

The potential for constructed wetlands to treat alkaline bauxite residue leachate: laboratory investigations

Buckley R.^{1,2} · Curtin T.^{1,2} · Courtney R.^{2,3}

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Abstract High alkalinity (pH > 12) of bauxite residue leachates presents challenges for the long-term storage and managements of the residue. Whilst the use of constructed wetlands is gaining in interest for its use in the treatment of alkaline waters, thus far, there is limited evidence of its suitability for treating NaOH dominated bauxite residue leachate. A series of batch trials were conducted to investigate the potential for constructed wetland conferred mechanisms (dilution water quality, contact with CO₂, and substrate type) for treating NaOH solutions to levels permissible for discharge ($p < 9$). Results demonstrate that significant reductions in solution pH can be achieved depending on the diluting water quality. Levels achieved may not always be suitable for direct discharge (i.e. pH ≤ 9), but further reductions occur with carbonation and soil contact. The extent of pH decrease and the timeframe required are influenced by soil quality, with greater efficiency observed in soils with higher organic matter content. Decrease in solution pH to discharge permit values are possible through a combination of the mechanisms occurring

in a constructed wetland. Formation of a calcite precipitate was observed in some treatments and further characterisation by XRD and XPS suggested surface coating with Na₂CO₃. It is therefore suggested that, under suitable conditions, constructed wetland technology can reduce leachate pH to <9 through mechanisms supporting the precipitation of sodium carbonate from solution. Further trials should investigate the activity under biological conditions representative of an operating constructed wetland.

Keywords Hyperalkaline · Passive treatment · Bauxite residue · Mine closure · Red mud

Introduction

Bauxite residue is the waste by-product generated by the extraction of alumina from bauxite ore via the Bayer process. Approximately 1–2 tonnes of residue are generated for every tonne of alumina produced, with an estimated global inventory of three billion tonnes that is growing at around 120 million tonnes per annum (Jones and Haynes 2011; Power et al. 2011).

The high alkalinity of bauxite residue presents challenging conditions for the long-term environmental management of BRDAs. Alkalinity exists in solid and solution as (1) entrained liquor (sodium hydroxide, sodium aluminate, and sodium carbonate), (2) calcium compounds, such as hydrocalumite, tricalcium aluminate, and lime, and (3) sodalite. Consequently, reserve alkalinity may maintain leachate pH of ca. 13 for several decades (Thorner et al. 1985) with potential leakage to surrounding environment representing a high environmental risk (Wang et al. 2015).

Even with novel techniques for the management of bauxite residue (e.g. carbonation and seawater neutralisation) it is acknowledged that further treatment of leachate is required

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✉ Courtney R.
ronan.courtney@ul.ie

¹ Department of Chemistry and Environmental Science, University of Limerick, Limerick, Ireland

² Materials and Surface Science Institute (MSSI), University of Limerick, Limerick, Ireland

³ Department of Life Sciences, University of Limerick, Limerick, Ireland

before it is suitable for direct discharge (Cooling 2007; Menzies et al. 2004). As a result, drainage from storage areas can pose an environmental risk and must be managed and drainage may need to be treated for many decades after closure (Hua et al. 2015).

Treatment of drainage waters by conventional methods is likely to be expensive, especially if it is to be continued for many decades after closure. A low-cost, passive option, such as a constructed wetland, is an attractive alternative (Hua et al. 2015). The application of constructed wetlands as elements of passive remediation systems for low pH sites is well documented and more recently the potential for wetland ecosystems and constructed wetlands to buffer high pH effluents has received attention (Mayes et al. 2006).

