



The potential for constructed wetland mechanisms to treat alkaline bauxite residue leachate: carbonation and precipitate characterisation

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Abstract

Leachates emanating from bauxite residue disposal areas are alkaline and require neutralisation prior to discharge. The use of passive technologies such as constructed wetlands has received increasing interest as possible treatments for alkaline leachates, including bauxite residues. Mechanisms proposed for wetland effectiveness have included calcite precipitation but it is not clear if such a pathway is feasible in the relatively low Ca residue leachates. Carbonation of Ca-spiked residue leachate treatments was conducted to observe rates of pH decrease and precipitate formation. For all treatments, carbonation effectively decreased pH to ca. 10.5 which remained stable following aeration. Decreases in Al content of 83–93% were also observed. Precipitates retrieved from carbonation experiments and from a constructed wetland trial were characterised using XRD, SEM, XPS and EDX. Calcium carbonates formed in Ca-spiked treatments and dawsonite precipitation occur in the absence of Ca. Rinsing of precipitates removes surface calcium indicating soluble forms adsorbed on precipitates. The results demonstrate that carbonation of bauxite residue leachate is an important component of passive treatments and neutralisation.

Keywords Alkaline drainage · Bauxite residue · Constructed wetlands · Neutralisation · Carbonation

Introduction

Bauxite residue is the waste by-product generated by the extraction of alumina from bauxite ore via the Bayer process. Globally, some 150 MT of bauxite residue are produced each year with an estimated stockpile of 3 billion tonnes (Evans 2016). These large volumes of bauxite residue are deposited in bauxite residue disposal areas (BRDAS) and can present

environmental risks, as bare areas are sensitive to erosion by wind and water, and can be regarded as a potential source of contamination (Zhu et al. 2018). Advances in the management of bauxite residue has increased the implementation of dry-stacking and the development of best practice techniques, such as mud farming, which increase dewatering of the mud making it easier to compact and consolidate the residue (Evans 2016; Gomes et al. 2017; Zhu et al. 2017).

Bauxite residue and associated leachate are inherently alkaline (pH 9–13) (Jones and Haynes 2011; Burke et al. 2013; Higgins et al. 2017; Kong et al. 2017a) resulting in challenges for its long-term management as the reserve alkalinity may maintain leachate pH of ca. 13 for several decades (Thornber et al. 1985). Thus, requirements for the management and treatment of such drainage waters may persist for many decades following closure of refinery and residue areas (Hua et al. 2015).

In the long term, conventional treatment methods, e.g. acid dosing, are likely to be expensive and energy intensive. Ideally, treatment of bauxite residues should best be conducted using a low-cost approach due to the vast amount of material present (Xue et al. 2018) and low-cost passive options such as a constructed wetland, offer attractive approaches for residue leachates (Hua et al. 2015; Higgins et al. 2017). The

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effectiveness of constructed wetlands for buffering alkalinity in steel slag leachates has been attributed to factors such as the presence of organic matter and macrophytes providing high specific surface area for precipitation, and biological processes such as microbial respiration producing appreciable concentrations of CO_2 in the rhizosphere (Mayes et al. 2006). More recently, the potential for constructed wetlands to treat alkaline bauxite residue leachates has received attention (Burke et al. 2013; Hua et al. 2015, 2018; Buckley et al. 2016; Higgins et al. 2016, 2017).

Alkaline bauxite residue leachates are characterised by high sodium content, and alkalinity removal through carbonation and other wetland mechanisms may not be as efficient as most Na compounds are highly soluble (Hua et al. 2015). Carbonation of bauxite residue slurries was found to be more effective where addition of Ca accelerated neutralisation (Han et al. 2017). Buckley et al. (2016) demonstrated the potential for wetland mechanisms, i.e. carbonation, water composition, organic content and soil absorption, to decrease pH of NaOH solutions to values of $\text{pH} < 9$. Adsorption of sodium carbonate onto calcite was suggested as a potential mechanism for decreasing alkalinity in calcium-spiked NaOH solutions but it is not clear if actual residue leachate will behave similarly, due to the more complex major ion matrix.

Based on the outcomes of work by Buckley et al. (2016) and plant growth trials conducted by Higgins et al. (2016), a field scale constructed wetland trial was initiated at Aughinish Alumina (Higgins et al. 2017). To simulate leachate quality anticipated from a closed BRDA, the wetland system received neat residue leachate ($\geq \text{pH} 13$) diluted with tap water to produce leachates of pH ca. 11 (Residue Solution 2007). This also resulted in increases in Ca content from 4.6 mg L^{-1} (neat leachate) to $20\text{--}60 \text{ mg L}^{-1}$ (wetland influent) (Higgins et al. 2017). While the potential for such a wetland to successfully buffer leachate pH to < 9 and remove contaminants was evidenced by Higgins et al. (2017), it was proposed that a key mechanism may be through the precipitation of CaCO_3 as suggested by Buckley et al. (2016) in NaOH solutions.

