

Permeable Reactive Barriers for mine water treatment in the UK: lessons from laboratory-scale applications

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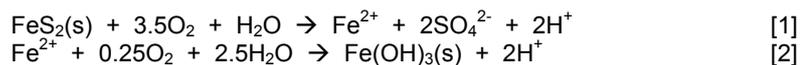
Keywords: Dodworth Colliery, mine drainage, permeable reactive barriers (PRBs), spoil heaps

ABSTRACT

Permeable reactive barriers (PRBs) for mine water remediation have found limited application in the UK to date, but there is an increasing need to address treatment of near-subsurface leachate from coal spoil, as these become the limiting factor to further environmental improvements in former coal mining areas. PRBs may well be an important option for passive treatment of such discharges. This paper reports the results of laboratory experiments to assess substrate suitability and likely performance of PRBs for acidic mine waters in the UK. Laboratory mesocosm experiments were conducted to investigate the effectiveness of substrates for remediation of the acidic Dodworth mine water in South Yorkshire, using findings from a study of substrate suitability for treatment of the highly acidic and metal-rich Shilbottle spoil heap drainage, Northumberland. Analyses of influent and effluent waters were also evaluated against findings from 1D models using PHREEQC, to assess likely contaminant removal mechanisms. Results indicate that metal attenuation in these laboratory mesocosms occurs via metal hydroxide precipitation, adsorption, and bacterial sulphate reduction leading to sulphide precipitation, with overall removal rates of 99.9% for Al, 86.5% for Cu, 70.5% for Zn and 33.3% for Co.

INTRODUCTION

Since the onset of the industrial revolution, coal mining has continued to be the predominant resource for power generation. Advances in technology have allowed mining of coal and ore bodies to continue to greater depths. During this mining, waste rock is loaded at the surface producing spoil heaps. This exposes potentially reactive media to the surrounding environment (Black & Craw, 2001) as spoil contains similar materials to those causing acidification within mine workings (Amos & Younger, 2003). When oxygenated water falls onto mine spoil it percolates through pores and cracks. Water-rock interaction results in contaminated water, which may drain from the spoil heap and enter surface waters, or can pass directly into underlying aquifers (Amos & Younger, 2001). The degree of contamination varies with residence time within the spoil. This production of polluted drainage is termed acid mine drainage (AMD) and primarily consists of low pH and increased dissolved metal concentrations, thus representing a significant source of aquatic pollution to UK watercourses (Younger, 2001). Production of acidity and dissolved metals results from the oxidation and hydrolysis of sulphide minerals (e.g. Blowes *et al.*, 2003):



Similar reactions involving other sulphide minerals can release various dissolved metals, such as copper and zinc (Benner *et al.*, 1997).

Permeable reactive barrier technology

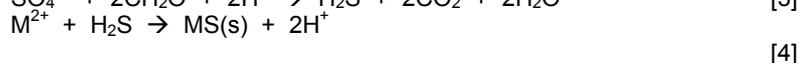
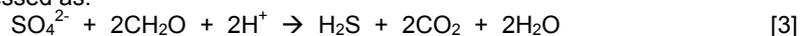
Amos & Younger (2003) define PRBs as:

“A vertical wall of reactive media, installed in the path of groundwater flow, to treat the groundwater in situ.”

PRB technology is gradually being accepted as a viable alternative to conventional groundwater remediation systems. The reactive media is permeable to groundwater flow and target contaminants are removed or altered by physical, chemical and/or biological means as the groundwater permeates through the PRB. These processes can include precipitation, sorption and oxidation/reduction (Amos & Younger, 2003). PRBs are attractive for the treatment of AMD, relative to other methods of remediation, as the treatment occurs in situ and is generally passive in nature (Herbert *et al.*, 2000).

Sulphate reduction

In natural settings, bacterial sulphate reduction acts to remove contaminated metals from solution (Dvorak *et al.*, 1992). Sulphate reducing bacteria use a variety of biochemical pathways to reduce sulphate by oxidation of organic carbon. This is generally expressed as:



Where CH₂O represents a generic carbon source, M²⁺ signifies mobile divalent metals and MS an amorphous or poorly crystalline metal sulphide (adapted from Benner *et al.*, 1997; Amos & Younger, 2003). The conditions within a PRB are particularly suited to sulphate reducing bacteria as oxygen ingress is impeded and carbon, nitrogen and phosphorous are provided, which are necessary for growth and reproduction (Benner *et al.*, 1997).

