In situ neutralisation of uncarbonated bauxite residue mud by cross layer leaching with carbonated bauxite residue mud

T.C. Santini [a,*], C. Hinz [a], A.W. Rate [a], C.M. Carter [b], R.J. Gilkes [a]

[a] School of Earth and Environment (M087), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
[b] Technology Delivery Group, Alcoa World Alumina Australia, PO Box 161, Kwinana, WA 6167, Australia

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ABSTRACT

Unameliorated residue mud from the Bayer process generates highly alkaline leachates (pH ca. 13) after deposition in storage areas. Pre-deposition treatment of bauxite residue mud (BRM) with CO_2 gas (carbonation) lowers leachate pH to ca. 10.5. Laboratory scale leaching columns were used to investigate the potential for *in situ* pH reduction in existing uncarbonated BRM deposits through exposure to carbonated mud leachate. Leachates from uncarbonated and carbonated residues in single and dual-layer column configurations were analysed for pH, electrical conductivity, carbonate and bicarbonate content, and element concentrations. Air-dried solids were analysed by X-ray diffraction before and after leaching.

Cross layer leaching lowers leachate pH from uncarbonated BRM. Leachate pH was significantly lower in dual layer and carbonated residue than in uncarbonated residue between one and 400 pore volumes leached. Carbonated residue porewater as well as dawsonite and calcite dissolution were identified as sources of (bi-)carbonate. Leachate concentrations of As, Cr, Cu, Ga and La were immediately reduced in dual layer treatments compared with uncarbonated residue. No element analysed exhibited a significantly higher leachate concentration in dual layer treatments than the highest observed concentration in single layer treatments. The implementation of dual layer leaching in the field therefore presents an opportunity to improve leachate quality from existing uncarbonated residue deposits and justifies further testing at field scale.
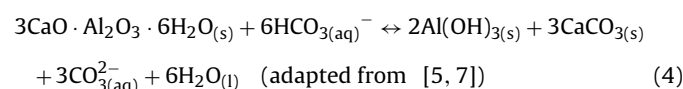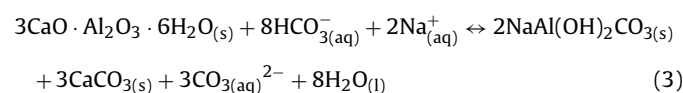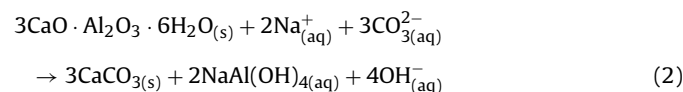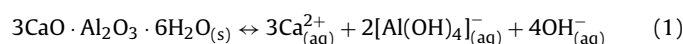
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1. Introduction

Caustic bauxite waste slurries contain alkalinity in the liquor (active alkalinity) and solid (reserve alkalinity) components. Despite dewatering and rinsing, deposited mud is approximately 48% w/w solids suspended in pH 13 liquor without application of a pH-lowering treatment [1,2]. After deposition, liquor alkalinity is slowly diluted by infiltration of rainwater; however, desorption of adsorbed hydroxide and carbonate and dissolution of alkaline solid phases such as tricalcium aluminate (TCA; $3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)}$), and at lower pH, sodalite ($Na_8Al_6Si_6O_{24}Cl_{2(s)}$), resupplies liquor alkalinity until the reserves of alkaline species and solids are exhausted [3–5].

Tricalcium aluminate is the main source of reserve alkalinity in bauxite residue [6]. Dissolution products of TCA depend on solution chemistry: without carbonate and bicarbonate present, TCA dissolves until chemical equilibrium prevails (Eq. (1)); in the presence of sufficient carbonate, calcite and sodium aluminate form (Eq. (2)); and in the presence of sufficient bicarbonate, calcite and dawsonite

($NaAl(OH)_2CO_{3(s)}$) or aluminium hydroxide will form (Eqs. (3) and (4)) [5]. Eqs. (1) and (2) generate $OH^-_{(aq)}$, and push the system above the carbonate/bicarbonate buffering pH ($pK_a = 10.25$).

$$3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)} \leftrightarrow 3Ca^{2+}_{(aq)} + 2[Al(OH)_4]^-_{(aq)} + 4OH^-_{(aq)} \qquad (1)$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)} + 2Na^+_{(aq)} + 3CO^{2-}_{3(aq)}$$
$$\rightarrow 3CaCO_{3(s)} + 2NaAl(OH)_{4(aq)} + 4OH^-_{(aq)} \qquad (2)$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)} + 8HCO^-_{3(aq)} + 2Na^+_{(aq)} \leftrightarrow 2NaAl(OH)_2CO_{3(s)}$$
$$+ 3CaCO_{3(s)} + 3CO_{3(aq)}^{2-} + 8H_2O_{(l)} \qquad (3)$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)} + 6HCO_{3(aq)}^- \leftrightarrow 2Al(OH)_{3(s)} + 3CaCO_{3(s)}$$
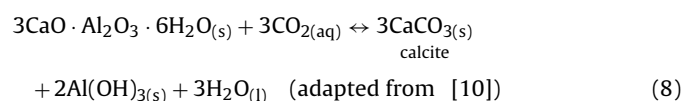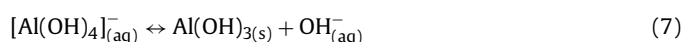$$+ 3CO^{2-}_{3(aq)} + 6H_2O_{(l)} \quad \text{(adapted from [5, 7])} \qquad (4)$$

The above reactions will proceed until either stocks of TCA are exhausted, or until calcium concentration increases so that the

* Corresponding author. Tel.: +618 6488 7346; fax: +618 6488 1050.
E-mail address: santit01@student.uwa.edu.au (T.C. Santini).

liquor is saturated with respect to TCA [5]. In a freely draining system exposed to rainfall, calcium concentration in the liquor would be unlikely to achieve saturation with respect to TCA, and any TCA present will continue to dissolve and release hydroxide [5]. Reserve alkalinity may maintain leachate pH ca. 13 for in excess of 20 years in uncarbonated bauxite residue deposits [3].

