Neutralisation of bauxite residue by carbon dioxide prior to acidic leaching for metal recovery

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Highlights

- High CO₂ concentrations reduce the bauxite residue alkalinity.
- Cancrinite forms upon decomposition of sodalite with high CO₂ concentration.
- High stability of aluminosilicate compounds with high sodium dissolution.
- Silica dissolution limits the recovery of metals by acidic leaching.
- The recovery of scandium is restricted by its chemical association to major elements.

Abstract

The present work considers the neutralisation of bauxite residue (red mud) with CO₂ as a potential technology for reducing the acid consumption in the acidic leaching step for metal recovery. The pH of bauxite residue was reduced during neutralisation by the transformation of hydroxide ions to (hydrogen) carbonate ions. Neutralisation at high CO₂ partial pressures and high temperatures reduces the alkalinity of the bauxite residue, but it leads to the stabilisation of silicate compounds such as cancrinite. After acidic leaching of the neutralised product with sulfuric acid, a decrease by 20% in the dissolution yield of Al, Fe, and Ti was observed, due to an insufficient amount of acid devoted to leaching as the transformation of calcite into bassanite and the polymerisation of silica consumed part of the acid. The recovery of Sc and La was reduced by approximately 10% in the material neutralised at high pressures and temperatures, while Y and Nd recovery was not influenced by the neutralisation. The difference in recovery yields is related to the different chemical association of minor elements with the major elements.

Key words: Neutralisation; carbon dioxide; bauxite residue; rare earths; red mud

1. Introduction

Bauxite residue (red mud) is the waste product generated during alumina production by the Bayer process and it is composed essentially of non-soluble elements such as iron and titanium minerals, undigested alumina minerals, sodium aluminium hydrosilicates, calcium minerals and significant amounts of minor and trace elements such as scandium, yttrium and lanthanides, i.e. the so-called rare earth elements (REEs) (Evans, 2016). Bauxite residue is an interesting source of REEs and especially scandium, but also of iron and titanium, while the residue after metal recovery can be used for low-carbon building materials (Binnemans et al., 2015). Scandium concentrations in Greek bauxite residue are about 120 mg/kg (Borra et al., 2015b), but it may reach up to 260 mg/kg in some bauxite residues (Borra et al., 2016) depending on the origin and mix of bauxite minerals (raw material). The scandium concentration in bauxite residue is much higher than its average abundance in the Earth's crust (22 mg/kg). Therefore, the recovery of scandium from bauxite residue could be of economical interest. In fact, scandium represents more than 90% of the value of the REEs present in bauxite residue.

Several methods for recovering valuable elements from bauxite residue have been reported (Borra et al., 2016). They are mainly based on hydrometallurgical and pyrometallurgical processes, or combinations of both. Pyrometallurgical processes allow a high recovery of scandium and other REEs (Borra et al., 2015a; Tanutrov et al., 2013), but the energy consumption is high. Minor elements can be recovered by acidic leaching with HCl, HNO₃, or H₂SO₄ (Abhilash et al., 2014; Borra et al., 2015a; Ochsenkühn-Petropulu et al., 2002, 1996), but co-dissolution of a significant amount of iron is a serious drawback for REE recovery (Borra et al., 2015b).

The alkalinity of bauxite residue is an important issue for metal recovery by acidic leaching because part of the acid must be used for the neutralisation of the alkaline products left behind after the Bayer process. This leads to a large acid consumption and makes the recovery of metals from bauxite residue often not economical. In order to reduce the amount of acid needed for neutralisation of bauxite residue and, consequently, to develop a more sustainable process for metal recovery, alternative neutralisation routes must be considered. The use of carbonic acid (H₂CO₃), formed during the dissolution of CO₂ in water, represents an inexpensive and safe technology for bauxite residue neutralisation. The use of this

reagent has shown promising results in terms of CO₂ sequestration and bauxite residue stabilisation for further safe disposal (Bonenfant et al., 2008; Hanahan et al., 2004; Lutpi and Zhu, 2010; Rai et al., 2013; Yadav et al., 2010). However, the use of CO₂ as a neutralisation reagent for bauxite residue as part of a flow sheet to reduce acid consumption during the metal recovery by acidic leaching has not been studied yet.

