Novel Developments in High-Shear Degassing Using Carbon Dioxide-Depleted Air to Precipitate Metal Contaminants: Sustainable Active Treatment Strategies for Circum-neutral Mine Water

Victoria Smyth[1], Max Gerke[1], Ryan Schultz[1], Julia Dent[1], Steven Pearce[1], Ben Gersten[2], Tom Williams[3] , Andrew Barnes[2]

[1]*Cambrian Environmental Technologies, UK, jdent@cambrianenvirotech.co.uk*

[2]*Geochemic Ltd., UK, abarnes@geochemic.co.uk*

[3]*Natural Resources Wales, UK, tom.williams@naturalresourceswales.gov.uk*

Abstract

The Sustainable Active Treatment (SAT) system has been developed as a novel process for treating circum-neutral mine water (CNMW) and recovering metals. The system's degassing process raises the pH of CNMW to alkaline levels, enabling the precipitation of metals such as zinc and lead. Recent developments introduce the use of carbon dioxide (CO_2)-depleted air, by a device stripping CO_2 from compressed air, that more effectively increases pH. Laboratory trials using CNMW from the disused Nant y Mwyn mine site in Mid Wales confirm the effectiveness of this technique, achieving enhanced metal precipitation compared with conventional air degassing. These advancements demonstrate SAT's potential as a sustainable and effective alternative treatment method for improving water quality and resource recovery from CNMW..

Keywords: Water treatment, zinc, degassing, abandoned mines

Introduction

Circum-neutral mine water (CNMW) is typical of historical metal mines in Mid Wales due to the presence of carbonate gangue and absence of sulfides such as pyrite (Warrender *et al.* 2011). CNMW often has high concentrations of metals such as zinc, lead, cadmium and copper due to their solubility over a wide pH range. Cambrian Environmental Technologies (CET) are developing a modular system for treatment of CNMW and recovery of metals, by combining treatment steps into a “treatment train” approach which include degassing and sorption (Dent *et al.* 2023, Marsden *et al.* 2021).

Industrial applications in mineral processing have readily demonstrated that the high shear reactor is an efficient aeration step. The creation of bubbles in water or droplets in air means the surface area for gas exchange is significantly increased, improving the gas transfer rate. The dispersion of bubbles in a liquid also minimises the distance that molecules need to move in order to come into contact with the gas-liquid interface, increasing reaction rates. CNMW from underground mine workings often contains higher levels of dissolved carbon dioxide (CO2) than typical surface conditions, resulting in depressed pH even in the presence of excess alkalinity. The excess CO2 can be removed by degassing, resulting in a rise in pH because of the presence of latent alkalinity. Reducing CO2 concentrations in mine water could therefore reduce the chemical demands of typical treatment systems (Geroni *et al.* 2011).

Henry’s gas law states that the amount of dissolved gas in a liquid is directly proportional to its partial pressure above the liquid. Minimisation of the partial pressure of a gas above a liquid shifts the equilibrium of the dissolved gas, encouraging it to be released from the liquid. The implications of this gas law were incorporated into modification of the SAT system to determine if the aeration step could be made more effective at degassing CO2. A series of laboratory experiments were set-up to test different media to 'scrub' compressed air of CO2 at different laboratory scales. The degassing step using 'scrubbed' compressed air was tested on CNMW from the Nant y Mwyn site in Mid Wales.

The Nant y Mwyn Mine is near Rhandirmwyn, 10 km north of Llandovery, Carmarthenshire. The mine consists of both underground workings and extensive spoil heaps, which are a source of zinc loading to the nearby river system. 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. Water from the Lower Boat Level was used in this trial. The minewater is circum-neutral and contains an average of 13 mg/L zinc.

Methods

A series of laboratory-scale trials using the SAT system were completed using mine water collected from the site in sealed intermediate bulk containers (IBCs). The chemistry of the mine water at Nant y Mwyn has been described previously (Dent *et al.* 2023, Marsden *et al.* 2021), abridged details are presented in Results Tab. 2. The SAT system uses the Aeroblast reactor which utilises high shear technology to aerate the mine water. The high shear conditions increase the generation of nanobubbles and the efficacy of degassing of CO_2 due to the increased surface area at the water/gas interface. Compressed air has previously been used as the main gas feed for the degassing step.

