

IRON AND MANGANESE REMOVAL IN A VERTICAL FLOW REACTOR FOR PASSIVE TREATMENT OF MINE WATER¹

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Abstract: Settling lagoons are a common feature of passive mine water treatment schemes but tend to require large surface areas, this makes them unfeasible in the numerous locations where space is limited. A novel pilot-scale vertical flow reactor has been built at the Taff Merthyr former colliery site. The vertical flow system is designed to replace conventional settling lagoons and decrease the surface-area requirements. To achieve this, the system is designed to take advantage of the surface-catalysed oxidation of Fe(II) on ochre surfaces and the (self)filtration of an ochre bed. This paper presents results from the first four months of operation and details iron and manganese removal. The system receives net-alkaline water from the abandoned colliery, the water quality is typically pH 6.9, with Fe_{TOT} of 9 mg/l. The results show that the vertical flow reactor achieves higher iron removal rates (typically between 10 and 20 g/m²/d) compared to the settling lagoon (typically < 5 g/m²/d). The vertical flow reactor achieves these removal rates with a smaller residence time, often half that of the settling lagoon. Manganese is present in the influent in low concentrations (~0.8 mg/l). Operating data show that about 50 % of Mn can be removed in the vertical flow reactor in 24 hrs compared to just 5 % in 24 hours in the settling lagoon. Longevity of the reactor will depend on maintaining an acceptable permeability in the bed. Although the permeability fell rapidly at first, the indications are that it is stabilising near to 10⁻⁴ m/s.

Additional Key Words: Surface catalysed iron oxidation

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Introduction

Ferruginous (Fe^{+2}) mine water discharges have long been acknowledged as being deleterious to receiving watercourses. The UK National Rivers Authority (now the Environment Agency) identified some 100 such discharges as the cause of significant pollution problems in the UK (NRA 1994). In the Eastern USA coalfields in excess of 8,000km of waterways and associated groundwaters have been identified as being directly affected (Cravotta and Trahan 1999).

In the UK, since the early 90's passive mine water treatment technologies have been favoured rather than active systems on the grounds of reduced costs and often favourable mine water chemistries (circumneutral or net-alkaline). The current best practice for the passive treatment of net-alkaline Fe^{+2} mine waters in the UK generally involves cascade aeration followed by further aeration and settlement of precipitated solids in lagoons. After passing through the lagoons, mine waters receive final treatment in surface flow wetlands. The intention is to remove 30-50% of the iron 'up-front' in the settlement lagoons before the mine water enters the wetland, thus allowing more effective sludge management and prolonged life of the wetland. However, these lagoons often need to be very large and considering the high population density of the UK it is no surprise that the UK's leading developer of passive treatment systems, the Coal Authority, regards restricted availability of land as the single greatest restraint on wider application of passive mine water treatment (Parker, 1997).

As an alternative to the conventional passive system, a vertical flow reactor has been developed and it has been demonstrated at small scale (about 1m^3) that it is possible to replace both the lagoons and the wetland at a substantially reduced treatment footprint. A larger version of the reactor has now been installed at the disused Taff Merthyr colliery in South Wales and the very early results of the operation have previously been presented (Sapsford et al., 2005). In the present paper the results for the first four months of continuous operation are presented, concentrating mainly on the removal efficiencies for Fe and Mn, along with the evolution of permeability in the ochre bed.

Design Concept for Vertical Flow Reactor

This has already been considered at depth in the paper presented at the 9th International Mine Water Association Congress in Oviedo in 2005 (Sapsford et al., 2005). The concept is not dissimilar to that considered in several recent publications (e.g. Jarvis and Younger (2001), Burke and Banwart (2002), Best and Aikman (1983), Younger (2000)) and relies on metal removal on the surfaces of ochre. However, in the Cardiff system, there are no media included for the ochre to accrete around; rather a bed of ochre is allowed to accumulate on top of a supporting gravel bed. It is anticipated that the ochre will achieve efficient Fe removal both by filtration of colloidal $\text{Fe}(\text{OH})_3$ particles by the ochre bed and by surface-catalysed oxidation of Fe^{+2} and subsequent accretion of Fe species around pre-existing particles in the accumulating bed.

