

## A novel method for passive treatment of mine water using a vertical flow accretion system

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### ABSTRACT

This paper introduces a novel method of mine water treatment, briefly reviews the science behind the concept and presents preliminary data from a range of different scale pilot systems. The largest pilot system (7.32m x 3.66m) is being operated at Taff Merthyr in South Wales, where it receives water (pH 6-7, Fe<sub>TOT</sub> ~ 8 -10 mg/l) from an abandoned coal mine. The mine water is piped into a tank where it flows down vertically through a gravel bed supported on a plenum floor. The water drains under the plenum and rises up and flows out over a weir. Iron removal is suspected to occur via two principal mechanisms: filtration of iron hydroxide particles (formed in the water column), and surface-catalysed oxidation of iron (II) (and precipitation) on solid iron (III) hydroxide surfaces. The data presented suggest that by harnessing these mechanisms it is possible to substantially decrease the surface area requirement for passive treatment schemes that have conventionally utilised large settling lagoons to remove iron.

### INTRODUCTION

The problem of ferruginous mine water discharges has long been acknowledged as being deleterious to the receiving environment. Receiving watercourses are initially impacted by damage to benthic organisms, smothered by the accumulations of 'ochre' (a generic name for the hydrous iron (III) oxide/hydroxide precipitates of variable composition common to mine water environments). This in turn leads to the destruction of the riverine food chain and can also have aesthetic impacts in recreational watercourses. The 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).

Systems devised to treat such mine waters can be typically be described as 'active' or 'passive'. Active treatment requires the continuous input of power for pumping, aeration and mixing plus the addition of treatment chemicals. These systems are often very responsive and controllable with a relatively small footprint but have high associated running costs. Passive treatments in contrast have no requirements in terms of power or chemicals, and consequently have lower operational costs. However, they often require a large area of land for effective treatment and are not a 'walk away' solution, i.e. they require maintenance.

Since the early 90's passive mine water treatment technologies have been favoured in the UK. This is due to a combination of factors; principally the lack of money available to treat discharges (caused by an absence of "polluter pays" legislation at the time of mine closures). Other reasons include; the required duration of treatment (possibly decades or more) and the actual mine water chemistries.

The current best practice for the passive treatment of net-alkaline ferruginous 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. This allows for more effective sludge management and prolongs the life of the wetland. However, in order to achieve 30-50% removal up front, the area of settlement lagoons often has to be very large. The reasons for this are threefold: 1) Large retention times are often required to give the oxidation of ferrous iron enough time to occur 2) Large surface areas are required to ensure sufficient oxygen transfer for the oxidation of iron (II) (Hustwit et al. 1992). 3) Large retention times are required to allow time for the settling out of the precipitated iron hydroxides which typically have very low settling velocities.

With these requirements for land area 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).

To address this problem, a treatment system is required that achieves similar or better up-front iron removal in a system with a reduced retention time and therefore smaller footprint.

### DESIGN CONCEPT FOR VERTICAL FLOW REACTOR

Cardiff University, in conjunction with the University of Newcastle-upon-Tyne and Mouchel Parkman, have developed a concept for the initial treatment stage of net-alkaline mine waters which aims to remove iron from net-alkaline mine waters in a more efficient manner than the settling lagoons conventionally used. The intention is to reduce the required residence time by accelerating the oxidation of iron (II) and changing the settling regime of solids that precipitate in the water column. This is achieved in the design by passing mine water down through an accreting and sedimenting bed of ochre.

This approach originated from previous research (Dey and Williams 2000) on the existing Gwenffrwd wetland (South Wales), which although designed to remove iron anaerobically as sulphide was found to be achieving high iron removal by an accreting and sedimenting a bed of ochre on the top surface.

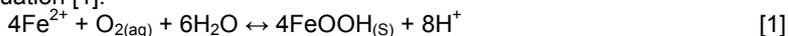
This idea was developed independently of the similar concepts developed by Jarvis and Younger (2001) and modelled by Burke and Banwart (2002), which in turn relates to a treatment process trialled by Best and Aikman (1983). These systems are 'roughing filters' (Younger, 2000). Mine waters are passed through reactors with media of high specific surface area (e.g. PVC trickling filter media, brushwood and blast furnace slag), iron removal occurs by ochre accretion (Younger, 2000) onto these surfaces.

In this novel system, there is 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 build up (and achieve efficient iron removal) both by 1) Filtration of iron hydroxide particles by the ochre bed and 2) Surface-catalysed oxidation of iron (II) and subsequent accretion of iron hydroxide around pre-existing iron hydroxide particles in the accumulating bed.

