# Field Trials of Low-Cost Permeable Reactive Media for the Passive Treatment of Circum-Neutral Metal Mine Drainage in mid-Wales, UK

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**Abstract** This paper addresses the ability of five low cost adsorbent/reactive materials to remove Zn, Pb and Cd from Fe-poor, circum-neutral pH metal mine water in mid-Wales, UK. Compost, iron ochre, basic oxygen furnace slag (BOS) blended with blast furnace slag, waste shell material and fly ash were used in a series of small-scale passive treatment cells to assess metal removal from mine drainage initially containing, on average, 23.5 mg/L Zn, 550 µg/L Pb and 50 µg/L Cd. Treatment plants contained between 2 and 20 kg of reactive media, with a 15 minute residence time and treated up to 1 L/minute. Fly ash from a peat fired power station was found to be the most effective material for metal removal, with over 99.9% Zn, Pb and Cd removed from over 1000 litres of water. The other materials tested initially achieved high levels of metal removal (with between 75 and 99.9% Zn, Pb and Cd removed), however all of the materials saturated with Zn after less than 200 litres of water had been treated. The results of the pilot-scale field trials can be scaled to demonstrate that a modest sized fly ash treatment cell only 2.7 x 2.7 x 1 metres in size would be sufficient to remove 90% of the total metal load from this mine (10 L/minute) for a one year period.

**Key Words** Passive treatment, low-cost reactive materials, circum-neutral pH metal mine water

## Introduction

Mine drainage from abandoned metal mines is a significant source of environmental contamination and ecological damage, with an estimated 200km of watercourses in the UK being affected (Younger, 2002). The European Union Water Framework Directive (WFD) (2000/60/EC) sets stringent targets for surface and groundwater quality, which must be met if UK watercourses are to reach the 'good' status stipulated by the directive. At present it is estimated that 9% of rivers in England and Wales are failing to meet the WFD targets as a direct result of pollution from abandoned mining areas (Johnston and Rolley, 2008). Thus the remediation of metal-rich discharges from former metal mines is becoming increasingly necessary if WFD targets are to be met.

The passive treatment of mine waters has become increasingly popular over the past 20 years as a result of its low operating and maintenance costs. In particular, low cost adsorbent/reactive materials (e.g. iron ochre, clay) are gaining significant attention as a result of their ability to achieve high levels of metal removal on a laboratory scale (e.g. 52.9 mg/g Zn by bentonite clay (Mellah and Chegrouche, 1997). Reactive/adsorbent materials are particularly suitable for metal removal in mining areas with circum-neutral pH drainage. This is because metal removal by adsorption is strongly dependent on solution pH, with metal cations such as Pb, Cu, Zn and Cd sorbing more readily at circum-neutral to moderately alkaline pH values (e.g. Dzombak and Morel, 1990). However many effective reactive /adsorbent materials are either fine-grained with a low permeability (e.g. clay) and/or expensive (e.g. activated carbon), which precludes their use in full-scale passive treatment systems. This paper therefore addresses the ability of several low cost adsorbent/reactive materials (including BOS slag, fly ash and iron ochre) to remove Zn, Pb and Cd from circum-neutral metal mine water in mid-Wales.

## Methods

Field trials were carried out at Bwlch former Pb/Zn mine, mid-Wales (UK) in early March 2010. The mine was worked extensively during the late 19th Century, with an estimated 5700 tonnes of Pb ore being produced during this period. The mineralisation at Bwlch is hosted in Lower Silurian siliceous turbidites and the primary sulfide minerals are galena (PbS) and sphalerite (ZnS) with secondary chalcopyrite ($CuFeS_2$) hosted within a quartz gangue. The absence of pyrite in the mineralisation means that the drainage waters are characterised by a circum-neutral pH (≈ 6.3) and low Fe concentrations (<0.2 mg/L). However, elevated concentrations of Zn (≤ 30 mg/L), Pb (≤ 1 mg/L) and Cd (≤ 0.1 mg/L) in the mine drainage cause significant failure of WQS for these parameters. This equates to annual Zn loading in the local river of up to 160 kg based on a discharge of 10 litres per minute.

