

# Mine water treatability studies for passive treatment of coal mine drainage

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## ABSTRACT

The closure of coal mines in the United Kingdom, and the subsequent rebounding of the groundwater has caused widespread pollution of watercourses. This has largely been through the deposition of hydrous ferric oxides, commonly known as ochre. This research has been conducted to further the understanding of the treatability of mine waters with respect to the rates of ferrous iron oxidation and particulate ferric iron settling that occur. Iron oxidation and settling rates were measured in freshly emerged mine waters using a 2.5 m high, 45 L capacity settling column, with periodic sampling from three different depths over a 48 hour duration. Mine waters with initial iron concentrations of between 3 mg/L and 18 mg/L, from sites across South Wales (UK) and New Zealand were tested. The results indicated that the limiting step for treatment on waters above pH 6 and below 18 mg/L iron was settling, which has significant implications for design interventions intended to increase treatment efficiency. The results also demonstrate the complexity of the mine water in relation to the rate of iron removal and the need for a test to determine the iron removal rate for individual mine waters. Furthermore the effect of decreased temperature on mine water treatability, which is important for understanding seasonal effects and the impacts of heat extraction from mine waters with heat pumps, was also examined, with results showing a decrease in mine water treatability at temperatures between 17.6 °C and 1.6 °C.

**Keywords:** Oxidation, settling, passive, heat extraction

## INTRODUCTION

Treatment of iron (Fe) bearing mine water using passive treatment systems has been occurring in the United Kingdom (UK) for two decades. A considerable amount of research has been conducted on the chemistry of the processes by numerous authors, which has been utilized in the design of passive treatment systems. These passive treatment systems in the UK are predominantly a combination of settling ponds and aerobic wetlands suitable for the circumneutral ferruginous mine waters issuing from former coal mines.

The design of past and current settling ponds has been based upon various criteria by different researchers. These include a 48 hour hydraulic retention time (NCB, 1982), anticipated Fe removal rate of 10 g/m<sup>2</sup>/d (Hedin, Nairn & Kleinmann, 1994) and 100 m<sup>2</sup> of pond area per L/s of mine water (PIRAMID, 2003). The calculation of the required area of wetlands is most often based upon one of two methods. The first was devised by Hedin, Nairn and Kleinmann (1994) and establishes a contaminant removal rate of 10 g/m<sup>2</sup>/d for a system that must meet regulatory standards or 20 g/m<sup>2</sup>/d for reasonable improvement (PIRAMID, 2003). Tarutis, Stark and Williams (1999) proposed that the removal rate of Fe in wetlands was by first order removal instead of zero order removal, which the previous criteria are based upon. These criteria produce sizably different scale treatment systems meaning that some are undersized, whilst others may be oversized (PIRAMID, 2003). Undersized schemes can lead to pollution incidents, whereas oversized schemes result in an unnecessary financial burden. A better understanding of the physicochemical processes influencing Fe removal for each site could reduce these uncertainties, taking into account the individual chemistry of the mine waters at each specific location.

The treatability of mine water with respect to the application of passive systems depends upon the rates of the processes governing Fe removal. Overall Fe removal in these systems requires (i) sufficient oxygen (O<sub>2</sub>) transfer into the water to satisfy the O<sub>2</sub> demand of ferrous iron (Fe(II)) oxidation (ii) adequate residence time for Fe(II) oxidation and (iii) sufficient residence time to remove particulate ferric iron (Fe(III)) through filtration, accretion, or settling. The widely accepted rate law for oxidation of Fe(II) in pH >4 indicates a reaction that is influenced most significantly by the variation in pH (Stumm & Lee, 1961; Hove, Van Hille & Lewis, 2007; Millero, Sotolongo & Izaguirre, 1987). Studies on the rate of particulate Fe(III) settling are sparse and are usually combined with Fe(II) oxidation studies. One study on particulate Fe(III) settling rates using settling columns and laboratory simulated mine waters focused upon circumneutral and high pH waters in the range of 6-10 and found that there was no significant difference between settling rates of Fe at each pH tested (Hove, Van Hille & Lewis, 2007). Settling rates of particulate Fe(III) were found to demonstrate first-order behavior with respect to the concentration of particulate ferric iron, with settling rates varying for different mine waters (Sapsford, 2013). Hedin & Nairn (1990) suggested that "Fe removal rates are correlated with Fe concentration" for wetlands, but whether this is applicable to settling ponds is unknown.

