An assessment of the current operation of the Coal Authority Six Bells Mine Water Treatment Scheme, South Wales

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Abstract

The Six Bells Mine Water Treatment Scheme is a semi-passive Coal Authority scheme within the South Wales Coalfield, near Abertillery. Hydrogen peroxide is used to promote iron and sulphide oxidation in the mine water.

This paper investigates the performance of the scheme over the last two decades whether the chemistry of the discharge has changed over time, and if hydrogen peroxide dosing is still required to effectively remove iron. Both iron and manganese in the mine water have decreased over time, with results suggesting that peroxide may no longer be required to fully treat the mine water.

Introduction

Over the last forty years coal mining has been phased out in the United Kingdom due to economic, environmental, and cultural reasons. This has resulted in environmental impacts in the years following closure, particularly in South Wales. Recovering groundwater in the old mines has flushed the products of pyrite oxidation and dissolution of siderite into the discharge water generating acidic to neutral high iron chemistry discharge waters.

The principles of mine drainage generation are well understood, with extensive research in the last 50 years due to the serious impact it can have on wildlife and ecology of river systems. Mine drainage imposes a significant threat across the South Wales Valleys, where such a concentrated band of vast, profitable coal mines existed. Coal mining has scarred the landscape and left behind an unmistakable legacy of orange, odorous contaminated water. Waters affected by mining can be acidic, circumneutral, basic, dilute, mineralised and saline (Nordstrom *et al*, 2015). The array of different chemical properties mine waters can exhibit often requires intricate water sampling investigations when planning what remediation strategies to impose. Remediation schemes aim to return water from its contaminated state by oxidising the water, promoting the oxidation and settling of dissolved metals, and eventually returning the pH to a circum neutral state by reducing acidity (Bowell *et al* 1999).

This paper presents an evaluation of one such scheme at the former Six Bells Colliery. This joint project between SRK Consulting, The Coal Authority and Cardiff University aims to assess the current operational effectiveness of the Six Bells Mine Water Treatment Scheme. The main focus is on the performance of the scheme, and whether the chemistry of the water has changed sufficiently over time (with respect to the iron loading) so as to no longer require hydrogen peroxide as an oxidising agent, and if the same productive treatment can be done without the expense of dosing.

Background

The Six Bells Colliery was in operation from 1895, located just to the south of Abertillery in the Ebbw Fach Valley. Closure occurred in 1986 following the miners' strike of the previous two years (Lawrence, 2009). After the cessation of pumping, groundwater began to fill the void space of the deep workings. Mine waters began discharging into the Ebbw Fach River by 1998, exhibiting the typical orange ochre staining associated with historic coal mining areas. As of 2001, this site was regarded as one of the most contaminated and significant mine drainage discharges in the UK (Jarvis *et al*, 2003), inflicting severe ecological and biological impacts within the Ebbw Fach River.

In 2000, The Coal Authority added the Six Bells mine drainage discharge to its list for treatment, with the preliminary treatment feasibility study of the discharge recommending a combination of passive and active remediation techniques. The scheme consists of two parallel settlement ponds, followed by an aerobic wetland, before the treated water is discharged into the Ebbw Fach River. Hydrogen peroxide (H_2O_2) dosing was implemented at the scheme, in lieu of an aeration cascade, due to restrictions, with topography and space, the high iron loading, and the potential for hydrogen sulphide odour. Hydrogen peroxide dosing accelerates the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), which promotes the settling of iron solids and removes the hydrogen sulphide by oxidation of the sulphide to sulphate.

An aeration cascade was constructed in 2013, and the mine water quality has steadily improved over the last two decades (reduced iron loading), so this study was conducted to assess the ongoing requirement of hydrogen peroxide dosing. Six Bells MWTS has been in operation for nearly 20 years, and, as with all mine water treatment schemes, regular assessment of the scheme performance is required, as treatment may need to be refined as the mine water chemistry matures.

