

In-Situ Hydrogen Peroxide Dosing Trials to Design Semi-Passive Treatment Schemes

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Abstract

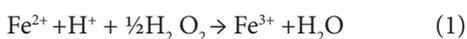
The oxidation kinetics of ferrous iron in coal mine water can be increased using hydrogen peroxide solution. To determine hydrogen peroxide demand the Coal Authority used desktop modelling based on a presumption that all mine waters had a similar behaviour for iron oxidation kinetics.

During the early stages of project design trials of hydrogen peroxide dosing were undertaken to study the behaviour in-situ of real mine water rather than in a laboratory with synthetic water. Both trials demonstrated the benefits of using actual mine water because it allowed for efficient and cost effective, semi-passive treatment schemes to be designed.

Keywords: Iron Oxidation, Hydrogen Peroxide

Introduction

Sometimes a passive coal mine water treatment scheme requires the addition of chemicals to increase the removal rate of iron, due either to a lack of available treatment area or a change in mine water quality or discharge requirements. This can be achieved using either hydrogen peroxide to increase the kinetics of the oxidation of ferrous to ferric ions (Leavitt 2010),



or sodium hydroxide solution to increase the solution pH. The rate of ferrous oxidation can be described by the rate equation (Stumm and Lee 1961),

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}][\text{O}_2][\text{OH}^-]^2 \quad (2)$$

The Coal Authority incorporated trials of hydrogen peroxide dosing of the coal mine water during the early stages of two projects which allowed for efficient and cost effective, semi-passive treatment schemes to be designed. These trials were undertaken at the Lynemouth treatment scheme (Northumberland, UK) and at the Polkemmet treatment scheme (West Lothian, UK).

Lynemouth Trial

Lynemouth treatment scheme, located on the site of the former Lynemouth Colliery, controls the water levels in the disused mine workings to prevent both pollution of the Morpeth aquifer, which supplies both drinking water and industrial supplies and uncontrolled discharges to surface. It consists of two treatment areas. Phase 1, built in 2013, consists of two 5,000 m² lagoons, in series, each preceded by a cascade. This could not pump sufficient water from the coalfield to prevent water levels rising in it. Consequently, Phase 2 was built in 2019, which consists of a cascade before three 4,000 m² lagoons in parallel; these collectively discharge into a second cascade that feeds two 5,500 m² lagoons in parallel. The combined treated water from Phase 1 and Phase 2 is discharged to the local beach outfall. The scheme has a discharge permit of 150 kg/d of iron.

Phase 2 substantially increased the water flow and the iron concentration at the scheme. During its design stage the Coal Authority became aware that there was insufficient land available for a passive treatment scheme so it was planned to implement hydrogen peroxide dosing at the site to improve the ferrous ion oxidation during high mine

water flows. An initial assessment of the 35%w/w hydrogen peroxide required was calculated. Firstly, from the equation, 0.35 ml of 35%w/w hydrogen peroxide per gramme of dissolved ferrous ions (Younger *et al.* 2002) which indicated that 330 L/d could be required. Secondly, Coal Authority data from similar schemes was used as a model, which indicated that 525 – 1140 L/day could be needed depending on raw water flows and iron concentrations. Both calculations gave a wide variation in the volumes for the hydrogen peroxide consumption, which made the selection of the correct treatment process difficult.

To enable the design of the hydrogen peroxide dosing system and improve the estimate for hydrogen peroxide consumption a series of trials were conducted. These on-site trials used Phase 1 aerated mine water which was pumped from its outlet channel into the test tank. A 1,000 L IBC was used for this because it was recognised that its 1 m² surface area and 1m depth would represent the active water column of a lagoon. Hydrogen peroxide (3%w/w) was continually dosed in-line between the channel and the IBC via a dosing rig. Water filled the IBC in upward flow mode and it was allowed to overflow from the IBC until the contents achieved a “steady state”. At this time both flows of water and hydrogen peroxide were stopped, the IBC isolated and the test began. This was a 48 hour period of batch reaction to simulate precipitation and settling in a lagoon. Samples were taken from near the water’s surface every three hours and analysed for total iron, ferrous ion and ferric ion concentrations. Six trials were carried out and the concentrations and dosing pump rates of hydrogen peroxide dosing are described in Table 1.

