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Chemical behaviour of the Wheal Jane bioremediation system

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Abstract

The effectiveness of remediation of the highly acidic and transition metal polluted mine water discharge from the Wheal Jane Mine by the Wheal Jane Passive Treatment Plant is described. The success of the remediation required that all the system components work as predicted. The study shows considerable success in the removal of key toxic metals and clearly demonstrates the potential for natural attenuation of acid mine drainage, particularly iron oxidation, by microbial populations. The Wheal Jane Passive Treatment Plant provides the only experimental facility of its kind.

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1. Introduction

Following the closure of coal and metal mines in recent years the problem of acid mine drainage (AMD) is becoming increasingly prominent (Younger, 1997). The most publicised accidental release was from the Wheal Jane Mine in 1992 following cessation of pumping a few months earlier (Younger et al., 2004). During this event and subsequent to it, a large quantity of highly acidic transition metal-rich flooded into the Carnon River and the Fal River/ Estuary (Younger et al., 2004; Neal et al., 2004).

Although there had been a long history of pollution from abandoned coal and metal mines across the UK, Wheal Jane produced the most spectacular incident and heightened awareness of the problems associated with acid mine drainage. In 1994, an active treatment plant and a pilot scale passive treatment plant were constructed at Wheal Jane, with the aim of treating the effluent from the mine and generating relatively clean water for discharge to the Carnon River. The passive wetland system was designed to treat the AMD as part of a long-term remediation study.

As noted by the Environment Agency (hhtp://www.swenvo.org.uk/environment/spot_poll.asp) "Large amounts of metals in water can kill aquatic life and decrease the diversity of plants. The economic cost of diffuse pollution by trace metals lies mainly in prevention or remediation (Ander et al., 2000). For

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example, the work done by the Environment Agency at Wheal Jane cost £3.4 million to set up, and continues to need £950 thousand per year to run."

The wetlands pilot plant consists of three schemes (Whitehead and Prior, 2004). These differ only in the pre-treatment utilised to modify the pH of the influent mine water: lime dosing to pH 5 (LD), an anoxic limestone drain (ALD) and no modification (lime free, LF). All three systems include:

- constructed aerobic reed beds designed to remove iron and arsenic;
- an anaerobic cell to encourage reduction of sulphate and facilitate removal of zinc, copper, cadmium and the remaining iron as metal sulphides;
- aerobic rock filters designed to promote the growth of algae and facilitate the precipitation of manganese.

Since the construction of the plant in 1994, extensive water quality, geochemical and biological data sets have been gathered present an opportunity to investigate the benefits of the passive treatment of mine water (Hall et al., 2004; Hallberg and Johnson, 2004; Johnson and Hallberg, 2004; Swash and Monhemius, 2004; Whitehead and Prior, 2004). As part of a DTI LINK initiative these data sets, together with more recent data, have been used to improve understanding of the physical, chemical and biological processes which underlie the technology of passive treatment system and the most suitable conditions for future bioremediation schemes.

In this paper, the overall chemical transformations occurring in the active and passive treatment plant are described. These transformations hold the key to describing the nature and effectiveness of the passive treatment plant and this is especially important given the uniqueness and environmental importance of the Wheal Jane PTP.

2. The active treatment system

The active treatment system was designed to treat the majority of the mine water flow. Initial design studies concluded that treatment using oxidation and chemical neutralisation would be the most cost-effective design. The EA commissioned the detailed design and construction of an active treatment plant. The plant consisted of high density sludge (HDS) treatment system, as shown in Fig. 1, and is described more fully by Coulton et al. (2003) and Brown et al. (2002). The treatment consists of three stages: in sequence,

- (i) mixing of mine water and sludge,
- (ii) aeration,
- (iii) clarification.

Water from the mine shaft is pumped using 6 pumps each with a total pumping capacity of $330 \ l \ s^{-1}$ to the treatment plant. Water from the mine drain, supernatant from the tailings pond and effluent from the pilot passive treatment plant are also treated by the system.