Reactive media

The type of reactive media is particularly important as this determines porosity occlusion. The chosen media controls reactivity and permeability, and must be chosen to maximise each over long periods of time. Preferential flow, which may evade reactive constituents, can be reduced by using a homogeneous mixture. However, as determined by Amos & Younger (2003), any one media is not sufficient to significantly reduce AMD pollution impacts, as best sulphate removal rates are achieved with a mixture of substrates.

Previous experience: Shilbottle Colliery, Northumberland

Amos & Younger (2003) investigated the effectiveness of various substrates to treat highly acidic and metal rich mine water at Shilbottle Colliery, Northumberland, by the use of laboratory mesocosm experiments. Results illustrated that a mixed media substrate of limestone chips, which generates alkalinity, and organic matter, to promote sulphate reduction, produced sufficient reductions in acidity and metal mobility, and perform best in terms of reactivity and permeability/hydraulic conductivity issues. This study led to the development of a full-scale PRB system at Shilbottle, installed in July 2001. In this, limestone gravel, composted horse manure and green waste was used as substrate at a ratio of 2:1:1, respectively. Younger *et al.* (2003) report that contaminated leachate is effectively treated by the PRB with favourable removal of target pollutants (table 1):

Table 1: Contaminant removal rates for the Shilbottle Colliery PRB

| pH increase (influent effluent) | Removal rates (%) | | | | |
|---------------------------------------|-------------------|------|----|------|------|
| | Fe | Al | Cu | Zn | Co |
| 3.29 - 7.20 | 96.1 | 88.1 | - | 78.3 | 63.9 |

Site description

Dodworth Colliery, South Yorkshire, is located approximately 3.2 km south-west of Barnsley (figure 1A). From the early 1870s onwards, the colliery worked a large area of coal from many different seams, with output typically being 1200 tons per day (Hill, 2000). Following many threats of closure during the mid-1960s and early 1980s, Dodworth Colliery finally closed in June 1987. The spoil tip area was acquired by Barnsley Metropolitan Borough Council in the early 1990s and limited remediation works were implemented during 1993/1994. This included capping the spoil, to limit water ingress, and the development of settling lagoons and reedbeds to treat run-off water. An extension of reedbed planting, plus the construction of a limestone pit, took place during the summer of 1996 (Naylor, 2002).

