PERGAMON

Water Research 37 (2003) 108–120

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Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate

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Received 8 March 2001; received in revised form 12 March 2002; accepted 27 March 2002

Abstract

Subsurface permeable reactive barriers (PRB) have been used to successfully treat acidic mine drainage in Canada and offer great potential for doing the same in the United Kingdom. A PRB for the treatment of colliery spoil leachate from a site near Newcastle upon Tyne, UK, has been designed. The selection of the reactive media to be used is of paramount importance, with particular reference to permeability and reactivity. A number of reactive media mixtures containing varying proportions of cattle slurry screenings, green waste compost, calcite limestone chips and pea gravel were prepared and their respective permeabilities and reactivities were investigated.

Media mixtures containing 50% 10 mm grade calcite limestone chips showed better alkalinity addition and metals removal than a blank containing 50% pea gravel. A media mixture containing 50% limestone chips and 50% green waste compost showed a 24 h period to achieve maximum addition of alkalinity and maximum removal of acidity and metals. Mixtures containing 25% green waste compost and 25% slurry screenings achieved maximum addition/removal in 4 h.

The likely presence of iron sulphide in samples drawn from test vessels during both test runs indicates that bacterial sulphate reduction is occurring in this composite. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acid mine drainage; Permeable reactive barriers; Bacterial sulphate reduction; Substrate characterisation

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1. Introduction

1.1. Acidic waters from colliery spoil

In recent years the arising of acidic groundwaters from recently abandoned coal mines has become a significant problem in the UK [1,2]. However, sources of acidic mine drainage are not limited to inundation of deep mine workings. Spoil heaps, containing the waste rock excavated during construction of shafts and access tunnels, contain similar materials to those causing the acidification of deep mine drainage. The percolation of oxygenated rainwater through the spoil heap removes acidity and metals from the spoil. The resulting contaminated water drains from the spoil heap and contaminates surface waters, or can pass directly into underlying aquifers.

One such spoil heap in Northeast England has been identified as the source of an acidic, ferruginous drainage that has caused significant pollution of a 2 km stretch of the nearby Stanley Burn [3]. A passive treatment wetland system, using bacterial sulphate reduction and limestone dissolution, has been found to treat the acidic drainage effectively and at minimum cost [4]. However, wetland-type passive treatment systems have large land area requirements. At sites where space is limited, alternative approaches to passive treatment may be necessary.

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PII: S0043-1354(02)00159-8

Nomenclature

PRB	permeable reactive barrier. A vertical wall of reactive media, installed in the path of groundwater flow, to treat the groundwater in situ
Eh	redox potential (mV)
mV	millivolt
ml	millilitre
$m\,s^{-1}$	metres per second (hydraulic conductivity or permeability)
$m\,day^{-1}$	metres per day (hydraulic conductivity or permeability)
kg	kilogram (mass)
$mg\,l^{-1}\,kg^{-1}$	milligrams per litre per kilogram (milligrams of substance removed from one litre of leachate by one kilogram of reactive media)
K	hydraulic conductivity or permeability (measured in metres per second or metres per day)
b	aquifer thickness (measured in metres)

1.2. Subsurface reactive barrier technology

The use of permeable, subsurface reactive barriers for remediation of groundwater pollution and contamination is becoming widespread in the United States and Canada [5–7].

The technology employs a vertical wall of reactive media, installed in the path of a contaminated groundwater flow, to remove or treat groundwater contaminants in situ. The reactive media is permeable to the groundwater flow and as it moves horizontally through the barrier, driven by natural hydraulic gradients, a variety of physical, chemical and/or microbiological processes remove the contaminants from the water. These processes can include precipitation, sorption, oxidation/reduction, fixation or degradation. The technology has been successfully used for the treatment of a variety of contaminants including the remediation of chlorinated aliphatic hydrocarbons [8], remediation of chromium VI [7] and the treatment of acidic mine drainage [9,10].

Several permutations of terms to describe the technology are in common use; these include ‘porous treatment walls’, ‘passive treatment walls’, ‘in situ permeable reaction walls’ and ‘in situ redox barriers’. The term permeable reactive barrier (PRB) will be used throughout this study.

There are generally two design configurations for reactive barriers. Funnel and gate systems, described by Starr and Cherry [11], use impermeable curtain walls to direct groundwater flow to treatment zones located between the ends of the curtain walls. Continuous barriers use a trench filled with reactive media across the entire width of the plume to be treated.

1.3. PRBs for the treatment of acid mine drainage

Blowes et al. [9] have investigated the use of organic substrates in PRBs to treat acid mine drainage. The study used a number of test cells constructed in the path of a plume of groundwater contaminated by metals and sulphate from the Nickel Rim tailings impoundment near Sudbury, Ontario, Canada. Results from the study showed significant reductions in iron and sulphate concentrations within a zone 1 m downgradient from the test cells.

The results from this study led to the development of a full-scale treatment system at the same location [10]. A PRB measuring 15 m wide (perpendicular to groundwater flow) × 4 m thick (parallel to groundwater flow) × 3.6 m deep was installed in August 1995. The aquifer is bounded on both sides and the base by bedrock and the reactive barrier was keyed into this feature to ensure all groundwater passed through, and not around, the treatment wall. Recently published results demonstrate effective treatment of the groundwater, in particular up to 90% removal of iron and raised pH [12]. Performance of this PRB was affected by variations in permeability (hydraulic conductivity) of the reactive media.

1.4. Reactive media selection for PRBs

A key element to the design of a PRB for successful treatment of contaminated groundwater is the selection of the reactive media. Gavaskar et al. [6] have identified five essential properties required for the reactive media:

- reactivity,
- permeability or hydraulic conductivity,
- environmental compatibility,
- availability and cost,
- stability.

The first two characteristics are of principle interest since these will have the greatest effect on success or failure of the treatment system. The latter three characteristics should not, however, be disregarded.

