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## ZINC REMOVAL FROM HARD, CIRCUM-NEUTRAL MINE WATERS USING A NOVEL CLOSED-BED LIMESTONE REACTOR

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**Abstract**—Zinc is an ecotoxic metal commonly associated with discharges from abandoned mines. Previous difficulties in removing zinc from circum-neutral mine waters with anaerobic wetlands have led to the development of a novel method to remove zinc from some mine waters of the North Pennine Orefield, UK. Geochemical modelling indicates that zinc carbonate (smithsonite,  $\text{ZnCO}_3$ ) should precipitate from these mine waters if pH can be raised from the ambient value of 7.5 to 8.2. It was postulated that this could be achieved through closed-system reaction with calcite, in a simple gravity-flow, sealed bed of limestone gravel (an “anoxic limestone drain” (ALD)). Previous applications of ALD technology have been for strongly acidic mine waters, with the intention of achieving wholesale alkalinity generation. In this new application, the ALD is meant to achieve a marginal increase in pH to encourage removal of zinc from the water by smithsonite precipitation. Testing of this concept by laboratory and field experiments has yielded encouraging results. The laboratory system gave an average of 50% reduction in zinc concentration over a 14 h retention period. The field system presently gives a 22% average reduction in zinc concentration over a similar retention time. With further development, it is hoped that ALDs could become a cheap and attractive unit process for treating drainage from abandoned mines, particularly in situations where conventional treatment is not feasible on economic or practical grounds. © 2000 Elsevier Science Ltd. All rights reserved

**Key words**—closed-system, limestone, mine, treatment, water, pollution, zinc

### INTRODUCTION

The Nent Valley lies within the North Pennine Orefield, UK. The area has experienced over two centuries of intensive mining activity for lead and zinc (Raistrick and Jennings, 1965; Dunham, 1990), that has left a legacy of contaminated land and river pollution (Nuttall and Younger, 1998). Ecotoxic metals leach from spoil heaps (created throughout the mining era) and tailings dams (created during the Second World War; Dawson, 1947). Contaminated land drainage and five disused mine adits also discharge metals into the River Nent. The mine waters in the Nent and neighbouring catchments have interacted with calcareous Carboniferous rocks and therefore have high hardness values (generally greater than 200 mg/l as  $\text{CaCO}_3$ ), high alkalinity values (generally greater than 100 mg/l as  $\text{HCO}_3^-$ ) and pH in the range 7.4–8.0. However, dissolution of sphalerite ( $\text{ZnS}$ ), a common ore mineral in this area, results in the

dominant anion in these mine waters being sulphate (150–200 mg/l), and in dissolved zinc concentrations in the range 3–8 mg/l. The mine waters also contain significant amounts of lead and cadmium, and of the ecotoxic metalloid arsenic (Table 1).

The zinc concentrations of the water and sediments of the River Nent are high enough to severely restrict aquatic biodiversity. Although zinc is a necessary trace element for mammals (Förstner and Wittman, 1981), it is toxic to fish and invertebrates at levels permitted in drinking water. When fish ingest zinc, it can accumulate in bones and vital organs (Calow and Petts, 1994). Externally, zinc can bind to the gill epithelium or suffocate the fish by binding to the body mucus layer, prompting excessive secretion of mucus (Alabaster and Lloyd, 1980; Handy and Eddy, 1990). Consequently the River Nent has an impoverished invertebrate fauna, and lack of food supply or direct toxicity results in a very sparse fish population.

