Article

Selective Leaching of Rare Earth Elements (REEs) from Eudialyte Concentrate after Sulfation and Thermal Decomposition of Non-REE Sulfates

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Abstract: Eudialyte, a sodium rich zirconosilicate, is one of the promising sources for REEs (rare earth elements), particularly for HREEs + Y (heavy rare earth elements and yttrium). The key challenge in hydrometallurgical processing is the prevention of silica gel formation and REE separation from resulting multi-element leach solutions. This study deals with the selective extraction of REE from eudialyte concentrate by selective roasting. In this method, metal ions are converted into sulfates, followed by the decomposition of non-REE sulfates in a roasting step and the water leaching of the calcine. The effect of acid addition, roasting temperature, roasting time, pulp density and leaching time is studied. For sufficient conversion of REEs into sulfates, sulfuric acid is added in excess. At a roasting temperature of $\geq 750\,°C$ sulfates of zirconium, hafnium, niobium, aluminum and iron decompose into sparingly soluble compounds, while REE and manganese sulfates remain stable up to a roasting time of 120 min. The silica present in the calcine is found to be metastable even after roasting. The amount of leached Si^{4+} is dependent predominantly on the pH value of the leaching medium. Applying the method, REEs can be efficiently separated from zirconium, hafnium, niobium, aluminum and iron. However, only diluted solutions can be produced. Water leaching of calcine at high solid/liquid ratios causes REE losses resulting from formation of double sulfates and gypsum. The acid excess removed from the reaction mixture in the roasting stage can be simply recovered by treatment of the gas phase.

Keywords: eudialyte concentrate; rare earth elements; separation; sulfation; selective roasting; leaching; stability of precipitated silica

1. Introduction

Currently, there are over 270 known minerals containing REEs (rare earth elements), of which ~43% are silicates, ~23% are carbonates and ~14% are phosphates/oxysalts [1]. Despite their high number, only a few have gained industrial importance so far. Light rare earth elements (LREEs: La–Eu) are mainly produced from bastnasite ($REEFCO_3$) and monazite ($REEPO_4$). On the other hand, heavy rare earth elements (HREEs: Gd–Lu) including yttrium are obtained mainly from xenotime ($REEPO_4$) and ion-adsorption type deposits [2].

In recent years, the demand—especially for HREEs—has risen strongly [3]. However, the reserves of the main sources, ion-adsorption type and xenotime deposits, are in comparison to bastnasite and monazite reserves extremely low [2]. Furthermore, the decomposition of xenotime concentrate is difficult [4] and the REE production from ion-adsorption type deposits causes environmental damage

including permanent loss of ecosystem, severe soil erosion, air pollution, biodiversity loss and human health problems [5].

Another promising sources for HREEs + Y are some peralkaline and apatite deposits. Generally, they contain higher amounts of REEs in comparison to ion-adsorption type deposits (peralkaline deposits ≤2 wt %; apatite deposits ≤1.5 wt %) [6]. However, due to the complex mining and extraction processes they have not gained industrial significance so far. Eudialyte group minerals (EGMs)—sodium rich silicates occurring in peralkaline deposits—are used sporadically as zirconium ore and are often enriched with REEs. The development of innovative approaches for the extraction of REEs from EGMs or apatite is of great importance for securing strategic raw materials supply and could revolutionize the rare earth market [1].

EGMs are characterized by low melting temperature and high solubility in diluted mineral acids [7]. The low resistance to acids makes eudialytes amenable for cheap leaching [8]. However, during leaching high amounts of silicic acid are released, which tends to gelate. To obtain a silica-free solution more demanding methods are required [9]. Furthermore, efficient and low priced subsequent separation of individual components from resulting multi-element solutions is a big challenge.

Several approaches have been described dealing with leaching of REEs from EGMs [9–11] and with REE separation from the resulting system [12–15] so far. A silica-free solution can be obtained by the pre-treatment of eudialyte with concentrated acid and subsequent water leaching. The REE separation is achieved by solvent extraction [12,13], by precipitation as carbonates [14] or by precipitation from Na_2SO_4/H_2SO_4-system [15].

Another possibility for selective REE extraction using H_2SO_4 is selective roasting. The method is based on the different thermal stability of sulfates of REEs and other metal ions. Selective roasting was originally developed for selective extraction of nickel and cobalt from lateritic ores [16] and has been patented for selective REE extraction from primary resources in 2017 [17]. The method has also been applied for REE recovery from secondary resources such as NdFeB magnets [18] as well as red mud [19]. The great advantage of the method in comparison to solvent extraction or precipitation is the very low chemical consumption and the possible recovery of acid excess from the gas phase [20].

In this study, the selective REE extraction from eudialyte concentrate by selective roasting is introduced. The main purpose of this investigation is to assess the applicability of the method to this mineral. Choosing appropriate parameters at each process stage, efficient REE separation from zirconium, hafnium, niobium, aluminum and iron is achieved by very low chemical consumption and without neutralization of acid excess. However, only diluted solutions can be obtained due to the high amounts of released sodium, potassium and calcium ions.

2. Materials and Methods

A study of eudialyte enrichment by wet high gradient magnetic separation delivered an ore concentrate from the Norra Kärr deposit for all experiments. The mineralogical and chemical composition of the used concentrate is given in Figure 1 and Table 1.
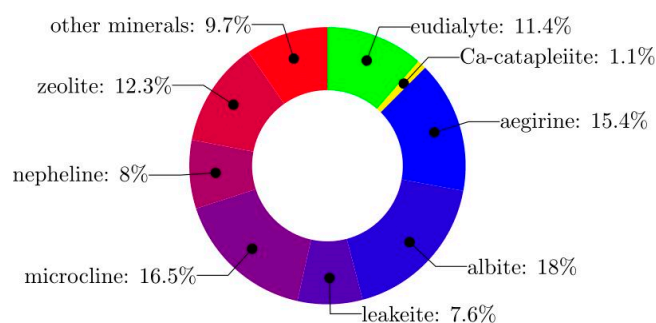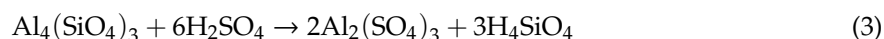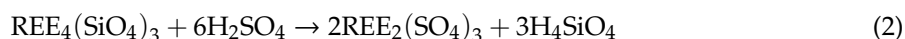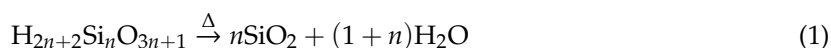

Figure 1. Mineral composition of the concentrate in wt % determined by mineral liberation analysis (MLA).