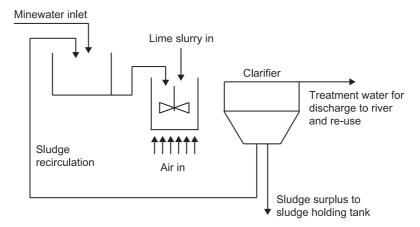


Fig. 1. The active treatment plant at the Wheal Jane Mine.

Mine water is pumped to treatment tanks where 5% lime slurry is added and the pH is raised to 9.5. Aeration takes place through a diffuser in the base of the tank and the fluid is kept mixed by means of a vertical paddle. The flow is split and directed to two parallel clarifiers where the solids settle out and are removed by mechanical rake to a sludge holding tank or are recirculated to the first stage mixing tank. The sludge in the holding tank contains between 30% and 40% solids and is piped to the tailings pond. The supernatant liquid from the clarifying stage is decanted and directed to a holding tank where it is re-used or discharged to the Carnon River (Fig. 1). The design capacity for the system is 440 l s⁻¹ and discharge consent has been approved for 350 1 s⁻¹ of treated water to the Carnon River. Residence time within the treatment system is approximately 30 min in the first and second stage tanks, and 25 min in the clarifiers. The system treated approximately 12.3 million cubic metres of water during the first 22 months of operation at an average rate of 200 l s⁻¹. It removed approximately 3200 tons of metal at a removal efficiency of 99.2%.

3. Description of the passive treatment system

The Passive Treatment Plant (PTP) consists of three separate systems each incorporating a series of aerobic and anaerobic cells and a rock filter with differing pre-treatment. The lime-dosed system incorporates a small lime dosing plant and precipitate trap (sludge channel); the Anoxic Limestone Drain (ALD) combines a small anoxic cell (pre ALD) and an anoxic limestone drain; the Lime Free System has no pre-treatment and acts as a control to the others. The mine water supply for all three systems originates from Jane's Adit, which is connected to Wheal Jane Mine workings. The mine water is transported underground via piping to the PTP. Early research at the site was undertaken during 1994–1997 (Hamilton et al., 1999) and the later DTI LINK project started in 1998.

The objectives of the differing treatment systems are as follows:

3.1. Lime dosing

Lime dosing is performed to raise the pH of the influent mine water without removing excessive

amounts of iron as this would contradict the principle of passive treatment. However, the level to which the pH can be raised without excessive precipitation occurring is constrained by the particular metals present and the levels of dissolved oxygen.

3.2. Anoxic limestone drain

The ALD (sludge channel) was designed to remove sufficient dissolved oxygen from the influent mine water to minimise the oxidation of iron and subsequent formation of iron (III) hydroxide in the ALD which may lead to the formation of a hard crust on the limestone, thus reducing rates of dissolution. The ALD was designed to raise the pH of the mine water by limestone dissolution and also to generate alkalinity. Design features of this system included a suitable retention time (1–2 days) to maximise alkalinity generation; the use of high grade limestone of a suitable particle size to allow sufficient permeability (20–40 mm surface area) and the fitting of an airtight cover to prevent oxygen ingress.

A number of modifications were carried out during the Pilot Study in an attempt to increase efficiency. As part of the modification works, the sludge channel was divided into two discrete longitudinal chambers and an airtight cover was added. A duplicate lime-dosing arrangement was introduced allowing simultaneous and independent of the influent mine water to both the ALD and Lime-dosed systems. In addition, the inclusion of an airtight cover allowed lime-dosing to a higher pH than was previously possible, due to the fact that under anaerobic conditions iron is found largely in its ferrous form which is soluble below approximately pH 8.5.

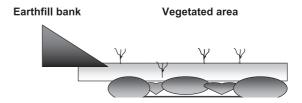


Fig. 2. Typical cross-section through aerobic cell, showing vegetation *Phragmites*, *Typha* and *Scirpus* and with substrate constructed in ridge and trough formation to maximise flow lengths.

Earth-filled bank Enclosed section Earth-filled bank

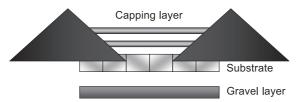


Fig. 3. Typical cross-section through anaerobic cell.

