Using Fe(II) adsorption and surface-catalysed oxidation for Fe(II) removal from predicted mine water discharges

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Abstract This study explores the possibility of using ferrous iron adsorption and surface catalysed oxidation within a reactor to remove dissolved iron loads from predicted mine water discharges. To assist in maximizing adsorption and surface-catalysed oxidation a steady state model has been adapted to the colliery discharges. The aim of this model is to assist in reactor design which would aid in alleviating the polluting alkaline mine water discharges that are expected. The envisaged reactor would allow Fe(II) removal on plastic trickling filter media anchored in a reactor receiving the discharge. Initial modelling shows that Fe(II) in the predicted mine water discharges can be removed through adsorption and surface-catalysed oxidation within a reactor. The modelled results show a that a reactor with surface a area of 18 895 m^2 and a water content of 11.7 m^3 is required for the discharge of 1.9 Ml day^{-1} from Treeton Colliery (South Yorkshire, UK)and a surface area 4006 m^2 and a total water content 1.4 m^3 is required for the remaining two discharges from Treeton and Silverwood collieries.

Key words adsorption; coal; ferrous iron; groundwater rebound; mines; modelling; reactor; surface pollution

INTRODUCTION

Extensive coal mining, both deep and opencast, has occurred in many parts of the world. A consequence of coal mining is the dewatering of large areas over wide areas by pumping. The closure of these mines leads to the cessation of this dewatering, which can lead to extensive flooding of mine workings. Consequently, unregulated mine water discharges occur as groundwater rebound takes place (Burke & Younger, 2000; Banks *et al.*, 1997). These discharges are often initially characterized by a low pH with high metal concentrations. However, many discharges which at first emergence exhibit a low pH and high metal concentration change to an alkaline pH with moderate metal concentrations over time (Younger, 1997).

The closure of three deep coalmines in South Yorkshire, UK, namely Treeton, Thurcroft and Silverwood, introduces the possibility of unregulated mine water discharges. Burke & Younger (2000) predicted a total flow of around 3.6 Ml day^{-1} with long term Fe(II) concentrations of around 20 mg l^{-1}. The three mines were operational from the early 1900s until the 1990s when the UK government commenced a mass

closure programme of the British Coal Industry. The three mines produced around
50 000 tonnes of coal per week employing a maximum of around 5000 men.
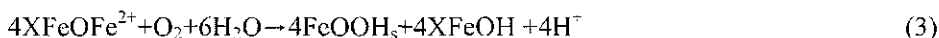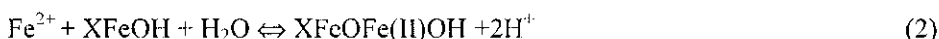
The mines were situated in the lower to upper coal measures of Carboniferous
strata and worked a number of seams with a low to medium sulphur content. The study
area is bounded to the east by Permian-Triassic strata.

Due to the large land requirements for mine water treatment using wetlands to
remove dissolved iron (Hedin *et al.*, 1994), this research explores the possibility of
using ferrous iron adsorption and surface-catalysed oxidation within a reactor model
containing high surface plastic trickling filter media using the geo-chemical code
Steadyql (Furrer *et al.*, 1989, 1990). This would assist in the design of a full-scale
reactor for the removal of Fe(II) from the predicted mine water discharges.

FE(II) ADSORPTION AND SURFACE-CATALYSED OXIDATION

Many mine water discharges in the UK (Banks *et al.*, 1997), exhibit uninterrupted and
expansive ochre (iron oxyhydroxide) accretion occurring at the base of receiving water
courses, with the upper part of the water column remaining clear of suspended
colloidal material.

The adsorption of aqueous Fe(II) species present in mine water discharges, occurs
onto the ochre surface, followed by rapid oxidation by dissolved O_2 and surface
precipitation as an Fe(III) mineral phase. The following stoichiometric reaction repre-
sents this transformation of adsorbed Fe(II) to freshly formed iron oxyhydroxide which
is irreversible under oxic conditions. A consequence of surface precipitation is
conservation of adsorption sites, represented as XFeOH, which react further, equations
(1)–(2), to adsorb Fe(II) species from solution, and catalyse their oxidation on the
FeOOH(s) surface, equation (3):

$$Fe^{2+} + XFeOH \Leftrightarrow XFeOFe^{2+} + H^+ \tag{1}$$

$$Fe^{2+} + XFeOH + H_2O \Leftrightarrow XFeOFe(II)OH + 2H^+ \tag{2}$$

$$4XFeOFe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH_s + 4XFeOH + 4H^+ \tag{3}$$

METHODOLOGY

The model developed to assist in the remediation of the predicted mine water
discharges expected from the abandoned coal mines of Treeton, Thurcroft and
Silverwood uses the geochemical code Steadyql (Furrer *et al.*, 1989, 1990). This is a
mathematical model for the speciation and oxidative precipitation of ferrous iron
(Burke & Banwart, 2002). The model formulates slow or irreversible reaction kinetics
with empirical rate laws and rapid reversible reactions as speciation equilibrium for a
single mixed flow through a reactor at steady state.