The objective of this paper is to evaluate the recovery of valuable metals after the reduction of bauxite residue's alkalinity by transformation of hydroxides into soluble carbonate compounds during the neutralisation by CO₂, at different conditions. Neutralisation with a mineral acid at similar conditions is compared to the neutralisation with CO₂. The neutralised solid fraction is leached with sulfuric acid at different concentrations to dissolve major and minor elements and the metal extraction efficiency is correlated with the neutralisation conditions. The acid consumption is also evaluated.

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 presses and room temperature drying. 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 using wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). Chemical analysis of minor elements was performed after complete dissolution of the bauxite residue by alkali fusion and acid digestion in 3% HNO₃ solution, followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) analysis. 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. Thermo-gravimetric analysis (TGA, Netzsch STA 409) were carried out in a nitrogen atmosphere from room temperature to 1000 °C at a heating rate of 10 °C/min in order to identify phase transformation and thermal decompositions in the bauxite residue.

Neutralisation at ambient conditions of bauxite residue with CO₂ gas was performed in a three-neck flask reactor (400 mL) with continuous agitation (magnetic stirrer at 478 rpm). Within the reactor, solid particles were mixed with water at a liquid-to-solid ratio, *L/S*, of 5:1. CO₂ gas (99.9925%, Air Liquide) was introduced continuously at defined flow rate, which was controlled with a flow meter. A diffuser (PTFE, pore size of 10 µm) was used to spread out the gas into the formed slurry.

High-pressure neutralisation experiments were carried out in a titanium autoclave (Parr Company, series 4560) varying the partial pressure of CO₂ and temperature. Bauxite residue and Milli-Q water were mixed during a period of 5 minutes in a beaker at a *L/S* of 5:1 at ambient conditions. The slurry was poured into the titanium vessel (200 mL) and mounted in the autoclave. Nitrogen gas at a pressure of 5 bar was used to remove the excess of oxygen gas inside the reactor, so that potential oxidative reactions could be prevented.

Neutralisation of bauxite residue with HCl (37%, Fisher Scientific) was performed with a *L/S* ratio of 5:1 in sealed polyethylene bottles by constant agitation using a laboratory shaker (Gerhardt Laboshake) at 200 rpm and 25 °C. The slurries after neutralisation were filtered using filter paper (pore size 0.45 µm) and diluted with 2% HNO₃ for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis for major elements (e.g., Al, Fe, Ca, Na, Si, Ti).

Leaching of the non-neutralised and the neutralised bauxite residue was carried out with sulfuric acid (95-97%, Sigma-Aldrich) with a *L/S* ratio of 10:1. The experiments were performed in the same laboratory shaker at 200 rpm and 25 °C. The leach solution (pregnant leach solution, PLS) was filtered using a syringe filter (pore size of 0.45 µm) and diluted with 2% HNO₃ for ICP-OES analysis for major and minor (e.g., Sc, Y, La, Nd) elements. Lutetium was used as internal standard during the analysis. A synthetic solution with a pre-defined concentration was used as reference.

3. Results and discussion

3.1 Characterisation of the bauxite residue

The concentrations of major elements in the form of oxides in our Greek bauxite residue sample are given in Table 1. Iron(III) oxide is the major oxide in the bauxite residue followed by alumina, calcium oxide, silica, titanium oxide and sodium oxide. In Table 2, the concentrations of selected REEs are shown. The concentrations of Sc, Y, La and Nd are shown because their concentrations in bauxite residue are relatively high.

Table 1: Major chemical components in the bauxite residue.

Compound	wt%
Fe ₂ O ₃	46.7
Al ₂ O ₃	18.1
CaO	8.5
SiO ₂	7.3
TiO ₂	5.8
Na ₂ O	2.8
Loss on ignition	8.5

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

Element	Concentration, g/tonne
Sc	121 ± 10
Y	76 ± 10
La	114 ± 15
Nd	99 ± 7

Mineralogical analysis allowed the identification of several mineral phases, based on iron (hematite, goethite), aluminium (gibbsite, diasporite, bayerite), calcium (calcite, calcium silicates and calcium alumino-silicates), sodium (sodalite, cancrinite) and titanium (rutile). Approximately 95% of the mineral phases were quantified using the Rietveld method (see Table S1 and S2). Table 3 describes the normalised (to 100% total) mineralogical composition of the bauxite residue sample. The quantification of mineral phases was analysed by taking into account the chemical composition of major elements obtained by XRF analysis (Table 1) with an estimated deviation error of approximately 10%.

