Treatment of zinc-rich acid mine water in low residence time bioreactors incorporating waste shells and methanol dosing

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ABSTRACT

Bioreactors utilising bacterially mediated sulphate reduction (BSR) have been widely tested for treating metal-rich waters, but sustained treatment of mobile metals (e.g. Zn) can be difficult to achieve in short residence time systems. Data are presented providing an assessment of alkalinity generating media (shells or limestone) and modes of metal removal in bioreactors receiving a synthetic acidic metal mine discharge (pH 2.7, Zn 15 mg/L, SO_4^{2-} 200 mg/L, net acidity 103 mg/L as $CaCO_3$) subject to methanol dosing. In addition to alkalinity generating media (50%, v.v.), the columns comprised an organic matrix of softwood chippings (30%), manure (10%) and anaerobic digested sludge (10%). The column tests showed sustained alkalinity generation, which was significantly better in shell treatments. The first column in each treatment was effective throughout the 422 days in removing >99% of the dissolved Pb and Cu, and effective for four months in removing 99% of the dissolved Zn (residence time: 12–14 h). Methanol was added to the feedstock after Zn breakthrough and prompted almost complete removal of dissolved Zn alongside improved alkalinity generation and sulphate attenuation. While there was geochemical evidence for BSR, sequential extraction of substrates suggests that the bulk (67–80%) of removed Zn was associated with Fe–Mn oxide fractions.

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1. Introduction

Acidic drainage from abandoned metal mines is a widespread and persistent form of aquatic pollution, discharging a range of contaminant metals (e.g. Cd, Pb and Zn) to surface waters [1,2]. While energy and cost-intensive treatment options are available for such discharges in the form of active chemical dosing (e.g. with lime to immobilise metals as hydroxides in a sludge: [3]), the abandoned nature of mine sites in many countries leaves absent or unclear legal liabilities for remediation, with the cost burden ultimately falling upon local, regional or national government. As such, the need for low-cost, low maintenance treatment systems for acidic metalliferous waters has been a focus for much research effort in recent years [3,4].

The development of bioreactors which harness bacterially mediated sulphate reduction have been widely tested since the pioneering observations of Tuttle et al. [5] on the effectiveness of acid-tolerant sulphate reducing bacteria (SRB) in removing metals as solid monosulphides from acid mine drainage. SRB perform the

key terminal reductive step for metal removal (Eqs. (1)–(2)) which is rate-limited by the supply of carbonaceous organic matter to the SRB which are degraded by primary heterotrophic bacteria (e.g. hydrolytic and fermentative bacteria).

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (1)$$

$$Me^{2+} + H_2S \rightarrow MeS_{(solid)} + 2H^+ \qquad (2)$$
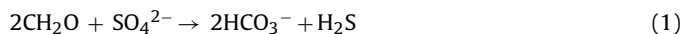
Sulphate-reducing bioreactors have been developed to field-scale treating coal mine drainage where principal contaminants of concern include Fe, Al and SO_4^{2-} [3,6]. Although there is clear evidence that some Zn and Cd removal occurs in some compost-based units around the UK and further afield [7], passive systems in which sulphate reduction will occur both vigorously and consistently enough to effect the removal of zinc (Zn) as ZnS to the low levels sufficient for compliance with surface water Environmental Quality Standards (EQS) have not yet been developed. The removal of Zn is of particular interest as it is both the most commonly encountered pollutant in rivers draining former metal mining districts in England and Wales [2].

In many wetlands and bioreactors the carbon source is initially present as labile cellulose-rich materials. This leaves more recalcitrant lignin-dominated material for later breakdown and limits supply of low-molecular weight carbonaceous material to SRB communities [8]. The necessity for replenishment of the

carbon source in compost wetlands has been long acknowledged [9], but it is something that can often be neglected in full-scale bioreactor operation and requires further attention to develop sustainable strategies for attaining treatment longevity. This problem is intensified in the UK where land availability is limited either through cost or topography (e.g. in upland ore fields where low gradient land is at a premium). As such the typical bioreactor residence times of 5–10 days (e.g. [10]) for high-yielding discharges are not usually feasible due to system sizing constraints. The use of refined organic products to stimulate microbial sulphate reduction has been successfully applied by workers elsewhere in the field of mine water remediation [11,12].

This study aims to (a) provide a comparative assessment of two alkalinity generating media: limestone and crushed whelk shells, a waste product from the shellfish processing industry, (b) provide an assessment of the response of bioreactor mesocosms to dosing with refined organic products and (c) offer insight into modes and rates of contaminant removal as a prelude to the pilot field testing of bioreactors.

2. Methods

2.1. Experimental configuration

Initial batch testing assessed the repeatability and efficacy of various organic wastes and alkalinity generating media in achieving geochemical conditions suitable for BSR (results reported in [13] provided in Supporting Information). The substrates identified combined (50%, *v.v.*); limestone or whelk shells, soft woodchip (30%), to provide adequate hydraulic conductivity through the column, farm manure (10%) which provides a carbon source and anaerobic digested sludge (10%), a by-product of primary sewage treatment and a source of SRB communities. Four columns (internal diameter 95 mm, length 400 mm) were set up with two columns of the same treatment in series with an intermediate aeration tank to facilitate CO_2 degassing (Fig. 1).

2900 cm^3 of each of the homogenised treatments was inserted into the columns then saturated to calculate the porosity of the substrates (Table 1) and active volume of water to facilitate residence time estimates. A Watson Marlow 300 series peristaltic pump was set up to give an approximate residence time of 12–14 h in each of the columns (Table 1).