There is a total of 47 chemical species available in the model, though only the ones
which are of concern and are typical in many discharging mine waters are included in
the input file. These species interact through fast reactions considered to be at
equilibrium. Species in solution are classed as mobile, and adsorbed species which are

retained on fixed solid mineral surfaces within the system are classed as immobile. Speciation equilibrium is solved by combining mass action laws and mass balances for all components, and solving iteratively, using initial estimates of the components. Thermodynamic constants are chosen from published literature and are conditional on ($I = 0.1$ M, $T = 25°C$). Redox speciation of Fe is included by defining both Fe^{2+} and Fe^{3+} as master species. The activity of $H_2CO_3^*$ and Fe^{3+} are fixed by solubility equilibrium with the phases $Fe(OH)_{3(s)}$ and $(CO_{2(g)})$, respectively. Empirical and kinetic rate laws defined in terms of relevant species concentration are formulated in the code using the following equation:

$$R = k \prod [X]_i^n \qquad (4)$$

where k is the relevant rate constant, $[X]_i$ is the concentration of the reactant species, i, and n is the reaction with respect to species i. Mass balance is defined as transport through a completely mixed reactor at steady-state (equation (5)) (defined in terms of mass flux (mol m^{-2} s^{-1}) per unit cross-sectional area of reactor across which flow occurs:

$$Q_{in} C_{in} = Q_{out} C_{out} \pm \text{reactions} \qquad (5)$$

where Q is water flow rate (dm^3 s^{-1}), C is concentration (mol dm^{-3}).

Oxygen diffusion is included in the model to determine the O_2 flux from the atmosphere to the reactor. The code uses units of flux (mol m^{-2} s^{-1}) to describe this mass transport, which corresponds to the mass flow per unit cross-sectional area of reactor across which flow occurs. This diffusion is described by linear mass transfer kinetics, where O_2 flux is proportional to the oxygen deficit that is the difference between the concentration of dissolved O_2 at saturation (C_{equil}) and the concentration of dissolved O_2 in the reactor (C_{actual}), equation (6).

$$\frac{dc}{dt} = \alpha \left(C_{equil} - C_{actual} \right) \qquad (6)$$

MODELLING

Successful calibration of the model was carried out using data from brush wood filter reactors at Kames Colliery, Scotland, UK (Best & Aikman, 1983). The brush wood filter reactor reduced the Fe(II) concentration in the discharge by between 50 and 80%, with relatively little change in pH (Fig. 1). Further removal may have been possible.

To model adsorption in the reactor the adsorption capacity (total number of adsorption sites, mol^{-1}) was defined. This was calculated by multiplying the adsorption density of an iron oxyhydroxide (1.00^{-7} moles dm^{-2}) by the adsorption area of solids in the reactor (dm^2). This was then divided by the total water volume of the reactor (dm^3). Calibration was achieved by varying the ratio of surface area:water volume in the reactor to give a calculated iron removal that was consistent with that removed.

Model simulations were carried out to assist in the design of the proposed reactors to treat the three predicted mine water discharges from the abandoned coal mines of Treeton, Thurcroft and Silverwood. The parameters used in the calibration, i.e.
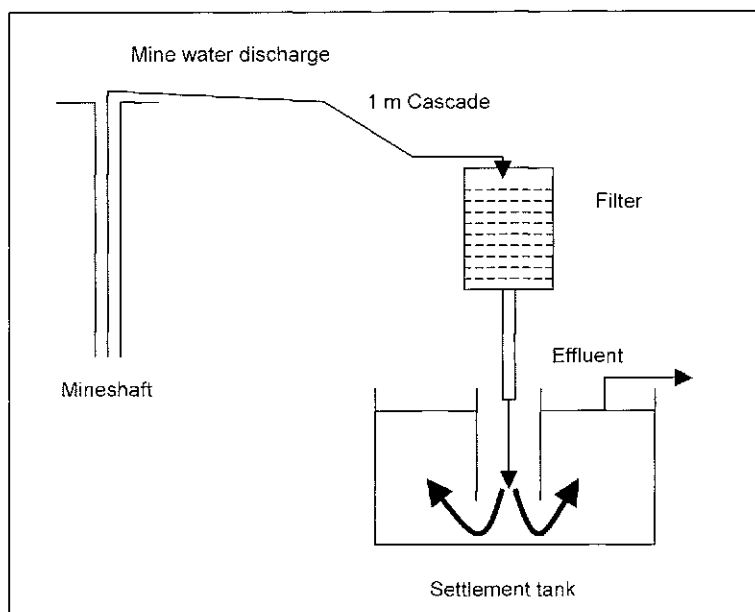
Fig. 1 Generalized diagram of the treatment system used at Kames Colliery and included in the model.