Aeration of the mine water prior to flowing into the settling pond is seen as an essential step in the treatment of ferruginous mine water (PIRAMID, 2003). This is to ensure that the Fe(II) is oxidized to Fe(III) so that it may precipitate in the settling pond. For some mine waters aeration cascades benefit by stripping dissolved carbon dioxide, therefore raising the pH and increasing the Fe oxidation rate (Geroni & Sapsford, 2011; Stumm & Lee, 1961; Hove, Van Hille & Lewis, 2007; Millero, Sotolongo & Izaguirre, 1987).

Temperature affects the treatability of mine water and the kinetics of Fe(II) oxidation (e.g. Stumm & Lee, 1961; Millero, Sotolongo & Izaguirre, 1987). Temperature might reasonably be expected to affect settling behavior of particulate Fe(III), although literature is interestingly lacking on this subject. Heat extraction from mine water has been demonstrated to be feasible and economic (Banks et al, 2004), however little consideration has been given to the effects it may have upon the treatability of the mine water. In the UK mine water is typically at a temperature of 10-12 °C year-round (Banks et al, 2004). Decreasing this temperature by the typical 5 °C (Banks et al, 2004), would be expected to cause a subsequent decrease in the rate of oxidation of the Fe(II) and possibly impact settling rates.

This paper aims to (i) demonstrate a method for examining the treatability of different circumneutral ferruginous mine waters, which shows the rates of Fe(II) oxidation and settling of particulate Fe(III) under quiescent conditions for different mine waters, (ii) demonstrate the effect of aeration versus non-aeration and (iii) assess the effect of temperature reduction on mine water treatability.

## METHODOLOGY

Iron removal tests were conducted for five mine waters from across South Wales and South Island in New Zealand. These studies were conducted using columns 2.5 m in height, (similar to a typical settling pond depth) and contained 45 L of mine water. Experiments were carried out on aerated and non-aerated mine water samples to determine the effects of aeration on the iron removal rates. Initial iron concentrations were between 3 mg/L and 17 mg/L. The experiments were run between 48 hours and 158 hours.

### Iron Removal Rates

#### *Mine Water Collection*

A number of mine waters from coalfields in South Wales and New Zealand were used in the study, including active coal mine sites and passive treatment schemes. All of the samples from South Wales were collected prior to any aeration cascades. The sites were four passive treatment systems in South Wales (Glyncorwg, Lindsay, Morlais, and Taff Merthyr) and one active mine in New Zealand, where the outfall from old mine workings pass over a waterfall prior to sampling. At each site 30 L containers were filled to the top to inhibit oxygenation in transit and transported back to the laboratory. Times varied from two hours to seven hours between sampling and commencement of the experiments.

#### *Settling Column*

The settling column was designed to replicate the processes occurring within a settling pond, although a difference in behavior might be expected where flow through the pond is not laminar. A relationship between the Fe concentration and column depth with time was determined by sampling every three hours from three sampling ports. An initial volume of 20 ml was extracted from each port and used to wash the beaker for each sample. A further 45 ml was extracted, from which 20 ml was used for total Fe analysis (i.e. particulate Fe(III) plus dissolved Fe(II)), 20 ml was filtered through a 0.2 µm syringe filter for total dissolved Fe and 5 ml was used for Fe(II) analysis. Prior to analysis 1 ml of 20% hydrochloric acid was added to the 20 ml samples.

Two settling columns were used for the water from each mine. In one column, the mine water was aerated by twice pouring the mine water between buckets held one meter above the other, in order to mimic the effects of an aeration cascade. In the second column, the non-aerated mine water was pumped directly from the 30 L container, through a pipe that passed down to the base of the column, thus minimizing the O<sub>2</sub> transfer into the mine water. The mine water was vigorously agitated in the sealed containers to re-suspend any sediment prior to being pumped into the columns. The columns were filled to within 0.05 m of the rim and remained undisturbed throughout the experiment.

