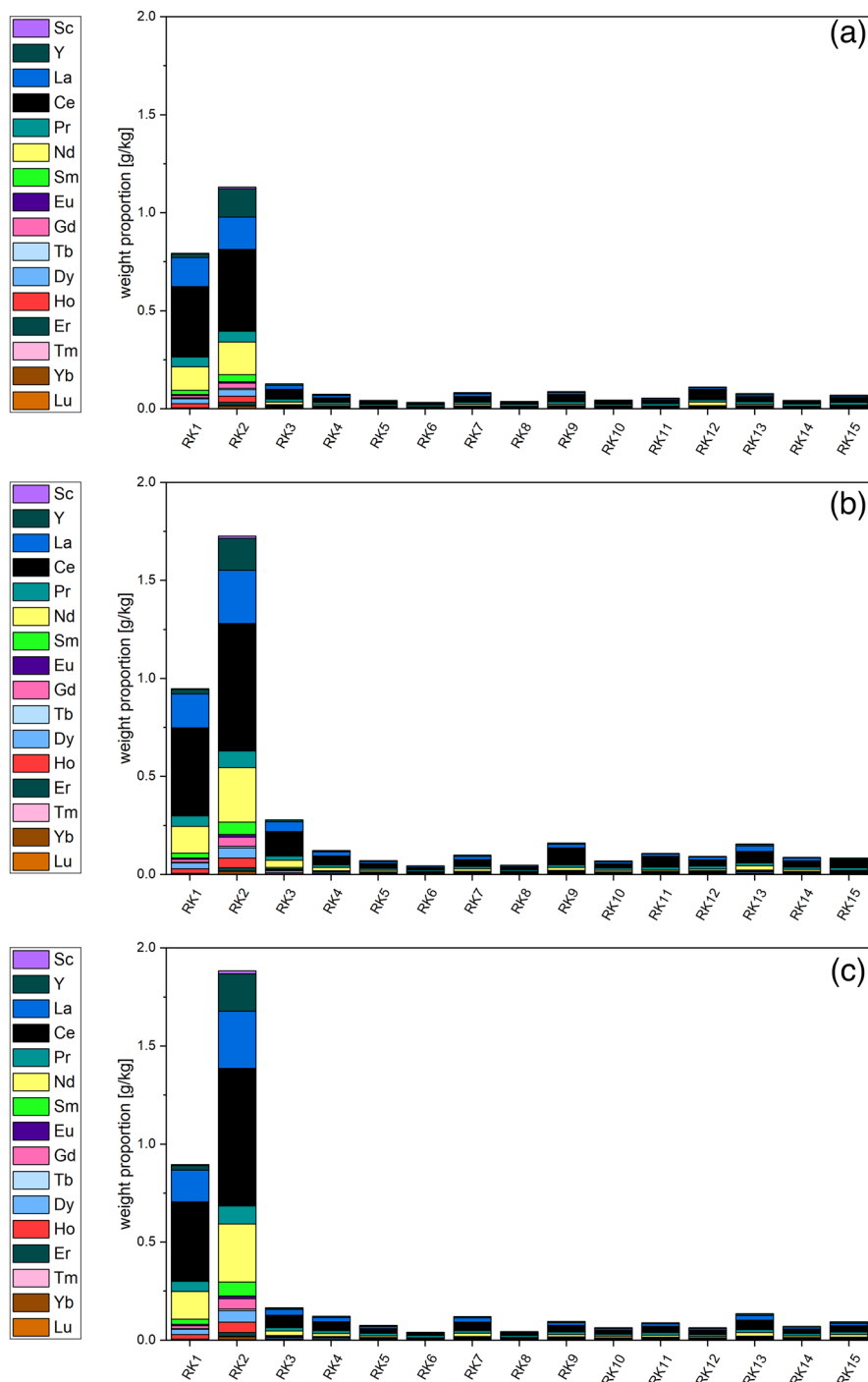
FIGURE 3 Weight proportion of REEs from different soil samples after concentrated acid treatment. (a) HNO_3, (b) H_2SO_4, and (c) HCl. Based on the results, the LREEs (light rare earth elements) were mainly recovered from the residual kaolinites. The investigation of all samples showed that only RK1 and RK2 are suitable for REE elution due to their elevated REE content.