Table 1. The chemical composition of the concentrate determined after lithium metaborate fusion by ICP-OES (Na, Mg, Al, Si, K, Ca, Fe) and by ICP-MS (REEs, Sc, Y, Mn, Zr, Nb, Hf, Th, U).

Valuable Components	Content (mg/kg)	Other	Content (mg/kg)
Sc	49	Na	71,600
Y	1908	K	60,700
La–Eu (LREE)	3669	Mg	2500
Gd–Lu (HREE)	1151	Al	78,500
		Si	197,000
Mn	3210	Ca	10,900
Zr	16,270	Fe	21,800
Hf	400	Th	20
Nb	882	U	21

The concentrate contains 11.4 wt % eudialyte ($Na_4(Ca,Ce)_2(Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$). Tailings mainly consist of albite ($NaAlSi_3O_8$), microcline ($KAlSi_3O_8$), ($NaFeSi_2O_6$), and zeolite ($Na_2AlSi_3O_{10}·2H_2O$). Over 65 wt % of eudialyte particles are completely liberated, the rest is associated with Ca-catapleiite, microcline and zeolite. The d_{80}-value of particles containing eudialyte is 55 μm.

The investigated separation process consists of three stages: sulfation, thermal decomposition of non-REE sulfates and REE water leaching. In the sulfation stage the concentrate was treated in a 60 mL alumina crucible with H_2SO_4 (96%, Acros Organic, Extra Pure) at a solid/liquid ratio of 200 kg/m^3 and a predefined acid addition n_{H^+}/m_{conc}. The mixture was homogenized and heated at 110 °C for 24 h to convert the released silica into the dehydrated form (Equation (1)) and the metal ions into sulfates (Equations (2) and (3)).

$$H_{2n+2}Si_nO_{3n+1} \xrightarrow{\Delta} nSiO_2 + (1+n)H_2O \tag{1}$$

$$REE_4(SiO_4)_3 + 6H_2SO_4 \rightarrow 2REE_2(SO_4)_3 + 3H_4SiO_4 \tag{2}$$

$$Al_4(SiO_4)_3 + 6H_2SO_4 \rightarrow 2Al_2(SO_4)_3 + 3H_4SiO_4 \tag{3}$$

The prerequisite for successful REE separation is the formation of sparingly soluble compounds of accompanying components during roasting. In general, metal sulfates have limited thermal stability and decompose into oxides and SO_3 at a given temperature (Equation (4)), while released SO_3 dissociates into oxygen and sulfur dioxide (Equation (5)) [21].

$$Al_2(SO_4)_3 + 6H_2SO_4 \xrightarrow{\Delta} Al_2O_3 + 3SO_3 \tag{4}$$

$$SO_3 \leftrightarrow SO_2 + 0.5O_2 \tag{5}$$

In the second process stage the dry acid/concentrate mixture was roasted in a pre-heated muffle furnace at $T_G = 650–850$ °C for $t_G = 30–240$ min. After heating, the mixture was cooled down to room temperature and pulverized.

All leaching experiments were conducted in a three-necked flask under stirring (KPG stirrer with moon-shaped stirrer blade, $r_{R,L} = 300$ rpm) at room temperature ($T_L = 20$ °C) and at a predefined pulp density (Equation (6)) for a given time t_L.

$$\varrho_{PD,L} = \frac{m_{conc.}}{V_{leaching\ medium}} \tag{6}$$

The composition of the liquid phase was analyzed by ICP-OES Analytik Jena PQ 9000 (Analytik Jena, Jena, Germany; Na, Al, Si, Ca, Fe) and ICP-MS Thermo Scientific XSERIES 2 (Thermo Fisher Scientific, Dreieich, Germany; internal standards: 10 μg/L Rh and Re; REEs, Mn, Zr, Hf, Nb). The pH value of the leachate was measured with a Pt–Ag/AgCl electrode saturated with a 3 M KCl solution (InLab Expert). The separation factor $\beta^S_{REE/(Zr,Hf,Mn,Nb,Al,Fe)}$ was calculated by Equation (7).

$$\beta_{\text{REE}/(\text{Zr,Hf,Mn,Nb,Al,Fe})}^{\text{S}} = \frac{\beta_{\text{REE}}}{\beta_{\text{Zr}^{4+}} + \beta_{\text{Hf}^{4+}} + \beta_{\text{Mn}^{2+}} + \beta_{\text{Nb}^{5+}} + \beta_{\text{Al}^{3+}} + \beta_{\text{Fe}^{3+}}} \qquad (7)$$

