Science of the Total Environment 408 (2010) 4877–4885

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Performance of a passive treatment system for net-acidic coal mine drainage over five years of operation

Romy Matthies *, Andrew C. Aplin, Adam P. Jarvis

School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

ARTICLE INFO

Article history:
Received 8 March 2010
Received in revised form 4 June 2010
Accepted 7 June 2010
Available online 6 July 2010

Keywords:
Coal mine drainage
Passive treatment
RAPS
Metals
Alkalinity

ABSTRACT

A full-scale passive treatment system (PTS) was commissioned in 2003 to treat two net-acidic coal mine water discharges in the Durham coalfield, UK. The principal aim of the PTS was to decrease concentrations of iron (<177 mg L^{-1}) and aluminium (<85 mg L^{-1}) and to increase pH (>3.2) and alkalinity (≥ 0 mg L^{-1} $CaCO_3$ eq). Secondary objectives were to decrease zinc (<2.8 mg L^{-1}), manganese (<20.5 mg L^{-1}) and sulfate (<2120 mg L^{-1}). Upon treatment, water qualities were improved by 84% in the case of Fe, 87% Al, 83% acidity, 51% Zn, 23% Mn and 29% SO_4^{2-}. Alkalinity (74%) and pH (95% as H^+) were increased. Area adjusted removal rates ($Fe = 1.49 \pm 0.66$ g d^{-1} m^{-2}; $acidity = 6.7 \pm 4.9$ g d^{-1} m^{-2}) were low compared to design criteria, mainly due to load limitation. Disregarding seasonality effects, acidity removal and effluent pH were stable over time. A substantial temporal decrease in calcium and alkalinity generation suggests that limestone is increasingly armoured. Once pH is no longer buffered by the carbonate system, metals could be remobilized, putting treatment efficiency at risk.

1. Introduction

Coal mine drainage can be enriched in iron, aluminium, manganese, trace metals (e.g. Pb, Cu, Ni, U, As, Zn and rare earth elements), sulfate and proton acidity (Kepler and Mc Cleary 1994, Yu and Heo 2001, Younger et al. 2002, Buil et al. 2007, Jena et al. 2007, Cravotta 2008, Botha et al. 2009, Janson et al. 2009, Wu et al. 2009). Such drainage can have harmful effects on a variety of receptors including water bodies, vegetation, fauna and infrastructure (Edwards et al. 1997, Jarvis and Younger 1997, Brown et al. 2002, Younger et al. 2002). As a consequence, a decrease of metal and proton acidity (with a commensurate increase in alkalinity) is necessary to allow controlled discharge.

Over the last 15 years, about 50 passive (and hybrid passive) treatment systems (PTS) have been installed in the UK for the purpose of treating (mostly net-alkaline) coal mine drainage with many more reported from Europe, North America, South Africa and some Asian countries (e.g. Hedin et al. 1994, Bhattacharya et al. 2008, Ji et al. 2008). For the passive treatment of net-acidic drainage ((metal and proton) acidity > alkalinity), Reducing and Alkalinity Producing Systems (RAPS) can be applied. RAPS are essentially combinations of anoxic limestone drains (ALD) and compost wetlands (Kepler and Mc Cleary 1994), but are vertical (downward) rather than horizontal flow systems. By removing dissolved oxygen from the water through aerobic microbial respiration, RAPS seek to prevent the oxidation, hydrolysis and precipitation of iron as oxide or hydroxide minerals (Younger et al. 2002). The precipitation of iron oxides is often a cause of failure of aerobic PTS because of the potential clogging of substrate pores and armouring of limestone. Alkalinity and pH are raised by the combined processes of limestone dissolution and anaerobic microbial respiration (e.g. bacterial iron and sulfate reduction, BFeR and BSR). Hydrogen sulfide, a product of BSR, then reacts with chalcophilic elements like Fe^{2+} to form mono and di-sulfides.

1.1. Study site

The Bowden Close (BCl, Fig. 1) passive treatment system is located 12 km southwest of Durham, northeast England, and treats one of more than 20 uncontrolled discharges of the Durham coalfield (Younger 1998). The three individual mine water discharges at Bowden Close are characterised by elevated concentrations of aluminium and iron, considerable amounts of zinc (compared to UK aquatic life standards), manganese and acidic pH. Trace amounts of arsenic, lead, nickel, chromium, cobalt, cadmium and copper have also been determined in the drainage (Fabian et al. 2006).

Discharges 1 and 2 derive from an abandoned flooded drift mine of the Harvey and Hutton coal seams (total sulfur = 1–5%), (Younger 1998). Discharge 3 emerges from a waste rock dump of the former Bowden Close colliery (Younger et al. 2003). During closure of the colliery in the 1960s, buildings were dismantled and the waste rock dump revegetated, but no attempt was made to prevent the generation

---

* Corresponding author. Tel.: +44 191 2464 903(office); fax: +44 191 222 692.
E-mail address: romy.matthies@ncl.ac.uk (R. Matthies).

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.06.009

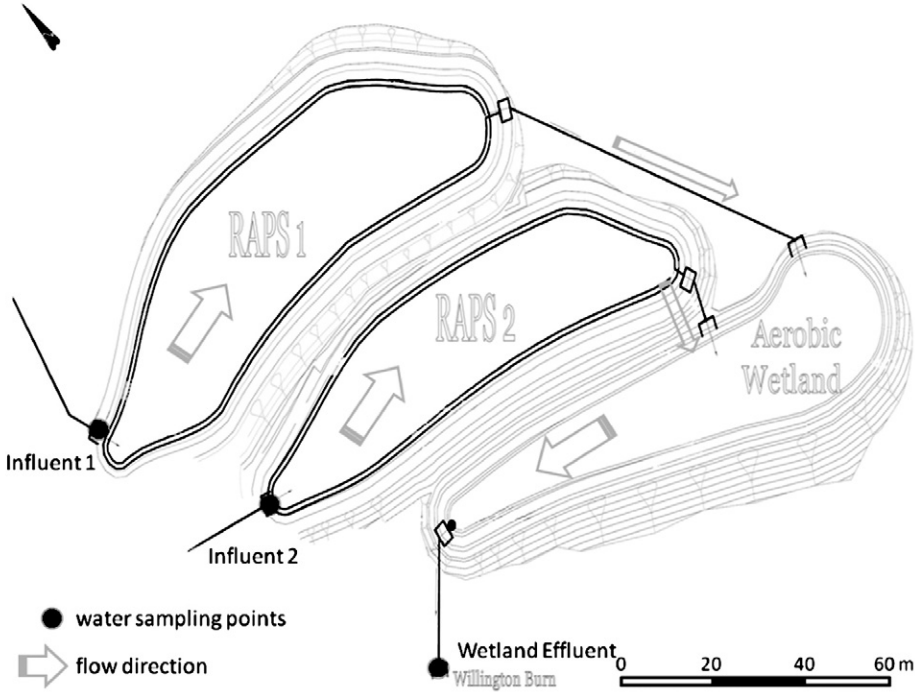

Fig. 1. The Bowden Close treatment scheme is composed of two parallel working Reducing and Alkalinity-Producing Systems (RAPS) and one aerobic reed wetland.

of acid mine drainage. Three decades after closure, it became apparent that the generated mine water had a severe impact on the water quality of the Willington Burn (a tributary of the River Wear) to which the drainage was discharged without prior treatment, and led to a decrease in diversity and abundance of invertebrates (Jarvis and Younger 1997). After the successful operation of a pilot-scale treatment plant between 1999 and 2001 (Younger et al. 2004), a full scale treatment system was installed in 2003. It consists of two parallel working RAPS (RAPS 1: designed area = 1728 m^2, actual area = 1511 m^2, length/width/depth = 86.3/4.5–22.5/0.8 m; RAPS 2: designed area = 4350 m^2, actual area = 1124 m^2, length/width/depth = 83.7/5–16.3/0.8 m) – filled with blended limestone gravel, horse manure and straw compost – which discharge into an aerobic wetland colonised with *Typha latifolia* and *Juncus effusus* (designed area = 1300 m^2, actual area = 990 m^2, length/width/depth = 88.8/5.3–19.5/0.9–1.0 m, Fig. 1). From the wetland outlet chamber, the treated water is discharged into the burn.