2.2. Column operation

A synthetic mine water was made through dissolving various laboratory grade salts in deionised water, with pH controlled with <5 mL of concentrated H_2SO_4. The synthetic feedstock was made up to replicate the constituent of a highly polluting metal mine discharge at Cwm Rheidol (Table 2) in Western Wales, UK (UK National Grid Reference SN 7302 7833), for which these tests were used to inform the design of a pilot treatment system.

Methanol was added to the feedstock from day 194 once dissolved Zn concentrations in the LS1 (LS = limestone) and SH1 (SH = whelk shell) effluents begin to rise consistently up until day 369. Following the method of [11], stoichiometry was used to determine the quantity of methanol required to remove 200% of the sulphate (a conservative dosing) in the influent water according to Eq. (1).

2.3. Water sampling and analyses

Samples were taken on a fortnightly basis over the course of the trial, with more intensive weekly sampling in both the early stages of the trial and following the addition of methanol. Samples were taken from the effluent of all four columns in addition to the influent

mine water. Flow rate was measured at each sample interval using a measuring cylinder and a stopwatch. Weekly measurements of sample pH, electrical conductivity, *Eh* and temperature were taken using a Myron 6P Ultrameter. Sample alkalinity was determined through titration of 10 mL of sample against 0.16 N sulphuric acid with Bromocresol-Green Methyl-Red indicator using a Hach digital titrator. Two 30 mL aliquots were acidified, one after filtration (0.45 μm cellulose nitrate filters) for total and dissolved metal analysis using a Varian Vista-MPX Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). 30 mL of sample was left unacidified and analysed for major anions (SO_4^{2-} and Cl^-) using a Dionex 100 ion chromatograph. Total organic carbon (TOC) and ammonia-col nitrogen (NH_3-N) were determined in the first two weeks of the trial until concentrations fell to residual levels and after methanol addition. TOC was determined using a Shimadzu 5000 TOC Analyser. NH_3-N was determined via Kjeldahl analysis [14]. Selected analyses were analysed using the PHREEQC geochemical code [15] in conjunction with the WATEQ4F database [16]. Analytical quality was tested via charge-balance (analyses with an electro-neutrality within ±5% are used).

Statistical analyses of the data were assessed using Minitab v15. Data were not normally distributed even after transformation therefore non-parametric tests were employed to compare performance between columns (shell versus limestone).

2.4. Sediment analyses

At the conclusion of the trial, destructive sampling of the drained column substrate was undertaken. Four replicate samples from each column were taken and air-dried prior to sequential extraction (following the method of [17]). Metal concentrations in extracts were determined using ICP-OES as per the water analyses and reported in the operationally defined phases of [17].

3. Results and discussion

3.1. Major trends

The trends in metal removal and major ion chemistry can be broadly separated into three main phases (Figs. 2 and 3) relating to addition of methanol: (1) an initial phase from day 1 to day 194 prior to any methanol addition, (2) the second phase covers the period when methanol was added to the feedstock from day 194 to day 369, and (3) the final two months of the trial after day 369 when methanol addition ceased. The first phase is characterised by the development of reducing conditions in the columns (settling at values in the region of −100 to −200 mV) and initial removal of all metals. After five months *Eh* begins to rise and breakthrough of dissolved Zn in the first column of each treatment occurs. The subsequent addition of methanol to the columns encouraged strongly reducing conditions (*Eh* between −100 and −300 mV) in all treatments (Fig. 2), sustained removal of all contaminant metals (Figs. 2 and 3) and enhanced alkalinity generation. The final phase of the test was assessing the response of the columns once the organic supplementation had ceased. An immediate and marked increase in effluent dissolved Zn concentrations, lesser alkalinity generation, diminished sulphate removal and less reducing conditions were apparent.

3.2. Acidity, alkalinity and pH

One consistent feature of the trial is the effective buffering of the acidic influent water in both the limestone and shell treatments. Alkalinity generation (between 80 and 160 mg/L as $CaCO_3$) and an effluent pH in the region of 6.6–7.6 (Fig. 2) have been maintained in the columns after initial flushing and dissolution of carbonate
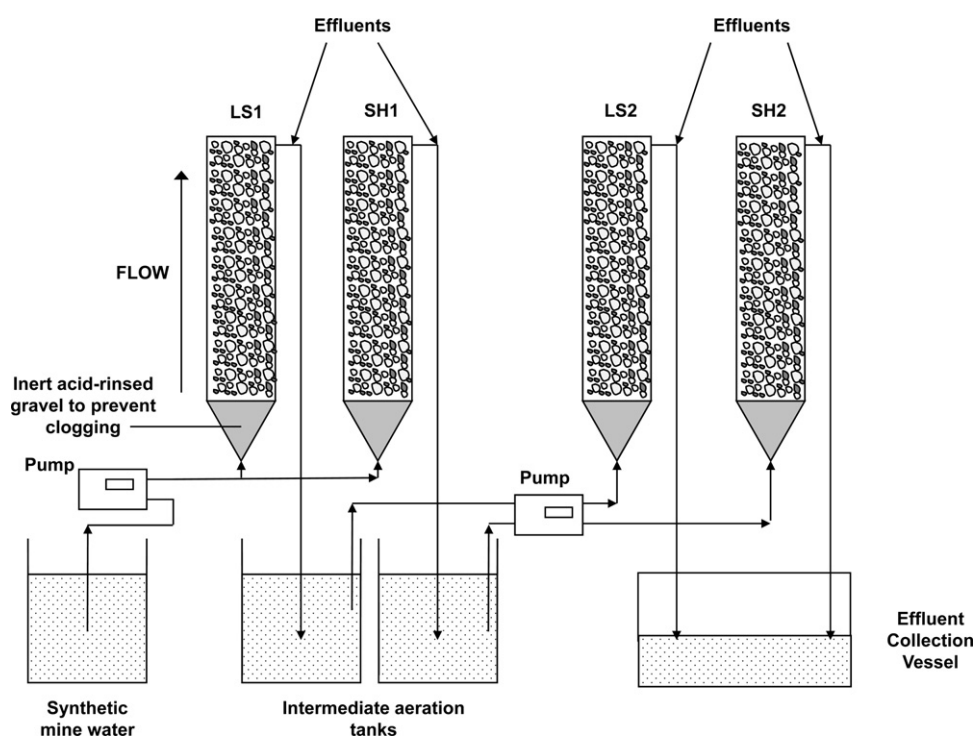
Fig. 1. Schematic diagram of the experimental set-up in column trials.

