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MINING AND THE ENVIRONMENT - UNDERSTANDING PROCESSES, ASSESSING IMPACTS AND DEVELOPING REMEDIATION

New perspectives on the passive treatment of ferruginous circumneutral mine waters in the UK

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Abstract This paper examines major physico-chemical processes during the passive treatment of ferruginous circumneutral drainage from abandoned coal mines in the UK. Data collected over several years of studies on mine water treatment systems shed new light on the relative importance of hydraulics, settling velocity, Fe(II) oxidation rates and cascade aeration, which, in turn, informs the design of future systems. This paper demonstrates that (1) the complex settling behaviour of Fe(III) precipitates may be described by a first-order volumetric process and that settling rate is different for different mine waters; (2) the hydraulic efficiency (ratio of time to peak tracer concentration to nominal residence time) of the settling ponds studied was widely variable at low flow rates in comparison to constructed wetlands; (3) aeration cascades contribute dissolved oxygen and lead to a rise in pH due to CO_2 degassing, which are very important in reducing the required time for iron oxidation and removal; (4) for at least 10 of the 30 sites examined, modelling of the rates of Fe(II) oxidation and particulate settling reveals that removal of iron is primarily dependent on settling rate; and (5) that substantial increases in pH can be brought about by forced aeration of mine water over several hours. Findings of this study apply to the majority of coal mine water treatment sites in the UK and may have broader application to other ferruginous waters with circumneutral pH or after treatment to increase pH.

Keywords Iron oxidation · Carbon dioxide degassing · Settling velocity · Hydraulic efficiency · Constructed wetlands · Settling ponds

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Introduction

Contaminated, iron-rich (ferruginous) drainage is one of the most pernicious and long-lasting environmental consequences of coal and metal mining. The problem mainly arises because of the ubiquity of the mineral pyrite (FeS_2) in metal deposits and coal-bearing strata that tend to oxidise upon exposure to the atmosphere, releasing sulphuric acid and dissolved iron. When acidic, it is termed acid rock drainage (ARD) or acid mine drainage (AMD); in such cases, the acidic nature of the mine waters often mobilise other metal/metalloid contaminants if present in the host rock (Kirby and Cravotta 2005; Cravotta 2008). The dissolved iron may persist after neutralisation of the ARD or AMD, particularly under anaerobic conditions.

This paper focuses on ferruginous circumneutral mine drainage from abandoned coal mines in the UK. The study reflects on 7 years of research by the author and also includes data provided by the UK Coal Authority, relating to the performance and geochemical behaviour of mine water treatment systems. The paper contains a number of key findings about the performance of the systems that will be useful to organisations or companies attempting to address mine water pollution problems. While the paper focuses on ferruginous circumneutral waters from coal mines rather than AMD, it is worth noting that the research is also applicable to the passive treatment of AMD as many schemes first involve neutralising mine water, followed by aerobic ponds and wetlands for further treatment. Thus, after the initial neutralisation of AMD to neutral pH, the processes for iron removal, i.e. oxidation of dissolved Fe(II) at circumneutral pH and precipitation and settling or accretion of the particulate Fe(III) produced, are the same as described here.

Ferruginous mine water: a UK perspective

Despite having a formerly large coal mining industry, almost all of the underground coal mining operations in the UK have ceased. Since coal mine abandonment and cessation of dewatering, groundwater has rebounded and continues to flush the products of pyrite oxidation from mine workings across the UK (Younger et al. 2002; Jarvis and Rees 2005). The result is the presence of both AMD and neutral mine drainages from all of the former coal fields. In many coal geological settings in the UK, limestone is abundant. Consequently, the acidic nature of the 'original' mine water has been neutralised, leaving iron as the principal contaminant; other contaminants such as manganese and aluminium may also be present in significant concentrations depending on the mineralogy of the coal-bearing strata and the pH and oxidation state of the drainage water. The iron, present as Fe(II), remains dissolved in the mine water, whilst access to atmospheric oxygen is restricted. On discharge from the mine and/or exposure to oxygen, the Fe(II) oxidises to Fe(III) which rapidly hydrolyses at circumneutral pH to what is often described as $Fe(OH)_3$ precipitates (Eq. 1). In reality, the composition and mineralogy of these solids vary considerably and are most conveniently described as hydrous ferric oxide (HFO) or 'ochre'.

$$\mathrm{Fe}^{2+} + {}^{1}/_{4}\,\mathrm{O}_2 + 2\,{}^{1}/_{2}\mathrm{H}_2\mathrm{O} = \mathrm{Fe(OH)}_3 + 2\mathrm{H}^+ \tag{1}$$

The environmental impact of this drainage (which is considerable) is not directly related to the toxicity of the water; the low solubility of Fe(III) at circumneutral pH results in low dissolved iron concentrations within a short distance from the point of discharge. Rather, it is the precipitation and accretion of ochre that blankets riverbeds that effectively smothers the benthos, leading to a significant reduction in biodiversity (Earle and Callaghan 1998).

Ferruginous mine drainage is one of the main legacy issues of coal mining in the UK because at the time of mine abandonment, prior to 2000, there was no 'polluter pays' legislation in place (Jarvis and Rees 2005). The UK government (via the Coal Authority) is responsible for remediating these discharges. To date, the Coal Authority has installed close to 60 treatment systems and continues to develop new schemes as well as refining those already in place to increase treatment efficiency and reduce costs.

