Optimising Circum-Neutral Mine Drainage Treatment By Implementing High Shear Degassing Into A Sustainable Active Treatment System

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Abstract

An alternative approach to treat circum-neutral metal mine drainage is being trialled using a degassing step within a sustainable active treatment (SAT) system. Typical discharges from Welsh metal mines have high dissolved CO_2 content and elevated alkalinity due to unique REDOX conditions. Although mine water has elevated alkalinity the pH is typically <7 upon discharge, keeping metals like Zn in solution. Degassing CO_2 raises the pH to >8.2, enabling metal removal by precipitating hydroxides or by sorbing to iron oxides. Degassing CO_2 is considered a potentially more sustainable, lower carbon and chemical-free method of removing metals from solution.

Keywords: Water treatment, CO_2 degassing, lead, zinc, mine drainage

Introduction

The removal and potential recovery of metals from circum-neutral mine drainage is a challenge, particularly in locations such as Wales where many historical mine discharges exist in remote areas. Metals such as Zn and Pb typically require a high pH (>8) to immobilise the soluble phase by precipitation/sorption, which is beyond the range achievable in many passive systems. Even if passive systems can be installed metal recovery can be difficult, and long-term performance is subject to uncertainty. Active treatment such as high-density sludge (HDS) is considered the only viable solution in many cases.

The approach taken within this study was to utilise well-established scientific principles used in passive water treatment, such as aeration and sorption, and integrate them into SAT to create an effective water treatment process for metal-contaminated circum-neutral mine water. This approach allows for cost-effective treatment of difficult to treat waters (circum-neutral with high Zn and Pb concentrations) and provides an opportunity to recover and reuse or resell metals from the treated water to potentially offset legacy site management.

Aeration is recognised as an opportunity in mine water treatment due to the effect of oxidation state on metal mobility. Dissolved gases such as CO2 also affect the carbonate system and ultimately solution pH, which in turn can be used for metal mobility manipulation (Marsden *et al.* 2021). Underground mine drainage waters are typically reducing and low in oxygen, and may be supersaturated with carbon dioxide due to reactions with host rocks such as limestone or by the oxidation of available organic carbon (Geroni *et al.* 2012). In Wales many circum-neutral mine waters are located in carbonate-rich host rock (Warrender and Pearce 2007), and thus circum-neutral mine waters may be affected by increased dissolved carbon dioxide. Previous studies on the aeration of mine drainage within treatment systems have shown that the chemistry of the mine water can be altered. The pH can rise by increasing the dissolved oxygen (DO) concentration as well as degassing of dissolved carbon dioxide (Kirby *et al.* 2009).

The use of the Maelgwyn Mineral Services (MMS) Aachen High Shear Reactor technology (fig. 1), more commonly used to enhance gold and silver leach kinetics through supersaturation of oxygen into slurry and mass transfer, has allowed for efficient aeration and degassing in a smaller physical area which is used to alter the pH of circum-neutral mine water. The theory of degassing circum-neutral mine water has been tested on a circum-neutral discharge from the abandoned Nant y Mwyn Pb-Zn mine in Mid Wales.

The degassing methodology at beaker trial level was also repeated on four additional samples of circum-neutral mine drainage waters from four separate Pb/Zn mines in Wales.

Site Background

Nant y Mwyn Mine is located in the village of Rhandirmwyn, 10 km north of Llandovery, Carmarthenshire. Underground workings and extensive spoil heaps are major sources of metals pollution to downstream watercourses, causing the River Tywi to fail Water Framework Directive (WFD) standards for Zn for approximately 25 km. A river system review (Coal Authority 2020) identified that clean-up at Nant y Mwyn would singularly benefit the failing waterbodies downstream, with no other major sources of metals pollution in the catchment.

The mine is geographically split into two sites, the Upper Boat Level (Nant y Bai tributary) and the Lower Boat Level (Nant y Mwyn tributary). The portal of the Lower Boat Level drainage adit is blocked and water discharges from the crown hole of an air shaft in-bye of the blockage. This mine water enters Church Terrace Tributary before joining the Nant y Mwyn and subsequently the River Tywi.