3. Results and Discussion

3.1. Effect of Roasting Time, Roasting Temperature and Acid Addition

The effect of roasting temperature and roasting time on leaching yields (primary y-axis) and concentrations (secondary y-axis) of REEs, Zr^{4+}, Hf^{4+}, Mn^{2+}, Nb^{5+}, Al^{3+}, Fe^{3+} at low solid/liquid ratio of 25 kg/m^3 is shown in Figure 2. At such a low pulp density the secondary effects such as precipitation or the salting out effect can be largely suppressed. Due to the similar behavior of zirconium and hafnium both elements were considered together.
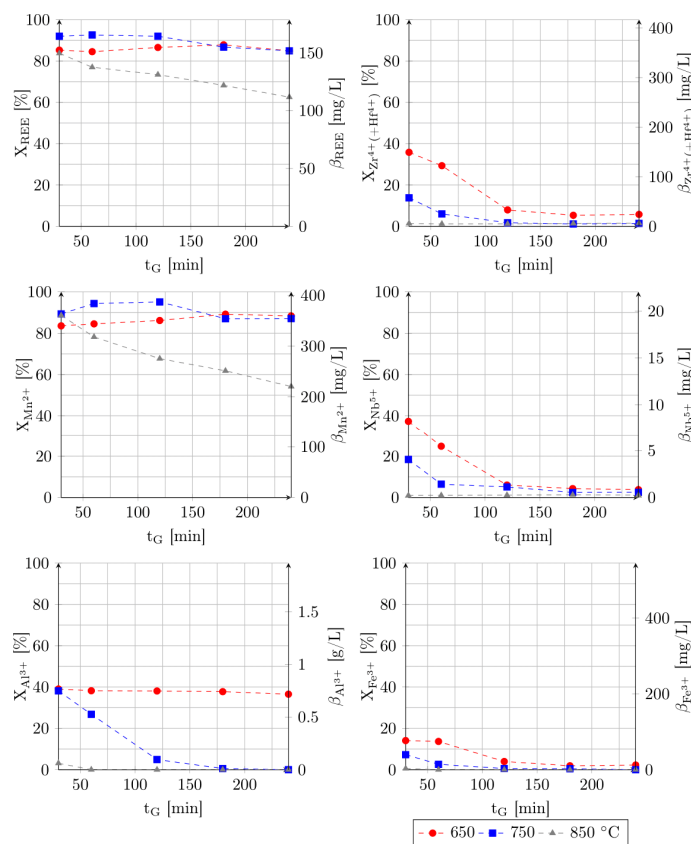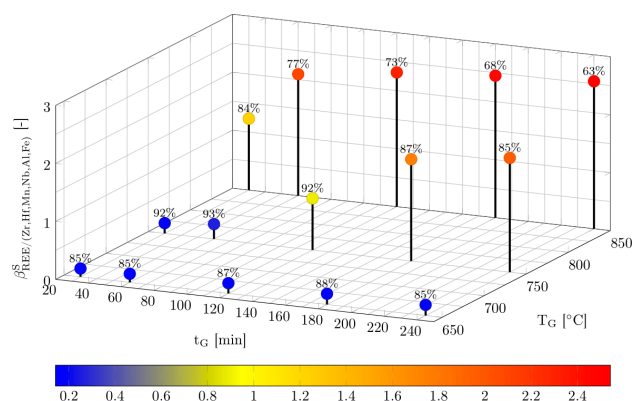

Figure 2. The effect of roasting temperature and roasting time on leaching yields (primary y-axis) and concentrations (secondary y-axis) of REEs, $Zr^{4+}(+Hf^{4+})$, Mn^{2+}, Nb^{5+}, Al^{3+}, Fe^{3+} ($n_{H^+}/m_{\text{conc.}}$ = 15 mmol/g; $\varrho_{\text{PD,L}}$ = 25 kg/m^3; T_{L} = 20 °C; t_{L} = 24 h; $r_{\text{R,L}}$ = 300 rpm).

At 650 °C leaching yields of REEs were high and independent of roasting time. In comparison, the concentration of zirconium (together with hafnium), niobium, and iron decreased sharply in the first 120 min at this temperature. It can be therefore concluded that sulfates of these metal ions decomposed at this temperature to sparingly soluble compounds. In contrast, higher temperatures were necessary to reduce the aluminum concentration. At 750 °C $\beta_{\text{Al}^{3+}}$ dropped from 748 mg/L to about 100 mg/L after 120 min. By extending the roasting time the aluminum content could be further reduced; however, this affected the REE yields negatively.

The separation factor $\beta_{\text{REE}/(\text{Zr,Hf,Mn,Nb,Al,Fe})}^{\text{S}}$ (Equation (7)) mainly depended on high aluminum concentration, which strongly increased at T_{G} = 750 °C and $t_{\text{G}} \geq$ 120 min (Figure 3). Due to the similar behavior of REEs and manganese the separation of both components could not be achieved.

Considering the highest achievable concentrations (leaching yield = 100%) of REEs and manganese of 164 mg/L and 72 mg/L, respectively, the maximum achievable separation factor was 2.3.
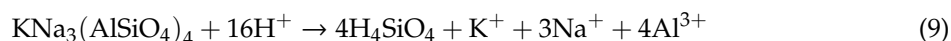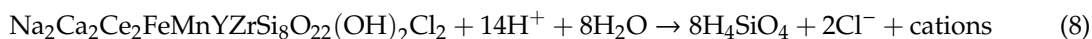

Figure 3. Effect of roasting temperature and roasting time on separation factor (y-axis, colored bar) and leaching yields of REEs in percent ($n_{H^+}/m_{conc.}$ = 15 mmol/g; $\varrho_{PD,L}$ = 25 kg/m³; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