fines in early weeks of the trial. Over the course of the trial there is a gradual decline in alkalinity, punctuated by an abrupt increase in alkalinity which was apparent in all treatments during the methanol addition phase (Fig. 2). Total alkalinity of effluent waters was significantly higher (Mann–Whitney $W = 458$, $P < 0.001$) in the

LS1 treatment during the methanol addition phase (day 194–369: median 173 mg/L as $CaCO_3$, range 64–234) compared to steady-state performance immediately prior to the methanol addition (day 8–193: median 98 mg/L as $CaCO_3$, range 54–183). Similarly significant (Mann–Whitney $W = 398$, $P < 0.001$) higher alkalinity was

Table 1
Summary of physical characteristics and operating conditions of columns (standard deviation in parentheses; $n = 102$ for flow, residence time and hydraulic loading calculations). LS1 and LS2; SH1 and SH2 = limestone and shell treatments 1 and 2 respectively. Estimates of specific surface assume spherical limestone clasts and thin (1 mm thickness) plate-like shells.

	LS1	LS2	SH1	SH2
Size fraction (limestone or shell)	5–20 mm	5–20 mm	5–20 mm	5–20 mm
Specific area (cm^2/g)	5.63	5.63	8.39	8.39
Initial porosity	0.41	0.44	0.41	0.45
Flow rate (L/day)	2.4 (0.1)	2.5 (0.3)	2.4 (0.2)	2.4 (0.1)
Residence time (h)	11.6 (0.6)	11.9 (1.2)	11.8 (0.7)	13.1 (0.6)
Hydraulic loading (day)	2.1 (0.1)	2.0 (0.2)	2.0 (0.1)	1.8 (0.1)
Total number of pore volume throughflows (after 422 days)	842.5	821.1	825.1	744.9

Table 2
Typical constituent of the influent water used in the column trials. Data for Cwm Rheidol Adit 6 courtesy of Environment Agency Wales.

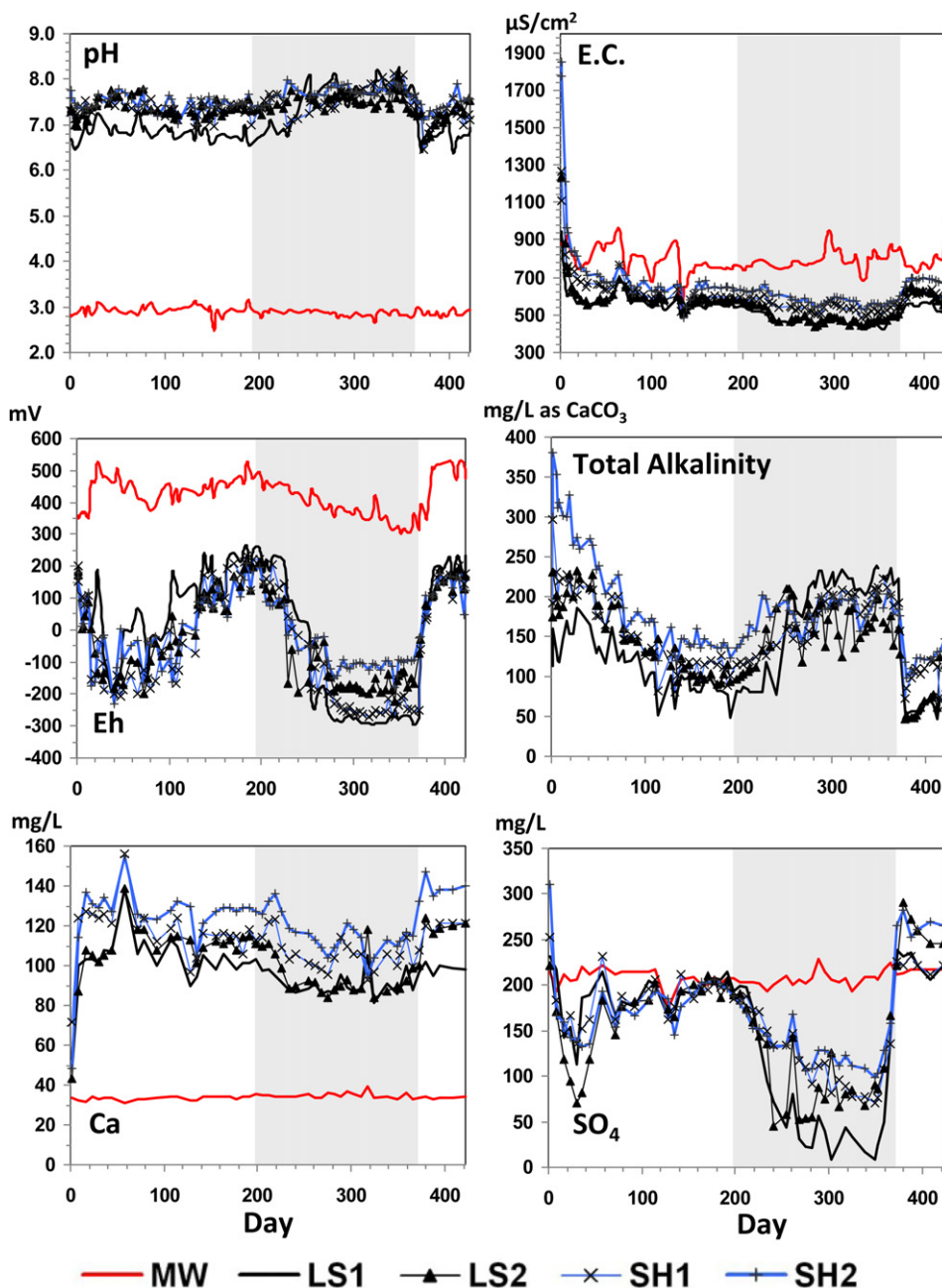| Parameter/species (mg/L unless stated)	Synthetic mine water	Cwm Rheidol adit 6 (data 1979–2008)		
		Mean	Standard deviation	N
pH	3.0	3.7	0.3	313
Electrical conductivity (μS)	400–800	400	174	68
Eh (mV)	350–450	–	–	–
Ca	30	27	14	227
Mg	10	10	6.1	228
Na	<0.5	7	0.7	27
K	0.5–1	1	1	27
SO_4	200–300	170	105	60
Cl	1–2	13	4	59
Zn	15	13	10	460
Pb	5	0.9	0.4	318
Cu	0.5	0.6	0.4	302
Fe	5	9	3.3	394
Mn	0.6	0.7	1.6	291
Al	<0.01	0.4	0.4	71