The outlets of the RAPS consist of perforated outlet pipe systems with granular fill surrounds underlying the reactive compost-limestone substrate to discharge the treated water (effluent) via an outlet chamber and underground aeration pipes into the wetland. The RAPS are also equipped with overflow pipes to allow a controlled discharge of surplus water (overflow) from the freeboard during high flow events and prevent erosion and potential failure of retaining embankments. Discharges 1 and 2 (influent 1) are directed into RAPS 1 and discharge 3 (influent 2) is directed into RAPS 2. Due to land restrictions, the three treatment ponds, but particularly RAPS 2, had to be downsized by up to four times.

The aim of the current investigation was to evaluate influent and effluent water qualities of the treatment system in order to assess the treatment performance of the active Bowden Close PTS (i.e. both RAPS and the aerobic wetland) with respect to Fe, Al, Mn, Zn and SO_4^{2-}, pH and alkalinity over the course of 5.5 years (Dec03–May09). Seasonal and annual trends have been assessed with a view to identifying the influence of changing influent concentrations and loads on treatment performance and making a preliminary evaluation of the likely overall lifetime of the system.

2. Materials and methods

Monthly surface water monitoring data from December 2003 to May 2009 were assessed in this study. During each sampling event, pH, electrical conductivity (EC), temperature (T), alkalinity (Alk), dissolved oxygen (DO since Jan 08) and flow rates (Q) were determined, along with total cation and anion concentrations. Filtered (<0.45 µm) samples for cation analysis were only sampled sporadically during this time and are not reported here. A Myron 6P Ultrameter was calibrated with pH 4, 7 and 10 and EC 1214 µS cm^{-1} standard solutions. Dissolved oxygen was analysed with an YSI 550A dissolved oxygen meter calibrated against atmospheric oxygen. Redox potentials were corrected to the standard hydrogen electrode. Alkalinity was determined by colorimetric titration (HACH AL-DT test kit) and total (metal and proton) acidity was calculated after Hedin et al. (1994). Flow rates were determined in triplicate by the bucket and stop watch method.

Acid-washed polyethylene bottles used for sampling were completely filled and stored at 4 °C in the absence of light. Samples for the determination of cations (Mg, Ca, Na, K, Fe, Al, Mn, Zn and S; since Jul 05: Si) were preserved with reagent grade nitric acid (1% v/v) and analysed within one month. Samples for sulfate and chloride determination were filtered (<0.45 µm, cellulose nitrate filters) and analysed within two weeks.

Anions were determined with an Ion Chromatograph (IC, type IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column). The IC was one-point calibrated (10 mg L^{-1} Cl^-, 20 mg L^{-1} SO_4^{2-}, detection limits = 0.5 mg L^{-1} SO_4^{-2}). Cation concentrations were quantified with an Inductively Coupled Plasma–Optical Emission Spectrometer (Vista MPX, CCP Simultaneous ICP–OES, Varian; detection limits = 0.01 mg L^{-1} except Al = 0.1 mg L^{-1}). Blanks, standard checks, replicates and standard reference materials (Thames river water: LGC6019, landfill leachate: LGC6175 and riverine water SLRS-3: National Research Council, Canada) were run alongside.

Statistical analyses were undertaken with SPSS 17.0. Statistical significance was assumed if $p<0.05$. Data were converted to a normal distribution by Blom's transformation. Missing data or data where $Q_{inf} \neq Q_{eff}$ were estimated by the median of the immediately previous and subsequent months.

3. Results and discussion

The raw data of the water monitoring are presented in Supplement 1 and are summarized in Table 1. Sequence charts for total concentrations of pH, net-acidity, treatment targets and flow rates in influents and the effluent of the PTS are shown in Fig. 2 and Supplement 2. Correlation coefficients of concentrations and loads from each sampling point are presented in Supplement 3.

3.1. Flow rates and retention times

Three-fold higher average flow rates were measured in influent 2 compared to influent 1 (Table 1). The highest flow rates were observed in late autumn to spring with maximum flow rates in December to February exceeding 200 L min^{-1} in influent 2 ($\bar{x}_{inf1} = 45$ L min^{-1}, $\bar{x}_{inf2} = 125$ L min^{-1}). Lowest flow rates ($\bar{x}_{inf1} = 9$ L min^{-1}, $\bar{x}_{inf2} = 33$ L min^{-1}) were measured during July to September.

Flow rates are linked to treatment performance in that they control hydraulic retention times, mixing and diffusional mass transfer (Jarvis and Younger 2000, Kadlec 2000, Giraldi et al. 2009). Tracer tests using bromide and sodium fluorescein indicated retention times varying from 4–8 days for RAPS 1 and from 4–6 days for RAPS 2, with effective velocities of 0.01 m h^{-1} (Wolkersdorfer et al. 2005). The mean residence time of water within the aerobic wetland was 1–2 days (Wolkersdorfer et al. 2005). Tracer concentration peaks were recorded at between 90 and 140 h (RAPS 1) and 120 h (RAPS 2). The first bromide was detected in the wetland effluent just one day after tracer injection (Wolkersdorfer et al. 2005), but dispersion effects resulted in tracer concentrations remaining above baseline concentrations even up to one month after tracer injection. This suggests that at least a fraction of the mine water may short-circuit via surface flow across the reactive substrate, while another portion appears to stagnate within the substrate. Preferential pathways are likely decreasing mean retention times (Amos and Younger 2003).

Short-circuiting was confirmed by measurements of the RAPS overflow pipes. Although the overflow pipes were installed for occasional use only, in 49% and 77% of all sampling events overflow was recorded in RAPS 1 and 2, respectively. On average, 50% (RAPS 1) and 65% (RAPS 2) of the influent water short-circuited over the RAPS substrate and was directly discharged via overflow pipes into the aerobic wetland. During the first five years of the treatment, overflows were quantified only in terms of flow rates. On no occasion were water qualities determined. However, recent measurements showed, that high but variable amounts of iron (>73% of total Fe), aluminium (>60% of total Al) and sulfate (>54% of total SO_4^{2-}) are removed in the freeboard of the RAPS, leading to overflow concentrations being different to those of the influents. Thus, the treatment performance of the individual ponds of the Bowden Close treatment scheme could not be estimated for the first years of treatment within an acceptable margin of error. Therefore, this paper reports the performance of the entire PTS (i.e. RAPS 1 + 2 plus the aerobic wetland).

Table 1
Arithmetic averages of physicochemical parameters and total element concentrations (2003–2009).

