WATER RESEARCH 43 (2009) 423–432

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Sizing criteria for a low footprint passive mine water treatment system

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ARTICLE INFO

Article history:
Received 15 May 2008
Received in revised form
20 October 2008
Accepted 27 October 2008
Published online 5 November 2008

Keywords:
Iron
Mine
Water
Treatment
Oxidation
Sizing

ABSTRACT

The objective of this paper is to present data from a novel vertical flow mine water treatment system, demonstrate how these data can be used to generate sizing formulae for this technology, and present a comparison between the size of system based on these formulae and those of conventionally designed passive systems. The paper focuses on passive treatment of circum-neutral ferruginous mine waters bearing up to 50 mg l^{-1} of iron in either ferrous or ferric form. The Vertical Flow Reactor (VFR) operates by passing mine water down through an accreting bed of ochre, the ochre bed being responsible for the intensification of iron removal by self-filtration and/or autocatalytic iron oxidation and precipitation. Key to the design and operation of the VFR system is the decrease in permeability in this ochre bed over time. The paper demonstrates that the VFR system can remove iron at many times the 10 g/m^2/day removal rate – an often employed figure for the sizing of aerobic settling ponds and wetlands. The paper demonstrates that VFRs are viable and novel passive treatment system for mine waters with a smaller footprint than conventional systems.

1. Introduction

Ferruginous mine waters are problematic to treat because of their widespread occurrence and longevity of discharge. So-called 'passive' treatment systems are often successfully implemented. For net-alkaline circum-neutral pH mine water in the UK these 'passive systems' typically comprise settlement lagoons in combination with constructed wetland (a technology widely used for wastewater treatment – e.g. Kadlec and Knight, 1996). The draw back to their application is often the necessity for large land area, which may be unavailable. The authors have designed and pilot tested a novel low footprint passive mine water treatment system for the removal of iron from mine waters (equally applicable to Fe contaminated groundwaters). The pilot plant successfully removed iron and manganese from the mine water (Sapsford et al., 2008).

Fig. 1 illustrates a schematic of the pilot system and Fig. 2 is a photograph of the system in operation at the abandoned Taff Merthyr colliery in South Wales. The pilot system referred to here as a Vertical Flow Reactor (VFR) is similar in concept to slow sand filters employed for water treatment or vertical subsurface flow filters used for wastewater treatment (e.g. Cooper, 1999) and operates by passing mine water down through a gravel bed which supports an accreting bed of ochre. Iron removal occurs by self-filtration by the ochre bed and heterogeneously catalysed iron oxidation and precipitation within the ochre bed. The concept of harnessing the autocatalytic nature of heterogeneous Fe(II) oxidation for mine water treatment has been investigated before as detailed in several publications (e.g. Best and Aikman, 1983; Jarvis and Younger, 2001; Burke and Banwart, 2002). However, in this VFR system, there are no media included for the ochre to accrete

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doi:10.1016/j.watres.2008.10.043

Nomenclature

W_2	solid loading (kg day^{-1}) to tank 2
$Q_{overflow}$	overflow rate (m^3 s^{-1})
Q	flow rate (m^3 s^{-1})
C_o	particulate iron concentration in the mine water influent to the system (mg l^{-1})
K	permeability (m s^{-1})
Fe(II)	ferrous iron concentration (mg l^{-1})
A	area (m^2)
$[O_2]$	dissolved oxygen concentration (mg l^{-1})
i	hydraulic gradient
$[H^+]$	hydrogen ion concentration (mg l^{-1})
ΔH	head difference (m)
k	pseudo-zeroth order rate constant for ferrous iron oxidation (mg l^{-1} s^{-1} at 25 °C)
x_B	bed thickness (m)
k'	pseudo-first-order rate constant for ferrous iron oxidation (s^{-1} at 25 °C)
K_p'	apparent permeability (s^{-1})
k_2	pseudo-first-order rate constant for heterogeneous ferrous iron oxidation (s^{-1} at 25 °C)
β	fitting constant
C_1	concentration of ferrous iron in Stage 1 effluent (mg l^{-1})
C_s	cumulative solids per unit area (kg m^{-2})
C_{in}	influent concentration to the CSTR (mg l^{-1})
n	fitting constant
V_1	volume of Stage 1 (m^3)
W	solid loading (kg day^{-1})
C_2	effluent concentration from the ochre bed (mg l^{-1})
t	system run time (days)
x	length of the flow path (m)
t_{ov}	time until tank overflows (days)
U	velocity (m s^{-1})

around, rather a bed of ochre is allowed to accumulate on top of a supporting gravel bed.

The combination of these mechanisms allows intensification of the iron removal process, thus allowing comparable treatment to conventional passive technologies (e.g. settling ponds and reed beds) but in a smaller footprint. To advance this technology as a potential treatment system, design criteria need to be formulated. This paper seeks to outline how sizing criteria can be derived from the results of the pilot-plant operation, and once formulated compare the required sizes with those required using conventional systems. This passive system is principally designed for the removal of iron from net-alkaline, circum-neutral pH mine waters.

2. Materials and methods

2.1. Pilot plant

The VFR pilot system was installed at the former Taff Merthyr colliery site in South Wales, where net-alkaline ferruginous mine water issuing from the mine is collected, pumped and treated in a system of conventional settlement lagoons and aerobic wetlands. The VFR comprises a commercially available steel-panelled water tank, with an internal baffle wall. The dimensions of the VFR pilot system are 7.32 m long by 3.66 m wide and 2.30 m deep, with a baffle wall 1.22 m from the end of the tank (see Fig. 1).

The 21.6 m^2 filter bed consists of a 100 mm thickness of 20 mm angular sandstone gravel, overlain by 100 mm of angular 6 mm sandstone gravel, a fillet of ordinary builder's sand was packed in against the walls to prevent short-cutting around the edges of the bed. The gravel bed is supported by a plenum floor comprising galvanised steel mesh sheets sitting atop 300 mm high concrete piers. Mine water passes down through this bed, into the under-drain, under the baffle wall and up into the rise chamber where it exits the system.

