Evidence

Mitigation of pollution from abandoned metal mines

Investigation of passive compost bioreactor systems for treatment of abandoned metal mine discharges

Science Report – SC090024/R3

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Miranda Kavanagh

Director of Evidence

Executive summary

The performance of compost bioreactor systems for the remediation of metal mine discharges has been investigated. The investigation has primarily focused on the simultaneous operation of two laboratory-scale reactors, one operated in a laboratory, the other under field conditions, and a pilot-scale reactor in the field at Nenthead, Cumbria. All three of these systems contained identical reactive substrates with a mixture of compost, wood chips and activated digested sludge, and were configured to have an initial hydraulic residence time of 19 hours. The primary interest was in the removal of the metal zinc, which is the most common pollutant in metal mine drainage. In addition, an equivalent pilot-scale reactor, but receiving a mine water of different characteristics, has been monitored at Cwm Rheidol, Wales. In this case interest was in both the removal of zinc and also the elevation of pH, which is low in the Cwm Rheidol water. The pilot-scale reactor at Nenthead operated for a 2-year period, from August 2010 to August 2012, while the system at Cwm Rheidol was commissioned in September 2010, and continues to operate at the time of writing. The principal conclusions from the research at Nenthead, which included the operation of the laboratory-scale systems, are as follows:

- Metal attenuation has taken place in all three systems but the quantity of metal removed has varied between systems. The laboratory and field columns show similar treatment efficiency with, on average, 98% and 94% respectively of the influent total zinc removed. Treatment efficiency in the pilot-scale system was significantly lower and showed far greater fluctuation with, on average, 68% of the influent total zinc removed. This difference appears to be primarily related to scale issues rather than environmental conditions, although there was evidence that the pilot-scale reactor did not perform as well when ambient temperature was low.

- A key process cited for removal of metals in compost bioreactors is bacterial sulphate reduction (BSR), which facilitates removal of metals as their solid sulphides. There was clear evidence that BSR was taking place in all three systems. Such evidence includes strongly positive saturation indices for metal sulphide solid phases during PhreeqC modelling and very high concentrations of both metals and acid volatile sulphides (AVS) in the substrate itself.

- Hydraulic conditions varied between systems and within systems. It appears that preferential flow paths may develop on occasion, but are perhaps short-lived. Full-scale design of such systems should factor in the possibility of residence times being less than calculated during design.

- Temperature appears to play an important role in the removal of metals within such bioreactors. Although the precise reason is not entirely clear, it would appear to be related to the suitability of conditions for sulphate reducing bacteria communities, and/or the maintenance of the reducing conditions that they require. Again, this may influence the performance of larger scale systems.

- Carbon additions, both slug and continuous, were made to the systems to investigate whether performance could be improved. Short-term results were ambiguous. Over the longer-term it appeared that continuous additions of small amounts of carbon were in fact beneficial to the pilot-scale system, but time was required for these beneficial effects to be manifested in improved performance. This is an area for further investigation.

- Microbial analyses successfully identified sulphate reducing bacteria (SRB), with the genus *Desulfobulbus* and genus *Desulfovibrio* predominating. The genetic sequences identified in the tank were closely related to those previously identified in treatment systems receiving metal-rich waste and in natural sediments contaminated with metals, suggesting that it is possible that the high metal conditions in these environments favour the selection of metal-tolerant SRB. It is not possible to conclude from the results exactly how important bacterial sulphate reduction is as a mechanism of metal removal, but it certainly appears to play some role. Further work to quantify its importance is recommended.
- It was not possible to conclude with confidence what the overall lifetime of a compost bioreactor would be. Although there was no apparent deterioration in the performance of the systems, it is not possible to extrapolate from the 2 years of data collected to conclude exactly what the lifetime would be, mainly because of difficulties in determining what individual factor ultimately determines lifetime (e.g. substrate porosity, metal toxicity etc).
- Preliminary assessments suggest that the substrate from the pilot-scale reactor tank would be classified as hazardous waste due to the elevated concentrations of zinc, but would still require pre-treatment due to the organics content.
- Metal recovery tests, using hydrochloric acid to recover metals from the substrate, suggest that there is clear potential to recover the metal from the substrate. This might reduce substrate disposal costs if the material could be reclassified as non-hazardous waste, but further work is required to establish whether the costs of metal recovery are lower than the savings in subsequent disposal costs.

Results from the Cwm Rheidol pilot-scale system corroborate the findings of the Nenthead investigation. The performance of the system was similar overall to the Nenthead system, despite the water being low pH and with a higher zinc concentration. Some key findings from the investigation at Cwm Rheidol that are of particular additional value to the findings at Nenthead are as follows:

- With suitable alkaline media included in the substrate, compost bioreactors can consistently elevate the pH of acidic mine drainage.
- Elevated iron concentrations create operational difficulties due to system clogging issues, which ultimately results in deterioration in system performance.
- The concentration of zinc in the substrate of the Cwm Rheidol reactor was substantially higher than in the Nenthead reactor. Nevertheless, the system continued to remove zinc, suggesting that even at such high concentrations toxic effects (which might influence the lifetime of such systems) were not evident, or at least not obvious from the performance data alone.

In March 2014 a large-scale compost bioreactor (Vertical Flow Pond) was commissioned at the Force Crag mine site in Cumbria. The results of the pilot-scale trial at Nenthead were directly used for the design of the Force Crag treatment system, which comprises two parallel compost units, each with a water surface area of approximately 800 m^2. The basis for the design of the Force Crag system is discussed in Section 6. In addition, some of the features included in the design to ensure that it operates effectively, and that it can be used to assist in the design of future systems, are detailed.

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- The Force Crag treatment system (Section 6) was an initiative funded by **Defra**, and was led by a partnership of the **Coal Authority, Environment Agency, National Trust and Newcastle University**. The detailed civil engineering design of the treatment system was undertaken by **Atkins**, and the construction contractor was **JN Bentley Ltd**.

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Tables and figures

1 Introduction

1.1 Background

Drainage from abandoned metal mines is an acute and pervasive form of aquatic pollution. The discharge of contaminant metals (e.g. zinc, lead, cadmium) to both surface and groundwaters has resulted in impacts on some 6% of surface water bodies in England and Wales according to a recent Defra and Environment Agency assessment (Mayes et al. 2009). Such discharges are known to remain sources of pollution for many decades, and even centuries (Younger et al. 2002), with only gradual improvements in water quality observed. For abandoned deep coal mines that were formerly part of the nationalised coal industry, remediation of polluted discharges is undertaken by the UK Coal Authority. The Coal Authority has constructed more than 50 full-scale treatment schemes for coal mine drainage to date, which collectively address a significant part of the national problem with respect to abandoned coal mines. However, the Coal Authority's remit has only recently extended to abandoned metal mine sites, which were not part of a nationalised industry. This remit allows the Authority to provide remediation services where funding from third parties becomes available. Prior to this, abandoned metal mine sites (and discharges from them) were effectively 'orphan' sites, with no responsible party to address pollution problems. Nevertheless, Defra and the Environment Agency recognise the need to tackle these issues in pursuance of improved national water quality, and in particular of meeting the objectives of the EU Water Framework Directive. It is for this reason that Defra and the Environment Agency commissioned the current study, a major focus of which has been the identification of the most sustainable, but simultaneously effective, treatment options for abandoned metal mine water discharges. This report therefore provides details of the results and conclusions of a 40-month-long laboratory and field investigation of 'passive' treatment options for abandoned metal mine drainage.

Much research effort in recent years has focused on the identification of low-cost, low-maintenance treatment options for the remediation of polluting discharges from abandoned metal mines. Such systems are referred to as 'passive' (as opposed to 'active' treatments, which are more intensive processes entailing the use of energy and chemicals). A review of passive treatment technologies for the remediation of such discharges was undertaken in the initial stages of this project. It revealed that many different types of passive treatment system are available, which operate with varying degrees of success. These range from proven technologies that have been implemented at full-scale, through technologies that appear to offer promise but have yet to be demonstrated at full-scale, to emerging technologies that have been investigated at laboratory-scale only. Full details of the review are given in Jarvis et al. (2011b). A key conclusion was that the most promising means of immobilising metals at the pH values typically achievable in passive treatment systems appears to be the use of anaerobic systems which encourage bacterial sulphate reduction in organic substrates in order to simultaneously generate alkalinity and immobilise metals as sulphides. A key requirement for the successful attenuation of metals within such systems appears to be the maintenance of microbial processes at sufficient rates to immobilise metals within a reasonable timeframe and thus in suitably sized systems. This is especially pertinent to the majority of metal mine discharges in the UK, which occur in upland areas with steep topography and therefore have limited land availability for large passive systems. Many recent studies have therefore focused on the identification of nutrient sources (typically carbon) for addition to the compost substrate in order to maximise rates of microbial processes and hence metal attenuation. Details of these studies are provided in Jarvis et al. (2011b).

It is apparent from the review that the majority of studies have been undertaken at laboratory-scale, under controlled conditions where temperature remains at approximately 20°C and there is less potential for invasion of new microbial colonies due to generally cleaner conditions than those found at actual mine sites. Additionally, the geometries of a laboratory-scale column are necessarily different to those of a pilot-scale reactor, and in turn of a full-scale system, and hydraulic conditions vary between them. In order to resolve these issues of environmental variability and engineering scale, laboratory-scale columns need to operate under field conditions with variable temperature and the development of a diverse microbial community.

With this in mind, the decision was made to explore enhanced passive treatment (EPT) using anaerobic systems which promote the removal of metals as their sulphides by bacterial sulphate reduction at both laboratory and field-scale. Such treatment entailed the periodic addition of carbon to passive bioreactors to enhance the rate of microbial processes. This approach offers a number of distinct advantages over alternative technologies, principally the success of previous experiments using this technology at laboratory-scale, the use of materials (such as manures, sewage sludge) that may otherwise be handled as a waste, and the possibility of offering habitat benefits where the systems can be colonised by reeds. The operation of a laboratory-scale column directly alongside, and simultaneously to, a pilot-scale reactor, in addition to an identical column in the laboratory, has enabled not only the identification of the geochemical and hydraulic processes occurring in each system but also an investigation into the scale-dependence of passive mine water treatment system performance. Similarly, the operation of a second pilot-scale reactor, treating water of a different chemistry, has enabled comparisons of system performance to be made for different influent water qualities.

Regardless of the technology used, passive treatment systems for the mitigation of pollution from abandoned metal mines have a finite life span, at which point the treatment substrate is considered exhausted or saturated. As metals cannot be eliminated or transformed by degradation, treatment systems are designed to accumulate and retain metals as precipitated or complexed minerals within the substrate. When such systems reach the end of their lifetime, saturated or exhausted substrates must be legally disposed of, ensuring minimal environmental impact, which necessarily comes at a high cost. Recovery of metals from these substrates may facilitate disposal of exhausted substrates as non-hazardous wastes and also be used to offset remediation running costs. A review of resource recovery options from the passive remediation of metal-rich mine waters was undertaken in the initial stages of this project (Gray et al. 2011), alongside the review of passive treatment technologies. The results of this review have been used to inform tests carried out to establish whether it is possible to recover metals from the treatment substrate by leaching techniques.

1.2 Previous work

The School of Civil Engineering & Geosciences (CEGs) at Newcastle University has previously carried out laboratory trials for the Environment Agency specifically aimed at identifying an effective passive treatment system for immobilisation of metals from a zinc-rich, acidic mine water discharge at Cwm Rheidol, Wales. The trials involved an assessment of different alkalinity-generating media (shells and limestone) within a compost bioreactor comprising an organic mix of wood chippings, manure and anaerobic digested sludge. The results of this work were published in Mayes et al. (2011) and demonstrate that sustained alkalinity generation and almost complete removal of dissolved zinc is possible when the laboratory columns are subject to methanol dosing. Figure 1 shows dissolved zinc concentrations during the course of the trial, with several distinct phases evident. An initial phase, characterised by the removal of dissolved zinc, is followed by zinc breakthrough[1] after around 5 months. The subsequent addition of methanol resulted in sustained removal of dissolved zinc once again, before an increase in effluent dissolved zinc concentrations occurred following the cessation of methanol addition towards the end of the trial.

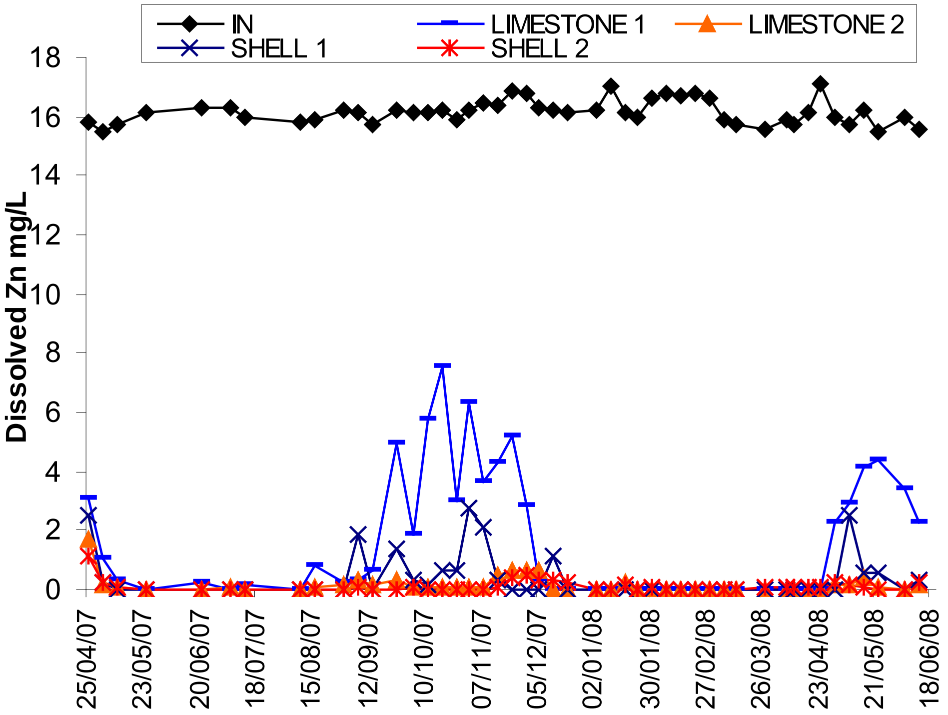

Figure 1. Effective removal of zinc in enhanced passive treatment laboratory-scale bioreactors (IN = influent concentration) (adapted from Mayes et al. 2011)

Following the success of these initial trials, further laboratory-scale continuous flow experiments have been undertaken by the CEGs team, funded by the Waste and Resources Action Programme (WRAP). These trials assessed the suitability of different substrate materials (PAS100 compost and farmyard manure) in passive bioreactors for the removal of metals from a synthetic zinc-rich, acidic mine water (Jarvis et al. 2011a). The results (Figure 2) once again demonstrate that sustained attenuation of zinc in such systems is possible but the addition of a carbon source appears to be necessary to maintain high removal rates. The work also evaluated different sources of carbon (liquid and solid) and different modes of addition (slug addition and semi-continuous addition) and concluded that the semi-continuous addition of liquid carbon offers the most promise as a means of maintaining metal immobilisation.

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[1] ‘Breakthrough’ refers to a sudden increase in effluent concentration, indicating failure of the system, with respect to zinc in this instance.

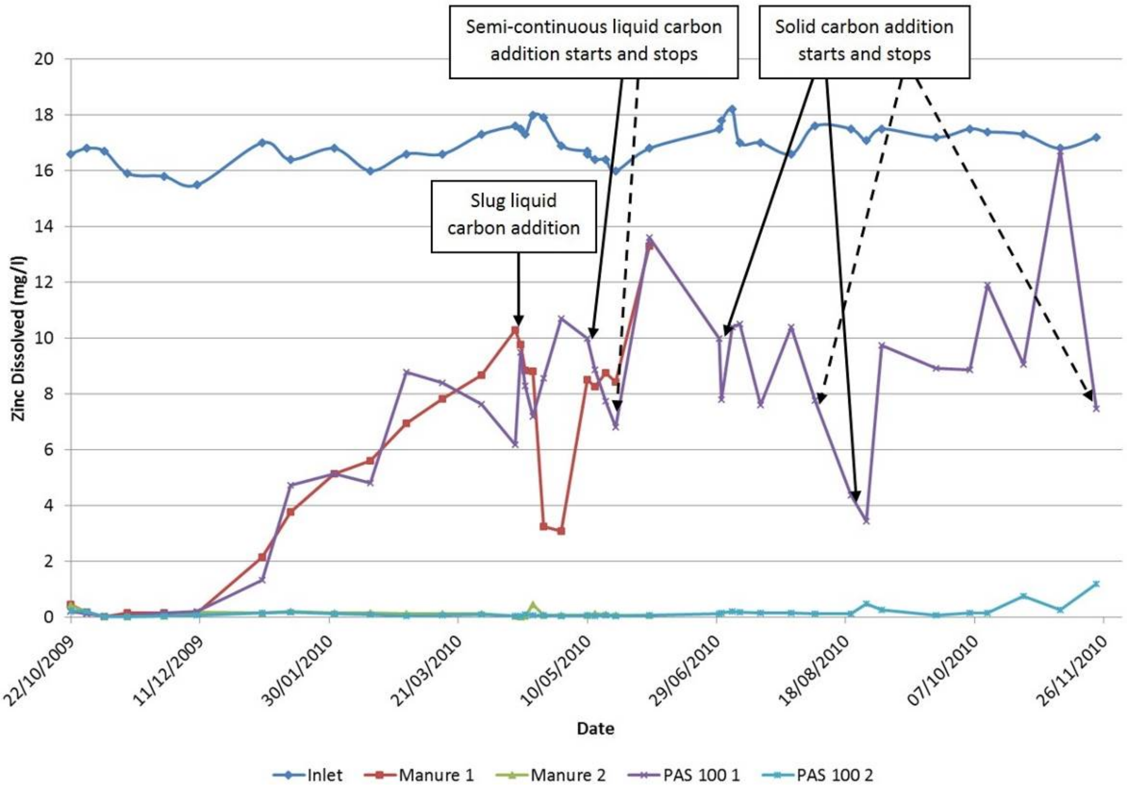

Figure 2. Trends in dissolved zinc concentrations in laboratory-scale bioreactors showing times when carbon additions start (solid arrows) and stop (dashed arrows) (from Jarvis et al. 2011a)

1.3 Location

1.3.1 Nenthead

A suitable location for a pilot-scale reactor to be operated under field conditions was identified in the grounds of the Nenthead Mines Heritage Centre in Cumbria, adjacent to the Rampgill Horse Level, from which mine water draining the Rampgill Mine Complex and Smallcleugh Mine discharges into the River Nent, a tributary of the River South Tyne. The area forms part of the Northern Pennine Orefield, which was mined intensively for lead and zinc until the early 20th century and the Rampgill discharge is one of several polluting discharges in the Nent Valley. As a consequence of these discharges, together with additional contamination from diffuse sources, the River Nent is severely impacted by metal-contaminated water and has been ranked third in the Northumbria River Basin District for prioritisation of impacted water bodies (Mayes and Jarvis 2009b). It is also ranked 22nd on the overall priority rank for impacted water bodies in England and Wales (Mayes and Jarvis 2009a).

Although the Rampgill discharge is not the most polluting in the Nent Valley, it nevertheless contains approximately 2–2.5 mg/L zinc, while it is circum-neutral with a pH of around 7–8. It is also polluted (though to a lesser degree) with cadmium, lead, copper and manganese. Most importantly, however, it contains low concentrations of iron and aluminium thereby limiting the potential for blockage of narrow diameter pipes with precipitates, a problem typically seen in pilot-scale reactors treating water with elevated concentrations of iron or aluminium. A summary of the Rampgill mine water chemistry is provided in Table 1.

Table 1. Summary chemistry data for the Rampgill Horse Level mine water discharge, where n represents the number of contributing samples and metal concentrations represent total concentrations

Parameter	Unit	Mean	Range	n
pH	pH units	7.74	6.88–8.62	85
Temperature	°C	8.89	5.8–12.5	84
Conductivity	µS/cm	589.5	389–681.4	85
Sulphate	mg/L	134	87–164	84
Bicarbonate	mg/L	192	126–290	84
Chloride	mg/L	13	8 - 16	84
Calcium	mg/L	52 - 93	80	84
Magnesium	mg/L	16 – 29	25	84
Sodium	mg/L	5.2 – 10.7	8.8	84
Potassium	mg/L	2.6 – 6.1	4.7	84
Zinc (total)	mg/L	2.32	1.69–4.50	83
Zinc (filt)^A	mg/L	2.16	1.58 – 2.16	84
Lead	mg/L	< 0.05	-	85
Cadmium	mg/L	< 0.01	-	85
Copper	mg/L	< 0.01	-	85
Iron	mg/L	0.33	0.1–2.72	83
Manganese	mg/L	0.15	0.08–0.56	82

^{A} Concentration reported is after filtering through a 0.45 µm filter

The use of a circum-neutral zinc-rich mine water in a pilot-scale investigation has a number of advantages. In particular, the Rampgill discharge is representative of a large number of mine waters nationally. Evidence for this was provided by the Defra/ Environment Agency-funded non-coal mines project, which showed that of the 257 known metal mine water discharges in England and Wales more than 80 have zinc concentrations greater than its Environmental Quality Standard (EQS) (unpublished data). In addition, unpublished data held by the Environment Agency reveals that more than 80% of all mine water discharges across the UK for which pH data are held have pH > 6. Thus, the results of this investigation will be relevant to many other similar discharges in England and Wales. Furthermore, for reasons outlined above, a highly acidic water would likely prove problematic to the operation of a pilot-scale reactor, principally because such waters contain elevated concentrations of iron which would almost certainly lead to the blockage of pipework and the possible armouring of reactive media. Besides, it is already known that the removal of iron and acidity is feasible via passive treatment, as proven by the many successful full-scale mine water treatment systems operating throughout the UK.

In addition to the chemistry of the Rampgill mine water discharge, the location of the pilot-scale reactor at the Nenthead Mines Heritage Centre possesses several additional advantages over alternative locations. These include factors such as security, which is essential for ensuring continuity of system operation, along with the provision of an electricity supply for the pumping of water from the Rampgill discharge to the pilot-scale reactor. Although it would be envisaged that any future full-scale systems would be operated under gravity where feasible, in order to maintain a consistent and continuous supply of water to a pilot-scale reactor, pumping represents a more desirable option due to problems of intermittent or decreasing inflow rates commonly observed in pilot-scale systems that operate under gravity due to the necessarily narrow diameter of inlet pipes. The use of electric pumps also enables the variation of flow as required in order to identify the optimum performance conditions.

1.3.2 Cwm Rheidol

Notwithstanding the above comments regarding the water chemistry at Nenthead, an analogous pilot-scale compost-based system, designed by the Newcastle University team and funded and installed by the Environment Agency, has been operating concurrently at Cwm Rheidol in West Wales. This system, which is somewhat larger than that at Nenthead, does treat acidic and iron-rich water, and is therefore serving as a very useful comparator to the Nenthead system.

The Cwm Rheidol metal mines complex was mined intensively for lead and zinc until the early 20th century. Discharges from two adits, No. 6 and No. 9, contribute high metal loads and acidity to the River Rheidol, which is severely impacted by metal-contaminated water. As a result of these discharges, and others, the River Rheidol is ranked top in the Western Wales River Basin District for prioritisation of impacted water bodies (Mayes and Jarvis 2009c). In fact, the extent of contamination is so great that it is also ranked top on the overall priority rank for impacted water bodies in England and Wales (Mayes and Jarvis 2009a).

The influent mine water to the pilot-scale reactor is taken from the Adit No.6 discharge which, although not as polluting as the Adit No. 9 discharge, contains approximately 13 mg/L zinc and is highly acidic with a pH of around 3.5. It also contains a higher iron concentration than the influent to the Nenthead reactors, at around 7 mg/L, and is polluted with lead, cadmium, copper and manganese. A summary of the Cwm Rheidol Adit No. 6 discharge is provided in Table 2.

Table 2. Summary chemistry data for the Cwm Rheidol Adit No. 6 mine water discharge, where n represents the number of contributing samples and metal concentrations represent total concentrations (Environment Agency Wales data, supplemented with Newcastle University data)

Parameter	Unit	Mean	Range	n
pH	pH units	3.9	3.4–4.7	59
Temperature	°C	11.0	5.6–18	48
Conductivity	µS	389.7	270.7–500	58
Eh	mV	307.1	15.8–457.4	32
Alkalinity	mg/L $CaCO_3$	22.2	0–70	43
Zinc	mg/L	12.8	9–16.8	59
Lead	mg/L	0.7	0.3–1.7	59
Cadmium	mg/L	0.035	0.027–0.044	59
Copper	mg/L	0.053	0.033–0.101	59
Iron	mg/L	7.2	2.5–18.4	58
Manganese	mg/L	0.6	0.4–0.8	59

1.4 Report structure

The report begins, in Section 2, with a description of the configuration of each reactor, including substrate composition and initial tests carried out to determine the hydraulic properties of the substrate. This section also includes an account of the monitoring protocol and a brief description of the experimental methods for sample collection and analysis. In addition, the configuration and experimental methods for the leaching tests for the potential recovery of metals are described in this section.

The main results section (Section 3) is structured to allow the assessment of each of the Nenthead reactors individually before comparisons are made between the different systems. Firstly, a comparison is made between the two laboratory-scale columns, in order to evaluate any effects that varying environmental conditions have on system performance. Secondly, the influence of engineering scale on metal immobilisation is considered by a comparison of the pilot-scale reactor and the laboratory-scale column located in the field. Due to the possible effects of a multitude of factors it is not possible to compare systems operating at different scales and under different environmental conditions. Therefore, no comparisons have been attempted between the laboratory reactor and the pilot-scale system.

Thus, the results of Nenthead systems' performance are presented and discussed in the following sections:

Section 3.1:	Laboratory-scale column
Section 3.2:	Laboratory-scale field column
Section 3.3:	Comparison of laboratory and field column performance
Section 3.4:	Pilot-scale reactor
Section 3.5:	Comparison of field column and pilot reactor performance

Section 4 presents results and discussion of the pilot-scale reactor at Cwm Rheidol (Section 4.1), before comparing these results with those of the Nenthead pilot-scale reactor (Section 4.2).

Section 5 details results of leaching experiments conducted to investigate the potential for metal recovery from treatment substrates. A discussion of system lifetime is presented, followed by a discussion of the results of waste classification tests. Finally, the results of preliminary experiments designed to explore the possibility of recovering metals from the used substrate are discussed.

In March 2014 a large-scale vertical flow pond (VFP) was constructed at the Force Crag mine site, Cumbria (a Defra-funded project executed by a partnership of the Coal Authority, Environment Agency, the National Trust and Newcastle University). The concept and process design for this treatment system was undertaken by Newcastle University. Many of the insights gained from the Nenthead pilot-scale trial were used directly in the design of this large-scale system. In Section 6 the design of this large-scale treatment system is therefore discussed, with close reference to the aspects of the design that were directly informed by the Nenthead trial. This section has been added as this information may well be of benefit to the design of future vertical flow pond systems for mitigation of pollution from other abandoned non-coal mine discharges across England and Wales.

2 System configuration, monitoring and methods

2.1 System configuration

2.1.1 Nenthead reactors

On the basis of previous work undertaken by the HERO Group using laboratory-scale continuous flow column experiments, as described in Section 1.2, a laboratory-scale reactor (internal diameter 105 mm, length 500 mm) was set up as shown in Figure 3. The actual column, operated in Newcastle University's Devonshire Building laboratories, is shown in Figure 4a. Mine water was collected weekly from the Rampgill Horse Level discharge and stored at 4°C. A Watson Marlow 300 series peristaltic pump was set up to transfer the mine water to the column, which was configured as an upwards flow reactor to prevent channelling of water and/or system blocking which would likely occur in such a small reactor if the water was allowed to flow downwards.

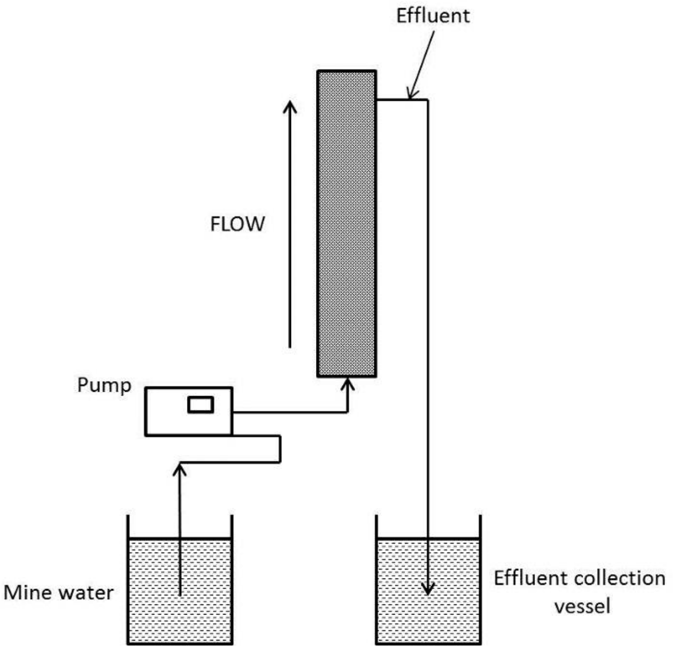

Figure 3. Schematic illustration of laboratory-scale continuous flow column operating in laboratory

An identical continuous flow column was set up in the field, alongside the pilot-scale reactor at the Nenthead Mines Heritage Centre, as shown in Figure 4b. A Watson Marlow 300 series pump was set up to transfer mine water from the Rampgill Horse Level discharge to the column.

Figure 4. Reactors for remediation of Rampgill mine water discharge: (a) laboratory-scale column in laboratory, (b) laboratory-scale column in field, (c) pilot-scale reactor

A pilot-scale reactor (length 2,500 mm, width 1,500 mm, height 1,000 mm) was installed at the Nenthead Mines Heritage Centre. Again, a Watson Marlow 300 series pump was set up to transfer mine water directly from the Rampgill Horse Level discharge to the reactor. A schematic illustration of the pilot-scale reactor is shown in Figure 5, while the reactor itself is shown in Figure 4c. Unlike the laboratory-scale reactors, the pilot-scale system was configured for the mine water to enter at the surface, then be constrained to flow downwards through the reactive media by gravity, to enter a pipe network at the base of the reactor. Effluent water was discharged via a variable height outlet pipe connected to the pipe network. Clearly the different hydraulic set-up of the laboratory-scale field column and pilot-scale reactor complicates interpretation of results relating to the influence of engineering scale. This is recognised as a possible weakness of the experimental set-up, but was considered the best approach given likely persistent problems of flow channelling/system blockage if the column reactor in the field had been configured as a downwards flow system.

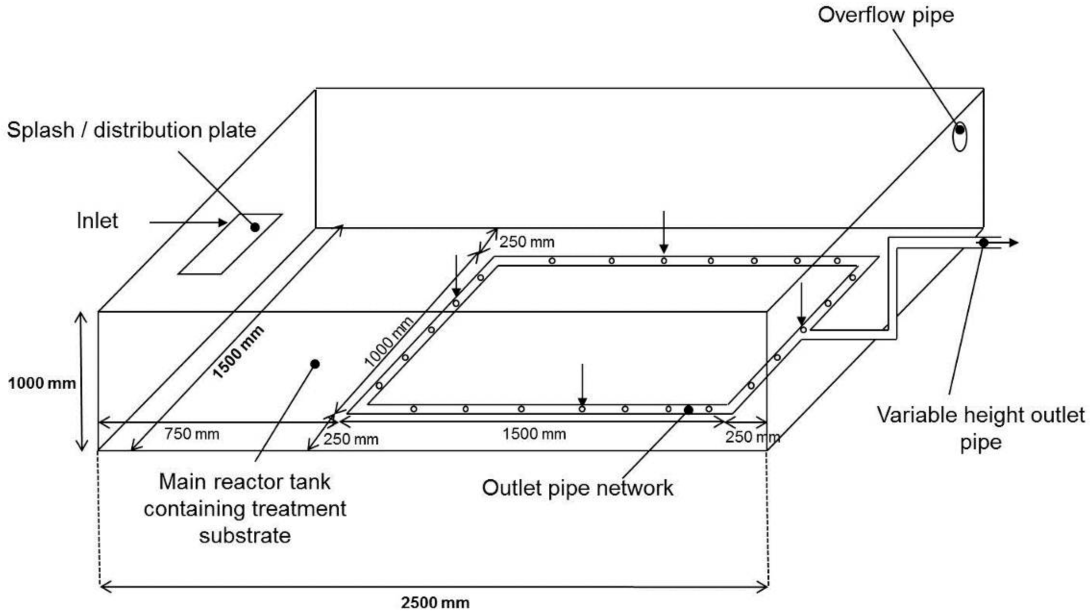

Figure 5. Schematic plan of pilot-scale reactor

The three reactors contained identical reactive substrates comprising PAS100 compost (45% v/v), wood chips (45%) and activated digested sludge from a municipal wastewater treatment plant (10%). Limestone gravel (~40–50 mm diameter clasts) was placed on the base of the reactors, principally to cover the pipe network in the pilot-scale reactor (to a depth of approximately 200 mm) to prevent clogging with solids. To ensure consistency, limestone gravel was also placed in the base of the two laboratory-scale columns, while a small amount of limestone gravel was mixed with the reactive substrate in all three reactors to aid permeability. The limestone also acts as a source of alkalinity although, in the case of the Rampgill mine water, which is circum-neutral, further alkalinity generation was not thought to be a necessity. The wood chips assist with provision of porosity, while the activated digested sludge is included as an initial source of available carbon (for metabolism of sulphate reducing bacteria). The compost, however, is the critical medium- to long-term source of carbon and encourages the development of anoxic conditions within the reactor (essential for the survival of sulphate reducing bacteria).

The substrates for each system were thoroughly mixed before 3,500 cm^3 (0.0035 m^3) of mixed substrate was inserted into each of the laboratory-scale columns and 2.25 m^3 of mixed substrate was inserted into the pilot-scale reactor. The substrates were then saturated and the volume of water added was recorded to facilitate the calculation of the initial substrate porosity and enable estimates of influent flow-rates necessary to achieve the required residence time. A bulk porosity of approximately 60% was calculated and Watson Marlow 300 series peristaltic pumps were set up for each reactor to give an approximate residence time of 19 hours. This necessitated an influent flow-rate of approximately 1.6–1.7 mL/min to each of the laboratory-scale columns and a flow-rate of around 1.1 L/min into the pilot-scale reactor.

2.1.2 Cwm Rheidol reactor

The pilot-scale reactor installed by the Environment Agency at Cwm Rheidol, shown in Figure 6, was larger than that installed at Nenthead, having the dimensions 4,500 mm length, 2,500 mm width and 1,200 mm height. Mine water was fed by gravity from the Adit No. 6 discharge and initially entered an inlet chamber (length 500 mm, width 2,500 mm, height 1,200 mm) adjoining the reactor, from which water drained into the reactor via a V-notch weir. The influent flow-rate was around 6 L/min. As with the Nenthead pilot-scale reactor, the system was configured for the water to enter at the surface, then be constrained to flow downwards through the reactive media by gravity, to enter a pipe network at the base of the reactor. Effluent water was discharged via a variable height outlet pipe connected to the pipe network.

