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EVALUATION OF THE RATE OF DECREASE IN THE IRON CONTENT OF WATER PUMPED FROM A FLOODED SHAFT MINE IN COUNTY DURHAM, ENGLAND

R.C. FROST*

Department of Civil and Structural Engineering, Teesside Polytechnic, Middlesbrough (Great Britain)

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ABSTRACT

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An attempt is made to provide a theoretical basis for the evaluation of field data relating to decreasing concentrations of iron in the drainage from flooded coal mines. It is thought that this will aid the formulation and adoption of policies aimed at abating the stream pollution caused by these discharges.

The removal of pyrite oxidation products from flooded mine workings is described as a convective mass-transfer process, and equations predicting an exponential decrease in their concentration with time are derived from theoretical considerations. In support of this model, the concentration of Fe, C_c (mg/l), in the water pumped from a flooded shaft mine was found to decrease with time, t (days), according to the regression equation:

$$\log C_c = 1.684 + 0.102 \log Q' - 0.000858t$$

where Q' was the instantaneous pumping rate (m^3/s).

The half-life of 350 days is compared with a value of 334 days calculated from literature data relating to small self-draining drift mines in the U.S.A.

The practical value of the model is illustrated by estimation of the volume of ferric hydroxide sludge that might be formed in a treatment facility.

INTRODUCTION

In a previous study (Cairney and Frost, 1975) it was reported that the concentration of Fe in the pumped discharge from a flooded coal mine in County Durham, England, decreased with time provided that the water level was kept fairly constant. Essentially similar observations have been made in other British coalfields (Lancashire River Authority, 1972; Welsh National Water Development Authority, 1975) and in the U.S.A. (Braley, 1954). Braley (1954),

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*Current address: Water Research Centre, Stevenage Laboratory, Elder Way, Stevenage, Hertfordshire, England.

for example, reported that the previously alkaline drainage from a deep shaft mine became acidic after the mine was abandoned, and the workings flooded, but that later, after nine months, it reverted back to an alkaline state.

A knowledge of the rate of decrease in the Fe content of flooded mine drainage will be a necessary prerequisite to the formulation, and adoption, of policies aimed at abating the stream pollution caused by the discharge of these waters. Should treatment of a given discharge be deemed necessary, this knowledge would be particularly useful in the estimation of sludge production rates.

The present paper attempts to provide a theoretical basis for the evaluation of field data, and is supported by an analysis of data obtained from Mainsforth pumping station, County Durham, England, in the period February—October, 1974.

THE FORMATION OF FERRUGINOUS AND ACIDIC COAL MINE DRAINAGE

It is generally accepted that acidic and or ferruginous coal mine drainage results from the oxidation of pyrite within the coal and associated strata, and from the removal of the oxidation products by inflowing groundwater. The formation of such drainage is a complex process, however, that belies the apparent simplicity of the overall reactions:

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4Fe^{2+} + 8SO_4^{2-} + 8H^+$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Reviews (Ohio State University Research Foundation, 1971; Morth et al., 1972; Frost, 1977, pp. 8—46) of the related literature should be consulted for a complete appraisal of the process.

It is apparent from the above reactions that the oxidation of pyrite is a heterogeneous reaction. Thus three sequential processes are involved in the formation of acidic and or ferruginous drainage:

(a) The transport of reactants to the oxidation sites.
(b) The oxidation of pyrite.
(c) The transport of oxidation products away from the oxidation sites.

