

Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching



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ABSTRACT

Bauxite residue (red mud) that is generated from karst bauxite ores is rich in rare-earth elements (REEs). The REEs can be recovered from bauxite residue by direct acid leaching but the extraction yields are generally low. The extraction yields can be increased by increasing the acid concentration but this will increase the dissolution of iron as well. Large amounts of iron in the leach solution create problems in the further recovery processes. Therefore, a combined sulfation–roasting–leaching process was developed to selectively leach the REEs while leaving iron undissolved in the residue. In this process bauxite residue was mixed with water and concentrated H₂SO₄ followed by drying, roasting and then leaching of the roasted product with water. Most of the oxides were converted to their respective sulfates during the sulfation process. During subsequent roasting, unstable sulfates (mainly iron(III) sulfate) decompose to their respective oxides. Rare-earth sulfates, on the other hand, are stable during roasting and dissolve during water leaching, leaving the iron oxides in the residue. The effect of the roasting temperature, roasting time and amount of acid on leaching of the different elements was studied. Decreasing the roasting temperature increased the dissolution of the REEs, but also that of iron and aluminum. Increasing the amount of acid led to higher REEs extraction. Acid to bauxite residue mass ratio beyond 0.75 at 650 °C increases the iron and aluminum dissolution due to increase in the iron(III) and aluminum sulfate amounts. The extraction of REEs slightly increased (<5%) with roasting time up to 2 h at 675 °C, but a further increase of the roasting time has a negative effect on the REEs extraction as the low amount of iron sulfate in the roasted mass increases the pH of the leach solution. About 60% of scandium and more than 90% of the other REEs can be dissolved at optimum conditions, while only a very small amount of iron (<1% of total iron) is solubilized. The residue after leaching was rich in Fe₂O₃, Al₂O₃, SiO₂ and CaSO₄·0.5H₂O.

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1. Introduction

Bauxite residue (red mud) is a waste generated during the Bayer process for alumina production. The annual global production of bauxite residue is about 140 million tons (Evans, 2015), while 2.7 billion tons of it is already stockpiled (Klauber et al., 2011). Storage of this material can pose an environmental challenge and space-consuming. However, bauxite residue that is generated from karst bauxite ores contains a significant amount of rare-earth elements (REEs). Practically all REEs end up in the bauxite residue during the Bayer process (Binnemans et al., 2015). Many researchers have

studied the direct acid leaching of bauxite residue for recovering REEs (Fulford et al., 1991; Ochsenkühn-Petropulu et al., 1996; Qu and Lian, 2013; Smirnov and Molchanova, 1997; Yatsenko and Pyagai, 2010), but the extraction yields are relatively low for the light REEs. These extraction yields can be improved by increasing the acid concentration, but an increase in acid concentration also leads to more iron dissolution into the leach solution (Borra et al., 2015). Large amounts of iron in the leach solution generate problems in the subsequent downstream processes, e.g. solvent extraction (Fulford et al., 1991). Therefore, iron removal from bauxite residue by smelting reduction prior to leaching could be an option for selective leaching of REEs (Binnemans et al., 2015; Borra et al., 2016; Logomerac, 1979; Sargic and Logomerac, 1974). However, high acid consumption, high temperature

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requirement during leaching, still considerable amount of iron dissolution are the major concerns in this route (Borra et al., 2016). Furthermore, large amounts of other impurities are also dissolved into the leach solution during direct and slag leaching, which generates large volume of effluents. Hence, a sulfation–roasting–leaching process was developed to selectively leach the REEs. This process was earlier developed for selective extraction of nickel and cobalt from iron rich lateritic ores (Guo et al., 2009; Kar and Swamy, 2000; Nicolas et al., 1968; Swamy et al., 2003) and recently applied for selective extraction of neodymium from neodymium–iron–boron (NdFeB) magnets (Önal et al., 2015).

Sulfation–roasting–leaching of a Greek bauxite residue was investigated in the present work for the purpose of REEs extraction. This is the first study for extraction of REEs from bauxite residue by this type of process. The effect of different process parameters including the amount of sulfuric acid, the roasting temperature, roasting time and different leaching parameters on the leaching efficiencies of the different elements were studied.

1.1. Sulfation–roasting–leaching

The flow sheet of the sulfation–roasting–leaching process consists of three major steps: (1) mixing the moistened feed material with concentrated sulfuric acid; (2) roasting and (3) leaching with water (Fig. 1). During acid mixing and the subsequent drying stages (e.g. sulfation), most of the oxides convert to their respective sulfates. As an example, at roasting temperatures of 600–700 °C, sulfates with low thermal stability such as iron(III) sulfate decompose to give their respective water-insoluble oxides (Eq. (1)).



The water-soluble rare-earth sulfates, on the other hand, are stable at such roasting temperature ranges (Bergmann, 1981) and they dissolve easily during the subsequent water leaching step leaving the iron oxides in the residue.

The main advantages of the sulfation–roasting–leaching process can be summarized as follows: (1) limited leaching of iron, titanium and aluminum; (2) no or very limited silica leaching, so that filtration problems can be avoided; (3) the possibility of (consumed) acid regeneration and therefore low acid consumption and (4) small volumes of waste water generation compared to direct leaching. Additionally, the pH of the residue after water

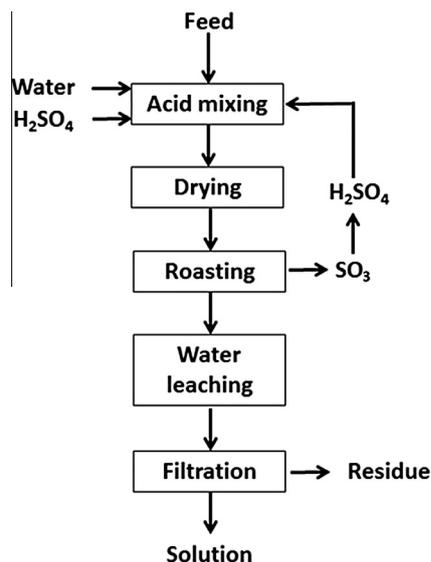


Fig. 1. Flow sheet of the sulfation–roasting–leaching process.

leaching is close to neutral and very low in sodium content (management and utilization of this stream in other applications is easier). The main drawback of this process is that it needs an extra processing (roasting) step.

