

Application of vertical flow reactors in New Zealand for removal of iron from AMD

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Abstract

This paper presents data on treatment trials of two low pH mine waters using vertical flow reactors (VFRs) - mine water treatment systems where mine water is directed through an unreactive gravel bed to encourage metal removal under aerobic conditions. Previous VFR studies have demonstrated their efficacy at iron (Fe) removal at circumneutral pH and at low pH in the UK; this study confirms the earlier work by showing that Fe can be removed at low pH at AMD sites in New Zealand. At one site, an active coal mine in New Zealand with AMD, up to 77% of the Fe is removed by a VFR. Some of this removal is attributed to filtering of particulate Fe(III) and microbial Fe(II) oxidation and heterogeneous precipitation. However, much of the removal is hypothesised to be from agglomeration and filtration of nanoparticulate colloidal-sized ferric iron precipitates. At a second site, the Bellvue Coal Mine AMD on the West Coast, one VFR treats anoxic water rich in Fe(II) from the mine pool (VFR-R) and another VFR treats oxidised water dominated by Fe(III) from the base of a cascade (VFR-O). Although Fe(II) is oxidised in the VFR-R, removal of Fe by the unit does not occur. On the contrary, up to 15% of the Fe is removed by the VFR-O, again largely contributed to agglomeration and filtration of nanoparticulate colloidal-sized ferric iron precipitates. The use of VFRs represents an inexpensive option for removing iron from low pH mine water without the requirement for pH adjustment.

Keywords: passive treatment, AMD, New Zealand, iron, vertical flow reactor.

Introduction

Passive treatment of acid mine drainage (AMD) typically involves the removal of elevated dissolved metal contaminants by precipitation or adsorption and pH adjustment through microbial alkalinity production or dissolution of alkaline material such as limestone or steel slag (Skousen and Ziemkiewicz, 1998; Watzlaf et al., 2004). For oxidising systems, the precipitation of metal oxides and hydroxides occurs as the pH increases and the solubility of the dissolved metals decrease. For reducing systems, precipitation of metals occurs through the formation of metal sulphides as sulphate is reduced to hydrogen sulphide by sulphate-reducing bacteria (Neculita et al., 2007).

One of the primary difficulties with passive treatment is the formation of iron hydroxide armouring layers on the treatment media (usually limestone) which inhibits dissolution of the limestone and can cause systems to fail (Ziemkiewicz et al., 1997; Hammarstrom et al., 2003). The focus of this study is on a technique that can minimise or reduce these difficulties by decreasing iron (Fe) concentrations in AMD prior to pH adjustment in a passive treatment system.

Dey et al. (2003) and Sapsford et al. (2007) developed a vertical flow reactor (VFR) which operates under aerobic conditions to remove Fe from circumneutral coal mine water by heterogeneous Fe(II) oxidation and precipitation and filtration of Fe(III)_(s) in an unreactive gravel support bed. Later work by Sapsford and Florence (2013), Sapsford et al. (2014) and

related publications, has shown that the same system can remove significant amounts of Fe from acidic mine drainage and hypothesise that much of this removal is through agglomeration and filtration of nanoparticulate-size colloidal ferric iron precipitates. In the work detailed here, the same VFR design is applied to two AMD sites in New Zealand.

Study sites

Active mine site with AMD

The first AMD study site is an active opencast coal mine. The AMD at the site issues from overburden waste rock dumps and contains relatively high concentrations of Fe, aluminium (Al) and manganese (Mn) and low pH.

Bellvue Coal Mine

The second AMD study site is the Bellvue Coal Mine, an underground mine located on the West Coast of the South Island approximately 15 km northeast of Greymouth. It operated from 1928 until 1964 and is currently abandoned. The entrance to the mine is on a hillside approximately 100 m above a nearby creek. An AMD water pool at the entrance drains to a cascade which flows down the slope to Cannel Creek. The water in the pool is in a reduced state, with approximately 20% of the Fe as Fe(II) and very low dissolved oxygen (DO) concentrations, and a pH of approximately 2.5 (West, 2014). As the AMD flows down the cascade, DO concentrations increase and Fe(II) oxidises to Fe(III) and some Fe hydroxides precipitate. The chemistry at the bottom of the cascade shows approximately 4% of the Fe as Fe(II). The Fe and Al concentrations are some of the highest recorded in New Zealand mine drainages.