In further experiments the sulfate content in the system was varied by changing the acid addition. Leaching yields and concentration of the considered metal ions in dependence on roasting time are shown in Figure 4.
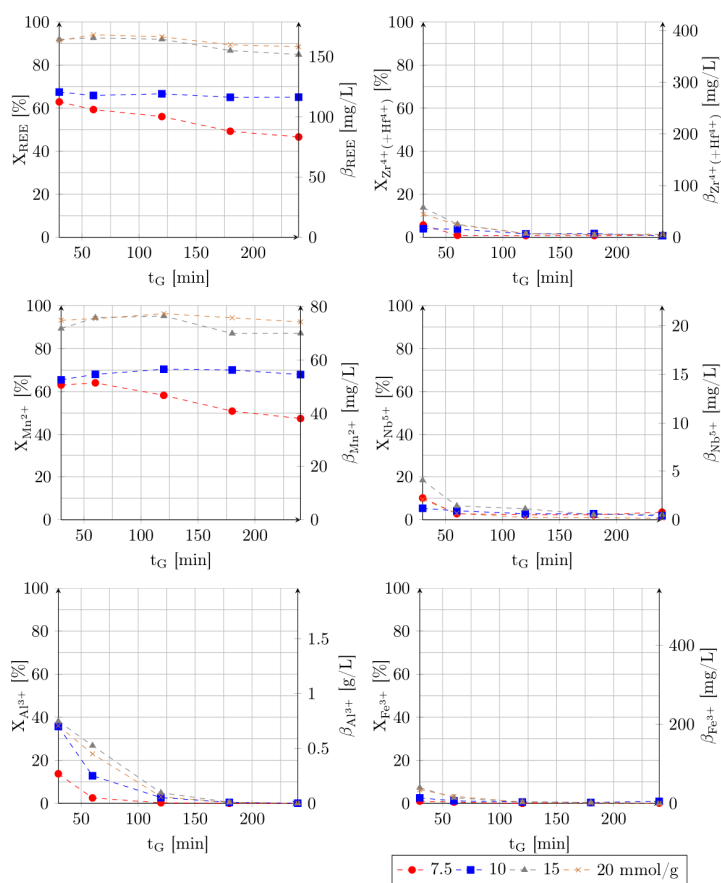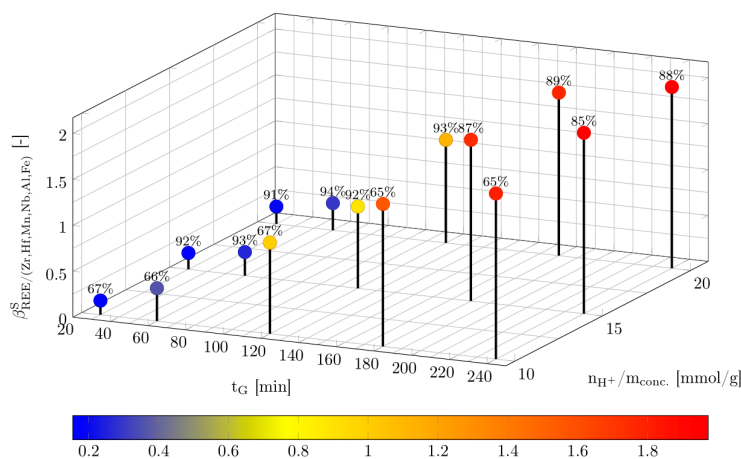

Figure 4. The effect of acid addition and roasting time on leaching yields (primary y-axis) and concentrations (secondary y-axis) of REEs, $Zr^{4+}(+Hf^{4+})$, Mn^{2+}, Nb^{5+}, Al^{3+}, Fe^{3+} (T_G = 750 °C; $\varrho_{PD,L}$ = 25 kg/m³; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

At an acid addition lower than 15 mmol/g the leaching yields of REEs were low and decreased slightly with roasting time. This indicated an insufficient amount of sulfate ions in the system. In the previous leaching study the theoretical acid consumption of 6.2 mmol/g was calculated considering Equations (8)–(10) describing the complete digestion of eudialyte (M = 1425 g/mol), nepheline (M = 584 g/mol) and zeolite (M = 352 g/mol) [9].

$$Na_2Ca_2Ce_2FeMnYZrSi_8O_{22}(OH)_2Cl_2 + 14H^+ + 8H_2O \rightarrow 8H_4SiO_4 + 2Cl^- + cations \tag{8}$$

$$KNa_3(AlSiO_4)_4 + 16H^+ \rightarrow 4H_4SiO_4 + K^+ + 3Na^+ + 4Al^{3+} \tag{9}$$

$$Na_2Al_2Si_3O_{10}{\cdot}2H_2O + 10H^+ \rightarrow 3H_4SiO_4 + 2Na^+ + 2Al^{3+} \tag{10}$$

Considering the determined acid consumption, it is evident that for achieving high REE yields the sulfuric acid should be added in excess. Further increase in sulfate content did not affect the behavior of all considered components. Accordingly, the separation factor changed hardly with acid addition (Figure 5).

Figure 5. Effect of acid addition and roasting time on separation factor (y-axis, colored bar) and leaching yields of REEs in percent (T_G = 750 °C; $\varrho_{PD,L}$ = 25 kg/m³; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

The determined pH values of solutions, which were prepared in discussed experiments, varied slightly and decreased with increasing roasting temperature and time (Figure 6).
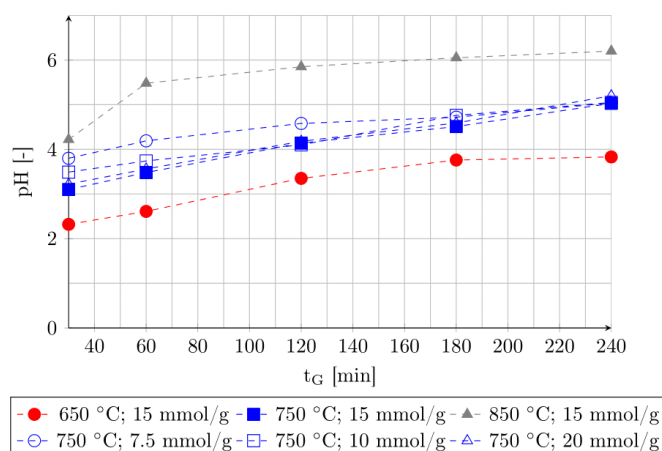

Figure 6. Effect of roasting time, roasting temperature and acid addition on pH value of leach solution ($\varrho_{PD,L}$ = 25 kg/m³; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

At the minimum pH value of 2.3 (650 °C; T_G = 30 min; 15 mmol/g), only 2.3% of the protons (5 mmol/L) remained in the calcine after roasting. The acid excess vaporized almost completely from the system during the first 30 min of roasting. However, according to the discussion above, an acid excess was necessary to achieve high yields of REEs. The great advantage of the process is the possibility to recover the vaporized acid by treatment of the gas phase [20]. Another approach for the reduction of the acid consumption is the previous separation of nepheline and zeolite from eudialyte which would reduce the required amount of acid and the process has significant costs. As it was shown in the leaching study, over 80% of the acid consumption is attributed to the leaching of these two minerals [9].