Table 3: Normalised mineralogical composition of the bauxite residue sample.

Phase	Chemical formula	wt%
Hematite	Fe_2O_3	36
Dicalcium-silicate (C_2S)	Ca_2SiO_4	12
Gibbsite	$\text{Al}(\text{OH})_3$	8
Hydrogrossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$	7
Diaspore	$\text{AlO}(\text{OH})$	7
Grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	5
Tricalcium-silicate (C_3S)	Ca_3SiO_5	5
Goethite	$\text{FeO}(\text{OH})$	5
Calcite	CaCO_3	4
Bayerite	$\alpha\text{-Al}(\text{OH})_3$	4
Sodalite	$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24}) \cdot x\text{NaOH} \cdot (8-2x)\text{H}_2\text{O}$	3
Calcium phyllo-dodeca-alumotetrasilicate	$\text{Al}_{12}\text{CaO}_{27}\text{Si}_4$	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

3.2 Neutralisation - leaching

The effect of neutralisation of bauxite residue with CO_2 gas on the acid consumption and the recovery of selected REEs from bauxite residue was evaluated in two consecutive experimental processes according to the diagram presented in Figure 1: (1) neutralisation of bauxite residue slurry with CO_2 gas, and (2) acidic leaching of the (non-) neutralised bauxite residue.

Figure 1: Flow sheet for neutralisation of bauxite residue, followed by metal recovery from neutralised bauxite residue by leaching with sulfuric acid.

3.3 Neutralisation of bauxite residue with water

Bauxite residue was washed with water to study the potential change in pH of bauxite residue with the removal of sodium hydroxide. The experiment was conducted in duplicate at a *L/S* ratio of 5:1. After a washing period of 24 h, the pH remained stable at 10.7, which corresponded to the original pH of our bauxite residue sample. This is due to the buffering activity of alkaline solids that are present in the sample (Gräfe et al., 2011). It was observed that about 8 wt% of the total sodium was removed from the solid matrix after washing, due to its chemical association to alumina-silicate compounds, such as sodalite and cancrinite (see Table 3). It has been reported that the solubility of alumino-silicates decreases with increasing presence of sodium carbonate (Zheng et al., 1998, 1997). However, there is a knowledge gap related to the solubility of silicate compounds remaining after the final separation stages of the Bayer process, so that it is difficult to assess the conditions at which such compounds become more or less soluble.

3.4 Neutralisation of bauxite residue with different gas flow rates

The studies were carried out in a reactor of 400 mL with gas flow rates of 0.008, 0.02, 0.1 and 0.25 L/min. The initial pH of the slurry, i.e. 10.7, decreased over a period of 2 hours with continuous gas blown through the reactor to an average value of 6.8 for all investigated flow rates (Figure 2). The most

remarkable changes were observed in the neutralisation rate, which was evaluated by considering the slope in the linear portion within the first 5 to 15 minutes of neutralisation on the corresponding curves in Figure 2. High gas flow rates lead to a high neutralisation rate due to a large amount of CO₂ injection (Figure 3), but not to an improvement of the amount of CO₂ sequestration due to the limit concentration of calcium. It has been reported earlier that CO₂ sequestration is enhanced by the precipitation of calcite, but is restricted by the calcium concentration in the bauxite residue (Han et al., 2017).

A threshold gas flow rate between 0.1 and 0.25 L/min was observed, above which a further increase in flow rate did not lead to an increase in neutralisation rate (the gas flow rate of 0.25 L/min is not shown in Figure 2 due to an overlap with the results for the gas flow rate of 0.1 L/min). In our study the maximum neutralisation rate was reached at a gas flow rate of 0.1 L/min.

Figure 2: Effect of CO₂ gas on the pH during the neutralisation of the bauxite residue sample (T : 25 °C, L/S : 5).

