magnesia [MgO] or witherite [$BaCO_3$]) mixed with a coarse inert matrix (wood chips). DAS had been tested previously at laboratory column, then field pilot scale and is currently successfully deployed full scale at two abandoned mines in SW Spain. In 2020, Natural Resources Wales (NRW) commissioned field pilot trials at Cwm Rheidol mine (Aberystwyth, Mid Wales) and Parys Mountain (Anglesey, North Wales) to test if this technology can be used to remediate acid mine waters at remote sites in a wet temperate maritime climate. These are two of the top five most polluting mines in Wales.

Cwm Rheidol discharges 9 T/yr of metals at a flow of 9 L/sec that enters the Afon Rheidol then Cardigan Bay. The main contaminants (by decreasing total concentration) are SO_4 (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 (0.38 mg/L), Cu (50 µg/L), Cd (40 µg/L), at pH 4.1.

Parys Mountain discharges 231 T/yr from the Dyffryn Adda adit at a flow of 12 L/sec that enter the Afon Goch Amlwch, which enters the Irish Sea. The main contaminants are SO_4 (2263 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), at pH 2.5.

The field trial at Cwm Rheidol has been operating since December 2020. For Parys Mountain, column trials have been carried out at the University of Huelva (Spain) in early 2021 to test the treatment train configuration at laboratory scale, the field trial commences in May 2021. This contribution presents initial results from the trials.

Methods

Dispersed Alkaline Substrate (DAS) is a passive treatment system for ARD (Acid Rock Drainage) with high metal concentrations, which was developed more than a decade ago to overcome clogging and passivation problems experienced with many other passive treatment systems for ARD. The fine-grained alkaline reagent (e.g., calcite [$CaCO_3$], caustic magnesia [MgO] or witherite [$BaCO_3$) in DAS provides a high specific surface area to increase dissolution rates and minimise passivation problems, while the coarse high surface matrix (e.g., wood chips) provides large pores where secondary minerals can precipitate without compromising substrate permeability, thus reducing clogging.

Calcite-DAS removes Al, Fe(III), Cu and Pb, while MgO-DAS removes divalent metals. Barium cations released by $BaCO_3$ dissolution react with dissolved sulphate

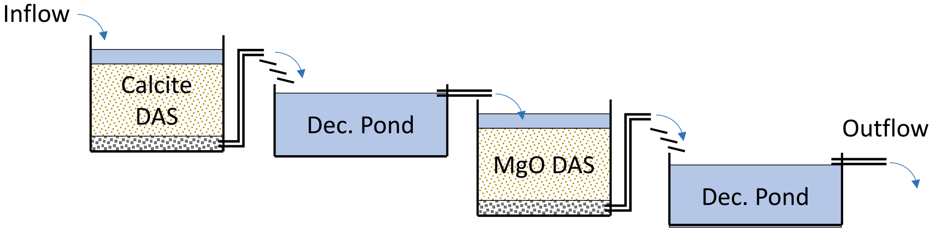

Figure 1 Schematic setup of the calcite-DAS + MgO-DAS reactors of the field trial at Cwm Rheidol.

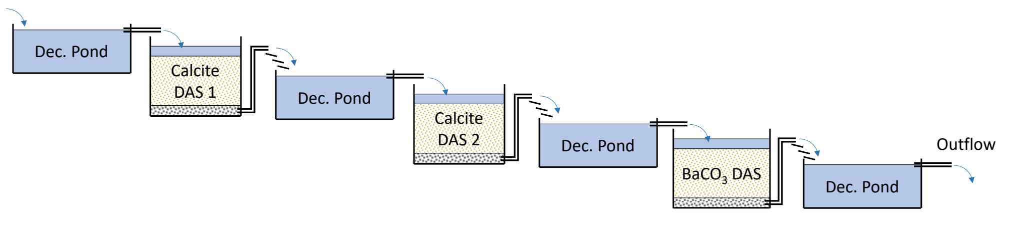

Figure 2 Schematic setup of the calcite-DAS + $BaCO_3$-DAS laboratory columns for Parys Mountain.

to precipitate as $BaSO_4$, which has a very low solubility. The increase of alkalinity (release of carbonate anions) may also induce precipitation of Ca and/or Mg as carbonates or hydroxides, thereby reducing the hardness of the treated water.

