Characteristics and treatment of mine water from three historical coal workings in Yorkshire, UK: interrelationships between rates in geochemical, environmental and operational processes

Robin S. Perry[1], A.W.L. Dudeney[2*], Brenda K.C. Chan[3]

[1] Elm House, 43 Brook Green, Hammersmith, London, W6 7EF, UK, robin.perry@ch2m.com
[2*] Centre for Environmental Policy, Imperial College London, Silwood Park Campus, Ascot, Berks SL6 7PY, UK, a.dudeney@imperial.ac.uk, corresponding author
[3] Formerly at Department of Earth Science & Engineering, Prince Consort Road, Imperial College London, SW7 2BP, UK, brendakc.chan@gmail.com

Abstract

Oxidation processes in three ferruginous coal mine water systems in Yorkshire, UK - studied over a period of some 20 years - are summarised. Filtered mine water samples from the Sheephouse Wood (SHW) system gave rates of iron(II) oxidation in homogeneous medium (determined in the laboratory in terms of the thermodynamic rate constant k) consistent with authoritative long-established literature reported for other aquatic systems. The calculated mean value of k was 2.35 x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (pH 6.4-7.0; relative standard deviation ±12.5%). For similar measurements in heterogeneous medium – in the presence of a set large excess of pre-precipitated hydrated iron(III) oxide, ochre (360 times by mass of initial dissolved ferrous iron) – a (conditional) rate constant k_c was found to be some two orders of ten greater. This represented an example of rate enhancement by autocatalytic reaction. Field measurements in a well-defined mine water channel at SHW provided semi-quantitative evidence that practical rates of mine water oxidation are also relatively greatly affected by seasonal environmental factors.

Observations of a pilot plant at the Woolley (W) system confirmed that net alkaline mine water was rapidly oxidised via autocatalytic reaction when passed through a tank containing a thick slurry of ochre. Carry-over of fine oxidised particulates tended to occur. Work at the full scale Bullhouse (BH) system, constructed with an unusually large lagoon, directed inlet pipework under water through settling ochre to optimise autocatalytic enhancement. Despite net acidity at this site, treatment met discharge objectives on oxidation and settlement for some 12 years, based on a long residence time (initially some 17 days). Progressive ochre build-up indicated a need thereafter for desludging. The results are discussed in terms of variable autocatalytic reaction, which is evidently normal in such systems, and, together with other parameters, relevance to the perceived state-of-the-art of treatment in coal mine water systems.

Key words: Coal mine water, oxidation rate, environmental character, mine water treatment

Introduction

Mine water (typically containing 5-100 mg/L Fe) from many thousands of abandoned coal and metal mines worldwide continues to cause, except where remediated, highly visible ochre and/or acid pollution. This can affect biodiversity, sometimes for as much as 1-10 km downstream from the discharge. Such discharges have received great attention on environmental grounds; in earlier days notably by the former US Bureau of Mines and former British Coal (e.g., reviewed in Dudeney, et al. 1994; Perry, 1997). Since 1994 many reports have been published internationally, e.g., the PIRAMID Guidelines (PIRAMID consortium, 2003) primarily on account of scientific, engineering and regulatory requirements relating to treatment or remediation. Analogous discharges or springs associated with many natural systems, have received similar attention, but more often on purely scientific grounds (e.g., Barrott, et al., 2014).

As part of this attention, fundamentals of geochemical processes occurring in emergent water from underground containing ferrous iron, and rate processes connecting them, have been studied over decades, and are mostly well documented. In particular, for synthetic and environmental waters under