Carbonation has been employed since 2006 as a pre-deposition pH reduction treatment at Alcoa's Kwinana (Western Australia) refinery [8]. Carbonation involves mixing carbon dioxide gas through residue slurry in pressure vessels, after thickening of the residue to remove excess liquor [9]. Residue pH is lowered by reaction of $CO_{2(g)}$ with alkaline liquor species such as $OH^-_{(aq)}$ and $Al(OH)^-_{4(aq)}$ (Eqs. (5)–(7)), and conversion of solid phases such as TCA to dawsonite and calcite (Fig. 1; Eqs. (3) and (8)). Only ca. 65% of TCA is consumed during carbonation [7], with the remainder available for dissolution during leaching according to Eqs. (1)–(4). Sodium aluminate also reacts directly with $CO_{2(aq)}$ to form dawsonite [10].

$$CO_{2(aq)} + OH^-_{(aq)} \leftrightarrow HCO^-_{3(aq)} \tag{5}$$

$$HCO_{3(aq)}^- + OH^-_{(aq)} \leftrightarrow CO^{2-}_{3(aq)} \tag{6}$$

$$[Al(OH)_4]^-_{(aq)} \leftrightarrow Al(OH)_{3(s)} + OH^-_{(aq)} \tag{7}$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O_{(s)} + 3CO_{2(aq)} \leftrightarrow \underset{calcite}{3CaCO_{3(s)}}$$
$$+ 2Al(OH)_{3(s)} + 3H_2O_{(l)} \quad \text{(adapted from [10])} \tag{8}$$

There are few treatment options for uncarbonated residue once deposited, meaning that alkaline leachate will continue to be collected after refinery closure in some cases. Seawater lowers leachate pH of uncarbonated residue to ca. 7 when applied surficially; however, the high salinity of seawater-leached residue inhibits plant growth [11]. Seawater also has undesirable effects on physical properties of residue, as it causes dispersion of fine particles, potentially creating surface hardpans and erosion issues. Seawater increases residue volume and decreases permeability through precipitation of layered double hydroxides [11]. Application of mineral acids would be expensive, although complete neutralisation could theoretically be achieved [3].

Leaching uncarbonated residue with a high (bi-)carbonate, low hydroxide solution (such as carbonated residue leachate) rather than rainwater (which contains relatively low concentrations of $HCO^-_{3(aq)}$, $CO^{2-}_{3(aq)}$, and $OH^-_{(aq)}$) may limit further release of adsorbed hydroxide and dissolution of OH^--containing minerals (such as TCA according to Eq. (1)), whilst still allowing export of free hydroxide present in the uncarbonated liquor as well as conversion of free hydroxide to carbonate through reaction with bicarbonate. Deposition of carbonated residue over old uncarbonated deposits provides a unique process opportunity in southwestern Australia in that carbonated residue is currently being produced at some refineries (including Alcoa Kwinana), and poses no additional environmental risk beyond that of the pre-existing uncarbonated deposit. If effective, such a treatment could 'neutralise[1]' uncarbonated residue deposits *in situ*, analogous to the use of permeable reactive barriers for treatment of contaminated groundwater plumes.

The study detailed herein aimed to assess the potential for pH reduction in a layered residue bed at a laboratory scale, evaluate the influence of factors affecting cross layer neutralisation, and identify any contaminants which may be mobilised during

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[1] Neutralisation in the context of this paper refers to lowering pH, not necessarily to a neutral (pH 7) value.

cross layer leaching. Leaching order (i.e. water flow from uncarbonated to carbonated, or carbonated to uncarbonated) and presence of a physical interface (providing potential for mineral precipitation and enhanced porewater mixing between layers) were factors considered likely to influence leachate quality. The following hypotheses were investigated: (a) leaching uncarbonated residue with carbonated leachate will result in decreased leachate pH compared to leaching uncarbonated residue with pure water; (b) pH of uncarbonated residue leachate will decrease after being leached through carbonated residue; (c) leaching order has a greater effect on leachate chemistry than a physical interface between the two residue types; (d) dissolution of TCA and sodalite will maintain a higher leachate pH from uncarbonated residue compared with carbonated residue; (e) carbonated residue leachate will have a higher initial carbonate and bicarbonate concentration than uncarbonated residue leachate; and carbonate and bicarbonate will be resupplied to carbonated residue leachate during extended leaching with water by dissolution of dawsonite and sodalite, (f) lowering pH through cross layer leaching will result in decreased leachate concentrations of trace elements such as As, Cr, Ga, La, Mo, U, and V compared with concentrations in single layer leachates.

2. Methods

Six treatments were compared to assess the potential of cross layer leaching as an *in situ* remediation technique. Two treatments consisted of a single short column containing uncarbonated (U) or carbonated residue (C) only; two treatments consisted of two short columns connected in series (U–C, C–U; with the first letter of each representing the residue type in the first (lower) column of the series); and two treatments consisted of single long columns containing two residue layers (UC, CU; with the first letter of each representing the residue type in the lower part of the column) (Fig. 2). U and C were single layer treatments, whereas U–C, C–U, UC, and CU were dual layer treatments.

2.1. Experimental setup

Leaching columns consisted of polycarbonate tubing (internal diameter 32 mm) inset with an O-ring at each end, sealed with polyvinylchloride (PVC) caps containing a single 2 mm internal diameter polyethylene connector as column inlets/outlets (Fig. 2g). Nylon mesh circles (mean pore size 50 μm) and perforated PVC board circles acted as filters to confine solid residue. PVC tubing connected the peristaltic pump to column inlets and sample vials to column outlets. 'Short' columns (35 mm length) were used for U, C, U–C, and C–U treatments; 'long' columns (70 mm length) were used for UC and CU treatments.

