

Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching



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ABSTRACT

In this work, the extraction of selected rare earth elements from bauxite residue by dry digestion method followed by water leaching was investigated. Kinetic studies performed with HCl and H₂SO₄ demonstrated that, at ambient temperatures, silica dissolution increases with increasing acid concentration, which leads to the formation of silica gel. Dissolution of silica is limited to less than 5 wt% by applying a two-step process: dry digestion of bauxite residue with HCl or H₂SO₄, followed by water leaching. The extraction of aluminium was low because of the low solubility of aluminosilicate compounds. The extraction of iron and titanium increased with increasing acid concentrations. High extraction of the rare-earth elements (REEs) were achieved with the HCl-based dry digestion method, but the concentration in the leachate was limited to approximately 6–8 mg L⁻¹. About 40 wt% of scandium was recovered with a high co-dissolution of iron, due to the occurrence of scandium (III) ions in the lattice matrix of iron(III) oxide. Dry digestion method with multi-stage circulation of the acid leaching solution significantly increased the REEs concentration up to 20 mg L⁻¹, while achieving an acid consumption of 788 g of HCl per kilogram of bauxite residue, and a significant reduction of water consumption (60%) relative to the single-stage acidic leaching method. The low water consumption allows to increase the filtration efficiency of the leach liquor due to the avoidance of silica gel formation.

1. Introduction

Bauxite residue (BR, also called red mud) is the waste product generated during alumina production from bauxite by the Bayer process (Patterson et al., 1986). It is composed essentially of compounds that are insoluble in concentrated sodium hydroxide solutions: iron and titanium minerals, undigested alumina minerals, sodium aluminium hydrosilicates and calcium compounds. It has been estimated that the annual global production of bauxite residue exceeds 150 million tonnes (Deady et al., 2016; Evans, 2016) and, according to numbers from the year 2007, about 2.7×10^9 tonnes have been already accumulated in tailing ponds, dry stacking and other dry disposal methods (Klauber et al., 2011). It is believed that today, this amount has increased to approximately 4×10^9 tonnes (Aluminium and the European Aluminium Association, 2015).

Bauxite residue represents an interesting source for major elements such as aluminium, iron and titanium, but also for rare-earth elements (REEs) (Binnemans et al., 2015). The chemical composition of bauxite residue shows a very wide variability, as it depends on the origin of the

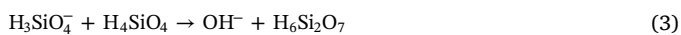
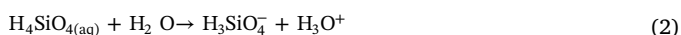
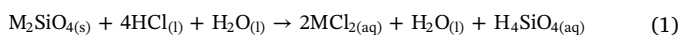
bauxite ore and the operational conditions during the Bayer process. A range on composition of minerals typically found on bauxite residue has been reported by Evans (Evans, 2016). REEs are normally associated to phosphate (e.g., monazite (REEPO₄)) and fluorocarbonate (e.g., bastnäsite (REECO₃F)) compounds (Mongelli, 1997). Bastnäsite is the most common host for rare-earth oxides in karst bauxites (Maksimovic and Panto, 1991; Mongelli, 1997). The enrichment factor of the rare earths in bauxite residue compared to bauxite is about a factor of two (Ochsenkuhn-Petropulu et al., 1994). The concentration of rare earths in bauxite residue may vary between 500 and 1700 mg kg⁻¹ (Akçil et al., 2017).

Scandium represents 95% of the economic value of the REEs present in bauxite residue (Borra et al., 2015b). Ores with a scandium content range between 20 and 50 mg kg⁻¹ are considered as resources and are worthy of exploitation (Shaoquan and Suqing, 1996). The highest concentration of scandium is found in Jamaica bauxite residue, with concentration as high as 260 mg kg⁻¹ (Borra et al., 2016a). This concentration is ten times higher than the average concentration of scandium in the Earth's crust. Several methods based on direct leaching by

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acids have been reported for recovering valuable metals from bauxite residue (Borra et al., 2016a; Liu and Li, 2015; Wang et al., 2011; Zhang et al., 2016a). The extraction efficiencies depend on the acid concentration with more extraction achieved at higher acid concentrations, but the amount of iron dissolution increases with acid concentration as well and this limits the REE concentration in the leachate (Borra et al., 2015b; Ochsenkuhn-Petropulu et al., 1994; Ochsenkuhn-Petropulu et al., 1996; Rivera et al., 2017). Although conventional direct acidic leaching of bauxite residue allows a high extraction of REEs with a low iron dissolution (Rivera et al., 2017), the concentration of REEs in the leachate (5–9 mg L⁻¹) is still about one hundred times lower than the iron concentration (about 900 mg L⁻¹), which hampers the extraction of REEs in further processing, for instance in the solvent extraction step (Onghena et al., 2017). However, the concentration of REEs in the leachate may be increased by a multi-stage treatment. The method has demonstrated promising results in terms of acid consumption reduction and enhancement of leaching efficiency, by which the concentration of metals in the leach liquor is increased (Onghena et al., 2017; Xia et al., 2015; Zhu et al., 2012). The application of the multi-stage leaching method to bauxite residue may increase the REE concentration in the leachate, although a high silica dissolution may also be expected, as well as an accumulation of major metals in the final leachate. A high silica dissolution leads to a greater silicon supersaturation index (SSI), which represents the ratio of dissolved silica with respect to the maximum silica solubility (Kokhanenko et al., 2016). The increase of SSI is considered to be the driving force for silica polymerization (Hamouda and Amiri, 2014; Tobler et al., 2009). In HCl or H₂SO₄ media, at relatively low pH values, i.e. below the isoelectric point for silica in the solution (pH_{iso} between 1.7 and 2.2) (Wilhelm and Kind, 2015), the hydrolysis of silica occurs very fast to produce H₄SiO₄ and H₃SiO₄⁻ (Eqs. (1) and (2)), which are the precursors for silica gel polymerization (Hamouda and Amiri, 2014; Zerda et al., 1986). Initially, silica monomers (e.g., H₄SiO₄, H₃SiO₄⁻) polymerize via dimers, trimers, etc. to cyclic oligomers (Si_{n+1}O_{m+2}OH), according to Eqs. (3) and (4). These oligomers continue to react until a gel network is formed via Ostwald ripening, i.e. dissolution of smaller particles and precipitation on larger particles, which finally results in the formation of an acidic silica gel (Tobler et al., 2009)



Among others, quartz, sodalite and cancrinite are the most abundant silica bearing minerals in bauxite residue, although silica gel is produced by the acidification of amorphous silicate minerals. Such compounds have a higher solubility in comparison to quartz, which makes these minerals of special interest for further research (Friedrich et al., 2016).

Silica gel formation represents a serious drawback in the extraction of metals from ores and process residues by hydrometallurgical methods because the gel solutions can no longer be filtered (Abkoshk et al., 2014; Queneau and Berthold, 1986; Shi et al., 2017; Zhang et al., 2016b). Additionally, this gelatinous precipitate may blind ore particles from further dissolution and reduce the leaching kinetics significantly. According to the literature, silica (and also iron) can remain undissolved when the bauxite residue is processed by the consecutive combination of sulfation, roasting and leaching processes, which also allows to achieve a high selectivity for REEs (Borra et al., 2016c; Onghena et al., 2017). However, this method is limited by the high energy consumption due to the decomposition of sulfates during roasting and evaporation of water during sulfation (Borra et al., 2016b). Another method, dry digestion, is an effective way to avoid the dissolution of amorphous silica from silicate minerals mainly because it

may take place at ambient conditions. The method consists in contacting silicate minerals with strong acids in a water-deficient system, i.e. a high solid concentration, by which silica is effectively rejected from the respective minerals (Dufresne, 1976). It is stated that in a water-deficient system, the interaction between the metal and the acid (i.e. formation of MSO₄ or MCl₂ with concentrated H₂SO₄ or HCl, respectively, where M represents the valuable metal) scavenges the available water of the system, so that no hydration of the silica is possible. This way, the silica polymerization is avoided, and the dehydrated silica (i.e. SiO₂) is readily filterable. The same principle applies in the so-called acid pugging and curing method, but the technique requires temperatures in the range of 100–200 °C (Amer et al., 2000). The dry digestion method is applied at ambient temperature, which represents its most remarkable advantage.