Mayes et al. (2006) also demonstrated calcite formation as pH reducing mechanism for steel slag discharges in wetland systems. However, the Ca content of leachates for bauxite residue from closed or legacy sites is uncertain with some projections expecting minimal Ca content from diluting waters (Buckley et al. 2016). On the other hand, high amounts of Ca are possible to result in leachates emanating from residue areas, as gypsum (CaSO_4) is commonly applied to bauxite residues as part of the revegetation process (e.g. Courtney et al. 2009; Courtney and Kirwan 2012; Zhu et al. 2017). Therefore, this study investigated the effects of carbonation on bauxite residue leachate containing different concentrations of Ca. Carbonation of residue leachate treatments was performed and changes in pH monitored. Precipitates formed were characterised to determine possible mechanisms for consuming leachate alkalinity within constructed wetlands.

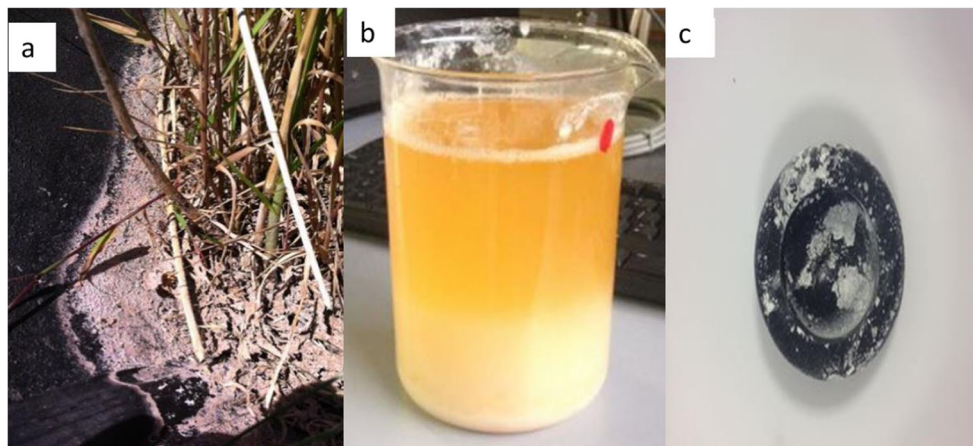
Materials and methods

Bauxite residue leachate ($\geq \text{pH} 13$) was obtained from the Aughinish Alumina bauxite residue disposal area (BRDA) in Ireland. Here, a constructed wetland has been in operation to assess the use of passive technologies for treating alkaline bauxite residue leachate (pH ca. 11). Neat leachate is diluted using a Programmable logic controller (PLC) system and pumped to the wetland at approximately $\text{pH} 10.5$ (Higgins et al. 2017). Operation of the trial identified precipitate forming on the plastic liner within the constructed wetland (Fig. 1a). Precipitates were retrieved and prepared in the laboratory for analysis.

Effect of carbonation on bauxite residue leachate pH

In order to determine the potential for constructed wetland mechanisms (carbonation) to decrease the pH of bauxite residue leachate, a series of treatments were used with varying Ca content. Ca content in treatments was chosen to reflect the

Fig. 1 Precipitates formed in a constructed wetland and b carbonated residue leachate from bulk beaker and c precipitated onto plastic washer



reported values for neat leachate, diluted leachates and leachates with added Ca likely to arise from rehabilitation procedures (Higgins et al. 2017). Residue leachate (\geq pH 13) collected from the BRDA was used to prepare a series treatments of varying Ca content (0, 100, 500, 1000 mg/L) by adding appropriate amounts of CaCl₂. Further, the Al content of leachate/Ca treatment samples was analysed before and after carbonation by ICP-OES. Each treatment of 1 L was covered and subjected to carbonation by bubbling a steady flow of CO₂ through the solution at 120 mL min⁻¹ (Table 1). A HDPE plastic washer was suspended in the solution to act as a site for precipitation, mimicking the plastic liner used in the constructed wetland where precipitate formation was observed (Fig. 1a).

During the carbonation experiments, the solution pH was continuously recorded using a data-logger every 2 min for 2 h. Once the pH of the solution had stabilised, the CO₂ flow was stopped and replaced by a flow of air ($>$ 120 mL min⁻¹) for 1 h, with pH recorded every 2 min. Precipitate formation was observed within the bulk leachate (Fig. 1b) and also on the plastic washer (Fig. 1c). A period of 30 min was observed to allow the precipitate to settle before being filtered using a Buchner funnel, “Whatman” filter paper (0.45 μ m pore size). Precipitates were air-dried for 24 h in preparation for further analysis.

Analysis of precipitates—SEM, XPS and XRD

Precipitates retrieved from the wetland and carbonation experiments were air-dried for 24 h. Precipitates formed in bulk solution were either analysed as described or were rinsed using deionised water (50–100 mL depending on the sample size) to remove soluble elements and analysed. This rinsing step was included as precipitation of Na₂CO₃ on calcite surfaces was reported by Buckley et al. (2016) following

carbonation of Ca-spiked NaOH solutions. This sodium carbonate precipitate is anticipated to be largely soluble. Precipitates were ground with a mortar and pestle and sieved to $<$ 20 μ m and placed in an oven at 105 °C for 5 h to eliminate moisture trapped in the samples. Samples of precipitates retrieved from bulk and plastic washer sources were then analysed by SEM (Hitachi FE SU-070) and XPS (Kratos AXIS 165 X-ray photoelectron spectrometer). XRD (Philips X’PERT PRO) analysis was conducted on bulk source precipitates only.