Columns were packed with 70:30 mixtures of sand (>99% quartz, Cook Industrial Minerals, Perth) and uncarbonated and/or carbonated BRM (Alcoa Kwinana bauxite residue storage facility, Perth). Incorporation of sand was necessary to increase hydraulic conductivity. Similar sand:residue ratios have been used in previous column leaching studies [12–14]. Sand:residue layers of 1 mm depth were tamped and the surface of each layer scratched lightly before packing the next layer to minimise between-layer ponding. Columns were filled with degassed MilliQ (Millipore GmbH, Eschborn, Germany) water by upwards injection and allowed to equilibrate for 57 h prior to commencement of continuous leaching. Columns were leached in upflow mode with degassed MilliQ water injected by a peristaltic pump at a rate of 5 mL per hour for 173.5 h; leachate samples were collected and analysed hourly for the first 20 h, and then at 31, 47.5, 66.3, 108, 120, and 173.5 h. Three replicates of each treatment were analysed. After leaching, effective pore volume was determined for one replicate of each
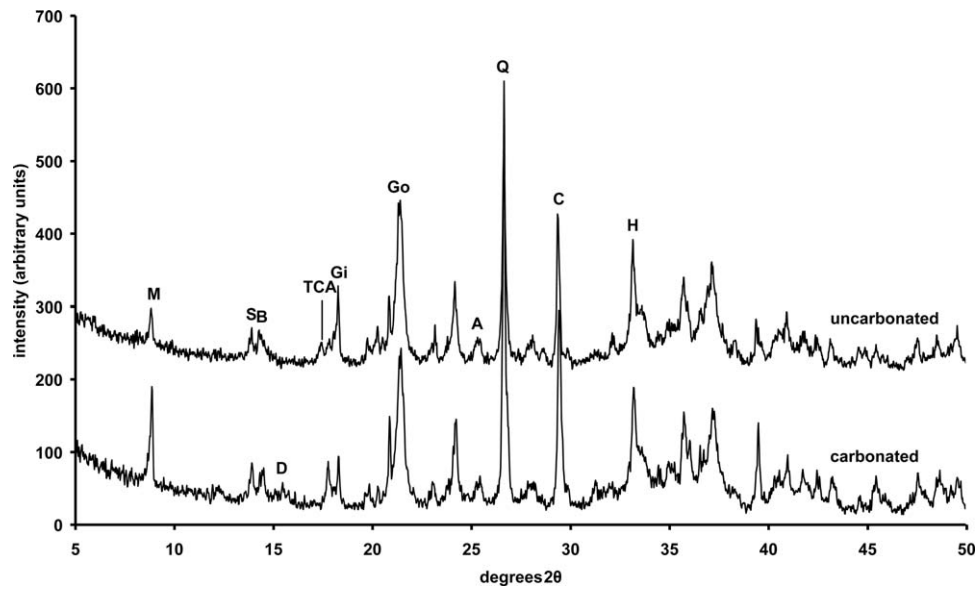
Fig. 1. XRD patterns for uncarbonated and carbonated bauxite residue mud prior to experimental leaching. Letters indicate location of the primary peak for each mineral (M: muscovite; S: sodalite (secondary peak labelled); B: boehmite; TCA: tricalcium aluminate; Gi: gibbsite; Go: goethite; A: anatase; Q: quartz; C: calcite; H: hematite; D: dawsonite).
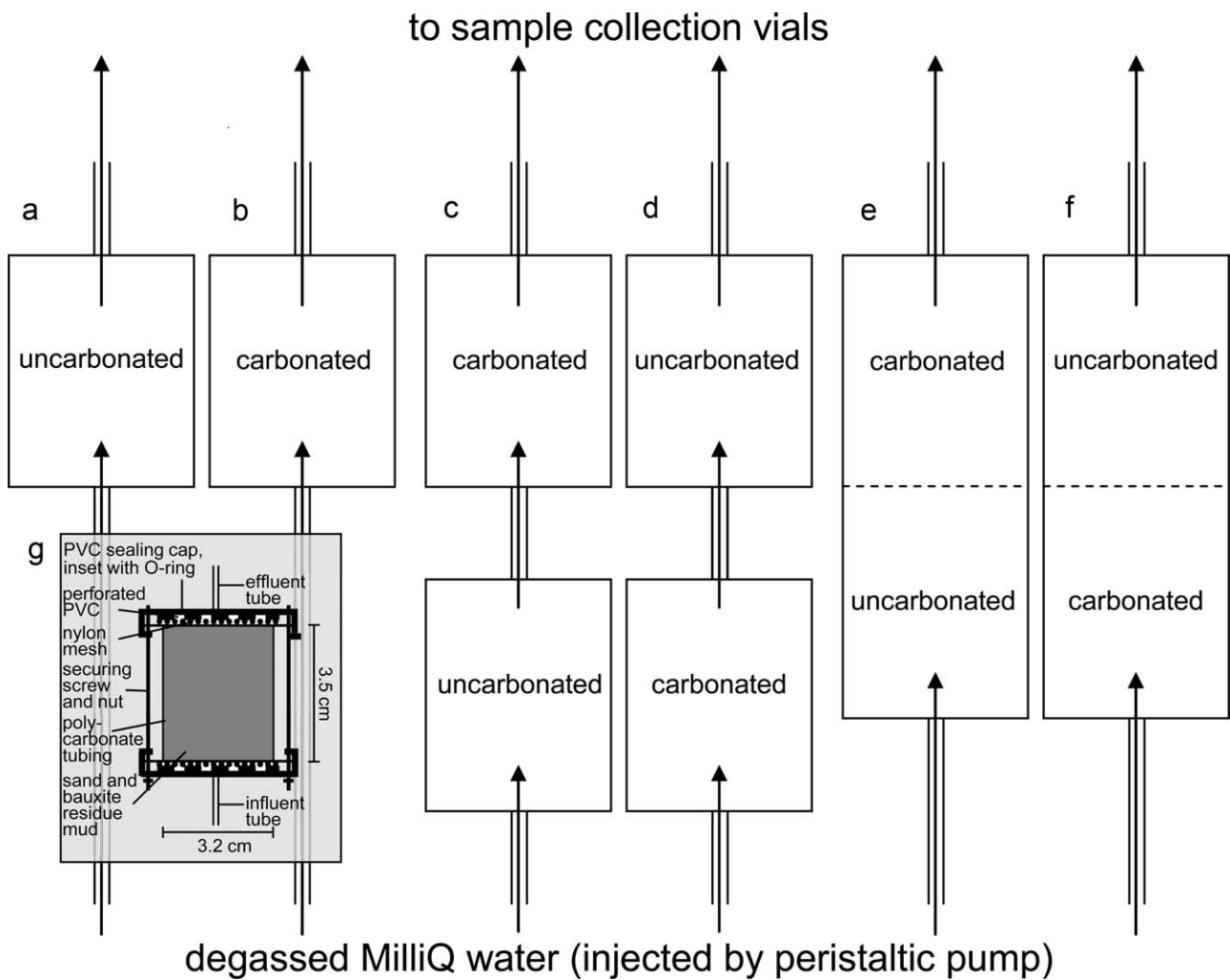

Fig. 2. Treatment configuration within leaching columns: (a) 'U' treatment; (b) 'C' treatment; (c) 'U–C' treatment; (d) 'C–U'treatment; (e) 'UC' treatment; (f) 'CU' treatment. Inset (g) indicates location of components within a 'short' (3.5 cm length of polycarbonate tubing) leaching column; location of components within 'long' leaching columns was identical, but used a 7 cm length of polycarbonate tubing.

Table 1
Physical column parameters as determined by 1 M potassium chloride tracer according to [14]. Porewater velocity, v; hydrodynamic dispersion, D; and dispersivity, α, values were converted to dimensionless terms to allow comparison of values between treatments.

Treatment	Bulk density ($g\,cm^{-3}$)	Pore volume (mL)	Observed porosity	v	D	α
U	1.99	2.18	0.077	1.96	1.65	0.84
C	1.94	2.55	0.091	1.76	1.14	0.65
U–C	1.96	6.16	0.109	1.88	2.60	1.38
C–U	1.96	5.33	0.095	2.44	2.60	1.07
UC	1.96	4.69	0.083	2.44	2.68	1.10
CU	1.96	4.89	0.087	2.15	2.63	1.22

treatment [15], assuming a constant solids volume within all treatments (Table 1). A 1 M KCl solution was used as a tracer, with a flow rate of 5 mL per hour.