Observations from volunteer wetlands, i.e. naturally occurring wetlands, have shown the potential for wetlands to buffer highly alkaline steel-slag influent water and represent a potential low-cost, environmentally sensitive approach to remediation of highly alkaline drainage (Mayes et al. 2006). The buffering properties of wetland soils are widely reported (e.g. Dunbabin and Bowmer 1992; Mayes et al. 2009), with alkaline influent waters buffered by a combination of: (1) high partial pressures of carbon dioxide ($p\text{CO}_2$) in wetland waters and substrates (e.g. Boyer and Wheeler 1989), arising from microbial respiration, which depress pH and can also accelerate rates of calcium carbonate (CaCO_3) precipitation, (2) cation exchange, and (3) the release of organic acids (e.g. Ross 1996; Mayes et al. 2009). Mechanisms underlying the functioning of these systems such as the choice of substrate, plant species, flow structure, and rates amongst others may be crucial to overall effectiveness (Kadlec and Wallace 2008). The specific mechanisms in constructed wetland technology for the treatment of alkaline leachates are understood only in broad terms (Mayes et al. 2006), and currently there is limited evidence of constructed wetland or other passive technology for the treatment of NaOH-derived alkaline bauxite residue leachates.

The aim of this study is to investigate the possibility of using a constructed wetland approach for reducing the pH of leachate arising from bauxite residue disposal areas (BRDAs). Depending on residue management techniques, leachate exhibits a pH of ~11–13 and the desired target is $\text{pH} \leq 9$ which is the permissible discharge value issued by regulators (EPA 2007). A constructed wetland was created on the Aughinish BRDA in Ireland with a view to testing the concept of wetland technology for treating bauxite residue leachate (Clune et al. 2015). A series of complementary batch trials were conducted to determine the effects of a number of parameters on wetland efficiency.

The role of surface diluting waters (runoff) and the properties conferred by constructed wetlands (e.g. CO_2 and organic/soil sites of activity) were evaluated for effectiveness in decreasing leachate pH. Experimentation was conducted to

determine the effects of different factors in decreasing residue leachate pH. These were diluting water quality, carbonation, calcium content, soil quality and organic content, and potential mechanisms for pH reduction.

Materials and methods

Neat residue leachate was taken from the bauxite residue disposal area at Aughinish ($52^\circ 37' 06'' \text{N}$, $9^\circ 04' 19'' \text{W}$). and diluted with deionised water (DI) at 100-fold dilutions up to 1:500 in order to determine possible starting ranges of leachates requiring wetland treatment. The sampling and dilution factors were based on earlier modelling work conducted to determine runoff/leachate pH from a closed BRDA (Residue Solutions 2007). Results are shown below.

	pH
Leachate	13.2
1/100	11.7
1/200	11.4
1/300	11.2
1/400	11.1
1/500	11.0

In order to remove possible variables within residue leachates (e.g. competing ions that could influence buffering) and to maintain consistency within treatments all subsequent batch trials were conducted using NaOH solutions as a synthetic bauxite residue leachate.

Effect of dilution on pH using different types of water

Neat bauxite residue leachate is hyperalkaline in the region of pH 13 (AQW, Burke et al. 2013) with anticipated dilutions factors for a closed BRDA in the region of 1:100–1:400 (Residue Solutions 2007). Solutions of NaOH of different molarities (0.1, 0.01, 0.001, 0.0001, and 0.00001 M) were prepared by dissolving analar grade NaOH pellets in different water samples. Water types used for diluting NaOH to the different molarities (deionised, rain, tap, and carbonated as well as the theoretical decrease). At each dilution, the pH of the solution was determined and graphed. Results shown are the mean of three replicates. Data was tested for normality, and Spearman's rank order correlations were performed to determine any relationships between decrease in pH and diluting water quality (starting pH, electrical conductivity (EC), soluble cations) using SPSS Version 21.

Rate of pH drop using different CO₂ flow rates during carbonation

In order to investigate the effect of carbonation on the pH of a NaOH solution, 0.1 M NaOH (pH 13) was fitted with a diffuser connected to a carbon dioxide cylinder and the beaker was partially covered. A steady flow of CO₂ was bubbled through the solution at 0, 20, 40, and 60 mL min⁻¹. The pH was recorded continuously (with measurements taken every 0.2 s) using a frequently calibrated PS-2008A datalogger system (SPARK) until the pH stabilised. Once the pH of the solutions had stabilised (after 1 h approx.), the CO₂ flow was stopped.