At both mine sites, combinations of calcite-DAS with either MgO-DAS or $BaCO_3$-DAS are being tested to determine which one performs best under site conditions. In this contribution, for conciseness we only present field results of calcite-DAS + MgO-DAS at Cwm Rheidol and laboratory results for calcite-DAS + $BaCO_3$-DAS for Parys Mountain.

The treatment train of the Cwm Rheidol field trial presented here (Fig. 1) consists of a calcite-DAS tank, a first decantation pond to oxidise and precipitate iron, an MgO-DAS tank and a final decantation pond to stabilise outflow pH due to CO_2 uptake from the atmosphere. The hydraulic residence time is about two days in each DAS tank and about three days in each decantation pond during the initial trial period reported here. Flow rates will be increased and hydraulic residence times decreased at later trial stages to optimise treatment performance and minimise space requirements for full-scale application.

The laboratory treatment train for Parys Mountain presented here (Fig. 2) contains two sets of calcite-DAS columns with decantation vessels to gradually remove the much higher iron concentrations, combined with a $BaCO_3$-DAS column and a final decantation vessel. The hydraulic residence times are similar to the Cwm Rheidol trial.

Results

Cwm Rheidol field trial

Results from the initial five months of field trial operation are presented below for pH, total Fe, Al and Zn.

The pH values (Fig. 3, left) increase from around pH 3.5 at the inflow of the calcite DAS tank to between pH 6.4 and pH 8.9 at the outflow of the calcite-DAS tank 3. The pH increases further to about pH 10.8 at the outflow of the MgO-DAS tank and then decline to about pH 9.6 at the outflow of the final decantation pond.

Influent total iron concentrations (Fig. 3, right) typically range between 5 mg/L and 25 mg/L. On 15th of March 2021, a very high total concentration of 130 mg/L was measured due to high particulate iron of 120 mg/L. Total iron concentration at the outlet of the calcite DAS tank decreases to an average value of 0.07 mg/L, about 0.03 mg/L at the outlet of the MgO-DAS tank and to below the detection limit of 0.03 mg/L at the outflow of the final decantation pond.

Total aluminium concentrations (Fig. 4, left) decrease from between 1.8 mg/L and 12.4 mg/L at the inflow to around 0.04 mg/L at the outlet of the calcite-DAS tank. Concentrations around the detection limit of 0.01 mg/L are observed at the outflow of the final decantation pond.

Total zinc (Fig. 4, right) is partially removed in the calcite-DAS tank, from inflow values between 9 mg/L and 40 mg/L to an average of 8.5 mg/L at the outlet of the tank. MgO-DAS removes virtually all remaining Zn, with concentrations at the outflow of the final decantation pond of around 0.18 mg/L.

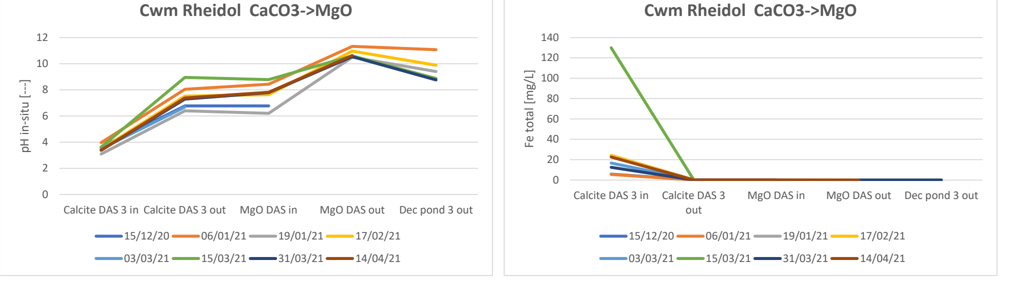

Figure 3 *Evolution of pH (left) and total iron concentrations (right) along the Cwm Rheidol treatment train.*