Waybrant et al. [13] have described the investigation and selection of reactive media for the barrier at the Nickel Rim site. Mixtures of sewage sludge, leaf mulch, wood chips, sheep manure and sawdust, in varying proportions, were assessed for reactivity, in terms of iron and sulphate removal, and permeability. Sewage sludge was found to significantly increase the concentration of nickel and sheep manure was found to have a relatively low reactivity. These two substrates were eliminated from further studies. Best sulphate removal rates were achieved with a mixture of substrates. The literature to date offers little guidance on the selection of suitable substrate mixtures. Accordingly, this paper documents the evaluation of permeability and reactivity of several possible PRB substrates for use in a subsurface reactive barrier for the remediation of acidic metalliferous drainage from a colliery spoil heap in the Northeast of England.

1.5. Site description

Shilbottle Colliery is approximately 56 km north from Newcastle upon Tyne and 4 km southeast from Alnwick (Fig. 1). Production started in 1926 and reached a peak in 1955, with a workforce of 756 producing 272 000 tons. The colliery closed in 1982 and the ownership of the spoil heap and responsibility for its remediation passed to Northumberland County Council in the early 1990s. A small spoil heap on the eastern part of the site was land filled and the 15 ha western heap was re-graded and landscaped. This western heap is located on the bank of the Tyelaw Burn, a tributary of the River Coquet. A number of surface drainage channels to intercept surface runoff and leachate drainage from the heap toe were constructed at this time. These directed contaminated seepage waters to a series of three aerobic reed-beds. Site topography and the aerobic nature of the metal removal mechanisms limit the effectiveness of this treatment system [14]. The majority of the discharge to the Tyelaw Burn is via subsurface flow and is not intercepted by this drainage system. PRB technology was therefore selected to treat the contaminated groundwater before it discharges into the Tyelaw Burn.

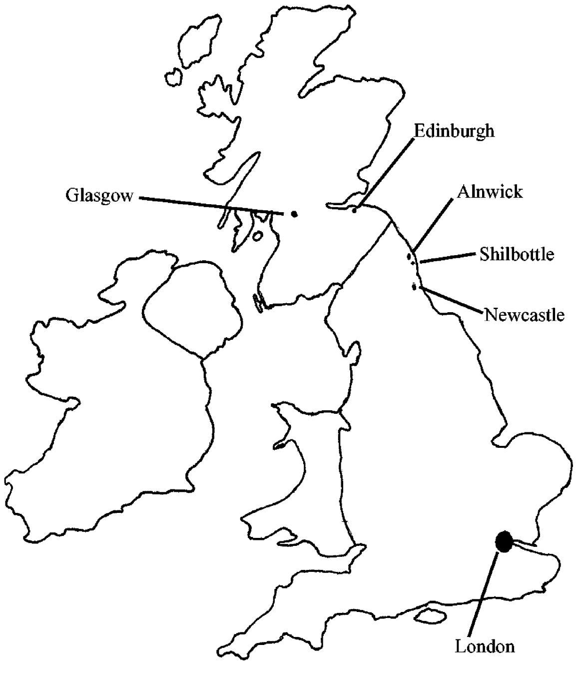

Fig. 1. Location of Shilbottle village

2. Methods

2.1. Field

A site investigation, in accordance with BS 5930 [15], was carried out. A site walkover identified a 200 m stretch of the southern end of the spoil heap as the source of the most contaminated groundwater. Samples from eight monitoring wells, three groundwater seepages and seven locations in the Tyelaw Burn were collected on five occasions. pH, Eh, temperature and conductivity were measured in the field with a portable Camlab Ultrameter or Palintest meter. Samples for metals analyses were collected in 125 ml polypropylene bottles and acidified with a few drops of concentrated nitric acid. Samples for anion analyses were collected in 250 ml polypropylene bottles. Ultimately, a holistic solution to the Shilbottle discharge was required and it was decided that filtration of the samples in the field might give under-measurement of analytes, leading to under-design of the PRB. Therefore, neither sample types were filtered in the field. This gave the added benefit of simplifying field procedures.

The permeability of the colliery spoil at the Shilbottle site was determined by conducting a single well, constant discharge pumping test, as described by Kruseman and de Ridder [16]. A Waterra Hydrolift positive displacement, constant discharge pump with 17 mm internal diameter Waterra tubing was used for the pumping test. The pumping test was carried out at a monitoring location at the toe of the spoil heap, close to the most polluting seepage. The ‘bucket and stopwatch’ principle was used to determine pump flow rate, the pump discharging into a graduated 25 l container. Recovery was monitored by measuring the water level in the borehole with an electronic dip-meter at 1-min intervals. The Theis recovery method [16] was used to determine the transmissivity and thickness of the colliery spoil (determined from drillers’ logs) allowed back calculation to a mean hydraulic conductivity value, using $K = T/b$.

2.2. Laboratory

Total iron, total manganese, total aluminium, total zinc and total copper were determined by flame atomic adsorption spectrophotometry using a Unicam 929 AA

Spectrometer and according to Section 3111 B (Direct Air–Acetylene Method) of the Standard Methods [17]. The concentrations of calcium, magnesium, potassium and sodium were determined by suppressed ion chromatography using a Dionex DX 100 Ion Chromatograph and according to Section 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity) of the Standard Methods [17]. Likewise, the concentrations of sulphate, fluoride, chloride and nitrate were determined by suppressed ion chromatography using the Dionex DX 100 Ion Chromatograph. All samples undergoing ion chromatography were injected into the chromatograph through a 670 μm filter to prevent possible damage to the chromatograph.

Gavaskar et al. [6] have described the procedures for determining reactivity on a continuous flow basis using column tests. A key issue is the residence time of leachate within the column, especially when compared with that achievable in the field. Younger et al. [18] have noted that residence times within PRBs can vary from 2 to 60 days. The residence time is also affected by the permeability of the selected media and, since a media had not yet been selected, it was not possible to carry out a truly representative column test. It was therefore decided to prioritise characterisation of the media permeability and in parallel conduct reactivity trials on a batch basis.

Permeability of possible PRB substrates was measured using constant head permeameters in upflow configuration. The upper end of the column was left open to allow the media under investigation to be surcharged with lead weights. This allowed the investigation of the effects of the media self-weight compressing the media and thus affecting permeability. The density and porosity of the media investigated were determined by mass–volume measurements and water displacement, respectively.

