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The potential for constructed wetlands mechanisms to treat alkaline bauxite residue leachate: carbonation and precipitate characterization

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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 characterized using XRD, SEM, XPS and EDX. Calcium carbonates formed in Ca spiked treatments and dawsonite precipitation occurs 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, **neutralization, carbonation**

1.0 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 is 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 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 neutralization (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 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 wetlands 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 (≥ 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 -60 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 characterized to determine possible mechanisms for consuming leachate alkalinity within constructed wetlands.

2.0 Materials and Methods

Bauxite residue leachate (≥ 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 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.

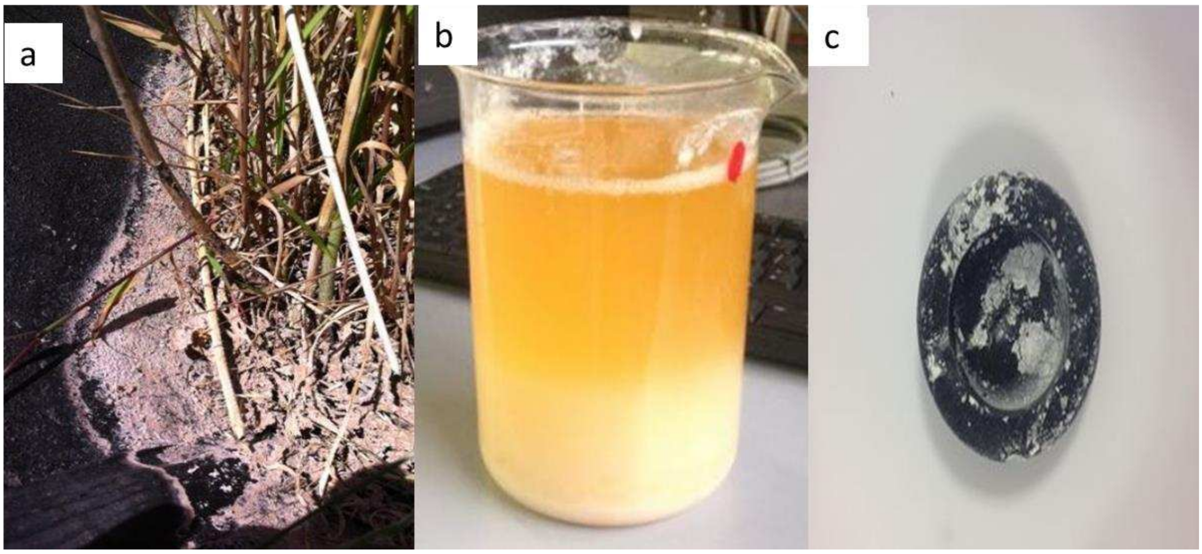

Figure 1. Precipitates formed in (a) constructed wetland and (b) carbonated residues leachate from bulk beaker and (c) precipitated onto plastic washer.

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 reported values for neat leachate, diluted leachates and leachates with added Ca likely to arise from rehabilitation procedures (Higgins et al. 2017). Residue leachate (≥ 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 $CaCl_2$. Further, the Al content of leachate/ Ca treatment samples were 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 CO_2 through the solution at 120 mL min^{-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 (Figure 1a).

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	

During the carbonation experiments, the solution pH was continuously recorded using a data-logger every two minutes for two hours. Once the pH of the solution had stabilised, the CO_2 flow was stopped and replaced by a flow of air (> 120 mL min^{-1}) for one hour, with pH recorded every 2 minutes. Precipitate formation was observed within the bulk leachate (Figure 1b) and also on the plastic washer (Figure 1c). A period of 30 minutes was observed to allow the precipitate to settle before being filtered using a Buchner funnel, “Whatman” filter paper (0.45 µm pore size). Precipitates were air dried for 24 hours 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 hours. 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 Na_2CO_3 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 µm and placed in an oven at 105°C for 5 hours 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.

3.0 Results

Various Ca ($CaCl_2$) amounts were added to batches of 1 L samples of bauxite residue leachate and these were tested for pH decrease by sparging with CO_2 gas. All residue leachate samples showed a significant drop in pH with ingassing of CO_2 (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 CO_2 was replaced with air and measured pH remained stable in leachate treatments with pH remaining below 10.4 following 60 mins of air bubbling (Figure 2b).