Methodology

Six Bells MWTS is located near the old village of Six Bells, now part of Abertillery, South Wales. The aim of this study is to evaluate the role of hydrogen peroxide dosing as an oxidising agent, and if the dosing can be reduced or stopped, allowing a discounted operational cost. The peroxide dosing was turned off for 2 days over a 4 day period (August 3rd to 6th 2021) to assess the difference in the scheme operation with and without dosing.

Field sampling occurred over four consecutive days. A total of eight sampling points were established at sequential points through the scheme, the first being raw mine water pumped from the shaft, and last being the reed bed outflow, just before its confluence with the Ebbw Fach River.

Analysis was completed at Cardiff University using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument. Samples were filtered into 25 ml plastic bottles using a 0.45 µm filter and 10 ml plastic syringe. This removed suspended iron from the solution. Samples were transferred to 15ml centrifugal tubes and were diluted by a factor of 5 (2 ml of sample and 8 ml of Milli-Q reference water) and subsequently acidified with 1 ml nitric acid (HNO_3). A correction was later made for the dilution to give native values.

Results

Review of Overall Water Chemistry

The main parameters that will be discussed are field parameters of pH, dissolved oxygen (DO), total suspended solids (TSS) and laboratory analysis of, alkalinity, iron (Fe), manganese (Mn), aluminium (Al) and sulfate (SO_4). These will indicate the efficiency of the scheme and also what processes are occurring in different parts of the system before the mine water is discharged.

Long-term trends of key parameters are presented in Figure 1. The pH is highly variable over the period of monitoring showing gradual increase over time. All values for pH lie within the permitted range for discharge.

Total and filtered iron concentrations and the ratio of filtered iron to total iron have been monitored. Total iron encompasses all the iron in the sample, while filtered iron only accounts for iron in the <0.45 µm fraction. Raw influent concentrations of total iron have generally shown a decrease, whilst outflowing concentrations have remained relatively constant (Figure 2). A large spike in total iron is observed at the end of 2011, rising to 43 mg/L before falling again, which is likely an artefact of the sampling methodology, or the sloughing of particulate iron from pipework. Concentrations in the outflow from settlement ponds 1 and 2 have also remained constant, at ~2 mg/L.

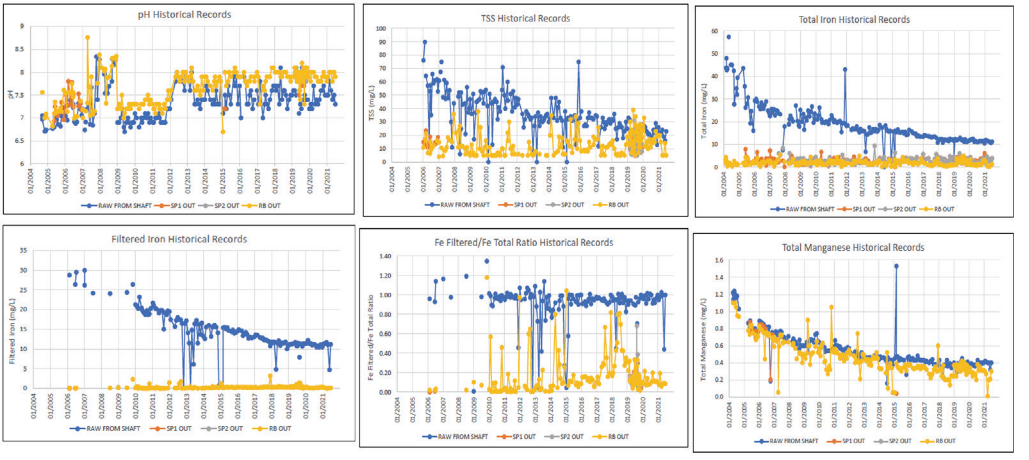

Figure 1 *Monitoring data from shaft mine water (raw from shaft), outflow from settlement ponds (SP1/2 OUT) and final discharge post reed beds (RB OUT). Monitoring data for the period 2004 to 2021. Source: The Coal Authority*

Outflowing loads are consistent, between 6 and 9 kg/day. Total iron removal rates have decreased from an average of 93% in 2004-2006 to 85% in 2019-present (Figure 3). Overall, similar iron levels at the outflow but reducing influent levels and that will lead to slight reductions in removal performance over time (Fig. 3).