2. Experimental

The bauxite residue used in this study was provided by Aluminium of Greece. The residue was first dried at 105 °C for 12 h. The dried sample was passed through 500 µm size sieve. Chemical analysis of the major elements was performed with wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400) whereas that of the minor elements was performed by complete dissolution of the bauxite residue by alkali fusion and acid digestion in a 1:1 (v/v) HCl solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. Thermo-gravimetric analysis (TGA, Netzsch STA 409) experiments were carried out in nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹. The mineralogy of the samples was studied by X-ray diffraction technique (XRD, Philips PW1830). The powder morphology was investigated by scanning electron microscopy (SEM, Philips XL30). The particle size of the samples was measured by laser particle size analysis (Malvern Mastersizer 3000). The results for particle size, SEM, TGA and XRD analysis of bauxite residue have already been reported elsewhere (Borra et al., 2015).

Analytical reagent grade sulfuric acid (95–97%) (Sigma–Aldrich) was used in the present study. During the acid mixing step (i.e. sulfation), the dried sample was moistened with deionized water (bauxite residue to water mass ratio is 1:0.4, unless specified) in a porcelain crucible and then mixed with concentrated sulfuric acid based on the experimental conditions. The addition of water was to ensure homogenous mixing. After mixing, samples were heated at 120 °C for 12 h to ensure complete sulfation of the bauxite residue. After drying, the samples were subsequently roasted at a set temperature for a selected time in a muffle furnace. Non-agitated leaching experiments were conducted at room temperature with deionized water in polyethylene bottles. Agitation leaching experiments were carried out in sealed polyethylene bottles by using a laboratory shaker (Gerhardt Laboshake) at 160 rpm and 25 °C. High-temperature leaching experiments were carried out in a 500 ml glass reactor fitted with a reflux condenser and placed on a temperature-controlled ceramic hot plate with a magnetic stirring system. After leaching, the solution was filtered with a syringe filter (pore size of 0.45 µm) and the obtained filtrate was diluted with acidified deionized water (Milli-Q, resistance 18.2 MΩ cm). The percentage extraction was calculated based on ICP-MS analysis of the clear leachate.

3. Results and discussion

3.1. Bauxite residue characterization

The chemical analysis of the bauxite residue used in this study is shown in Tables 1 and 2. Table 1 shows that the bauxite residue

Table 1
Major chemical components in the bauxite residue sample (Borra et al., 2015).

	wt%
Fe ₂ O ₃	44.6
Al ₂ O ₃	23.6
CaO	11.2
SiO ₂	10.2
TiO ₂	5.7
Na ₂ O	2.5

is rich in iron oxide and alumina. Table 2 shows that the total REE content in the bauxite residue is about 0.1%. Borra et al. reported that the bauxite residue used in this study is a very fine material with d_{90} less than 10 μm and contains small agglomerates (Borra et al., 2015). They also found by XRD analysis that it contains different phases like hematite, goethite, gibbsite, diaspor, calcite and cancrinite.

3.2. Effect of roasting temperature on leaching

After sulfation at 120 °C, the samples (acid to residue ratio 1:1) were roasted at different temperatures for 1 h. XRD patterns of these samples are shown in Fig. 2. At 120 °C, most of the components are converted to their respective sulfates. Calcium sulfate has already lost its bound water molecules at that temperature. Iron(III) sulfates contain chemically bound water together with H_2SO_4 . Some peaks of unreacted hematite and diaspor were also observed. This means that iron(III) oxide and alumina are not completely converting to their respective sulfates at 120 °C. With increase in the temperature, iron(III) sulfate starts losing water. Aluminum sulfate and titanium oxysulfate are also observed in the XRD pattern. No significant changes were observed in the XRD pattern until 600 °C. Further increase in temperature to 650 °C, resulted in partial decomposition of iron(III) sulfate to iron oxide. Iron(III) sulfate was fully decomposed to iron oxide at 700 °C. Calcium sulfate was still stable at this temperature.

Fig. 3 shows TGA–DSC analysis of the sulfated sample (sulfuric acid to bauxite residue mass ratio of 1:1). The weight loss below 350 °C is due to the removal of physical and chemical water and excess sulfuric acid. The small weight loss and peak around 500 °C may be due to titanium sulfate decomposition. The combined weight loss and peaks between 600 and 750 °C is due to the decomposition of aluminum and iron(III) sulfate. These temperatures are higher compared to the literature values that are shown in the Table 3. This is due to several reasons: (1) the values given in the table are starting temperatures for decomposition; (2) the complex nature of the bauxite residue sample; (3) the high heating rate used in this study. Based on the XRD and DSC–TGA results, roasting experiments were conducted between 650 and 700 °C.

Experiments were carried out at 650, 675 and 700 °C to investigate the effect of temperature on the dissolution behavior of iron and other elements. Samples were prepared with 1:1 mass ratio of (sulfuric acid)-to-(bauxite residue). Fig. 4 shows the effect of roasting temperature on extractions of REEs and major elements. The extraction yields of all REEs slightly decrease with increasing roasting temperature. It is obvious that higher roasting

temperatures will increase the decomposition kinetics of metal sulfates. Also, the dissolution of aluminum, iron and titanium decreases with increasing roasting temperature. These results are in agreement with the expectations. On the other hand, dissolution sodium and calcium remains practically constant because their sulfates decompose only at very high temperatures. Iron and aluminum extractions are lower when roasting is performed at 700 °C compared to extractions after roasting at 650 °C. By increasing the temperature from 650 °C to 700 °C, it is possible to decrease the iron and aluminum extractions from 23 wt% to about <1 wt% and from 38 wt% to ~20 wt%, respectively. Very little or no silicon was observed in the leach solutions of the sulfation–roasting process, which is a promising result in view of further processing steps such as filtration and solution purification.