Although there exist no literature reports on the application of dry digestion to bauxite residue, researchers have reported promising results on the use of this technique for extraction of metals from eudialyte (Davris et al., 2017; Friedrich et al., 2017, 2016; Voßenkaul et al., 2017), but also from different silicate minerals for zinc and manganese extraction (Dufresne, 1976; Groot et al., 2013; Kazadi et al., 2016; Zhang et al., 2016b).

The objective of this paper is to evaluate the extraction of REEs from bauxite residue by dry digestion with concentrated mineral acids (i.e. HCl, H₂SO₄), followed by water leaching. Valuable metals can be effectively washed out by using this method since silica polymerization does not occur, which significantly can improve the filterability of the leach liquor. Direct leaching experiments of bauxite residue are performed with HCl and H₂SO₄ at different concentrations in order to study the behaviour of silicon during acid leaching over time. A multi-stage leaching was applied after dry digestion to increase the REEs concentration in the leachate. The process has been compared with the conventional direct acidic leaching method in terms of selected REEs and iron concentration, and acid consumption.

2. Material and methods

The bauxite residue studied in this paper was kindly provided by Aluminium of Greece (Agios Nikolaos, Greece). It originates from a mixture of karst and lateritic bauxites. It was received from the alumina refinery after dewatering by filter pressing and drying at room temperature. Upon arrival in the lab, the sample was further dried at 105 °C for 24 h. Chemical analysis of the major elements in bauxite residue was performed by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Chemical analysis of the minor elements was performed after complete dissolution of the bauxite residue by alkali fusion and acid digestion in 3 vol% HNO₃ solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. The alkali fusion was carried out by mixing 0.5 g of bauxite residue with 1.5 g of sodium carbonate and 1.5 g of sodium tetraborate decahydrate, followed by heating the mixture in a platinum crucible at 1100 °C for 30 min. The mineralogy of the samples was studied by X-ray powder diffraction (XRD, Bruker D2 Phaser). The obtained data were evaluated with EVA V.3.1 (Bruker AXS) and quantified with Topas-Academic V.5, using the Rietveld method.

Leaching experiments of bauxite residue over time were performed in a 150 mL glass reactor with HCl (37 vol%, Fisher Scientific) and H₂SO₄ (95–97 vol%, Sigma-Aldrich) solutions of a fixed concentration (0.5, 1.0 and 1.5 N) at ambient conditions, i.e. 25 °C. The experimental set-up consists of a hot-plate magnetic-stirrer device, a pH-electrode (Hamilton, VWR) and a thermocouple (Pt100, VWR). Within the reactor solid particles were mixed with 100 mL of the corresponding solution at a liquid-to-solid ratio (L/S) of 5:1. The entire experiment lasted for 60 min, in which aliquots (about 2 mL) of slurry were extracted from the glass reactor at specific time intervals. The mixtures were continuously agitated during the whole experiment to ensure a homogenous suspension. Each aliquot was filtered using a syringe and a

0.45 μm filter (CHROMAFIL PET-45/25 Polyester), and diluted with 2 vol% HNO_3 for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis for silicon. Lutetium was used as an internal standard. A pre-prepared liquid solution was used as a reference sample during each chemical analysis by ICP-OES. The chemical composition of the reference sample considers: 30 mg L^{-1} of Al and Fe, 18 mg L^{-1} of Si and Ti, 40 mg L^{-1} of Na and 0.12 mg L^{-1} of Sc. The experiments were conducted at ambient temperature, i.e. 25 $^\circ\text{C}$. The pH of each sample was measured with the same pH probe. At the end of each experiment, the remaining reactor content was filtered through a Buchner filter (VWR® Grade 413 Filter Paper, Qualitative, 5 μm retention), and the solid filter cake was dried (24 h, 105 $^\circ\text{C}$) and stored for further XRD analysis.

Dry digestion experiments were initiated by mixing 2 g of sample with 2 mL of concentrated acid. The desired water-to-acid ratio, W/A, was reached through dilution with Milli-Q water (18.2 M Ω cm). The time of digestion and leaching was evaluated during 24 h. After digestion, the paste was washed with 10 mL of Milli-Q water. The experiments were performed at 25 $^\circ\text{C}$ in sealed polyethylene bottles with constant agitation (200 rpm) using a laboratory shaker (Gerhardt Laboshake). The pregnant leach solution (PLS) was filtered using a syringe filter (pore size of 0.45 μm) and diluted with 2 vol% HNO_3 for ICP-OES analysis of major (Al, Fe, Ti) and minor elements (Sc, Y, La, Nd).

Multi-stage leaching was performed by repeating the dry digestion process five times, i.e. five stages, each time on a virgin red mud sample, but instead of leaching with water during the second and following cycles, the leachate of the previous cycle was used as the liquid phase. Since a small volume of the leachate is lost during filtration, the volume of the leachate after filtration is less than 10 mL. Therefore, extra water was added in each cycle to maintain a 5:1 L/S ratio. Each cycle, about 8.5 mL of the leachate of the previous cycle was mixed with approximately 1.5 mL of ultrapure water to achieve exactly 10 mL of leach solution and used as the liquid phase for leaching. Aliquots of PLS (1 mL) were extracted at the end of each cycle, which were diluted with 2 vol% HNO_3 for ICP-OES analysis. All other steps were performed in the same way as described above.

All the experiments were carried out in triplicate to ensure reproducibility of the results. The errors were determined as the standard deviations on the results.

3. Results and discussion

3.1. Characterization of the bauxite residue

The chemical analysis of the major elements present in bauxite residue is shown in Table 1. Bauxite residue has a high content of iron and aluminium. In Table 2, the concentrations of scandium, yttrium, lanthanum, and neodymium are shown because their concentrations are among the highest for the REEs in bauxite residue. Mineralogical analysis allowed the identification of several mineral phases (Table 3), rich in iron (hematite, goethite), aluminium (gibbsite, diaspore, bayerite), calcium (calcite, calcium silicates and calcium aluminosilicates), sodium (sodalite, cancrinite) and titanium (rutile).

Table 1
Major chemical components in the bauxite residue.

Compound	Concentration, wt%
Fe	33
Al	10
Ca	6
Si	3
Ti	3
Na	2
Loss on ignition	8.5

Table 2
Selected rare-earth elements composition of the bauxite residue sample (Borra et al., 2015b).

Element	Concentration, mg kg^{-1}
Sc	121 \pm 10
Y	76 \pm 10
La	114 \pm 15
Nd	99 \pm 7

Table 3
Mineralogical composition of the bauxite residue sample (estimated relative error 10%).

