

# Mechanisms of Iron Removal during Passive Treatment of AMD in a Vertical Flow Reactor

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## ABSTRACT

This paper presents data from a field trial for the passive removal of Fe from circa pH 3 metal mine water. In a 1 m<sup>3</sup> intermediate bulk container (IBC) converted into a vertical flow reactor (named here the VFR), mine water was passed through in a downward direction through an unreactive reactive gravel bed under aerobic saturated conditions. The VFR was deployed for a period of 414 days at the Cwm Rheidol mine, an abandoned historic Pb/Zn mine in Wales, UK that discharges circa pH 3 AMD with average Fe concentrations of 95 mg/L. Removal of iron, as high as (85%) was shown with an average of 65% achieved over the trial period from an average flow of 0.38 L/min. Results were encouraging, a very simple system providing an option to treat acidic coal mine drainage where iron is the principal contaminant or pre-treat 'metal mine' water by removing the bulk of the Fe as an iron-rich sludge to help prevent clogging of subsequent treatment stages for more environmentally toxic elements. The Fe removal mechanism is thought to be predominantly by the crystal growth and/or aggregation and filtration of nanoparticulate Fe(III) in the VFR. Centrifugation of influent water samples from site indicated that 80 – 90 % of the Fe in the inflow water is present as Fe(III)<sub>(s)</sub> particles < 35 nm. Microbial Fe(II) oxidation is suspected to be important along the flow path before water enters the VFR and to a small extent within the VFR. Analysis of the sludge indicates that schwertmannite is the dominant mineral phase.

**Keywords:** mine water, passive treatment, vertical flow reactor, Wales/UK

## INTRODUCTION

Historically, north and south Wales, Cornwall and the midlands were extensively mined for base metal sulphides and coal. It is estimated that there are tens to thousands of abandoned mining facilities including onshore mining and quarrying sites (Palumbo-Roe and Colman, 2010). The clean-up of water from abandoned coal mines is the responsibility of the UK Coal Authority, but since the introduction of the Water Framework Directive in 2006, the Coal Authority and Natural Resources Wales have been working closely together to find long-term, low cost treatments options for the clean-up of the metal mines.

National Resources Wales (formerly known as the Environment Agency Wales) published the Metal Mines Strategy for Wales (Johnston, 2004) which lists the top fifty most polluting sites in Wales that were identified, following the monitoring of 5042 km of river stretches, 108 km of which failed ecosystem objectives as a direct consequence of pollution from abandoned mines (Jarvis et al., 2007). 38 of those top 50 sites are located in the Mid-Wales district of Ceredigion.

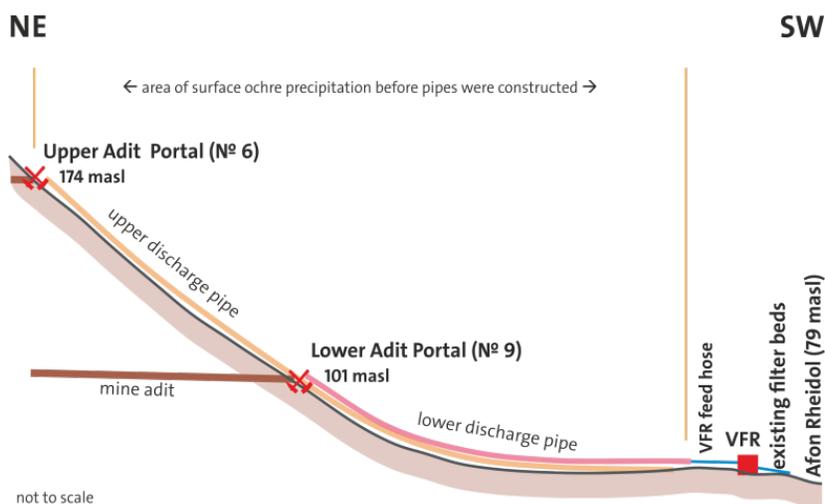
Metal mine water is commonly treated by active means, where chemicals are added to raise the solution pH and precipitate metals and metalloids. This tends to form a high volume of sludge, which, if containing metals other than Fe, for example, Zn, Pb, Cd may be classified and disposed of as hazardous waste, further adding capital and operational costs. Consequently, active treatment might be impractical, bearing in mind that the Coal Authority is a governmental organisation and mine water can continue to pollute for tens to hundreds of years. As such, active treatment is not currently considered for application to the majority of discharges in former UK mining regions. Furthermore, the metal mining areas tend to be concentrated in remote steep sided valleys, where access is difficult and a lack of basic infrastructure, such as power, exists. For this reason, the adoption of passive treatment is favoured. However, passive treatment options for metal mine drainage are not well developed in the UK.