A flow gauge attached to the Aeroblast was continuously monitored to determine when 100 L has gone through the shearing column; this loop is referred to as one 'Pass'. The length of each batch run (BR) was determined by the number of 'Passes' the same 100 L of minewater went through. At the end of each BR the mine water was drawn from the top of the tank into waste storage, the tank was cleaned and then re-filled with mine water from the IBCs.

The primary form of analysis was real-time pH from the top of the Aeroblast tank, which was monitored using a Metler-Toledo meter (pH Sensor InLab® 413 IP67). Gas and water pressures within the Aeroblast circuit (system gauges) were continuously monitored for consistency. Dissolved oxygen (YSI multiparameter probe), temperature (Metler + YSI), and atmospheric pressure (YSI) were also noted.

To test the theory that the concentration of CO_2 in the input gas was limiting the pH raise in the degassed water, three different trials were completed. An initial trial to test the concept utilised a pressurised nitrogen (N_2) gas canister connected to the Aeroblast circuit as this would supply 0% CO_2. Secondly, two different vessels were filled with milled waste concrete to act as a chemical "scrubber" to remove CO_2 from compressed air. Resultant gas from one large column of milled concrete (50 cm media length, saturated with water) was fed to a 1 L mine water sample. A system consisting of smaller columns, in-series, which were filled with damp, milled concrete (3x 18 cm media length) between an air compressor and the Aeroblast circuit were used to affect a pH change in 100 L mine water samples. Up to two in-line vessels, utilising commercially available (dry) scrubbing media were also installed between an air compressor and the Aeroblast circuit, ultimately, to a higher flow rate and air pressure. Each means of supplying CO_2-depleted gas to the mine water sample was tested independently from the other, with various gas pressures and flow rates. The scenarios included in the trials are shown in Tab. 1.

The ability of the scrubbers to remove CO2 was monitored using a Vaisala GMP252 CO2 monitoring probe and Insight™ software. The commercial scrubbing media was a mixture of calcium hydroxide and sodium hydroxide. The waste concrete was freshly milled by jaw crusher to reduce the impact of weathering and generate media 'pellets' of less than 3 cm.

Water samples were collected at regular intervals from the top of the Aeroblast tank for analysis by ICP-MS to assess how the gas mix trials affected contaminant precipitation. The difference between the dissolved metals concentrations and the total metal

Table 1 Overview of degassing scenarios assessing reduction in the concentration of CO2 within input gasses via various 'scrubbing media'.

Scrubbing Media	CO_2 min. (µg/L)	CO_2 mean (µg/L)	Media length (cm)	Column diameter (cm)	Mean gas flow rate (L/hr)	Max. air pressure (Bar)	Mine water vessel size (Litres)
Nitrogen (N_2)	n/a	n/a	n/a	n/a	15	4.5	100
Commercial (dry)	0	14	36	7	20	4.5	100
Concrete (damp)	0	60	54	7	6	6	100
Concrete (saturated)	0	14	50	15	Unavailable	2	1

concentration indicates the amount that has precipitated i.e. is no longer dissolved. The amount of precipitation was calculated from the dissolved and total metals in the initial mine water source and then again at 10 Passes, 20 Passes and 30 Passes.

Results

Changes in pH and dissolved metals concentrations of the trials using CO_2-depleted air or N2 gas are shown in Fig. 1 and Tab. 2. Overall, all three trials successfully raised the pH to over 8, which is required for the precipitation of ionic zinc in the mine water. The trials were compared where those where only compressed air was used as the gas source (no depletion of CO_2).

Trials with compressed air in the 100 L Aeroblast circuit ran at higher flow rates and pressures than N2 and scrubbed air (i.e. CO_2-depleted) in the same apparatus, yet the pH of the mine water failed to surpass pH 8 at 20 Passes. When trialled with N2 pH 8 was surpassed within approximately 8 Passes. When using air scrubbed with commercial scrubbing media, the pH of the mine water