near neutral conditions (pH 5-8), the rate of aerial oxidation under homogeneous aqueous conditions (i.e., at low concentration of iron(II) or Fe^{2+}, in the absence of significant precipitation) is well established and quantified in terms of a fundamental rate constant (k), while (generally faster) rates under heterogeneous, autocatalytic, conditions (i.e., at higher initial concentration in the presence of significant precipitated solid), are known in less precise terms of 'increased rate at increased solids content'; e.g., Stumm and Lee (1961), Davison and Seed (1983) and Stumm and Morgan (1996). However, despite the implied wealth of published information, uncertainties remain in the literature, especially in relation to mine water effluent from sedimentary coal-bearing strata. A recent paper dealing with mine water in Wales, UK (Geroni and Sapsford, 2011), reported much higher values of the constant than previously recorded. Thus, one objective of the present paper is to re-visit fundamental factors affecting rates of oxidation, especially those relevant to remediation of discharges from disused coal mines. The rate of oxidation of iron is re-determined in terms of k from previously unpublished data and also in terms of a 'conditional' constant, quantified for a representative set of autocatalytic conditions in contact with a substantive mass of ochre.

As another part, related flow processes underground and in the open environment, have been similarly studied and the general principles largely elucidated. Thus, partial oxidation of sulphide strata underground typically leads to the formation and mobilisation of iron(II), which, once out in the open, is progressively oxidised to iron(III) downstream of a source. However, conditions are usually poorly defined: effective direct access to reactive strata underground is normally impractical while emerging water often flows in an ill-defined channel or direct into a receiving stream. In particular, for ochreous mine water, many studies have tracked levels of contamination and interactions downstream from a discharge, but with limited access to details of processes spatially and temporarily. A second objective is thus to provide new data and discussion on such time-dependent processes, especially regarding environmental exposure and seasonal effects on mine water, employing flow from underground in an unusually well-defined mine water channel (leet).

As a third part, many polluting discharges have been successfully treated. In addition to fundamental and environmental data, treatment scheme design and operation has taken account of multifarious site-specific conditions and relevant regulation. Thus, unsightliness and toxicity associated with the generation of ochre and acidity have been alleviated at many operating and disused mine workings, with treated water discharged to the environment. In the UK, under the auspices of the Coal Authority (Coal Authority, 2014), a growing number of full scale mine water treatment schemes (now more than 70) treat ochreous mine water from abandoned coal mines. However, notwithstanding many years of development leading to a largely successful generalised approach (Table 1), a number of issues remain for improvement, e.g., matching plant configuration optimally to local conditions, reacting effectively to changing operational conditions as plants age, optimising the use of special geochemical effects (especially autocatalysis) and developing generally acceptable markets for recovered ochre. Once again rates of change are central, especially rates of oxidation and sedimentation in operational plant and changes occurring to system aging. Therefore, a third objective is to touch on issues around the interdependence of fundamental, environmental and treatment plant characteristics, and their different impacts on rates of change.

To introduce the provisions of Table 1, the perceived state of the art includes mine water capture, channel/cascade aeration, lagoon/wetland ochre settlement/deposition, water overflow to a local river, and gravel bed dewatering/drying of ochre for periodic recovery. Thus, the table encompasses the main technical requirements for effective removal of ochre, which are normally optimisation of rates of oxidation, settlement, dewatering and drying; typically translated into maximum effective turbulence for oxidation, quiescent water volume/surface area for adsorption/settling, and open solid standing area for water removal from ochre. Pumping is often needed to control underground levels and lift mine water to a plant level; and chemical dosing is sometimes employed (in addition to aeration) to enhance rates of oxidation and, perhaps, reduce the land area needed for treatment. Processes can also be intensified (at a cost) by selective use of mechanical equipment such as an industrial centrifuge. The table is thus an attempt to collect together technologies employed to maximise effectiveness of iron removal (particularly process rates), despite differences in local conditions, e.g., in land character, availability and accessibility for construction, linkage to mine water

sources and drainage, environmental enhancement and other issues consistent with regulatory planning approval.