Fig. 2. Major physico-chemical parameters and selected major ions in influent mine water (MW) and column effluents during the trial. Grey shading indicates period of methanol dosing.

reported in the SH1 treatment during methanol addition (median 188 mg/L as $CaCO_3$, range 188–223) than in preceding un-dosed phases also (median 115 mg/L as $CaCO_3$, range 81–150). There was no corresponding increase in Ca^{2+} in effluent waters of these treatments during this period (Fig. 2). Ca^{2+} in effluent of LS1 and SH1 were significantly ($P < 0.001$) lower during methanol addition than the preceding phase. This suggests that the additional alkalinity is not a product of increased limestone dissolution and the patterns is most likely explicable due to the enhanced sulphate reduction during the methanol addition phase (Eq. (1)). Indeed, the additional alkalinity from BSR will depress calcium carbonate dissolution due to elevated pH and this appears to be the case here.

Table 3 summarises key metrics with regard alkalinity generation and acidity removal over the course of the trial to contrast the effects of the substrates used. The key patterns to highlight

are (1) the bulk of the alkalinity generation and acidity removal occurs within the first column of each treatment (see acid load removed and $CaCO_3$ load added) and (2) the consistently greater alkalinity generation in the SH1 treatment compared to the LS1 treatment. The total acid load removed is marginally greater in LS1 than SH1 (although overall the combined shell treatments perform slightly better), but alkalinity in effluents and the total loading of $CaCO_3$ added are 12% and 19% higher respectively in SH1 than LS1. While similar volumes of alkalinity generating media were used, the actual weights differed. These mass differences are accounted for by the acidity removal efficiency (as defined by [18] as the g of acidity (as $CaCO_3$) removed per day per t of limestone (or shells in this case) used). Acidity removal efficiency was significantly greater in the SH1 treatment (median 86.8, range 40.6–163.0) than the LS1 treatment (median 55.6, range 22.6–103.1; Wilcoxon Signed

Table 3
Characteristics of columns with regard acidity removal and alkalinity generation. Mean (net acidity, alkalinity) and median (pH, CaCO$_3$ and acid loads, removal efficiency) shown with standard deviation (where mean data) or range (median data) in parenthesis, $n = 101$ for pH, alkalinity and CaCO$_3$ load, $n = 49$ for all other parameters.

	Mine water	LS1	LS2	SH1	SH2
pH	2.9 (2.5–3.2)	6.9 (6.4–8.3)	7.4 (6.7–8.0)	7.4 (6.5–8.1)	7.6 (7.0–8.0)
Net acidity (mg/L as CaCO$_3$)[a]	103.3 (18.5)	−131.4 (62.8)	−140.9 (45.3)	−146.49 (42.3)	−178.5 (49.0)
Influent acidity load (g/m^2/day)	–	8.7 (1.7)	0.6 (0.5)	8.8 (1.9)	0.7 (0.3)
Acid load removed (g as CaCO$_3$/year)	–	213.9	6.3	208.3	13.1
Total alkalinity (mg/L as CaCO$_3$)	0 (0)	136.1 (62.1)	143.9 (47.1)	153.2 (47.4)	182.1 (56.3)
CaCO$_3$ load added (g as CaCO$_3$/year)[b]	–	139.3	20.7	172.6	13.4
Acidity removal efficiency[c]	–	55.6	1.6	86.8	5.5

[a] Net acidity (mg/L as CaCO$_3$) = $(50(10^{(3-pH)}) + 2\,C_{Fe}/55.85 + 2\,C_{Mn}/54.94 + 2\,Zn/65.39 + 2Pb/207.2)$ − alkalinity, where C_{Fe}, C_{Mn}, C_{Zn} and C_{Pb} are concentrations of dissolved elements.