Figure 6. Pilot-scale reactor for remediation of discharge from Adit No. 6 at Cwm Rheidol

The reactive substrate within the reactor comprised (by volume) 50% shells, 30% coarse wood chips, 10% PAS100 compost and 10% anaerobic digested sludge. Limestone granules (approximately 100 mm in diameter) were placed on the base of the reactor, to a depth of approximately 200 mm, to cover the pipe network and prevent clogging with solids. The shells, wood chips and compost were thoroughly mixed before approximately 6.75 m^3 of substrate was inserted into the reactor. The anaerobic digested sludge, which was in liquid form, was spread across the substrate at a depth of 300 mm and again across the top of the substrate at a depth of 600 mm. Unlike the pilot-scale reactor at Nenthead, the substrate in the Cwm Rheidol system contained a significant proportion of alkalinity-generating media, in the form of shells, due to the acidic nature of the influent mine water. The wood chips assisted with permeability while the compost was the main source of carbon for metabolism of sulphate reducing bacteria and encouraged anoxic conditions. The anaerobic digested sludge acted as an initial source of available carbon.

2.2 Monitoring

2.2.1 Nenthead reactors

Samples were collected by the HERO Group from all three systems on a weekly basis, as far as possible, over the course of the trial, although the harsh winter conditions at Nenthead during 2010/11 resulted in unavoidable problems with sample collection (difficulties in reaching Nenthead, frozen reactors and pump failures) at times. Samples were collected from the effluent of all three systems in addition to the influent mine water and were analysed for total and dissolved[2] cations, major anions and dissolved organic carbon (DOC). The complete analytical suite is given in Table 3. Measurements of influent and effluent pH, Eh, electrical conductivity, water temperature and total alkalinity were also taken on each sampling occasion together with influent and effluent flow-rates (effluent flow-rate only in laboratory-scale reactors).

Table 3. Analytical suite for influent and effluent water samples with cation analysis performed on total and dissolved samples (using a 0.45 µm filter)

Parameter	Unit
DOC	mg/L
Chloride	mg/L
Sulphate	mg/L
Calcium	mg/L
Magnesium	mg/L
Sodium	mg/L
Potassium	mg/L
Iron	mg/L
Manganese	mg/L
Aluminium	mg/L
Zinc	mg/L
Lead	mg/L
Copper	mg/L
Cadmium	mg/L
Nickel	mg/L
Chromium	mg/L
Arsenic	mg/L
Silicon	mg/L

2.2.2 Cwm Rheidol reactor

Samples were collected from the Cwm Rheidol pilot-scale reactor by the Environment Agency on an approximately twice-monthly basis, with additional periodic sample collection by the HERO Group. Samples were collected from the influent and effluent of the pilot-scale reactor, together with two mid-depth sampling ports, and were analysed for total and dissolved cations and major anions. The complete analytical suite was somewhat larger than that for the Nenthead systems but, for comparative purposes, only the determinands listed in Table 3 were used in the study. Measurements of influent and effluent pH, Eh, electrical conductivity, water temperature and total alkalinity were also taken on each sampling occasion together with influent and effluent flow-rates.

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[2] Note that we refer to ‘dissolved’ cations throughout this report, even though that portion of water that passes through a 0.45 µm filter may not only contain truly dissolved phase metals; ‘filtered’ would be more strictly accurate, but dissolved is more common in regulatory circles.

2.3 Methods

2.3.1 Water sampling and analysis

Nenthead reactors

Measurements of influent and effluent pH, Eh, electrical conductivity and water temperature were taken on each sampling occasion using a pre-calibrated Myron L 6P Ultrameter. Total alkalinity was also determined at the time of sample collection using a Hach Digital Titrator with 1.6N sulphuric acid (pilot-scale reactor) or 0.16N sulphuric acid (laboratory-scale reactors) with a Bromcresol-Green Methyl-Red indicator, with results given in units of mg/L as calcium carbonate ($CaCO_3$). The direct analysis of sulphide concentration in the influent mine water and effluent waters from the field column and pilot-scale reactor was also carried out during the final 10 months of the trial using a Merck Microquant colorimetric sulphide field test kit.

All water samples were analysed within the HERO Group laboratories at Newcastle University. For each sample, two aliquots of 30 mL were acidified with 1% v/v nitric acid, one after filtration through a 0.45 µm filter, for the analysis of total and dissolved cations using a Varian Vista-MPX Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). During the final 10 months of the trial, an additional aliquot of 30 mL was passed through a 0.1 µm filter, acidified with 1% v/v nitric acid and analysed for dissolved cations as above. A further 30 mL aliquot was left un-acidified for anions analysis using a Dionex DX320 ion chromatograph. Samples were also collected for DOC in 30 mL glass bottles and acidified with 1% v/v hydrochloric acid before analysis on a Shimadzu TOC-5050A analyser. All samples were preserved at 4°C prior to analysis.

Cwm Rheidol reactor

Water samples collected from the Cwm Rheidol pilot-scale reactor by the Environment Agency were analysed in its own laboratories. Measurements of influent and effluent pH, Eh, electrical conductivity and water temperature were taken on each sampling occasion and total alkalinity was also determined at the time of sample collection.

Samples periodically collected from the Cwm Rheidol reactor by the HERO Group were analysed as per the samples collected from the Nenthead reactors (see above). The sampling protocol followed was also the same as that given above for the Nenthead reactors.

2.3.2 Substrate analysis

Nenthead reactors

Samples of substrate were collected from the pilot-scale reactor at Nenthead after one week of operation and again after 8 months of operation for microbiological analysis. Samples were also collected after 8 months of operation from both the laboratory column and the field column. All samples were preserved at minus 80°C until analysis. The methods, results and conclusions of the preliminary microbiological analysis are presented in Section 3.4.3 (*Microbiology*) and in Appendix A of this report.

Samples of substrate were also collected from the pilot-scale reactor after 10 months of operation for the metal recovery leaching tests. On this occasion, three samples were collected from the upper surface of the substrate at the influent end of the reactor. The samples were air-dried and then subjected to Aqua Regia digestion with subsequent ICP-OES analysis to determine their metal content. A sample from the original substrate mixture was also air-dried and subjected to Aqua Regia digestion to act as a control sample. Following the leaching tests (full details given in Section 2.4 and Section 5), Aqua Regia digestion was again undertaken to determine the new metal contents.

Further extensive sampling of the substrate was undertaken during decommissioning of the pilot-scale reactor to determine the metal removal mechanisms. A total of 24 samples were collected in a grid arrangement, 12 from just below the substrate surface and the remaining 12 from a depth of approximately 23 cm, to ascertain any spatial variability in metal content. Samples were also collected from the same locations for microbiological analysis and all samples were preserved at minus 20°C until analysis. The geochemical analysis took the form of an Acid Volatile Sulphide/Simultaneous Metal Extraction (AVS/SEM) approach to determine both acid volatile sulphide and metal contents. The AVS/SEM method of Allen et al. (1993) was used, with the exception that hydrogen sulphide (H_2S) was purged from the sample for 3 hours as recommended by APHA (2005) to ensure that all AVS was recovered, rather than just 1 hour as recommended by Allen et al. (1993). A limited number of samples were also subjected to Aqua Regia digestion with subsequent ICP-OES analysis to compare metal contents with those determined by the AVS/SEM method. It is important to note that the recovery of metals via the AVS/SEM method is by digestion in hydrochloric acid at room temperature, while Aqua Regia digestion uses nitric acid and hydrochloric acid at up to 165°C. The Aqua Regia method is therefore more effective at recovering metals, and higher concentrations would be expected via this method.

Three samples of substrate from the pilot-scale reactor were also collected during decommissioning for waste classification hazard assessment. This included a hazard assessment, comprising a wide-ranging chemical analysis of the materials, followed by single-stage Waste Acceptance Criteria (WAC) testing (two-stage testing was not possible due to high organic matter content of the substrate). These analyses were conducted for Newcastle University by the UKAS accredited laboratory Environmental Scientific Group.

Cwm Rheidol reactor

Samples of substrate were collected from the pilot-scale reactor at Cwm Rheidol after 21 months of operation for geochemical and microbiological analysis. The samples for geochemical analysis were preserved at 4°C until they were air-dried and subjected to Aqua Regia digestion with subsequent ICP-OES analysis to determine their metal content. The samples for microbiological analysis were preserved at minus 20°C until analysis.

2.4 Metal recovery leaching tests

Leaching tests have been carried out to determine whether it may be possible to recover metals from the treatment substrate. There is no established protocol for conducting experiments of this type, and therefore the experiments were designed by the Newcastle team. The experiments were undertaken in three phases: an initial batch test using three different lixiviants[3] (hydrochloric acid, distilled water, ammonium sulphate/ammonia solution) to establish the rate at which metals are leached from the

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[3] A lixiviant is a hydrometallurgical term that refers to a liquid used to selectively extract a particular metal (in a hydrometallurgical context usually from an ore, but obviously in the current context from the treatment substrate).

substrate, and then two subsequent phases in which continuous flow columns were set up through which a fixed volume of lixiviant was recycled through the substrate.

3 Results and discussion: Nenthead

3.1 Laboratory-scale column

3.1.1 System performance

Metal removal

The following section will focus on the removal of zinc, since this is the principal metal contaminant in the Rampgill mine water, and indeed in metal mine drainage across England and Wales. Given the lower solubility products of the sulphides of other metals, such as copper, cadmium and lead (Jarvis et al. 2011b), these metals will likely form a sulphide more readily than zinc. Thus, if a system can be shown to successfully attenuate zinc then it can be expected that it will also remove these other metals to an equal or greater extent.

Total zinc concentrations in the influent mine water and total and dissolved zinc concentrations in the effluent water from the laboratory column are presented in Figure 7. Note that dissolved zinc concentrations in the influent are not shown since zinc in the Rampgill mine water is predominantly in its dissolved form and thus there is little difference between total and dissolved zinc concentrations. The mean influent zinc concentration is slightly lower than that given in Table 1 for the Rampgill mine water. This reflects some attenuation of zinc during storage (e.g. adsorption to sides of storage vessel).

Following a decline in total and dissolved zinc concentrations over the initial 4 months of operation, effluent concentrations generally stabilised around 0.06 mg/L total zinc and 0.03 mg/L dissolved zinc for a further 4 months. Both total and dissolved effluent zinc concentrations subsequently showed a slight rise after a slug addition of carbon was made on 9 May 2011, before decreasing to their pre-carbon addition levels where they remained for a further 7 months, although there is evidence of greater fluctuation since the onset of continuous carbon addition from 31 May 2011. Further discussion on the influence of carbon addition on system performance is provided in Section 3.1.2. Towards the end of the trial both total and dissolved effluent zinc concentrations showed a gradual increase to reach 0.2 mg/L (total zinc) and 0.14 mg/L (dissolved zinc) at the time the system was decommissioned. This may indicate the onset of zinc breakthrough, although it should be noted that the influent zinc concentration also showed a steady increase over the final 4 months of the trial and the higher effluent concentrations may simply reflect this.

Other metals (lead, cadmium and copper) were below detection limits in both the influent mine water and effluent water throughout the duration of the trial.

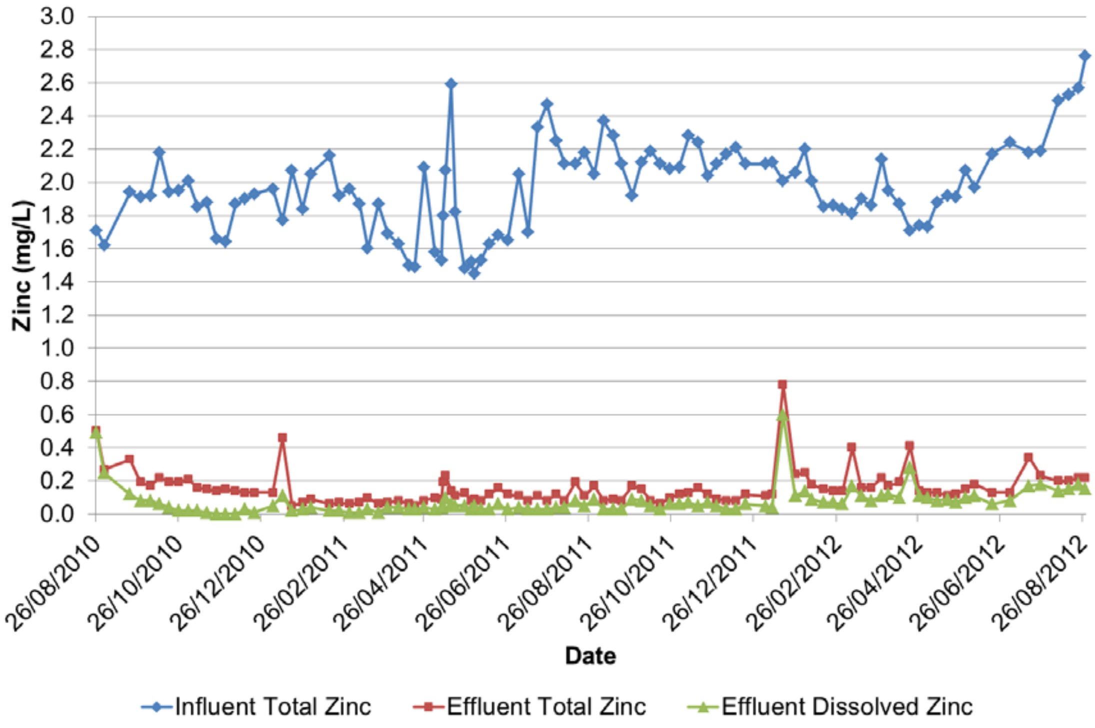

Figure 7. Influent and effluent zinc concentrations in laboratory column

In terms of treatment performance, the column removed, on average, 92% of the influent total zinc and 96% of the influent dissolved zinc, which equates to an area-adjusted removal rate of around 0.5 g/m^2/day and a volume-adjusted removal rate of the order of 1.3 g/m^3/day. Treatment efficiency and volume-adjusted removal rates for dissolved zinc are presented in Figure 8. Although treatment efficiency remained consistently above 95% for the initial 16 months of the trial (with a mean of 97%), a clear reduction in efficiency can be seen in the latter 8 months, albeit over 90% of the influent dissolved zinc was removed, for the most part, and the mean efficiency was still 93%.

The volume-adjusted removal rate, on the other hand, showed greater variation throughout the duration of the trial, ranging from 0.8 g/m^3/day to 1.9 g/m^3/day, with a general increase in removal rate discernible in the latter stages. On closer inspection, these variations are seen to be related to influent zinc concentration, which has also shown an increase towards the end of the trial (see Figure 7). Increases in influent zinc concentration were not matched by a rise in effluent zinc concentrations of the same magnitude during the initial 16 months of the trial, and hence treatment efficiency remained at 97%. In the final 8 months, as noted above, effluent zinc concentrations also increased, resulting in a reduction in treatment efficiency. This indicates that, prior to the rise in effluent zinc concentrations towards the end of the trial, treatment performance improved during periods of higher influent zinc concentration. It appears, therefore, that the system is only capable of removing zinc to a minimum concentration (around 0.03 mg/L), irrespective of the influent concentration, and suggests that greater removal rates may be achieved with higher influent zinc concentrations. The overall conclusion of these observations is that the system is load-limited and that the volume-adjusted removal rate is a function of the amount of zinc added to the system, which is itself a function of influent zinc concentration and flow-rate. Based on the mean influent dissolved zinc load, the maximum possible volume-adjusted removal rate for dissolved zinc is 1.36 g/m^3/day which, when compared with the mean actual volume-adjusted removal rate of 1.30 g/m^3/day, shows that the system has been 96% efficient in its removal of zinc.

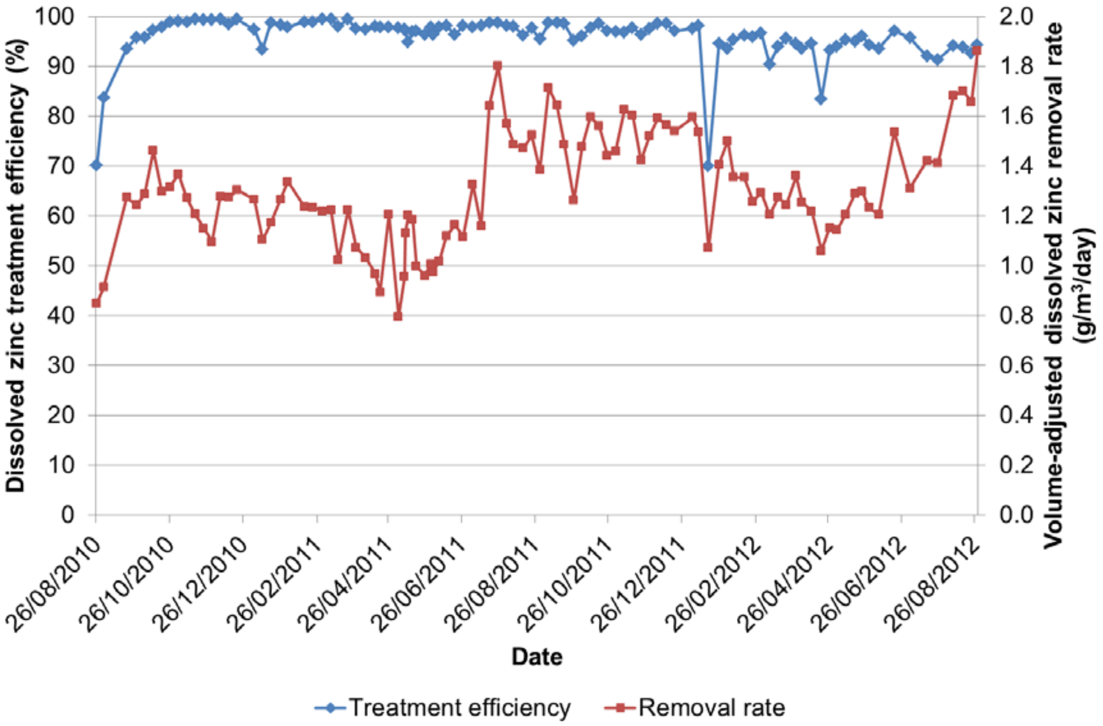

Figure 8. Treatment efficiency and removal rate of dissolved zinc in laboratory column

pH and alkalinity generation

The pH and total alkalinity of the influent mine water and effluent water from the laboratory column are shown in Figure 9. The effluent water showed a slightly lower pH throughout the trial than the influent mine water but remained greater than 7, and is still within the range pH 5–7 which is required for sulphate reducing bacteria to thrive (Cohen 1996). Total alkalinity, on the other hand, was consistently greater in the effluent water than in the influent mine water for the initial 9 months of operation, suggesting that alkalinity generation was taking place within the laboratory column. On average, around 30 mg/L as $CaCO_3$ alkalinity was generated. Following the onset of continuous carbon additions at the end of May 2011, however, influent and effluent alkalinity became comparable, with limited alkalinity generation taking place. Given the small increase in calcium concentration observed between the influent and effluent waters (Figure 10), some of the alkalinity generated in the early stages of the trial may be attributed to dissolution of limestone gravel within the reactive substrate. There is no indication from Figure 10, however, of a subsequent reduction in effluent calcium concentration (and therefore alkalinity generation attributed to limestone dissolution) suggesting that the additional alkalinity generation prior to the onset of continuous carbon additions may have been a result of bacterial sulphate reduction, a chemical product of which is the bicarbonate ion which is the major component of alkalinity in a water of this pH. Carbon additions were made directly to the influent feed water to the column, and it is notable that influent alkalinity is more variable after the commencement of carbon additions. It is not therefore clear whether the decreased generation of alkalinity post-carbon additions is due to some reaction of the organic liquid with the alkalinity in the influent water, or whether it is due to some form of inhibition of alkalinity generation within the column reactor itself, or whether it is a combination of both.

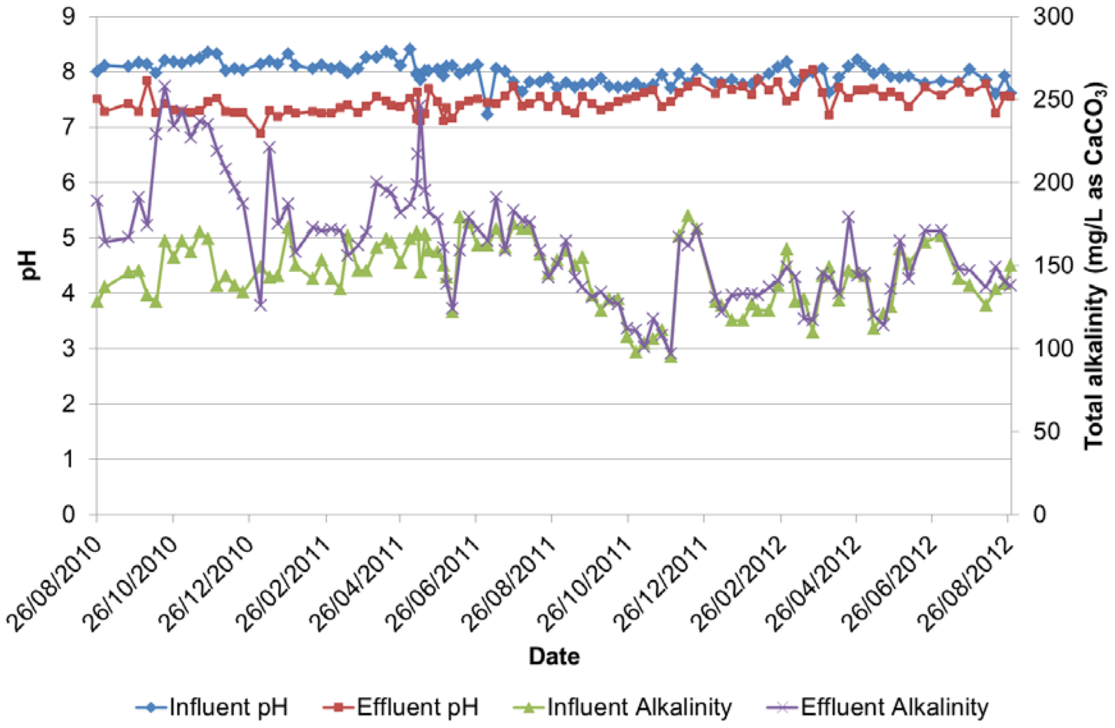

Figure 9. Influent and effluent pH and total alkalinity in laboratory column

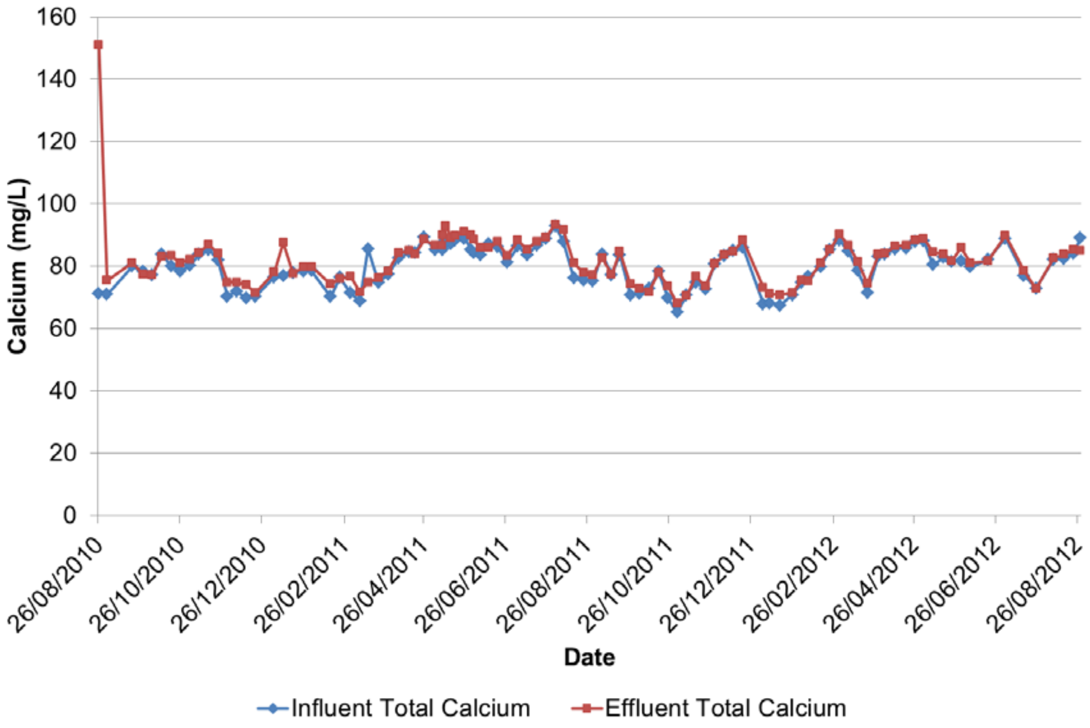

Figure 10. Influent and effluent calcium concentrations in laboratory column

3.1.2 Influence of carbon addition

Although breakthrough of zinc did not occur in the effluent from the laboratory column, the influence of carbon addition on system performance was assessed by the addition of a 20 mL slug of liquid carbon (brewery waste) to the column on 9 May 2011. Analysis of the liquid carbon showed it to contain 48,000 mg/L total organic carbon

(TOC) (and low metal concentrations). The effluent total and dissolved zinc concentrations following this carbon addition are shown in Figure 11. It is clear that a rise in both total and dissolved effluent zinc concentrations occurred immediately after the carbon addition, and then concentrations returned to their pre-carbon addition levels after a period of around 10 days. Reasons for this deterioration in performance are unclear as yet, since previous work (Jarvis et al. 2011a) has shown that the addition of an identical volume of carbon to a similar column resulted in a decrease in effluent zinc concentrations. Similarly, following the commencement of continuous carbon addition on 31 May 2011, in the form of 20 µL brewery waste per 1.0 L of influent mine water (which equates to an addition of 50 µL per day), effluent zinc concentrations showed an initial increase, particularly noticeable for total zinc, and although they subsequently decreased, greater fluctuations in zinc concentration continued. To assess whether the relatively low influent zinc concentration[4] necessitates the addition of a smaller volume of carbon, the volume of carbon added to the system was reduced by half, on 11 October 2011, to 10 µL brewery waste per 1.0 L of influent mine water (which equates to an addition of 25 µL per day). However, there is no indication that this reduction in volume had an impact on system performance, with effluent zinc concentrations continuing to fluctuate and a general rise was apparent towards the end of the trial, as discussed above.

Despite this apparent reduction in performance of the system following carbon addition, with the exception of the first few days after the slug addition of carbon, treatment efficiency in terms of total zinc removal remained above 90%, and in terms of dissolved zinc removal above 95%, until the final 8 months of the trial when a reduction in system efficiency was observed. As mentioned in Section 3.1.1, the volume-adjusted zinc removal rate actually showed an increase following carbon additions, but this is related to a concurrent increase in influent zinc concentration.

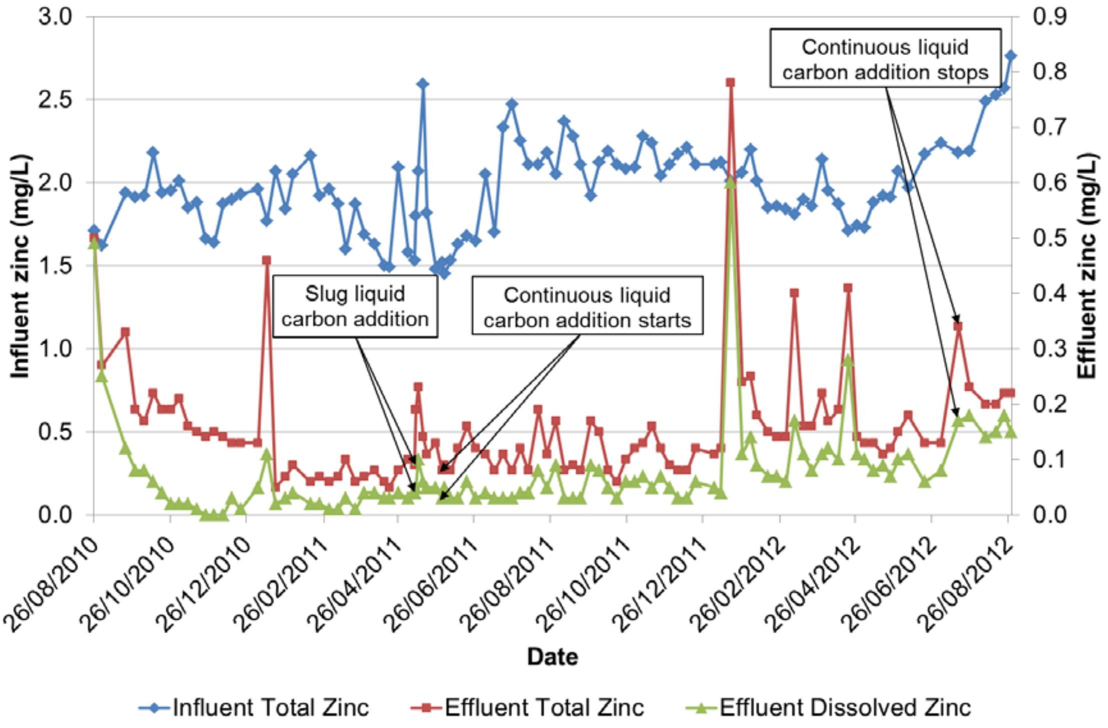

Figure 11. Influent and effluent zinc concentrations in laboratory column showing periods of carbon addition

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[4] Compared to an influent zinc concentration some 6 times greater used in previous work reported by Jarvis et al. (2011a), in which a similar volume of carbon proved successful

3.1.3 Factors influencing performance

Redox potential

The Eh in the influent mine water and effluent water from the laboratory column throughout the trial is shown in Figure 12. After an initial decline in Eh in the effluent water following the commencement of the trial, moderately anoxic conditions were established with an Eh of between -200 mV and -300 mV. Exceptions in January, February and March 2011, when conditions momentarily became less reducing, can be explained by changes in either the temperature[5] or chemistry of the influent mine water. Discounting these occasions, Eh values remained below -200 mV until the addition of carbon on 9 May 2011 when there was an immediate rise in Eh to over 100 mV. Reducing conditions returned shortly afterwards, presumably showing the short-lived effects of the carbon addition. However, following commencement of the continuous carbon addition at the end of May 2011, Eh of the effluent water fluctuated greatly for the subsequent 2 months before oxidising conditions became established for the remainder of the trial. This provides further evidence that the carbon additions had a negative impact on the bacterial sulphate reduction process, although it should be noted that the Eh measurements reported here are likely to overestimate the actual Eh value within the column. Once the effluent water was discharged from the column it became aerated and the Eh was seen to gradually rise. Given sample collection took a period of at least 1 hour (due to low flow-rates), the recorded Eh values are likely to be far higher than the actual in situ values within the column. Nonetheless, conditions clearly became less reducing following the onset of carbon additions.

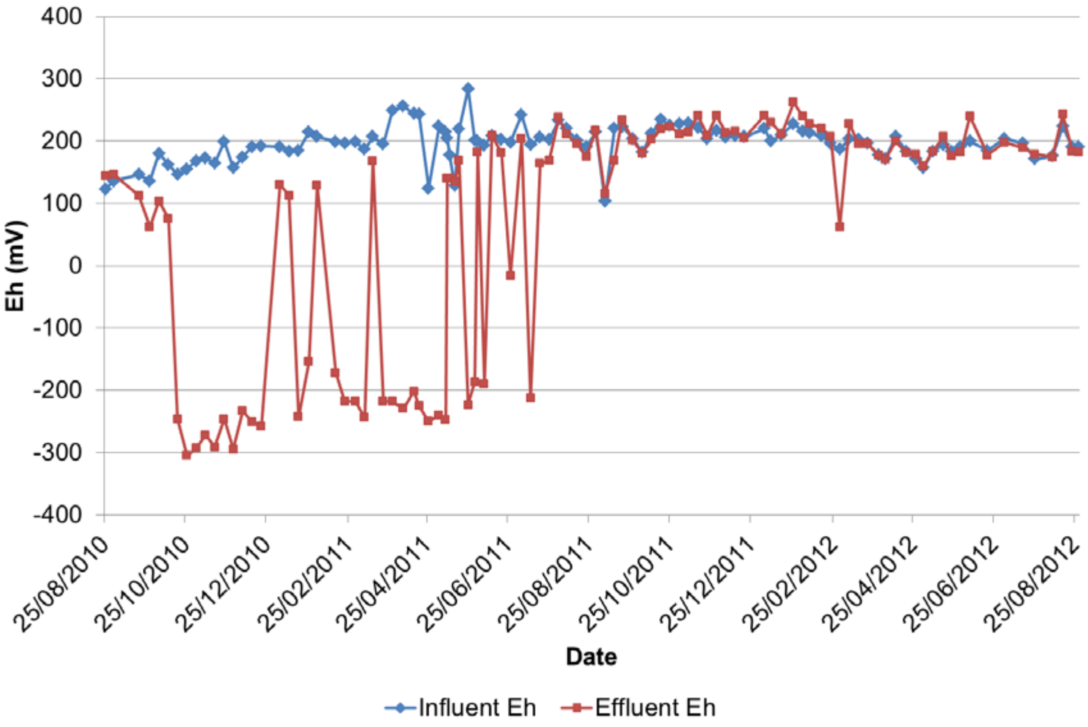

Figure 12. Influent and effluent redox potential in laboratory column

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[5] Changes in temperature of water used in the laboratory column were due to the inadvertent, but short-lived, use of mine water that had only recently been taken from cold storage and which, therefore, had not reached room temperature.

Sulphate

Sulphate concentrations were measured by ion chromatography. The influent sulphate concentration, and the change in sulphate concentration between influent and effluent, is shown in Figure 13. Apart from the odd exceptions, which coincide with periods when conditions became less reducing (Figure 12), sulphate concentrations in the column effluent were lower than influent concentrations until the commencement of carbon additions, indicating that sulphate attenuation was taking place within the column. Although there was a short-term increase in the amount of sulphate removed by the treatment system following the slug addition of carbon, within 2 weeks of the addition there was little change between influent and effluent sulphate concentration, and this trend continued throughout the period of continuous carbon addition. There is no indication that this pattern is related to changes to influent sulphate concentration. From the changes in sulphate concentration between influent and effluent it therefore appears that the addition of carbon, rather than enhancing bacterial sulphate reduction, has resulted in a decline in bacterial sulphate reduction.