2.2. Analyses

Leachate was analysed for pH, EC, carbonate and bicarbonate content immediately after collection; subsamples of leachate were filtered with 0.22 μm cellulose acetate filters, acidified, and stored at 4 °C for determination of element concentrations (Al, As, Ca, Cr, Cu, Ga, La, Mo, Na, S, Si, U, V) using an Inductively Coupled Plasma Optical Emission Spectrometer (Optima 5300 DV; PerkinElmer, Waltham, MA, USA). Carbonate and bicarbonate content was determined by potentiometric titration against 0.1 M HCl [16] in a solution of degassed MilliQ water with an automatic titrator (DL55; Mettler Toledo, Columbus, OH, USA), and carbonate content was corrected for contributions from aluminate and hydroxide. Aluminate content was calculated from Al content, assuming precipitation as $Al(OH)_{3(s)}$ by pH 8.3, and hydroxide content was calculated from pH data. Results of all leachate analyses

were transformed to standard pore volumes by linear interpolation of observed values for adjacent data points. Repeated measures analysis of variance (ANOVA) was used to compare treatments for statistical significance at the $\alpha = 0.05$ level (Genstat; VSN International, Helensburgh, NSW, Australia [17]).

Solid material from one replicate was used for XRD analyses. Material < 0.5 mm was separated from each air dried residues, ground with an agate mortar and pestle, and packed into aluminium sample holders for XRD analysis. Random powder XRD patterns were obtained between 3 and 70 degrees 2θ using CuK$_\alpha$ radiation with a diffractometer (Philips PW1830; Panalytical, Almelo, The Netherlands). Minerals were identified by comparison with reference mineral peak listings [18]. Anatase was used as an internal standard to calculate relative changes in residue mineral content after leaching by comparison of mineral peak area ratios, as it was considered unlikely to dissolve or precipitate under experimental conditions. This assumption was supported by geochemical modelling in PHREEQC (v 2.13.2 [19]) which predicted very minor transformations.

3. Results and discussion

3.1. Leachate chemistry

Cross layer leaching significantly reduced leachate pH below that of pure uncarbonated residue (U) leachate for up to 400 pore volumes of leaching (Fig. 3). Initially, significantly higher leachate pH was observed in U–C (pH 10.8) and UC (pH 11.0) treatments than in C (carbonated residue only; pH 10.4) treatment; however, this difference became non-significant after 200 pore volumes. Carbonated (C) leachate pH (10.0–10.7) was significantly lower than that of U leachate (11.2–13.3) throughout the entirety of leaching. Leachate pH of all treatments significantly decreased between one
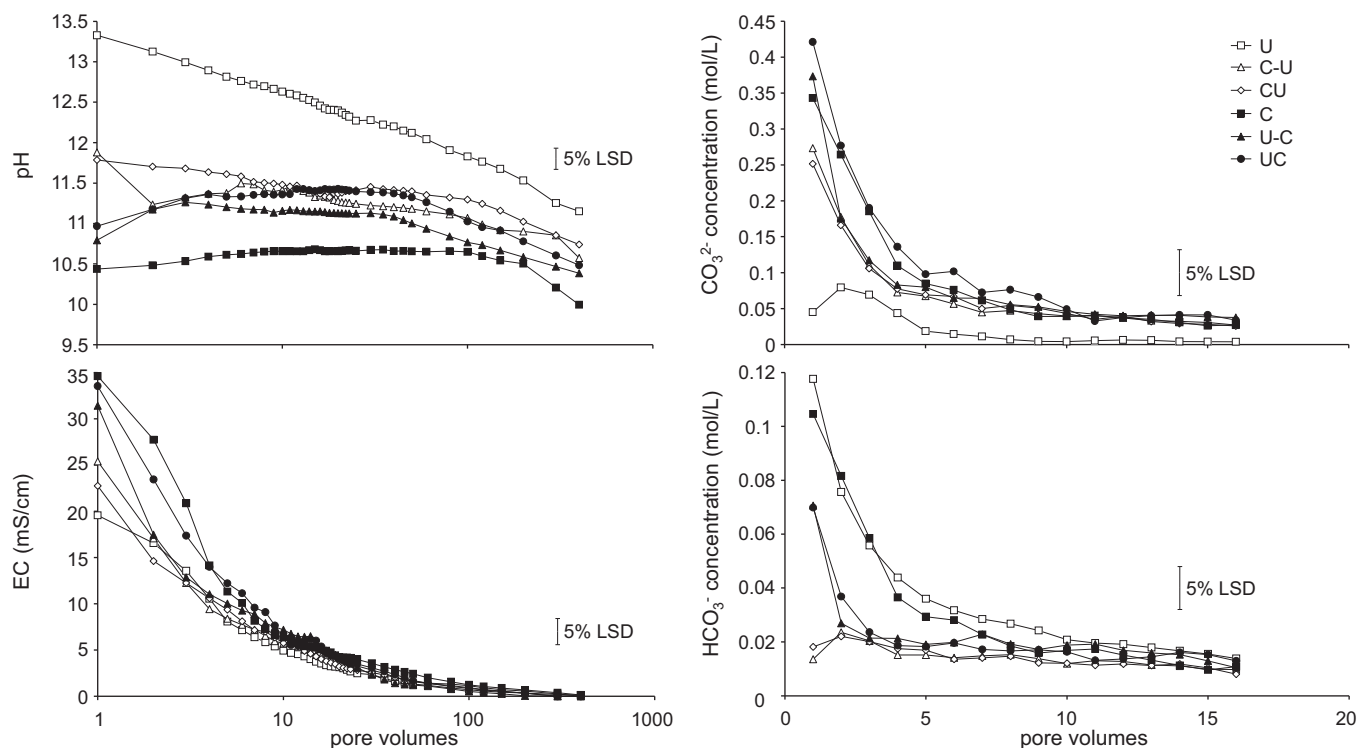

