Introduction
Coal mining in the United Kingdom (UK) has gone through a full rise and fall cycle, output rose constantly through the 18th century reaching a zenith output around 1913. The 20th century saw a continual decline until the last deep coal mine closed in 2015. In 1994, it was estimated that 200 km of UK rivers and streams were affected by coal minewater discharge (NRA 1994).

During active coal mining, the underground workings are “dewatered” to maintain a safe working environment, and to reduce water ingress creating mostly dry conditions which prevent the mobilisation of contaminants. Once pumping ceases and the water table rebounds, pyrite is exposed to oxygen, water and bacterial catalysts, and the oxidation of pyrite is stimulated producing acid mine drainage. Ideal conditions are created in abandoned workings for the oxidation products, ferrous iron (Fe²⁺), sulfate (SO₄²⁻) and free acidity, to be dissolved and carried out of the mine as minewater discharge into the surrounding watercourses.

Minewater discharge from pyrite oxidation may have serious environmental consequences for aquatic ecosystems as it did in the Pelenna valley in the South Wales Coalfields. Following the cessation of active mining operations, the coal workings flooded and minewater discharged into the river system, Nant Gwenffrwd and Nant Blaenpelenna, tributaries of the Afon Pelenna. The two tributaries were stained orange with iron concentrations elevated for approximately 7 km downstream to the confluence with the River Afan (Edwards et al. 1997). The aquatic species were thought to be impoverished from a combination of increased acidity, toxic effects of metals and from the smothering effect of ochre on the benthic zone of the watercourse (Wiseman 2002).

In 1992, a study was initiated to establish the impact that minewater discharge was having on the environment. The recommendations from the study were to reduce iron concentrations by 95% and 50% in the Nant Gwenffrwd and Nant Blaenpelenna respectively, so that iron concentrations would be below the required 1 mg/L and the pH would be between 6-9 in the Afon Pelenna. This was expected to provide suitable conditions for recolonisation by salmonid fish (Ishemo and Whitehead 1992). It was decided that the most suitable and cost-effective remediation of the tributaries would be to passively treat the minewater discharge through constructed wetlands.
Between 1995 and 1999, a three-phase passive wetland scheme was constructed to treat five minewater discharges; this was one of the first passive minewater treatment wetlands within the UK and Europe. Different passive constructed wetland configurations were implemented based on the incoming minewater discharge.

The configurations used were considered novel as they were mainly based on work at the time in the USA of Hedin et al. (1994) and Kepler and McCleary (1994). The scheme was known as the River Pelenna Minewater Project before the Coal Authority took over management of the scheme that is now known as the Coal Authority Pelenna Minewater Treatment Sites (MWTS).

**Site Description**

The Pelenna MWTS consist of five constructed wetlands, Whitworth No.1, Garth Tonmawr and Whitworth A, B and Gwenffrwd, located near Tonmawr village, South Wales approximately 11 km northeast of Port Talbot. Tonmawr lies within the Pelenna valley through which the Nant Gwenffrwd and Nant Blaenpelenna flow into the Afon Pelenna. The Afon Pelenna is a tributary of the river Afan, which flows into the sea at Port Talbot.

The three-phase passive wetland scheme was constructed to treat minewater discharge in the Pelenna valley. This paper only discusses Whitworth No.1 and Garth Tonmawr as they have comparable constructed wetland designs and are of similar age.

**Whitworth No.1**

Whitworth No.1 was the first phase, completed in October 1995 and comprised of four parallel cells. The incoming discharge was split into each cell of which two were aerobic and two were anaerobic. The aerobic cells were expected to remove iron by oxidation and hydrolysis while iron was expected to be reduced by sulfur reducing bacteria (SRB) in the anaerobic cells. Different substrates and vegetation types were utilised for each cell; this was largely due for experimental purposes with the results used to inform the construction of phase II and III. The wetland is constructed in precast concrete with a geomembrane basal liner (SRK 1994).

