Hydraulic and biotic impacts on neutralisation of high-pH waters

Helena I. Gomes [a,*], Mike Rogerson [a], Ian T. Burke [b], Douglas I. Stewart [c], William M. Mayes [a]

[a] School of Environmental Sciences, University of Hull, Cottingham Road, Hull, HU6 7RX, UK
[b] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[c] School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK

HIGHLIGHTS

- Cascade systems lower pH and alkalinity more successfully than ponds.
- Biofilms promote neutralisation in all systems due to CO_2 from respiration.
- Photosynthesis and respiration in biofilms induce a diurnal effect at high pH.
- The hydraulic configuration has more influence on neutralisation than biofilms.

GRAPHICAL ABSTRACT
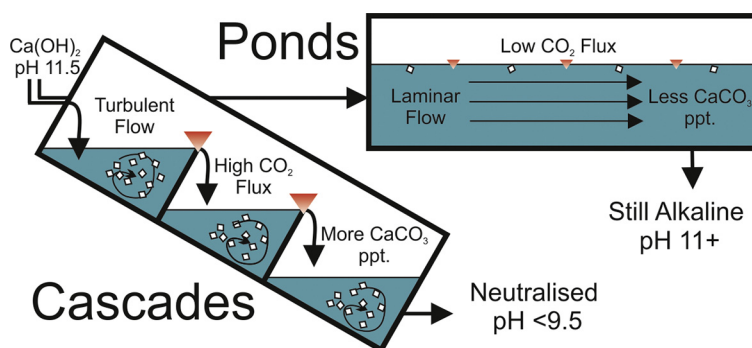
ARTICLE INFO

ABSTRACT

The management of alkaline (pH 11–12.5) leachate is an important issue associated with the conditioning, afteruse or disposal of steel slags. Passive in-gassing of atmospheric CO_2 is a low cost option for reducing $Ca(OH)_2$ alkalinity, as $Ca(OH)_2$ is neutralised by carbonic acid to produce $CaCO_3$. The relative effectiveness of such treatment can be affected by both the system geometry (i.e. stepped cascades versus settlement ponds) and biological colonization. Sterilized mesocosm experiments run over periods of 20 days showed that, due to more water mixing and enhanced CO_2 dissolution at the weirs, the cascade systems (pH $11.2 \rightarrow 9.6$) are more effective than settlement ponds (pH $11.2 \rightarrow 11.0$) for lowering leachate alkalinity in all the tested conditions. The presence of an active microbial biofilm resulted in significantly more pH reduction in ponds (pH $11.2 \rightarrow 9.5$), but had a small impact on the cascade systems (pH $11.2 \rightarrow 9.4$). The pH variation in biofilm colonized systems shows a diurnal cycle of 1 to 1.5 pH units due to CO_2 uptake and release associated with respiration and photosynthesis. The results demonstrate that, where gradient permits, aeration via stepped cascades are the best option for neutralisation of steel slag leachates, and where feasible, the development of biofilm communities can also help reduce alkalinity.

1. Introduction

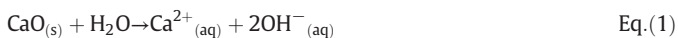In recent years, there has been a growing interest in passive treatment of sites impacted by highly alkaline leachates, mirroring the use of constructed wetlands to treat acid mine drainage (Buckley et al., 2016; Higgins et al., 2015; Higgins et al., 2017; Mayes et al., 2009b). Wetlands are a low-cost approach that can improve water quality parameters, such as pH, alkalinity, total dissolved solids, and also lower metal concentrations in alkaline leachates (Banks et al., 2006; Buckley et al., 2016; Higgins et al., 2015; Mayes et al., 2009b; Valipour and Ahn, 2015). Wetland-based passive remediation has been

* Corresponding author.
  E-mail address: h.gomes@hull.ac.uk (H.I. Gomes).

demonstrated at some alkaline waste legacy sites and shown promise in leachate neutralisation (Banks et al., 2006; Mayes et al., 2009a). Understanding the physical, chemical and biological processes that occur in wetlands, and their relative importance in altering leachate chemistry is essential for optimising their design and operation.

Steel slags are a high volume (170–250 Mt. a^{-1}) byproduct associated with steelmaking much of which is stored, at least temporarily, in land based repositories (Gomes et al., 2016). Hydration of CaO and Ca$_2$SiO$_4$ phases within the slag (Eqs. (1) and (2)) results in the production of highly alkaline leachates (pH 11–12.5; Mayes et al., 2008).

$$CaO_{(s)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad \text{Eq.(1)}$$

$$Ca_2SiO_{4\ (s)} + 3H_2O \rightarrow 2Ca^{2+}_{(aq)} + H_3SiO_4^- + 3OH^-_{(aq)} \qquad \text{Eq.(2)}$$

where steel slag leachate emerges to atmosphere this often is associated with precipitation of CaCO$_3$ in tufa like systems (Mayes et al., 2008; Riley and Mayes, 2015), due to interaction with atmospheric CO$_2$, resulting in the net reaction (Eq. (3)) (Boylan et al., 2016; Clark et al., 1992; Greenwood and Earnshaw, 2012):

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} + CO_{2(g)} \rightleftarrows + Ca_2CO_{4(s)} + H_2O_{(1)} \qquad \text{Eq.(3)}$$
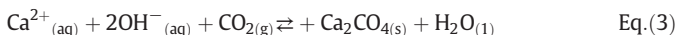
So aeration of Ca(OH)$_2$ containing steel slag leachate potentially offers a mechanism for pH neutralisation prior to discharge. Microbial activity can also act to enhance this effect due to CO$_2$ release to the leachate from biomass during respiration (Buckley et al., 2016; Higgins et al., 2015; Mayes et al., 2009a). Also, the emergent vegetation and organic debris provides a high specific surface area for nucleation of carbonate precipitation reactions (Vacca et al., 2005). However, despite the microbial diversity in steel slag leachate (Roadcap et al., 2006), the establishment of viable biofilm communities and plants in high pH water is difficult (Higgins et al., 2016), and no plant life is observed until the pH has been partially reduced (pH < 10; Mayes et al., 2009b). The importance of biological mechanisms, and particularly their diurnal and seasonal variations, are not well understood and this is currently an impediment to full-scale system adoption.

Naturally occurring alkaline springs can provide valuable insight into the conditions under which rapid CaCO$_3$ precipitation can occur. Natural systems that buffer pH most rapidly do not resemble pond systems, but rather stepped cascades (Veysey and Goldenfeld, 2008) in which flow velocity is a primary control on CaCO$_3$ precipitation rates, and thus the effluent water chemistry (Dreybrodt et al., 1997; Hammer et al., 2010; VeyseyII et al., 2008). Therefore, treatment systems optimized for Ca(OH)$_2$-rich steel slag leachates may function better if they are designed to resemble natural tufa cascade systems rather than the pond systems often employed in constructed wetlands.