Physico-chemical processes during mine water treatment

Ferruginous mine waters from abandoned coal mines in the UK tend to be circumneutral and either net alkaline or slightly net acidic and contain ferrous iron (Fe(II)). Representative Coal Authority data show an average (with standard deviation and number of sites) Fe(II) concentration of 23 mg L^{-1} (±13.2 mg/L, n=34) and pH 6.7 (±0.6, n=21). Treatment for these mine waters is achieved through cascade aeration, followed by settling lagoons (settling ponds) and constructed wetlands. The schemes are mostly passive, although often the mine water is pumped to the treatment system. The settling lagoons are designed to remove a significant proportion of the iron load up front, leaving the wetlands to polish the remaining iron from the discharge. There are numerous processes thought to occur in the wetland including biologically assisted sequestration of iron in the wetland substrate either as oxides or sulphides, depending on the Eh, or sorption onto organic matter; uptake by plants is minimal (Younger et al. 2002). Despite these processes, the removal mechanisms which account for the vast majority of iron removal from the water are Fe(II) oxidation (see Eq. 2) and separation of the ochre produced, whether by settlement, filtration or accretion. Thus, the overall efficacy of these systems for iron removal is dependent upon the rates of Fe(II) oxidation, settling rates of particulate Fe(III) and the system residence time. Note that from here on, the term 'settling rate' is used as a catch-all term to describe both the rates of settling and filtration/accretion processes.

The common and widely cited empirical rate law for Fe(II) oxidation at pH of >4 (e.g. Stumm and Lee 1961) is as follows:

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k[\mathrm{Fe(II)}][\mathrm{OH}^-]^2 P_{\mathrm{O}_2} \tag{2}$$

[Fe(II)]	Molar concentration of Fe(II)
$[OH^-]$	Molar concentration of OH^-
P_{O_2}	Partial pressure of O_2 (in atmosphere)
k	Rate constant (mole per atmosphere per minute)

Laboratory-determined values for k have been published by a number of authors, including Shenk and Webber (1968), Davison and Seed (1983) and Liang et al. (1993), and are all within the range 1.5 (±0.5)×10^{13} mol^{-2} atm^{-1} min^{-1} (Stumm and Lee 1961) to 3.2×10^{13} mol^{-2} atm^{-1} min^{-1} (Millero et al. 1987) at 20.5–25 °C. Previous work by Geroni and Sapsford (2011) found that values for the rate constant k determined in the field appear to be 1–3 orders of magnitude greater than this. The rate of Fe(II) oxidation has been shown to be temperature dependent with estimates of activation energy in the range 29±2 kJ mol^{-1} (Millero et al. 1987) to 96 kJ mol^{-1} (Stumm and Lee 1961). The water dissociation constant K_w is also temperature dependent, thus requiring correction of $[OH^-]$ accordingly (where $[OH^-]=K_w/10^{-pH}$). The reported values for k determined by Geroni and Sapsford (2011) in the field take account of these temperature effects.

A common observation at passive circumneutral mine water treatment schemes is that the pH is often higher at the outflow than the inflow. The pH increases when carbon dioxide (CO_2) degases from the mine water (e.g. Geroni et al. 2012). High levels of CO_2 are derived from microbial respiration and reaction of the original mineral acidity with limestone. When underground, the mine water/mineral system is 'closed', and high levels of dissolved CO_2 can accumulate in the water. When the water emerges, this excess CO_2 will degas until equilibrium with the atmospheric partial pressure of CO_2 is reached. Of note in Eq. 2 is the second-order dependence on $[OH^-]$, i.e. an inverse square relationship with $[H^+]$, meaning changes in pH have a substantial influence on the rate of Fe(II) oxidation. It is for this reason that the degassing of CO_2 from mine water is of particular interest as the associated increase in pH can dramatically reduce the residence time required to ensure complete Fe(II) oxidation. An increase in pH of 1 unit results in a 100-fold increase in Fe(II) oxidation rate.

There is little in the literature concerning the actual settling behaviour or rate of settling of precipitated ochre in mine water treatment systems. An exception, the study by Hove et al. (2007), demonstrates how the prevailing pH can influence the nucleation rate, mineralogy and final particle size distribution of iron precipitates in treatment systems, but their results show that, interestingly, there was a little discernable difference between settling rates of particles formed at pH values between 6 and 10. This paper aims to present settling data along with another important parameter, the hydraulics of the treatment system, in order to provide a full picture of all parameters controlling Fe removal. The literature on hydraulics in chemical reactor engineering (e.g. Levenspiel 1999) demonstrates that 'conversion' for all processes with positive reaction order is maximum under ideal plug flow conditions. Accordingly, for optimal iron removal within open ponds or wetlands of a given design, flow should be as close to plug flow as possible, though this is, as will be demonstrated, often not the case in practice. Interestingly, the exception to the preference for plug flow in reactors (in this context, lagoons/wetlands) occurs for certain instances where autocatalytic behaviour is occurring in reactors designed for low conversion (Levenspiel 1999). In most instances, high conversion is desirable in a treatment lagoon or wetland; thus, plug flow is desirable in most cases.

Methods

Aeration cascade analysis

The data in this paper are supplemented by an analysis that was conducted by consultants (Opus International Consultants 2011) on behalf of the Coal Authority into the current performance of operational aeration cascades (see Table 1). The report details studies of oxygenation of mine waters and pH changes, based on methods used by Geroni et al. (2012). Note that the author of the current study did not collect these data but is reporting results (with permission) from this study. Two Hanna HI-9828 multi-parameter probes were calibrated on site and deployed, one at the top and bottom of the cascade. Typically, data were collected for approximately 1 h with the meters set to log values of pH, dissolved oxygen (DO) and electrical conductivity (EC) every 15 s. All other works described below and used for this study were completed by the author of this paper.