Long-term ratios of filtered iron to total iron show a contrast between inflowing ratios and outflowing. Inflowing ratios remain constant at a near 1:1, whilst outflowing ratios fluctuate heavily, averaging a 0.1:1 ratio until 2017, where it increases to an average of 0.3:1, before falling back to its original ratio.

Total manganese concentrations have decreased over time, from an approximate 1.2mg/L in 2004, to most recently 0.4mg/L.

Hydrogen Peroxide Assessment

Hydrogen peroxide dosing was introduced to tackle sulfide odour and to oxidise ferrous iron in the mine water. Assessment of the benefit of peroxide addition shows slightly lower pH in the settlement ponds, presumably reflecting hydrogen ion liberation

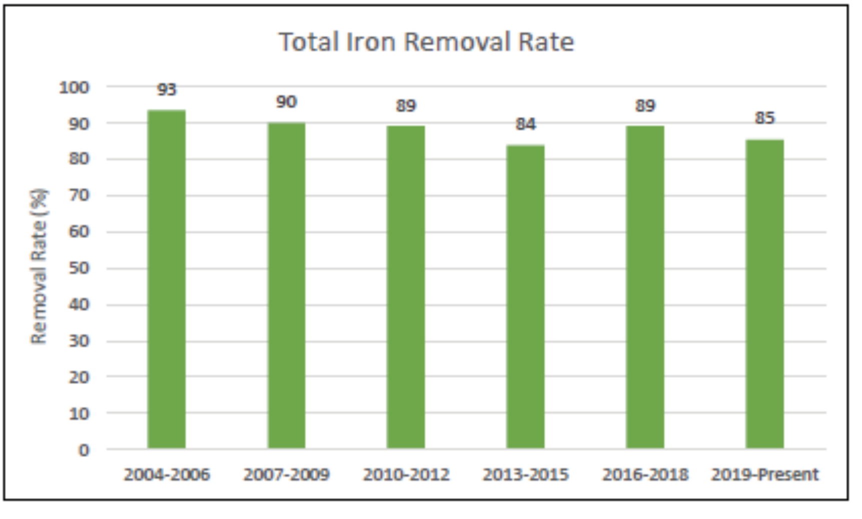

Figure 2 *Long-term total iron removal rates at Six Bells broken down into 3 year periods from 2004 to the present day.*

on oxidation of ferrous iron at different stages of the treatment system (Figure 4). Incoming total iron concentrations exhibit a very similar trend for peroxide dosed (peroxide on) and natural waters (peroxide off). A clear drop in concentrations can be seen for both waters through settlement pond, with dosed water concentrations slightly lower at 3.96 mg/L compared to 4.12 mg/L. Iron loads inflowing to the system are also very similar, at 45.36 kg/day and 46.66 kg/day, respectively. Outflowing loads were measured at 3.2 kg/day and 3.97 kg/day. Removal rates are 93% for dosed waters compared to 91% for natural waters. Filtered iron concentrations show a stark contrast when compared to one another (Figure 3). Natural water concentrations greatly reduce through the settlement pond, from 10.2 mg/L to 0.07 mg/L, whilst dosed waters remain constant. Inflowing loads are significantly higher for natural waters, at 47.95 kg/day, compared to only 0.82 kg/day for dosed waters. Output loads are much closer, measured at 0.09 kg/day (natural) and 0.13 kg/day (dosed). Removal rates show waters without hydrogen peroxide have 100% efficiency against only 84% for hydrogen peroxide dosed waters.