This study investigates the hydrochemistry of steel slag leachate treatment in mesocosm experiments using two different hydraulic settings – settlement ponds and stepped cascades. The relative importance of physicochemical and biomediated processes on CaCO$_3$ precipitation was investigated by undertaking experiments in both configurations with and without biofilm colonization. The objectives were to understand the controls on pH neutralisation in each system and thus to make recommendations for the effective design of passive treatment schemes for real-world alkaline leachates.

2. Materials and methods

2.1. Steel slag leachate

Basic oxygen furnace (BOF) steel slag was collected from Yarborough, Scunthorpe, UK (53°35′07.3″N 0°35′35.5″W) on December 2014 and April 2015. Steel slag leachate was produced in the laboratory by leaching steel slag with deionized water (15 MΩ cm ELGA Purelab water). Leachate was prepared in a 100 L vessel containing deionized

water and slag in the ratio of 10:1 by weight. The vessel was mixed by extracting water from the bottom and returning it to the top using a Hozelock Cyprio pump. After 48 h the pH value stabilized at 11.2 ± 0.1, and the conductivity was 826 ± 258 μS cm^{-1} (n = 80), which are similar to leachate springs in the field (11 < pH < 11.5; Mayes et al., 2008). Periodically during the experiment, fresh BOF slag was added to the 100 L vessel to maintain leachate composition. After conditioning in contact with slag, the leachate was transferred to a 100 L storage vessel before use in mesocosms. Table 1 presents the average composition of the steel slag leachate, and compares it with water at the site where the slag originated (Scunthorpe, UK).

2.2. Mesocosm experiments

Pond and cascade systems were established to have the same internal volume of water (0.04 m^3) and the same surface area of the stored water (0.22 m^2). The pond configuration consisted of a Perspex box 102 cm long, 22 cm wide and 16.5 cm tall (Fig. 1), whereas the cascade configuration is 32 cm tall, has two steps at equal distance (30 cm) and an 8.4° inclination. Chalk limestone gravel (4.5 kg autoclaved for 30 min at 135 °C, 1 cm < diameter < 2.5 cm) was placed in the bottom of the ponds and cascades to provide a suitable surface for calcium carbonate precipitation (Rogerson et al., 2008a).
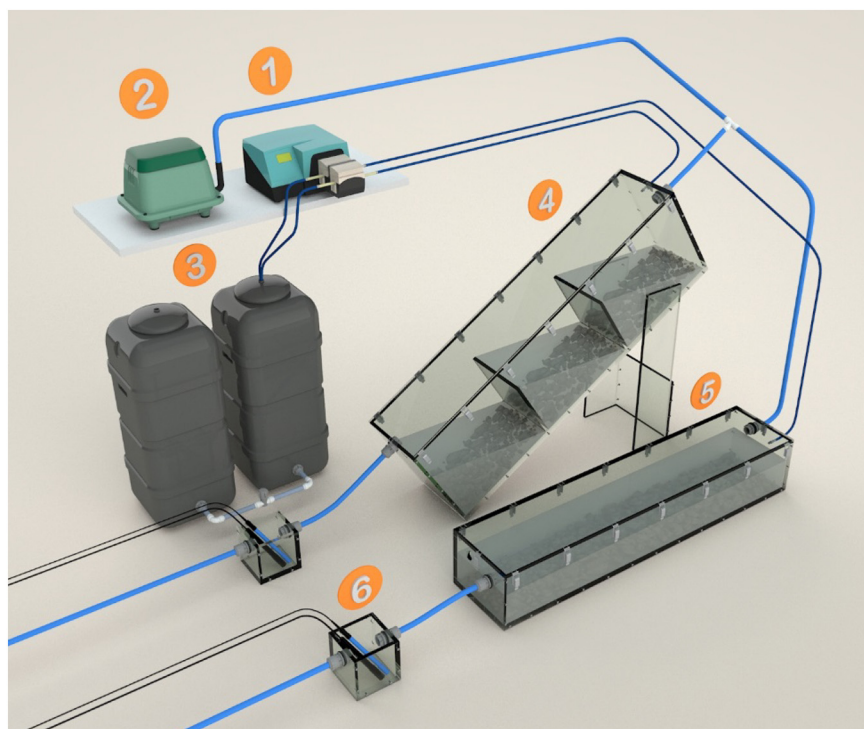
Mesocosms were prepared in duplicate. The sterilized experiments were initially filled with sythetic slag leachate, whereas the biofilm experiments were primed with lower pH leachate (Table 1) before the start of the tests. The pond/cascades were closed by transparent perspex lids to prevent colonization by unwanted microbes, and air was circulated under the lid using an HIBLOW HP40 pump. Flow was commenced by continuously injecting synthetic steel slag leachate into both the

Table 1
Composition of the synthetic steel slag leachate used in the mesocosm experiments and during the biofilm incubation and comparison with the range of values found in Scunthorpe and in steel slag leachate in the UK (Hull et al., 2014; Mayes et al., 2008).

Determinand	Synthetic slag leachate (average values, n = 80)	Synthetic slag leachate used during initial biofilm colonization (average values, n = 3)	Water samples from Scunthorpe (average values, n = 15)	Range of reported UK leachate values
pH	11.2 ± 0.1	10.6 ± 0.2	11.1 ± 1.1	10.3–11.9
Conductivity (μS cm^{-1})	826 ± 258	734 ± 132	2554 ± 2432	438–7879
Major elements (mg L^{-1})				
Ca	93 ± 24	90 ± 10	10.7 ± 10.2	11–239
Mg	0.2 ± 0.2	1.5 ± 0.5	5.8 ± 9.9	1–12
K	4.3 ± 2.9	12.4 ± 4.4	41.1 ± 42.9	18–293
Na	45 ± 36	50.3 ± 22.5	300 ± 314	24–83
Al	1.4 ± 0.4	0.6 ± 0.1	0.6 ± 1.2	0.013–0.5
Si	3.6 ± 2.2	6.0 ± 0.2	3.9 ± 4.8	0.203–7.7
Sr	0.1 ± 0.1	0.2 ± 0.01	0.3 ± 0.6	0.2–4
Trace elements (μg L^{-1})				
As	<15	<15	35 ± 12	na
Ba	25 ± 21	14.7 ± 0.3	19 ± 19	4.6–42.5
Cd	<0.5	<0.5	<0.5	<0.1–0.3
Cr	<1	<1	<1	<5–22
Cu	<0.3	<0.3	<0.3	<5–70
Fe	<0.6	<0.6	42 ± 27	54–920
Ga	<2	<2	12 ± 11	na
Li	5 ± 2	6 ± 0.4	80 ± 68	4.4–822
Mn	<0.1	<0.1	<0.1	5.4–160
Mo	<3	<3	<3	2.8–45
Ni	<2	<2	<2	0.3–70
Pb	<9	3.4 ± 2.2	<9	<5–70
V	83 ± 64	109 ± 3	68 ± 87	1.6–120
Zn	<2	<2	<2	2–40

na – not available.

