THE ROLE OF DISSOLVED CARBON DIOXIDE IN GOVERNING DEEP COAL MINE WATER QUALITY AND DETERMINING TREATMENT PROCESS SELECTION[1]

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Abstract. Field and laboratory measurements of mine waters emerging from abandoned deep coal mines in the UK have shown that CO_2 partial pressures (pCO_2) may be more than 100 times greater than atmospheric levels. Measured values of acidity vary significantly with time due to degassing of CO_2 from such samples. The evolution (i.e. decrease) of pCO_2 with time is described. The significance of these findings for mine water treatment process selection is discussed, and plans for future research in this area are outlined.

Additional Key Words: acidity, alkalinity, pH, bicarbonate, carbonic acid, thermodynamic mass action

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Introduction

Effective treatment of mine waters crucially depends upon raising pH in the case of acidic discharges, and then precipitating insoluble metal (oxy)hydroxides or sulfides within the confines of the treatment system. Two generic treatment options are available for this purpose: active treatment utilises alkaline chemicals (e.g. $Ca(OH)_2$ or NaOH) and energy (for pumping, dosing etc) to raise pH and rapidly immobilise and remove metals. Passive treatment, in contrast, employs gravity and naturally occurring biogeochemical processes to attenuate mine water pollution (Younger *et al.*, 2002) e.g. constructed wetlands. In both cases a clear and reliable understanding of the mine water quality is an essential prerequisite of effective treatment system design. In particular, it is vital to know whether the discharge is net-acidic or net-alkaline (i.e. acidity > alkalinity or *vice versa*) (Hedin *et al.*, 1994). It is this that will determine the appropriate type of passive system (PIRAMID Consortium, 2003), whether chemicals are required for active treatment and, if they are, the quantities / strength required (Younger *et al.*, 2002). Given the extent of mine water pollution, and the substantial costs of treatment (the UK Coal Authority invested approximately £8 million in mine water treatment schemes in 2004 alone (Jarvis *et al.*, 2005)), there is clearly both an environmental and an economic incentive to ensure treatment systems are correctly designed.

Accurately determining acidity and alkalinity concentrations is clearly essential in the design of such treatment systems. Ordinarily these variables are measured using titration against a strong acid (for alkalinity) or base (for acidity) to pH 4.3 and 8.2 respectively (APHA, 1998). However, discharges from abandoned coal mines often have carbon dioxide partial pressures (pCO_2) far in excess of atmospheric partial pressure (3.55×10^{-4} atm.), due to release of CO_2 within the workings under confined conditions. Hedin and Watzlaf (1994), for example, have shown mine water pCO_2 as high as 10^{-1} atm. The elevated pCO_2 in these mine waters effectively contributes to acidity in the form of aqueous CO_2 (or carbonic acid, $H_2CO_3^*$), but upon emergence to the surface exsolution of CO_2 occurs until equilibrium with atmospheric conditions is reached, in accordance with Henry's Law. The exsolution of CO_2 can be represented by the reaction shown as Equation 1 (Stumm and Morgan, 1996).

$$H_2CO_3^* \leftrightarrow CO_2(g) + H_2O \qquad -\log K = 1.47\ (25^\circ C, I=0M) \qquad (1)$$

Thus, as the reaction proceeds to the right, under atmospheric conditions, acidity concentration decreases. However, concentrations of individual inorganic carbon species are a function of pH. In the case of mine water discharges this complicates matters, since abandoned coal mine discharges typically contain elevated iron concentrations, and high Al concentrations in the case of the most acidic outflows. In the surface environment Fe^{+2} iron is oxidised to Fe^{+3} iron, which subsequently undergoes hydrolysis to form an (oxy)hydroxides precipitate, as illustrated by Equations (2) and (3) (Younger *et al.*, 2002).

$$2\,Fe^{+2} + \tfrac{1}{2}O_2 + 2H^+ \leftrightarrow 2\,Fe^{+3} + H_2O \qquad (2)$$

$$2\,Fe^{+3} + 6H_2O \leftrightarrow 2Fe(OH)_3 + 6H^+ \qquad (3)$$

The net result of these reactions is the release of 4 protons, which therefore causes a decrease in pH. Thus, on the one hand acidity concentrations may decrease due to exsolution of CO_2, and yet on the other pH may decrease due to hydrolysis of ferric iron.