The neutralisation by CO₂ gas in water involves a number of chemical reactions. The first chemical reaction is the dissolution of CO_{2(g)} in water to form CO_{2(aq)} (equation 1), which reacts with water to form carbonic acid. The concentration of CO₂ in aqueous solution, i.e. CO_{2(aq)}, can be determined from Henry's law (equation 2).

$$[\text{CO}_{2(\text{aq})}] = K_{\text{CO}_2} (P_{\text{CO}_{2(\text{g})}}) \quad (2)$$

where K_{CO_2} represents Henry's law constant of CO_2 , equal to 3.38×10^{-2} (mol/L/atm) (Reddy and Balasubramanian, 2014), and $P_{\text{CO}_2(\text{g})}$ is the partial pressure (in atm) of CO_2 gas in the atmosphere. At ambient conditions, P_{CO_2} depends on the number of CO_2 molecules dissolved in water and, consequently, on the magnitude of the gas flow rate. Therefore, a high gas flow rate leads to a large dissolution of CO_2 molecules in water and, thus, to an increase in P_{CO_2} . The interaction between CO_2 and water leads to the formation of carbonic acid H_2CO_3 , which is a weak acid (equation 3). Dissolution of H_2CO_3 in water involves two dissociations. The first dissociation is related to the formation of the hydrogen carbonate (bicarbonate) ion, HCO_3^- (equation 4), while the second dissociation involves the dissociation of the hydrogen carbonate ion into the carbonate ion, CO_3^{2-} (equation 5). Both chemical reactions involve the release of H^+ ions into the solution, leading to a decrease in pH until equilibrium is reached. For instance, the final pH attained after 2 hours of neutralisation with CO_2 gas corresponds to the pH associated to the first chemical decomposition of the carbonic acid, i.e. the formation of the hydrogen carbonate ion, when the gas was introduced continuously into the reactor.

The pH of the neutralised sample was measured for 2 days after the end of the experiment (no CO_2 was blown inside the reactor, and the slurry was left at ambient conditions and in steady state). An increase of the pH to an average value of 9.3 was observed (Figure 2), due to the presence of unreacted sodalite and hydroxide compounds that buffer the bauxite residue (Cooling et al., 2002; Khaitan et al., 2009b). This rebound of pH has been already reported by other researchers (Han et al., 2017; Kirwan et al., 2013; Rai et al., 2012; Sahu et al., 2010). It is evident that in the absence of continuous CO_2 gas injection, the concentration of $\text{HCO}_3^-/\text{CO}_3^{2-}$ is limited and, consequently, alkaline anions in solution such as $\text{Al}(\text{OH})_4^-$ ($pK_{\text{a}} \sim 10.2$) and OH^- ($pK_{\text{w}} = 14$) (Gräfe et al., 2011) start buffering the pH of the slurry (Sahu et al., 2010).

In bauxite residue, alkalinity is mainly stored in compounds such as hydrogrossular and sodalite, which have a buffer capacity between pH 11 and 8 (Kirwan et al., 2013), respectively. Hence, at pH around 6.8, the decomposition of such compounds may take place with the partial dissolution of Na and Ca. The dissolution of the major elements Al, Fe, Ti and Si starts occurring at pH values below 6 (Borra et al., 2015b). According to Figure 3, about 10 to 12 wt% of the total sodium content was dissolved. However, as already was described in section 3.3, about 8 wt% of sodium is readily soluble in water, therefore only an additional 2 to 4 wt% of sodium reacts with the carbonic acid. During the carbonation process (dissolution of CO₂ gas in water), the carbonate and hydrogen carbonate ions may react with Na⁺ ions present in solution to form Na₂CO₃ and/or NaHCO₃ according to reactions 6 and 7. However, these two compounds have a relatively high solubility in water (30.7 and 8.7 g/100 g water at 25 °C, respectively). Most of the sodium remains in the solid matrix mainly associated to alumina-silicates compounds (see Table 3).

The carbonate and hydrogen carbonate ions may also react with Ca²⁺ ions according to reactions 8 and 9. CaCO₃ tends to precipitate due to its low solubility (1.4×10⁻³ g/100 g water at 25 °C). The solubility of CaHCO₃ is relatively high (solubility of CaHCO₃: 16.6×10⁻³ g/100 g water at 25 °C), causing the elements to remain in solution. However, the chemical association of calcium to silicate compounds limits the concentration of Ca²⁺ ions. Consequently, less than 5 wt% of Ca was dissolved during neutralisation (Figure 3).

