

Innovative Passive Treatment Technologies for UK Metal Mine Water

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Abstract

UK metal mine waters are challenging to treat due to highly variable chemistry, the need for very low residual metal concentrations and system footprints constrained by limited land availability. This paper presents results from the first 300 days of operation of three 50 m² Vertical Flow Reactors (VFRs) treating mildly acidic mine water. Excellent Fe and Mn removal and effective polishing of Cu, Ni and Cd were observed. Zn removal was more variable and dependent on pH with seasonal effects noted. Findings inform design, optimisation and media reuse for passive treatment schemes.

Keywords: Vertical flow reactors, metal mine waters, pilot-scale trials

Introduction

The Water and Abandoned Metal Mines (WAMM) programme was established in 2011 to address pollution from abandoned metal mines, which affects approximately 1,500 km of rivers across England. These mines, once central to Britain's industrial heritage, now release harmful metals into waterways, damaging aquatic ecosystems and impacting economic activity. The programme is a partnership between the Mining Remediation Authority (formerly the Coal Authority), the Environment Agency and the Department for Environment, Food and Rural Affairs (Defra). It is primarily funded by Defra to support delivery of the statutory Environment Act target: to halve the length of rivers polluted by harmful metals from abandoned metal mines by 2038.

Many mine sites are located in rural and/or upland landscapes where the availability or suitability of land can be limited, restricting the feasibility of more conventional passive treatment technologies. To address this, the WAMM Programme has initiated pilot-scale research trials across the UK, including the Coombe Mine Water Treatment Scheme (MWTS), where pilot-scale Vertical Flow Reactors (VFRs) are being investigated to treat mine water from Coombe Adit. The mine water is net-acidic and contains Fe,

Mn, Zn, Cu, As, Ni and Cd at concentrations sufficient to pollute the receiving river. The Coombe MWTS consists of four pilot-scale VFRs, each with an area of 50 m² (5 m × 10 m) and a depth of 2 m. These were constructed utilising the findings from small-scale field trials (Okeme *et al.* 2025). Treatment media tested include granite and limestone, enabling investigation of both oxidation-driven and alkalinity-driven removal pathways. The nature and thickness of the media in the VFRs are described in Table 1. Target retention times (RT) in the limestone portion of VFR 2 and VFR 3 are broadly reflective of the RT in the limestone reactors of the original trial (Okeme *et al.* 2025), with a nominal RT on average of 2.8 and 2.5 hrs in the limestone section of VFR 2 and 3 respectively compared to ≈ 3 hrs in the limestone reactors of the METAL-SolVER trial. Average flow rates over the trial were of 0.4 L/s for VFRs 1 and 2 and 0.5 l/s for VFR 3. VFR 4 was not in use for this trial.

Results and Discussion

CO₂ degassing is an important phenomenon in VFRs, in common with coal mine waters (see Geroni *et al.* 2012). This is most clearly demonstrated by the data for VFR 1 which contained only granite media. A pH rise is observed as water passes through VFR 1,



Table 1 Vertical Flow Reactor (VFR) configuration and media details.

	Media type and size	Media layers and depth
VFR 1	Granite gravel 6 mm	Top layer: Depth of 200 mm
	Granite gravel 20 mm	Bottom layer: Depth of 150 mm
VFR 2	Granite gravel 6 mm	Top layer: Depth of 200 mm
	Limestone gravel 2-6 mm	Middle layer: Depth of 200 mm
	Granite gravel 20 mm	Bottom layer: Depth of 150 mm
VFR 3	Limestone gravel 2-6 mm	Top layer: Depth of 400 mm



Figure 1 General arrangement of the four VFRs at Coombe MWTS.



Figure 2 VFR 1 and its aeration rose, showing iron accumulation on the surface of the media layer.

with loss of the temporary acidity due to CO_2 degassing (compare “raw” influent mine water and “VFR 1” effluent in Figure 3). Bubbles were clearly seen escaping from the influent water for all VFRs and from the VFR media, leaving small holes visible in accumulated ochre. It is not known whether these are due to entrained air subsequently escaping, but it is feasible that these could be evidence of CO_2 degassing. In VFRs 2 and 3 the more substantial pH rise is due also to reaction with limestone.