Methods

Three VFR treatment tanks were installed at the study sites (one at the active mine site and two at the Bellvue Coal Mine) in April 2014. At the Bellvue Coal Mine, one system was configured to take water directly from the mine pool (the anoxic, reduced AMD) and the other was configured to take water from the bottom of the cascade (oxidised AMD).

The system (Fig. 1), mirroring the systems in Sapsford et al. (2007) and Sapsford and Florence (2013), uses a 1 m³ intermediate bulk container (IBC) as a VFR treatment tank. A 100 mm gravel bed layer (of unreactive 10 mm greywacke gravel), supported by a layer of 30 mm chips of the same material was used in the base of the tank upon which precipitate is allowed to accumulate. IBCs have an outlet at the bottom of the tank which has a standard fitting which can be opened and closed manually. Inside the tank, underneath the gravel bed a length of coiled slotted drainage pipe was attached to the outlet valve which allowed the treated water to be collected and directed up through a swan neck outlet. A length of hose was fitted to that outlet valve to act as a swan neck mechanism so that the driving head within the container could be adjusted; the head was set to 200 mm.

Monitoring of the influent and effluent for the systems was conducted on a fortnightly basis in 2014 and on a monthly basis in 2015. Samples for total Fe including suspended particulate Fe and dissolved Fe were taken directly from the mine water using a disposable Plastipak syringe and stored in a sample bottle and acidified with 0.1 ml of 20% (v/v) HNO₃. Samples for filtered Fe were taken in the same way except that first they were filtered using disposable

0.45 μm syringe filters. These samples were analysed by ICP-OES. Samples for Fe(II) were measured in the field immediately upon collection using Hach Method 8146 (1,10 Phenanthroline Method) and concentrations determined through absorbance using a Hach DR/2400 Portable Spectrophotometer. All field pH/DO measurements were taken using a portable YSI 556 multi-probe system, calibrated against known standards in the field. Influent and effluent flow measurements were taken during each site visit by timing the length of time to fill a measuring cylinder.

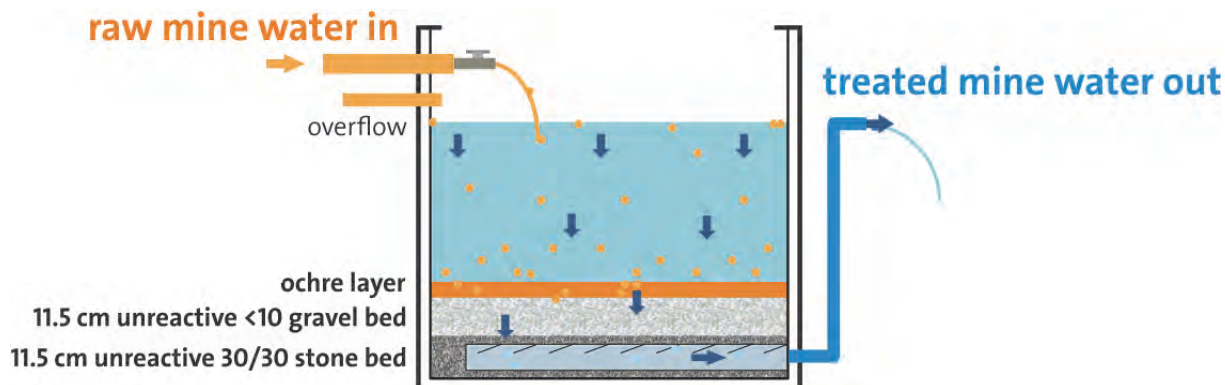


Figure 1. Schematic of a VFR (from Sapsford et al., 2015).

Results and discussion

The results for Fe removal are given in Figs 2-4. Fe(II) is the spectrophotometrically determined aqueous Fe(II) concentration. Fe-Filt is the concentration of Fe in all its forms that has passed a 0.45 μm filter. The portion of Fe that passed a filter that is not Fe(II) is shown in yellow. Fe-Tot is the sum of dissolved iron (both Fe(II)_(aq) and Fe(III)_(aq)) + particulate Fe suspended in the water. The portion of Fe capture by a filter (particulate Fe > 0.45 μm) is shown in grey. Presented in this way, changes to the concentrations of Fe in each of these categories can be identified between the inlet and outlet of the VFRs.