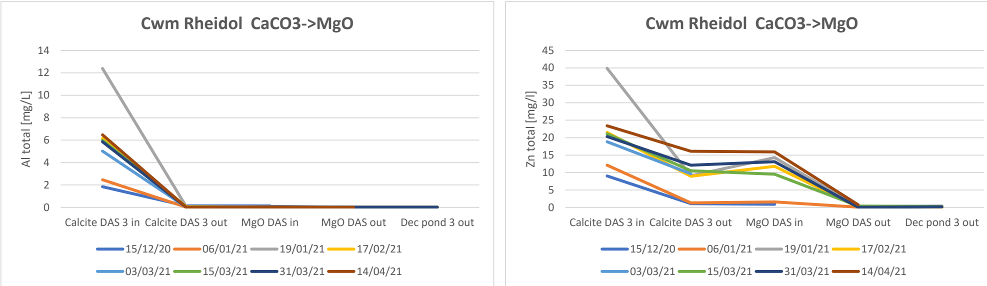

Figure 4 *Evolution of total Al (left) and Zn concentrations (right) along the Cwm Rheidol treatment train.*

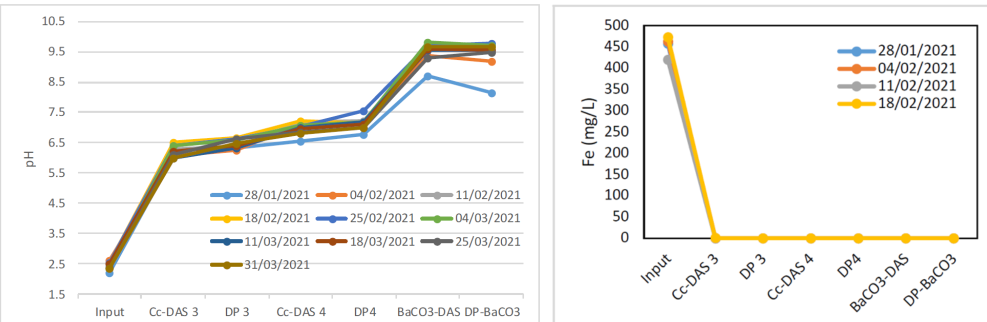

Figure 5 *Evolution of pH (left) and total iron concentrations (right) along the Parys Mountain laboratory columns.*

Parys Mountain column trial

Results from the initial two months of laboratory trial operation are presented below for pH, total Fe, Al and Zn.

Inflow pH is around pH 2.4 throughout the trial (Fig. 5, left). At the outflow of the first calcite-DAS column, it increases to around pH 6.4, to around pH 6.7 at the outflow of the second calcite-DAS column and to around pH 9.5 at the outflow of the $BaCO_3$-DAS column.

Influent total Fe concentration (Fig. 5, right) was around 450 mg/L, and decreased to less than 0.1 mg/L at the outflow of the first calcite-DAS column.

Similar to iron, Al (inflow concentration arounf 60 mg/L; Fig. 6, left) was completely removed in the first calcite-DAS column. Zn (Fig. 6, right) had an inflow concentration of arounf 55 mg/L, with little removal in the first calcite-DAS column. Some Zn (with decreasing efficiency) was retained in calcite-DAS column 2 and decantation pond 2, but throughout the trial all remaining Zn was retained in the $BaCO_3$-DAS tank.

Sulphate concentrations (Fig. 7, left) in the inflow were around 2300 mg/L, and they decreased to around 2100 mg/L in the outflow of the first calcite-DAS column. They remained approximately constant in the first decantation pond, second calcite-DAS column and second decantation pond for all sampling rounds except the first round in January 2021. Sulphate concentrations decreased considerably to between 100 mg/L and 500 mg/L at the outflow of the $BaCO_3$-DAS column, with a decreasing trend in sulphate removal efficiency. Sulphate removal was likely due to precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) in the first calcite-DAS column, and due to barite ($BaSO_4$) precipitation in the $BaCO_3$-DAS column.