Fig. 3. Leachate pH, electrical conductivity (EC) (mS/cm), carbonate and bicarbonate concentration (mol/L) during continuous leaching. Data points represent the mean of three replicates interpolated to standard pore volume increments. 5% LSD bar represents 5% least significant difference (time × treatment) from repeated measures ANOVA. Note that pH and EC data are displayed as logarithmic pore volumes to 400 pore volumes leached; whereas carbonate and bicarbonate are displayed as linear pore volumes to 16 pore volumes leached.
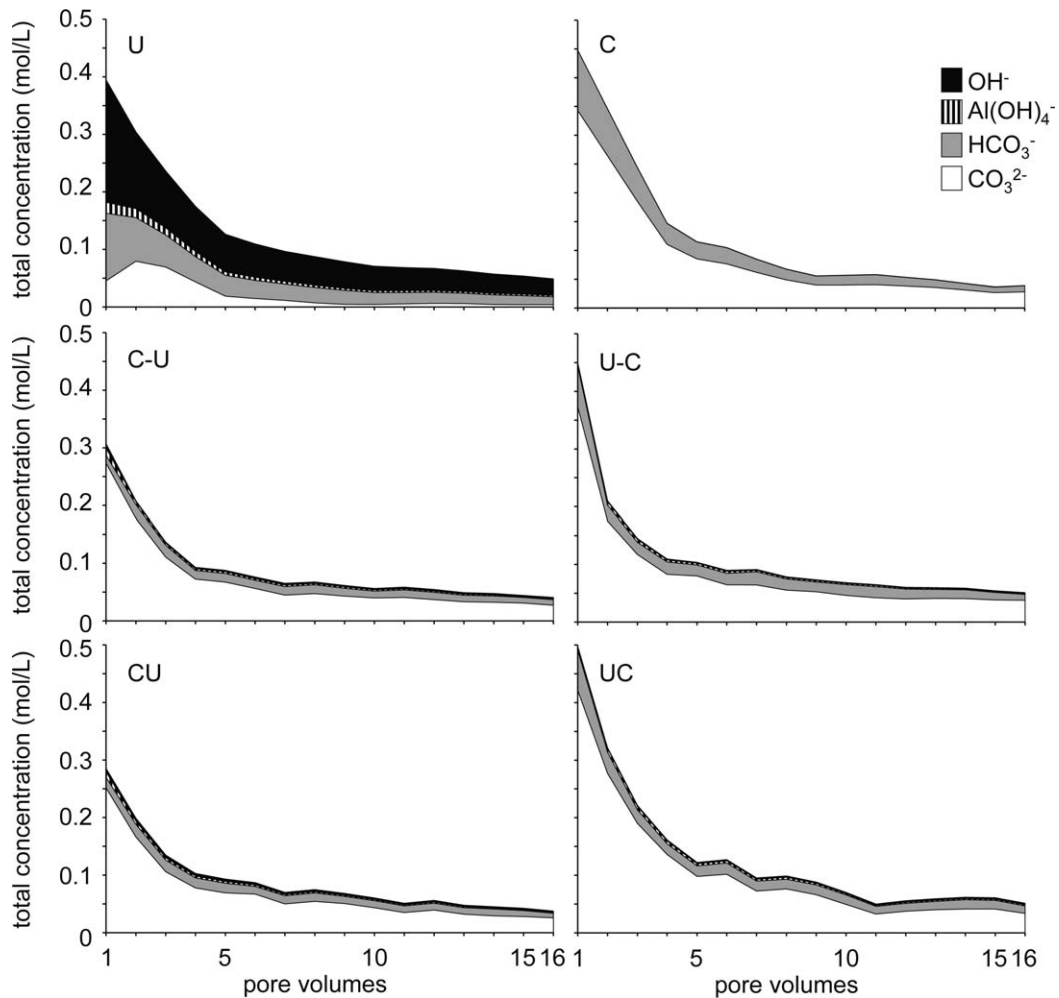
Fig. 4. Total leachate alkalinity, split into contributions from OH^- (calculated from pH), $Al(OH)_4^-$ (calculated from Al content), CO_3^{2-} (calculated from titratable alkalinity to pH 8.3 minus hydroxide and aluminate alkalinity), and HCO_3^- (calculated from titratable alkalinity to pH 3.7 minus contributions from carbonate). Note that data is displayed to 16 pore volumes as no Al leachate data is available beyond this point.

and 400 pore volumes leached. Initially, leachate ECs for C, U–C and UC were significantly higher than those for U, C–U and CU (Fig. 3); the final residue leached before leachate exit appears to control EC in the early stages of leaching due to porewater washout. There were no significant differences in leachate EC between treatments after four pore volumes leached. Leachate EC of all treatments significantly decreased between one and 400 pore volumes leached.

Carbonate concentration was initially significantly lower in U leachate than for any other treatment; this difference became non-significant by three pore volumes leached, and leachate carbonate concentrations were not significantly different between any treatments after nine pore volumes (Fig. 3). Leachate carbonate concentration of all treatments except single layer U decreased significantly between one and 16 pore volumes leached. Leachate bicarbonate concentrations of all dual layer treatments were significantly lower than that of single layer treatments between one and four pore volumes leached (Fig. 3). Fig. 4 appears to indicate that some of the bicarbonate present in single layer leachate is converted to carbonate during leaching in dual layer treatments. No significant differences in leachate bicarbonate concentrations existed after six pore volumes leached. Leachate bicarbonate concentrations of all treatments except C–U and CU significantly decreased between one and 16 pore volumes leached.

Contributions to alkalinity in U and C single layer treatments differs substantially, with over half the initial alkalinity present in U

leachate coming from hydroxide, and around 75% of the total initial alkalinity present in C leachate coming from carbonate (Fig. 4). Total alkalinity was initially higher for C, U–C, and UC treatments than U, C–U and CU treatments. Treatments with the same layering order show similarities in leachate alkalinity contributions.

Na, S, and Al were the three elements present in the highest concentrations in leachates. This is a consequence of caustic soda used in the Bayer process to dissolve gibbsite and boehmite, which also liberates S as sulfate from impurities in the feed bauxite. Although present in significant concentrations (20–830 mg/L), sulfate behaviour is not relevant to the neutralisation behaviour of these systems and will not be discussed further.

Dual layer leachate Al concentrations were initially significantly lower than U leachate and significantly higher than C leachate; however, there were no significant differences in Al concentration between dual layer leachates and single layer leachates after six pore volumes (Fig. 5). After nine pore volumes leached, there were no significant differences in Al concentration between U and C leachate. Leachate Al concentrations followed trends for leachate pH, which fits with predictions of Al partitioning between gibbsite and free Al (as $Al(OH)_4^-$) described elsewhere for bauxite residue [20].

