

# Assessment and experimental passive treatment of zinc-rich net alkaline minewaters, Nent Valley, UK

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**Abstract:** The Nent Valley has experienced more than two hundred years of intensive lead and zinc mining activity that ended in the early 1900's. Consequently the River Nent is presently impacted by five metalliferous mine water discharges and the vast quantities of spoil and tailings material situated along the banks of the river represent diffuse sources of contamination. Elevated zinc concentrations that typically exceed the EQS (Environmental Quality Standard) limit of 0.5mg/l for a river of this type have led to a lack of fish and invertebrates in the main river. The mine waters are typically net-alkaline with zinc concentrations ranging from 1-8mg/l and sulphate concentrations around 200mg/l. The mine waters also contain lower concentrations (<1mg/l) of other ecotoxic metals such as lead, cadmium and arsenic. Previous attempts at zinc removal from net-alkaline mine waters using conventional compost wetland technology have proved unsuccessful because of the predominance of carbonate-bound zinc species at neutral pH. A passive treatment scheme for these mine waters has been developed with the support of computer geochemical modelling. This treatment mechanism relies on zinc removal by precipitation as the carbonate (smithsonite ( $ZnCO_3$ )) following calcite dissolution under closed-system conditions in a sealed limestone bed. The treatment system has been tested both in the laboratory and the field with promising results. It is hoped that with development this technology may provide a cheap and effective method for removing zinc from net-alkaline mine waters passively.

## 1 INTRODUCTION

The Nent Valley lies in Cumbria in the most northerly part of the North Pennine Orefield UK and has experienced over two centuries of intensive lead and zinc mining activity (Raistrick & Jennings, 1965; Dunham, 1990). A legacy of contaminated land and river pollution remains (Nuttall & Younger, 1999). Ecotoxic metals leach from spoil heaps and tailings material (created from spoil re-working during the Second World War; Dawson, 1947), and five disused mine adits discharge metal-rich waters to the River Nent. The lead-zinc deposits are Mississippi Valley type, hosted by cyclic Carboniferous rocks that are underlain by a Lower Palaeozoic basement intruded by Devonian granites. The presence of limestone ensures that the mine waters in the Nent and neighbouring catchments are circum-neutral. Dissolution of sphalerite ( $ZnS$ ), one of the ore minerals in the area has resulted in minewaters with sulphate as their dominant anion (150-200mg/l) and in dissolved zinc concentrations of 3-8mg/l. Other ecotoxic metals such as lead and cadmium are also present in lower concentrations. The River Nent has its headwaters above the village of Nenthead and flows for 8km in a westerly direction to join the River South Tyne below the town of Alston (which

is the highest market town in England at 300masl). The River South Tyne is environmentally significant in terms of its fisheries and water resources. Zinc concentrations in water and sediments are sufficiently high to severely restrict aquatic biodiversity either by direct toxicity or by lack of invertebrates for food supply. Although zinc is a necessary trace element for mammals (Förstner & Wittman, 1981) it is toxic to fish and invertebrates at levels permitted in potable water. Fish can accumulate zinc in bones and vital organs following ingestion (Calow & Petts, 1994) and externally zinc can bind to the mucus on the body surface of the fish which leads to excessive secretion of mucus and eventually suffocation (Alabaster & Lloyd, 1980; Handy & Eddy, 1990). In other mining areas zinc predominates as the free ion ( $Zn^{2+}$ ) in solution but speciation modelling has shown that zinc in the Nent Valley mine waters is strongly complexed with carbonate ions (Nuttall & Younger, 2000).

## 2 CHEMICAL CHARACTERISATION OF MINE WATERS

Assessment of mine waters has been carried out monthly over a two-year period and is discussed more fully in Nuttall & Younger (1999). Five mine water discharges and one drainage from the contaminated land surrounding the site of the smelt mill were sampled. The average chemistry of these discharges is shown in Table 1. Major ion chemistry was also plotted on Stiff and Piper diagrams, which revealed that all of the minewaters except Croft to conform to the calcium-sulphate hydrochemical facies. Croft discharge displays the more usual calcium bicarbonate chemistry typically associated with limestone groundwaters. The high sulphate concentration of the other mine waters can be attributed to the effects of decomposition of sulphide minerals