Active mine site with AMD

Data was collected at the VFR at the active mine site with AMD on 15 occasions between April 2014 and May 2015. The mean data (\pm Stdv) was as follows: flow rate = 0.48 ± 0.18 L/min; Influent pH = 3.22 (pH converted to H^+ concentrations for calculation); Effluent pH = 3.04; Influent DO = 7.70 ± 0.83 mg/L; Effluent DO = 8.28 ± 1.23 mg/L. The mean total Fe removal was 45% with a high of 77% and a low of 8.3%. The mean Fe removal rate was 11 $\text{g}/\text{m}^2/\text{d}$ with a high of 29 $\text{g}/\text{m}^2/\text{d}$ and low of 0.61 $\text{g}/\text{m}^2/\text{d}$.

A summary of the Fe removal (in various forms) is given in Fig. 2. The total concentration of Fe decreases for each sampling event. A portion of this decrease can be attributed to filtration of particulate Fe > 0.45 μm (note the decrease in “Fe-Tot” in Fig. 2) as well as bacterial oxidation of Fe(II) and likely precipitation as schwertmannite (note the decrease in “Fe(II)”). However, the remaining decrease in Fe is likely through agglomeration and filtration of nanoparticulate-size colloidal ferric iron precipitates which can pass through a 0.45 μm filter, as hypothesised in Sapsford and Florence (2013) and Sapsford et al. (2014) for other VFRs (note the decrease in Fe-Filt, especially from September 2014 to present). This hypothesis is further supported by Zanker et al. (2002), who documented the presence of colloidal particles

of schwertmannite and jarosite between 1.3 and 5 nm in diameter (0.0013 to 0.005 μm) comprising up to 15% of the Fe concentration in pH 2.7 AMD.

Performance of this VFR has significantly improved over the last several months, possibly due to enhanced auto-catalytic oxidation and precipitation of Fe as the layer of Fe hydroxides builds up in the system. No removal of Al or Mn occurs in the system.

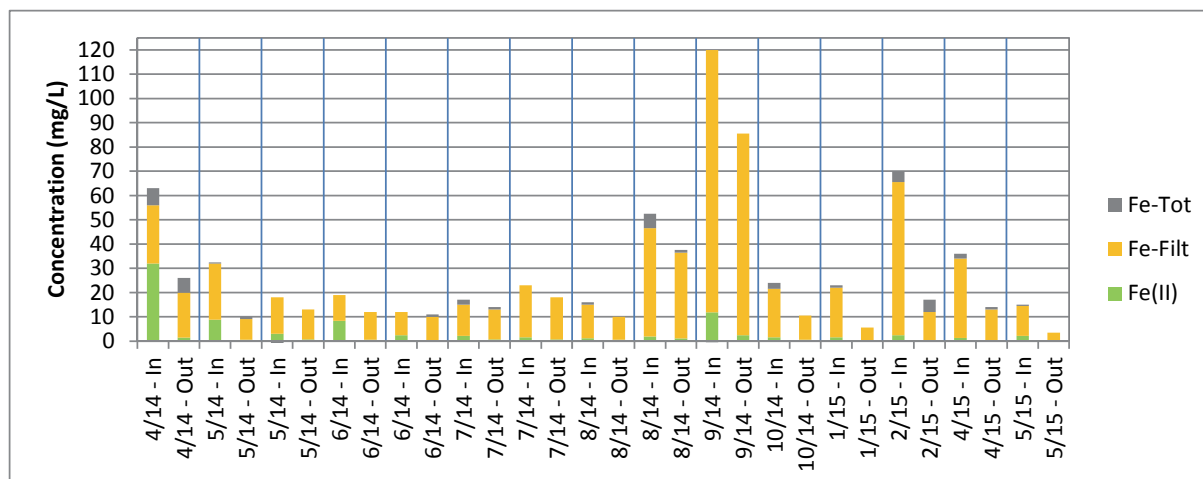


Figure 2. Active mine site Fe concentrations for VFR influent (In) and effluent (Out).

Bellvue Coal Mine

There are two VRFs at the Bellvue Coal Mine, one taking reduced, anoxic water from the mine pool (VFR-R) and the other taking oxidised water from the bottom of the cascade (VFR-O). VFR-R was monitored on 12 occasions and VFR-O was monitored on 8 occasions.