Looking outside of the UK many countries have developed and deployed a host of these passive technologies (*e.g.* anoxic limestone drains) for treating metal-rich AMD (Brodie et al., 1991, Hedin et al., 1991, Skousen, 1991). Passive mine water treatment is commonly achieved via harnessing of naturally occurring physiochemical and biological processes, for example the manipulation of solubility via changes in pH by reaction with limestone (Blowes et al., 2003), altering the redox conditions through the use of organic matter (Lottermoser, 2007, Wildeman et al., 1993), the addition of high surface area materials used to provide sorption sites (Jarvis and Younger, 2001, Younger, 2000) or the use of low cost reactive materials (Warrender et al., 2011). The longevity of these treatments can be compromised by clogging due to the Fe (or Al) precipitates formed during the neutralisation of AMD with limestone or other alkalinity producing systems (Younger et al., 2002). This study considers these treatment methods with a modular approach, whereby a system such as a VFR could be used to remove Fe (as the bulk contaminant) from AMD. Such a technology could be deployed where Fe alone is the contaminant of concern (*e.g.* acidic coal mine drainage) or as a pre filter for Fe removal where Fe and other solubilized metals such as Zn occur together, thus allowing prolonged longevity for the second metal removal stage. The benefits of this would be the reduction of the volume of the 'hazardous' waste and the production of a clean (in terms of free of organics) iron-rich sludge that could have reuse value. The focus of this study is therefore to test the VFR as an Fe removal pre-treatment system for AMD.

On its course through the system, mine water passes down through the gravel bed support media. The vertical flow design reduces the footprint compared to more traditional systems that require large areas of land. Sapsford et al. (2007) detailed the testing of a VFR achieving 50% Fe removal from circum-neutral (pH 6–7) coal mine drainage with Fe concentrations of 8–10 mg/L. Iron removal occurred via filtration of iron hydroxide particles (formed in the water column) and surface-catalysed oxidation of Fe(II) (and precipitation) of Fe(III) hydroxide surfaces. This paper reports the results and possible Fe removal mechanisms of a VFR trialled for removal of Fe from pH 3 mine water.

## METHODOLOGY

The system was adapted from the original design used in the initial field trial at the Taff Merthyr site in South Wales (Dey et al., 2003), using a modified 1 m<sup>3</sup> intermediate bulk container (IBC, see fig. 1 in Sapsford, Florence, Pope and Trumm, these proceedings). A length of coiled, slotted drainage pipe was placed in the bottom of the tank. 30 mm angular coarse grained siliceous chips were added to the container to secure the pipe and provide a stable base on top of which a 200 mm depth layer of 5–10 mm grain size siliceous gravel was added (Fig. 2). A down flow of mine water was then maintained through the water column and through the ochre bed. Driving head was set via a swan neck mechanism through which the treated water was discharged. The VFR was set up alongside the River Rheidol to take a proportion of the flow from the lower number 9 adit discharge pipe of the Cwm Rheidol mine located at the base of the mine. Water was piped to the VFR under gravity from the adit discharge pipe (Fig. 1).



**Figure 1** Schematic cross section of the upper number 6 adit and the lower number 9 adit and the location of the VFR at Cwm Rheidol. masl: meters above sea level.

### Field data and water sampling

All field measurements of pH, EC, ORP and temperature were taken using Hanna combination meters HI-9828. The dissolved oxygen (DO), electrical conductivity and pH probes were calibrated at each site visit using the manufacturer's calibration procedure set out in the operator's manual. Flow rates were measured using the bucket-and-stop-watch-method.