Phase	Chemical formula	Concentration, wt%
Hematite	Fe_2O_3	36
Grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	13
Dicalcium-silicate (C ₂ S)	Ca_2SiO_4	12
Gibbsite	$\text{Al}(\text{OH})_3$	8
Diaspore	$\text{AlO}(\text{OH})$	7
Tricalcium-silicate (C ₃ S)	Ca_3SiO_5	5
Goethite	$\text{FeO}(\text{OH})$	5
Calcite	CaCO_3	4
Bayerite	$\alpha\text{-Al}(\text{OH})_3$	4
Sodalite	$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24})\cdot x\text{NaOH}(8-2x)\text{H}_2\text{O}$	3
Calcium-aluminium-silicate (CAS)	$\text{Al}_{12}\text{CaO}_{27}\text{Si}_4$	2
Rutile	TiO_2	2
Cancrinite	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2\cdot 2\text{H}_2\text{O}$	1

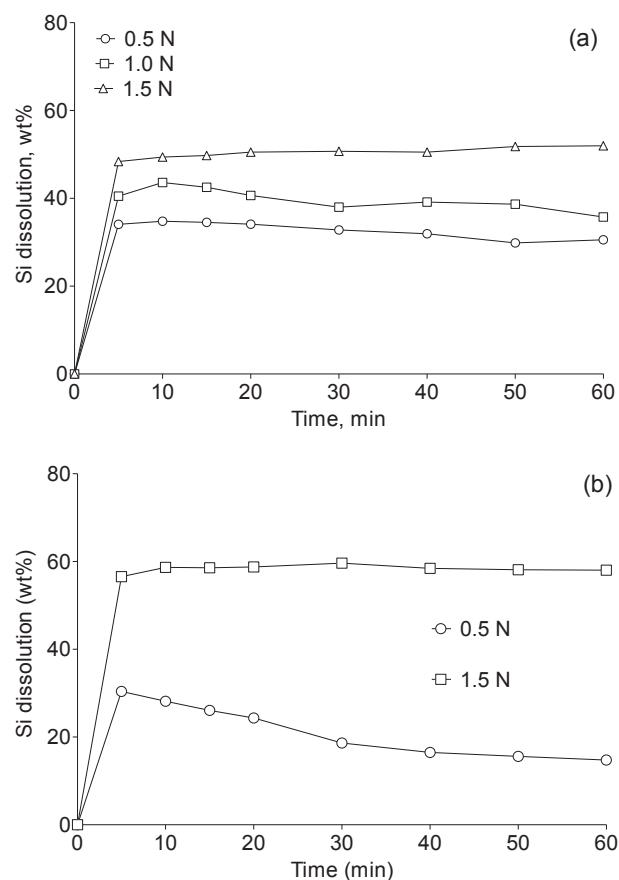


Fig. 1. Effect of (a) HCl and (b) H_2SO_4 concentration on the dissolution of silicon (Si) during leaching of bauxite residue sample (L/S: 5, 200 rpm).

3.2. Silicon dissolution behaviour

The behaviour of silicon dissolution over time was studied during the direct acid leaching of bauxite residue. The experiments were conducted with mineral acids at different concentrations. Fig. 1 describes the effect of HCl and H₂SO₄ on the dissolution of silicon as a function of time at different concentrations. At ambient temperature, the dissolution of silicon in the leach solution increases with increasing acid concentration, and the maximum dissolution was obtained between the first 5–10 min of chemical reaction. In hydrochloric (or sulfuric) acid media, silicates dissolve from the bauxite residue by forming H₄SiO₄ and H₃SiO₄⁻ according to Eqs. (1) and (2). These monomers polymerize to cyclic oligomers (Si_{n+1}O_{m+2}·OH), according to Eqs. (3) and (4), which react until a gel network is formed via Ostwal ripening, i.e. formation of an acidic silica gel (Tobler et al., 2009).

The lowest silicon dissolution was observed with the lowest acid concentration due to the reduction of the monomer's solubility as consequence of a fast reactivity of the acid with solid particles (Wilhelm and Kind, 2015). The initial concentration of silicon in the solution was about 2.0–2.3 g L⁻¹ when the bauxite residue started being leached with 0.5 N of HCl and H₂SO₄, i.e. within the first 3–4 min, which represents the minimal concentration of silicon in the leachate for silica gel formation.

The highest silicon dissolution was observed at 1.5 N H₂SO₄. This suggests that silicate compounds, such as grossular, C₂S and C₃S (Fig. 2), are much more soluble in H₂SO₄ than in HCl. The low concentration of these compounds in the leached samples indicates a favoured dissolution of these compounds in H₂SO₄ media rather than in HCl.

3.3. Dry digestion followed by water leaching

Direct acid leaching experiments revealed the importance of mineral acid concentration during silica gel formation. As it was discussed in the previous section, silica polymerization can be limited by avoiding the hydrolysis of silica. The dry digestion method allows to treat silicate minerals with highly concentrated mineral acids in a water-deficient system at ambient conditions (Dufresne, 1976). The effect of dry digestion of bauxite residue on silica depletion, acid consumption and the extraction of selected REEs from bauxite residue was evaluated at ambient conditions in two consecutive experimental processes, according to the diagram depicted in Fig. 3: (1) dry digestion of bauxite residue with highly concentrated mineral acid, and (2) subsequent water leaching and filtration of the digested bauxite residue sample.

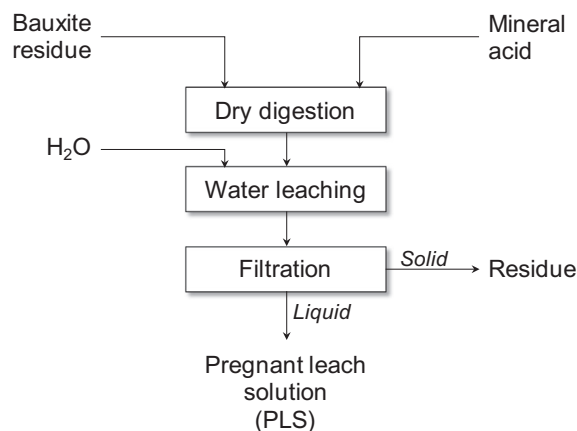


Fig. 3. Flow sheet for dry digestion of bauxite residue, followed by metal extraction from the digested bauxite residue by water leaching.

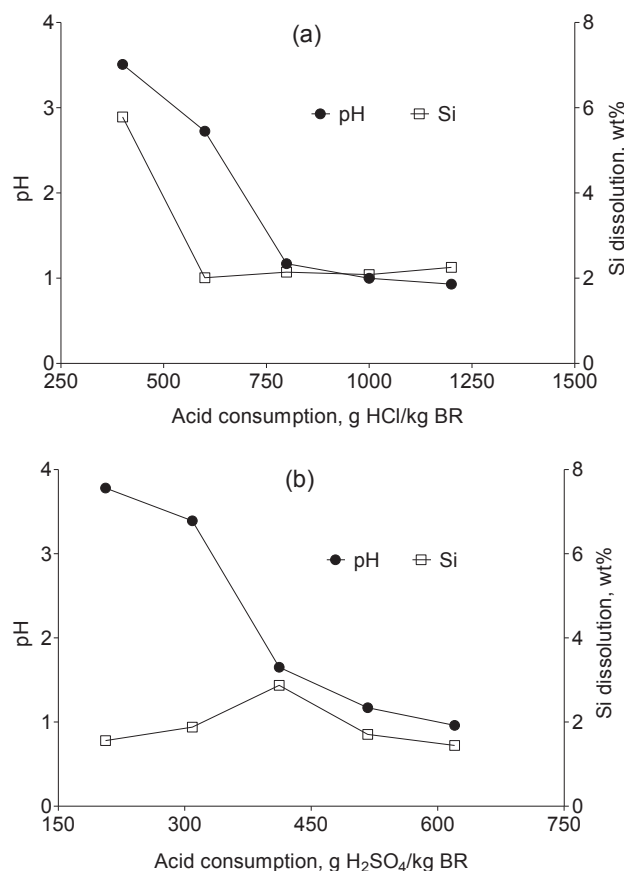


Fig. 4. Effect of (a) HCl and (b) H₂SO₄ consumption on the pH and silicon (Si) dissolution after dry digestion-water leaching processing. (BR: bauxite residue, L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, T: 25 °C, 200 rpm).

