Passive Leached Water Mine (P.L.W.M.) – A sustainable approach to mine water remediation and metals extraction

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Abstract

Although there is little active mining in Wales, legacy mine sites still cause large scale environmental disruption; limiting grazing time in fields affected by metals leaching from spoil heaps, and over 200 km of rivers are impacted by historic metal mines. Furthermore, the transition to "green" technologies is necessitating an increase in mining, and the realisation of supply security, of both traditional and "critical" metals such as Rare Earth Elements (REE), Cobalt and Lithium. Passive Leached Water Mine (PLWM) remediation is a new technology developed by X-ray Minerals Service Ltd (XMS) and Durham University which seeks to address both of these issues.

Introduction

PLWM technology is both passive (relying on gravity to enable waters to pass through the filter media with no pumping required) and is highly effective at remediating mine waste water contaminated with (potentially critical) metals. Furthermore, there is also the potential to recover these extracted metals as a valuable by-product of the process. In this paper, the results of the latest trial (part funded by the Welsh Government SMARTCymru scheme) at Pugh's Adit, Cwmystwyth (Figure 1) will be presented and discussed. The first field test demonstrated the technical and commercial feasibility of the process. A 200 L filter unit with a retention time of 20 min, treating 85,000 L of water over 10 days in December 2019 recovered 80% of Pb, 75% Zn, 70% Ni,70% of Co and 92% of REE. Following this in May 2021, a larger industrial research phase of work enabled a 1000 L filter to be run at the same rate over 58 days, treating up to 500,000 litres of water. This longer test extracted 1kg of both Pb and Zn from Pugh's Adit.

XMS is currently further developing the technology, through an 18-month part funded Innovate UK SMART award, enabling a 1 year, 4000 L filter test to be undertaken. We are envisaging that by the end of this project, the full remediation capacity of this filter technology will be determined, in terms of water initial and variable concentrations, pH, seasonal changes, filter media reusability as well as operations costs and positive environmental impact.

Alginate material fundamentals

Alginate forms the basis of our filter material. It is well studied and descripted (Draget and Taylor 2011, Mohammed *et al*. 2022) and its robust nature, forming egg-box gel structure after a (divalent) cation is introduced, makes it versatile to be used across applications, (Hu *et al*. 2021) . In the case of the alginate (and PLWM), metal adsorption series has been established (Equation 1), through experimental work (Haug 1961) and corroborated by (Wang 2016). It can be seen that Pb has higher affinity than Ca which in turn has higher affinity than Zn, Ni and Co.

$Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+}$, Zn^{2+}, $Ni^{2+} > Mg^{2+}$ (Equation 1)

The binding mode also is different for these elements, with Ca inducing the known egg-box configuration while Zn inducing a weak and less homogenous structure, (Hu *et al*. 2021) This different configuration and binding modes should play a role on the performance of the initial Ca-alginate egg-box structure, on any multi-metal adsorption process, along with pH, initial