Parameter	Influent 1	Influent 2	Wetland effluent
T	9.6 ± 2.2	9.5 ± 1.7^{63}	10.1 ± 5.2^{63}
pH	5.77 ± 0.98	$\underline{5.00 \pm 0.62}^{63}$	6.89 ± 0.49^{63}
EC	845 ± 129	1617 ± 570^{63}	1430 ± 517^{63}
Eh	330 ± 120	360 ± 80^{63}	220 ± 66^{63}
Alk	25 ± 23	12 ± 20^{63}	115 ± 79^{63}
Acd	73 ± 81	315 ± 173	30 ± 24
DO*	8.3 ± 1.6^{10}	7.6 ± 0.6^{10}	n.m.
Q	33 ± 28^{61}	100 ± 89^{65}	124 ± 125^{61}
SO_4^{2-}	369.9 ± 105.9^{63}	$\underline{1074.6 \pm 553.4}^{62}$	$\underline{670.2 \pm 331.5}^{62}$
Ca	102.2 ± 19^{63}	173.8 ± 60.3^{62}	218.4 ± 111.5^{62}
Fe	$\underline{19.7 \pm 21.9}^{63}$	$\underline{70.9 \pm 48.7}^{62}$	$\underline{5.9 \pm 5.5}^{62}$
Al	$\underline{6.1 \pm 7.5}^{63}$	$\underline{33.0 \pm 19.1}^{61}$	$\underline{1.9 \pm 2.7}^{62}$
Mn	$\underline{1.1 \pm 0.4}^{63}$	$\underline{7.4 \pm 4.5}^{62}$	$\underline{4.4 \pm 3.0}^{62}$
Zn	$\underline{0.2 \pm 0.1}^{63}$	$\underline{1.2 \pm 0.7}^{62}$	$\underline{0.3 \pm 1.3}^{62}$

Average ± standard deviation^n, concentrations = mg L^{-1} except pH, Eh = mV (raw data corrected for the standard hydrogen electrode), Q = flow L min^{-1}, EC = µS cm^{-1}, T = °C, Alk, alkalinity and Acd, acidity = mg $CaCO_3$ eq L^{-1}), DO, dissolved oxygen = mg L^{-1} measured between 2008 and 2009, n = sample size: 64 unless otherwise indicated, n.m. = not measured; underlined values indicate exceedance of guideline limits for UK environment guidelines (compiled from Environmental Quality Standards, Dangerous Substances Directive-List II (76/464/EC), Drinking Water Directive (98/83/EC), Freshwater Fish Directive (78/659/EEC) and Surface Water (River Ecosystem) Regulation (1994/1057)).

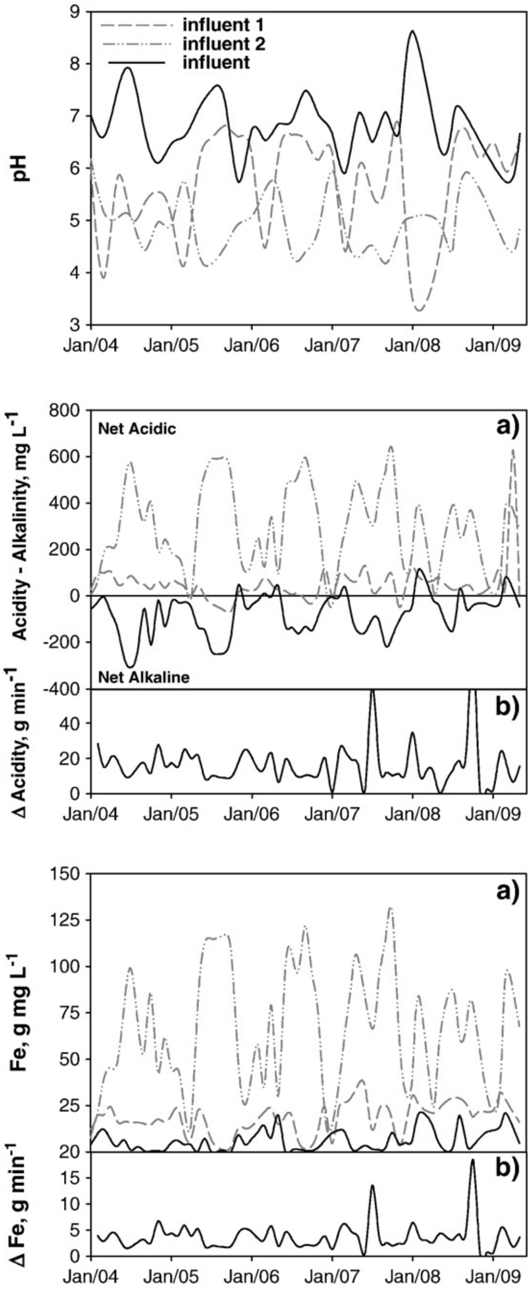

Fig. 2. Sequence charts of a) pH, net-acidity and total iron concentrations in influent 1, 2 and the wetland effluent; and b) element removal rates; alkalinity and acidity in $CaCO_3$ eq.

Overall, tracer tests showed that retention times largely exceeded the recommended minimum of 14 h (Younger et al. 2002, Wolkersdorfer et al. 2005) which were set as design criteria for Bowden Close RAPS (Fabian et al. 2005). In similar treatment systems, retention times varied between 4–8 h and 2.4–27 days (Kepler and Mc Cleary 1995, Demchak et al. 2001, Watson et al. 2009).

3.2. Influent water chemistry

Our data are similar to historic, pre-treatment mine water data (Younger 1998). Influent 2 was net acidic (Fig. 2). Influent 1 was largely net-acidic with about four-fold lower acidity compared to influent 2 (Table 1, Fig. 2a, b). The average alkalinity in influent 1 was two-fold higher than in influent 2 and likely originated from the dissolution of Ca–(Mg)-carbonates (Hedin et al. 1994), siderite (Younger 1998) and ankerite (Prieto and Mery Duitama 1999). Redox potentials and dissolved oxygen concentrations indicated oxidizing conditions (Table 1).

Major ions are predominantly present in the filtered fraction (<0.45 µm filter pore size, unpublished data) which made it reasonable to use total concentrations for the assessment of water types. The mine drift water (influent 1, Fig. 3) is a calcium–magnesium–sulfate water, similar to other uncontrolled discharges of the Durham coalfield (Younger 1998). In influent 2, iron and aluminium showed average concentrations similar to Ca, Mg and SO_4^{2-} (i.e. Ca–Mg–Fe–Al–SO_4^{2-} water type).

Correlations between total concentrations and physicochemical parameters were poor in influent 1 except for the pH-alkalinity and sodium-chloride couples (r>0.8, Supplement 3). The pH and alkalinity are of course closely linked through the carbonate system ($CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+$). Element concentrations in influent 2 are positively correlated to each other and inversely to flow rates (Fig. 4), indicating dilution processes, probably by infiltrating meteoric water into the waste rock dump. Alkalinity and pH showed negative correlations compared to other element concentrations (r<−0.5) in influent 2 which could be related to the increasing instability of the metals (e.g. Al and Fe) at higher pH which causes increased hydrolysis and precipitation as (hydr)oxides.

Compared to influent 1, total concentrations of sulfate, iron, manganese, aluminium and zinc are enriched in influent 2, typically by three to six times. Compared to north east England average stream concentrations, enrichments are as follows: ($Fe_{inf1} \times 78$, $Fe_{inf2} \times 253$, $Mn_{inf1} \times 69$, $Mn_{inf2} \times 465$, $Al_{inf1} \times 87$, $Al_{inf2} \times 468$, $Zn_{inf1} \times 75$, $Zn_{inf2} \times 448$, $S_{inf1} \times 23$, $S_{inf2} \times 67$ (Salminen 2005, de Vos and Tarvainen 2006). Average, minimum and maximum concentrations of influents and the effluent were compared to several UK environmental guidelines (Table 1). Although these guidelines are not directly applicable to mine water but rather to the receiving surface water bodies, the comparison indicates the degree of contamination encountered at Bowden Close. In the influents, iron, zinc and manganese (all filtered fraction) exceeded aquatic life standards. Additionally, the average and 95th percentile of sulfate in influent 2 exceeded the guideline limit (400 mg L^{-1}). The pH did not comply with the minimum level of 6 in influent 2 ($Q_{95} = 5.8$). Iron, manganese, zinc, sulfate and pH were identified as main treatment targets. No guideline limit exists for aluminium. Nonetheless, due to its toxicity and potentially suffocating effects on aquatic biota (Nordstrom 1982, Havas and Likens 1985, Havens and Heath 1989, Havens and Heath 1990) it was included in the list of treatment targets.