At each of the 34 site visits between 2011-05-17 to 2012-07-04, filtered and unfiltered water samples were collected from the inflow and outflow. For the filtered samples, 0.2  $\mu\text{m}$  Acrodisc PF syringe filters fitted to Plastipak syringes were used. In this study, the term filtered is used to describe samples that pass a 0.2  $\mu\text{m}$  filter and is not a definition used to describe 'dissolved' species. All water samples were collected in 30 mL containers and rinsed with the sample and acidified with  $\text{HNO}_3$  to stabilize the water chemistry. Samples collected on site were placed immediately into a dark cool box and stored at 4 °C until analysis was possible. Samples were analysed using a Perkin Elmer Optima 2100DV ICP-OES. Filtered unacidified inflow and outflow samples were also collected for sulphate analysis using a Dionex<sup>®</sup> ICS-2000 Ion Chromatography System. Whilst samples for Fe total and Fe filtered were collected and analysed from each sample visit, Fe(II) was only measured on 11 of the sampling intervals. On the occasions that Fe(II) was measured in the field, filtered samples were analysed using a potable Merck NOVA60 spectrophotometer with appropriate Merck Fe test cells. Samples collected for Fe(II) analysis in the laboratory using a Hitachi U1900 spectrophotometer, were filtered and acidified with 20% (v/v) HCl. Samples for Fe(II) that could not be analysed on the same day were frozen until analysis was possible.

### Centrifugation

A centrifugation method adapted from Hüttig and Zänker (2004) was used to determine the Fe particle size distribution in the unfiltered inflow water. In this context, truly dissolved relates to a particle size of less than 50 nm, which is close to the 20 nm cut off between “truly dissolved” and colloids suggested by Shiller (2003). 20 tubes of fresh mine water were collected in the field (10 × 2 to duplicate the experiment). Parallel centrifugation of each 2 × 50 mL of raw water was carried out at rotor speeds calculated as per Table 1 at rotor speeds of 300, 500, 700, 1000, 3000 and 5000 over a period of 1 h and 3500 rpm (rounds per minute) over a period of 2 h due to the limitation of the centrifuge instrument speed. Equivalent RCF values (relative centrifugal force, which is equivalent to the *g*-force used in table 1) at a given point in the centrifuge tube were calculated according to the equation 1:

$$RCF = 11.18 \times r \times U^2 / 1000 \quad [1]$$

Where *r*: distance between the rotation axis and the particle in the centrifuge tube in cm and *U*: rpm rounds per min. After centrifuging, the supernatant was syringed from the centrifuge tube using a pipette. The sample was transferred to a new sample container, acidified with 20% nitric acid and the total unfiltered Fe concentration analysed by ICP-OES.

**Table 1** Centrifuge parameters and calculated values

| RPM  | <i>t</i> , h | <i>g'</i> , - | <i>d</i> , nm |
|------|--------------|---------------|---------------|
| raw  | -            |               |               |
| 0    | 1            |               |               |
| 300  | 1            | 283           | 683           |
| 500  | 1            | 474           | 417           |
| 700  | 1            | 659           | 293           |
| 1000 | 1            | 945           | 207           |
| 2000 | 1            | 1889          | 101           |
| 4000 | 1            | 4181          | 50            |
| 5000 | 1            | 5254          | 39            |
| 3500 | 2            | 3913          | 35            |

The maximum size of the particles still present in the supernatant was calculated with an assumed density of the colloids and under the assumption of a spherical form of the particles in accordance with equation 2:

$$d = 18 \eta \ln(r_1 / r_0) / (\rho_2 - \rho_1) \omega^2 t \quad [2]$$

with *d* diameter of particle in cm,  $\rho_2$  density in g cm<sup>-3</sup> (3.96 g cm<sup>-3</sup> for ferrihydrite), *r*<sub>0</sub> distance of water level in vial to rotation axis before taking sample in cm, *r*<sub>1</sub> distance of water level in vial to rotation axis after taking sample in cm, *t* duration of centrifuging in s,  $\eta$  viscosity of water at 25 °C (0.008941 g cm<sup>-1</sup> s),  $\rho_1$  density of water at 25 °C (0.997 g cm<sup>-3</sup>) and  $\omega$  angular velocity in s<sup>-1</sup> =  $U \times 2\pi / 60$ .

