

## Passive Removal of Iron from AMD Using VFRs

Devin Sapsford, Kay Florence, James Pope and Dave Trumm

1. School of Engineering, Cardiff University, United Kingdom
2. CRL Energy Ltd / University Canterbury, New Zealand

### ABSTRACT

This paper presents data on treatment trials of three low pH mine waters and one circumneutral mine water in the UK and New Zealand 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 removal at circumneutral pH; this study demonstrates that significant removal of iron (as high as 85%) can be achieved at low pH (~3), within a practicable treatment area using the VFR system. The iron removal rate varies between the four study sites. The difference is attributed to the mechanism of removal which is suspected to be the agglomeration and filtration of nanoparticulate colloidal-sized ferric iron precipitates in addition to microbial Fe(II) oxidation and heterogeneous precipitation. The use of VFRs represents an inexpensive option for removing the majority of iron from low pH mine water without the requirement for any pH adjustment. The study also confirms the VFR's applicability to iron removal from circumneutral mine water.

**Keywords:** vertical flow reactors, nanoparticulate iron, filtration

## INTRODUCTION

Passive mine water treatment involves a number of physicochemical and microbiological strategies for the removal of dissolved species of concern. Removal of metals is either achieved via harnessing of naturally occurring physicochemical and microbiological processes, for example the manipulation of solubility via changes in pH (e.g. by reaction with limestone) or redox conditions (through contact with organic matter) or through sorption processes. Removal of iron (Fe) is the focus of the present study.

In general, at pH below 9, the divalent Fe(II) species are highly soluble and do not readily form salts or hydroxide precipitates. Fe(III) solubility is such that under oxic conditions numerous Fe(III)-bearing phases precipitate (hereafter termed Fe(III)<sub>(s)</sub>) over the pH spectrum. In acid mine drainage (AMD) environments it is common for the Fe hydroxy-sulfate mineral schwertmannite to form (e.g. Bigham et al, 1996) as well as jarosite-alunite minerals. Ferrihydrite and goethite dominate at higher pH (> 4). It is difficult to predict the exact solubility because of the heterogeneity of mineral products and the corresponding paucity of unanimity in thermodynamic data for Fe in the literature. Fe(II) is meta-stable under acidic oxidizing abiotic conditions due to slow oxidation kinetics but is widely reported to be microbiologically catalyzed (e.g. Kirby et al, 1999), with the production of aqueous Fe(III) species or Fe(III) phases depending on the pH.

Iron is often the principal contaminant of concern from coal mine AMD and generally the approach to treatment is to contact the mine water with reagents to raise the pH to circumneutral pH or higher to accelerate Fe(II) oxidation and minimize Fe solubility. The reagents include lime, limestone, caustic soda, slag, in different configurations depending on whether the treatment is active or passive or semi-passive. In active treatment schemes the resultant particulate Fe(III) will either be removed by polymer dosing and clarification; in passive systems a limestone drain, slag bed or RAPS will be used to raise pH ahead of settling ponds and/or aerobic wetlands which are used to settle and filtrate the suspended particulate Fe(III). In passive systems the rise in pH also accelerates the oxidation of Fe(II) to precipitate Fe(III)<sub>(s)</sub> and may be augmented by the addition of hydrogen peroxide or other oxidants in semi-passive treatment schemes.

### Vertical Flow Reactors

Dey et. al (2003), Sapsford et. al (2008), and Sapsford and Williams (2009) and related publications detail a vertical flow system which operates under aerobic conditions to remove Fe from circumneutral coal mine water by (self)filtration of Fe(III)<sub>(s)</sub> supported by a gravel support bed and also heterogeneous Fe(II) oxidation and precipitation. This was based on earlier observations in the literature as well as observations from the field concerning the ubiquity of Fe(III) precipitates forming on vertical flow RAPS. There are a number of related publications concerning heterogeneous Fe(II) oxidation harnessed for treatment (e.g. Best and Aikman, 1983, Jarvis and Younger, 2001). Some authors have investigated harnessing low pH microbial Fe(II) oxidation (e.g. Burgos et al, 2004). This paper examines the application of VFRs to AMD. The specific aims of this study are to: (i) present data from field trials of VFRs operating at a low pH abandoned lead (Pb) – zinc (Zn) metal mine site in the UK and two AMD sites and one neutral mine drainage site in New Zealand (South Island), and (ii) to highlight the removal chemistry of iron in these systems.