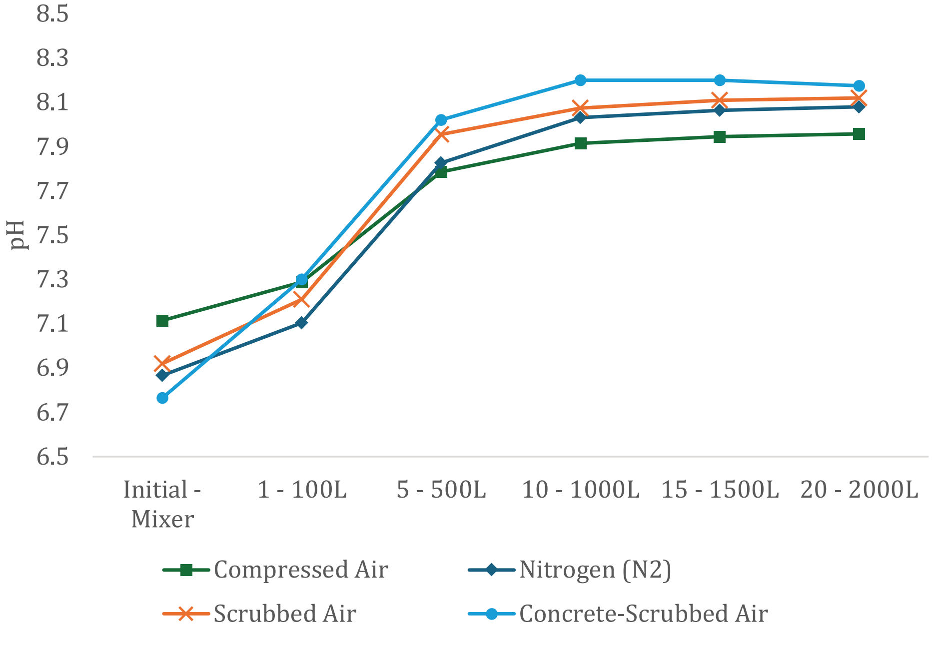

Figure 1 *Spatial distribution of the sulfur content in the coal seam President 1 resulting from Kriging interpolation of data from 45 exploration drillings in the western Ruhr area, depicted by the white circles. The black rectangle roughly represents the area of the longwall mining operation.*

surpassed pH 8, in a similar number of passes as when N2 (0% CO_2) was used as the input gas (Fig. 1).

At the lowest flow rates, the input exhaust gas mix generated by the larger column of crushed concrete (50 cm length, saturated) reduced the CO_2 concentration to 0 mg/L, which was maintained at < 20 mg/L (0.002%) for almost 80 hours. For the smaller columns of crushed concrete media (3x 18 cm, damp), installed in series for the 100 L Aeroblast circuit, flow rates were low but pH 8 was surpassed after 6 Passes. The maximum pH achieved (pH 8.16) was very similar to when N_2 and compressed air scrubbed with commercial (dry) media had been installed in the Aeroblast circuit. Homogeneity of the grain size of the milled waste concrete was improved upon for the smaller vessels, from the larger one, by selective sieving but flow rates could not exceed 10 L/min, which is too low to reach the target pH of 8.3.

It was noted during the experiments that the use of a stirrer within the Aeroblast tank appeared to draw CO_2 from the atmosphere and kept the pH lower.

Alongside the complete removal of CO_2 from the gas input, the air flow rate was proven to play an important role in the pH increase (Tab. 2). Further investigations using compressed air scrubbed by the dry, commercial media were able to reach higher gas flow rates, yielding pH results above the target 8.3.

The increase in pH for each 100 L mine water sample had a marked effect on the quantity of metal precipitate. When the pH was raised over 8, a fine, pale, precipitate formed in the 100 L mine water sample, obscuring the view of the agitator and the base of the Aeroblast tank. This precipitate did not form in the 100 L trials using only compressed air as the mine water remained close to pH 8, even after 45 Passes. It is theorised that this precipitate is a zinc hydroxide based on the chemistry of the inflow and outflow water (confirmation due with ongoing testing).

Implications of the pH increase for metals precipitation are considered in more detail in Fig. 2 and Fig. 3. The starting concentration of zinc per sample ranged from approximately 10 mg/L to 14 mg/ L. Almost all zinc (Fig. 2) was precipitated in the higher flow rate trials, where the tank pH went above 8.3 in BRs of 30 Passes. Lead, copper and cadmium also readily precipitated at this pH. Fig. 3 illustrates the precipitation of these three metals (Pb, Cu, Cd) by the reduction in dissolved concentrations.