This was repeated for NaOH solution made up with 100 mg/L Ca, and the formation of a white precipitate was observed. This precipitate was filtered using a Buchner funnel with a vacuum pump and dried. The resulting white solid was analysed by XPS using a Kratos AXIS 165 X-ray photoelectron spectrometer. In preparation for XPS analysis, the precipitate was ground with mortar and pestle into a powder and attached to a double-sided vacuum-compatible tape. Samples were analysed using an Al X-ray source (1486.58 eV) at 10 mA and 15 kV. Calibration was carried out using the C1s line at 284.8 eV. The charge neutraliser prevented charging of the samples during analysis.

The precipitate was also analysed by powder XRD using a Philips X'PERT PRO XRD, between 0° and 80° 2θ. In preparation for analysis, all samples were ground with a mortar and pestle to a homogeneous size and placed on zero background discs.

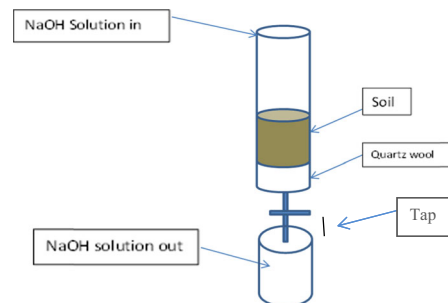
Effect of soil organic matter content on pH over time

To investigate the role of soil properties in buffering NaOH a combination of soil treatments with varying organic content were prepared. Solutions of NaOH were treated with different combinations of compost and perlite, and the pH was monitored over time. Fifty milliliters of NaOH at pH 10.5, 11.7, and 13 was placed into 6 × 100 mL beakers. Five grams of soil was added to each beaker in different ratios; 0, 20, 40, 60, 80, and 100 % compost to perlite; (e.g. 0 % = 5 g perlite, 100 % = 5 g compost, 20 % = 1 g compost, 4 g perlite). A blank solution of 50 mL 0.1 M NaOH in a 100-mL beaker was also prepared. The pHs of these solutions were recorded initially and periodically over 120 h.

Measuring capacity of soil and perlite to reduce pH of NaOH solution

The efficiency of different soil types to reduce the pH of NaOH solution was measured using vertically clamped column (cylindrical separator funnel) with quartz wool placed in the bottom to prevent solids entering the tap. For each soil

type, 1 g of soil was placed on the quartz wool and 0.1 M NaOH (pH 11.7) solution continuously poured through the column and released through the tap at an approximate flow rate of 1 mL min⁻¹. The solution exiting the column was collected in 25-mL aliquots, and the pH of each aliquot was measured. The flow through the column was continued until the pH stabilised. The capacity of the solid for reducing the pH was calculated by determining the amount of solution that was passed through the column before the pH stabilised.



Experimental set up for investigating the capacity of soils to reduce pH.

Experimental set up for investigating the capacity of soils to reduce pH

Results

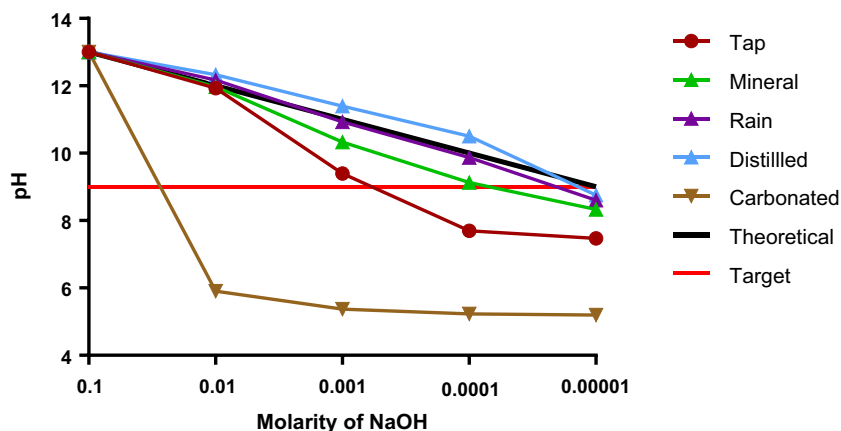
Figure 1 presents the variation of pH with dilution using the indicated water types. Included also in the figure is the theoretical pH, which is calculated from the NaOH molarity (OH concentration). The dashed horizontal line at pH 9 shows the target discharge pH. To reach a pH of 9, a theoretical dilution of 1:10,000 is required. The overall trend, for all water types, shows a drop in pH with dilution with distilled water being the least effective. The most effective water type for reducing the pH is carbonated water with tap water also relatively effective.