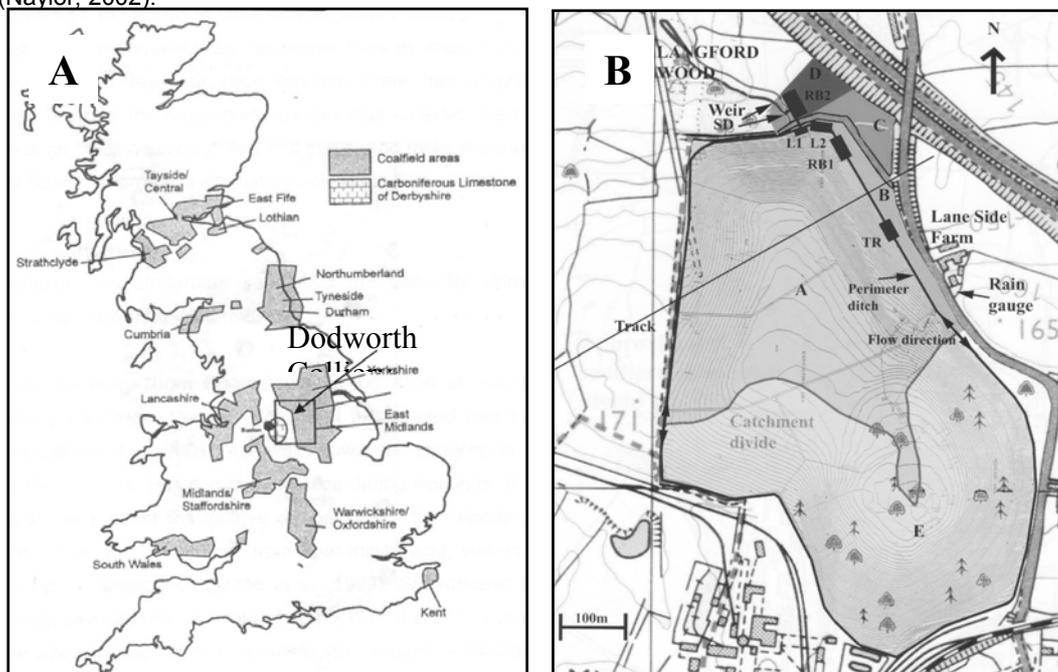


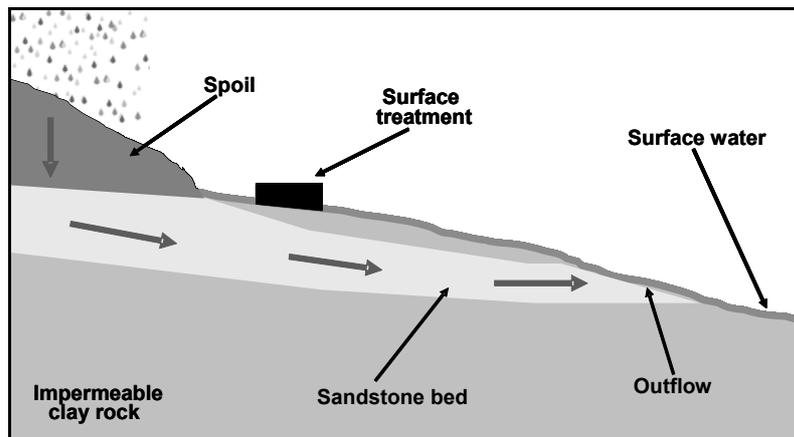
Figure 1: The coalfields of the UK (A) and a plan of Dodworth Colliery showing surface treatment (B) (Banks *et al.*, 1997; Hine, 2002)

The remediation of any contaminated water that drains to the surface, where it is channelled to the series of settling lagoons and reedbeds (figure 1B), has been successful, as mobile metals are precipitated and the acidity is therefore reduced. A study by Hine (2002) illustrates the success of the surface remediation (table 2):

Table 2: Quality of Dodworth spoil waters pre- and post-treatment (Hine, 2002)

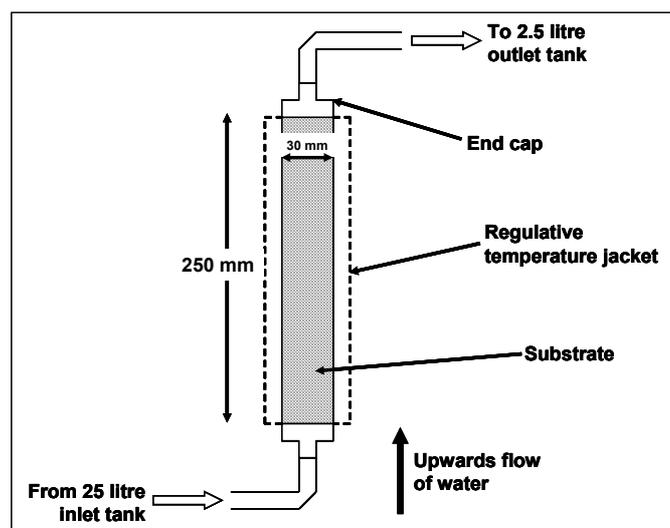
| Date | Influent (mg/l) | | | Effluent (mg/l) | | |
|------------|-----------------|------|-----|-----------------|------|-----|
| | pH | Fe | Al | pH | Fe | Al |
| 28/09/1994 | 4.7 | 14.2 | 0.9 | 7.6 | 12.0 | 0.2 |
| 11/10/1994 | 4.4 | 41.3 | 6.0 | 7.1 | 0.6 | 0.1 |

Bottrell (2003) discovered that a proportion of spoil drainage was infiltrating into an underlying confined sandstone aquifer. Any contaminated water that enters this sandstone bed is largely unchanged in its chemistry, as the layer is dominated by fracture flow, thus residence and water-rock contact time is low. Groundwater from the sandstone aquifer enters surface waters beyond any surface treatment, causing a pollution problem (figure 2). The feasibility of addressing this problem with PRB technology is being assessed. The laboratory trials which form part of this assessment are described below.

**Figure 2: Cross-sectional view at Dodworth (not to scale)**

MATERIALS AND METHODS

Two, laboratory based, PRB columns were constructed using PVCu industrial drain piping. In order to best simulate real conditions, without requiring excessive volumes of input contaminant solution, lengths of 0.25 m, 30 mm diameter columns were chosen. Both barriers were bottom fed from a 25 litre influent tank via one outlet. This was to ensure equal flow rate across both barriers. Individual outlet tubes discharged effluent water into separate 2.5 litre tanks (figure 3). Inert quartz sand was used in end caps to encourage uniform flow entering and leaving the substrate.