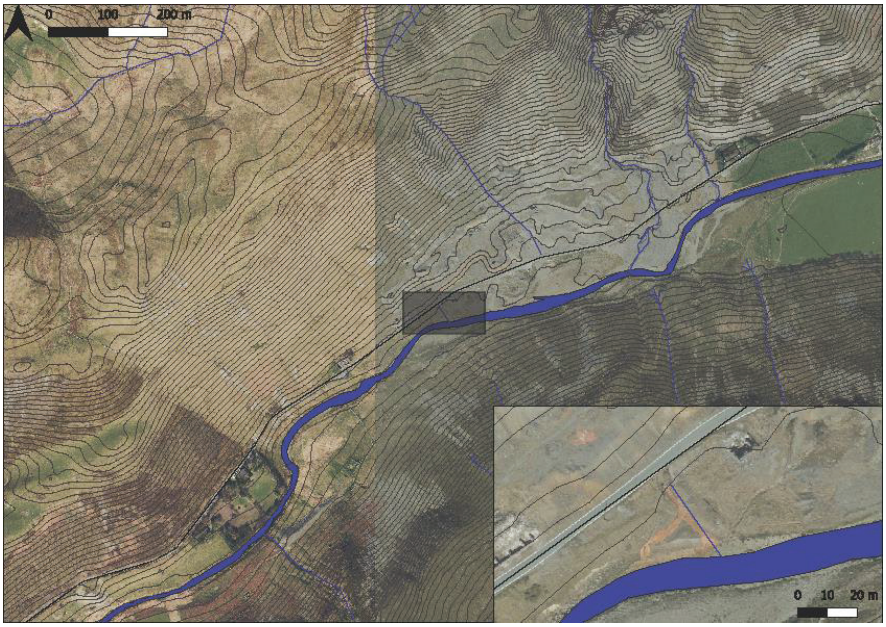

Figure 1 *Aerial imagery and elevation contour map of the old mine area of Cwmystwyth Lead mine. River Ystwyth and streams are in blue, while Pugh's Adit is shown at the bottom right on a different observation scale.*

metal concentration, temperature, and contact time (Montazer-Rahmati *et al*. 2011)

Materials and field trial set-up

Alginate beads

Starting with alginate raw material, beads were made in the lab, using tap water and onsite by mixing with water at Cwmystwyth, by dripping into a non-toxic gelling agent to form 5mm semi spherical filter beads.

Filter unit

For this field trial, 2 X 2 filter units were used in parallel, Filters A & B and Filters X & Y, all with same volume capacity of 225 L. In Filters A & B, the lab-made alginate beads were used, while in Filters X & Y, the on-site alginate beads were used.

End-to-end system water flow description

Water flow from Pugh's Adit is controlled by a metal box, connected by pipe to our filter system, (Figure 2). It has been established from the previous internal research projects that 20 min retention time through the two filter units, translated to 3 L/min water flow through the filter media, is a cost-effective rate for high metal remediation. An entry water flow of 7-8 L/min was regulated for achieving a complete passive flowing system.

Water analysis

Water samples were collected over the period of the trial, at the inlet of the filter units, after filter A, and filter X, and after filter B and filter Y, which constitutes the treated water

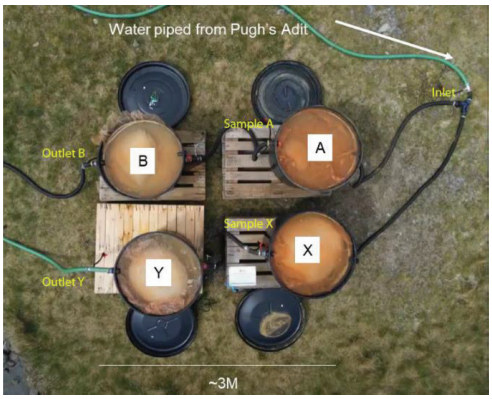

Figure 2 *Aerial imagery of filter A-B and filter X–Y, as laid out during the field trial. Water pipe from Pugh's Adit, filter units, A, B & X, Y as well as sampling points Inlet, Sample A, Outlet B, Sample X and Outlet Y are annotated. System's footprint is 3 m × 3 m.*

concentrations. Water samples were kept in a cool box and sent for analysis the next day. All analysis was done with ICP-OES/MS at Greenwich University, with NIST 1640a being the used standard.

Results

The following results correspond to a field trail during May-July 2021, for assessing how filter media would respond in temperature fluctuation in our testing area of Cwmystwyth mine. This 2-months test was part of a set of field trials assessing filter media performance to higher or lower temperature and rainfall, spanned from November 2020 to August 2021.

The key findings of the series of trials study demonstrated that:

- General changes in temperature and rainfall did not affect filter performance.
- The filters were not affected by freezing (although pipe work did freeze leading to a blockage of water to the filter which will be rectified by insulating pipework in the future)
- The filters did not dry out when water levels fell to the extent that the filter system lost the necessary head to have waste-water flow through it. They stayed damp in the filter and continued to work when flow recommenced.