### Study Sites

#### *Cwm Rheidol*

The Cwm Rheidol former Pb/Zn mine was operated between 1848 and 1917 and is located within the mid-Wales Orefield approximately 12 km east of Aberystwyth north of the river Rheidol. The mine is part of a big mine complex situated just below the village of Ystumteum, on the steep southerly face of the Rheidol Valley which runs ESE to WNW. The AMD issues from two adits. Cwm Rheidol is classified as one of the top 50 polluting metal mines in Wales and put forward as a priority site for remediation in the Metal Mines Strategy for Wales report by Johnston (2004).

Despite this mine complex having been abandoned for almost a century, AMD is still contributing almost half the Zn and Pb loading to the River Rheidol (Edwards and Potter, 2007).

### *Bellvue Mine*

Bellvue Coal Mine is an underground mine located on the West Coast of the South Island of New Zealand 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 the creek. The water in the pool is in a reduced state, with the majority of iron as Fe(II) and very low dissolved oxygen (DO) concentrations, and a pH of approximately 2.5. As the AMD flows down the cascade, DO concentrations increase and Fe(II) oxidises to Fe(III) and some Fe hydroxides precipitate. The Fe and aluminum (Al) concentrations are some of the highest recorded at NZ mines.

### *Active Mine Site with AMD, New Zealand*

The second AMD site in New Zealand is an active opencast coal mine. The AMD at the site issues from overburden waste rock dumps and contains relatively high concentrations of Fe, Al, and Mn and low pH.

### *Active Mine Site with neutral drainage, New Zealand*

The neutral drainage site in New Zealand is an underground active coal mine. The neutral drainage issues from an old adit on the site and contains relatively low concentrations of Fe and a neutral pH.

## **METHODOLOGY**

### **UK VFR**

The system (see Figure 1) was adapted from the original design used in initial field trial at the Taff Merthyr site in South Wales (Dey et al, 2003), using a 1 m<sup>3</sup> intermediate bulk container (IBC) adapted to become a VFR treatment tank. A 100 mm gravel bed layer (of unreactive siliceous 5 mm chips), supported by a layer of 30 mm chips of the same material was used in the base of the tank upon which ochre 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 mine water was conducted as follows: Samples for total iron (Fe-Tot) 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) HNO<sub>3</sub>. Samples for filtered Fe (Fe-Filt) were taken in the same way except that first they were filtered using disposable 0.2 µm syringe filters. These samples were analyzed by ICP-OES. Samples for Fe(II) were either measured in the field using a portable Merck SQ NOVA60 spectrophotometer with appropriate Spectroquant<sup>®</sup> Fe test cells or acidified with HCl and placed immediately into a dark cool box and stored at 4° C until analysis in the laboratory by the 2'2-bipyridyl solution method using a Hitachi U1900 spectrophotometer. All field pH/DO measurements were taken using Hanna combination meters, calibrated at each site visit. Influent and effluent flow measurements were taken by timing the length of time to fill a measuring cylinder.