Table 1 Average data for the metalliferous discharges in the Nent Valley

| Site Name         | pH   | SO <sub>4</sub> <sup>2-</sup><br>mg/l | Zn<br>mg/l | Pb<br>mg/l | Cd<br>mg/l | Alkalinity<br>as HCO <sub>3</sub> | Hardness as<br>CaCO <sub>3</sub> |
|-------------------|------|---------------------------------------|------------|------------|------------|-----------------------------------|----------------------------------|
| Caplecleugh Level | 7.47 | 163                                   | 6.9        | 0.05       | 0.01       | 180 mg/l                          | 302 mg/l                         |
| Rampgill Level    | 7.53 | 163                                   | 7.1        | 0.189      | 0.008      | 146 mg/l                          | 300 mg/l                         |
| Nentsberry Haggs  | 7.52 | 250                                   | 7.8        | 0.004      | 0.007      | 217 mg/l                          | 396 mg/l                         |
| Croft             | 7.34 | 71                                    | 1.3        | 0.004      | 0.003      | 218 mg/l                          | 243 mg/l                         |
| Rampgill Drainage | 7.11 | 106                                   | 1.5        | 0.09       | 0.008      | 96 mg/l                           | 193 mg/l                         |
| Nent Force Level  | 7.15 | 181                                   | 3.1        | 0.005      | 0.005      | 220 mg/l                          | 336 mg/l                         |

## 3 DEVELOPMENT OF A TREATMENT STRATEGY

Previous attempts at removing zinc from circum-neutral mine waters using a compost based wetland have proved unsuccessful because of the fact that zinc is strongly bound to carbonate in the circum-neutral environment (Younger, 1997).

The Eh-pH diagram that was devised from the work of Hem (1972) provided the key to the development of a treatment strategy (Figure 1). The diagram suggests that there is a narrow pH range (approximately pH 7.5-8.0) over which zinc can be removed from natural waters as the stable carbonate mineral smithsonite ( $ZnCO_3$ ). Hence smithsonite precipitation offers a possible process for the removal of zinc from mine waters, assuming that the correct physical and chemical conditions can be achieved. In order to determine these conditions, simple geochemical modelling was carried out using the WATEQ4F code (Ball & Nordstrom, 1991). This is particularly useful for this application because its associated database has been developed mainly in the field of mine water research. More detailed discussion of the modelling is provided in Nuttall & Younger (2000).

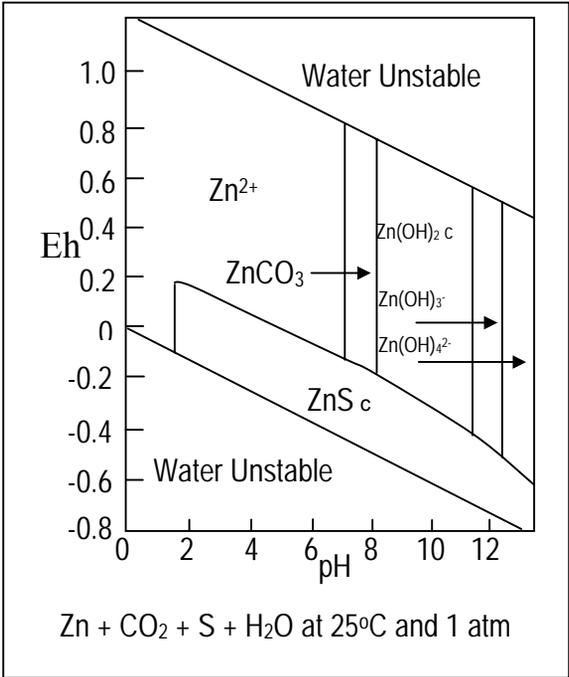


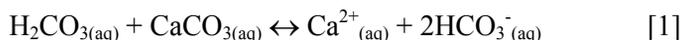
Figure 1 Eh-pH diagram devised by Hem (1972)

Modelling showed that as pH increases the concentration of hydroxyl bound species ( $Zn(OH)_2^0$ ) and carbonate bound species ( $ZnCO_3^0$ ,  $Zn(CO_3)_2^{2-}$ ) increases resulting in a decrease in the concentration of the free zinc ion ( $Zn^{2+}$ ) and the sulphate bound species ( $ZnSO_4^0$ ). Increased concentrations of carbonate species at pH 8.2 lead to optimum smithsonite saturation for this mine water (amorphous zinc oxide ( $ZnO$ ) is also saturated at this pH).

In order to apply these findings towards a treatment strategy ways in which mine water pH could be raised were considered. Lime dosing is one option; however large operating costs would be incurred for which there is no revenue

source. An anoxic limestone drain (ALD) provides a passive treatment option. These systems are already proven as a pre-treatment step for acidic mine waters which are then passed through wetlands (Hedin et al., 1994). In that application ALDs generate alkalinity and increase pH in order to optimise the bacterial conditions necessary for metal removal in the wetland. For zinc-rich circumneutral systems, the theory is somewhat different and relies upon closed system dissolution of limestone.