Positive and significant correlations were found for the overall decrease in NaOH pH with calcium content ($r=0.92$, $p=0.02$) and electrical conductivity ($r=0.92$, $p=0.01$) of diluting waters. The higher the conductivity or calcium content then the greater the ability to reduce the pH. However the most dramatic fall in the pH was associated with the carbonated water.

A significant characteristic of constructed wetland technology for the treatment of alkaline waste streams is the high partial pressure of CO₂ that biological activity confers. All NaOH samples showed a significant drop in pH with ingassing of CO₂ (Fig. 2) with the rate of decrease fastest for higher flow of CO₂, (3 min) compared to the slowest rate of 20 mL/min requiring 7.5 min for pH to drop below 9. Regardless of CO₂ flow rate, all solutions stabilised at pH 6.5 for the duration of the experiment (up to 20 min).

In NaOH solutions containing calcium (500 mg/L Ca), a white precipitate was observed following carbonation (Fig. 1).

Fig. 1 pH of different molarity NaOH solutions in diluting waters



XRD analysis of this precipitate matched that of calcite (CaCO_3) (Supplementary Information Figure 1). Subsequent XPS analysis was conducted, and elementally it was found to be composed of calcium, carbon, and oxygen but also significant quantities of sodium (Supplementary Information Figure 2). Relative atomic amounts of each of these elements are given in Table 1.



White precipitate formed in carbonated NaOH solution made in Ca solution

White precipitate formed in carbonated NaOH solution made in Ca solution

A more in-depth analysis of the XP spectra revealed that the dominant species was Na_2CO_3 , sodium carbonate. This was based on the surface composition which contained 24 at.% Na^+ and 12.7 at.% C as carbonate.

High resolution XP spectrum of the C 1s peak is shown in Supplementary Information Figure 3a. The contributions of different types of carbon species can be clearly observed. 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) on the high energy surface of the solid. This carbon is known as adventitious carbon and is commonly observed on all solid surfaces that have been exposed to the atmosphere. There is also evidence of low levels of other carbon types (286.1 eV – C–O and 288 eV O=C–O).

Supplementary Information Figure 2 shows the high resolution XP spectra of the O 1s and Na 2s peaks. The oxygen peak is made up of two different peaks which would indicate the presence of two different oxygen types. The larger oxygen peak at 531.1 eV is representative of carbonate and oxygen from organic sources is represented by the peak at 532.4 eV. The two peaks observed for the calcium Ca 2p peak is representative of Ca^{2+} . The peak for the Na 1s species (not shown) was a single peak centred at 1071.1 eV and is representative of Na^+ .

Table 2 summarises the characteristics of the various species detected from the high resolution spectra with peak assignment and the atomic percentage of all species. From the quantification and the Na to carbonate ratio, it seems that the dominant phase of the sample is sodium carbonate, Na_2CO_3 . The sodium atomic

Fig. 2 Rate of pH decrease during carbonation using various flow rates of CO_2 (0.1 M NaOH)