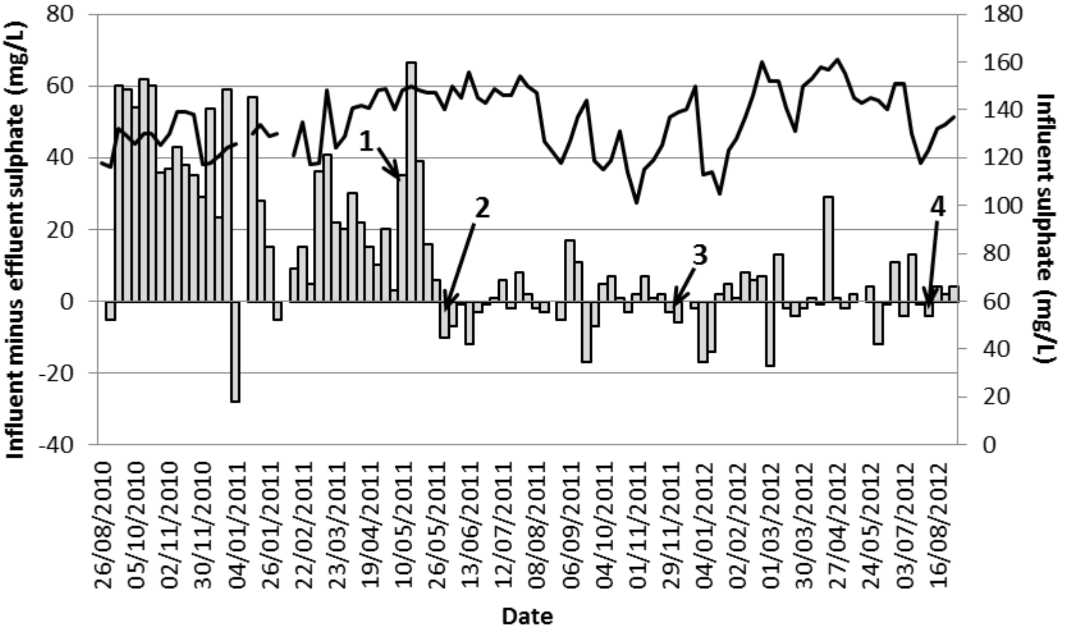

Figure 13. Influent sulphate concentration (line), and difference between influent and effluent sulphate concentrations (columns), in the laboratory column (numbered arrows indicate: 1 – slug addition of carbon; 2 – continuous carbon addition commences; 3 – volume of carbon added continuously reduced; 4 – carbon addition ceases)

Microbiology

In an initial round of microbiological analysis, in 2011, samples from both laboratory-scale columns were analysed to attempt to identify the presence of sulphate reducing bacteria, but the majority of the samples analysed were from the pilot-scale reactor. The samples from the pilot-scale reactor comprise triplicate samples of unused substrate (effectively a control sample), together with 12 samples taken from the reactor after 8.5 months of operation, and just before carbon additions were made.

Microbial analysis was conducted via polymerase chain reaction (PCR) of extracted genomic DNA using primers that detected total bacterial populations and dissimilatory sulphite reductase (DSR) functional genes. A series of analyses were undertaken at various dilutions, and all using negative controls and procedural blanks. Analysis showed the presence of bacterial communities in all samples. However, none of the results of this suite of analyses indicated the presence of active bacterial sulphate reduction (despite the odour of hydrogen sulphide routinely associated with the columns and pilot-scale reactor, which suggests that bacterial sulphate reduction was certainly occurring). Further tests, using different procedures and primers, to target known sulphate reducing bacteria populations, were therefore undertaken in March 2013. However, only samples from the pilot-scale tank were analysed in the second round of microbiological tests, and therefore the results are reported in Section 3.4.3 of this report.

Hydraulic conditions

The laboratory column was set up with an influent flow-rate of 1.6–1.7 mL/min to provide an initial hydraulic residence time of approximately 19 hours, based on bulk porosity measurements and the time taken to fill the pilot-scale reactor. In order to investigate the effects of engineering scale on system performance it was imperative that all systems had the same initial hydraulic conditions, and therefore the two laboratory-scale reactors were configured to have the same initial residence time as the pilot-scale reactor. Two tracer tests, using a sodium fluorescein tracer, were undertaken on the laboratory column, after 6 and 12 months of operation respectively, in order to determine any changes in hydraulic residence time. The results are presented in Figure 14, where it can be seen that the peak sodium fluorescein concentration was observed on both occasions after around five to six hours from the start of the test. This indicates that the actual hydraulic residence time was significantly lower than the predicted calculation of residence time based on substrate pore volume and flow-rate. This may be due to the development of preferential flow paths through the reactive substrate, possibly driven by settlement/compaction of the substrate. Despite this short hydraulic residence time, the laboratory column continued to remove approximately 96% of the influent dissolved zinc, which suggests a highly efficient system for the removal of zinc.

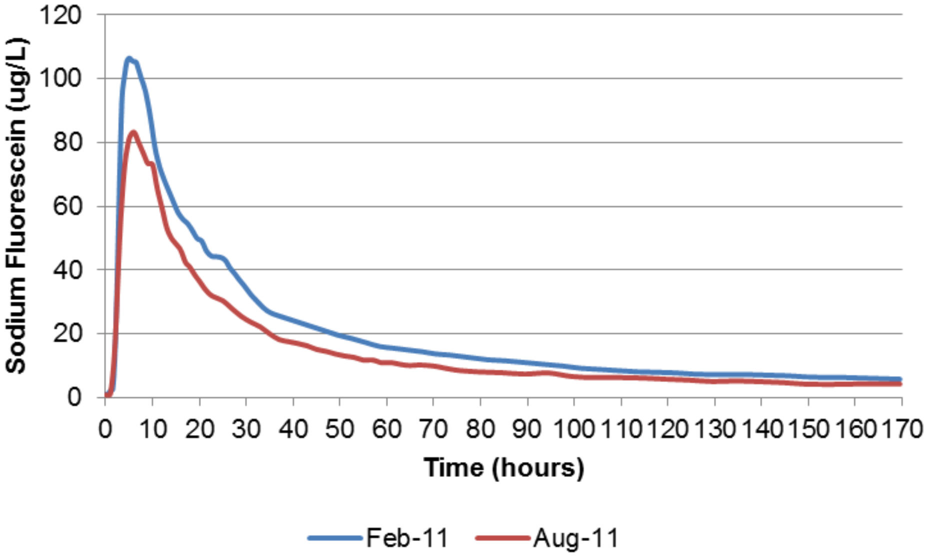

Figure 14. Laboratory column tracer test results for February 2011 and August 2011

3.2 Laboratory-scale field column

3.2.1 System performance

Metal removal

Total zinc concentrations in the influent mine water and total and dissolved zinc concentrations in the effluent water from the field column are shown in Figure 15. Gaps in the data series during the winter months represent periods where it was not possible to travel to Nenthead to collect samples, or times when the column was frozen due to extreme temperatures. Clearly, the column consistently removed zinc throughout the course of the trial, with effluent total zinc concentrations generally around 0.15 mg/L and effluent dissolved zinc concentrations on average approximately 0.08 mg/L. As with the laboratory column, both total and dissolved effluent zinc concentrations showed a gradual increase towards the end of the trial but this may reflect a similar increase in influent zinc concentration. The effluent concentrations are slightly higher than those for the laboratory column (Section 3.1.1) but this is due to some attenuation of zinc during storage resulting in a slightly lower influent (and therefore effluent) zinc concentration in the laboratory column. Unlike the laboratory column, for logistical reasons continuous carbon additions were not made to the field column, although a slug addition of carbon was made on 9 May 2011. This appeared to have little effect on effluent zinc concentrations. The high influent zinc concentration of 4.5 mg/L recorded in April 2011, along with similar smaller peaks in October 2011 and April 2012, were due to disturbance of sediment in the adit which resulted in a high particulate content in the samples. The influent dissolved zinc concentration on these occasions, by contrast, was only 1.9 mg/L, 2.15 mg/L and 2.01 mg/L respectively.

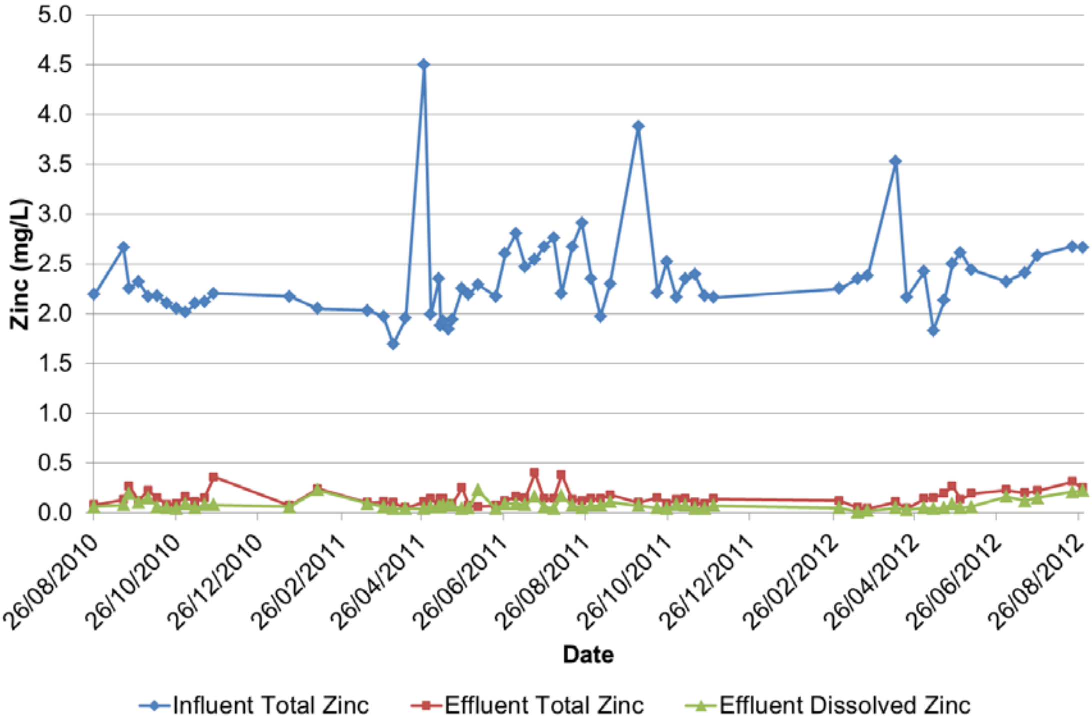

Figure 15. Influent and effluent zinc concentrations in field column

In terms of treatment performance, the field column removed, on average, 94% of the influent total zinc and 96% of the influent dissolved zinc, which equates to an area-adjusted removal rate of approximately 0.6 g/m^2/day and a volume-adjusted removal rate of around 1.4 g/m^3/day. These values are very similar to those reported for the laboratory column (Section 3.1.1). Treatment efficiency and volume-adjusted removal rates for dissolved zinc are given in Figure 16. Treatment efficiency showed rather more variation for the field column than for the laboratory column, although it remained above 90% for almost the whole period. Similarly, the volume-adjusted removal rate for dissolved zinc, as with the laboratory column, showed significant variation throughout the trial and appeared to reflect changes in influent zinc concentration (see Figure 15). Overall, the volume-adjusted removal rate varied between 1.0 g/m^3/day and 2.0 g/m^3/day, with the exception of one occasion in October 2011 when the flow-rate to the column was very low and hence the calculated removal rate was also low. As with the laboratory column, the field column appears to be load-limited and the removal rate is therefore a function of the zinc load added to the system. Based on the mean influent dissolved zinc load, the maximum possible volume-adjusted removal rate for dissolved zinc is 1.45 g/m^3/day which, when compared to the mean actual removal rate of 1.39 g/m^3/day, shows that the system has been 96% efficient in its removal of zinc.

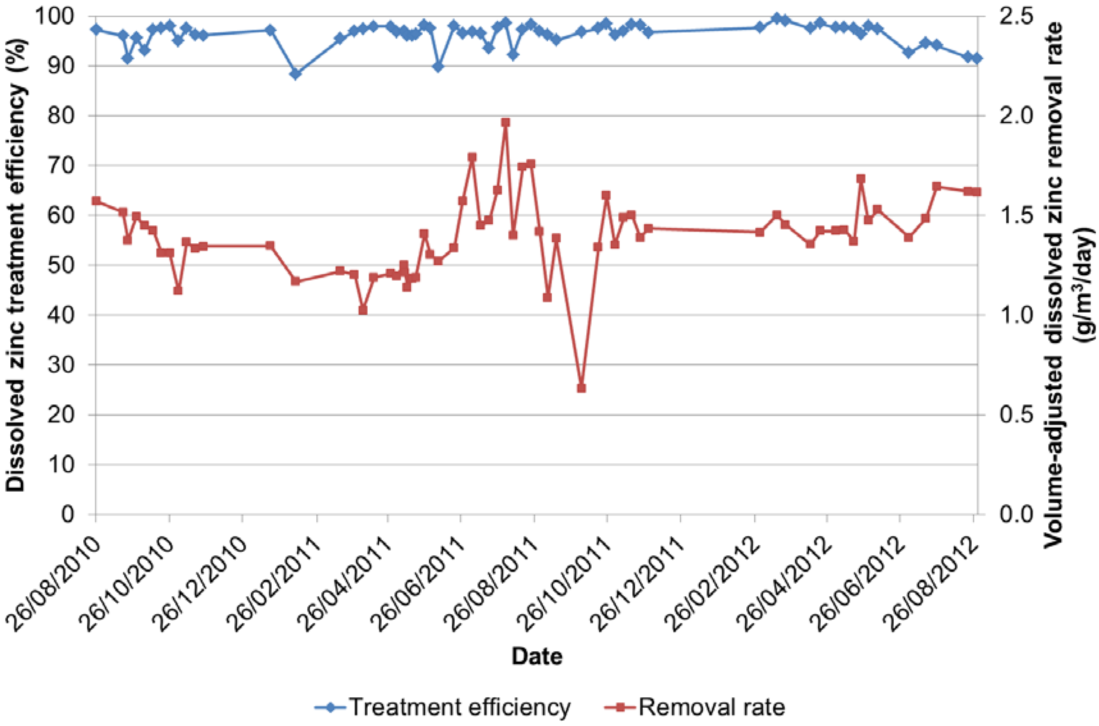

Figure 16. Treatment efficiency and removal rate of dissolved zinc in field column

pH and alkalinity generation

The pH and total alkalinity of the influent mine water and effluent water from the field column are presented in Figure 17. Unlike the laboratory column, in which effluent pH was consistently lower than influent pH, in the field column the effluent pH was generally slightly higher than the influent pH for much of the trial and consistently so for the final 5 months. The effluent pH remained above 7.1 throughout the trial and is therefore within the range required for sulphate reducing bacteria to thrive, although at times it exceeded 8.0 and was thus, if anything, slightly too high (Cohen 1996). Total alkalinity, on the other hand, in both the influent and effluent waters, showed wide variation with no clear pattern of alkalinity generation noticeable. At times, up to 50 mg/L as $CaCO_3$ alkalinity was generated in the column but such periods were short-lived. Similarly, influent and effluent calcium concentrations showed far greater variation in the field column (Figure 18) than in the laboratory column and showed a clear correlation with total alkalinity. This suggests that during periods when alkalinity generation was taking place within the field column it could be attributed to dissolution of limestone gravel within the reactive substrate. Unlike the laboratory column, however, there is no indication of possible additional alkalinity generation resulting from bacterial sulphate reduction.

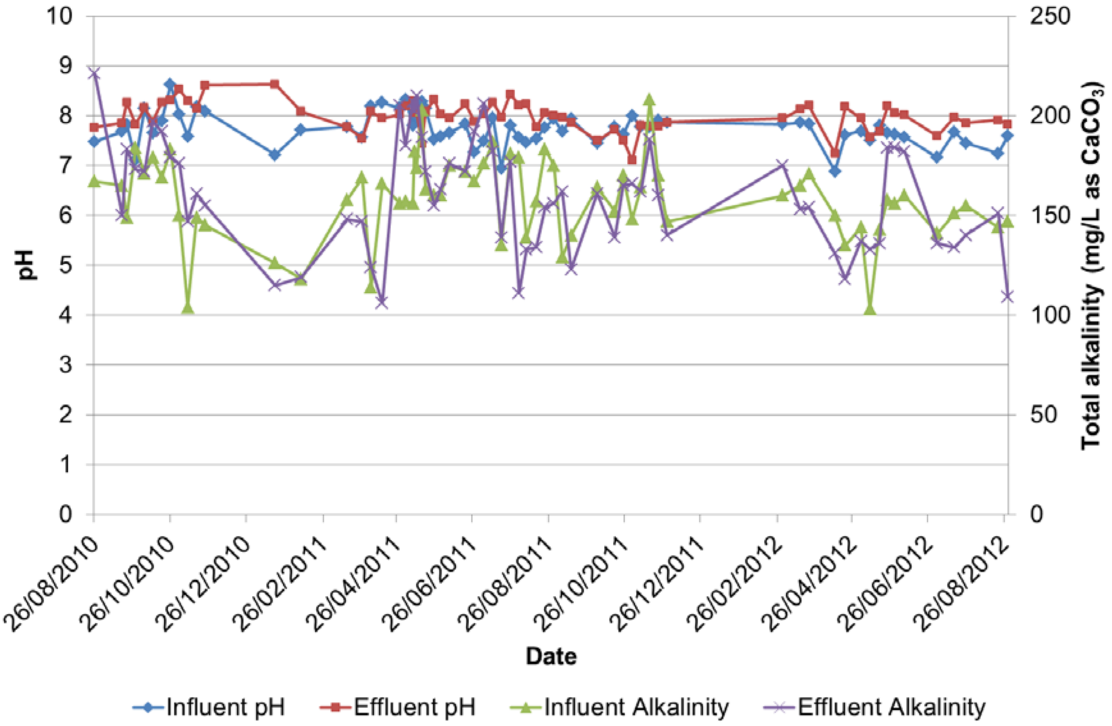

Figure 17. Influent and effluent pH and total alkalinity in field column

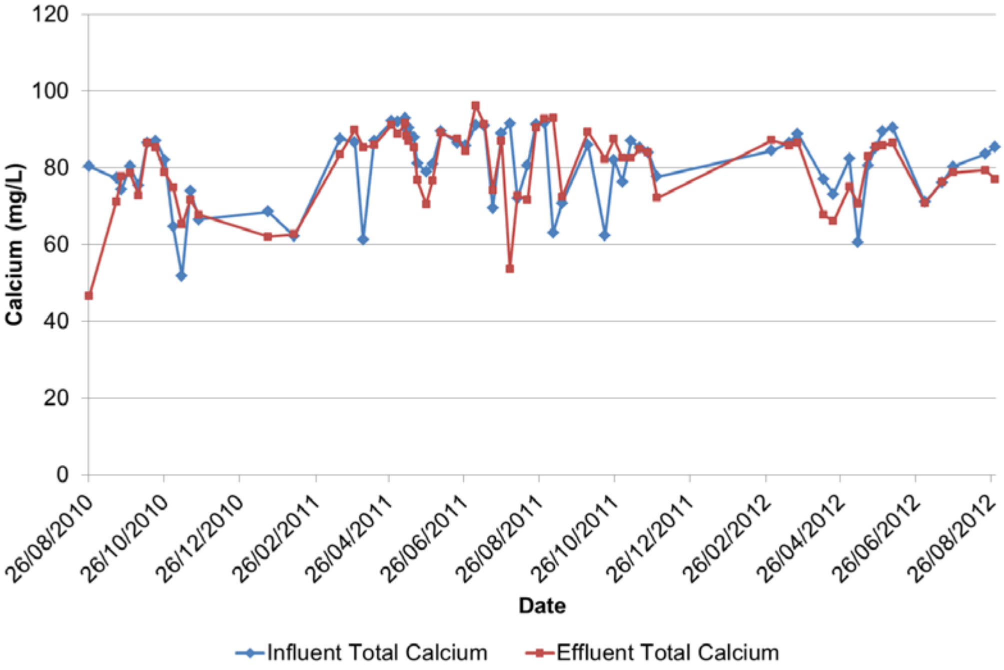

Figure 18. Influent and effluent calcium concentrations in field column

3.2.2 Influence of carbon addition

As with the laboratory column, breakthrough of zinc did not occur in the effluent of the column but the influence of carbon addition on system performance was assessed by the addition of a 20 mL slug of liquid carbon (brewery waste) to the column on 9 May 2011. The effluent total and dissolved zinc concentrations following this carbon addition are shown in Figure 19. The greater variation in effluent zinc concentrations is apparent from this figure with total zinc ranging from 0.05 mg/L to 0.4 mg/L. Following the carbon addition, apart from a small increase in both total and dissolved effluent zinc concentrations, very little impact can be seen on treatment performance. Treatment efficiency remained above 92% and a slight decrease in volume-adjusted zinc removal rate was recorded but these minor effects were short-lived. Due to logistical reasons it was not possible to examine the influence of continuous carbon addition on the field column but its impact on the laboratory column and pilot-scale system are described elsewhere in this report.

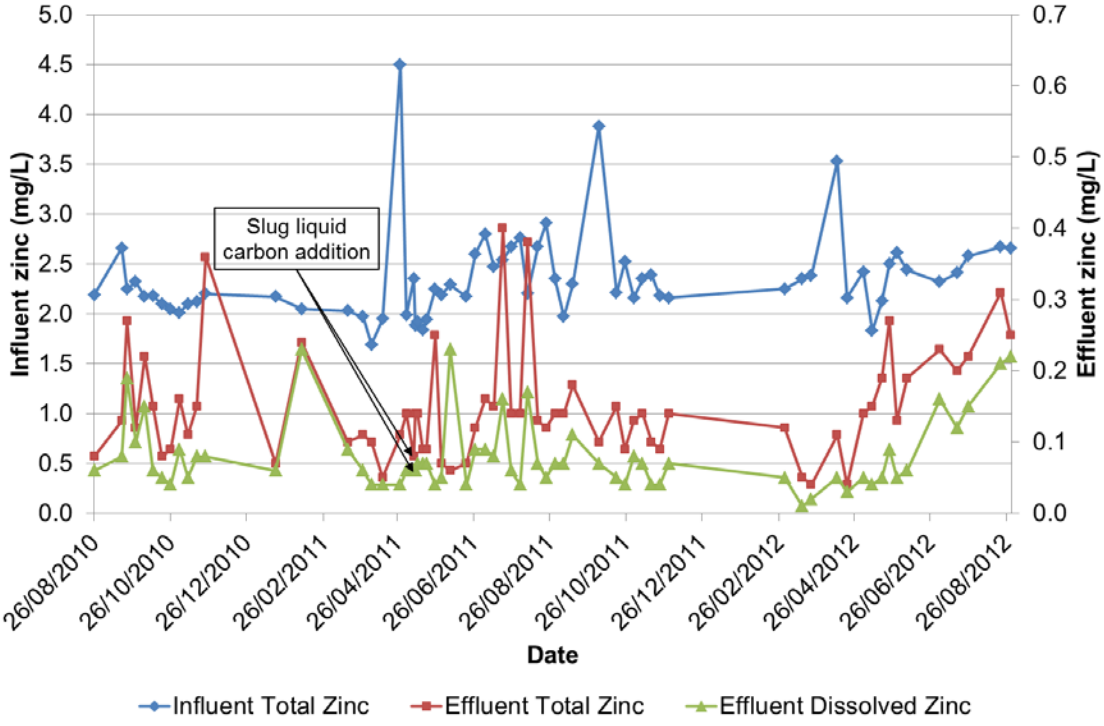

Figure 19. Influent and effluent zinc concentrations in field column showing the point of carbon addition

3.2.3 Factors influencing performance

Redox potential

The Eh in the influent mine water and effluent water from the field column over the duration of the trial are shown in Figure 20. As with the other parameters described above, Eh showed far greater variation in the field column than in the laboratory column (Figure 12). For the first 3 months of the trial, conditions were mildly oxidising but over the following 6 months anoxic conditions were present for short periods, with Eh reaching a minimum of -100 mV. Over the remainder of the trial, however, moderately anoxic conditions appeared to become established (with one exception) with Eh varying between -39 mV and -230 mV during this period. It should again be noted here, however, that, due to the low flow-rate, sample collection from the field column took at least 1 hour and once discharged from the column the effluent water became aerated. Thus, the recorded Eh values are likely to be considerably higher than the in situ values within the column. Therefore, the persistence of oxidising conditions during the first 9 months of the trial does not necessarily mean that conditions were not in fact anoxic within the column.

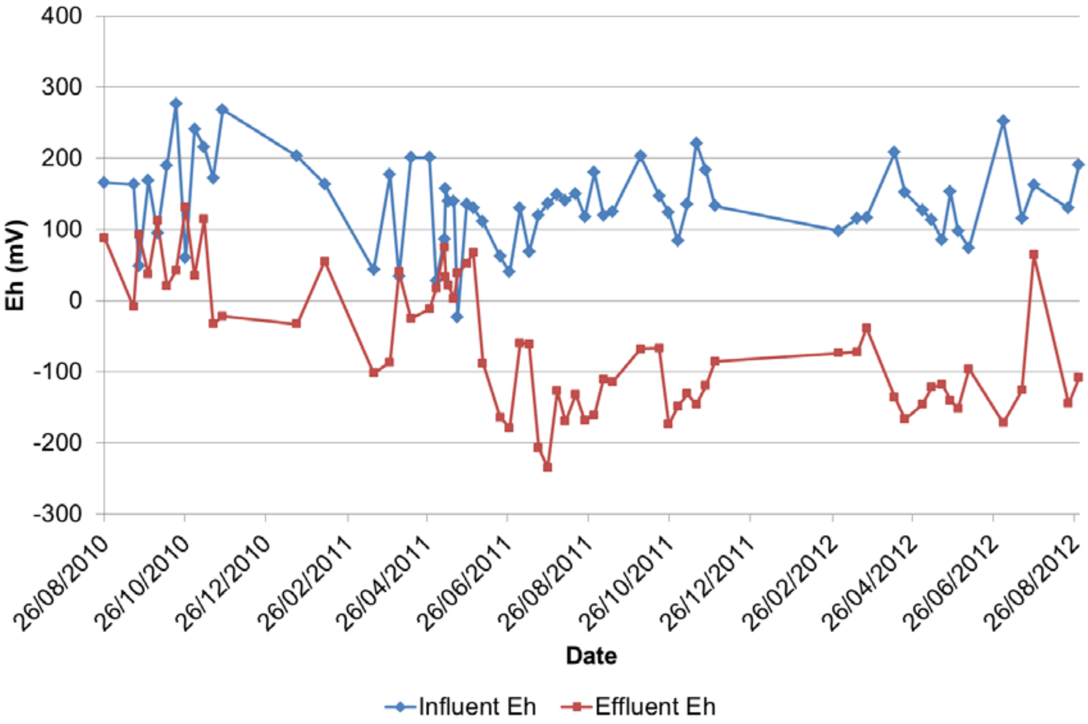

Figure 20. Influent and effluent redox potential in field column

Sulphate

Influent sulphate concentration, and the difference between influent and effluent concentration, is shown in Figure 21. In general, effluent sulphate concentrations were lower than influent sulphate concentrations throughout the trial, with the odd exceptions. As with the laboratory column, this implies that bacterial sulphate reduction is occurring. However, as with the laboratory column, the slug addition of carbon on 9 May 2011 appeared to have no impact on the extent of sulphate reduction.

Inspection of Figure 21 suggests that there may have been a seasonal influence on the removal of sulphate within the column and, therefore, on the extent to which bacterial sulphate reduction occurred. Specifically, it appears that there was greater reduction of sulphate during the warmer, summer months. Plotting sulphate removed (influent sulphate minus effluent sulphate concentration) against temperature suggests that there is indeed a relationship (Figure 22). Furthermore, there is also an inverse relationship between sulphate removed and effluent dissolved zinc concentration; that is, the greater the sulphate removed the lower the effluent dissolved zinc concentration (Figure 23). The implication is that bacterial sulphate reduction is encouraged by warmer temperatures, with consequent impacts on the efficiency of treatment in terms of metal removal. As expected, this is not a pattern that is observed in the equivalent column in the laboratory, since temperatures are constant at around 20°C.

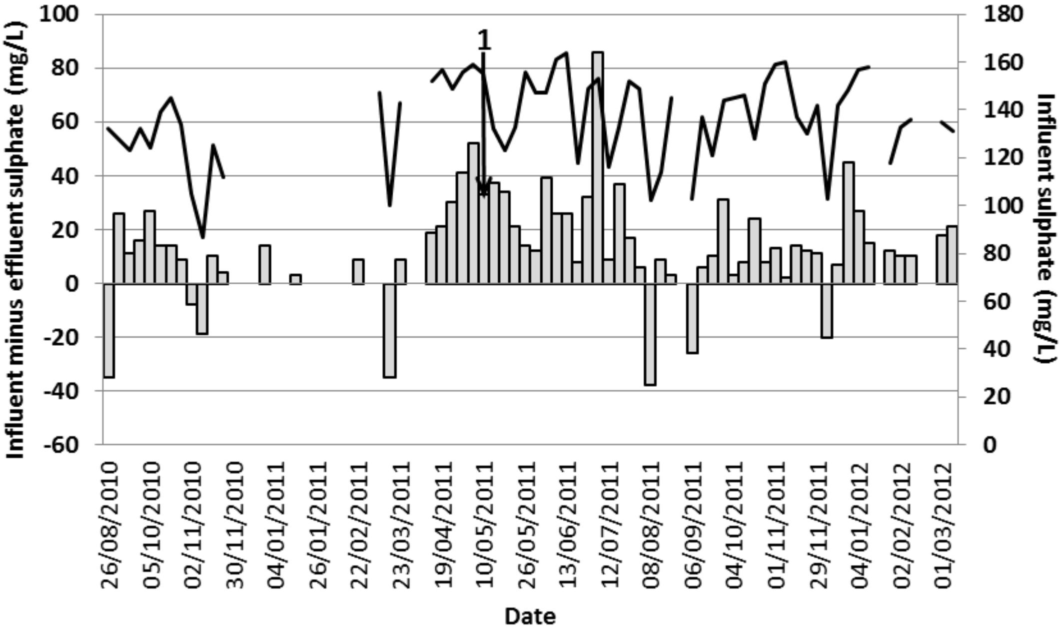

Figure 21. Influent sulphate concentration (line), and difference between influent and effluent sulphate concentrations (columns), in the laboratory-scale field column (numbered arrow indicates: 1 – slug addition of carbon)

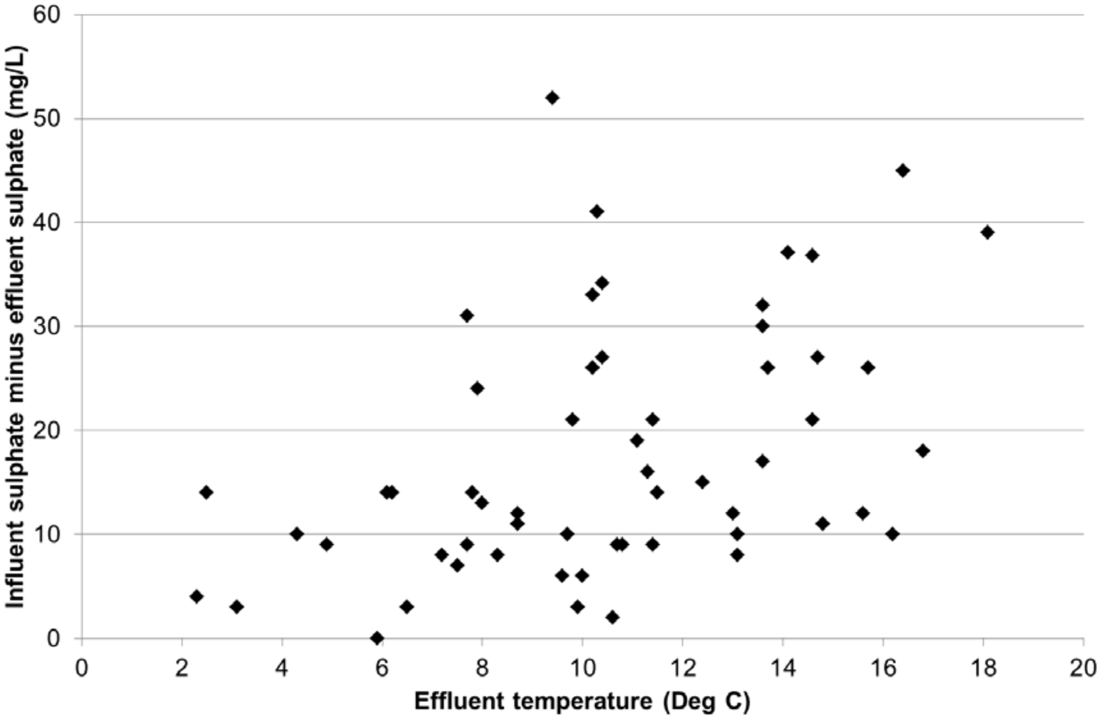

Figure 22. Relationship between effluent temperature and sulphate removed in the field column

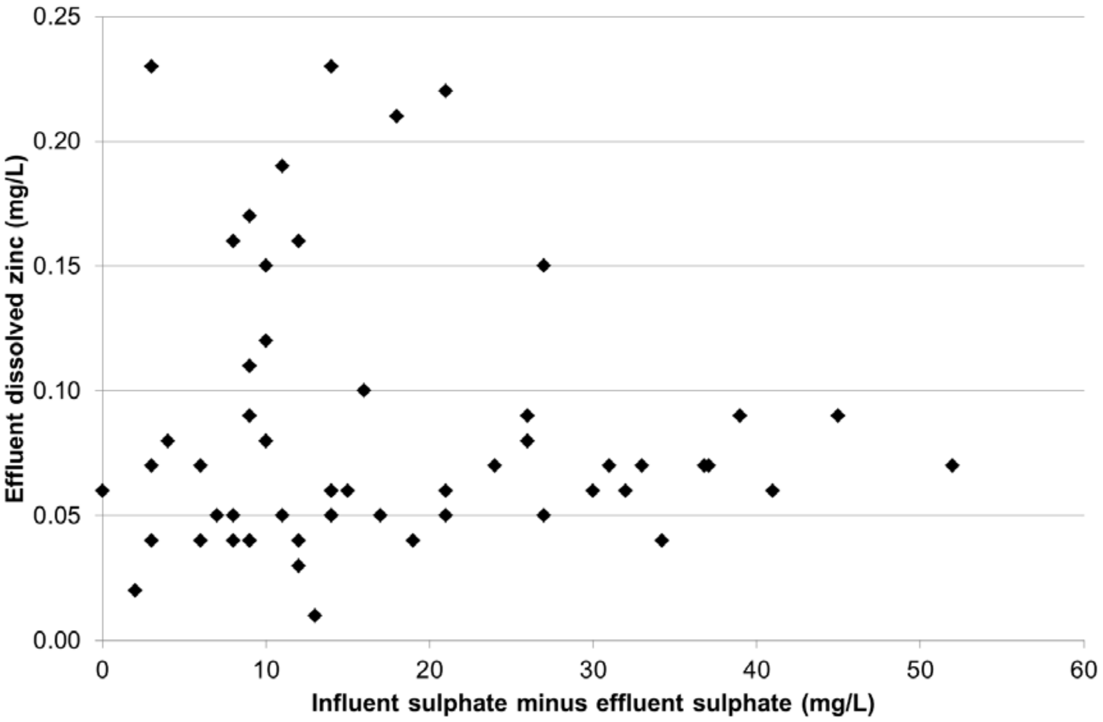

Figure 23. Relationship between sulphate removed and effluent dissolved zinc concentration in the field column

Microbiology

As noted in Section 3.1.3, a first round of microbiological analyses were undertaken on substrate from both the laboratory column and the field column, but failed to identify any sulphate reducing bacteria groups. In a subsequent round of analyses only samples from the pilot-scale tank were analysed, and these results are reported in Section 3.4.3 of this report.