The pilot plant was operated between June 2006 and May 2007, the influent flow rate to the system was varied and the chemistry of the influent and effluent from the pilot plant was monitored regularly using standard probes and sampling techniques. The VFR was operated allowing a 'variable head' arrangement. The water depth in the down flow chamber is dictated by the driving head that develops to overcome the increase in bed depth and decrease in permeability in the ochre bed as it collects. The depth was initially a minimum, but over time the depth increased to a maximum of 0.84 m (the height of the overflow).

2.2. Water sampling and analyses

Measurements of pH were made using a Hanna H1991003 meter and probe and Dissolved Oxygen (DO) using a Hanna H19145 meter and probe. Water samples for 'total' and

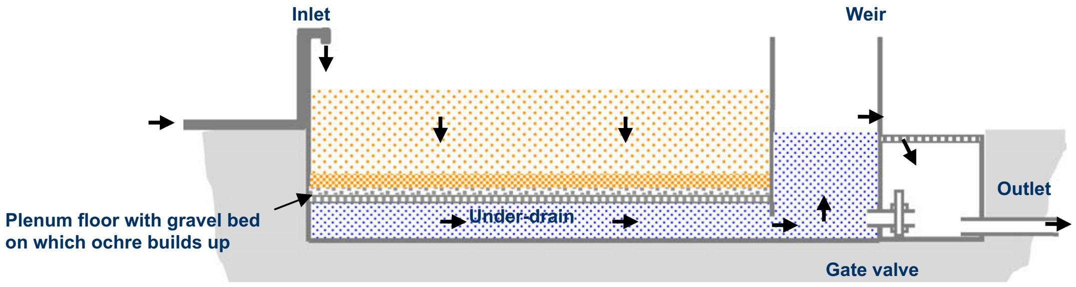

Fig. 1 – Schematic of the Vertical Flow Reactor (VFR) (Sapsford et al., 2008).

Fig. 2 – Photograph of the VFR in operation.

'dissolved' (filtered through a 0.45 μm cellulose nitrate filter) metals were collected and acidified, and these samples were analysed for total metals on an ICP-OES (Perkin Elmer Optima 2100). VFR effluent flow rates were measured using the 'bucket and stopwatch' method. Cumulative flow rates were derived using flow rates as measured on the sampling day and assuming that flow rates between sampling times varied linearly. The cumulative ochre solids were calculated using cumulative flow data and by assuming that the measured iron removal rates continued until the next monitoring period. Permeability calculations for the ochre/gravel bed required a head difference to be measured, this was done by measuring the level of water in the two chambers shown in Fig. 1.

2.3. *Proposed treatment scheme*

This paper principally concerns the generation of sizing criteria for the VFR. As such it is necessary to outline the two guiding design principles around which the models developed in the discussion are based upon. These guiding principles are:

1. Iron in the mine water is considered to be either entirely particulate or entirely dissolved. Combinations of particulate and dissolved iron will be considered from the design models for these compositional extremes.
2. The design model should consider the requirement for periodic removal of ochreous sludge from the system without operational downtime.

These considerations can be satisfied by using one tank that is split into sections, creating parallel tanks (see Fig. 3). This allows treatment to occur in one 'active' tank, whilst the other parallel tank: i) is available to be de-sludged and recommissioned, ii) acts as an overflow tank to ensure treatment of the mine water when the first tank fails and iii) can receive storm flow. These design criteria are accordingly directed at such a design and the other considerations given above.

The VFR could be operated in a number of configurations, analogous to the modes of operation of a slow sand filter. The chosen mode of operation will dictate the design of the system. The pilot plant was operated with 'variable head'. In this mode of operation the head is dictated by the permeability of the bed and the level of water above the ochre bed increases to overcome the increasing ochre depth and decreasing permeability in the bed. The advantage of this is that it requires no maintenance and will continue until the system overflows. The disadvantages are that initially the residence time above the bed is low (detrimental to homogenous iron oxidation) and that the flow velocity is throttled by the ochre bed itself (any physical damage to the ochre bed results in rapid flow at the point of damage and cause scouring of the bed). The system would possibly work more effectively operating at 'constant head', this has the potential advantage of maximising the residence time above the bed for homogenous Fe(II) oxidation and preventing scour from bed damage. Constant head filtration is usually achieved by use of a control valve on the effluent flow pipe to throttle the flow through the system, in conjunction with a weir to control the head difference between the downflow and upflow chambers. However, this is not chosen here because this would have the disadvantage that regular site visits will be needed to monitor the permeability and manipulate the head.

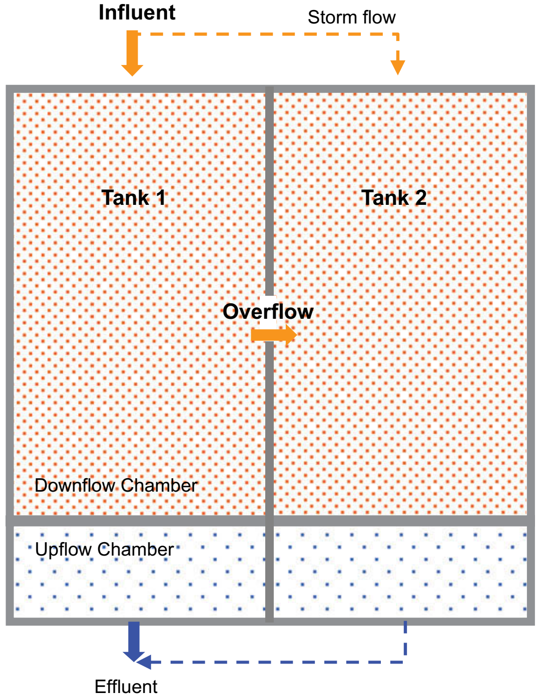

Fig. 3 – Plan-view schematic of two VFRs in parallel.

After the first VFR tank begins to overflow into the second (i.e. A overflows to B (see Fig. 3)) then tank A is operating under 'Declining Filtration Flow'. The rate of filtration through the bed decreases as the permeability does. For sizing criteria the head at which the system overflows (which was 0.84 m in the pilot plant) has been increased to a standard 1 m for the overflow in the system as outlined in this paper.

3. Pilot-plant results

Table 1 presents influent and effluent water quality results from the 11 month VFR pilot-plant trial. Over the monitoring

Table 1 – Flow rates, water quality and performance data for the VFR.