Influence of Solution and Surface Chemistries on the Oxidation of Fe(II) (Fe^{+2}) Species

Passive treatment of net-alkaline Fe^{+2} waters involves retaining the water for a sufficient time to allow the Fe^{+2} iron load to be oxidised and precipitate out as some form of hydrous ferric oxide (FeOOH or ochre) as given by Eq. [1]:



The Fe(III) (Fe^{+3}) solid phases (ochre) produced are usually amorphous, gelatinous precipitates with varying composition dependant upon the mine water chemistry, with time these may convert to more crystalline phases such as goethite. At circumneutral pH the formation of these solids is irreversible under oxic conditions. The overall rate of the reaction (Eq.1) at circumneutral pH can be described by the following empirical rate law:

$$R = - \frac{d[\text{Fe(II)}]}{dt} = k [\text{Fe(II)}] [\text{O}_2] [\text{H}^+]^{-2} \quad [2]$$

The pH dependence of the reaction changes from $\log R \propto [\text{H}^+]^{-2}$ to $\log R \propto [\text{H}^+]^{-1}$ below pH 5, and becomes independent of pH below pH 3. This was interpreted by Millero (1985) as due to the parallel oxidation of Fe^{+2} iron and its hydroxo complexes (see also Werhli, 1990; Burke and Banwart, 2002).



Each Fe^{+2} species has its own rate of reaction with dissolved O_2 (see rate constants in Table 1), equation [6] gives the rate law (Burke and Banwart, 2002) which expresses the sum of the parallel pathways, where the subscript i refers to an individual Fe^{+2} species (see equations [3] – [5]), and the subscript T refers to the total concentration of Fe^{+2} .

$$- \frac{d[\text{Fe(II)}]_T}{dt} = \sum k_i [\text{Fe(II)}]_i [\text{O}_2] \quad [6]$$

The actual rates for the reactions described are determined by the production of the superoxide anion (O_2^-) because this is considered (Millero 1985; Werhli 1990) to be the first and rate-determining step in the 4-electron reduction of O_2 during its reaction with dissolved Fe(II). The much faster rates of reaction for the hydroxo Fe^{+2} complexes is because OH^- serves as an effective electron bridge, facilitating the transfer of electrons from Fe^{+2} .

The speciation of Fe^{+2} is pH dependant, $\text{Fe}^{2+}_{(\text{aq})}$ tends to dominate the Fe speciation in the acidic to circumneutral pH range whilst $\text{Fe}(\text{OH})^+_{(\text{aq})}$ and $\text{Fe}(\text{OH})_{2(\text{aq})}$ dominate in higher pH solutions. The 6-orders of magnitude difference between rate constants for Fe^{+2} , $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2$ (see Table 1) explains why Fe oxidation rates show such a pronounced difference over a range of pH values (increasing sharply at high pH), reflecting the change in Fe^{+2} speciation with pH.

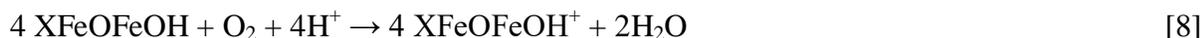
Table 1. Rate constants for oxidation of Fe^{+2} species, where k_i is the 2nd-order rate constant for equation [6].

Fe(II) species	2 nd -order rate constant	
Fe^{+2}	$k_1 = 7.9 \times 10^{-6}$	$\text{M}^{-1}\text{s}^{-1}$
$\text{Fe}(\text{OH})^+$	$k_2 = 25.1$	$\text{M}^{-1}\text{s}^{-1}$
$\text{Fe}(\text{OH})_{2(\text{aq})}$	$k_3 = 7.94 \times 10^{+6}$	$\text{M}^{-1}\text{s}^{-1}$

Heterogeneous catalysis of Fe(II) oxidation

It has long been established that surface-catalysed oxidation of Fe^{+2} occurs on Fe_2O_3 surfaces in the circumneutral pH range (e.g. Tamura et al., 1976; Wehrli 1990).

At pH values of between 5-6, Fe^{+2} in solution exists principally as $\text{Fe}^{2+}_{(\text{aq})}$ and correspondingly the homogenous rate of oxidation is still low (compared to the rate at higher pH where FeOH^+ , $\text{Fe}(\text{OH})_2$ dominate). In the same pH range and above, the introduction of ochre results in the adsorption of Fe(II) and the formation of Fe(II)-surface complexes (where 'X' denotes a surface) which can react with dissolved O_2 (Zhang et al., 1992; Burke and Banwart., 2002):



Wehrli (1990) used data from Tamura et al. (1976) to estimate a 2nd-order rate constant for the adsorbed Fe^{+2} species. The estimate ($5.01 \text{ M}^{-1}\text{s}^{-1}$) is 6-orders of magnitude larger than the rate constant for $\text{Fe}^{+2}_{(\text{aq})}$ and comparable to the rate constant for the $\text{Fe}(\text{OH})^+$ hydroxo complex in solution (see Table 1). Again the larger rate constant (and therefore rate of reaction) for the surface species is attributable to the presence of oxyanions (this time associated with the hydrated mineral surface) which facilitate electron transfer.