### *Inorganic Elements Analysis*

For the samples collected in South Wales total Fe was measured using a Perkin and Elmer Optima 2100DV inductively coupled plasma-optical emission spectrometer against certified standards. In New Zealand total Fe was determined using a portable Hach spectrophotometer with FerroVerr as the reagent. Iron concentrations above 3 mg/L were diluted using deionized water before analysis on the spectrophotometer. Ferrous iron from mine waters in Wales was determined spectrophotometrically using a Hitachi U1900 spectrophotometer at a wavelength of 510 nm. The reagent used was 1,10-phenanthroline at Fe concentrations less than 15.0 mg/L. The mine water samples in New Zealand were measured using a portable Hach spectrophotometer with Hach Fe(II) reagent. Fe(II) concentrations above 3.0 mg/L were diluted using deionized water before analysis on the Hach spectrophotometer.

### *Data Logging*

Throughout the duration of the experiment dissolved oxygen (DO), pH and temperature were measured using a HANNA 9828 multi-parameter probe. The probe was immersed in the mine water within the column at a height of 1.86 m. Calibration of the probe was undertaken before each experiment. Temperature, pH and DO were also measured in the field when the mine water was collected.

### **Heat Abstraction**

Mine water collected from Taff Merthyr in South Wales was used for the heat abstraction experiments and was obtained in the same manner and analyzed using the same techniques as the column experiments above. The mine water was cooled during transport by storing in a cool box at reduced temperatures prior to refrigeration. The mine water in both columns was aerated prior to transfer into the column.

### *Settling Column*

Two settling columns were used, one was kept at room temperature of 17.6°C and the second stored in a fridge at 1.6°C. The settling columns were 20 L square barrels, 0.55 m in height, 0.20 m in width and 0.20 m deep, filled to within 0.05 m of the rim. Samples were extracted from 0.1 m below the surface of the mine water. The experiment was repeated using different temperatures of 12.9°C for the room temperature and 4.3°C in the fridge.