3.2.3 | Elution of kaolinite residues for REE recovery with diluted acids

One focus of our study is the optimization, cost reduction, and development of a more environmentally friendly REE-elution process from kaolinite. Therefore, in order to pursue these objectives, we have replaced the concentrated mineral acids with diluted ones and verified the elution efficiency of these reagents.

In this regard, we have conducted a series of analogous elution experiments with diluted nitric acid (15%), hydrochloric acid (5%), and sulfuric acid (19%)—a dilution factor of approximately 4.5 compared to the concentrated acids. In Figure 4, it becomes evident that concentrated acids are beneficial for a one-step elution process for RK2. Between 46% and 76% of REEs can be accessed in a single elution step, resulting in weight fractions larger than 1 g/kg in all cases. This one-step
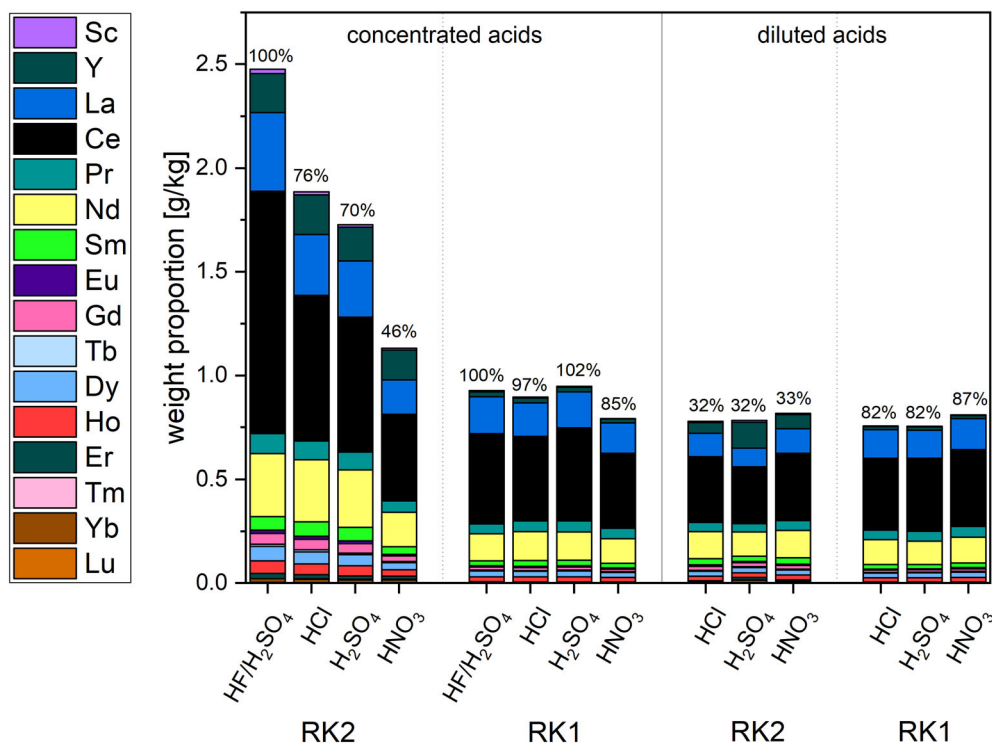
FIGURE 4 Summary of REE weight proportions after a single elution process from different soil samples RK2 and RK1. Concentrated (left set of columns) and diluted acids (right set of columns) are shown. RK2: Conc. hydrochloric acid 1.89 g/kg, conc. sulfuric acid 1.73 g/kg, and conc. nitric acid 1.13 g/kg of REEs were achieved after one single elution process from an overall REE content of 2.48 g/kg (HF/H$_2$SO$_4$ column). Using diluted acids for RK2, a single elution process resulted in values around 0.8 g/kg. RK1: almost the entire amount of REEs can be achieved in a single elution process using conc. acids. Amounts reaching 0.9 g/kg. Only conc. nitric acid is less effective with only 85% REEs. In the case of diluted acids, values of about 0.8 g/kg were observed.

efficiency drops to around 32% for diluted acids. In the case of RK1, the elution efficiency is significantly increased. Independent of the type and its concentration, this efficiency increases to values of 82 to >99%. Even the difference in efficiency for concentrated compared with diluted acids in the case of RK1 is marginal. Unfortunately, the accessed weight fraction of REEs is around 0.9 g/kg in all cases due to the overall lower REE content in RK1.