When carbonic acid (created from the reaction between water and atmospheric carbon dioxide) is in contact with limestone under atmospheric (open) conditions (equation 1), limestone dissolution takes place (Appelo & Postma, 1993):



The reaction proceeds until calcite saturation is achieved and an equilibrium pH is attained. If the same reaction occurs under closed conditions (i.e. with no replenishment of carbon dioxide from the atmosphere), carbonic acid concentration decreases as dissolution proceeds. The equilibrium pH reached in this system will be higher than that of the open system (Freeze & Cherry, 1979). It was therefore hypothesised that if Nent Valley mine water (in this case from Caplecleugh adit) was passed through an ALD, the pH attained within the system would be sufficiently high to precipitate smithsonite as this would become the solid limiting solubility (Mann & Deutscher, 1980). The high concentrations of sulphate in these mine waters will also influence the solubility of calcite by the common ion effect (Freeze & Cherry, 1979). The net result of the closed system and the sulphate concentrations makes the mine water more aggressive to calcite leading to smithsonite precipitation.

#### 4 LABORATORY AND FIELD EXPERIMENTS

The concept was tested in the laboratory using a sealed polythene box which had been filled with 10-15mm size limestone and had influent and effluent ports added to the bottom and top of opposite sides of the container. Mine water was supplied by a small pump from a 20 litre storage vessel. A 14 hour retention time was chosen as this has been suggested for the ALDs that treat coal mine drainage in the US (Hedin *et al.*, 1994). Limestone high in calcium carbonate was chosen because those richer in magnesium carbonate have a lower solubility. Daily influent and effluent samples were taken analysed by atomic absorption spectrophotometry (AAS). pH was difficult to measure because of sample degassing. The system ran from the end of March 1998 until the beginning of October 1998 for a total of 105 days. The performance of the system is shown in Figure 2.

The pilot scale field reactor was constructed at the beginning of August 1998 to treat a small portion of flow from the Caplecleugh adit. A double 2m by 5m plastic bag was filled with four tonnes of 30mm limestone and pipe unions were

attached for the influent and effluent ports. The ALD was then sealed and covered by a tarpaulin to prevent punctures, and the material previously removed from the site was used to bury the ALD. Samples of mine water and effluent were taken daily by staff of a nearby visitors centre. The system was sampled over 154 days and the performance of the system is shown in Figure 3.