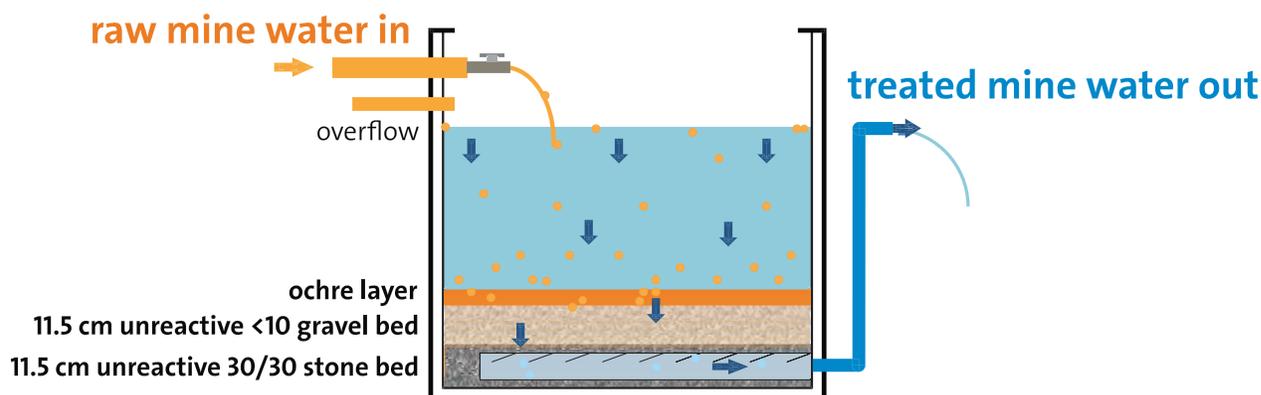


Figure 1 Schematic of Cwm Rheidol VFR

### New Zealand VFRs

The systems installed in NZ used the same configuration as the one installed at Cwm Rheidol in the UK. Monitoring of the influent and effluent for the systems was conducted as follows: Samples for total iron (Fe-Tot) 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) HNO<sub>3</sub>. Samples for filtered Fe (Fe-Filt) were taken in the same way except that first they were filtered using disposable 0.45 µm syringe filters. These samples were analyzed 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 by timing the length of time to fill a measuring cylinder.

## RESULTS AND DISCUSSION

The results for iron removal are given in Figures 2 – 5. Further explanation of the bar charts presented is required with respect to the meaning of the reported breakdown of iron. Fe-Tot (total iron) is the sum of dissolved iron (both Fe(II)<sub>(aq)</sub> and Fe(III)<sub>(aq)</sub>) + particulate iron suspended in the water. Fe-Filt (filtered iron) is the concentration of iron in all its forms that has passed a 0.2 µm filter (0.45 µm for New Zealand data) and Fe(II) is the spectrophotometrically determined aqueous Fe(II) concentration. Presented in the stacked format it can be seen what proportion of the total iron exist in each category, and how each form of iron is changing through the VFRs. Images of the VFR beds are given in Figure 6.

### UK VFR

The Cwm Rheidol (UK) VFR was monitored 21 times between August 3, 2011 and July 4, 2012; of this data, Fe(II) analyses were included 11 times, and so the data set presented here is for these 11 monitoring occasions. For these times the mean data (± Stdv) was as follows: flow rate = 0.34 ± 0.29 L/min; Influent pH = 2.97 ± 0.63; Effluent pH = 2.98 ± 0.67; Influent DO = 7.69 ± 1.34 mg/L; Effluent DO = 6.45 ± 1.39 mg/L. The mean total Fe removal was 70% with a high of 85% and a low of 36%. The mean Fe removal rate was 30 g/m<sup>2</sup>/d with a high of 87 g/m<sup>2</sup>/d and low of 3.7 g/m<sup>2</sup>/d. Iron accumulated on the VFR bed after 11 months of continuous operation is shown in Figure 6 (a).

A summary of the Fe removal (in various forms) is given for the Cwm Rheidol VFR in Figure 2. It can be seen that there is always Fe removal observed in the VFR, but the first thing to note is that removal of particulate Fe > 0.2 µm is not solely responsible for the observed removal of Fe in the system, nor is there a substantial change in pH which would explain Fe removal. Where Fe(II) is

present in the influent it is seen to dramatically decrease on passage through the VFR indicating the presence of active acidophilic Fe(II) oxidizers (this was in fact confirmed by a concurrent microbial study by Prof B Johnson, Bangor University, UK) which probably oxidize Fe(II) and precipitates the resultant Fe(III) as schwertmannite. However, it is interesting to note that on all occasions (except for '1') the decrease in Fe(II) between inlet and outlet is not sufficient to explain the observed decrease in Fe-Filt.