3.3. Effect of sulfuric acid amount on leaching

A series of experiments were carried out by varying the mass ratio of sulfuric acid to bauxite residue from 0.25 (1:4 ratio) to 1 (1:1 ratio). The samples were roasted for 1 h at the fixed temperature of 650 °C. After roasting, the samples were leached with water for 7 days without agitation. Fig. 6 shows the extraction of the REEs and major elements in the leachate with increasing initial acid to residue ratio. As seen in Fig. 5, the REEs extraction dramatically increases with increasing acid to bauxite residue mass ratio up to 0.5:1. With further increase, this effect becomes less pronounced. Particularly, the extraction of scandium was 64 wt% at acid to bauxite residue mass ratio of 1:1. An additional experiment was performed to evaluate whether extraction of scandium could be increased beyond this value with an acid to bauxite residue mass ratio of 2:1. However, even with this higher ratio the extraction of scandium remained unaffected. It was reported that the maximum iron conversion in sulfation–roasting to iron(III) sulfate is around 60–70 wt% (Güler et al., 2008). That could be the reason for the poor scandium extraction since scandium(III) oxide is locked in the iron(III) oxide lattice (Borra et al., 2015; Brookins et al., 1983). Another reason for the poor scandium extraction might be due to the lower decomposition temperature of scandium compared to that for other REEs, except cerium. However, unlike scandium, cerium starts decomposing below 700 °C to cerium oxysulfate, which is soluble in slightly acidic conditions. The maximum extraction yields of the other REEs are between 85 wt% and 95 wt%. The increase in REEs dissolution with increasing acid addition is due to the enhanced reactivity at higher acid to bauxite residue ratios. Adding more sulfuric acid leads to an increased conversion of the oxides to sulfates which eventually improves the extraction. The extraction yields of both iron and aluminum increase with increasing addition of acid. Titanium follows the same trend. This is also a consequence of the increasing sulfate formation when more acid is added. In this case, more iron and aluminum sulfates can be decomposed and hence more of these sulfates will remain after the roasting treatment. The remaining iron, aluminum and titanium sulfates are all dissolved in the leaching step since they are quite soluble in water. Sodium and calcium dissolution remains constant at 100 wt% and ~30 wt%, respectively, in the examined range of acid addition. That is because of the fact that the added sulfuric acid is primarily consumed by sodium- and calcium-containing phases. Even at 0.25:1 acid to bauxite residue ratio, both types of phases already transformed to their respective sulfates. The primary consumption of acid for neutralization of alkali compounds in a bauxite residue was reported earlier by Borra et al. (2015). Although calcium-containing phases transform to their sulfate form easily, calcium dissolution is low due to the fact that calcium sulfates have very low solubility in water (Myerson, 2002) (http://www.kayelab.npl.co.uk/chemistry/3_2/3_2.html).

Table 2
REEs composition of the bauxite residue sample (Borra et al., 2015).

	g/ton
Sc	121
Y	76
La	114
Ce	368
Pr	28
Nd	99
Sm	21
Eu	5
Gd	22
Tb	3
Dy	17
Ho	4
Er	13
Tm	2
Yb	14
Lu	2

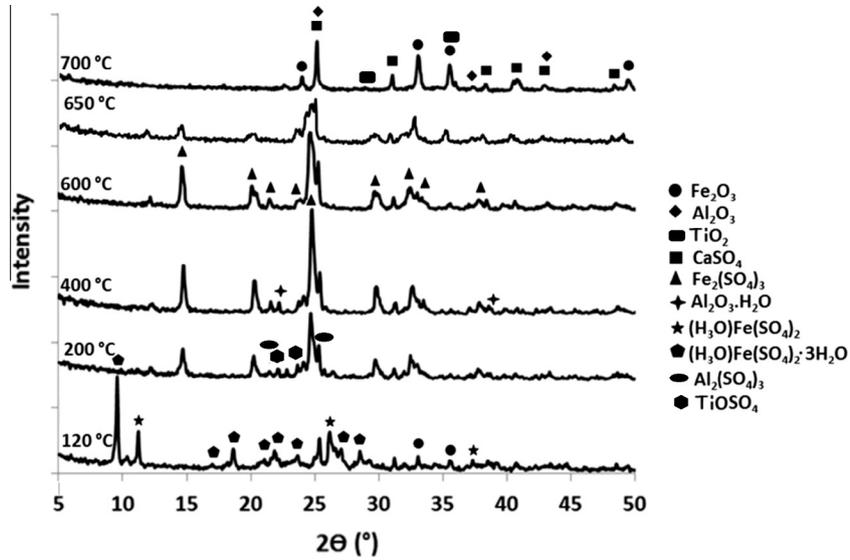


Fig. 2. XRD patterns of samples roasted at different temperatures (sulfuric acid to bauxite residue ratio 1:1, roasting time: 1 h).

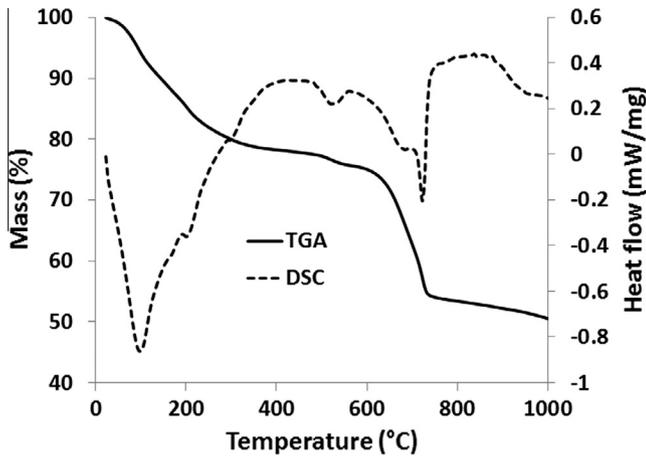


Fig. 3. TGA and DSC curves of the sulfated bauxite residue sample.