Leachate Na concentrations were initially significantly higher for C, U–C, and UC treatments than for U, C–U, and CU treatments, which may be due to porewater displacement as carbonated
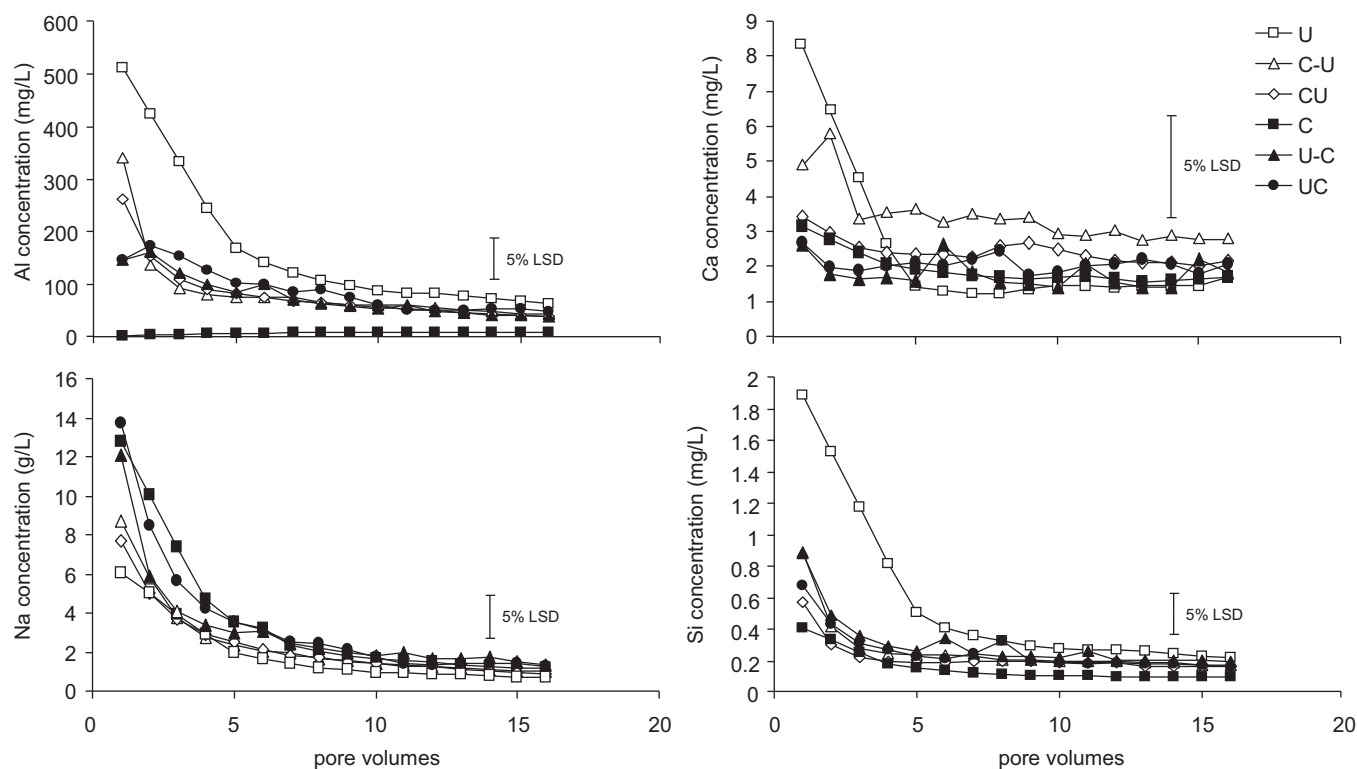
Fig. 5. Leachate Al, Ca, Na, and Si concentrations during continuous leaching. Data points represent the mean of three replicates interpolated to standard pore volumes. 5% LSD bar represents 5% least significant difference (time × treatment) from repeated measures ANOVA. Initial porewater concentrations in uncarbonated residue were Al: 1200 mg/L; Ca: below detection limit; Na: 14 g/L; Si: 3 mg/L. Initial porewater concentrations in carbonated residue were Al: 4 mg/L; Ca: 1 mg/L; Na: 36 g/L; Si: 2 mg/L.

residue contains higher initial porewater concentrations of Na. There were no significant differences between treatments after four pore volumes for Na (Fig. 5).

Cross layer leaching significantly reduced leachate Si concentrations below that of U leachate for between one and four pore volumes (Fig. 5). Leaching behaviour for Si does not appear to be controlled by the residue leached before exit of leachate from the columns, which implies that mineral precipitation/dissolution (predominantly sodalite) controls leachate chemistry rather than porewater displacement.

Calcium concentrations were significantly higher in U leachate than in other treatment leachates after one pore volume; after which no treatments experienced any significant differences in leachate Ca concentration (Fig. 5). This indicates that mineral dissolution, probably of TCA at the elevated pH initially observed in uncarbonated residue leachate, is occurring in response to leaching, as initial porewater Ca concentrations in uncarbonated residue were below the detection limit. Calcite and TCA have been previously identified as solubility controlling phases for calcium in leached bauxite residue mud [20]. Calcium leaching appeared to reach a steady state in all treatments after five pore volumes leached, at concentrations well above the detection limit of 0.35 mg/L.

The leaching behaviour of several transition metals (Cr, Cu, Mo, V) and other elements of interest (As, Ga, La, U) present in considerable concentrations in single layer residue leachates was also followed to identify potential risks associated with implementing dual layer treatments. This is particularly relevant in remediation of old uncarbonated deposits. For all transition metals and elements of interest except Mo and U, carbonation significantly reduced initial leachate concentrations from single layer uncarbonated residue (Figs. 6 and 7). Leachate uranium concentrations are initially higher in C, U–C and UC treatments than U, C–U and CU; however, the difference in uranium concentrations in dual layer treatments

becomes non-significant by two pore volumes leached. This initial difference is probably due to complexation of uranium by carbonate and bicarbonate resulting in increased mobility for treatments containing carbonated residue, analogous to a carbonate heap leach method [21]. An explanation of Mo leaching behaviour is limited by the lack of an identified solubility controlling phase (cf. [20]) but is possibly related to the pH-dependence of molybdate adsorption.