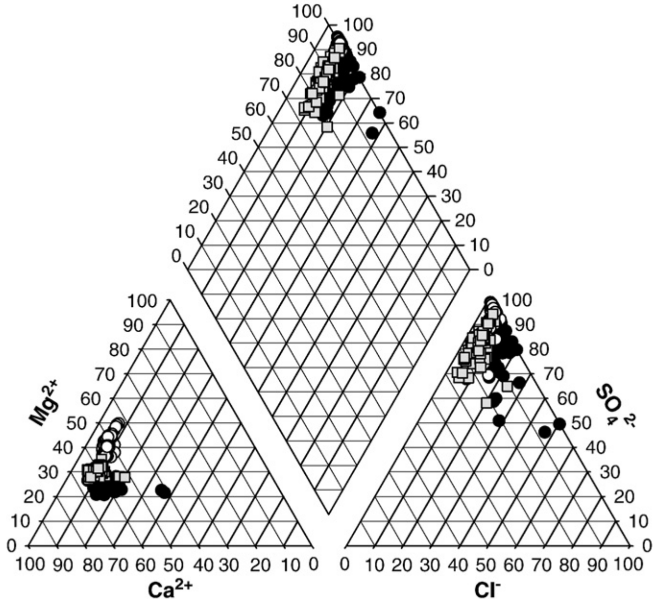

Fig. 3. Piper plot of influents 1 and 2 and the effluent (Ca, Mg, Na + K; Cl^-,SO_4^{2-},CO_3^{2-} + HCO_3^-).

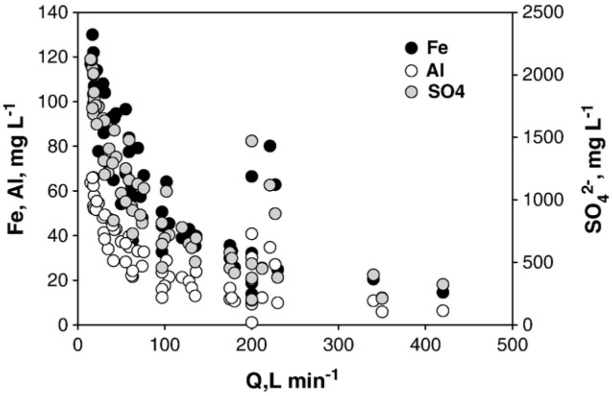

Fig. 4. Iron, aluminium and sulfate concentrations in influent 2 compared to flow rates.

3.3. Effluent water chemistry

The Bowden Close effluent is characterized by circum-neutral pH (>5.7, Fig. 2), and most waters are net-alkaline. The effluent water is characterised as a Ca–Mg–SO_4^{2-}(–HCO_3^-) water type (Fig. 3). Compared to influents, acidity, iron, aluminium and sulfate are significantly depleted, although zinc and manganese are significantly depleted compared to influent 2 only. The alkalinity is significantly enriched and proton acidity is depleted. Effluent element concentrations and electrical conductivities in the effluent are inversely correlated to flow rates (Supplement 3). However, this was not the case for iron, aluminium and zinc (r<0.27), which could be an effect of the overflow and flushing of hydrous oxides in the surface sediment. As discussed earlier, increased flow rates favour horizontal flow which could lead to resuspension of the surface ochre sludge during high flow events. Despite the considerable improvement of the mine water quality by the passive treatment, concentrations of some contaminants still exceeded guideline limits. This was particularly the case for sulfate and manganese, and occasionally for iron and zinc (Table 1).

3.4. Treatment performance

Evaluating pollutant concentrations in mine water is an essential part of the assessment of toxicity effects to environmental receptors. However, to discuss the performance of the treatment system, element loads (g d^{-1}) have to be calculated to assess element mass balances. Overall, the Bowden Close PTS received a mean acidity load of 30.2 kg acidity $CaCO_3$ eq per day (range: 2.2–118 kg). The waste rock dump drainage (influent 2) contributed more than 88% of the total acidity load. Contaminant loads are positively correlated to each other in influents as well as in effluents (Supplement 3). However, correlations between influent loads and element removal loads are generally low $r<0.7$ or insignificant (e.g. Mn).

Treatment efficiencies are calculated based on the differences in concentration between the influent and effluent sampling points (Wieder 1993). This approach has the disadvantage that flow rates, element loads and the area of the treatment system are not considered. Hence, outcomes are relative and not comparable to other treatment facilities. Here, we calculated load efficiencies ($\Delta L\% = 100(Linf - Leff)Linf^{-1}$; L_{inf} = influent load including influent 1 and influent 2 ($g\ d^{-1}$), L_{eff} = effluent load ($g\ d^{-1}$)) and average load removal rates ($\Delta L = L_{inf} - L_{eff}$, $g\ d^{-1}$).

Area adjusted removal rates (AR, $g\ d^{-1}\ m^{-2}$) are most commonly used for the assessment of the treatment performance. Thus, the average load removal is adjusted to the surface area of the system ($AR = \Delta LA^{-1}$; A = surface area). However, because RAPS are vertical flow systems and because of the increased depths compared to aerobic PTS, it is logical to evaluate treatment performance on a volume-adjusted basis (Mayes et al. 2009), which has been done here as well ($VR = AR{*}d{*}n_e$, d = depth, n_e = effective porosity (0.3–0.5)). These metrics of treatment performance assume zero-order removal kinetics.

Treatment performance and total mass removal since system commissioning are summarized in Table 2. Overall, the effectiveness of contaminant removal is in the order: aluminium > iron > (acidity) > zinc > sulfate > manganese.

Average acidity removal rates ($6.7\ g\ d^{-1}\ m^{-2}$) were low compared to literature sizing criteria for RAPS treatment schemes of 20–30 $g\ d^{-1}\ m^{-2}$ (Nairn and Mercer 2000, Demchak et al. 2001, Watzlaf et al. 2002, PIRAMID Consortium 2003, Ziemkiewicz et al. 2003, Riefler et al. 2008) and also compared to removal rates reported from other RAPS schemes (0–293 $g\ d^{-1}\ m^{-2}$); (Nairn and Mercer 2000, Danehy et al. 2001, Demchak et al. 2001, Ziemkiewicz et al. 2003, Bhattacharya et al. 2008). Nairn and Mercer (2000) measured mean iron removal rates of 17 $g\ d^{-1}\ m^{-2}$ compared to 1.5 $g\ d^{-1}\ m^{-2}$ in Bowden Close. Hedin et al. (1994) reported average sulfate removal rates of 5.2 $g\ d^{-1}\ m^{-2}$ for compost wetlands; lower than those observed in Bowden Close (8.0 $g\ d^{-1}\ m^{-2}$). Expressed as mass removal per litre and day, Bowden Close ($\bar{x} = 291 \pm 249\ mg\ d^{-1}\ L^{-1}$) removed sulfate in the same order of magnitude as obtained from column and batch experiments reported by Cruz Viggi et al. (2010) and citations therein. Average area adjusted removal rates of manganese were about one order of magnitude lower than those measured in aerobic wetlands monitored by Hedin et al. (1994). Zinc removal rates are low compared to those reported by Mayes et al. (2009) and to most references cited therein.

3.5. Seasonality and annual trends

To assess seasonal changes and trends in the treatment performance it is necessary first to address variations in influent water characteristics. Both influents showed significant seasonality both in terms of concentrations and loads (e.g. Fe; Fig. 2). Flow rates varied significantly over the course of a year and were negatively correlated to electrical conductivities ($r_{inf1/inf2} = -0.39/-0.79$), suggesting that changes in concentrations are primarily driven by dilution effects, also observed in other mining areas (Mac Causland and Mc Tammany 2007). The non-linear, exponential correlation of Q and EC and the major ions in influent 2 (Fig. 4) suggests additional factors, such as mineral precipitation and mixing with other waters, may also influence element concentrations. Despite the considerably lower concentrations for most parameters over the winter and early spring period, highest element loads were recorded during February to April due to the significantly higher flow rates.

