REMEDIATION OF CIRCUM-NEUTRAL, LOW-IRON WATERS BY PERMEABLE REACTIVE MEDIA

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Abstract

Research into the remediation of contaminated waters has generally concentrated on the treatment of Fe-rich, acidic waters where the mechanisms of metal removal are well understood. However, many former mining areas of the British Isles are characterised by circum-neutral, low-Fe drainage with high levels of dissolved Zn, Pb and Cd (e.g. mid Wales, North Pennines and the Irish Republic). These waters present a challenging target for remediation, as the low Fe content of many of these waters means that treatment by co-precipitation of metals with Fe-oxyhydroxides is not viable. This paper reports the results of preliminary experiments comparing metal removal rates between selected circum-neutral and acid mine drainage waters. Batch screening studies were conducted by reacting 5 common reactive materials (zero valent iron, activated carbon, compost, limestone and fly ash) with circum-neutral mine drainage from geologically different sources. The Nenthead Pb-Zn mine in the north Pennines is carbonate hosted with drainage typically containing 7 mg L^{-1} Zn, 0.02 mg L^{-1} Pb and 0.01 mg L^{-1} Cd. The Bwlch Pb-Zn mine in mid Wales is siliciclastic hosted and typically contains 22 mg L^{-1} Zn, 2.4 mg L^{-1} Pb, and 0.05 mg L^{-1} Cd. These results were compared to drainage from a notorious acid mine drainage site in north Wales, Parys Mountain Cu mine, which typically contains 27 mg L^{-1} Zn, 0.06 mg L^{-1} Cd, 0.04 mg L^{-1} Pb. The experiments have yielded very encouraging results, with Zn, Pb and Cd removal from the circum-neutral waters generally occurring more rapidly than from the acidic water. All reactive materials showed over a 90% reduction in Zn, Pb and Cd concentrations over a 10 minute reaction period for the Bwlch and Nenthead waters (pH 6.2 and 7.3, respectively). In contrast, a longer reaction period of 30-60 minutes was required to reduce concentrations in the Parys Mountain water (pH 2.5) to the same extent. Fly ash derived from a peat-fired power station was the most effective material for the removal of all metals from solution, with over 98% of Zn being removed after only 2 minutes. The presence of carbonate in the mine water was shown to impede in the removal of Pb from solution, but aid in the removal of Zn, possibly a result of the precipitation of zinc carbonate. Overall, these findings demonstrate the potential of common reactive materials to remediate a range of mine sites with circum-neutral drainage. The rapid reaction rates imply that short residence times are required, hence allowing smaller treatment systems to be utilised for remediation in such areas.

Introduction

Mine drainage from both metal and coal mines sites is a continual source of environmental contamination and ecological damage. Many former mining areas of the UK are characterised by abandoned spoils heaps and extensive underground workings, which now leach grossly contaminated waters into local watercourses. This often causes them to fail Environmental Quality Standards by up to several orders of magnitude for decades or even centuries after mining ceases.

The chemistry of mine drainage can vary significantly and is dependent upon a number of factors, including the geochemical conditions at the point source of weathering, the chemistry of the ore deposit and the nature of the host rocks and gangue minerals. Until recently, attention has tended to focus on the ferruginous acidic discharges that emanate from many abandoned metal mine sites, i.e. 'Acid Mine Drainage' (AMD) (e.g. Nordstrom et al., 2000). In reality, however, many metal-laden mine discharges are characterised by a circum-neutral pH due to either (i) an absence of pyrite in the ore, hence minimising the acid generating potential on site, or (ii) the presence of a carbonate host rock or gangue, which effectively neutralises any acidity produced (Blowes et al., 2003). Many historical mining areas in the British Isles are characterised by such circum-neutral, low-Fe drainage, including the North Pennines (Nuttall and Younger, 2000), mid Wales and Southern Ireland (Aslibekian et al., 1999).