Settling rate determinations

To investigate the settling behaviour and settling rate of particulate ochre in mine waters, samples were collected from four sites across South Wales, UK, and were used for laboratory-based 'long tube' settling experiments. A plastic settlement cylinder, 2.5 m tall with an internal diameter of 20.3 cm, was fabricated with tapping points at heights of 61, 122 and 183 cm from the bottom of the tube. Fifty litres of mine water sample was collected from the outlet of the first lagoon of each test site (Lindsay, Taff Merthyr, Morlais and Six Bells). The samples were then transported back to the laboratory and left for further 3 days to allow complete oxidation of Fe(II). The 50-L sample was then agitated and pumped in to the top of the settlement cylinder using a peristaltic pump. Compressed air was introduced at the lowest tapping point for 20 min to thoroughly mix and resuspend the particulate matter in the settling column. The airline was removed, and initial water samples ($t=0$ min) were taken from each of the three sampling ports. These water samples were taken by drawing out 50 mL from each tapping point into a collection beaker, slowly over a period of a minute. A 25-mL subsample was taken and acidified with 1 mL of 3 M nitric acid (HNO_3) in order to dissolve the particulate iron, and the samples were analysed for iron by ICP-OES. Further samples were taken periodically (intervals between 20 min and hours for up to 1.2 days) from each tapping point; although with subsequent sampling, 30–50 mL of water was flushed slowly from the tapping points into a waste beaker to minimise contamination from the previous sampling occasion.

Tracer tests

Six tracer studies were carried out between November 2007 and August 2008 at the Lindsay and Taff Merthyr mine water treatment schemes in South Wales, UK. The tracer used was NaCl, either 10 or 40 kg was used (amounts indicated in Fig. 4) and the NaCl was first dissolved in 50 L of mine water and introduced into the mine water over approximately 1 min. For the first set of tracer tests (28-11-07 to 14-03-11), effluent conductivity was measured using a Consort K912 logging

Table 1 Summary of cascade data from mine water treatment sites across the UK (data derived from Opus International Consultants UK 2011)

Site no.	Site	Flow[a] ($L\ s^{-1}$)	Cascade width (m)/no. of steps/height (m)	Mean at cascade top				Mean at cascade bottom			
				(n)	Temp (°C)	pH[b]	DO ($mg\ L^{-1}$)	(n)	Temp (°C)	pH[b]	DO ($mg\ L^{-1}$)
1	Acomb	26	2.1/5/–	250	11.73	6.83	4.33	245	11.78	6.36	9.92
2	Aspull Sough (1)	24	4/5/0.5	243	11.78	6.31	4.85	248	11.94	6.60	8.34
3	Aspull Sough (2)	24	4/5/0.5	232	12.84	6.95	7.33	252	12.87	7.29	9.56
4	Bates (1)	179	5.5/3/0.8	241	13.76	6.68	3.90	243	13.76	7.02	8.33
5	Bates (2)	188	5.5/3/0.8	482	13.81	6.64	3.27	482	13.79	6.99	7.21
6	Bates (3)	–	–	244	13.81	6.70	6.60	246	13.80	6.93	7.06
7	Bates (4)	–	–	267	13.82	6.54	5.22	295	13.79	6.94	8.29
8	Blenkinsopp	27	2/7/0.1	251	12.84	6.30	3.94	241	12.85	6.59	8.18
9	Blindwells (1)	294	30/6/0.5	397	11.71	6.31	0.34	396	11.84	6.69	6.09
10	Blindwells (2)	294	30/6/0.5	243	11.70	6.30	0.37	241	11.74	6.70	6.55
11	Bridgewater	55	–	251	11.98	6.95	9.50	267	12.06	7.23	9.64
12	Clough Foot	24	3/5/0.5	259	10.08	5.91	4.62	246	10.87	6.23	9.28
13	Cuthill	17	0.5/70/–	1,229	11.02	6.50	3.23	234	10.67	6.91	7.63
14	Deerplay	23	2.8/4/–	238	10.74	6.64	0.01	237	10.69	6.93	8.46
15	Ewanrigg	7	2/5/0.5	261	12.15	6.48	4.88	254	12.38	6.82	7.93
16	Francis (1)	162	15/5/0.5	243	13.98	6.39	0.33	238	13.97	6.47	6.39
17	Francis (2)	162	15/5/0.5	242	14.00	6.38	0.33	240	13.98	6.46	6.35
18	Hockery Brook	13	4/5/0.5	251	13.00	6.27	4.52	241	13.08	6.60	7.46
19	Kibble (1)	–	–	249	15.30	6.80	6.47	239	15.32	6.77	6.81
20	Kibble (2)	–	–	242	15.23	6.82	5.76	245	15.26	6.88	8.26
21	Kibble (3)	–	–	266	15.23	6.85	5.38	241	15.21	6.91	8.04
22	Lindsay (1)	15	1.9/3/0.4	251	15.12	7.04	5.00	255	15.14	7.23	7.76
23	Lindsay (2)	15	0.5/36/0.1	237	16.36	7.54	6.94	250	16.36	7.90	7.33
24	Minto	44	0.7/6/0.3	255	15.33	6.50	0.14	248	15.37	6.60	3.70
25	Morlais	–	2/3/0.3	243	14.16	6.81	0.45	241	14.20	6.91	3.94
26	Smithy Brook	15	3.5/5/–	264	12.90	6.83	4.00	261	12.87	7.14	8.54
27	Taff Merthyr (1)	–	0.4/8/0.1	242	12.01	7.14	2.59	245	12.03	7.23	6.25
28	Taff Merthyr (2)	–	0.4/9/0.1	242	12.05	7.17	3.66	257	12.11	7.23	5.86
29	Whittle	24	1.2/3/0.38	238	9.95	6.71	1.74	241	9.98	6.83	7.28
30	Woolley	131	5/4/–	289	16.33	7.28	0.10	278	16.30	7.66	7.84