Table 2
Removal rates and amounts of treatment parameters.

Parameter	Load Efficiency	Load Removal	Total Removal	Area adj. Removal	Volume adj. Removal
Acidity	83	24.2 ± 17.9	48.6	6.7 ± 4.9	17 ± 13
Iron	84	5.41 ± 2.4	10.6	1.49 ± 0.66	3.8 ± 3
Aluminium	87	2.48 ± 1.3	4.9	0.69 ± 0.35	1.9 ± 2
Manganese	23	0.11 ± 0.18	0.22	0.03 ± 0.05	114 ± 274
Zinc	51	48.3 ± 138	0.94	13 ± 38	43 ± 101
Sulfate	29	29.1 ± 23.7	56.9	8.04 ± 6.5	27.1 ± 44

Average ± standard deviation, load efficiency in %, load removal in $kg\ d^{-1}$ except Zn ($g\ d^{-1}$), total removal in tons (Dec03–May09), area adjusted removal rates in $g\ d^{-1}\ m^{-2}$ except Zn ($mg\ d^{-1}\ m^{-2}$), volume adjusted removal rates in $g\ d^{-1}\ m^{-3}$ except Zn, Mn ($mg\ d^{-1}\ m^{-3}$).

Physicochemical parameters and element loads showed significant seasonal variations in influents (except alkalinity, EC (influent 1), Mn, Al and Zn (influent 2)). However, annual means showed no significant changes throughout the five years, i.e. there was no long term trend (tested with moving average (span = 12) and seasonal decomposition). This indicates that AMD generation in the waste rock dump and the mine processes have stabilised and are largely controlled by *juvenile* acidity formation (i.e. acidity that is generated during the oxidation of sulfide minerals) (Younger 1998).

Despite the seasonality in influent chemistry, removal rates did not show clear temporal patterns and were characterized by non-stationarity and heteroscedastisity. This is possibly a combined effect of the two influents, dispersion and short-circuiting but could here not be unravelled.

On 6 out of 66 occasions, respectively, a net increase of manganese was observed across the treatment system, i.e. effluent loads exceeded influent loads. In 27 occasions, a net sulfate increase was observed. This could be related to increased exchange of interstitial waters at higher flow rates or remobilization via desorption, redissolution and ion exchange.

The removal of the seasonality by running median (span = 12) did not lead to any clear trends. Annual average removal rates and seasonal average removal rates were not significantly different for any treatment performance parameter. Cumulative curves of removal rates (Fig. 5) suggest that despite the time dependent increasing variance and occasional remobilisation of manganese and sulfate, no indication was found for a change in the treatment performance of Bowden Close for the principal treatment parameters (Al, Fe, Zn, Mn and SO_4^{2-}).

Removal trends observed in Bowden Close differ from similar treatment systems (e.g. Wieder 1993, Hedin et al. 1994, Woulds and Ngwenya 2004). In the latter, the lowest acidity removal rates occurred during winter months whereas highest removal rates occurred in summer. This was not the case in Bowden Close, where

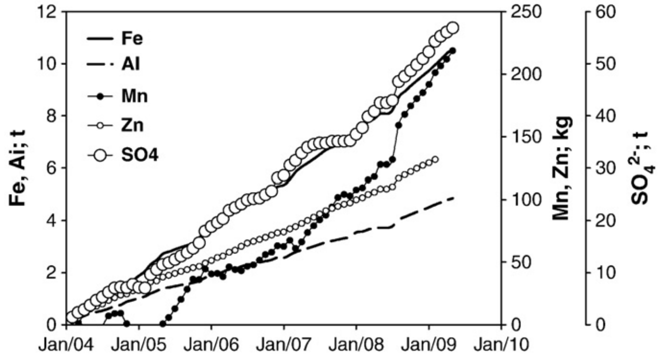

Fig. 5. Cumulative curves of iron, aluminium, zinc, manganese and sulfate removal over 5.5 years of passive treatment.

the highest removal rates coincide with the highest influent loads (February and March). A comparison of loads of influent acidity and acidity removal rates (Fig. 6) revealed significant positive correlation ($r>0.6$, without outliers: $r>0.88$). This indicates that acidity removal was mostly load limited (particularly at influent acidity loads <25 g min^{-1} $CaCO_3$ eq), of first order and the reason why seasonal removal patterns of other PTS were not repeated in Bowden Close.

However, during high flow events (filled circles on Fig. 6), increased horizontal flow in the RAPS probably led to increased short-circuiting of the water over the RAPS and an overall decrease in retention time in the treatment scheme. Treatment performance declined during these periods. This assumption is supported by the fact that these “outliers” occurred at average overflow: effluent flow ratios of 4.6 (in RAPS 2), i.e. four times more water was short-circuited over the reactive RAPS substrate than infiltrated into it.

3.6. Removal processes for main contaminants

Potential sinks for metals in PTS have been widely discussed (Kepler and Mc Cleary 1994, Younger et al. 2002). Due to the lack of filtered element concentrations, potential removal processes were estimated based on removal ratios, correlation coefficients (Supplement 3) and multiple regression.

Redox sensitive iron and sulfur are often believed to be preferentially removed as sedimentary sulfide minerals (FeS, FeS_2) in anaerobic PTS (Younger et al. 2002). From the average S:Fe removal ratio of 3.6 ± 2.4 (range: -1.8 to 11.3; Fig. 7) it is apparent that a number of removal processes are potentially occurring in parallel within the system including the removal of sulfides (S:Fe = 1 (FeS), = 2 (FeS_2)) and oxyhydroxysulfates (S:Fe = 0.125–0.167, e.g. schwertmannite (Bigham et al. 1996)). However, despite the strong correlation between iron and sulfur removal rates ($r = 0.81$), the excess sulfur removed by the PTS over iron suggests that a significant fraction of sulfur is removed independently of iron. This was confirmed in an earlier study that showed that the dominant sulfur sinks were organic sulfur, elemental sulfur and oxyhydroxysulfates (Matthies et al. 2009).

The principal aluminium sinks in this kind of treatment system are oxyhydroxysulfates and (hydr)oxides (Younger et al. 2002). Manganese was net removed in the substrate during May to October whilst in November to April it was potentially net-released. Temperature, iron removal, effluent pH and the mobilization of calcium had a significant impact on the removal of manganese (multiple regression, Eq. (1)). The mobilization of calcium had the highest importance (i.e. highest standardized $\beta = -0.69$) of all predictor variables (T, Ca, Fe and H^+):

$$\Delta Mn = -214 + 25.6T - 0.023Ca + 0.032Fe - 6.3*10^5 H^+ \quad (1)$$

ΔMn = manganese removal rates (mg min^{-1}),
T = temperature in °C determined in influents,
Ca = calcium mobilization (mg min^{-}),
Fe = iron removal (mg min^{-1}),
H^+ = effluent pH (in H^+),
standard errors ($stderr_{const} = 50.8$, $stderr_T = 4.6$, $stderr_{Ca} = 0.001$,
$stderr_{Fe} = 0.005$, $stderr_H = 2.07*10^5$;
standardized β ($\beta_T = 0.21$, $\beta_{Ca} = -0.69$, $\beta_{Fe} = 0.327$, $\beta_{pH} = -0.124$)

No multicollinearity (i.e. linear relationship) between the predictor variables was observed. It is apparent that most manganese was removed at higher temperatures and circum-neutral to alkaline effluent pH. More manganese was removed when iron removal was high, suggesting co-precipitation. It is unclear, however, how the negative relation between calcium mobilization (potentially caused by limestone dissolution) and manganese removal can be interpreted. Sequential extractions of the RAPS substrates (unpublished data) indicated that more than 50% of the total manganese was bound to carbonates. Whether the precipitation of calcium carbonates, supersaturated in RAPS effluents, could favour the coprecipitation of manganese has to be assessed further.