The introduction of water quality guidelines and the EU Water Framework Directive (2000/60/EC) have meant that remediation of polluted watercourses is becoming increasingly necessary in order to reduce contaminant concentrations to legal guidelines. Traditional 'active' methods of treatment have high associated operating costs and, as a result, 'passive' treatment systems have emerged as an attractive alternative remediation technology over the past 15 years. At present, several methods of passive water treatment are in use in the UK, including aerobic wetlands, anaerobic compost wetlands, Reducing and Alkalinity-Producing Systems (RAPS), limestone filter beds and subsurface reactive barriers (Younger, 2000).

Permeable Reactive Barriers (PRBs) have gained popularity in recent years owing to their ability to treat a range of contaminants with minimal operating and maintenance costs. These are engineered walls of reactive materials that are installed in the path of a contaminant plume to both control the rate of groundwater flow and to provide *in-situ* remediation of contaminants. PRB technology relies on natural groundwater gradients to move the contaminant plume through the zone of reactive materials (Morrison et al., 2002). Contaminants are removed by either adsorption onto the surface of the reactive material or by a combination of chemical, physical and biological reactions, which promote precipitation or stabilisation of contaminants. PRBs offer a significant advantage over many passive treatment technologies, as they have minimal land requirements and do not demand significant above-ground infrastructure. The efficiency of metal removal using PRBs has shown to be strongly dependent on groundwater hydrochemistry. pH and major ion content in particular play a major role.

Remediation of circum-neutral, low-Fe mine waters

At present, the majority of passive treatment plants in the British Isles treat acidic, ferruginous waters at abandoned coal and metal mine sites, where the mechanisms of metal removal are well understood and treatment is aided by high concentrations of Fe in solution. Remediation of these waters may involve simply buffering the pH to above the pH of iron hydrolysis, effectively removing metal contaminants by co-precipitation with iron (e.g. Whitehead and Prior, 2005). Conversely, treatment of circum-neutral, low-Fe waters is generally considered more difficult, as the low iron content of many of these waters means that remediation is not aided by the co-precipitation of metals with iron (oxy)hydroxides. Many of these circum-neutral mine drainage waters are also located in areas with carbonate bedrock, meaning that drainage waters may be characterised by high major cation (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) and carbonate concentrations, which are known to affect remediation by competing for sorption sites on the reactive materials (Van Geen et al., 1994). As a result these circum-neutral, low-Fe waters are considered difficult to remediate using traditional passive treatment methods. The primary aim of this research was to determine whether a range of traditional reactive materials can be used to effectively remove metals from circum-neutral mine waters. A series of mines from the UK and Ireland were selected based on their hydrochemistry and pH. This paper reports a small selection of the data from two sites with circum-neutral mine drainage in the North Pennines (Nenthead) and mid Wales (Bwlch). These results were compared to drainage from an acid mine drainage site in north Wales (Parys Mountain Cu mine).

Sample sites

1. The Nent Valley in the North Pennines was intensively exploited for Pb and Zn for over two centuries. The Caplecleugh Level (NY 781 436) was the principal level exploited from Nenthead and the adit now drains a large complex of workings from the Nenthead area. The calcareous host rocks for the Pb-Zn deposits ensure that the water draining from the mine is characterised by a circum-neutral pH.
2. Bwlch Pb-Zn mine site (SN 703 825) is located approximately 8 miles east of Aberystwyth and was worked extensively during the 19th Century, with galena and sphalerite being the primary ore minerals extracted. Although the site was partially remediated during the late 1990s, monitoring data show that drainage waters still contain significant quantities of Zn, whilst the low pyrite content of the ore generates drainage characterised by a circum-neutral pH.
3. Parys Mountain (SH 438 912) lies in north-east Anglesey and was the world's largest Cu producer during the 18th and 19th Centuries. Although the main period of extraction on site ceased in 1904, oxidation of sulphide minerals within the spoil heaps has meant that the site is characterised by acidic, metal-rich ferruginous drainage waters.