As a consequence of the formation of, and rapid reaction of the adsorbed Fe^{+2} species, the lower pH boundary of rapid Fe^{+2} oxidation is effectively lowered in the presence of the Fe_2O_3 (*ochre*) surface (Burke and Banwart, 2002). The surface oxidised iron then precipitates as fresh surface:



The continual precipitation of new solid oxide also means that surface sites are preserved and the reaction is in effect autocatalytic.

Site description

Taff Merthyr is an abandoned colliery, approximately 15 miles north of Cardiff in South Wales (UK). Mine water from the abandoned workings drains underground to a sump at low elevation at the site. From this sump, mine water is pumped up to a central distribution chamber; the flow is intermittent because the pumps are controlled by a float switch within the sump. The water drains from the distribution chamber and discharges at about 100 L/s into four settling lagoons each of surface area 1235 m^2 , which in turn drain by gravity through surface flow reed beds before discharging to the river Taff (Coal Authority, 2001). The Fe concentrations in the mine water are presently between 8 and 10mg/l.

The Vertical Flow Reactor

The Vertical Flow Reactor (VFR) large pilot-scale system (see Fig. 1) comprises a bespoke, commercially available, galvanised steel tank, 7.32m long by 3.66m wide and 2.30m deep, with a baffle wall 1.22 m from the end of the tank. The inside of the tank including all exposed concrete surfaces has been sealed with bituminous paint. Mine water is piped under gravity into the tank from the distribution chamber at the Taff Merthyr mine site. The flow rate into the tank

is controlled by an adjustable ball valve; the maximum flow rate delivered through the pipe is ~ 4 l/s ($14.4 \text{ m}^3/\text{h}$). The mine water flows down through a 100 mm bed of sandstone gravel, which sits on a plenum floor. The plenum floor is made of galvanised steel mesh sheets sitting on top of 300mm high concrete support pillars. This means that the whole gravel bed is under-drained by a large void space; the design is intended to improve the uniformity of flow through the ochre and gravel bed, reduce the possibility of blinding in the under-drain and allow access to clear blockages.

Water flows through this under-drain, under the baffle wall and up through into a rise chamber. The mine water discharges over an adjustable weir into an overflow chamber where a pipe takes the water away to discharge back into the existing wetland system. The adjustable weir allows control of the depth of water in the system and can also be adjusted (when the permeability of the ochre bed decreases) to allow a driving head to be developed between the two chambers. The whole system can be drained through a gate valve (see Fig.1) which is kept shut during normal operation. There is an overflow cut into the baffle wall at the top (see Fig. 2) which means in the event of the bed blinding, water will overflow and the system will work as a conventional settling lagoon.

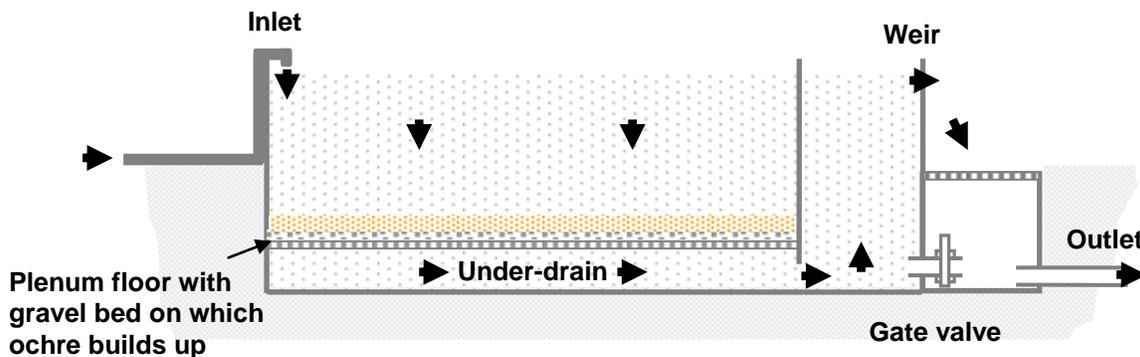


Figure 1. Schematic of the VFR (7.32m long by 3.66m wide and 2.30m deep) pilot-scale system at Taff Merthyr

