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CSB 4

(March 2004)

case study bulletin

CL:AIRE case study bulletins provide a source of information on the characterisation and remediation of specific sites in the UK. This case study bulletin describes the active and passive treatment of mine water at Wheal Jane Tin Mine in Cornwall.

Definitions of words written in bold type may be found in the Glossary of Terms within the Publications section of the CL:AIRE website at http://www.claire.co.uk

Mine Water Treatment at Wheal Jane Tin Mine, Cornwall

1. INTRODUCTION

The Wheal Jane tin mine is located within the Carnon River valley in Cornwall (see Figure 1), approximately 7 miles southwest of the town of Truro. It operated as a tin mine from at least the early 18th century until 1991 when it was closed and abandoned under the Mines and Quarries Act.

Closure of the mine resulted in the termination of mine dewatering operations and a rise in water levels. In January 1992, there was a sudden and uncontrolled release of highly contaminated **mine water** into the Carnon River and Fal estuary. **Oxidation** of the iron rich mine water generated orange-brown discolouration over a downstream drainage area of more than 6.5 x 10^6 m^2 including parts of Falmouth Docks. The highly conspicuous nature of the contaminated plume led to the event attracting worldwide media attention (Brown et al., 2002).

Emergency pumping and treatment from the Wheal Jane **adit** to the **mine tailings area** was immediately carried out by the owners Carnon Consolidated Ltd. Environmental impact and remedial studies were initiated in 1994 by Knight Piésold UK, now Scott Wilson Piésold, on behalf of the National Rivers Authority (NRA), now the Environment Agency (EA), for both **active** and **passive treatment systems**.

In 1994 a pilot passive treatment system (PPTP) was constructed to carry out research into possible long term passive remedial solutions at the site. An active treatment system was constructed and became operational in 2000.

The purpose of this Case Study Bulletin is to describe the construction and performance of both the active and passive treatment systems at the site with special emphasis on the passive system.

2. ACTIVE TREATMENT SYSTEM

The active treatment system was designed to treat all of the mine water flow. Pilot studies concluded that treatment using oxidation and **chemical neutralisation** would be the most cost effective design. In 1999 Hyder (now United Utilities Industrial Ltd) won a contract from the Environment Agency, using technology provided by Unipure Environmental Inc, to design and build the treatment plant and operate it for a period of ten years. The plant was commissioned in 2000.

A **high density sludge** (HDS) treatment system was the preferred design and this is described more fully by Coulton et al., (2003) and also in Brown et al., (2002). Treatment consists of three stages:

- mixing of mine water and **sludge**
- **aeration**
- **clarifying**

Water from the mine shaft is pumped using 6 pumps each with a pumping capacity of 55 l/s (total capacity 330 l/s) to the treatment plant. Water from the **toe drain**, **supernatant** from the tailings pond and effluent from the pilot passive treatment plant are also treated by the system.

Mine water is pumped to the first stage treatment tank where it is mixed with re-circulated sludge using a water to sludge ratio between 25:1 and 50:1. The pH is raised to approximately 8.5. The fluid flows into the second stage aeration tank where a 5 % lime slurry is added. 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 pH in this stage is 9.25. The fluid is piped by gravity and dosed with a **polymer flocculant** at a rate of 2.5 g/l. 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 re-circulated to the first stage mixing tank. The sludge in the holding tank contains between 30 % - 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. A schematic diagram of the process is shown in Figure 2.

Figure 1: Aerial view of the Wheal Jane Mine complex. Left background shows tailings pond. The pilot passive treatment plant (PPTP) is shown occupying the Carnon River valley in the foreground left to right. Source: Scott Wilson Piésold

The **design capacity** for the system is 440 l/s and a discharge consent has been approved for 350 l/s of treated water to the Carnon River. **Residence time** within the treatment system is approximately 30 minutes in the first and second stage tanks, and 25 minutes in the clarifiers. The system treated approximately 12,310,000 m^3 of water during the first 22 months of operation at an average rate of 200 l/s. It removed approximately 3,200 tonnes of metal at a removal efficiency of 99.2 %.