This article reports the results of a preliminary investigation of the hydrochemical evolution of a mine water, from its first emergence from abandoned coal mine workings to its eventual discharge to a river some 2.3 km downstream. This particular mine water, at Sheephouse Wood, South Yorkshire, provides an opportunity to study changes in acidity and pH as the mine water runs along its own channel, undiluted, for the full length of its course to the river. Supporting the results of this investigation, other mine waters in the UK have also been assessed for CO_2 partial pressure and its influence on mine water geochemistry in the surface environment.

The implications of the findings of this investigation, for future monitoring of mine waters and design of treatment systems, are discussed. The investigation discussed was a preliminary assessment only, and potential drawbacks are highlighted. Plans for further research, with the objective of providing more accurate measurements of the evolution of pCO_2 in mine waters, with a view to optimising treatment, are outlined.

Study sites

The Sheephouse Wood mine water discharge emerges from an abandoned coal mine adit approximately 5 km west of the small town of Stocksbridge, and 40 km east of Manchester. The adit formerly provided access to several collieries, which worked the Halifax Hard seam of coal. These workings were largely abandoned in the early part of the 20th century, and mine water now emerges from the adit in an uncontrolled manner, following mine water rebound. The mine water discharges into a channel that carries the mine water from the adit to the Little Don river (at National Grid Reference SK 247 994). This channel was constructed specifically in order that the mine water would not flow into the Underbank reservoir, a water supply resource. Along its 2.3 km length, there are no other inputs to this channel, other than the minor contribution of rainfall events. Thus, it is an ideal site for investigating the evolution of acidity and pH without the complications of diluting inputs.

The nature of the discharge has been known to vary, particularly with respect to flow-rate, pH and acidity concentration. It is not entirely clear why this is the case, but the discharge is influenced by rainfall events, and it is also prone to sudden high-volume ‘flushes’ of heavily contaminated water. It is presumed that these flushing events are the result of a recurring event in which sediment builds up in a flow path within the workings, causing a constriction in flow-rate, followed by sudden release as the pressure of water behind it overcomes the blockage. This occurred most spectacularly in February 2002, when an estimated 15,000 m^3 of grossly polluted water emerged in little over a day, closing the trunk road below it for nearly a week.

Field and laboratory methods

Monitoring of the discharge for specific investigation of the role of CO_2 in mine water evolution at Sheephouse Wood was undertaken by IMC Consulting Engineers Ltd (2003). The pH, conductivity and temperature were measured on site using a calibrated Myron Company 6P Ultrameter. Alkalinity and acidity measurements were also made in the field, using a Hach field titration kit. Alkalinity was measured by titration using 1.6N H_2SO_4 and a phenolphthalein indicator, whilst acidity was measured using 1.6N NaOH and a methyl red-bromcresol green indicator. Acidity concentration was also calculated, using the method of Hedin *et al.* (1994), shown as Equation 4.

$$\text{Acidity}_{calc}\ (\text{mg/L as } CaCO_3) = 50[2\ Fe^{+2}/56 + 3\ Fe^{+3}/56 + 2Mn/55 + 3Al/27 + 1000(10^{-pH})] \quad (4)$$

APHA (1998) recommends the use of H_2O_2 and boiling for determination of acidity for waters with elevated pCO_2, such as those described here. In determining 'Hot acidity', as this is commonly termed, CO_2 is intentionally driven off, and Fe and Mn oxidised, and therefore "CO_2 acidity" is not included in the acidity concentration (as it has been degassed) (e.g. Kirby and Cravotta, 2005). However, evidence presented below suggests that the elevated pCO_2 in mine waters may (a) require considerable time to degas without physico-chemical intervention and (b) the elevated pCO_2 may consequently inhibit effective treatment in some cases. In order to make a preliminary assessment of both the contribution of CO_2 to total acidity, and to assess how quickly CO_2 will degas without physico-chemical intervention, titrations have therefore been made here without preliminary boiling, albeit the potential for greater variability of results is recognised.

Metal ion concentrations were measured, using ICP-OES, by an accredited UK commercial laboratory. Anion concentrations were also determined by a commercial laboratory, but using Ion Chromatography (APHA, 1998).

Measurements of field determinands (and simultaneous collection of samples for cation and anion analysis) were made at intervals down the length of the channel receiving the mine water; 6 sample locations were used in all, the first at the entrance to the adit, and then at intervals of 250 m, 500 m, 1,000 m, 1,500 m downstream and, finally, at 2,300 m.

The interpretation of these data, below, is new to this article (with kind permission from the UK Coal Authority for use of the data).