Discussion

These trials confirm that a crucial driver for the removal of CO_2 from CNMW, and therefore increase in mine water pH, is the proportion (or partial pressure) of CO_2 in the gas used in degassing. Nitrogen has the largest partial pressure differential (100% gas is not CO_2) however, the use of compressed N_2 canisters in remote environments, where this system is proposed to be used, are impractical for use and maintenance.

The CO_2 proportion in air is anticipated to be variable but approximately 0.03–0.04%. Following the scrubbing processes utilised in these degassing trails, the difference in CO_2 concentration from the original gas composition (i.e. air) appears negligible compared with the marked effect the change has on the reaction to increase the mine water pH. The correlation between the reduction in CO_2 concentrations in the gas feed and the largest increase in pH change in the mine water, indicate the importance of CO_2 in regulating mine water pH.

The concrete media seemed to outperform other options but higher flow rates are required to reach the target pH than those

Table 2 *Results for pH (averaged maxima) and selected dissolved metal concentration changes in mine water by gas flow rate.*

	Aeroblast 'Passes'	pH	Zinc µg/l	Lead µg/l	Cadmium µg/l	Copper µg/l
Initial mine water	n/a	6.86	10750	113	37.2	24.5
Lower gas flow	20	8.13	5656	31.3	31.3	4.6
Higher gas flow	30	8.54	2070	8.4	28.0	1.5

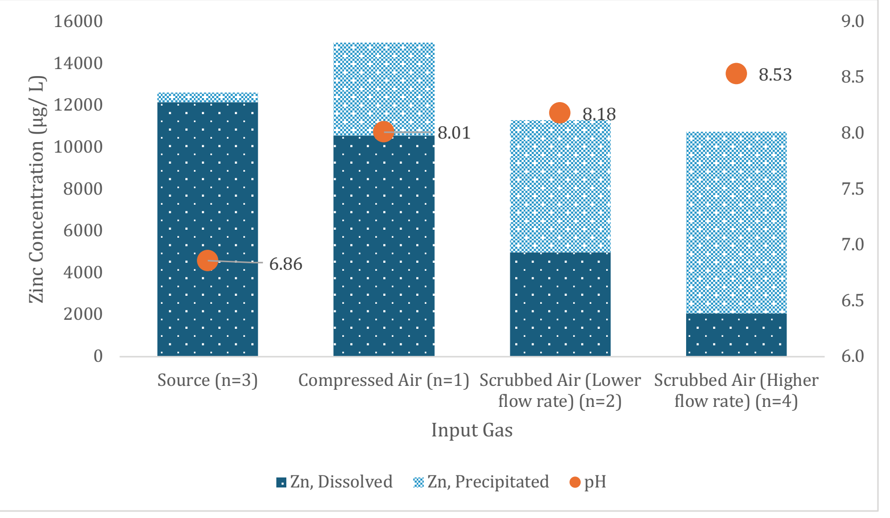

***Figure 2** Zinc precipitate in mine water at batch run end by gas mix, against pH in 100 L tank.*

employed in the BRs. The higher pH reached at low flow rates was also when no agitation occurred within the 100 L in the Aeroblast tank. Results therefore look similar to the initial tests with commercial media, which were agitated, but did not work effectively at the higher flow rates necessary to consistently surpass 8.3.

At the higher air flow rates, the residence time through the concrete scrubbing media was greatly reduced and as such, the CO_2 removal was not as effective. The reactivity of the recycled concrete is linked to the homogeneity of the material both in terms of reactive surface area and reactivity of available minerals, which will need to be