In other mining fields, zinc is often associated with acidic drainage from abandoned mines. In such waters, zinc is predominantly present in solution as  $\text{Zn}^{2+}$ , which is readily treatable by alkali dosing to form a hydroxide solid, or by sulphate re-

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

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

duction to form a sulphide. However, in hard, net-alkaline mine waters such as are found in the Nent Valley, zinc is predominantly present as a carbonate complex ( $\text{ZnCO}_3^0$ ), as illustrated by Table 2.  $\text{ZnCO}_3^0$  will not readily react to form non-carbonate solids. For this reason, attempts to use aerobic passive treatment technology to precipitate zinc from these waters as a sulphide have not been very successful (Younger, 1997a). While conventional alkali dosing could be used, this is not feasible at long-abandoned mine sites (such as those in the Nent Valley) where there are no revenue streams to pay for treatment and no clear legal liabilities for pollution remediation. The best hope in such cases is to devise a capital-intensive remedial strategy, where a single "spend" can achieve lasting results with little or no ongoing running costs. Such a strategy is likely to be based upon passive treatment technology (Hedin *et al.*, 1994) using wetlands, anoxic limestone drains (ALDs) and similar devices (Younger, 1997b). While compost wetlands have proved successful at removing zinc from net-acidic mine waters (Knight Piésold, 1998), they have been found to be far less suited to removing zinc from circum-neutral mine waters in the North Pennines (Younger, 1997a). The search for an appropriate passive treatment technology for the Nent Valley mine waters has led to consideration of an alternative process route. The selected process is based upon closed-system dissolution of calcite coupled with precipitation of the zinc (as a carbonate, hydrated carbonate and/or oxide). This paper describes the concept of this alternative process, and laboratory field testing of its feasibility.

#### TREATMENT CONCEPT

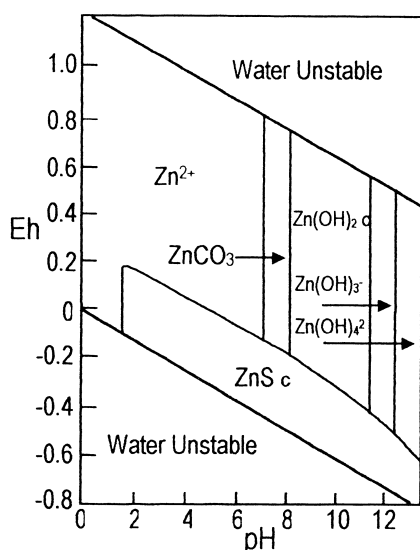
The work summarised in the Eh–pH diagram of Hem (1972) (Fig. 1) indicates that zinc can form a stable carbonate mineral (smithsonite,  $\text{ZnCO}_3$ ) over

a narrow pH range (approximately pH 7.5–8.0) in natural waters. Therefore, if the correct physical and chemical conditions could be achieved, smithsonite precipitation could offer a process for removing zinc from net-alkaline mine waters. In order to determine the "correct physical and chemical conditions" for these particular mine waters, simple geochemical modelling was carried out using the well-known WATEQ4F code (Ball and Nordstrom, 1991). This code is particularly suited for this task, as it is based upon a database developed mainly in the context of mine water research.

Differences in mineral phase saturation and zinc speciation were examined by entering the raw field data, and then adjusting the pH and Eh values to determine the consequent changes in speciation of these waters. An Eh range of –150 to –500 mV was modelled to reflect the consequences of passing mine water through an anaerobic wetland. The change in Eh gave no change in mineral phase saturation or zinc species distribution, reflecting the results of the disappointing field experiments reported by Younger (1997a). As the average pH of one of the main mine waters (Caplecleugh) is 7.47, a pH range of 6–8.5 was modelled. The results showed that changing pH causes a change in species distribution (Table 2). For example comparing species distribution at pH 6 and 8.2 shows that at pH 8.2 a greater concentration of carbonate bound zinc species exists. Overall the WATEQ4F results show that over the pH range 6–8.5, the species distribution changes in the following way: as pH increases the concentration of carbonate bound ( $\text{ZnCO}_3^0$ ,  $\text{Zn}(\text{CO}_3)_2^{2-}$ ) and hydroxyl bound species ( $\text{Zn}(\text{OH})_2^0$ ) increases at the expense of the free zinc ion ( $\text{Zn}^{2+}$ ) and the sulphate bound species ( $\text{ZnSO}_4^0$ ). The change in mineral phase saturation over the pH range is displayed in Fig. 2. The presence of the increased concentrations of carbonate bound species at pH 8.2 results in the optimum sat-

