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A novel approach to mine water treatment

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Abstract

The current best practice for the passive treatment of net alkaline ferruginous mine waters in the UK generally involves pre-treatment, through cascade aeration and settlement, followed by final treatment in surface flow wetlands. The intention is typically to remove 30–50% of the iron 'up-front' in the settlement lagoons before the mine water enters the wetland. This approach allows for more effective sludge management and prolongs the life of the wetland. However, in order to achieve 50% removal up front the area of settlement lagoons is often very large.

Cardiff University has developed an alternative concept for the pre-treatment stage employing autocatalytic oxidation and ochre accretion within an ochre bed without any supporting media. This approach was discovered through research studies on the existing Gwenffrwd anaerobic wetland, which was found to be achieving high iron removal by this process. Preliminary trials undertaken on behalf of Parkman indicate that the retention times required for this approach may be significantly reduced compared to those of conventional pre-treatment settlement lagoons, and that with correct design it is possible to remove over 90% of the dissolved iron. This approach offers a promising new passive technology for the pre-treatment stage and a potential alternative to wetlands with a substantially smaller footprint.

This paper presents the results of some preliminary trials on mine waters undertaken by Cardiff University and Parkman. It evaluates the applicability of this approach, and includes both technical and practical aspects of design and implementation.

Key words: autocatalytic oxidation, dissolved iron, mine water, ochre accretion, passive technology, pre-treatment stage, retention time, vertical flow system

INTRODUCTION

The problem of ferruginous mine water discharges has long been acknowledged as being deleterious to the surrounding environment. 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). With ever-increasing restrictive legislation being enacted globally an economic control of the problem is paramount.

Usually the control of the discharges is only possible by tertiary systems, i.e. collection and treatment, due to the lack of planning during the development of the mine and the absence of proven in-mine technologies for mine water remediation. Tertiary treatment systems can be active, passive or sometimes a mixture of both. Active treatments are defined as requiring the continuous input of energy for pumping, aeration and mixing, plus the addition of treatment chemicals. These systems can be very responsive and controllable, often with a relatively small footprint, but have a high associated running cost. Passive treatments, in contrast, avoid the continuous input of either energy for equipment or chemicals (Burke and Banwart 2002) in the treatment process and 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. The duration of the treatment for the removal of contaminants is also another unknown factor that adds further uncertainty to the financial liability (Burke and Banwart 2002). In the UK the

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preferred method of treatment of the discharge is predominantly passive-based, due to the duration factor, which outweighs the extra costs incurred in purchasing the land.

The current best practice for the passive treatment of ferruginous mine waters in the UK generally involves pre-treatment, through cascade aeration and settlement, followed by final treatment in wetlands. This approach usually applies to mine waters that are net alkaline (Hedin *et al.* 1994), including most discharges from flooded underground mine workings (Banks *et al.* 1997). The intention is typically to remove 30–50% of the iron 'up-front' in the settlement lagoons before the mine water enters the wetland. This approach allows for more effective sludge management and prolongs the life of the wetland. However, in order to achieve 50% removal up front, the area of settlement lagoons is often large, due to the very low settling velocities associated with the precipitated iron hydroxides. The settlement lagoons also pose a problem in the further treatment of the collected sludge for disposal. Once the lagoons are drained, the sludge concentration is only between 2 and 5% (Widowson 2002). It therefore requires further dewatering prior to disposal.

After research studies on the existing Gwenffrwd anaerobic wetland (Dey and Williams 2000) an alternative concept for the pre-treatment stage employing autocatalytic oxidation and ochre accretion was developed. This idea was developed independently of the concept developed by Jarvis and Younger (2001) and Burke and Banwart (2002) but employs the same process mechanism. The autocatalytic oxidation of dissolved Fe(II) to precipitated Fe(III) is well documented (Wehrli 1990; Zhang *et al*. 1992) and is the reason for the furring of pipes and channels in the delivery of the mine water discharges to treatment sites.