Date	VFR flow (l/s)	Cumulative throughput (m^3)	pH influent	pH effluent	DO influent ($mg\,l^{-1}$)	DO effluent ($mg\,l^{-1}$)	Influent Fe ($mg\,l^{-1}$)	Effluent Fe ($mg\,l^{-1}$)	Influent Mn ($mg\,l^{-1}$)	Effluent Mn ($mg\,l^{-1}$)	Fe removal ($g/m^2/day$)	Fe removal (%)	Mn removal ($g/m^2/day$)	Mn removal (%)	Cumulative Fe (kg)	Cumulative ochre solids (kg)	Head difference (cm)
04/06/2006	0.34	59	[a]	[a]	[a]	[a]	8.38	0.12	0.78	0.66	11.2	99	0.16	15	0.5	0.9	0.01[b]
06/06/2006	0.34	118	6.26	6.52	5.33	5.02	7.84	0.11	0.75	0.57	10.5	99	0.24	24	0.9	1.8	0.01[b]
08/06/2006	0.48	200	6.59	6.76	5.30	5.98	9.07	0.13	0.81	0.67	17.2	99	0.27	17	1.7	3.1	0.01[b]
14/06/2006	0.46	439	6.79	6.95	4.59	5.08	8.65	0.06	0.84	0.37	15.8	99	0.87	56	3.7	7.0	0.01[b]
20/06/2006	0.91	911	7.07	6.98	4.90	6.18	7.82	0.46	0.74	0.38	26.8	94	1.31	49	7.2	13.4	3.5
28/06/2006	0.94	1550	7.02	7.14	2.63	5.01	8.51	0.50	0.74	0.31	30.1	94	1.60	58	12.3	23.0	4.0
07/07/2006	0.97	2293	[a]	[a]	[a]	[a]	7.72	0.25	0.73	0.21	29.0	97	2.02	71	17.9	33.3	[a]
11/07/2006	0.99	2631	6.89	6.88	2.48	4.73	7.64	0.21	0.66	0.23	29.4	97	1.70	65	20.4	38.0	11.5
28/07/2006	0.15	3469	[a]	[a]	[a]	[a]	7.57	0.00	0.74	0.00	4.5	100	0.44	100	26.7	49.9	[a]
20/08/2006	0.01	3508	[a]	[a]	[a]	[a]	8.12	0.00	0.76	0.00	0.3	100	0.03	100	27.0	50.5	[a]
16/09/2006	2.2	4079	[a]	[a]	[a]	[a]	9.32	1.47	0.78	0.65	69.1	84	1.11	16	31.5	58.8	46.0
22/09/2006	1.4	5012	6.79	7.00	[a]	[a]	8.90	2.99	0.77	0.49	33.1	66	1.55	36	37.0	69.1	55.0
29/09/2006	0.73	5656	6.67	6.57	2.54	2.65	8.48	0.01	0.76	0.01	24.7	100	2.20	99	42.5	79.3	59.0
05/10/2006	0.27	5915	[a]	[a]	[a]	[a]	7.74	0.36	0.61	0.27	8.0	95	0.37	56	44.4	82.8	[a]
09/10/2006	0.24	6003	[a]	[a]	[a]	[a]	7.26	0.45	0.79	0.31	6.5	94	0.46	61	45.0	84.0	[a]
16/10/2006	0.57	6248	6.73	6.69	4.42	3.57	7.21	0.20	0.04	0.04	16.0	97	0.00	0	46.7	87.2	70.0
20/10/2006[c]	0.34	6405	6.86	6.93	3.83	3.83	6.49	0.08	0.66	0.30	8.7	99	0.49	55	47.7	89.0	49.0
15/11/2006[c]	0.83	6907	6.46	6.93	3.72	5.73	6.66	1.94	0.72	0.26	15.7	71	1.53	64	50.1	93.5	84.5
17/11/2006	0.97	7063	6.66	6.54	3.70	5.46	6.86	1.97	0.74	0.38	19.0	71	1.40	49	50.9	94.9	72.0
27/11/2006	0.93	7884	6.86	6.98	3.91	5.96	5.08	2.97	0.62	0.28	7.8	42	1.26	55	52.6	98.1	84.0
05/12/2006	1.03	8561	6.18	6.19	3.72	7.04	4.91	2.16	0.60	0.23	11.3	56	1.52	62	54.5	101.6	84.0
07/12/2006	1.04	8740	6.67	6.59	4.76	6.24	4.74	1.35	0.58	0.20	14.1	72	1.58	66	55.1	102.7	118
14/12/2006	0.8	9296	6.39	6.48	3.42	4.35	5.05	0.62	0.60	0.16	14.2	88	1.41	74	57.5	107.3	140
05/01/2007	0.56	10589	6.79	7.05	3.86	4.18	5.35	0.51	0.61	0.11	10.8	90	1.12	82	63.8	119.0	101
24/01/2007	0.5	11459	6.85	[a]	[a]	[a]	4.79	0.00	0.59	0.06	9.6	100	1.06	90	67.9	126.8	74.0
15/02/2007	0.27	12191	6.92	7.12	4.90	6.60	4.65	0.04	0.61	0.01	5.0	99	0.66	99	71.3	133.0	56.5
23/02/2007	0.71	12588	6.32	6.71	3.90	5.70	13.62	1.57	0.67	0.20	34.2	88	1.33	70	76.1	142.0	[a]
06/03/2007	0.58	13073	[a]	[a]	[a]	[a]	5.35	0.96	0.54	0.12	10.2	82	0.98	78	78.2	145.9	[a]
23/03/2007	0.43	13712	7.13	7.55	3.42	6.70	6.41	0.38	0.67	0.05	10.4	94	1.07	93	82.1	153.1	87.0
13/04/2007	0.38	14456	6.76	6.42	4.43	4.19	7.11	0.01	0.71	0.00	10.8	100	1.08	100	87.4	163.0	82.5
24/04/2007	0.37	14840	6.37	6.61	3.42	3.53	6.56	0.05	0.72	0.00	9.6	99	1.06	100	89.9	167.7	81.5
01/05/2007	0.23	15043	[a]	[a]	[a]	[a]	6.84	0.19	0.72	0.00	6.1	97	0.66	100	91.2	170.2	50.0
04/05/2007	0.22	15157	6.77	6.57	1.91	5.91	7.11	0.17	0.72	0.00	6.1	98	0.63	100	92.0	171.6	47.0
09/05/2007	0.14	15257	6.49	6.63	1.11	5.81	6.17	0.06	0.68	0.00	3.4	99	0.38	100	92.6	172.8	34.0
10/05/2007	0.22	15286	6.48	6.63	[a]	[a]	7.20	0.03	0.66	0.00	6.3	100	0.58	100	92.8	173.2	57.5
13/05/2007	0.25	15375	6.25	6.42	2.17	4.33	6.16	0.08	0.64	0.00	6.1	99	0.64	99	93.4	174.2	55.5

a Not measured.