The design of Whitworth No.1 changed between 2006 and 2009 to allow the cells to flow in series from cell 4 to cell 1, due to a reduction in wetland performance. Cell 1 and 4 became settlement ponds while cell 2 and 3 became aerobic wetlands as illustrated in Figure 2.
The Garth Tonmawr constructed wetland is illustrated in Figure 3 and consists of a settlement lagoon, two reducing and alkalinity producing systems (RAPS) cells and two anaerobic cells. The settlement lagoon promotes iron oxidation and hydrolysis and allows heavier particles to settle out before being further treated. The RAPS cells are anaerobic and make use of a limestone bed overlain with substrate. The water moves through the substrate, which allows some precipitation of metals before the limestone buffers the acidity of the minewater.

Methods

Water quality data analysis
Natural Resources Wales (NRW) provided long-term water sampling data for the Pelenna MWTS. This included data from river samples up and downstream, and the inlet and outlet of the wetlands.

Using the statistical programme R, the data was standardised by making box and whisker plots and removing any outliers in the data before processing with Excel. The data was reduced to 5 years prior to construction of each wetland until January 2017. Access was used to align the months of the long-term data at each monitoring station to plot long-term trends and determine the removal rate in and out of each wetland.

PHREEQC was used to determine the redox potential (Eh) of the minewater at the inlets and outlets. The initial run produced a list of possible species present within the water and an estimated concentration of each species that included Fe$^{3+}$ and Fe$^{2+}$, which were subsequently used in the redox calculations to determine the Eh (Appelo and Postma 2006).

Ochre sampling and analysis
Three ochre samples were collected from the four cells at Whitworth No.1. The samples were prepared by drying and crushing before elemental composition was analysed using an Olympus Innov-X X-ray Fluorescence (XRF) analyser.

The samples were also acid leached and the leachate analysed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the mobile elements released from the ochre under acidic conditions.

Results and Discussion

Performance Assessment
When the Whitworth No.1 cells operated in parallel, there was an apparent increase in acidity and a decrease in the sulfate removal efficiency, which may be explained by a reduction in SRB due to unfavourable condi-
SRB occur under anaerobic conditions at medium to high pH (Bass Becking et al. 1960). Whitworth No.1 made use of a flow distribution chamber to distribute the incoming minewater to each of the four cells; this likely increased the acidity at the inlet. It is thought that the decrease in pH at the inlet and the decreased performance of the anaerobic cells was the reason for the change in design to series cells.

The dissolved iron removal rate has remained high and variable throughout the monitoring period (Table 1) although the total iron removal rate has decreased to 76% in the current period. The iron Eh-pH diagram created for Whitworth No.1 indicates that the conditions are suitable for iron oxidation (Bass Becking et al. 1960), with Fe(OH)₃ deposition. The iron is susceptible to spikes in acidity within the wetland and according to the Eh-pH diagram this would create conditions for the Fe(OH)₃ to be reduced to Fe²⁺. From the 2010-2014 period, the wetland appears to be a source of sulfate rather than a sink.

This decrease in performance at Whitworth No.1 may be from a combination of factors. Firstly, reduced hydraulic retention due to the system short-circuiting through preferential flow paths potentially created during blockages or periods of high rainfall.

Secondly, the lack of specific oxidation and reduction conditions needed to remove iron. The change in Cell 2 from anaerobic to aerobic may have caused the pyrite formed during bacterial sulfate reduction, to be oxidised. This requires ferric iron to be available, which may be the case as not all the ferrous iron will be converted through cells 4 and 3. This is supported by the XRF results, which show that cell 2 is only retaining 28% iron within the ochre while cells 4 and 3 are retaining above 50% and cell 4 is retaining above 40%. The ICP-MS results are an indication of what would be released from the ochre under acidic conditions. This also supports the above suggestion as 7.1 mg/g was released from the sediment in cell 2 while 6.9, 6.6 and 6.5 mg/g were released from cells 3, 4 and 1, respectively.