The ratio of filtered iron to total iron begins much higher for natural waters at 1.03:1, compared to 0.02:1 for peroxide dosed waters. The raw ratio then drops significantly to 0.02:1 at the end of the settlement pond, identical to the ratio of the dosed waters at this point in the scheme (0.02:1). The raw waters remain at 0.02:1 until they are output, however the dosed waters rise slightly to 0.04:1.

Concentrations of total manganese remain relatively stable until the reed bed, where dosed waters decrease from 0.36 mg/L to 0.29 mg/L, and natural waters from 0.38 mg/L to 0.26 mg/L (Figure 4). Inflowing loads are identical regardless of hydrogen peroxide dosing, at 1.68 kg/day. Output is slightly higher for the dosed waters at 1.25 kg/day compared to 1.12 kg/day for natural waters. Removal rates for peroxide dosed waters were measured at 26% and natural waters at 33%.

Discussion

Since its inception in 2004, the Six Bells discharge pH has varied between 7 and 8 pH, and increasing pH is not a main priority when operating the site. However, a period of decreased pH can be observed between

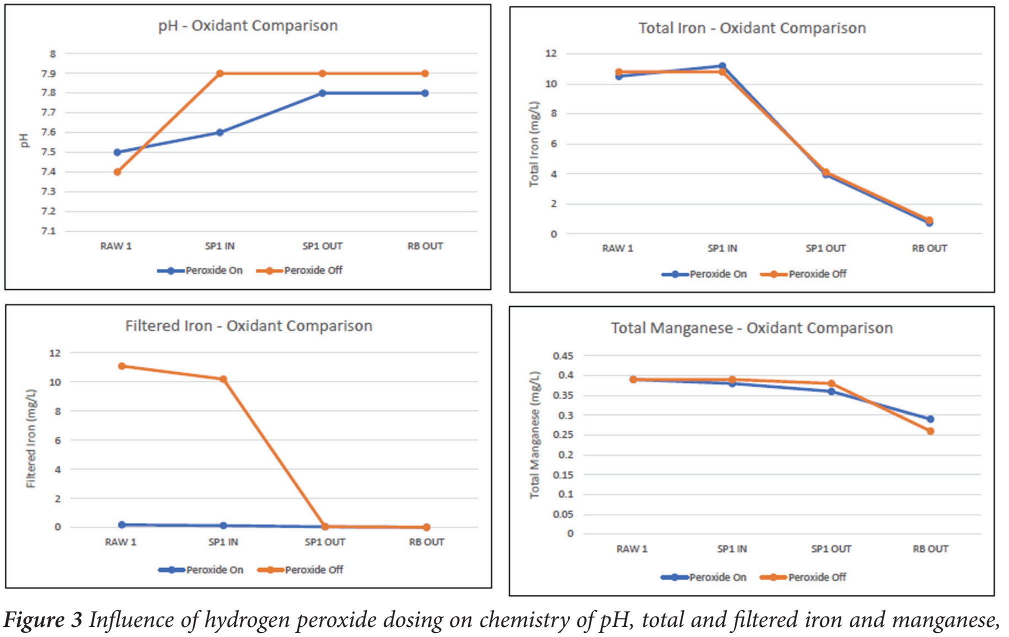

Figure 3 Influence of hydrogen peroxide dosing on chemistry of pH, total and filtered iron and manganese, Six Bells MWTS.

the end of 2009 and the beginning of 2012. This cannot be the result of changes at the site on an operational level, as the only major change, the aeration cascade, was constructed the following year. A likely explanation for the decreased period is that of insufficient groundwater recharge.

Six Bells has maintained a consistent removal rate for both total and filtered iron of above 85% since 2004. Total iron removal rates have shown some sign of decrease, dropping from 93% in 2004-2006 to 85% from 2019 onwards. Analysis of the field samples shows a removal rate of 93%, which suggests this decline may have been temporary, or the field sample is not indicative of the longer-term trend. Relatively high removal rates imply oxidation and subsequent hydrolysis reactions are occurring. The majority of iron is removed through the settlement ponds, indicating they are performing as intended, with the iron being successfully oxidised in the scheme.