The surface-catalysed oxidation of iron (II) in the near acidic – circumneutral pH range is an attractive mechanism to exploit in a treatment system for mine waters of the appropriate pH range (which in fact brackets a large number of mine waters in the UK). The chemistry of ferrous iron oxidation and its catalysis by hydrous iron (III) oxides (ochre) surfaces is outlined below.

### CHEMISTRY OF FERROUS IRON OXIDATION

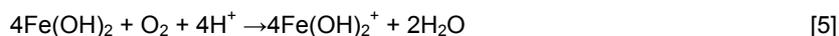
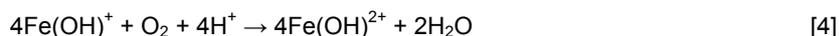
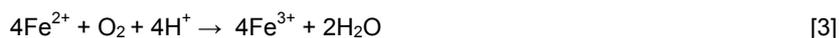
Passive treatment of net-alkaline ferruginous waters involves retaining the water for a sufficient time to allow the iron (II) load to be oxidised and precipitate out as some form of hydrous iron (III) oxide (ochre) as given by Equation [1]:



The iron (III) solid phases 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 iron (II) and its hydroxo complexes (see also Werhli, 1990; Burke and Banwart, 2002).



Each Fe(II) species has its own rate of reaction with dissolved oxygen (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(II) species (see equations [3] – [5]), and the subscript *T* refers to the total concentration of Fe(II).

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

The actual rates for the reactions described are determined by the production of the superoxide anion ( $\text{O}_2^-$ ) because this is considered (Millero 1985; Werhli 1990) to be the first and rate-determining step in the 4-electron reduction of oxygen during its reaction with dissolved Fe(II). The much faster rates of reaction for the hydroxo Fe(II) complexes is because  $\text{OH}^-$  serves as an effective electron bridge, facilitating the transfer of electrons from Fe(II).

The speciation of Fe(II) is pH dependant,  $\text{Fe}^{2+}_{(\text{aq})}$  tends to dominate the iron 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  $\text{Fe}^{2+}$ ,  $\text{Fe}(\text{OH})^+$  and  $\text{Fe}(\text{OH})_2$  (see Table 1) explains why iron oxidation kinetics show such a pronounced difference over a range of pH values (increasing sharply at high pH) reflecting the change in Fe(II) speciation with pH.

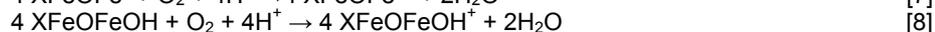
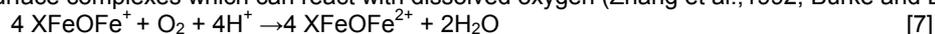
**Table 1 Rate constants for oxidation of Fe(II) species, where  $k_i$  is the 2<sup>nd</sup>-order rate constant for equation [6].**

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

**Heterogeneous catalysis of Fe(II) oxidation**

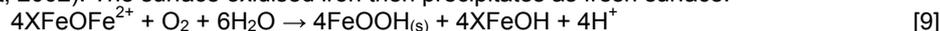
It has long been established that surface-catalysed oxidation of Fe(II) occurs on iron (III) oxide surfaces in the circumneutral pH range (e.g. Tamura et al., 1976; Wehri 1990).

At pH values of between 5-7, Fe(II) in solution exists principally as Fe<sup>2+</sup><sub>(aq)</sub> and correspondingly the homogenous rate of oxidation is still low (compared to the rate at higher pH where FeOH<sup>+</sup>, Fe(OH)<sub>2</sub> dominate). In the same pH range and above, the introduction of iron (III) oxide solids results in the adsorption of Fe(II) and the formation of Fe(II) surface complexes which can react with dissolved oxygen (Zhang et al., 1992; Burke and Banwart., 2002):



Wehri (1992) used data from Tamura et al. (1976) to estimate a 2<sup>nd</sup>-order rate constant for the adsorbed Fe(II) species. The estimate (5.01 M<sup>-1</sup>s<sup>-1</sup>) is 6 orders of magnitude larger than the rate constant for Fe<sup>2+</sup><sub>(aq)</sub> and comparable to the rate constant for the Fe(OH)<sup>+</sup> 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(II) species, the lower pH boundary of rapid Fe(II) oxidation is effectively lowered in the presence of the iron (III) oxide (*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.