The difference in filtered and total iron removal also supports this suggestion as the iron particulates may be released from cell 2 and are not fully settling out in cell 1 before the discharge is released into the Nant Blaenpeleenna. These reactions also explain the increase in sulfate in the wetland as sulfate is released during pyrite oxidation and during release of previously bound metal sulfides.

It should be noted that aluminium and manganese concentrations are low but appear to be sufficiently removed from the wetland. The removal rate of both constituents increased with the change in design, which may be due to an increased retention time. Aluminium precipitation occurs around pH 5 and under the net acidic conditions aluminium oxidation is expected (Hedin et al. 1994). This is supported by the Eh-pH diagram where aluminium is in the oxidised form Al(OH)₃. According to the Eh-pH diagram, manganese is in Mn²⁺ form suggesting that the manganese is being precipitated as metal sulfides rather than oxidised. Oxidation of manganese occurs at around pH 8 (Stumm and Morgan 1981).

The discharge from the outlet at Whitworth No.1 has been within the pH 6-9 range required for the Afon Pelenna. The dissolved iron concentrations represented by the filtered iron was supposed to be reduced by 95% in the Nant Gwenffrwrd to be below 1 mg/L in the Afon Pelenna. This means that the filtered iron concentrations at the outlet should be approximately 1.98 mg/L; this has been achieved in the last two years but not over the 22-year life, with an average of 2.34 mg/L. The dissolved iron would therefore be expected to be around 1 mg/L in the Afon Pelenna due to dilution in the Nant Blaenpeleenna.

At Garth Tonmawr, iron oxidation and hydrolysis are occurring as designed (Table 2), as evidenced by surface ochre on the first three cells. The dissolved iron removal rates show a small decrease over time to about 90% in the current period with oxidising conditions.

Garth Tonmawr has a net-acidic mine-water discharge and so it was decided to implement RAPS cells within the wetland. The RAPS cells seem to have decreased in efficiency quite quickly as the acidity in the discharge is progressively less buffered in the wetland.
Table 1. Summary of the long-term data at Whitworth No.1

<table>
<thead>
<tr>
<th>Date</th>
<th>Flow (m³/s)</th>
<th>pH</th>
<th>Total Fe (mg/L)</th>
<th>Filt Fe (mg/L)</th>
<th>Filt Mn (mg/L)</th>
<th>Filt Al (mg/L)</th>
<th>SO₄ (mg/L)</th>
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<tr>
<td>1995-1999</td>
<td>Inlet: 0.003</td>
<td>6.3</td>
<td>22.97</td>
<td>20.99</td>
<td>1.97</td>
<td>0.065</td>
<td>346</td>
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<td>Outlet: 6</td>
<td>7.0</td>
<td>3.95</td>
<td>3.23</td>
<td>1.08</td>
<td>0.010</td>
<td>298</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
<td></td>
<td>83</td>
<td>85</td>
<td>45</td>
<td>85</td>
<td>14</td>
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<tr>
<td>2000-2004</td>
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<td>6.3</td>
<td>2.38</td>
<td>2.21</td>
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<td>6.0</td>
<td>24.27</td>
<td>22.13</td>
<td>1.88</td>
<td>0.091</td>
<td>334</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
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<td>90</td>
<td>90</td>
<td>54</td>
<td>83</td>
<td>6</td>
</tr>
<tr>
<td>2005-2009</td>
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<td>5.8</td>
<td>25.63</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>332</td>
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<td></td>
<td>Outlet: 7</td>
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<td>0.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>274</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
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<td>97</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>2010-2014</td>
<td>Inlet: 0.005</td>
<td>6.2</td>
<td>19.40</td>
<td>17.51</td>
<td>1.65</td>
<td>0.098</td>
<td>271</td>
</tr>
<tr>
<td></td>
<td>Outlet: 7</td>
<td>7.0</td>
<td>2.40</td>
<td>2.08</td>
<td>0.63</td>
<td>0.011</td>
<td>273</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
<td></td>
<td>88</td>
<td>88</td>
<td>62</td>
<td>88</td>
<td>-0.6</td>
</tr>
<tr>
<td>2015-Present</td>
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<td>6.2</td>
<td>19.32</td>
<td>18.55</td>
<td>1.72</td>
<td>0.116</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
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<td>90</td>
<td>61</td>
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<td>2.34</td>
<td>0.81</td>
<td>0.012</td>
<td>288</td>
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<tr>
<td></td>
<td>Removal Rate (%)</td>
<td></td>
<td>86.8</td>
<td>88.3</td>
<td>55.5</td>
<td>86.8</td>
<td>7.1</td>
</tr>
</tbody>
</table>