Removal rates of manganese have generally increased, from 10% in 2004-2006 to 24% within the last 3 years. Manganese precipitation is difficult to predict and analyse due to its many oxidation states. Abiotic oxidation and complete removal will usually occur above pH 9 (Jacobs *et al*., 2014). Six Bells mine water has a pH of between 7-8, which is not high enough for purely abiotic oxidation. However, as the iron content is over four times greater than the manganese concentration, co-precipitation can occur (Jacobs *et al*., 2014). As iron forms iron hydroxide (Fe(OH)3) and precipitates, small amounts of manganese can co precipitate with the ochre flocs within the settlement ponds.

Iron is oxidised preferentially over manganese and will only begin to undergo oxidation when iron has been reduced significantly. The main portion of manganese removal occurs biotically in the reed bed once the majority of iron has been removed. This explains the low rate of manganese removal at Six Bells, which sits at 26% currently. A jump in manganese removal rate occurred after 2013 due to the construction of the aeration cascade, rising from 15% in 2010-2012, to above 20% from then on. The aeration cascade increased dissolved oxygen within the settlement ponds, likely accelerating the oxidation rate of iron, in turn having a direct effect on oxidation of manganese.

Seasonal variability of metal concentrations within mine water can play a huge part in the effectiveness of the scheme throughout the year. Manganese and iron concentrations are most susceptible to this (August *et al*., 2002). Flow rate would only partially vary at Six Bells as the mine water is pumped at a continuous 40 L/s, however, manganese and iron concentrations may drop in summer compared to winter months.

Despite the short duration of the testwork, the addition of hydrogen peroxide (H_2O_2) appears to now have little effect on the pH at Six Bells. Waters without dosing show a quicker pH increase through the scheme, starting at 7.4 and increasing to 7.9. These conditions are still more than enough for the oxidation of iron. Total iron removal rates are almost identical regardless of hydrogen peroxide addition, with waters at Six Bells experiencing a 2% decrease when dosing is turned off. Removal rates remain over 90%, suggesting that the aeration cascade supplies enough dissolved oxygen (DO) to the settlement ponds to sufficiently promote iron oxidation and counteract the loss of H_2O_2.

Filtered iron concentrations experienced the biggest variation. After dosing, raw filtered iron concentrations were measured at 0.19 mg/L, whilst when dosing was turned off, they rose to 11.1 mg/L. The results indicate that iron oxidation is almost complete and this would infer that the peroxide is causing rapid oxidation of dissolved iron by the time it reaches the top of the cascade.

Manganese removal rates increase when peroxide dosing is turned off, at 33% compared to 26%. Concentrations decrease quicker in the settlement ponds when dosed, likely as the iron is oxidised faster, which would remove manganese via sorption within iron hydroxides (Stumm and Morgan, 1981). Waters without dosing remove a significant amount of manganese through the reed bed. This is most likely explained by formation of insoluble Mn2+ oxides at low oxygen fugacity and mobilization of Mn in higher oxidation systems.

Conclusions

Total iron concentrations output from Six Bells have averaged 2 mg/L. Removal rates have decreased 8% since its inception, despite a lower incoming load. Filtered iron removal rates remain exceptionally high, which will be promoted by the addition of hydrogen peroxide. The majority of iron is removed through the settlement ponds rather than the reed bed, suggesting the ponds are working as expected. Manganese concentrations at Six Bells are relatively low, with removal rates of around 26%. Manganese removal is mainly conducted through the reed bed once iron has been preferentially oxidised. An increase in residence time may bolster removal rates, shown by the significant jump in 2013, presumed to be a result of additional aeration by the aeration cascade. From the short-term assessment conducted, hydrogen peroxide dosing at Six Bells had limited benefit over an entirely passive treatment process. The aeration cascade, implemented in 2013, now provides sufficient dissolved oxygen levels for the reduced concentrations of contaminants it receives, and an additional longer term and closely monitored trial (3-6 months) is now required to assess scheme performance without peroxide dosing.

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