Table 1. Hydrochemistry of Bwlch, Nenthead and Parys Mountain waters (all values in mg L^{-1}).

	Host rock for deposit	pH	Zn	Pb	Cd	Fe	Ca	Mg
Nenthead	Calcareous	7.3	7	0.02	0.01	0	46	24
Bwlch	Siliciclastic	6.2	22	2.40	0.05	0.02	26	8
Parys Mountain	Volcanics	2.5	27	0.04	0.06	106	10	47

Preliminary batch screening study methodology

Batch screening studies were used as an initial method to compare metal sorption onto a range of traditional reactive materials using waters from the three sites listed above. The primary aim of these initial experiments was to determine whether metal removal from circum-neutral mine waters is comparable to the removal of metals from acid mine waters.

Six commonly-used reactive materials were selected for screening, including Zero Valent Iron (ZVI), activated carbon, limestone chippings (500-1000 μm), compost and fly ash from a peat-fired power station. These materials were reacted with a constant volume of mine water selected from Bwlch, Nenthead and Parys Mountain. Batch screening studies were designed with two main variables: (i) weight of reactive material and (ii) reaction time. The 'weight' experiments were carried out by separately reacting 0.1, 0.5, 1.0, 5.0 and 10.0 g of the five reactive materials with 50 mL of the three mine waters. Relatively large masses of reactive materials were used for these initial experiments to evaluate the behaviour of the reactive materials with the mine waters. Samples were shaken using a reciprocal shaker for 30 minutes and then filtered through Whatman No.1 filter papers into acid washed 60 mL HDPE bottles. The pH of the samples was recorded prior to acidification. The 'time' experiments were conducted by separately reacting 5 g of the five reactive materials with 50 mL of Nenthead, Parys Mountain and Bwlch waters. The samples were shaken for varying lengths of time (2, 5, 10, 20, 30, 60, 180, 360 minutes) in order to allow reaction rates to be determined. All experiments were carried out in acid washed 125 mL conical flasks, with quality control being ensured though preparation of three replicates for each sub-experiment. All samples were analysed for Cu, Fe, Zn, Mg, Ca by Atomic Absorption Spectrophotometry (AAS) and for Na and K by Atomic Emission Spectrophotometry (AES). Analysis of trace metals was carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Results and Discussion

All reactive materials were effective at removing Pb, Zn and Cd from the three water types (Bwlch, Nenthead and Parys Mountain) (Fig. 1), although the relative proportion of metal removal was dependent on the type of reactive material and the hydrochemistry of the raw, untreated water. In general, metal removal from the circum-neutral waters (Bwlch and Nenthead) was greater and occurred more rapidly than from the acidic water. For example a 10 minute reaction period was generally sufficient to achieve over 90% Pb, Zn and Cd removal from Bwlch and Nenthead waters, whilst a longer reaction period of between 30 and 60 minutes was required to reduce metal concentration in the Parys Mountain water to the same extent. These higher amounts of metal removal from the circum-neutral waters may be explained by the strong pH-dependence of sorption, with increased sorption generally occurring at higher pH (e.g. Stahl and James, 1991).

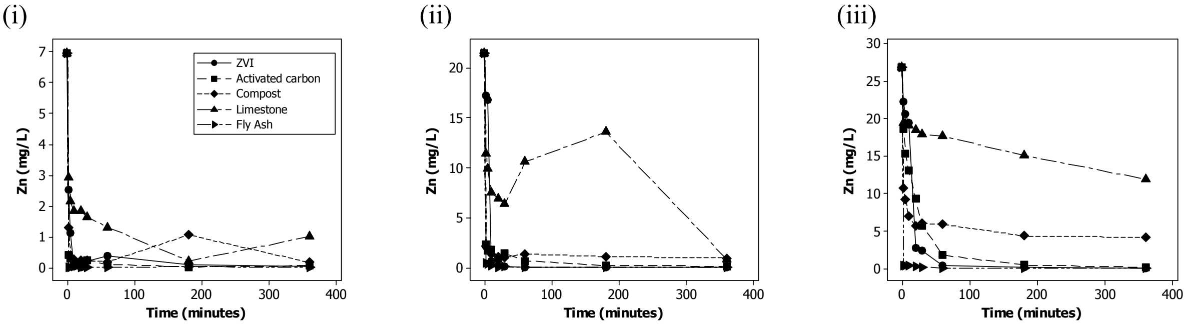
(i) (ii) (iii)

Figure 1. Zinc removal from (i) Nenthead (ii) Bwlch and (iii) Parys Mountain waters (starting concentrations given in Table 1).