3.2. Effect of Leaching Time and pH Value of Leaching Medium

In further experiments the influence of leaching parameters on the REE yields and the separation was investigated. For this purpose a calcine was used, which was roasted 2 h at 750 °C. Figure 7 depicts the concentration of REEs, manganese, zirconium (together with hafnium), aluminum and iron in dependence on leaching time.
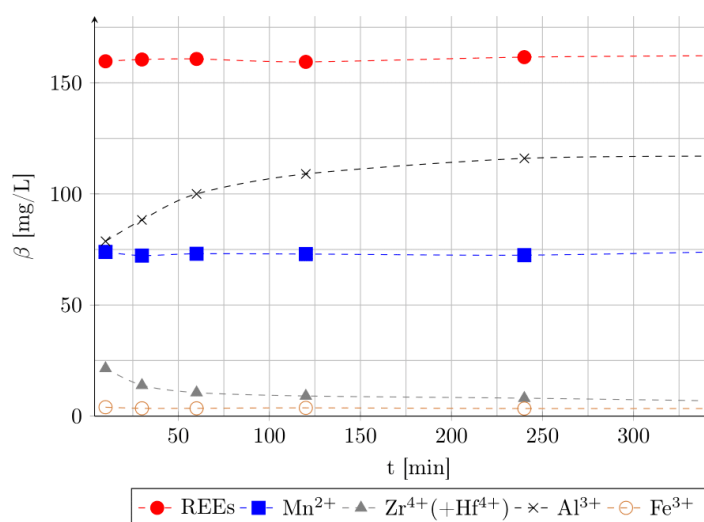

Figure 7. Effect of time on leaching of REEs, $Zr^{4+}(+Hf^{4+})$, Mn^{2+}, Nb^{5+}, Al^{3+}, Fe^{3+} ($n_{H^+}/m_{conc.}$ = 15 mmol/g; T_G = 750 °C; t_G = 2 h; $\varrho_{PD,L}$ = 25 kg/m³; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

The REEs and manganese were leached from calcine in high yields within 10 min and their concentrations did not change in the investigated period of time. On the other hand, the concentrations of zirconium (together with hafnium) and iron decreased and the concentration of aluminum increased with time. According to the Monhemius's hydroxide-precipitation diagram (1997) [22] the solubility of zirconium and iron at pH of 4 is below 10^{-5} mol/L (<1 mg/L) and the solubility of aluminum is about 10^{-2} mol/L (~270 mg/L). It is likely that the change in concentrations over time can be attributed to the hydrolysis of unconverted metal sulfates (Equations (11) and (12)) and the hydroxide precipitation of iron (Equation (13)) and zirconium.

$$Al_2(SO_4)_3 \leftrightarrow 2Al^{3+} + 3SO_4^{2-} \tag{11}$$

$$Fe_2(SO_4)_3 \leftrightarrow 2Fe^{3+} + 3SO_4^{2-} \tag{12}$$

$$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3 \downarrow \tag{13}$$

This indicated an incomplete conversion of metal ions into sparingly soluble compounds during roasting. To confirm the statement, the pH value of solution was varied in further experiments (Figure 8).
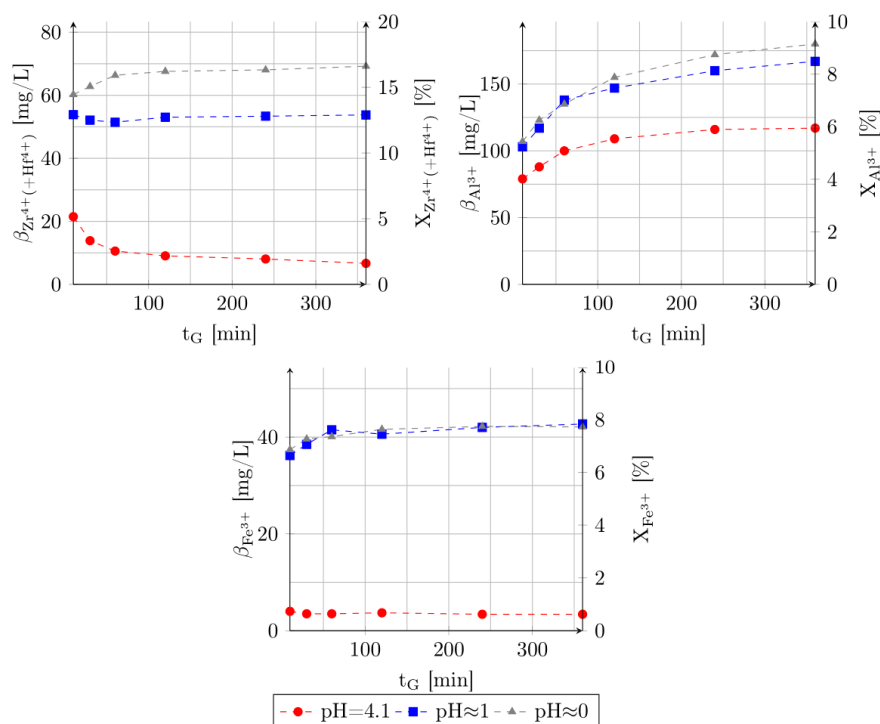
Figure 8. Effect of acidity of leaching medium on separation of $Zr^{4+}(+Hf^{4+})$, Al^{3+} and Fe^{3+} ($n_{H^+}/m_{conc.} = 15$ mmol/g; $T_G = 750$ °C; $t_G = 2$ h; $\varrho_{PD,L} = 25$ kg/m^3; $T_L = 20$ °C; $t_L = 24$ h; $r_{R,L} = 300$ rpm).

The rise in acidity of the leaching medium caused a significant increase in the amount of leached metal ions significantly and confirmed the assumption. The consequence of this is that the separation is caused not only by the conversion of non-REE sulfates into sparingly soluble compounds but also by lowering of their solubility resulting from the removing the acid excess from the system.