Hydraulic conditions

Two tracer tests, using a sodium fluorescein tracer, were undertaken on the field column after 7 months and 12 months of operation respectively, to determine any changes in hydraulic residence time from the initial 19 hours. The results are shown in Figure 24. After 7 months of operation, the hydraulic residence time (indicated by the peak sodium fluorescein concentration) had decreased to around 14 hours but in the second tracer test, carried out after 12 months of operation, the hydraulic residence time appeared to have increased again to approximately 17 hours. In contrast to the laboratory column, in which hydraulic residence time was seen to significantly decrease to around 5 to 6 hours during the initial 6 months (Section 3.1.3), the development of preferential flow paths within the reactive substrate does not appear to have occurred in the field column to the same extent. It is difficult to draw any firm conclusions about the reasons for these differences.

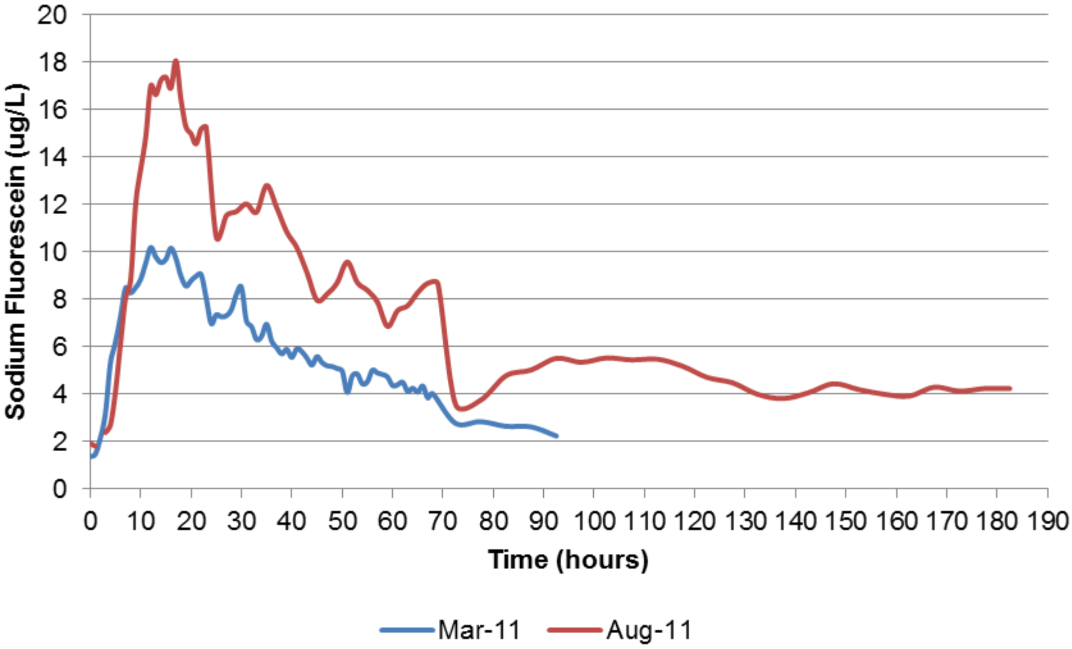

Figure 24. Field column tracer test results for March 2011 and August 2011

3.3 Comparison of laboratory and field column performance

3.3.1 Comparisons in system performance

The laboratory and field columns showed similar treatment efficiency with, on average, 92% of the influent total zinc and 96% of the influent dissolved zinc removed within the laboratory column compared to 94% of the influent total zinc and 96% of the influent dissolved zinc removed within the field column. The field column, however, displayed greater fluctuation in efficiency, ranging from 88% to 99% while the laboratory column consistently removed between 95% and 99% of the influent zinc until the final 8 months of the trial when efficiency dropped but still remained above 90% for the most part. In terms of volume-adjusted removal rates, both the laboratory and field columns showed similar removal rates of 1.3 g/m^3/day and 1.4 g/m^3/day respectively, although a general increasing trend was evident in the laboratory column towards the end of the trial. Both systems also appeared to be load-limited in that the removal rate was a function of the influent zinc load, which is itself related to influent zinc concentration and flow-rate. Given that the flow-rate remained constant in the laboratory column, the removal rate was linked only to influent zinc concentration, which showed an increase during the latter stages, hence the observed rise in removal rate during the same period. The field column, on the other hand, was subject to fluctuating influent flow-rates (particularly during the winter months) as well as influent zinc concentration. The dependence of removal rate on influent zinc concentration is confirmed by linear regression, which gives coefficients of determination (R^2) of 0.89 for the laboratory column and 0.80 for the field column.

With regard to other parameters, alkalinity generation appears to have been greater (prior to carbon additions) in the laboratory column than in the field column, while anoxic conditions (as indicated by Eh readings) were established fairly readily in the laboratory column but not until the last 15 months in the field column, although there were short periods prior to this when conditions were anoxic. There is clear evidence that sulphate attenuation was taking place within both the laboratory and field columns throughout the trial, which is indicative of bacterial sulphate reduction. Notwithstanding this comment, there is evidence of a relationship between effluent water temperature and sulphate removed, and sulphate removed and effluent dissolved zinc concentration, in the field column (Figures 22 and 23), suggesting a degree of performance control by environmental conditions. Such relationships are absent in the laboratory column, as would be expected given the constant ambient environmental conditions.

3.3.2 Influence of hydraulic conditions

Clearly there were differences in performance between the laboratory and field columns despite similar treatment efficiencies and volume-adjusted removal rates. Given that the two systems contained identical volumes and mixtures of reactive substrate, and were subjected to the same influent flow-rates, any variations in performance would seem to be due to different environmental conditions. Despite identical influent flow-rates and initial hydraulic residence times, however, the hydraulic conditions within the laboratory and field columns have appeared to differ. The substantial decrease in residence time in the laboratory column during the first 6 months of operation indicates the development of preferential flow paths but this does not appear to have been the case in the field column, with residence time decreasing only slightly during the first 7 months of the trial and subsequently increasing again. Nevertheless, the laboratory column, despite such a low residence time, continued to remove upwards of 90% of the influent zinc. This suggests a highly efficient system for the removal of zinc. It does, however, make direct comparisons in performance between the two systems difficult since, not only have the systems operated under different environmental conditions, but also varying hydraulic conditions.

3.3.3 Influence of environmental conditions

The two laboratory-scale systems operated under different environmental conditions. In particular, the laboratory column was operated in a controlled temperature environment of around 20°C, whereas fluctuating temperatures, including freezing conditions during the winter months, were experienced by the field column at Nenthead. The limited number of samples collected from the field column during the winter prevent a comprehensive assessment of the effect of temperature on treatment performance but there are indications from Figures 15 and 16 that effluent zinc concentrations rose during the winter and, as a result, treatment efficiency and volume-adjusted removal rates decreased. Furthermore, Figures 22 and 23 suggest that the ambient temperature may influence the degree of sulphate reduction, which is in turn reflected in the treatment performance with respect to zinc attenuation.

3.4 Pilot-scale reactor

3.4.1 System performance

Metal removal

Total zinc concentrations in the influent mine water and total and dissolved zinc concentrations in the effluent water from the pilot-scale reactor are presented in Figure

25. The high influent zinc concentration of 4.5 mg/L recorded in April 2011, along with similar smaller peaks in October 2011 and April 2012, were due to disturbance in the adit which resulted in a high particulate content in the samples. Although both total and dissolved zinc were clearly removed within the pilot-scale reactor, effluent concentrations were significantly higher than those measured in the laboratory-scale reactors. Despite initial effluent concentrations lower than 0.5 mg/L, concentrations rose to around 1 mg/L (total zinc) over the winter months before decreasing again to around 0.5 mg/L during the spring. Following the slug addition of carbon on 9 May 2011, both total and dissolved effluent zinc concentrations increased temporarily before a more general increasing trend, particularly for total zinc, became apparent following the onset of continuous carbon addition at the end of May 2011. During the final 10 months of the trial, however, effluent zinc concentrations decreased again, possibly related to a reduction in the volume of carbon added to the system. Further discussion on the variation in zinc concentration and the influence of carbon addition on system performance is provided in subsequent sections.

In terms of treatment performance, the pilot-scale reactor removed a lower proportion of zinc than both the laboratory-scale reactors with, on average, 68% of the total zinc and 84% of the dissolved zinc removed. This equates to an area-adjusted removal rate of approximately 0.5 g/m^2/day and a volume-adjusted removal rate of around 0.9 g/m^3/day for total zinc. For dissolved zinc, the mean area-adjusted removal rate was approximately 0.6 g/m^2/day and the mean volume-adjusted removal rate was around 1.0 g/m^3/day. Despite the lower treatment efficiency of the pilot-scale reactor, the area-adjusted removal rates were very similar to those in the laboratory-scale reactors while the volume-adjusted removal rates were only slightly lower.

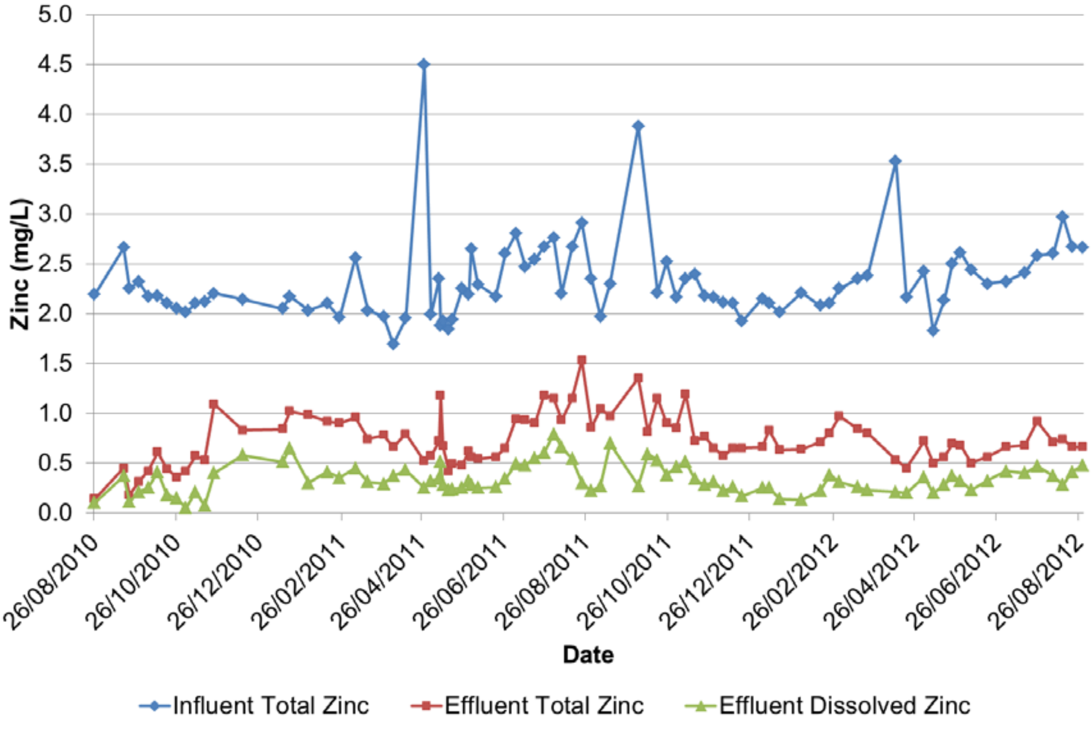

Figure 25. Influent and effluent zinc concentrations in the Nenthead pilot-scale reactor

Treatment efficiency and volume-adjusted removal rates for total and dissolved zinc over the duration of the trial are presented in Figures 26 and 27 respectively. In contrast to the laboratory-scale columns, in which treatment efficiency remained relatively constant (albeit the field column did show some variation), there was significant variation in treatment efficiency in the pilot-scale reactor. This is particularly apparent for total zinc, for which treatment efficiency decreased from an initial 93% (such a high efficiency in the early stages is probably the result of sorption/co-precipitation of zinc onto fresh surfaces) to a minimum of 50% before gradually increasing again. The slug addition of carbon on 9 May 2011 saw an immediate and substantial reduction in treatment efficiency for total zinc to only 37%, but this was short-lived (presumably reflecting the rapid passage of carbon through the system) and efficiency increased again before beginning a more general decrease after the commencement of continuous carbon additions at the end of May. As with the effluent zinc concentrations, however, treatment efficiency increased again during the latter 10 months of the trial, possibly related to a reduction in the volume of carbon added to the system. The treatment efficiency for dissolved zinc (Figure 27) showed slightly less variation, ranging from 95% to around 70%, but there was a similar significant reduction in efficiency following the slug addition of carbon followed by a gradual decrease after continuous carbon additions began. Towards the end of the trial, however, an improvement in dissolved zinc treatment efficiency was observed as the system consistently removed between 80% and 90% of the influent dissolved zinc. Again, it is possible that this improvement was related to a reduction in the volume of carbon added to the system.

The volume-adjusted removal rate similarly showed great variation over the course of the trial and, especially for total zinc, appears to follow the same pattern as treatment efficiency. This differs from the laboratory-scale columns, in which removal rate was closely related to influent zinc concentration. The total zinc removal rate varied between 0.16 g/m^3/day and 2.5 g/m^3/day in the pilot-scale reactor, with the principal cause of such variation being changes in flow-rate. Problems during pumping of the mine water to the reactor, in particular freezing temperatures during winter, resulted in a widely varying influent flow-rate. Since the volume-adjusted removal rate is based on the influent flow-rate, such variations are reflected in the removal rate. Thus, as with the two laboratory-scale reactors, the pilot-scale reactor appears to be load-limited, with the removal rate a function of the influent zinc load. This is highlighted by the high volume-adjusted removal rate of 2.5 g/m^3/day on the occasion when the influent zinc concentration increased to 4.5 mg/L.

Similarly, the volume-adjusted removal rate for dissolved zinc varied between 0.2 g/m^3/day and 1.8 g/m^3/day and was closely related to influent flow-rate. Based on the mean influent zinc load, the maximum possible volume-adjusted removal rate is 1.3 g/m^3/day (total zinc) and 1.2 g/m^3/day (dissolved zinc) which, when compared to the mean actual removal rates of 0.9 g/m^3/day (total zinc) and 1.0 g/m^3/day (dissolved zinc), shows that the system has been 68% efficient in its removal of total zinc and 84% efficient in its removal of dissolved zinc.

During the final 10 months of the trial, additional samples of influent mine water and effluent water from the pilot-scale reactor were passed through a 0.1 µm filter and analysed for metal concentrations. Dissolved zinc concentrations in the effluent water samples were significantly lower than those reported above (from samples passed through a 0.45 µm filter), with less than 0.1 mg/L zinc consistently present. This indicates that the zinc present in the samples of water passed through a 0.45 µm filter occurred as very small particles, less than 0.45 µm in diameter. Given the discussion below in Section 3.6, it is feasible that these particles may be particles of zinc sulphide generated within the reactor, in which case treatment efficiency was almost 100%.

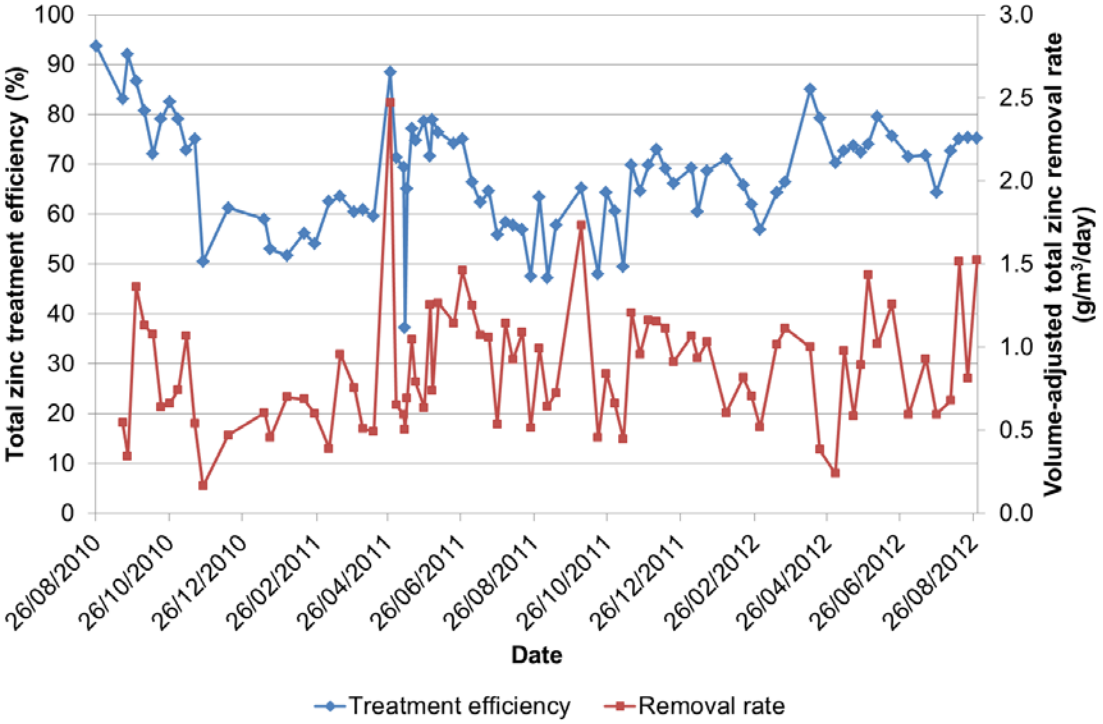

Figure 26. Treatment efficiency and removal rate of total zinc in the Nenthead pilot-scale reactor

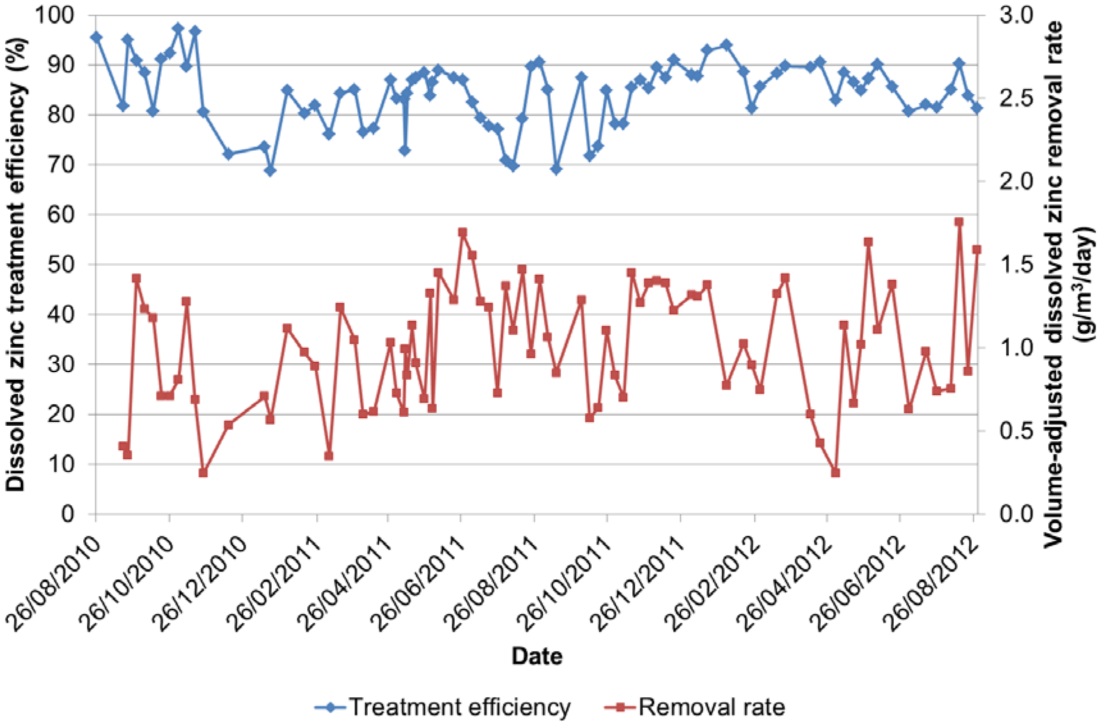

Figure 27. Treatment efficiency and removal rate of dissolved zinc in the Nenthead pilot-scale reactor

pH and alkalinity generation

The pH and total alkalinity of the influent mine water and effluent water from the pilot-scale reactor are shown in Figure 28. The effluent pH varied between 6.9 and 8.7 with a higher pH recorded during the initial 7 months of the trial followed by a clear decrease until stabilising around 7.2 to 7.5 for the remainder of the trial. During this latter period, effluent pH was consistently lower than influent pH although prior to the decrease, in general, the effluent water showed a slightly higher pH than the influent mine water. Reasons for this sudden decrease in pH in the effluent water are unclear but pH remained greater than 7.0 (the only exception being when influent pH was also below 7.0) and was thus within the range required for sulphate reducing bacteria to thrive (Cohen 1996). As with the field column, particularly in the early stages of the trial, if anything pH was slightly too high with occasions when it was greater than 8.0. The influent pH, however, remained below 8.0 for the most part.

Total alkalinity, in both the influent and effluent waters, varied throughout the trial, with no clear pattern of alkalinity generation apparent. In the early stages, when effluent pH was higher, alkalinity in the effluent water was, in general, slightly greater than that in the influent mine water but, after the onset of carbon additions, very little alkalinity generation took place within the reactor until the final 6 months of the trial when effluent alkalinity was consistently greater than influent alkalinity. Some of the alkalinity generated in the initial 7 months may be attributed to dissolution of limestone gravel within the reactive substrate, since effluent calcium concentrations during this time were slightly higher than influent calcium concentrations (Figure 29). However, in the latter stages of the trial, little limestone dissolution appears to have taken place since influent and effluent calcium concentrations were comparable. The additional alkalinity generation may have therefore resulted from bacterial sulphate reduction.

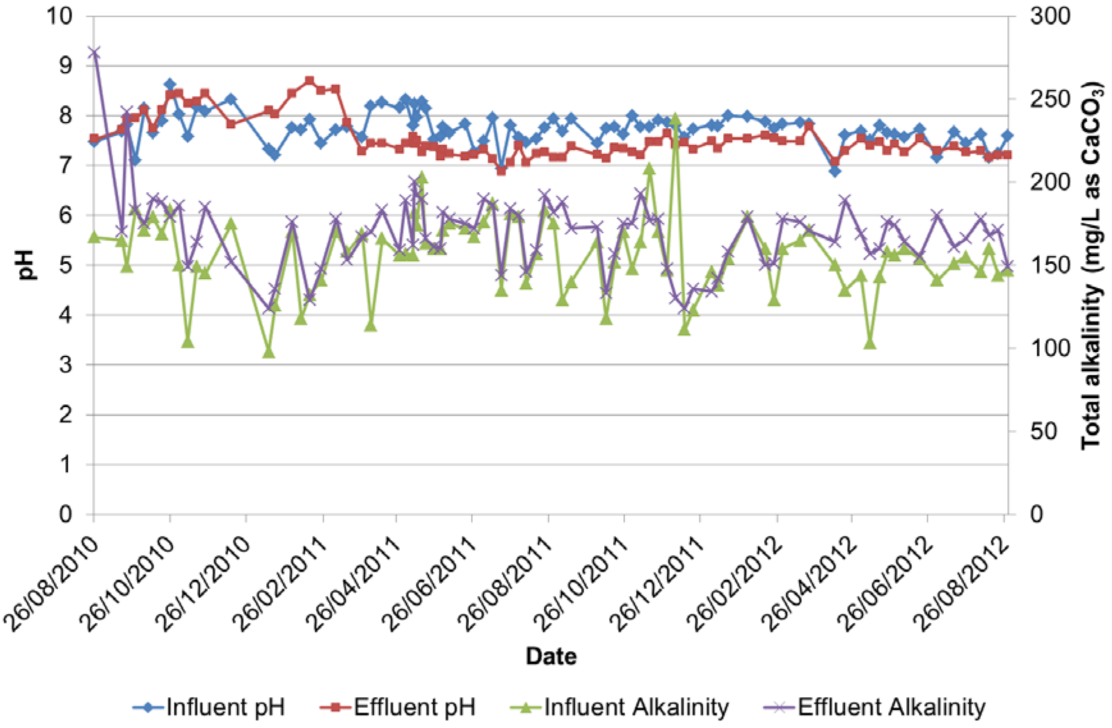

Figure 28. Influent and effluent pH and total alkalinity in the Nenthead pilot-scale reactor

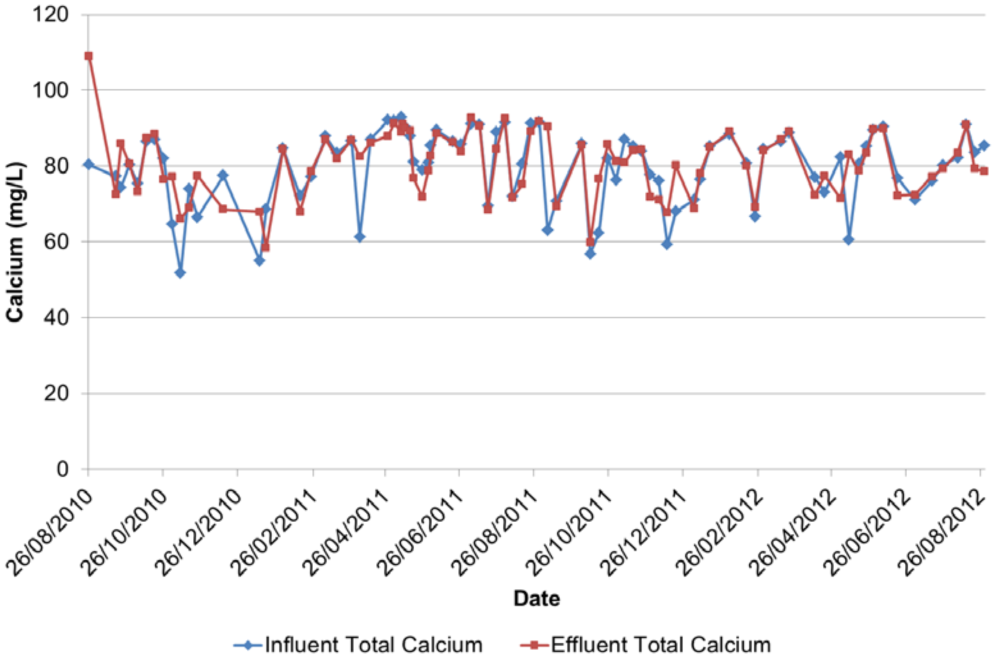

Figure 29. Influent and effluent calcium concentrations in the Nenthead pilot-scale reactor

3.4.2 Influence of carbon addition

The influence of carbon addition on the performance of the pilot-scale reactor was assessed by the addition of a 13 L slug of liquid carbon (brewery waste, directly added to the water surface at the influent end of the tank) to the reactor on 9 May 2011. The volume of carbon added was analogous to that injected into the laboratory-scale reactors, taking into account the different scales of the systems. The effluent total and dissolved zinc concentrations (together with the influent total zinc concentration) following this carbon addition are shown in Figure 30. An immediate increase in both total and dissolved zinc concentrations in the effluent water after the carbon addition is apparent, before concentrations returned to their pre-carbon addition levels after a period of around 7 days. Thus, although the slug addition of carbon had a negative impact on system performance, the effect was relatively short-lived, lasting less than a week. The impact can also be clearly seen in Figures 26 and 27, where total zinc treatment efficiency reduced from almost 70% to 37% immediately after the carbon addition and dissolved zinc treatment efficiency decreased from 83% to 73%. Reasons for this deterioration in system performance are unclear but it is possible that a slug addition represents too great a volume of carbon and promotes the activity of other groups of bacteria (e.g. methanogens) which out-compete the activity of the sulphate reducing bacteria which are required for metal removal.

Following the commencement of continuous carbon addition on 31 May 2011, in the form of approximately 34 mL of brewery waste added to the reactor on a daily basis (again as direct injection to the surface of the tank at the influent end), a small decrease in total and dissolved zinc concentrations in the effluent water was observed for a period of around a week. However, concentrations then showed a gradual increase and, despite a concurrent rise in influent zinc concentrations, a decrease in treatment efficiency to 47% (total zinc) and 70% (dissolved zinc) suggests that continuous carbon additions of this form, at least at this feed-rate, also have a negative impact on system performance. It is uncertain as yet why the carbon additions have had such an impact on system performance, given previous work using similar volumes of carbon (albeit at laboratory-scale) has proved successful. To assess whether the relatively low influent zinc concentration in the Rampgill mine water (compared to the influent zinc concentration in previous work reported by Jarvis et al. (2011a) which was some six times greater) necessitates the addition of a smaller volume of carbon, the volume of carbon added to the system was reduced by half, on 11 October 2011, to approximately 15 mL of brewery waste daily. A subsequent decrease in both total and dissolved effluent zinc concentrations occurred over the following 4 months before concentrations rose again slightly towards the end of the trial. It is unclear whether this decrease in effluent zinc concentration was solely related to the reduction in carbon but, over the same period, treatment efficiency also improved (Figures 26 and 27) and there are signs that alkalinity generation was taking place within the reactor (Figure 28), possibly due to bacterial sulphate reduction.

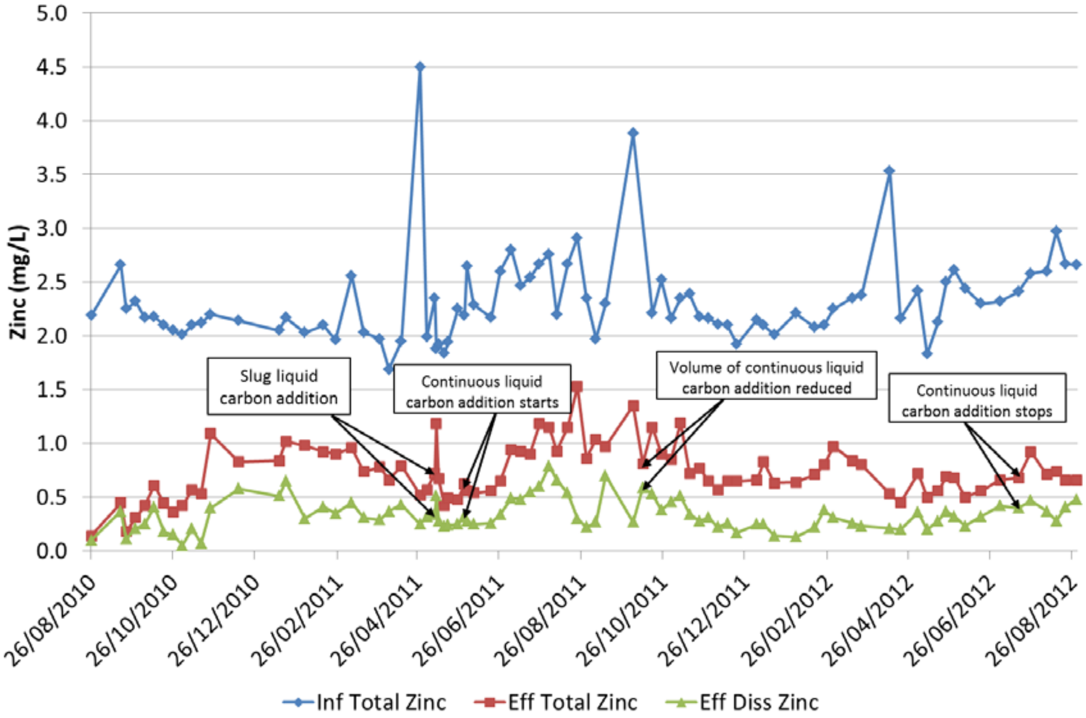

Figure 30. Influent and effluent zinc concentrations in the Nenthead pilot-scale reactor showing periods of carbon addition

3.4.3 Factors influencing performance

Redox potential

The Eh in the influent mine water and effluent water from the pilot-scale reactor over the course of the trial is shown in Figure 31. After an initial decline in Eh in the effluent water during the first month of the trial, anoxic conditions were established and have remained throughout the rest of the trial, with values as low as -360 mV recorded. A significant drop in effluent Eh is apparent immediately following the slug addition of carbon in May 2011, and conditions remained more anoxic throughout the period of continuous carbon addition. This indicates that, despite an apparent negative impact on system performance, the addition of carbon to the reactor resulted in the development of more reducing conditions which are essential for the development and sustainability of sulphate reducing bacteria. One possible reason that the more reduced conditions did not appear to result in commensurate decreases in zinc concentration (as zinc sulphide, via bacterial sulphate reduction) is if too much carbon was being added, which may favour methanogenesis over sulphate reduction. However, this possibility was not explored experimentally, for example by monitoring methane emissions.

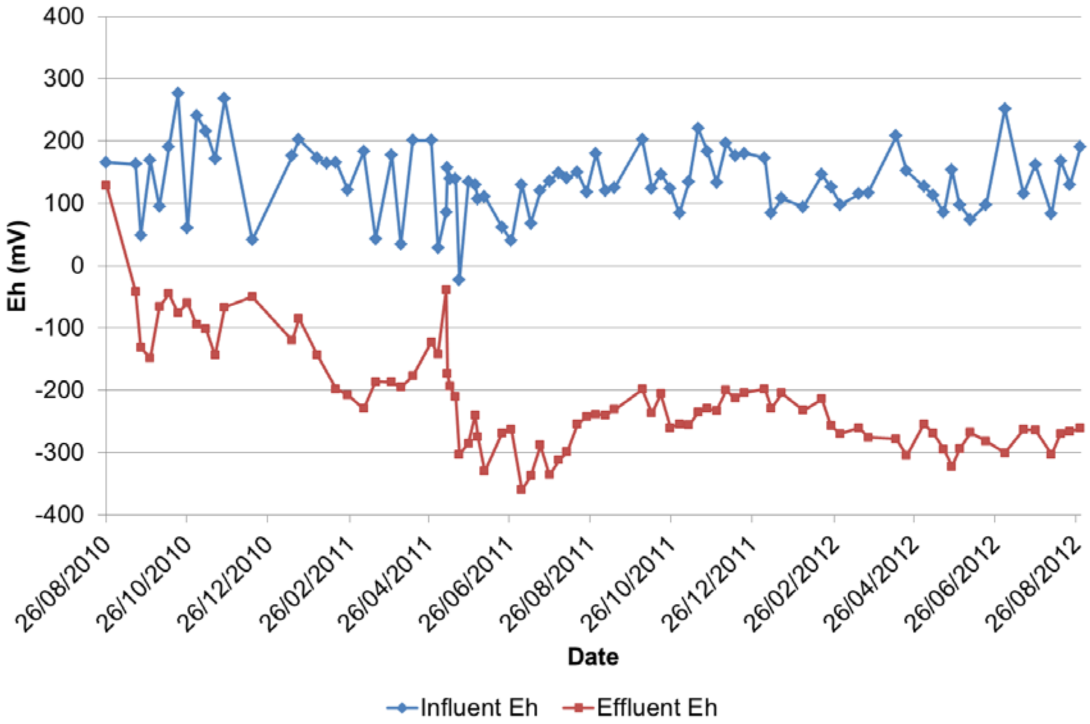

Figure 31. Influent and effluent redox potential in the Nenthead pilot-scale reactor

Sulphate and sulphur

Sulphate concentrations in the influent and effluent waters to the pilot-scale reactor are presented in Figure 32. With the odd exception, effluent sulphate concentrations were lower than influent sulphate concentrations over the duration of the trial, indicating that some attenuation of sulphate was taking place. Occasions when effluent sulphate concentration is higher than influent concentration relate to dilution of the raw water by rainfall events which are not reflected in the effluent samples collected.