VFR-R

The mean data (\pm Stdv) for the VFR-R was as follows: flow rate = 0.46 ± 0.1 L/min; Influent pH = 2.60; Effluent pH = 2.58; Influent DO = 1.51 ± 1.07 mg/L; Effluent DO = 4.32 ± 1.03 mg/L. It can be seen from Fig. 3 that removal of Fe was not observed in this VFR. On the contrary, Fe in the outlet is consistently higher than the concentration in the inlet. This may be a consequence of the sampling locations. The inlet sample is collected from the surface of the mine pool, however, the AMD feeding the system comes from the base of the pool and flows via a siphon through a 60 m long pipeline down the cascade to the system. It is possible that higher Fe concentrations are present at the base of the pool and/or that Fe had previously precipitated within the pipeline and is now dissolving and feeding into the reactor. Additional samples will be collected to investigate this possibility.

Despite the lack of removal of Fe, Fe(II) decreases across the VFR for approximately half of the sampling events, indicating, as with the other sites, an active Fe(II) oxidising microbial community, although in this case the resultant Fe(III) is clearly not precipitating in the VFR.

Poor performance of the VFR-R may be primarily due to the low pH conditions, coupled with the high percentage of Fe present as Fe(II) in the inlet water. PHREEQC modelling (not shown) indicates that the water is only slightly oversaturated with respect to schwertmannite (SI of 0.37).

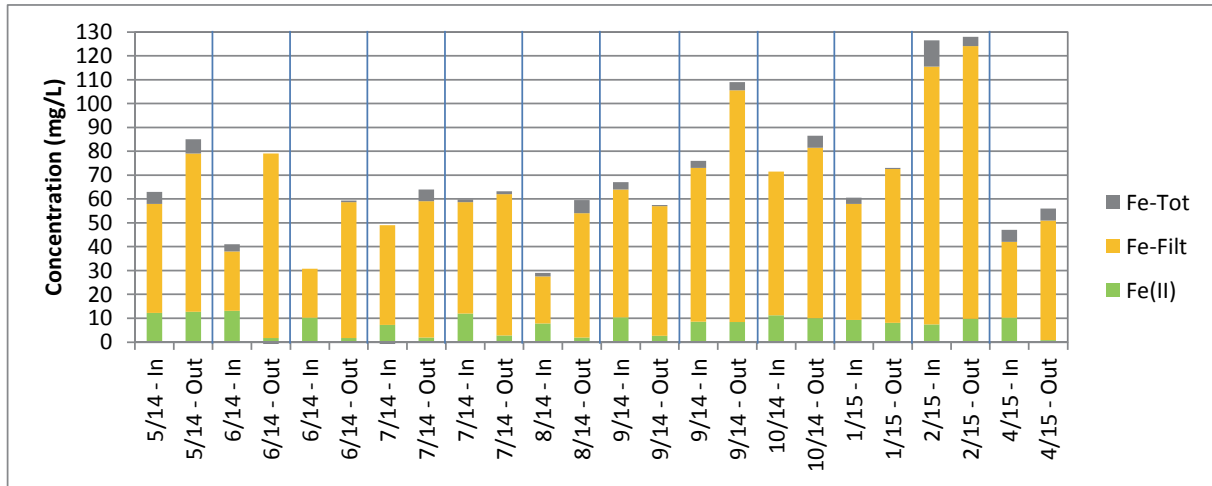


Figure 3. Bellvue Coal Mine Fe concentrations for VFR-R influent (In) and effluent (Out).

VRF-O

The mean data (\pm Stdv) for the VFR-O was as follows: flow rate = 0.43 ± 0.08 L/min; Influent pH = 2.59 (pH converted to H^+ concentrations for calculation); Effluent pH = 2.62; Influent DO = 10.04 ± 0.37 mg/L; Effluent DO = 9.97 ± 0.85 mg/L. Unlike the VRF-R, some removal of Fe is evident (Fig. 4). The mean total Fe removal was 5.4% with a high of 15% and a low of 0%. The mean Fe removal rate was 3.0 g/m²/d with a high of 3.5 g/m²/d and low of 0 g/m²/d.