[a] Approximate flows based on either average abstraction rates for the month of measurement, spot pump rate data or spot flow measurements

[b] pH data computed from $-\log_{10}$ (mean $[H^+]$)

conductivity meter. Flow rates were calculated from measured velocities which were found using vertical axis flow meter (impellor) positioned at three fifths of the water depth. The number of impellor revolutions was taken over 15-min intervals to give an average flow velocity. After repeating these measurements three times, mean calculated velocities were then multiplied by channel cross-section area (using measured depths) to give calculated flows. The second phase of tracer studies (18-07-08 to 15-08-08) used Hanna HI-9828 multiparameter data logging probes to log the pH, DO, temperature and conductivity of the inlet and outlet waters. A FLOWSYS Doppler flow meter was used to log flow every 10 s for the duration of the tracer tests.

Batch aeration experiments

Mine water used in the batch aeration studies were taken from the following mine water treatment sites: Lindsay, Taff Merthyr, Tan Y Garn, Glyncastle, Corrwg, Blaenavon, Morlais and Ynysarwed. Twenty litres of ‘fresh’ mine water was collected from the influent of each site and immediately sealed underwater to minimise the release of dissolved CO_2. The samples were then returned back to the laboratory as quickly as possible (within 70 min). Upon returning, 10 L of sample was transferred into a bucket at the bottom of which was a manifold comprising two connected rings of perforated MDPE pipework (Ø 5 mm). The perforated manifold was connected to a pressurised air supply (maintained at approximately 2.5 bar) to allow sample aeration/air stripping over 14 h. Two Hanna HI-9828 multi-parameter data meters were used to log pH, EC and DO at 10-s intervals, and the data were then downloaded and $[H^+]$ averaged.

Results and discussion

Cascade aeration and CO_2 degassing

Table 1 gives the results of the cascade analyses. As would be expected, DO increased from the top to the bottom of the cascade for all sites. Averages (with standard deviation) across all sites monitored ranged from 3.66 mg/L (±2.51 mg/L) to 7.48 mg/L (±1.42 mg/L) at the top and bottom of the cascades, respectively. It is interesting to note that in almost all cases, the pH also rises across the cascades from pH 6.69 (±0.35) to pH 6.90 (±0.36), the exception being Acomb where net acidity from Fe(II) oxidation and hydrolysis results in a pH decrease. This rise in pH is due to CO_2 degassing from the circumneutral, net-alkaline mine waters (see also Geroni et al. 2012).

Particulate iron settling rates

Figure 1 gives the results of the settling experiments for the Lindsay mine water. The results are given as concentration of iron at each sampling port (of different heights from the bottom of the column) with time. Data from the other tests are not shown but followed the same trends. The results of the tests show unusual settling behaviour, neither the ‘line settling’ nor the ‘flocculent settling’ that is commonly observed in settling of suspensions. Both types of common settling produce distinctive plots in the form of concentration versus time for the different depths. The data from the settling of particulate ochre in mine water do not follow these typical settling trends. The settling behaviour is similar to that observed by Pizarro et al. (1995) for HFO colloids settling in a lake. One possible explanation is that the suspended particles are mostly stable, but occasionally, groups of particles accrete, or ‘snowball’, and settle very rapidly (loosely analogous to rain falling from a cloud). As the measured iron concentrations in Fig. 1 were constant across sampling heights, the data for each time interval were averaged over the entire column volume, and a plot of ln[Fe] versus time (see Fig. 2) reveals that the decrease in average concentration of suspended particulate iron over the entire depth of the column can be successfully described by first-order kinetics for all of the experiments. Parameterisation of settling in the form of a volumetric first-order removal constant not only describes the experimental data well but is a useful form for combination with a first-order volumetric rate constant for Fe(II) oxidation such that iron removal in a passive mine water treatment scheme can be approximated by two steps (Sapsford and Watson 2011):

$$\mathrm{Fe(II)}_{(aq)} \text{- - -} \; k' \text{- - -} \longrightarrow \mathrm{Fe(III)} \text{ - - -} \; k_2 \text{ - - -} \longrightarrow \text{Settled Fe(III) (ochre)} \tag{3}$$

where k' is the pseudo-first-order Fe(II) oxidation rate constant (discussed in detail in the following section), Fe(III) is the suspended particulate iron and k_2 is the settling rate constant (settling here is also used to describe accretion).

