Field Trials of Dispersed Alkaline Substrate to Passively Treat Highly Polluted Acid Mine Drainage at two Emblematic Abandoned Mines in Wales

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Abstract

Dispersed alkaline substrate is a passive treatment technology for sites with high metal concentrations and has been trialled successfully at field pilot-scale at two mine discharges. At the abandoned Cwm Rheidol lead-zinc mining complex, a two-step DAS system operated for over one year, removing Fe, Al, Zn, Pb, Cd and other metals. At Parys Mountain, a volcanogenic massive sulphide deposit which was the world's largest copper mine in the 18th century, a three-step DAS system is removing Fe, Cu, Zn, Al, SO_4 and other contaminants. DAS achieved very high metal removal rates for all contaminants of potential concern.

Keywords: ispersed alkaline substrate, passive mine water treatment, remediation, clogging, passivation

Introduction

Acid mine drainage (AMD) is a major cause of water contamination worldwide. Conventional treatment plants can be expensive to build and operate, and application at remote sites may be impractical. Passive treatment systems, which only require naturally available energy sources and infrequent maintenance, may be an economical option to treat these waters. When used to treat water with high metal concentrations or high acidity loads, they are however prone to loss of permeability and reactivity or may require excessively large land areas. Moreover, the passive removal of high concentrations of divalent metals (e.g., Zn, Mn, Cu, Pb, Ni, Cd) poses major challenges.

Methods and Field Sites

Dispersed Alkaline Substrate

Dispersed alkaline substrate (DAS) is an innovative passive treatment technology that can be implemented at sites with high metal concentrations (Roetting *et al.* 2006, 2008a, 2008b, 2008c). DAS consists of a fine-grained alkaline reagent mixed with a coarse matrix. The fine grain size of the alkaline reagent increases the dissolution rate due to the increased specific reactive surface area and therefore reduces armouring, while the coarse matrix provides a large pore space to store precipitates and retard clogging.

Calcite-DAS provides the main source of alkalinity to neutralise the bulk acidity of the mine drainage by buffering the pH between 6 and 8, efficiently removing trivalent metals such as Fe(III) and Al, but not divalent metals. Removal of divalent metals is achieved in an additional DAS reactor containing magnesium oxide or barium carbonate. MgO hydration and dissolution buffers the pH between 9 and 10. In this pH range, most divalent metals display very low solubility and are readily removed. If BaCO3 is used instead of MgO, the system also removes SO4, and the hardness that was added in the calcite-DAS reactor(s).

In the trials reported here, two different types of wood flakes were mixed with the DAS materials. In some of the reactors, fresher (mainly ash) wood cuttings were used. In other reactors, pine wood shavings were used.

Cwm Rheidol

The Ystumtuen or Cwm Rheidol mining complex is located 15 km east of Aberystwyth, Ceredigion, and includes the mines of Cwm Rheidol, Ystumtuen (early records dating back to 1698), Penrhiw, Bwlchgwyn and Llwynteifi. The five mines are connected underground, enabling the extensive workings to drain to the Afon Rheidol via adits No. 6 and No. 9, which emerge on the steep valley slopes. Both discharges are acidic and contain elevated concentrations of metals including Zn, Pb and Cd. These discharges are subsequently contributing to the Afon Rheidol, failing European Water Framework Directive (WFD) standards for Zn and Cd for 18 km downstream of the mine to its tidal limit. Adit 6 (discharging at a higher elevation) has a higher flow rate but lower concentrations and a higher pH than Adit 9 (discharging at a lower elevation). The main contaminants in the combined discharge (flow-weighted average during the period 2015 – 2019) in the combined discharge are SO4 (216 mg/L), Zn (20.3 mg/L), Fe (17.8 mg/L), Al (5.5 mg/L), Mn (0.95 mg/L), Pb (0.62 mg/L), Ni (0.28 mg/L), Cu (50 µg/L), Cd (40 µg/L), and the combined pH is approximately 4.1. The average composition of Adit 9 water in the same period is SO4 (824 mg/L), Zn (85.5 mg/L), Fe (126 mg/L), Al (29 mg/L), Mn (4 mg/L), Pb (0.01 mg/L), Ni (1.26 mg/L), Cu (100 µg/L), Cd (120 µg/L), with a pH of 3.0.