Reactant transport

Since oxygen will be the ultimate electron acceptor (oxidant) within a given system, the pyrite will be fixed in position, and water may be assumed to be present either as liquid water or vapour, the only reactant transport that must be considered is that of oxygen. A consideration of the solubility of oxygen in water, together with the stoichiometry of the pyrite oxidation reactions and the iron and sulphate concentrations commonly observed in ferruginous and acidic drainage, indicates that it is possible for only a minor proportion of the oxygen required to have entered the system as oxygen dissolved in the flowing groundwater (I. Barnes and Clarke, 1964; H.L. Barnes and Romberger, 1968; Smith et al., 1969). Furthermore, the oxygen diffusivity in water is only $1 \cdot 10^{-4}$ of that in air (Coulson and Richardson, 1964). Thus it may be assumed that essentially all oxygen must be transported to the oxidation sites in the gaseous phase (Shumate and Smith, 1968; Shumate et al., 1969; Morth et al., 1972), and that any pyrite submerged by groundwater or mine water is effectively precluded from further oxidation.

In view of the above, the kinetics of pyrite oxidation need not be considered in this treatment. This is fortuitous since considerable disagreement exists as to whether the oxidation is brought about by purely chemical means (Lau et al., 1970; Smith and Shumate, 1971), or whether it is bacterially catalysed (Ashmead, 1955, 1956; Singer and Stumm, 1969; Walsh and Mitchell, 1975). This subject will be reviewed in a subsequent paper.

Oxidation product transport

Since the removal of pyrite oxidation products is brought about by flowing groundwater, their removal from a mine will depend upon the prevailing hydrological and hydrogeological conditions. Workers at the Ohio State University (Shumate and Smith, 1968; Shumate et al., 1969; Morth et al., 1970, 1972; Smith and Shumate, 1971) have identified three principal mechanisms (gravity-diffusion, leaching and flushing) by which oxidation products are removed from drift mines lying above the water table.

The first of these, gravity-diffusion, is the diffusion of oxidation products from highly concentrated condensates, formed at the oxidation sites, into nearby flowing water; whilst leaching results from the intermittent passage of water through channels and cracks in the roof strata during, and after, periods of intense precipitation. The third mechanism, that of flushing, includes and supercedes the others, and takes place upon the inundation of the oxidised pyrite.

Commonly, the drainage from non-flooded shaft mines in Great Britain is not significantly effected by the removal of pyrite oxidation products — though there are exceptions to this (Ashmead, 1955, 1956). Presumably, therefore, the gravity-diffusion and leaching mechanisms are relatively non-effective in many of these deep mines, and pyrite oxidation product removal is mainly effected by the flushing mechanism upon the flooding of the workings. Possible reasons for this are discussed elsewhere (Frost, 1977, pp. 152—158).

THE FLUSHING PROCESS — THEORETICAL CONSIDERATIONS

Provided that the concentration of Fe (or of SO_4) is not controlled by mineral solubility factors, maximum mine drainage concentrations will be limited by the rates of release of Fe from the (former) oxidation sites and by dilution factors. The flushing process, therefore, may be considered as the convective mass transfer of oxidation products from the highly concentrated solutions at, and surrounding, the oxidation sites. The vast majority of these sites should lie within the fragmented rock matrix (goaf) remaining after the coal has been extracted, and the roof allowed to collapse.

The overall mass transfer process may be broken down into three distinct phases (Coulson and Richardson, 1968, pp. 278–282):

(a) The dissolution of pyrite oxidation products within the channels and pores of the rock fragments. This should occur so rapidly as to have negligible effect on the overall rate, and may be ignored.

(b) Molecular diffusion through solutions within the tortuous channels and pores of the rock fragments.

(c) Diffusion from the concentrated solutions at the outer surfaces of the rock fragments into the convective flows of mine drainage. Mass transfer in this phase is by a combination of molecular and eddy diffusion through a a surface film surrounding the rock fragment — the thickness of the film being dependent upon the convective flow conditions.

In general, the upper limit for the overall rate of mass transfer from the oxidation sites will be prescribed by the rates of diffusion through the pores of the rock fragments. If the overall rate were solimited, it would be reasonable to assume that the rate of loss of oxidation products from the individual rock fragments would, at any given time, be directly related to the amount remaining. Changes in the convective flow conditions – resulting from variations in the pumping rate and regime (whether pumping is continuous or intermittent), and from variations in the groundwater inflow rate – would exert no control. Thus the rate of removal of oxidation products could be expected to decrease exponentially with time, dependent only upon the amounts of oxidised pyrite remaining and on the (constant) nature of the diffusional paths within the rock fragments.