Five low-cost adsorbent/reactive materials were selected for the field trials; compost, basic oxygen furnace slag (BOS), iron ochre precipitate from a passive coal mine water treatment system, waste shell material from a seafood processing plant and fly ash from a peat-fired power station. These materials were employed in a series of five treatment cells 230 × 380 × 295 mm in size. The cells were designed to allow a maximum influent flow of 1 litre per minute and the bed thickness in each tank was calculated to give a residence time of approximately 15 minutes. In practice, however, the flow rates were ultimately controlled by the permeability of the materials and the head (which could be varied by an adjustable swan neck on the side of the tank) (Figure 1a). The crushed shell material (primarily whelk shells) was crushed to <5 mm and a 100 mm bed thickness was used. The tank containing the BOS slag also utilised a bed thickness of 100 mm. The compost, fly ash and iron ochre were mixed with sand to ensure adequate permeability and maintain flow rates. A 50:50 (w/w) compost and sand mixture was used (bed thickness = 100 mm) and the fine-grained nature of the fly ash and ochre (<65 µm) required them to be 'sandwiched' as a 20 mm thick layer between two layers of fine sand in order to prevent loss of reactive material from the bottom of the treatment cells (see Figure 1b). All treatment cells were run until breakthrough occurred or a steady-state effluent profile was achieved. Here, breakthrough is defined at a value of $C/C_0 = 0.1$ (or 90% metal removal) as this approximates to the removal of Pb from the Bwlch mine drainage to below EU WQS guidelines. Adopting the same definition for Zn or Cd however gives breakthrough values which are too low to be achieved, and thus for consistency, Zn and Cd breakthrough are also defined at $C/C_0=0.1$.

The treatment cells were deployed in the field for a two-and-a-half week period. Sampling was carried out hourly during the first six hours of the field trial, and approximately every 48 hours thereafter. At each sampling interval field measurements of flow rate, pH, Eh and electrical conductivity (EC) were carried out and influent and effluent samples were collected for metals analysis. All water samples were filtered to <0.45 µm and acidified to 0.5% v/v $HNO_3$ in the field. Samples were then immediately returned to the laboratory and stored at 4°C prior to analysis. An additional un-acidified sample was also taken for analysis of sulfate, chloride and nitrate.

## Results and Discussion

The results of the field trials are illustrated in Figure 2, which demonstrates that the materials varied in terms of their ability to remove metals from solution. Fly ash from a peat fired power station proved the most effective material, with concentrations of Zn, Pb and Cd reduced to below detection limits (and below EU WQS concentrations) in the first 1000L of water treated over a six day period. The other materials tested initially achieved high levels of metal removal (with between 75 and 99.9% Zn, Pb and Cd removed), however these rapidly saturated and effluent metal con-

(*a) Field Reactors*

*(b) Ochre sandwiched between sand*

***Figure 1*** *Set-up of the field trials* centrations rose steadily back to influent levels. Zinc breakthrough ($C/C_0 = 0.1$) occurred particularly rapidly after 4, 30 and 200 L for BOS slag, waste shell material and compost, respectively. This is likely to be a function of the high influent Zn concentrations (average = 23.5 mg/L) and relatively high flow rates compared to the volume of reactive material (0.11 – 0.89 L/minute) (Figure 2), which means that the metal adsorption capacity of the reactive materials is rapidly reached. Cadmium removal patterns were similar to those of Zn, with breakthrough curves for both elements being almost identical for the BOS slag, waste shells and peat fly ash treatment tanks (Figure 2). The removal of Pb, however, was generally maintained over longer time periods than Zn and Cd by all materials, with compost in particular removing over 80% of the Pb from 8000 litres of water. The flow rate of all treatment cells was measured throughout the field trials and was ultimately controlled by the material permeability. Average flow rates varied from a minimum of 0.11 L/minute (peat fly ash) to 0.89 L/minute (waste shell material). The low permeability of the iron ochre cell meant that flow rates were extremely low (<0.01 L/hr) and sufficient head could not be attained in order to achieve higher flow rates. This tank was consequently discontinued after approximately 12 hours.

The results of the field trials were scaled to determine the approximate size (mass and volume) of each reactive material that would be required to treat all the effluent from Bwlch mine (approximately 10 L/min and 23.5 mg/L Zn) to breakthrough concentrations for a one-year period. The results are given in Table 1, which shows that 90% of the Zn load could be removed from Bwlch discharge for 1 year using a treatment cell as small as 2.7 × 2.7 × 1 metres. Although the results of the field trials demonstrate that flow rates were slowest in the peat fly ash and compost treatment tanks, the scaled results show this is not overly detrimental to the estimated size of a full-scale