Those trials in which no dosing occurred corresponded to a passive treatment scheme. The results did not fit Eq. (2) proposed by Stumm and Lee (1961) since the curve for iron removal against time was sigmoidal (Fig 1) and fitted the logistic equation,

$$\eta = \frac{[Fe]_{out}}{[Fe]_{in}} = \frac{L}{1+e^{-k(t-t_0)}} \tag{3}$$

where η is % removed, L is the maximum efficiency for the tests, t_0 is the midpoint of the S-shaped curve, k is the slope of the curve at the mid-point. Sigmoidal graphs are associated with autocatalytic mechanisms (Moore and Pearson 1981), a characteristic of which is that the reaction is catalysed by one of its products. No attempt was made to confirm this for this particular mine water and further research is required to explain these results.

For the trials that were dosed the results followed a second order rate reaction (Fig 2),

$$\frac{1}{[Fe]_{out}} = \frac{1}{[Fe]_{in}} + At_{res}, \text{ where } A = B[H_2O_2]^c \tag{4}$$

and t_{res} is residence time, B and c are empirical curve fitting parameters ($B = 9.2527 \times 10^{-5}$ and $c = 1.9702$) and $[H_2O_2]$ expressed as μL of 100 %w/w hydrogen peroxide per L of mine water treated.

From Eq. (4), it was calculated that 220 L/d 35%w/w hydrogen peroxide could be required to dose Phase 2. An estimate 35-80% lower than the previous calculations for volume used.

During the building of Phase 2, 35%w/w hydrogen peroxide was dosed into Phase 1 to allow it to treat higher water flows. Dosing was transferred to Phase 2 for commissioning to minimise the risk of an environmental incident whilst its flows were established. Initially dosing was at 187 L/d (130 ml/min). The average total iron load in the Phase 2 discharge was 26.3 kg/day and the average total iron load for the scheme was 67.6 kg/day or 45.1% of the 150 kg/day permitted discharge. Encouraged by this, the dosing was decreased step wise to determine the minimum for the scheme. The doses used, water flows and its iron contents are in Table 2 and the corresponding iron loadings achieved for Phases 1 and 2 and the scheme are in Table 3.

Table 1 Hydrogen peroxide concentrations and dosing rates used in Lynemouth trials.

Test	1	2	3	4	5	6
100 %w/w H ₂ O ₂ , ($\mu\text{L/L}$)	0	5	10	0	15	20
H ₂ O ₂ Pump rate, (mL/min)	0	36	72	0	109	145

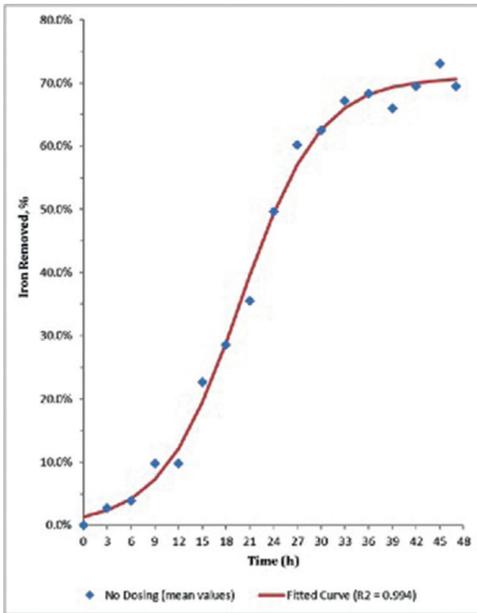


Figure 1 Lynemouth - Iron removed without dosing.

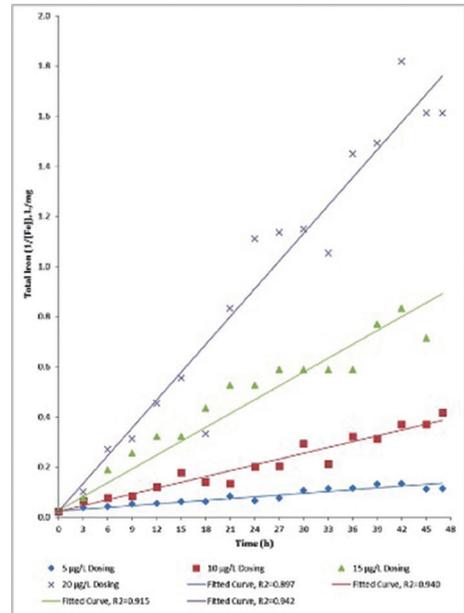


Figure 2 Change in total iron with time, with dosing.