Iron is a secondary contaminant of concern for this system, but its removal as a filter cake on top of the upper layer of granular granite media (see Figure 2) also allows the use of limestone in subsequent treatment, which otherwise has a tendency to become armoured/blinded with iron precipitates (as has been demonstrated in

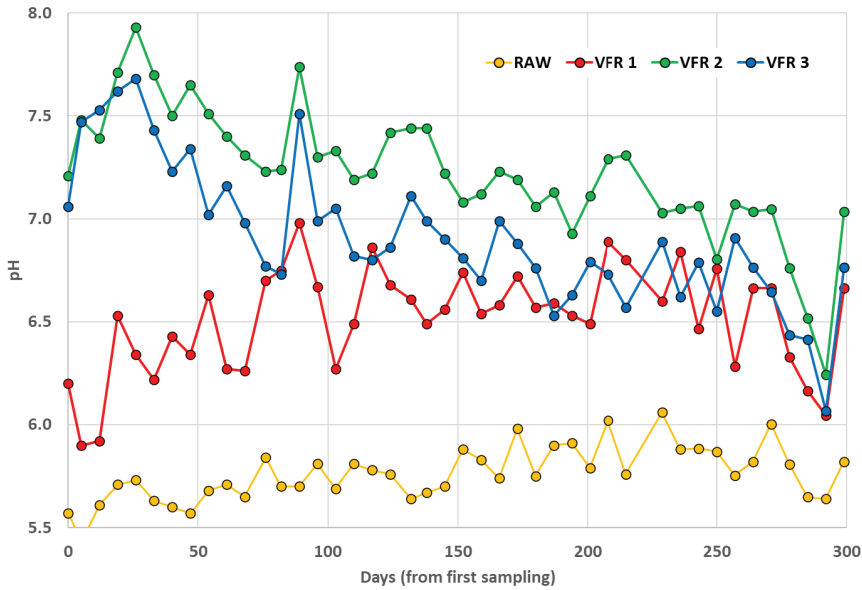


Figure 3 A plot of pH versus time for raw mine water and the effluent from VFRs 1–3.

many mine water treatment systems). Iron removal was excellent, with effluent total iron concentrations for VFRs 1–3 being commonly lower than the detection of the analysis used (<0.01 mg/l) over the entire period of the trial. That the same Fe removal results were obtained for VFR 1 (no limestone) shows that the effectiveness of iron removal in VFRs for this mine water does not require the further pH increase from limestone dissolution. It is interesting to note that at the pH of the influent (pH 5.5–6) the literature reported rates of homogenous Fe(II) oxidation suggest an expected half-life of days (Stumm and Morgan 1997), whereas the Fe(II) oxidation and precipitation is observed here are happening in hours. This is likely due to heterogenous catalysis by ochre considerably enhancing Fe(II) oxidation kinetics (Barnes *et al.* 2009). These findings are important evidence for the application of VFRs for Fe removal in coal and metal mine water treatment schemes. Despite the excellent iron removal and consequent accumulation of ochre on top of the media, sufficient hydraulic conductivity of the VFRs was maintained allowing for continuous operation over the trial.