A total of four different treatment train configurations were tested at Cwm Rheidol (Figure 1):

- Treatment train 1: Calcite DAS + BaCO3 DAS (using fresh ash wood cuttings), fed with combined Adit 6+9 water. This treatment train was operated from December 2020 until October 2022.
- Treatment train 2: Calcite DAS + MgO DAS (using dried pine wood shavings), fed with combined Adit 6 + 9 water.

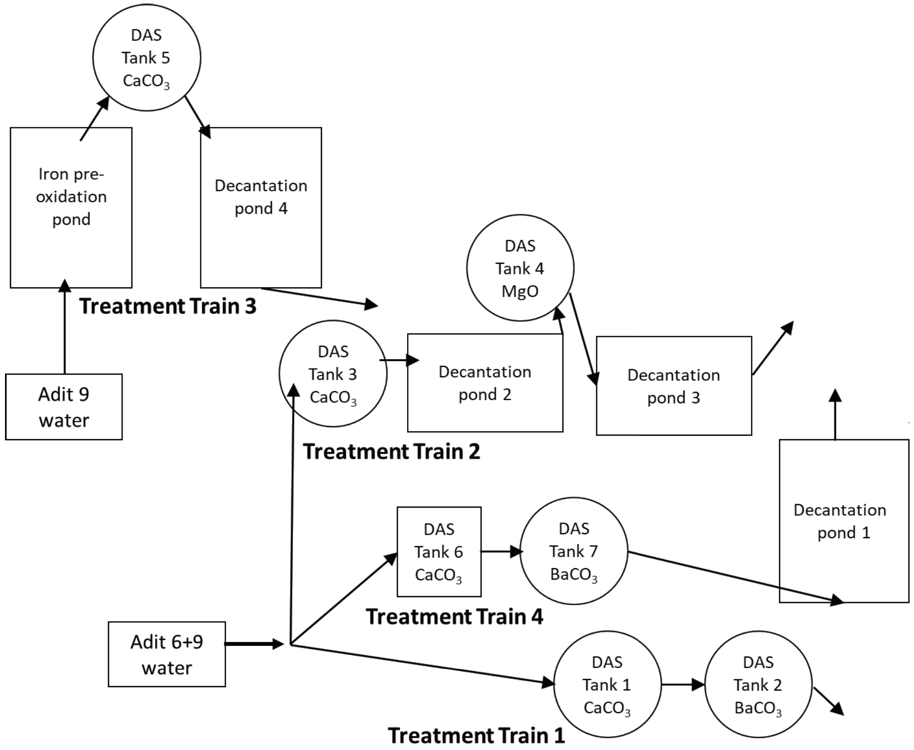

***Figure 1** Schematic site layout of the Cwm Rheidol DAS pilot trial.*

This treatment train was operated from December 2020 until October 2022.

- Treatment train 3: Calcite DAS only (using fresh wood cuttings), with pre-oxidation pond, fed with Adit 9 water only. This treatment train was operated from December 2020 until December 2021.
- Treatment train 4: Calcite DAS + BaCO3 DAS (using dried pine wood shavings), fed with combined Adit 6+9 water. This treatment train was operated from April 2022 until October 2022.

Parys Mountain

Parys Mountain Mine was the world's largest source of copper in the 18th Century. Today the site is a valuable resource for tourism, research and education, but is also one of the biggest single point sources of pollution in Wales, discharging more dissolved metals into the Irish Sea than the River Mersey, despite having less than 0.3% of the flow.