Figure 3: Effect of gas flow rate on the dissolution of Na and Ca from the neutralised bauxite residue and CO₂ injected (BR: bauxite residue, T : 25 °C, L/S : 5, t : 2 h).

Neutralisation with a strong acid, such as HCl, may cause a substantial reduction of the material's alkalinity, depending on the acid concentration (Khaitan et al., 2009a). The addition of acid in a pH range between 6 and 7 involves the partial decomposition of silica compounds, but also of calcite. Hence, an increase of Na and Ca dissolution is expected. Figure 4 describes the effect of acid concentration on the pH and on Na and Ca dissolution in the bauxite residue sample. A higher dissolution of Na and Ca in comparison to neutralisation with carbonic acid (formed during the dissolution of CO₂ in water) was observed. However, it is necessary to highlight the significant difference in the corresponding cost associated to the use of mineral acids or CO₂ for neutralisation. The price of the acid may reach a value of up to 200 USD/tonne (www.sunsirs.com), while the use of CO₂ is a less expensive reagent, because it can be obtained from the gas emissions generated during the alumina production (Bayer process). In addition, the use of CO₂ for neutralisation may help to reduce the greenhouse effect due to its removal from the industrial flue gases.

Figure 4: Neutralisation of bauxite residue with mineral acid and Na and Ca dissolution at different acid concentration (HCl, T : 25 °C, L/S : 5, t : 24 h).

3.5 High pressure neutralisation

The effect of CO_2 partial pressure on the dissolution of sodium and calcium and on pH, during neutralisation of the bauxite residue, is shown in Figure 5. The increase of CO_2 partial pressure leads to an increase of sodium dissolution, and to a very small increase in the dissolution of calcium due to the relatively high solubility of $\text{CO}_{2(g)}$ in water (0.14 g CO_2 /100 g water at 25 °C). The pH of the slurry remained around 9.2. Figure 6 describes the effect of temperature during neutralisation of bauxite residue with 30 bar of CO_2 partial pressure. A significant increase in sodium dissolution was observed when the temperature increased. The concentration of calcium in solution decreased due to the precipitation of calcite when the temperature was increased. The solubility of CO_2 in water decreases with an increase in temperature at constant partial pressure of the CO_2 in the gas phase above the bulk liquid, but it does increase when its partial pressure above the solution increases and, consequently, the concentration of $\text{HCO}_3^-/\text{CO}_3^{2-}$ also increases. This relationship can be summarised by combining Le Châtelier's principle, i.e. the shift of the chemical equilibrium in the direction at which the pressure is released, and Henry's law, i.e. the increase in concentration of the gas in the liquid when the partial pressure increases (see equation 2). The effect of temperature on the solubility reduction of CO_2 becomes less significant when the CO_2 partial pressure is increased (Santos et al., 2013). The decrease

in alkalinity with the increase of temperature may be explained by the reduction of sodalite concentration (see Figure 8).

Figure 5: Dissolution of Na and Ca during neutralisation at different CO₂ partial pressures (T : 25 °C, L/S : 5, t : 2 h).

Figure 6: Dissolution of Na and Ca during neutralisation at different temperatures (P_{CO_2} : 30 bar, L/S : 5, t : 2 h)

The identification of phase transformation and thermal decomposition in the non-neutralised and neutralised bauxite residue was confirmed by thermo-gravimetric analysis (Figure 7). The mass loss between 270 and 600 °C is due to the loss of chemically bound water, mainly from goethite (between 292 and 355 °C) (Rizov, 2012), gibbsite (between 300 and 400 °C) and diasporite (between 400 and 600 °C) (Agatzini-Leonardou et al., 2008). The first endothermic peak on the differential thermogravimetry (DTG) curve describes the dehydration of gibbsite to form both boehmite and α -alumina, i.e. between 270 and 320 °C (Klopprogge et al., 2002). The dehydration peak of gibbsite is more intense in the highly

neutralised sample than in the non-neutralised one, presumably due to its chemical transformation into grossular when Ca and Na were dissolved (Whittington and Cardile, 1996), i.e. during the carbonation period. The second endothermic reaction is observed at 510 °C and it is attributed to the decomposition of diasporé (Atasoy, 2005). The mass loss between 600 and 800 °C was much more pronounced in the neutralised sample compared to the non-neutralised bauxite residue, due to the release of relatively more CO₂ from the neutralised sample as a consequence of the decomposition of CaCO₃ (Agatzini-Leonardou et al., 2008) formed during neutralisation.