Table 1 Typical sequences of oxidative mine water treatment processes and ochre isolation from abandoned coal mines in the UK

Process	Means	Purpose	Equipment
Water capture	Forced flow (gravity)*	Provide process head and required water level underground	Pump (channel flow)
Water conditioning	Aeration (dosing/aeration)	Increase DO/reduce CO_2 causing iron oxidation (enhance rate)	Open cascade/channel (chemical plant**)
Water/ochre disengagement	Settlement/ deposition	Reduce linear flow, causing sedimentation of ochre and overflow of clarified water	Lagoon and/or con-structed wetland
Ochre dewatering	Filtration	Remove occluded water	Gravel filter bed
Ochre drying	Exposure	Evaporate adsorbed water	Gravel filter bed

*Items in brackets are occasionally relevant alternatives **Adding lime, caustic soda or peroxide

The present work has been based on field study, and on associated laboratory study, carried out over a period of some 20 years with ochreous mine water from discharges and treatment products primarily involving Coal Authority treatment schemes at Sheephouse Wood (SHW), Bullhouse (BH) and Woolley (W) in Yorkshire (UK National Grid refs: SK232000, SE215028 and SE319132, respectively). The three systems have basic similarities governed by geochemistry at near neutral pH (and broadly consistent with Table 1). All three operate with pumping but no dosing (termed 'pumped passive'). However, they have many distinctions in detail, e.g., in iron concentration, flow rate and flow path and different site-specific conditions - especially different access, surface topography, land availability and technological development. For example, mine waters at SHW and BH have shown no effective diminution in iron concentration (*Ca* 30 and 50 mg/L Fe, respectively) over many years at the point of emergence from underground (adit) while at W, a progressive decrease has continued since 1994 from >100 to <10 mg/L Fe. Flow rates are typically some 2, 1 and 5 x 10^3 m^3/day, respectively, but greater in winter. Typical initial pH ranges at BH, SHW and W are 5.5-6.5, 5.9-6.6 and 7.5-8.0, respectively, while final values on samples after equilibration in air are correspondingly 3.5-4.0, about 5.5-6.0 and 7.0-7.5 (net acid, slightly net acid and net alkaline).

Fundamental and environmental rate processes, mainly rate constants and flow characteristics of iron oxidation, were determined on samples taken at SHW (at the adit and along the mine water leet), while corresponding applied issues, here mainly considering autocatalysis, were studied at W (pilot plant) and BH (full scale plant).

Oxidation rate constants

Sampling, sample management and analysis were undertaken in general accordance with established methods (e.g., Greenberg, et al., 1992). On-site analyses were made with commercial electronic probes for pH, DO, and CO_2. For iron analysis rapid colorimetric methods based on absorbance of the red Fe(II)-o-phenanthroline complex at 510 nm were used. Specific experimental rationales, procedures and quality assessments are reported in detail in Perry (1997). For precise determination of k, mine water samples, taken at the SHW adit in 500 mL plastic bottles, were immediately purged (preserved) with carbon dioxide gas for 10 minutes (using a small gas cylinder, delivery tube and glass frit), sealed and stored in a cool box at 4ºC for transport to London. Subsequent measurements were carried out in a specially constructed reaction chamber. Results were converted to plots of log Fe(II) versus time and values of k calculated from the slope of the straight line so obtained, based on the standard equation (eqn 1), valid for pH 5-8 (Stumm and Lee, 1961), relating the rate of oxidation to

the concentration of iron(II), the square of the activity of hydroxyl ion (constant at buffered pH) and the partial pressure of oxygen (constant at set inlet flow rate):

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)](a_{OH^-})^2pO_2 \qquad (1)$$

For comparison of homogeneous and heterogeneous oxidation, 20 ml wet ochre was added to aged mine water, together with quantities of iron(II) sulphate and sodium bicarbonate sufficient to yield 5 mg/L Fe^{2+} and 250 mg/L HCO_3^-, respectively, once mixed. The precise proportion of ochre present was determined as 1.81 g/L by washing, oven drying and weighing a separate 20 ml of wet ochre. Kinetic experiments were carried out as above at pH 6.0 and 10º C.