Ca concentrations (Fig. 7, right) increased from about 50 mg/L at the system inflow to around 370 mg/L at the outflow of the first calcite-DAS column, indicating that the removal of metals and acidity was driven by calcite dissolution. Ca decreased only marginally in the first decantation pond, second calcite-DAS column and second decantation pond, but dropped dramatically to between 10 mg/L and 40 mg/L at the outflow of the $BaCO_3$-DAS column, demonstrating that $BaCO_3$-DAS is also capable of removing again the hardness that was added due to calcite dissolution in the previous treatment steps. Ca removal in the $BaCO_3$-DAS column is likely due to alkalinity release from $BaCO_3$ dissolution and subsequent calcite precipitation. The performance of calcite + $BaCO_3$-DAS system is consistent with results obtained previously in column trials treating acid mine drainage from Spain (Torres *et al.*, 2018).

Conclusions

The results to date obtained from the field and laboratory trials are promising and indicate that remediation of both mine discharges is possible using DAS technology. If successful, this passive treatment system will provide a proven cost-effective option to treat differing maritime metal mine waters from different geological sources of the massive sulphide deposit at Parys Mountain to warm brine epigenetic vein type lead zinc deposits of the Mid Wales Orefield. This new treatment tool can be applied in optioneering to reduce the pollutant load, develop resilience, reverse the derogation of Water Framework Directive (WFD) failing waterbodies and restore river health. This is especially relevant at remote maritime sites where other treatment systems cannot be applied either due to excessive treatment costs or land requirements.

Acknowledgements

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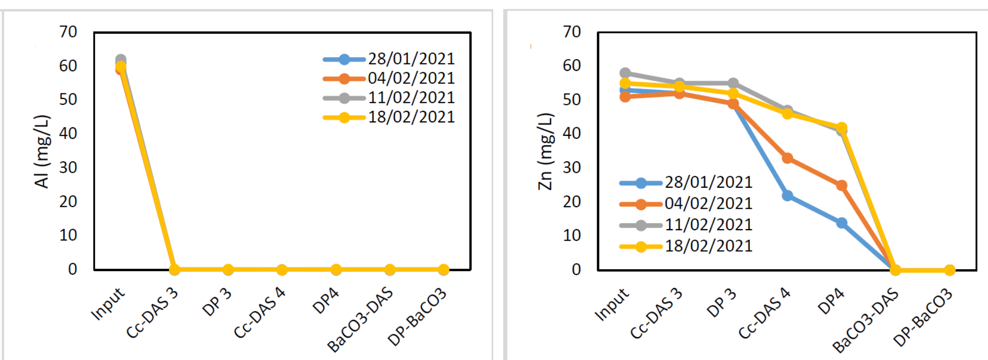

Figure 6 *Evolution of total Al (left) and Zn concentrations (right) along the Parys Mountain laboratory columns.*

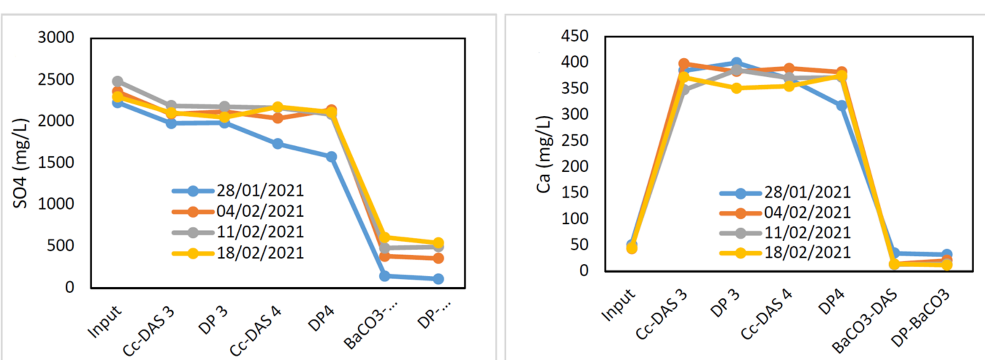

Figure 7 *Evolution of total sulphate (left) and Ca concentrations (right) along the Parys Mountain laboratory columns.*

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