The media were hand placed in 25 l plastic tubs to within 10 cm of the tub rim. Groundwater was collected, in 25 l narrow necked containers filled to the brim to minimise potential oxygenation, from the site on the previous day and stored in a refrigerator overnight. Test solution was carefully poured into each tub and oxygen displaced from the media voids allowed to escape to the surface. Each media was allowed to saturate for about 10 min, each tub was then topped up to the brim with test solution and plastic airtight lids fitted so that the majority of the lid was in contact with the test solution, thereby minimising potential oxygenation of the test solution during the study. Approximately, 13 l of test solution was added to each tub. The chemical composition of the test solution, as analysed at the beginning of the reactivity trial, is given in Table 1.

Table 1
Composition of test solution

Determinant	Unit	Measurement
pH		4.24
Eh	mV	174
Alkalinity	mg l^{-1} as $CaCO_3$	0 (by deduction)
Acidity (calculated)	mg l^{-1} as $CaCO_3$	4807
Fe^{2+}	mg l^{-1}	1190
Mn^{2+}	mg l^{-1}	279
Al^{3+}	mg l^{-1}	411
Na^{+}	mg l^{-1}	183
K^{+}	mg l^{-1}	0
Mg^{2+}	mg l^{-1}	216
Ca^{2+}	mg l^{-1}	496
SO_4^{2-}	mg l^{-1}	14752
Fl^{-}	mg l^{-1}	423
Cl^{-}	mg l^{-1}	850
NO_3^{-}	mg l^{-1}	123

Samples were drawn from a tube near the base of the tub, a clamped tube allowed nitrogen gas from a bladder to occupy the headspace generated as samples were removed. Approximately, one tube volume (25–40 ml) was purged from the sample tube before collecting the samples. Measurement of pH, Eh and temperature was made immediately using a Jenway 3310 bench pH meter. Alkalinity was determined immediately by titration of a 25 ml sample with N/50 sulphuric acid as per section 2320 B of the Standard Methods [17]. In keeping with the holistic treatment objective previously stated, samples were not filtered prior to analysis. Samples for metals analysis were acidified with a drop of concentrated nitric acid. Metals and anions analyses were made as previously described.

During the first run of the reactivity test a black precipitate was seen to be present in some vessels. Analysis of this was made using a Hitachi S-2400 Scanning Electron Microscope with EDAX analysis. The precipitate was collected and prepared for this analysis by two different methods. Samples of the water containing the precipitate were drawn off, filtered through a standard glass fibre GF/A filter and dried at 105°C for 24 h. At the end of the first reactivity batch test, precipitate that had sorbed to the walls of the glass sample draw-off tube was scraped and washed off with de-ionised water into a porcelain dish. Excess water was removed by evaporating over a steam bath and the precipitate was then dried for a few hours at 105°C. It was noted that, as the water in the dish was driven off, black precipitate on the sides of the dish changed to an orange colour. All preparations were stored in a dessicator until analysis could be carried out.

3. Substrates investigated

It was intended to use bedded cattle manure, comprising straw and faeces, as the reactive media. This material is known to be a rich source of sulphate reducing bacteria, the bacteria being present in large numbers in the animals intestine, it is widely available at low cost in the area, and has been used successfully in a number of passive treatment systems in the UK [4,19]. The permeability properties were soon found to be unsatisfactory and a number of media composites were produced and investigated (Table 2). The principle mixtures, #1 and #2, contained varying amounts of calcite limestone chips, green waste compost and cattle slurry screenings. The slurry screenings are a fine, solid by-product from the mechanical screening of cattle slurry. It was anticipated that these would be easy to handle, would mix easily and intimately with other media types and act as a rich source of sulphate reducing bacteria. Green waste compost was included since there is a composting facility close to Shilbottle and therefore a plentiful, low cost supply of this material is available. This material is the resulting product from the aerobic composting of organic household waste and garden waste such as hedge trimmings and grass clippings.

The number of media composites investigated was limited to four to keep the number of samples collected and analyses required manageable and to reflect the local availability of the various composite ingredients. Selection of mixtures to be investigated began by assuming a mixture of 50% limestone chips, 25% compost and 25% slurry screenings (composite #1) as the preferred choice. Benner et al. [10] found favourable results with a 20% municipal compost, 20% leaf compost, 10% wood chips and 50% pea gravel mixture. In the event that the permeability of #1 proved too low, composite #2 contained 75% limestone chips, 12.5% compost and 12.5% slurry screenings. In order to compare the effects of including limestone in the mixture, composite #3 was identical to composite #1 but with pea gravel replacing the limestone chips. Finally, composite #4 contained 50% limestone chips and 50% compost to assess the effects of excluding slurry screenings from the mixture.

It was expected that when the barrier is constructed the composite mixture will be proportioned on-site by excavator bucket loads, and the mixtures were therefore proportioned on a volumetric basis and simple ratios of composition were deliberately selected.

Batch reactivity tests were carried out twice. During the first run, samples were collected daily for 7 days and then once at 10 days and once at 36 days. After this, the vessels were drained and refilled with more groundwater collected from the same source. It was noted that composite #2 had performed less effectively than the other three mixtures and so this composite was excluded from further studies. A black precipitate, which was present in samples drawn off from media #1 and #3, was collected for analysis at this stage. Samples for the second run were collected after 0, 4, 8, 12, 24, 28, 32, 36, 48, and 72 h.

Due to similarities in composition, it was anticipated that media #3 and #4 would have permeability similar to that of #1 and so the permeability of these mixtures was not determined.