Results

Various Ca (CaCl₂) amounts were added to batches of 1-L samples of bauxite residue leachate, and these were tested for pH decrease by sparging with CO₂ gas. All residue leachate samples showed a significant drop in pH with ingassing of CO₂ (Fig. 2a) with the rate of decrease fastest for highest concentration of Ca (1000 mg/L), compared to the slowest rate for 0 mg/L. Rate of decrease was slower with decreasing Ca content, and regardless of Ca concentrations, all leachate solutions stabilised in the region of pH 10.07–10.4 for the duration of the carbonation experiment (up to 120 min).

Following carbonation, the CO₂ was replaced with air and measured pH remained stable in leachate treatments with pH remaining below 10.4 following 60 min of air bubbling (Fig. 2b).

The aluminium content in the leachate treatments before and after carbonation is shown in Table 2. Concentrations were in the region of 490 mg L⁻¹ decreasing in all treatments following carbonation by 83–93%.

Precipitate formation was observed for all treatments following carbonation and formed both as bulk within the beakers (Fig. 1b) and on the plastic washers within the beakers (Fig. 1c).

Table 1 Bauxite residue leachate treatments and locations of precipitate formation and treatment

| Treatment | Description | ID | Bulk precipitate | Precipitate from washer |
|-----------|---------------------------------------|----|------------------------|-------------------------|
| A | Leachate + Ca 1000 mg L ⁻¹ | A1 | precipitate not rinsed | |
| | Leachate + Ca 1000 mg L ⁻¹ | A2 | precipitate rinsed | |
| | | A3 | | not rinsed |
| B | Leachate + Ca 500 mg L ⁻¹ | B1 | precipitate not rinsed | |
| | Leachate + Ca 500 mg L ⁻¹ | B2 | precipitate rinsed | |
| | | B3 | | not rinsed |
| C | Leachate + Ca 100 mg L ⁻¹ | C1 | precipitate not rinsed | |
| | Leachate + Ca 100 mg L ⁻¹ | C2 | precipitate rinsed | |
| | | C3 | | not rinsed |
| D | Leachate + Ca 0 mg L ⁻¹ | D1 | precipitate not rinsed | |
| | Leachate + Ca 0 mg L ⁻¹ | D2 | precipitate rinsed | |
| | | D3 | | not rinsed |
| W | Precipitate from wetland | WP | precipitate not rinsed | |

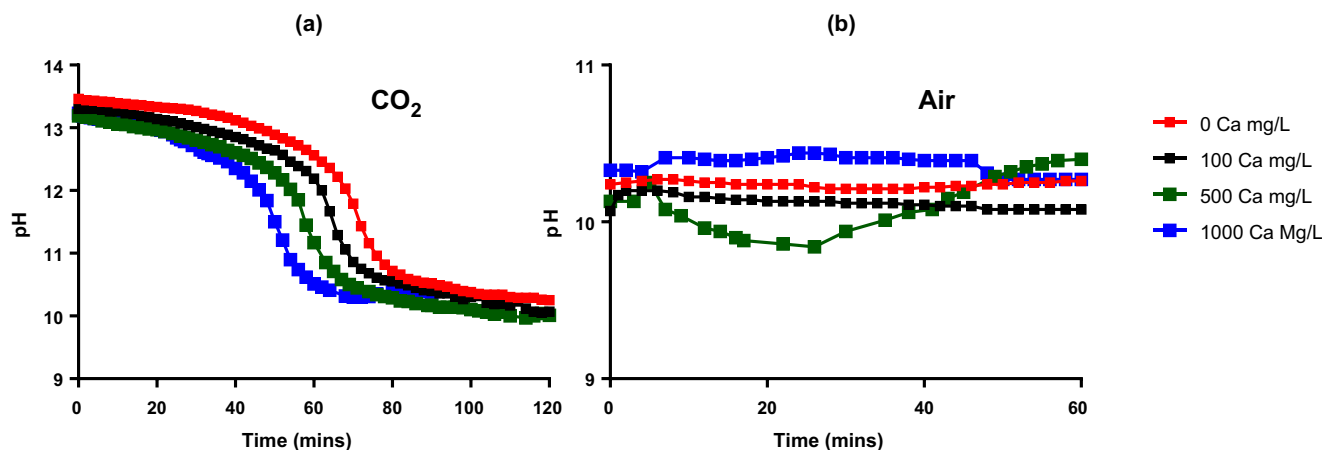


Fig. 2 Change in pH residue leachate of **a** varying Ca concentration over time with carbonation and **b** following air bubbling

XRD

XRD analysis of the precipitates from the constructed wetland and for Ca-treated leachates (bulk) was dominated by calcite (CaCO_3) (Table 3). Another calcium carbonate mineral (vaterite) was also found. For precipitates formed following carbonation of leachate without Ca, the dominant peak matched dawsonite ($\text{NaAlCO}_3(\text{OH})_2$). Washing/rinsing of the sodium aluminium carbonate hydroxide (dawsonite) precipitate removed traces of calcite, indicating surface adsorption of a soluble phase.