The characteristic smell of hydrogen sulphide was evident close to the effluent pipe throughout the trial. Direct measurement of sulphide concentration in both the influent mine water and the effluent water during the final 10 months of the trial revealed influent sulphide concentrations to be less than 0.1 mg/L while effluent sulphide concentrations were between 1 and 2 mg/L. This strongly suggests that sulphide was indeed being generated within the reactor via bacterial sulphate reduction, which is discussed further in Section 3.6.

It is unclear whether carbon additions influenced the amount of sulphide generated, although immediately following the slug liquid carbon addition there was a sharp increase in sulphide concentration. There is no indication of an increase in sulphate attenuation or sulphide generation since the onset of continuous carbon additions however. Again, it is not clear whether this may have something to do with increased activity of methanogens.

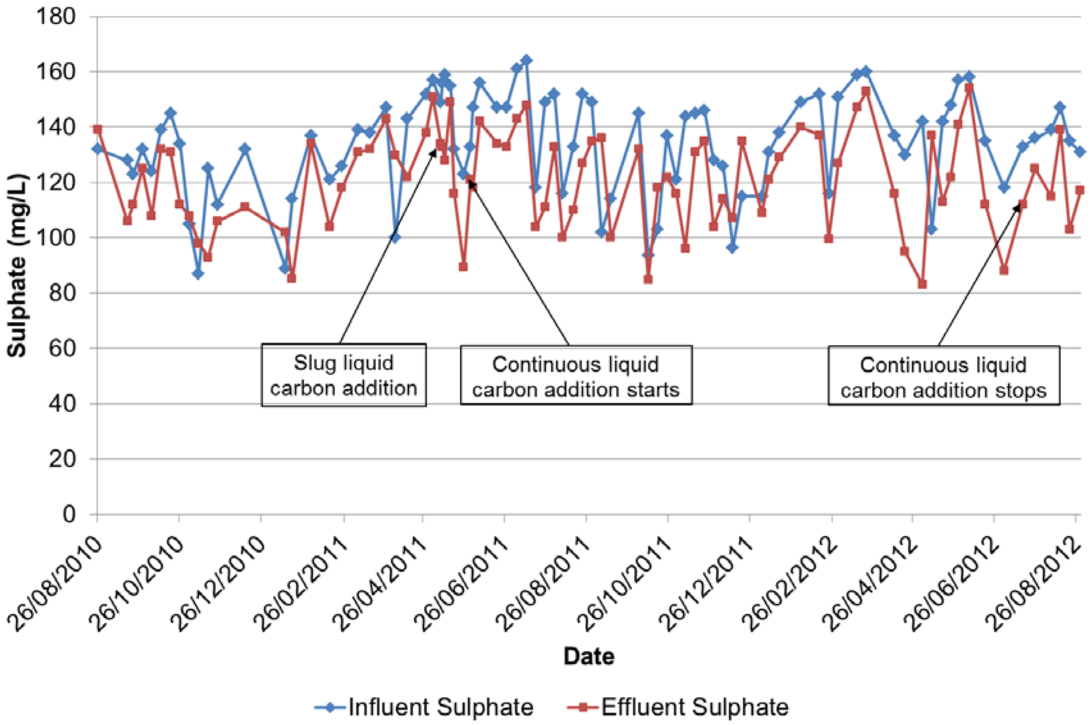

Figure 32. Influent and effluent sulphate concentrations in the Nenthead pilot-scale reactor

Microbiology

As noted previously, a first round of microbiological analyses were undertaken (in 2011) on substrates from the laboratory column, field column, and pilot tank, but all failed to identify sulphate reducing bacteria groups using a targeted polymerase chain reaction (PCR) based approach aimed at the amplification of a diagnostic gene sequence (dsrA) coding for the enzyme dissimilatory sulfite reductase. In a subsequent round of analysis, in March 2013, only samples from the pilot-scale tank were analysed. In these later experiments the PCR reaction conditions were optimised to facilitate successful PCR amplification. Amplification of the target gene fragment is required for subsequent confirmation of its presence in the original sample by visualisation using gel electrophoresis. Once the gene fragment is identified it is cloned in order to isolate gene sequences of individual organisms in the sulphate reducing bacteria community. These isolated fragments can then be sequenced to identify DNA sequence compositions. Individual sequences are then compared in terms of their similarity to those obtained from cultured sulphate reducing organisms and also sulphate reducing gene sequences recovered from other environments in which sulphate reducing bacteria have been identified.

In this round of molecular analysis sulphate reducing bacteria were successfully identified. The key findings were as follows:

- The dominant sulphate reducing bacterial groups identified were from the Deltaproteobacteria most similar to the family Desulfobulbaceae (genus *Desulfobulbus*) and the family Desulfovibrionaceae (genus *Desulfovibrio*).
- The sulphate reducing bacteria groups identified in the tank substrate were predominantly most similar to groups previously identified in non-marine environments, which is consistent with the freshwater conditions of the tank.

- Many of the sequences in the Nenthead tank substrate were also closely related to those previously identified in water treatment system substrates, and in particular those systems designed to treat metal-rich wastewaters. Nenthead sequences were also related to those recovered from metal-contaminated natural sediments. It is possible therefore that the high metal concentration conditions in the Nenthead treatment system, and other treatment systems for metal-rich wastewaters, favour the selection of metal-tolerant sulphate reducing organisms.

A phylogenetic tree summarising these findings is included in this report as Appendix A. The phylogenetic tree provides a graphical representation of the genetic relatedness of Nenthead sequences to both laboratory cultured sulphate reducing groups and those organisms identified in treatment systems/other environments. Each terminal branch in the tree represents an individual gene sequence identified by its species or clone name, its database accession number and a short source description.

It is not possible to draw conclusions about the absolute importance of sulphate reduction as a mechanism of metal removal from these data. However, these findings clearly show that sulphate reducing organisms are present and, coupled with other lines of evidence, suggest that bacterial sulphate reduction certainly plays some role in the immobilisation of metals in the treatment tank.

Further insight into the importance of bacterial sulphate reduction could be gained from undertaking further microbiological analysis. Specifically, quantification of sulphate reducing bacteria numbers may prove useful, since any correlation of bacterial numbers with solid phase metal and acid volatile sulphide concentrations in the substrate would imply the attenuation of metals may be directly related to bacterial sulphate reduction.

Substrate analyses

Samples of reactive substrate were collected from the pilot-scale reactor after 10 months of operation and were air-dried and then subjected to Aqua Regia digestion to determine their metal content. The samples were collected from the upper surface of the substrate at the influent end of the reactor. In addition, a sample from the original substrate mixture was also air-dried and subjected to Aqua Regia digestion for use as a comparison. The results are shown in Table 4. Clearly, there has been significant accumulation of metals, in particular zinc, within the substrate, which is consistent with the removal of metals within the system as shown by the water quality analyses (Section 3.4.1). The mean zinc content of the spent substrate was 5,789 mg/kg, which is considerably higher than the 340 mg/kg of zinc contained within the original substrate mixture. Although some variation exists between samples (especially for lead), for the most part the results are consistent indicating that the metal content does not vary substantially, at least in that part of the reactor. More discussion of the substrate composition, following decommissioning of the treatment tank after 24 months of operation, is provided in Section 3.6.

Table 4. Analysis of metal content in the Nenthead pilot-scale reactor substrate

Sample	Zinc (mg/kg)	Lead (mg/kg)	Cadmium (mg/kg)	Copper (mg/kg)	Iron (mg/kg)
Original	340	65.4	1.0	139	11,381
Sample 1	5,193	183	9.8	86.7	14,491
Sample 2	5,506	154	10.5	49.3	9,863
Sample 3	6,669	453	12.0	67.3	11,650

Hydraulic conditions

Tracer tests, using a sodium fluorescein tracer, were carried out on the pilot-scale reactor after 3 months, 7 months, 12 months and 23 months of operation to determine any changes in hydraulic residence time from the initial 19 hours. The results are presented in Figure 33. During the early stages of the trial, the hydraulic residence time reduced to around 14 hours after 3 months. Together with compaction of the substrate, this probably reflects the development of some preferential flow paths within the substrate. By 7 months' duration, the hydraulic residence time had decreased further to 7.5 hours but the following tracer test, after 12 months of operation, showed that the residence time had increased again to 14.5 hours. The reduction between 3 and 7 months may indicate further development of preferential flow paths through the substrate but, despite such a short residence time, the system was still removing over 60% of the influent zinc at this time. The subsequent increase in hydraulic residence time over the following 5 months of the trial may, in part, be due to a drop in water level within the reactor over several days in April, caused by a power cut which turned the pumps off and allowed part of the substrate to dry out. When pumping resumed, and the water level rose, disturbance of the substrate may have blocked the previously formed preferential flow paths thereby resulting in an increase in hydraulic residence time. The final tracer test, at the end of the trial, showed that the residence time had remained relatively constant during the preceding 11 months, decreasing only slightly to 11 hours. It is difficult to be absolutely conclusive about the reasons for the variability in hydraulic residence time, but these results certainly illustrate the dynamic nature of such bioreactors, particularly in the early stages of their operation. Given that only four tracer tests were undertaken, it is not possible to draw any clear conclusions regarding any relationship between measured hydraulic residence time and zinc removal. For such an analysis influent flow-rate has to be used as a proxy for residence time (i.e. higher influent flow-rates are assumed to result in lower hydraulic residence times).

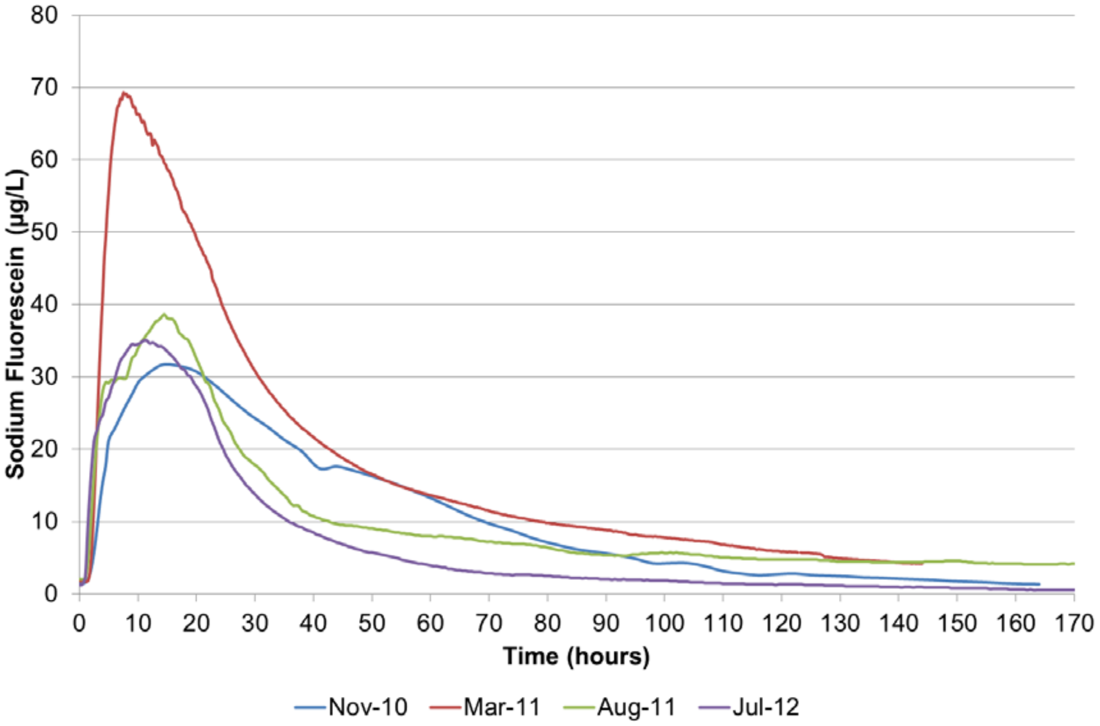

Figure 33. Nenthead pilot-scale reactor tracer test results for November 2010, March 2011, August 2011 and July 2012

3.5 Comparison of field column and pilot-scale reactor performance

3.5.1 Comparisons in system performance

There are clearly significant differences in performance between the field column and the pilot-scale reactor. Whereas treatment efficiency in the field column remained above 90% for almost all of the trial (albeit showing more variation than in the laboratory column), the removal of total zinc in the pilot-scale reactor fluctuated between 50% and 93% of the influent zinc (and dropped even lower following a slug addition of carbon). Similarly, the volume-adjusted removal rates for both total and dissolved zinc showed substantial variation in the pilot-scale reactor, ranging from 0.16 g/m^3/day to 2.5 g/m^3/day for total zinc, although it should be noted that the highest removal rate was measured on a sample which had a particularly high influent zinc concentration. If this sample was excluded the highest removal rate would have been 1.7 g/m^3/day. In contrast, the volume-adjusted removal rate for zinc in the field column varied less, fluctuating between 1.0 g/m^3/day and 2.0 g/m^3/day. As with the laboratory and field columns, the removal rate in the pilot-scale reactor appeared to be load-limited and therefore a function of the influent zinc load. However, flow-rate in the pilot-scale reactor showed greater variation. Hence the influent zinc load varied more and, as a consequence, so did the zinc removal rate. The importance of influent flow-rate on the volume-adjusted zinc removal rate in the pilot-scale reactor is highlighted by linear regression, which gives a coefficient of determination (R^2) of 0.84 compared to only 0.06 in the field column. The influent zinc concentration has a much greater effect on the volume-adjusted zinc removal rate in the field column with a coefficient of determination (R^2) of 0.80 compared to 0.15 in the pilot-scale reactor.

3.5.2 Influence of hydraulic conditions

The field column and the pilot-scale reactor were subjected to the same environmental conditions. Therefore, any variations in performance must be due to differences in engineering scale and hydraulic conditions. As reported above, both the field column and the pilot-scale reactor were configured to have identical initial hydraulic residence times of 19 hours. However, the field column was designed as an upwards flow reactor to limit channelling of water and clogging, while the water in the pilot-scale reactor was constrained to flow downwards by gravity. As a consequence, hydraulic conditions developed differently within the two systems over the duration of the trial. More specifically, while the hydraulic residence time in the field column appeared to decrease only slightly during the initial 7 months, before increasing again, a significant reduction in hydraulic residence time to 7.5 hours was observed in the pilot-scale reactor over the same time period. This indicates greater development of preferential flow paths in the pilot-scale reactor, likely as a result of the downwards flow configuration. The residence time did, however, show an increase towards the end of the trial, possibly due to disturbance of the substrate and the blocking of previously formed preferential flow paths. It is possible that the lower treatment efficiency of the pilot-scale reactor was, in part, due to this reduction in hydraulic residence time, but it is not possible to be conclusive. Given the heterogeneous nature of the compost materials used in these reactors it is difficult to envisage how it would be possible, in larger applications, to avoid at least some problems with variable residence times. However, even in the downwards flow configuration, by keeping the media saturated, and with a water cover, such short-circuiting problems should be comparatively limited (compared to a surface flow wetland, for example).

3.5.3 Influence of environmental conditions

Although the field column and pilot-scale reactor operated under the same environmental conditions, the collection of a greater number of samples from the pilot-scale reactor during the winter allowed a more thorough assessment of the effects of temperature on system performance. As reported in Section 3.3.3, there are indications that effluent zinc concentrations in the field column rose during the winter and there was a concurrent decrease in treatment efficiency and volume-adjusted removal rate. This is highlighted further by the pilot-scale reactor. It can be seen from Figures 25 to 27 that effluent zinc concentrations showed a clear increase over the period November 2010 to March 2011, before decreasing again, while treatment efficiency and removal rate displayed a reduction during the same period. The commencement of continuous carbon additions at the end of May 2011 resulted in an increase in effluent zinc concentration and therefore it has not been possible to study the impact of temperature on system performance after this date.

The variation in total zinc treatment efficiency with temperature in the pilot-scale reactor can be seen in Figure 34. Evidently, there is a clear relationship between the two variables during the early stages of the trial, with a decrease in treatment efficiency from over 90% to 50% as temperature dropped from 12°C to 2°C (note that this is temperature of the effluent water recorded when a sample was taken, the temperature at Nenthead dropped substantially below this during the winter period). A subsequent increase in treatment efficiency to over 70% can then be seen as temperature increased during the following spring. Although not so obvious, once carbon additions were made at the end of May, there is still evidence of a possible relationship between effluent temperature and treatment efficiency.

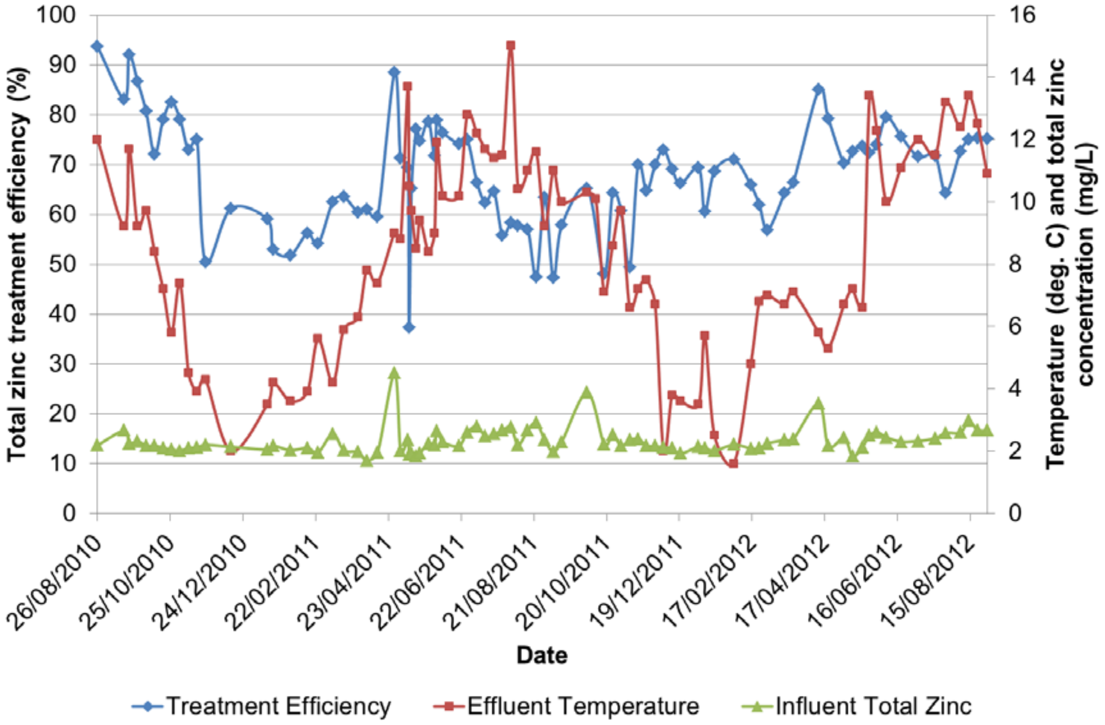

Figure 34. Treatment efficiency and effluent temperature in the Nenthead pilot-scale reactor

Further confirmation of the relationship between effluent temperature and effluent zinc concentration is shown in Figure 35. Note that the data presented here cover the initial 8 months of the pilot-scale reactor operation and excludes data following carbon addition from the beginning of May 2011. A decrease in effluent zinc concentration is seen with increasing effluent temperature. This indicates that environmental conditions, in particular temperature, may play an important role in the removal of metals within such systems. It is unclear, as yet, why this is the case but since the rates of bacterial reactions typically increase with temperature it is possibly linked to the maintenance of reducing conditions essential for the development and sustainability of the important microbial communities which act to remove metals as their sulphides via bacterial sulphate reduction. The redox conditions in the effluent water from the pilot-scale reactor were presented in Figure 31. Although a clear relationship between Eh and temperature is not apparent, in general the highest Eh values, and therefore least reducing conditions, were recorded during the period of lowest temperature.

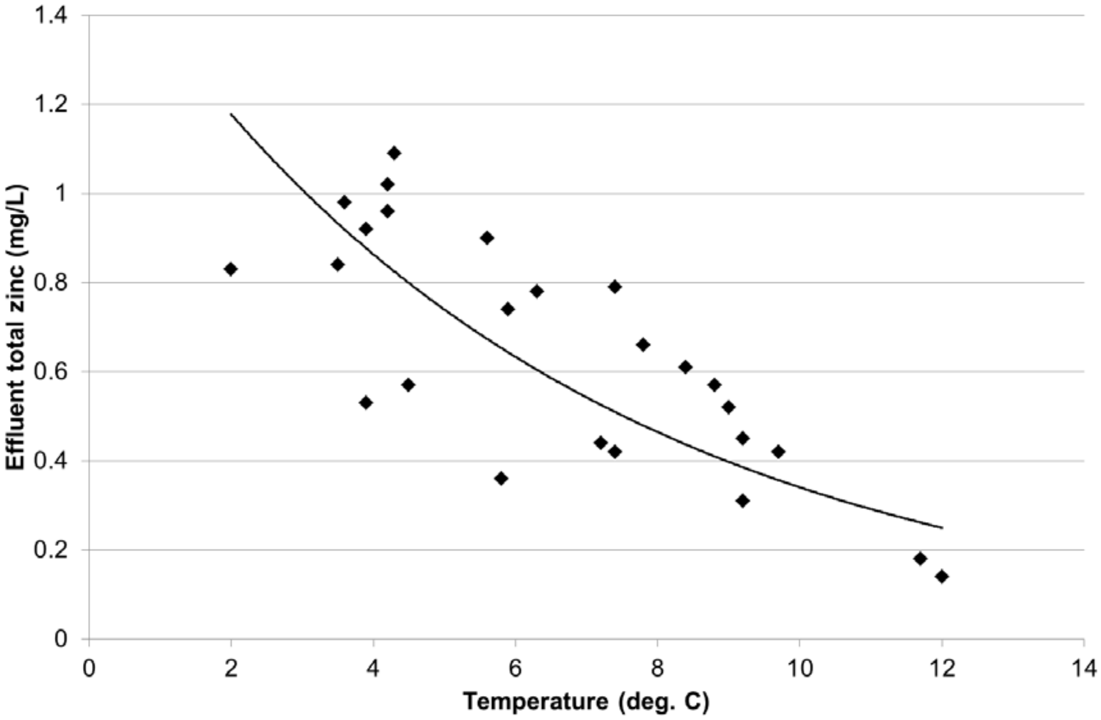

Figure 35. Relationship between effluent temperature and total zinc concentration in the Nenthead pilot-scale reactor

3.6 The importance of bacterial sulphate reduction

A key process cited in the attenuation of divalent metals in compost bioreactors is bacterially mediated sulphate reduction, which facilitates the immobilisation of metals as sulphides in the form MS (where M is a divalent metal ion). An important objective of the investigation of the system was to gain an understanding of the key mechanisms involved in the retention of metals (especially zinc) within the pilot-scale treatment system. Analysis of the results of routine water quality data (the influent and effluent data presented earlier in this report) suggests that bacterial sulphate reduction is indeed an important mechanism in the removal of divalent metals. Specifically:

- There are measurable decreases in both sulphate and zinc concentrations between influent and effluent. The mean reduction in concentration of sulphate is 17.4 mg/L (Figure 32), whilst the mean reduction in zinc concentration is 1.66 mg/L (Figure 25)
- The figures for the reduction in concentrations of both sulphate and zinc (above) indicate that the ratio of sulphate retained to zinc retained within the tank is high. Assuming that the sulphate is retained in the tank via

microbial reduction to sulphide, then this would favour the immobilisation of zinc as its sulphide, since there is an excess of sulphide to zinc.

- pH and redox potential are critical influences on the behaviour of metals. Over the last year of monitoring of the pilot-scale system mean effluent pH was 7.33 and mean effluent redox potential (Eh) was -262 mV, which would favour the formation of ZnS, as opposed to any other solid zinc phase.
- Preliminary analysis of the effluent water quality data using the geochemical modelling software PhreeqC also suggests that zinc monosulphide is the only solid zinc phase that is likely to form a solid within the treatment tank.

After ceasing operation of the pilot-scale system at Nenthead the tank was drained in a controlled manner, and solid samples of the compost substrate were recovered for analysis (Figure 36).

Figure 36. Excavation of the upper layer of compost substrate

A range of analyses were performed on the substrate, the results of which provided further evidence that bacterial sulphate reduction was a key process in the attenuation of zinc. Specifically:

- There are very high concentrations of both acid volatile sulphide (up to 9,000 mg/kg) and zinc (up to 12,200 mg/kg) in the compost substrate. Acid volatile sulphide is the type of sulphide that would be associated with metal sulphides formed by bacterial sulphate reduction.
- In the majority of the samples analysed the ratio of sulphide to zinc is high, indicating that there is a plentiful supply of sulphide to form a solid with zinc (and suggesting that the sulphate removed by the treatment system is indeed retained in the substrate as a sulphide). The ratio of sulphide to zinc appears to be higher in the lower layers of compost, suggesting that there is capacity for retention of more metal within the treatment system.
- Although concentrations of metals such as manganese, cadmium, lead and nickel are very low in the Rampgill mine water discharge, there were measurable concentrations in the compost substrate after 2 years. This suggests that these metals too are immobilised, despite being present in only very low concentrations in the mine water. Furthermore, these metals appear to be accumulating in the same areas of the substrate as the zinc, perhaps suggesting that they too are immobilised by bacterial sulphate reduction.

4 Results and discussion: Cwm Rheidol

4.1 Pilot-scale reactor

4.1.1 System performance

Metal removal

Total zinc concentrations in the influent mine water and total and dissolved zinc concentrations in the effluent water from the pilot-scale reactor at Cwm Rheidol are presented in Figure 37. Dissolved zinc concentrations in the influent water are not shown since zinc in the Cwm Rheidol discharge, as in the Rampgill discharge at Nenthead, is predominantly in its dissolved form and thus there is little difference between total and dissolved zinc concentrations.

Although initial effluent zinc concentrations (both total and dissolved) were very low, of the order of 0.48 mg/L total zinc and 0.15 mg/L dissolved zinc (such low concentrations in the early stages of operation are probably the result of zinc removal by sorption/co-precipitation onto fresh surfaces), they quickly rose over the first 3 months to reach peaks of 8.76 mg/L total zinc and 7.62 mg/L dissolved zinc. Thereafter, there appeared to be a seasonal pattern in zinc removal with effluent concentrations decreasing during the summer of 2011 before increasing again over the following winter. Dissolved zinc concentrations reached a minimum during summer 2011 of less than 0.005 mg/L, representing almost 100% efficiency in terms of dissolved zinc removal at this time.

In January 2012 a sharp increase in effluent dissolved zinc concentration occurred until there was little difference between total and dissolved zinc concentrations. This indicates that, in contrast to the previous 12 months of the trial, when the majority of zinc in the effluent water was present in particulate form, the effluent zinc became predominantly dissolved. There is no obvious explanation for this deterioration in performance of the system in terms of dissolved zinc removal, although it should be noted that the authors were not as closely involved in the operational control of the Cwm Rheidol reactor as they were with the Nenthead system. For instance, at the same time that effluent dissolved zinc concentrations rose, a substantial increase was also evident in the effluent flow-rate, which was at times significantly greater than the influent flow-rate. Reasons for this are unknown but it is likely to have had an impact on system performance. Further discussion of this issue, and its effects on the hydraulics of the system, is given in Section 4.1.2. Over the same period, from January 2012, total zinc concentrations in the effluent water also remained higher than they had been during the summer of 2011, with only a slight decrease in concentration apparent from the preceding winter.

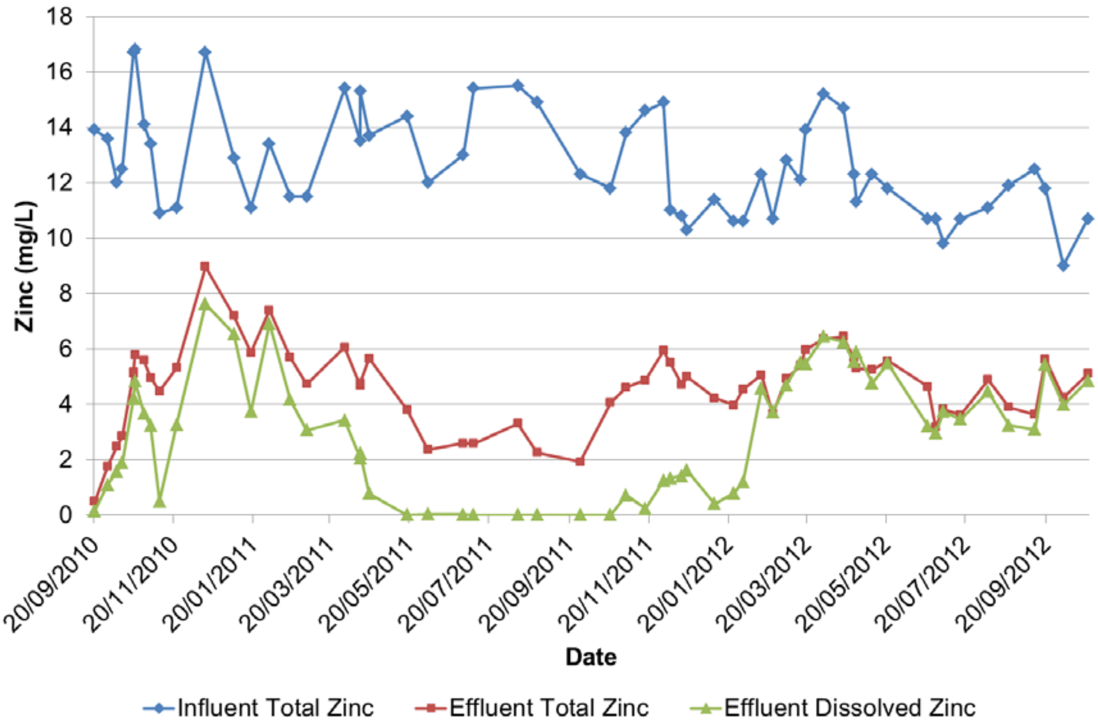

Figure 37. Influent and effluent zinc concentrations in the Cwm Rheidol pilot-scale reactor

In terms of treatment performance, the pilot-scale reactor at Cwm Rheidol removed, overall, a slightly lower proportion of zinc than the pilot-scale reactor at Nenthead with, on average, 63% of the total zinc and 76% of the dissolved zinc removed. In contrast, the area-adjusted and volume-adjusted removal rates for zinc were significantly higher at Cwm Rheidol, with a mean area-adjusted removal rate of approximately 3.6 $g/m^2/day$ and a mean volume-adjusted removal rate of 4.5 $g/m^3/day$ for total zinc. For dissolved zinc, the mean area-adjusted removal rate was 4.3 $g/m^2/day$ while the mean volume-adjusted removal rate was 5.3 $g/m^3/day$. These higher removal rates reflect the higher influent zinc load to the Cwm Rheidol system compared to the zinc load entering the Nenthead reactor, and are consistent with the earlier suggestion that these systems may become load-limited.

Treatment efficiency and volume-adjusted removal rates for total and dissolved zinc over the duration of the trial are presented in Figures 38 and 39 respectively. As with the pilot-scale reactor at Nenthead, there was significant variation in treatment efficiency for both total and dissolved zinc. However, treatment efficiency in both cases can be seen to have followed the same seasonal pattern as effluent zinc concentrations (Figure 37), at least until the final 9 months of the trial. For total zinc, treatment efficiency reduced from an initial 96% to a minimum of 44% in the winter of 2010/11 before increasing again, to around 84%, during the summer of 2011. Despite a similar reduction in treatment efficiency over the following winter, system performance did not improve to the same extent during the summer of 2012 with treatment efficiency at around 52% at the end of the trial. Similarly, for dissolved zinc, treatment efficiency reduced from an initial 99% to a minimum of 48% in the winter of 2010/11 before increasing again, to almost 100%, during the summer of 2011. As with total zinc, a subsequent decrease in dissolved zinc treatment efficiency can be seen over the following winter but system performance did not significantly improve during the summer of 2012 with treatment efficiency at around 55% at the end of the monitoring period. As noted above, the reduction in system performance during the final 9 months of the trial may be related to the substantial increase in effluent flow-rate observed over the same period but it is difficult to draw any firm conclusions from the available data.

The volume-adjusted removal rate similarly showed significant variation over the course of the trial but did not show the same seasonal pattern as effluent zinc concentrations and treatment efficiency. The total zinc removal rate varied between 0.7 g/m^3/day and 12.9 g/m^3/day, with the principal cause of these variations, as in the Nenthead pilot-scale reactor, being changes in influent flow-rate. Although the mine water was transferred by gravity to the Cwm Rheidol system, thus eliminating the problems which occurred at Nenthead due to pumping, the flow-rate still varied and was particularly high during the first month of the trial. Since the volume-adjusted removal rate is based on the influent flow-rate, such variations are reflected in the removal rate. Ignoring the early data when the influent flow-rate was high, the volume-adjusted removal rate for total zinc was typically in the range 2 to 6 g/m^3/day. The reactor thus appears to be load-limited, as were the Nenthead systems, with the removal rate a function of the influent zinc load. This is highlighted by the higher volume-adjusted removal rates calculated for the Cwm Rheidol system than for the Nenthead pilot-scale reactor, since both influent flow-rate and influent zinc concentrations were higher at Cwm Rheidol. The volume-adjusted removal rate for dissolved zinc showed a similar pattern to that for total zinc, varying between 0.8 and 14.6 g/m^3/day, and was closely related to influent flow-rate. Ignoring the early data, when influent flow-rate was particularly high, the volume-adjusted removal rate for dissolved zinc was typically in the range 3 to 7 g/m^3/day. Based on the mean influent zinc load, the maximum possible volume-adjusted removal rates are 7.2 g/m^3/day (total zinc) and 7.1 g/m^3/day (dissolved zinc), compared to the mean actual removal rates of 4.5 g/m^3/day (total zinc) and 5.3 g/m^3/day (dissolved zinc).