4. Results

4.1. Permeability

The pumping and recovery periods were 810 and 1140 s, respectively. Data for the first 300 s

Table 2
Media composites investigated (percentage composition by volume)

Designation	Description	Comments
Manure	100% bedded cattle manure	Rejected at early stage due to low permeability
#1	50% limestone chips 25% slurry screenings 25% compost	Provisionally assumed as preferred mixture, subject to investigation results
#2	75% limestone chips 12.5% slurry screenings 12.5% compost	Investigated in case permeability for media #1 was found to be too low
#3	50% pea gravel 25% slurry screenings 25% compost	Chosen with objective of identifying effect of adding limestone to mixture, i.e. experimental blank to #1
#4	50% limestone chips 50% compost	Chosen with objective of identifying effect of excluding rich source of sulphate reducing bacteria

Table 3
Permeability results

Surcharge mass (kg)	0	4.2	12.6	25	39
Cattle manure	—	6.12 m day^{-1}, 7.1×10^{-5} m s^{-1}	2.08 m day^{-1}, 2.4×10^{-5} m s^{-1}	1.11 m day^{-1}, 1.3×10^{-5} m s^{-1}	—
#1	625 m day^{-1}, 7.2×10^{-3} m s^{-1}	—	—	650 m day^{-1}, 7.5×10^{-3} m s^{-1}	570 m day^{-1}, 6.6×10^{-3} m s^{-1}
#2	67 m day^{-1}, 7.8×10^{-5} m.s^{-1}	—	—	—	—

— denotes the media was not tested under these conditions.

($t = 810-1110$) and the last 60 s ($t = 1890-1950$) of the recovery period were excluded as per [16]. Cumulative flow during the drawdown was measured as 40 l, giving a flow rate of 0.0494 l s^{-1}. Permeability results for the media tested are given in Table 3. Borehole lithology showed water inflow through two horizons: the colliery spoil (0.52 m) and an underlying sandy clay layer (1.10 m). Given the requirement for $K_{\text{media}} \geqslant 10 \times K_{\text{spoil}}$ [10] it was necessary to establish the maximum likely permeability of the spoil; this value is arrived at using a minimum value for aquifer thickness 'b'. In this case, an aquifer thickness of 0.52 m was used, i.e. assuming that inflow to the borehole is primarily through the colliery spoil. The maximum value for the in situ spoil permeability is calculated as 5.5×10^{-5} m s^{-1} (4.76 m day^{-1}). This figure is closely comparable with that obtained by Benner et al. [10] for the fine grained sand aquifer (2×10^{-5} m s^{-1}) at the Nickel Rim site.

The cattle manure shows a permeability of 7.1×10^{-5} m s^{-1} for a surcharge of 4.2 kg. This media could not be tested under zero surcharge since the flow of water through the media was found to lift the media out of the column. The permeability was found to dramatically decline as surcharge was increased, 2.4×10^{-5} m s^{-1} for 12.6 kg surcharge and 1.3×10^{-5} m s^{-1} for 25 kg surcharge.

Composites #1 and #2 could be tested under zero surcharge conditions and gave permeability values of 7.2×10^{-3} and 7.8×10^{-4} m s^{-1}, respectively. This part of the investigation was carried out concurrently with the media composite reactivity trials. Composite #2 showed poor reactivity and effects of surcharge upon permeability were therefore not investigated. Composite #1 showed permeability values of 7.5×10^{-3} m s^{-1} for a surcharge of 25 kg and 6.6×10^{-3} m s^{-1} for a surcharge of 40 kg. This shows a minor variation in permeability with surcharge.

4.2. Reactivity

Results from the second run of batch tests are presented in Figs. 2–8. For these tests it was assumed that all media were fully acclimatised, having been exposed to acidic groundwater in anaerobic conditions for 36 six days during the initial test run.

Media #1 and #3 showed a rapid rise in pH from 4.2 to 6.0 (#3) and 6.3 (#1) over the first 4 h of contact (Fig. 2). Within 24 h of contact these levels stabilised to 5.9 (#3) and 6.2 (#1). Media #4 showed a much slower change, taking 24 h to reach pH 6.2 and stabilising to pH 6.3 after 36 h of residence in the vessel.

Redox potential effects were similar, media #1 and #3 reached minima of –54 and –70 mV, respectively, in 4 h and stabilised to around –45 and –70 mV, respectively, after 24 h. The redox potential in vessel #4 declined much more slowly, reaching a stabilised minimum of –70 mV after 36 h.

Effects on alkalinity, acidity and metals concentrations are expressed in terms of removal (addition in the case of alkalinity) per litre of water and per kilogramme of media. The expression removal is made with reference to the concentrations at the beginning of the test, i.e. mass removed = (mass at $t = 0$)−(mass at $t = t$).

Media #1 shows the greatest addition of alkalinity during the first 4 h of contact (53 mg l^{-1} kg^{-1}, Fig. 3). This dropped over the following 8 h period to a stable level of 47 mg l^{-1} kg^{-1}. After 48 h, the addition rate increased to 58 mg l^{-1} kg^{-1}. Media #3 showed a similar form of reaction, but taking 8 h to reach maximum addition of 30 mg l^{-1} kg^{-1} and then declined to a stable level of around 20 mg l^{-1} kg^{-1}. Media #4 behaved in a distinctly different fashion, taking 48 h to reach maximum alkalinity addition (52 mg l^{-1} kg^{-1}) and then declining slightly after this period to 48 mg l^{-1} kg^{-1}.

The trends described above apply to acidity, iron, and manganese removal (Figs. 3–6), that is media #1 and #3 showed greatest removal during the first 4 h of contact and this diminished within 24 h of contact to a stable level. Media #1 performed consistently better than media #3. Media #4, however, took 24 h to establish greatest removal and then remained at this level for the remainder of the investigation. This level of performance is consistently better (i.e. greater removal per litre per kilogramme) than that for media #1.

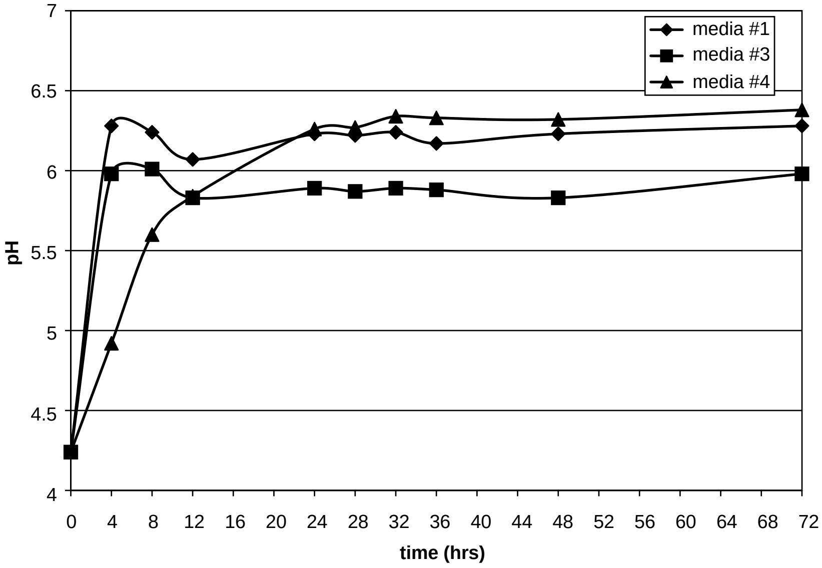

Fig. 2. pH effects.