3.3. Aerobic treatment

The aerobic cells, shown in Fig. 2, were designed to remove iron as ferric hydroxide/oxyhydroxide, with arsenic removal by co-precipitation and adsorption onto the iron precipitate. The cells were designed to have a 5-10 year lifespan before it was expected that the accumulated metal precipitates would fill the available freeboard. However, in practice, significant accumulation of ochre in both lime dosed and lime free systems have been mainly confined to the first three of five cells. The key parameters in the aerobic cell design were oxygen availability and pH maintenance. Sufficient oxygen for the oxidation of ferrous iron is obtained via diffusion from the atmosphere. This is achieved by maintaining a water depth no greater than 300mm within the cell to aid transport of oxygen by reeds to the rooting zone and division of the aerobic system into five discrete cells separated by weirs. The two principal factors of concern when sizing the cells to maintain a suitable pH are the quantity of iron loading (the dominant target metal) and the pH of the influent mine water which determines the effectiveness of the bicarbonate buffering system.

3.4. Anaerobic cells

The anaerobic system, as shown in Fig. 3, consists of a closed cell between earth filled banks and capped

above to prevent air entering the cell and sealed beneath by a clay and gravel layer. The cell is filled with a substrate of fresh organic material which acts as a source of carbon for bacteria. The construction was designed to remove cadmium, copper, zinc and residual iron. Removal occurs through the formation of metal sulphides which are the product of a reaction between metals present and hydrogen sulphide. The hydrogen sulphide is present due to reduction of sulphates in the mine water by bacteria, principally of the *Desulphovibrio* family. In order for the bacterial community to function they require a sulphate source, carbon in a readily available form and a pH range of pH 5–8.

The anaerobic cells were designed to have a 30-year lifespan, after which the cell substrate would require substantial replenishment with organic matter. In reality, however, it was necessary to add fresh organic matter/sulphate reducing bacterial inoculum (cattle manure) during the pilot study in order to enhance cell performance.

The size of the anaerobic cell is based upon a volumetric metal loading factor and a surface area loading factor. Through experience of passive treatment in the USA, Knight Piesold suggest that the metal loading rate should be approximately 0.3 mol metal m³ day⁻¹ and the surface area loading factor is 20 m² l⁻¹ min⁻¹ when pH<5. It is thought that at a lower pH this loading factor may be reduced.

3.5. Rock filters

The rock filters consist of pools of water separated by rock banks and have been designed to promote the growth of algae, as well as the removal of manganese as an oxide, along with a reduction in the BOD of the anaerobic cell effluent. In order to increase efficiency of this 'polishing stage', the filter was designed to maximise algal growth through sufficient light penetration and surface area within cell. Experimental results indicate that manganese removal is typically in

Table 1 Summary of mean chemistry in the lime free system, all units mg/l except pH

Lime free system	Ca	Mg	Na	K	Cl	SO_4	DO	pН	Al	As	Cd	Cu	Fe	Mn	Zn
Adit	433.6	39.3	177.3	19.0	407.3	1649.5	1.4	3.9	48.6	2.7	0.1	0.4	143.6	21.4	82.0
After aerobic cells	457.7	40.6	177.3	18.1	393.9	1522.9	8.6	2.9	56.5	0.0	0.1	0.5	35.3	23.9	84.6
After anaerobic cells	510.8	47.3	203.9	22.9	388.5	1610.4	2.5	3.8	70.3	0.0	0.0	0.0	52.3	27.3	47.1
After rock filters	520.6	48.6	199.1	25.9	393.0	1636.1	8.0	3.1	75.8	0.0	0.0	0.1	12.7	27.6	51.3

Table 2 Summary of chemistry in the anoxic limestone drain system, all units mg/l except pH