Results and discussion

Key chemical data of the mine water discharge at Sheephouse Wood, and its quality as it flows down the channel to its discharge point into the River Little Don, are shown in Table 1.

The data in Table 1 indicate that this mine water is net-acidic (i.e. acidity > alkalinity). However, using the method of calculation of acidity proposed by Hedin et al. (1994) (Equation 4), which has been shown to correlate well with measured acidity concentrations (variation of just 6%; Hedin et al., 1994); there is significant variation between measured and calculated concentrations, as illustrated in Table 2.

The data in Table 2 clearly shows two things. Firstly, the acidity concentration of this mine water decreases with time as the water flows down its dedicated channel (it takes an estimated 1.3 hours for the water to reach the point 2300 m downstream; IMC Consulting Engineers Ltd, 2003). Secondly, the calculated acidity concentration is typically in the order of 40% less than the measured concentration for all samples except those 1500 and 2300 m downstream of the mine adit (by which time the measured concentration has dropped by approximately 40-50%). However, samples of water that were collected simultaneously, and then stored in bottles with no head space for a period of 4 days, showed vary little variation from the field measurements of acidity concentration (column 3 of Table 2). The conclusion therefore is that acidity concentration is decreasing due to reactions occurring as the mine water flows down the channel. It is conceivable that this relates to buffering reactions occurring as a consequence of contact with materials on the channel bed. Since the channel bed material largely comprises hydrous ferric oxide (HFO) precipitates, this seems unlikely, but it is nevertheless an avenue for future research.

Table 1. Evolution of water quality of the Sheephouse Wood mine water from its emergence to the surface (0 m) to its discharge to river (2300 m) (data from IMC Consulting Engineers Ltd, 2003).

Distance from adit (m)[1]	pH	Measured acidity (mg/L as $CaCO_3$)	Calculated HCO_3^- (mg/L)[2]	Ferrous iron (mg/L)	Total iron (mg/L)
0	5.30	231	36.0	67.9	68.1
250	5.66	216	40.8	65.6	66.2
500	5.70	176	36.0	67.4	68.0
1000	5.86	200	39.6	62.4	63.9
1500	5.70	124	33.6	61.1	64.8
2300	5.22	128	6.0	54.9	60.7

1 0 m is discharge from abandoned mine adit

2 HCO_3^- concentration is calculated by multiplying the measured alkalinity concentration by 1.22.

Table 2. Temporal and spatial differences between measured and calculated acidity concentrations of the Sheephouse Wood mine water discharge (percentage differences compared to field measurement of acidity shown in parentheses) (Data from IMC Consulting Engineers Ltd, 2003).

Distance from mine adit (m)	Measured acidity (mg/L as $CaCO_3$) at T_0[†]	Calculated acidity (mg/L as $CaCO_3$) at T_0[‡]	Measured acidity (mg/L as $CaCO_3$) at T_4[††]
0	231	122 (-47.2%)	220 (-4.8%)
250	216	119 (-44.9%)	223 (+3.3%)
500	176	122 (-30.7%)	152 (-13.6%)
1000	200	116 (-42.0%)	138 (-31.0%)
1500	124	119 (-4.0%)	137 (+10.5%)
2300	128	114 (-10.9%)	130 (+1.6%)

† Acidity concentration measured on site at time of sample collection, using method described in Field and laboratory methods section.

†† Acidity concentration measured as above, but 4 days after collection, during which time sample was stored in a sealed polyethylene bottle with no head space.

‡ Calculated using equation (4), as shown in Field and laboratory methods section.

The calculated acidity concentration does not vary greatly along the course of the channel. Inspection of iron concentration data, illustrated in Table 1, illustrates why: Fe is the main contributor to the mineral acidity component of the calculation, and concentrations do not decrease significantly along the course of the channel (a decrease in total iron concentration from 68.1 mg/L at the adit mouth (0 m) to 60.7 mg/L 2300 m downstream). Neither does the pH vary greatly (Table 1), which represents the proton acidity component of the acidity calculation.