[b] Calculated from mass balance of dissolved Ca^{2+} loading between influent and effluent of each column (and therefore does not reflect any additional alkalinity generation from BSR).

[c] Acidity removal efficiency is the acidity load in g (as CaCO$_3$) removed per day per t of limestone (or shells) in the system

Rank Test, $W_+ = 1225$, $P < 0.001$). This is a likely feature of the higher specific surface area of the shells permitting greater dissolution of carbonate minerals than with the more spherical limestone clasts (Table 1).

The actual acidity load the columns were subjected to was relatively modest compared to similar applications, which usually quote maximum acidity loads of 30 g acidity/m^2 day for RAPS systems (6) and less than 10 g acidity/m^2 day compost-based anaerobic wetlands (19). However, the bulk of acidity load design guidance for coal mine drainage treatment arises from Fe and Al [4,6,20], which are of comparatively lesser significance in most examples of UK metal mine drainage [2].

3.3. Metal removal

Both Pb and Cu in the effluent of all columns fell close to or below detection limits after week 2 of the trial (Fig. 3). The total concentrations of Pb and Cu become steady after week 2 of the trial, both at ~10% of the influent mine water concentration. Dissolved Pb and Cu are consistently below detection limits in the effluents of all columns and breakthrough does not occur at any point in the trial. Concentrations of particulate Cu and Pb in column effluents show occasional spikes, particularly during the phase of methanol addition. The column effluent was designed in such a way that occasionally the effluent port would build up a slight head of water (due to surface tension around the aperture) prior to pulsing out under gravity. This led to some entrainment of fines from the sediment surface which may account for many of the occasional spikes in particulate metal concentration. Beyond the occasional spikes, there is a consistent increase in particulate Cu, Pb, Fe and Zn release shortly after methanol addition. Such issues have been found in similar bioreactor systems [21] and could be easily circumvented in full scale systems through deployment of a polishing reedbed or settlement lagoon [3]. The more aerobic conditions early in the trial were conducive to the formation of ferric oxide deposits around the influent and effluent of the columns which were absent during methanol addition phases. The saturation index data in Supporting Information (Table S1) highlight the saturation of a range of iron oxide phases (e.g. goethite, hematite, magnetite) during the non-dosed phases in all columns and undersaturation of such phases during the methanol addition phase. Ferric iron oxide deposits are well-regarded sinks for divalent metals [22,23] and sediment extraction data (see Section 3.6) highlight the importance of Fe and Mn oxide phases as metal sinks in the columns here. As such, the release of these phases immediately after methanol addition either through dissolution or colloidal material may account for some of the metal export from the columns. Iron shows similar patterns to the metals described above with most Fe attenuated within the columns during the pre-methanol addition phase. Despite the diminished removal rate of Fe

immediately after methanol addition, effluent concentrations of Fe remain well below influent values throughout the trial with mean treatment efficiencies of 97% (LS1) and 98% (SH1).

Removal of Mn from mine waters typically demands oxidation of Mn(II) species at elevated pH of around 8–10 [4] or through microbially mediated oxidation onto dolomites or limestones [24]. Mn was not anticipated to be removed in significant quantities in these trials and was included in the synthetic mine water to offer an accurate reflection of the solute composition of the mine water. Unlike the other metals monitored there is no significant sustained attenuation of Mn in any of the columns (Fig. 3) and is present almost entirely in dissolved form. Such a pattern is expected given the solubility of Mn sulphides; metal monosulphides are thought to precipitate sequentially according to their solubility product, and MnS is the last of the metals most commonly found in UK metal mine drainage to form a monosulphide on this basis (the theoretical order of formation is CuS, PbS, ZnS, CdS, NiS, FeS, MnS; [19]). There is slight attenuation of Mn in the columns (up to 48% removal in the LS1 treatment, Fig. 3) during the period when methanol was added, but effluent Mn rises to influent values almost immediately after methanol addition is ceased suggesting that the Mn removal mechanism is dependant on the more reducing conditions and/or perhaps increased biological activity when methanol is added. The sequestration of Mn in hydroxides has been noted in other bioreactor systems [21] receiving sulphate rich, acid waters and may be an important here given the elevated pH during methanol dosing.

Total Zn concentrations in the column effluents were quite erratic throughout the trial with occasional peak values associated with flushing of fine sediment from the column effluent (Fig. 3). The first column of each treatment show effective removal of dissolved Zn (>99% treatment efficiency) in the first four months of the trial. Following the breakthrough of dissolved Zn in the effluent of the SH1 and LS1 treatments, the dissolved Zn curves showed a steady rise until the methanol addition commenced. There is an immediate downturn in effluent dissolved Zn after methanol addition to concentrations below detection limits (<0.001 mg/L) which are sustained until 1 week after methanol addition ceased on day 369. Once methanol addition had ceased, dissolved Zn in the effluent of LS1 and SH1 rose again, implying that ongoing Zn removal (in the order of 90% efficiency for the subsequent 2 months) can be sustained at least for a moderate period after methanol addition has ceased. The data suggest that any readily available low molecular weight organic compounds within the substrate (i.e. in the manure and sludge fractions) were exhausted in the first four months of the trial, possibly because the rate of utilisation of carbon available to SRB exceeds the rate at which heterotrophic bacterial communities are able to break down the more recalcitrant higher molecular weight organic compounds present in the substrate.