Excluding Fe(II)<sub>(aq)</sub> which is accounted for analytically, the other species that could be reasonably expected to be present and pass a 0.2 μm filter are Fe(III)<sub>(aq)</sub> and nanoparticulate Fe(III)<sub>(s)</sub>. The definition of what is truly 'dissolved' and 'particulate' is largely operationally defined, but Waychunas et al (2005) have reported nanoparticles in mine water. The removal of dissolved/nanoparticulate Fe seems to be occurring within the VFR. PHREEQC modelling (not shown) indicates that a range of Fe(III) minerals (including schwertmannite) are oversaturated and able to precipitate. It is possible that the residence time (mean 39 hrs) in the VFR allows time for kinetically constrained hydrolysis of Fe(III) to occur, however, according to Combes et al., (1989) precipitation of Fe can be viewed as Fe(III) phases forming from solution beginning as small clusters of octahedral Fe(O, OH, OH<sub>2</sub>)<sub>6</sub> units that evolve into larger polymeric units with time, eventually reaching colloidal sizes. It is also feasible that heterogeneous nucleation is important in the VFR system.

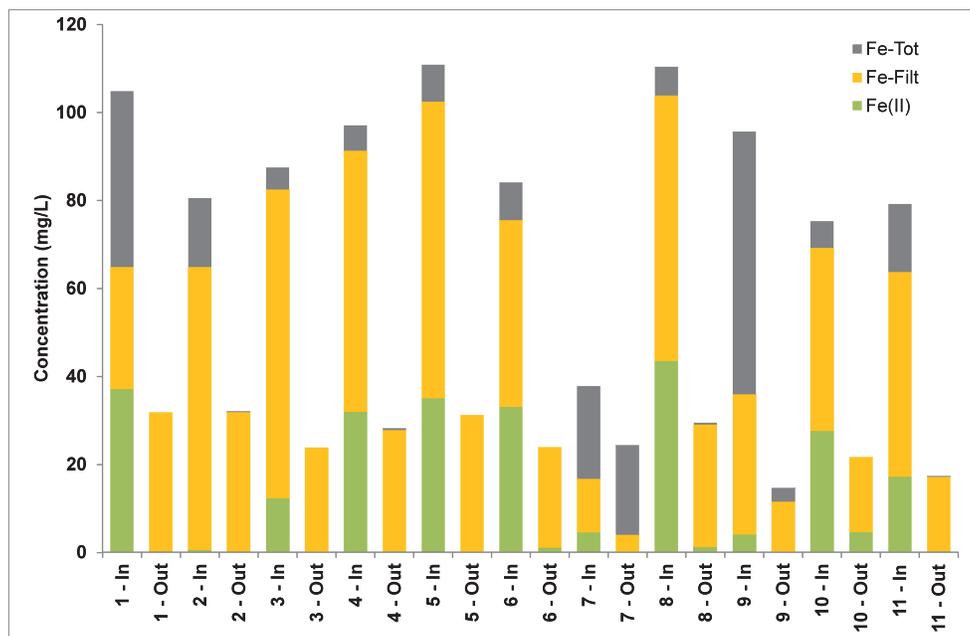


Figure 2 Cwm Rheidol (UK) iron concentration data for VFR influent (in) and effluent (out) on sampling occasions 1 - 11