However, a consideration of the relatively low bulk porosity, approximately 0.1, of the areas of roof fall (National Coal Board, 1972) suggests that it might well be diffusion in phase (c) that effectively limits the overall rate of mass transfer. If this were the case it would imply that variations in the groundwater inflow rate, and in the pumping rate and regime, might exert significant control over the rate at which pyrite oxidation products are flushed from the workings, and on their concentration in the mine drainage.

MODEL DERIVATION

Consider the transfer of ferrous iron from one channel within a rock fragment of the goaf towards a convective flow — as depicted in Fig.1. Assume that the flow conditions are at steady state, i.e. that the convective flow rate, q, is constant with time. Assume further that the overall rate of mass transfer is determined by the transfer rate across a surface film on the external surface of the rock fragment.

The diffusional path, O—S, of the Fe(II) within the rock fragment is generally complex and diffusion is in an unsteady state. Consequently, no concentra-

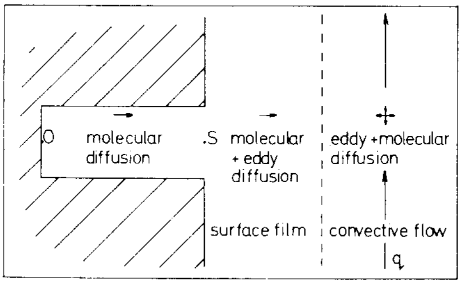

Fig. 1. Diagrammatic representation of the convective mass transfer of oxidation products from flooded pyrite oxidation sites.

tion profile can be proposed. However, it would seem reasonable to suggest that the concentration, C_S, at the end of the diffusional path is indicative of the total amount of Fe (II), O_{OXP}, remaining within the fragment. Within time limits such that C_S remains within the same order of magnitude one may make an approximation, therefore, and state that:

$$C_S = pO_{OXP} \tag{1}$$

where the proportionality factor p is assumed constant.

The transfer of Fe (II) across the surface film is also an unsteady state process since C_S will decrease with time. All available evidence (Braley, 1954; Morth et al., 1972; Cairney and Frost, 1975), though, suggests that the overall rate decreases slowly with time. Consequently the convective mass transfer may be considered a quasi-steady state process, i.e. approximately steady state over limited periods of time. A mass transfer coefficient, k_c, may then be defined for the transfer of Fe (II) from the surface of the fragment by:

$$N = k_c A(C_S - C_q) \tag{2}$$

where N is the rate of mass transfer through a cross-sectional area A, and C_q is the concentration of Fe (II) in the convective flow.

In this quasi-steady state process, the total mass transfer rate, N, may be equated to the rate of loss of Fe (II) from the channel volume:

$$-dO_{OXP}/dt = k_c A(C_S - C_q) \tag{3}$$

The flushing process may be described as the dispersal of highly concentrated solutions surrounding the former pyrite oxidation sites by convective flows of relatively low Fe concentration. If the assumption that $C_S >> C_q$ is made, eq. 3 reduces to:

$$-dO_{OXP}/dt = k_c A C_S \tag{4}$$

Combining eqs. 1 and 4 yields:

$$-dO_{OXP}/dt = pk_c A O_{OXP} \tag{5}$$

The rate of Fe loss from the channel volume may be considered equal to the

Fe load (qC_q) of the convective flow. Thus the concentration of Fe in the convective flow is given by:

$$C_q = -q^{-1}(\mathrm{d}O_{\mathrm{OXP}}/\mathrm{d}t) \tag{6}$$

Combining eqs. 5 and 6 yields:

$$C_q = q^{-1}pk_cAO_{\mathrm{OXP}} \tag{7}$$

Assuming constant flow conditions, and that k_c is also constant with time, differentiation of eq. 7 with respect to time yields:

$$\mathrm{d}C_q/\mathrm{d}t = q^{-1}pk_cA\,(\mathrm{d}O_{\mathrm{OXP}}/\mathrm{d}t) \tag{8}$$