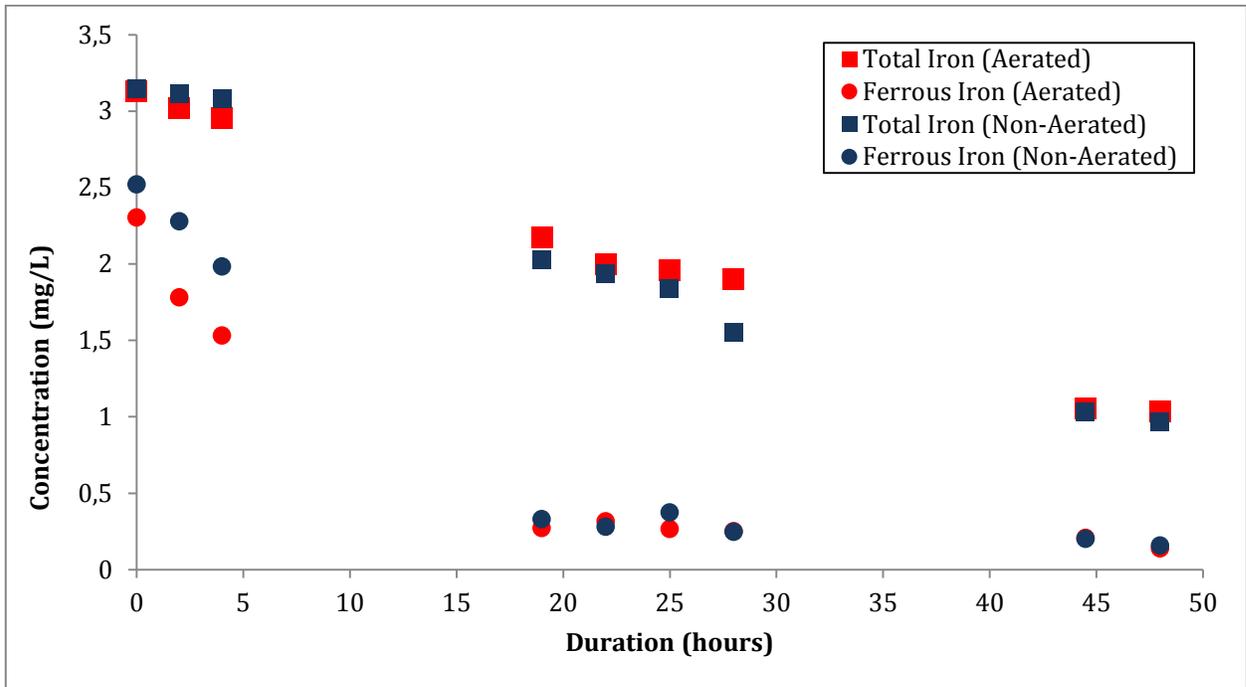
## RESULTS AND DISCUSSION

### Iron Removal Rate & Aeration

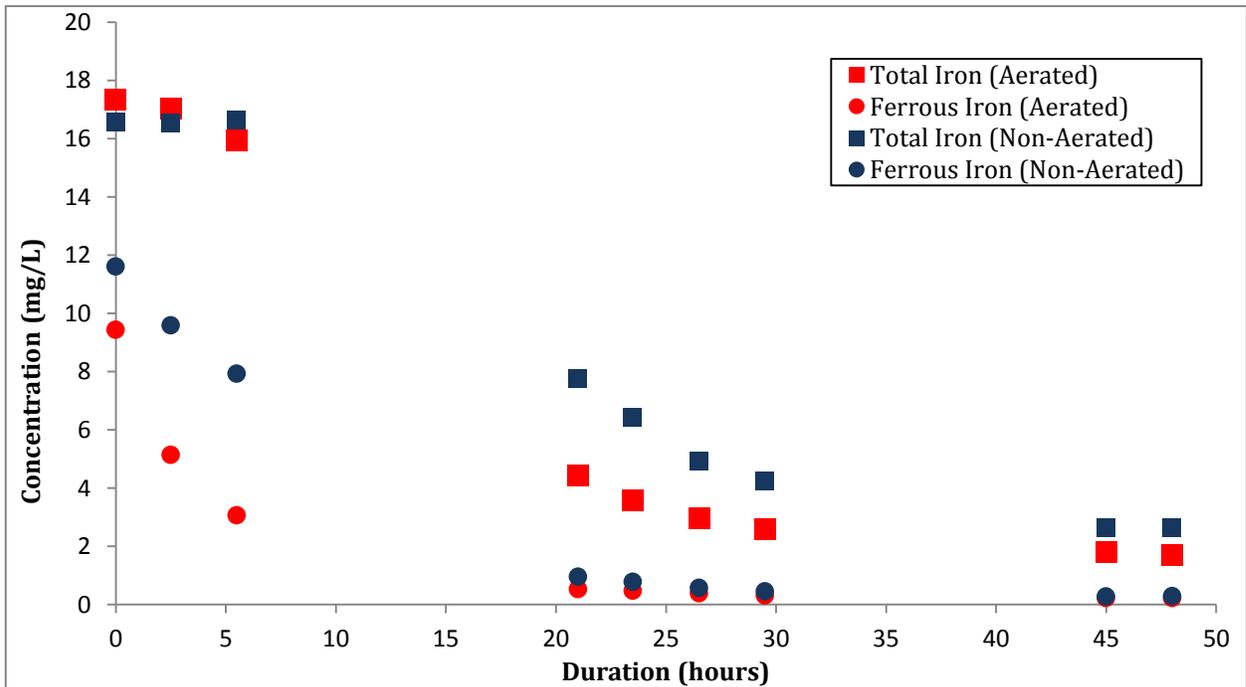
The following can be inferred from the data presented below. Aeration of the mine water made little difference to the overall removal of iron for the mine water at Glyncoirwg (Figure 1), which was roughly linear with an iron removal rate of 0.07 mg/L/hr. This indicates that for this mine water particulate settling was likely to be the rate limiting step. At Lindsay (Figure 2) the data indicates that particulate settling was likely the rate limiting step for this mine water, with similar removal of total Fe after 48 hours between the aerated and the non-aerated columns. The impact of aeration on the Lindsay mine water is more evident and it is noteworthy that after 20–30 hours the majority of Fe was in particulate Fe form, which may have been easier to remove (by filtration) if the water was passing through an aerobic wetland at these times. Total Fe removal in Figure 2 did not follow a linear trend over the duration of the experiment at Lindsay. The mine water for Morlais was most clearly impacted by the aeration as seen in Figure 3, with the total Fe removal in the aerated column being approximately 58% lower in concentration than in the non-aerated column after 48 hours. This indicates that for this mine water, both the Fe(II) oxidation rate and particulate Fe(III) settling rate are important in the overall treatability of the mine water. Again the overall iron removal is approximately linear over the duration of the experiment and is circa 0.20 mg/L/hr.