Most of the mine drainage from the site currently discharges from the Dyffryn Adda Adit into the Afon Goch Amlwch. The main contaminants (average during the period 2015 – 2019) in the discharge are SO_4 (2,263 mg/L), Fe (646 mg/L), Zn (78 mg/L), Al (73 mg/L), Cu (42 mg/L), Mn (16 mg/L), As (0.67 mg/L), Co (0.42 mg/L), Ni (160 µg/L), Cd (150 µg/L), Pb (20 µg/L). The average pH is 2.5.

Due to the high Fe concentrations at Parys Mountain, it was necessary to install two $CaCO_3$-DAS tanks in sequence (each followed by an aeration cascade and decantation pond) ahead of an MgO-DAS or $BaCO_3$-DAS tank to completely remove the Fe and Al before the water contacts the third DAS treatment stage. Two treatment trains were installed (Figure 2): Train 1 with MgO as the final treatment step and Train 2 with BaCO3 as the final treatment step. All DAS tanks were filled using fresh wood cuttings.

Contaminant removal efficiency calculations

Relative removal efficiencies r of metals and metalloids are calculated using the following equation:

$$r = \frac{c_{in} - c_{out}}{c_{in}} \times 100\%,$$

where c_{in} is the inflow concentration and cout is the outflow concentration.

Results

Cwm Rheidol

Table 1 displays median inflow and outflow total concentrations in treatment train 1.

In treatment train 1, removal efficiencies of >99% are calculated for Al, Cd, Fe, Pb and Zn. Removal efficiencies are 98.9% for Ni, 97.6% for SO_4, 83.6% for Cu, 78.8% for Cr, and 56.4% for Mn. Alkalinity increases substantially, but also organic carbon, total hardness, Ca, K, Mg, and Sr.

In treatment train 2, removal efficiencies of >99% are observed for Al, Cd, Fe, Mn, Pb, and Ni. Removal efficiencies are 98.1% for Cu, 82.2% for Cr, 63.9% for Sr, 56.4% for Mn, and 15.7% for SO_4. Mg, as expected, increases in its median concentration after the MgO-DAS tank. Organic carbon also increases, but less than in Train 1.

In treatment train 3, removal efficiencies of >99% are observed for Al and Cd. High removal efficiencies are also noted for Cu (98.5%), Cr (95.8%), Pb (83.1%), and Fe

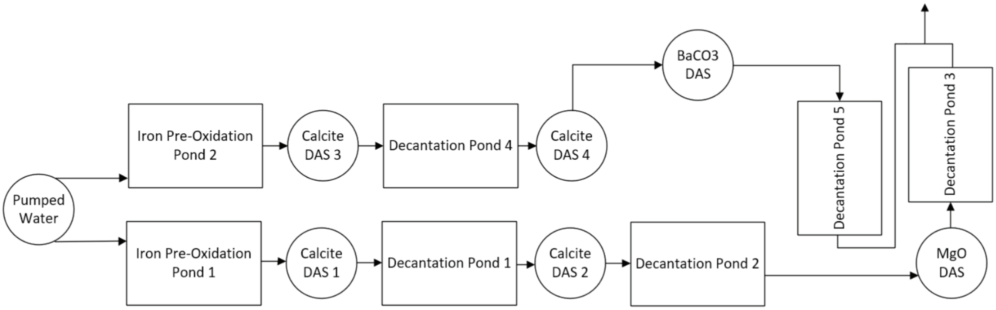

***Figure 2** Schematic site layout of the Parys Mountain DAS pilot trial.*

(77.0%). Removal efficiencies between 3.6% and 27.2% are observed for Li (6.0%), Mg (3.6%), Mg (7.9%), Na (13.5%), Ni (14.7%), SO4 (11.6%), and Zn (27.2%).

In treatment train 4, removal efficiencies of >99% are observed for Al, Fe, and Pb. 98.8% of Cd, 97.0% of Cu, 95.8% of Zn, 90.5% of SO4, 84.5% of Ni, 84.1% of Cr, and 79.4% of Mn are also removed.

In terms of absolute removal, the largest contributions to metal mass load reduction across the treatment trains are achieved for Zn, Fe, Al, Mn, and Pb.