Table 2 Trial parameters employed during Phase 2 commissioning (mean values).

Trial	35 %w/w H ₂ O ₂ Dosed to Phase 2 only	Mine Water Total Iron mg/L	Water Flow Phase 1 L/s	Water Flow Phase 2 L/s	Discharge Total Iron Phase 1 mg/L	Discharge Total Iron Phase 2 mg/L
	L/d					
Trial 1	187	51.2	71.8	107.9	6.6	2.8
Trial 2	151	45.1	61.1	103.1	5.2	2.8
Trial 3	118	42.6	64.0	108.0	5.9	2.0
Trial 4	89	49.5	70.0	110.6	5.9	2.6
Trial 5	54	51.9	71.0	99.8	5.8	2.7
Trial 6	22	48.5	69.4	110.3	5.2	3.2
Trial 7	0	48.2	70.2	111.0	5.3	3.5

Table 3 Trial results achieved during Phase 2 commissioning (mean values).

Trial	35 %w/w H ₂ O ₂ Phase 2 only	Discharge Iron Load Phase 1	Discharge Iron Load Phase 2	Discharge Iron Load Total
	L/d	kg/d	kg/d	kg/d
Trial 1	187	41.3	26.3	67.6
Trial 2	151	28.3	24.6	52.7
Trial 3	118	32.9	18.9	51.8
Trial 4	89	35.8	25.1	60.8
Trial 5	54	35.8	24.0	59.8
Trial 6	22	31.0	30.2	61.2
Trial 7	0	32.1	33.6	65.7

For all the trials, the daily iron load in the discharge ranged from 34.5-45.1% of the permitted discharge of 150 kg/d total iron. Indeed with no dosing to the scheme the iron load was 43.8% of the permitted discharge which provided a margin of safety should either an increase in iron concentration or an increase in flow occur.

Polkemmet Trial

Polkemmet treatment scheme, located near Whitburn, West Lothian, is a semi-passive treatment scheme that has no cascade. Oxidation of ferrous iron is achieved with 35%w/w hydrogen peroxide solution injected into the mine water transfer pipe at the headwork. The mine water is transferred about 230 m to three lagoons. Two lagoons (1160 m² and 1344 m²) operate in parallel and the combined discharges feed a third lagoon (1485 m²). The discharge from the third lagoon feeds a single reed bed (3200 m²). The Coal Authority decided to refurbish the scheme for several reasons. Firstly, it cannot abstract sufficient mine water to maintain the below ground level, which historically has led to several uncontrolled discharges at surface. Secondly, its reed bed is severely overgrown and is not working correctly; furthermore, it cannot be isolated or easily maintained. Thirdly, the current lagoons have low residence times and experience short-circuiting. Fourthly, it has a high operating cost because it uses 35 %w/w hydrogen peroxide to oxidise the ferrous iron and bring about the precipitation of ferric hydroxide. Currently, it uses 429 L/d 35%w/w hydrogen peroxide equivalent to 157 t/y.a

The refurbishment, planned for 2021–2023, will include constructing a cascade and two new reed beds, re-piping the existing lagoons so that they operate in parallel and constructing two new primary lagoons. There is insufficient land available for a fully passive scheme and although a cascade has been included to decrease both the reliance on hydrogen peroxide use and operating cost, it is

anticipated that some dosing will be required.

Trials were conducted to inform the design of the dosing system and estimate hydrogen peroxide consumption. For these, mine water was taken from the riser main to pass down a cascade. It was calculated that the mine water delivered, at 3m height, a 0.5 L/s flow that decreased sharply so it was unlikely that this flow could be attained if a fully representative 4m high cascade was used. A two-stage cascade (stage 1, 2.5 m high; stage 2, 1.5 m high), Fig 3, with intermediate pumping was used. If sized for 0.5 L/s (Younger *et al.* 2002) the cascade would be narrow and unstable therefore it had a larger width to flow ratio of 150. Hydrogen peroxide (7.71%w/w) addition was to the aerated mine water in the buffer tank whilst a pipe mixer provided additional mixing. The water filled a 1000 L IBC in upward flow mode and overflowed from the IBC until the contents achieved a “steady state”. At this time both flows of water and hydrogen peroxide were stopped, the IBC isolated and the 48 hour test period began. Samples were taken from near the water’s surface every three hours and analysed for total iron, ferrous ion and ferric ion concentrations. Hydrogen peroxide concentrations and dosing pump rates used in the twelve trials are collated in Table 4.