The mine water Taff Merthyr indicates that for this mine water particulate Fe(III) settling is the rate limiting step and thus controls the overall removal of iron for this mine water (Figure 4). Iron oxidation rates are different between the aerated and non-aerated mine waters, but this has negligible impact on the overall Fe removal rate. The mine water at the active mine site in New Zealand (Figure 5) shows a case where there is no requirement for the oxidation of Fe(II) and that all the Fe is in the form of particulate Fe(III), thus Fe removal is solely governed by the rate of settling.

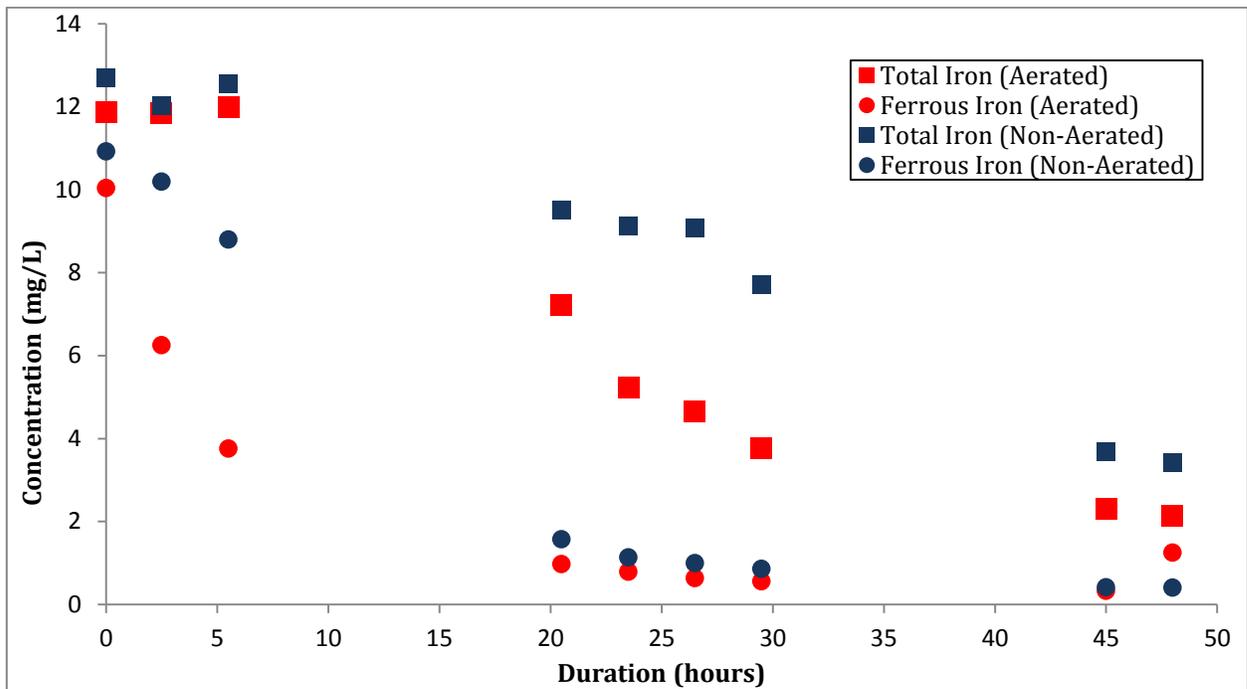
The Fe(II) and total Fe concentrations between the three sampling ports in the columns were found to be very similar in all cases, typically within 4.4% and 3.0% of each other for total Fe and Fe(II) respectively. Consequently the average value between the three sampling ports was used to create the following Fe concentration versus time graphs. This means that the settling rates of Fe(III) are irrespective of the depth, which has implications for design of settling lagoons.