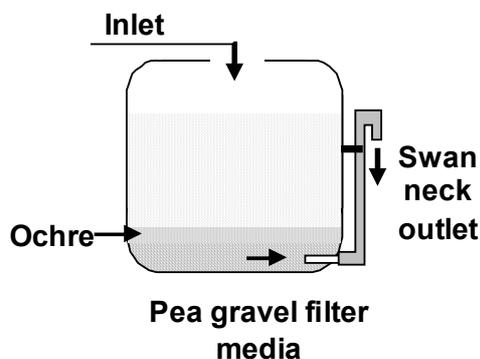
**PRELIMINARY TRIALS****Worsely Delph**

Preliminary trials undertaken at the Worsley Delph mine water discharge in Manchester involved flowing mine water through a small (30cm x 30cm) bed of sand for a week. Results (see Table 2) indicated that the retention times required for this approach may be significantly reduced compared to those of conventional pre-treatment settlement lagoons and that the iron removal rates may exceed 90% (see Dey and Williams 2001).

**Taff Merthyr IBC**

Further to the encouraging results of initial investigations into iron removal using a vertical flow system at Worsley Delph with very small flow rates, on-site trials were performed the Taff Merthyr mine water treatment scheme in South Wales. At Taff Merthyr, 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 where the water discharges (~ 100 L/s) into four settling lagoons (~1200 m<sup>2</sup> each), which in turn drain (by gravity) through reed beds (surface-flow) before discharging to the river (Coal Authority, 2001). The iron concentrations in the mine water are typically between 8 and 10mg/l.

For the trials a 25mm internal diameter plastic hose was used to supply mine water (siphoned from the base of an aeration cascade which is part of the existing treatment system) to the test cell. The test cell used was a 1 m<sup>3</sup> Intermediate Bulk Container (IBC), the bottom of which was lined with 100 mm of pea gravel (<10mm) to act as filter media on which the bed of ochre could accumulate. The water level in the cell was controlled by a 'swan neck' plastic pipe, attached to the outlet tap of the IBC. The duration of the test was ~ 4 months.

**Figure 1: Schematic of test cell (a 1m<sup>3</sup> IBC) configuration at Taff Merthyr****Results from preliminary trials**

A brief summary of the results from the preliminary trials is shown in Table 2 below. The results show that iron removal far in excess of 50 % can be achieved with reasonably short retention times (~90 mins). These figures compare well with the NCB (1982) guidance to allow 48 hours of retention time for the removal of 30 mg/l Fe. It also compares well with the performance of the settlement lagoons at Taff Merthyr, which remove about 50% of the iron with a retention time of about 18 hours. In terms of iron removal rates, the Taff Merthyr IBC trial removed between 26 and 79 g/m<sup>2</sup>/day (Dey and Williams 2001). For the Worsley Delph tests removal rates were similar, varying between 18 and 48g Fe/m<sup>2</sup>/day (see Dey and Williams 2001). These values compare very favourably with the values of 10 – 20 g/m<sup>2</sup>/d which are typical iron removal rates in conventional passive ponds and wetlands (Hedin & Nairn, 1992).

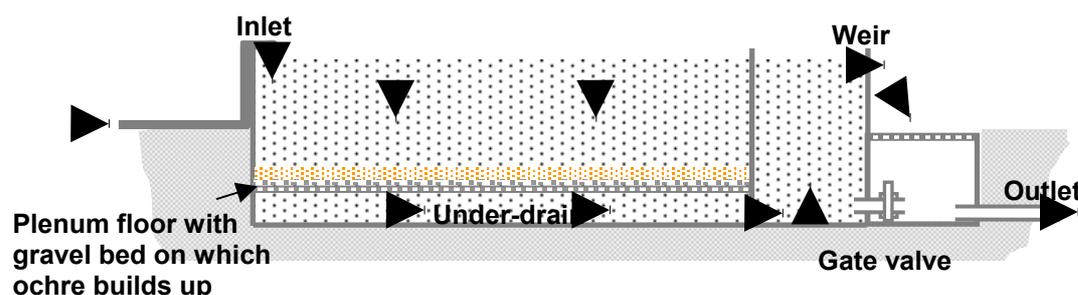
**Table 2 Results from Worsley Delph and Bridgewater Canal study, and Taff Merthyr IBC study (Dey and Williams 2002)**

Trial	Total iron in (mg/l)	pH	Flow rate (l/hr)	Retention time (hrs)	Iron removal %
<i>Worsley Delph</i>	14	6-7	2	23.0	97
<i>Worsley Delph</i>	14	6-7	4	11.5	95
<i>Worsley Delph</i>	14	6-7	6	7.7	94
<i>Taff Merthyr IBC</i>	10	6-7	3	300	89
<i>Taff Merthyr IBC</i>	10	6-7	135	6.7	81
<i>Taff Merthyr IBC</i>	10	6-7	144	6.3	93
<i>Taff Merthyr IBC</i>	10	6-7	171	5.3	88
<i>Taff Merthyr IBC</i>	10	6-7	648	1.4	51

#### TAFF MERTHYR LARGE PILOT-SCALE SYSTEM

After the success of the preliminary trials, Cardiff University successfully won funding from the UK Engineering and Physical Science Research Council (EPSRC) to build and operate a pilot-scale mine water treatment system based on the same vertical flow principle as in the initial trials.