Fig. 1. Mesocosm experimental setup: ① peristaltic pump, ② air pump, ③ steel slag leachate tanks, ④ stepped cascade, ⑤ rectangular pond, ⑥ monitoring sensors (pH and conductivity).

ponds and cascades by a peristaltic pump (Series 300, Watson-Marlow, Falmouth, UK) and overflowed into an outlet pipe. The leachate flow rate was 6 mL min^{-1} for both treatments which gave a pond/cascade residence time of 4.6 days. This is consistent with similar applications for constructed wetlands for analogous mineral rich or high ionic strength waters (Kusin, 2013; Zahraeifard and Deng, 2011). A single cascade experiment was conducted where there was no ventilation under the lid for the first 15 days. All pond and cascade experiments were run in a windowless, air-conditioned laboratory (ambient air temperature 20 ± 1 °C). Biofilm experiments were subjected repeatedly to 12 h light (6.82 klux; Thorn Lopak 250 W HPS-T Na lamp, 10 pm to 10 am) and 12 of darkness. Detailed information on the experimental conditions can be found in SI section S1.

2.3. Chemical analysis

Electrodes were placed in the effluent of the ponds/cascades to continuously monitor pH and electrical conductivity (EC), using Pinpoint pH and EC—freshwater hardness monitors, American Marine Inc. (Fig. 1). The pH and EC data were logged every 10 min via a webcam connected to a computer running WebCamImageSave software and then transferred into a text file (txt) by Watchman software, following the approach of Rogerson et al. (2008b). The influent pH and conductivity were also measured in a daily sample in a Jenway 3540 pH and conductivity meter. Total and carbonate alkalinity was measured daily in filtered (0.22 μm, MCE Membrane Millex HA) 50 mL samples from the leachate influent and the effluent from the ponds/cascades using a Mettler Toledo T50 titrator (Method HU40). At the same time, 10 mL water samples were taken, filtered (0.22 μm, MCE Membrane Millex HA) and preserved with a few drops of HNO$_3$ (Romil SpATM Super Purity Acid). Aqueous trace metal concentrations were measured using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A certified reference material (CRM-ES AT-1529, lot number 1319108) was used for quality control. Mineralogy of precipitated phases was determined by XRD on a PANAlytical Empyrean diffractometer operating in Bragg-Brentano

geometry using copper Kα1 radiation (λ = 1.540546 Å), and a PIXEL detector.

2.4. Data analysis

Analysis of variance (ANOVA) was carried out in SPSS Statistics 22 (IBM). The leachate composition varied slightly during the first three days after fresh slag was added to the leachate preparation vessel, so data from the period when this leachate was injected into the ponds/cascades is omitted from the statistical analysis (a similar equilibration period for BOF slag was observed by De Windt et al. (2011). Before the ANOVA, the assumptions were evaluated (Levene's test) and determined to be satisfied, particularly the equality of variance and the data distribution (approximately normal). The geochemical analysis was undertaken using PHREEQC Interactive 3.3.7–11,094 (USGS) and the LLNL database.

3. Results

3.1. Mesocosm experiments

Fig. 2 displays the pH and conductivity variation in the mesocosm experiments. In the sterilized systems (Fig. 2a), the pH values in the effluent of the cascades are, in most cases, 1–1.5 pH units lower than those measured in the ponds. The average pH of the sterilized pond effluents was 11.0 ± 0.1 (n = 7365), while that of the cascade effluents was 9.6 ± 0.5 (n = 6015). In a parallel unventilated cascade test, the pH values were initially similar to the sterilized pond experiments, until ventilation was commenced, when the pH dropped to values similar to those observed in the other sterilized and fully ventilated cascade tests (SI Fig. S1).

The pH behaviour of biofilm colonized pond and cascade systems (Fig. 2b) is strikingly different to the sterilized systems (Fig. 2a), due to a well-defined diurnal cycle with minima occurring at 3 am and maxima occurring at 3 pm in both hydraulic settings. The average pH in the colonized pond effluents during the day was 10.0 ± 0.6 (n = 4467), while in the cascade effluents it was 9.4 ± 0.6 (n = 3894). The average
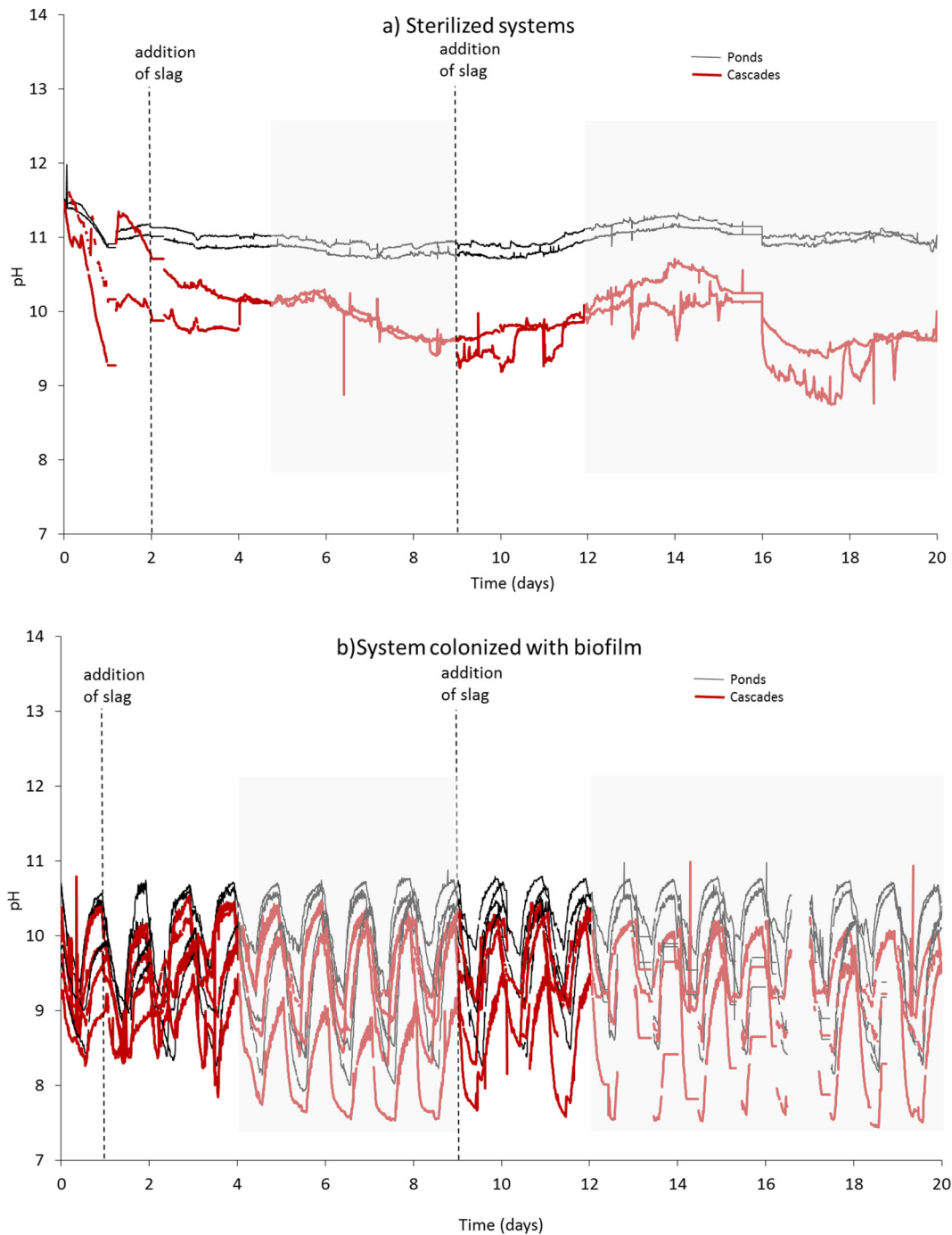
Fig. 2. pH values in the a) sterilized and b) colonized mesocosm experiments. The grey areas mark the data used for the analysis after a 3 day equilibration period after the addition of fresh slag.