A cascade was beneficial because the first stage increased the dissolved oxygen from 5.1% to 84.7%. Stage 2 did not increase the dissolved oxygen further because the water was nearly saturated with oxygen, which restricted its ability to absorb more oxygen. Aeration increased the raw mine water from pH 6.33 (mean) to pH 6.77 (mean) due to carbon dioxide degassing.

Unlike Lynemouth, those results for the non-dosing trials did not show a sigmoidal curve which suggested that no autocatalytic mechanism was promoting the ferrous oxidation (Fig 4). Polkemmet mine water is partially oxidised and contains about 10-15% ferric iron. It’s aerated, undosed, water oxidised much faster than Lynemouth’s, after

Table 4 Hydrogen peroxide concentrations ($\mu\text{L/L}$) and dosing rates (mL/min) for Polkemmet trials.

Test	1	2	3	4	5	6	7	8	9	10	11	12
100 %w/w H ₂ O ₂	0.0	2.5	12.5	17.5	20.0	1.0	7.5	0.0	10.0	15.0	5.0	0.0
H ₂ O ₂ Pump rate,	0	44	221	310	354	18	133	0	177	265	88	0

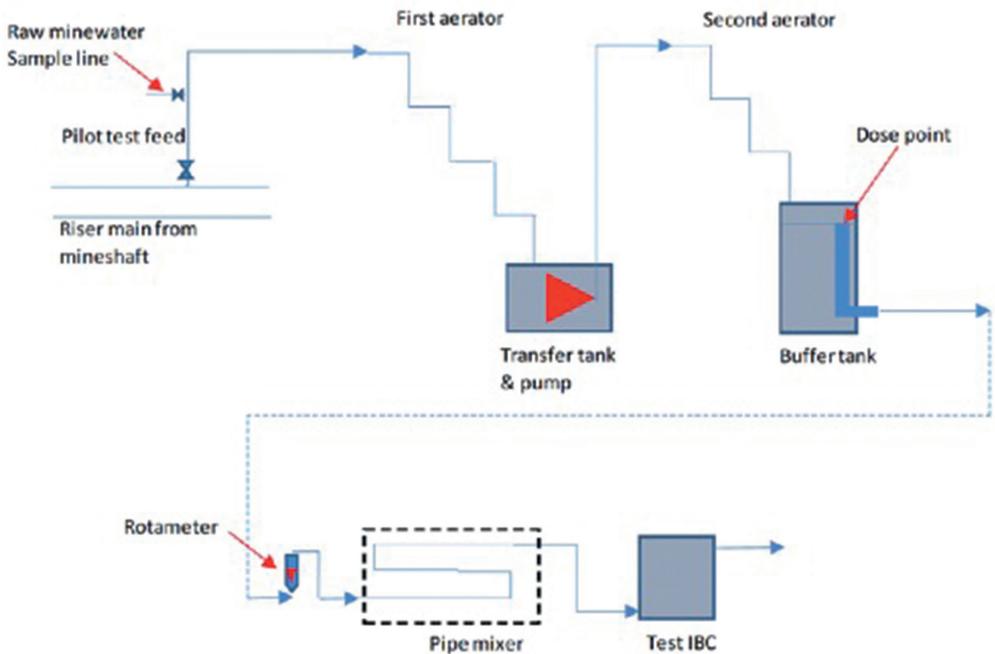


Figure 3 Layout of Equipment for Polkemet Test Work.

15 hours iron removal was 79.4% compared to the 22.7% iron removal of Lynemouth. Laboratory and field studies have shown that precipitated hydrous ferric oxides can catalyse the oxidation of ferrous ions adsorbed on their surfaces (Tamura 1980, Dempsey 2002, Geroni 2011). The presence of ferric iron,

and associated hydrous ferric oxides, may be promoting a much faster oxidation of the ferrous iron than the suggested autocatalytic mechanism.