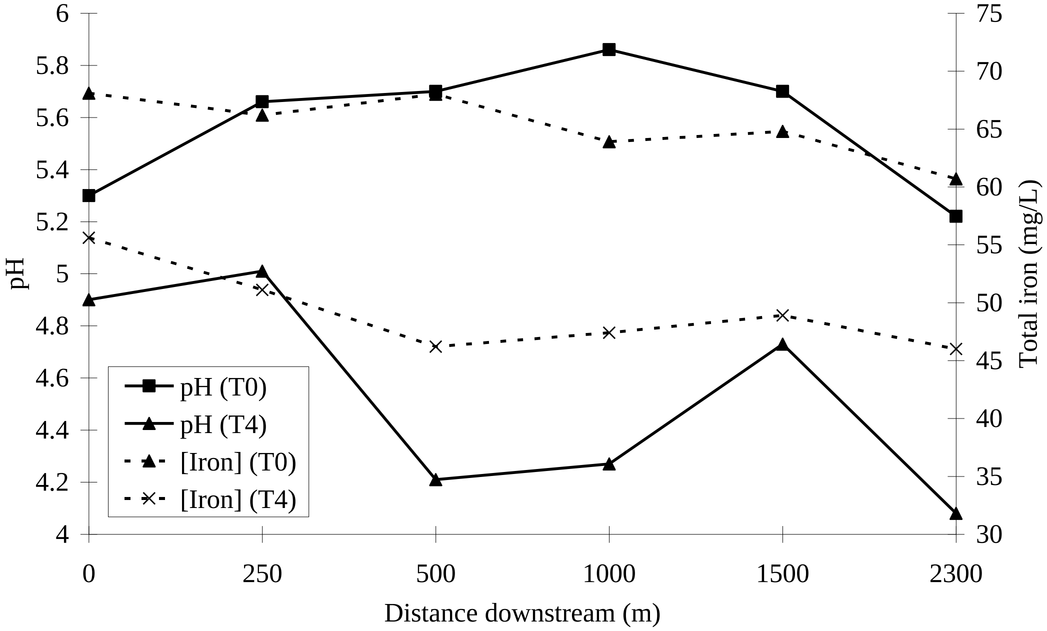

Figure 1. Variation of pH and total iron concentration of Sheephouse Wood mine water samples over a 4-day period (T0 represents field measurements and T4 indicates analyses of the same water 4 days later).

Where we do see significant variations in iron concentration and pH are when we compare samples analysed in the field (T_0) with replicate samples analysed 4 days later (T_4), as illustrated in Fig. 1. Iron concentrations in the water column decrease, presumably as a consequence of precipitation of HFO along the course of the channel. Since this occurs via reactions (2) and (3), above, protons are released, resulting in a decrease in pH. Consequently, we have the counter-intuitive phenomena of acidity concentration and pH *both* decreasing along the course of the channel.

The role of CO_2 in influencing the variation of acidity can be investigated by invoking the relevant thermodynamic mass action laws for the carbonate system which, adjusted for temperature according to the method of Stumm and Morgan (1996), are shown in Equations (5) and (6).

$$K_1 = 10^{-1.30} = \frac{[H_2CO_3]}{PCO_2(g)} \tag{5}$$

$$K_2 = 10^{-6.44} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \tag{6}$$

These mass action laws can be rearranged to solve for pCO_2 as shown in Equation 7 (after Neal, 1988).

$$pCO_2 = \frac{[H^+][HCO_3^-]}{K_1K_2} \tag{7}$$

Assuming the ion activity coefficient of HCO_3^- to be approximately 0.85 (Stumm and Morgan, 1996), it is then possible to solve for pCO_2, using the HCO_3^- and pH data for the Sheephouse Wood discharge collected by IMC Consulting Engineers Ltd (2003). Table 3 illustrates the derived partial pressures of CO_2 using these data, and reveals that pCO_2 of the mine water at first emergence appears to be approximately 400 times greater than atmospheric pCO_2 ($10^{-3.45}$ atm), and remains at least 80 times greater than atmospheric pressure along the entire length of its channel.

Table 3. Derived pCO_2 values using pH and bicarbonate concentration (Equation (7))

Distance downstream (m)	Calculated pCO_2 (atm)
0	1.38×10^{-1}
250	6.8×10^{-2}
500	5.5×10^{-2}
1000	4.2×10^{-2}
1500	5.1×10^{-2}
2300	2.8×10^{-2}