night time pH in the pond effluents was 9.5 ± 0.7 ($n = 4478$) and in the cascade effluents was 8.9 ± 0.7 ($n = 3894$) (Fig. 3). The magnitude of the diurnal pH cycle in both colonized systems was between 1 and 1.5 pH units, and there was a longer term trend towards lower pH values during the experiment.

Dissolved inorganic carbonate (DIC) was estimated by deduction of OH^- and other dissolved alkali species (e.g. Al, Si) from the total alkalinity (USGS, 2012). The DIC in the influent water was 1.4 ± 0.4 mmol L^{-1} ($n = 28$) (Fig. 4 and SI Figs. S2, S5 and S8). The concentration of DIC in the influent varied during the experiments (SI Figs. S5 and S8). The DIC in the sterilized pond effluents was 0.2 ± 0.1 mmol L^1 ($n = 56$), while in the cascade effluents it was 0.1 ± 0.1 mmol L^1 ($n = 46$). The average

DIC in the colonized pond effluents during the day was 0.3 ± 0.1 mmol L^1 ($n = 40$), while in the colonized cascade effluents was 0.2 ± 0.1 mmol L^1 ($n = 40$). The average night time DIC in the pond effluents was 0.3 ± 0.1 mmol L^1 ($n = 72$) and in the cascade effluents was 0.2 ± 0.1 mmol L^1 ($n = 61$).
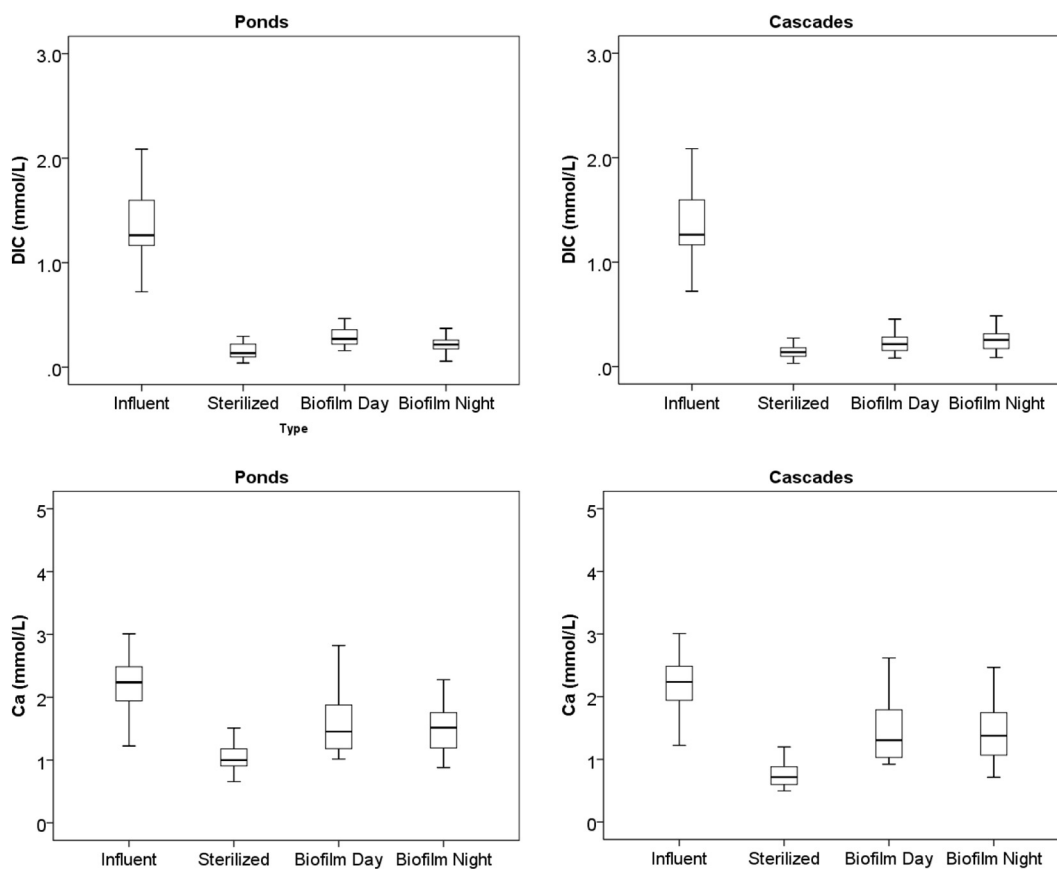
The average calcium concentration in the in the influent water was 2.5 ± 0.8 mmol L^{-1} (100.5 ± 30 mg L^{-1}, $n = 28$) and it varied during the experiments (SI Figs. S4 and S6). In the sterilized pond effluents it was 1.1 ± 0.3 mmol L^{-1} (42.5 ± 10.8 mg L^{-1} $n = 56$), while in the cascade effluents it was 0.8 ± 0.2 mmol L^{-1} (30.4 ± 7.8 mg L^{-1}, $n = 46$). The average calcium concentration in the colonized pond effluents during the day was 1.6 ± 0.5 mmol L^{-1} (63.0 ± 18.5 mg L^{-1}, $n = 40$),
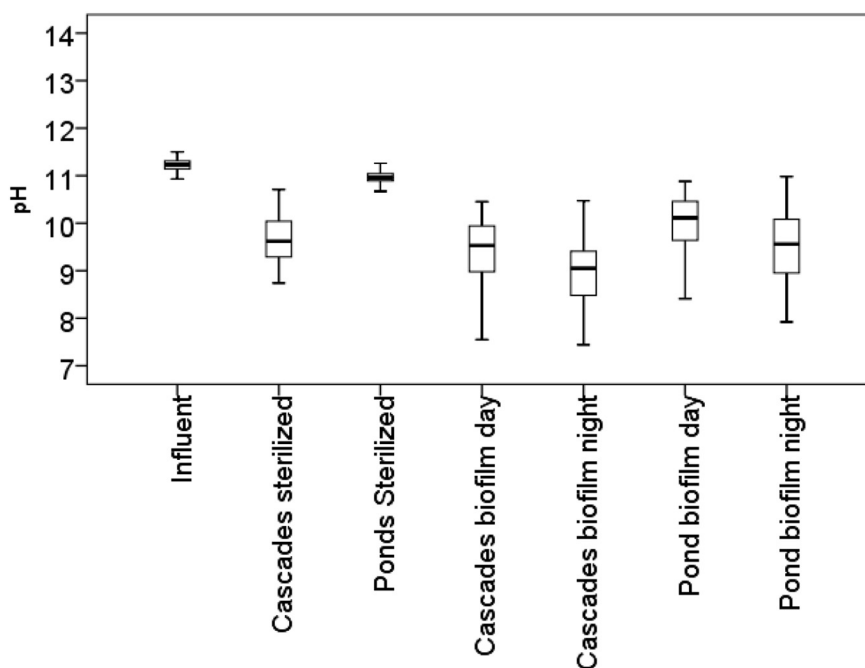
Fig. 3. Boxplots (data range, quartile range and median values) of the pH values measured in the influent and the effluent of the sterilized and colonized by biofilm ponds and cascades, during day and night in the biofilm experiments.