**Figure 3: Schematic of laboratory PRB (not to scale)**

The reactive substrate was chosen owing to its success at Shilbottle Colliery (table 3). White Spar limestone was chosen as the primary alkalinity generating media as it was determined, via acid leaching, to be pure carbonate. This was graded to diameters between 2.4 – 6.8 mm. All media were homogenised as much as possible and

both barriers were filled, with identical substrate ratios, to similar densities (mean: $1030.05 \pm 1.35 \text{ kg/m}^3$) to ensure uniformity.

Table 3: Mass ratio and basic composition of substrates used

| Substrate | Mass ratio | Composition |
|------------------------|------------|-----------------------------|
| White Spar limestone | 2 | Pure carbonate |
| Composted horse manure | 1 | CH ₂ O (N, P, K) |
| Green waste | 1 | - |

Untreated mine water, from Dodworth, was collected at the inlet to the first settling lagoon (TR lagoon, figure 1B). This was used as the influent solution for both barriers. Influent samples were taken in situ. Effluent samples were initially collected every day, then more infrequently. All aqueous samples were acidified (cations only) and refrigerated until analysis. Samples were analysed for cations and anions using ICP-OES and DIONEX Ion Chromatography, respectively.

Isotopic sulphur ($\delta^{34}\text{S}$) analysis, on influent and effluent waters, was carried out using a Micromass Isoprime Mass Spectrometer coupled to an Environmental Analyser, against known standards comprising seawater sulphate and chalcopyrite sulphide.

Once dismantled, each barrier was divided into four, equal horizontal sections for sulphide extraction. Quantitative sulphide concentrations were determined using the Chromous Chloride method.

RESULTS AND DISCUSSION

Contaminant concentrations decrease and alkalinity and the $\delta^{34}\text{S}$ isotope increase as a result of treatment by the PRBs, which were run over a 20 day time period. These are tabulated as a mean for both barrier effluent samples (table 4):

Table 4: Quality of water pre- and post-PRB treatment (mean)
N.B. Iron concentrations were at non-detectable levels in both influent and effluent waters

| | mg/l | | | | | | | | |
|--------------------------|------|-------|--------|------|------|------|-------------------------------|-------------------------------|-----------------------|
| | pH | Al | Ca | Co | Cu | Zn | HCO ₃ ⁻ | SO ₄ ²⁻ | $\delta^{34}\text{S}$ |
| Influent | 4.00 | 15.36 | 327.79 | 0.15 | 3.26 | 0.61 | 8.07 | 1597.38 | 12.82 |
| Effluent (day 20) | 7.50 | 0.01 | 373.49 | 0.10 | 0.44 | 0.18 | 185.14 | 1585.95 | 14.63 |

Under laboratory conditions, the PRB succeeds in removing target contaminants effectively (table 5), with a flow rate of $0.15 \text{ cm}^3/\text{s}$ and a retention time of 35 minutes (approximate values).

Table 5: Contaminant removal rates

| pH increase | Removal rates (%) | | | |
|-------------|-------------------|------|------|------|
| | Al | Cu | Zn | Co |
| 4.00 - 7.56 | 99.9 | 86.5 | 70.5 | 33.3 |

Alkalinity generation

Effluent pH increases from 4.0 (day 0) to approximately 7.5 after day 3, which is essentially maintained throughout the experiment (figure 4A). Calcium concentrations in the effluent are 13-35% higher than influent values. Bicarbonate exhibits a similar trend with concentrations rising by over 2000% (figure 4B).