Methods

Measurements of pH and oxidation-reduction potential and temperature measurements were made using a Hanna H1991003 meter and probe, Dissolved Oxygen (DO) using a Hanna H19145 meter and probe. Water samples (24 ml) were collected and acidified using 1ml of 25% HNO_3 , these samples were analysed for total metals on an ICP-OES (Perkin Elmer optima 2100), in this paper total metals measured in this way are given the sub-script suffix 'TOT' e.g. Fe_{TOT} . Water samples were also taken and filtered in the field through a $0.45 \mu\text{m}$ cellulose nitrate filter paper before acidifying the samples for ICP analysis as described above, in this paper metals measured in this way are denoted with a sub-script suffix of 'FILT $0.45 \mu\text{m}$ ', for example ' $\text{Fe}_{\text{FILT } 0.45 \mu\text{m}}$ '. Alkalinity measurements were made in the field using a HACH digital titrator. $\text{Fe}^{+2}_{(\text{aq})}$ and $\text{SO}_4^{-2}_{(\text{aq})}$ measurements were made in the field using a Hach DR-890 portable colorimeter. Water quality measurements were made and samples taken from the interior of the

tank. Sample ports built into the tank (see Fig. 2) were opened and connected to a Sheffield flow-through cell, this allowed insertion of the appropriate probes into water draining from the sampling ports without atmospheric contamination.



Figure 2. Photographs of large pilot-scale system at Taff Merthyr

Flow rates were measured at the point of ingress into the tank using the ‘bucket and stopwatch’ method. Flow rates were later corrected for the times when the pumps were not on by multiplying values by 0.75 (reflecting the estimated on/off times of the pumps bring water to the distribution chamber). Permeability calculations for the ochre/gravel bed require a head difference to be measured; this was done by measuring the level of water in the two chambers shown in Fig 2.

Results and Discussion

Influent chemistry

Table 2 shows some typical water quality parameters measured for the influent water into both the Vertical Flow Reactor (VFR) and the pre-existing settling lagoon. Of particular note is the circumneutral pH and high alkalinity which is typical of net-alkaline Fe^{+2} discharges from coal mines in the UK. The discrepancy between Fe_{TOT} and Fe^{+2} suggests that Fe^{+3} is present in the influent. The discrepancy between Fe^{+2} could be caused by uncertainty in the in-situ analysis, although the difference is consistently $> 20\%$ between measured Fe^{+2} and filtered Fe in the field (data not shown). Another possibility is that the Fe^{+2} is partially oxidising before the Fe^{+2} is measured, however this is unlikely because the HACH reagent quenches Fe^{+2} -oxidation immediately. The difference between the values of $\text{Fe}_{\text{FILT } 0.45\mu\text{m}}$ and Fe^{+2} dissolved are more likely due to the presence of Fe^{+3} solids of less than $0.45\ \mu\text{m}$ in size. There is no difference between Mn_{TOT} and $\text{Mn}_{\text{FILT } 0.45\ \mu\text{m}}$ suggesting all the Mn present in the influent is dissolved.

Table 2. Typical chemistry of influent mine water

Parameter		Number of samples
pH	6.92	13
ORP versus Ag/AgCl ₂	-26 mV	13
Conductivity	950 µS/cm	1
Dissolved Oxygen	3.1 mg/l	13
Alkalinity (as CaCO ₃)	233 mg/l	10
Fe _{TOT}	9.3 mg/l	12
Fe _{FILT 0.45 µm}	8.9 mg/l	9
Fe(II)	6.8 mg/l	13
Mn _{TOT}	0.8 mg/l	10
Mn _{FILT 0.45µm}	0.8 mg/l	9
Sulphate	230 mg/l	13
Temperature	12.0 °C	12

Flow rates and permeability of the system

The influent flow rate has varied from less than 0.5 l/s to about 2.5 l/s over the course of the system operation, shown in Fig. 3 (a). This variation is in part deliberate, the influent flow rate was varied using the ball valve on the influent pipe so that different flow rates (and the corresponding residence times) could be trialled and the effect on iron removal rates recorded. However, the decrease in flow rates shown for the last 4 data points was due to the gradual blocking of the influent pipe with ochre accumulation.