Anoxic limestone drain system	Ca	Mg	Na	K	Cl	SO_4	DO	pН	Al	As	Cd	Cu	Fe	Mn	Zn
Adit	433.6	39.3	177.3	19.0	407.3	1649.5	1.1	3.9	48.6	2.7	0.1	0.4	143.6	21.4	82.0
After LD	462.8	39.0					0.3	5.5	41.2	0.4	0	0	106.7		
After ALD	556.3	39.5	174.4	19.1	393.2	1588.5	0.6	6.0	12.9	0.3	0.0	0.0	112.0	24.3	60.2
After aerobic cells	546.1	39.4	170.0	19.4	385.8	1531.5	7.8	3.6	8.9	0.0	0.1	0.0	25.3	23.6	48.4
After anaerobic cells	503.5	39.2	154.6	32.2	372.7	1323.5	2.1	5.9	8.6	0.0	0.0	0.0	17.6	22.6	1.0
After rock filters	464.0	37.4	147.3	36.0	338.1	1150.4	9.7	6.6	3.3	0.0	0.0	0.0	2.2	12.2	4.9

the order of 2 g Mn m⁻² day⁻¹ with the presence of a sufficiently dense algal mat.

3.6. Passive treatment plant operation and sampling strategy

Passive treatment systems are based upon physical, chemical and biological mediated processes. The reed, algal and bacterial communities require a period of time to become established and reach maturity. Therefore a period of stabilization was required in order to allow a full evaluation of the performance of the individual components in each system. At least a year of growth is required before the ecology can be said to have reached maturity. In the Wheal Jane project there were in fact 3 years of routine management of the system prior to DTI project.

Management of the Pilot Plant has been kept to a minimum to ensure that the treatment is indeed 'passive'. Aerobic cell management has been aimed at promoting reed and algal growth to support the microbial community, as and when required. The anaerobic cells have been operated in one of two ways, either 'in-series', with the cell receiving influent mine water from the final aerobic cell, or 'in-parallel', with the cell receiving pre-treated mine water or raw mine water in the case of the Lime Free System. Rock filter management mainly consists of periodic weeding of the rock banks to prevent blockages and the

application of a general purpose NPK fertilizer during the summer to encourage algal growth.

Chemical monitoring was undertaken on a weekly basis and divided into (a) in situ monitoring of temperature, dissolved oxygen (DO), pH, redox potential (Eh) and electrical conductivity, and (b) laboratory analysis of samples taken at key points across the site. Samples were analysed for a broad range of determinands including pH, Dissolved Oxygen (DO), redox potential, alkalinity, dissolved metals and anions. All metal analysis was undertaken using an ICP-OES in duplicate on both ultra-sonic and crossflow nebulisers to account for the large variations in concentrations detected. All analysis was completed within a week of collection at site in accordance with UKAS and BS5750 quality assurance controls.

4. Overall chemical behaviour

Tables 1, 2 and 3 give a basic statistical summary of the chemistry for the three systems in the passive treatment plant. There are many notable features of this data such as the extremely high sulphate concentrations, low Dissolved Oxygen, low pH and high metal content in the Adit water that feed the passive treatment system. This is typical of acid mine drainage and is the cause of the considerable damage that can be inflicted on streams by the highly acid waters: Neal et al. (2004)

Table 3 Summary of mean chemistry in the lime dosed system, all units mg/l except pH

Lime dosed system	Ca	Mg	Na	K	Cl	SO ₄	DO	pН	Al	As	Cd	Cu	Fe	Mn	Zn
Adit	433.6	39.3	177.3	19.0	407.3	1649.5	1.0	3.8	48.6	2.7	0.1	0.4	143.6	21.4	82.0
After lime doser	445.2	38.6	177.3	18.6	396.6	1663.1	5.4	4.6	43.6	1.6	0.1	0.4	136.0	23.5	80.8
After aerobic cells	445.8	38.2	176.5	18.4	394.5	1579.5	7.3	2.8	45.5	0.0	0.1	0.4	41.8	23.2	80.8
After anaerobic cells	462.5	41.0	179.3	20.3	402.8	1550.8	2.8	3.2	50.9	0.0	0.0	0.0	43.8	24.1	34.5
After rock filters	475.7	42.1	185.0	23.6	412.6	1591.2	7.5	3.0	55.8	0.0	0.0	0.1	13.2	24.8	45.6