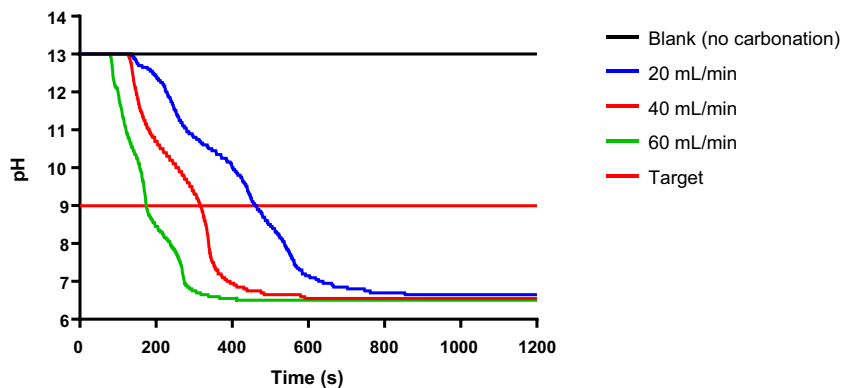


Table 1 XPS analysis of the relative amounts of the indicated elements in the precipitated form following the carbonation of 0.1 M NaOH containing 500 mg/L Ca

Name	Binding energy (eV)	Atomic % conc.
Na _{1s}	1071.0	24.7
O _{1s}	531.1	42.2
Ca _{2p}	346.5	1.2
C _{1s}	284.7	30.4
Cl _{2p}	199.0	2.2

concentration is 24.3 %, and the carbonate CO₃⁻ concentration is approximately half of that value at 12.7 at. %.

Soil composition is an important factor in constructed wetland efficiency. The effect of organic matter content in soil on pH of varying strength NaOH solutions is shown in Fig. 3. The starting pH in this series of experiments was pH 10.7–13. A greater difference can be seen in pH drop over time at the lower starting pH using the different soil treatments.

At pH 13, all soil treatments significantly lowered NaOH pH for the duration of the test period. However, results were still above pH 10. Atmospheric carbonation (blank with stirring) reduced solution pH, but levels were still > pH 11.5.

Effect of organic matter content is more evident with starting pH 11.7. All soil treatments resulted in a pH reduction to less than the target value of pH 9. Soil treatments with an organic matter content of >50 % achieved a pH of <7.

With a solution starting pH 10.7 atmospheric carbonation resulted in a short term decrease to pH 9 but this rebound to pH 9.5. Soil treatment with no organic matter (perlite alone) displayed a similar result to that observed for the pH 11.7 with pH <9 achieved, but the time to reach this target was quicker. All soil treatments containing organic matter achieved a pH of <7 with treatments of higher organic content (>50 %) resulting in pH of <6.

Three locally available soil types were also characterised (Table 3) and tested for their potential to treat NaOH solution

Table 2 Relative amounts of the indicated elements in the precipitated form following the carbonation of 0.1 M NaOH containing 500 ppm Ca

Name	Species	Position (eV)	Atomic % conc.
Na _{1s}	Na ⁺	1071.0	24.7
O _{1s}	Carbonate	531.1	33.2
O _{1s}	Organics	532.4	9
Ca _{2p}	Ca ²⁺	346.5, 350.0	1.2
C _{1s}	C-C, C-H	284.8	1.2
C _{1s}	C-O	286.1	13.9
C _{1s}	O=C-O	288.0	2.3
C _{1s}	Carbonate	289.3	12.7
Cl _{2p}	Cl ⁻	198.9, 200.5	2.2

(Fig. 4). The capacity of each soil to buffer NaOH is also presented (Fig. 5).

Soil samples display different capacities for reducing pH in NaOH solution. The best performing soil had a relatively low soil pH, higher carbon content, and effective cation exchange capacity compared to the other soils.