Zinc removal was poorly correlated to other parameters (Supplement 3). Unpublished data of sequential extractions of RAPS sediments indicated that more than 40% of zinc is remobilised from the substrate upon treatment with 6 N HCl and could represent both zinc in sulfides or coprecipitated zinc onto hydroxides.

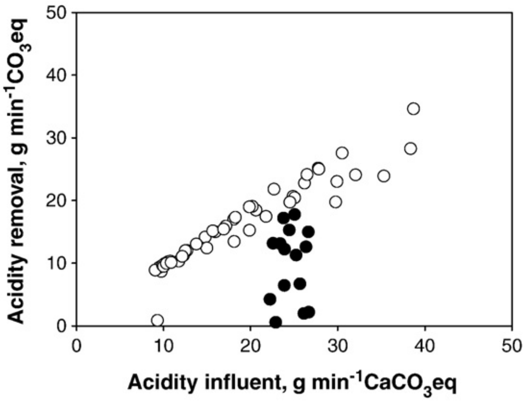

Fig. 6. Acidity influent load versus acidity removal, samples represented by filled circles are possibly caused by short-circuiting of the water during high flow events; regression equation of the remaining samples: $\Delta acidity_{rem} = 1.7 + 0.8 acidity_{inf}$; $r = 0.79$.

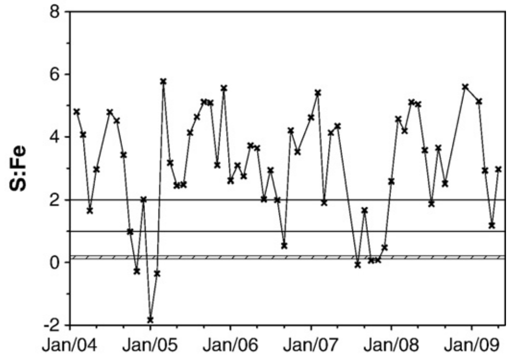

Fig. 7. Sulfur: iron removal ratios in Bowden Close; lines indicate S:Fe ratios of (1) FeS and (2) FeS_2; the shaded area indicates S:Fe ratios (0.125–0.166) of oxyhydroxysulfates (Bigham et al. 1996); negative S:Fe values indicate net removal of either sulfur or iron or both; outliers were excluded.

3.7. Alkalinity generation

The longevity of the treatment system depends on two principal factors: the generation of bicarbonate alkalinity and the pore volume available for the accumulation of metal sludge which crucially influences substrate permeability.

The increase in net-alkalinity in the PTS is a complex process driven by the sum of alkalinity generating processes (e.g. limestone dissolution and anaerobic respiration processes), metal acidity generating processes (precipitation of hydroxide minerals, e.g.: $Fe^{3+} + H_2O \rightarrow Fe(OH)_3 + 3H^+$) and proton acidity consuming processes (e.g. $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$). The net-alkalinity generated by a PTS is often estimated (Eq. (2)) by the sum of total amount of (metal and proton) acidity removed (in calcium carbonate equivalent) and the *surplus alkalinity* (i.e. the increase in bicarbonate alkalinity generated by the PTS from limestone dissolution and anaerobic respiration). It is recognised that multiple other processes may also contribute to the overall net alkalinity and acidity removal, but the key processes are accounted for in this equation.

$$\text{Net alkalinity} = \text{Acidity Removal} + \text{Surplus Alkalinity}. \tag{2}$$

Acidity removal = Influent—Effluent acidity loads;
Surplus alkalinity = Effluent—Influent Bicarbonate Alkalinity Loads

The equation is based on two principal statements: (i) the release of calcium from the PTS is an indicator for the dissolution of limestone, i.e. limestone alkalinity (e.g. Kepler and Mc Cleary 1995, Riefler et al. 2008), and (ii) the unaccounted bicarbonate generation is a product of the removal of sulfate by microbial reduction (BSR, $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$) (Hedin et al. 1994, Kepler and Mc Cleary 1994, Jarvis and England 2002).

This approach may be complicated by the following reasons: I) organic substrates can function as a net source of calcium (total Ca concentration ≈ 9.4–65.2 g kg^{-1}) during degradation (Stewart et al. 2000, Guo et al. 2001, Ji and Kim 2008) though compared to the 50% limestone in the substrate, this is likely to be a minor calcium source; II) Calcium can be retained in the substrate by precipitation as carbonate or sulfate (e.g. calcite and gypsum) (e.g. Barton and Karathanasis 1999, Herbert et al. 2000), and by assimilation, sorption and ion-exchange ; III) Analysis of PTS sediments (e.g. Herbert et al. 2000, Neculita et al. 2008, Matthies et al. 2009) showed that the removal of sulfate largely occurs as organic sulfur or oxyhydroxysulfates and only minor amounts of chalcophilic elements were retained in sulfides; IV) Non-BSR anaerobic respiration processes (e.g. anaerobic NO_3^-, Fe^{3+}, Mn^{4+} reduction and methanogenesis) are sources of CO_2 but are mostly neglected in the treatment performance discussion; V) Sequential extractions of RAPS sediments showed that only a fraction of iron and aluminium (<72%) were recovered in the (hydr) oxide phase (e.g.: $Al^{3+} + H_2O \ Al(OH)_3 + 3H^+$) (Matthies et al. 2009), i.e. other removal processes likely have not contributed to the generation of proton acidity.

As a consequence of these limitations, limestone alkalinity can be both over- or underestimated (points (I) and (II), respectively); biologically derived alkalinity can be over- and underestimated (points (III) and (IV), respectively) and the alkalinity that is consumed based on the removal of metal acidity can be overestimated (point (V)). These potentially complicating factors need to be borne in mind when interpreting the mechanisms of alkalinity generation in PTS.

It was shown in previous sections that pH and alkalinity of the mine water were raised by the PTS throughout the more than five years of treatment. Effluent pH and alkalinities always exceeded 5.7 and 9 mg L^{-1} $CaCO_3$ eq, respectively. One way analysis of variance on alkalinity loads showed that increases were significantly different both seasonally and annually. Multiple regression (equation 3) did not lead to a clear identification of the main processes influencing the increase in pH and release of alkalinity. However, calcium mobilisation accounts for only 17% of the variation in alkalinity, suggesting that a considerable portion of alkalinity derives from processes other than limestone dissolution, e.g. anaerobic microbial respiration. Furthermore, bicarbonate was generated even in circumstances in which there was no net-generation of calcium in the treatment system. The cumulative curve of the net-alkalinity generation was constant throughout the time of monitoring (Fig. 8) indicating a constant overall treatment performance of the system. The bulk of the variation of the net-alkalinity ($R^2_{adj} = 87\%$) was explained by three variables: i) the removal of iron ($\beta = 0.88$), ii) the increase in calcium ($\beta = 0.40$) and iii) the decrease in aluminium ($\beta = 0.35$).