3.3.1. Silica dissolution after dry digestion of bauxite residue

Fig. 4 shows the effect of acid consumption on the pH and silicon dissolution after water leaching. The acid consumption increases due to an increase in the acid concentration, which leads to a dramatic reduction of the pH. The lowest silicon dissolutions were observed with H₂SO₄ rather than with HCl. This was due to the preferential dissolution of silicate compounds in H₂SO₄ (see Fig. 2). In HCl media, silicon dissolution was reduced from 6 wt% when the acid consumption was 400 g HCl/kg BR to about 2 wt% with an acid consumption of 1200 g HCl/kg BR. However, dry digestion with sulfuric acid caused only 1.5 wt% of silicon dissolution with a much lower acid consumption (620 g H₂SO₄/

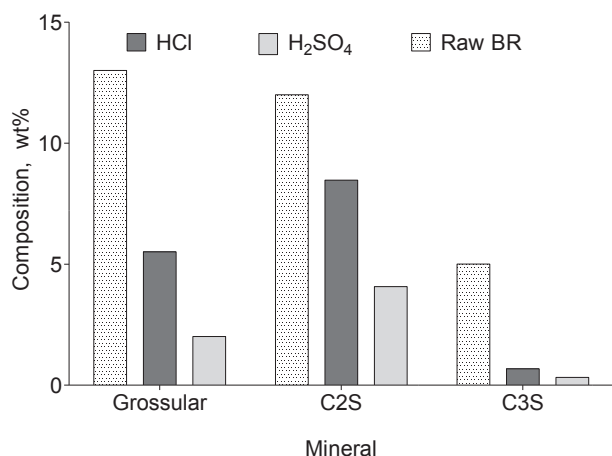
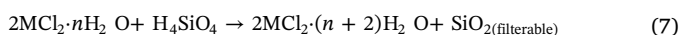
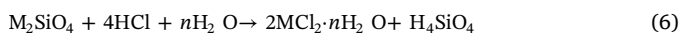
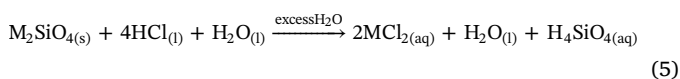


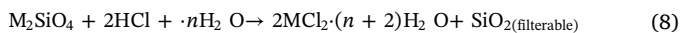
Fig. 2. Concentration of selected mineralogical phases in the solid after acidic leaching with HCl and H₂SO₄ (acid concentration: 1.5 N, t: 1 h, T: 25 °C, L/S: 5).

kg BR). This is due to the fact that sulfuric acid releases two protons per molecule, whereas this is only one proton in the case of hydrochloric acid. The acid consumptions were defined as function of pH by using different mineral acids. It must be noticed that the dissolution yields achieved by this method were much lower than the one previously described in Section 3.2 by direct leaching (Fig. 1), and even much lower than the values reported in the literature (Borra et al., 2015b; Rivera et al., 2017). Only about 5 wt% of silicon was soluble over the whole acid consumption range. The standard error of silicon was less than 0.05% with HCl, while with H₂SO₄ was less than 0.1%.

The lowest amount of silicon dissolution achieved with this method was due to the low amount of water used during the process, which avoids the hydrolysis of silica. When a silicate compound is in contact with an excess of water in acidic media, i.e. conventional direct acid leaching of bauxite residue, the silicon liberation and the subsequent generation of silicic acid results in the silica gel formation according to Eq. (5). However, when the amount of water is restricted, the reaction proceeds according to Eq. (6). As this is an intermediate step, the partially hydrated metal ion reacts further with silicic acid, diminishing the condensation of monomeric silicic acid according to Eq. (7).



The overall reaction is represented in Eq. (8). It is postulated that in a water-deficient system, the produced chloride scavenges the available water. Thus, hydration of silica may be restricted and so is the silica polymerization. The dehydrated silica (i.e., SiO₂) can be readily filterable (Dufresne, 1976; Kazadi et al., 2016). The same principle is applied in H₂SO₄ media (Eq. (9)).



3.3.2. Metal extraction with dry digestion method

The extraction of major and minor elements was evaluated after applying the dry digestion method. The effect of acid concentration on the extraction of aluminium, iron and titanium is depicted in Fig. 5. At lower acid consumption, aluminium was easily leachable in both acidic media compared to iron and titanium. The extraction of aluminium increased with higher acid concentrations until a maximum of about 30 wt% was reached. As expected, iron and titanium dissolution gradually increased with the increase in acid consumption. A further increase in acid concentration did not lead to an improvement of aluminium extraction, due to the low dissolution of aluminium-silicate compounds, such as C₂S and C₃S, and gibbsite. As it is described in Fig. 6, these compounds were identified not only in the raw bauxite residue, but also after dry digestion with HCl and H₂SO₄. Grossular demonstrated a higher decomposition after dry digestion with HCl than with H₂SO₄, while cancrinite was not identified after leaching, presumably because it is totally decomposed by dry digestion. The XRD pattern also revealed that the intensity of gibbsite was increased prominently after dry digestion with HCl, presumably due to the low solubility of gibbsite at ambient temperature (Zhao et al., 2013).

Fig. 7 describes the effect of acid concentration on the leaching of selected REEs. The extraction of REEs gradually increased with increasing acid concentration. However, the lowest extraction yields were achieved by using H₂SO₄ during the dry digestion stage (Fig. 7b), which confirms the results already reported in the literature (Borra et al., 2015b; Boudreault et al., 2015; Ochsenkühn-Petropulu et al., 1996; Rivera et al., 2017). The difference in extraction yield of scandium between dry digestion with HCl and H₂SO₄ can be explained by the co-

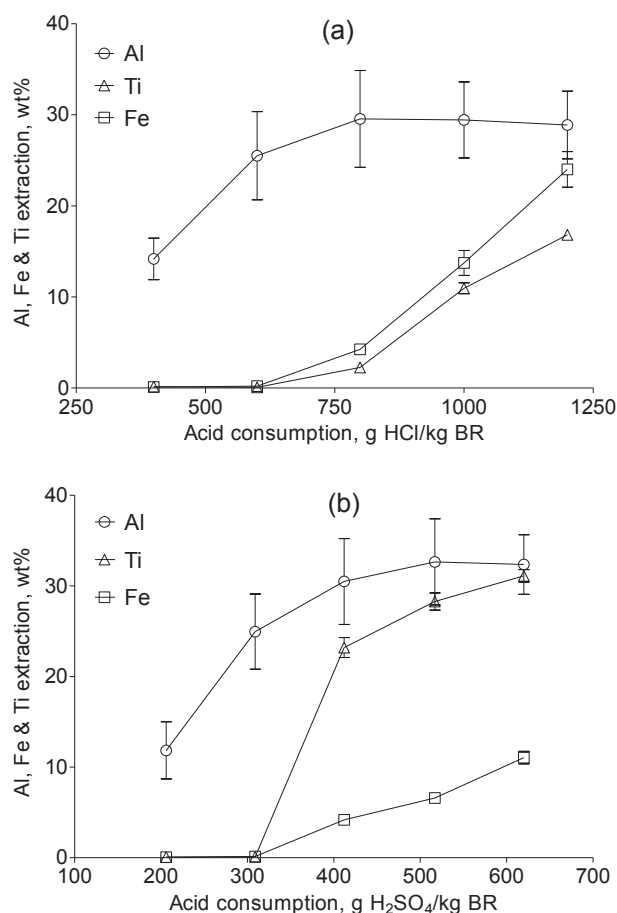


Fig. 5. Effect of acid consumption on the extraction of aluminium (Al), iron (Fe) and titanium (Ti) after water leaching. Dry digestion with (a) HCl and (b) H₂SO₄ (L/S: 5, $t_{\text{digestion}}$: 24 h, t_{leaching} : 24 h, 200 rpm). The standard error of Fe in H₂SO₄ is below 0.1%.