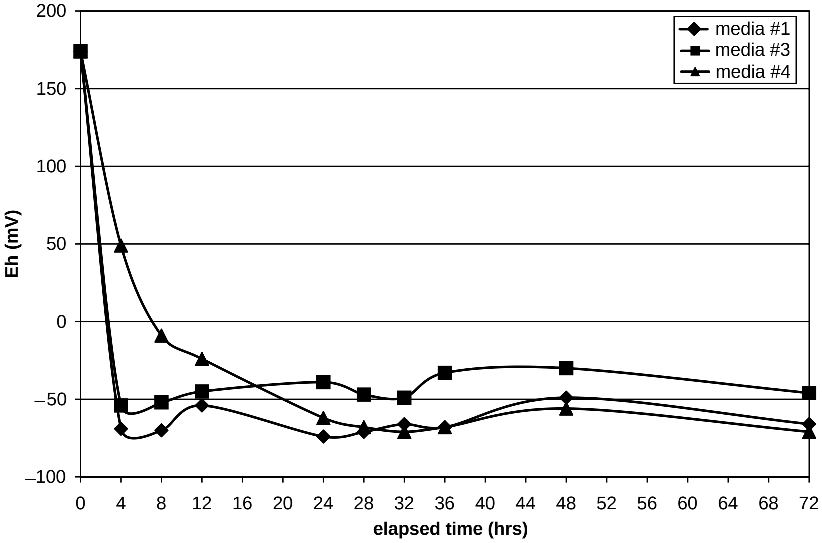

Fig. 3. Eh effects.

It is believed that the asymptotic level of metals removal attained by all media is due to the sealed system reaching equilibrium conditions.

Media #1 and #3 showed very similar and stable levels of aluminium removal from the outset of the experiment (16.0 and 15.7 $\mathrm{mg\,l^{-1}\,kg^{-1}}$, respectively). Media #4 took approximately 24 h to reach its maximum removal of 15.5 $\mathrm{mg\,l^{-1}\,kg^{-1}}$.

Results for sulphate removal vary substantially within the test period. Media #1 and #4 show maximum removal at 24 h, whilst media #3 shows maximum removal at 36 h. Over the duration of the test period, all media show removal of sulphate in the order of 200–300 $\mathrm{mg\,l^{-1}\,kg^{-1}}$. Of these, media #4 shows greatest removal ($\sim$300 $\mathrm{mg\,l^{-1}\,kg^{-1}}$) whilst media #1 shows least removal ($\sim$200 $\mathrm{mg\,l^{-1}\,kg^{-1}}$). It is noted that the time series maxima and minima coincide with maxima and minima for the redox potential data. It is possible that these phenomena are related. Alternatively, the fluctuations could be an artefact of the enclosed system achieving equilibrium.

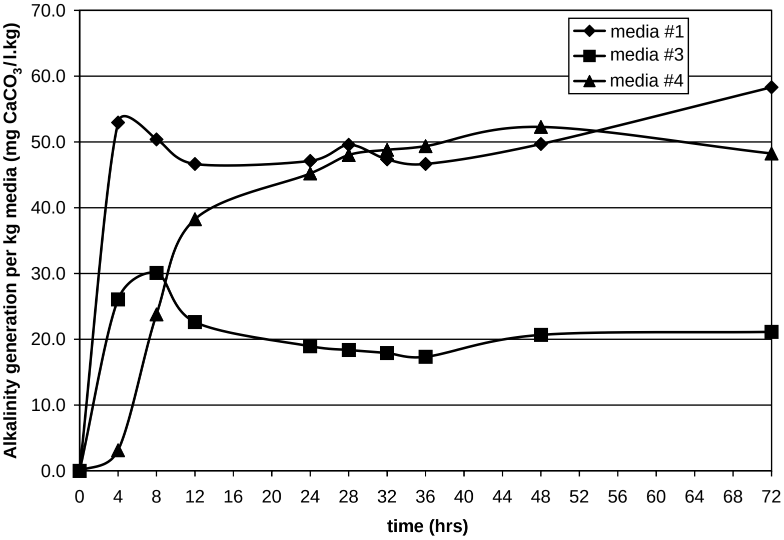

Fig. 4. Alkalinity generation.

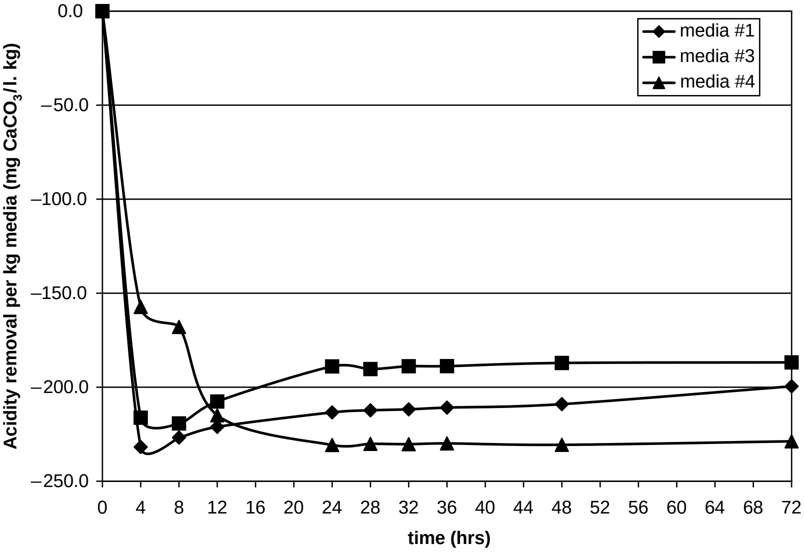

Fig. 5. Acidity removal.