Table 2. Table of zinc species concentrations (all in mg/l) at different pH values (modelled using WATEQ4F)

Species	pH 6.0	pH 7.0	pH 7.47	pH 7.8	pH 8.0	pH 8.2	pH 8.5
Zn	4.948	4.595	3.935	3.078	2.417	1.731	0.869
$\text{ZnCO}_3^0$	—	1.004	2.507	4.111	5.023	5.564	5.302
$\text{Zn}(\text{CO}_3)_2^{2-}$	—	—	0.300	1.029	1.954	3.343	6.037
$\text{ZnHCO}_3$	2.310	2.131	1.801	1.382	1.065	0.744	0.355
$\text{ZnOH}^+$	—	—	1.263	—	—	0.090	0.090
$\text{Zn}(\text{OH})_2^0$	—	—	—	0.156	0.310	0.553	1.106
$\text{ZnSO}_4^0$	1.582	1.471	1.263	0.991	0.779	0.560	0.282



Zn + CO<sub>2</sub> + S + H<sub>2</sub>O at 25°C and 1 atm

Fig. 1. Eh-pH diagram devised by Hem (1972).

uration of the mineral phase smithsonite for this mine water. By comparison, at pH 6 no carbonate (except bicarbonate) bound zinc species exist (Table 2) and the solution is undersaturated with respect to smithsonite. At pH 8.2 WATEQ4F also shows that the system is saturated with amorphous zinc oxide (ZnO).

Several ways in which the pH of the mine water could be raised to 8.2 were considered. One option would be lime dosing; however, the continuous dosing with reagents would incur large operating costs for which no revenue source exists. The obvious passive treatment option is to use an anoxic lime-

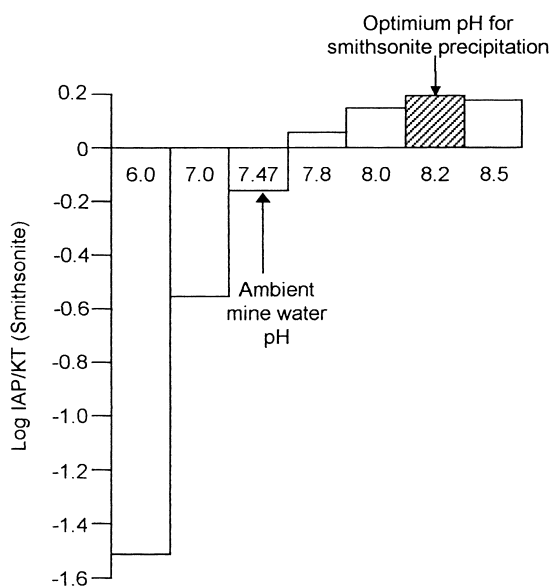
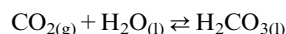


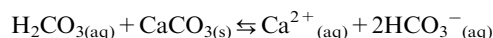
Fig. 2. Graph of smithsonite saturation at various pH values (modelled using WATEQ4F).

stone drain (ALD). Such systems have been previously used as a pre-treatment step for acidic mine waters entering compost based wetlands (Hedin *et al.*, 1994), in that case being used to generate large amounts of alkalinity as well as increasing pH to optimise conditions for anaerobic bacterial activity in the compost wetlands. However, in this case, the theory is slightly different and dependent upon closed-system dissolution of limestone.