Arsenic, chromium, copper and gallium leaching displayed similar behaviour, with all dual layer treatments exhibiting significantly lower leachate As, Cr, Cr and Ga concentrations than U leachate for between one and four pore volumes leached. Gallium leaching behaviour was similar to that of Al leaching because Ga substitutes for Al in many Al-bearing minerals, and is released into solution during the Bayer process as $Ga(OH)_4^-$, which behaves similarly to $Al(OH)_4^-$ under alkaline conditions [22]. Lanthanum leaching was significantly lower for dual layer treatments than single layer uncarbonated residue for between one and three pore volumes leached (Fig. 7). For the purpose of our discussion, the control on La mobility (mineral dissolution, desorption, etc.) is not important. However, La behaviour did not mimic P leaching behaviour and the solubility of $La(OH)_3$ would be expected to decrease with increasing pH, while the solubility of La-carbonates would be expected to decrease with increasing carbonate concentration. Control of La leaching is therefore unlikely to be due to dissolution of La phosphates, hydroxides, or carbonates. Vanadium leaching followed Na leaching patterns, although explanation of this behaviour is also limited by the fact that previous studies have not identified a mineral controlling V solubility. Minerals controlling solubility of the transition metals and elements of interest discussed above, as well as the possible contribution of adsorption to leaching behaviour of these elements, requires further investigation by more sensitive analytical techniques (synchrotron-based μXRF and XRD of leached and unleached thin sections, for example). Differences in leachate element concentrations between all treatments became
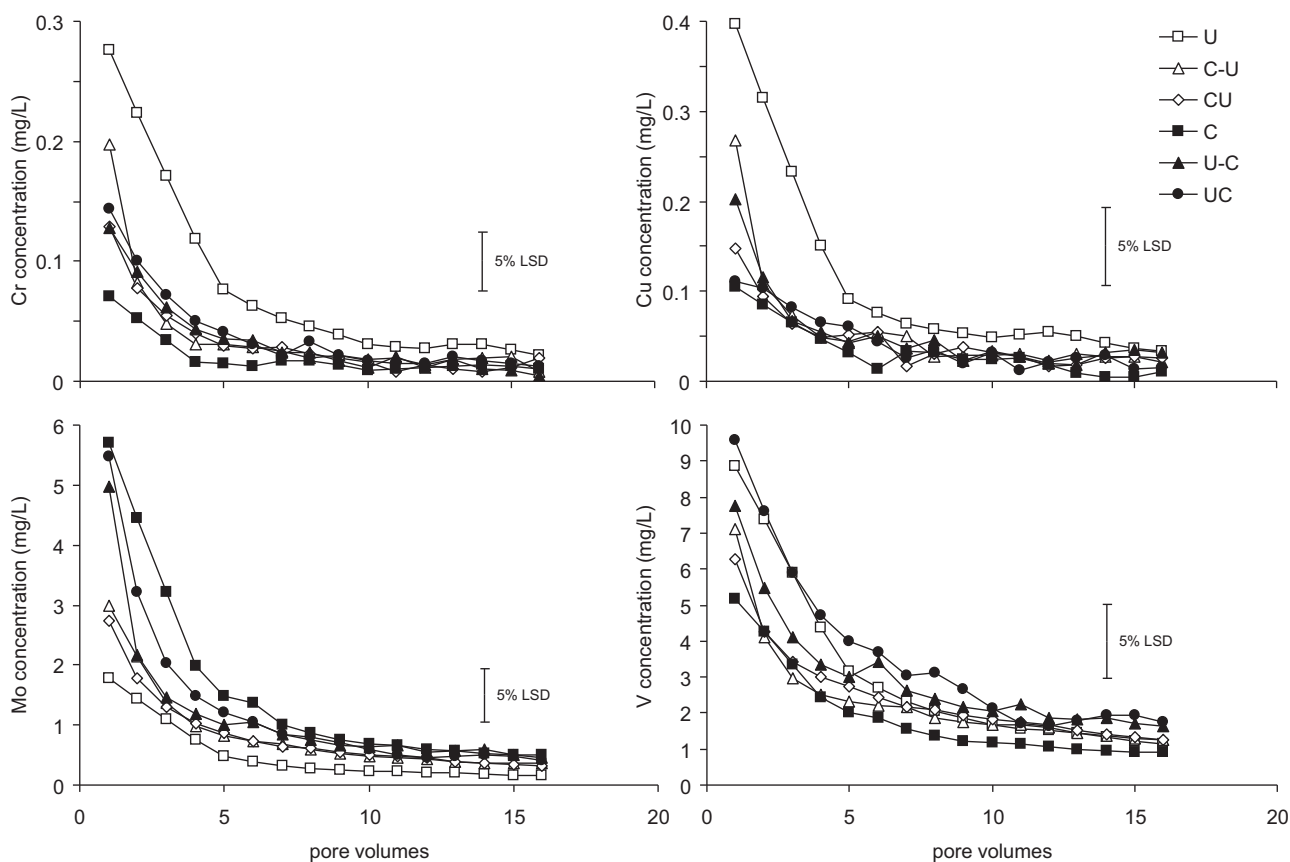
Fig. 6. Leachate Cr, Cu, Mo, and V concentrations during continuous leaching. Data points represent the mean of three replicates interpolated to standard pore volumes. 5% LSD bar represents 5% least significant difference (time × treatment) from repeated measures ANOVA.

non-significant between four and ten pore volumes leached (four: La, U; five: Cu, V; six: Cr; seven: As, Mo; ten: Ga).

After 16 pore volumes leached, there were no significant differences in leachate element concentrations between any treatments, despite there still being significant differences between treatments in leachate pH (Fig. 3). The initially high values of most analytes combined with similar observed porewater velocities in treatments suggest that dissolution/release kinetics may be slower than the flow rate employed in this study, resulting in significant initial differences between treatments (after the 57 h equilibration period) which diminish rapidly over time as leaching continues.

At no time during the entirety of leaching did dual layer leachate concentrations for any element analysed exceed the highest leachate element concentration observed for single layer treatments. Field-scale trials may therefore be performed with the knowledge that they are 'risk-neutral' under similar flow conditions; that is, that leachate quality is unlikely to deteriorate. Although a low flow rate (5 mL/h) was used in this study, the influence of chemical or physical nonequilibrium may alter results in the field where lower flow rates are likely.

3.2. Solids mineralogy

Changes in dawsonite, calcite, TCA, and sodalite contents were probably caused by dissolution or precipitation which contributed to changes in leachate chemistry; other minor changes in mineral contents are attributed to translocation of particles and are therefore not presented here. As expected, TCA and sodalite dissolve during leaching, and are likely to maintain high pH in uncarbonated bauxite residue leachate (Table 2). This is supported by leachate data for between one and ten pore volumes leached, with significantly higher hydroxide and aluminate concentrations in uncarbonated residue than for all other treatments, which contain carbonated residue (Figs. 3–5). Dawsonite, sodalite, and calcite were observed to dissolve in carbonated residues, and are likely to maintain moderately high pH in carbonated leachates (Table 2). Dissolution of dawsonite and calcite in carbonated residue is consistent with leachate carbonate concentrations being significantly higher in carbonated residue leachate than uncarbonated residue leachate for between one and three pore volumes leached (Fig. 3).

Leaching uncarbonated residue with carbonated leachate had only a small effect on TCA dissolution; however, it does appear to supply the carbonate/bicarbonate required to transform TCA to calcite and dawsonite as per Eqs. (2)–(4). Dawsonite is stable in 1 M sodium carbonate and calcium carbonate solutions at 50 °C and pH 9–12 [23], but becomes unstable once CO_2 fugacity (i.e. solution carbonate) drops below 0.1 in seawater at 40 °C [24]. Dawsonite therefore probably dissolves after precipitation according to Eq. (3) during extended leaching as carbonate and bicarbonate reserves

Table 2
Change in mineral:anatase ratio relative to unleached residue samples (%), rounded to nearest 10%. Mineral:anatase ratio is calculated by areas under the mineral primary peak in sample X-ray diffraction patterns. N/P indicates mineral was not initially present and did not precipitate.