precipitation of scandium with calcium during the chemical transformation of calcite into bassanite in H₂SO₄ media (Fig. 6) (Voßenkaul et al., 2017). Additionally, scandium(III) ions are present in the iron(III) oxide lattice (Zhang et al., 2017), which limits its complete dissolution. Iron dissolution was much higher when dry digestion was performed with HCl (Fig. 5) compared to H₂SO₄ dry digestion, which explains the higher extraction of scandium in a HCl-based dry digestion procedure upon a significant amount of iron dissolution (about 25 wt% in HCl) (Fig. 8). Although the elemental correlation between scandium and the major elements is less clear with H₂SO₄ in comparison to HCl dry digestion, scandium dissolution does not depend on the extraction of aluminium, but it may have some correlation with the dissolution of titanium. It has been reported that REEs, with the exception of scandium, tend to be associated to perovskite phases, which makes the dissolution in acidic solutions very difficult (Shrivastava et al., 2004; Zheng et al., 2016). No correlation between yttrium and the other metals was found, which may indicate that yttrium is not bonded to other metals in this particular bauxite residue, but the extraction depends only on acid concentration.

The extraction of neodymium and lanthanum was higher with the HCl-based dry digestion (about 37 wt%) in comparison to H₂SO₄-based dry digestion (about 20 wt%). Leaching of both elements tends to be positively correlated due to their similarities in atomic and ionic radii (Fig. 9) (Borra et al., 2015a; Lei et al., 1986). However, in HCl media, the extraction depends on scandium dissolution (Fig. 10). No trend between the selected lanthanides and scandium was found in the sample subjected to dry digestion with H₂SO₄. (Figure S1 in the Supplementary Material), presumably due to the occurrence of a double sulfate precipitation (Duyvesteyn, 2012).

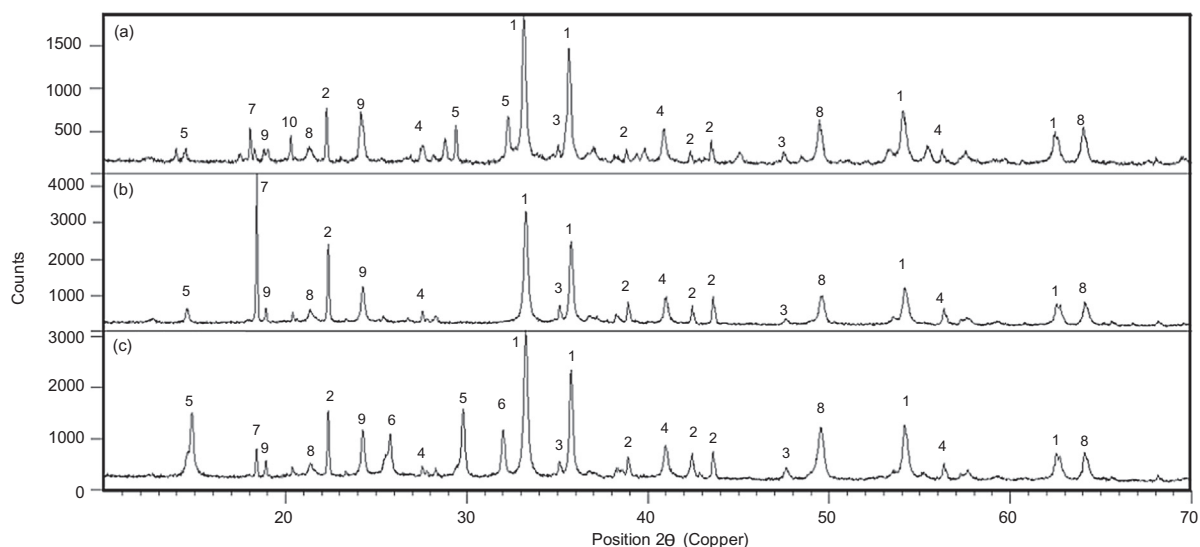


Fig. 6. XRD pattern of (a) raw bauxite residue and, water-leached samples after dry digestion with (b) 1000 g HCl/kg BR and (c) 517 g H₂SO₄/kg BR (BR: bauxite residue, L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm). 1: Hematite; 2: diaspor; 3: perovskite (CaTiO₂); 4: C₂S; 5: grossular; 6: bassanite (CaSO₄ 0.5H₂O); 7: gibbsite; 8: goethite; 9: C₃S; 10: cancrinite.

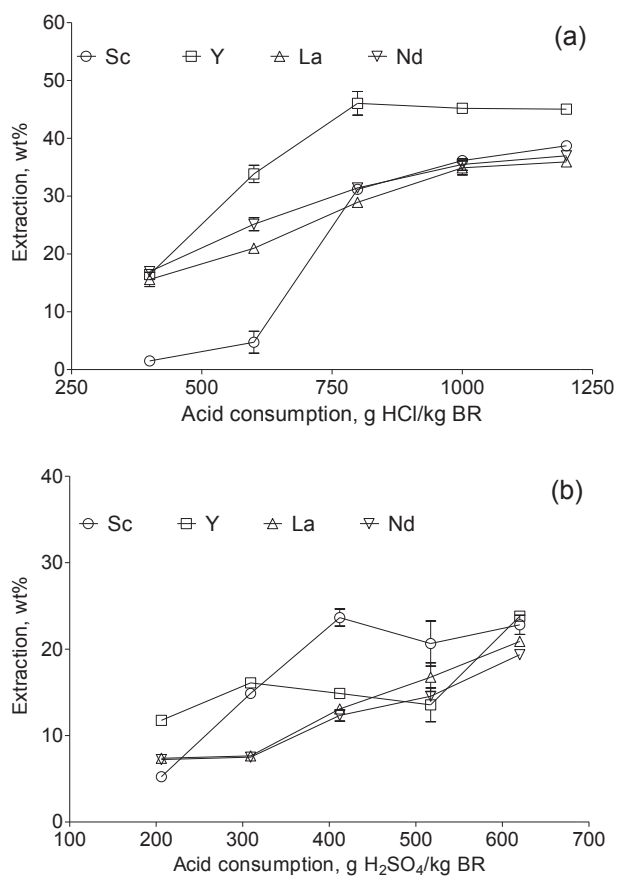


Fig. 7. Effect of acid consumption on the extraction of scandium (Sc), yttrium (Y), lanthanum (La) and neodymium (Nd) after water leaching. Dry digestion with (a) HCl and (b) H₂SO₄ (L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm). The error bars represent the standard error of the mean for experiments performed in triplicate.