Perhaps the most informative metric for bioreactors or RAPS systems are volumetric removal rates, particularly given that land
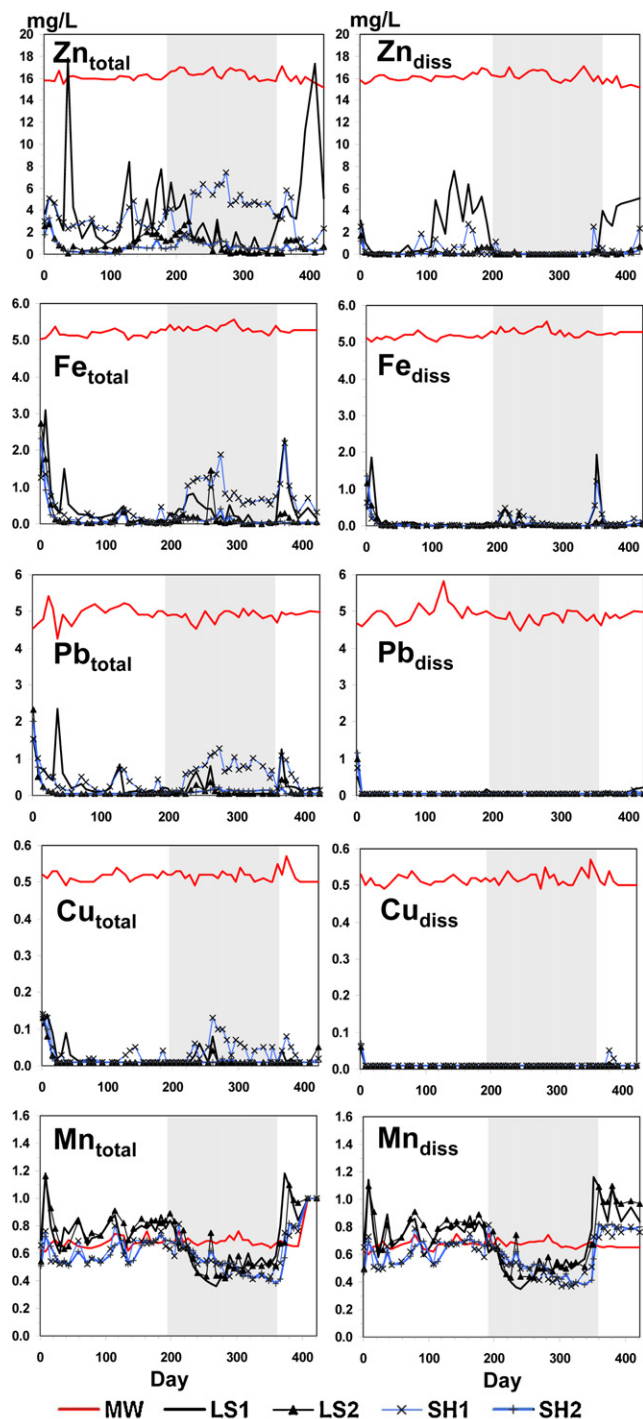
Fig. 3. Selected total and dissolved metal concentrations in influent mine water (MW) and column effluents. Grey shading indicates period of methanol dosing.

area is a crucial constraint on full scale systems (efficiency metrics, such as percentage metal removal, fail to account for such engineering considerations). In this case peak removal of 15.4 g Zn/m^3/day (LS1) and 16.7 g Zn/m^3/day (SH1) were apparent when there was complete removal of dissolved Zn. Given the load limitation (i.e. effluent concentrations below detection limits) it is not possible to speculate on the maximum feasible Zn removal rates in the columns. Although comparisons between laboratory and field systems should be exerted with extreme caution, the mean Zn removal rate in the LS1 and SH1 treatments (9.9 and 11.4 g Zn/m^3/day, respectively) compares favourably with other reported

passive systems such as sorbent based filters [23], algal mats [25] and limestone drains [26]. This may be anticipated with the semi-passive approach to treatment, but does reinforce the promise for pilot field testing of these bioreactor systems for Zn removal in a small land footprint.

3.4. Other water quality considerations

The use of by-products (and organic wastes in particular) in treatment systems demands careful evaluation to ensure no leaching of environmentally significant chemical species occurs from the system. Both the shell treatments show an exponential decline in Na and Cl concentrations in the early phases of the trial falling from initial peaks of 123 and 151 mg/L in SH2 on day 1 to values less than 5 mg/L on day 18. TOC and NH$_3$-N were monitored early in the trials giving initial peak values of 101 and 70.6 mg/L, respectively, both recorded in the SH2 treatment. These initial peaks are most likely associated with the flushing of organics (most notably, the liquid anaerobic digested sludge) from the columns. A subsequent fall in TOC and NH$_3$-N occurs by day 2 of the trial, to 15.7 and 1.7 mg/L for TOC and NH$_3$ respectively. Spot measurements of TOC during the methanol addition phase were made, showing TOC to rise to between 10 and 40 mg/L in the column effluents shortly after methanol addition on day 205, but subsequently falling to below <0.5 mg/L in subsequent spot samples one month later. NH$_3$-N column effluent values remained below detection limits (of 1 mg/L) during spot samples in the methanol addition phase. These data show that while there is some flushing of TOC and potentially high NH$_3$-N concentrations shortly after start-up, and with the case of TOC during initial supplementation with methanol, there is no sustained export of TOC and NH$_3$-N. Although sulphide was not directly measured, treatment of bioreactor water prior to discharge for sulphide would be required. This could be achieved in passive oxidation units that are routinely deployed in mine treatment [3].