Table 4
Median removal rates of major elements at Wheal Jane Passive Treatment Plant, 1999–2001 (LD—lime dosed system, ALD—anoxic limestone drain system, and LF—lime free system)

System	Al (%)	Cd (%)	Cu (%)	K (%)	Mg (%)	Mn (%)	Na (%)	S (%)	Zn (%)
LD	65	78	73	24	37	54	30	47	66
ALD	90	98	95	41	41	60	33	39	73
LF	35	53	42	-2	26	45	20	37	47

provide a comparison of adit and River Carnon water quality in relation to sources and dynamics.

The chemistry of the three systems show that the metal reductions vary significantly and it is noticeable that there is a broad difference in the capacity of each system to remove metals in addition to a wide variance between elements, as shown in Table 4.

Interim results of the water chemistry appear to support the original research carried out at the site from 1994 to 1998 (Fig. 4). All systems appear to remove soluble Fe from the AMD, with removal primarily taking place in the first two aerobic cells. The ALD configuration has the highest removal rate with a median of 99.5%, with the LD and LF systems removing a median of 96.5% and 94.8%, respectively.

The relationship between potential and pH at sites across the passive treatment plant have been mapped (Fig. 5) to allow the interpretation of element speciation within the three treatment systems using adapted Pourbaix diagrams (Pourbaix, 1974).

These theoretical diagrams depict the thermodynamically most stable form of an element, as a function of potential and pH and show the relative stability of an element and its predominant form under a range of environmental conditions. This simple analysis has allowed theoretical determination of which chemical equilibrium equations which could be included in the model for each element considered. However, recent work (Johnson and Hallberg, 2004; Hall et al., 2004; Hall and Puhlmann, 2004) indicate that most of the transition between metal speciation forms is controlled by microbial behaviour. Thus using equilibrium approaches is not the best approach. Hall et al. (2004) and Hall and Puhlmann (2004) has conducted a series of laboratory and field experiments to determine the reaction rate controls and has found that the processes are generally first order microbiologically controlled reactions with measurable reaction rates. Thus, it is possible to take this into account when modelling to the processes at Wheal Jane and other bioremediation systems.

Spatial variations in pH, dissolved oxygen, conductivity, redox and BOD at the pilot passive treatment plant were determined. The system variations of these parameters were important and they allowed the environmental conditions within each section or reach of the three systems to be analysed. The maximum, minimum and inter-quartile ranges for each reach were calculated for all parameters for the period June–November 1996, to allow limits to be established and determination of important processes to aid model development. Dissolved oxygen plots for this period

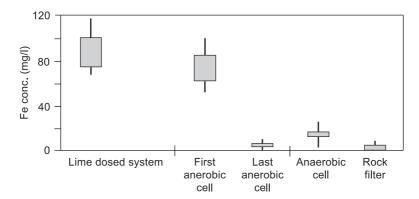


Fig. 4. Iron concentrations down the Wheal Jane Pilot Passive Treatment Plant (June-November 1996).

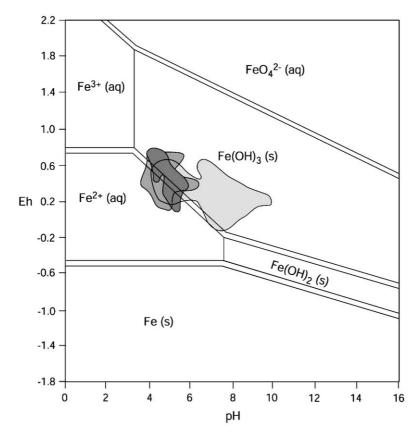


Fig. 5. Adapted Pourbaix diagram illustrating iron speciation within the three treatment systems at Wheal Jane Pilot Passive Treatment Plant.

(Fig. 6) show that although heavily depleted in the anaerobic cell, the final stages of the treatment process in the rock filter are sufficient to return the DO

concentration to levels recorded at the end of the final aerobic cell. This indicates DO reaeration is an important process in this section of the treatment plant.