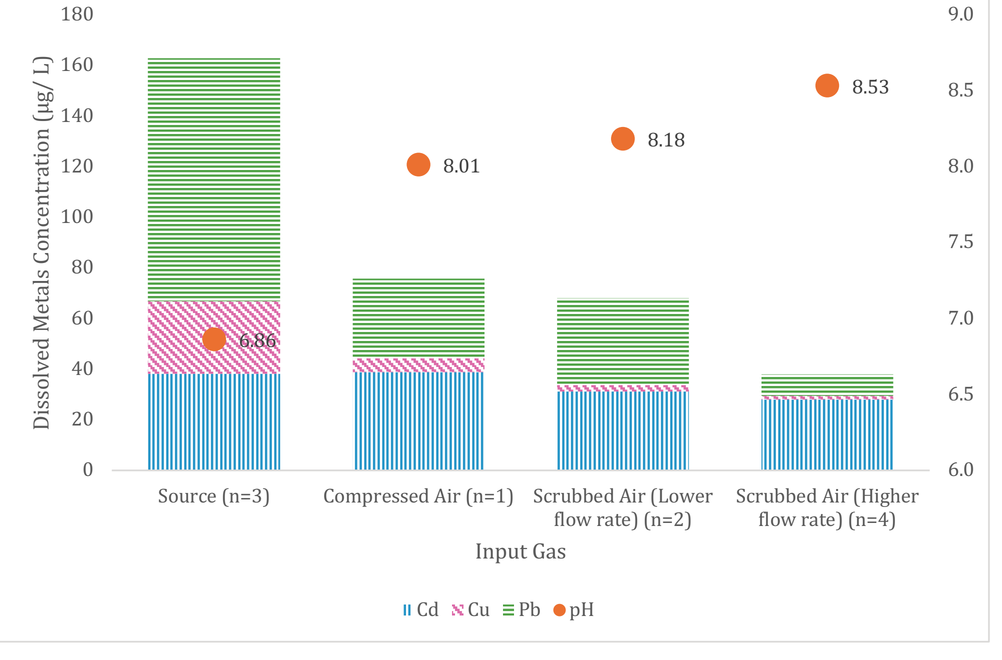

***Figure 3** Select metals concentrations at batch run end by gas mix, against pH in 100 L tank.*

compensated by material preparation and gas residence time.

Further investigations will use a larger volume for the scrubber system to improve residence times (both soda lime and concrete) and ensure this element is working as effectively as possible.

Conclusions

The findings from this study demonstrate that the gas mix used in degassing plays an important role in altering the condition of mine water pH because adjustments to pH are highly sensitive to CO_2 concentrations in the gas input. The incorporation of a "scrubber" to reduce CO_2 concentrations was therefore an effective means to increase pH during degassing. Re-purposing of used concrete, to act as a CO_2 scrubbing media, in the degassing step of the SAT system exhibits feasibility although requires further investigation to improve current constraints.

This paper only describes the recent trials on the degassing stage of the SAT system. Ultimately, the SAT system will incorporate two more stages to maximise the removal and recovery of contaminant metals (primarily zinc) via filtration and sorption elements. Investigations are still ongoing to finalise the design of the "treatment train" that will reduce the dissolved zinc from 10 mg/L to a target of 10–100 µg/L. Parameters for continuous running of the system have been chosen based on the results from the BRs that achieved a pH raise beyond 8.3 and are ongoing.

Overall, the trials demonstrated that a semi-active treatment system using scrubbed air or N_2 to degas CO_2 from mine water was effective at raising pH within the range required for precipitating metals of interest. This system could reduce reagent consumption associated with traditional treatment systems.

Acknowledgements

The authors thank the Wales Metal Mines Programme, funded by Welsh Government, for allowing these results to be published.

References

Coal Authority (2020) Metal Mine Failing Waterbodies Assessment. – Overview Report OP16-154/F13/0.

Geroni JN, Sapsford DJ, Florence K (2011) Degassing CO_2 from mine water: implications for treatment of circumneutral drainage. Mine Water

Dent, Julia; Pearce, Steven; Savage, Rhys; Marsden, James; Schultz, Ryan; Williams, Tom; Stanley, Peter; Roberts, Mark; Barnes, Andrew; Gersten, Ben (2023): Optimising Circum-Neutral Mine Drainage Treatment By Implementing High Shear Degassing Into A Sustainable Active Treatment System. – In: Stanley, P.; Wolkersdorfer, C.; Wolkersdorfer, K., Mugova, E.: IMWA 2023 – Y Dyfodol | The Future. – p. 129–134; Newport, Wales, UK (International Mine Water Association)

Marsden J, Pearce S, Sambrook T, Dent J, Barnes A (2021) Site specific optimisation assessment of cirucm-neutral water treatment using a cost-treatability curve assessment. IMWA 2021 Proceedings: Mine Water Management for Future Generations (2021) 334–339.

Warrender R, Pearce N, Perkins W, *et al* (2011) Field Trials of Low-cost Reactive Media for the Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK. Mine Water and the Environment 30:82–89. https://doi.org/10.1007/s10230-011-0150-8