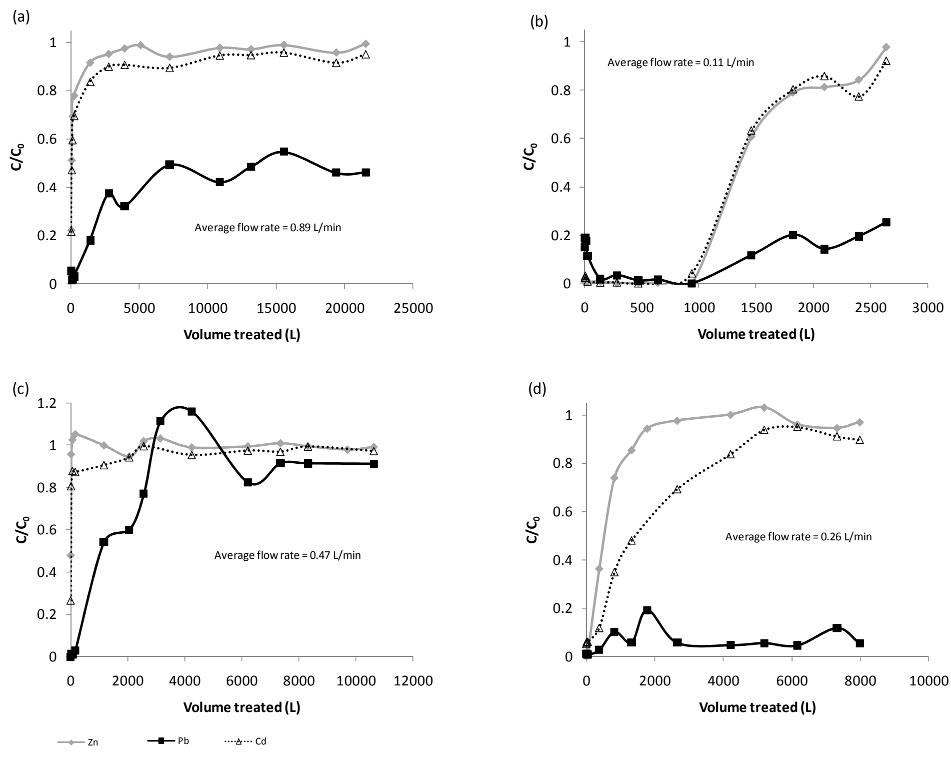


***Figure 2*** *Removal of Zn, Pb and Cd by (a) waste shell material; (b) peat fly ash; (c) BOS slag and (d) compost, where $C_0$ = influent concentration and C = effluent concentration. Average influent concentrations are: Zn = 23.5 mg/L, Pb = 0.5 mg/L and Cd = 0.05 mg/L*

*__Table 1__ Mass and volume of each material required to remove 90% of metal load from Bwlch mine discharge for a 1 year period*

| Material | Mass required (tonnes) | Area of treatment cell (metres)* |
|---|---|---|
| Peat fly ash | 7.5 | 2.7 x 2.7 |
| Waste shell material | 8333 | 81.6 x 81.6 |
| Compost | 56.9 | 9.7 x 9.7 |
| BOS slag | 18,718 | 144 x 144 |

* Assuming a bed thickness of 1 metre

treatment cell. For example a compost treatment cell approximately 9.7 × 9.7 × 1 metres in size could remove over 90% of the total metal load from Bwlch. However, BOS slag and waste shell material are less suitable materials for full-scale treatment, with treatment cells needing to be much larger (up to 144 × 144 × 1 metres in size) in order to treat the same metal load.

## Conclusions

The results of the field trials demonstrate that the reactive materials are variable in terms of their metal removal ability. Although all of the materials initially achieved high levels (>75%) of metal removal, they were generally not tolerant of the high metal concentrations over extended time periods. Zinc in particular was found to be difficult to remove from the circum-neutral pH drainage using the adsorbent materials tested. Fly ash from a peat fired power station was found to be the most effective material for metal removal, with over 99.9% Zn, Pb and Cd removal from 1000 litres of water. Although this cell had a lower flow rate than the other reactive materials tested (≈ 0.11 L/s), scaling the field results to full-scale shows that a modest sized treatment cell only 2.7 × 2.7 × 1 metres in size would be sufficient to remove in excess of 90% of the total metal load over a one year period.

## References

Dzombak DA and Morel, FMM (1990) Surface complexation modelling: hydrous ferric oxide. John Wiley and Sons, New York.

Johnston D and Rolley S (2008) Abandoned mines and the Water Framework Directive in the United Kingdom. In: Rapantova, N & Hrkal, Z (Eds.) Mine Water and the Environment. – Paper #128; Ostrava (VSB – Technical University of Ostrava).

Mellah A and Chegrouche S (2007) The removal of zinc from aqueous solutions by natural bentonite. Water Research 31, p 621—629

Wantanaphong J, Mooney SJ and Bailey HE (2004) Suitability of natural and waste materials as metal sorbents in Permeable Reactive Barriers (PRBs). Environmental Chemistry Letters 3(1).

Younger PL (2002) Mine water pollution from Kernow to Kwazulu-Natal: Geochemical remedial options and their selection in practice. Scott Simpson Lecture 2002. Geosci. Southwest England. Proceedings of the Ussher Society 10, p 255—266.