3.3. Stability of Silica

High amounts of released Si^{4+} is the main drawback by leaching of eudialyte concentrates [9]. The presence of silica in solution causes problems in subsequent operations such as liquid–liquid extraction, ion exchange processes and electrolysis [23]. The stability of SiO_2 in the calcine was investigated in dependence on roasting time, temperature and the amount of mineral acid (Figure 9).
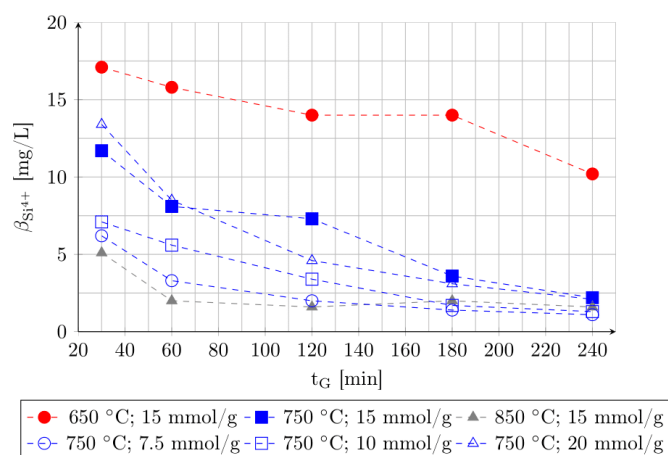
Figure 9. Effect of roasting time, roasting temperature and acid addition on the stability of SiO_2 ($\varrho_{PD,L} = 25$ kg/m^3; $T_L = 20$ °C; $t_L = 24$ h; $r_{R,L} = 300$ rpm).

Apparently, a decrease in the roasting temperature and an increase in acid addition led to a higher solubility of Si^{4+}. In order to provide a better understanding of the influence of both parameters on the SiO_2 stability present in the calcine, the acidity of leach solution and the roasting temperature were further varied. The measured Si^{4+} concentrations versus time are shown in Figure 10.
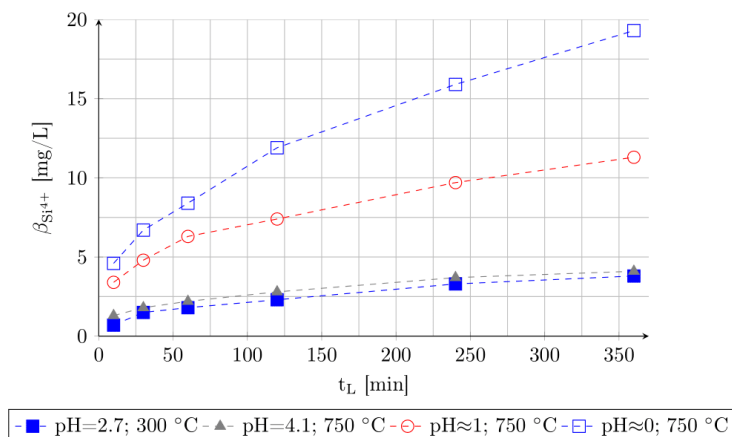
Figure 10. Effect on roasting temperature and pH value of leaching solution on the SiO_2 stability present in the calcine ($n_{H^+}/m_{conc.}$ = 15 mmol/g; t_G =2 h; $\rho_{PD,L}$ = 25 kg/m^3; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

The SiO_2 stability was strongly dependent of the pH value of the leaching medium, while the temperature variation had a marginal effect. The presence of additional acid in the leaching medium accelerated the release of Si^{4+} significantly. From this it can be deduced that the SiO_2 present in the calcine was in a metastable form even after roasting at high temperatures. Therefore, the removal of acid excess during roasting also plays an important role in regard to the contamination of the leach solution with Si^{4+}.

3.4. Effect of Pulp Density during Leaching

Finally, the effect of the increase in solid/liquid ratio was investigated by leaching of the calcine obtained by T_G = 750 °C and t_G = 120 min. The increase in pulp density affected the leaching yield of REEs negatively, especially of LREEs (Table 2).

**Table 2.** Effect of pulp density on concentrations and leaching yields (X) of REEs, LREEs, HREEs + Y, Mn^{2+}, $Zr^{4+}(+Hf^{4+})$, Nb^{5+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Na^+ and Si^{4+}, on separation factor and pH value of the leach solution ($n_{H^+}/m_{conc.}$ = 15 mmol/g; T_G = 750 °C; t_G = 2 h; $\varrho_{PD,L}$ = 25 kg/m^3; T_L = 20 °C; t_L = 24 h; $r_{R,L}$ = 300 rpm).

$\rho_{PD,L}$(kg/m^3)	25	50	100	200	300
β_{REE} (mg/L) (X (%))	164 (92)	322 (90)	624 (88)	1043 (73)	1229 (57)
β_{LREE} (mg/L) (X (%))	91 (91)	178 (89)	345 (87)	508 (64)	469 (39)
β_{HREE+Y} (mg/L) (X (%))	74 (93)	144 (91)	279 (89)	535 (85)	760 (80)
$\beta_{Mn^{2+}}$ (mg/L) (X (%))	76 (95)	149 (93)	290 (91)	584 (91)	891 (92)
$\beta_{Zr^{4+}(+Hf^{4+})}$(mg/L)	7 (2)	8 (1)	25 (2)	110 (3)	252 (5)
$\beta_{Nb^{5+}}$(mg/L)	1 (5)	1 (3)	4 (5)	18 (10)	43 (17)
$\beta_{Al^{3+}}$(mg/L)	97	148	505	1030	1580
$\beta_{Fe^{3+}}$(mg/L)	3	7	18	61	149
$\beta^S_{REE/(Zr,Hf,Mn,Nb,Al,Fe)}$	0.89	0.78	0.74	0.58	0.42
$\beta_{Ca^{2+}}$(mg/L) (X (%))	240 (88)	470 (87)	558 (52)	506 (23)	523 (16)
β_{Na^+}(mg/L)	820	1670	3280	6420	9410
$\beta_{Si^{4+}}$(mg/L)	4	8	14	22	31
pH value	4.1	3.9	3.8	3.7	3.6

The REE losses at high solid/liquid ratios are consistent with the results of a previous work [9], which were explained by the formation of double sulfates and REE incorporation into the precipitated gypsum structure. The gypsum precipitation can be recognized by the decrease in the leaching yields of Ca^{2+}. On the other hand, the strong decrease in LREE leaching yields indicates the formation of double sulfates. The presence of calcium and sodium (together with potassium) ions hampers the production of highly concentrated solutions even after the removal of the acid excess and the conversion of most of the accompanying components in sparingly soluble compounds.