The aluminium hydroxide Bayerite ($\text{Al}(\text{OH})_3$) was also found in treatments containing high Ca content. Hydrocalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) was found only in the CW precipitate and halite in the rinsed high Ca content, possibly due to presence of Cl from CaCl_2 .

XPS analysis on the precipitates formed within the beaker (Fig. 1b) was elementally composed of calcium, carbon and oxygen but also significant quantities of aluminium and sodium (Table 4) were also observed. Rinsing of precipitates appreciably decreased amounts of Na for all precipitates except those from the 0 mg Ca L^{-1} treatment, indicating dominance of soluble phases.

Precipitates removed from the plastic washers (Fig. 1c) contained similar concentrations of Na compared to their bulk precipitate counterparts but did not contain Ca. These

precipitates also exhibited lower O and Al concentrations whilst C was much higher.

The precipitate formed on the CW liner had significant Ca content but did not contain Na. Higher levels of Si compared to other precipitates were also observed. This was most likely from the soil substrate within the wetland. All other precipitates were dominated by oxygen, sodium, aluminium and Ca. Washing of precipitates resulted in low Na content for each treatment, indicating that the Na component readily dissolves.

SEM characterisation of calcite precipitates from leachates containing Ca treatment showed that the minerals are of variable shapes and sizes (Supplementary data—Fig. 1a–1d). Each sub-region within the matrix had relatively uniform composition and four different chemically discrete phases were identified. For samples A–D, the Al content was low and Ca content high. This agrees with XRD analysis, e.g. low dawsonite and high calcite.

Negligible Ca content for the treatments D1 and D2 also confirms absence of calcite, as found by XRD. Samples retrieved from the plastic washer had markedly higher Na content than their corresponding bulk precipitate and much lower Ca content.

The XPS assessment of the precipitates was backed up by elemental analysis using SEM–EDX (Table 5). Precipitate from the 0 mg Ca L^{-1} (rinsed and unrinsed) had oxygen, sodium and aluminium as major elements with Si as a trace element. XPS assessment of precipitates was in agreement with EDX with no Ca found on the precipitates retrieved from the washers.

High-resolution XPS spectra showing the C 1s peak from each sample is shown in Supplementary Information Fig. 2. The contributions of different types of carbon species are clearly observed for the bulk precipitates formed within the beakers. The carbon peak, centred at a binding energy of 289.3 eV, is characteristic of carbonate species. The largest peak situated at 284.8.4 eV is due to the adsorption of organic carbon (C–C, C–H). This carbon is known as adventitious

Table 2 Al content in leachate/Ca treatments before and after carbonation

| Treatment | Al content (mg L^{-1}) Before carbonation | Al content (mg L^{-1}) After carbonation | % Decrease |
|-----------|---|--|---------------|
| A | 491 | 81 | 83 |
| B | 456 | 70 | 84 |
| C | 468 | 41 | 91 |
| D | 489 | 32 | 93 |

Table 3 XRD characterisation of precipitates

| | Sample | PHASES (in order of prominence in XRD patterns) | | | | |
|----|--------------------------------|---|--------------|-----------|---------------|--|
| A1 | 1000 mg L ⁻¹ | Calcite | Vaterite | Bayerite | | |
| A2 | 1000 mg L ⁻¹ rinsed | Calcite | Halite | Bayerite | Hydrocalumite | |
| B1 | 500 mg L ⁻¹ | Calcite | Dawsonite | | | |
| B2 | 500 mg L ⁻¹ rinsed | Calcite | Vaterite | Dawsonite | Bayerite | |
| C1 | 100 mg L ⁻¹ | Calcite | Dawsonite | | | |
| C2 | 100 mg L ⁻¹ rinsed | Calcite | Dawsonite | | | |
| D1 | 0 mg L ⁻¹ | Dawsonite | Calcite | | | |
| D2 | 0 mg L ⁻¹ rinsed | Dawsonite | | | | |
| WP | Wetland precipitate | Calcite | Hydrocalcite | Quartz | | |

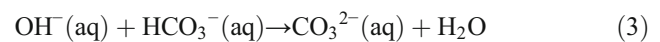
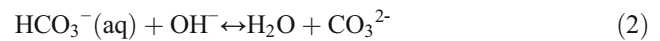
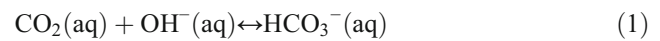
carbon and is commonly observed on all solid surfaces that have been exposed to the atmosphere. By contrast, samples precipitated onto the washer and removed from the constructed wetland are dominated by a single C peak at 284 eV.