While the elution process for RK1 cannot be optimized further, there is potential for RK2. We therefore varied the elution acid amount and performed a multi-step elution to enhance the REE recovery outcome. Doubling the acid amount during one elution step did not significantly influence the elution efficiency for RK2, as illustrated in Figure 5. The elution capacity of the acids is therefore not the limiting factor in this process. However, the resulting weight proportion of REEs recovered remained approximately at 0.9 g/kg. Therefore, a multi-step elution process was tested to enhance the elution efficiency in the case of diluted acid treatment.

Here, an elution step was performed three times for RK2 using the same parameters as for the one-step case.

With a total weight content REEs of 1.38 g/kg in a three-time elution process using diluted hydrochloric acid and 1.19 g/kg in diluted sulfuric acid, the weight proportions of REEs increased by 69% for hydrochloric acid, by 37% for sulfuric acid, and by 24% for nitric acid in comparison to a single step elution. After each elution step, the REE content in the elution medium was evaluated, and all results are summarized in Figure 5.

3.3 | Dissolution processes during REE recovery

Not only rare earth elements are accessed in the elution series. It is also necessary to determine the amount of non-REE ions that are accessed by the aforementioned processes. This knowledge is crucial for all upcoming processes like REE adsorption and enrichment using bacteria and REE separation in principle. All elements present in the elution solvents were quantified by ICP-OES analyses.

Out of all present elements in kaolinite (Figure 6, HF/H$_2$SO$_4$ column), mainly aluminum, iron, lead, alkali-
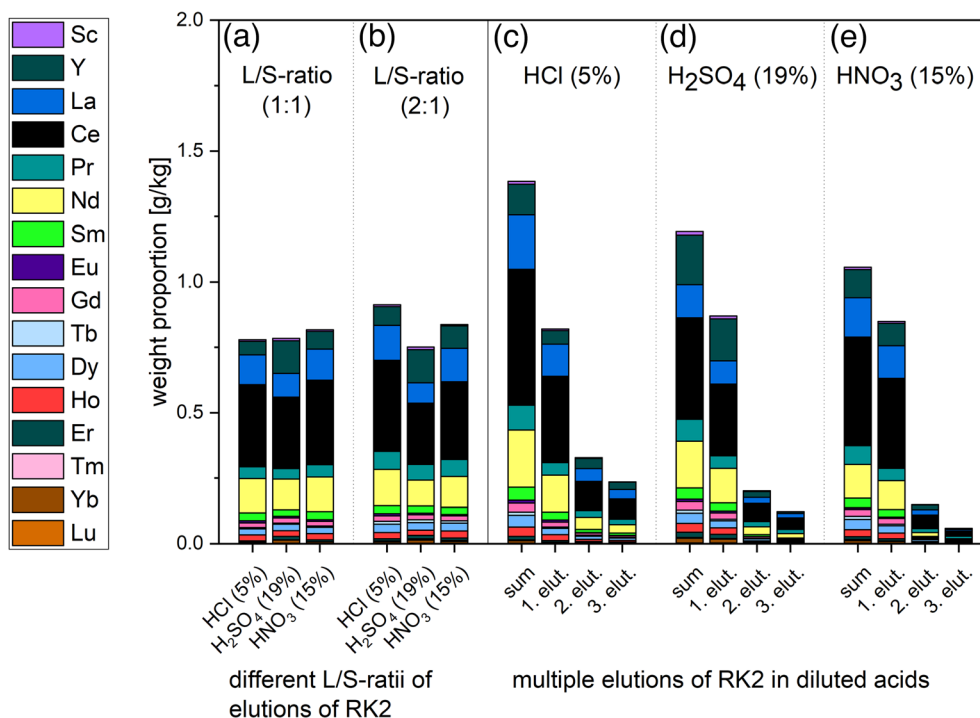
FIGURE 5 REE recovery from different soil samples after liquid/solid ratio variation and multiple diluted acid treatment. Results are denoted after varying the liquid–solid ratio (L/S ratio) from (a) 1:1 to (b) 2:1 in diluted HCl, dil. H_2SO_4, and dil. HNO_3. REE weight proportion of RK2 soil samples after diluted acid treatment in a multiple elution process (3 times) using (c) HCl, (d) H_2SO_4, and (e) HNO_3. After multiple elution of RK2 in dil. acids, an increase of REE recovery to 1.38 g/kg with HCl, 1.19 g kg with H_2SO_4, and 1.06 g/kg with HNO_3 were observed, which translates to 69% (dil. HCl), 37% (dil. H_2SO_4), and 24% (dil. HNO_3) increase compared with a one-step elution process (data see Figure 4).
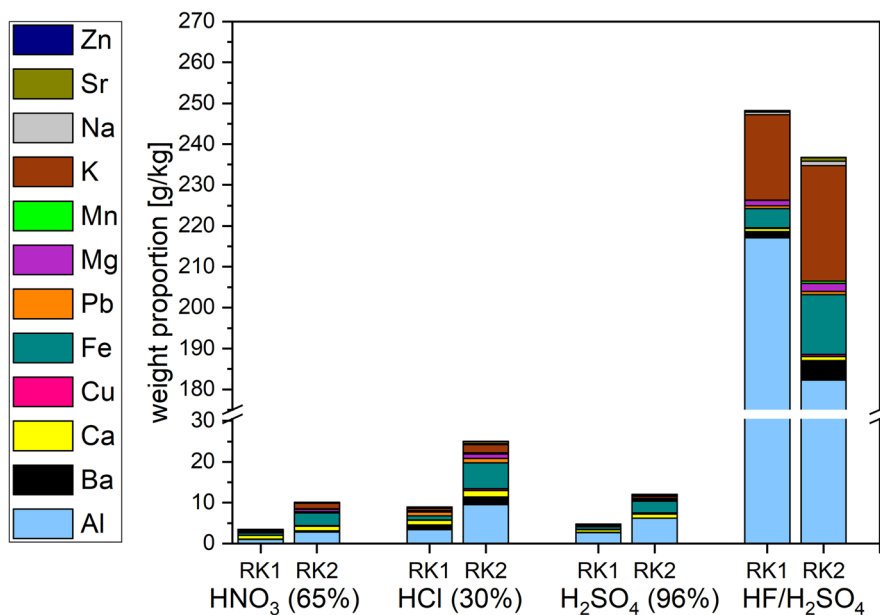