### PHREEQC Modelling

A full water analysis was used for chemical thermodynamic modelling with PHREEQC interactive Version 3.1.1.8288 (2013-12-05) and the WATEQ4F database (6895 2012-08-21 18:10:05Z) extended with kinetic data of schwertmannite.

### Sludge analysis

Samples for XRD analysis were dried overnight at 60 °C, finely ground and placed in a slide window covered by glass plate, amorphous samples were scanned for 12 h. Settling velocities of the Cwm Rheidol sludge from within the VFR were calculated by measuring the distance at which the particles settled over time.

## RESULTS AND DISCUSSION

### Fe inflow and outflow concentrations

The data for iron show that average removal for Fe(total) is 65% on the sampling occasion across the 13 months period (Table 2). Fe removal rates remained consistent throughout the trial period and the flow rates stabilised between days 33 and 387 averaging 0.39 L/min (Fig. 3), which shows that after the initial drop, the permeability of the bed did not decrease significantly over time. On average, about 85% of the Fe in the influent is Fe-filtered (*i.e.* passing a 0.2 µm filter) and on average 99% of the effluent iron passes a 0.2 µm filter. The removal of Fe-Filtered is on average 53 mg/L (Table 1). This demonstrates that the VFR removes Fe(III) of < 0.2 µm, where the Fe could either be particulate (smaller than 0.2 µm, *i.e.* colloidal or nanoparticulate) or truly dissolved. Likely candidates for the removal of Fe-Filtered are (i) Microbial Fe(II) oxidation and precipitation of a Fe(III) solid phases (ii) Filtration of particulate-Fe(III)<sub>(s)</sub> which is < 0.2 µm and/or (iv) adsorption of dissolved Fe(III) to HFO followed by precipitation (self-seeding crystal growth). These are discussed in more detail below.



**Figure 2** Left, initial stages of filling the VFR; centre: Ochre inside the VFR (after draining tank); right: ochre precipitates taken directly from the VFR.

Table 2 VFR field parameter measurements.