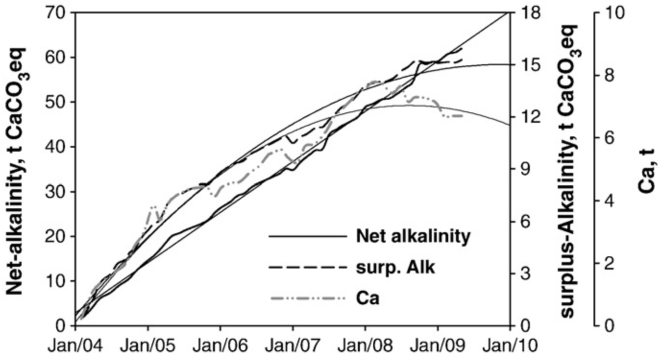

Fig. 8. Cumulative curves (and regression curves) of the generation of net alkalinity and surplus alkalinity and mobilization of calcium.

$$\text{Net}-\text{alkalinity} = -1.67{*}103375 + 0.67\text{Ca} + 4.49\text{Fe} + 3.19\text{Al}. \tag{3}$$

Net − alkalinity = generation of alkalinity (mg min^{-1}),
Ca = calcium remobilization rate (mg min^{-1}),
Fe = iron removal (mg min^{-1}),
Al = aluminium removal (mg min^{-1}),
standard errors ($stderr_{const} = 1.44{*}10^3$, $stderr_{Ca} = 0.10$, $stderr_{Fe} = 0.33$, $stderr_{Al} = 0.62$

There was no significant long term change in effluent pH. However, the cumulative curve of surplus alkalinity and calcium (Fig. 8) follows first order logarithmic behaviour and significant decreases in annual bicarbonate generation and calcium mobilization were observed. There are two potential reasons for this behaviour. If the bulk of calcium mobilized is derived from limestone dissolution, a decrease in calcium concentrations in the effluent could be caused by armouring of the limestone gravels with secondary mineral precipitates (Huminicki and Rimstidt 2008). Secondly, since calcium carbonate is supersaturated in RAPS effluents (unpublished data), carbonate precipitation could partially account for the decrease in alkalinity and calcium. In addition, the apparent decrease in bicarbonate generation could also be related to a decelaration of anaerobic respiration processes. It has been widely reported that the ageing organic substrate of PTS is increasingly depleted in short chained organic molecules, essential for heterotrophic sulfate reducing bacteria (SRB) (Cocos et al. 2002). The remaining organic matter is increasingly enriched in cellulose and lignin that have to be pre-digested, e.g. by fermentative bacteria and converted into lower molecular weight compounds which can be utilised by SRB (Tsukamoto et al. 2004, Zagury et al. 2006). More work is necessary to unravel the principal cause of the decrease in alkalinity generation. Currently, a study is underway to identify the principal source of carbon by application of stable carbon isotopes.

4. Conclusions

More than five years of passive treatment data for two net-acidic coal mine discharges from northeast England have been assessed in this study. The treatment system performed reasonably well for the removal of iron, aluminium and acidity, and constantly increased pH and alkalinity. Manganese, zinc and sulfate were partially removed in the system, but occasionally remobilized. Removal ratios of iron and sulfate indicated that in addition to sulfide minerals, other Fe, S sinks exist. Manganese removal as a carbonate is to be confirmed and so are the reasons for its seasonal remobilisation. It is critical to expand the study with interstitial water and solid phase sediment analytical data of the three treatment ponds.

Trend analysis indicated that removal rates of the main contaminants, though seasonal, were constant over the five years of monitoring. This is encouraging in that despite the increase in surface ochre sludge and significant overflow through the RAPS, the treatment system still performs well after more than five years of operation. However, a significant decrease in calcium and bicarbonate mobilization, possibly caused by the armouring of limestone, suggests that regeneration of the system may be required in the near future.

To increase the life time of the PTS it is recommended to remove the surface sludge covering the RAPS in order to increase the freeboard and promote downward flow. Also controlled flushing of secondary precipitates (Kepler and Mc Cleary 1997, Watzlaf et al. 2002) have been shown to increase the void space. However, this will be of limited use to remove surface precipitates from the apparently armoured limestone. It appears unavoidable therefore that the reactive substrate will have to be replaced as soon as pH is no longer sufficiently buffered to avoid redissolution of mineral precipitates which could lead to the remobilisation of the target elements. Replacement of PTS substrate is a major undertaking, particularly with respect to disposal of the spent substrate, which can be very costly, especially if the only disposal route is to landfill. Therefore, investigations of the type discussed here provide valuable insight into both the longevity of such PTS and the overall costs and benefits of PTS for remediation of pervasive waste streams such as mine water pollution.

Acknowledgements

The authors thank the EPSRC, Environment Agency, the Institute for Research on Environment and Sustainability and the School of Civil Engineering and Geosciences (Newcastle University) for funding the project and staff of the HERO group for assistance in field and labwork. H.A.B. Potter and two anonymous reviewers provided valuable comments on an earlier draft of this manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2010.06.009.

References

Amos PW, Younger PL. Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate. Water Res 2003;37:108–20.

Barton CD, Karathanasis AD. Renovation of a failed constructed wetland treating acid mine drainage. Environ Geol 1999;39(1):39–50.

Bhattacharya J, Ji S, Lee H, Cheong Y, Yim G, Min J, Choi Y. Treatment of acidic coal mine drainage: design and operational challenges of Successive Alkalinity Producing Systems. Mine Water Environ 2008;27(1):12–9.

Bigham JM, Schwertmann U, Traina SJ, Winland RL, Wolf M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim Cosmochim Acta 1996;60(12):2111–21.

Botha M, Bester L, Hardwick E. Removal of uranium from mine water using ion exchange at Driefontein mine. International Mine Water Conference, Pretoria, South Africa; 2009. p. 19–23. October.

Brown M, Barley B, Wood H. Minewater treatment technology, application and policy. Dorchester: IWA; 2002.

Buil B, Gomez P, Gaffafon A, Turmero MJ. Factors controlling mobility of heavy metals and rare earth elements in a stream affected by mine drainages (NW Spain). In: Loredo Lopez J, editor. 23 rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacion y Prospeccion de Minas, University of Oviedo, Oviedo, Spain; 2007. p. 14.-19. June.

Cocos IA, Zagury GJ, Clement B, Samson R. Multiple factor design for reactive mixture selection for use in reactive walls in mine drainage treatment. Water Res 2002;36(1): 167–77.

Cravotta CA. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: constituent quantities and correlations. Appl Geochem 2008;23(2):166–202.

Cruz Viggi C, Pagnanelli F, Cibati A, Uccelletti D, Palleschi C, Toro L. Biotreatment and bioassessment of heavy metal removal by sulphate reducing bacteria in fixed bed reactors. Water Res 2010;44(1):151–8.

Danehy TP Hilton T, Watzlaf GR Johnson F, Busler SL Denholm CF, Dunn MH. Advancement in vertical flow-hybrid passive treatment systems. West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA; 2001. p. 4. April.

de Vos W, Tarvainen T. Geochemical atlas of Europe. Part 2: interpretation of geochemical maps, additional tables, figures, maps, and related publications. Espoo: Geological Survey of Finland; 2006.

Demchak J, Morrow T, Skousen J. Treatment of acid mine drainage by four vertical flow wetlands in Pennsylvania. Geochem Explor Environ Anal 2001;1(1):71–80.

Edwards PJ Bolton CP, Ranson C, Smith AC. The river Pelenna minewater treatment project. Abandoned Mines: Problems and Solutions. Environment Agency, Sheffield, UK; 1997. p. 20.-21. March.

Fabian D, Aplin AC Younger PL. In: Loredo J, Pendas F, editors. Geochemical performance of a Reducing and Alkalinity-Producing System (RAPS) for the passive treatment of acidic mine drainage at Bowden Close, United Kingdom. Oviedo, Spain: Mine Water: Mine Closure; 2005. p. 5.-7. September.

Fabian D, Jarvis AP Younger PL, Harries ND. Contaminated land: Applications in real environments (CL:AIRE), London; 2006.

Giraldi D, de'Michieli Vitturi, M, Zaramella M, Marion A, Iannelli R. Hydrodynamics of vertical subsurface flow constructed wetlands: tracer tests with rhodamine WT and numerical modelling. Ecol Eng 2009;35(2):265–73.

Guo M, Chorover J, Rosario R, Fox RH. Leachate chemistry of field-weathered spent mushroom substrate. J Environ Qual 2001;30:1699–709.

Havas M, Likens GE. Changes in Na influx and outflux in Daphnia magna as a function of elevated Al concentrations in soft water at low pH. Proceedings of the National Academy of Science; 1985.