When using by-products or wastes in passive treatment systems the potential release of contaminants from the substrate (e.g. metals when initially in contact with an acidic water) is a potential concern given the moderate concentrations of metals (Zn and Pb in particular) that are reported in sewage sludge and agricultural manure [27]. There was no evidence of significant initial flushing in this case (effluent metal concentrations did not exceed influent concentrations, while concentrations of As, Cd, Co and Ni remained below detection limits of 10 μg/L throughout the trial).

3.5. Sulphate

In this study, sustained removal of dissolved Fe, Cu and Pb, and especially dissolved Zn, has been observed (albeit the latter showing breakthrough into column effluents on two occasions: Fig. 3). While the overarching intent of bioreactors such as the one described here is to remove divalent metals as sulphides, it may not always be the case that bacterial sulphate reduction is the dominant, or even a significant, mechanism for metal removal [28]. However, there are several lines of direct and modelled geochemical evidence suggesting sulphate reduction is an important process in attenuation of metals during the study, particularly during the methanol addition phase. The first of these relates to the additional alkalinity generation during the methanol addition phase, which was not driven by increased dissolution of calcite. *Eh* measurements themselves reported an immediate lowering of *Eh*, to highly anaerobic conditions, in all treatments upon addition of methanol. While these values are close to those quoted for sulphate reduction (~−240 mV; [29]), it should be noted that the *Eh* measurements reported here are likely to consistently underestimate the actual *Eh* value in the pore waters of the columns and potentially subject to oft-quoted inaccuracies of hand-held proprietary meters [29].
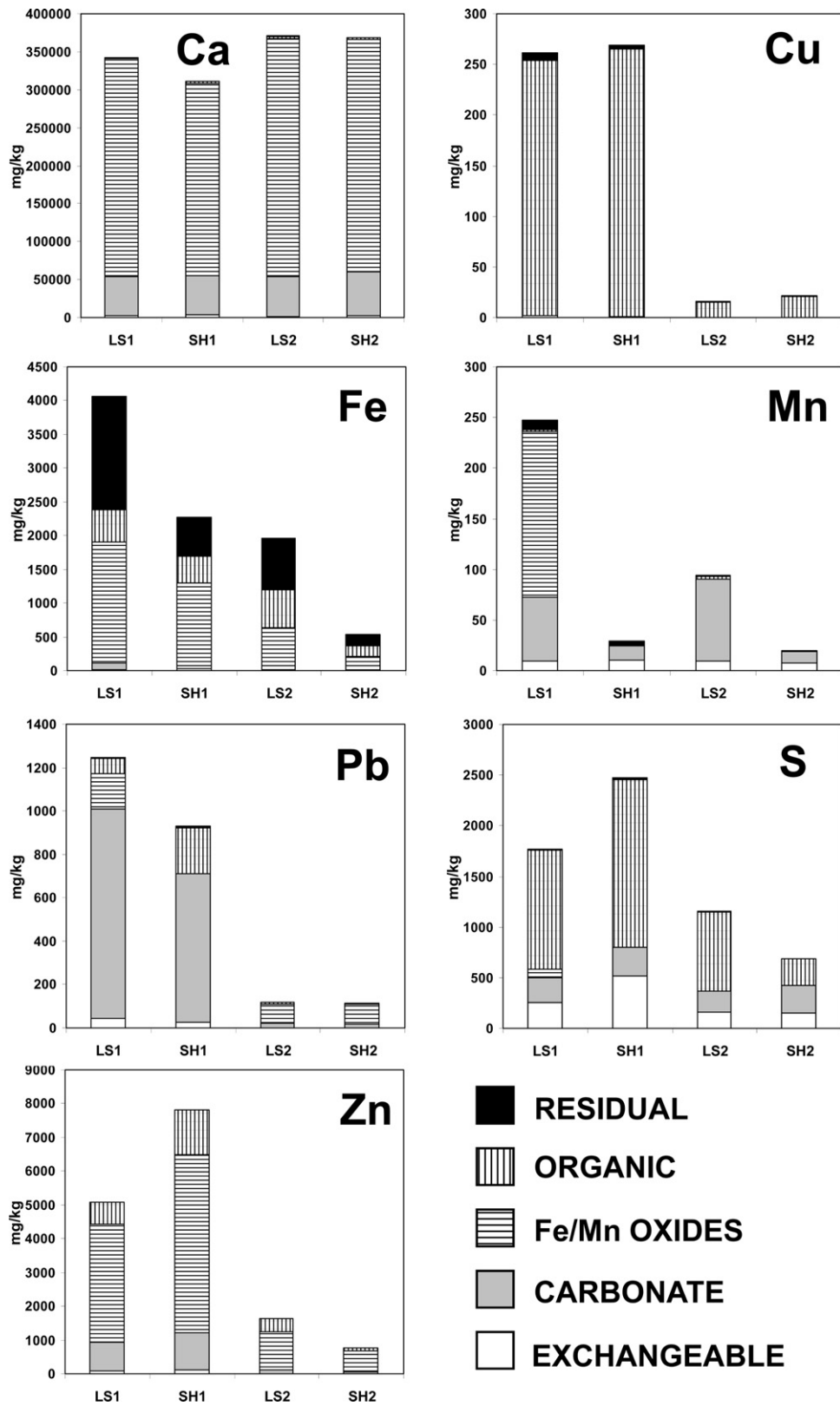
Fig. 4. Mean concentrations of selected elements in the operationally defined fractions of [17] after sequential extraction.