3.4. Dry digestion method with multi-stage circulation of acid leaching solution

In order to decrease the water consumption and enhance the leaching efficiency of REEs, the multi-stage leaching method was studied by considering a constant acid consumption. According to Figs. 5

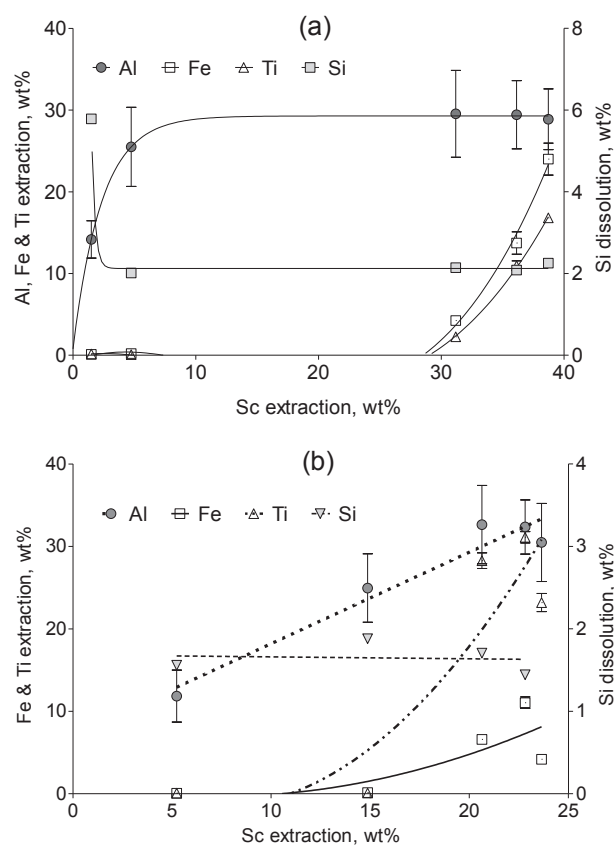


Fig. 8. Extraction behaviour of scandium (Sc) as function of Al, Fe, Ti and Si dissolution after water leaching. Dry digestion with (a) HCl and (b) H₂SO₄ (L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm). The error bars represent the standard error of the mean for experiments performed in triplicate. Trend lines do not represent measurement data, but are added just to aid in detecting trends.

and 7, the lowest Al/Fe leaching ratio (i.e. 2:1) was obtained under the acid consumptions of 788 g HCl/kg BR and 412 g H₂SO₄/kg BR. The same acid consumptions allow a relatively high REEs extraction without bringing too much iron into the solution (about 4 wt%). In this leaching technique, the obtained leachate is filtered and repeatedly contacted again with dry-digested solid samples in multiple leaching

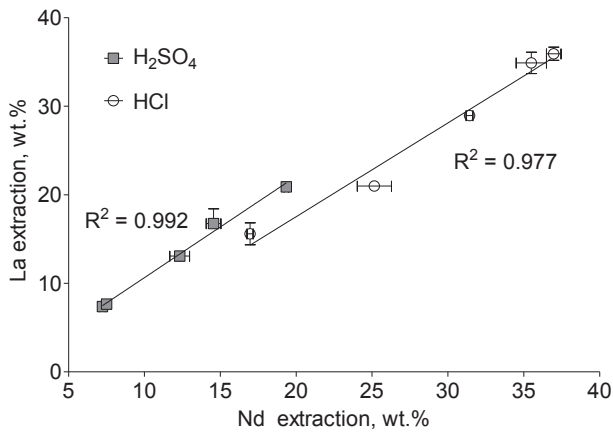


Fig. 9. Correlation between extraction of lanthanum (La) and neodymium (Nd). Dry digestion with HCl and H₂SO₄ (L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm). The error bars represent the standard error of the mean for experiments performed in triplicate.

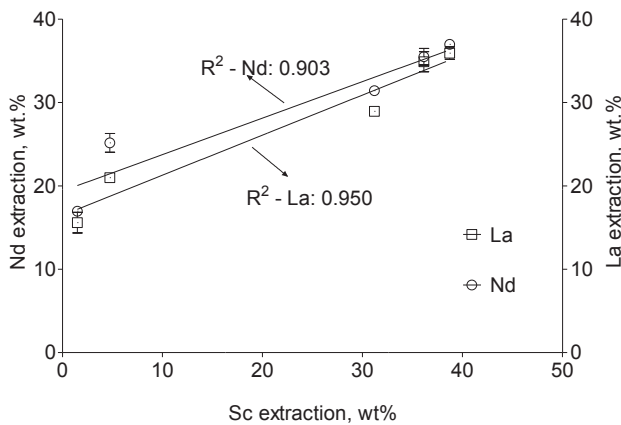


Fig. 10. Correlation between extraction of lanthanum (La) and neodymium (Nd) with scandium (Sc) in HCl-based dry-digested bauxite residue sample with (L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm). The error bars represent the standard error of the mean for experiments performed in triplicate.

stages (Fig. 11). Consequently, a more concentrated leachate is obtained and less water is consumed. The corresponding dry-digested samples were prepared in each stage by mixing the same mentioned

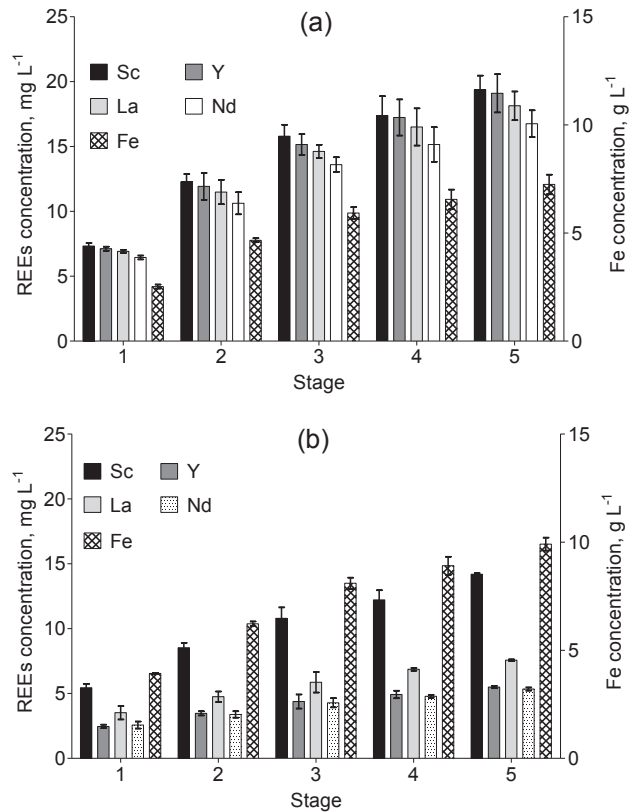


Fig. 12. Concentration of selected rare earths (expressed in mg L⁻¹) and iron (expressed in g L⁻¹) in the leachate after water leaching of each stage. Dry digestion was performed with (a) 788 g HCl/kg BR and (b) 412 g H₂SO₄/kg BR (L/S: 5, t_{digestion}: 24 h, t_{leaching}: 24 h, 200 rpm).

amount of acid. The water leaching step was always performed in a 5:1 L/S ratio.

The concentrations of the selected REEs and iron in the leachate after each stage are summarized in Fig. 12. A single-stage dry digestion-water leaching limits the final concentration of REEs in the leachate to approximately 6–8 mg L⁻¹. However, the concentration of REEs increased during the following leaching stage. The treatment of fresh bauxite residue with a pre-defined quantity of acid allows to obtain the same extraction yields described in Section 3.3.2 (Fig. 7). Moreover, the