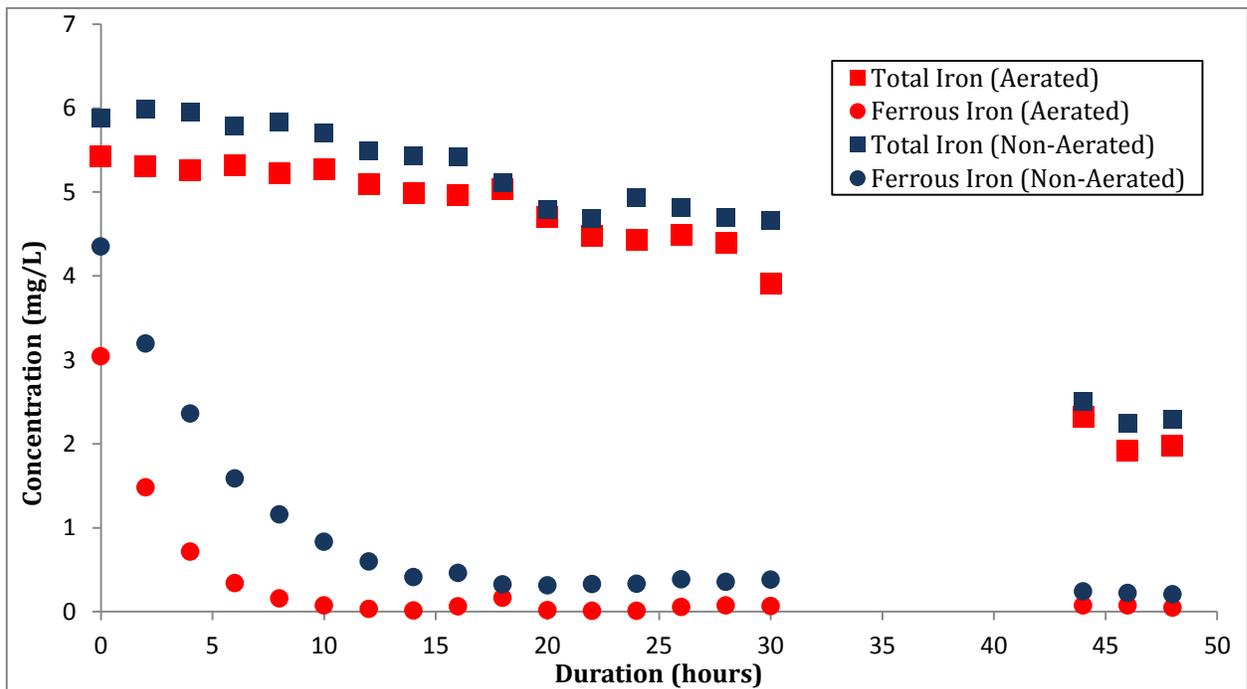
**Figure 1** Change in Fe(II) and total Fe concentration with time in column at Glyncorrwg. Mean pH and initial DO during test = 6.52 and 4.99 mg/L respectively for aerated and 6.17 and 3.44 mg/L for non-aerated



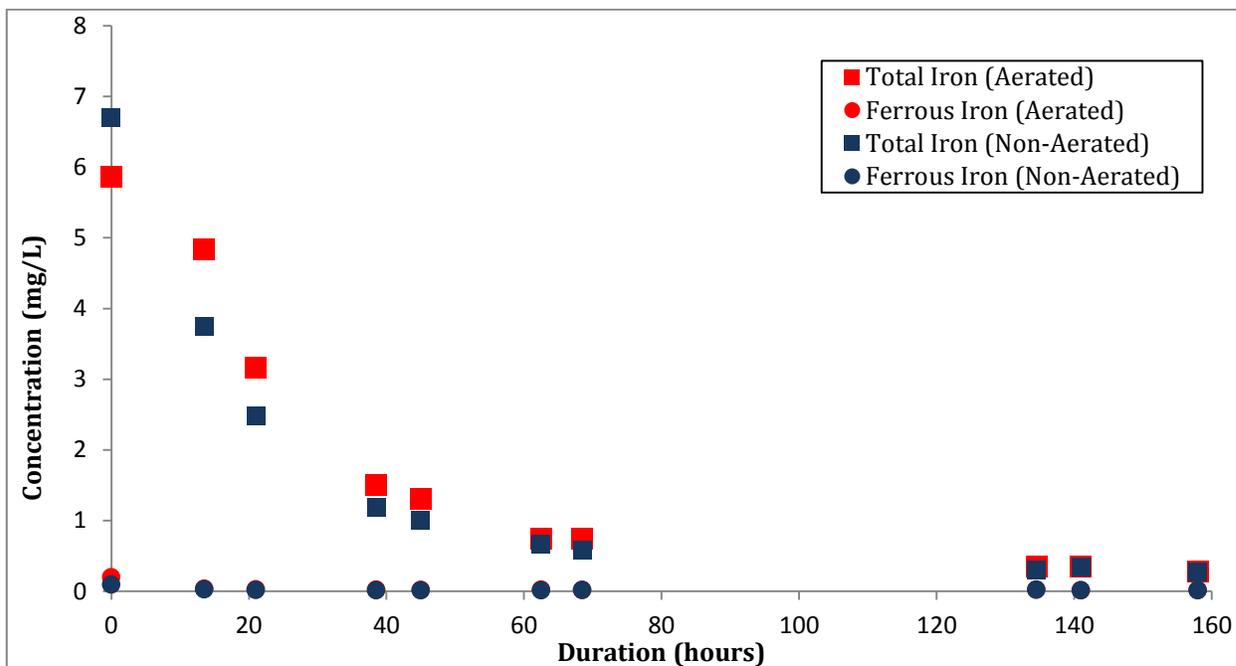
**Figure 2** Change in Fe(II) and total Fe concentration with time in column at Lindsay. Mean pH and initial DO during test = 6.58 and 8.00 mg/L respectively for aerated and 6.59 and 2.67 mg/L for non-aerated