Discussion

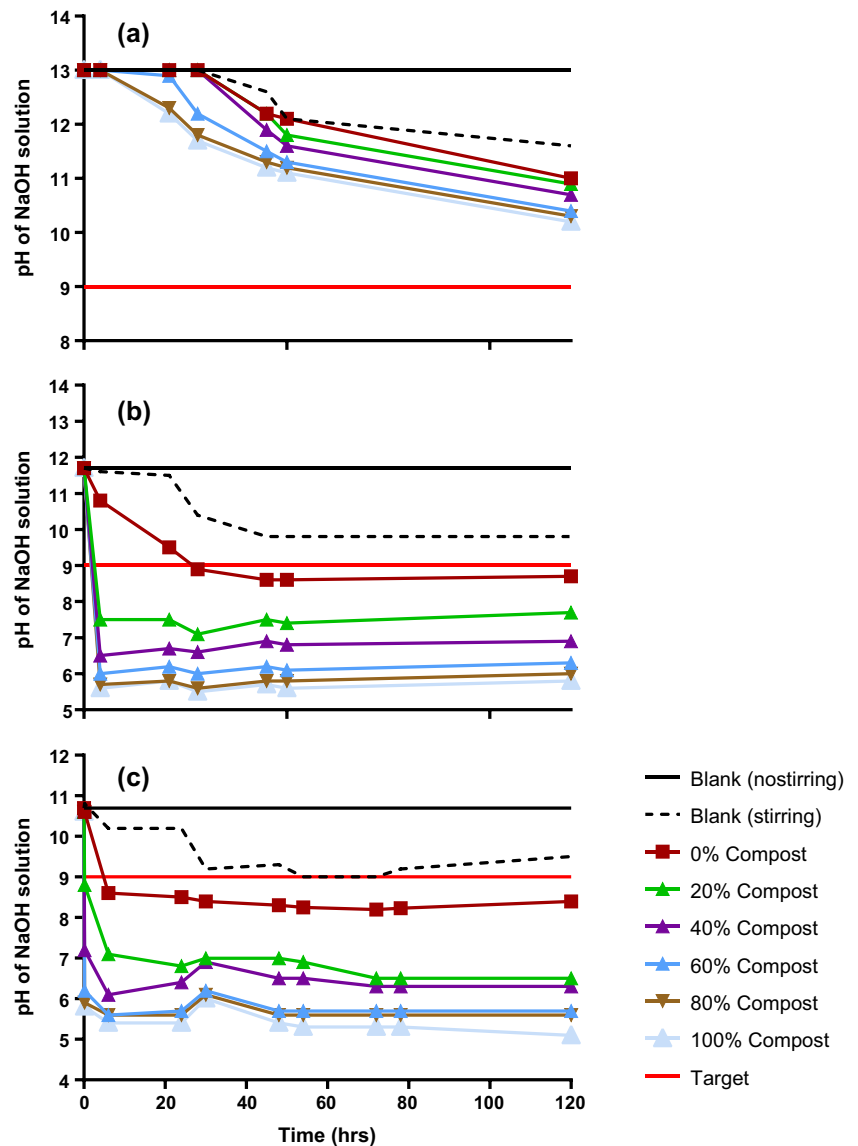
In the environmental management of solid phase bauxite residue (red mud), the role of amendments such as gypsum in decreasing pH is recognised (Courtney and Timpson 2005). The role of such practises in influencing runoff and leachates from BRDAs is largely unknown.

Neat leachate was high in pH, but it is anticipated that in a closed and landscaped BRDA that neat residue leachate (ca. pH 12+) will be substantially diluted by runoff thus resulting in a reduced pH of waters requiring treatment. However, the amount of diluting water needed to reduce the pH to an acceptable level (less than pH 9) varies significantly depending on the water types used. Moreover, in instances where some form of management is carried out on the residue, substantially lower pH occurs. Recent developments in ‘mud farming’, where residues are trafficked by amphibious equipment to ‘squeeze out’ excess moisture content followed by ploughing and harrowing (World Aluminium 2014), have shown decreases in residue slurry pH from 11.9 to 10.6 (Clohessy 2015). It is therefore anticipated that leachate quality in final closed BRDAs should be substantially improved.

Neutralisation of bauxite residue leachate has been demonstrated using additives of HCl, gypsum, and seawater (Burke et al. 2013). Seawater has also been used by Couperthwaite et al. (2014) who compared seawater and nanofiltered seawater (double cation content) for neutralising leachate and observed that the nanofiltered was effectively twice as fast. It was also observed that volume of seawater required to achieve pH reductions was considerably less when nanofiltered seawater was used, and a pH of <9 was only achieved with nanofiltered seawater. Although management of residue leachates have not received the same level of attention, it is evident that composition of waters diluting the neat leachates will be important factors in determining pH of leachate requiring treatment or discharge. For example, gypsum, acid and acidic gypsum amended residue has yielded leachate with Ca content of 20–435 mg/L after eight pore volumes (Ippolito et al. 2005).