The water flowing out from treatment trains 1 and 3, which used fresh wood cuttings to mix the DAS materials, displayed a dark colour and a strong rotten egg smell, indicative of bacterial sulfate reduction reactions. In trains 2 and 4, which used dried pine wood shavings, the outflow was clear and odourless.

Parys Mountain

Table 2 Table 1 displays median inflow and outflow total concentrations in treatment train 1.

In treatment train 1, removal efficiencies of >99.8% are observed for Al, Cd, Cu, Fe, and Zn. Removal efficiencies are 98.5% for Mn, 96.6% for Cr, 96.2% for Ni, and 89.9% for Pb. Median SO$_4$ removal is 16.9% in train 1.

In treatment train 2, removal efficiencies of >99.8% are observed for Al, Cd, Cu, Fe, and Zn. Removal efficiencies are 99.0% for Ni, 89.9% for Pb, 87.5% for Mn, 96.7% for Cr, and 92.9% for SO$_4$. Sr increases substantially across train 2, both in the CaCO$_3$-DAS tanks and the BaCO3-DAS tank.

In terms of absolute removal, the largest contributions to metal mass elimination in both treatment trains are achieved for Fe, Al, Zn and Cu. All four contaminants are removed within the CaCO$_3$-DAS tanks.

***Table 1** Median inflow and outflow water quality of the Cwm Rheidol DAS treatment trains during the trial period (total concentrations unless otherwise stated).*

Parameter	Unit	Adit 6 + 9 mixed	Train 1 out	Train 2 out	Train 4 out	Adit 9	Train 3 out
pH	---	3.48	7.86	9.42	8.17	2.93	6.92
Alkalinity	mg/L	0	310.0	62.5	175.0	0	265.0
Diss. Oxygen	mg/L	10.42	4.61	7.58	n.d.	7.90	6.83
Org. Carbon (Filt.)	mg/L	0.74	59.90	3.38	6.82	0.53	29.10
Redox Pot.	mV	433.8	8.1	29.3	67.3	456.1	8.3
Hardness	mg/L	121.8	394.7	277.6	190.8	346.9	945.9
Al	mg/L	5.69	0.02	0.01	0.03	29.90	0.02
Ba	mg/L	0.01	51.40	0.05	5.23	0.01	0.02
Ca	mg/L	29.3	106.0	30.4	47.7	71.2	298.0
Cd	mg/L	0.0445	0.0001	0.0003	0.0007	0.1295	0.0004
Cr	mg/L	0.0024	0.0005	0.0005	0.0005	0.0120	0.0005
Cu	mg/L	0.0534	0.0087	0.0010	0.0016	0.0971	0.0015
Fe	mg/L	16.70	0.10	0.03	0.04	101.00	23.20
K	mg/L	0.97	1.37	1.00	0.96	0.82	1.28
Li	mg/L	0.10	0.10	0.10	0.10	0.18	0.17
Mg	mg/L	12.8	15.1	46.2	15.6	44.1	42.5
Mn	mg/L	0.98	0.43	0.01	0.25	4.57	4.21
Na	mg/L	10.4	4.6	7.6	8.2	7.9	6.8
Ni	mg/L	0.284	0.003	0.002	0.057	1.33	1.14
Pb	mg/L	0.736	0.005	0.002	0.002	0.012	0.002
SO$_4$	mg/L	229.0	5.6	207.0	24.6	841.0	743.0
Sr	mg/L	0.07	1.08	0.03	0.46	0.24	0.38
Zn	mg/L	20.70	0.21	0.41	1.07	89.20	64.90

n.d.: not determined

SO4 removal also accounts for an important decrease of total contaminant mass in the $CaCO_3$-DAS tanks of both trains, with substantial additional SO4 removal achieved in the $BaCO_3$-DAS tank, but not in the MgO-DAS tank. The removal of SO_4 and Zn in the $CaCO_3$-DAS tanks was likely due to the reducing conditions that developed in the tanks, promoted by the fresh wood cuttings. The water flowing out from both trains displayed a dark colour and a strong rotten egg smell, indicative of bacterial SO_4 reduction reactions.