The overall stoichiometry for the oxidation of adsorbed Fe(II) by ionic oxygen is shown in Eq. 1:

$$O_{2(aq)} + 4Fe^{2+} + 6H_2O \leftrightarrow 4FeOOH_{(S)} + 8H^+ \qquad (1)$$

However, the chemistry is not that simple and the aqueous Fe(II) is never solely in solution as a free ion but as a variety of species, some of which are hydrolysed. These species, adsorbed on to the Fe(III) oxide mineral surface, are significantly more reactive than the adsorbed ionic Fe^{2+} (Burke and Banwart 2002). The authors state that autocatalytic oxidation by adsorption on to the oxide surface and accretion is attractive as an approach to mine water treatment, as the reactive surface of the catalyst does not decrease with time.

The Gwenffrwd system was found to operate successfully by accreting ochre on the surface of a compost bed through which mine water flowed vertically. From this observation an alternative to more conventional treatments was conceived, which involves autocatalytic oxidation within an ochre bed in a vertical flow system. The novelty of this approach relates to the removal of iron within an ochre bed, rather than in any supporting substrate or media.

Preliminary trials undertaken at the Worsley Delph mine water discharge in Manchester, on behalf of Parkman, 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% (Dey and Williams 2001). The vertical flow system also permits under-drainage that will naturally dewater and thereby thicken the sludge prior to disposal.

Subsequent trials were undertaken at Taff Merthyr to confirm earlier findings.

METHODOLOGY

The on-site trials were performed at the site of the new Taff Merthyr mine water treatment scheme in South Wales. At the site, the existing mine water treatment entails pumping the mine water from the old mine workings to a central chamber, prior to distribution to four large settlement lagoons that supply 16 reed beds (Coal Authority 2001). The average iron concentration in the mine water is approximately 10 mg/L.

For the trials, a 25 mm internal diameter plastic hose was used to supply mine water, at 10 mg/L Fe, to the test cell under gravity. The benefits of aerating the mine water prior to treatment (Burke and Banwart 2002) were exploited as the mine water was siphoned from the base of the *in situ* aeration cascade. For the test cell a 1 m^3 intermediate bulk container (IBC) was employed with a 100 mm base of pea gravel (<10 mm) acting as a filter medium. Control of the flows to the test cell was by a gate valve; this was subsequently removed in order to increase the flow rate, and levels in the cell were controlled by a 'swan neck' arrangement. Figure 1 illustrates the test set up and Figure 2 shows the test cell on site.

For the trials, several feed flow rates were investigated and the level of iron removal monitored. The concentrations of iron entering and exiting the test cell were recorded, together with the flow rate through the cell and the iron concentration in the discharge from the existing treatment settlement lagoon. Iron analysis was performed at the Cardiff School of Engineering laboratories by a Perkin Elmer P400 Inductively Coupled Plasma (ICP) emission spectrophotometer.