The reaction of atmospheric carbon dioxide and rainwater produces carbonic acid:



When carbonic acid comes into contact with limestone under atmospheric (open) conditions, dissolution of limestone takes place (Appelo and Postma, 1993):



Dissolution takes place until a saturated solution of calcite is achieved, at which point equilibrium pH will have been reached. If carbonic acid interacts with limestone under closed-system conditions (i.e. carbon dioxide is not replenished from the atmosphere), the carbonic acid concentration will decrease as dissolution proceeds. When the closed system reaches equilibrium, the pH attained will be higher than that of an equivalent open system (Freeze and Cherry, 1979). It is therefore hypothesised that smithsonite precipitation should occur if the mine water is passed through a closed-system limestone bed, promoting a rise in pH. If CO<sub>2</sub> becomes trapped within the closed environment of an anoxic limestone drain, both the partial pressure of CO<sub>2</sub> and the Ca<sup>2+</sup> concentration will increase, leading to a net rise in pH and concomitant decrease in the solubility of zinc as smithsonite becomes the solid limiting solubility (Mann and Deutscher, 1980). These mine waters are high in sulphate (from oxidation of sulphide ores) and typically have sulphate concentrations of over 100 mg/l. The presence of this amount of sulphate influences the solubility of calcite due to the common ion effect (Freeze and Cherry, 1979). The combination of the presence of sulphate and the closed-system conditions make the mine water more aggressive towards calcite which leads to bicarbonate ions, hydroxide ions and zinc ions being produced. The resulting increase in pH leads to the solubility product of smithsonite being exceeded. Smithsonite should then precipitate out of solution, lowering the dissolved zinc concentration. It would also seem feasible that the calcium present might react with the sulphate to precipitate gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

#### LABORATORY TESTING OF CONCEPT

A laboratory scale anoxic limestone drain (ALD) was constructed to determine whether the correct environmental conditions for zinc precipitation as

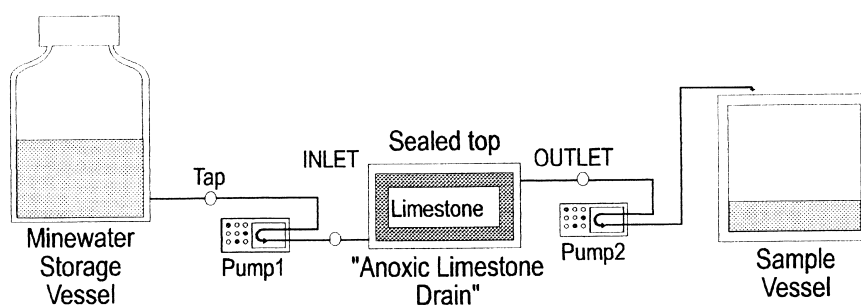


Fig. 3. Diagram of laboratory anoxic limestone drain apparatus.

the carbonate smithsonite ( $\text{ZnCO}_3$ ) could be achieved. The construction of this system is detailed in Fig. 3. The system was constructed using a 5 l polyethylene container. Inlet and outlet connectors were fitted at the bottom of one side of the box (inlet) and at the top of the opposite side of the box (outlet). A low flow rate was chosen for the reactor in order for it to be practical to run the lab-scale reactor using real mine water. Mine water was supplied from a 20 l glass storage vessel that was replenished approximately every four days. Flow rates were calibrated and measured using a measuring cylinder and stopwatch. A 14 h retention time was suggested in literature (Hedin *et al.*, 1994); however this was for ALDs which currently receive acidic water. The limestone used in the experiment was of the size range 10–15 mm which had a void space of 50%, when the polyethylene container was filled the reactor had a volume of 2.8 l. Grey Carboniferous limestone was chosen because it contains a higher proportion of  $\text{CaCO}_3$  (~95%) than the locally abundant brown limestone which is richer in dolomite  $\text{MgCa}(\text{CO}_3)_2$ . Dolomite is less soluble than  $\text{CaCO}_3$ ; hence carbonate dissolution would have taken longer had brown limestone been used. As far as possible, daily samples of influent mine water and reactor effluent were taken in polyethylene bottles and fixed with nitric acid. These

samples were analysed for total zinc using atomic absorption spectrophotometry (AAS) (Unicam 929 AA with acetylene/air mixture). Occasionally, anion samples would also be taken and analysed for sulphate, nitrate, chloride and fluoride. pH and alkalinity measurements were attempted although this was difficult because by the time the sample bottle had filled, the sample had reacted with the atmosphere and degassing of  $\text{CO}_2$  had occurred. The system ran from the end of March 1998 until the beginning of October 1998 for a total of 105 days. The performance over that time is detailed below (Table 3 and Fig. 4).