It can be seen from Fig. 2 that the settling rates are different for different mine waters, although the rates are very similar for Taff Merthyr and Lindsay. It seems likely that the settling rate is influenced by site-specific conditions, specifically the mine water chemistry which will influence the surface charge on the precipitates (zeta potential) and, hence, the tendency for particles to repel or attract on another (e.g. Barnes et al. 2009). Organic particles may also

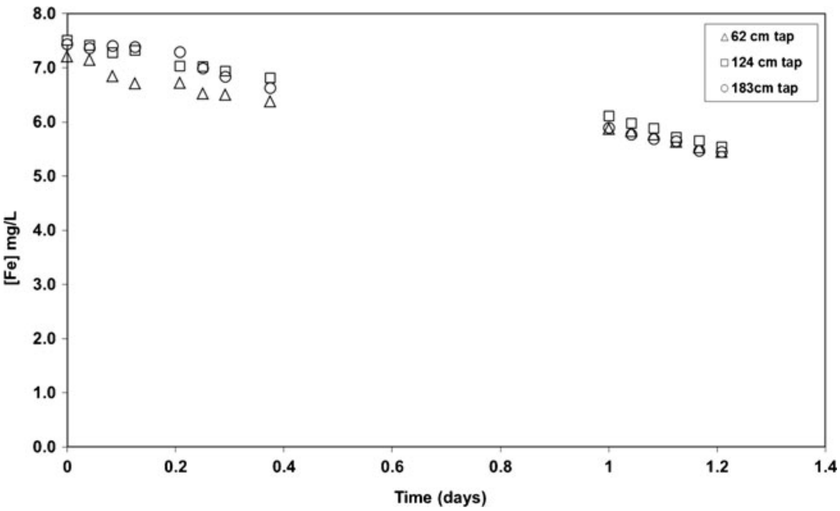

Fig. 1 Results from settling column for Lindsay mine water showing change in the concentration of suspended particulate iron concentration with time

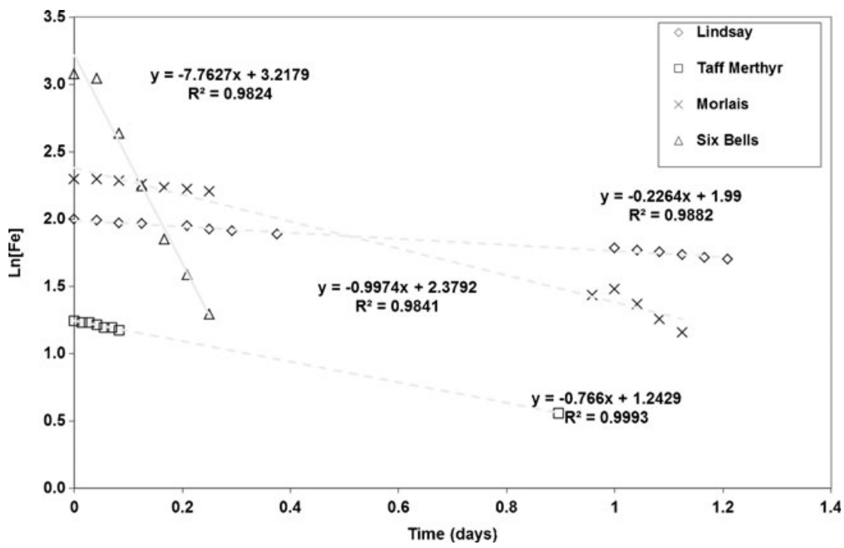

Fig. 2 Data for settling experiments plotted on characteristic first-order ln plot to determine settling rate constant for changes in the concentration of suspended particulate iron concentration with time

be important in acting as natural flocculants (Pizzaro et al. 1995). Values for k_2 vary between 0.23 and 7.76 day^{-1} (cf. Pizzaro et al. 1995). The maximum settling rate for UK mine water systems has previously been estimated from analysis of the Coal Authority treatment performance database and was found to be 12.5 day^{-1} (Sapsford and Watson 2011). This upper limit was only found for wetlands, thus, in reality, probably reflecting filtration/accretion as the cause of more rapid ‘settling’.

Theoretical framework to consider k' and k_2

If Eq. 2 is recast for conditions of fixed pH and DO, then Fe(II) oxidation becomes a pseudo-first-order process as described by Eq. 4, with k' as the pseudo-first-order rate constant defined in Eq. 5:

$$-\frac{d\mathrm{Fe(II)}}{dt} = k'[\mathrm{Fe(II)}] \tag{4}$$

where

$$k' = k\mathrm{P}_{\mathrm{O}_2}[\mathrm{OH}^-]^2 \tag{5}$$

The overall rate of Fe removal from solution can then be described by a rate equation which combines both oxidation and settling steps with the settling rate constant (k_2). Removal of iron [i.e. in the form of oxidised settled Fe(III) (ochre)] in the mine water treatment system can then be calculated by applying standard relationships for first-order reactions and sequences of first-order reactions (e.g. Stumm and Morgan 1996; Levenspiel 1999). Equation 6 describes the decrease in concentration of dissolved Fe(II) with time. Equation 7 describes the concentration of suspended Fe(III) with time (note that all Fe(III) can be assumed to exist as particulate in the circumneutral pH range considered here). Equation 7 takes into account both the production of suspended particulate Fe(III) through the oxidation of Fe(II) as in Eq. 6 and the attenuation of the suspended particulate Fe(III) through settling. Thus, the total iron in the water column can be determined at any time t by Eq. 8, by combing expression for the dissolved Fe(II) with time (Eq. 6) and the expression for the suspended particulate Fe(III) with time (Eq. 7).