Analysis of the results from the dosed trials identified that they followed a second order reaction, Eq. (4), similar to Lynemouth,

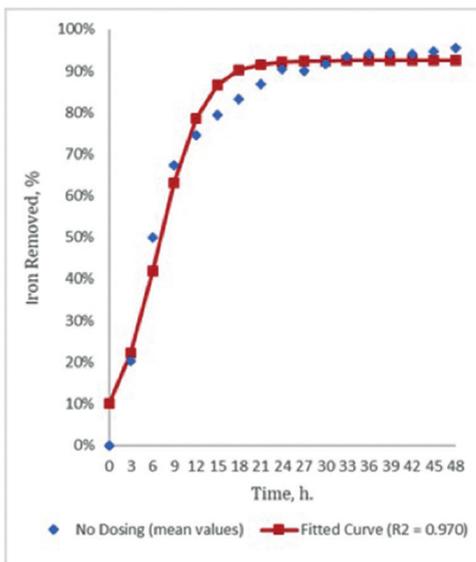


Figure 4 Polkemet - Iron removed without dosing.

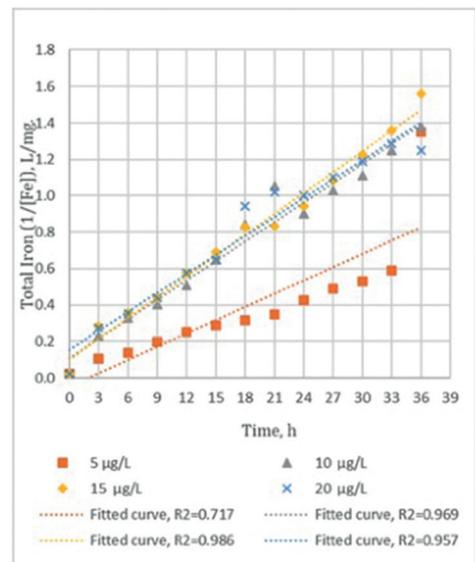


Figure 5 Change in total iron with time, with dosing.

where the empirical curve fitting parameters were $B = 8.480 \times 10^{-3}$ and $c = 0.4989$ and $[H_2O_2]$ expressed as μL of 100 %w/w hydrogen peroxide per L of mine water treated. The observed faster rate of iron removal without dosing suggests that the need for hydrogen peroxide could be much decreased compared with the 429 L/d currently used but this would depend on the cascade's efficiency to aerate the abstracted mine water. It was calculated that 100-200 L/d 35%w/w hydrogen peroxide could be required.

Conclusions

Previously the Coal Authority's approach to designing dosing systems applied desktop modelling and a prior knowledge that assumed that mine waters had a similar behaviour for iron oxidation kinetics during dosing. This work demonstrated that desktop models can calculate a higher volume of hydrogen peroxide needed to be dosed compared with the results obtained from trials on real mine water. In addition, the mine waters in these trials demonstrated markedly different behaviours that were specific to each site. Results from Lynemouth suggested that an autocatalytic mechanism contributed to the oxidation of ferrous iron in the undosed trials and further research is needed to confirm this.

Desktop modelling suggested that Lynemouth needed to be dosed with 330 L/d 35%w/w hydrogen peroxide. A second order rate equation derived from the on-site test results calculated 220 L/day was needed. A saving of 110 L/d or 45 t/y in chemical used. Dosing continued during Phase 2 commissioning to minimise the risk of an environmental incident whilst scheme flows were established. It was progressively decreased such that when it was stopped the iron load of the discharge remained substantially less than its 150 kg/d maximum discharge limit. This result suggested that the model from the trial did not accurately reflect the scheme's true performance. Indeed, the model does not take into account the actual residence times in the lagoons, which may have to be

included as an empirical factor to improve it. Work is underway to determine the actual residence times.

The results for the Polkemmet trials confirmed that a cascade would be substantially beneficial to provide aeration and some carbon dioxide degassing and one has been included into the new scheme's design. Provision has also been made for dosing equipment in it, as the mine water is considered marginal in terms of treatment through passive oxidation alone.

This work demonstrated the benefits of undertaking hydrogen peroxide dosing test work on site using actual mine water because it allowed for efficient and cost effective, semi-passive treatment schemes to be designed. Furthermore, it provided an equation that the Coal Authority will be able to use in the future to model hydrogen peroxide dosing at treatment schemes.

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