while in the cascade effluents it was 1.4 ± 0.5 mmol L^{-1} (57.2 ± 19.1 mg L^{-1}, n = 40). The average night time calcium concentration in the pond effluents was 1.5 ± 0.4 mmol L^{-1} (59.5 ± 15.0 mg L^{-1}, n = 72) and in the cascade effluents it was 1.5 ± 0.4 mmol L^{-1} (57.4 ± 16.3 mg L^{-1}, n = 61). Calcite was the only mineral precipitate detected in the experiments.

Fig. 4. Boxplots (data range, quartile range and median values) of estimated dissolved inorganic carbonate (DIC) in mmol L^{-1} and measured calcium concentrations (mmol L^{-1}) in the influent and the effluent of the sterilized and colonized ponds and cascades, during day and night in the biofilm experiments.

3.2. Hydrogeochemical modelling

Saturation indices (SI) were modelled using PHREEQC (USGS). Fig. 5 shows the boxplots of the saturation indices for calcite ($CaCO_3$) in the conditions tested. In all the experiments, the SI of calcite in the effluent is much lower than the influent, but typically oversaturated with respect to calcite. However, there were periods where the effluent is undersaturated with respect to calcite. In the colonized systems, during the night, the saturation index (SI) values of the first quartile were between -1.2 and -0.8 for cascades, and between -0.4 and -0.1 for ponds. In sterilized experiments and in colonized experiments during the day, cascades had the lowest saturation indices. Since the precipitation rate of calcite depends on SI (Inskeep and Bloom, 1985), a lower calcite precipitation is expected in biofilm systems.

3.3. Statistical (ANOVA) analysis

A two-way repeated measures ANOVA considered the type of system and presence of biofilm as factors for the totality of data. In the colonized systems, the factors were the type of system and the presence of light (day/night). The ANOVA determined that there was a statistically significant difference between cascades and ponds for all the parameters considered (Table 2). Also, there was a statistically significant difference between the equivalent sterilized and colonized systems for all the parameters considered, except carbonate alkalinity. The interaction effect – whether there is more impact on pH from colonization and hydraulics than could be explained by the two influences alone – was also significant for all parameters, but the values of η^2 are below 0.2, meaning that the interaction effect between the two factors explains little of the determinants variance. For total and carbonate alkalinity, the type of system is the most relevant factor, explaining 49% and 81% of the variance of those parameters, respectively.

In the colonized systems, all the parameters considered are significantly different between cascades and ponds and between day and night, except for calcium concentration (Table 2). The interaction effect between the type of system and the presence of biofilm (Table 2) is only significant for conductivity and total alkalinity, but the η^2 are below 0.2. The effect size of the type of system explains 60% of the carbonate alkalinity variance in the colonized systems. For calcium, the presence of

biofilm is the most important factor, as it can explain 56% of the variance.

4. Discussion

4.1. Effect of mesocosm geometry on leachate neutralisation

The influent water supplied to both sterilized cascade and pond systems had high pH and contained high concentrations of Ca^{2+} and dissolved inorganic carbonate (DIC). The Ca^{2+} was derived from slag leaching (Eqs. (1) and (2)), but the source of DIC is presumed to be due to CO_2 dissolution during the leachate make-up stage (Eq. (3)). Upon entering the mesocosm systems, where ample limestone surfaces were present to act at nucleation points, the saturation index in the effluent is reduced. Therefore, Ca^{2+} and DIC removal were observed in both the cascade and pond systems. Values estimated from water flow and average Ca^{2+} loss found that 30 g and 25 g calcite was precipitated during cascade and pond experiments respectively. However, pH reduction was only observed in the cascade mesocosm. This is attributed to high CO_2 ingress occurring in this system. This was supported by the observation in the parallel unventilated cascade experiment, where pH reduction did not occur until aerated conditions were established. CO_2 ingress is maximised in cascading systems due to the occurrence of reduced diffusive boundary layer thickness within film-flow sites (Dreybrodt et al., 1996) at the cascade overflows. Turbulent mixing of water at the overflows also helps prevent stagnant regions from forming, exposing the whole water mass to CO_2 ingress. In contrast, in the pond system, CO_2 dissolution can only occur via diffusion across the water surface, which limits the volume of water that can equilibrate with air (Chanson, 2004).