b Estimate for use in permeability calculations.

c Influent pipe was completely blocked for a period of time between 20/10/06 and 15/11/06.

period the influent water was of circum-neutral pH (mean = pH 6.67 ± 0.26) and contained (mean total values ± stdv) Fe = 7.15 ± 1.73 mg l^{-1}, Mn = 0.68 ± 0.13 mg l^{-1}, and Dissolved Oxygen (DO) = 3.68 ± 1.10 mg l^{-1}. Table 1 shows that the effluent typically had more dissolved oxygen than the influent reflecting uptake across the water surface and during turbulent entry of the influent. The often observed slight increase in pH through the VFR was probably due to CO_2 degassing. The data in Table 1 have been used to formulate the sizing criteria presented in this paper.

Iron removal in the VFR was generally excellent, the system often displayed close to 100% removal, the exceptions were times where the system overflowed or where the velocities were too high (>4 m day^{-1}). In terms of the often used design rate of 10 g/m^2/day (Hedin et al., 1994), removal rates were often in excess of this despite the fact that such low concentrations of Fe normally give rise to low removal rates.

The VFR system demonstrated the ability to filter out particulate iron hydroxide very effectively. Visual inspection of the ochre and gravel bed after 11 months of operation revealed that filtration occurs by cake filtration rather than by the gravel bed, the gravel bed acting simply as a permeable support for the cake. In this way the system is analogous to slow sand filtration where the bulk of the physical filtration occurs in the schmutzdecke. Experience at running the pilot plant would suggest that the velocity through the ochre bed should not be more than 4 m day^{-1}, and preferably 3 m day^{-1} or less. However, it is not known whether the poorer iron removal efficiency above these velocities is due to ochre being scoured from the bed or whether it is poorer rates of Fe(II) oxidation due to decreased residence time in the ochre bed. The latter explanation is deemed more likely and for the purposes of this paper it is assumed that particulate iron can be completely removed by the bed, this is certainly true for lower flow rates (and hence velocities) where iron removal was virtually 100% (see Table 1).

Although the removal of iron using a VFR design is the focus of this paper, a brief summary of the manganese removal is included because the two contaminants often occur together in mine and groundwaters. The often high levels (circa 100%, see Table 1) of manganese removal in the VFR were unexpected because of the documented slow kinetics of Mn oxidation at the pH of the influent water, the low concentrations (see Table 1) resulting in lower oxidation rates, and the presence of Fe(II) > 1 mg l^{-1} (which inhibits MnO_2 precipitation). The manganese removal rates observed (g/m^2/day) were often higher than the values of 0.5–1 g/m^2/day recommended for use in sizing aerobic wetlands for Mn removal (Hedin et al., 1994). The better than expected Mn removal rates observed have been attributed to heterogenous and microbial catalyses within the ochre bed (Sapsford et al., 2008).

4. Discussion

4.1. Permeability model

Having demonstrated at pilot scale that a VFR system has the capacity to treat ferruginous mine water, attention is turned to engineer the system more fully with consideration of the actual operation of such a system. The following model has been constructed using the data collected from the VFR pilot presented in Table 1. The ochre provides the resistance to flow in the VFR. Flow through the ochre bed is described by Darcy's Law:

$$Q = KAi \qquad (1)$$

where Q = flow rate ($m^3\,s^{-1}$), K = permeability ($m\,s^{-1}$), A = area (m^2), and i = hydraulic gradient = head difference ΔH (m)/bed thickness x_B (m).

The change in bed thickness (x_B) over time is not known, so exact values of K for the bed cannot be calculated. However, only an apparent permeability K_p' is required for modelling purposes.

$$K_p' = \frac{K}{x_B} \qquad (2)$$

and therefore:

$$K_p' = \frac{Q}{A\Delta H} \qquad (3)$$

To be of utility for the sizing of other systems, it is necessary to relate the head developed in the pilot system to a quantifiable parameter in all systems. It is possible and useful to derive an empirical relationship between the K_p' and the cumulative solids deposited per square meter of filter bed (C_s), over time. The cumulative mass of solids deposited on the bed was calculated by calculating the cumulative iron deposited on the entire bed using the iron removal data, see Table 1. This figure was then adjusted to cumulative solids based on a dry solids content of 53% Fe. This figure is a mean value obtained from the strong acid digest of three dried ochre samples from the VFR system, taken at the time of decommissioning. Note that it is not actually necessary to do this conversion, but the conversion is done here for completeness. The cumulative solids deposited per square meter were then calculated by dividing by the filter bed area (21.6 m^2).

The results of the plot of K_p' versus C_s are shown in Fig. 4. The best fit equation generated gives the design information required. The general trend appears to be of an initial rapid decrease in apparent permeability, followed by a more gradual decrease. The deviation from the actual results increases at higher data points suggesting that the curve would overestimate the decrease in apparent permeability. This is satisfactory for the purposes of these sizing guidelines, since it

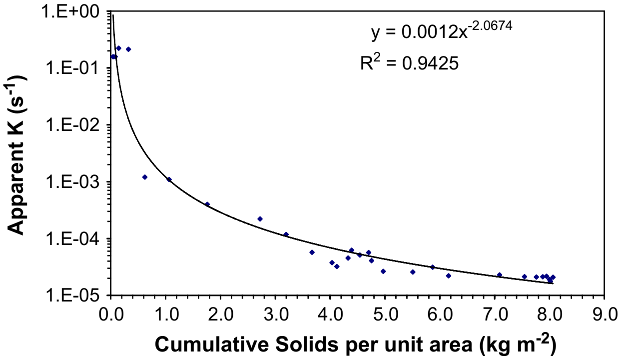

Fig. 4 – Apparent permeability K_p' (s^{-1}) versus cumulative solids per unit area of filter bed (kg m^{-2}).

should lead to conservative estimates of design lifetime (see below).