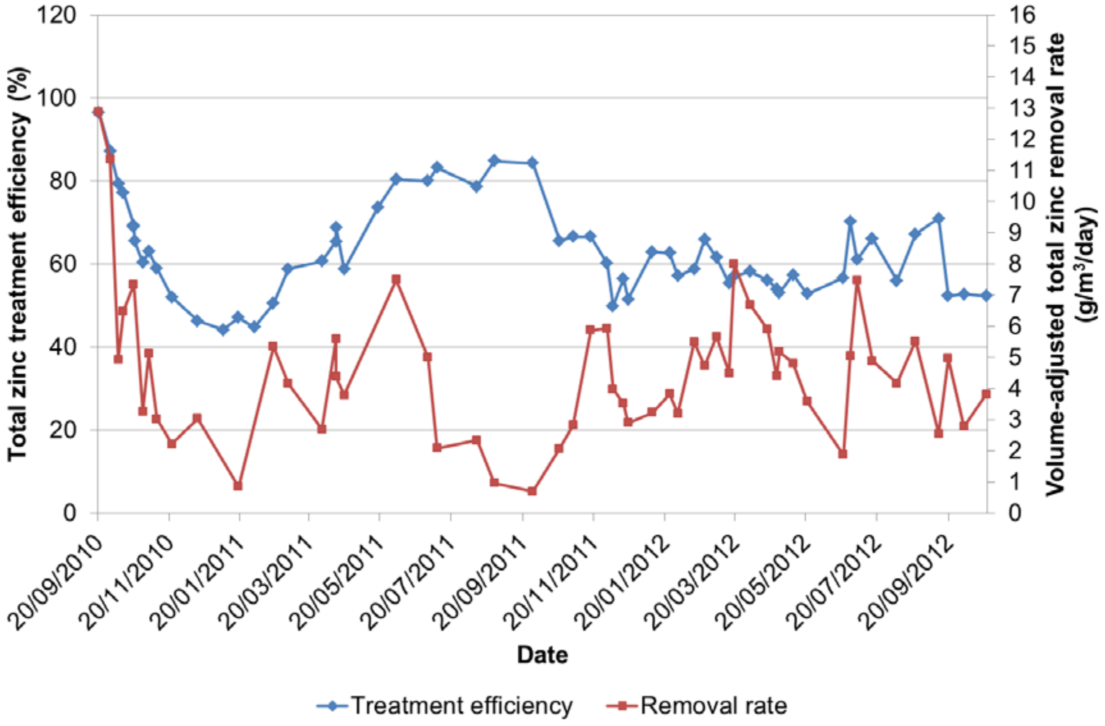

Figure 38. Treatment efficiency and removal rate of total zinc in the Cwm Rheidol pilot-scale reactor

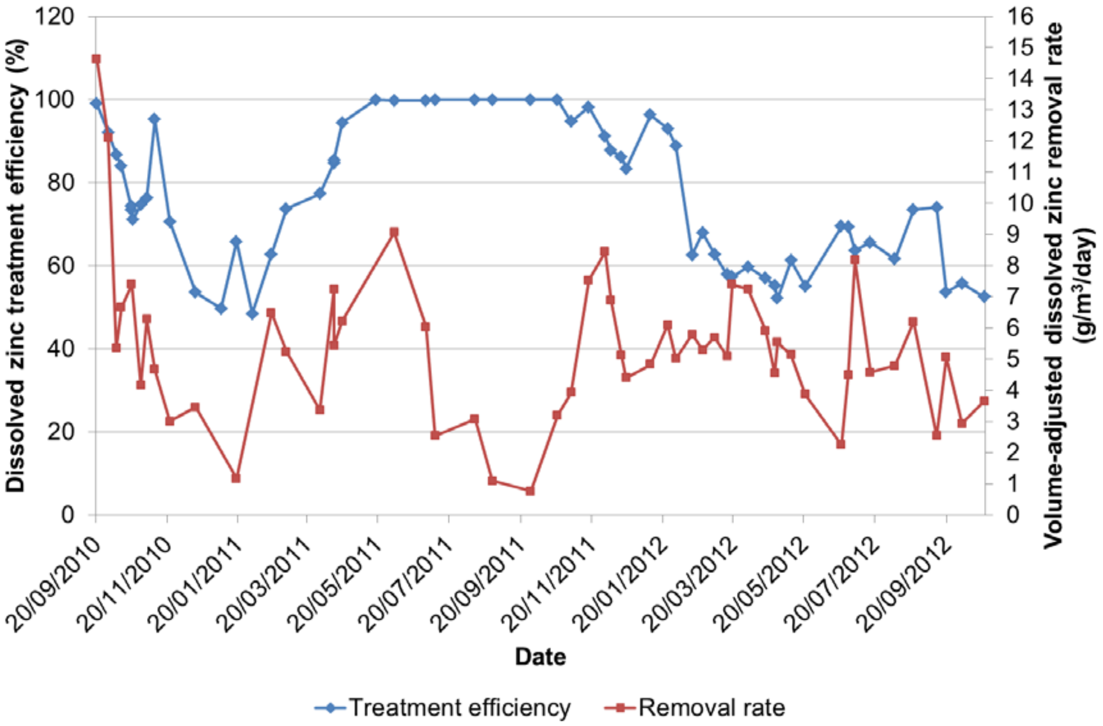

Figure 39. Treatment efficiency and removal rate of dissolved zinc in the Cwm Rheidol pilot-scale reactor

Other metals, in particular lead, showed even higher treatment efficiencies with, on average, 98% of the total lead and 99% of the dissolved lead removed within the system. In terms of removal rates, the mean area-adjusted removal rate for lead was 0.3 g/m^2/day (both total and dissolved) while the mean volume-adjusted removal rate for lead was 0.4 g/m^3/day (total and dissolved). Despite little variation in treatment efficiency, the volume-adjusted removal rate for lead, like that for zinc, was closely related to influent flow-rate and, as such, varied throughout the trial, ranging from 0.04 g/m^3/day to around 1.0 g/m^3/day.

pH and alkalinity generation

The pH of the influent mine water and the effluent water from the pilot-scale reactor, together with the total alkalinity of the effluent water, are shown in Figure 40. The total alkalinity of the influent water is not shown since, for the most part, influent pH was lower than 4.5 and thus there was no alkalinity present. A clear pH increase occurred within the reactor for the duration of the trial. The influent pH varied from around 3.4 to 4.7 while the effluent pH varied from 6.3 to 7.9. Similarly, alkalinity generation took place throughout the course of the trial. Despite gaps in the data, which represent occasions when alkalinity of the effluent water was not measured, over 50 mg/L as $CaCO_3$ alkalinity was typically produced. Given the substantial increase in calcium concentration (up to 60 mg/L) between the influent and effluent waters, shown in Figure 41, it is apparent that a large proportion of this alkalinity generation can be attributed to dissolution of shells within the substrate and limestone clasts on the base of the reactor. There is an indication, towards the end of the trial, that the amount of alkalinity generation, together with effluent calcium concentrations, reduced, but this coincided with the increase in effluent flow-rate discussed above and, as such, probably reflects a shorter hydraulic residence time within the system. It is impossible to conclude from these results whether any of the observed alkalinity generation could be attributed to bacterial sulphate reduction.

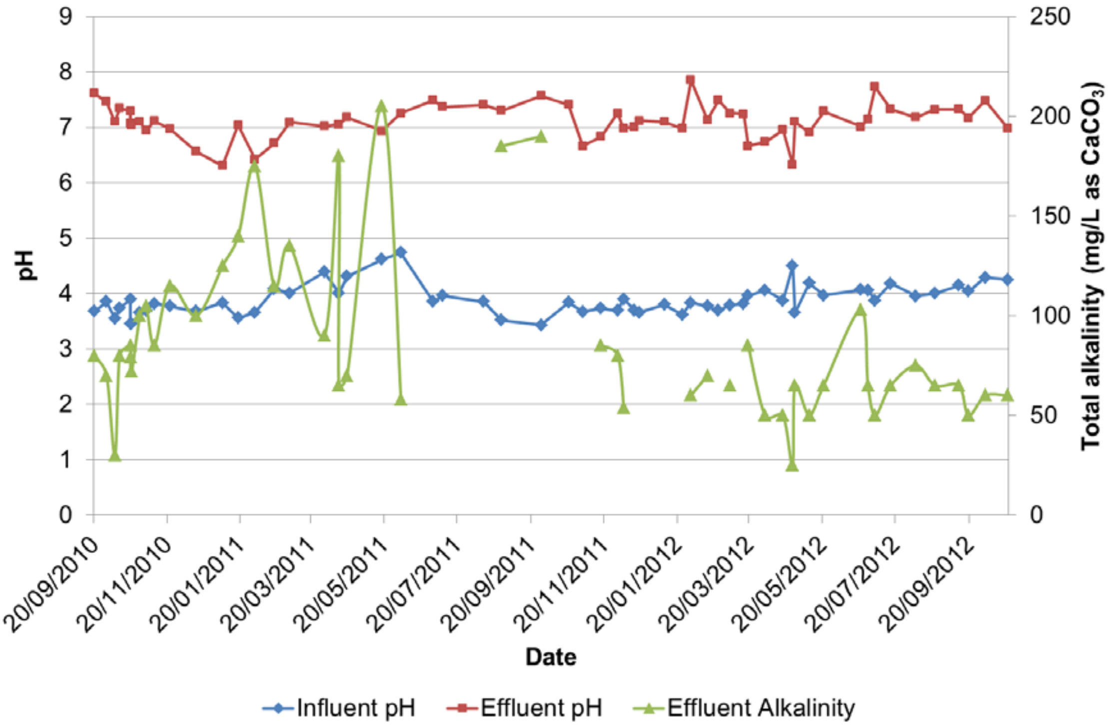

Figure 40. Influent and effluent pH and total alkalinity in the Cwm Rheidol pilot-scale reactor

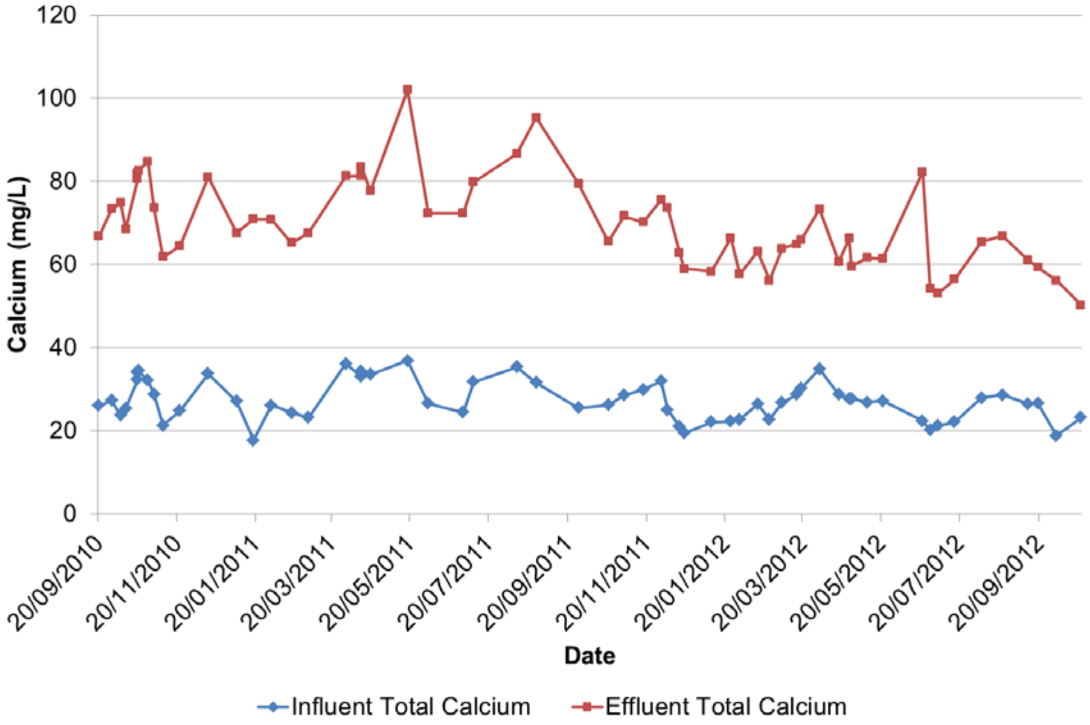

Figure 41. Influent and effluent calcium concentrations in the Cwm Rheidol pilot-scale reactor

4.1.2 Factors influencing performance

Redox potential

Because of unreliable data for Eh in the influent mine water and effluent water from the pilot-scale reactor, it has not been possible to assess the influence of redox conditions on system performance.

Sulphate

Sulphate concentrations in the influent and effluent waters to the pilot-scale reactor are shown in Figure 42. At the beginning of the trial, both influent and effluent sulphate concentrations were comparable but there are indications that, towards the end of the trial, sulphate attenuation was taking place within the reactor. However, limited data are available for sulphate concentration during the final 9 months of the trial making it difficult to draw any firm conclusions.

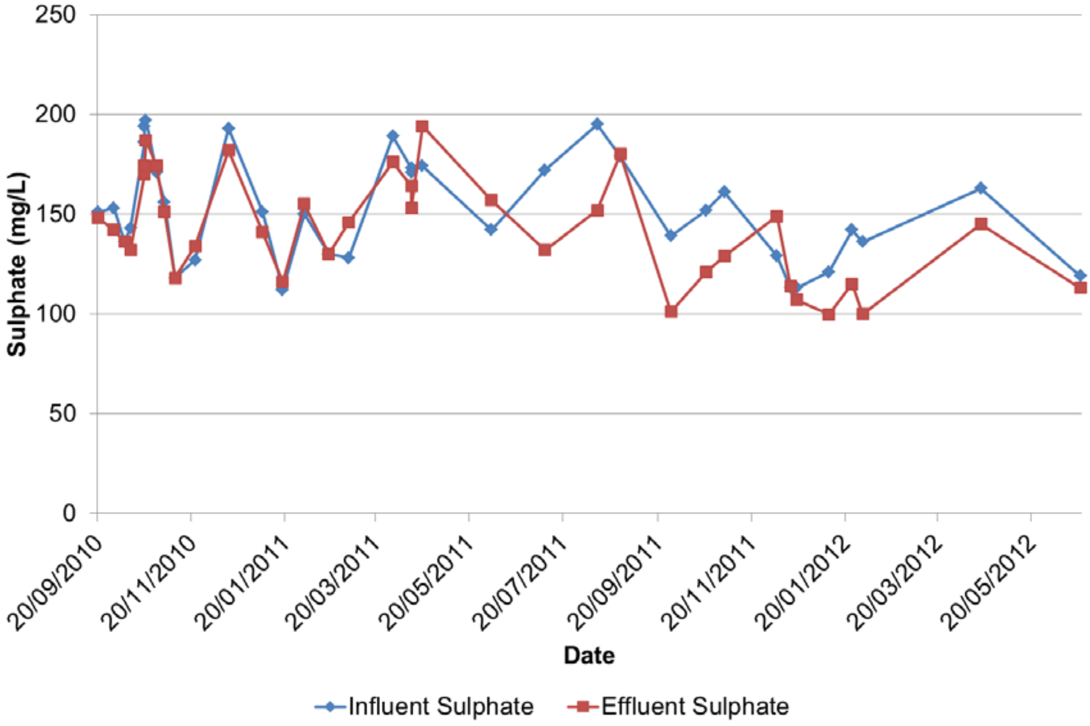

Figure 42. Influent and effluent sulphate concentrations in the Cwm Rheidol pilot-scale reactor

Substrate analyses

Samples of reactive substrate were collected from the reactor after 21 months of operation. They were air-dried and then subjected to Aqua Regia digestion to determine their metal content. The samples were collected from the upper surface of the substrate at six locations, which were spread across the reactor in order to assess any spatial variation. At two of these locations triplicate samples were collected. The locations are indicated in Figure 43, and the results for metals analysis of substrate from each of these locations are shown in Table 5.

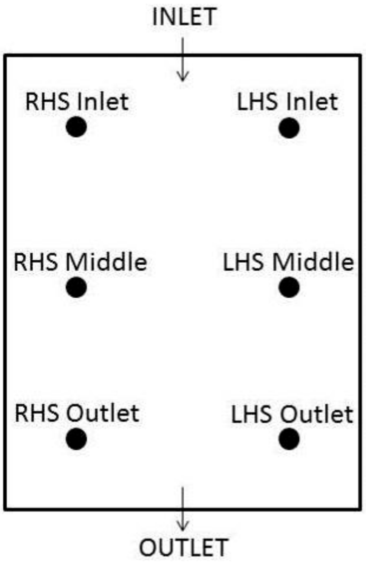

Figure 43. Locations from which substrate samples were collected from the surface of the Cwm Rheidol compost bioreactor

The substrate analyses indicate very high concentrations of zinc throughout the upper layer of compost within the system (2.1–3.8% by weight), as well as elevated concentrations of lead, cadmium, copper and iron. Clearly this is consistent with the attenuation of these metals within the treatment system. Overall the highest concentrations of metals are on the right hand side of the tank towards the inlet, immediately adjacent to the inlet to the tank. There is variability between specific metals, however, and there is no clear pattern to the distribution. It is notable that where triplicate samples have been taken the concentrations of metals across triplicates are very similar (< 3.5% difference), suggesting that the values given in Table 5 are both accurate and representative. Some of the zinc concentrations in Table 5 are more than three times higher than the highest recorded concentrations in the substrate of the Nenthead treatment tank (and almost all of them are at least double) (see Section 3.6). These high values suggest that these compost substrates have a very high capacity for retention of metals.

Table 5. Analysis of metal content in the Cwm Rheidol pilot-scale reactor substrate

Sample	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Mn (mg/kg)	Fe (mg/kg)
RHS Inlet 1	35,647	6,809	67.5	575	280	5,154	17,784
RHS Inlet 2	36,331	6,969	68.4	588	282	5,314	18,248
RHS Inlet 3	36,843	7,013	67.8	593	280	5,289	18,203
LHS Inlet	25,790	1,779	76.0	183	305	3,180	15,286
RHS Middle	21,265	1,937	92.1	181	228	2,198	14,672
LHS Middle	38,327	4,393	68.5	396	359	4,078	15,771
RHS Outlet 1	25,643	2,692	61.1	258	264	3,517	21,622
RHS Outlet 2	26,159	2,715	61.2	258	264	3,617	22,082
RHS Outlet 3	25,917	2,687	59.9	253	259	3,536	21,673
LHS Outlet	28,441	2,339	86.5	231	305	2,742	16,104

There are also correlations between zinc concentration in the substrate and other metal concentrations in the substrate (Figure 44). Specifically, lead, copper and manganese all show positive correlations with zinc, illustrating that the loci of zinc accumulation are also the zones of accumulation of these other metals.

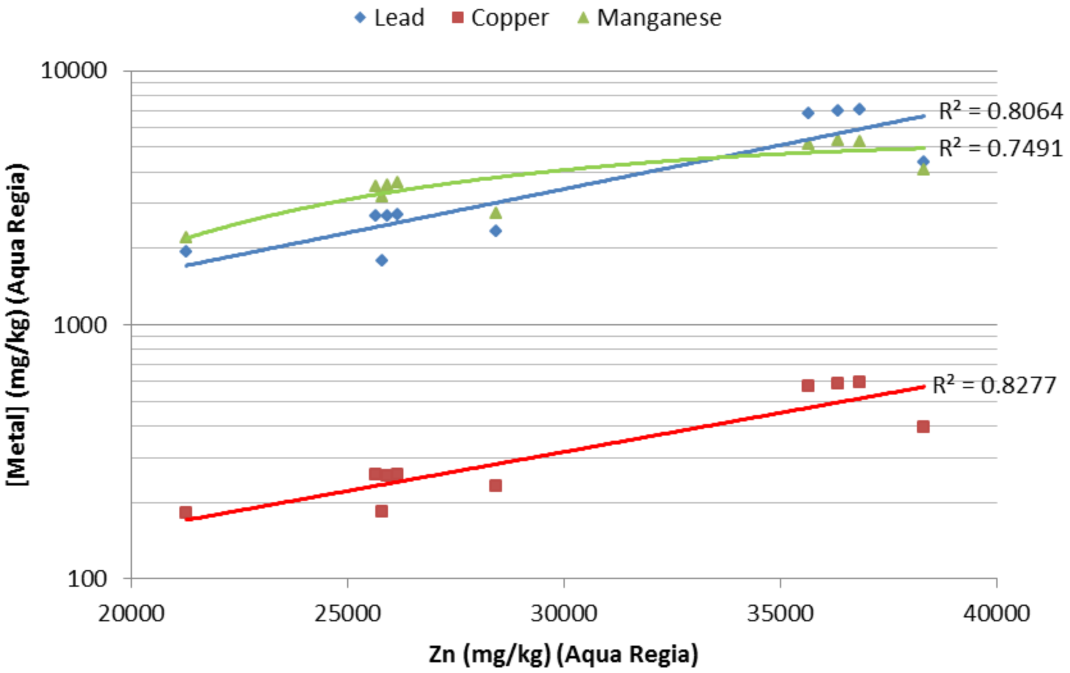

Figure 44. Relationship of zinc concentration in Cwm Rheidol substrate (via Aqua Regia analysis) to concentrations of manganese, copper and lead

Hydraulic conditions

Tracer tests, using a sodium fluorescein tracer, were carried out on the pilot-scale reactor after 7 months, 15 months, 19 months and 21 months of operation to determine any changes in hydraulic residence time from the design residence time of 14 hours. The results are shown in Figure 45. It is clear that during the initial 15 months of operation the hydraulic residence time, approximated by the time to reach peak sodium fluorescein concentration, was substantially greater than 14 hours, being of the order of several days. This was due to the influent flow-rate to the reactor having been reduced to around 2 L/min from the design flow-rate of 6 L/min during this period. By 19 months, the influent flow-rate had been increased to 4.5 L/min and the hydraulic residence time was 14 hours, the same as the design residence time. By 21 months, however, the peak fluorescein concentration occurred after only around 4 hours. It is difficult to reach any firm conclusions about variability of hydraulic conditions in the reactor when both influent and effluent flow-rates varied throughout the trial. The long residence time calculated during the early stages of operation can be explained by a low influent flow-rate and, although this was rectified by the time of the later tracer tests, the effluent flow-rate during the final 9 months appeared to increase and at times was significantly higher than the influent flow-rate. It is not known why this occurred but it indicates significant changes in the hydraulic conditions of the system, possibly due to the development of preferential flow paths (which in turn may have partly been related to ‘blinding’ by iron hydroxide solids on the surface of the compost substrate), and is probably the reason for the low hydraulic residence time calculated in the final tracer test. Nevertheless, when influent flow-rate was close to the design rate, the hydraulic residence time was calculated to be that targeted at the beginning of the trial.

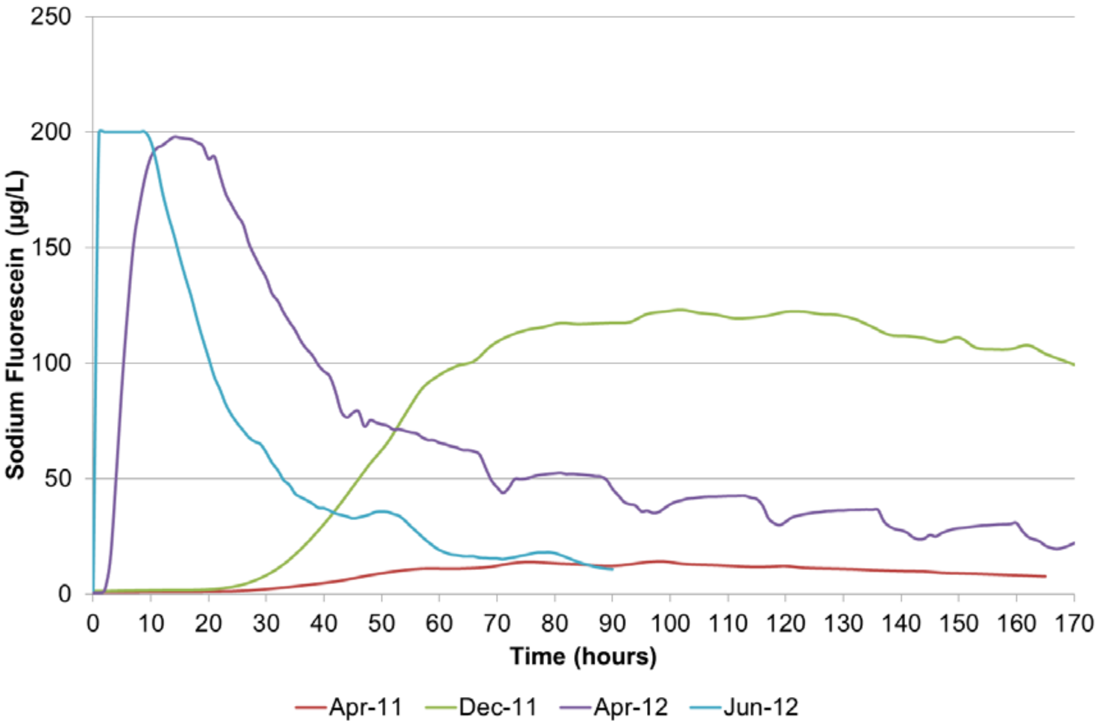

Figure 45. Cwm Rheidol pilot-scale reactor tracer test results for April 2011, December 2011, April 2012 and June 2012

Environmental conditions

The effect of temperature on the performance of the pilot-scale reactor at Cwm Rheidol is clearly apparent from Figure 46, which shows the variation in total zinc treatment efficiency and the temperature of the effluent water over the course of the trial. Despite limited temperature data at times, the seasonal pattern in effluent temperature is obvious. The total zinc concentration in the influent mine water is also shown for comparative purposes but this remained relatively constant and any variation in effluent zinc concentration could therefore not be attributed to changes in the influent concentration.

As discussed above, until the final 9 months of the trial a seasonal pattern in treatment efficiency could be identified and this can be seen to correlate well with effluent water temperature (Figure 46). As the temperature of the water dropped from 12°C to 3.7°C in the early stages of operation, the total zinc treatment efficiency similarly decreased from 96% to 44%. A subsequent increase in temperature during the summer of 2011, to as high as 16°C, was matched by a corresponding increase in treatment efficiency, to reach a peak of around 85%. Although both effluent water temperature and treatment efficiency subsequently dropped over the following winter, the relationship appeared to break down, with treatment efficiency remaining relatively constant during the spring and summer of 2012 despite an increase in effluent temperature. This coincided with changes in the hydraulics of the system, seen by an increase in the effluent flow-rate, which, as noted above, would have an impact on treatment efficiency.

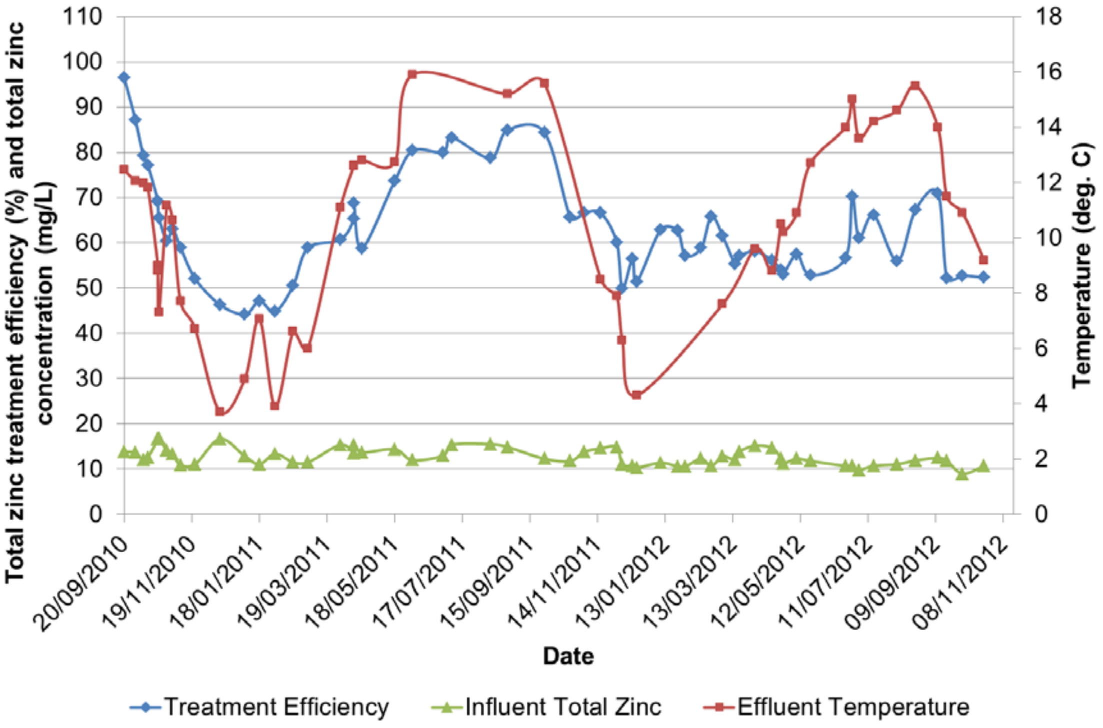

Figure 46. Treatment efficiency and effluent temperature in the Cwm Rheidol pilot-scale reactor

Further confirmation of the relationship between effluent water temperature and the total zinc concentration in the effluent water is shown in Figure 47. Note that the data presented here cover the whole period of the trial, including the latter stages when the relationship between effluent water temperature and treatment efficiency was less obvious (Figure 46). A marked decrease in effluent zinc concentration with increasing temperature can be seen, indicating that temperature plays an important role in the removal of metals within such systems (directly or indirectly). As discussed above, for a similar relationship seen in the Nenthead pilot-scale reactor, it is unclear why temperature plays such an important role but it may be linked to the maintenance of reducing conditions which are essential for the development and sustainability of sulphate reducing bacteria populations. Due to unreliable data, it has not been possible to compare Eh of the effluent water at Cwm Rheidol with temperature.

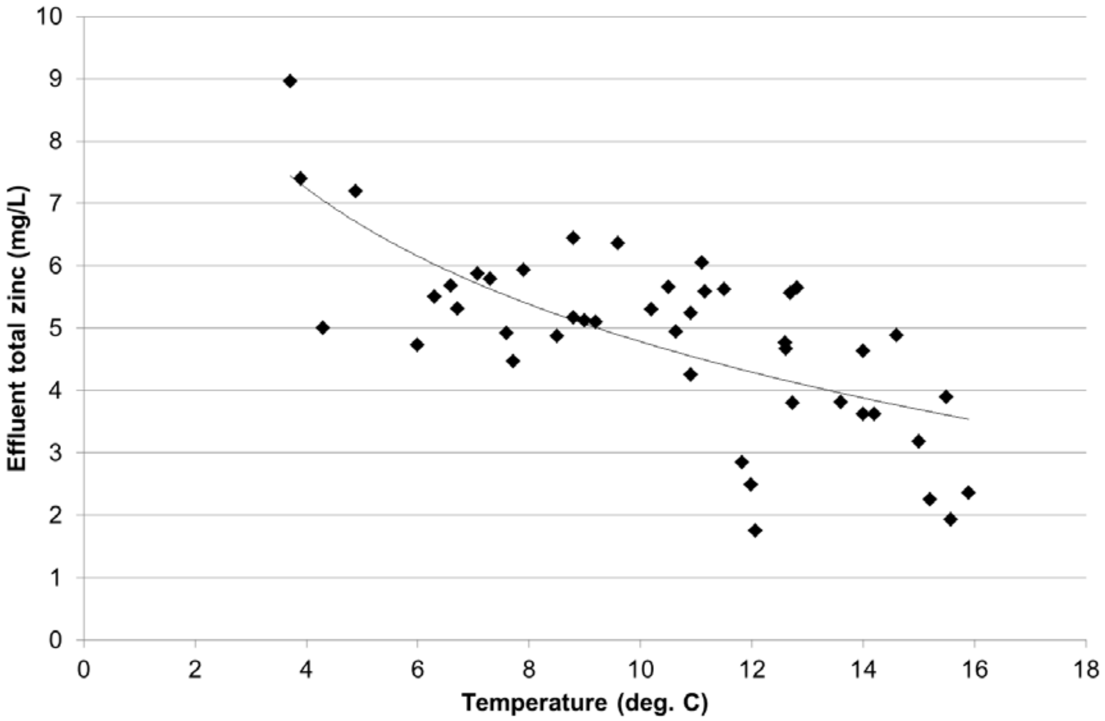

Figure 47. Relationship between effluent temperature and total zinc concentration in the Cwm Rheidol pilot-scale reactor

4.2 Comparison of Nenthead and Cwm Rheidol pilot-scale reactor performance

4.2.1 Comparisons in system performance

The pilot-scale reactors at Nenthead and Cwm Rheidol showed similar treatment efficiency with, on average, 68% of the total zinc and 84% of the dissolved zinc removed in the Nenthead reactor compared to 63% of the total zinc and 76% of the dissolved zinc at Cwm Rheidol. In both systems, treatment efficiency fluctuated widely, with Cwm Rheidol, in particular, showing an apparent seasonal pattern. Although the mean treatment efficiencies were slightly lower for Cwm Rheidol than for Nenthead, the dissolved zinc concentration decreased to less than 0.005 mg/L at Cwm Rheidol during the period when effluent temperatures were at their highest, despite higher influent concentrations than at Nenthead. This represents almost 100% removal of dissolved zinc within the system at that time.

In terms of volume-adjusted removal rates, those for Cwm Rheidol were substantially greater than the rates calculated for the Nenthead system, principally due to the higher influent zinc load at Cwm Rheidol, which provides further evidence that the systems are load-limited. To clarify, the Cwm Rheidol mine water has a mean zinc concentration of 12.8 mg/L while the Rampgill discharge at Nenthead has a mean zinc concentration of 2.32 mg/L. Furthermore, the influent flow-rate at Cwm Rheidol was approximately 4.5 L/min compared to 1.1 L/min for the pilot-scale reactor at Nenthead. These higher influent zinc loads resulted in a mean volume-adjusted removal rate for total zinc at Cwm Rheidol of 4.5 g/m^3/day, compared to 0.9 g/m^3/day at Nenthead, while for dissolved zinc the mean volume-adjusted removal rates were 5.3 g/m^3/day at Cwm Rheidol and 1.0 g/m^3/day at Nenthead. In both systems, variations in volume-adjusted removal rate appeared to be primarily influenced by influent flow-rate.

With regards to other parameters, the pH increased significantly within the Cwm Rheidol reactor, as did total alkalinity, as a result of dissolution of shells and limestone which made up a greater proportion of the substrate than at Nenthead. The pH in the influent mine water at Nenthead is already circum-neutral and hence there was no requirement for alkalinity generation within the reactor. Despite this, some alkalinity generation took place prior to the onset of carbon additions and some of this may have resulted from bacterial sulphate reduction. It is not possible to conclude whether additional alkalinity generation took place at Cwm Rheidol, above that attributed to dissolution of calcium carbonate.

In terms of sulphate concentrations, there is evidence that sulphate attenuation was taking place within the Nenthead reactor, which could be attributed to bacterial sulphate reduction, but insufficient data for the Cwm Rheidol system prevents any firm conclusions being drawn.