4.2. Effect of biofilms on leachate neutralisation

In the biofilm colonized systems, the difference between the cascade and pond systems is much more modest, and both types of mesocosm effectively reduced pH to <10. Less Ca^{2+} was removed, and therefore, less calcite will have formed in biofilm containing experiments than in sterilized systems, despite increased availability of DIC from respiration (estimates from water flow and average Ca^{2+} loss indicate that 18 g and
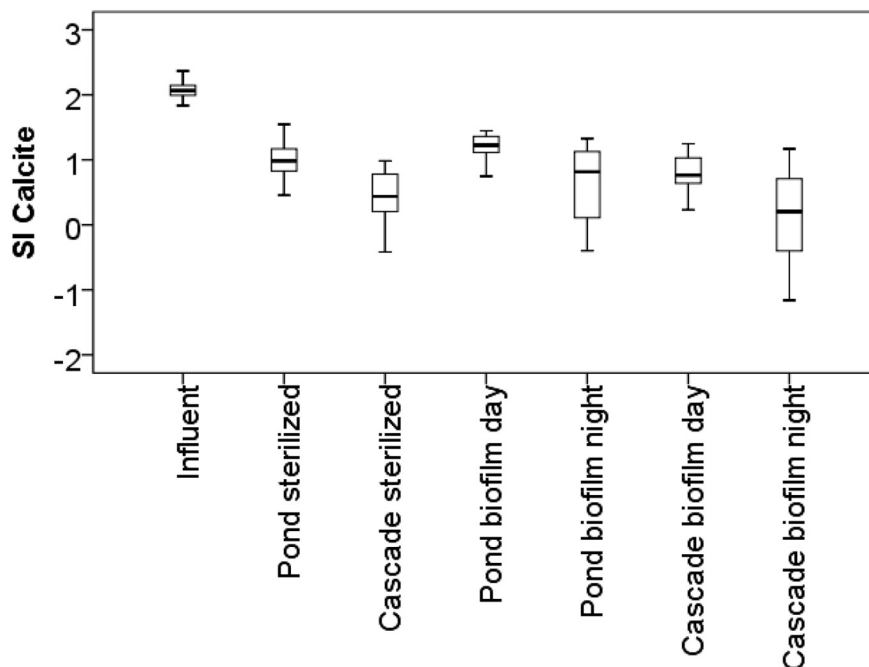

Fig. 5. Variation in the calculated saturation indices (SI) of calcite ($CaCO_3$) in the mesocosm experiments.

Table 2
Results of the two-way repeated measures ANOVA considering the totality of data and detailing for the biofilm colonized systems. Values marked in bold are statistically significant.

Sterilized and colonized systems

	Type of system (ponds/cascades)	Presence/absence of biofilm	Interaction effect
pH	$F_{(1, 5689)} = 17,685.507$, $\eta^2 = 0.37$, $\mathbf{p < 0.001}$	$F_{(1, 5689)} = 14,164.122$, $\eta^2 = 0.24$, $\mathbf{p < 0.001}$	$F_{(1, 5689)} = 1,680.463$, $\eta^2 = 0.04$, $\mathbf{p < 0.001}$
Conductivity	$F_{(1,13,455)} = 7864.844$, $\eta^2 = 0.37$, $\mathbf{p < 0.001}$	$F_{(1, 5803)} = 24,046.263$, $\eta^2 = 0.39$, $\mathbf{p < 0.001}$	$F_{(1, 5803)} = 2151.209$, $\eta^2 = 0.08$, $\mathbf{p < 0.001}$
Total alkalinity	$F_{(1, 46)} = 193.305$, $\eta^2 = 0.49$, $\mathbf{p < 0.001}$	$F_{(1, 46)} = 10.022$, $\eta^2 = 0.03$, $\mathbf{p < 0.001}$	$F_{(1, 46)} = 34.087$, $\eta^2 = 0.10$, $\mathbf{p < 0.001}$
Carbonate alkalinity	$F_{(1, 45)} = 1208.417$, $\eta^2 = 0.81$, $\mathbf{p < 0.001}$	$F_{(1, 45)} = 2.831$, $p = 0.099$	$F_{(1, 45)} = 47.471$, $\eta^2 = 0.05$, $\mathbf{p < 0.001}$
Calcium	$F_{(1, 45)} = 9.474$, $\eta^2 = 0.03$, $\mathbf{p = 0.004}$	$F_{(1, 45)} = 171.338$, $\eta^2 = 0.56$, $\mathbf{p < 0.001}$	$F_{(1, 45)} = 8.501$, $\eta^2 = 0.02$, $\mathbf{p = 0.006}$

Biofilm colonized systems

	Type of system (ponds/cascades)	Day/night	Interaction effect
pH	$F_{(1, 3583)} = 1,680.288$, $\eta^2 = 0.16$, $\mathbf{p < 0.001}$	$F_{(1, 3583)} = 2,265.159$, $\eta^2 = 0.12$, $\mathbf{p < 0.001}$	$F_{(1, 3583)} = 0.866$, $p = 0.352$
Conductivity	$F_{(1, 3668)} = 71.443$, $\eta^2 = 0.002$, $\mathbf{p < 0.001}$	$F_{(1, 3668)} = 1,299.864$, $\eta^2 = 1.34 \times 10^{-3}$, $\mathbf{p < 0.001}$	$F_{(1, 3668)} = 641.902$, $\eta^2 = 6.25 \times 10^{-4}$, $\mathbf{p < 0.001}$
Total alkalinity	$F_{(1, 39)} = 193.152$, $\eta^2 = 0.42$, $\mathbf{p < 0.001}$	$F_{(1, 39)} = 111.252$, $\eta^2 = 0.32$, $\mathbf{p < 0.001}$	$F_{(1, 39)} = 16.001$, $\eta^2 = 0.02$, $\mathbf{p < 0.001}$
Carbonate alkalinity	$F_{(1, 36)} = 346.256$, $\eta^2 = 0.60$, $\mathbf{p < 0.001}$	$F_{(1, 36)} = 133.355$, $\eta^2 = 0.25$, $\mathbf{p < 0.001}$	$F_{(1, 36)} = 2.053$, $p = 0.161$
Calcium	$F_{(1, 36)} = 2.850$, $p = 0.1$	$F_{(1, 36)} = 1.237$, $p = 0.273$	$F_{(1, 36)} = 0.983$, $p = 0.328$

17 g calcite precipitated in the cascade and ponds, respectively). Precipitation of $CaCO_3$ can reduce concentrations of co-precipitating divalent metals and constitute a natural sink of carbon, thereby contributing to carbon sequestration (de Montety et al., 2011).

The lower calcite precipitation may arise from the inhibition of crystal formation by dissolved organic matter associated with the biofilm itself (Lin et al., 2005), suggesting binding of dissolved organic mass onto growing crystal surfaces and dissolved ions. However, the saturation index (SI) of the solution did not increase. On the contrary, due to their lower pH, the SI of the biofilm colonized systems was lower becoming negative during the night. Calcite precipitation in hyperalkaline polluted sites possibly occurs via a reaction path involving organic carbon-Ca^{2+} complexes within the biofilm itself, in close analogy to naturally occurring carbonate-forming systems (Rogerson et al., 2010; Saunders et al., 2014; Shiraishi et al., 2008).