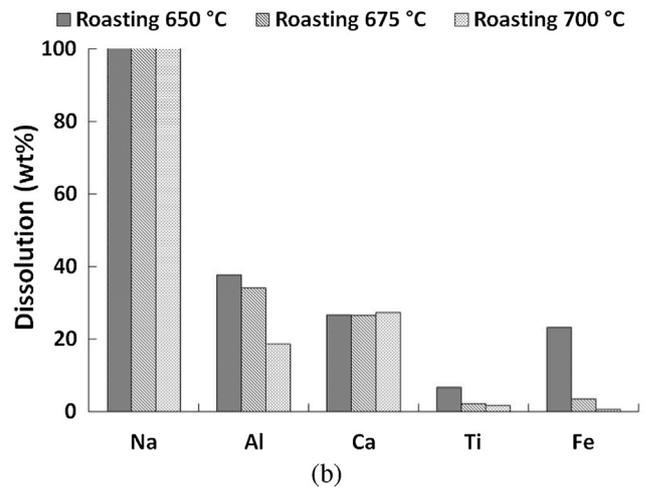
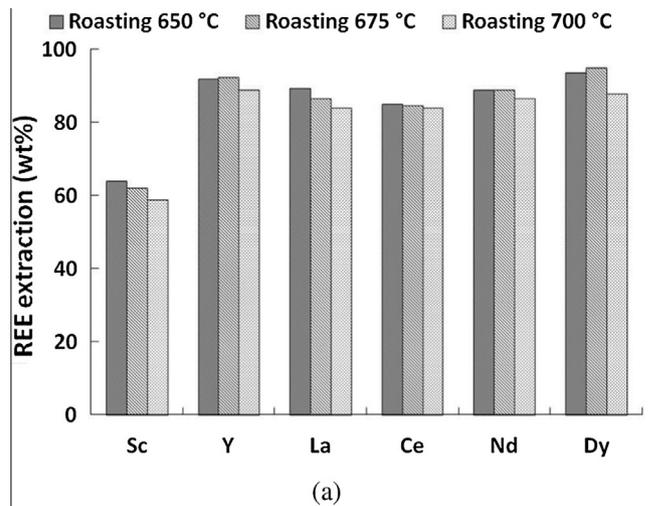


Fig. 4. Effect of roasting temperature on leaching of (a) REEs and (b) major elements (acid to bauxite residue ratio: 1:1, roasting duration: 1 h, non-agitated leaching duration: 7 days, L/S ratio: 50).

Table 3
Stability of metal sulfates of interest.

Compound	Onset of thermal decomposition (°C)	Heating rate (°C/min)	Source
Iron(III) sulfate	545	5	Tagawa (1984)
Aluminum sulfate	524	5	Tagawa (1984)
Calcium sulfate	>1000	-	Stern (2000)
Titanium(IV) oxysulfate	430	-	Stern (2000)
Sodium sulfate	870	-	Stern (2000)
Scandium(III) sulfate	700	10	Li et al. (2005)
Yttrium(III) sulfate	850	2.5	Bergmann (1981)
Cerium(III) sulfate	666	5	Tagawa (1984)
	700	-	Bergmann (1981)
Neodymium(III) sulfate	800	1.5	Bergmann (1981)
Lanthanum(III) sulfate	840	2.5	Bergmann (1981)

3.4. Effect of roasting duration on leaching

Roasting experiments were conducted for different durations to understand the effect of roasting time on dissolution of REEs and major elements. In these experiments samples were prepared with a constant sulfuric acid to bauxite residue mass ratio 1:1. Samples were roasted at 675 °C for different durations. Finally, non-agitated

room-temperature leaching has been performed for 7 days. Fig. 6 shows the effect of roasting duration on leaching of REEs and major elements. The REEs extraction slightly increases with roasting time

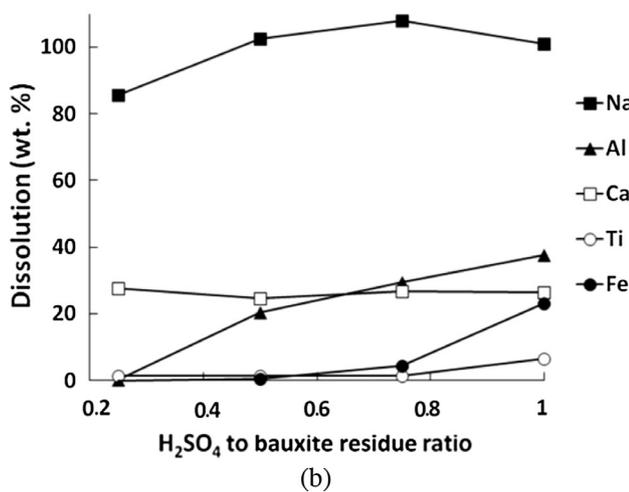
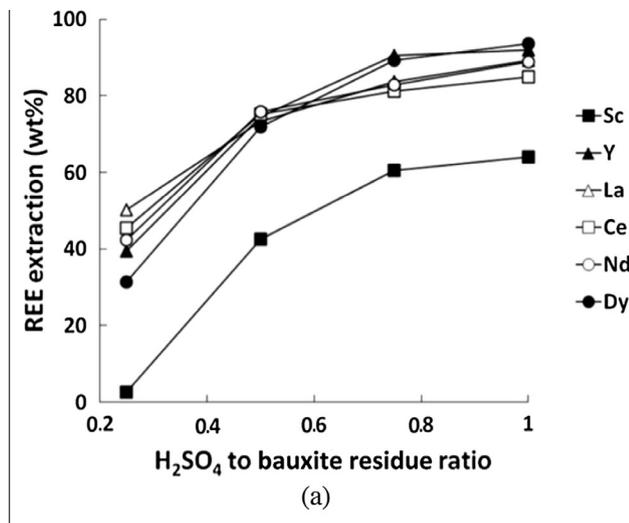


Fig. 5. Effect of the acid to bauxite residue ratio on leaching of (a) REEs and (b) major elements (roasting temperature: 650 °C, roasting duration: 1 h, non-agitated leaching duration: 7 days, L/S ratio: 50).