Combining eq. 6 and 8 yields:

$$-\mathrm{d}C_q/\mathrm{d}t = pk_cAC_q \tag{9}$$

A solution of this differential equation is:

$$C_q = C_{q0}\exp(-pk_cAt) \tag{10}$$

where C_{q0} is the value of C_q at time $t = 0$.

This analysis has only described the convective mass transfer from one rock fragment to a single steady state convective flow, whilst the systems of interest are of infinitely greater complexity. By analogy, however, the time varying concentration, C, of Fe in the drainage from an area of flooded workings may be described by:

$$C = C_0\exp(-kt) \tag{11}$$

or, in logarithmic form, by:

$$\ln C = \ln C - kt \tag{12}$$

where C_0 is the value of C at time $t = 0$, and k is an effective overall mass transport coefficient. In general, k will be dependent upon the total surface area of the flooded rocks, the geometry of the system, the amount of Fe remaining within the system, and the number, distribution, flow rates and relative flow rates of the component mine water feeders.

ANALYSIS OF THE DATA FROM MAINSFORTH PUMPING STATION, FEBRUARY—OCTOBER 1974

The location and history of Mainsforth pumping station has been described in an earlier report (Cairney and Frost, 1975). For the period considered here, the mine water was maintained at a fairly constant level of −37.8 m AOD by pumping at a long-term average rate of approximately 0.1894 $\mathrm{m^3/s}$ (2500 gpm). In order to reduce power costs pumping was restricted, whenever possible, to the hours $19^{\mathrm{h}}00^{\mathrm{m}}$—$07^{\mathrm{h}}00^{\mathrm{m}}$ Mon.—Sat., and $12^{\mathrm{h}}00^{\mathrm{m}}$ Sat.—$07^{\mathrm{h}}00^{\mathrm{m}}$ h Mon. For a variety of reasons pumping could not be restricted solely to these times, and continuous pumping had also to be resorted to. This led to a range of instantaneous pumping rates (0.1515—0.4167 m^3/s; 1500—5500 gpm) being employed over the period, achieved by various combinations of the pumps installed in the two adjacent shafts.

The mine drainage at Mainsforth is derived from the Permian Magnesian Limestone which overlies the Coal Measures. Generally, the rate of inflow of groundwater from this source is not seasonally variable. The absence of appreciable levels of Fe and SO_4 in the drainage from the non-flooded workings (Cairney and Frost, 1975; Frost, 1977, pp. 95—114) indicates that the rates of Fe removal brought about by the gravity-diffusion and leaching mechanisms are insignificant.

A previous report (Cairney and Frost, 1975) demonstrated that intermittent pumping leads to considerable short-term variations in the mineralisation of the discharged water. This stems from the stratification of drainage within the shafts of flooded mines, and reproducible samples of the pumped discharge may only be taken after several hours of pumping have elapsed. All of the analyses for total Fe, C_c, listed in Table I were performed on samples collected between the times 05^h30^m and 06^h30^m, i.e. after atleast 10 h of pumping had elapsed.