There was a marked difference between the day and night time conditions in the biofilm systems; the first time such a diurnal cycle has been described for a pH 11.5 system. However, this observation is consistent with previous studies at slightly lower pH, which showed that the balance between photosynthesis and respiration are the dominant processes influencing in-stream diurnal variation, with the uptake of dissolved CO_2 by net photosynthesis during the day and net production of CO_2 during the night by respiration (release of CO_2 leads to neutralisation, and CO_2 uptake has the opposite effect) (de Montety et al., 2011; Gammons et al., 2015). This diurnal cycle indicates that the phototrophic metabolism is predominant, taking up CO_2 photosynthetically during the day, and then release some of it by respiration at night. The photoautotrophic metabolism increases pH and shifts the bicarbonate/carbonate equilibrium towards carbonate, thus increasing the SI of calcite. During the night, respiration releases CO_2 to solution that lowers pH.

4.3. Implications for treatment of $Ca(OH)_2$ containing leachate

In both the sterilized and colonized settings, cascades are more effective than ponds for lowering pH (Table 3). Statistical analysis showed that presence or absence of cascades was more important for driving changes in performance than whether biofilm was present or not. Therefore, the addition of cascades provides a means of notably improving the performance of passive remediation systems where discharge licenses set a limit on pH (usually ≤9), using a relatively simple change in the physical configuration of the system, where topography permits.

To maximise abiotic pH and alkalinity decrease at remediation sites that are not conducive to biological processes (e.g. visibly devoid of benthic biofilms and macrophytes), leachate management efforts should not only seek to maximise the ratio of surface area to flow but also maximise the turbulent mixing within the flow path. This is less important at sites heavily colonized by biomass, as respired CO_2 will mitigate the differences driven by mixing and gas dissolution into thin film-flows (Blanken et al., 2017; Li et al., 2016). Nevertheless, there was significantly increased gas dissolution in the cascade experiments compared to pond experiment and so an advantage to a stepped geometry even when colonized.

It is advantageous to encourage biomass growth in pond systems. Thus future work should focus on the characterisation of high pH tolerant communities and seek opportunities to transplant inocula to constructed wetlands. In biomass containing systems, it is important that time of day is incorporated into sampling and monitoring strategies. The time-variable control on hydrochemistry is complicated by the non-linear pattern of day-night changes observed. In our simple model systems, minimum pH occurs 5 h after dark, and the maximum pH was recorded 5 h after lighting. The delay between light/dark and pH maximum/minimum may reflect the buffering capacity of the water, and the absorption kinetics of respired CO_2 at night, and photosynthetic consumption of CO_2 in the day. However, the precise diurnal pattern is likely to vary between sites and even between reaches of a single site as a consequence of water flow, hydrochemistry, biomass, temperature and light exposure. For example, at Warm Springs Ponds (Montana, USA) the pH maxima occur in mid-to-late afternoon and

Table 3
Qualitative assessment of the efficacy of the tested systems (★- low, ★★- medium, ★★★ - high) on lowering pH, carbonate alkalinity, and calcium.

Type of system	Time of day	pH	Carbonate alkalinity	Calcium
Sterilized cascades		★★	★★	★★★
Colonized cascades	Day	★★	★★	★★
	Night	★★★	★★★	★★
Sterilized ponds		★	★	★★★
Colonized ponds	Day	★★	★★	★★
	Night	★★	★★★	★★

minima just before dawn (Gammons et al., 2007). The asymmetry in the diurnal cycle observed in the field may indicate that temperature also affects metabolic rate, reflecting that maximum (minimum) temperatures occur in the early afternoon (just before dawn) in the field.

Our results also show that calcite has formed in all the systems investigated, generating conditions conducive to (contaminant) metal co-precipitation within carbonates and removing alkalinity from the steel slag leachate (Mayes et al., 2008). Highest mean effluent calcite SI occurs in the pond systems colonized by biofilm during the day, and the relatively high disequilibrium of this system means that further precipitation is more likely downstream treatment zone. As uncontrolled precipitation of calcite could be problematic for invertebrate fauna in streams (Hull et al., 2014), this is not desirable. Counter to this, calcite saturation in the colonized flumes systems during the night can reach negative values (Fig. 5), meaning that no more precipitates are forming despite ongoing CO_2 generation by respiration. The potential diurnal cycling of elements between the solution and the precipitate reflects similar features reported for circum-neutral systems (Jones et al., 2015; Rogerson et al., 2010), and complicates the behaviour of ions precipitated within or co-precipitated with calcite. Diurnal remobilisation of presumed stable mineral phases further emphasises the need for understanding the time of day as a factor in field analysis and further undermines the ability of spot-sampling to evaluate a site effectively. In addition, it is desirable to assure residence times longer than 24 h in passive treatment systems.

5. Conclusions

Stepped cascades perform better than settlement ponds at lowering the pH of steel slag leachate, particularly in the absence of biofilms. Biofilms slightly improve the pH reduction in cascade systems and significantly improve the pH reduction in pond systems, but result in slightly less Ca^{2+} removal from solution in both systems. Also, when biofilm are present, both the pH value and calcium concentration exhibit a diurnal variation due to photosynthesis and respiration, with maximum pH reduction occurred during the night, but maximum calcite precipitation occurred during the day. In summary, wherever possible, passive remediation systems for lowering the pH of steel slag leachate should be designed to incorporate thin film-flow and turbulent mixing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.05.248.

References

Banks, M.K., Schwab, A.P., Alleman, J.E., Hunter, J.G., Hickey, J.C., 2006. Constructed wetlands for the remediation of blast furnace slag leachates, Publication FHWA/IN/JTRP-2006/03. Joint Transportation Research Program, Indiana Department of Transportation and Purdue University, West Lafayette, Indiana http://dx.doi.org/10.5703/1288284313362.

Blanken, W., Magalhães, A., Sebestyén, P., Rinzema, A., Wijffels, R.H., Janssen, M., 2017. Microalgal biofilm growth under day-night cycles. Algal Res. 21, 16–26.

Boylan, A.A., Stewart, D.I., Graham, J.T., Trivedi, D., Burke, I.T., 2016. Mechanisms of inorganic carbon-14 attenuation in contaminated groundwater: effect of solution pH on isotopic exchange and carbonate precipitation reactions. Appl. Geochem. https://doi.org/10.1016/j.apgeochem.2016.12.006.

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.

Chanson, H., 2004. Environmental Hydraulics for Open Channel Flows: Butterworth-Heinemann.

Clark, I.D., Fontes, J.-C., Fritz, P., 1992. Stable isotope disequilibria in travertine from high pH waters: laboratory investigations and field observations from Oman. Geochim. Cosmochim. Acta 56, 2041–2050.

De Windt, L., Chaurand, P., Rose, J., 2011. Kinetics of steel slag leaching: batch tests and modeling. Waste Manag. 31, 225–235.

Dreybrodt, W., Lauckner, J., Zaihua, L., Svensson, U., Buhmann, D., 1996. The kinetics of the reaction $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$ as one of the rate limiting steps for the dissolution of calcite in the system $H_2O \cdot CO_2 \cdot CaCO_3$. Geochim. Cosmochim. Acta 60, 3375–3381.