4.2.2 Influence of hydraulic conditions

While the pilot-scale reactor at Nenthead was configured to have a hydraulic residence time of 19 hours, the reactor at Cwm Rheidol was designed to have a residence time of 14 hours. Tracer tests, using sodium fluorescein, were undertaken on both reactors to investigate changes in hydraulic conditions during operation but variations in influent flow-rate between tracer tests at Cwm Rheidol have made it difficult to compare results. In the early tracer tests, when influent flow-rate was low, the hydraulic residence time was of the order of days but, towards the end of the trial, the effluent flow-rate increased which resulted in a shorter than expected hydraulic residence time. The increase in effluent flow-rate, however, indicates that a change in hydraulic conditions had taken place within the reactor.

At Nenthead, on the other hand, influent flow-rate remained the same when each tracer test was undertaken, allowing comparisons to be made. A significant reduction in hydraulic residence time was observed during the first 7 months of the trial, possibly indicating development of preferential flow paths, but towards the end of the trial the residence time appeared to increase.

What is clear is that the maintenance of a constant flow-rate is critical to maintaining a consistent residence time within the reactors, and that having a residence time that is too short (due to higher than design flow-rates) may result in poor performance (as appears to have happened at the Cwm Rheidol system). Even where residence flow-rates are maintained at a constant rate, however, variations in residence time appear to be possible (as was observed at Nenthead), suggesting that flow-routing through these systems does change with time, and not necessarily in a predictable fashion. This would perhaps suggest that conservative design of larger scale systems would be prudent, to accommodate periods of lower than expected residence times.

4.2.3 Influence of environmental conditions

There is evidence in both pilot-scale reactors, at Cwm Rheidol and Nenthead, that temperature plays an important role in system performance. In particular, in the Cwm Rheidol reactor, there was a clear seasonal pattern in treatment efficiency, with increased treatment efficiency during periods of higher effluent water temperature, and vice versa. The addition of carbon to the Nenthead reactor resulted in an increase in effluent zinc concentrations and it has thus not been possible to study the impact of temperature on performance of the system since then. Nevertheless, prior to carbon addition, there was a clear relationship between treatment efficiency and effluent water temperature. Similarly, both systems have shown a decrease in effluent zinc concentration with increasing temperature. It is unclear why temperature has such a pronounced impact on system performance but it may be linked to the maintenance of reducing conditions which are essential for the development and sustainability of sulphate reducing bacteria, and/or it may be that the activity of the sulphate reducing bacteria is directly limited by low temperatures.

This is clearly an issue for scaling such systems up to full-scale, and in particular for how they would perform (cf. any targets for downstream water quality) during the colder months of the year. However, neither is it clear whether a much larger scale system may have the capacity to maintain more constant temperatures within the substrate itself, which would limit the impact of low temperature.

5 Results and discussion: system longevity and renovation

5.1 Introduction

The discussion thus far has demonstrated that both the Nenthead and Cwm Rheidol pilot-scale compost bioreactors have worked effectively over the 2 years for which they have operated. These passive treatment units are often advocated on the basis of their low operational costs, but to truly appreciate what the costs of these systems are it is necessary to consider the entire life cycle of such a system. At some point a full-scale compost bioreactor for metal mine drainage remediation would need renovation, and this raises two key questions:

- How long will the system operate before such renovation is required?
- What would be the cost of such renovation?

This section of the report considers these difficult questions, specifically by considering the following:

- Insights on system lifetime from the pilot-scale units.
- Waste classification of the substrate from the Nenthead system for the purposes of disposal to landfill.
- Possibilities for recovery of metals from the substrates.

Each of these issues is discussed in this section. For the final one of these issues a suite of experiments have been conducted to investigate the principles of metal recovery from such substrates, and the results are discussed below.

5.2 System lifetime

In theory there may be a number of factors that may individually, or in combination, determine the absolute lifetime of a passive bioreactor, including:

- physical compaction of the substrate resulting in plugging;
- plugging of the system due to accumulation of metal precipitates and other solid debris introduced to the system;
- exhaustion of available carbon for sulphate reducing bacteria;
- toxic / inhibitory effects of metals and/or sulphides on the sulphate reducing bacteria.

With respect to the first two of these, porosity of the substrate in the Nenthead treatment system was measured both at the outset of the trial and also during decommissioning 2 years later. The bulk porosity (i.e. including limestone at the base of the tank as well as compost over it) of the treatment substrate at the commencement of operation of the system was measured as 62%. Upon decommissioning porosity tests on the compost substrate were repeated on samples of both the upper and lower layers of compost. These tests revealed porosity of the upper and lower layers to be 40% and 32% respectively. These figures suggest that there was a substantial reduction in porosity over the 2 years of the trial, and therefore that compaction and clogging may compromise system lifetime. However, it is not possible to conclude whether this reduction in porosity is an ongoing trend, or whether in fact porosity reduction occurred rather rapidly over the first months of operation but has since been rather limited. Any trend of decreasing porosity would be anticipated to be mirrored by decreasing residence time of water in the reactor, but this is not observed from the results of tracer tests at Nenthead (Figure 33), which actually show the residence time to be rather similar at the end of the trial to what it was initially. No equivalent porosity data are available for the Cwm Rheidol system unfortunately, but there is no question that the presence of elevated iron concentrations, which result in precipitation of iron within the system, will impact on the porosity of the substrate more significantly than for water without high iron content. For the design of any full-scale systems which will receive ferruginous water, careful consideration will need to be given to how to limit plugging due to iron precipitates.

There was no evidence of carbon exhaustion in the Nenthead or Cwm Rheidol reactors. Although the impact of the carbon additions made to the Nenthead system were ambiguous over the short-term, inspection of system performance since continuous, low feed-rate additions have been made suggest that the performance has been both improved and more consistent since that time. It is not possible to conclude whether this is coincidence or a result of the carbon additions, but earlier laboratory tests certainly show that carbon additions improve performance (Figure 1). Therefore although the results from the pilot-scale reactor are not conclusive, there would appear to be scope for ensuring that carbon exhaustion should not be a limitation to system lifetime.

With respect to toxicity effects, a variety of studies have been conducted to assess what specific concentrations of metals prove toxic to sulphate reducing bacteria, and the results of some of these investigations are summarised by Neculita et al. (2007). There is difficulty in determining a specific concentration at which any individual metal is toxic to the sulphate reducers, due to a variety of factors such as the understanding of the exact degree to which the bacteria are exposed to the metal, and the potential influence of other metals present. Typically a figure of 15–20 mg/L is identified as the concentration above which zinc becomes toxic to sulphate reducing bacteria, which is above that of the influent water of both the Nenthead and Cwm Rheidol systems (and it is worth noting that this is above the concentration of zinc found in the majority of the UK's abandoned metal mine water discharges). However, analyses of the substrates from the two systems reveal substrate zinc concentrations of up to 38,000 mg/kg (Table 5). Data from the Nenthead system also show that there are highly elevated sulphide concentrations (Section 3.6). In neither case though is there any evidence of deteriorations in system performance that cannot be ascribed to other factors (e.g. residence time being too short in the Cwm Rheidol system in the later months of operation).

Although there is no direct evidence that any of these factors were compromising the performance of the pilot-scale reactors at Nenthead, or even Cwm Rheidol, it is not possible to conclude with certainty that such issues would not become significant over longer periods of operation. Extrapolating in some way from the results of the Nenthead and Cwm Rheidol systems to estimate system lifetime is not possible, since it is simply not known whether there may be some critical 'tipping point' beyond which the systems will cease to function effectively (e.g. if there is a particular substrate zinc concentration above which the metal will become toxic to sulphate reducing bacteria). Therefore, the best way forwards is to minimise the possibilities of system lifetime being shortened by:

- Reducing the potential for system plugging by (a) keeping the substrate depth as shallow as possible, (b) maximising the initial substrate porosity as far as possible without restricting the potential for development of anoxic conditions and (c) removing iron prior to introduction of mine water to the compost substrate, or having an effective maintenance strategy for removing iron precipitates from the substrate surface.

- Ensuring that the initial substrate composition is rich in available carbon, and planning for the need to introduce additional carbon at some point in the future (e.g. by identifying suppliers of such carbon-rich additives and trialling these in laboratory tests ahead of the point at which they may need to be deployed in any full-scale system).
- Keeping the metal loading rate to the substrate as low as practically feasible (bearing in mind that volumetric removal rate tends to decrease with influent metal loading), for which there will need to be a trade-off between metal loading rate and absolute system size (i.e. the lower the loading rate the larger the system size).

5.3 Waste classification of Nenthead substrate

Eventually it would be anticipated that a compost bioreactor would cease working effectively due to some combination of the factors discussed in Section 5.2, above. At such a point it would probably be necessary to dispose of the compost substrate, or treat it in some way such that it could be reused. To begin to establish the full life-cycle costs of such systems, the substrate from the Nenthead pilot-scale system was subjected to waste classification to determine what type of landfill could receive the material (e.g. inert, non-hazardous, hazardous). This is because the cost of disposal per unit volume/mass varies depending on the classification of the waste. WRAP (2012) reports that the median UK gate fee cost for non-hazardous waste is currently £21/tonne, while the median cost of disposal of hazardous waste (not containing asbestos) is £29/tonne. Both of these figures exclude landfill tax and haulage. For illustration, the median cost of non-hazardous waste disposal including landfill tax was reported as £85/tonne (WRAP 2012), and therefore the landfill tax is a substantial proportion of the overall cost of disposal.

Three sub-samples of substrate from the Nenthead treatment system were subjected to waste classification hazard assessment and testing for a Waste Acceptance Criteria (WAC) suite of analysis. The analysis was contracted to Environmental Scientifics Group (ESG), which also provided an outline interpretation of the results with respect to disposal options.

A hazard assessment of the chemical data relating to the substrate was undertaken by ESG using the CATWASTE^{SOIL} model, the outputs from which showed that all three samples would be classified as hazardous on the basis of the zinc content, which would be considered ecotoxic (the Zn concentrations reported by ESG were 7,564 mg/kg, 8,300 mg/kg and 10,630 mg/kg, which are comparable to the 9,000 mg/kg determined by Newcastle University analysis).

Subsequent to this WAC testing was undertaken. Due to the high total organic carbon (TOC) content it was not possible to conduct a full two-stage WAC test, and therefore only a one-stage test was undertaken. ESG concluded that concentrations of most substances tested in the WAC were low and therefore the material did not exceed threshold concentrations for hazardous waste, but that high TOC content (> 27%) and high values for loss on ignition (LOI) (46.0–48.2%) meant that some form of pre-treatment would be required prior to disposal '…to either reduce the organic matter content of the material or its hazardous properties i.e. content of zinc'.

ESG therefore concluded that the material could be suitable for disposal to hazardous landfill subject to a reduction in organic content such that the material complied with

WAC thresholds for TOC and LOI. Alternatively, if the zinc content could be reduced then it might be feasible to reclassify the material as non-hazardous subject to further testing. It has not been possible to establish what ‘threshold’ concentration of zinc (or zinc compound) in the waste renders it ecotoxic, or indeed whether this is an absolute value or variable depending on results of leaching tests or equivalent. In principle it should be possible to lower the zinc concentration of the waste (by some form of recovery), or prevent the concentration being exceeded by limiting the operational lifetime of the treatment system. It is therefore strongly recommended that the precise limit values for zinc are established, in order to then determine the most effective way of managing wastes from such treatment systems.

5.4 Metal recovery tests

The findings of the waste classification testing suggest that reduction of the concentration of zinc in the used substrate would yield the most beneficial results in terms of costs of final disposal (reduction of organic content would need to be undertaken in any case for the material to be disposed of to a hazardous landfill). For this reason a suite of proof-of-principle experiments has been undertaken with the substrate from the pilot-scale tank to establish whether it is possible to recover the metals (specifically zinc in this case) from the substrate. These experiments were based upon the same principles used in ‘heap leach’ approaches for metal recovery in mining operations, in which a lixiviant is trickled through metal ore to recover metals into the lixiviant, which then forms a ‘pregnant’ solution of the recovered metal for subsequent processing.

In this case, the lixiviants used were hydrochloric acid and ammonium sulphate solution. Although the acid lixiviant was always anticipated to be the more effective, an alkali lixiviant is sometimes used in actual heap leach operations, and was therefore used here for comparison. In addition distilled water was used with metal-rich substrate to act as a lixiviant control, and unused substrate was used with the HCl lixiviant as a substrate control. The experiments comprised the following phases:

1. Establishment of the ratio of solid (substrate) to liquid (lixiviant) required to ensure constant pH during subsequent tests. This was done for the hydrochloric acid lixiviant only, since it was assumed that the substrate may have neutralising potential, but not acidity generating potential.

2. ‘Slurry’ tests, which were essentially jar tests to establish the mass of zinc that could be recovered, and the time taken for recovery of zinc, during mixing of substrate with lixiviant.

3. Continuous recycle tests, which comprised recirculating as small a volume of possible of one lixiviant (HCl) through a sample of substrate (conducted in duplicate).

4. A repeat of the continuous recycle tests, but introducing the HCl lixiviant as an aerosol rather than a drip-feed.

Only the results of steps 2 to 4 of these experiments are reported here, since step 1 was essentially a necessary preliminary step to inform step 2.

Prior to commencement of the tests triplicate Aqua Regia digestion analyses of the used substrate were performed to establish the concentration of zinc associated with the substrate. These results showed that the substrate had an approximate mean concentration of 5,500 mg/kg zinc during steps 2 and 3, and this figure is used for assessment of the success of the metal recovery tests. The success of step 4 of the experiments is discussed separately.

5.4.1 Slurry test results

The key results for step 2 of the metal recovery tests are illustrated in Figure 48, which shows triplicate results for zinc recovery for each of the hydrochloric acid and ammonium sulphate lixiviants.

During the test using HCl maximum pH reached was 2.48, and minimum was 1.53. pH generally increased over the duration of the test. For the ammonium sulphate lixiviant, maximum pH reached was 9.98, and minimum was 9.78, with no obvious pattern over the duration of the tests (supporting the assumption that the substrate had no acidity generating potential).

Figure 48 indicates that the HCl lixiviant rapidly and effectively leached zinc from the substrate. After 4 hours over 70% of the original zinc content (5,500 mg/kg) of the substrate had been recovered, and over 85% had been recovered after 24 hours. The ammonium sulphate lixiviant was less effective; a mean of 35% zinc recovery after 4 hours, a little over 50% after 24 hours, and a mean of 60% after 48 hours. Metal recovery in both the lixiviant control and substrate control experiments was negligible by comparison.

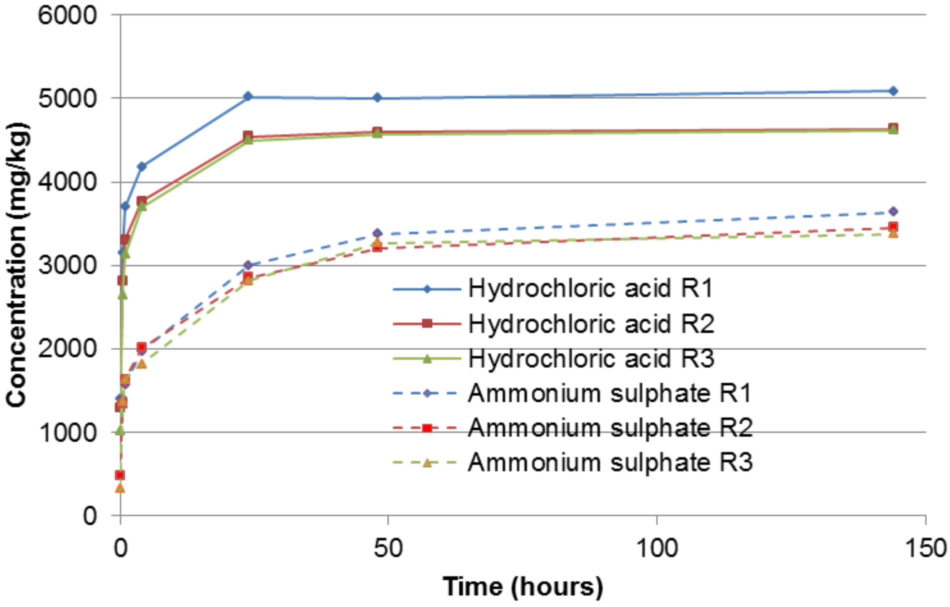

Figure 48. Zinc recovery over time using hydrochloric acid and ammonium sulphate lixiviants in metal recovery slurry tests

These results conform to scientific expectation given that solid zinc phases are at their most soluble at low pH. The speed of recovery of metals is insightful in terms of possible full-scale application.

Interestingly, the comparative effectiveness of the two lixiviants appears to be different depending on the metal. In particular, iron was recovered noticeably more effectively by the HCl lixiviant than the ammonium sulphate lixiviant, as illustrated in Figure 49. Initial iron concentration in the substrate was 12,000 mg/kg (mean from Aqua Regia digestions). While neither lixiviant recovered the same percentage iron as they did zinc, it is still noteworthy that the HCl was able to recover approximately 25% of the iron, while the ammonium sulphate recovered less than 0.5% of the iron. This suggests that there may be a possibility to selectively recover metals using different lixiviants.

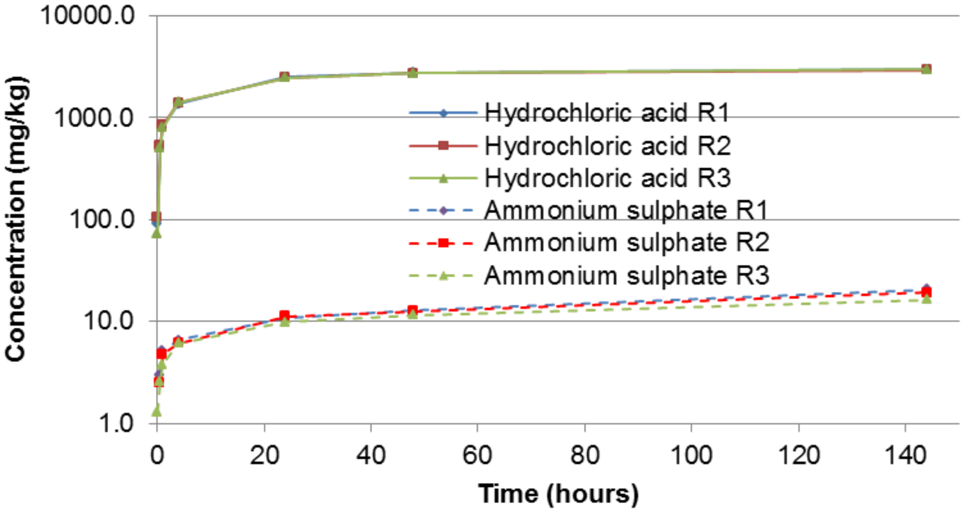

Figure 49. Iron recovery over time using hydrochloric acid and ammonium sulphate lixiviants in metal recovery slurry tests

5.4.2 Continuous recycle tests (drip-feed)

The continuous recycle tests were set up as conceptually illustrated in Figure 50. Two sets of duplicate columns were set up, all containing used substrate from the pilot-scale tank, but one set using concentrated HCl as the lixiviant, and one set using distilled water as the lixiviant. In all cases distilled water was passed through the substrate continuously until such time as the substrate had become saturated (the substrate was dry initially), to prevent the need to add additional acid during the test itself. Analysis of the water used to saturate the substrate showed that it had removed a negligible mass of zinc from the substrate.

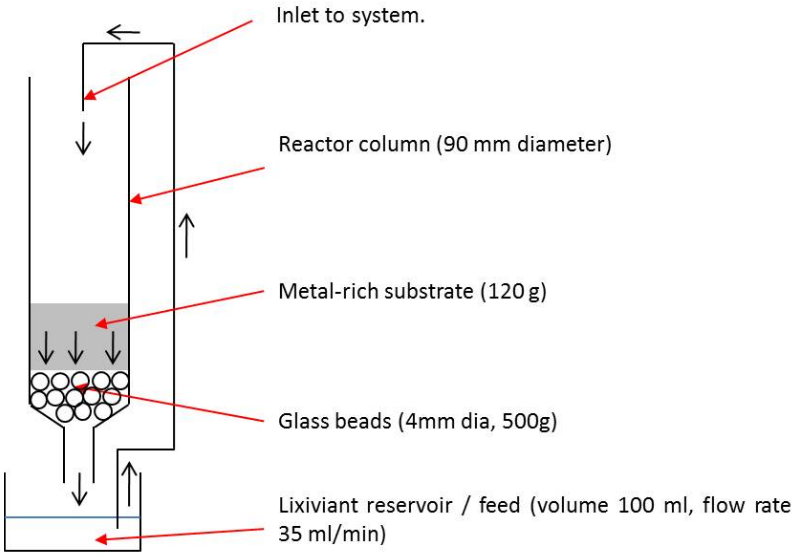

Figure 50. Conceptual illustration of experimental set-up for the continuous recycling metal recovery experiments

During the subsequent tests the distilled water control duplicates recovered negligible zinc, and therefore are not discussed further. The key results from this experiment, for the HCl lixiviant, are shown in Figure 51. The results shown are mean values from the two duplicates, since results from each were very similar.

It can be seen from Figure 51 that the recovery of zinc is rapid, with maximum zinc mass recovered in the lixiviant recorded after just 1 hour. The ~60 mg zinc in the lixiviant at 1 hour equates to 9.3% of the total mass of zinc in the used substrate originally. After this point the mass of zinc in the lixiviant actually decreases, presumably due to attenuation of zinc within the substrate, which in turn may be a function of the gradually increasing pH of the lixiviant itself (Figure 51). The gradual elevation of pH is assumed to be due to some neutralisation capacity in the substrate. After 94 hours 50 mL of additional HCl was added to the acid reservoir, which resulted in a drop in pH and increased mass recovered, though the mass of zinc in the lixiviant did not return to its 1 hour maximum.

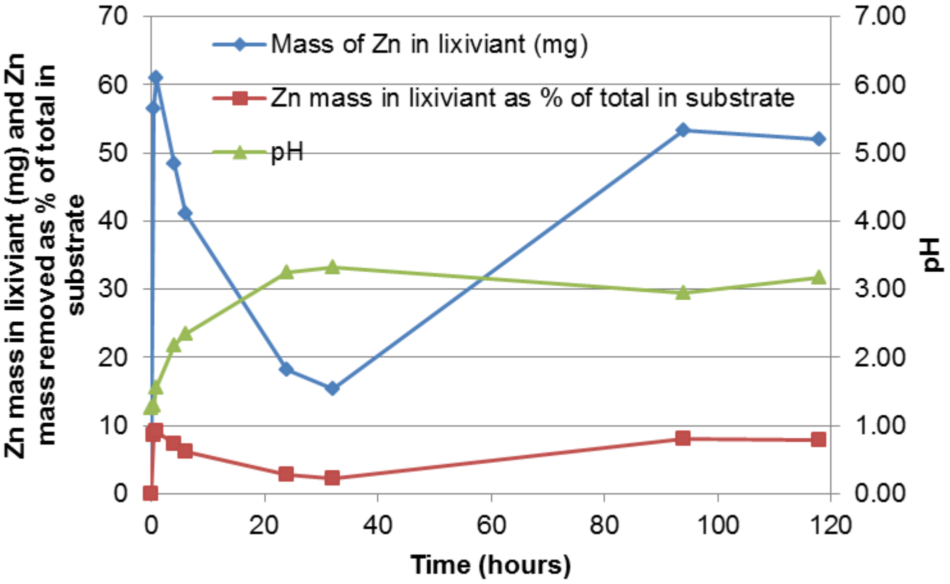

Figure 51. Mass of zinc recovered during continuous recycle recovery experiments, also showing variation of pH during the tests, and the mass of zinc recovered as a percentage of total zinc mass in substrate

Clearly, recovery of a little under 10% of the total zinc mass is far less than was recovered during the initial slurry tests (70% recovery after 4 hours). The reason for this is not thought to relate to a problem with the principles of the process, but is more likely an operational issue with the experimental set-up. Specifically, introduction of the acid to the column was as a drip-feed from a fixed point, and therefore the acid dripped onto the same point on the surface of the substrate throughout the experiment. Although observations showed that the entire width of the substrate in the column had been wetted with acid by the conclusion of the experiments, it is nevertheless likely that the acid followed a preferential flow path vertically through the substrate. Thus, a large proportion of the metal on that particular flow path may have been recovered, but as a percentage of the total mass in the substrate this amount would be relatively small. Further experiments were therefore conducted in which the lixiviant was introduced as an aerosol, in an effort to ensure even distribution of the acid across the substrate surface and therefore reduce potential for short-circuiting.

5.4.3 Continuous recycle tests (aerosol injection)

In a final suite of experiments HCl lixiviant was introduced to four columns (one control containing unused substrate and triplicate columns containing used substrate) as an aerosol rather than a drip-feed in an effort to reduce the possibilities of short-circuiting.

In each case lixiviant was recirculated through the substrate for a total period of 15 hours, broken into stages of 2 hours, 6.5 hours and 6.5 hours. After each stage acid was allowed to drain from the substrate. The acid reservoir was then topped up, and the next stage of recirculation commenced. In total 520–575 mL of acid was used per column (which equates to 21.3–23.6 mL of 0.5 M HCl, since the acid used as lixiviant was diluted 0.5 M HCl). The volume of substrate in each column was 0.82 L, and the weight of substrate in each column was approximately 120 g (dry weight). Triplicate sub-samples of the substrate used in each column were subjected to Aqua Regia digestion prior to the experiments and after the 15 hours of leaching. The results of this experimentation are shown in Table 6.

Table 6. Results of metal recovery tests (Nenthead substrate) introducing acid lixiviant as aerosol (see text for further details; all units in mg/kg except % values)

Column number		Replicate 1	Replicate 2	Replicate 3	Mean Zn removed	
					mg/kg	%
1, 2, 3	Initial [Zn]	6,228	6,858	6,556	-	-
1	Final [Zn]	3,233	3,785	4,148	2,825	43.1%
2	Final [Zn]	4,094	3,869	3,954	2,575	39.3%
3	Final [Zn]	3,592	3,731	3,863	2,818	43.0%

The results presented in Table 6 show that approximately 40% of the zinc has been removed from the substrate, and there is good reproducibility of results between the three identical columns. Given that these were only proof-of-principle tests these are considered positive results. The significance of them is that reducing the zinc content substantially may result in the substrate being classified as non-hazardous, rather than hazardous, waste. Alternatively, it may be possible to reuse the substrate if the reason for it ceasing to be effective in treating mine water was its zinc content. With respect to disposal to landfill, if recovery of metal for the purposes of re-classification of the substrate as non-hazardous waste is the objective, it will be necessary to establish the specific hazardous/non-hazardous threshold zinc concentration for zinc to determine what the target needs to be for metal recovery. This information is not known to the authors of this report, but is presumably a value used in the CATWASTE$^{\mathrm{SOIL}}$ model used in classification. It is strongly recommended that this issue is investigated further, as noted previously.

However, the promising results in terms of metal removal need to be tempered with an appreciation of the proportion of acid to substrate used in these experiments. If the volumes of acid and substrate used in these experiments are any guide, then a larger scale recovery operation would require large volumes of acid. For example, extrapolating directly from the proportions used in these experiments, in the region of 25–30 m^3 of 0.5 M HCl (and around 500–600 m^3 of water) would be required to recover 40% of the zinc from 1,000 m^3 of compost substrate.

It is important to stress that these experiments were only preliminary in nature, and it may well be possible to improve experimental set-up and operation to improve results. Nevertheless, there is clearly a need to look more closely at these issues of metal recovery and substrate disposal routes, both in terms of appropriate technologies for metal recovery and in terms of costs and benefits of metal recovery versus unit and absolute costs for disposal to different landfill types. Establishing the exact limit values for zinc-containing wastes to non-hazardous and hazardous landfills is recommended as a priority action in light of the findings of this work.

6 Large-scale compost bioreactor design: The Force Crag Vertical Flow Pond (VFP)

6.1 Introduction

In March 2014 a large-scale compost bioreactor was constructed at the Force Crag mine site, Cumbria. This scheme was a Defra-funded project completed by a partnership comprising the Coal Authority, Environment Agency, the National Trust and Newcastle University. The conceptual and process design for this treatment system was undertaken by Newcastle University. The detailed civil engineering design of the treatment system was undertaken by Atkins, and the construction contractor was JN Bentley Ltd. Many of the insights gained from the Nenthead pilot-scale trial were used directly in the design of this large-scale system. A specific objective of the Force Crag treatment system is for it to be used to investigate the potential utility of compost bioreactors for the mitigation of other abandoned non-coal mine water discharges across England and Wales. Because of the potential importance of this treatment system for future management of abandoned non-coal mine waters, and because much of its design was based around results presented in this report, it is therefore logical to report here on the design of the Force Crag treatment system. In particular, the discussion here focuses on how the Nenthead trial data were used to inform design, and also highlights the features of the Force Crag VFP system that have been included specifically to ensure that maximum benefit can be gained from it in terms of understanding the performance of the system and deriving design criteria for future systems.

The term ‘compost bioreactor’ has been used to describe the pilot-scale treatment systems at Nenthead and Cwm Rheidol throughout this report. At Force Crag the treatment system has been called a vertical flow pond (VFP), but this is synonymous with the term compost bioreactor; the mode of operation of the Force Crag treatment system is identical to that of the Nenthead pilot-scale unit. The term VFP has been adopted as it is in common usage internationally for this type of system (especially in the USA).

6.2 Background to Force Crag mine

The Force Crag mine, Cumbria, is located at the head of the valley of the Coledale Beck, approximately 7 km west, and slightly south, of Keswick (NGR NY199216). The main mine site lies at an elevation of 275 m a.s.l. (above sea level), though the abandoned mine workings extend west by a horizontal distance of approximately 1 km, to an elevation of 600 m a.s.l. The mine was worked for barite ($BaSO_4$), sphalerite (ZnS) and galena (PbS). The workings were mined predominantly during the early 20th century, but finally closed in 1992. Force Crag was the last working mine in the Lake District. The mine and surrounding land is owned by the National Trust.

There are a total of 9 levels into the workings (Level 0 to Level 7 - with Level 0 being at the lowest elevation, and Level 7 at the highest elevation – and the High Force cross cut level), all of which are interconnected. A very small volume of water discharges from Level 0, but the main conduit from which mine water discharges to the surface is Level 1. As with many other abandoned non-coal mine sites diffuse mining pollution is an issue at this site (e.g. Gozzard et al., 2011; Mighanetara et al., 2009), but Level 1 has repeatedly been shown to be by far the most important point source of pollution to the receiving watercourse, the Coledale Beck. When the opportunity arose to construct a large-scale passive treatment system at the Force Crag site it was therefore logical to target the Level 1 discharge for remediation.

Table 7 presents summary water quality data for the Level 1 discharge.

Table 7. Summary water quality data for the Level 1 mine water discharge from the Force Crag mine for the period 12/2011 to 06/2014 (unpublished data of Environment Agency and Newcastle University)

Variable	Range	Mean	n[A]
Flow (L/s)	8.5 – 24.4	14.8	21
pH	5.6 – 7.7	6.8	25
HCO_3^- (mg/L)	8.5 – 26.8	16.7	28
Cl (mg/L)	4.7 – 7.6	5.7	28
SO_4 (mg/L)	16.0 – 39.5	26.6	28
Ca (mg/L)	5.1 – 14.5	9.5	28
Mg (mg/L)	1.95 – 5.00	3.30	28
Na (mg/L)	2.40 – 3.60	2.95	28
K (mg/L)	0.32 – 0.62	0.46	28[C]
Fe (mg/L)	0.26 – 1.08	0.52	28
Mn (mg/L)	0.29 – 0.76	0.51	28
Al (mg/L)	0.05 – 0.20	0.08	28
Zn (total) (µg/L)	1730 – 4660	2997	28
Zn (filt) (µg/L)[B]	1710 – 4550	2950	28
Pb (µg/L)	25.0 – 87.9	43.6	28[D]
Cu (µg/L)	1.80 – 8.57	5.11	28[E]
Cd (µg/L)	5.00 – 20.00	14.24	28[F]
Ni (µg/L)	10.00 – 20.00	16.09	28

[A] number of samples
[B] Concentrations reported are after filtering through 0.45 µm filter
[C] 5 samples measured by ICP-OES below detection of 1.00 mg/L; value of 0.50 mg/L used for calculation of summary statistics
[D] 6 samples measured by ICP-OES below detection of 50 µg/L; value of 25 µg/L used for calculation of summary statistics
[E] 13 samples measured by ICP-OES below detection of 10 µg/L; value of 5 µg/L used for calculation of summary statistics
[F] 2 samples measured by ICP-OES below detection of 10 µg/L; value of 5 µg/L used for calculation of summary statistics

The Level 1 mine water is poorly mineralised, with low concentrations of all major ions. This includes sulphate concentration, which is a ubiquitous constituent of mine waters arising from abandoned metal sulphide mine workings; 16.0 – 39.5 mg/L is a low concentration of sulphate by comparison to many other mine waters across England and Wales (the Rampgill mine water, at Nenthead, has a sulphate concentration in the range 87–164 mg/L, for example; Table 1). Table 7 illustrates that zinc is the main contaminant metal of concern in terms of absolute concentration. Although other metals may also be of concern in terms of Environmental Quality Standards in the Coledale Beck, zinc sulphide has a greater solubility product than Cu, Cd and Pb (Diaz et al., 1997)[6], which means that zinc should be attenuated as its sulphide sequentially after these other metals. Therefore successful removal of zinc will likely result in successful removal of these other metals.

6.3 Design considerations

6.3.1 System size and substrate

Given the successful performance of the Nenthead pilot-scale unit, the size of the VFP system at Force Crag was determined directly from the Nenthead results. Approaching the design of the Force Crag VFP in this way was logical given the broad similarity of the Rampgill mine water at Nenthead (Table 1) to the Level 1 water at Force Crag (Table 7), the availability of the same treatment system substrate materials, and the similar environmental conditions at the two sites (the Nenthead site is at 440 m a.s.l., compared to the Force Crag site at an elevation of 275 m a.s.l., for example). Nevertheless, this approach is not without risks, which include:

1. Directly scaling results from a pilot-scale unit comprising 2.25 m^3 of substrate to a full-scale treatment system containing in the order of 1,000 m^3 of substrate
2. Assuming that the reactive substrate will perform in the same way in a different system, since there is a growing body of anecdotal evidence that this may not be the case, even where the same substrate is used.

In a wider sense, while it is hoped that the empirical guidance below may prove useful for the design of future systems of this sort, there is no question that design considerations need to be made on a site-specific basis, particularly with respect to variations in water quality. For example, the potential process implications of higher contaminant metals concentrations and low pH would need to be considered in the case of an acidic water, and both process and operational implications would need to be factored into design for a water with elevated iron concentrations. Lab- and / or pilot-scale experiments are therefore advisable, prior to full-scale design and installation, to establish the viability of passive treatment using VFP technology for a particular mine water.