The rise in the solid/liquid ratio in the leaching stage caused a strong increase in the concentrations of accompanying components compared to REEs and this affected the separation process negatively. It is interesting to note that at high $\varrho_{TD,L}$ values the concentrations of $Zr^{4+}(+Hf^{4+})$ and Fe^{3+} were higher in comparison to the solubility of $Zr(OH)_4$ and $Fe(OH)_3$ at the corresponding pH value [22]. A possible explanation is the solubility enhancement of Fe^{3+} and $Zr^{4+}(+Hf^{4+})$ in the presence of sulfate ions. Further reasons could be the presence of iron in the eudialyte in various oxidation states [24] or a partial Fe^{3+} reduction to Fe^{2+} by other metal ions present in the solution during water leaching, which has a higher solubility in the weakly acidic range compared to Fe^{3+} [22].

To assess the described method one leaching experiment of dehydrated acid/concentrate mixture was conducted at $\varrho_{PD,L}$ = 100 kg/m³ omitting the thermal decomposition stage (Figure 11).
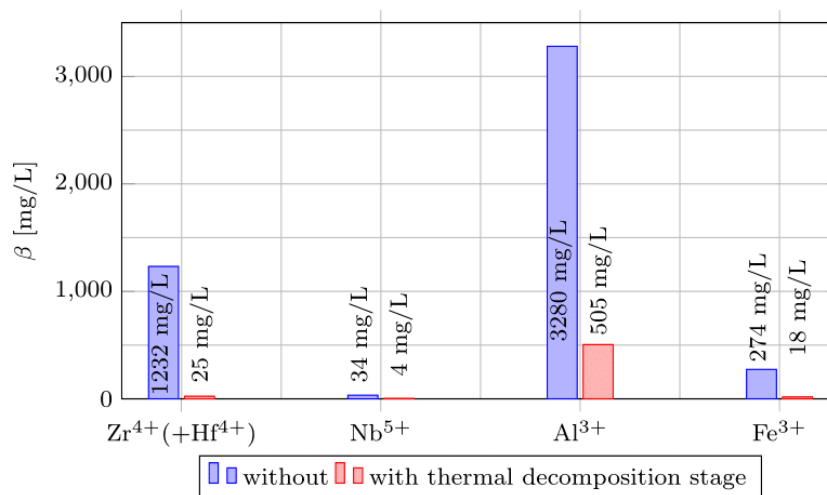
Figure 11. Effect of roasting stage on leaching yields of $Zr^{4+}(+Hf^{4+})$, Nb^{5+}, Al^{3+} and Fe^{3+} at $\varrho_{PD,L}$ = 100 kg/m³.

Roasting caused a significant decrease in concentration of $Zr^{4+}(+Hf^{4+})$, Nb^{5+}, Al^{3+} and Fe^{3+} by at least 85% for Al^{3+}. In particular, the concentration of $Zr^{4+}(+Hf^{4+})$ was most strongly affected, which could be reduced by 98%.

4. Conclusions

In this study, the selective leaching of REEs after sulfation and thermal decomposition of non-REE sulfates was investigated. Due to the similar thermal stability of $MnSO_4$ and $REE_2(SO_4)_3$, the separation of Mn^{2+} and REEs was not possible. However, the concentrations of $Zr^{4+}(+Hf^{4+})$, Nb^{5+}, Al^{3+} and Fe^{3+} could be significantly reduced choosing appropriate parameters in each process stage by at least 85%.

Beside the thermal decomposition of non-REE sulfates the separation process was driven by the pH value of the leaching medium. High yields of REEs (≥90%) and a high separation factor $\beta^S_{REE/(Zr,Hf,Mn,Nb,Al,Fe)}$ (≥0.78) were achieved by adding the sulfuric acid in excess acid, by roasting the dehydrated mixture at 750 °C for 2 h and by water leaching at low pulp density ($\rho_{PD,L} \leq 50$ kg/m³). The acid excess should be removed from the reaction mixture in the roasting step in order to prevent the hydrolysis of undecomposed non-REE metal sulfates.

Water leaching of calcine at high solid/liquid ratios of >100 kg/m^3 resulted in significant REE losses up to 43% at $\varrho_{PD,L} = 300$ kg/m^3. The losses were most likely due to the formation of double sulfates and gypsum; high levels of sodium, potassium and calcium ions in the system hampered the production of concentrated solutions strongly.

In addition, the stability of SiO$_2$ formed during acid digestion was analyzed. Even after roasting, SiO$_2$ remained in a metastable form. To reduce the amount of released Si^{4+} during leaching the pH value of the solution should be 5 to 6.

In summary, the investigated method allows efficient REE separation with a yield of approx. 90% from zirconium, hafnium, niobium, aluminum and iron just by heat treatment at 750 °C without additional chemicals. However, only diluted solutions can be produced, which contain high amounts of Ca^{2+}, Na$^+$ and Mn^{2+} at $\varrho_{PD,L} = 50$ kg/m^3 of up to 470 mg/L, 1670 mg/L and 149 mg/L, respectively. The efficiency of the method decreases with an increasing content of soluble Na$^+$ and Ca^{2+} ions present in the raw material. In regards to the considered concentrate, the amount of Na$^+$ and Al^{3+} can be reduced by previous separation of nepheline (KNa$_3$(AlSiO$_4$)$_4$) and zeolite (Na$_2$Al$_2$Si$_3$O$_{10}$) from eudialyte, e.g., by wet high intensity magnetic separation [25]. Both are completely decomposed by H$_2$SO$_4$ in the first process stage increasing the acid consumption significantly and releasing high amounts of Na$^+$, Al^{3+} and Si^{4+} [9]. Another possible option to concentrate REEs and to separate them from remained impurities is the subsequent liquid–liquid extraction. According to the literature, naphthenic acid is suitable for this task [26,27].