In Fig. 3 (b) is displayed the calculated coefficient of permeability based on the thickness of the gravel bed (100 mm) and the measured head differences between the inlet and outlet chambers of the VFR. Initially the permeability was relatively high (0.64 m/s), with values typical of gravel beds. After the second week, the permeability has decreased to values of around 3×10^{-4} m/s, typical of clean sands and sand-gravel mixtures. The increase in permeability for the 12/08/05 was due to interference with the VFR on the 02/08/05. The VFR was drained to the half-way mark by opening up the gate valve shown in Fig.1. This resulted in high flow rates within the tank which lead to scouring of the gravel and removal of some of the accumulated ochre. The permeability was consequently higher on the 12/08/05; however the system rapidly recovered to permeabilities of $\sim 10^{-4}$ m/s thereafter.

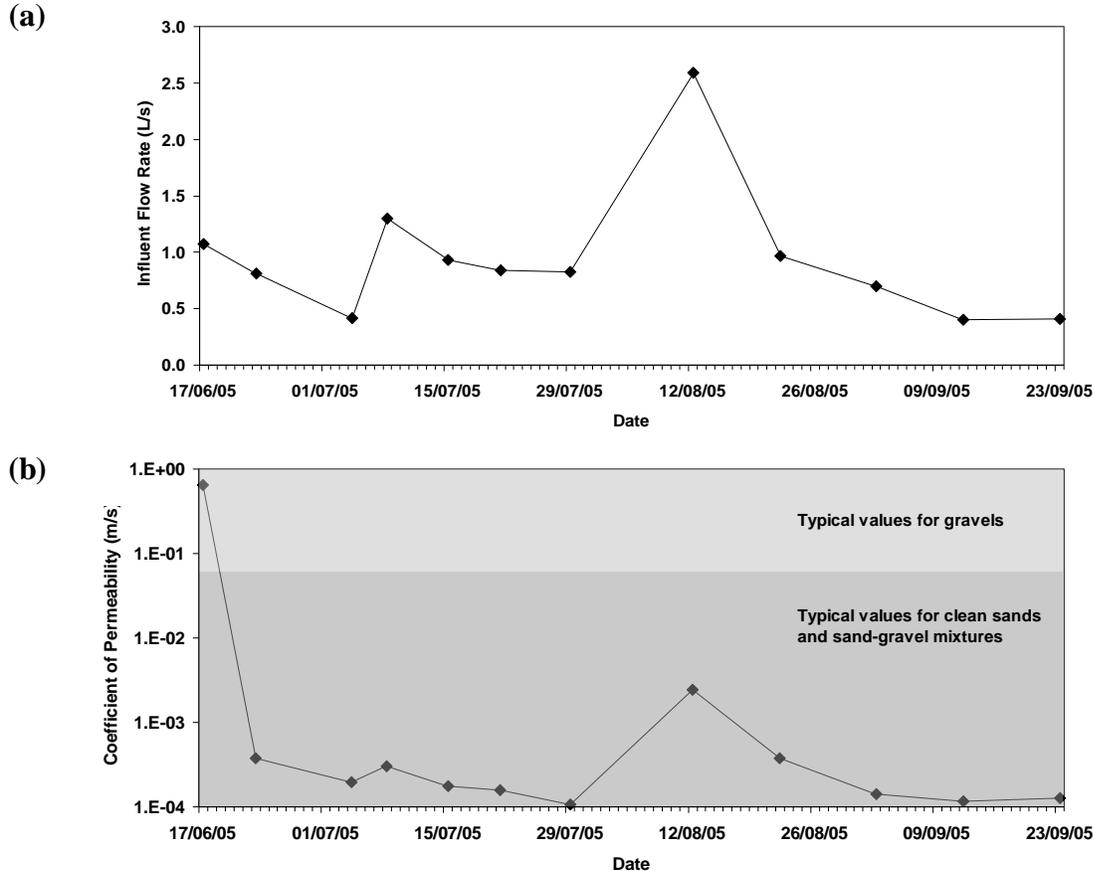


Figure 3. (a) Influent flow rates and (b) Permeability of the VFR

Influent and effluent iron and manganese chemistry

Iron is removed in the VFR as can be seen from Fig. 4(a), influent waters bearing between 7.8 – 10.1 mg/l of Fe and effluent waters bearing between 2.2 and 8.1 mg/l. The amount of Fe^{+2} in the ranges from 3.1 to 7.6 mg/l. The effluent water consistently has lower concentrations of Fe^{+2} than the corresponding influent (see Fig. 4(b), ranging between 0.24 and 3.45 mg/l. Thus showing that Fe^{+2} is being oxidised in the VFR.