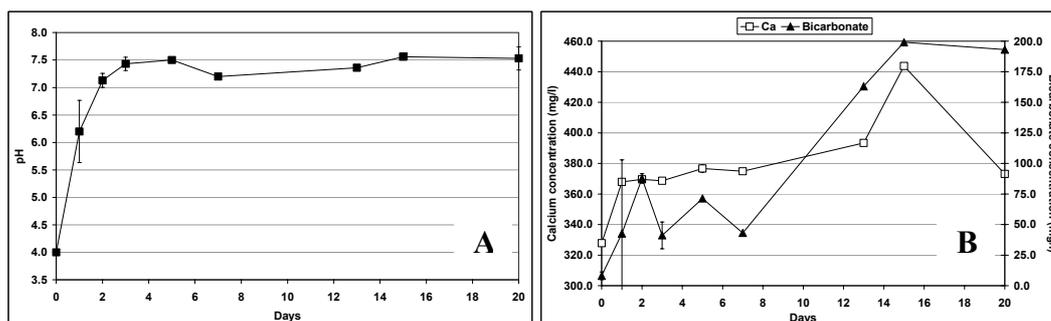


Figure 4: Change in pH (A) and calcium and bicarbonate (B) as a function of time (mean)

Calcium and bicarbonate values correlate with a 99.5% confidence level, indicating they originate from carbonate dissolution within the barrier. The resulting alkalinity increases the pH to neutral. The rise in pH generates aluminium precipitation as a hydroxide solid, which readily occurs above pH 5.0. Findings from PHREEQC show the system is supersaturated with amorphous aluminium hydroxide, gibbsite ($\text{Al}(\text{OH})_3$) and alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), which are all stable at neutral pH and under anoxic conditions.

Bacterial sulphate reduction

Cobalt, copper and zinc follow similar trends (figure 5A). All decrease rapidly from initial effluent concentrations (day 0) and, following a small increase on day 3, concentrations remain low. Sulphate concentration and $\delta^{34}\text{S}$ values are inversely proportional, with a 99.0% confidence correlation level. Both exhibit an opposite trend from day 5 onwards (figure 5B).

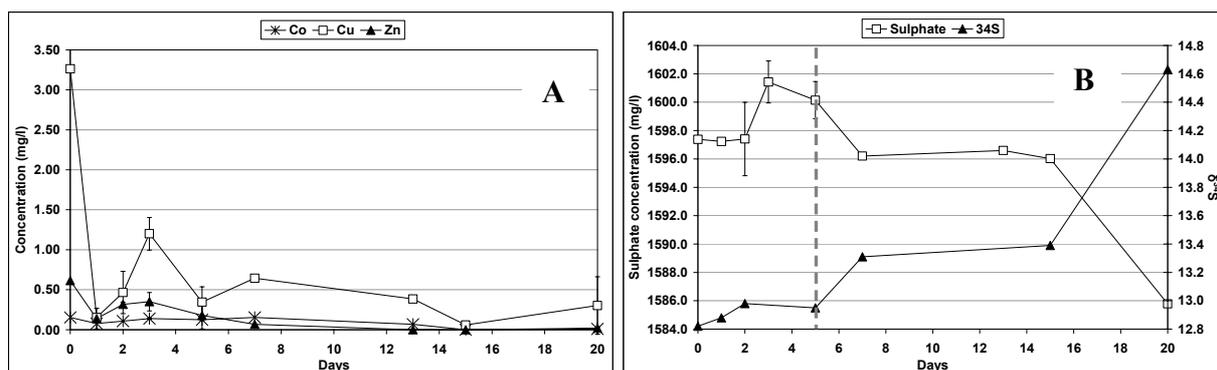


Figure 5: Change in cobalt, copper and zinc concentration (A) and sulphate concentration and $\delta^{34}\text{S}$ values (B) as a function of time (mean)

An initial reduction in metal concentration can be attributed to adsorption onto organic material. Once sorption sites become unavailable, breakthrough occurs, around day 3, and metal concentrations temporarily increase. By day 5 concentrations fall once more. This is a result of initial bacterial sulphate reduction illustrated by a decrease in sulphate concentration and an increase in the $\delta^{34}\text{S}$ isotope, which is an indication of sulphide production. Cobalt, copper and zinc readily form sulphides due to bacterial sulphate reduction. Sulphate reduction occurs subsequent to day 5 (dashed line, figure 5B), due to time taken for the system to become anoxic, indicated by the presence of methane (CH_4) and hydrogen sulphide (H_2S) gas from PHREEQC results. Sulphide concentrations within each barrier are low (0.11 – 0.37%), however, saturation indices, from PHREEQC, indicate that the system is supersaturated with respect to sphalerite.