Industrial waste gases (SO₂ & CO₂) have been used to neutralise solid bauxite residues (Cooling 2007; Khaitan et al. 2009; Kirwan et al. 2013; Wang et al. 2015) and atmospheric carbonation used on BRDAs (Clohessy 2015). Kirwan et al. (2013) highlighted that CO₂ neutralisation beyond the pH of approximately 10 is impractical due to the conversion of residue

Fig. 3 pH of NaOH solutions (a 0.1 M, b 0.01, and c 0.001 M) versus time in soils of varying organic content



tricalcium aluminate (TCA) to calcite and $\text{Al}(\text{OH})_3$. Absence of solid phase alkalinity in the NaOH solutions presents a preferable matrix to residue/leachate. In the current study, carbonation (bubbling of CO_2) of the high pH solutions resulted in a rapid drop in pH (Fig. 2) from pH 13 to pH <7 in 2.5 min. Carbonation of bauxite residue leachate has not been previously

studied, but in a study of water geochemistry in a bauxite residue lake deposit, Czop et al. (2011) observed a decrease in pH with depth and attributed this, in part, to in gassing of atmospheric CO_2 . Mayes et al. (2006) observed significantly lower pH in steel-slag leachates treated by volunteer wetlands and attributed this to precipitation of calcite due to the high partial pressure of CO_2 within the rhizosphere.

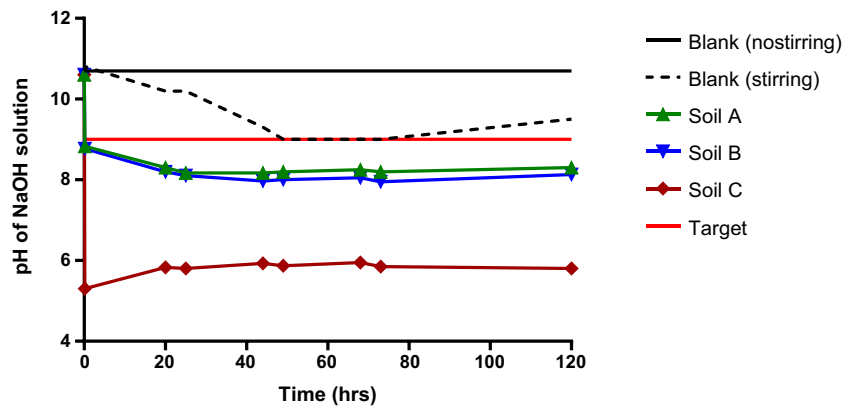
Introduction of seed particles or crystal nuclei to medium have been shown to induce the crystallisation process with calcite providing nucleation spots for amorphous calcium carbonate clusters a well-accepted mechanism (Nancollas and Reddy 1971; Salek et al. 2016). The formation of calcite and consumption of alkalinity previously demonstrated in alkaline steel-slag leachates is also attributed to the relatively high Ca content of these waters (Mayes et al. 2006). In the current study, carbonation of NaOH solutions in the presence of Ca resulted in the formation of calcite, with XPS analysis

Table 3 Selected characteristics of different soil types

	Compost	Soil A	Soil B	Soil C
pH	5.9	7.9	7.8	5.6
EC ($\mu\text{S cm}^{-1}$)	203	163	199	142
Ca (mg/kg)	Not determined	37,940	41,380	2270
ECEC (meq/100 g)	Not determined	35.5	35.1	44.9
Org C (%)		1.92	2.96	3.69

ECEC effective cation exchange capacity

Fig. 4 pH of NaOH solutions versus time with 5 g soil/50 mL solution



demonstrating sodium carbonate on the surface. It is possible that the sodium carbonate adsorbs onto the surface of the precipitating calcite. Wetland systems confer high specific surface areas for precipitation (Mayes et al. 2009) and as such the soils, plant, and organic debris may act as seeding site for sodium carbonate formation.

