The potential for semi-passive mine water treatment by CO_2 stripping at Ynysarwed, S. Wales

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Abstract In the Spring the of 1993 the Ynysarwed mine water discharge in South Wales became a serious problem affecting a 12km length of the Neath Canal. As a result of the severity of the discharge, pH 3.5, 400mg/L Fe, a combination of active and passive treatment steps were installed. Chemical dosing was stopped in 2009 as conditions had improved pH>5, 100mg/L Fe. The existing mine water treatment scheme is in the process of being reviewed. Different treatment options are being considered including stripping dissolved CO_2 from the mine water, thereby maintaining mildly acidic pH and accelerating Fe(II) oxidation rates.

Key Words oxidation rate, CO_2 degassing, aeration, active treatment.

Introduction
What's next for the Ynysarwed Minewater discharge? After many years of low flow the Ynysarwed minewater discharge near Neath in South Wales became a serious problem in the Spring of 1993 affecting a 12km length of the Neath Canal. The severity of this discharge (400mg/L Fe, pH 3.5) and sensitivity of the affected water body resulted in the deployment of a combination of active and passive treatment steps, comprising mechanical aeration with calcium/magnesium hydroxide addition and flocculent dosing/Lamellae plate clarification followed by a constructed wetland to provide final polishing. It was envisaged that active treatment would only be required for a decade at which point the iron concentration would be sufficiently low as to be treatable by passive means alone. Chemical dosing was stopped in 2009 with all water being discharged directly into the reed beds. Despite the reduced influent iron concentration of <100mg/L and pH>5 the site sometimes struggles to meet target effluent iron concentrations. Thus the existing mine water treatment scheme is in the process of being reviewed. Different treatment options are being considered including innovative approaches. This paper provides a snapshot of current system performance and demonstrates the potential for treating this water by stripping dissolved CO_2 stabilising the pH in the mildly acidic region and thereby increasing Fe(II) oxidation rates.

Methods
CO2 degassing experiments
Fresh minewater was collected from the adit and returned to the lab for degassing experiments. The pH, temperature, and dissolved oxygen (DO) were measured (only selected data presented here) using two hand held Hanna combination meters HI-9828 while 8l of the water was aerated and degassed using a compressed air line. Both meters were calibrated according to manufacturers instructions prior to experimentation. Measurements were logged every 10 seconds. Two 15ml samples of the mine water were taken at the beginning and end of the experiment and acidified with 4 drops of 20% nitric acid. One of the samples was passed through a 0.8/0.2μm Acrodisc PF syringe filter prior to acidification to remove Fe(III) particulates and was taken to be representative of dissolved Fe(II) concentration. All Fe samples were then analysed by ICP-OES. Acidity and Alkalinity were determined using Hach digital titrators with cartridges containing 1.6N NaOH and H_2SO_4 respectively. Acidity titrations were carried out to an end point of pH 10.4 to determine total acidity as described by Stumm and Morgan (1996). This end point was chosen as a pH of 10.4 ensured that all Fe(II) was oxidized on the timescale of the titration and so a true comparison of the acidity generated at the beginning and end of the experiment could be made. Alkalinity titrations were carried out using a bromcresol green methyl red indicator and were titrated until the colour change from green to pink was observed.

Site survey

A survey was conducted of the reed beds and distribution channels at the Ynysarwed site. Dissolved oxygen (DO), pH, and conductivity were determined using two Hanna HI-9828 multi-parameter data logging probes which were deployed in unison, and programmed to log a reading every 10 seconds. After sampling for 10—15 minutes at each point, logging was discontinued and average values across the time period determined. On the day that the site survey was carried out 0.6 L/sraw mine water was being treated by a pilot scale plant for the production of high density sludge (HDS) before being recirculated into the main influent stream to the reed beds. Blocks containing flocculent and magnesium hydroxide were also being added periodically at the distribution weir just ahead of the reed beds. Acidity, alkalinity and iron concentrations were determined in the same way as for the CO_2 degassing experiments.

Results and Discussion

A schematic outline of the passive part of the Ynysarwed treatment scheme is shown in Figure 1. The influent water is pumped from an adit 0.5km to the North East of the site. 0.6L/s of the flow is then diverted through the HDS plant before being returned to the bulk flow and pumped into a distribution chamber where the flow splits, with half going through the smaller wetland (a) to the left and half through the larger wetland (b) to the right. The pump transferring the water from the adit to the wetland is cycled on and off throughout the day with peaks in flow of 15—16 L/s through each of the wetlands giving an average flow of 8.4 L/s (16.8 L/s total).

Figure 2 shows changes in concentration of Fe(II) and Fe(III) across the site. The initial sample was taken at point (1) as the water emerges from the adit. The drop in total iron between the adit (1) and the start of the wetlands (2) and (5) can be accounted for by the partial diversion of 0.6 L/s through the HDS pilot plant and ochre accretion in the transfer pipe. In the HDS plant the water is aerated and the pH increased to accelerate iron oxidation before being returned to the main pipe. This also accounts for the increase in pH between the adit and sample points (2) and (5).

Contrary to initial expectations total iron removal is higher across the smaller wetland than across the larger one. Historic data from the site shows that this is consistently the case, though the reasons for this are not clear. One possible explanation would be better hydraulics e.g. less short cutting in the small wetland.