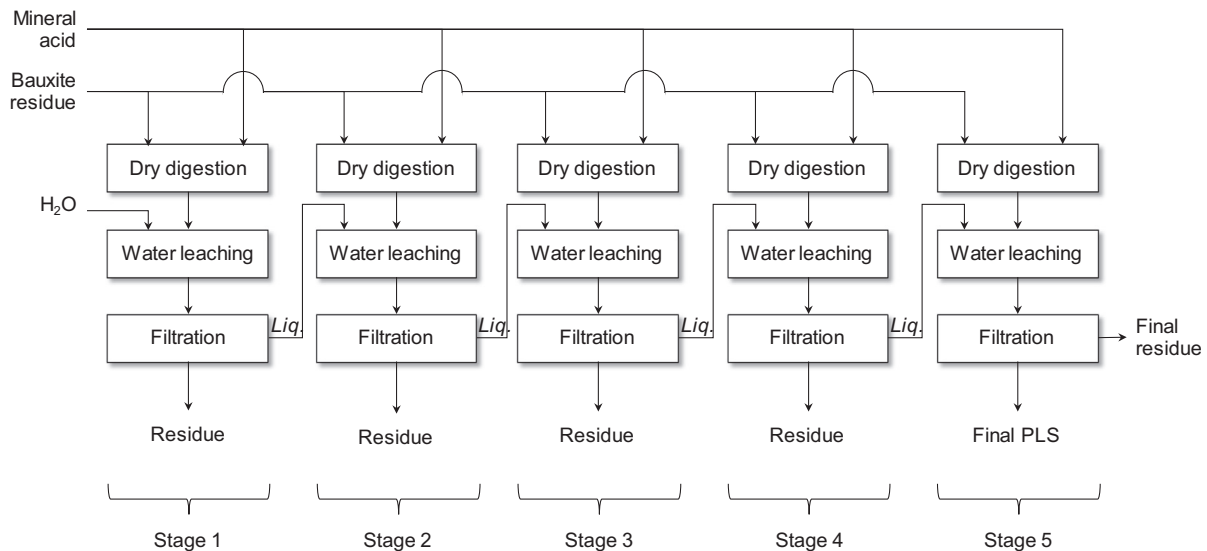


Fig. 11. Conceptual process flow sheet for dry digestion of bauxite residue with a multi-stage leaching.

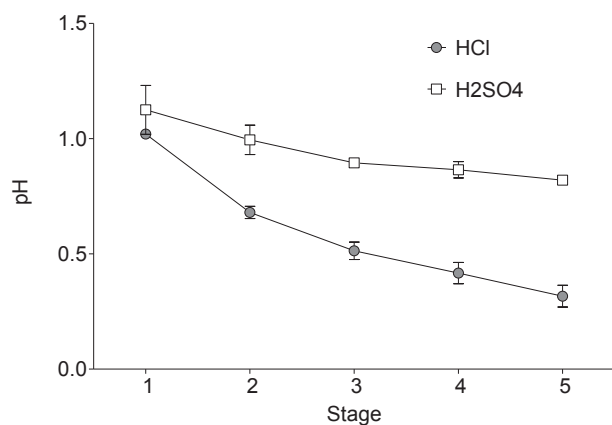


Fig. 13. Change of the pH of the leachate in the different stages of multi-stage leaching with 788 g HCl/kg BR and 412 g H₂SO₄/kg BR (L/S: 5, $t_{\text{digestion}}$: 24 h, t_{leaching} : 24 h, 200 rpm).

enrichment was much more significant for the HCl-based method than for the H₂SO₄-based method. During multi-stage leaching with HCl, the scandium concentration increased from 7.3 mg L⁻¹ in stage 1 to a concentration of 19.3 mg L⁻¹ in stage 5, while the concentration of yttrium, lanthanum and neodymium increased from an average value of 6.8 mg L⁻¹ in stage 1 to an average of 18 mg L⁻¹ in stage 5, more than twice the concentration observed by a single-stage method. During multi-stage leaching with H₂SO₄, the scandium concentration increased from 5.4 mg L⁻¹ in stage 1 to 14.2 mg L⁻¹ in stage 5, while the concentration of yttrium, lanthanum and neodymium increased from an average value of 3 mg L⁻¹ in stage 1 to a concentration about 8 mg L⁻¹ in stage 5. Note that the concentration of silicon in both systems, i.e. HCl and H₂SO₄, remained below 0.5 g L⁻¹ (Figure S2 in the Supplementary Material), so that no gel formation took place during the different stages. Therefore, the multi-stage leaching allows to successfully increase the concentration of REEs, but also the concentration of major metals. When HCl was used, a higher concentration of iron was obtained in comparison to the H₂SO₄-based method. This was caused by the lower pH values achieved with HCl in the different stages (see Fig. 13), but also due to the low solubility of silicate compounds (Fig. 2). The concentration of aluminium was similar with both acids (about 12 g L⁻¹ in stage 5), but the concentration of titanium was slightly higher with H₂SO₄ (4 g L⁻¹ in stage 5) in comparison to the concentration achieved with HCl (0.5 g L⁻¹ in stage 5) (Figure S2 in the Supplementary Material). Purging part of the leach liquor during the multi-stage treatment of bauxite residue can help to reduce the concentration of major metals, in particular of iron.

The present method allows to process much more bauxite residue with a significant decrease in water consumption (Fig. 14). The water consumption was reduced from 5.5 cm³ H₂O/g BR in stage 1 to about 2.3 cm³ H₂O/g BR in stage 5. This was caused by the treatment of fresh bauxite residue and the low amount of water added during the different stages. An increase in bauxite residue processing may help to reduce the inventories and costs associated with storing, which are major concerns for the alumina producers. Nevertheless, this method still needs more investigation at a larger scale, as the obtained reduction in water consumption may vary as a function of the chemical and physical properties of the different bauxite residue samples.

Table 4 compares the results of the direct (single-stage) acidic leaching and results obtained with the dry digestion method with multi-stage circulation of the acid leaching solution. Dry digestion method with multi-stage circulation of solution leads to a reduction in water consumption of about 60% and 48% when HCl and H₂SO₄ are considered, respectively. During multi-stage leaching, the enrichment of REEs is three to four times higher than the concentration achieved with a single-stage leaching method, particularly with HCl, while the iron

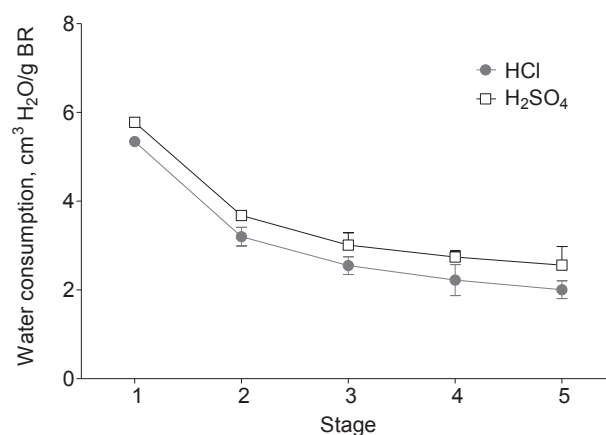


Fig. 14. Water consumption in the different stages of multi-stage leaching with 788 g HCl/kg BR and 412 g H₂SO₄/kg BR (L/S: 5, $t_{\text{digestion}}$: 24 h, t_{leaching} : 24 h, 200 rpm).

concentration increases significantly. Therefore, a severe reduction in the REE/Fe leaching ratio is obtained, i.e. less selective leaching of REEs. However, as it was discussed in Section 3.3, hydrolysis of silica does not occur and polymerization can be avoided with the dry digestion technique, which may lead to a significant improvement of the filtration efficiency for further processing of the leach liquor.

The residue generated after leaching is rich in silica and low in sodium content. It can also be rich in CaSO₄ when H₂SO₄ is considered in the process. For instance, the residue can be further studied for their applicability in building materials or cementitious binder.