The graph in Fig. 4 gives:

$$K_p' = \beta C_s n \tag{4}$$

where K_p' = apparent permeability (s^{-1}), β = fitting constant = 0.0012, C_s = cumulative solids per unit area ($kg\,m^{-2}$), and n = fitting constant = −2.0674.

Eq. (3) can be rearranged to:

$$\Delta H = \frac{Q}{AK_p'} \tag{5}$$

and Eq. (4) substituted into Eq. (5), which is then rearranged to give C_s as a function of Q, A and ΔH:

$$\log[C_s] = \frac{\log[Q] - \log[\Delta HA\beta]}{n} \tag{6}$$

Values of Q, A and ΔH can then be entered into the equation for design purposes. The maximum ΔH permissible is dictated by the height of the overflow. For demonstration purposes $\Delta H = 1$ m is used. With knowledge of the maximum ΔH, the C_s value at which the system would overflow (and therefore system lifetime) can be determined for a given flow and area.

4.2. *Filtration model*

The VFR can function purely as a filter removing particulate iron hydroxide or at the other extreme, operate as a catalytic bed removing iron by heterogeneous catalysis of Fe(II) oxidation and subsequent accretion of iron hydroxide. In this model the bed is functioning as a filter bed only. With the knowledge of the particulate Fe influent concentration and assuming 100% removal of this particulate iron by the bed (see Section 3) a time until the system overflows (t_{ov}) can be determined for different influent particulate iron concentrations and different hydraulic loadings ($m^3\,m^{-2}\,day^{-1}$). It is convenient to express C_s as:

$$C_s = \frac{Wt}{A} \tag{7}$$

where W = solids loading ($kg\,day^{-1}$) and t = system run time (days).

Therefore it is possible to calculate t when C_s has reached the limit determined from Eq. (6) and the VFR system begins to overflow (t_{ov}). This provides useful design guidance for the expected flows and concentrations and also relates it to the required frequency of system de-sludging – an extremely important aspect for the long-term operation of VFRs. Example curves are given in Figs. 5 and 6 along with example loadings from other passive mine water treatment systems in South Wales.

4.2.1. *Overflow calculations*

The previous calculations give t_{ov}, the time until the system overflows (where $\Delta H = 1$ m). Of design importance is the ability to estimate the overflow rate and therefore Fe loading after t_{ov} has been reached. This indicates that the loading to the receiving environment or further treatment tanks that would be expected as t_{ov} is exceeded.

The recommended designs suggest having two identical tanks side-by-side (see Fig. 3), so that the first tank overflows into a second identical tank for continued treatment after t_{ov}. Therefore after t_{ov} has been reached the mine water will be treated in two locations, one portion of the water will flow through the bed in the first tank (Tank 1) whereas the remainder will overflow into the second tank (Tank 2) and be treated there. Thus after t_{ov} is exceeded, Tank 1 operates in 'declining filtration' mode. It is necessary in this situation to calculate the declining rate of filtration (flow) which in turn depends on the rate of decrease in K_p'. Rearranging Eq. (5) and differentiating with respect to time:

$$\frac{dQ}{dt} = \left(\frac{dK_p'}{dt}\right) A\Delta H \tag{8}$$

(Note: $A\Delta H$ is constant.)

dQ/dt can be approximated by calculating $\Delta Q/\Delta t$. $\Delta K_p'/\Delta t$ was first found by first calculating the additional C_s deposited by Q in 1 day (the chosen time step) at the given influent iron concentration. Secondly, by recalculating Q based on the new C_s, then iterating this calculation dQ/dt can be approximated. From this it is possible to estimate dQ/dt into Tank 2 by how much flow is overflowing into Tank 2 (i.e. Q into Tank

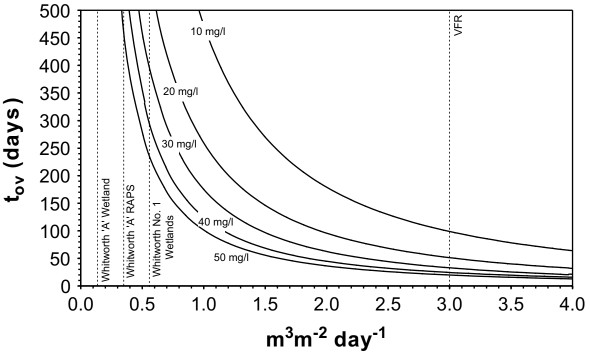

Fig. 5 – Time until a VFR system would overflow (t_{ov}) for different hydraulic loadings and influent particulate Fe concentrations. Example of hydraulic loadings from the pilot VFR and Whitworth treatment systems (data from Wiseman, 2002) is also given.

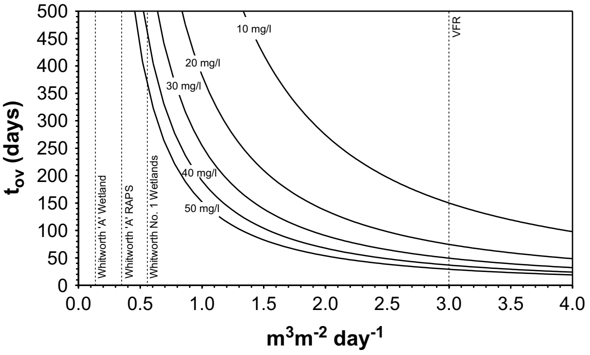

Fig. 6 – Time until a 2 × Tank VFR system would overflow (t_{ov}) for different hydraulic loadings and influent particulate Fe concentrations. Example hydraulic loadings from the pilot VFR and Whitworth treatment systems (data from Wiseman, 2002) are also given.

$B = Q_{Tot} - Q_{Tank\ 1}$). With the flow into Tank 2 known it is then possible to calculate the loading into Tank 2 (W_2):

$$W_2 = Q_{overflow} C_o \tag{9}$$

where C_o = particulate Fe concentration in the mine water influent to the system.