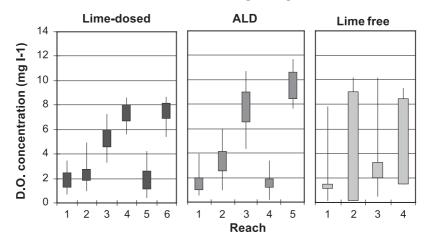


Fig. 6. Spatial variations in dissolved oxygen at Wheal Jane Pilot Passive Treatment Plant showing low initial DO, rising DO through the aerobic cells and the rock filters but low DO in the anaerobic zones (reaches 5, 4 and 3 in the three systems).

5. Discussion of detailed chemical processes

The addition of lime to the mine water can rapidly raise the pH to high levels and simultaneously precipitate all iron, manganese and base metals from solution. Indeed this is the basis of the present 'active' treatment of the bulk of the mine water from Wheal Jane, as discussed above. At pH<5 chemical precipitation is relatively slow and yet substantial removal of Fe(II) from solution at pH values of 3.5-4.5 was observed in all three treatment systems. The oxidation of Fe(II) and subsequent hydrolysis of Fe(III) to form the ochre deposits is associated with the production of acidity. These reactions result in a lowering of the pH of the mine water as Fe(II) is oxidised. The speed and extent of oxidation within the aerobic cells suggests a microbiological mechanism. Laboratory studies showed that the bulk of this activity which was associated with the sediment from the reed beds could be stopped by boiling or filtering sediment slurries which would kill or remove bacteria from the slurries respectively. Moreover, the reaction had a distinct temperature optimum of about 35 °C. This was compelling evidence for a biological mechanism of iron oxidation that was particularly effective in the pH range of 3.5-4 but activity declined as pH approached 3. The dominant iron oxidising microorganisms were shown to be a previously undescribed group of moderately acidophilic bacteria (see Hallberg and Johnson, 2004). There was little evidence for the presence of the classical extremely acidophilic iron oxidising bacteria such as Acidithiobacillus ferrooxidans presumably because as the pH fell to levels favouring their activity the concentration of Fe(II) in solution was too low to support extensive growth. Additional work has shown that the dominant moderately acidophilic bacteria within the PTP are also found in other mine waters throughout the UK.

5.1. Performance of the aerobic cells

Over the study period the flow rates of mine water to all treatments varied between 0.2 and 0.4 l s⁻¹ and the concentration of Fe(II) ranged between 5 and 90 mg l⁻¹. The lowest concentrations followed periods of wet weather. In the Lime dosing system adjustment of the pH to 4.5 minimised the precipitation of iron in the sludge channel leading from the lime dosing unit to

the first aerobic cell. Loss of iron from solution was initially rapid on discharge to the cell but the rate of oxidation soon decreased. Monthly samples taken over an annual cycle showed that, on average, 52% of the Fe(II) in the inflow was removed by the first aerobic cell (area=187 m²). The average aerial removal rate was 4 g m⁻² day⁻¹, which is less than half of the slowest rate encountered commonly in aerobic wetlands receiving neutralised ferruginous mine waters (Younger et al., 2002). In the second aerobic cell (area=240 m²) concentrations of Fe(II) decreased further and approximately 90% of Fe(II) in the inflow was removed over the two cells. A residual concentration of Fe(II) usually remained in solution. The ochre in cell 1 had a high water content (approximately 50%) and was very light flocculent prone to resuspension.