up to 1 h. Further increase of roasting time has a negative effect on the REEs dissolution due to the increasing amount of sulfates that are decomposed to oxysulfates and oxides which are insoluble in water or due to hydrolysis of REEs caused by the high pH of the leach solutions (due to iron and aluminum sulfates decomposition). There is no significant change in the dissolution of calcium, sodium and silicon. The extraction of iron, aluminum and titanium decreases with an increase in roasting time, again because of the increased amount of sulfates that are decomposed. Titanium dissolution is gradually decreased and reaches its minimum after 1 h of roasting. The iron extraction shows a sharp decline in the first hour of roasting. After 1 h, the decrease is more gradual until it reaches zero dissolution between 2 and 3 h. The aluminum dissolution decreases more gradually and is completely decomposed to Al_2O_3 after approximately 4 h of roasting. Results show that the ferric sulfates are more easily decomposed compared to aluminum sulfates. This was also observed by Guo et al. (2009). If roasting is performed at a higher temperature, the roasting time needed for selective leaching will be shorter. The optimal roasting time is determined considering two main factors: REEs dissolution and iron (and aluminum) dissolution. Based on the results, the optimal roasting time at 675 °C is between 1 and 2 h. At this temperature, REEs dissolution is still high, while iron and aluminum dissolution

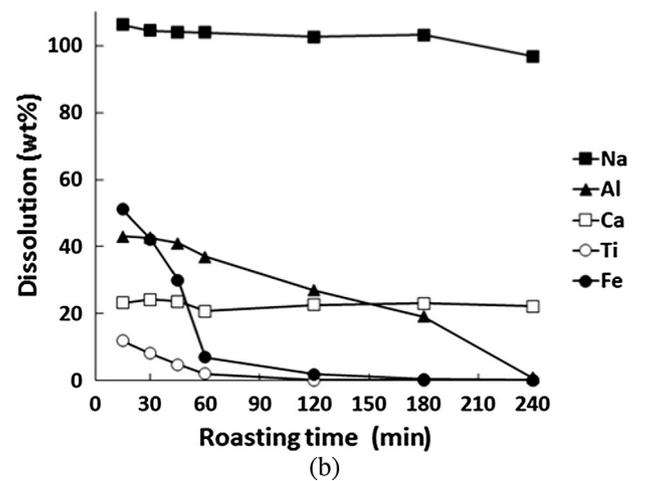
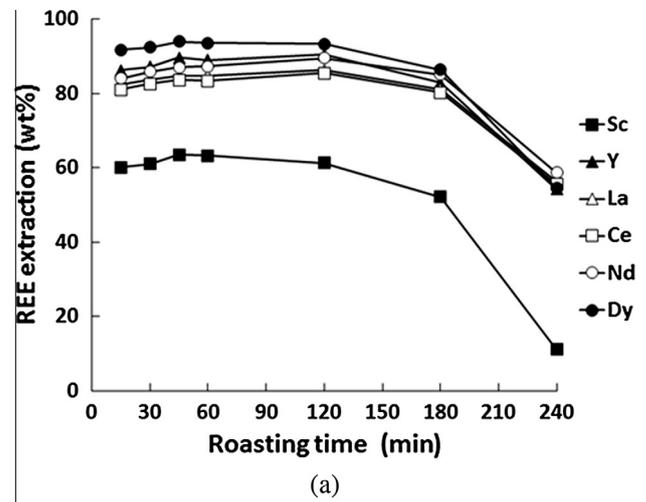


Fig. 6. Effect of the roasting time on leaching of (a) REEs and (b) major elements (acid to bauxite residue ratio 1: 1, roasting temperature: 675 °C, non-agitated leaching duration: 7 days, L/S ratio: 50).

are low. The optimal roasting time for roasting at higher temperatures can be shortened since the metal sulfates are decomposed faster.

3.5. Water addition during mixing

The bauxite residue is moistened with deionized water before sulfuric acid is added. The aim of moistening is to improve the mixing of the acid with the bauxite residue and therefore aid the conversion of metal oxides to sulfates (Guo et al., 2009; Swamy et al., 2003). Fig. 7 shows the REEs dissolution in the leachates for a sulfation roasting process with water addition in the sample preparation step and for one without water addition. The samples were roasted for one hour at 700 °C and were subjected to 7 days of non-agitated room-temperature leaching. The extraction of REEs is almost halved when no water is added. This is due to the improper mixing of the sulfuric acid with the bauxite residue which causes a decrease in the amount of sulfates formed (Önal et al., 2015). Water to bauxite residue ratio beyond 0.2 however, does not affect the recoveries.

3.6. Effect of leaching conditions

Leaching experiments were conducted without agitation at different time intervals for samples roasted at 650 °C for 1 h. The

sulfuric acid to bauxite residue mass ratio was fixed at 1:1. In Fig. 8, REEs and major element dissolutions are given with respect to leaching time for non-agitated room-temperature leaching. It can be seen that the leaching time has an important influence on the dissolution behavior of the REEs. Up to 85–95 wt% of the yttrium, lanthanum, cerium, neodymium and dysprosium could be extracted. After six days of leaching, a maximum was reached for all these REEs – except for scandium – and their dissolution values remain constant. The effect of duration on the dissolution of scandium differs from that of the other REEs. It first increases rapidly during the first day, later on stagnates and remains around a maximum of about 64 wt%. The effect of leaching duration on the dissolution behavior of the major elements (sodium, aluminum, calcium, titanium and iron) is less significant. Already after one day of leaching, the dissolution values of the major elements reached stationary levels. The dissolution of the major metals into the leachate is relatively high due to the large amount of sulfuric acid added (1:1 acid to residue mass ratio) and the low roasting temperature (650 °C). Additional leaching experiments were conducted at higher temperature (80 °C) and at 25 °C with agitation (160 rpm). High temperature leaching lowers recoveries. The use of higher temperatures was not further investigated thoroughly as an increase in temperature is known to decrease the solubility of REEs (Table 4). Fig. 9 shows the effect of agitation time on leaching of REEs and major elements. It shows that REEs dissolution reached a maximum in 2 days where the major elements require only 1 day.