Fig. 1 shows a plot of log[Fe(II)] versus time, identified with the integrated form of eqn (1) and approximated, for constant pH and pO_2, as a straight line having slope $(k/2.30)(a_{OH^-})^2pO_2$. Similarly to Stumm and Lee (1961) and Davison and Seed (1983), a_{OH^-} and pO_2 can be calculated, respectively, from pH (making use of the temperature dependent ionic product of water) and pO_2 (from direct measurement). Thus, k can be determined. In the present work, seven replicate runs carried out in the range pH 6.4-7.0, were used to calculate a mean value of k of 2.35 x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (relative standard deviation ±12.5%). This value compares favourably with the range of rate constants determined up to 1983 and thus with the variable 'universal' rate constant given as (1.5-3.0) x 10^{13} $M^{-2}atm^{-1}min^{-1}$ (Davison and Seed, 1983). Lower precision quoted in the earlier work (e.g., relative standard deviation ±48.5%) may be attributed in part to difficulties of reliable measurement and control of pH during iron(II) oxidation, for which the rate of reaction increases some 100 fold for each pH unit increase and precipitating hydrated iron(III) oxide progressively interferes with measurements.
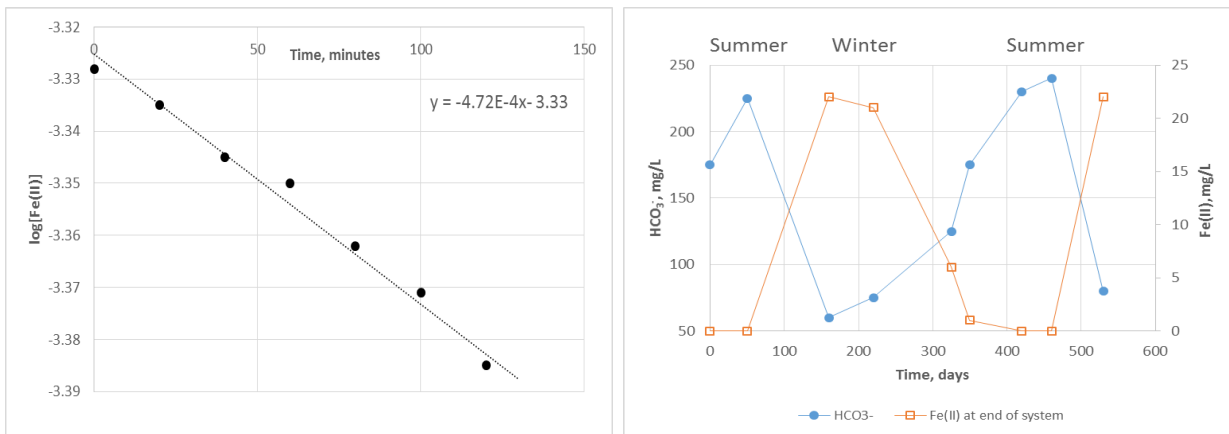
Figure 1 *Left: plot of log[Fe(II)] against time at 10ºC, pH 6.7, pO_2 0.20, initial Fe^{2+} 30 mg/L. Right: plot of seasonal variation of iron(II) concentration at far end of leet in relation to initial bicarbonate concentration. Initial iron(II) 30-45 mg/L (Summer) and 25-30 mg/L (Winter).*

An analogous plot of log[Fe(II)] versus time (not shown) for a semi-synthetic mine water at pH 6.0 and 10 ºC, initially containing 5 mg/L Fe^{2+} and 1.81 g/L ochre (dry mass, but not pre-dried), i.e., a mass large enough to overwhelm any second order effects. Once again, a good straight line was obtained having much greater slope than without added ochre. Six replicate samples, gave an average value of a conditional constant (termed $k_{1.81}$) of 2.05 x 10^{15} $M^{-2}atm^{-1}min^{-1}$ (relative standard deviation ±9.1%) This $k_{1.81}$ is some 87 times greater than k, equivalent to increasing pH by approximately one unit.