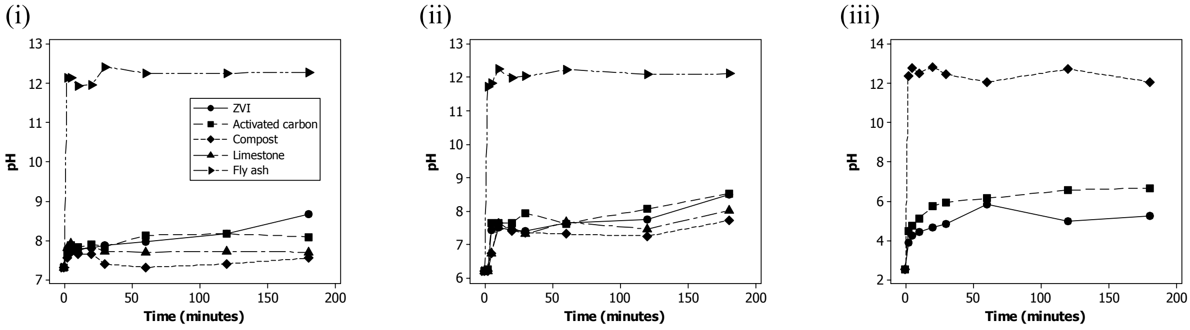
(i) (ii) (iii)

Figure 2. Sample pH for (i) Nenthead (ii) Bwlch and (iii) Parys Mountain waters.

Although metal removal from the circum-neutral waters occurred more rapidly than from the acidic mine water, the relative proportion of contaminant removal was dependent upon the metal of interest and the hydrochemistry of the mine water (Fig. 3). For example Pb removal occurred most rapidly from the Bwlch water, whilst Zn removal occurred more rapidly from the Nenthead water (originally sourced from a carbonate-hosted Pb-Zn mine). The latter may be explained by the formation of zinc carbonate $ZnCO_3$ (smithsonite) at pH values between 7.5 and 8 (Nuttall and Younger, 2000). The higher initial pH (7.3) of the untreated Nenthead mine water meant that only a small increase in pH, and hence a shorter reaction time, was required to promote smithsonite precipitation. In comparison, Bwlch and Parys Mountain waters (initial pH values of 6.2 and 2.5, respectively) required greater increases in solution pH and hence longer reaction times to allow smithsonite to precipitate.