| Date       | Flow rate (L/min) |      | pH   |        | D.O (mg/L) |     | ORP (mV) |       | Temp (°C) |       | Fe-Tot (mg/L) |       | Fe-Tot Removal % |       | Fe (Filt) Removal % |       | Fe (II) (mg/L) |       | Δ Fe-Filt (mg L) | RT (hrs) |
|------------|-------------------|------|------|--------|------------|-----|----------|-------|-----------|-------|---------------|-------|------------------|-------|---------------------|-------|----------------|-------|------------------|----------|
|            | E                 | I    | E    | I      | E          | I   | E        | I     | E         | I     | E             | I     | E                | I     | E                   | I     | E              | I/E   |                  |          |
| 2011-06-21 | 0.71              | 2.98 | 3.01 | 8.47   | 7.33       | 684 | 716      | 13.54 | 14.14     | 126   | 60.81         | 51.74 | 126.59           | 65.3  | 48.42               | na    | na             | 61.29 | 16               |          |
| 2011-07-11 | 0.46              | 3.29 | 3.38 | 7.54   | 7.81       | 670 | 742      | 15.41 | 18.01     | 23.25 | 17.1          | 26.45 | 16.45            | 15.8  | 3.95                | na    | na             | 0.65  | 24               |          |
| 2011-07-20 | 0.38              | 3.33 | 3.26 | 9.51   | 4.12       | 670 | 764      | 14.37 | 16.04     | 119.6 | 41            | 65.72 | 116.2            | 41.16 | 64.58               | na    | na             | 75.04 | 31               |          |
| 2011-08-03 | 0.25              | 3.03 | 3.09 | 5.83   | 4.38       | 678 | 763      | 16.97 | 16.26     | 104.9 | 31.37         | 70.10 | 64.87            | 31.82 | 50.95               | 37.1  | <0.2           | 33.05 | 47               |          |
| 2011-08-11 | 0.11              | 2.58 | 3.05 | 6.49   | 5.89       | 758 | 776      | 17.88 | 19.64     | 80.56 | 32.09         | 60.17 | 64.87            | 31.82 | 50.95               | 0.58  | <0.2           | 33.05 | 85               |          |
| 2011-08-22 | 0.3               | 3.42 | 3.58 | 6.9    | 4.30       | 673 | 710      | 15.27 | 14.48     | 146.2 | 53.34         | 63.52 | 138.7            | 52.45 | 62.18               | na    | na             | 86.25 | 48               |          |
| 2011-08-30 | 0.2               | 3.03 | 3.02 | 8.35   | 6.66       | 673 | 762      | 12.02 | 12.64     | 155.1 | 53.9          | 65.25 | 135.5            | 51.18 | 62.23               | 10.2  | na             | 84.32 | 59               |          |
| 2011-09-19 | 0.2               | 3.05 | 3.00 | 5.66   | 5.55       | 767 | 678      | 12.88 | 12.19     | 87.54 | 23.63         | 73.01 | 82.5             | 23.86 | 71.08               | 12.3  | <0.2           | 58.64 | 70               |          |
| 2011-09-25 | 0.29              | 3.04 | 3.06 | 8.85   | 5.40       | 663 | 757      | 12.28 | 14.05     | 101   | 20.75         | 79.46 | 77.17            | 20.19 | 73.84               | na    | na             | 56.98 | 30               |          |
| 2011-09-26 | 0.24              | 2.83 | 2.63 | 7.66   | 4.08       | 668 | 728      | 16.01 | 19.67     | 84.91 | 18.13         | 78.65 | 72.2             | 17.76 | 75.40               | na    | na             | 54.44 | 58               |          |
| 2011-10-04 | 0.26              | 2.5  | 2.41 | 9.20   | 6.31       | 664 | 718      | 12.40 | 12.26     | 97.09 | 28.19         | 70.97 | 91.31            | 27.78 | 69.58               | 32    | <0.2           | 63.53 | 60               |          |
| 2011-10-07 | 0.24              | 2.65 | 2.68 | 7.19   | 6.73       | 741 | 724      | 15.08 | 15.38     | 110.9 | 28.91         | 73.93 | 102.5            | 31.23 | 69.53               | 35    | <0.2           | 71.27 | 52               |          |
| 2011-10-21 | 0.31              | 3.01 | 3.15 | 7.70   | 10.02      | 638 | 648      | 10.44 | 11.46     | 84.13 | 23.64         | 71.90 | 75.53            | 23.92 | 68.33               | 33.1  | 1              | 51.61 | 40               |          |
| 2011-11-04 | 0.19              | 2.88 | 2.59 | 9.32   | 6.10       | 662 | 727      | 10.52 | 9.47      | 37.82 | 24.35         | 35.62 | 16.68            | 3.97  | 76.20               | 4.44  | <0.2           | 12.71 | 50               |          |
| 2011-11-18 | 0.2               | 2.77 | 2.63 | 9.16   | 7.75       | 359 | 722      | 11.14 | 10.96     | 110.4 | 29.45         | 73.33 | 103.93           | 29.05 | 72.05               | 43.5  | 1.18           | 74.88 | 72               |          |
| 2012-01-02 | 0.1               | 2.45 | 2.37 | 9.13   | 6.83       | 718 | 726      | 6.75  | 6.74      | 95.67 | 14.56         | 84.78 | 35.83            | 11.53 | 67.82               | 4     | <0.2           | 24.3  | 112              |          |
| 2012-03-18 | 0.23              | 2.38 | 2.32 | 7.07   | 6.45       | 773 | 741      | 9.18  | 10.81     | 79.15 | 23.51         | 70.30 | 72.32            | 24.74 | 65.79               | na    | na             | 47.58 | 38               |          |
| 2012-06-07 | 1.1               | 3.08 | 2.54 | 8.30   | 7.20       | 476 | 448      | 13.04 | 14.09     | 102.1 | 24.28         | 76.22 | 91.17            | 24.49 | 73.14               | na    | na             | 66.68 | 6                |          |
| 2012-06-30 | 1.1               | 4.86 | 4.94 | 6.60   | 5.54       | 505 | 492      | 14.37 | 13.63     | 75.3  | 20.37         | 72.95 | 69.26            | 21.6  | 68.81               | 27.6  | 4.6            | 47.66 | 10               |          |
| 2012-07-04 | 0.75              | 2.87 | 2.92 | 7.42   | 5.89       | 485 | 516      | 13.40 | 12.51     | 79.2  | 17.31         | 78.14 | 63.69            | 17.1  | 73.15               | 17.2  | <0.2           | 46.59 | 15               |          |
| Mean       | 0.38              | 2.83 | 2.77 | 7.8175 | 6.217      | 646 | 693      | 13.15 | 13.72     | 95.04 | 29.33         | 67.11 | 80.86            | 28.33 | 63.4                | 21.42 | 0.69           | 52.53 | 46               |          |