A preliminary economic analysis of the processes was developed in order to assess the economic feasibility of pilot-scale test (Table 5). The analysis considered the extraction of titanium and selected rare-earth elements, as oxides, by the methods described in Table 4. The results are given for 1 tonne of bauxite residue processed by a single unit, i.e. single-stage process. During multi-stage leaching, 5 stages were considered. It has been reported that the operating cost of bauxite residue may vary between 4 and 12 USD/tonne, which mainly depends on the site remediation (Evans, 2016). However, the consumption of bauxite residue was considered as a benefit in this preliminary evaluation, as the material is a liability to the company (Evans, 2015). The price of acid used in the calculation was taken from www.alibaba.com, while the price of titanium dioxide was taken from USGS Minerals (Bedinger, 2017). REE prices were taken from mineralprices.com. For the scandium oxide price two values were considered: (1) market price (accessed on 13/12/2017) and (2) half of the market price. This is to check the decrease in margin if there is a price drop for scandium oxide due to increase in production from the proposed processes. Hence, two margins were calculated. The cost associated to electrical energy and further recovery processes (e.g. solvent extraction, ion exchange), as well as labor and equipment was not considered in these preliminary calculations.

The profit margins of these methods are shown in Fig. 15. It is evident from this Figure that recovery of scandium is very important. The results show that the margins are not going below zero at the current price of scandium oxide. Instead, the margins are significantly improved by considering multi-stage leaching, in particular with H₂SO₄. This is mainly because of the high consumption of bauxite residue and the low consumption of water with multi-stage leaching. Furthermore, multi-stage leaching allows to decrease the large volumes of effluents generated during direct leaching, which also leads to an improvement of the profit margin. The margin described by multi-stage leaching with H₂SO₄ is slightly higher than the margin depicted by multi-stage leaching with HCl, because of the lower acid consumption and higher titanium extraction. However, the profit margin does not show a significant improvement when half of the scandium price is considered. Indeed, the margin goes below zero when multi-stage

Table 4
Comparison between single-stage direct acidic leaching and dry digestion with a five-stage circulation of acid solution in terms of selected REEs, iron and aluminium concentration.

Parameters	Direct leaching with H ₂ SO ₄	Multi-stage leaching with HCl	Multi-stage leaching with H ₂ SO ₄
Acid consumption, g acid/kg BR	438	788	412
Water consumption, kg H ₂ O/kg BR	5	2	2.6
Scandium concentration, mg L ⁻¹	5	19	14
Yttrium concentration, mg L ⁻¹	4	19	2.5
Lanthanum concentration, mg L ⁻¹	3	18	7.6
Neodymium concentration, mg L ⁻¹	2	17	5.3
Iron concentration, g L ⁻¹	0.9	7	10
Aluminium concentration, g L ⁻¹	2.5	12.5	12
Leaching ratio Al/Fe, g g ⁻¹	2.8	1.8	1.2
Leaching ratio selected REE/Fe, mg g ⁻¹	15.6	10.4	3.0

Table 5
Preliminary comparative economic analysis of the processes studied in this investigation.

Direct leaching with H ₂ SO ₄			
	Mass (tonne)	Unit price (USD/tonne)	Value (USD)
<i>Costs</i>			
Acid	0.412	-200	-82.4
Water	5	-1	-5
<i>Benefits</i>			
Bauxite residue	1	10	10.0
TiO ₂	1.68E-02	1.5E+03	25.2
Sc ₂ O ₃	7.42E-05	4.2E+06	311.8
Y ₂ O ₃	5.58E-05	6.0E+03	0.3
La ₂ O ₃	3.08E-05	2.0E+03	0.1
Nd ₂ O ₃	2.42E-05	4.2E+04	1.0
Margin 1	-	-	261.0
Margin 2	-	-	105.1
Multi-stage leaching with H ₂ SO ₄			
	Mass (tonne)	Unit price (USD/tonne)	Value (USD)
<i>Costs</i>			
Acid	2.06	-200	-412
Water	2.6	-1	-2.6
<i>Benefits</i>			
Bauxite residue	5	10	50.0
TiO ₂	6.23E-02	1.5E+03	93.5
Sc ₂ O ₃	1.98E-04	4.2E+06	830.8
Y ₂ O ₃	6.35E-05	6.0E+03	0.4
La ₂ O ₃	8.07E-05	2.0E+03	0.2
Nd ₂ O ₃	5.66E-05	4.2E+04	2.4
Margin 1	-	-	562.7
Margin 2	-	-	147.3
Multi-stage leaching with HCl			
	Mass (tonne)	Unit price (USD/tonne)	Value (USD)
<i>Costs</i>			
Acid	3.94	-200	-788
Water	2.6	-1	-2.6
<i>Benefits</i>			
Bauxite residue	5	10	50.0
TiO ₂	9.24E-03	1.5E+03	13.9
Sc ₂ O ₃	2.97E-04	4.2E+06	1247.5
Y ₂ O ₃	2.42E-04	6.0E+03	1.5
La ₂ O ₃	2.13E-04	2.0E+03	0.4
Nd ₂ O ₃	1.95E-04	4.2E+04	8.2
Margin 1	-	-	530.9
Margin 2	-	-	-92.9

leaching with HCl is applied. This is due to the low amount of titanium extracted with HCl media, despite the high amount of extracted scandium. Therefore, the simultaneous recovery of REEs and titanium oxide is the key factor to ensure a positive profit margin.

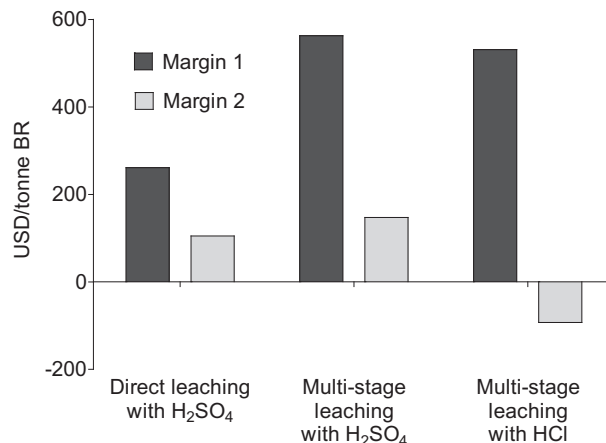


Fig. 15. Profit margin for three leaching methods at current REEs price (source: <http://mineralprices.com>, accessed on 13th of December 2017).

4. Conclusions

Kinetic studies demonstrated that, at constant temperatures, the dissolution of silicon in the leachate increases with increasing acid concentration, due to the high solubility in water of the orthosilicic acid at decreasing pH. High silicon dissolution leads to an increase of the silica saturation index and, therefore, to the formation of silica gel. Reducing the hydrolysis of silica is key to avoid silica polymerization during acidic leaching of bauxite residue.

The two-step processing of bauxite residue by dry digestion and subsequent water leaching demonstrated a high extraction of REE while at the same time preventing silica polymerization. The extraction of aluminium, iron and titanium increased with increasing acid concentration. However, only up to 30 wt% of aluminium can be recovered by this method due to the poor solubility of alumino-silicate compounds in water. The HCl-based dry digestion method allowed the extraction of much more REEs, particularly scandium, compared to H₂SO₄-based dry digestion. However, about 40 wt% of scandium was recovered alongside 25 wt% of iron dissolution, due to their simultaneous occurrence in the lattice matrix of iron(III) oxide. A single-stage dry digestion-water leaching limits the final concentration of REEs in the leachate to approximately 6–8 mg L⁻¹, but it was significantly increased up to 20 mg L⁻¹ by considering the same acid consumption in a multi-stage leaching, particularly with HCl. By considering the dry digestion and water leaching methods as processes integrated in a multi-stage treatment, much more bauxite residue can be processed for REEs extraction without demanding too much water for the process. The low water consumption allows to increase the filtration efficiency of the leach liquor due to the avoidance of silica gel formation.

The preliminary comparative economic analysis shows that dry digestion with H₂SO₄ and multi-stage leaching is the most interesting method for the extraction of scandium and titanium from bauxite

residue. However, this method needs to be studied in pilot-scale. The method looks promising, but further studies are required to increase the extraction of scandium.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mineng.2018.01.023>.

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