#### RESULTS OF THE LABORATORY EXPERIMENTS

The laboratory ALD ran for approximately three months during which time it proved successful at removing a considerable amount of zinc from the mine water. The system was sampled over a period of 105 days and in this time approximately 430 l of mine water were treated. The average influent zinc concentration was 5.54 mg/l and the average effluent concentration was 2.70 mg/l. The average percentage removal rate of zinc was 50%. In terms of loadings, the system removed 1.4 g of zinc in 105 days. Calculations of some kinetic constraints were performed to determine the amount of zinc

Table 3. Total performance of laboratory anoxic limestone drain

	ALD Performance								
	time (h)	flow (l/h)	total vol (l)	av. IN Zn conc. (mg/l)	av. IN load (mg Zn)	av. OUT Zn conc. (mg/l)	av. OUT load (mg Zn)	load removed (mg Zn)	% load removed
<i>Date</i>									
March (24th–31st)	184	0.19	35.55	4.74	168.53	0.64	22.70	145.83	86.53
April (1st–30th)	720	0.19	139.10	5.92	823.44	1.46	202.45	620.99	75.41
May (1st–11th)	264	0.16	51.00	5.01	255.62	1.91	97.29	158.33	61.94
May (12th–15th)	96	0.16	15.38	5.21	80.16	2.48	38.15	42.02	52.41
May (28th–30th)	72	0.16	11.53	5.54	63.91	2.18	25.13	38.78	60.68
June (1st–17th)	408	0.14	65.36	5.32	347.92	2.51	164.06	183.86	52.84
June (29th–30th)	48	0.14	6.62	10	40.39	4.76	31.52	8.87	21.97
July (1st–17th)	408	0.14	56.30	6.32	355.76	3.67	206.47	149.29	41.96
July (20th–31st)	288	0.14	39.74	5.42	215.54	3.66	145.43	70.11	32.53
Aug (3rd–4th)	48		6.62	5.85	38.77	3.79	25.09	13.68	35.28
Average values	—	—	—	5.54	239.01	2.70	95.83	143.18	52.16
Totals	2536	—	427.23	55.44	2390.01	27.04	958.29	1431.76	

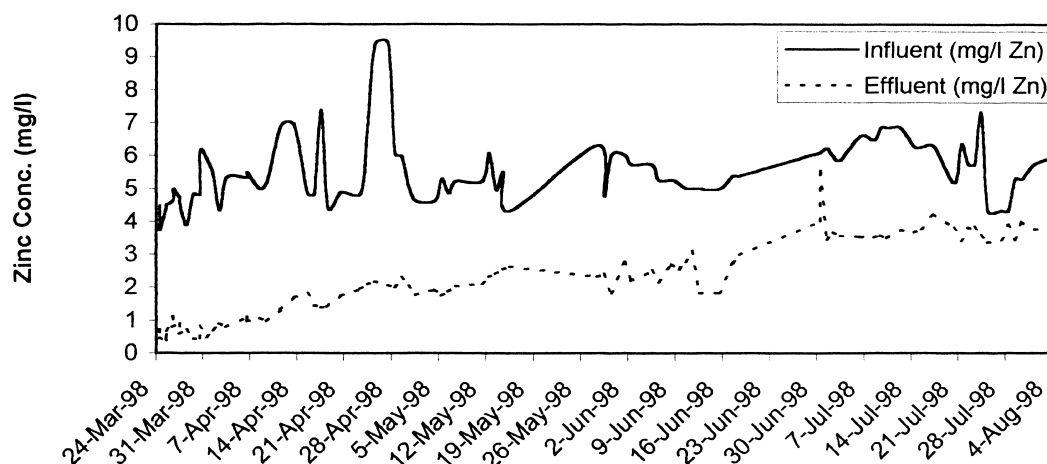


Fig. 4. Graph of results from the laboratory anoxic limestone drain.