Discussion

The role of carbonation in the rhizosphere of wetlands treating alkaline wastewaters has been reported for steel slag leachates (Mayes et al. 2006) and bauxite residue leachate (Higgins et al. 2017). Czop et al. (2011) studied the hydrogeochemistry of a lake inundated with bauxite residue and attributed the lower pH in surface waters to interaction with atmospheric CO₂ (Czop et al. 2011). Carbonation has also been previously shown to decrease pH in bauxite residue slurries, aged deposits (Kirwan et al. 2013; Rai et al. 2013; Han et al. 2017; Kong et al. 2017b) and in NaOH solutions (Buckley et al. 2016). Reduction in Al content from the current study of 83–95% is slightly less than those of Higgins et al. (2017) who observed a ca. 97% following wetland treatment.

Higgins et al. (2017) also reported reduction to pH 8 and the greater efficiencies are attributed to the mechanisms conferred by wetlands such as relatively high levels of CO₂ in wetland waters and substrates, formed as a product of both aerobic and anaerobic microbial respiration (Mayes et al. 2006). Additional wetland properties include high specific surface area for precipitation due to organic matter and macrophytes. Findings from the current study also indicate that that CO₂ ingress (carbonation) alone is not sufficient to produce optimal treatment of alkaline residue leachate.

Reduction in residue pH is by reaction of CO₂(g) with alkaline liquor species such as OH⁻(aq) and Al(OH)₄⁻(aq) (Eqs. 1, 2)



Limitations to achieving pH < 10 in carbonated bauxite residue was noted by Kirwan et al. (2013) and attributed to conversion of tricalcium aluminate (TCA) in the residue.

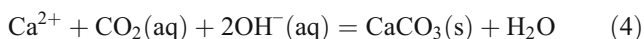
Table 4 XPS elemental quantification in atomic % for elements in wetland treatment precipitates

| Treatment and precipitate origin | O 1s | C 1s | 1s | Ca 2p | Na 1s | Si 2p | Al 2p | S 2p | Cl 2p | P 2s | Fe 2p | N 1s | Mg 1s |
|---|------|------|-----|-------|-------|-------|-------|------|-------|------|-------|------|-------|
| A1 1000 mg Ca L ⁻¹ Bulk precipitate not rinsed | 47.9 | 29.2 | 1.1 | 11.0 | 5.0 | | 5.1 | 0.2 | 0.5 | | | | |
| A2 1000 mg Ca L ⁻¹ Bulk precipitate not rinsed | 48.3 | 28.9 | 1.5 | 12.2 | 0.1 | 0.9 | 7.6 | 0.4 | | | | | |
| A3 1000 mg Ca L ⁻¹ Bulk precipitate rinsed | 23.2 | 68.8 | | | 5.7 | | 1.1 | 0.7 | 0.6 | | | | |
| B1 500 mg Ca L ⁻¹ Precipitate from washer | 52.0 | 23.6 | 1.0 | 3.8 | 4.7 | | 14.2 | | | 0.7 | | | |
| B2 500 mg Ca L ⁻¹ Bulk precipitate rinsed | 52.9 | 23.3 | 0.9 | 3.5 | 2.2 | | 17.1 | | | | | | |
| B3 500 mg Ca L ⁻¹ Precipitate from washer | 22.9 | 68.5 | | 0.6 | 5.1 | | 2.0 | | 0.6 | | | | |
| C1 100 mg Ca L ⁻¹ Bulk precipitate not rinsed | 53.8 | 22.7 | 0.4 | 0.9 | 6.3 | | 15.8 | | | | | | |
| C2 100 mg Ca L ⁻¹ Bulk precipitate rinsed | 54.3 | 21.4 | 0.9 | 1.5 | 4.1 | | 17.8 | | | | | | |
| C3 100 mg Ca L ⁻¹ Precipitate from washer | 27.2 | 64.6 | | | 6.2 | | 1.2 | 0.4 | 0.4 | | | | |
| D1 0 mg Ca L ⁻¹ Bulk precipitate not rinsed | 46.4 | 35.0 | 0.3 | | 5.2 | | 13.1 | | | | | | |
| D2 0 mg Ca L ⁻¹ Bulk precipitate rinsed | 55.1 | 20.8 | 0.5 | | 5.0 | | 18.6 | | | | | | |
| D3 0 mg Ca L ⁻¹ Precipitate from washer | 24.8 | 67.2 | | | 6.5 | | 1.0 | 0.4 | 0.2 | | | | |
| WP Wetland precipitate | 30.1 | 59.3 | | 3.5 | | 1.0 | 2.7 | 0.4 | | | 0.3 | 2.5 | 0.2 |