Figure 1 Aachen reactor cartridge that introduces gas under pressure to generate fine gas bubbles

Initial degassing tests

In 2021 water samples were collected from the Lower Boat Level discharge for beaker trials and a laboratory scale trial of the Aachen High Shear Reactor to assess the feasibility of degassing mine water to adjust pH as part of a larger treatment system. Field measurements taken at the site at a later sampling date (autumn 2022) (Table 1) show the effect of natural degassing from the shaft discharge, down the stream to the flow gauging station weir, and further downstream in the Church Terrace Tributary. The overall elevation change is approximately 6 metres. Small increases in DO and pH are seen from natural degassing downstream.

The mine water samples were taken to Geochemic Ltd (Geochemic) laboratory for the treatability study. Active aeration, by sparging the raw mine water sample with air, was completed at beaker scale and the pH of the solution recorded during this process. The test gives an indication of the expected pH change following loss of volatiles that are not in equilibrium with the atmosphere (such as the degassing of CO2 and SO2 gasses). The resultant pH increase during the initial degassing beaker trial is shown in Fig. 2, which overall showed a pH increase of 1.3 units.

In summer 2021 a larger sample (c.500 L) of Nant y Mwyn mine water was collected using submersible pumps directly from the shaft discharge. This was transported to Geochemic Ltd laboratory for use in a trial of the Aachen High Shear Reactor for degassing of the raw mine water. The tank capacity of the Aachen was 100 L, the liquid flow 1,540 L/hr and the air flow rate set as 20 Ln/min. Time was recorded and this was combined with the water and airflow rates were used to calculate the number of passes through the Aachen, where a pass indicates a full circulation of the Aachen system. Data is typically presented as a pass through the system rather than by time. The pH results from the initial trial of the Aachen system on Nant y Mwyn raw mine water are shown in Fig. 3. The pH was successfully increased from an initial pH 6.7 to pH 8.3, which is the targeted pH for Zn removal.

Table 1 *Field measurements at Nant y Mwyn indicating variation due to distance from adit and potential degassing.*

Parameter	Unit	Nant y Mwyn – LB1 at shaft pool	Nant y Mwyn at weir	Nant y Mwyn in stream edge of the property	Nant y Mwyn – water pumped through pipe during collection
Date-time	-	14/09/22 – 11:30	14/09/22 – 11:33	14/09/22 – 11:35	14/09/22 – 13:30
Temperature	°C	10.2	10.3	10.3	13.5
Dissolved oxygen	%	34	38	50	40
Specific conductivity	µS/cm	301	300	300	301
pH	s.u.	6.6	6.4	6.6	6.8
ORP	mV	230	211	186	172

Extended beaker trials

Following the success of degassing the water from Nant y Mwyn a further set of samples were gathered from potentially suitable abandoned mine site discharges in Mid Wales. These included Nant y Mwyn (lower boat level), Level Fawr, Pugh's Adit (Cwmystwyth), Frongoch and Van Mine (fig. 4). The samples were collected in autumn 2022 after a relatively dry summer, with most of England and Wales being under drought conditions. As such, it can be expected that the flow rates were at the lower end of the range experienced at the sites.

The raw mine water was used to complete aeration and adsorption beaker trials by Geochemic's laboratory to test the potential treatability of each mine water by the degassing process. The pH of the mine water samples was continuously monitored whilst the sample was degassed using air sparging. The aim of this aeration step is to allow CO_2 dissolved in the water to be released as gas, raising the pH. The change in pH of the degassing stage are shown in Fig. 5. The pH of all mine water samples increased, but the range of increase varied. Pugh's Adit and the Van Mine duplicate pH increased the least, at around 0.3 pH