Leaching experiments were conducted at different L/S ratio to see its effect on dissolution of REEs and major elements (Fig. 10). It shows that the effect of L/S ratio on REEs dissolution is insignificant. Also no change in the dissolution of sodium, aluminum, titanium and iron was observed. Iron dissolution is less than 1% at all L/S ratios. Calcium dissolution is drastically decreased with decrease in L/S ratio due to the solubility limit. From the results it can be concluded that REEs can be selectively dissolved even at low L/S ratios with low calcium in the solution. Fig. 10 also shows that it is possible to use low L/S ratio to minimize solution volumes without sacrificing extraction efficiency. The absolute concentrations of REEs and major elements in the leach solution at L/S ratio of 5 are shown in Table 5. It is difficult to remove the iron completely from the leach solution. However, decrease in iron concentration definitely decreases the number of processing steps in further processes such as solvent extraction or ion exchange.

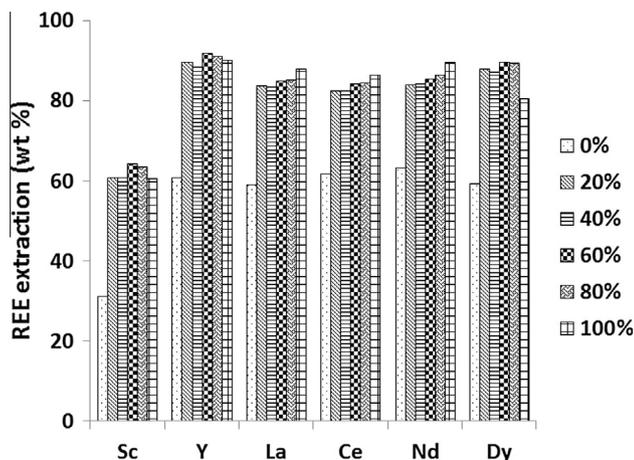


Fig. 7. Effect of the amount of water addition during sulfation on leaching (acid to bauxite residue ratio: 1:1, roasting temperature: 650 °C, non-agitated leaching duration: 7 days, L/S ratio: 50).

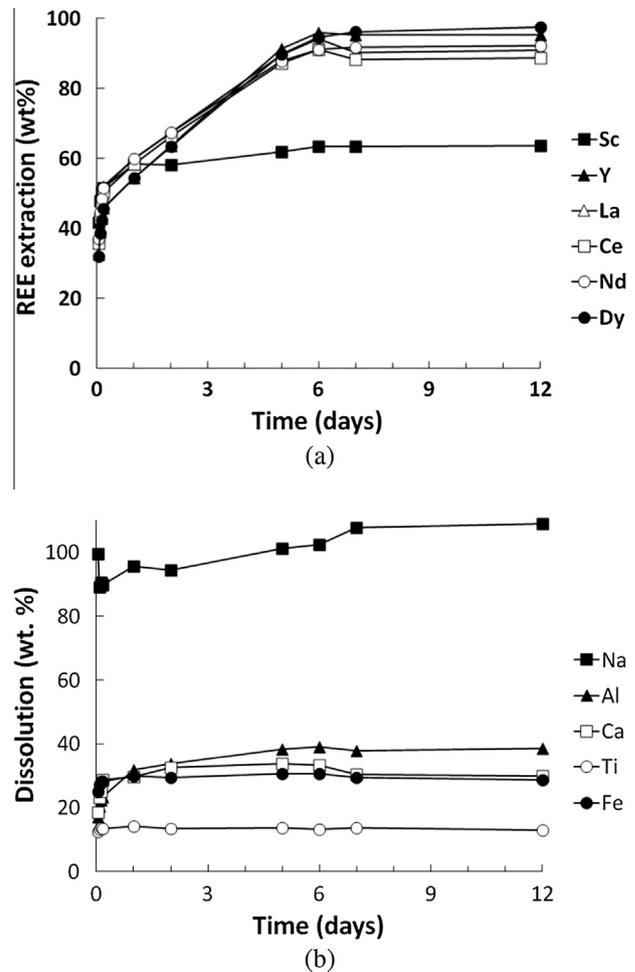


Fig. 8. Effect of leaching duration on non-agitated leaching of (a) REEs and (b) major elements (roasting temperature: 650 °C, roasting duration: 1 h, acid to bauxite residue: 1, L/S ratio: 50).

Table 4
Solubilities of rare earth sulfates (Kaye and Laby Online, 2005; Lide, 2004).

Compound	Solubility in water at 20 °C (g/100 ml)	Solubility in water at 100 °C (g/100 ml)
Sc ₂ (SO ₄) ₃	10.3	Highly soluble
Y ₂ (SO ₄) ₃	7.5 (16 °C)	2 (95 °C)
La ₂ (SO ₄) ₃	2.3 (25 °C)	0.7
Ce ₂ (SO ₄) ₃	9.5	2.25
Nd ₂ (SO ₄) ₃	7.1	1.2
Dy(SO ₄) ₃	4.1	2.7 (40 °C)
Na ₂ SO ₄	19.1	42.2
CaSO ₄	0.274	0.189
Al ₂ (SO ₄) ₃	36.4	98.1
Fe ₂ (SO ₄) ₃ ·9H ₂ O	400	–

3.7. Relationship between pH and dissolution of different elements

It was observed from the leaching results that the pH of the leach solution affects the dissolution of different elements in the solution. The pH of the leach solutions was typically between 2.3 and 6.5 in the studied conditions and is closely associated with the elemental composition of the roasted sample. It mainly depends on the amount of iron(III) sulfate (and to a lesser extent aluminum sulfates) present after the roasting step. It was observed that when higher amounts of ferric and aluminum sulfate remain after roasting, the pH is lower. For instance, the leach solution of a sample roasted at a 700 °C has a higher pH than the solution of