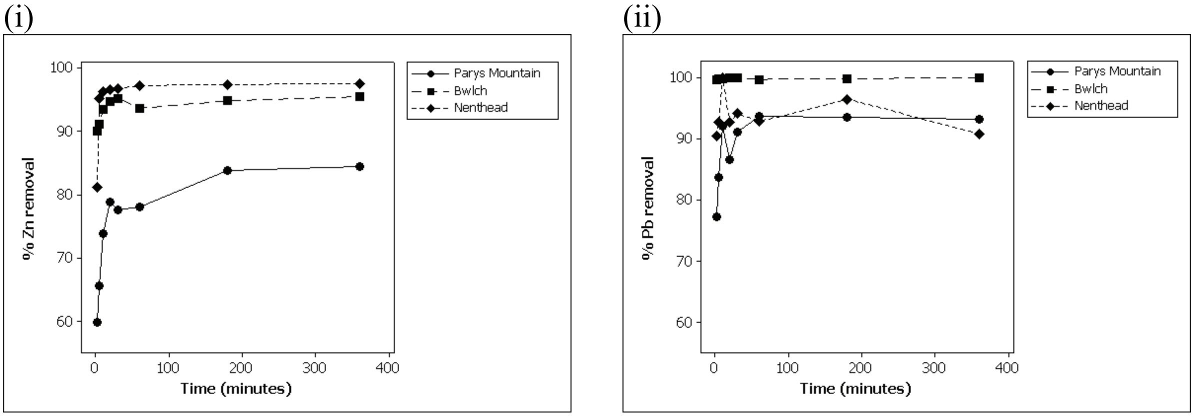

Figure 3. Comparison of (i) Zn and (ii) Pb removal from Bwlch, Nenthead and Parys Mountain waters by compost.

1. Comparison of reactive material performance

All tested materials proved efficient at removing metals from solution, with a general efficacy order of fly ash > ZVI > activated carbon > compost > limestone chippings. Fly ash showed the highest removal capacity for Pb, Zn and Cd from all waters, with metal removal occurring very rapidly. This is thought to be related to the extremely alkaline nature of the fly ash, with only a 2 minute reaction time being sufficient to raise solution pH to approximately 12 in all waters. This pH increase would be sufficient to cause metal precipitation as hydroxides, possibly accounting for the high rates of metal removal by this reactive material. Activated carbon, ZVI and compost were also capable of achieving over 90% Pb, Zn and Cd removal from the three water types. The dominant metal removal mechanisms were thought to be sorption and reductive precipitation. For example metal removal by ZVI occurs by a combination of reductive precipitation and metal adsorption onto the surface of the reactive material (Blowes et al., 2003). In comparison, metal removal by activated carbon and compost occurs primarily by sorption onto the organic substrate.

In general, the limestone chippings were found to be the least effective for the removal of Pb, Zn and Cd, particularly from the acidic Parys Mountain water. Metal removal by limestone is thought to occur by a combination of sorption and precipitation of metal carbonates on the reactive material surface (García-Sánchez and Álvarez-Ayuso, 2002). The limited efficiency by the limestone chippings may therefore be related to its relatively small surface area and hence the limited number of sorption sites compared to the other reactive materials used in this study.

2. Effect of reaction time

The time-dependent behaviour of metal removal was determined by varying the contact time between the reactive materials and the three waters. As expected, increasing the reaction time resulted in greater amounts of metal removal, although the rates and quantities of metal removal were dependent on the reactive material, the metal of interest and the attendant water chemistry. The time required to reach equilibrium varied for all metals, reactive materials and water types. In general, Zn and Pb removal plateaued after approximately 60 minutes, whereas a reaction period of 180 minutes was required before Cd removal reached its maximum.

3. Effect of mass of reactive material

As expected, increasing the mass of reactive material resulted in higher metal removal rates from Bwlch, Nenthead and Parys Mountain waters. This is related to the increased number of surface sites available for metal sorption, allowing greater quantities of metals to be removed from solution. Again, the results demonstrate that metal removal from the circum-neutral Bwlch and Nenthead waters is more effective, with only 1 g of reactive material required in 50 mL of mine water to reduce metal concentrations by over 80%. This can be compared to the 5 g of material required in Parys Mountain water to reduce Zn, Pb and Cd concentrations to the same extent.

Conclusions

The preliminary batch screening studies produced very encouraging results in terms of the potential of traditionally-used reactive materials to remediate circum-neutral, low-Fe mine waters. The findings demonstrate that reaction rates are rapid and smaller quantities of reactive materials are required to achieve significant removal of Pb, Zn and Cd from circum-neutral mine waters compared to acidic mine waters. The results demonstrate the potential of these reactive materials to treat mine waters from a number of further sites in the British Isles with circum-neutral drainage. Furthermore, the rapid reaction rates observed have significant implications for the residence times required for PRBs and other passive treatment systems. This could significantly reduce the land area required for treatment systems in areas with circum-neutral mine drainage.

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