Although Mn is present in only small concentrations (influent containing between 0.83 and 0.70 mg/l) the results shown in Fig. 4(c) are interesting, especially because Mn is notoriously difficult to remove from mine waters due to its slow oxidation kinetics at circumneutral pH. It is encouraging to report that Mn removal is improving over the course of operation of the VFR reaching a maximum of ~ 55 % removal. It should be noted that the retention time of the VFR was higher at these times, approaching 24 hours. However, the Mn effluent from the pre-existing Taff Merthyr settling lagoon (which has a designed residence time of at least 24 hrs) was only removing 5% of the influent Mn on the same day (data not shown). Although by the time the water had flowed through the settling lagoon and onward through a large reed bed and the sum residence time is of the order of days, 87 % of the Mn had been removed (data not shown). Data from Nuttall (2003) shows that iron hydroxide flocs can scavenge Mn from water, in the VFR water flows through a bed of ochre flocs, this seems a likely explanation for the larger Mn removal in the VFR compared to the settling lagoon. Heterogeneous catalysis of Mn oxidation

on ochre surfaces and subsequent co-precipitation with iron hydroxide may also be an important mechanism explaining the increasing manganese retention in the VFR.

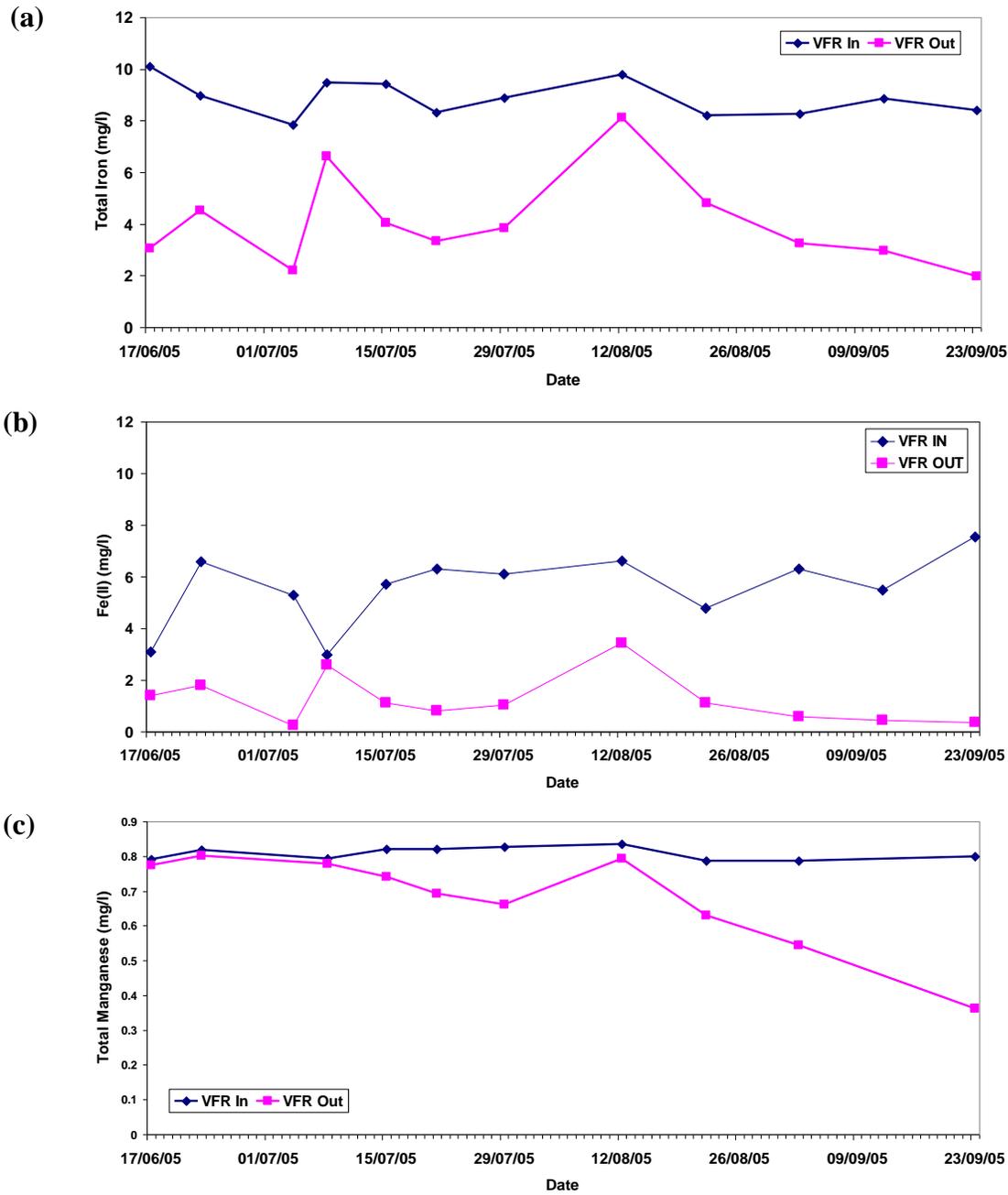


Figure 4. (a) Total iron (b) Fe(II) and (c) Total manganese in the influent and effluent water of the VFR since operation began