Filt: filtered, Tot: total, I: influent, E: effluent

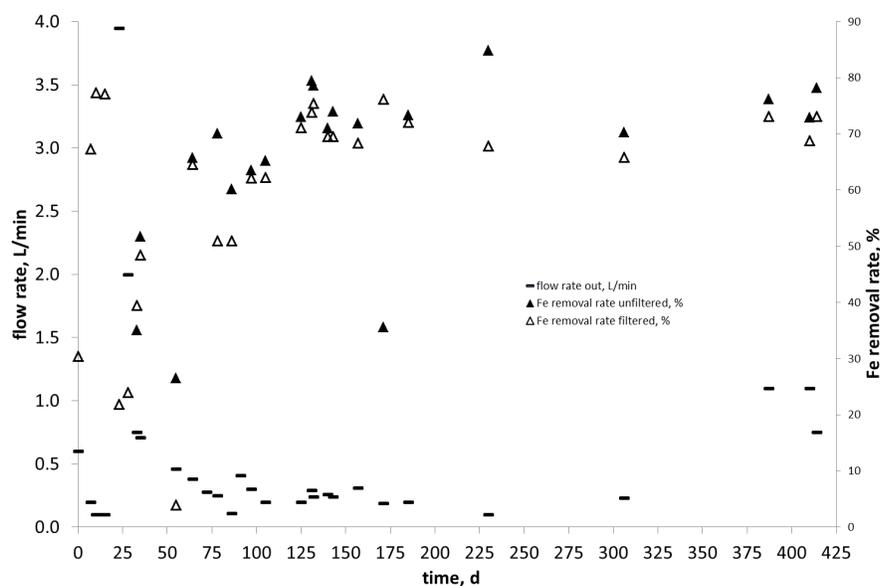


Figure 3 Filtered and unfiltered Fe(total) removal rate and flow rate of the VFR over time

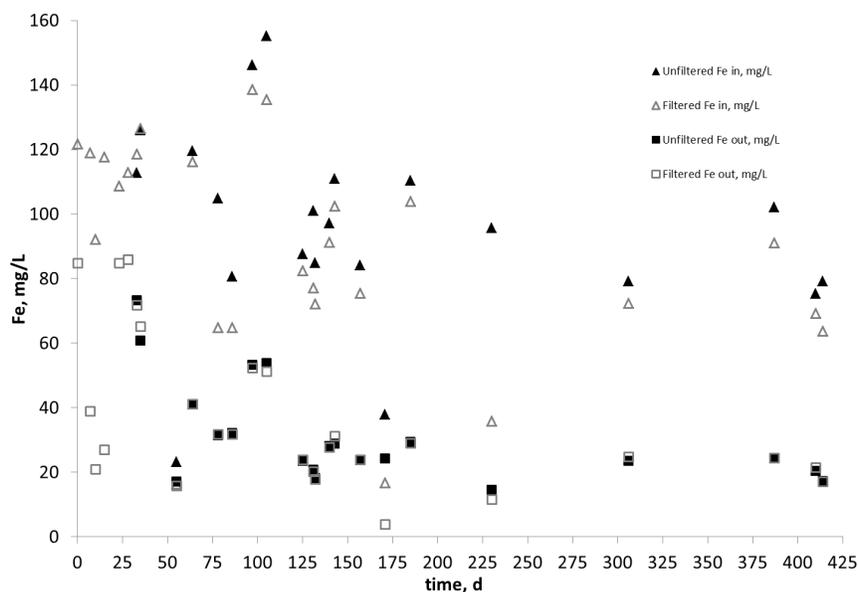


Figure 4 Filtered and unfiltered VFR inflow and outflow Fe(total) concentrations over time