Figure 7: TGA (left y-axis) and DTG (right y-axis) curves of the non-neutralised (BR) and neutralised (NBR) bauxite residue sample.

Figure 8 describes the change in composition of selected mineralogical phases. The composition of calcite, C₂S, cancrinite and sodalite are shown as their concentration significantly changed during neutralisation (BR = non-neutralised bauxite residue, NBR = neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HP NBR = high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPT NBR = high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5)....

Table S2). The calcite content increases when the CO_2 partial pressure and temperature increased. Nonetheless, the amount of CO_2 consumed during the formation of calcite at high pressure and temperature registered at only 1 wt%. Formation of calcite may be explained by the decomposition of C_2S , and also by the partial decomposition of cancrinite (Kirwan et al., 2013). However, strong neutralisation conditions (temperature and pressure) lead to an increase in the concentration of cancrinite as a consequence of sodalite decomposition (Barnes et al., 1999). Silicate compounds such as cancrinite and grossular became more stable in the neutralised samples rather than in the non-neutralised bauxite residue, due to the decrease of SiO_2 solubility with the increase of Na_2CO_3 concentration in the slurry (Zheng et al., 1998).

Figure 8: Change of composition in selected mineralogical phases. BR: non-neutralised bauxite residue, NBR: neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HPNBR: high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

3.6 Leaching of neutralised bauxite residue

Figure 9 shows the effect of acid concentration on the pH of the solution for both neutralised and non-neutralised bauxite residue. Evidently, the pH decreases and the acid consumption increases when the acid concentration is increased. However, neutralised samples achieved lower pH values compared to the non-neutralised material. Furthermore, the sample neutralised with high pressure and temperature registered the lowest pH values, even with the same acid consumption as for the non-neutralised samples. This is due to the lower pH of the sample after neutralisation with high pressure and

temperature. As it was already described in the previous section, during the neutralisation step, high CO_2 concentration enhances the reduction of the sample alkalinity as a consequence of sodalite decomposition. Figure 10 reports the pH values of the sample with and without neutralisation before acidic leaching.

Figure 9: Effect of acid concentration (H_2SO_4) on the pH in the non-neutralised and neutralised bauxite residue sample, and acid consumption (T : 25 °C, L/S : 10, t : 24 h). BR: non-neutralised bauxite residue, NBR: neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HPNBR: high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

Figure 10: Initial pH of the non-neutralised bauxite residue and the resulting pH of the bauxite residue after neutralisation. BR: non-neutralised bauxite residue, NBR: neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HPNBR: high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

The effect of acid concentration on the leaching of Al, Fe and Ti is shown in Figure 11. Neutralisation at ambient conditions did not result in an improvement of the extraction efficiencies. Indeed, the major

metal recoveries from the neutralised sample with high calcite and cancrinite concentration, i.e. samples neutralised with high CO₂ partial pressure, were the lowest with higher acid consumption compared to the non-neutralised sample. This is due to the lack of acid available for leaching, caused by the transformation of calcite into bassanite and the partial decomposition of silicate compounds. As it is shown in Figure 12, a further increase in the extraction of Al, Fe or Ti from the highly neutralised sample is limited by 50 wt% of Si dissolution, even upon further increasing the acid concentration. An increase in silica dissolution leads to a larger supersaturation of silicon, which is considered as the driving force for polymerisation, i.e. gel formation (Hamouda and Amiri, 2014; Tobler et al., 2009). Polymerisation of silica represents a common problem during leaching of silicate minerals (Abkhoshk et al., 2014; Shi et al., 2016; Zhang et al., 2016), which may be promoted by low pH values and high temperatures (Voßenkaul et al., 2016), resulting in problems of solid-liquid separation that increase the required acid consumption and affect the selective recovery of metals.

Figure 11: Effect of acid concentration on the extraction of (a) Al, (b) Fe and (c) Ti (H_2SO_4 , L/S : 10, T : 25 °C, t : 24 h). BR: non-neutralised bauxite residue, NBR: neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HPNBR: high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

Figure 12: Extraction behaviour of Al, Ti and Fe as function of Si dissolution after acidic leaching of bauxite residue sample neutralised at 150 °C and P_{CO_2} : 30bar (H_2SO_4 , L/S : 10, T : 25 °C, t : 24 h).