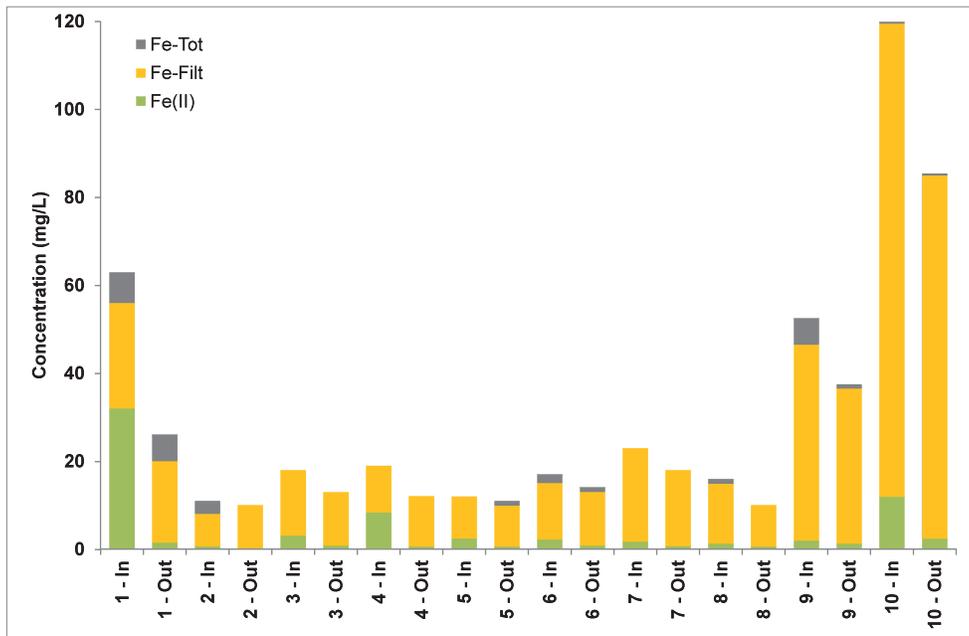


Figure 3 Active mine site with AMD (NZ) iron concentration data for VFR influent (in) and effluent (out) on sampling occasions 1 – 10

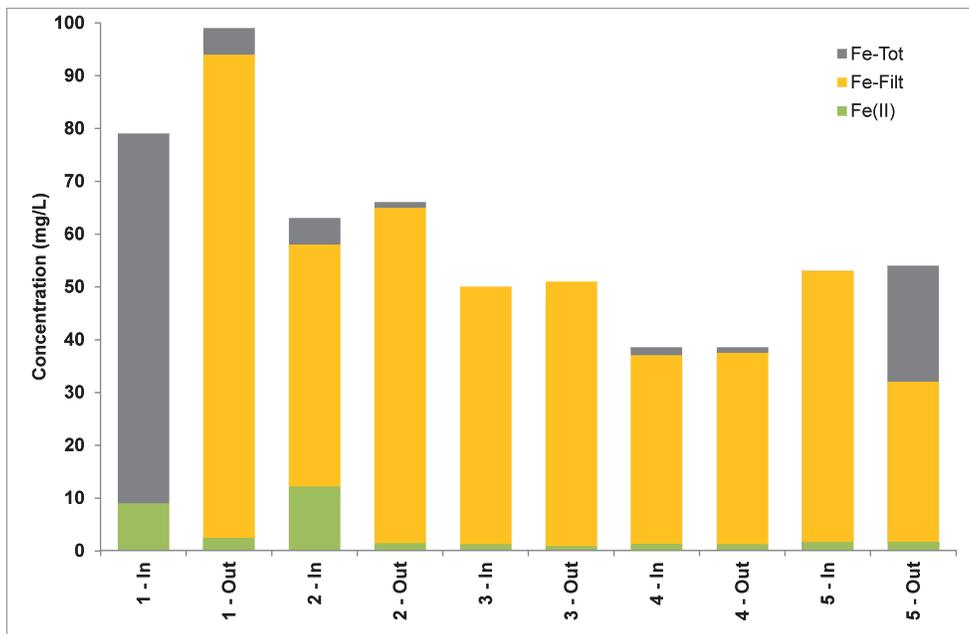


Figure 4 Bellvue (NZ) iron concentration data for VFR influent (in) and effluent (out) on sampling occasions 1 – 11