Table 5 Summary data of EDX (SEM)

| Treatment and precipitate origin | O | Na | Mg | Al | Si | Ca |
|----------------------------------|------|------|-----|------|------|------|
| A1 | 57.6 | 12.2 | | 20.2 | 0.8 | 41.9 |
| A2 | 63.7 | 0.9 | | 7.4 | 0.6 | 59.3 |
| A3 | 58.2 | 32.8 | | 22.3 | 5.4 | 2.9 |
| B1 | 60.5 | 9.5 | | 16.1 | 0.5 | 39.4 |
| B2 | 62.3 | 4.7 | | 22.8 | 1.1 | 31.7 |
| B3 | 48.4 | 34.1 | | 16.2 | 0.2 | 1.5 |
| C1 | 60.9 | 18.9 | | 43.2 | 1.5 | 6.0 |
| C2 | 67.3 | 10.7 | | 45.3 | 1.3 | 11.6 |
| C3 | 52.6 | 44.0 | | 28.4 | 0.6 | 2.1 |
| D1 | 59.8 | 22.0 | | 45.9 | 1.8 | 0.3 |
| D2 | 60.9 | 13.6 | | 52.6 | 2.6 | 0.3 |
| D3 | 46.3 | 67.7 | | 6.7 | | |
| WP | 66.1 | | 4.4 | 6.3 | 14.2 | 29.2 |

Han et al. (2017) examined additions of Ca to address this and achieved pH of less than 9 with carbonation. For the current study, the faster drop in pH with increasing Ca content is in agreement with Han et al. (2017) who reported its effectiveness in decreasing alkalinity and leading to formation of calcite (4).

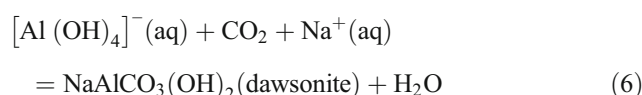
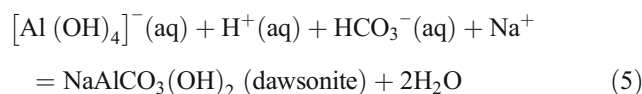


In the cases of both Kirwan et al. and Han et al., pH values achieved following carbonation were much lower than for the current study, but conversely, we did not find a pH rebound. These findings indicate formation of stable precipitates consuming alkalinity, namely calcite but also dawsonite for treatments without Ca additions and there was no evidence of alkaline producing phase TCA. Hellevang et al. (2005) suggested that dissolution of dawsonite may occur once there is a drop in CO₂ partial pressure but there was no evidence of this in the relatively short time frame observed in the current study. Stability of the alkaline consuming mechanism with carbonation can be supported by the long-term effect observed for the constructed wetland treating leachate (Higgins et al. 2017) but wetland substrate and vegetation contribute to this removal efficiency. With the evidence from Gomes et al. (2017) on the effects of atmospheric carbonation from using cascades for decreasing pH in alkaline waters, this would indicate the potential for passive treatment technologies in the treatment of bauxite residue leachates.

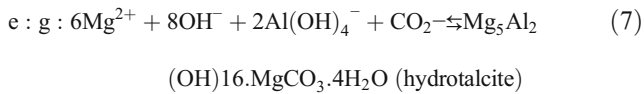
Formation of calcium carbonates (calcite) following carbonation of Ca-spiked bauxite residue slurries (Han et al. 2016) and NaOH solutions (Buckley et al. 2016) has been reported. Other calcium carbonates, such as aragonite, result from neutralisation of bauxite residue with seawater (Couperthwaite et al. 2014). Buckley et al.

(2016) also suggested that calcite acted as nuclei for further adsorption of sodium carbonates in carbonated NaOH solutions. Calcite peaks dominated in the current study with the exception of the 0 mg Ca L⁻¹ where dawsonite formed. Secondary carbonates, such as vaterite, were also identified in the treatments with higher Ca content. Although no Ca was added to treatments D1 and D2, calcite was observed and may be due to the small amount of Ca content present in bauxite residue leachate (ca. 4.6 mg L⁻¹) (Higgins et al. 2017) which suggest that calcite formation may play a role in carbonation of residue leachate, even where dilution with other waters is minimal. Traces of Ca were also found by EDX analysis but calcite peaks disappeared following rinsing. This implies that the calcite was quite fine grained and it dissolved quickly in the rinse solution.

All samples except the 1000 mg Ca L⁻¹ displayed dawsonite peaks. Several authors claim that dawsonite precipitation is observed when bauxite residue is carbonated (Jones et al. 2006; Clark et al. 2015; Xue et al. 2016) but this has not previously been reported for residue leachate. Using bauxite residue diluted at 5:1 rate, Jones et al. (2006) reported that dawsonite formation is a major control on alkalinity for CO₂-neutralised red muds by either of the reactions (5, 6). Declercq et al. (2008) also reported dawsonite formation following CO₂ injecting of Na-rich brines. It is suggested that dawsonite formation is through CO₂ and HCO₃⁻ reaction with aluminosilicates and under elevated CO₂ conditions (Hellevang et al. 2005; Johnston et al. 2010).