Iron and manganese concentration within the VFR

Table 3 shows Fe^{+2} iron and total MN concentrations within the VFR at 8 different sampling points (see Fig. 5). At each sampling point samples were taken from different depths (heights above gravel bed). Surface water samples (1.4 m above gravel bed) were taken directly. Samples from within the water column (0.6 m above gravel bed) and samples taken below the ochre bed (in the gravel bed) were taken from sampling ports built in to the system. The influent concentration of 6 mg/l Fe^{+2} is different from measurements of 2-3 mg/l in water at the surface of the VFR. This shows that significant Fe^{+2} oxidation is occurring upon exposure to the atmosphere, aeration is also promoted by the turbulent mixing of influent water at the point of entry into the VFR. The results also show that the remaining Fe^{+2} iron removal (oxidation) is occurring mostly within the ochre bed. Manganese removal is clearly taking place within the ochre bed rather than in the water column, which supports the idea (e.g. Nuttall, 2003) that ochre is an effective scavenger of dissolved Mn, possible removal mechanisms being adsorption onto ochre (with possible surface-catalysed oxidation) and co-precipitation with iron hydroxide.

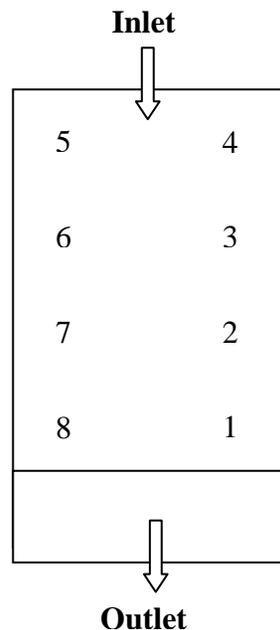


Figure 5 Plan view of the VFR with numbered sampling points shown

Iron removal rates in the VFR and lagoon

Fig. 6 (a) shows that the VFR system is already achieving Fe removal rates that are used as guide removal rates ($10 - 20 \text{ g/m}^2/\text{d}$) for the design of aerobic wetlands and lagoons for conventional passive systems (Hedin & Nairn, 1992). The VFR also shows better Fe removal rates than the existing settling lagoons at Taff Merthyr which are removing on average $\sim 4 \text{ g/m}^2/\text{d}$. Fig. 6 (b) is a plot of the calculated iron removal rates for the VFR and the lagoon versus residence time. Generally, the VFR is achieving higher Fe removal rates with a shorter residence time. It can be seen that at times, the VFR is achieving 2-3 times the Fe removal rate of the lagoon in approximately half the residence time.

Table 3. Fe(II) and Mn_{TOT} concentrations within VFR tank, Inlet concentrations: Fe(II) = 6 mg/l, Mn = 0.7 mg/l

Sampling Point	Fe(II) (mg/l)			Mn _{TOT} (mg/l)		
	<i>Height above gravel bed</i>			<i>Height above gravel bed</i>		
	1.4 m	0.6m	0	1.4 m	0.6m	0
1	2.4	2.1	0.8	0.7	0.7	0.4
2	2.4	2.2	0.6	0.7	0.7	0.3
3	3.1	2.2	0.1	0.7	0.7	0.1
4	3.4	2.3	1.2	0.7	0.7	0.4
5	2.2	2.2	0.3	0.7	0.7	0.1
6	3.6	2.1	0.8	0.7	0.7	0.4
7	2.5	2.1	0.6	0.7	0.7	0.2
8	2.5	2.3	0.2	0.7	0.7	0.2