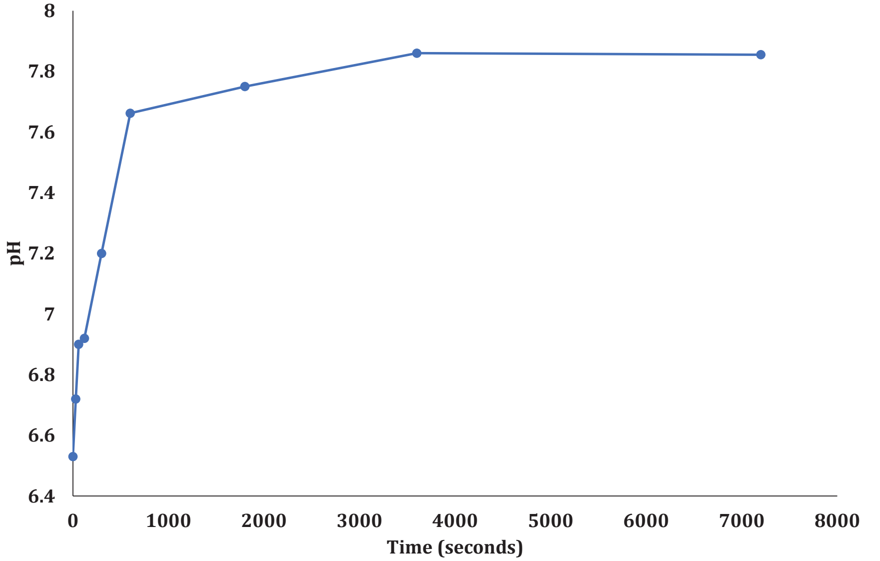

Figure 2 *Initial pH change following the beaker degassing test on Nant y Mwyn mine water.*

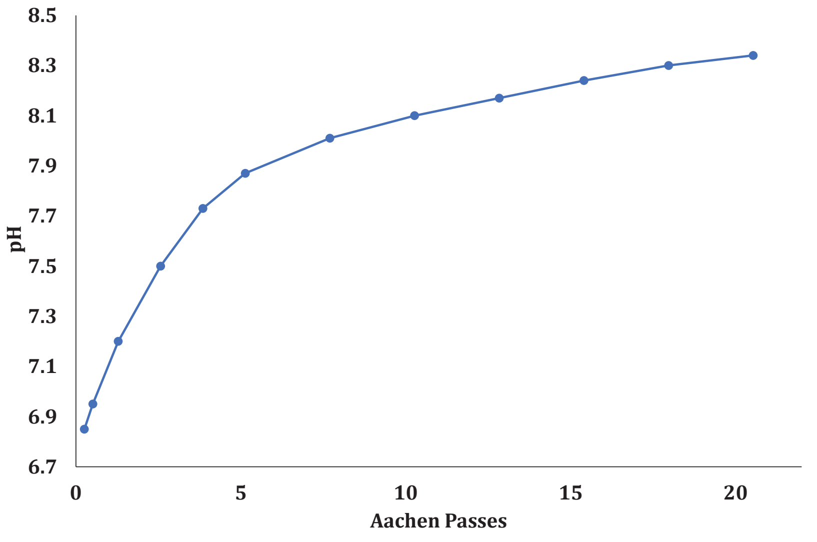

***Figure 3** Initial laboratory trial of degassing Nant y Mwyn mine water using the Aachen High Shear Reactor*

units, however the second Van Mine sample increased by 0.6 pH units. The pH increase at Frongoch and Level Fawr was much greater at 1.3 and 1.5 pH units respectively. This is equivalent to the 1.3 pH units achieved in the original Nant y Mwyn degassing beaker trial. Frongoch, Level Fawr and Nant y Mwyn only showed an increase in pH following commencement of degassing, however, Van Mine and Pugh's Adit both showed a dip in the pH before it then began to increase. It is believed that this dip could be related to latent acidity due to oxidation of reduced iron and/or sulfur species in the mine water.