porosity and residence time were used, and the velocity given by Burke & Younger (2000) was included into the model. However, surface area using design parameters from plastic trickling filter media was varied in the model to achieve maximum removal of Fe(II) within the proposed reactors.

Only the Fe(II) loadings were predicted by Burke & Younger (2000), and therefore, it was necessary to assume a pH and oxygen level. A slightly saturated oxygenated discharge with a neutral pH was chosen for all three of the predicted surface discharges. This is typically the case in many mature discharging mine waters in the UK (Younger, 1996).

RESULTS

The model suggests that this technology within a reactor where surface area is maximized can be used to remove Fe(II) from the predicted discharges by the three collieries. The modelled results suggest that a surface area within a reactor of 4006 m^2 with a total water content of 1.47 m^3 is necessary to remove the iron from the small discharges at Treeton and the larger discharge at Silverwood. A larger surface area of 18 895 m^2 within a reactor with a total water content of 11.7 m^3 is required for complete removal at the remaining large discharge at Treeton. Selected remaining reactor parameters used in the input file of the model are shown in Table 1.

Table 1. Selected reactor parameters used in the model.

	Silverwood discharge 1.5 Ml day^{-1}	Treeton discharge 1.9 Ml day^{-1}	Treeton discharge 0.2 Ml day^{-1}
Reactor radius (m)	0.45	0.9	0.45
Reactor length (m)	2.1	4.2	2.1
Porosity (%)	94.4	94.4	94.4
Volume of solids (m^3)	7.4	59.8	7.4
Adsorption capacity (M l^{-1})	2.72×10^{-04}	1.60×10^{-04}	2.72×10^{-04}

CONCLUSION

The results suggest that the surface-catalysed oxidation of iron can be successfully used to remove iron loadings from mine water discharges. For increased reactor efficiency a smaller surface area may be used for the lesser discharge from Treeton Colliery. However, if sufficient surface area cannot be found from suitable surface media that would fit into a reactor, then a larger reactor volume may be needed to accommodate the surface area and total water volume given in Table 1.

Due to the pH dependence of Fe(II)$_{aq}$ adsorption the influent alkalinity of the discharge will play a major role in the efficiency of surface-catalysed oxidation. If the influent alkalinity is low then a greater surface area will be required. Where the alkalinity is not known for predicted discharges, then larger surface areas may be installed as a precaution against the effect of low alkalinity concentrations.

REFERENCES

Banks, D., Burke, S. P. & Gray, C. (1997) The hydrogeochemistry of coalmine drainage and other ferruginous waters in North Derbyshire and South Yorkshire, UK. *Quart. J. Engng Geol.* **30**, 257–280.

Best, G. A. & Aikman, D. I. (1983) The treatment of ferruginous groundwater from an abandoned colliery. *Water Pollution Control* **82**(4), 537–566.

Burke, S. P. & Banwart, S. (2002) A geochemical model for removal of iron(II) (aq) from mine water discharges. *Appl. Geochem.* **17**(4), 431–443.

Burke, S. P. & Younger, P. L. (2000) Groundwater rebound in the South Yorkshire Coalfield: a first approximation using the GRAM model. *Quart. J. Engng Geol.* **30**, 149–160.

Furrer, G., Westall, J. & Sollins, P. (1989) The study of soil chemistry through quasi-steady-state models. I Mathematical definition of problem. *Geochim. Cosochim. Acta* **53**, 595–601.

Furrer, G., Sollins, P. & Westall, J. (1990) The study of soil chemistry through quasi-steady-state models: acidity of soil solution. *Geochim. Cosmochim. Acta* **54**, 2363–2374.

Hedin, R. S., Narin, R. W. & Kleinmann, R. L. P. (1994) Passive treatment of coal mine drainage. *US Bureau of Mines Information Circular 9389.*

Younger, P. L. (1996) Hydrogeochemistry of minewaters flowing from abandoned coal workings in County Durham. *Quart. J. Engng Geol.* **28**, 101–113.

Younger, P. L. (1997) The longevity of minewater pollution: a basis for decision making. *Sci. Total Environ.* **194/195**, 457–466.