Once a daily value of C_s is calculated then t_{ov} for Tank 2 can be calculated by finding the number of days until $\Delta H = 1$. By substituting Eq. (4) into Eq. (5):

$$\Delta H = \frac{Q}{A \beta C_s^n} \tag{10}$$

Design curves for two tanks in parallel are shown in Fig. 6. Interestingly, dividing a given area into two sections results in a longer lifetime than for a single tank of the same area as the two tanks combined. This is because in the first scenario despite the tank overflowing the ochre bed in Tank 1 is still permeable and continues treating a large proportion of the flow. In the single tank situation once the overflow height is reached the whole system fails. It is therefore recommended that for any given loading the treatment area is divided into separate tanks. This is advantageous in prolonging the time before ochre de-sludging is required compared to a single tank and also allows the temporary decommissioning and de-sludging of one tank whilst treatment continues in the other tank(s).

Fig. 7 gives the relationship between flow rate and required area for influent particulate iron concentrations of 10, 20, 30, 40 and 50 mg l^{-1} for a two tank VFR system that has a design lifetime of 1 year before de-sludging is required. Also displayed in Fig. 7 the size of wetland (or settling pond) that would be built using the 10 g/m^2/day guidelines. It can be seen that the VFR system always requires less area for the same treatment. The removal rates that correspond to these influent concentrations are: 17, 21, 23, 26 and 28 g/m^2/day. Note that as the influent concentration increases so does the removal rate (this is related to the flattening of the apparent permeability with solids deposited in Fig. 4). It can be seen from Fig. 6 that an influent particulate iron concentration of 50 mg l^{-1} could be removed for a year with less area than a conventional system would require to remove 20 mg l^{-1}.

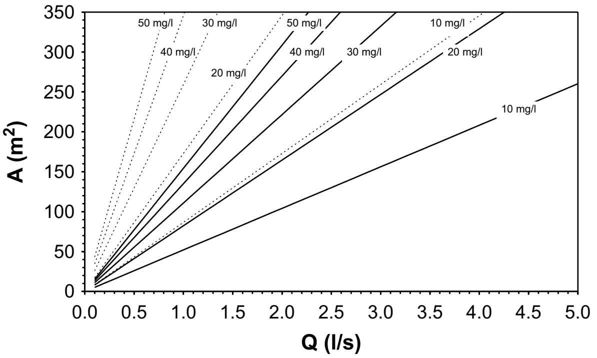

Fig. 7 – Design curves for determining the required area of a 2 × tank VFR for 1-year continuous operation with different flow rates (Q) and influent particulate Fe(III) concentrations (solid lines). Compare with design curves generated using the 10 g/m^2/day metric (dashed lines).

Further decreases in footprint could be achieved for a VFR system if the maintenance frequency is increased. Therefore a site specific balance can be struck between the requirement for reduced land take and the frequency of de-sludging. Whilst division of the treatment area into discrete tanks is advantageous, the number of divisions must not be high enough to lead velocities in excess of the recommended 4 m day^{-1} in any particular tank, to reduce the possibility of bed scour.

There are reasons to believe that design curves give an underestimate of the time until the 2 × Tank system overflows. One reason is that the best fit curve in Fig. 4 slightly underestimates the apparent permeability at later times. The other is that the modelling above implicitly assumes that the design curve relating C_s to K_p' is correct for all throughputs. There is reason to believe that as an incorrect assumption. This assumption negates the possibility that at lower velocities, the compressive force experienced by the ochre bed also decreases, resulting in less compression and the maintenance of higher permeability in the ochre. Measurements of the permeability of ochre from another vertical flow system, the Whitworth 'A' RAPS at Pelenna, South Wales (Reilly, 2001), indicate a permeability of circa 4×10^{-5} m s^{-1}. The actual permeability of the ochre from the pilot VFR (based on recorded thickness of ochre and last recorded head difference) was circa 1×10^{-6} m s^{-1}, 40 times less permeable than the Whitworth 'A' ochre. The superficial velocity at Whitworth 'A' is in the region of 0.35 m day^{-1} (see Figs. 5 and 6) whilst the superficial velocity in the Taff Merthyr pilot VFR was typically around 3 m day^{-1}, and occasionally more than double this. Again, this would imply that the permeability model presented above may overestimate the decrease in permeability for systems with lower throughputs than the pilot VFR.

4.3. *Fe(II) oxidation model*

The above design calculations assume 100% iron removal, which is a reasonable assumption when all of the iron intercepted by the gravel bed is in the oxidised solid form and the system is working simply as a filter. However, most of the time mine drainage contains ferrous iron which confounds the design guidance above (unless sufficient residence time is provided before the gravel bed to allow the ferrous iron to oxidise and precipitate).

To model the removal (by oxidation, precipitation and filtration) of Fe(II) in the VFR system it is essential to consider the homogenous and heterogenous kinetics of Fe(II) oxidation. Despite papers encouraging the use of first-order (concentration dependant) equations to model iron removal in full scale mine water treatment systems (e.g. Tarutis et al., 1999), generally zero-order formulations are preferred (Younger et al., 2002), probably because of the complexity of predicting realistic residence time distributions (Kadlec, 2000) and the relative contribution of the various Fe removal processes e.g. Fe oxidation kinetics (both homogenous and heterogenous), settling and filtration of iron particulates, adsorption and diffusion in and out of the wetland substrate and sequestration as sulphides. However, removal of Fe(II) in the VFR system can be modelled as a first-order process (where sufficient buffering is present and DO is constant), because once oxidised and hydrolysed the iron is retained in the filter bed.

For homogenous Fe(II) oxidation the common empirical rate law for iron oxidation at pH > 4 is cast by Stumm (1992) as:

$$-\frac{\mathrm{dFe(II)}}{\mathrm{dt}} = \frac{k[\mathrm{Fe(II)}][\mathrm{O_2}]}{[\mathrm{H^+}]^2} \tag{11}$$

where sufficient buffering is present (giving relatively constant pH) and at fixed [O_2] Eq. (11) can be formulated as a pseudo-first-order rate, dependant on the Fe(II) concentration alone.

$$-\frac{\mathrm{dFe(II)}}{\mathrm{dt}} = k'[\mathrm{Fe(II)}] \tag{12}$$

From field oxidation experiments using the Taff Merthyr mine water (data not shown) a value of the rate constant k in Eq. (11) was determined to be $7.52 \times 10^{-13}\ \mathrm{mg\,l^{-1}\,s^{-1}}$ (at 25 °C). Therefore for a given [O_2] and pH, k' can be used to calculate oxidation rates. k' can also (and was in the calculations below) be corrected for the temperature of the intended site using the Arrhenius expression and an activation energy of 96 $\mathrm{kJ\,mol^{-1}}$.