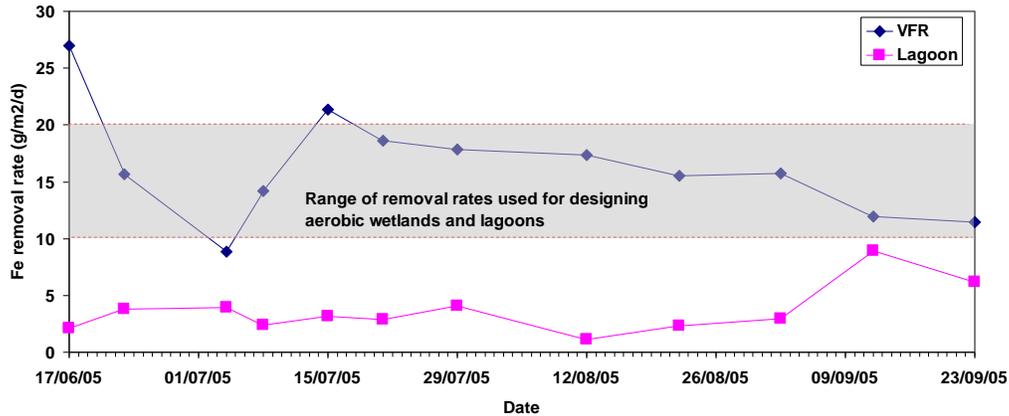
Summary

A novel system for the treatment of net-alkaline mine waters has been developed and a pilot-scale plant built and operated for almost 4 months. The system is designed to capitalise on the surface-catalysed oxidation of Fe⁺² on ochre surfaces and the (self)filtration of the ochre bed. Initial results show that the VFR is outperforming (in terms of iron removal g/m²/d) a conventional settling lagoon which is being operated in parallel to it. The VFR is also achieving higher removal rates in a shorter residence time. The VFR is also achieving appreciably better Mn removal than the existing settling lagoon. The permeability of the ochre and gravel bed (which is seen as key to its effective operating time) is currently of the order of 10⁻⁴ m/s, similar to that of a clean sand. It is anticipated that the permeability of the ochre bed will decrease over time. However, the operational lifetime of the VFR can be extended by removing blocks from the ‘stock and block’ weir, creating more driving head to overcome the decreasing permeability, eventually the gate valve (see Fig. 1) can be opened allowing approximately 2 m of driving head to develop.

The higher iron removal rates (g/m²/d) of the VFR system means that a smaller footprint could be employed to attain the same Fe removal rates as the existing settling lagoon. In addition to providing Fe removal with a reduced footprint, the vertical flow reactor has additional advantages over current systems. When drained, settlement lagoons contain ochre sludge with 2 and 5% solids. Further dewatering is therefore required to allow economic disposal. By diverting the influent and allowing the VFR system to fully drain the accumulated ochre sludge could be dewatered. Such systems can be used to thicken sludges to 25-35% dry

solids within a few weeks (NCB, 1982) and make ochre disposal more economic. Ochre recovered from a vertical flow reactor would be ‘clean’ (i.e. not mixed with compost or wetland plants), this would also make the ochre more amenable to recycling.

(a)



(b)

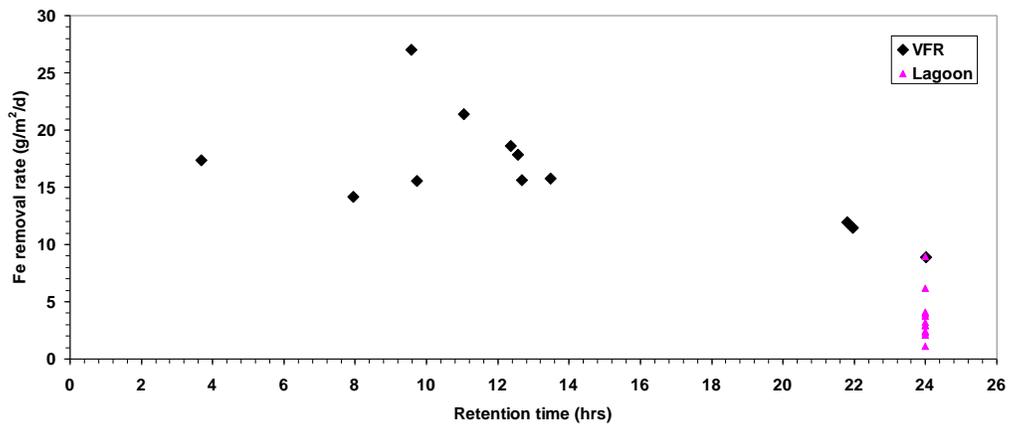


Figure 6. (a) Iron removal rates in the VFR and lagoon over the duration of plant operation and (b) Iron removal rates versus retention times for the VFR and settling lagoon

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