Focusing more on the analytical findings of the May-July test, the first samples (inlet and filter outlets) were taken on 26/05/2021, with overall sampling placed every 1–4 days until 23/07/2021. The main elements of interest monitored were Pb and Zn, followed by Ni, Co and Total_REE elements (In + Lanthanides). The inlet concentrations of these elements along with the Environmental Quality Standard (EQS) for Pb at 1.2 ug/L and Zn at 15 ug/L, are given in Figure 3. For both elements, the concentrations found over the course of the trial were above those environmental guidelines as established in the Water Framework Directive. For the EQS of Zn, the ambient background concentration of the area is taken into account, as well.

Interestingly, it can be clearly seen how different elements are related to each other. As Pb (Figure 3, top left) and Zn (Figure 3, top right) are the main elements of interest, in the second row the total REE concentration and Ni, Co concentrations are plotted, respectively. The concentration response of REEs is following that of Pb, while Ni and Co is following that of Zn, demonstrating elemental relevance of the expected metalliferous mineralogy of galena (PbS) and sphalerite (ZnS).

Assessing the performance of filter A–B and filter X–Y, on adsorbing Pb, Zn measured

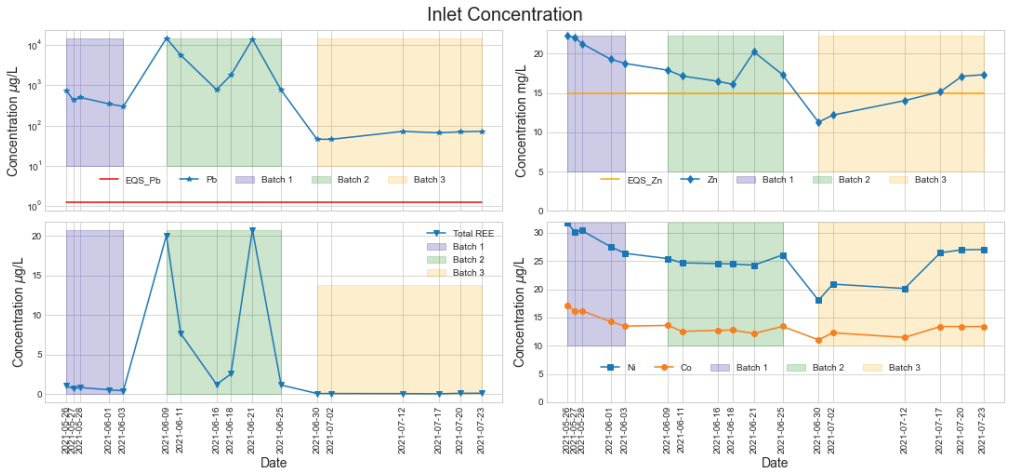

Figure 3 Inlet concentration time series of Pugh's Adit, as collected at the inlet of the filter system and analysed, between 26/05/2021 and 23/07/2021. Different batches of collected samples, Batch 1, Batch 2 and Batch3 dates are shaded accordingly.

at the outlet of each linear set-up, Figure 4, it can be said that, both exhibited very high adsorption capability removing Pb from the water, despite the fact that filter X–Y alginate beads were made with river water.

Zinc was problematic. To start with, the filters were highly effective, however this, combined with the order of magnitude higher level of zinc in the waste water compared to other elements, meant that the filter media was quickly overwhelmed. Therefore, for the majority of the filter test, Zn adsorption was not as good as for Pb. If the Batch 1 pattern of Zn is carefully observed (Figure 4, top right), the effluent concentrations for the first three incidents, is between 25–50 % of the inlet, while after that the filter system seems saturated in Zn. Similarly, for filter X–Y (Figure 4, bottom right), the first concentration incidents show a good Zn adsorption while for the rest of the trial, the filter is also saturated with Zn.

Total adsorption % was calculated and presented in Figure 5 for filter A & B and filter X & Y. It can be seen that the difference in adsorption capacity based on the initial water used for constructing filter media, tap water vs river water, has a small effect. It should be noted that for Pb (in both filter system) and for Batch 1, the adsorption % drops, while for Batch 2 reaches 99% Pb recovery, before it drops below 60% for Batch3. That can be described as an anomalous recovery pattern, while on the other hand Zn, starts with a 40% total recovery in both filter systems, fluctuating downwards to 0% or negative % (meaning filter desorbs Zn into the water). One explanation for Pb adsorption pattern is the destructive behaviour of Zn towards the Ca-alginate structure as discussed previously, for Batch 1, which is minimised for Batch 2 & Batch3, allowing higher adsorption % for Pb, consistent for both filter systems.