$$[\mathrm{Fe(II)}]_t = [\mathrm{Fe(II)}]_0 e^{-k't} \tag{6}$$

$$[\mathrm{Fe(III)}]_t = k'[\mathrm{Fe(II)}]_0\left(e^{-k't} - e^{-k_2t}\right)/(k_2 - k') \tag{7}$$

$$\begin{aligned}[\mathrm{Fe}]_t = [\mathrm{Fe(II)}]_t + [\mathrm{Fe(III)}]_t = [\mathrm{Fe(II)}]_0 e^{-k't} \\ + k'[\mathrm{Fe(II)}]_0\left(e^{-k't} - e^{-k_2t}\right)/(k_2 - k')\end{aligned} \tag{8}$$

where

$[\mathrm{Fe(II)}]_t$	Fe(II) concentration at time t (in milligrams per litre)
$[\mathrm{Fe(II)}]_0$	Initial Fe(II) concentration (in milligram per litre)
$[\mathrm{Fe(III)}]_t$	Suspended particulate Fe(III) concentration at time t (in milligram per litre)
$[\mathrm{Fe}]_t$	Total concentration of iron [suspended particulate Fe(III) + dissolved Fe(II)] in water at time t (in milligram per litre)
k'	Pseudo-first-order oxidation rate constant (per day)
k_2	First-order sedimentation rate constant (per day)
t	Residence time (days)

Equation 8 was used to compute $[\mathrm{Fe}]_t$ for influent concentration of Fe(II) and t iterated until $[\mathrm{Fe}]_t$=0.05 $[\mathrm{Fe(II)}]_0$, i.e. 95 % removal of total iron from the mine water. Two different illustrative values of k were used (within range from Geroni and Sapsford 2011) with different values of pH, which, together with k and known values of DO and temperature, define k'. Being first-order relations, the fractional removal is independent of the values given for $[\mathrm{Fe(II)}]_0$. This equation makes several simplifying assumptions such as ideal plug flow hydraulics and fixed DO and pH to calculate the required residence time for treatment. Despite this, some important trends can be derived using Eq. 8, which reveal the relative importance of pH and Fe(II) oxidation rate versus settling rate of ochre for mine waters where initial Fe(II) levels are low enough not to require a reaeration stage.

Figure 3 illustrates changes in Fe concentrations over time calculated using Eq. 8 and presented as residence time required for 95 % iron removal from waters initially containing only Fe(II). Several example curves showing potential relations between retention time and pH are given for different values of k' and k_2 (Fig. 3). The following conclusions can be drawn from studying these potential relations shown in Fig. 3:

1. By controlling k', pH can have a significant effect on the residence time required for iron removal. At lower pH, Fe(II) oxidation becomes the rate limiting step (i.e. $k'<k_2$); in this region, the required residence time for 95 % removal changes as pH changes. At higher pH, Fe(II) oxidation is sufficiently fast that particulate settling becomes the rate-limiting step for iron removal in the system (i.e. $k'>k_2$), and above pH 7, the required residence time for 95 % removal of iron becomes independent of pH and dependent solely on k_2.
2. For mine waters with a low k', cascades may provide significant increases in pH and, hence, increase k' with commensurate reductions in the required residence time of a treatment scheme. Figure 3 has the pH changes (see references to Table 1) plotted, and it can be seen that a relatively small adjustment in pH (between pH 6.4 and 6.8) could result in reductions in the required residence time for 95 % iron removal. However, it is also worth noting that, for about ten of the sites, the pH data before degassing lie to the right of the 95 % removal curve, and thus is already sufficiently high that the required residence time for treatment is independent of pH.
3. As k is increased (a higher value is shown by the dashed line in Fig. 3), the pH at which settling becomes rate limiting is lowered. In the mine waters studied in Geroni and Sapsford (2011), it was noted that the values of k varied considerably for different mine waters and were noted to be higher for sites with lower pH. The implication therefore is that settling is always likely to be the rate-limiting step for iron removal in a well-oxygenated system at circumneutral pH. Interestingly, this provides an explanation for the origin and relative success of the National Coal Board ‘rule of thumb’ (PIRAMID Consortium 2003) of applying a standard residence time of 48-h retention time as a design stipulation for lagoons/ponds, a design rule which is independent of pH and initial iron concentration, i.e. comparable to the straight line sections of the curves in Fig. 3.