Table 1 shows changes in pH, acidity and alkalinity across the site. It can be seen that large changes in alkalinity correlate with large changes in acidity. This is to be expected because as iron oxidises the acidity generated is consumed by the available alkalinity resulting in an overall reduction of both. In addition to this CO_2 degassing across the site will also account for a proportion of the reduction in acidity.
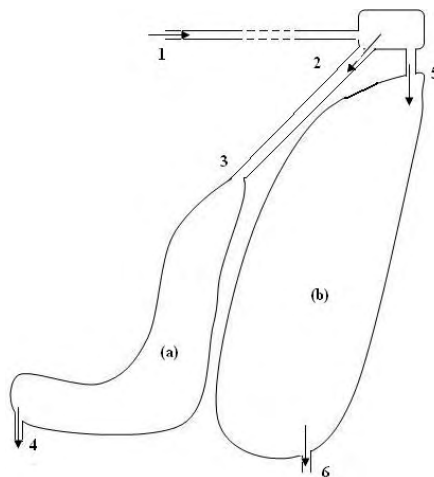

Figure 1 Schematic outline of Ynysarwed wetlands. Small lagoon (a) 3080m², Large lagoon (b) 6800m.²HDS plant located between sample points 1 and 2
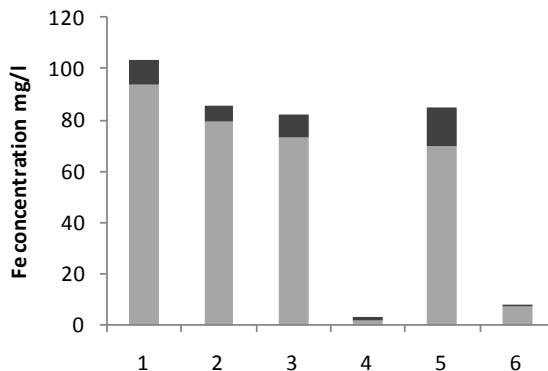
Figure 2 Variation in Fe concentration across the site, Fe(II) light gray, Fe(III) dark grey

Table 1 Comparison of total iron concentration, pH and alkalinity (mg/L CaCO₃ equivalent) across the site

Survey point	Total Fe (mg/l)	pH	Alkalinity	Acidity
1	103.5	5.77	132	400
2	85.4	6.32	119	321
3	82.2	6.59	109	319
4	3.0	6.64	11.0	84
5	84.5	6.60	139	334
6	8.1	6.28	17.5	102

Numerous definitions of alkalinity and acidity have been suggested by a variety of authors (Kirby and Cravotta 2005 and references therein) and are applied depending on the pH of the water being tested and the end usage for which the data is required. Decisions taken about whether or not to treat a minewater discharge actively or passively are often based on calculations of net acidity or net alkalinity as defined by (Hedin et al 1994) where:

Net acidity (meq/l) = Total permanent(metal + proton) acidity – total alkalinity

In these cases, acidity is generally measured by titration in the field and so has considerable contribution from dissolved CO_2 which cannot be considered to be permanent acidity (Kirby et al. 2009). A number of recent publications have highlighted the importance of this difference in accurately determining the potential of a minewater to be treated without chemical dosing including McAllan et al (2009).

Figure 3 shows the change in pH of the mine water over a 20h period with continuous aeration. Previous experiments conducted by the authors suggest that the majority of oxidation takes place within the first 2h with dissolved CO_2 dropping from 0.286 to 0.0142mg/L (modelled using PHREEQCi (Parkhurst and Apello 1999) with the phreeq.dat database) over that time. Both the acidity and alkalinity decreased as expected from 400 to 51, and 132 to 7 respectively. The pH dropped from an initial value of 5.78 to 5.72 and Fe(II) dropped from 93.7 to 2.79.

The magnitude of the reduction in Fe(II) over the timescale of this reaction is surprising given the pH conditions. The half life for homogeneous Fe(II) oxidation in a well aerated solution can be calculated using published rate constants to be of the order of days at pH 5.8. The most likely explanation for the observed oxidation rate is accelerated oxidation via the heterogeneous mechanism with Fe(II) adsorbing onto the surface of the newly formed hydrous ferric oxide (HFO) precipitates. This was an unexpected outcome given the results of Sung and Morgan (1980) who stated that autocatalytic iron oxidation is not important below pH 7.
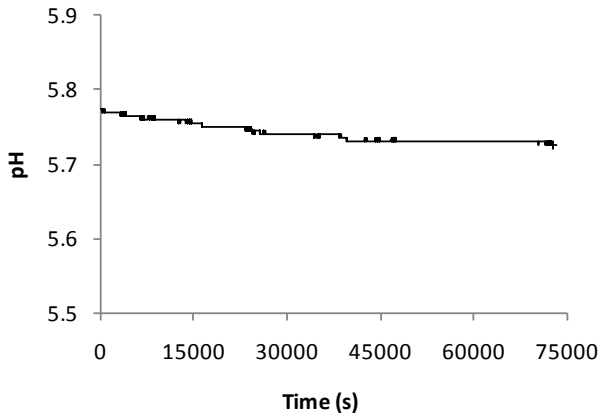
Figure 3 *Change in pH with aeration and CO₂ degassing*

Conclusions

The results of the site survey show that the effluent water at Ynysarwed is currently meeting the discharge consent for Fe(II) concentration. Comparison with the degassing studies of fresh minewater suggests that this is likely to be because of the slightly elevated pH resulting from the HDS trial plant. The results presented here show that 97% iron removal can be achieved and the mine water can be brought within the discharge limit for iron by aeration and degassing alone. Previous work carried out by the authors at this site shows that iron concentrations can be reduced to acceptable levels for discharge in around 2 hours (assuming that the same gas transfer efficiencies can be achieved at larger scale). With current flow rates a 60m³ tank would provide a 2 hour residence time for iron oxidation. Continuous agitation and circulation of the HFO precipitates would ensure maximum oxidation rate by including the heterogenous as well as the homogeneous oxidation pathway.

Acknowledgements

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