FIGURE 6 Weight proportion of non-REEs after elution of RK1 and RK2 samples in concentrated acids (HNO_3, HCl, and H_2SO_4). The HF/H_2SO_4 value represents the entire amount of all ions after dissolution. As expected for kaolinite, aluminum represents the main component.

and alkaline earth metals were found in solution. In Figure 6, the highest concentration of secondary metals (25.03 g/kg) was found after the elution of RK 2 in concentrated hydrochloric acid. In comparison, 8.94 g/kg is

dissolved for RK1 in a similar process. The total metal ion contents after treatment of RK1 (4.18 g/kg) and RK2 (12.04 g/kg) with concentrated sulfuric acid are much lower than in concentrated hydrochloric acid and slightly

FIGURE 7 Weight proportion of non-REEs from RK1 and RK2 samples in diluted acids. (HNO₃, HCl, and H₂SO₄).
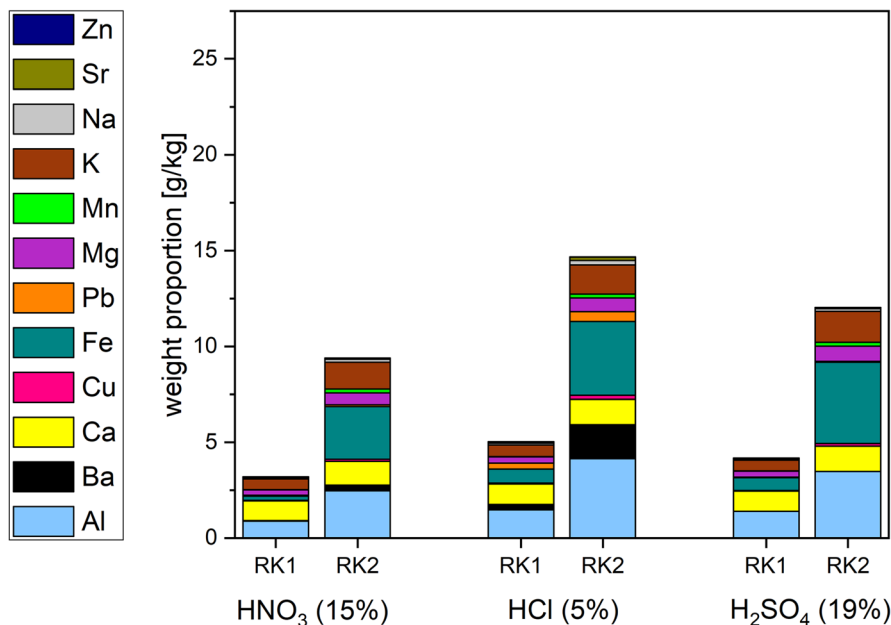
larger than in nitric acid (Figure 6). For the latter acid, we have achieved the lowest values of secondary metal extraction, 10.07 g/kg for RK2 and 3.44 g/kg for RK1.