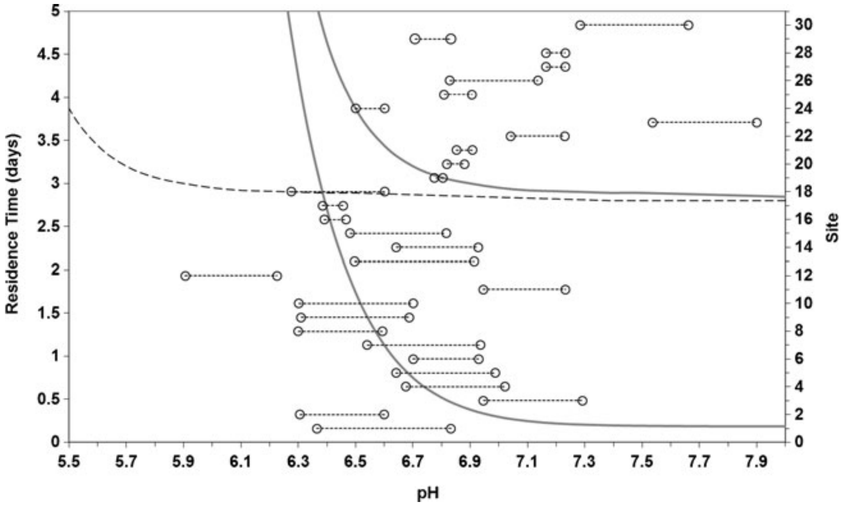

Fig. 3 Graph showing the required residence time for 95 % total iron removal for mine waters (derived from using Eq. 8) with different values of k' and k_2. In the diagram, the *solid grey lines* are as follows: *upper solid grey line* uses k' values derived from $k=3\times10^{14}$ $\mathrm{mol^{-2}\,atm^{-1}\,min^{-1}}$, DO=8.5 mg $\mathrm{L^{-1}}$, temperature=12 °C, $k_2=0.8$ $\mathrm{day^{-1}}$; *lower solid grey line* uses the same values but with $k_2=12.5$ $\mathrm{day^{-1}}$; the *dashed line* is derived from a $k=3\times10^{16}$ $\mathrm{mol^{-2}\,atm^{-1}\,min^{-1}}$, DO=8.5 mg $\mathrm{L^{-1}}$, temperature=12 °C, $k_2=0.8$ $\mathrm{day^{-1}}$; the *right-hand* y-axis gives pH data of mine water treatment sites as listed in Table 1, and the *markers* indicate the pH at the *top* (*left-hand side*) and *bottom* (*right-hand side*) of aeration cascades, except for sites 1 and 19 where there was a slight pH decrease

Tracer tests

Figure 4 shows three examples of tracer tests run in settling lagoons at the Taff Merthyr and Lindsay sites. The measured effluent conductivity trends are mirrored by Cl concentrations in the effluent (data not shown). It can be seen for the tests run on 14-03-08 and 18-07-08 that the lagoons studied display very different hydraulic residence time distributions (also known as 'exit age distribution' (Levenspiel 1999)) as revealed by the tracer compared to wetlands (data shown in Fig. 5). At typical design flows, both the Lindsay and Taff Merthyr lagoons resulted in a very dispersed flow regime, and note that the meaning of 'dispersion' used here is used as per Kadlec and Wallace (2008). In fact, the tracer results show that the mean retention time of the tracer in the systems is actually longer than the nominal retention time (i.e. volume/flow), suggesting that the tracer must have remained in stagnant zones of water and was only gradually released from the system.

By contrast, the tracer test run on 15-08-08 showed much more plug-like flow similar to that observed for wetlands in Fig. 5. Under normal conditions, water at Taff Merthyr runs through two parallel settling lagoons, but in this example, one lagoon was closed off (for maintenance purposes). This effectively doubled the flow through the remaining lagoon which accounts for the reduced nominal residence time compared to 14-03-08. Under these conditions, the hydraulic efficiency as per Persson et al. (1999) is 0.97 [calculated as the ratio of time of peak tracer concentration (t_p) to nominal residence time with the system approaching idealised plug flow conditions as hydraulic efficiency approaches unity]. The data therefore suggest that higher flows lead to greater hydraulic efficiency. Based on many field observations, the authors posit that this may be because, at low throughputs, there is insufficient turbulent mixing through the water column caused by the incoming water, such that influent water skates across the top of the lagoon (an effect that could be exacerbated by temperature stratification within the lagoon). Furthermore, wind-driven turbulence may contribute to a much dispersed flow at low throughputs.

Flow through the wetlands is plug-like in all cases observed in this study (cf. Kusin et al. 2010). Figure 5 shows characteristic well-defined 'tight' peaks indicative of limited dispersion. This is probably due to the higher advective velocities compared to lagoons (reed beds typically being circa 0.4 m in depth versus around 2 m for lagoons) and the attenuation of dispersion mechanisms by reeds (Kadlec and Wallace 2008). Despite the more plug-like flow, it can be seen that the hydraulic efficiency in the case of Lindsay is low (0.31), revealing short-circuiting. The deviation from ideal plug flow and the hydraulic efficiencies of unity that are seen reveal the profound influence of hydraulics on the effective residence time of water in each treatment system, in effect reducing substantially their effective volume, something that can be addressed by an improved design.

Batch aeration

The results of the batch aeration of mine water samples are shown in Table 2. It can be seen that there is a substantial increase in the pH of the mine water after aeration. This is a result of CO_2 stripping from the mine water and has been modelled elsewhere for a number of coal mine discharges by Geroni et al. (2012). The high pH end point of many of the mine waters reflects the original contact with carbonate minerals. It is worth noting that not only can CO_2 stripping raise pH and increase Fe(II) oxidation rate but, by reducing the acidity of the water, can also reduce the required lime dose (equating to substantial financial savings) for many mine waters.

Improving passive mine water treatment

Despite the success of current passive mine water treatment schemes in the UK, there is a continued requirement to

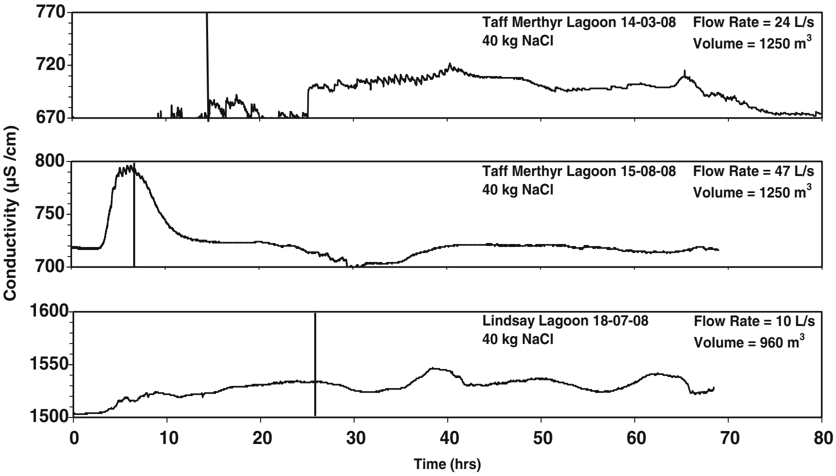

Fig. 4 Effluent conductivity for lagoons at Taff Merthyr and Lindsay during tracer tests. Nominal retention time is marked with a *vertical line*