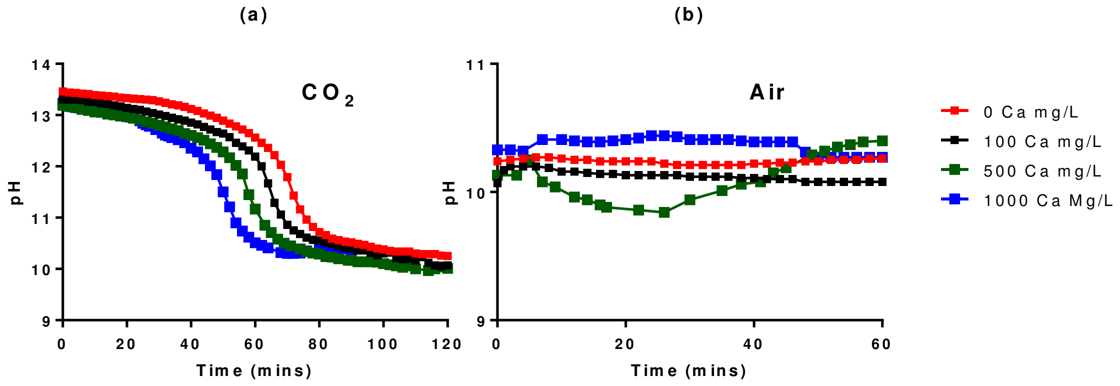

Figure 2. **Change in pH residue leachate of (a) varying Ca concentration over time with carbonation and (b) following air bubbling**

The aluminium content in the leachate treatments before and after carbonation are shown in Table 2. Concentrations were in the region of 490 mg L^{-1} decreasing in all treatments following carbonation by 83-93%.

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

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

XRD

XRD analysis of the precipitates from the constructed wetland and for Ca treated leachates (bulk) were 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 ($NaAlCO_3(OH)_2$). 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 ($Al(OH)_3$) was also found in treatments containing high Ca content. Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) was found only in the CW precipitate and halite in the rinsed high Ca content, possibly due to presence of Cl from $CaCl_2$.

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	Hydrotalcite	Quartz	

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

XPS analysis on the precipitates formed within the beaker (Fig 1b) were 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 (Figure 1 c) 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.

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

SEM characterization of calcite precipitates from leachates containing Ca treatment showed that the minerals are of variable shapes and sizes (Supplementary data - Figure 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 Figure 2. The contributions of different types of carbon species is 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 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.

4.0 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 CO_2 (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% are 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 CO_2 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 CO_2 ingress (carbonation) alone is not sufficient to produce optimal treatment of alkaline residue leachate.

Reduction in residue pH is by reaction of $CO_2(g)$ with alkaline liquor species such as $OH^{-}(aq)$ and $Al(OH)_4^{-}(aq)$ (Eqs. 1, 2)

$$CO_2(aq) + OH^{-}(aq) \leftrightarrow HCO_3^{-}(aq) \qquad (1)$$

$$HCO_3^{-}(aq) + OH^{-} \leftrightarrow H_2O + CO_3^{2-} \qquad (2)$$

$$OH^{-}(aq) + HCO_3^{-}(aq) \rightarrow CO_3^{2-}(aq) + H_2O \qquad (3)$$

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. 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).

$$Ca^{2+} + CO_2(aq) + 2OH^{-}(aq) = CaCO_3(s) + H_2O \qquad (4)$$

In the cases of both Kirwan et al. and Han et al., pHs 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 CO_2 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 contributes 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. 2017) and NaOH solutions (Buckley et al. 2017) have been reported. Other calcium carbonates, such as aragonite, result from neutralization of bauxite residue with seawater (Couperthwaite et al. 2014). Buckley et al. (2015) 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 treatment D1 & 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 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 CO_2 -neutralized red muds by either of the reactions (5, 6). Declercq et al. (2008) also reported dawsonite formation following CO_2 injecting of Na-rich brines. It is suggested that dawsonite formation is through CO_2 and HCO_3^- reaction with aluminosilicates and under elevated CO_2 conditions (Hellevang et al. 2005; Johnston et al. 2010).

$$[Al(OH)_4]^- (aq) + H^+ (aq) + HCO_3^- (aq) + Na^+ = NaAlCO_3(OH)_2 \text{ (dawsonite)} + 2H_2O \qquad (5)$$

$$[Al(OH)_4]^- (aq) + CO_2 + Na^+ (aq) = NaAlCO_3(OH)_2 \text{ (dawsonite)} + H_2O \qquad (6)$$

Seawater neutralisation of bauxite residue slurry utilises the soluble Ca^{2+} and Mg^{2+} 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.

e:g: $6Mg^{2+} + 8OH^{-} + 2Al(OH)_4^{-} + CO_2{-} \leftrightarrows Mg_5\ Al_2\ (OH)16.MgCO\ _3.4H_2O$ (hydrotalcite) (7)

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 (Figure 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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