Figure 13 describes the XRD pattern of non-neutralised and neutralised bauxite residue samples after acidic leaching. The most notorious effect of silica gel polymerisation is observed in the large decrease of Al dissolution upon gibbsite precipitation. Cancrinite was not identified after leaching, presumably because it is totally decomposed by sulfuric acid, although some sodium alumino silicates compounds were recognised on both diffractograms.

Figure 13: XRD pattern of non-neutralised and neutralised bauxite residue sample after acidic leaching (1.6 N H_2SO_4). BR: non-neutralised bauxite residue, HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

Figure 14 shows the effect of acid concentrations on the leaching of selected REEs. Extraction of Sc, Y, La, and Nd are shown because their concentrations are relatively high in bauxite residue. The dissolution of Sc and Y increased with a decrease in pH and it reached a maximum when the acid concentration was 0.7 N. The lowest recoveries of Sc and La were achieved in the sample neutralised at high pressure and temperature. The leaching of Y and Nd was not affected by CO_2 neutralisation, due to their smaller ionic radii compared to Sc and La. However, the extraction of La and Nd could be enhanced by increasing the acid concentration.

Figure 14: Effect of acid concentration on extraction of selected REEs (H_2SO_4 , L/S : 10, T : 25 °C, t : 24 h). BR: non-neutralised bauxite residue, NBR: neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HPNBR: high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPTNBR: high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar, T : 150 °C, L/S : 5).

Figure 15 describes the extraction behaviour of Sc and Y from the highly neutralised sample as function of Al, Fe and Ti dissolution. Although Y recovery was not affected by the neutralisation (Figure 14), the extraction of both Sc and Y is limited by the dissolution of major metals. Up to 40 wt% of Sc and 60 wt% of Y is leached with negligible amount of Fe dissolved. Urbain and Sarkar (1927) were the first to report on the chemical association between Sc and Fe, and recently Borra et al. reported that up to 50% of Sc can be extracted from bauxite residue without bringing a significant dissolution of Fe into the solution (Borra et al., 2015b), which is confirmed by our results. A similar association trend as between Sc/Y and Fe seems to exist between Sc/Y and Ti, although much higher amounts of Ti (30 wt%) are dissolved at high levels of Sc and Y leaching. A different relation exists with Al: above 15 wt% of Al dissolved, Sc and Y leaching are independent of Al dissolution. No chemical associations of Sc and Y with major elements other than Fe have been reported so far in literature. In the association with Fe and Ti dissolution, the extent of Y leaching is 1.5 times higher than that of Sc leaching.

Figure 15: Extraction behaviour of (a) Sc and (b) Y as function of Al, Ti and Fe dissolution after acidic leaching of the bauxite residue sample neutralised at 150 °C and P_{CO_2} : 30bar (H_2SO_4 , L/S : 10, T : 25 °C, t : 24 h).

The extraction behaviour of La and Nd from the highly neutralised sample is shown in Figure 16 as function of Al, Fe and Ti dissolution. The correlation between the extraction of La or Nd and the dissolution of the major elements is less clear. Again, above a certain threshold of La or Nd dissolution (between 0 and 12 wt% in our results), no relation between La or Nd leaching exists with Al dissolution. A similar behaviour can be even suggested for Fe and Ti, where La and Nd leaching is independent from Fe and Ti dissolution from ca. 20 wt % extraction of La or Nd. However, the leaching of La and Nd is determined by the amount of free H^+ ions in solution, which are consumed during the dissolution of major elements and during the decomposition of silicate compounds (Abhilash et al., 2014).

Figure 16: Extraction behaviour of (a) La and (b) Nd as function of Al, Ti and Fe dissolution after acidic leaching of the bauxite residue sample neutralised at 150 °C and P_{CO_2} : 30bar (H_2SO_4 , L/S : 10, T : 25 °C, t : 24 h).