Using the least mean squares method, a linear regressional analysis of the variation of log C_c with t yields:

$$\log C_c = 1.647 - 0.000943t \tag{13}$$

TABLE I

Data for the analysis of the variation in Fe concentration at Mainsforth from 20/2/74 (day *143*) to 11/10/74 (day *377*)

Day No.	Q' (m^3/s)	C_c* (mg Fe/l)	Day No.	Q' (m^3/s)	C_c* (mg Fe/l)
143	0.1894	31.3	*261*	0.2652	24.0
150	0.1515	28.6	*268*	0.3030	26.6
156	0.1894	32.2	*275*	0.3030	26.6
162	0.3030	29.8	*283*	0.3030	24.0
171	0.2652	30.0	*290*	0.3030	23.4
176	0.3030	35.7	*297*	0.3030	23.4
191	0.3030	28.3	*303*	0.3030	24.0
200	0.3030	26.0	*310*	0.2652	22.2
205	0.3409	31.0	*317*	0.2652	23.2
214	0.3409	25.9	*325*	0.2652	23.0
219	0.3409	29.6	*333*	0.2273	23.0
227	0.4167	26.5	*345*	0.1515	18.6
228	0.4167	28.5	*355*	0.1894	21.8
234	0.3788	23.4	*361*	0.1894	21.0
241	0.3788	24.8	*368*	0.1515	20.0
248	0.3788	28.7	*371*	0.1515	18.7
256	0.3030	27.2	*377*	0.1136	16.5

*The subscript c denotes that the discharged water comprises two components, and is not just drainage from the flooded workings (Frost, 1977).

where t is the number of days post 30/9/73 (date at which pumping to hold the water at a constant level recommenced), with a correlation coefficient of 0.896 statistically significant at the 0.1% level.

The data of Table I also yields that the Fe content of the discharge increases with increasing pumping rate. This may be shown by assuming that the data may be fitted to a semi-empirical equation of the form:

$$C_c = C_{c0}\ Q'^n \exp(-kt) \tag{14}$$

where Q' is the instantaneous pumping rate (m^3/s), and n is a constant. A multiple linear regressional analysis of the correlation of log C_c with log Q' and t yields:

$$\log C_c = 1.684 + 0.102 \log Q' - 0.000858t \tag{15}$$

with a multiple correlation coefficient of 0.914 significant at the 0.1% level; and with partial correlation coefficients of 0.409 significant at the 5% level, and of 0.878 significant at the 0.1% level, for the partial correlation of log C_c with log Q' and t, respectively.

DISCUSSION

The high level of statistical significance associated with the correlation coefficient relating log C_c to t provides strong support for the hypothesis that the rate of pyrite oxidation product removal decreases exponentially with time. From eq. 15 a half-life, $t_{1/2} = \log 2/k$, of 350 days may be calculated. This compares well with a value of 334 days which may be derived from the data of Morth et al. (1972).

Morth et al. (1972) were concerned with the removal of pyrite oxidation products from small self-draining drift mines in the U.S.A. Considering the diversity in scale between the mines studied, the similarity in the $t_{1/2}$ values suggests that a minimum value of approximately 300 days might exist — reflecting the limiting rates of diffusion of oxidation products in the rock containing the oxidised pyrite. Some support for this tentative conclusion is provided by the observed rates of decrease in Fe and SO_4 content of drainage from other mines in County Durham, England. Half-lives of 641—1817 days were determined (Frost, 1977, pp. 244—253) and it was suggested that these flooded areas were subjected to less vigorous convective flows.

The statistically significant dependence of the Fe concentration on the pumping rate might be interpreted as being due to increased rates of mass transfer at higher pumping rates. However, a consideration of the mean residence time of the drainage within the flooded workings at Mainsforth — estimated to be in excess of 217 days — suggests that the effect of any such influence would, in all likelihood, be masked by that of antecedent pumping rates (and regimes). It has been demonstrated (Frost, 1977) that the influence of pumping rate probably results from the variable rate at which the more mineralised drainage from the flooded areas is discharged, whilst the drainage from the higher non-flooded seams is discharged at an essentially constant rate.