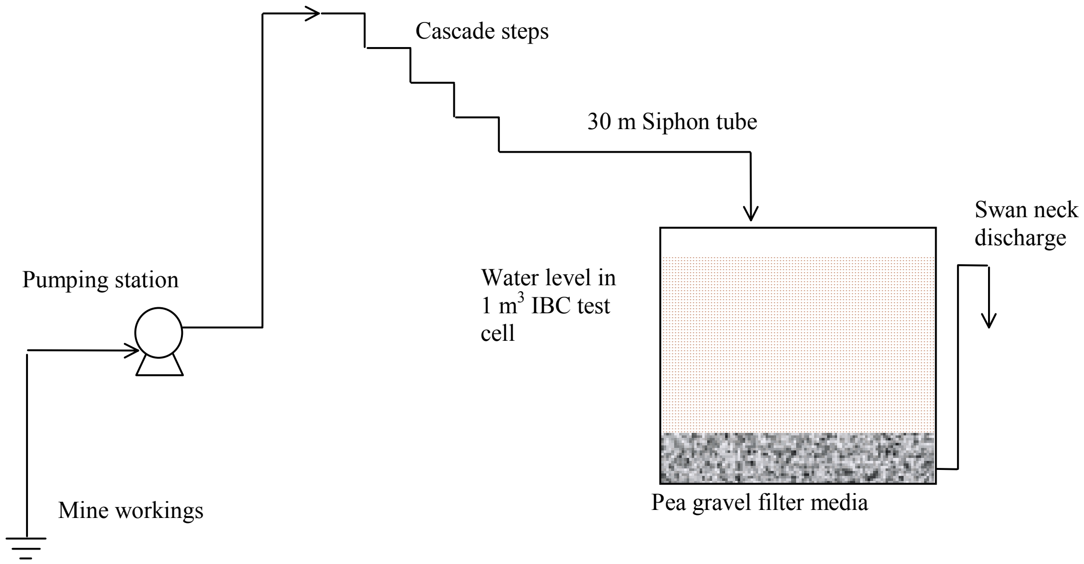

Figure 1. Schematic of test cell configuration

Figure 2. Photograph of test cell on site at Taff Merthyr mine water treatment scheme

Table 1. Results of variation in flow rate with iron removal and corresponding retention time in the treatment cell

Feed rate (L/min)	Average % removed	Retention time (h)
0.05	89	300
2.25	81	6.7
2.40	93	6.3
2.85	88	5.3
10.80	51	1.4

Table 2. Iron removals by existing lagoons at Taff Merthyr

Date	% removed
12 July	54
24 July	36
30 July	89
02 August	40
06 August	45

RESULTS

Since installation in late June, the test cell at Taff Merthyr has run continuously (to the current date of 1 September). When changes to flow rate or retention times were made, the system was not monitored until the time taken for four complete reaction vessel volume changes had elapsed to ensure that the new equilibrium was attained. Table 1 shows the effect of variation of feed flow rate on iron removal.

During the test trials, the performance of the existing settling lagoons was also monitored. Table 2 shows the performance of these lagoons on selected dates.

The estimated flow rate to four settlement lagoons of approximate area 2500 m^2 at Taff Merthyr is 50 L/sec. This translates to a retention time of about 42 hours.

DISCUSSION

The results of the larger scale trials at Taff Merthyr confirm the results found at Worsley Delph (see Table 3). Both trials show that relatively little retention time is required to remove a high percentage of the dissolved Fe(II). This observation is in agreement with well-documented abiotic autocatalytic oxidation of Fe(II),

Table 3. Results from Worsley Delph and Bridgewater Canal study, average iron concentration 14 mg/L (Dey and Williams 2002)

Flow rate (L/h)	Iron Total (mg/L)	Iron % removed	Retention time (h)	Approximate operating time (h)
2	0.4	97	23	72
4	0.7	95	11.5	96
6	0.8	94	7.7	72

1. Approximate operating time indicates time between starting test and sampling discharge

which is rapid under circum-neutral conditions (Evangelou and Zhang 1995). To achieve the specified design criteria of 50% up-front iron removal, results suggest that a retention time of less than 90 minutes is required. This compares very favourably with design guidance for settlement (NCB 1982) that recommends 48 hours retention for treatment of mine waters with up to 30 mg/L iron content. It also compares extremely well with the performance of the settlement lagoons at Taff Merthyr, which remove about 50% of the iron with a retention time of about 42 hours. This approach therefore appears to offer a very attractive alternative to conventional settlement ponds as pre-treatment for mine waters.

The results also suggest that this type of approach may offer an attractive alternative to wetland treatment, since effluent mine waters with iron concentration less than 1 mg/L can be achieved with moderate retention times. The following comparison illustrates this point, although it should be noted that the efficiency of the vertical system under discussion is dependent on retention time rather than treatment area, and therefore the area of the vertical systems calculated below is sensitive to the depth of water in the trial.