Heterogeneous Fe(II) oxidation rates are less clearly defined in the literature, but are (depending on the amount of Fe(III) present, pH and DO) up to two orders of magnitude faster than the homogenous rates (e.g. Barnes et al., 2007). Values for the maximum pseudo-first-order heterogeneous rate constant (k_2) derived from the literature (and conditions) are given in Table 2. Note that all of these studies had a relatively small concentration of Fe(III) compared to the VFR ochre bed where Fe(III) concentration was measured at approximately 150 g/l.

With consideration of literature values and calculated estimates from the pilot-plant data (not shown) for design purposes a conservative estimate of the heterogeneous rate constant (k_2) = 100 $\mathrm{d^{-1}}$ (at 10 °C) for a constant bed thickness of 0.05 m is made. Although a simplification for the purposes of calculations, the use of a constant product of x_B and k_2 in the these calculations (see Eq. (14)) may be partly justified by the fact that although initially the ochre bed is much thinner the associated catalytic effect is probably higher because of the enhanced contact with non-compressed sludge. Over time the sludge compresses (as evidenced by the decrease in apparent permeability Fig. 4) and the pore velocity will increase (residence time decrease) and effective surface area of the sludge probably decreases. It should be noted that this value is applied universally without consideration of ochre depth, temperature, pH, DO or microbiological effects. Hopefully future research will be able to give better estimates. It should also be noted that according to the proposed rate law of Tamura et al. (1976) the heterogeneous catalysis is less sensitive to pH (proportional to 1/[H^+]) than the homogenous oxidation rate (proportional to 1/[H^+]^2) making the application of a constant rate constant between pH 6 and 7 reasonable for the net-alkaline circum-neutral pH mine water considered in this work.

Table 2 – Maximum pseudo-first-order heterogeneous rate constant (k_2) and reaction conditions reported in the literature.

Fe(II) ($\mathrm{mg\,l^{-1}}$)	Fe(III) ($\mathrm{mg\,l^{-1}}$)	pH	O_2 ($\mathrm{mg\,l^{-1}}$)	Temperature (°C)	k_2 ($\mathrm{d^{-1}}$)	Reference
10.7	140	6.8	0.40	25	907	*Park and Demspey, 2005*
3.0	600	6.7	35.4	25	723	*Tufekci and Sarikaya, 1996*
10.0	200	6.5	8.5	25	457	*Barnes et al., 2006*

For the purposes of modelling, the VFR reactor can be split into two separate reaction stages: the water above the ochre bed (Stage 1) and the ochre bed itself (Stage 2). The Fe(II) concentration in the effluent from each of these stages is dependant upon the rate of Fe(II) oxidation within each, the volume (which changes in each due to head differences) or depth, the flow rate and the nature of the flow through each stage. In order to predict the general behaviour of the system it assumed that pseudo-first-order kinetics for Fe(II) oxidation apply and that the flow through the stages is ideal that Stage 1 acts as a Continuously Stirred Tank Reactor (CSTR) and the Stage 2 acts as a plug-flow reactor. The former assertion is supported by field measurements of relatively constant Fe(II) concentrations at different locations within Stage 1 (see Sapsford et al., 2006) and also from a Computational Fluid Dynamics (CFD) modelling that was undertaken on the VFR using the FLUENT package.

The concentration of the effluent from Stage 1 can be calculated using:

$$C_1 = \frac{QC_{\mathrm{in}}}{Q + K'V_1} \tag{13}$$

where C_1 = concentration of Fe(II) in Stage 1 effluent ($\mathrm{mg\,l^{-1}}$), C_{in} = influent concentration to the CSTR ($\mathrm{mg\,l^{-1}}$), Q = flow rate through the VFR ($\mathrm{mg\,l^{-1}}$), k' = homogenous rate constant ($\mathrm{s^{-1}}$), and V_1 = volume of Stage 1 ($\mathrm{m^3}$).

The plug-flow-reaction equation for Stage 2 is given by

$$C_2 = C_1\,\mathrm{e}^{(-k_2 x)/U} \tag{14}$$

where C_2 = effluent concentration from the ochre bed ($\mathrm{mg\,l^{-1}}$), C_1 = influent concentration to the ochre bed ($\mathrm{mg\,l^{-1}}$) from Stage 1, k_2 = heterogeneous first-order decay constant ($\mathrm{s^{-1}}$), x = length of the flow path (m), and U = velocity ($\mathrm{m\,s^{-1}}$).

The above equations can be arranged such that an area is calculated for a specific flow rate, Fe(II), pH and DO to a target of 1 $\mathrm{mg\,l^{-1}}$ in the effluent. Note that the volume and the corresponding residence time of the post-ochre bed system are irrelevant because any iron whether dissolved or particulate that passes the ochre bed is considered untreated.

The design of the system is based on an initial water depth of 0.5 m (above the bed). The system is designed to overflow when the head difference is 1 m – although this is only relevant to determine the time until the system overflows. To be conservative the Fe(II) oxidation that occurs in the water column is always considered to occur in a volume of 0.5 × area as this represents the minimum volume (and therefore residence) time of the water in Stage 1, the actual volume (and therefore residence time) will increase over time as the necessary driving head develops.

It is therefore possible to define two equations to describe Fe(II) oxidation in the system – one equation describing oxidation in Stage 1, using k' according to Eq. (12) and the other describing oxidation in the ochre bed using $k_2 = 100\ \mathrm{d}^{-1}$.