### Oxidation of Fe(II) and precipitation of Fe(III)(s)

Where Fe(II) analyses were performed in the field, it was apparent that Fe(II) only made up a small proportion of the influent Fe (highest observed was 42 % of the influent Fe-Filtered on 18-11-11). Fe(II) was removed in the VFR, with 7 of the 11 sampling occasions falling below the detection limit of the spectrophotometric method used (0.2 mg/L). The minimum removal of Fe(II) was 83 % on 30-06-12 (note: with only a short residence time of 10 h). Thus it is clear that despite Fe(II) being variable, it was typically a small component of the Fe-Filtered and that it was removed effectively in the VFR. Based on the microbial analyses (Florence, 2014) and the published rates for abiotic and biotic Fe(II) oxidation at low pH, the proposed mechanism for the observed results is microbial Fe(II) oxidation.

However, the change in filtered Fe between the influent and effluent cannot be simply explained by the oxidation of Fe(II), and in all of the cases observed during sampling the removal of filterable influent iron that initially passes a 0.2  $\mu\text{m}$  filter cannot be explained by oxidation of iron (II) to an insoluble Fe(III) product. Thus the dominant removal for filterable iron must involve changes in dissolved Fe(III) or colloidal to nanoparticulate Fe(III) that passes the 0.2  $\mu\text{m}$  filter.

### Iron removal mechanism: Precipitation versus filtration of nanoparticulate-Fe(III)(s)

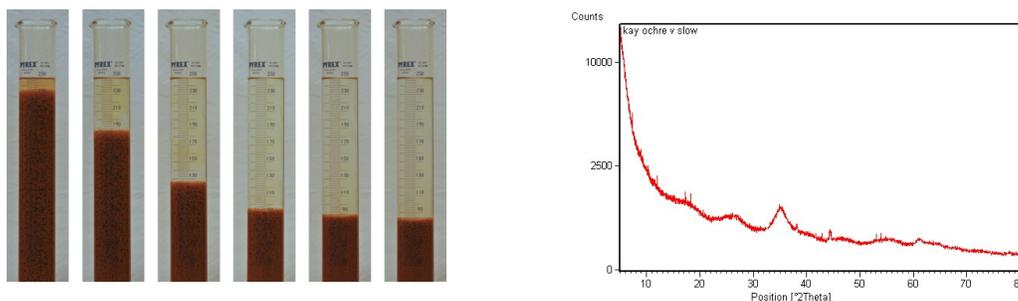
70% of the Fe in the inflow passing a 0.2  $\mu\text{m}$  filter is retained in the VFR (Fig. 4). On average, the remaining 30% of the inflow Fe is still present in the outflow. Water at Cwm Rheidol is typically well oxidised. The remaining 30% of the Fe that is not being removed was Fe(III) in either truly dissolved form (single solvated Fe(III) ions) or particulate Fe(III)<sub>(s)</sub> of < 200 nm. A centrifuge study was used to examine the size distribution for possible particulate Fe(III). The Fe data showed that Fe does decrease as centrifugation speed increases, however 87% of the iron measured in the raw mine water was still present after centrifugation for 2 h at 3500 rpm which corresponds to a stokes diameter of 35 nm. This means that on the sampling occasion, the Fe present in the mine water sample was less than 35 nm in size. This suggests that the Fe removal mechanism in the VFR involves either (i) precipitation and filtration of dissolved Fe(III) as it grows from molecular clusters to larger sizes range precipitates or aggregation and filtration of nanoparticulate Fe(III) < 35 nm in size that was present in the VFR influent.

At this scale, given the very small size of the particles involved, it becomes somewhat arbitrary what the operational definition of dissolved and particulate iron is. There is no general consensus in

the literature, under which threshold size particles can be considered “truly dissolved”, and the distinction between the two is analytically challenging (Mudashiru, 2008). Commonly, 1–1000 nm are called colloids, 1–100 nm are nanoparticles and several authors call particle sizes under 30–50 nm “truly dissolved” (Daughney et al., 2004). Yet, 1 nm is still larger than the size of a molecule which is in the range of several Ångströms but in the range of hydrated ions (Ranville and Schmiermund, 1999). As such, it could be viewed as the removal mechanism working in the system is providing retention time for the growth of ferric iron from truly dissolved state to particles large enough to be filtered out in this the VFR. Based on the results of the centrifuging and this definition of colloid ranges, it can therefore be suggested that the removal mechanism occurring in the VFR is one or a combination of nanoparticle filtration or precipitation and aggregation of truly dissolved (*i.e.* originally molecular-scale) Fe. The role of heterogeneous ‘seeding’ by the precipitated solids in the system is also potentially very important but it is not possible to distinguish this mechanism from the field data collected.