**Figure 3** Change in Fe(II) and total Fe concentration with time in column at Morlais. Mean pH and initial DO during test = 6.06 and 5.01 mg/L respectively for aerated and 6.36 and 3.23 mg/L for non-aerated



**Figure 4** Change in Fe(II) and total Fe concentration with time in column at Taff Merthyr. Mean pH and initial DO during test = 7.09 and 8.52 mg/L respectively for aerated and 7.11 and 2.62 mg/L for non-aerated



**Figure 5** Change in Fe(II) and total Fe concentration with time in column at active mine site in New Zealand. Mean pH during test = 6.48 for aerated and 6.48 for non-aerated

### Heat Abstraction

Experiment one was conducted at a mean water temperature of 1.6 °C for the refrigerated sample and 17.6 °C for the room temperature sample. Experiment two was conducted at 4.3 °C for the refrigerated sample and 12.9 °C for the room temperature sample. The Fe removal rates have a similar linear relationship between total Fe concentration and time to the previous column tests at Taff Merthyr.

Reduction in temperature in experiment one shows a decrease in the Fe removal rate between the room temperature sample and the refrigerated sample, with a difference in final Fe concentration of 0.8 mg/L after 48 hours. A similar decrease was seen in experiment two, with a difference in final total Fe concentration of 0.9 mg/L after 48 hours. Comparing the experiments shows that the Fe removal rates are variable and not solely dependent upon temperature, as the removal rate at 4.3 °C and 12.9 °C is higher than that recorded at 17.6 °C.

**Table 1** Iron removal rates for mean temperatures of 1.6–17.6 °C, pH 6.4–6.8 and initial DO 6.0–6.2 mg/L, duration of 48 hours

Mean Temperature (°C)	Initial Fe(II) Concentration (mg/L)	Final Fe(II) Concentration (mg/L)	Initial Total Fe Concentration (mg/L)	Final Total Fe Concentration (mg/L)	Fe Removal Rate (mg/L/h)
1.6	2.32	0.12	5.13	2.24	0.03
17.6	2.49	0.27	4.85	1.39	0.07
4.3	3.22	0.13	5.13	2.09	0.07
12.9	3.30	0.13	5.20	1.24	0.08

## CONCLUSION

In conclusion, the findings of this study were as follows:

- (i) Particulate Fe(III) settling displays unusual settling behavior where the concentration is seen to decrease concurrently and equally at different heights within a column of quiescent mine water.
- (ii) For mine waters of similar character (low Fe concentration, pH 6.0–7.5, DO 2.62–8.52 mg/L) the treatability of the mine waters is different and show instances where the relative rates of Fe(II) oxidation and particulate Fe(III) settling becomes more or less important. This information is very important for design, particularly where treatment efficiency is trying to be increased. The data presented thus demonstrate the importance of mine water treatability studies for each new mine water to be treated.
- (iii) Decreasing the temperature of the mine water by between 8.6–16°C leads to a reduction in the treatability of the mine water.

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