4. Conclusions

The two-step processing of bauxite residue via neutralisation and subsequent leaching establishes the effect of CO₂ gas as neutralisation reagent on the extraction efficiencies of metal recovery via acidic leaching. The minimum pH attained after neutralisation in our bauxite residue with CO₂ was 8.6. Further pH decrease is limited, because of the chemical association of sodium to the sparsely soluble silicate compounds. The increase of temperature leads to a strong decomposition of silicate minerals, which allows the reduction of alkalinity upon carbonation of sodium and calcium. However, the intensification of neutralisation at elevated temperatures and high CO₂ partial pressures leads to the formation of calcite and cancrinite, the latter upon decomposition of sodalite. Silicate compounds became more stable in the neutralised samples rather than in the non-neutralised bauxite residue, due to the decrease of SiO₂ solubility with a high sodium dissolution. The extraction of Al, Fe and Ti was reduced due to the insufficient availability of acid caused by acid consumption for the chemical transformation of calcite into bassanite and the polymerisation of amorphous silica. The recovery of Sc from highly neutralised bauxite residue is lower compared to that from the less neutralised, or even non-neutralised, one due to its chemical association with major elements. The recovery of La and Nd is determined by the acid concentration upon a limit recovery of major elements and high silica polymerisation.

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7. Supplementary material

Table S1: Full mineralogical composition analysis (wt%) of the bauxite residue samples.

Phase	Chemical formula	BR	NBR	HP NBR	HPT NBR
Hematite	Fe_2O_3	34	34	37	37
Dicalcium-silicate (C_2S)	Ca_2SiO_4	11	8	2	3
Gibbsite	$\text{Al}(\text{OH})_3$	8	9	5	3
Hydrogrossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$	7	7	9	6
Diaspore	$\text{AlO}(\text{OH})$	7	8	6	6
Grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	5	8	10	8
Tricalcium-silicate (C_3S)	Ca_3SiO_5	4	4	3	4
Goethite	$\text{FeO}(\text{OH})$	4	4	5	5
Calcite	CaCO_3	4	4	5	9
Bayerite	$\alpha\text{-Al}(\text{OH})_3$	4	3	3	3
Sodalite	$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24}) \cdot x\text{NaOH} \cdot (8-2x)\text{H}_2\text{O}$	3	2	1	1
Calcium phyllo-dodeca-alumotetrasilicate	$\text{Al}_{12}\text{CaO}_{27}\text{Si}_4$	2	2	3	2
Rutile	TiO_2	2	1	3	3
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	1	4	7
Total		95	96	95	96
Unidentified		5	4	5	4

BR = non-neutralised bauxite residue , NBR = neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5), HP NBR = high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPT NBR = high-pressure and high-temperature neutralised bauxite residue (P_{CO_2} : 30 bar , T : 150 °C, L/S : 5).....

Table S2: Normalised mineralogical composition (wt%) of the bauxite residue samples (cf. Table S1) .

Phase	Chemical formula	BR	NBR	HP NBR	HPT NBR
Hematite	Fe_2O_3	36	35	39	39
Dicalcium-silicate (C_2S)	Ca_2SiO_4	12	8	3	3
Gibbsite	$\text{Al}(\text{OH})_3$	8	9	5	3
Hydrogrossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$	7	7	9	6
Diaspore	$\text{AlO}(\text{OH})$	7	8	6	6
Grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	5	8	11	9
Tricalcium-silicate (C_3S)	Ca_3SiO_5	5	4	3	4
Goethite	$\text{FeO}(\text{OH})$	5	4	5	5
Calcite	CaCO_3	4	5	5	9
Bayerite	$\alpha\text{-Al}(\text{OH})_3$	4	3	3	3
Sodalite	$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24}) \cdot x\text{NaOH} \cdot (8-2x)\text{H}_2\text{O}$	3	2	1	1
Calcium phyllo-dodeca- alumotetrasilicate	$\text{Al}_{12}\text{CaO}_{27}\text{Si}_4$	2	2	3	2
Rutile	TiO_2	2	2	3	3
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	1	4	7
Total		100	100	100	100

BR = non-neutralised bauxite residue , NBR = neutralised bauxite residue at ambient conditions (q_{CO_2} : 0.25 L/min, T : 25 °C, L/S : 5),
 HP NBR = high-pressure neutralised bauxite residue (P_{CO_2} : 30 bar, T : 25 °C, L/S : 5), HPT NBR = high-pressure and high-temperature
 neutralised bauxite residue (P_{CO_2} : 30 bar , T : 150 °C, L/S : 5).....