With a maximum loading of 156 g Fe/day the removal rates for the vertical system tested at Taff Merthyr varied between 26 and 79 g Fe/m^2/day (omitting the extra long retention time). For the Worsley Delph tests removal rates were similar, varying between 17.5 and 47.5 g Fe/m^2/day. For the high flow rate trial at Taff Merthyr these removal rates are nearly four times greater than those quoted by Hedin *et al.* (1994) of 20 g Fe/m^2/day (abandoned mined land criteria). Improved aerial treatment rates could easily be achieved for the Worsley Delph trial by increasing the depth of water from 0.3 m and therefore increasing the retention time. The removal achieved by the Gwenffrwd anaerobic wetland system is approximately 28 g Fe/m^2/day (Dey and Williams 2000) but at a retention of about 50 hours.

Jarvis and Younger (2001) using the same autocatalytic mechanism reported removal rates of 0.09 and 0.05 g Fe/m^2/day. However, they argued that the retention time must be taken into account, as their reactor was treating the water in just over a minute and 6 minutes respectively, compared to an average 3.5 days of a typical wetland. This gave them a removal rate of 34 to 82 g Fe/m^2 compared to a corrected rate of 3 to 6 g Fe/m^2 for the wetland. Applying the same correction mechanism to both the Taff Merthyr and Worsley Delph results gives between 93 and 1354 g Fe/m^2 and between 18.3 and 148 g Fe/m^2 respectively. These results show that the vertical treatment system also potentially offers an attractive alternative to surface flow wetland treatment.

However, in this vertical flow design the overall permeability of the system must be considered. In order to treat 10.8 L/min at Taff Merthyr in the 1 m^3 test cell a vertical Darcy velocity of 2×10^{-4} m/s must be maintained. Assuming a vertical hydraulic gradient of 1, this Darcy velocity is equal to the permeability requirement of the filter and ochre bed. This is close to the permeability of a clean sand (Craig 1987). The sludge relies on its very low solids content and open structure for its permeability. As the sludge layer accretes, the weight of the overlying sludge compresses the ochre and the permeability of the bed decreases (Dey and Williams 2000). Results from previous testwork suggest that the permeability of the bed of sludge rapidly decreases to the order of 10^{-5}m/s. This suggests that the system could fail in a relatively short period of time as the sludge layer thickens. Without the benefit of data on the permeability of sludges accreted in this way, it is appropriate to allow a greater area for treatment than indicated by the retention alone.

Currently, at Taff Merthyr 0.5 ha of settling lagoons are used to treat approximately 50 L/s of mine water. If the vertical flow system were to be installed to remove 50% of the iron, assuming a retention time of 90 minutes, the volume of the vertical system would be 270 m^3, which at an operational depth of 1 m is equivalent to 270 m^2, i.e. approximately 5% of the area required at Taff Merthyr. If the area was increased by a factor of 10 to 2500 m^2 to accommodate uncertainty regarding vertical permeability, the minimum vertical velocity could be reduced by a factor of 10 to 2×10^{-5} m/s, thereby increasing the systems' life and still occupying less land than conventional settling lagoons. This increase in size would also have the effect of increasing retention time and removing a much greater proportion of the iron than the existing treatment system. From Table 2, the average iron removal by the Taff Merthyr settling lagoons is approximately 50%, and the increased size of the vertical flow system should remove between 80 and 90% of the iron (see Table 1). A decrease in depth of the system could compensate for this if removal of the majority of the iron in a pre-treatment system was considered undesirable.