On average, for Batch1, Batch 2 and Batch 3, different metal recovery % was achieved, as shown in Table 1. No standard deviations of concentrations are given, as the scope of that trial was to assess, at a high level only, adsorption efficiency of filter material. Furthermore, the adsorption patterns of Pb and for the REE show some irregularity through the three batches, which is a point for further research during the 1-year trial imminently commencing. All standard

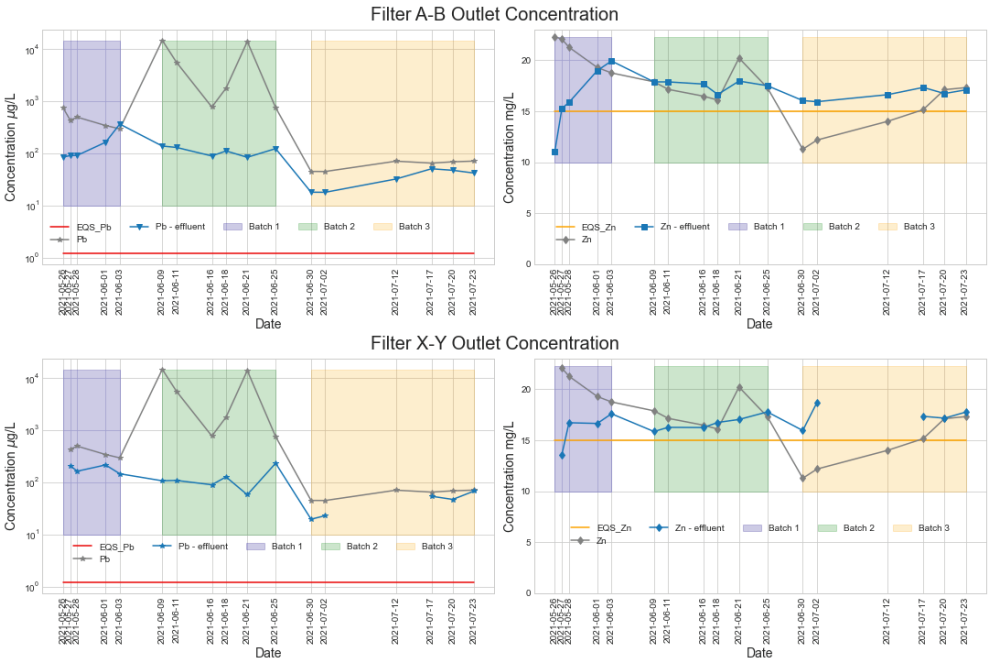

Figure 4 *Effluent concentrations of Pb and Zn for both filter systems, A-B (top row) & X-Y (bottom row). Blue lines are the effluent concentrations while grey lines are the inlet concentrations plotted for comparison.*