Mn removal versus time is shown in Figure 4. Mn is not removed in VFR 1, likely due to relatively low pH impeding the oxidation kinetics. In VFRs 2 and 3 Mn is removed from almost the beginning of the trial. The removal is attributed to the limestone layers in VFR 2 and 3 acting to boost the pH of the mine water upon contact through dissolution of calcite. A plot of effluent Mn concentration versus pH (not shown) indicates that at $\text{pH} > 6$ the Mn is effectively removed. The rapid removal might have initially involved sorption, but Mn(II) oxidation and precipitation of MnO_2 was rapidly established, evidenced by accumulation of black precipitate in the limestone of VFR 3 and subsequent analyses (not shown). Once MnO_2 precipitate has accumulated, the well-known autocatalytic oxidation mechanism (Stumm & Morgan 1997) and additional biotic effects become more important. The establishment of a zone of catalysing MnO_2 precipitate during early operation of VFR 2 and 3 may explain why VFR 2 and 3 continue to remove Mn later in the trial when compared to the lack of removal in VFR 1, which is of comparable pH (Figure 3). Differences in pH dependence of sorption to calcite surfaces present in VFR 2 & 3 (but not

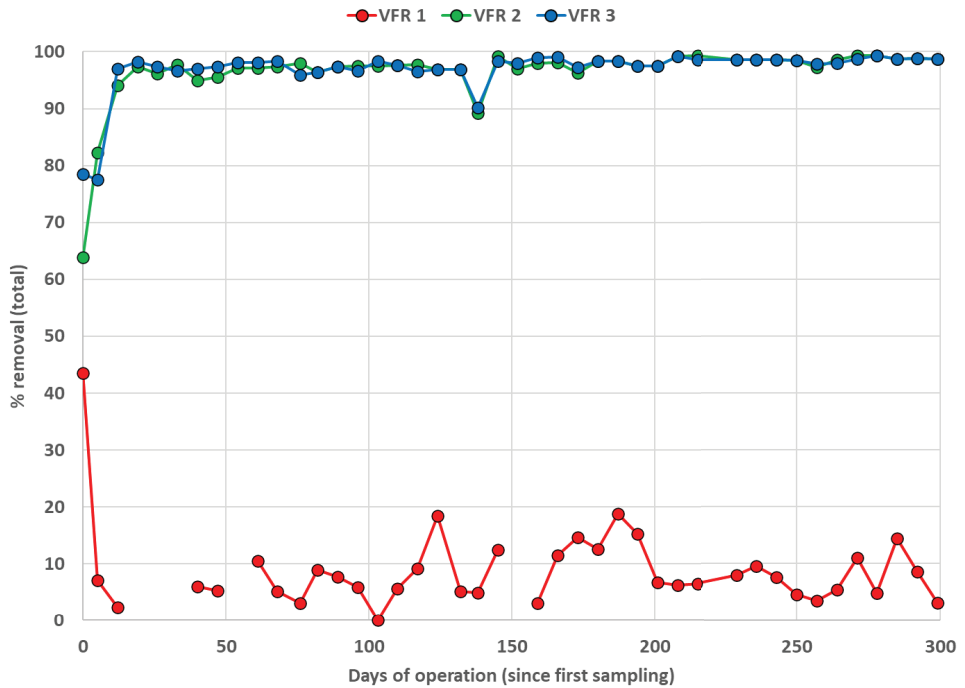


Figure 4 A plot of Mn removal % versus time in VFRs 1–3

VFR 1) and/or formation of MnCO_3 may also be important in the continued removal.

Zn removal with time is shown in Figure 5. This shows excellent removal at the beginning of the trial for VFRs 2 and 3, and then a decrease over time, with the latest data suggesting a stabilisation in the range of 20–50% removal. In terms of load removal (by calculation combining flow data) over the 300 days, 50% and 51% of the Zn load has been removed for VFR 2 and 3 respectively. Whilst this is promising removal for a simple granite/limestone bed, the system is not performing as well as in the previous small-scale trial (Okeme *et al.* 2025). The likely explanation is that unlike in the original trials, the CO_2 content of the water was not fully degassed in VFRs 2 and 3 which constrains the pH rise upon contact with limestone. Interestingly, this is in-line with the sorption edge for Zn adsorption on to amorphous or hydrous manganese oxides (Pretorius & Linder 2001; Gadde & Laitinen 1974). The most recent data for the system (not shown) shows increasing recovery of Zn removal rates indicating possible seasonal effects in the system.