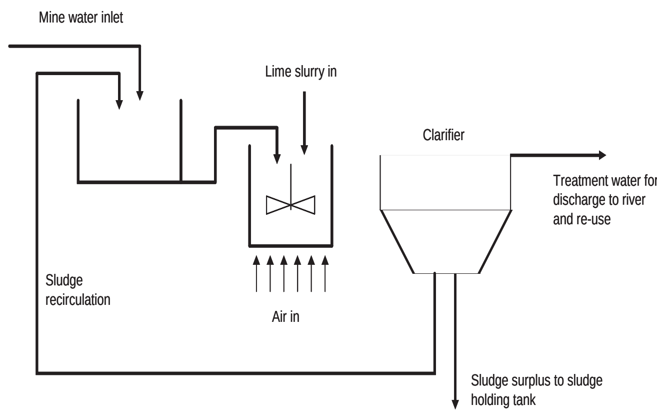

Figure 2: Schematic active treatment system (adapted from Brown et al., 2002).

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Table 1: Average composition of the mine water from the Wheal Jane tin mine (1995-1998).

Parameter	Value
Fe	150 mg/l
Zn	2.5 mg/l
As	2.5 mg/l
Cd	0.12 mg/l
Cu	0.5 mg/l
Mn	20 mg/l
Al	50 mg/l
SO_4^{2-}	300 mg/l
pH	3.9

3. PASSIVE TREATMENT SYSTEM

3.1 Pilot Passive Treatment Plant (PPTP) Design

The complexity of the Wheal Jane mine water chemistry (average composition shown in Table 1 using data from 1995-1998) required a combination of the (then) available passive treatment options to solve the problem. The PPTP consisted of three separate systems each containing the following principal treatment components:-

- 5 **artificial reed beds** (**aerobic cells**) to facilitate precipitation of iron as ferric hydroxide/oxyhydroxide (**ochre**) with arsenic removal by co-precipitation onto the iron precipitate
- an **anaerobic cell** to encourage bacterial reduction of sulphate, and hence increase **alkalinity** (and pH), and facilitate precipitation of metals (Cu, Zn, Cd and any remaining Fe) as metal sulphides
- shallow **rock filters** to promote the growth of algae and consequently raise the pH of the water and precipitate manganese

The three systems differed in the pre-treatment used to increase the pH of the influent mine water as follows:-

- **Lime dosing** to a pH of 4.5 (LD system)
- Passage through an **anoxic (without oxygen) limestone drain**, after initial passage through a small anoxic cell (ALD system)
- No treatment (lime free) so raw mine water flowed directly to the aerobic cells (LF system)

The PPTP has a maximum design flow capacity of 0.6 l/s and can receive short term flows of up to 1.9 l/s (Brown et al., 2002). This represents less than 1 % of the total mine water discharge from the Wheal Jane mine.

An aerial view showing the layout of the PPTP is shown in Figure 1 with a schematic diagram of the three systems shown in Figure 3. A summary report on the performance of the PPTP was published in 1998 reporting gross chemical changes throughout the PPTP. This suggested that water quality objectives for discharge of the effluent to the Carnon River were regularly exceeded and the PPTP was showing inconsistent performance. In 1999, the Mining Industry Research Organisation (MIRO) coordinated a research consortium, funded by the DTI/LINK scheme, to investigate the chemical and microbiological processes throughout the PPTP. Research was conducted by Universities of Bangor and Reading, Imperial College (also funded by Environment Agency), Camborne School of Mines and Centre for Ecology and Hydrology (CEH), with support from several industrial partners. The concept of using artificial or natural wetlands, and indeed ALD systems, is not new but rarely have they been used to treat such an aggressive mine water discharge. Understanding of the fundamental underlying processes within this system would not only show where the system components were breaking down but also aid future design and optimisation of alternative passive treatment systems.

3.2 Colonisation by Introduced Plant Species

The **base substrate** for the artificial reed beds was fine mine tailings and all the cells were planted with a 50:50 mixture of *Phragmites* and *Typha*. In addition the LD and ALD cells were planted with approximately 100 *Scirpus*. The LD and ALD systems provided alternative ways of increasing the pH of the influent mine water and it was considered that the bullrush would establish more readily at the higher pH.