The decreased performance in the RAPS cells may be due to changed water levels affecting flow through the substrate and limestone beds. The overflow means that some water is bypassing the cell and will not be buffered by alkalinity.

The performance of the wetland has still been maintained, which may be due to the increase in pH at the Garth Tonmawr discharge to above pH 6, which is suitable for microbiological catalysts to increase iron oxidation and buffer the pH (Bass Becking et al. 1960).

The sulfate removal rates in Garth Tonmawr have been poor because conditions to promote sulfate reduction were not implemented during the construction of the wetland. Aluminium concentrations of the discharge are low, but the removal rate has remained high (85%) even though it has decreased over time, this may be due to a reduced hydraulic retention time. The manganese removal rate is low due to poor oxidising conditions in the wetland. Metal sulfides are unlikely to precipitate out of the water as the conditions do not favour SRB and therefore the manganese would not be expected to coprecipitate to manganese sulfide.

The discharge from the outlet at Garth Tonmawr has been within the pH 6-9 range required in the Afon Pelenna. The dissolved iron concentration is required to be reduced by 50% in the Nant Blaenpelenna to reach the 1 mg/L standard in the Afon Pelenna; this would require a dissolved iron concentration of 14.5 mg/L, which has been consistently reached over each 5-year period.

Effect of wetland design on performance

Both wetlands had high iron removal rates and a similar capacity to buffer acidity indicating that both parallel and series cells can perform well if designed correctly and maintained. Whitworth No.1 showed an initial increase in performance when the wetland design changed to operate in series, this may be due to an increased practical hydraulic retention time, which allows for further chemical and biological processes to take place.

Wiseman (2002) showed that the aerobic cells were performing better than the anaerobic cells at Whitworth No.1. Anaerobic cells are more sensitive to fluctuations in water level from blockages than aerobic cells because the water will flow under higher pressure and may move to the surface of the cell or create openings in the substrate which are likely to become preferential flow paths or alternatively, the cell may completely dry up affecting the microbes in the cell. The limiting factor for anaerobic cells will be carbon if the
anaerobic and redox conditions are preserved to support SRB while the limiting factor for the aerobic cell appears to be space rather than the cell becoming exhausted.

The change in design at Whitworth No.1 has altered the anaerobic cell to an aerobic cell. This has changed the cell from reducing conditions to oxidising conditions and consequently there is evidence for pyrite oxidation and release of iron sulfides once sorbed in the cell. Cell 4, which was an anaerobic bed was cleared of substrate and is now a settlement lagoon which appears to be promoting iron oxidation and hydrolysis as ochre is floating on the surface.

**Conclusions**

Even though these wetlands are not performing as designed they are still removing the dissolved iron and buffering the pH to suitable concentrations. This indicates that these wetlands are resilient to change and that they may be somewhat over designed. It appears that more simplistic designs would have produced similar results and that the more complex the cell configuration the less likely they are to last the design life. This is mostly due to higher maintenance requirement for more complex cells. It is therefore concluded that regular maintenance is essential for efficient performance.

**Acknowledgements**

I thank the Commonwealth Scholarship Commission, which funded my Cardiff University Master’s thesis on which the paper is based. In addition, I thank the Coal Authority and Severn Trent Services for allowing me to access and collect samples from the Coal Authority Pelenna Minewater Treatment Sites and the Natural Resources Wales for providing the long-term water database. A special thank you to Peter Brabham, Tim Jones and Rob Bowell for their supervision of my thesis and for their contribution to the paper.

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