The VFRs also displayed excellent polishing of Cu, Ni and Cd. Cu was removed from a mean of 64 $\mu\text{g/l}$ in the influent to a mean of 1 and 2 $\mu\text{g/l}$ in the effluents from VFRs 2 and 3 respectively. Ni was removed from a mean of 60 $\mu\text{g/l}$ in the influent to a mean of 2 $\mu\text{g/l}$ for both VFRs 2 and 3. Cd was removed from a mean of 2 $\mu\text{g/l}$ in the influent to a mean of 0.5 $\mu\text{g/l}$ for both VFR 2 and 3.

Conclusions

The VFR trials have shown remarkable removal of Fe and Mn which may have very important implications for mine water treatment in general. The VFR trials have also demonstrated that permeability of the ochre layer was not an issue for the duration of the trial. Furthermore, excellent removal of Ni and Cu was noted despite the very low concentrations in the influent, showing that the system can polish these effectively to very low levels. Zn removal was not as high, with 50–51% of the total influent Zn load removed (in VFRs 2 and 3), although still notable given these are very simple aerobic granite/limestone reactors. However, effluent concentrations of Zn were generally not as low

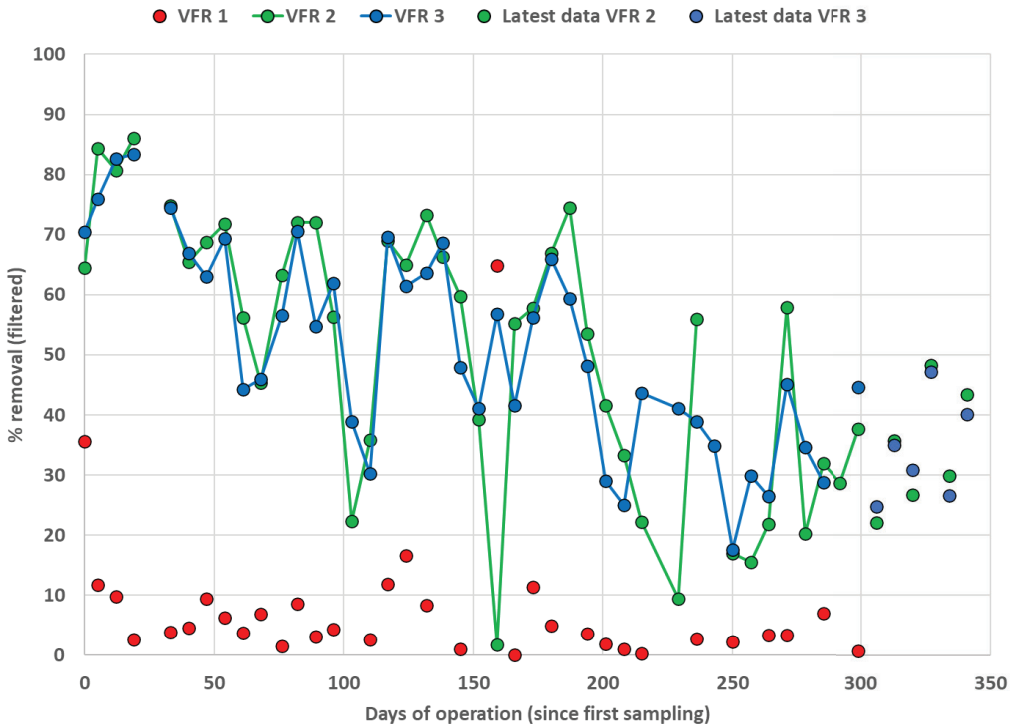


Figure 5 A plot of Zn removal versus time for VFRs 1 – 3, including latest data from VFRs 2 and 3.

as those achieved during earlier trials because of dissolved CO₂ restricting the pH rise when contacting limestone. It is important that CO₂ is degassed as this will lead to higher pH and better co-removal of Zn by adsorption to MnO₂ precipitated on the VFR media.

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