High amounts of lead were observed after the hydrochloric acid process, and moderate amounts were retrieved with the nitric acid treatment. In contrast, no Pb^{2+} ions were found after sulfuric acid treatment due to the low solubility of $PbSO_4$ (Figures 6 and 7). K and Fe were dissolved in the expected large amounts. Still, the concentration of both elements is lower when using sulfuric acid compared to the other two acids. This phenomenon is most likely due to the solubility of the salts formed, which could be of interest for further processing of REEs.

The elution processes in concentrated sulfuric and nitric acid yielded similar amounts of non-REE metals. Again, the highest metal content was determined for the elution in concentrated hydrochloric acid (see Figure 6). Therefore, based on these data, the application of hydrochloric acid is rather unsuitable for REE recovery, particularly for the purification of the REE extracts.

The environmentally friendly elution in diluted nitric, hydrochloric, and sulfuric acid was investigated with regard to the secondary metals (Figure 7). For RK2, the proportion of metals is higher in hydrochloric acid (14.69 g/kg) than in the elution with nitric and sulfuric acid (9.38 and 12.03 g/kg, respectively). For RK1, the dissolution behavior is similar to RK2, except that the overall values are lower. The content of Fe ions is higher in RK2 than in RK1, which is a consequence of the fabrication process of RK2 where magnetic fractions were accumulated during the kaolinite purification process at AKW. Compared to elution with diluted sulfuric and nitric acid, the total non-REE metal contents after elution

with concentrated acids are only slightly higher. The clear exception is hydrochloric acid. In this case, the differences in total proportions are minor, but the individual proportions differ to varying degrees, for example, the Al proportions (see Figures 6 and 7).

4 | CONCLUSIONS

In the present study, the elution of adsorbed REEs of 15 different kaolinite samples (RK1–RK15) was investigated using various acids in a microwave-assisted elution process. RK1 and RK2 samples showed the highest accessible REE outcome in weight percentages, while the other mineral samples (RK3-RK15) comprising only a minor proportion of REEs. After phase analysis, five different phases were identified in RK1 and RK2, although kaolinite is the major phase with contents >80%. The elution efficiency for REEs via ion exchange in concentrated acids for RK2 samples increases in the following order: HNO_3 < H_2SO_4 < HCl. For RK1, similar efficiencies could be observed, as the REE accessibility for each concentrated acid lies well over 80%. During the applied elution process, secondary metal ions are eluted or dissolved from the samples. These metal ions are disadvantageous for the following REE separation and work up processes. According to our study, in the case where concentrated acids are applied, a sulfuric acid elution process seems to be the most preferable one.

Another intention of this study was to enable a more environmentally friendly REE recovery process by using diluted acids. With diluted acid solutions, the elution potential does not exceed a REE weight proportion of

0.8 g/kg when dissolving REEs from clays in an one-step elution process. Moreover, the elution efficiency can be enhanced through a multiple-step process. In the multiple-step process, the diluted hydrochloric acid provided the highest increase in REE content compared with a one-step elution process, with lower values for diluted sulfuric acid and for diluted nitric acid.

Furthermore, the application of diluted acids in an elution process is advantageous for subsequent process steps, such as the metal recovery by bio-sorption, which proceeds under pH 5–6 conditions. The optimization of the elution process, which is performed in a discontinuous batch process to a semi-continuous method, is a challenging task in the future. Future studies should address the potential of this developed elution process for the recovery of REE in large-scale industrial processes.

CONFLICT OF INTEREST STATEMENT
All authors declare no conflict of interest. This manuscript has not been submitted or published elsewhere.

DATA AVAILABILITY STATEMENT
The data presented in this study are available upon request from the author.

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