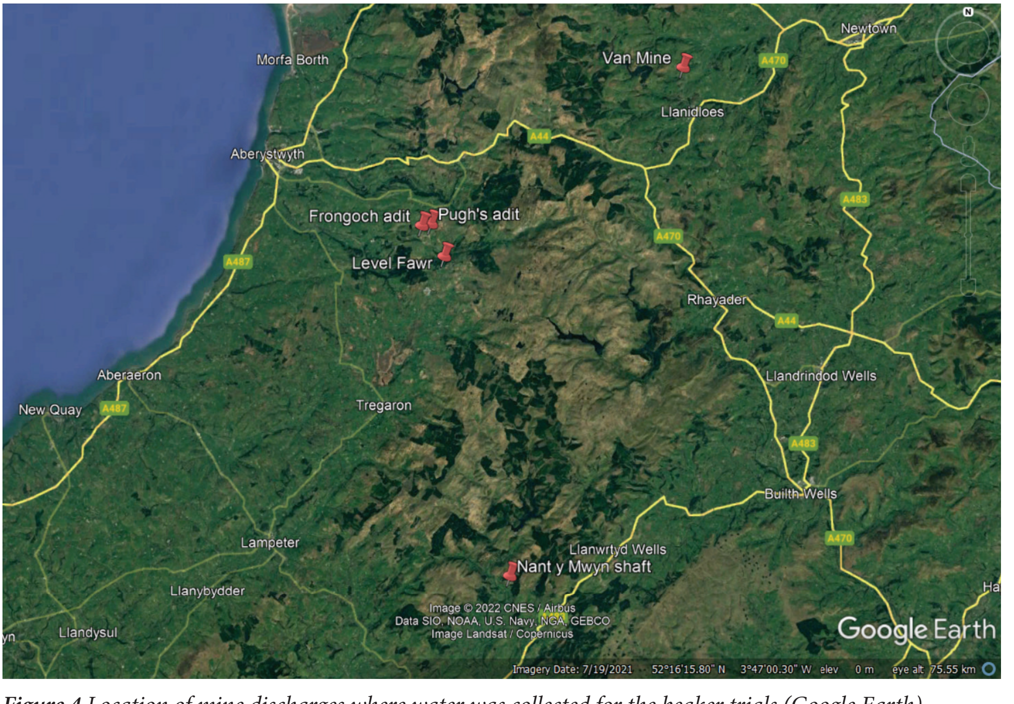

***Figure 4** Location of mine discharges where water was collected for the beaker trials (Google Earth)*

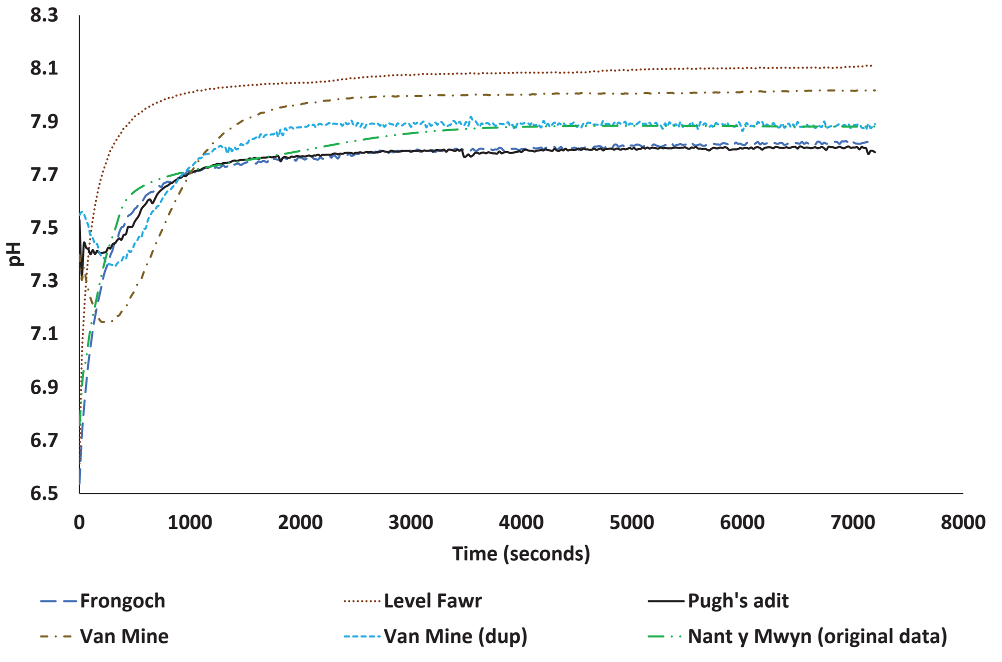

Figure 5 *pH increase in different mine waters following degassing.*

The second part of the beaker trials was to test the effect of adding FeOx as an adsorbent at 10 g/L to the degassed mine water. The metal removal rates are shown in Fig. 6. Following the adsorption step 100% of Pb was removed from all sites other than Van, where 72% of Pb was removed. Level Fawr showed the highest removal rate of Zn at 98% (the final concentration was 40 µg/L), followed by 85% in the Van mine water (the final concentration was 415 µg/L). Nant y Mwyn Zn removal was at around 60%, which is similar to the initial beaker trial results (remaining concentration 6,072 µg/L). Frongoch and Pugh's Adit showed lower Zn removal rates, only 45% and 38% respectively, relating to concentrations of 9,800 and 16,670 µg/L respectively. Cd was removed by over 50% in all the mine waters, and up to 90% in Level Fawr. Cu was also successfully removed in all mine waters where it was present. Co was removed in some mine waters (Level Fawr and Nant y Mwyn) but concentrations remained similar in the others. Mn was removed from Frongoch, Pugh's Adit and Van Mine waters, but not from Nant y Mwyn.