PRACTICAL APPLICATIONS

Though ferruginous drainage such as that described above can seriously pollute a receiving stream, the $t_{1/2}$ value indicates that chronic pollution might persist for no longer than five years. In the North East Coalfield (and others) of Great Britain there are many such discharges. Taking both of these factors into consideration, together with the generally non-acidic nature of the drainage and the difficulty attached to its treatment, any proposed treatment of ferruginous mine waters in NE England, and similar areas, would not appear to be justified.

It is generally recognised that the predominantly ferric hydroxide sludge produced when (neutral) ferruginous mine drainage is oxidised and allowed to settle is voluminous, difficult to handle, and poses a major disposal problem. Should the treatment of a pumped discharge be deemed necessary, therefore, knowledge of the rate of decrease in the Fe concentration would be desirable since estimates of the sludge production rate, and thus sludge handling and disposal costs, could then be made.

Assuming a design effluent Fe concentration of X kg Fe/m^3, the sludge production rate, dV_{SL}/dt (m^3/d), may be given by:

$$dV_{SL}/dt = Q(C-X)/FS \qquad (16)$$

in which

C = average concentration of Fe in the discharged mine water (kg/m^3)
S = average concentration of sludge solids produced (kg/m^3)
F = fraction of dried sludge solids consisting of Fe
Q = daily pumping rate (m^3/d)

Thus the cumulative volume of sludge produced in T days will be given by:

$$V_{SL} = \int_0^T \frac{Q}{FS}\,[C_0\exp(-kt) - X]\,dt \qquad (17)$$

i.e.:

$$V_{SL} = \frac{Q}{FS}\left[\frac{C_0}{k}\,\{1 - \exp(-kt)\} - XT\right] \qquad (18)$$

Data pertaining to Mainsforth for the period Feb.—Oct. 1974 may be substituted into eq. 18 together with representative values for F, S and X of 0.53, 75 kg dried solids/m^3 and 0.005 kg Fe/m^3, respectively. V_{SL} is plotted as a function of time in Fig.2. A settlement basin (lagoon) could be designed to hold all of the sludge produced — at the end of its useful life the basin might then be backfilled. Alternatively the basin could be desludged at intervals. Local circumstances, together with a comparison of the detailed costs of sludge withdrawal and the capital cost of lagoon construction, would dictate which was the most practicable and least costly method. In this example it would probably be most economic to construct a lagoon capable of holding the entire

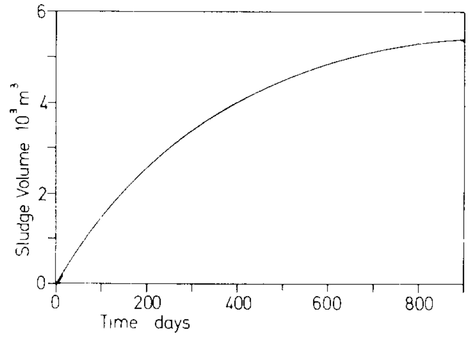

Fig. 2. Sludge production in a hypothetical treatment facility.

volume of sludge produced in the lifetime of the hypothetical treatment facility. This may be deduced from a comparison of the total volume of sludge likely to be produced, approximately 5400 m^3, with the basin volume (65,500 m^3) providing a nominal hydraulic retention time, of say two days, sufficient to achieve oxidation of the Fe (II) and settlement of enough ferric hydroxide to meet effluent standards.

CONCLUSIONS

The flushing of pyrite oxidation products from flooded mine workings may be described as a convective mass-transfer process. As predicted by a theoretical analysis of this process, the concentration of Fe in the drainage from a constant volume of flooded workings decreases exponentially with respect to time.

It is possible that a value of approximately 300 days may be a limiting value to the half-lives of these decay curves – reflecting the limiting rates of diffusion of oxidation products in the rock fragments comprising the areas of roof-fall (goaf).

A knowledge of the rate of decrease in the concentration of Fe in the drainage will assist in the decision as to whether a given discharge should be treated or not. If treatment is decided upon, this knowledge will enable some estimate of the sludge production rates to be made, and assist in the design of the treatment facility.

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