References

1. Chakhmouradian, A.R.; Wall, F. Rare Earth Elements: Minerals, Mines, Magnets (and More). *Elements* **2012**, *8*, 333–340. [CrossRef]
2. Krishnamurthy, N.; Gupta, C.K. *Extractive Metallurgy of Rare Earths*, 2nd ed.; Publisher: Boca Raton, FL, USA, 2015.
3. Goodenough, K.M.; Wall, F.; Merriman, D. The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations. *Nat. Resour. Res.* **2018**, *27*, 201–216. [CrossRef]
4. Qi, D. Extraction of Rare Earths from RE Concentrates. In *Hydrometallurgy of Rare Earths*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 1–185.
5. Yang, X.J.; Lin, A.; Li, X.-L.; Wu, Y.; Zhou, W.; Chen, Z. China's ion-adsorption rare earth resources, mining consequences and preservation. *Environ. Dev.* **2013**, *8*, 131–136. [CrossRef]
6. Hoshino, M.; Sanematsu, K.; Watanabe, Y. REE Mineralogy and Resources. In *Handbook on the Physics and Chemistry of Rare Earths*; Bünzli, J.C., Pecharsky, V.K., Eds.; Elsevier: Amsterdam, The Netherlands, 2016; Volume 49, pp. 129–291.
7. Krasikov, S.A.; Upolovnikova, A.G.; Sitnikova, O.A.; Ponomarenko, A.A.; Agafonov, S.N.; Zhidovinova, S.V.; Maiorov, D.V. Phase formation during the carbothermic reduction of eudialyte concentrate. *Russ. Metall. (Met.)* **2013**, *2013*, 482–485. [CrossRef]
8. Lipin, B.R.; Boynton, W.V. Geochemistry and Mineralogy of Rare Earth Elements. In *Reviews in Mineralogy*; Mineralogical Society of America: Chantilly, VA, USA, 1989; Volume 21.
9. Balinski, A.; Atanasova, P.; Wiche, O.; Kelly, N.; Reuter, M.A.; Scharf, C. Recovery of REEs, Zr(+Hf), Mn and Nb by H$_2$SO$_4$ leaching of eudialyte concentrate. *Hydrometallurgy* **2019**, *186*, 176–186. [CrossRef]

10. Davris, P.; Stopic, S.; Balomenos, E.; Panias, D.; Paspaliaris, I.; Friedrich, B. Leaching of rare earth elements from eudialyte concentrate by suppressing silica gel formation. *Miner. Eng.* **2017**, *108*, 115–122. [CrossRef]

11. Voßenkaul, D.; Birich, A.; Müller, N.; Stoltz, N.; Friedrich, B. Hydrometallurgical Processing of Eudialyte Bearing Concentrates to Recover Rare Earth Elements Via Low-Temperature Dry Digestion to Prevent the Silica Gel Formation. *J. Sustain. Metall.* **2017**, *3*, 79–89. [CrossRef]

12. Davidson, T. *Amended and Restated Prefeasibility Study-NI 43-101-Technical report for the Norra Kärr Rare Earth Element Deposit*; 0465-RPT-014 Rev 1; GBM: Gränna, Sweden, 2015.

13. Litvinova, T.E. Development of Physico-Chemical Bases of Hydrometallurgical Processing of Rare-Metal Eudialyte Ores. Ph.D. Thesis, Saint Petersburg Mining University, Saint Petersburg, Russia, 1998.

14. Ma, Y.; Stopic, S.; Friedrich, B. Hydrometallurgical Treatment of an Eudialyte Concentrate for Preparation of Rare Earth Carbonate. *Johns. Matthey Technol. Rev.* **2019**, *63*, 2–13. [CrossRef]

15. Motov, D.L.; Leshtaeva, T.G. *Khimicheskaya Tekhnologiya Redkometall'nogo syr'ya (Chemical Technology of Rare-Earth Raw Materials)*; Nauka: Moscow, Russia, 1966; pp. 16–26.

16. Zubryckyj, N.; Evans, D.J.I.; Mackiw, V.N. Promotion Agents in the Sulphation of Oxidized Nickel and Cobalt Bearing Ores. U.S. Patent 3,367,740A, 6 February 1968.

17. Naumann, D.; Goode, J.R. Rare Earth Ore Processing Methods by Acid Mixing, Sulphating and Decomposing. Patent WO2017,1009,33A1, 22 June 2017.

18. Önal, M.A.R.; Borra, C.R.; Guo, M.; Blanpain, B.; Van Gerven, T. Recycling of NdFeB Magnets Using Sulfation, Selective Roasting, and Water Leaching. *J. Sustain. Metall.* **2015**, *1*, 199–215. [CrossRef]

19. Borra, C.R.; Mermans, J.; Blanpain, B.; Pontikes, Y.; Binnemans, K.; Van Gerven, T. Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching. *Miner. Eng.* **2016**, *92*, 151–159. [CrossRef]

20. King, M.; Moats, M.; Davenport, W. *Sulfuric Acid Manufacture*, 2nd ed.; Elsevier: Oxford, UK, 2013.

21. Stern, K.H.; Weise, E.L. *High Temperature Properties and Decomposition of Inorganic Salts. Part 1. Sulfates*; U.S. Department of Commerce National Bureau of Standards: Washington, WA, USA, 1966.

22. Monhemius, A.J. Precipitation diagrams for metal hydroxides, sulfides, arsenates and phosphates. *Trans. Inst. Min. Metall.* **1977**, *86*, C202–C206.

23. Terry, B. The acid decomposition of silicate minerals part II. Hydrometallurgical applications. *Hydrometallurgy* **1983**, *10*, 151–171. [CrossRef]

24. Schilling, J.; Wu, F.-Y.; McCammon, C.; Wenzel, T.; Marks, M.A.W.; Pfaff, K.; Jacob, D.E.; Markl, G. The compositional variability of eudialyte-group minerals. *Mineral. Mag.* **2011**, *75*, 87–115. [CrossRef]

25. Forrester, K.; Leijd, M.; Oczlon, M.; Holmström, H.; Saxon, M. Beneficiation of rare earth element enriched eudialyte from the Norra Kärr peralkaline intrusion with wet high intensity magnetic separation. In Proceedings of the Conference of Metallurgists, Vancouver, BC, Canada, 28 September–1 October 2014.

26. Qi, D. Extractants Used in Solvent Extraction-Separation of Rare Earths: Extraction Mechanism, Properties, and Features. In *Hydrometallurgy of Rare Earths*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 187–389.

27. Zhang, J.; Zhao, B.; Schreiner, B. *Separation Hydrometallurgy of Rare Earth Elements*, 1st ed.; Springer International Publishing: Basel, Switzerland, 2016.