Environmental oxidation rates

At SHW mine water, once in the open, flowed along the leet approximately 3 km, with a tracer-estimated residence time of approximately 90 minutes, before discharge to the River Little Don. Notwithstanding responses to rainfall, leaf fall and routine maintenance (including sweeping-off loose accretion) the mode of flow was quite uniform, normally exhibiting laminar 'plug' flow over most of

the length, but turbulent flow (reminiscent of an aeration cascade) during a final steep 200 m descent to the river. The pH increased as dissolved carbon dioxide evolved, giving final values of approximately 7-8 and 1.7-15 mg/L, respectively, at the point of discharge to the river. Turbidity also increased via iron oxidation and precipitation, acid so generated being largely consumed by reaction with contained bicarbonate. The pH was substantially higher in summer throughout the system (largely because of less dissolved carbon dioxide and more bicarbonate), but in inverse relation to iron(II) discharged to the river. As shown in Fig. 1 (right), iron was essentially fully oxidised in summer (equivalent to an average oxidation rate of roughly 0.3 mg(Fe)/L/min), but most of it (20-30 mg/L) remained un-oxidised in winter (rate effectively zero), even though the water was 100% air-saturated by the far end of the leet.

A picture emerges from one end of the leet to the other of gas exchange between carbon dioxide and air, iron oxidation ranging from near zero to essentially complete depending upon the season, and, despite substantial exposed leet surface area subject to significant progressive fouling, a low proportion of undisturbed ochre retention (as accretion). Such observations are apparently consistent with the basic characteristics and environmental behaviour of many mine water discharges, albeit most exhibiting less controlled dispersion. Additionally they provide an unusually precise indication of the (large) variations in seasonal geochemical characteristics of mine water emerging from underground and flowing in the open environment.

Applied rates

In order to re-assess (at pilot scale) catalytic oxidation as the basis of a separate intensified 'passive' process, coal mine water at W was first employed because of ready access to a well-defined mine water source (bleed) at the pump head and ochre from the drying beds there. In 1997, mine water feed (typically 7 L/min containing 27 mg/L Fe^{2+}) was passed for several days through a thick, slowly stirred, ochre slurry (approximately 0.75 m^3 containing approximately 15 vol% ochre) contained in a 1 m^3 tank fitted at one end with a submerged inlet manifold and at the other with an overflow pipe to two similar settling tanks in sequence. The slurry was prepared by 'blunging' (in this case treading) mine water with ochre from the W drying beds. Suitably blunged ochre slurry (*cf* ceramic 'slip') formed a dense medium, with a 'mud line' below supernatant mine water, which gravitated up and through towards the outlet. Routine analyses showed iron(II) to be barely detectable at the outlet. Thus, these early results confirmed that catalytic adsorption and oxidation were relatively efficient when mine water was suitably mixed with a large excess of ochre.

However, carry-over of fine-grained ochre particles contained more iron than that entering, except at very slow flow rate, and (unless occasionally replenished) the dense medium was slowly degraded. Thus, downstream bulk solid-liquid separations were expected to partially negate any benefits of more rapid oxidation and denser deposition. In fact, in more conventional processes, oxidation and ochre disengagement from the bulk of water often occur essentially together, so a greatly increased rate of oxidation after full aeration may not be helpful as a similar lagoon or wetland volume would still be needed to retain the finer sized solid.

The BH mine water treatment scheme provided an opportunity, at full scale, to examine a modified form of autocatalytic oxidation. This scheme, associated with workings on the same coal seam as SHW, but separated from it by an underground fault, was one of the earliest Coal Authority treatment schemes, operational since 1998 (Laine and Dudeney, 2000). It relies in part on pumps delivering raw mine water to the lagoon, in this case via a 0.8 km pipeline (in some respects mirroring the leet system at SHW), which transports the water up some 26 m in elevation, along a flat stretch, down some 8 m and through an aeration cascade to the main settling lagoon. Treated mine water is pumped back along the same route before discharge. The system relies on an exceptionally large void for ochre settlement (the main settling lagoon of capacity some 50 000 m^3), made available in nearby older, near-surface, coal workings after (timely) completion of pipe-clay quarrying there by Hepworth Building Products. This provided a relatively long working retention time initially (17-25 days) and overall lifetime to full with sludge (16-20 years), but left no space (or apparent need at the time) for a substantial 'polishing' wetland and drying bed. To make full use of the retention time (and mitigate the effects of relatively large 'net acidity' in this mine water), inlet pipes to the lagoon were directed