However, plant growth in the LD and LF systems was very poor (see Figures 4 and 5) probably due to the low pH (pH=4.5 and 3.9 respectively) and the low nutrient content of the substrate and inflowing mine water. In contrast the growth in the ALD system was extensive, presumably due to the higher pH (pH=6) of the effluent in addition to essential nutrients leaching from the manure within the pre-ALD cell. Indeed the aerobic cells of the ALD became colonised by other submerged wetland plants, particularly the floating club rush, to densities that could have a detrimental effect on the treatment process. It is unlikely that the introduced plants in the LD and LF systems would contribute directly to the treatment process other than providing a limited supply of nutrients for microbial populations.

3.3 Chemical / Biological Processes

The addition of lime to the mine water can rapidly raise the pH to 12 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. However, at pH values <5 chemical precipitation is very slow and yet substantial removal of Fe(II) from solution at pH values of 3.5 to 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** (see equations 1 and 2). These reactions result in a lowering of the pH of the mine water as Fe(II) is oxidised.

$$Fe^{2+} + 1/4\,O_2 + H^+ \longrightarrow Fe^{3+} + 1/2\,H_2O \qquad (1)$$

$$Fe^{3+} + 3\,H_2O \longrightarrow Fe(OH)_3 + 3\,H^+ \qquad (2)$$

These reactions are well known but the speed and extent of oxidation within the aerobic cells suggested a microbiological mechanism. Laboratory studies showed

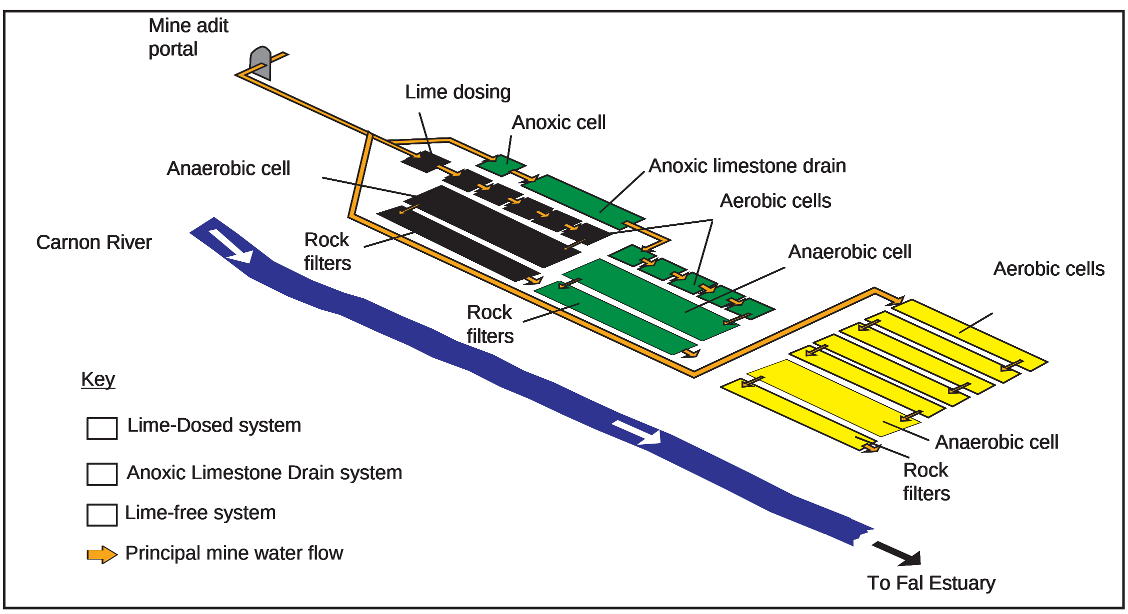

Figure 3: Schematic representation of the three systems within the pilot passive treatment system.

Figure 4: Colonisation of the lime free system aerobic cells by introduced plants. Source: G.Hall

Figure 5: Growth of the introduced reed species in the lime dosed system compared to luxuriant growth in the aerobic cells of the ALD system in the background. Source: G.Hall

that the bulk of this activity was associated with the sediment from the reed-beds and 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 ºC. 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 un-described group of moderately **acidophilic** bacteria. 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 PPTP are also found in other mine waters throughout the UK.