Seawater neutralisation of bauxite residue slurry utilises the soluble Ca²⁺ and Mg²⁺ content of the water to convert alkaline species to form products such as hydrotalcite (Kirwan et al. 2013; Couperthwaite et al. 2014) and mixing of leachate with acidic saline waters has also yielded the product (Santini and Fey 2012). Although not reported for freshwater systems, the precipitate found within the constructed wetland contained hydrotalcite and had the highest Mg content of all precipitates. Magnesium content in the soil and influent for the constructed wetland treating residue leachate was approximately 5000 mg kg⁻¹ and 10 mg/L with, respectively (Higgins et al. 2017), allowing for Mg supply to hydrotalcite formation. Further, increases in oxide-bound magnesium within the soil were recorded and the mechanism for removal in carbonate precipitates is likely.



The wetland precipitate also contained quartz as well as higher values for Si. The occurrence of quartz is likely to be from soil entrainment. Carbonation of bauxite residue can produce soluble salts (Wang et al. 2015) and Buckley et al. (2015) reported evidence of sodium carbonates on calcite precipitate following carbonation of Ca-spiked NaOH solutions. In the current study, rinsing of calcite precipitates resulted in decreased Na content (Tables 4 and 5) indicating that Na removal may be due to formation of readily soluble Na-carbonates. Precipitates recovered from the plastic washers did not display Ca peaks and were similar in composition to unrinsed precipitates at 1000 mg L^{-1} . Buckley et al. (2015) suggested the possibility of sodium carbonates forming on calcite following carbonation and the plastic washer may similarly act as a site of precipitation. Further removal and adsorption of sodium, and other leachate contaminants will be increased on contact with the constructed wetland soil and vegetation. Wetland systems confer high specific surface areas for precipitation (Mayes et al. 2006) and Higgins et al. (2017) reported significant increases in both soluble and carbonate bound Na, and in carbonate bound Ca in soil samples retrieved from a constructed wetland treating bauxite residue leachate.

Conversion of alkaline phases to carbonates is an important component of constructed wetland treatment of bauxite residue leachates. The reactions are slower in the absence of Ca (Fig. 2a) and as evidenced by Buckley et al. (2015). Thus, composition of influent waters will influence the degree of alkaline buffering in wetlands treating residue leachates. Soil properties will also contribute to contaminant removal efficiency and wetland longevity. The current study confirms the role of carbonation within constructed wetlands in the treatment of alkaline bauxite residue leachate, but as reported by Buckley et al. (2015) and Han et al. (2017), the efficiencies may be improved through additions of Ca and/or other cations. Cascade systems such as those reported by Gomes et al. (2017) could be employed as a preliminary step in residue leachate treatment producing influents of circa pH 10.5 thereby reducing alkalinity loading to wetlands and contributing to longevity of wetland systems. Results demonstrate the potential for constructed wetland mechanisms to buffer alkaline bauxite residue leachate in low Ca conditions.

Conclusions

The data provided here demonstrates that carbonation and calcite precipitation play a positive role in passive treatment of bauxite residue leachates. Calcite formation is evident in low Ca waters, but where Ca is absent, the precipitation of

dawsonite occurs. Addition of Ca to residue leachate may be considered prior to discharge to passive treatment systems as this improves both the rate pH reduction observed and the volumes of calcite available to buffer pH values over the longer term. Leachate pH reduction via carbonation is viewed as a vital step prior to discharge into constructed wetland systems.

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References

- Buckley R, Curtin T, Courtney R (2016) The potential for constructed wetlands to treat alkaline bauxite residue leachate: laboratory investigations. *Environ Sci Pollut Res* 23:14115–14122
- Burke IT, Peacock CL, Lockwood CL, Stewart DI, Mortimer RJ, Ward MB, Renforth P, Gruiz K, Mayes WM (2013) Behavior of aluminum, arsenic, and vanadium during the neutralization of red mud leachate by HCl, gypsum, or seawater. *Environ Sci Technol* 47:6527–6535
- Clark MW, Johnston M, Reichelt-Brushett AJ (2015) Comparison of several different neutralisations to a bauxite refinery residue: potential effectiveness environmental ameliorants. *Appl Geochem* 56:1–10
- Couperthwaite SJ, Johnstone DW, Mullett ME, Taylor KJ, Millar GJ (2014) Minimization of bauxite residue neutralization products using nanofiltered seawater. *Ind Eng Chem Res* 53:3787–3794
- Courtney R, Kirwan L (2012) Gypsum amendment of alkaline bauxite residue—plant available aluminium and implications for grassland restoration. *Ecol Eng* 42:279–282
- Courtney RG, Jordan SN, Harrington T (2009) Physico-chemical changes in bauxite residue following application of spent mushroom compost and gypsum. *Land Deg Dev* 20:572–581
- Czop M, Motyka J, Sracek O, Szuwarzyński M (2011) Geochemistry of the hyperalkaline Gorka pit Lake (pH > 13) in the Chrzanow region, southern Poland. *Water Air Soil Pollut* 214:423–434
- Declercq J, Oelkers EH, Aagaard P (2008) Experimental determination of the dawsonite dissolution/precipitation rates and their application to CO₂ sequestration. *Geophys Res Abstr* 10:08482
- Evans K (2016) The history, challenges, and new developments in the management and use of bauxite residue. *J Sustain Metall* 2:316–331
- Gomes HI, Rogerson M, Burke IT, Stewart DI, Mayes WM (2017) Hydraulic and biotic impacts on neutralisation of high-pH waters. *Sci Tot Environ* 601:1271–1279
- Han YS, Ji S, Lee PK, Oh C (2017) Bauxite residue neutralization with simultaneous mineral carbonation using atmospheric CO₂. *J Hazard Mater* 326:87–93
- Hellevang H, Aagaard P, Oelkers EH, Kvamme B (2005) Can dawsonite permanently trap CO₂? *Environ Sci Technol* 39:8281–8287
- Higgins D, Curtin T, Pawlett M, Courtney R (2016) The potential for constructed wetlands to treat alkaline bauxite-residue leachate: *Phragmites australis* growth. *Environ Sci Pollut Res* 23:24305–24315
- Higgins D, Curtin T, Courtney R (2017) Effectiveness of a constructed wetland for treating alkaline bauxite residue leachate: a 1-year field study. *Environ Sci Pollut Res* 9:8516–8524
- Hua T, Haynes RJ, Zhou YF, Boulemant A, Chandrawana I (2015) Potential for use of industrial waste materials as filter media for removal of Al, Mo, as, V and Ga from alkaline drainage in constructed wetlands—adsorption studies. *Water Res* 71:32–41