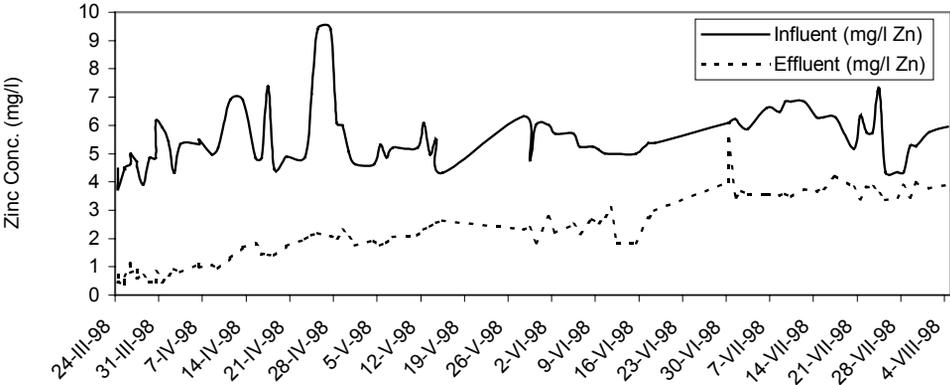


Figure 2 Graph of results from the laboratory anoxic limestone drain

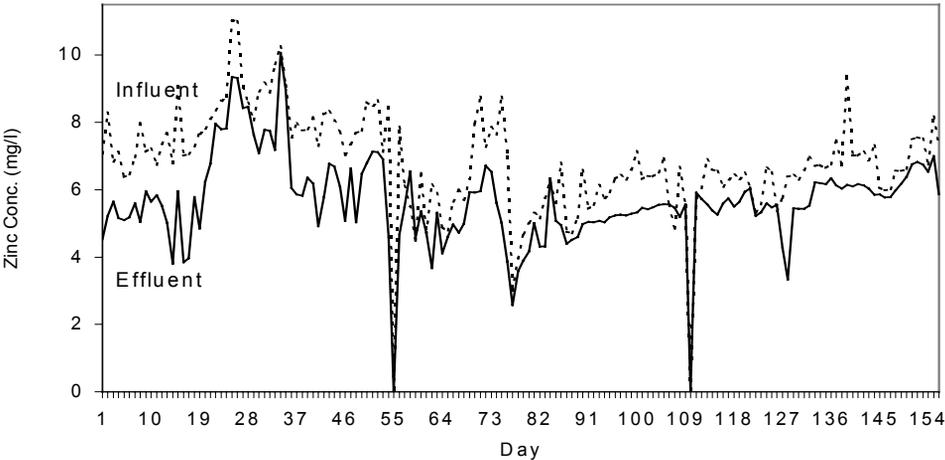


Figure 3 Graph of results from the field anoxic limestone drain

**5 EXPERIMENTAL RESULTS**

The laboratory ALD successfully removed zinc from mine water over a period of around three months (Figure 2). Initial high removal rates are due to sorption of zinc onto the fresh limestone. In general, removal rates were better when the influent zinc concentration was higher. Over the 105 day experiment,

approximately 430litres of mine water were treated. The average percentage removal rate was 50%, and the system removed 1.4g of zinc.

The field ALD also removed zinc from mine water (Figure 3) over a period of 154 days. Initial removal rates were around 36% but then declined to an average of 16% over the whole experiment. During the course of the experiment  $2.8 \times 10^5 \text{m}^3$  of mine water were treated and 327g of zinc was removed (i.e. approximately 2g per sampling day). The percentage removal rate for the pilot scale reactor was lower than for the laboratory reactor probably because a larger size of limestone was used and also because the temperatures in the field (mine water temperature is 10°C) is lower than laboratory temperatures (20°C). Although the removal rates are lower, the system was still removing zinc from mine water after a period of 10 months. Experiments suggest that the design could be improved by adding baffles to prevent short circuiting within the system and by incorporating a degassing step into the system (perhaps by using two ALDs instead of one).

## 6 CONCLUSIONS

The river Nent has zinc concentrations toxic to fish and invertebrates. Attempts at using anaerobic wetlands to remove zinc from circum-neutral mine waters have been unsuccessful due to the difference in zinc speciation between the acidic and circumneutral environments. Computer modelling has shown that mine water pH must be increased to 8.2 in order to remove zinc from mine water as smithsonite. An anoxic limestone drain should allow the ambient pH of mine water to be raised to 8.2. Laboratory and field experiments have shown that zinc can be removed from mine waters using an ALD at rates of between 16 and 50% for a 14 hour retention time.

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## **Ocena i eksperymentalne bierne oczyszczanie alkalicznych wód kopalnianych bogatych w cynk, Nent Valley, Wielka Brytania**

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**Streszczenie:** Intensywna eksploatacja ołowiu i cynku w Nent Valley, zakończona w początkach XX wieku, trwała ponad dwa stulecia. W konsekwencji rzeka Nent jest obecnie zanieczyszczona przez pięć wypływów wód z byłych kopalń kruszców, a olbrzymie ilości odpadów usytuowane wzdłuż jej brzegów stanowią rozproszone źródło zanieczyszczeń. Zwiększone koncentracje cynku, przekraczające zwykle 0,5 mg/l limitu dla rzeki o tym typie doprowadziły do wyginięcia ryb i bezkręgowców w głównej rzece. Wody kopalniane są typowo alkaliczne z koncentracją cynku 1-8 mg/l i siarczanów około 200 mg/l. Zawierają one również mniejsze koncentracje (<1 mg/l) innych ekotoksycznych metali takich jak ołów, kadm, i arsen. Wcześniejsze próby usunięcia cynku z wód kopalnianych przy użyciu konwencjonalnej metody filtrów roślinnych nie powiodły się z powodu dominacji cynku związanego z węglanami przy neutralnym pH. W związku z tym dla rozpatrywanych wód opracowano model biernego oczyszczania przy zastosowaniu geochemicznego modelowania komputerowego. Mechanizm oczyszczania opiera się na usuwaniu cynku przez strącanie węglanu cynku (smitsonit ( $ZnCO_3$ )), po rozpuszczeniu kalcytu w warunkach zamkniętego systemu w szczelnej warstwie wapienia.

System oczyszczania był testowany zarówno w laboratorium jak i w terenie z obiecującymi wynikami. Istnieje szansa, że technologia ta może dostarczyć tanią i efektywną metodę biernego usuwania cynku z alkalicznych wód kopalnianych.