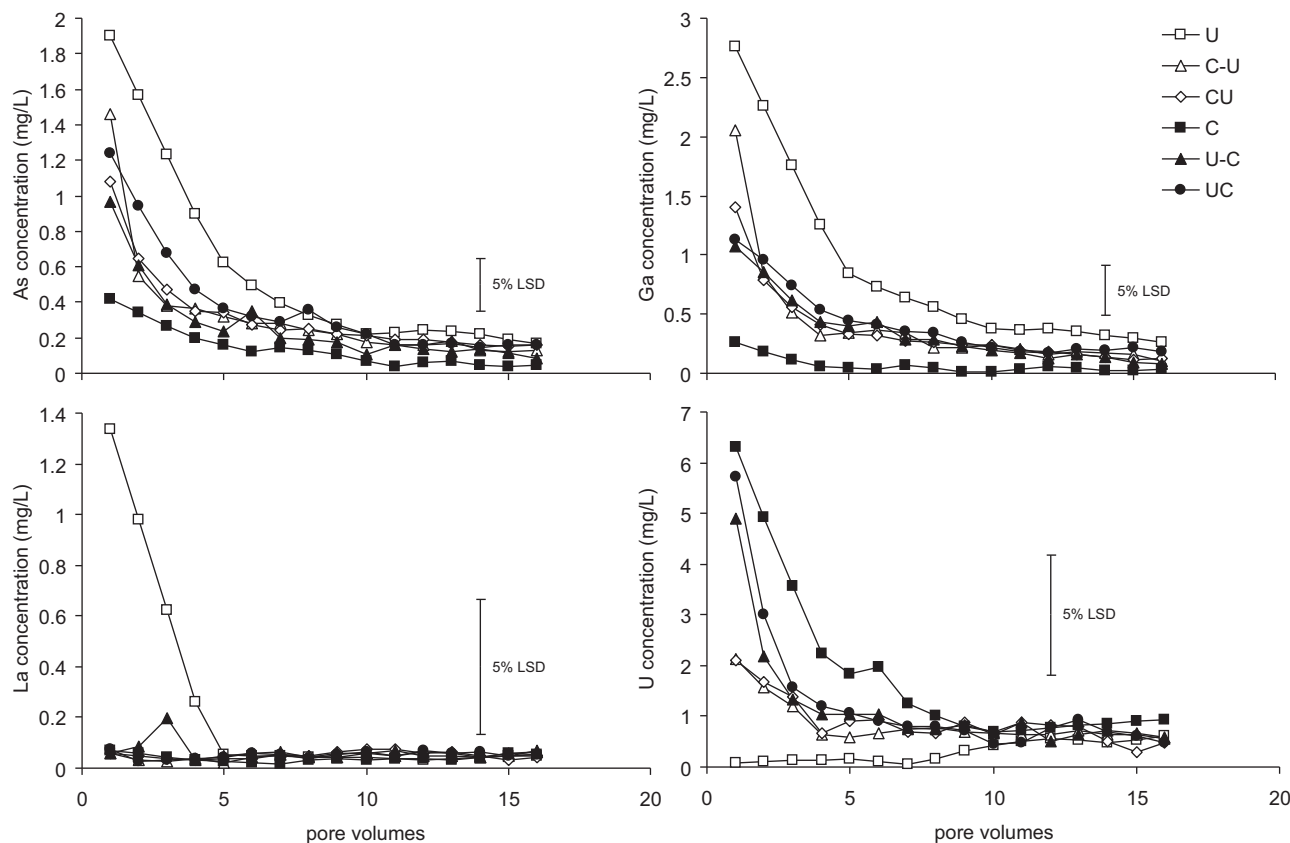| Treatment	Layer	Calcite	Dawsonite	Sodalite	TCA
U	U	0	N/P	−20	−30
C–U	U	40	N/P	0	−30
CU	U	30	N/P	−20	−20
C	C	−30	−100	−40	N/P
U–C	C	0	−100	−10	N/P
UC	C	−20	−100	−20	N/P

Fig. 7. Leachate As, Ga, La, and U concentrations during continuous leaching. Data points represent the mean of three replicates interpolated to standard pore volumes. 5% LSD bar represents 5% least significant difference (time × treatment) from repeated measures ANOVA.

are exhausted. Note that the (bi-)carbonate present in carbonated leachate that is represented in Eqs. (2)–(4) may be a product of both initial porewater chemistry following carbonation (Eqs. (5) and (6)) and dawsonite and calcite dissolution in carbonated residue.

Sodalite was stabilised in uncarbonated residue when exposed to carbonated residue leachate (Table 2); this may be due to the higher Na and carbonate/bicarbonate contents of carbonated residue leachate compared to uncarbonated residue leachate (Figs. 3–5), because the solubility of sodalite decreases as solution Na_2CO_3 concentration increases [25]. Some of the carbonate which stabilises sodalite may be removed by precipitation as calcite as per Eq. (2) in the CU treatment during the initial equilibration period, accounting for the larger change in calcite:anatase and sodalite:anatase ratios in the U layer of the CU treatment compared to the C–U treatment (Table 2). Initial observed carbonate concentration for CU was lower than for the C–U treatment; however, this difference was not significant (Fig. 3).

Calcite and sodalite in carbonated residue appear to be partially stabilised when exposed to uncarbonated leachate, whereas dawsonite completely dissolves. This may be due to the high pH of uncarbonated leachate (11.5–13 for the majority of leaching), at which values dawsonite could reasonably be expected to dissolve; however, calcite and sodalite, which buffer at around pH 8.5, would be expected to be less soluble at higher pH and carbonate concentration than when being leached with deionised water.

Error may arise in the use of mineral:anatase ratios for semiquantitative analysis due to anatase particle translocation (anatase can exist as particles of diameter < 0.1 μm) and the presence of different mineral assemblages in residue pre- and post-leaching causing alteration of relative peak areas. This is difficult to eliminate; however, thin section microscopy and energy dispersive spectrometry analysis of leached residue samples at various depths

along leaching columns did not indicate significant accumulations of Ti in particular layers (data not shown).

3.3. Conclusions

Results from this small-scale column leaching study indicated that cross layer leaching is an effective treatment for the neutralisation of uncarbonated bauxite residue. Leachate pH remained significantly different between uncarbonated residue and dual layered residue treatments until 400 pore volumes leached. Initial porewater (bi-)carbonate content, as well as that which results from dawsonite and calcite dissolution is likely to have caused this observed pH difference between treatments. The behaviour of TCA was consistent with previous studies [5,7], with TCA dissolution linked to elevated leachate pH.

No element analysed exhibited a significantly higher leachate concentration in dual layer treatments than the highest leachate concentration observed for that element in single layer treatments. Leachate concentrations of As, Cr, Cu, Ga and La were immediately and significantly reduced in dual layer treatments compared to uncarbonated residue treatments. Significant reductions in leachate concentrations of several transition metals and other elements of interest were observed in dual layer treatments compared to uncarbonated residue over the first four pore volumes of leaching, representing a considerable and immediate improvement in leachate quality for uncarbonated deposits remediated by leaching from an overlying carbonated layer.

The implementation of dual layer leaching in the field therefore represents potential improvement upon current practices. However, field-scale trials of this remediation approach are also required to evaluate the influence of additional factors beyond the scope of this study, including variable flow cycles and leaching rates

induced by seasonal rainfall and evaporation patterns. Macropore flow resulting from surface cracking during residue drying can occur; and rainwater chemistry, which is typically slightly more acidic and saline than deionised water, may also affect reactions observed in this study.

Acknowledgments

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