In the Anoxic lime drain (ALD) system, the first aerobic cell of the ALD system has an area of 224 m² and, on average, 90% of the Fe(II) present in the inflow was precipitated over the cell. The monthly average aerial removal rate was 7.6 g m⁻² day⁻¹ almost double the removal by the first cell of the LD system. The ochre precipitates were closely associated with the extensive plant root systems and there was some evidence that plant biomass was so high that preferential flow lines of the mine water were developing in the cell. These 'flow lines' did not appear to affect performance but did have the potential to decrease the residence time of mine water in the cell. In the LimeFree (LF) system, the aerobic cells in this scheme were larger, presumably due to anticipated slower reaction times, than in the other systems with each cell having an area of 8175 m². However, iron oxidation and subsequent precipitation was very rapid with a monthly average of 77% of Fe in the inflow being removed in only one quarter of the area of the first cell (aerial removal rate 5.8 g m⁻² day⁻¹). A typical distribution of Fe(II) with distance along the cell is shown in Fig. 6. The decrease in reaction rate was almost certainly due to the fall in pH associated with hydrolysis of Fe(III). The precipitated iron deposits were consolidated in nature with a water content of approximately 15%. The oxidation of Fe(II) to Fe(III) will catalyse the oxidation of As(III) to As(V). Compared to Fe the concentration of As in the mine water was relatively low and therefore a small amount of iron precipitation would lead to the removal of a substantial portion of As from solution. Indeed, As was removed to below detection levels within the first aerobic cell of all systems and accumulated in the ochre deposits to concentrations approaching 0.1% (w/w).

5.2. Performance of anaerobic cells

The anaerobic cells (or compost bioreactors) are underground chambers filled with a mixture of straw, sawdust and manure. The straw and sawdust provided solid substrate support and also served as a long-term source of organic carbon for the sulphate reducing bacteria (SRB). The manure was added as an immediate source of organic carbon and inoculum for SRB. Regular monitoring of the effluent from these bioreactors over 2 years revealed they were not functioning as expected. The effluent contained more soluble iron, as Fe(II), than the influent. It was confirmed that solid suspended Fe(III) was entering the reactors from the aerobic cells. This iron would not only affect the redox potential within the reactor but could also be reduced to Fe(II) and appear as soluble iron in the effluent thus reversing the process of iron oxidation from the aerobic cells. Moreover, the anaerobic processes did not increase alkalinity to a great extent and the pH of the effluents rarely exceeded 5.5. At such low pH some metal sulphides are not stable and hence removal of residual iron and other base metals was poor. The reason for low anaerobic activity was not clear although experience with the LF compost bioreactor may have provided some clues. Fracture of the main mine water feed-pipe to the LF system in 2001 led to its shutdown for almost 12 months. To protect the compost bioreactor from wash-out by sulphate deficient rainwater, the reactor was sealed. When the flow of mine water resumed a marked difference in the chemistry of the effluent was observed. After four months of continuous operation following the shutdown, the pH of the effluent was consistently between 6 and 7 and concentrations of sulphide, Zn and Fe were below levels of detection. Moreover, the numbers of sulphate reducing bacteria (SRB) detected in the effluent (cells being washed out by the flow) were 100 times greater than numbers detected in the effluent from LD and ALD reactors. It appears that the long shutdown period had somehow conditioned the bioreactor to operate as predicted. Observations

suggest an enrichment of SRB that were better adapted to growth and activity under conditions within the bioreactors in the presence of effluent from the aerobic cells. The SRB in cattle manure would be better adapted to conditions within the rumen rather than those of acidic mine water and the routine function of the compost bioreactors at the PPTP required enrichment of suitable SRB.

5.3. Performance of the rock filters

The rock filters are a series of 10 shallow pools containing small granite pebbles to encourage colonisation by algae. In theory, the consumption of CO₂ during oxygenic photosynthesis would raise the pH of the water and at pH values in excess of 8 the oxidation and precipitation of manganese would be favoured. The low pH of the effluent from the anaerobic cell did little to favour extensive growth of algae. Moreover, the oxidation of Fe(II) and free sulphide in the aerobic environment of the shallow pools would cause lower pH conditions. These systems were only partially effective for removal of manganese. In the initial phase of this study the rock filters of the LF system behaved as in the LD and ALD systems. However, following the shutdown of the LF system the average pH of the inflow to the LF rock filters was approximately neutral. This pH (and the essential nutrients that would leach from the organic wastes in the compost bioreactors) was more favourable for production of algae. Indeed following the 'conditioning' shutdown there was a correlation between high pH and manganese removal (concentrations of Mn as low as 0.5 mg/l) throughout the rock pools. The observations showed little effect of seasonality but it should be expected that algal productivity would be lower in winter due to shorter daylight hours and lower temperatures.