Saturation indices prepared for 8.30 am samples collected during trial 2 are presented in Table 4. Saturation indices are shown for selected minerals of relevance to observed changes in water quality in trial 2, calculated as log(IAP)/K_T values using WATEQ4F [20]. Values significantly below zero (<-0.1) indicate the water to be under-saturated with respect to the mineral in question (so that it would tend to dissolve in the water if present), whereas values $>+0.1$ indicate super-saturation (so that the mineral tends to precipitate from the water). Equilibrium is denoted by values around 0.0 (in practice: $-0.1<$equilibrium$<+0.1$).

5. Discussion

5.1. Permeability

Benner et al. [10] have suggested that the optimum permeability for a reactive barrier is one order of magnitude greater than that of the aquifer in which it is constructed. The cattle manure shows permeability value similar to that of the colliery spoil and therefore does not satisfy this requirement. Furthermore, the measured permeability is significantly affected by surcharging mass. The surcharging mass is analogous

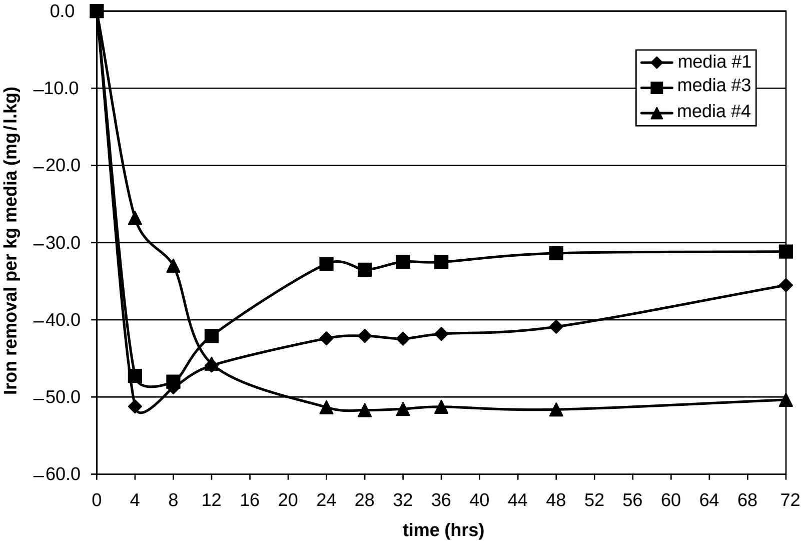

Fig. 6. Iron removal.

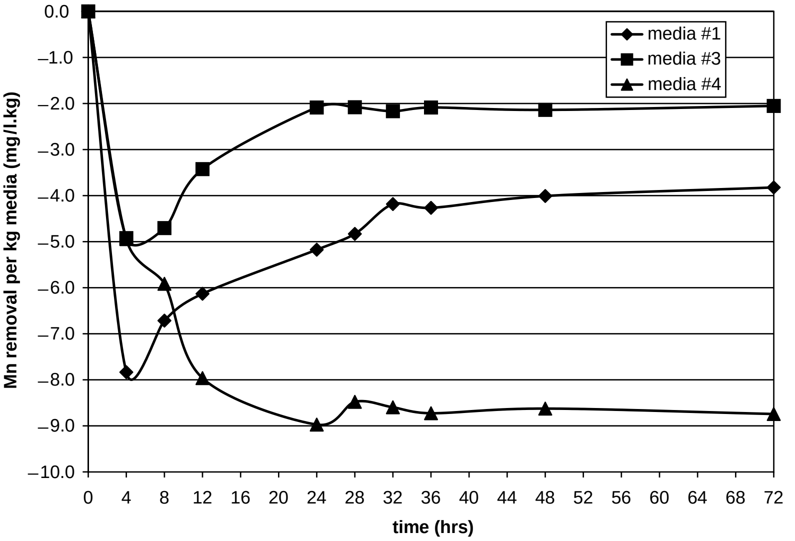

Fig. 7. Manganese removal.

to the self-weight of the media: at a given point in the reactive barrier the media will be experiencing a compressive force due to the weight of media above it. It therefore follows, and these results support this statement, that the permeability of a barrier using cow manure as the reactive media will vary with depth and flow within the barrier will therefore be affected.

A key requirement to successful treatment using reactive barrier technology is the need to avoid preferential flow or 'channelling' within the barrier. This is achieved by using a homogeneous mixture. The cattle manure was found to be very inhomogeneous due to layers of straw and compaction by handling equipment. Overall, the manure was highly unsuitable for use in the reactive barrier and it was therefore excluded from further studies.

Given the requirement for $K_{\text{media}} \geqslant 10 \times K_{\text{spoil}}$, composite #2 would appear to be the most suitable choice. However, reactivity tests carried out concurrently with the permeability investigation showed consistent poor reactive performance from this media and it was excluded from further studies. It is interesting to note that composite #1, with the lower proportion of

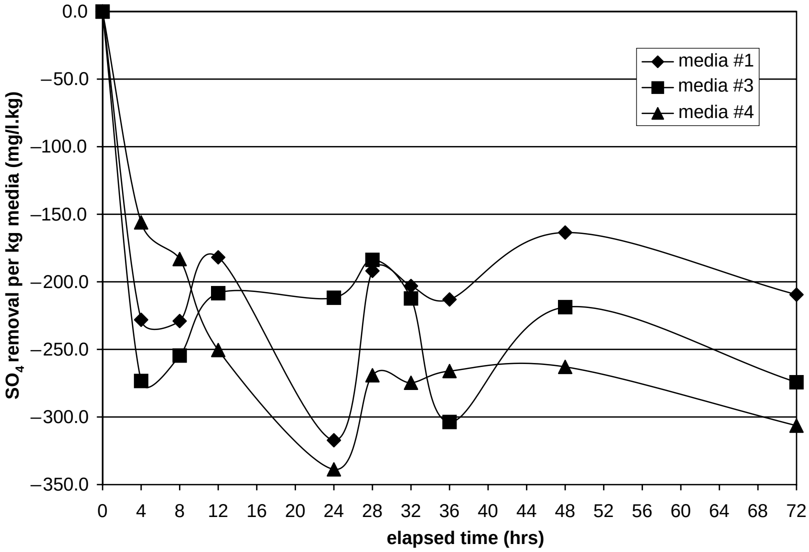

Fig. 8. Sulphate removal.