Dreybrodt, W., Eisenlohr, L., Madry, B., Ringer, S., 1997. Precipitation kinetics of calcite in the system $CaCO_3$-H_2O-CO_2: the conversion to CO_2 by the slow process $H^+ + HCO_3 \rightarrow CO_2 + H_2O$ as a rate limiting step. Geochim. Cosmochim. Acta 61, 3897–3904.

Gammons, C.H., Grant, T.M., Nimick, D.A., Parker, S.R., DeGrandpre, M.D., 2007. Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system. Sci. Total Environ. 384, 433–451.

Gammons, C.H., Nimick, D.A., Parker, S.R., 2015. Diel cycling of trace elements in streams draining mineralized areas—a review. Appl. Geochem. 57, 35–44.

Gomes, H.I., Mayes, W.M., Rogerson, M., Stewart, D.I., Burke, I.T., 2016. Alkaline residues and the environment: a review of impacts, management practices and opportunities. J. Clean. Prod. 112 (Part 4), 3571–3582.

Greenwood, N.N., Earnshaw, A., 2012. Chemistry of the Elements. Elsevier.

Hammer, Ø., Dysthe, D.K., Jamtveit, B., 2010. Travertine terracing: patterns and mechanisms. London, Special Publications]->Geol. Soc. Lond., Spec. Publ. 336, 345–355.

Higgins, D., Courtney, R., Curtin, T., Clune, L., 2015. Use of constructed wetlands for treating BRDA leachate and run-off. In: Pontikes, Y. (Ed.), Bauxite Residue Valorisation and Best Practices, Leuven, Belgium, pp. 53–60.

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. 24, 8516–8524.

Hull, S.L., Oty, U.V., Mayes, W.M., 2014. Rapid recovery of benthic invertebrates downstream of hyperalkaline steel slag discharges. Hydrobiologia 736, 83–97.

Inskeep, W.P., Bloom, P.R., 1985. An evaluation of rate equations for calcite precipitation kinetics at pCO$_2$ less than 0.01 atm and pH greater than 8. Geochim. Cosmochim. Acta 49, 2165–2180.

Jones, A., Rogerson, M., Greenway, G., Mayes, W., 2015. Zinc uptake from circumneutral mine drainage in freshwater biofilms: new insights from in vitro experiments. Mine Water Environ. 34, 295–307.

Kusin, F.M., 2013. A review of the importance of hydraulic residence time on improved design of mine water treatment systems. World Appl. Sci. J. 26 (10), 1316–1322.

Li, T., Piltz, B., Podola, B., Dron, A., de Beer, D., Melkonian, M., 2016. Microscale profiling of photosynthesis-related variables in a highly productive biofilm photobioreactor. Biotechnol. Bioeng. 113, 1046–1055.

Lin, Y.-P., Singer, P.C., Aiken, G.R., 2005. Inhibition of calcite precipitation by natural organic material: kinetics, mechanism, and thermodynamics. Environ. Sci. Technol. 39, 6420–6428.

Mayes, W.M., Younger, P.L., Aumônier, J., 2008. Hydrogeochemistry of alkaline steel slag leachates in the UK. Water Air Soil Pollut. 195, 35–50.

Mayes, W.M., Aumonier, J., Jarvis, A.P., 2009a. Preliminary evaluation of a constructed wetland for treating extremely alkaline (pH 12) steel slag drainage. Water Sci. Technol. 59, 2253–2263.

Mayes, W.M., Batty, L.C., Younger, P.L., Jarvis, A.P., Kõiv, M., Vohla, C., et al., 2009b. Wetland treatment at extremes of pH: a review. Sci. Total Environ. 407, 3944–3957.

de Montety, V., Martin, J.B., Cohen, M.J., Foster, C., Kurz, M.J., 2011. Influence of diel biogeochemical cycles on carbonate equilibrium in a karst river. Chem. Geol. 283, 31–43.

Riley, A.L., Mayes, W.M., 2015. Long-term evolution of highly alkaline steel slag drainage waters. Environ. Monit. Assess. 187, 1–16.

Roadcap, G.S., Sanford, R.A., Jin, Q., Pardinas, J.R., Bethke, C.M., 2006. Extremely alkaline (pH > 12) ground water hosts diverse microbial community. Ground Water 44, 511–517.

Rogerson, M., Pedley, H.M., Wadhawan, J.D., Middleton, R., 2008a. New insights into biological influence on the geochemistry of freshwater carbonate deposits. Geochim. Cosmochim. Acta 72, 4976–4987.

Rogerson, M., Pedley, H.M., Wadhawan, J.D., Middleton, R., 2008b. New insights into biological influence on the geochemistry of freshwater carbonate deposits. Geochim. Cosmochim. Acta 72, 4976–4987.

Rogerson, M., Pedley, H., Middleton, R., 2010. Microbial influence on macroenvironment chemical conditions in alkaline (tufa) streams: perspectives from in vitro experiments. London, Special Publications]->Geol. Soc. Lond., Spec. Publ. 336, 65–81.

Saunders, P., Rogerson, M., Wadhawan, J.D., Greenway, G., Pedley, H.M., 2014. Mg/Ca ratios in freshwater microbial carbonates: thermodynamic, kinetic and vital effects. Geochim. Cosmochim. Acta 147, 107–118.

Shiraishi, F., Bissett, A., de Beer, D., Reimer, A., Arp, G., 2008. Photosynthesis, respiration and exopolymer calcium-binding in biofilm calcification (Westerhöfer and Deinschwanger Creek, Germany). Geomicrobiol J. 25, 83–94.

USGS, 2012. Alkalinity and acid neutralizing capacity. U.S. Geological Survey TWRI Book 9 Chapter 6.6.

Vacca, G., Wand, H., Nikolausz, M., Kuschk, P., Kästner, M., 2005. Effect of plants and filter materials on bacteria removal in pilot-scale constructed wetlands. Water Res. 39, 1361–1373.

Valipour, A., Ahn, Y.-H., 2015. Constructed wetlands as sustainable ecotechnologies in de-centralization practices: a review. Environ. Sci. Pollut. Res. 1–18.

Veysey, J., Goldenfeld, N., 2008. Watching rocks grow. Nat. Phys. 4, 310–313.

VeyseyII, J., Fouke, B.W., Kandianis, M.T., Schickel, T.J., Johnson, R.W., Goldenfeld, N., 2008. Reconstruction of water temperature, pH, and flux of ancient hot springs from trav-ertine depositional facies. J. Sediment. Res. 78, 69–76.

Zahraeifard, V., Deng, Z., 2011. Hydraulic residence time computation for constructed wetland design. Ecol. Eng. 37, 2087–2091.