### Sludge Composition and settling behaviour

The consistency of the sludge that accumulated within the tank was unusual and noteworthy: The sludge looked like it had been polymer dosed. Settling velocity experiments showed that the VFR precipitates had comparable settling rates to polymer dosed HDS sludge yet remained permeable throughout the field trial (Fig. 5, left). Bacterial presence is thought to be responsible for the unusual consistency of the flocs in the VFR (Fig. 2, right), which was supported by a supporting microbiological study (Florence, 2014). Sulphur analysis of the VFR sludge showed the sample to contain 4.4% sulphur which is an indication of that schwertmannite was formed. This is also consistent with XRD analysis (Fig. 5, right) that showed peaks of an amorphous Fe(III) (hydroxy) oxide that is characteristic of aged schwertmannite (Peretyazhko et al., 2009).



**Figure 5** Left, settling properties of the precipitates that formed in the VFR at 15, 60, 120, 194, 240 and 284 s settling time. Right, XRD analysis of VFR ochre. The peaks at around 15, 35 and 45°2θ are characteristic for schwertmannite.

### PHREEQC modelling

In support of the field and laboratory analyses of Fe speciation, PHREEQC modelling, suggests that Fe predominantly exists as Fe(III) (91%) and to a lesser degree of Fe(II) (9%) in the influent. The dominating Fe(III) and Fe(II) species are  $\text{FeSO}_4^+$  (81%) and  $\text{FeSO}_4^0$  (9%) respectively. Likely important phases that were predicted oversaturated for the mine water were K-jarosite and schwertmannite.

### Iron removal in the context of the study site

Studying the layout of the mine is important as this helps to depict the chemical reactions responsible for the site being a producer of AMD (Fig. 1) and how the VFR is removing Fe from the mine water. Hydrolysis and oxidation of Fe(II) to Fe(III) occurs in the extended adits and mine workings prior to reaching the VFR. The adit length (600 m), flow rate (3 L/min) and a convex channel (0.5–1 m wide and 0.05 deep) results in a flow of approx. 0.10 m/min; data which is used to calculate the distance at which particles > 0.2 μm will settle based on Stoke’s law. This was found to be 300–500 m. The first reaction occurring is the partial ochre precipitation in the adits (reaction 3):



Mine water is further aerated and agitated during the pipe transport and more ochre forms in the pipe. The mine water that is now collected from the adit discharge pipe and drained to the VFR contains the following aqueous components (based on PHREEQC results):



Solubility calculations and the chemical analysis at the discharge pipe shows, that part of the iron remains truly dissolved (and passes through the VFR), but that the water is still oversaturated with iron phases and able to precipitate iron, potentially as (nano-)particles < 0.2 μm in the acid mine water according to equation 3. In the VFR, due to the slow flow, prolonged residence time and intimate contact with precipitates compared to the adit and pipe flow, the (nano-)particles and/or dissolved Fe are removed. Yet, some of the dissolved Fe(III) remains in solution according to the solubility of the controlling Fe-phase at this pH (schwertmannite) and passes through the VFR without being removed.

## CONCLUSION

The VFR trial at the abandoned Cwm Rheidol mine was effective at removing a large proportion of the Fe from low pH AMD. Whilst further work is required to understand the precise mechanisms of Fe removal in the VFR, where chemical, environmental and biological conditions are conducive, the VFR system has excellent potential as a Fe removal system for 'pre-treatment' (to remove a bulk of the iron) at metal mines such as Cwm Rheidol or to remove Fe from acidic coal mine drainage. Based on the results of the 13 month trial, a 50 m × 35 m VFR could remove approximately 70% of the Fe from the number 9 adit at Cwm Rheidol for at least a year without maintenance.

## ACKNOWLEDGEMENTS

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