removed per  $\text{cm}^2$  of the reacting surface area within each rig. The following assumptions were made. Each grain of limestone within the rig was assumed spherical. 80% of the surface area of each spherical limestone grain was assumed available for reaction (i.e. 20% was taken up by grain contacts). Finally the porosity of each limestone filled reactor was assumed to be 50% (which laboratory experiments showed to be a fair approximation). The laboratory ALD was calculated to have a zinc removal rate of  $1.45 \times 10^{-8} \text{ mol/day/cm}^2$ .

#### FIELD TESTING

The pilot scale field reactor was constructed at the beginning of August 1998 to treat a small portion of flow from one of the abandoned mines (Capeleugh). The field reactor was built by filling a large ( $2 \times 5 \text{ m}$ ) "double plastic bag" with limestone gravel. The "double plastic bag" was simply one heavy-duty polyethylene bag placed inside another to prevent leaks. Four tonnes of limestone were shovelled into the bag. At the sealed end of the polyethylene, a plastic pipe sealed into the polyethylene served as the effluent port. When the bag

was full with limestone, the bag was sealed and another pipe attached to serve as the influent port. A tarpaulin was draped over the top of the filled bag to help protect it from punctures and to further prevent light penetration. The material previously removed from the site was finally replaced on top of the filled bag of limestone to provide additional cover.

Samples of the Capeleugh mine water and field ALD effluent were taken daily (as far as possible) by staff of a nearby visitors centre. Measurements of pH, alkalinity, conductivity, flow and DO were made sporadically as the opportunity arose. In the laboratory, analysis of the influent and effluent samples was performed for zinc, calcium, magnesium, sodium, and potassium using AAS. Every week, samples were also analysed for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$  using a Dionex DX-100 ion chromatograph. The performance of the field ALD is documented in Table 4 and Fig. 5.

#### RESULTS OF FIELD EXPERIMENTS

The field ALD has run for approximately three months during which time it has removed appreci-

Table 4. Total performance of field anoxic limestone drain to date

	time (h)	flow (l/h)	total vol (l)	av. IN Zn conc. (mg/l)	ALD performance		av. OUT load (mg Zn)	load removed (mg Zn)	% load removed
					av. IN load (mg Zn)	av. OUT Zn conc. (mg/l)			
<i>Date</i>									
Aug (6th–17th)	288	65.00	18720.00	7.12	133286.40	5.37	100526.40	32760.00	24.58
Aug (19th–23rd)	120	65.00	7800.00	7.53	58734.00	4.52	35256.00	23478.00	39.97
Aug (25th–31st)	84	65.00	5460.00	8.11	44280.60	6.74	36800.40	7480.20	16.89
Sept (1st–6th)	384	65.00	24960.00	8.93	222892.80	7.65	190944.00	31948.80	14.33
Sept (21st–27th)	168	65.00	10920.00	7.72	84302.40	6.00	65520.00	18782.40	22.28
Oct (8th–18th)	132	65.00	8580.00	7.34	62977.20	5.94	50965.20	12012.00	19.07
Oct (29th)	24	65.00	1560.00	6.49	10124.40	5.36	8361.60	1762.80	17.41
Nov (3rd–6th)	96	65.00	6240.00	5.41	33758.40	4.46	27830.40	5928.00	17.56
Average values	—	—	—	7.33	81294.53	5.76	64525.50	16769.03	21.51
Totals	1296	—	84240.00	58.65	650356.20	46.04	516204.00	134152.20	—