Sulphate concentrations in the column effluent are less than influent concentrations until sulphate values converge on influent values when Zn breakthrough occurs in the LS1 and SH1 treatments (Fig. 3). This does suggest that in the early phases of the trial there is some sulphate attenuation taking place. Geochemical modelling (Table 3) suggests that in the early stages of the trial the waters are not sufficiently reducing for any sulphide phases to be supersaturated. However, this may be a feature of the potential inaccuracies associated with *Eh* measurement of waters collected from sampling ports on the columns, as opposed to accurate measurement of *Eh*

within the columns. After methanol addition there is a rapid fall in effluent sulphate values in all treatments. This fall is particularly pronounced in the LS1 treatment where up to 75% of the influent sulphate is attenuated in the column during the methanol addition phase. Geochemical modelling also shows the waters to be consistently supersaturated with respect to FeS (precipitate), sphalerite (ZnS), wurtzite (ZnS) and amorphous ZnS, during the methanol addition phase, while they remain undersaturated in antecedent and subsequent phases (Supporting Information Table S1).

3.6. Sediment analyses

Destructive sampling of the substrates and subsequent sequential extraction was undertaken to assess the metal sinks and mobility in the substrate. The contaminants of concern show consistent patterns between treatments, but differing dominant sinks are apparent for different elements (Fig. 4). Total concentrations of Cu are apparent in LS1 and SH1 of 262 and 269 mg/kg, respectively, of which 96–98% was recovered in the organic fraction. The dominance of the organic fraction as a sink for copper is noteworthy given (1) the organic fraction is often considered the fraction where sulphides are recovered (e.g. [30]); a pattern reinforced by the high proportion (38–66%) of sulphur recovered in this experiment and, (2) Cu is sequentially the first of those of contaminants of interest here to form a sulphide, according to the metal sulphide solubility products of the contaminant metals present in this water [19]. Fe is associated with the hydrous ferric oxide (32–55%) and residual phases (25–41%) but also with the organic phase (12–30%). Total Mn mass recovered is low and reflects the low removal rates in the columns. Mn concentrations are higher in the sediments of the limestone treatments (mean of 171 mg/kg) than shell treatments (mean of 24.5 mg/kg) and the bulk of the Mn is associated with carbonate (26–86%) and Fe/Mn oxide phases (in LS1 only). Whether this is indicating some preference for removal of Mn on the limestone surface (4) in oxic portions of the column is unclear.

Pb is predominantly associated with carbonate fractions in the first column treatments (74–78% of Pb) and Fe/Mn oxides in the second column (71–84%). Between 2 and 23% of the Pb is associated with the organic fraction, with peak values recorded in SH1. A similarly small association of Zn with the organic fraction is also apparent. A minimum of 12% (SH2) and maximum of 25% (LS2) were found in the organic fraction. The dominant sink for Zn is the Fe/Mn oxide fraction (67–80%) with a minor component (7–17%) associated with carbonates. The patterns suggest that removal of Zn as a sulphide may only be of peripheral importance as an attenuation mechanism in the columns and again highlights the importance of HFO deposits as a sink for Zn, a pattern documented in many other trials [23,31] and appear to be important in this case. Clearly the less anoxic conditions in the initial and final phase of the trial are more conducive to the formation of HFO deposits (see Supporting Information) and less likely to promote sulphate reduction. As such, the analyses from the trial conclusion may likely underestimate the importance of organic fraction sinks, particularly during the methanol addition phase.

While the carbonate fraction appears to be a less important sink for contaminants (with the exception of Pb), it is interesting to note that it is a more prominent sink for metals in the shell treatments than the limestone (Fig. 4) with the exception of Mn. This could be explained readily by the greater specific surface area of the shells relative to limestone.

4. Conclusions

Comparative assessment of alkalinity generating media showed significantly greater acidity removal efficiency in systems comprising waste whelk shells than those with limestone clasts. Where

available, waste shells offer the additional environmental benefits of both taking a waste product from one industry (shellfish processing) to remediate the polluting legacy of another industry (metal mining) and circumvents the need for quarrying virgin limestone.

Metal removal in both systems showed similar patterns, with effective removal of Pb and Cu throughout the trial. As with many other sulphate reducing bioreactor systems, the removal of Zn was more erratic. Cu was predominantly associated with organic phases, Pb with carbonate phases and Zn with Fe/Mn oxides.

Treatment longevity for Zn appears to demand supplementation of carbon source for low residence time systems such as those trialled here. Given logistical constraints (available land area/costs, high loadings rates of some of the most environmentally significant discharges), such dosing will likely be necessary for full-scale deployment. Future research should assess the viability of alternative liquid carbon amendments (preferably by-products such as agricultural wastes or brewery wastes) and assess scope for manipulating microbial communities (e.g. through innocula) to enhance bacterially mediated sulphate reduction for divalent metal removal. As with all laboratory studies developing mine drainage treatment systems, future research efforts should evaluate larger field-scale systems and aim to transpose promising laboratory performance into effective long-term field treatment.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.07.073.

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