Havens KE, Heath RT. Acid and aluminum effects on freshwater zooplankton: an in situ Mesocosm study. Environ Pollut 1989;62(2–3):195–211.

Havens KE, Heath RT. Phytoplankton succession during acidification with and without increasing aluminum levels. Environ Pollut 1990;68(1–2):129–45.

Hedin RS, Nairn RW, Kleinmann RLP. Passive treatment of coal mine drainage. IC9389, Bureau of Mines US Department of the Interior, Washington, DC; 1994.

Herbert RB, Benner SG, Blowes DW. Solid phase iron–sulfur geochemistry of a reactive barrier for treatment of mine drainage. Appl Geochem 2000;15:1331–43.

Huminicki DMC, Rimstidt JD. Neutralization of sulfuric acid solutions by calcite dissolution and the application to anoxic limestone drain design. Appl Geochem 2008;23(2):148–65.

Janson E, Gzyl G, Banks D. The occurrence and quality of mine water in the Upper Silesian coal basin, Poland. Mine Water Environ 2009;28:232–44.

Jarvis A, England A. Operational and treatment performance of a unique Reducing and Alkalinity Producing System (RAPS) for acidic leachate remediation in Lancashire, UK. In: Merkel BJ, Planer-Friedrich B, Wolkersdorfer C, editors. Uranium in the Aquatic Environment. Freiberg, Germany: Springer; 2002. p. 15.-21. September.

Jarvis AP, Younger PL. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK. Chem Ecol 1997;13:249–70.

Jarvis AP, Younger PL. Passive treatment of net-acidic mine waters: Field experiences in the UK, 7th International Mine Water Association Congress. International Mine Water Association, Ustron, Poland; 2000. p. 11.-15. September.

Jena VK, Jaiswal NK, Patel KS. Arsenic and other toxic elements in coal leachates of Korba: a review of central India. In: Loredo Lopez J, editor. 23 rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacíon y Prospección de Minas, University of Oviedo, Oviedo; 2007. p. 14.-19. June.

Ji S, Kim S, Ko J. The status of the passive treatment systems for acid mine drainage in South Korea. Environ Geol 2008;55(6):1181–94.

Ji SW, Kim SJ. Lab-scale study on the application of In-Adit-Sulfate-Reducing System for AMD control. J Hazard Mater 2008;160(2–3):441–7.

Kadlec RH. The inadequacy of first-order treatment wetland models. Ecol Eng 2000;15: 105–19.

Kepler DA, Mc Cleary EC. Successive Alkalinity-Producing Systems (SAPS) for the treatment of acidic mine drainage. International Land Reclamation and Mine Drainage Conference and the 3rd International Conference on the Abatement of Acidic Drainage, Pittsburgh, USA; 1994.

Kepler DA, Mc Cleary EC. Successive Alkalinity-Producing Systems (SAPS). 16th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA; 1995.

Kepler DA, Mc Cleary EC. Passive aluminium treatment successes. 18th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA; 1997. p. 15.-16. April.

Mac Causland A, Mc Tammany ME. The impact of episodic coal mine drainage pollution on benthic macroinvertebrates in streams in the Anthracite region of Pennsylvania. Environ Pollut 2007;149(2):216–26.

Matthies R, Aplin AC, Boyce AJ, Jarvis AP. Is bacterial sulfate reduction a dominant process for the removal of iron in reducing and alkalinity producing systems? ICARD: Proceedings from the 8th International Conference on Acid Rock Drainage, Skelleftea, Sweden; 2009. p. 21.-24. May.

Mayes WM, Potter HAB, Jarvis AP. Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. J Hazard Mater 2009;162(1):512–20.

Nairn R, Mercer M. Alkalinity generation and metals retention in a successive alkalinity producing system. Mine Water Environ 2000;19(2):124–33.

Neculita C-M, Zagury GJ, Bussière B. Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: II. Metal removal mechanisms and potential mobility. Appl Geochem 2008;23(12):3545–60.

Nordstrom DK. The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3–SO_3–H_2O at 298 K. Geochim Cosmochim Acta 1982;46(4):681–92.

PIRAMID Consortium. Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters. Newcastle: University of Newcastle; 2003.

Prieto G, Mery Duitama L. Environmental impacts and acid drainage of coal mining in Cundinamarca Department, Colombia. Seville, Spain: International Mine Water Conference; 1999.

Riefler RG, Krohn J, Stuart B, Socotch C. Role of sulfur-reducing bacteria in a wetland system treating acid mine drainage. Sci Total Environ 2008;394(2–3):222–9.

Salminen R. Geochemical atlas of Europe. Part 1: background information, methodology and maps. Espoo: Geological Survey of Finland; 2005.

Stewart DPC, Cameron KC, Cornforth IS, Main BE. Release of sulphate-sulphur, potassium, calcium and magnesium from spent mushroom compost under field conditions. Biol Fertil Soil 2000;31:128–33.

Tsukamoto TK, Killion HA, Miller GC. Column experiments for microbiological treatment of acid mine drainage: low-temperature, low-pH and matrix investigations. Water Res 2004;38(6):1405–18.

Watson IA Taylor K, Sapsford DJ Banks D. Tracer testing to investigate hydraulic performance of a RAPS treating mine water in South Wales. ICARD: Proceedings from the 8th International Conference on Acid Rock Drainage, Skelleftea, Sweden; 2009. p. 21.-24. May.

Watzlaf GR, Kairies CL, Schroeder KT, Danehy T, Beam R. Quantitative results from the flushing of four reducing and alkalinity-producing systems. West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA; 2002. p. 16.-17. April.

Wieder RK. Ion input/output budgets for five wetlands constructed for acid coal mine drainage. Water Air Soil Pollut 1993;71(3–4):231–70.

Wolkersdorfer C, Hasche A, Göbel J, Younger PL. Tracer test in the Bowden Close passive treatment system (UK): preliminary results, 56. Berg- und Hüttenmännischer Tag: Behandlungstechnologien für bergbaubeeinflusste Wässer, Freiberg; 2005.

Woulds C, Ngwenya BT. Geochemical processes governing the performance of a constructed wetland treating acid mine drainage, Central Scotland. Appl Geochem 2004;19:1773–83.

Wu P, Tang C, Liu C, Zhu L, Pei T, Feng L. Geochemical distribution and removal of As, Fe, Mn and Al in a surface water system affected by acid mine drainage at a coalfield in Southwestern China. Environ Geol 2009;57(7):1457–67.

Younger PL. Coalfield abandonment: Geochemical processes and hydrochemical products. In: Nicholson K, editor. Energy and the environment: Geochemistry of fossil, nuclear and renewable resources. Environmental geochemistry series, vol. 1 Insch. Mac Gregor Science; 1998.

Younger PL, Banwart SA, Hedin RS. Mine water: hydrology, pollution, remediation. London: Kluwer; 2002.

Younger PL, Jayaweera A, Elliot A, Wood R, Amos P, Daugherty A, Martin A, Bowden L, Aplin AC, Johnson DB. Passive treatment of acidic mine waters in subsurface-flow systems: exploring RAPS and permeable reactive barriers. Land Contam Reclam 2003;11(2):127–35.

Younger PL, Jayaweera A, Wood R. A full-scale Reducing and Alkalinity-Producing System (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham, CL:AIRE Annual Project Conference. London: University College; 2004.

Yu J-Y, Heo B. Dilution and removal of dissolved metals from acid mine drainage along Imgok Creek, Korea. Appl Geochem 2001;16(9–10):1041–53.

Zagury GJ, Kulnieksa VI, Neculita CM. Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment. Chemosphere 2006;64(6):944–54.

Ziemkiewicz PF, Skousen JG, Simmons J. Long-term performance of passive acid mine drainage treatment systems. Mine Water Environ 2003;22(3):118–29.