Precipitation of sodium carbonates can occur in environments with low Ca content. Marion (2001) reported cation analysis of several alkaline natural waters (pH 10.13–10.19). At Na contents of 6.23–7.49 mol/kg (water) and undetected calcium, precipitation of trona at 21 °C was predicted. It was also noted that for trona to precipitate at ≤25 °C requires high alkalinity, low P-CO₂, and high pH (>9.7) or nahcolite is the stable solid phase. Trona has been observed precipitating from high alkalinity natural waters in the pH range from 9.8 to 10.2.

The pH buffering capacity of soils is associated with a number of soil properties and include the mineral (ion exchange reactions) and organic constituents. It is clear that organic solids have the capability of reducing pH and this property is likely to be important in a wetland operation. From the pH drop and the amount of solution needed to bring the pH back up to the starting level, the compost was found to be capable of neutralising 27.4 mmole of NaOH per gram of solid. The perlite, on the other hand, only had a capacity of

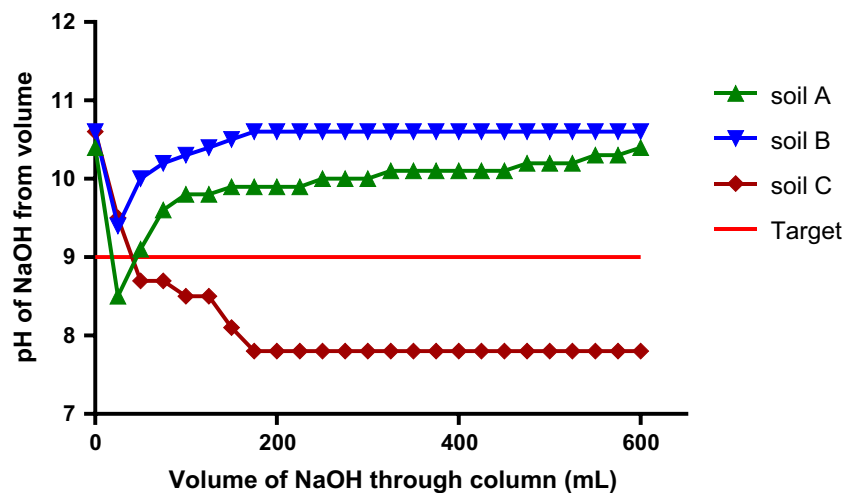
neutralising 0.9 mmole NaOH. Cation exchange and the production of organic acids can lower the pH of alkaline waters (Ross 1996), and studies by Kõiv et al. (2009) have also demonstrated the mineralised peat filters can be effective in lowering pH of alkaline waters with reductions from ca. pH 9 to 7.5 achieved over a 4-month period. Decreases observed in the current study are much greater than this, but observations were for a shorter period. Capacity of soils to effectively buffer NaOH solution over time warrants further research.

Similarly, the three soil samples taken from test areas for wetland soil demonstrated varying levels of efficiency in decreasing NaOH pH and capacity to buffer. From the analysis of the soils, soil C exhibited highest organic carbon and effective cation exchange capacity together with the lowest pH in comparison to the other soils and would indicate that these characteristics are important for reducing pH of leachates within wetlands.

Conclusion

The data presented here demonstrate that reduction in NaOH solution pH is possible using mechanisms associated with

Fig. 5 pH of NaOH solution through soil columns



constructed wetland technology and provide a promising foundation for further research and development of constructed wetlands in treating alkaline bauxite residue leachates.

Role of diluting water in initial buffering of neat leachate warrants further investigation. Properties conferred by constructed wetlands, namely soils with high CEC and biological activity leading to CO₂ generation, can effectively decrease NaOH pH to values that meet discharge targets. Whilst precipitation of calcite consumes alkalinity and offers a site of nucleation for sodium carbonate to form, presence of Ca is not essential to the process. Further work is recommended to investigate the potential for soil/plant systems to treat alkaline bauxite residue leachates.

This study is the first step in determining the use of constructed wetland technology for use in treatment of leachate waters from bauxite residue storage areas. The next stage is to examine the plant growth and biological activity under NaOH conditions and to determine if the wetland system can effectively buffer the pH to <9.

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