Conclusions

All treatment trains at both field trial sites achieved very high metal removal rates during the trial period.

Overall, treatment performance for most metals was similar for the treatment trains, and most metals were almost completely removed within the $CaCO_3$-DAS tank of each train. Only Mn and SO^4 displayed no or low removal in the $CaCO_3$-DAS tanks and required MgO-DAS (for Mn) or $BaCO_3$-DAS (for Mn and SO_4) to improve removal efficiency.

One issue in the trial performance at both sites was unpleasant odour and dark discolouration of the water flowing out of treatment trains that used fresh wood cuttings in the DAS reactors, due to reductive microbiological reactions. These unwanted reactions were prevented by using dried pine wood shavings, which demonstrated excellent results in treatment trains 2 and 4 at Cwm Rheidol. The pine shavings have natural antimicrobial properties and release much less organic carbon.

At Parys Mountain, substantial amounts of Fe were removed in the iron pre-oxidation ponds (on average, about 150 mg/L in each train) and in the decantation pond after the first $CaCO_3$-DAS tank in each train (on average about 150 mg/L in train 1 and about 100 mg/L in train 2). The iron pre-oxidation ponds had however particularly very long residence times (about eight days), which

Table 2 Median inflow and outflow water quality of the Parys Mountain DAS Treatment Trains (total concentrations unless otherwise stated).

Parameter	Unit	Inflow	Train 1 Outlet	Train 2 Outlet
pH	---	2.51	9.41	8.13
Alkalinity	mg/L	n.d.	n.d.	n.d.
Dissolved Oxygen	mg/L	2.7	5.1	5.1
Organic Carbon (Filt.)	mg/L	3.15	114.6	55.1
Redox Potential	mV	461.3	84.1	136.8
Hardness	mg/L	601.3	2111.5	931.2
Al	mg/L	69.85	0.013	0.022
Ba	mg/L	0.01	0.40	2.53
Ca	mg/L	75.7	52.3	223.0
Cd	mg/L	0.146	0.00015	0.00033
Cr	mg/L	0.0150	0.0005	0.0005
Cu	mg/L	36.6	0.006	0.012
Fe	mg/L	615.00	0.40	0.26
K	mg/L	1.4	27.3	20.5
Li	mg/L	0.16	0.12	0.18
Mg	mg/L	102.0	641.5	106.0
Mn	mg/L	17.4	0.27	2.2
Na	mg/L	18.6	53.7	30.3
Ni	mg/L	0.151	0.006	0.002
Pb	mg/L	0.020	0.002	0.002
SO_4	mg/L	2040	1695	145
Sr	mg/L	0.13	0.14	2.15
Zn	mg/L	62.65	0.11	0.24

n.d.: not determined

may be prohibitive for a full-scale application. Modifications to the pilot system in 2023 (already commissioned) will test the use of a vertical flow reactor (VFR, e.g., Sapsford and Williams 2008) instead of the iron pre-oxidation pond in train 1, to compare the iron removal performance for a lower treatment plant footprint.

The main differences in treatment performance between trains using MgO-DAS or $BaCO_3$-DAS were as follows:

- Trains with MgO achieved greater removal of Mn and Zn and displayed lower increases in Ba and Sr. The outflowing water had however higher concentrations of SO_4, K, hardness and a more alkaline pH.
- Trains with $BaCO_3$ achieved greater removal of SO4, had lower concentrations of K and hardness, more near-neutral pH values, but higher Ba and Sr concentrations.

The field trials have been successful and demonstrate the ability of the DAS system to be considered for scaling up to full sized treatment plants at both sites.

Acknowledgements

This study is funded by the joint Metal (Non-Coal) Mine Programme of NRW and The Coal Authority sponsored by Welsh Government. We extend our thanks to Dr Nina Menichino, Team Leader, Evidence Portfolio, Programmes and Processes at NRW for supporting this paper.

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