The large pilot-scale system comprises a 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 tank is a commercially available bespoke steel panelled water tank set in a concrete base. The inside of the tank was sealed with bituminous paint. Mine water is piped (under gravity) into the tank from the distribution chamber at the Taff Merthyr mine site (as described above). The flow rate into the tank can be controlled by an adjustable ball valve; the maximum flow rate delivered through the pipe is ~ 4 l/s (14.4 m<sup>3</sup>/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 and reduce the possibility of blinding in the under-drain.



**Figure 2 Schematic of the large (7.32m long by 3.66m wide and 2.30m deep) pilot-scale system at Taff Merthyr**

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 over 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 Figure 2) which is kept shut during normal operation. There is an overflow cut into the baffle wall at the top (see Figure 3) which means in the event of the bed blinding, water will overflow and the system will work as a conventional settling lagoon.



Figure 3 Photographs of large pilot-scale system at Taff Merthyr

Table 3 Initial results from the large pilot-scale vertical flow reactor at Taff Merthyr

Vertical Flow Reactor						
Parameter	Week 1			Week 2		
Flow Rate	1.43 l/s			0.93 l/s		
Residence Time	~ 12 hrs			~ 18 hrs		
	Inlet	Outlet	Removal	Inlet	Outlet	Removal
<i>Fe TOT</i>	8.0 mg/l	3.8 mg/l	53 %	8.6 mg/l	3.8 mg/l	56 %
<i>Fe(II)</i>	3.1 mg/l	1.4 mg/l	55 %	6.6 mg/l	1.8 mg/l	73 %
<i>pH</i>	6.36	6.72		6.70	6.37	
<i>ORP</i>	51 mV	55 mV		121 mV	73 mV	
<i>Dissolved Oxygen</i>	7.1 mg/l	6.1 mg/l		3.5 mg/l	3.8 mg/l	
<i>Alkalinity</i>	200 mg/l	180 mg/l		180 mg/l	180 mg/l	

### Results and discussion

At the time of writing this paper, the pilot scale system pictured above has been running for 2 weeks. Table 3 gives some initial readings taken using portable meters and a HACH colorimeter. In the 2 week period of the experiment so far, no appreciable depth of ochre has had time to accumulate, nevertheless the results are already extremely encouraging, with over 50% of the total iron being removed. Iron removal rates of 24 g/m<sup>2</sup>/d and 18 g/m<sup>2</sup>/d can be calculated from the data (the filter bed is ~ 22 m<sup>2</sup>) in Table 3. The system is already achieving the upper ranges of iron removal (10 – 20 g/m<sup>2</sup>/d) expected from conventional passive systems (Hedin & Nairn, 1992) and improving on the existing settling lagoons at Taff Merthyr which (based on data collected at the same time as the data in Table 3) are removing ~ 9 g/m<sup>2</sup>/d. It is anticipated that the iron removal rates of the vertical flow system will increase as a bed of ochre builds on top of the gravel bed.

In addition to providing iron 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. If the influent to the tank is diverted and the effluent valve opened, vertical flow reactors under-drain the accumulated ochre sludge. 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.

### FUTURE WORK

The large-scale pilot system will be operated for two years, weekly sampling of the inlet and outlet waters of both the vertical flow reactor and the existing settling lagoon will allow direct comparisons of the iron removal efficiency of both systems. Further more intensive sampling at different depths within the tank will also take place frequently, allowing the chemistry of the system to be resolved. The sampling programme will run in conjunction with geochemical modelling of the processes within the treatment system, field data can be used to validate the results of modelling work. The permeability of the ochre bed will also be routinely monitored, because it will be the parameter that ultimately controls the length of time that the system can be successfully operated before desludging is required.

The data yielded from the various chemical and physical investigations will hopefully produce a new treatment option for treating ferruginous mine waters and provide better insight in to the chemical processes at work in passive treatment systems.

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