3.4 Performance of the Aerobic Cells

Over the study period the flow rates of mine water to all treatments varied between 0.2 l/sec and 0.4 l/sec and the concentration of Fe(II) ranged between 5 mg/l and 90 mg/l. The lower concentrations followed periods of wet weather.

3.4.1 Lime dosing (LD) 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 m^2). The average areal removal rate was 4 $gm^{-2}d^{-1}$, which is less than half of the slowest rate commonly encountered in aerobic wetlands receiving neutralised ferruginous mine waters (Younger et al., 2002). In the second aerobic cell (area = 240 m^2) 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, flocculant and prone to **resuspension**.

3.4.2 Anoxic lime drain (ALD) system

The first aerobic cell of the ALD system has an area of 224 m^2 and, on average, 90 % of the Fe(II) present in the inflow was precipitated over the cell. The monthly average **areal removal rate** was 7.6 $gm^{-2}d^{-1}$ 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.

3.4.3 Lime free (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 817.5 m^2. 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 (areal removal rate 5.8 $gm^{-2}d^{-1}$). A typical distribution of Fe(II) with distance along the cell is shown in Figure 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 usually above 0.1 % (w/w).

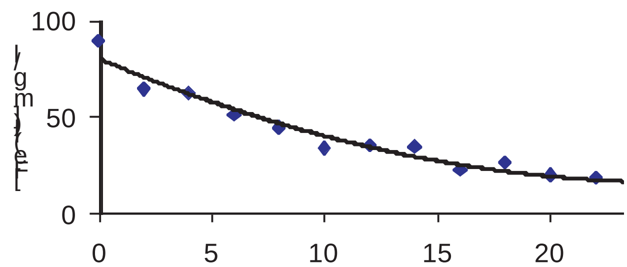

Figure 6: Typical distribution of Fe(II) concentration with distance along the first aerobic cell of the lime free system. The total length of this cell is 109m.

3.5 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.

3.5.1 LD and ALD systems

Regular monitoring of the effluent from these bioreactors over 2 years revealed they were not functioning as expected. The effluent contained more soluble iron (exclusively 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 appear to increase alkalinity to a great extent and the pH of the effluents rarely exceeded 5.5. At this 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.

3.5.2 LF system

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 4 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 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 would appear 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.

3.6 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 CO_2 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.

3.6.1 LD and ALD systems

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 not very effective for removal of manganese.

3.6.2 LF system

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 (see Figure 7). 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.

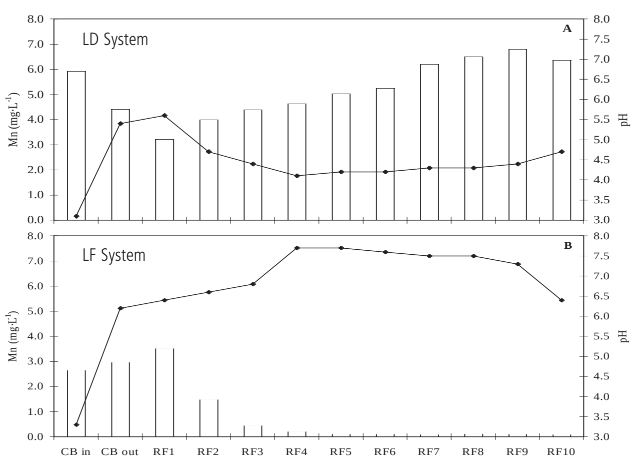

Figure 7: Manganese and pH trends in the compost bioreactor influent (CB in) and effluent (CB out) and in each of the 10 rock filter pools (RF1-RF10). The samples were taken in April, 2002, from the LD (A) and LF (B) systems. Bars show soluble manganese and the lines show pH.

3.7 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 aluminium 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 re-directed 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 existing 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.

4. CONCLUSIONS

Remediation of the aggressive mine water discharge from the Wheal Jane mine by the PPTP 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. 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 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 PPTP provides the only experimental facility of its kind in Europe (if not the world) and only by modification of the existing flow regimes can alternative treatment options be put to the test.

Acknowledgements

This bulletin was prepared by CL:AIRE staff from information provided by members of the Wheal Jane Project research consortium.

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