IMPLICATIONS FOR FUTURE TREATMENT SYSTEM DESIGN

This new approach to removal of iron from net alkaline mine waters offers significant potential to reduce the size and costs of future mine water treatment systems. To date, the applicability of this type of approach has been demonstrated at bench-scale for two net alkaline mine waters with iron concentration 5–15 mg/L. Based on the authors' experience working on numerous UK coal mine waters, this water quality range describes a significant proportion of the major mine water discharges from coalmines in the UK. The construction of such a system is more complex than conventional settlement lagoons, since there is a requirement for a filter layer and under drains, as well as valves for backwashing the filter and an overflow to provide for any excess flows. The major constraint is the need for a head of water, since the water has to enter from the top and exit the bottom of the system. These systems are therefore suited to sites with changes of elevation of at least 2 m over the treatment area. It is possible that shallow (0.3 m) systems could be cost effective, and in this case there may be potential for their construction on more level sites.

As well as reduced costs and area these systems offer the potential to dry sludges on site, without use of additional equipment, since the operation can be adapted so that the system acts as an under drain for the sludge if the influent water is diverted, whilst the effluent valve remains open. Such systems can be used to thicken sludges to 25–35% dry solids within a few weeks (NCB 1982).

The vertical treatment system also has the advantage of being amenable to failsafe design, since, if the vertical bed clogs, the water will overflow and the system will operate as a conventional settlement pond.

Certain aspects of these systems remain unproven and should be addressed before construction at full scale. The main issues relate to the potential for the system to clog due to reduction in the permeability of the ochre or precipitation of ochre within the filter medium. Evidence to date suggests that this should not be a problem in the medium term, since the Gwenffrwd system has been operating successfully in this manner for several years. It is likely that these problems would be minimised by designing systems to remove iron to low concentrations. This would minimise the potential for precipitation of iron in the filter medium. Furthermore, systems with a high flow rate per unit area of bed, i.e. low retention time or deep systems with relatively small footprint, may be problematic, since these systems require a higher permeability in the bed than those with a lower flow rate per unit area.

Other uncertainties relate to:

- general effects of scaling up;
- applicability to mine waters with different chemistry;
- seasonal variations in performance.

FURTHER RESEARCH

The main activity, which would add confidence to the applicability of vertical accretion as a means of treating mine waters, as described in this paper, would be operation of a pilot system at a field scale for several years to assess the potential ochre permeability and clogging effects. It is recommended that this is progressed rapidly, so that the opportunity to treat other mine waters using this approach can be taken and the resultant potential financial and land area savings achieved.

Further research is also required to determine the range of mine water chemistries to which this approach can be applied. This should include trials to assess the effects of high and low iron concentrations, net acidity, pH and the potential to treat other metals present in mine waters.

Once established as a workable approach, it would be appropriate to develop design guidance based on an understanding of the factors that control the rate of iron removal in such systems. The guidance should include: range of treatable chemistries and iron removal versus retention time for different chemistries (iron concentration, net alkalinity/acidity, pH, Eh); optimum and maximum vertical velocity; minimum and maximum sludge thickness and minimum and maximum operating water depth.

Typically, it is operational experience that then provides the best guide to operational problems and their solutions and general operational efficiency. It would be sensible to begin considering these problems and attempting to design them out at as early a stage as possible. Issues, which need to be addressed, are likely to be desludging frequency, design and operation of the backwashing system and operation of an under drain for sludge drying.

CONCLUSIONS

The vertical flow treatment system has proved to be very effective at iron removal. Typical removals of 90% can be consistently achieved with moderate retention times of six to eight hours. A removal rate of 50% has been achieved with a retention time of 90 minutes. Very high rates of iron removal can be achieved per unit area, 79 g Fe/m^2/day;

When compared to the existing settling lagoons at Taff Merthyr, a vertical treatment system can meet the same design specification of 50% iron removal in a fraction of the area: 250 m^2 compared to the existing 5000 m^2.

Accreted iron removal rates can be several times greater than those of surface flow wetlands, and under-drainage design of the vertical treatment system will enable improved dewatering of the sludge during maintenance. This system clearly offers potential for significant financial savings compared to current best practice in the UK, and deserves serious consideration and investment to develop future design guidance.

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