The metal removal rate for Zn, the target metal, was very high where the initial concentrations are lower (Level Fawr and Van Mine). As such, the removal rate from Frongoch, Pugh's Adit and Nant y Mwyn is likely limited by the amount of FeOx added during the beaker trials. A higher amount would be expected to increase removal rates, increasing the efficiency of Zn removal. Overall, there is metal removal recorded at all sites (fig. 6), suggesting this system could be adapted to work at all sites tested during this assessment.

Conclusions

The results presented outline the potential efficacy of incorporating active aeration steps into a SAT system for manipulating pH in circum-neutral mine water to better allow precipitation or sorption of targeted metal species removal, such as Zn, Pb and Cd. A similar pH increase was successfully achieved in all four mine waters tested, confirming the approach may have wider applications and is not restricted to the original study site.

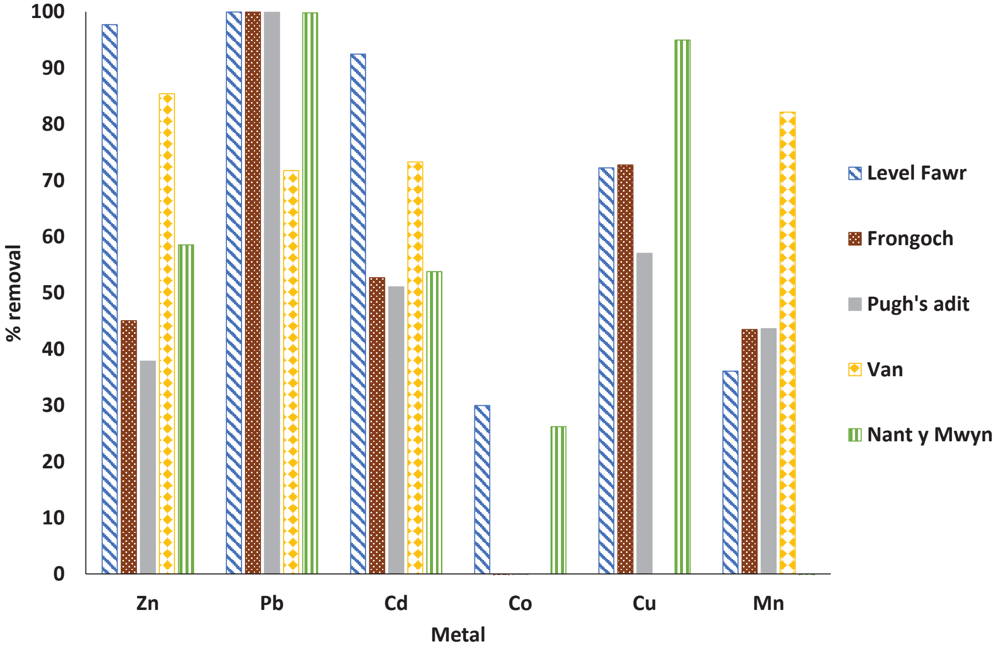

Figure 6 Metal removal in mine water discharges following degassing and FeOx treatment.

The environmental and economic value of incorporating a degassing step into a SAT system provides a more sustainable, lower carbon and chemical-free alternative to HDS systems.

Acknowledgements

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