Permeability

Using the change in flow rate and measured head differences, the change in hydraulic conductivity (figure 6), throughout the experiment, was calculated using Darcy's Law:

$$K = \frac{Q}{A i} \quad [5]$$

- K = hydraulic conductivity (m/s)
 Q = flow rate (m^3/s)
 A = cross sectional area (m^2)
 i = hydraulic gradient

A rapid decrease in hydraulic conductivity is observed (due to initial saturation of the column) and sustained suggesting that geochemical processes, such as adsorption and precipitation, create porosity occlusion, which reduces flow rate and, thus, permeability. Porosity increase due to calcite dissolution could produce the peak, seen at approximately day 5, but due to the subsequent decrease it is probably due to experimental error.

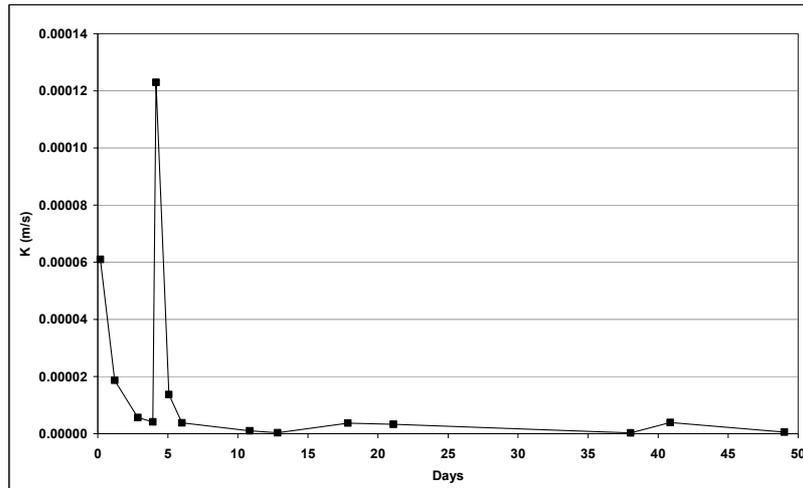


Figure 6: Change in hydraulic conductivity as a function of time (mean)

Field implementation

Using hydrological data relating to the site at Dodworth, hydraulic conductivity values calculated for this type of PRB implementation, in situ, show that the depth required, for the observed flow, is ~6.0 m (Bottrell, 2003). Due to the confined nature of the sandstone aquifer, a maximum depth of only 3.0 m is allowed, indicating that a PRB with the substrate mix investigated in this study is not practical. With more research into suitable reactive substrates however, PRB treatment is a feasible method of remediation at Dodworth Colliery.

CONCLUSIONS

Spoil heaps are created due to removal of waste rock during mining. Under atmospheric conditions reactive material, within the spoil, produces contaminated water. This may infiltrate into underlying aquifers, which drain to surface waters, creating a pollution problem.

PRBs may be an option for treating sub-surface contaminated water, by removing target contaminants. Reactive substrate must be chosen to ensure the longevity of reactivity and permeability. The reactive media within a PRB at Shilbottle Colliery was chosen for its alkalinity generating and sulphate reducing properties, and is effective at decreasing contaminant concentrations.

Using contaminated mine drainage, from Dodworth Colliery, and substrate composition implemented at Shilbottle, laboratory mesocosm experiments were erected to assess the effectiveness of decreasing contaminant concentrations (figure 7).

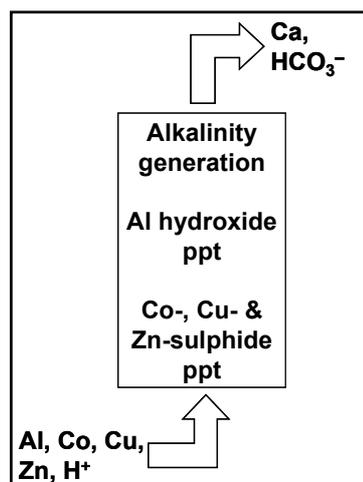


Figure 7: Geochemical changes occurring within the PRB

- a. Contaminant removal rates were high indicating the effectiveness of substrate reactivity.
- b. Dissolution of carbonate material generates alkalinity, which increases pH and precipitates aluminium hydroxides.
- c. Although in its infancy, sulphate reduction removes divalent metals from solution and decreases sulphate concentration, indicated by an increase in isotopic $\delta^{34}\text{S}$ values within effluent waters.
- d. Hydraulic conductivity values decrease rapidly due to porosity occlusion, reducing substrate permeability.

Although the required depth is too large, when applying results to field scale situations, the success of the PRB at Shilbottle suggests that this method of sub-surface treatment is a viable option to treat contaminated water at Dodworth, with more research needed to assess the suitability of reactive substrates.

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