- Hua T, Haynes RJ, Zhou YF (2018) Potential use of two filter media in constructed wetlands for simultaneous removal of as, V and Mo from alkaline wastewater - Batch adsorption and column studies. *J Environ Manage* 218:190–199
- Johnston M, Clark MW, McMahon P, Ward N (2010) Alkalinity conversion of bauxite refinery residues by neutralization. *J Hazard Mater* 182:710–715
- Jones BE, Haynes RJ (2011) Bauxite processing residue: a critical review of its formation, properties, storage, and revegetation. *Crit Rev Env Sci Technol* 41:271–315
- Jones G, Joshi G, Clark M, McConchie D (2006) Carbon capture and the aluminium industry: preliminary studies. *Environ Chem* 3:297–303
- Kirwan LJ, Hartshorn A, McMonagle JB, Fleming L, Funnell D (2013) Chemistry of bauxite residue neutralisation and aspects to implementation. *Int J Miner Process* 119:40–50
- Kong XF, Li M, Xue SG, Hartley W, Chen CR, Wu C, Li XF, Li YW (2017a) Acid transformation of bauxite residue: conversion of its alkaline characteristics. *J Hazard Mater* 324:382–390
- Kong XF, Guo Y, Xue SG, Hartley W, Ye YZ, Cheng QY (2017b) Natural evolution of alkaline characteristics in bauxite residue. *J Clean Prod* 143:224–230
- Mayes WM, Younger PL, Aumo J (2006) Buffering of alkaline steel slag leachate across a natural wetland. *Environ Sci Technol* 40:1237–1243
- Rai SB, Wasewar KL, Mishra RS, Mahindran P, Chaddha MJ, Mukhopadhyay J, Yoo C (2013) Sequestration of carbon dioxide in red mud. *Desalin Water Treat* 51:2185–2192
- Residue solutions (2007) Residue management sustainability review Alughinish alumina limited. Residue solutions Pty Ltd., Brisbane
- Santini TC, Fey MV (2012) Synthesis of hydrotalcite by neutralization of bauxite residue mud leachate with acidic saline drainage water. *Appl Clay Sci* 55:94–99
- Thomber MR, Taplin JH, Hughes CA (1985) A mineralogical and chemical investigation of various Alcoa red mud waste materials, restricted investigation report no. 1592R. CSIRO division of mineralogy and geochemistry, Perth
- Wang X, Zhang Y, Lv F, An Q, Lu R, Hu P, Jiang S (2015) Removal of alkali in the red mud by SO₂ and simulated flue gas under mild conditions. *Environ Prog Sustain Energy* 34:81–87
- Xue S, Kong X, Zhu F, Hartley W, Li X, Li Y (2016) Proposal for management and alkalinity transformation of bauxite residue in China. *Environ Sci Pollut Res* 23:12822–12834
- Xue SG, Li M, Jiang J, Millar GJ, Li CX, Kong XF (2018) Phosphogypsum stabilization of bauxite residue: conversion of its alkaline characteristics. *J Environ Sci China*. <https://doi.org/10.1016/j.jes.2018.05.016>
- Zhu F, Hou JT, Xue SG, Wu C, Wang QL, Hartley W (2017) Vermicompost and gypsum amendments improve aggregate formation in bauxite residue. *Land Degrad Dev* 28:2109–2120
- Zhu F, Cheng QY, Xue SG, Li CX, Hartley W, Wu C, Tian T (2018) Influence of natural regeneration on fractal features of residue microaggregates in bauxite residue disposal areas. *Land Degrad Dev* 29:138–149