Based on the results of the pilot-scale trials at Nenthead, full-scale design of the Force Crag VFP needed to take account of the difference between the calculated residence time ('time to fill') and measured residence time (taken as time of emergence of peak concentration of a conservative tracer for simplicity), with the ultimate objective of designing a system to have an actual residence time of ~ 14 – 15 hours.

To calculate the time to fill, the porosity of the limestone and of the compost mix was measured during the Nenthead trial, both at the outset and at the completion of the 2 year trial. Limestone porosity was constant at 50%, as expected. Compost porosity varied with both depth and time, but on average was also around 50%. Comparison of the actual peak residence time of water within the Nenthead reactor (Figure 33) with the calculated time to fill showed that the actual peak residence time was less than the calculated residence time, and therefore to achieve an actual residence time of 15 hours the calculated residence time (time to fill) needed to be multiplied by a factor of 1.3. Whilst it is recognised that the hydraulic behaviour of the full-scale system at Force Crag may not mirror that of the Nenthead pilot-scale system (especially given the

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[6] Note that the mean concentration of nickel in the Level 1 water is less than the EQS of 20 µg/L (the EQS is an annual average), and therefore attenuation of this metal, which has a sulphide solubility product lower than that of zinc, is not an objective of treatment.

difference in scale), this was nevertheless the starting point for design of the larger system.

On this basis, Table 8 provides the volume and area of compost required (assuming 0.2 m limestone and 0.5 m compost depth) to achieve actual residence time of 15 hours for the various flow rates shown. A 0.5 m depth of compost is selected here as this is the actual depth that was used in the Force Crag VFP system (as opposed to the 0.4 m depth used in the Nenthead trial).

Table 8. Estimated volumes and areas of compost required to achieve a 15 hour residence time in a VFP for various flow-rates (volumes and areas are rounded to nearest 5 m^3 or m^2; see text for further details)

Discharge flow-rate (L/s)	Volume of compost (m^3)	Area of compost (m^2)[A]
1	140	300
2	280	585
3	420	865
4	560	1140
5	700	1425
6	840	1700
7	985	1970
8	1125	2250
9	1265	2520
10	1400	2810

[A] The calculation assumes a trapezoidal basin with equal length and width dimensions and internal slopes of 1:2.5, and that the 0.5 m layer of compost would be underlain by 0.2 m depth of limestone. The absolute area within the retaining embankments (that is, at crest level) would be greater than this due to the requirement for water cover over the compost and freeboard. Multiple basins may be advisable for higher flows, which would also increase absolute footprint.

It will be apparent from the dimensions in Table 8, especially for the higher flow-rates, that multiple basins may be advisable, particularly for the purposes of maintenance. For example, using an excavator to remove compost substrate from the VFPs, as and when it becomes exhausted, becomes more logistically difficult with larger basin sizes. It is also the case that having two parallel VFP units permits temporarily ceasing flow to one unit, whilst continuing to treat water in the second unit, for example if one of the VFPs requires maintenance. Adopting such an approach for future systems is therefore strongly advisable for all but the very smallest of design flow-rates.

The Force Crag VFP treatment system has a design flow-rate of 6 L/s, and comprises two parallel VFP units, each with a design flow-rate of 3 L/s. The volume and area of compost in each VFP is very similar to the figures given in Table 8 for such a flow (slight differences being due largely to engineering constraints on site). The substrate in the Force Crag VFPs is the same as that used at Nenthead, albeit the suppliers were different in order to limit transport distances: PAS100 compost (45% v/v), wood chips (45%) and activated digested sludge from a municipal wastewater treatment plant (10%). Limestone gravel was used for the underdrain layer, as at Nenthead, although clast size is approximately 20 – 30 mm in the Force Crag system (~40–50 mm in the Nenthead system). Figure 52 illustrates the VFP system during construction, and clearly shows the limestone and compost layers.

The effluent waters from the two Force Crag VFPs merge into a single pipe, from where the water discharges to a small aerobic wetland before returning to the Coledale Beck.

Figure 52. The two Force Crag VFPs during construction, with compost substrate being placed on top of limestone layer in VFP1 (Photograph © John Malley, National Trust)

6.3.2 Hydraulics and flow control

Maintaining good hydraulics and close flow control to any mine water treatment system is important. For the Force Crag VFP system this was especially critical given that it is planned to use the system to investigate the utility of such technology at other sites across England and Wales. The overall flow of mine water through the treatment system, from Level 1, via the treatment system back to the Coledale Beck, is shown in Figure 53. Flow from Level 1 is via a pipe, to a chamber from where mine water is diverted to the treatment system. Because the flow-rate from Level 1 is variable (see Table 7) the amount of water flowing to the treatment system is controlled by a gate valve, such that a little more than is required to go to the treatment system is allowed through (about 8 L/s, compared to design flow-rate of 6 L/s). Any excess passes back to the Coledale Beck. Level 1 water is then split, approximately evenly, in order to feed water to each of the VFPs. Additional valves are available for flow control after the flow has been split, but the main structures for control (and adjustment) of flow into the two VFPs are the penstocks. These structures are discussed further below. Sharp-crested V-notch weirs are used to measure flow-rate into each of the VFPs. Flow measurement can also be undertaken, using a bucket and stopwatch, at the outlet pipes from the two VFPs. The flows from the two VFPs then combine before discharging through the aerobic wetland, and final discharge back to the Coledale Beck is via another V-notch weir, for final flow measurement.

It was vital that design of the large-scale treatment system at Force Crag ensured that water was able to flow in a controlled and measured way, just as it did in the pilot-scale system at Nenthead. In this respect there were four key elements to hydraulics and flow control at the Force Crag treatment system:

1. **Inlet to the VFPs**: It was essential that a constant flow could be maintained to the VFPs, but also that flows could be incrementally adjusted to one or both VFPs as required
2. **VFP drainage pipe network**: The network of perforated pipes at the base of each of the VFPs had to permit water to flow freely, and without hydraulic short-circuiting, over the long-term
3. **VFP outlet pipes**: The outlet pipes control the water level in the VFPs, and these needed to be both adjustable (to adjust water level in the ponds) and also accessible to allow sampling and *in situ* monitoring

4. **Flow measurement**: At all key points through the treatment system there had to be facilities to accurately and reliably measure flow-rate.

Each of these four key elements is discussed in more detail below.

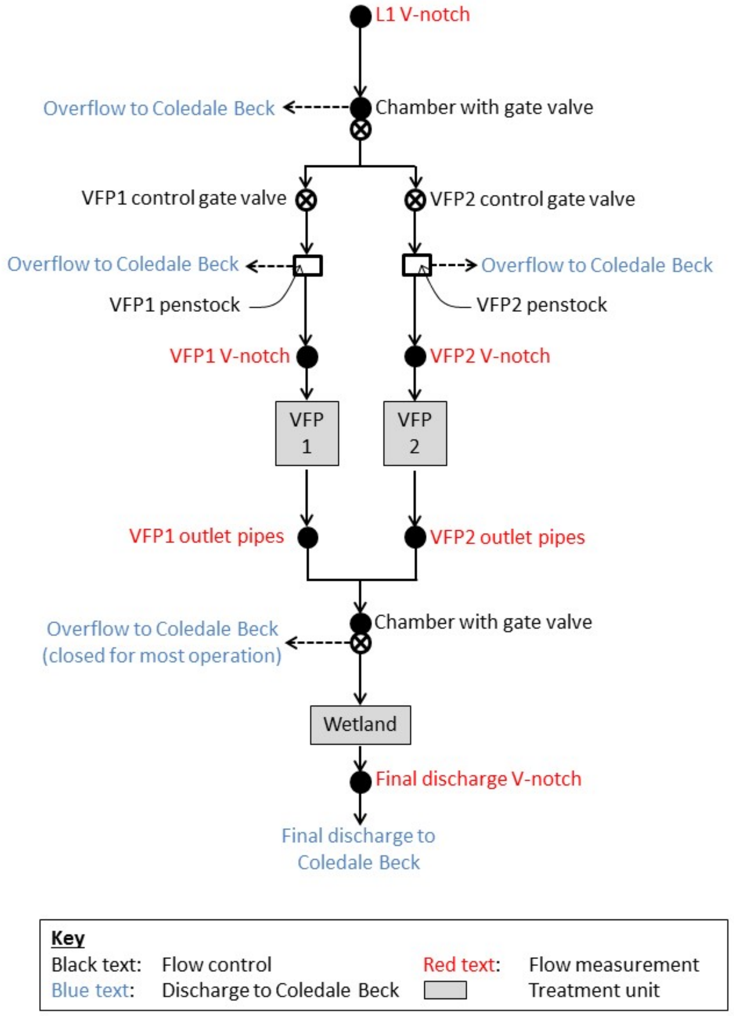

Figure 53. Schematic illustration of flow of mine water through the Force Crag treatment system (note that VFP1 and VFP2 penstocks are contained in a single chamber (see Figure 54), but are separated here for illustrative purposes)

Inlet to the VFPs

Figure 54 illustrates the inlet arrangement to the VFPs at Force Crag. The selection of the design flow-rate of 6 L/s was determined by reviewing historic flow data for the Level 1 adit. In order to ensure that the design flow-rate could always be maintained it was ensured that the design flow-rate was less than the lowest recorded flow from the adit. Table 7 indicates that the lowest recorded flow is 8.5 L/s, although older data (not shown here) suggest that the 7 L/s is the lowest flow measured. For that reason the initial design flow-rate was set at 7 L/s. Subsequent engineering constraints resulted in slightly smaller VFPs than originally planned, and therefore the design flow was reduced to 6 L/s.

A flow of approximately 8 L/s is allowed to flow through the gate valve below Level 1 (Figure 53). The flow is then split into two separate pipes, in which there are two further gate valves to allow throttling of flow, but the main flow control structures are the two penstocks. The details of the overall structure of the penstocks are shown in simplified form in Figure 54. In essence the flow-rate of water to the two VFPs is controlled by downward operating penstocks. Unlike conventional penstocks, in this instance water overflows the top of the penstocks, not underneath them. The reason conventional penstocks were not used was because variable hydraulic head behind each of the penstocks (as seemed possible) would have resulted in the release of a variable flow of water from the chamber. This in turn would have resulted in variable flow-rate to the VFPs, which was not desirable. This is because it is important to maintain constant flow over a period of time, even when flow from Level 1 varies, to understand the performance of the treatment system at this specific flow-rate. Once confidence is gained in the performance at this flow-rate, then the flow-rate might be adjusted up or down to investigate how flow-rate influences performance. Such information is crucial for the purposes of future design.

Each of the downward operating penstocks effectively controls hydraulic head by allowing water to pass over them. These penstocks move up and down on spindles, and therefore very fine control of water level in the penstock chambers is possible.

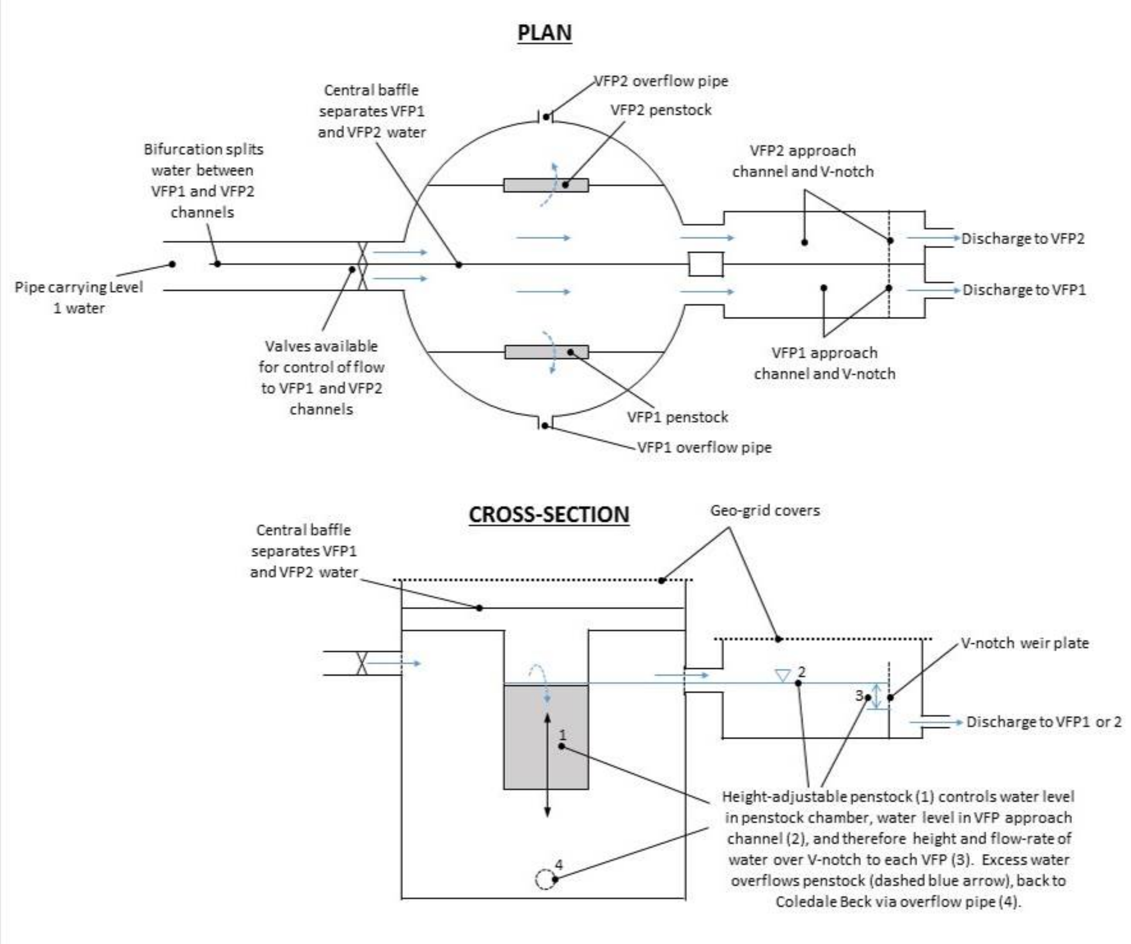

Figure 54. Simplified schematic plan and cross-section of the VFP inlet and flow control structure (not to scale; see text for further details)

The penstock chambers are hydraulically connected (via pipes) to the approach channels to each of the VFPs (see Figure 54), and therefore the water level in the approach channels is the same as that in the penstock chamber. There is a 20° V-notch weir at the end of each approach channel. Flow-rate is accurately measured over these V-notch weirs, and each of the penstocks is adjusted until the desired flow-rate is achieved.

Pipe systems, using valves to control flow, can be used to good effect in many water treatment applications. Although pipe valves have been used at two locations through the Force Crag system, where close control of flow is required open channel flow control systems were desirable, mainly because many mine waters contain elevated iron concentrations. Iron can rapidly accrete in pipes and valves resulting in decreasing flows. Although iron concentration in the Level 1 water is not especially high, it is still elevated enough to result in deposition on surfaces (Table 7). Open channels also accrete iron, but cleaning is far more straightforward.

Nevertheless, given the flow-rates involved, the VFP inlet structures at Force Crag are perhaps more heavily engineered than would likely be necessary for future systems (the penstocks are housed in a 2.1 m diameter manhole ring for example, and the VFP approach channels are 3 m long). This is because of the crucial need to have very close flow control at the Force Crag system so that design criteria for future systems can be derived. It may be feasible to adopt similar design principles for future systems (e.g. open channels with variable height overflows) but at lower engineering cost, since slightly less precise flow control may be acceptable.

VFP underdrainage pipe network

Just as schematically illustrated in Figure 5, at the base of each of the VFPs there is an underdrainage pipe network. To maximise understanding of the operation of the system, and also to provide flexibility in operation, the underdrainage network in each VFP at Force Crag is divided into 4 quadrants of equal area. In total there is a perforated pipe length of approximately 345 m in VFP1 and 360 m in VFP2. These 100 mm internal diameter pipes were supplied by a manufacturer with perforations. They have 3 by 7 mm diameter perforations at 35 mm intervals around the pipe, at approximately 80 mm centres along the length of the pipe. The combined area of orifices in the underdrainage network in each VFP is far greater than the area of the influent pipe to each VFP (approximately 30 times greater). The perforated pipes are also protected by the 200 mm layer of limestone overlying them. For both of these reasons blockage of these pipes would appear to be very unlikely.

VFP outlet pipes

Because there are 4 distinct underdrainage pipe networks in each VFP, there are also 4 outlet pipes from each VFP. As is common practice with VFPs, the outlet pipes are elevated such that the invert level of the outlet pipes controls the water level within the VFPs. The height of the 4 outlet pipes (and therefore water level in the VFPs) is also adjustable, as the board in which they are housed can be raised or lowered using chains accessible from ground level (thus avoiding the need to enter a confined space). The actual arrangement of these outlet pipes is shown in Figure 55.

Flow from each outlet pipe can be reduced or stopped entirely using valves at the end of each quadrant of underdrainage pipe. This might be done, for example, in an effort to overcome any problems with hydraulic short-circuiting that many be encountered. It would also be possible to ‘flush’ each VFP, as each outlet pipe can be lowered to the same level as the underdrain network, though this would likely only be done if there were problems with the underdrain networks becoming blocked.

The water chemistry of the VFP outlet waters is critical to understanding the performance of the system. For that reason it was ensured during the design that each of the outlet pipes was safely accessible for the purposes of both collecting samples for analysis, and measuring flow-rate by bucket-and-stopwatch.

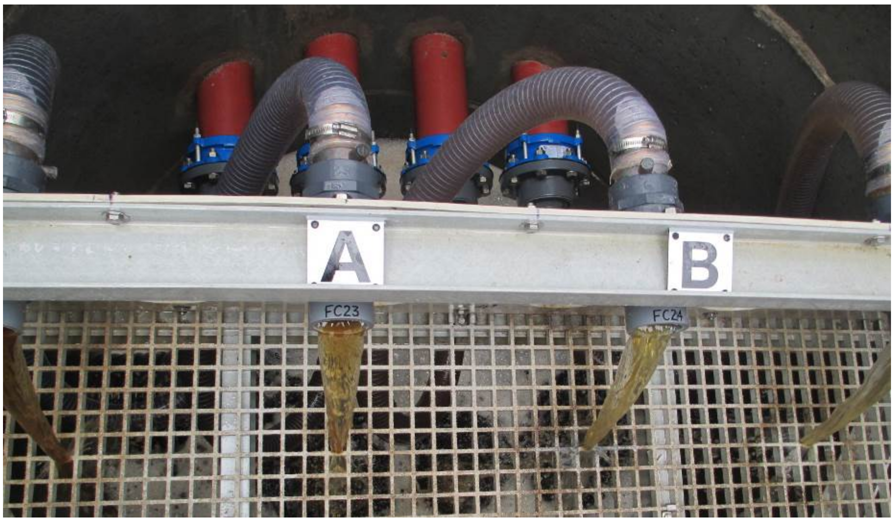

Figure 55. VFP outlet pipe arrangement at Force Crag (see text for details; note the photograph is taken less than 24 hours after system commissioning, and therefore the effluent water is temporarily discoloured) (Photograph by Newcastle University)

Flow measurement

Measurement of flow-rate is critical in treatment systems of this sort, as it permits the calculation of contaminant loading rates into, and out of, the treatment system. These data are essential for assessing system performance and developing design criteria for future systems.

As indicated on Figure 53, facilities for flow measurement have been installed at key points throughout the treatment system at Force Crag. As noted above, measurement of flow from the VFP outlet pipes is achieved using the bucket-and-stopwatch method. In addition, sharp-crested V-notch weirs have been installed at (see Figure 53):

- Level 1 (90° V-notch)
- Inlet to VFP1 (20° V-notch)
- Inlet to VFP2 (20° V-notch)
- Final effluent from the treatment system (90° V-notch)

To ensure accuracy of flow measurement, sharp-crested weirs (synonymous with thin-plate weirs) are designed and installed following the guidance of BS ISO 1438:2008 *Hydrometry – Open channel flow measurement using thin-plate weirs*.

6.4 Summary

The Force Crag VFP treatment system is the first of its kind in the UK. Pollution from abandoned non-coal mines is a widespread and severe problem across much of England and Wales (Mayes et. al., 2009), and therefore the particular significance of the Force Crag treatment system is that it may well be the blueprint for the design of similar systems in the future.

The Force Crag treatment system was designed on the basis of the results of the pilot-scale treatment trial at Nenthead. In particular, the understanding gained at Nenthead of the relationships between hydraulic performance and metal removal efficiency were used directly to size the treatment system at Force Crag. Such an approach is not without risks, not least amongst which are the assumptions that performance will be equivalent despite the very substantial increase in system scale, and that the compost substrates used as the main treatment media in such systems will perform in the same way.

The mine waters at Nenthead and Force Crag are of rather similar chemical quality, which was advantageous. In designing future systems it should not be assumed that VFP systems will perform similarly for mine waters with different chemical characteristics (e.g. low pH, higher metals concentrations); the relatively low cost of lab- and pilot-scale trials, on a case-specific basis, may still be advisable given the substantial capital costs of a full-scale system.

Notwithstanding these comments, there is little doubt that the Force Crag treatment system will serve as a blueprint for future systems. Given this, a crucial aspect of its design was ensuring that maximum benefit could be gained from it in terms of understanding the treatment process and deriving reliable design criteria for future systems. It is for this reason that such close attention was paid to the provision of complete and reliable flow control and flow and water quality monitoring infrastructure. These facilities will allow for the collection of the data required to design future systems. Whilst future systems may not require quite the same level of provision in terms of flow control and flow and water quality monitoring infrastructure, their design should nevertheless benefit from some of the principles outlined here.

7 Conclusions

The performance of compost bioreactor systems for the remediation of metal mine discharges has been investigated. The investigation has primarily focused on the simultaneous operation of two laboratory-scale reactors, one operated in a laboratory, the other under field conditions, and a pilot-scale reactor in the field at Nenthead, Cumbria. All three of these systems had identical reactive substrates containing a mixture of compost, wood chips and activated digested sludge, and were configured to have an initial hydraulic residence time of 19 hours. In addition, an equivalent pilot-scale reactor, but receiving a mine water of different characteristics, has been monitored at Cwm Rheidol, Wales. The pilot-scale reactor at Nenthead operated for a 2-year period, from August 2010 to August 2012, while the system at Cwm Rheidol was commissioned in September 2010, and continues to operate at the time of writing. The principal conclusions from the research at Nenthead, which included the operation of the laboratory-scale systems, are as follows:

- Metal attenuation has taken place in all three systems but the quantity of metal removed has varied between systems. The laboratory and field columns show similar treatment efficiency with, on average, 98% of the influent total zinc and 94% of the influent dissolved zinc removed within the laboratory column compared to 94% and 96% of the influent total and dissolved zinc respectively, removed within the field column. Treatment efficiency in the pilot-scale system, however, was significantly lower and showed far greater fluctuation with, on average, 68% of the influent total zinc and 83% of the influent dissolved zinc removed. The results quite clearly show that the performance of the pilot-scale unit is markedly different to the performance of the laboratory-scale units. Although this appears to be primarily related to scale issues rather than environmental conditions, since the laboratory-scale units in the field and in the laboratory performed similarly, there is evidence that the performance of the pilot-scale treatment system was affected by temperature, with poorer performance during low temperatures. It is not clear why these temperature effects were not seen in the laboratory-scale system operating in the field, but there were operational problems with this small unit during the winter months, which may have masked any effects.
- The volume-adjusted removal rate of metals is load-limited, and therefore a function of the influent metal load. Thus, although relatively low dissolved zinc removal rates of, on average, 1.2 $g/m^3/day$ in the laboratory column, 1.4 $g/m^3/day$ in the field column and 1.0 $g/m^3/day$ in the pilot-scale reactor have been calculated, this is partly due to the comparatively low influent zinc concentration. On occasions when influent zinc concentrations were higher, significantly higher removal rates were observed.
- There is clear evidence that bacterial sulphate reduction was taking place in all three systems. Both water quality data, and analyses following destructive sampling of the treatment substrate at decommissioning, all point towards immobilisation of metals as their sulphides, via bacterial sulphate reduction, as a key process in the attenuation of metals. Such evidence includes greater removal of sulphate from the mine water than zinc, appropriate pH and Eh conditions for the formation of zinc sulphide, and very high concentrations of both metals and acid volatile sulphides (AVS) in the substrate itself.
- Anoxic conditions became established fairly readily within the laboratory column and remained (apart from brief periods which can be accounted for)

until the onset of carbon additions. In contrast, in the field column, redox conditions showed greater variation with moderately reducing conditions only established in the latter 3 months of the trial. This may explain why bacterial sulphate reduction did not appear to be taking place to the same extent in the field column as in the laboratory column. In the pilot-scale reactor, there has been an overall decreasing trend in Eh, which corresponds with an increasing trend in sulphide generation, and again points to bacterial sulphate reduction as a key process in metal attenuation.

- Hydraulic conditions have differed between the systems, despite the same initial conditions. However, there is no clear pattern to these variations. It appears that preferential flow paths may develop on occasion, but are perhaps short-lived. In the case of the pilot-scale reactor, residence time at the end of the trial was in fact similar to that at the start of the trial. Nevertheless, this variability suggests that full-scale design of such systems should factor in the possibility of residence times being less than calculated during design.

- Temperature appears to play an important role in the removal of metals within such bioreactors. Over the first year of operation in particular there was a clear relationship between effluent temperature and treatment efficiency within the pilot-scale reactor, with a decrease in treatment efficiency observed as temperature dropped over the winter period and a subsequent increase as temperature rose during the spring. The reason for this apparent temperature dependence is not entirely clear, but would appear to be related to the suitability of conditions for sulphate reducing bacteria communities, and/or the maintenance of the reducing conditions that they require. It is hoped that close monitoring of the Force Crag VFP system will offer further insights to this issue.

- The addition of carbon, both slug and continuous additions, appeared to have a negative impact on system performance. An immediate increase in effluent zinc concentration (and a corresponding decrease in treatment efficiency) was observed in the laboratory column and pilot-scale reactor following a slug addition of carbon, while little impact was seen in the field column. Following the commencement of continuous carbon additions to the laboratory column and pilot-scale reactor, a slight increasing trend in effluent zinc concentrations is apparent. Reasons for this deterioration in performance are unclear, but it is possible that too much carbon was added, with the consequence that populations of bacteria other than the sulphate reducers began to dominate the bacterial community as a whole, and were out-competing the sulphate reducers. However, while the short-term impacts of the carbon additions were not clear, the performance of the pilot-scale reactor over the final year of operation was much more consistent than in the first year, and the commencement of this improved performance coincided with the commencement of semi-continuous additions of small volumes of carbon additive. It is possible therefore that the carbon additions were in fact beneficial, but time was required for these beneficial effects to be manifested in improved performance. This is certainly an area for further investigation.

- Microbial analyses conducted in 2011 failed to identify sulphate reducing bacteria (SRB). A second round of analyses, in 2013, used an optimised method, and sulphate reducing bacteria were successfully identified. The SRB identified were most similar to those of the genus *Desulfobulbus* and genus *Desulfovibrio*. These groups are most commonly associated with non-marine environments, which is consistent with the freshwater conditions of the treatment tank. The genetic sequences identified in the tank were also closely related to those previously identified in treatment systems receiving metal-rich waste and in natural sediments contaminated with metals. This suggests that it is possible that the high metal conditions in these environments favour the selection of metal-tolerant SRB. Although it is not possible to conclude from these results exactly how important bacterial sulphate reduction is as a mechanism of metal removal, alongside other lines of evidence it certainly suggests bacterial sulphate reduction plays some role in metal immobilisation. Further microbiological work, to quantify numbers of SRB, may prove insightful, especially if SRB numbers correlated with metal and acid volatile sulphate concentrations (AVS), as this would strongly implicate bacterial sulphate reduction as an important mechanism of metal removal within the treatment system.

- Despite the large volume of new data collected, and the insights gained, it is not possible to conclude with confidence from these investigations what the overall lifetime of a compost bioreactor would be. Although the porosity of the substrate in the Nenthead pilot-scale tank has decreased over the 2 years of operation, there is no indication that this is an ongoing trend, and neither is it reflected in shorter hydraulic residence times. Other factors that may influence the overall lifetime of such systems, such as metal toxicity to sulphate reducing bacteria, do not appear to have had any detrimental effect on the pilot-scale reactor, despite the presence of very high concentrations of zinc in the substrate. Nevertheless, it is possible that there is an upper limit of zinc concentration, which had not been reached in the Nenthead reactor, beyond which toxic effects may be observed, resulting in deterioration in reactor performance.

- Preliminary assessments of the substrate from the pilot-scale reactor tank have been made with a view to assessing what classification of waste the material would be for the purposes of landfill disposal. The results suggest that the material would be classified as hazardous waste due to the elevated concentrations of zinc (which would be considered ecotoxic). If the material was to be disposed of as hazardous waste it would need pre-treatment in any case, since the organic content of the material was determined to be too high for disposal as hazardous waste. Alternatively, if the zinc concentrations in the substrate could be lowered it might be possible to have the material reclassified as non-hazardous waste.

- Metal recovery tests have been undertaken to establish whether, in principle, it is possible to recover the zinc immobilised within the treatment substrate following exhaustion of the substrate. ‘Slurry’ tests, using a hydrochloric acid lixiviant, show good recovery of zinc; up to 85% recovery. Subsequent continuous recirculation tests initially produced much less positive results, with only ~10% zinc recovery. Modifications to the experimental set-up, specifically the introduction of the hydrochloric acid as an aerosol, resulted in much improved performance, with reductions of ~40% in the zinc content of the substrate. The results suggest that there is clear potential to recover the metal from the substrate, most likely to lower the cost of substrate disposal, but further work is required to establish whether the costs of metal recovery are lower than the savings in subsequent disposal costs.

The results from the Cwm Rheidol pilot-scale system largely corroborate the findings of the Nenthead investigation. The performance of the system was similar overall to the Nenthead system, despite the water being low pH and with a higher zinc concentration.

Some key findings from the investigation at Cwm Rheidol that are of particular additional value to the findings at Nenthead are as follows:

- With suitable alkaline media included in the substrate, compost bioreactors can consistently elevate the pH of acidic mine drainage.
- Elevated iron concentrations (evident at Cwm Rheidol but not at Nenthead) unquestionably create operational difficulties, primarily due to system clogging issues, which in turn impacts on hydraulic residence time, which results in deterioration in system performance.
- The concentration of zinc in the substrate of the Cwm Rheidol reactor was substantially higher than in the Nenthead reactor because the zinc loading to the system was much higher. Nevertheless, the system continued to remove zinc, suggesting that even at such high concentrations toxic effects were not evident, or at least not obvious from the performance data alone.

In March 2014 a large-scale compost bioreactor (Vertical Flow Pond) was commissioned at the Force Crag mine site in Cumbria. The results of the pilot-scale trial at Nenthead were directly used for the design of the Force Crag treatment system, which comprises two parallel compost units, each with a water surface area of approximately 800 m^2. The basis for the design of the Force Crag system is discussed in Section 6. In addition, some of the features included in the design to ensure that it operates effectively, and that it can be used to assist in the design of future systems, are detailed.

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Appendix A: Phylogenetic tree of sulphate reducing organisms identified in the Nenthead treatment tank substrate

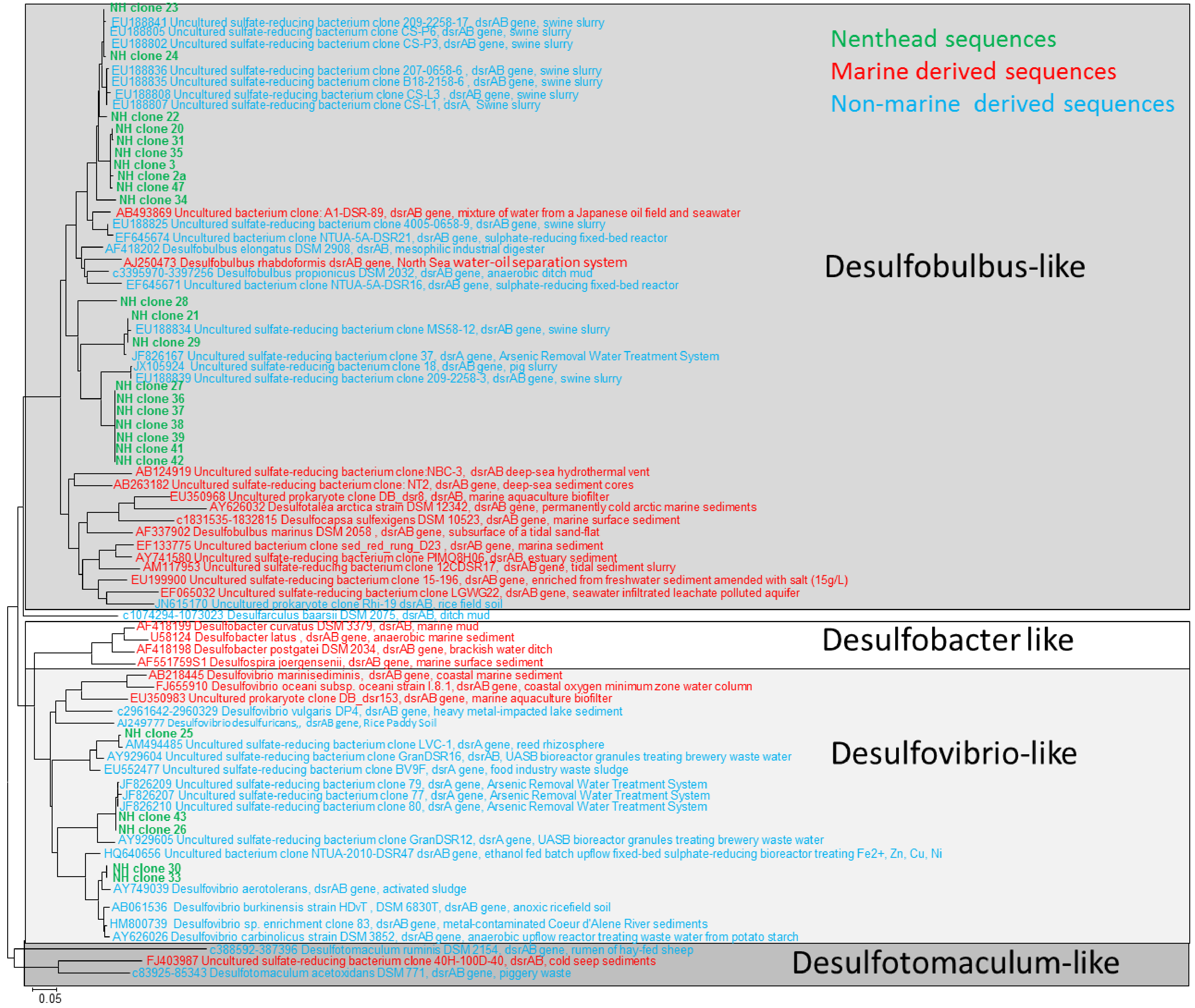

Figure A1. Phylogenetic tree showing similarity of gene sequences identified in the Nenthead tank substrate (green text) compared to cultured sulphate reducing organisms and sulphate reducing organisms previously found in similar environments (see the microbiology subsection of Section 3.4.3 for details)

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