Table 4
Saturation indices

Media no.	Mineral / Sampling date	Gypsum	Anhydrite	Ferrihydrite	Siderite	Rhodocrosite
	7-9-1999	0.11	−0.10	−4.74	<-15	<-15
1	8-9-1999	0.23	0.02	−3.37	1.38	0.94
	9-9-1999	0.25	0.03	−2.99	1.38	0.97
	10-9-1999	0.26	0.04	−3.05	1.57	1.08
3	7-9-1999	0.11	−0.10	−4.74	<-15	<-15
	8-9-1999	0.17	−0.04	−3.68	0.78	0.32
	9-9-1999	0.16	−0.06	−3.68	0.77	0.29
	10-9-1999	0.13	−0.08	−3.48	0.95	0.47

Saturation indices for selected minerals of relevance to observed changes in water quality in trial 2, calculated as $\log(\mathrm{IAP})/K_T$ values using WATEQ4F [20]. Values significantly below zero (<-0.1) indicate the water to be under-saturated with respect to the mineral in question (so that it would tend to dissolve in the water if present), whereas values $>+0.1$ indicate super-saturation (so that the mineral tends to precipitate from the water). Equilibrium is denoted by values around 0.0 (in practice: $-0.1<$equilibrium $<+0.1$).
Note on mineral compositions: Gypsum—$CaSO_4 \cdot 2H_2O$; Anhydrite—$CaSO_4$; Ferrihydrite—$FeOH_3$; Siderite—$FeCO_3$; Rhodocrosite—$MnCO_3$.

limestone chips, shows a permeability approximately one order of magnitude greater than composite #2. This result was contrary to the expectations of the authors and the results found by Benner et al. [10]. Determination of the porosity values of the media showed that media #1 had the highest porosity (34%), followed by media #2 (33%). The limestone chips alone were found to have porosity 32%. It is therefore apparent, and logical, that the porosity of the mixtures affects their permeability values. As to why the porosity increases as organic fraction increases, it is suggested that the angular chips pack closely when no organic material is present. The addition of organic material may partially occupy the voids between the chips, pushing the chips further apart and thus increasing the porosity and availability of flow paths.

Results from the surcharge trials show that, while the permeability of media #1 is affected slightly by surcharge, this effect is not significant enough to substantially affect the flow regime within the barrier. Media composite #1 is therefore expected to perform satisfactorily with regard to the surcharge conditions likely to be experienced within the Shilbottle reactive barrier.

5.2. Reactivity

It can be clearly seen that media #1 offers greater addition of alkalinity and removal of metals and acidity than media #3. The logical conclusion is therefore that the inclusion of limestone chips in the media mixtures is beneficial. These two media also clearly show a short period of time in which treatment is optimal, typically during the first 4 h of contact. This reduces within 24 h: what is seen as a decline in removal is an actual increase in observed concentrations of iron and manganese. This phenomenon has been observed at several passive treatment sites in England and is generally referred to as the 'honeymoon' period. This period is typically characterised by impressive levels of metals and acidity removal which later decline to a lower 'operational' level. This honeymoon period is caused by reversible sorption of metals to 'fresh' (i.e. uncontaminated) organic material. After a duration of exposure metals are released from the organics back to solution, accounting for the observed rise in concentrations.

Media #4 exhibits very different characteristics. Approximately, 8 h pass before the pH level falls to that generally recognised as acceptable for bacterial sulphate reduction to occur (pH 5–6, [21]). It is therefore suggested that possible inhibited activity of sulphate reducing bacteria could be a cause for this substrate's poor performance (in terms of iron removal) during the first 8 h of exposure. It is interesting to note that after 24 h the performance of this mixture is consistently superior to that of media #1. Media #4 does not appear to exhibit reversible metal sorption within the time period of the study (72 h). There are a number of possibilities: the study may have terminated before desorption from the organics began, or the organic material used in this mixture may exhibit only one way sorption of metals onto the mixture. This aspect of the study requires further investigation.

Gavaskar et al. [6] have already justified the need for caution in applying batch test results to dynamic flow situations. Nevertheless, taking this advice into account, the results are sufficiently encouraging to support some prediction of full-scale performance. Residence time within the proposed reactive barrier at Shilbottle is estimated as 1.7 days. This estimate is based on groundwater flow rate per unit cross sectional area at the toe of the spoil heap of $0.19\,m^3\,day^{-1}$, barrier thickness of 1 m and media porosity of 32%. The results from this study, notwithstanding the points raised in the discussion above, suggest an acidity removal of $211\,mg\,l^{-1}\,kg^{-1}$ media may cautiously be expected if media #1 were used as the reactive material.

An image from the scanning electron microscope is shown in Fig. 9. The sample under analysis is filtrate collected from vessel #1 during the first set of reactivity tests, the fibres comprising the glass filter can be clearly seen. Analysis of the crystalline structure on the left of the image showed its composition to be predominantly calcium, sulphur and oxygen. This structure is almost undoubtedly gypsum (calcium sulphate).

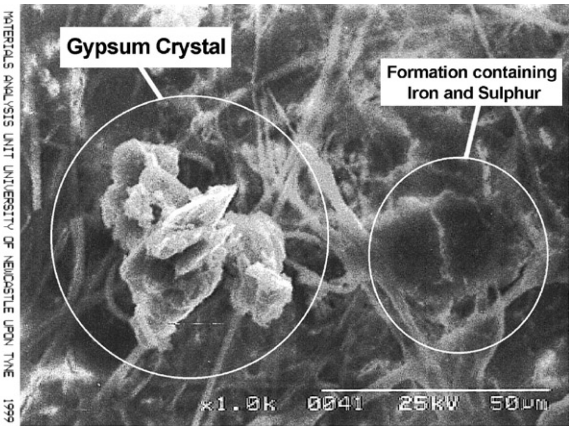

Fig. 9. Scanning electron microscope showing gypsum crystal and formation containing iron and sulphur.