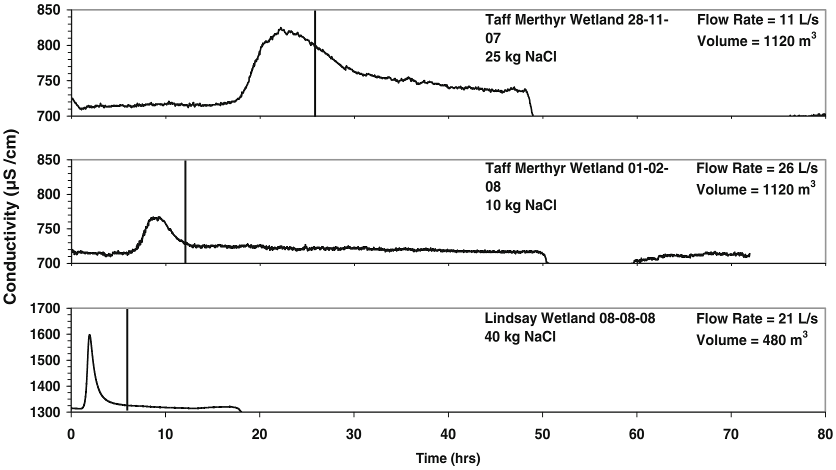

Fig. 5 Effluent conductivity for wetlands at Taff Merthyr and Lindsay during tracer tests. Nominal retention time is marked with a *vertical line*

reduce the land take of these systems. Sizing becomes an issue where land is unavailable and because larger size systems inevitably mean increased capital expenditure in the civil engineering work. To reduce the area required for treatment, the rate of iron removal in mine water treatment systems must be increased. This study has given some insights into potentially fruitful solutions as follows:

1. Improved hydraulics: It has been shown that hydraulics are often poor in mine water treatment systems. Improvements can be achieved by the installation of flow control structures such as baffles as was clearly demonstrated by Wolkersdorfer (2011). Even a small percentage increase in the performance of a settling lagoon is advantageous for the longevity of the whole treatment system. Sludge management can substantially improved by dropping out more iron in the lagoons because lagoon desludging is relatively easy (PIRAMID Consortium 2003), and this has commensurate benefits for the treatment wetlands by reducing the need for intrusive ochre sludge removal which might disturb the habitat and ecosystem value of the reed beds.
2. Settling rate has been shown to be independent of depth (in this study, up to depths of ~2m) but dependent on residence time. Building deeper settling lagoons (with longer residence time) would make more effective use of a given land area. This is caveated, however, with the need to make sure that influent is uniformly distributed and well mixed across the entire depth, which may be possible with appropriately placed baffles.
3. System size could be dramatically reduced if both the rate of oxidation and settling were accelerated. Changes in pH can be induced by aggressive CO_2 stripping/aeration to reduce the Fe(II) half-life to the order of minutes to seconds. Settling would then be limiting, but this could be accelerated by the use of coagulants, polymer flocculants and other means of solid/liquid separation (e.g. filtration; see Sapsford and Williams 2009). Many of these improvements (and commensurate savings in capital expenditure) would however result in higher operational expenditure which would have to be balanced over the lifetime of the treatment scheme but may be the only option where land availability is constrained.

Table 2 pH of net-alkaline mine water before and after prolonged (14 h) aeration/degassing

Mine water	Start pH	End pH
Lindsay	7.01	8.66
Taff Merthyr	6.36	8.44
Glyncastle	6.42	8.25
Corrwg	5.97	7.89
Blaenavon	6.17	8.16
Morlais	6.55	8.25
Ynysarwed	5.78	8.16
Tan-y-Garn	5.16	7.75
Six Bells	6.72	7.85

Conclusions

This paper has summarised physico-chemical and hydraulic data collected over many years of research on mine water treatment systems. Trends have been determined that have potentially important ramifications for both the science and engineering aspects of mine water treatment systems. The main findings can be summarised as follows:

1. Fe(III) hydroxide precipitates exhibit complex settling behaviour. Settling of these precipitates can be described by a first-order process with rates varying for different mine waters.
2. The hydraulic efficiency of the settling ponds studied was generally shown to be poor (short circuiting

and very dispersed flow) in comparison to constructed wetlands—an observation that may be related to influent water not mixing over the entire depth of the pond at the point of entry and/or wind-driven dispersion.

3. Aeration cascades not only contribute dissolved oxygen but also (importantly in some cases) lead to a consistent rise in pH due to CO_2 degassing.
4. It was shown via modelling that small increases in pH (e.g. from CO_2 degassing) may be very important for reducing the required residence time for some circumneutral mine water treatment systems but that for at least 10 of the 30 sites examined (and probably the majority) of sites in the UK, the removal of iron is solely dependent on the rate at which particulate iron is removed by settling and/or accretion.

In conclusion, this paper has attempted to take a fresh look at mine water treatment systems to reveal important information for the improved design of future systems, particularly in terms of intensification of iron removal.

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