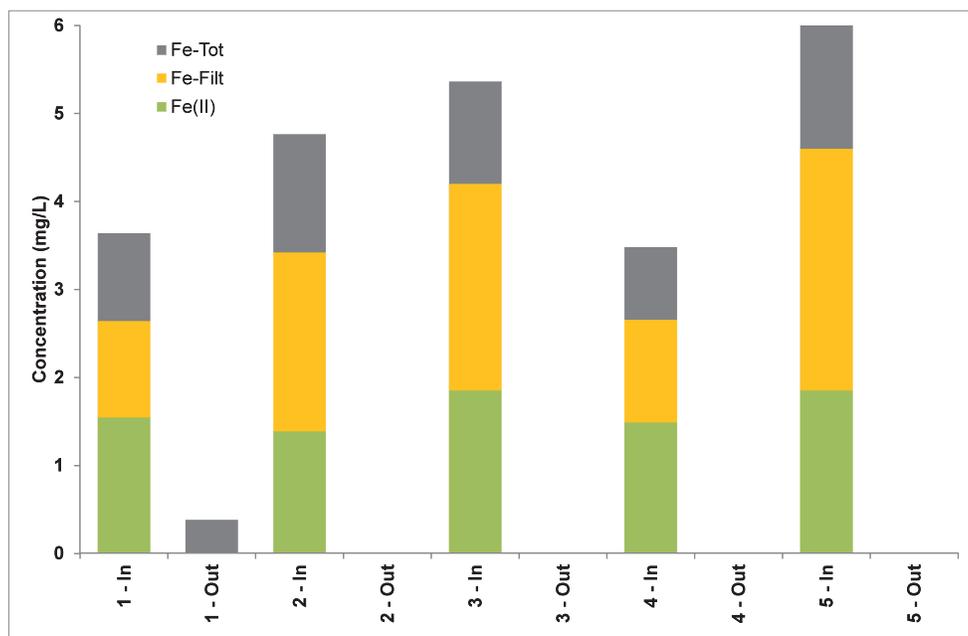


Figure 5 Active mine site with neutral mine drainage (NZ) iron concentration data for VFR influent (in) and effluent (out) on sampling occasions 1 – 10

Regardless of the removal mechanism (which warrants further research) the data show that the VFR is effective at removing a large proportion (70%) of the iron from the discharge. The full mine water discharge at Cwm Rheidol is circa 10 L/s. Based on an average flow of 0.34 L/min going through the 1 m<sup>2</sup> bed of the VFR, a VFR of 1765 m<sup>2</sup> (e.g. dimensions 50 m x 35 m) could remove circa 70% of the iron from the full discharge continuously for at least one year without the need for maintenance.

### New Zealand VFRs

#### Active mine site with AMD

The VFR at the active mine site with AMD was monitored on 10 occasions between April 30, 2014 and September 11, 2014. The mean data ( $\pm$  Stdv) was as follows: flow rate =  $0.47 \pm 0.06$  L/min; Influent pH =  $3.19 \pm 0.14$ ; Effluent pH =  $3.06 \pm 0.11$ ; Influent DO =  $8.03 \pm 0.66$  mg/L; Effluent DO =  $8.77 \pm 0.89$  mg/L. The mean total Fe removal was 28% with a high of 59% and a low of 8.3%. The mean Fe removal rate was 8.2 g/m<sup>2</sup>/d with a high of 26 g/m<sup>2</sup>/d and low of 8.3 g/m<sup>2</sup>/d. Iron accumulated on the VFR bed after six months of continuous operation is shown in Figure 6 (b).

Despite being a slightly higher pH mine water than Cwm Rheidol in the UK, the Fe removal is consistently less for this VFR, however significant Fe removal is still occurring Figure 3. Fe(II) is generally a small proportion of the influent Fe, meaning that the Fe-Filt is likely either Fe(III)(aq) or nanoparticulate to colloidal Fe(III)<sub>(s)</sub>. As with the Cwm Rheidol VFR, Fe(II) when present is seen to decrease through the VFR indicating the presence of active Fe(II) oxidizing microbes.

Unlike Cwm Rheidol, the decrease in Fe(II) through microbial oxidation and precipitation could explain the overall decrease in Tot-Fe between in and out for many of the observed sampling occasions, but not always, suggesting that there is another mechanism responsible for removing Fe-Filt as was observed at Cwm Rheidol. All of the removal could be accounted for by accumulation of particulate and nanoparticulate Fe(III). The pH at here is higher than at Cwm Rheidol, yet removal is lower suggesting the controls on Fe solubility are slightly different between sites. In summary

despite these differences with Cwm Rheidol the VFR at the New Zealand active mine site with AMD is effective at removing a proportion (28%) of the Fe from the discharge.

*Bellvue*

The Bellvue VFR was monitored on five occasions between May 7, 2014 and September 2, 2014. The mean data ( $\pm$  Stdv) was as follows: flow rate =  $0.46 \pm 0.06$  L/min; Influent pH =  $2.58 \pm 0.06$ ; Effluent pH =  $2.57 \pm 0.03$ ; Influent DO =  $8.55 \pm 3.22$  mg/L; Effluent DO =  $9.98 \pm 1.07$  mg/L. It can be seen from Figure 4 that removal of Fe was not observed in this VFR. Figure 6 (c) shows that after four months of operation the gravel showed no signs of ochre build up (Note 1-In data for Fe-Filt is missing). Interestingly, it can be seen that despite the lack of removal of Fe, Fe(II) decreases across the VFR indicating, as with the other sites, an active Fe(II) oxidizing microbial community, although in this case the resultant Fe(III) is clearly not precipitating in the VFR.