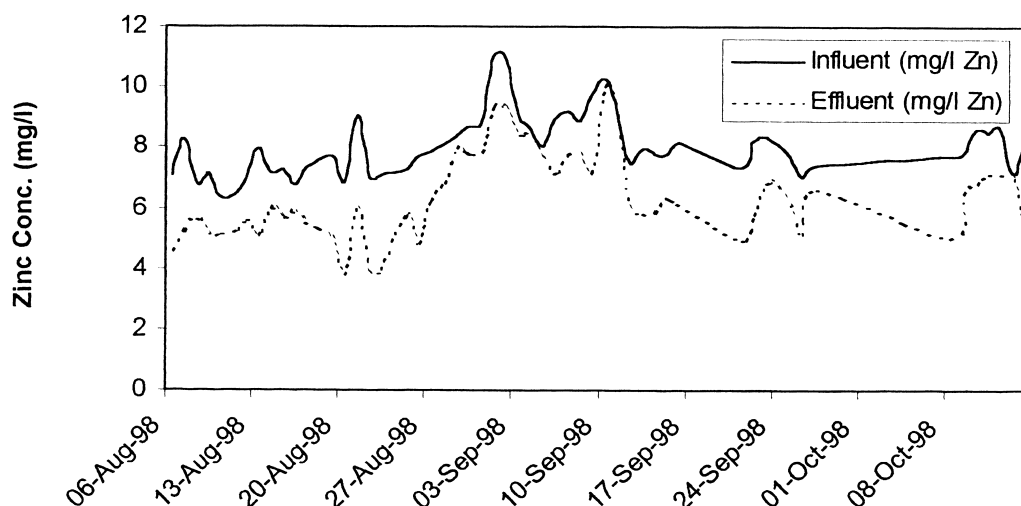


Fig. 5. Graph of results from the field anoxic limestone drain to date.

able zinc from the mine water (Table 4). The system was sampled over a period of 54 days and in this time approximately 84 240 l of mine water have been treated. The average influent zinc concentration to date is 7.33 mg/l and the average effluent concentration to date is 5.75 mg/l. The average percentage removal rate of zinc to date has been 22% (Fig. 5). In terms of loadings, over the 54 day period of operation, the system has removed 134 g of zinc. Calculation of the kinetic constraints as described in the previous section gave the field ALD a zinc removal rate of  $1.8 \times 10^{-8}$  mol/day/cm<sup>2</sup>.

#### DISCUSSION

Both the laboratory and field systems worked effectively in removing zinc from the mine water. The laboratory system had an average zinc removal rate of 50% while the field system gave a removal rate of 22%. The difference in the performance of these two systems is probably due to:

- the difference in temperature between the laboratory (20°C) and the field ( $\leq 10^\circ\text{C}$ )
- the difference in limestone particle size between the lab rig (10–15 mm) and the field rig (35 mm).

Difficulties have been encountered in measuring the pH of the ALD effluent, again due to degassing, so the rise in pH cannot be compared with that expected on theoretical grounds. While the fact that the two systems do remove zinc could never be taken as “proof” of the concepts upon which the system was based, the results at least encourage perseverance with this new approach to zinc removal from similar mine waters. Current experiments (to be the subject of a future paper) are examining whether improved zinc removal can be

achieved by running two ALDs in series, with venting of CO<sub>2</sub> between them to restore the aggressivity of the water with respect to calcite.

#### CONCLUSIONS

The River Nent contains concentrations of zinc that are toxic to fish and invertebrates.

Zinc has proved difficult to remove from circum-neutral mine waters by using anaerobic wetlands due to the dominance of different zinc species between the acidic and circum-neutral aquatic environments.

Computer modelling shows the optimum pH for zinc phase precipitation to be 8.2

At this pH the mineral phases produced will be smithsonite (ZnCO<sub>3</sub>) and an amorphous zinc oxide (ZnO).

An anoxic limestone drain should allow the ambient pH of mine water to be raised from 7.47 to 8.2.

Laboratory and field experiments have shown that zinc can be removed from mine waters with an anoxic limestone drain, at rates of between 22 and 50% for a 14 h retention time.

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