6. Operational considerations

A number of problems were identified with the existing configuration of the PPTP:

(i) The purpose of the pre-ALD cell was to ensure that the mine water was anaerobic on entering the ALD. If oxygen was present, the production of Fe(III) would cause 'armouring' of the limestone, prevent contact between limestone and mine water, and prevent dissolution to increase pH. This worked very efficiently. However, the mine water contained up to 100 mg l⁻¹ Al and as the pH increased within the ALD this was selectively precipitated as a gel and blocked flow within the drain. This happened very frequently during the study and eventually the anoxic limestone drain system was abandoned. The mine water flow was redirected to a second lime dosing unit and lime was added to adjust the pH of the inflowing mine water to values similar to that during operation of the ALD. At this time the plant growth in the aerobic cells was sufficiently well established so it was not dependent on the supply of nutrients from the ALD. It was considered that conversion to a second lime dosed system would have little effect on the performance of the aerobic cells.

- (ii) The area of the aerobic cell was far in excess of that required to remove the iron at the operational flow rates. The present observations show that to lower the iron concentration in the inflow by 90% required only 10%, 20% and 40% of the total area of aerobic cell in the LF, ALD and LD systems, respectively. Clearly there is more capacity for iron precipitation within the present system. However, this capacity could not be filled by simply increasing the flow rate (and therefore iron load) to the system. As previously noted, the hydrolysis of Fe(III) rapidly lowered the pH to levels limiting the activity of the moderate acidophilic bacteria. Increasing the load of iron to the system would only result in higher concentrations of iron when activity became inhibited. This could be overcome by distributing the flow to different areas of the aerobic cell or introducing alkalinity producing systems at intervals along the cells.
- (iii) The failure of the anaerobic cells (compost bioreactors) in the LD and ALD systems to function as predicted was surprising. The low pH of the inflow to these cells would be a factor but ultimately anaerobic activity should produce alkalinity and raise the pH. Closing the reactor in the LF system for a period of months

- appeared to change the operating conditions which could be related to the enrichment of active populations of SRB. These must have also been present within the LD and ALD systems but the continuously flowing mine water prevented them developing to suitable numbers to influence the chemistry of the anaerobic cells.
- (iv) The successful removal of Mn by the rock filters in the LF system was related to the high pH of the effluent from a correctly functioning compost bioreactor. The poor performance of the rock filters in the LD and ALD systems was almost certainly due to the low pH of the effluent from the anaerobic cells in these systems.
- (v) The LF system was the only truly passive treatment system within this project. The effective removal of iron, successful functioning of the anaerobic cell and subsequent removal of Mn in the rock filters demonstrates that within the PPTP this system has the most potential for development as a treatment option.

7. Conclusions

Remediation of the highly acidic and transition metal polluted aggressive mine water discharge from the Wheal Jane Mine by the Wheal Jane Passive Treatment Plant required that all the system components work as predicted. Clearly this was not the case and this research programme has gone some way to explain where theoretical concepts were breaking down. However, the programme also clearly demonstrated the potential for natural attenuation of acid mine drainage, particularly iron oxidation, by microbial populations, and the subsequent removal of key toxic metals. The lime free (LF) system was passive and, at least over the period of this study, was also sustainable. The present design of the lime free PPTP system has the capacity to efficiently precipitate iron from a greater volume of mine water. Indeed it is estimated that the flow rate could be increased by a factor of 10 (Hall et al., 2004) provided that either (i) the increased flow is distributed to different areas of the aerobic cells, or (ii) a means to increase the pH of the mine water is introduced at regular intervals in the aerobic cells. However, it cannot be predicted if the

anaerobic treatment cells or rock filters could also maintain performance with the increased flow rate through the plant. The Wheal Jane Passive Treatment Plant provides the only experimental facility of its kind and only by modification of the existing flow regimes can alternative treatment options be put to the test.

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