The darker, amorphous mass, seen on the right, was found to contain predominantly iron, sulphur, calcium, potassium, silicon, and oxygen with lesser amounts of magnesium, aluminium, phosphorus and chloride. Analysis of other similar features showed the typical major constituents to be iron, sulphur, calcium and oxygen with aluminium and silicon appearing in some analyses. Significant silicon peaks occurred in those samples on the glass filters and these peaks are therefore attributed to the glass filter.

It is suggested that the amorphous mass is a combination of iron sulphide, a typical by-product of bacterial sulphate reduction in anaerobic, ferruginous waters, and calcium sulphate. The amorphous shape is attributed to iron sulphide forming on top of, or being included within, the gypsum crystals.

It is highly unlikely that iron sulphides were present in the cattle slurry screenings prior to the experiment. Iron is not known to be a major constituent of cattle slurry. Furthermore, iron monosulphides are aerobically unstable and would have degenerated whilst the slurry screenings were stored in the outdoor manure heap on the farm.

Solids scraped from the walls of the glass sample tubes were found to change to an orange colour during preparation (drying) for SEM analysis. SEM analysis of these samples was therefore excluded, however, this degeneration is indicative of iron, present in the black solid, oxidising during the drying process.

It is interesting to note that formation of the black precipitate was observed for media #1 during the second reactivity test run. For both test runs, formation of this precipitate was not observed for composite #4. This evidence appears to suggest that bacterial sulphate reduction is occurring in composite #1 but not in composite #4. If this is the case then the effective metal removal exhibited by this composite must be attributable to some other mechanism or combination of mechanisms.

The saturation indices for gypsum show super-saturation in absolutely every case, lending support to the deduction that precipitation of gypsum occurs within the reaction vessel. The above also explains some of the sulphate loss from solution. In terms of molar concentrations and assuming that all calcium left solution as gypsum (a conservative assumption, since calcite was also approaching equilibrium by 10 September 1999, saturation index -0.06), an equal molar concentration of SO_4 would be removed to form $CaSO_4 \cdot 2H_2O$ (gypsum). This could explain the $0.0018\,mol\,l^{-1}$ of sulphate loss by precipitation of gypsum, out of a total net sulphate loss of about $0.06\,mol\,l^{-1}$ over the 4 days. This means that about 3% of sulphate lost from solution can be explained by the precipitation of gypsum, with the remainder presumably forming amorphous sulphides. Interestingly, the measured Eh values were still too high for pyrite or marcasite precipitation to be predicted, however, this could be explained by some aeration of the samples during extraction and measurement.

Some of the other minerals listed in the table are interesting also. The anhydrite saturation index remains level at the saturation point, but never becomes super-saturated, which suggests gypsum is the only $CaSO_4$ phase of importance. Ferrihydrite (ochre) is strongly under-saturated throughout, which means it would dissolve if present in the substrate, and therefore cannot explain iron loss from solution. Indeed, iron would not be expected to be removed from solution as ochre in an oxygen-free environment as found in the reaction vessel. Some other phase(s) need(s) to be invoked to explain iron loss therefore; iron sulphides are an obvious postulate, but interestingly siderite ($FeCO_3$) also could be a strong candidate, with super-saturation developing in both media for all sampling times except experiment start (i.e. 7 September 1999, 8:30am).

The net loss of some $40–70\,mg\,l^{-1}$ of manganese from solution is also consistent with the super-saturation of rhodocrosite ($MnCO_3$) predicted by the code and is in line with data and deductions from other PRBs presented by Younger et al. [18]. The relatively slow removal of manganese from solution in this manner is consistent with recent reports of slow precipitation kinetics for rhodocrosite in anaerobic aquatic environments [22].

6. Conclusions

1. Subsurface reactive barriers have been used to successfully treat acidic mine drainage in Canada and offer great potential for doing the same in the UK.
2. The selection of the reactive media to be used is of paramount importance, with particular reference to permeability and reactivity.
3. Constant head permeability tests, with various surcharge conditions applied to the media under test, have shown that unadulterated cattle manure is unsuitable for use due to poor permeability and inhomogeneity.
4. Media mixtures containing 50% 10 mm grade calcite limestone chips showed better alkalinity addition and metals removal than a blank containing 50% pea gravel.
5. Media mixtures containing cattle slurry screenings, a finely divided, easily handled form of cattle manure, showed reversible sorption of iron and manganese. Optimum removal occurred in the first 4 h of contact and ‘operational’ removal occurred after 24 h of residence time.
6. The media mixture containing 50% limestone chips and 50% green waste compost showed a 24 h period to achieve maximum addition of alkalinity and maximum removal of acidity and metals. Mixtures containing 25% green waste compost and 25% slurry screenings achieved maximum addition/removal in 4 h.
7. The media mixture containing 50% limestone chips and 50% green waste compost did not exhibit reversible iron and manganese sorption within the time period of the study (72 h).
8. The likely presence of iron sulphide in samples drawn from composite #1 during both test runs indicates bacterial sulphate reduction is occurring in this composite. It is unclear what mechanism(s) are responsible for metals removal in composite #4.

Acknowledgements

The authors would like to thank Northumberland County Council, and in particular Aln Elliott, Project Manager, Environment Directorate for funding the site investigation. Karen Johnson (Civil Engineering Department, University of Newcastle upon Tyne), Adam Jarvis (formerly Civil Engineering Department, University of Newcastle upon Tyne and now with IMC Ltd), and Paula Canteli (Escuela de Minas, Oviedo, Spain) are thanked for their help with the site investigation and laboratory analyses. Finally, Pat Johnston and Fiona Read (Civil Engineering Laboratories, University of Newcastle upon Tyne) are thanked for their support.

The second author acknowledges the funding of the European Commission's PIRAMID project (EVK1-CT-1999-000021) for the later stages of the work.

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