under the water surface, thereby aiding distribution and preventing channelling to the outlets (Dudeney, et al., 2000). As the system aged, inlet water came into contact with increasing quantities of ochre suspension and sediment and was thus increasingly subject to catalytic iron oxidation – perhaps offsetting effects of reduced free volume as ochre accumulated. In any event, the system operated efficiently for more than 12 years, with little iron discharged (Fe typically <5 mg/L), net acidity in the effluent being fortuitously absorbed by natural alkalinity in the river. However, more recent large winter flows (>2000 m^3/day), greater iron content (>60 mg/L) and longer operation (some 16 years in 2014) have led to excessive particulate overflow and renewed contamination in the receiving river as the lagoon became increasingly filled with ochre. There is a need to de-sludge the lagoon and suitably dispose the ochre: major undertakings at this site.

An alternative enhancement of rates, predating considerations of autocatalytic reaction highlighted, was studied in an earlier pilot plant (Dudeney, et al., 1994, Perry, 1997) operating on SHW mine water. It employed chemical (alkali) dosing and (polyacrylamide) flocculation, which respectively increased rates of oxidation and disengagement (settling), to facilitate treatment at a space-restricted site. The pilot plant was sited near the far end of the leet but was designed to model a full scale treatment system near the SHW adit. The design was one of the first to be examined on modern environmental grounds for full scale treatment following the (then) recent closure of many UK coal mines; and was based on a gravity fed operation occupying a restricted area of land between the leet (and the adjacent A616 trunk road) and the receiving river. However, although the scheme proved technically satisfactory, the land envisaged turned out to have disadvantages, e.g., periodic water saturation and difficulty of access. Being close to the adit, the design would also have required some form of forced aeration to expel dissolved carbon dioxide ahead of dosing. More recent studies, e.g., Jarvis (2006), were spurred by a catastrophic mine water breakout at the site (which closed the A616 road for several days). A new plant, finally commissioned in 2014, instead elevates the mine water 25-30 m to a larger relatively flat area above the former mine (on the other side from the river), which has been made available for un-dosed treatment. For this purpose a hydrostatic dam, borehole and pump system are employed to shut off the original leet system and raise the water to the treatment system. The surface layout conforms to the treatment state-of-the-art (Table 1), and no doubt benefitting from a measure of autocatalytic reaction. Observation in April 2016 indicated satisfactory operation based on pumped mine water, although some seepage occurred direct from the hillside. Ochre management is based on a built-in dewatering and drying system, designed to be routine, thus avoiding the situation developed at BH.

Conclusion

Eqn (1) indicates the main variables affecting the rate of iron oxidation as iron(II) and oxygen concentration, and (especially) pH. Based on this equation, the present work confirmed that the homogeneous rate of oxidation of iron in coal mine water (determined as the fundamental rate constant) is consistent with measurements on other (synthetic and environmental) waters. However, under environmental and practical mine water treatment conditions, the present work also highlights additional factors, notably autocatalysis of iron(II) oxidation and seasonal change (particularly of ambient temperature and bicarbonate concentration) have large effects on practical rates of oxidation. Evidently such rates can be increased, in principle at least, by effective control of variables, e.g., by minimising carbon dioxide and optimising autocatalysis. Nonetheless, as significant variation in all variables should be considered as normal in particular schemes, between schemes and with the age of schemes, practical oxidation rates are not usefully generalised (or quantified). Additionally, because discharge consents may be based on total iron content in effluent, effective retention (settlement) of oxidised iron is as important as iron(II) oxidation: increase in oxidation rate may not be helpful if particulates are ineffectively retained. Of course, siting and configuration of treatment schemes also have different impacts; as emphasised here between chemical dosing on a site of limited size and access, and passive treatment on an elevated site subject to seepage via porous strata. Differences in design and outcomes mentioned exemplify the types of changes that can be consequent on prioritisation of a secure and practical procedure, consistent with regulatory approval, including constraints in matching plant configuration optimally to local conditions.

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