*New Zealand active mine site with neutral mine drainage*

The VFR at the New Zealand active mine site with neutral mine drainage was monitored on five occasions between June 27, 2014 and September 1, 2014. The mean data ( $\pm$  Stdv) was as follows: flow rate =  $0.46 \pm 0.05$  L/min; Influent pH =  $7.46 \pm 0.03$ ; Effluent pH =  $7.52 \pm 0.10$ ; Influent DO =  $10.56 \pm 0.19$  mg/L; Effluent DO =  $10.51 \pm 0.38$  mg/L. The mean total Fe removal was 98% with a high of 100% and a low of 90%. The mean Fe removal rate was  $1.2$  g/m<sup>2</sup>/d with a high of  $5.3$  g/m<sup>2</sup>/d and low of  $2.0$  g/m<sup>2</sup>/d. Note that these are seemingly low but actually these are relatively high given the very low Fe concentration.

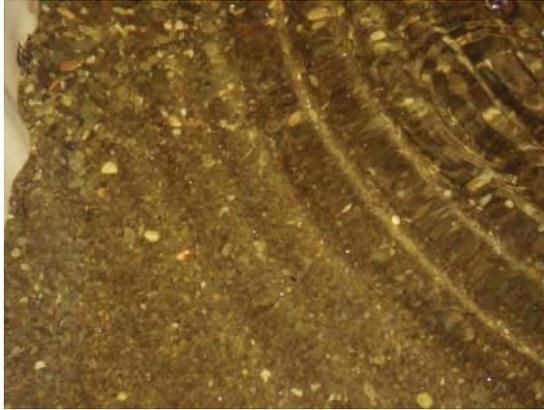
Overall Fe removal was excellent. Note that the pH is circumneutral and as such, Fe(II) should be rapidly oxidized either homogeneously or heterogeneously within the VFR and particulate Fe(III) removed by filtration/accretion. This observed performance is in line with earlier VFR studies (see references above) conducted at circumneutral pH. It is noteworthy in Figure 5 that Fe(II)  $\neq$  Fe-Filt, despite the circumneutral pH suggesting that colloidal Fe(III) precipitates are passing the filter. On four of the five sampling occasions Fe was removed to below the detection limit of the spectrophotometer. This demonstrates that the VFR can be used to polish Fe levels down to very low levels as a last stage in treatment, and can replace wetlands in this function, which has the commensurate benefits for waste management of the arising ochre.



(a) Cwm Rheidol VFR, 11 months operation



(b) New Zealand active mine site with AMD VFR, 5 months operation, contours caused by underlying gravel



(c) Bellvue VFR, 4 months operation, note no precipitate in evidence.

**Figure 6** Photographs of gravel bed after operation of the VFRs

## CONCLUSION

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

- Where Fe is present as particulate Fe(III) it can be effectively filtered out in a VFR. Even at a low pH of circa pH 3, depending on the phase controlling Fe solubility, significant proportion of Fe can be in particulate form (albeit nanoparticulate) and/or supersaturated and able to be removed in a VFR where (self)filtration and precipitation occurs. This means that for many acid mine waters, significant removal of the principal contaminant can be achieved by a simple filtration-type system. This is of particular significance to coal mine AMD where Fe is the principle contaminant. Even slight pH change should be enough to remove much of the Fe.
- The precipitate and/or the gravel substrate hosts Fe(II) oxidizing microbes resulting in demonstrable Fe(II) oxidation. The activity of Fe(II) oxidizers is important in AMD treatment, but the data presented here shows removal of what appears to be 'dissolved' Fe may not always be due to Fe(II) oxidizers.
- An example scale up for the Cwm Rheidol mine water suggests that 70% of the Fe from the full discharge at that site of 10 L/s could be treated continuously for at least one year without removing the precipitate by a VFR of 42 m × 50 m.

## ACKNOWLEDGEMENTS

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