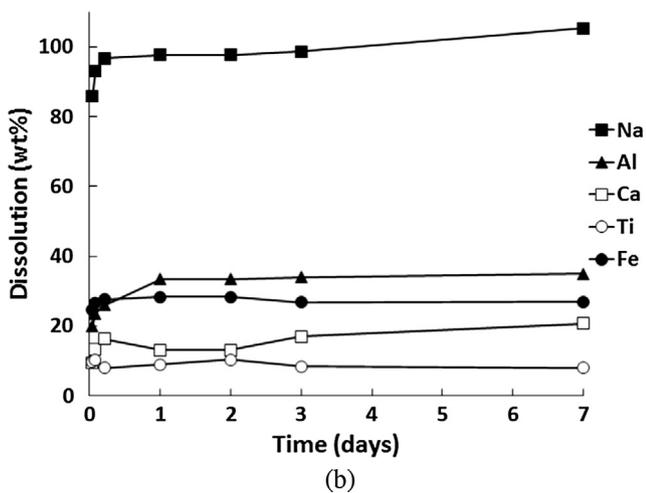
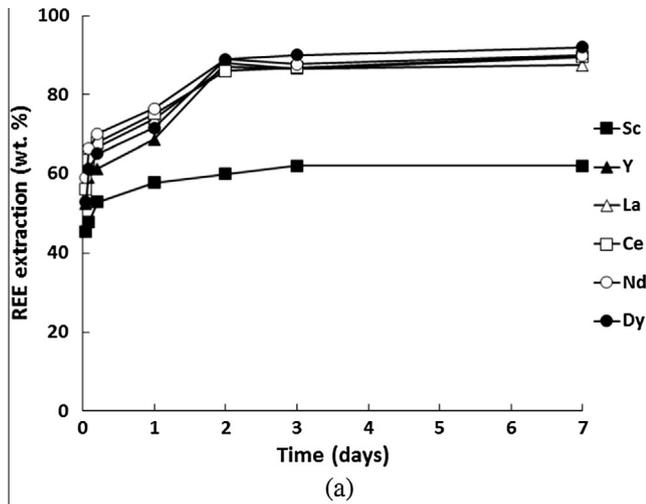


Fig. 9. Effect of leaching duration on agitated leaching of (a) REEs and (b) major elements (roasting temperature: 650 °C, roasting duration: 1 h, acid to bauxite residue: 1, L/S ratio: 50, leaching duration: 7 days).

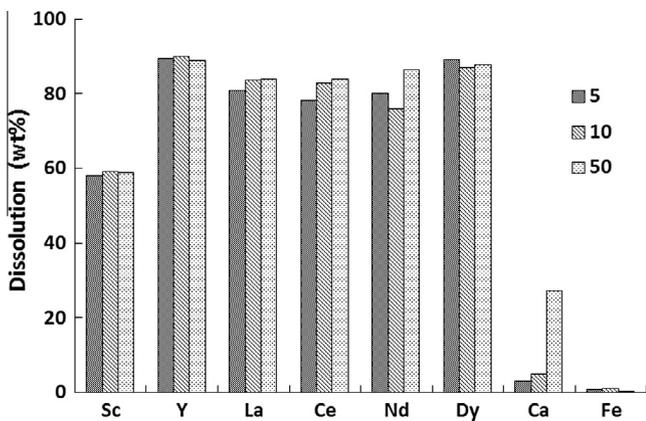


Fig. 10. Effect of L/S ratio on dissolution of different elements (roasting temperature: 700 °C, roasting duration: 1 h, acid to bauxite residue: 1, non-agitated leaching duration: 7 days).

a sample roasted at 650 °C. Fig. 11 shows the effect of pH on the dissolution of scandium, iron, aluminum and cerium. Other elements are not shown in the figure for the sake of readability. The results show that with increase in pH, initially iron starts to

Table 5

Concentration of REEs and major elements in the leach solution (roasting temperature: 700 °C, roasting duration: 1 h, acid to bauxite residue: 1, non-agitated leaching duration: 7 days, L/S ratio: 5).

	ppm
Sc	15
Y	13
La	19
Ce	62
Nd	17
Dy	3
Na	3859
Al	4638
Ca	441
Ti	82
Fe	450

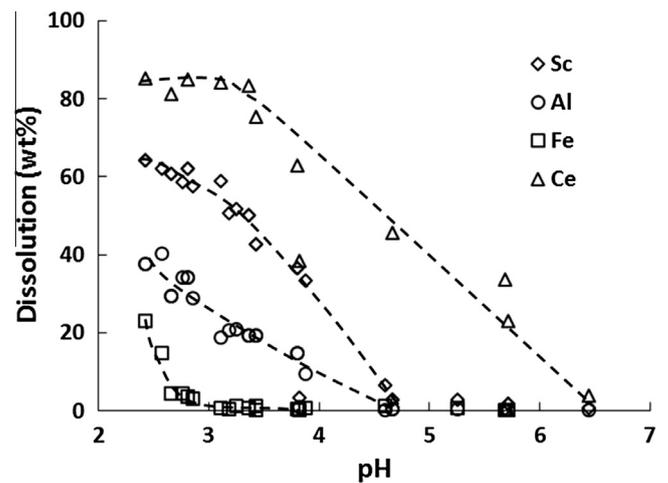


Fig. 11. Effect of pH on dissolution of different elements.

precipitate followed by aluminum, scandium and cerium. The pH of precipitation is higher for cerium and other REEs compared with scandium. No change in the dissolution of calcium and sodium was observed with respect to pH. All these pH values are more or less in agreement with their respective Pourbaix diagrams (Takeno, 2005). These results are in a good agreement with phase equilibria calculations using FACTSAGE® 6.4.