For Stage 1, $V_1 = 0.5\ A$ can be substituted into Eq. (13) giving:

$$C_1 = \frac{QC_{\text{in}}}{Q + K'0.5A} \tag{15}$$

At the end of the period of VFR operation the ochre within the bed was found to have a solids content of only 15% (w/v) (Sapsford et al., 2008). A high effective porosity is therefore assumed, thus allowing calculation of the water velocity through the bed using $U = Q/A$. For Stage 2, $U = Q/A$ can be substituted into Eq. (14) to give

$$C_2 = C_1\ \mathrm{e}^{(-k_2 xA)/Q} \tag{16}$$

Eq. (15) can be substituted into Eq. (16)

$$C_2 = \left(\frac{QC_{\text{in}}}{Q + k'0.5A}\right)\mathrm{e}^{(-k_2 xA)/Q} \tag{17}$$

Using this equation the relationship between Q and A (the area required for the filter bed) can be found using numerical iteration. The area was numerically iterated using the Solver tool in Microsoft Excel until $C_2 = 1\ \mathrm{mg\,l}^{-1}$ which is the target effluent concentration. Fig. 8 presents the relationship between Q and A, based on conservative assumptions, for a VFR treating different concentrations of influent Fe(II) at pH 6.5, DO saturation and 10 °C (close to typical mine water temperature) giving $k' = 0.67\ \mathrm{day}^{-1}$.

Note that as the pH of the influent water decreases the dependence of system area on satisfying a volume above the bed to provide residence time for the homogenous Fe(II) oxidation diminishes (as this rate slows dramatically) and the role of the ochre bed in overall Fe(II) oxidation becomes more and more important. Consequently the design area becomes proportional to the flow velocity that is slow enough to allow the required oxidation to occur in the ochre bed and is virtually independent of water depth above the bed. However, some depth of water is needed to ensure even flow distribution through the ochre bed.

Fig. 8 also shows the design curves for the VFR compared to those generated using the 10 g/m^2/day metric (Hedin et al., 1994). It can be seen that much less surface area is required to treat the mine water using the VFR system, this is more apparent at higher Fe(II) loadings and/or lower pH where the importance of the ochre bed in the oxidation of Fe(II) becomes more important at defining the overall rate of Fe(II) oxidation in the system. The removal rates that correspond to the influent concentrations 10, 20, 30, 40, and 50 $\mathrm{mg\,l}^{-1}$ Fe(II) are: 23, 35, 47, 58 and 68 g/m^2/day, respectively. These are removal rates for a single VFR. As described earlier the favoured design would be to have two tanks side-by-side, this doubles the area required for the VFR (×2) system, but nevertheless removal rates are all still higher than 10 g/m^2/day. Note also that the comparison is made at pH 6.5, for lower pH water the zero-order formulation may underestimate the wetland area required because it does not take into account the precipitous decrease in the Fe(II) oxidation rate with decreasing pH in this range. For a given area the time until the system overflows can be determined as explained in Section 4.3.

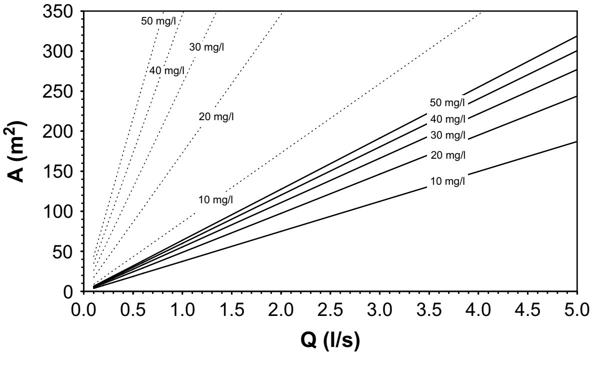

Fig. 8 – Design curves for determining the required area of a VFR for different flow rates (Q) and influent dissolved Fe(II) concentrations, pH 6.5, 10 °C and DO sat (solid lines). Compare with design curves generated using the 10 g/m^2/day metric (dashed lines).

For sites where area is limited but there is significant height difference across the site (e.g. a hillside), the design area calculated for the VFR (for Fe(II) oxidation) could be divided amongst two (or more) VFR cells arranged in series, with the proviso that superficial velocity through the ochre bed in any one cell does not exceed ~4 m day^{-1}.

In situations where there is a combination of ferrous iron and total iron in the influent the following calculations should be made. Firstly a calculation is made of an area based on the assumption that all the iron in the influent is particulate, using the sizing approach used in Section 4, the area chosen is dependant upon the required time between de-sludging. Secondly, a calculation of required area needed for the oxidation of the Fe(II) using Eq. (17) should be made. The correct option would be to base the design on the larger area of the two calculated.

4.4. *Ochre removal*

Periodically, prior to the designed overflow time being reached (once yearly in the preceding examples), ochre will need to be removed from the VFR system to re-establish the permeability. Ochre removal can be achieved in a number of ways. Typical practice for removing ochre sludges from passive mine water treatment systems involves the use of mobile 'sludge-gulpers' and these should work equally well on the VFR sludge. Alternatively, the VFR can be drained down and the ochre scraped out either manually (e.g. with shovels for smaller systems) or using a back-hoe for larger systems. When water is emptied the ochre on the gravel bed will be underdrained, over time this should aid ochre consolidation and dewatering, thereby facilitating removal of the ochre.

5. Conclusions

The data from the pilot study has shown that VFRs can be used to passively remove iron and manganese from circumneutral mine waters. Data from the pilot plant have been used to formulate sizing equations for removal of particulate ferric iron and dissolved ferrous iron. These calculations show that a viable treatment can be achieved using a substantially smaller footprint than would be required for conventional wetlands and/or settling lagoons.

The VFR system can be designed to work as a filter or as a Fe(II) oxidising system, or a combination of both. VFRs can be used for complete treatment of mine water or used as a unit process at different stages in a combined treatment scheme. There are a number of key considerations that need to be taken into account when designing a VFR system. Those are the influent Fe(II) and particulate iron concentration, influent pH, DO and temperature, the required frequency of desludging, VFR depth, VFR area and the height of the overflow. Multiple VFR systems can be run in parallel, and in series or both. Where site topography allows, it is recommended that the designed treatment area should be divided into a series of descending parallel VFRs – thus maximising the advantages that both configurations offer. Whether used by themselves or together in a process train with conventional passive treatment systems, aerobic vertical flow reactors have the potential to be a useful contribution to the toolbox of passive mine water treatment techniques, especially for sites where land area is restricted.

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