In approximately half of the sampling events, a portion of the treatment can be attributed to removal of particulate Fe > $0.45 \mu m$, and, as with the VFR at the active mine site, some removal of Fe < $0.45 \mu m$ occurs, suggesting removal of nanoparticulate Fe. In six of the sampling events, Fe(II) concentrations decrease through the reactor (by up to 57%), suggesting an active Fe(II) oxidising microbial community. Overall performance appears to be improving in 2015, possibly due to autocatalytic precipitation of Fe hydroxides and heterogeneous nucleation in the VFR system.

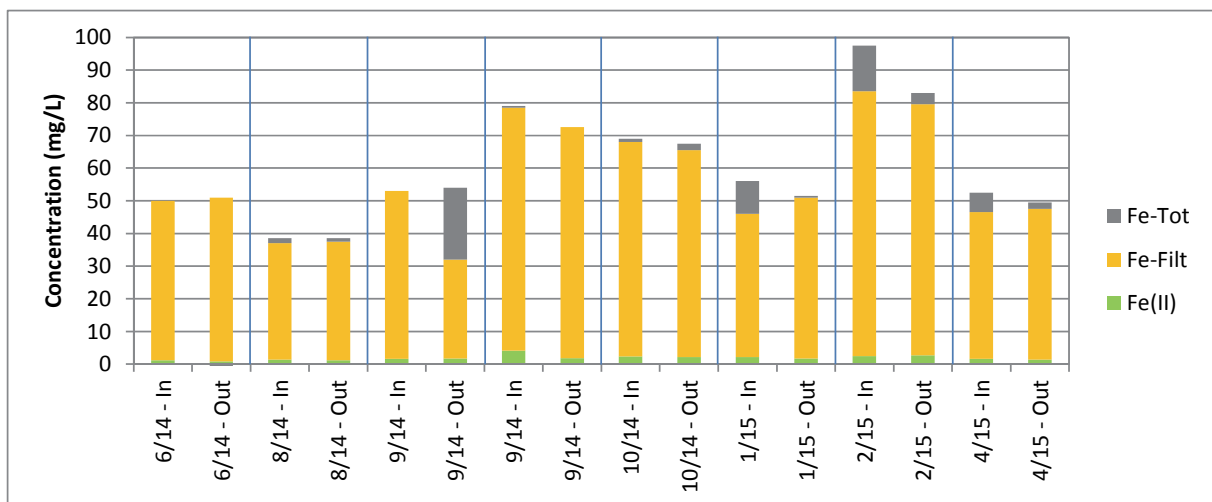


Figure 4. Bellvue Coal Mine Fe concentrations for VFR-O influent (In) and effluent (Out).

The better performance of the VFR at the active mine site compared to the two VFRs at the Bellvue Coal Mine may be a consequence of the much lower pH of the Bellvue AMD.

Sapsford et al. (2015a) found that mixing high alkalinity sea water with AMD at a site in the UK raised the pH enough to improve performance of a VFR treating low pH AMD. Cannel Creek near the Bellvue AMD has a pH of approximately 6.5. Field and laboratory experiments are underway to determine a suitable mixing ratio to raise the pH of the Bellvue AMD enough to precipitate Fe in the VFRs.

Conclusions

In conclusion, the findings of this study were as follows:

- (1) Application of a VFR system for removal of Fe from AMD sites in New Zealand can be successful under the right conditions. The VFR system lowers the concentration of Fe by filtration and removal of particulate Fe(III) > 0.45 μm and nanoparticulate-size colloidal Fe < 0.45 μm . The gravel substrate in the system likely hosts Fe(II) oxidising microbes, resulting in demonstrable Fe(II) oxidation.
- (2) At an active mine site in New Zealand with AMD, a VFR was found to remove up to 77% of the Fe, much of this in the nanoparticulate-size range. Improved performance over the last several months may be due to increased auto-catalytic oxidation and precipitation of Fe as the layer of Fe hydroxides builds up in the system.
- (3) At the Bellvue Coal Mine AMD site, removal rates for a VFR treating oxidised AMD rich in Fe(III) range from 0% to only a maximum of 15%. A second VFR at the Bellvue site treating reduced anoxic AMD rich in Fe(II) shows no removal of Fe. It is possible that the pH at the Bellvue site is too low for adequate formation of nanoparticulate-size colloidal ferric iron. Preliminary modelling suggests that the water is only slightly oversaturated with respect to schwertmannite.

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