3.8. Leach residue

The residue of the leach solution was characterized by SEM-EDX and XRD. The results depicted in Figs. 12 and 13 originate from a sample treated with a sulfuric acid to bauxite residue mass ratio of 1:1 and roasted at 700 °C for 1 h, followed by seven days of non-agitated room temperature leaching. XRD analysis indicates hematite, alumina, calcium sulfate hemihydrate, titania and silica as the major phases. The SEM image shows that the material is very fine and porous. In addition, SEM-EDX analysis identified calcium sulfate and aluminum oxide. Other individual phases were difficult to detect because of the fineness of the material. Considering the mineralogy and morphology of the sample, the residue could be used as a raw material in clinker production for ordinary Portland cement, OPC (Pontikes and Angelopoulos, 2013). Compared to bauxite residue produced today, the leach residue offers a major advantage since all sodium is dissolved into the leach solution and hence the final sodium content is very low. Since this is a pre-requisite for clinker production, the new leach residue could be introduced at higher levels in the raw meal formulations, than

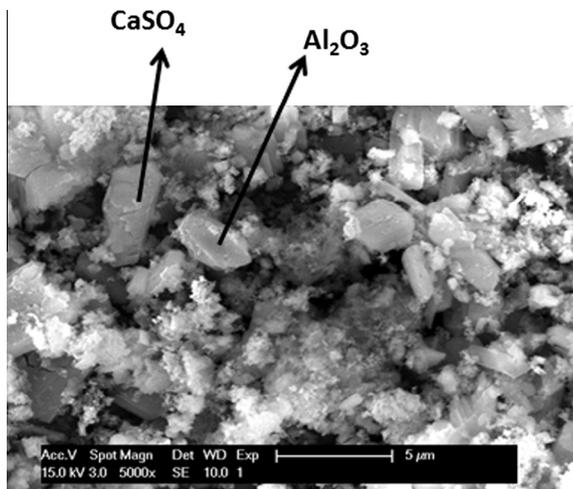


Fig. 12. SEM image of the leach residue (roasting temperature: 700 °C, roasting duration: 1 h, acid to bauxite residue: 1, L/S ratio: 50, non-agitated leaching duration: 7 days).

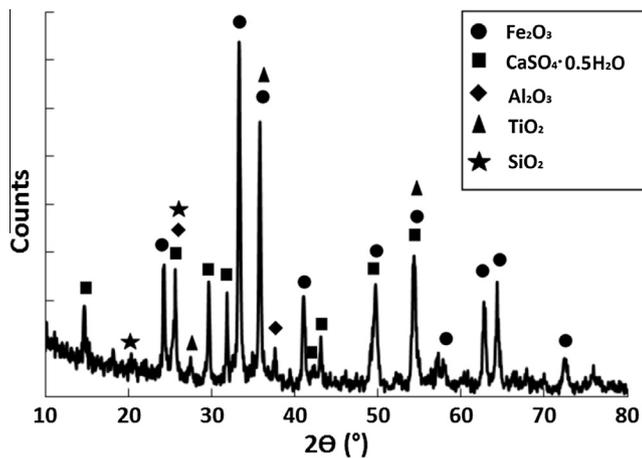


Fig. 13. XRD of the leach residue (roasting temperature: 700 °C, roasting duration: 1 h, acid to bauxite residue: 1, L/S ratio: 50, non-agitated leaching duration: 7 days).

the approx. 3 wt% today for bauxite residue. Interestingly, the composition of the material is also exceptionally attractive for non-OPC clinkers, belite, calcium sulfo-ferro-aluminates in particular (Iacobescu et al., 2013). In this type of clinkers, gypsum is added as a raw material and both iron and alumina levels are much higher compared to OPC; an overview can be retrieved elsewhere (Pacheco-Torgal et al., 2013). Another possibility is to explore the application of the residue in blended cements (Pera et al., 1997). In that approach, the presence of calcium sulfate hemihydrate is a benefit and will substitute the addition of gypsum in the OPC clinker. Still, the pozzolanic properties of the new residue need to be investigated in detail.

3.9. Preliminary economic analysis

A preliminary economic analysis of the process is shown in Table 6, including the estimated costs of consumed reagents and values of the generated products. While the calculations are based on the 50 g scale experiments, the results are given for 1 ton of bauxite residue. The extraction values for Sc and other REEs are 60% and 80%, respectively. The consumption of bauxite residue is represented as a positive benefit as the material is a liability to the company.

Table 6

Preliminary economic analysis of the proposed process (production unit is 1 ton of bauxite residue).

	Weight (ton)	Unit price (US\$/ton)	Value (US\$)
Costs			
Acid	0.38	200	–76
Water	10	1	–10
Benefits			
Bauxite residue	1	10	10
Sc ₂ O ₃	111 · 10 ^{–6}	2.5 · 10 ⁶	277
Other REEs	740 · 10 ^{–6}	–	16
Residue	1.06	10	11
Margin	–	–	228

The acid used at optimized conditions was one ton per ton of bauxite residue. However, the consumption during the process is around 0.38 ton (based on theoretical calculations). The remainder will report to the gas phase and can be used for acid regeneration. The acid price used in the calculation was taken from <http://www.alibaba.com/>. REEs prices were taken from USGS 2013 Minerals yearbook (Gambogi, 2015). Total REEs value except scandium is the sum of the amount recovered multiplied by their respective price. As mentioned earlier, the residue generated in the process can be considered for application in cementitious binders. The profit margin amounts to about 228 US\$. However, it should be noted that the cost of sulfation, roasting, further recovery processes (e.g. solvent extraction, ion exchange etc.), labor, equipment and energy was not considered in these preliminary calculations.

4. Conclusions

A sulfation–roasting–leaching process was developed to selectively leach REEs from bauxite residue (red mud). Most of the elements in the bauxite residue convert to their respective sulfates during sulfation. Iron and aluminum sulfates decompose to their respective oxides at temperatures around 700 °C. Decrease in the roasting temperature increases the iron, aluminum and titanium dissolution. Increase in the roasting time beyond certain duration decreases the dissolution of iron, titanium, and REEs. At a roasting temperature around 700 °C for a roasting duration of 1 h and with a sulfuric acid to bauxite residue mass ratio of 1:1, ca. 60 wt% of scandium and >80 wt% of other REEs can be extracted after room temperature leaching for 7 days without agitation or for 2 days with agitation. However, scandium attains maximum dissolution within 1 day for both the cases. The dissolution of some of the major elements expressed as a fraction of their total availability was found to be very low compared to the direct acid leaching method: less than 1%, for Fe and Ti and less than 20%, for Al. No silicon dissolution was observed. Sodium was completely soluble and calcium was soluble up to the solubility limit of its sulfate in water. A decrease in L/S ratio does not affect the dissolution of REEs and major elements except calcium; however, it increases the REEs concentration in the leach solution. The pH of the residue generated after leaching is close to neutral and has attractive chemistry and crystalline phase assemblage for other applications, e.g. cementitious binders.

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