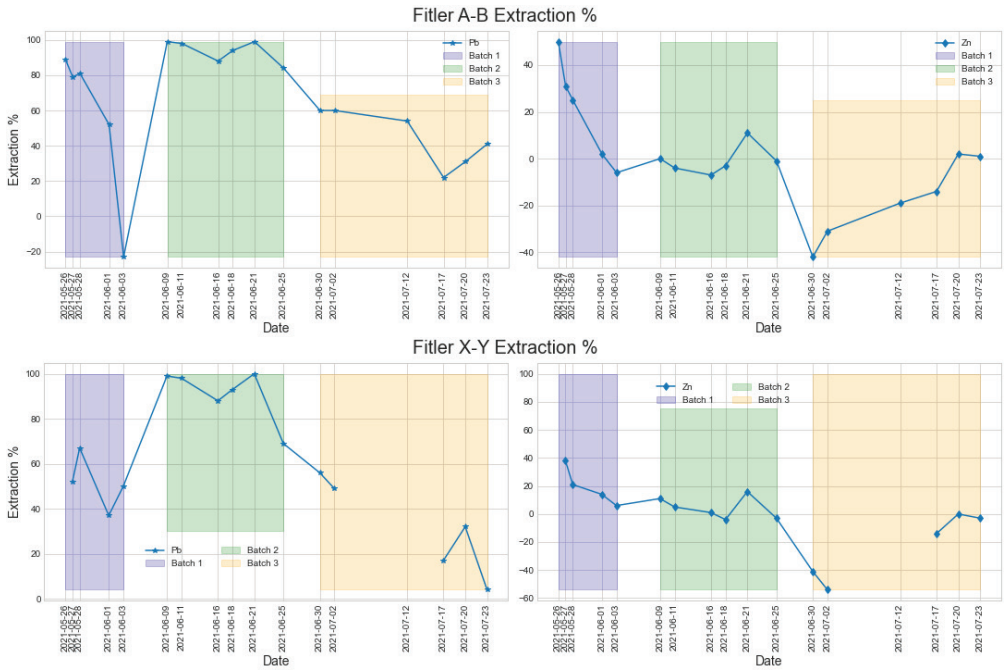

Figure 5 Extraction % of Pb and Zn for filter A-B (top row) and filter X-Y (bottom row).

practise, for water analysis, and element concentration reporting, is to be followed during this extended trial.

Social and economic value

- After this series of trials, and despite of the small relative scale of treated water, we deem the results as having a positive environmental impact for the old mine area and the river system in overall. It demonstrates the ability of a simple and adaptable technology as a solution for treating mine waste water. Additionally, the local community has also being interested of this technology implementation seeing the positive outcomes for improved river water quality, affecting livestock and other local activities. We envisage that the 1-year long trial will further establish the technology for the described benefits
- Despite this test being on a small, industrial research scale, over 500,000 litres of water were treated, leading to the removal of ~1kg of Zinc and Lead (and 10s of grams of Rare Earth Elements and Lithium). Furthermore, lab-based research has demonstrated the feasibility of extracting these metals in a form amenable to commercial extraction. As described above, the main control on removal efficiency appears to be the overloading of the filter media by Zinc. The addition of a new dosing system will be implemented in the imminent new large-scale test of the filter system, tackling the Zinc oversaturation media

Table 1 Average metal recovery % of key elements for Batch 1, Batch 2, Batch 3

Filter A–B	Pb	Zn	REE	Ni	Co
B1	56%	20%	35%	19%	14%
B2	94%	-1%	90%	-3%	-3%
B3					
Filter X–Y					
B1	52%	20%	33%	20%	15%
B2	78%	4%	86%	2%	1%
B3	32%	-22%	-20%	-23%	-13%

effects. If successful, it is expected that metal removal will increase, highlighting the real potential to "remine" metals during the water remediation process. We look forward to presenting the results of this test in a future IMWA conference.

Conclusion

In this work it was demonstrated a new passive technology for mine water treatment. The system was employed at a highly Pb and Zn contaminated abandoned mine stream, showcasing a strong potential water mine clean up, with highest metal adsorption of over 90% across the course of a 2-months trial. Due to high adsorption of other valuable elements such as REE, Ni, Co and potentially Cu, this technology can have a positive impact on partially covering operational costs of system deployments. Batch experiments of spent filter media re-charging, with concomitant metal recovery, show strong results of using the same bead media volume for several adsorption/ desorption cycles, further reducing the operational costs.

As it was apparent from results shown above, Zn has saturating / destructive effects on the system. For more efficient adsorption, several established precipatation solutions are being considered, prior to water entering the main filter system.

In attempt to make beads on-site, river water was used successfully, having minor effect on final adsorption capacity and life of filter system, thereby massively reducing the need to transport raw materials to a remediation site, making it highly suitable for remote rural sites, and lowering the cost of transport and making the technology more practical.

Acknowledgements

We wish to acknowledge the support provided to this project through the SmartCymru funding scheme.

Authors would like to thank Chris Hughes, a retired X-Ray Mineral Services, Technical Development Manager, for leading this work the past years. His commitment to the project was beyond valuable.

Also, thanks should be extended to the many Durham University and the Greenwell Group students, who worked in the lab and the field trials, completing significant part of the research, with their work being the basis of our technical understanding of the filter media.

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