If the same pH and HCO_3^- data are used to solve for H_2CO_3, by rearranging Equation (6), it transpires that mine water H_2CO_3 concentration would be in excess of 500 mg/L. Since total measured acidity is just 231 mg/L, this cannot be the case. If there are errors in the analytical data, one would expect these to relate to the measured acidity and alkalinity concentrations, since both of these measurements rely on operator observation of an indicator colour change, which is somewhat subjective. Largest magnitude errors are likely to occur with the measurement of alkalinity concentration, since absolute concentrations are quite low (typically < 40 mg/L as $CaCO_3$). An alternative approach to calculating pCO_2 is to assume that the difference between measured and calculated acidity concentration (Table 2) is attributable to elevated pCO_2 (present in the water column as H_2CO_3 at the pH of this water), which subsequently degasses, resulting in the convergence of measured and calculated concentrations (note similarity of measured and calculated values of acidity at 1500 m and 2300 m downstream of the mine water adit). Thus, this provides a value for the concentration of H_2CO_3, which can then be used to solve for HCO_3^- using Equation (6). Table 4 shows the values for H_2CO_3 concentration (simply the difference between measured and calculated acidity), the derived bicarbonate concentration, and the newly derived pCO_2 values. Manipulating the data in this way suggests that the measured bicarbonate concentration may be in excess of actual concentrations. This in turn results in the derived pCO_2 values being somewhat less than those calculated in Table 3, above. Nevertheless, the pCO_2 calculated for the mine water, with correction for HCO_3^-, is still two orders of magnitude greater than atmospheric conditions.

Table 4. Derived pCO_2 following correction of HCO_3^- concentration data

H_2CO_3 (measured acidity minus calculated acidity) (mg/L)	Derived HCO_3^- concentration (mg/L)	Calculated pCO_2 after correction of HCO_3^- concentration (atm) (see text for explanation)
109	7.8	3.5×10^{-2}
97	15.8	3.1×10^{-2}
54	9.7	1.7×10^{-2}
84	21.7	2.7×10^{-2}
5	0.9	2.0×10^{-3}
14	0.8	5.0×10^{-3}

Although field titration for alkalinity determination has the dual attractions of simple measurement and low cost, manipulating the data in this way illustrates the possible inaccuracies of this method. One of the objectives of future work in this area (see below) is to evaluate approaches to alkalinity determination that offer increased confidence in results while maintaining the ease of measurement and low cost, which are attractive to implementers of mine water treatment schemes.

Implications for mine water management

The Sheephouse Wood mine water is not the only coal mine discharge that shows this phenomenon of elevated pCO_2. At Shepley Dyke, another mine water in Yorkshire, IMC Consulting Engineers Ltd (2003) reported even greater discrepancies between measured and calculated acidity concentrations, as illustrated in Table 5.

The data from Shepley Dyke suggest that at this site the contribution of aqueous CO_2 to acidity is even greater than that at Sheephouse Wood. Furthermore, the occurrence of elevated pCO_2 in this water renders it net-acidic, but comparison of the calculated values of acidity with alkalinity data indicates the water to be net-alkaline. This would have very significant implications for the selection of treatment units at this site, and yet simple aeration of the water would appear to be sufficient to transform the water from net-acidic to net-alkaline, via exsolution of CO_2 (cf. the downstream decrease in acidity at Sheephouse Wood).

Table 5. Discrepancies between measured and calculated acidity concentrations at the Shepley Dyke mine water, Yorkshire, UK (from IMC Consulting Engineers Ltd, 2003).

Measured acidity (mg/L as $CaCO_3$)	Calculated acidity (mg/L as $CaCO_3$)
300	32
251	29
100	6
139	12
120	31
125	31

Anecdotal reports from other waters in the UK, yet to be analysed for pCO_2, also suggest that CO_2 is present at elevated partial pressures. For example, one mine water in Northumberland is reported to actually "fizz", due to rapid CO_2 degassing, as it emerges at the surface (personal communication, Adrian England, White Young Green Ltd, UK). CO_2 is also thought to be present at elevated partial pressures at the UK's largest mine water treatment plant at Wheal Jane, Cornwall (personal communication, Chris Bullen, Unipure Europe Ltd, UK). This mine water actually emerges from an abandoned tin mine, which raises the question as to the source of the dissolved CO_2 (dissolution, under closed conditions, of carbonate minerals has been postulated, but not experimentally confirmed). Here, the apparent consequence of the elevated CO_2 partial pressures is a requirement to over-dose with lime in the first stage of treatment, at an additional cost that would appear to amount to an equivalent of in excess of US $100,000 dollars per year (personal communication, Chris Bullen, Unipure Europe Ltd, UK). Simple agitation, or purging with air, might result in cost savings of tens of thousands of dollars, at minimal capital outlay at this particular site.

Conclusions and future work

The data presented suggest that elevated CO_2 partial pressures may be a significant contributor to acidity in mine waters emerging from deep workings, with pCO_2 values in the order of 100 times greater than atmospheric pCO_2. This has significant implications for mine water treatment, not only in terms of initial design of treatment units, but also in terms of operational costs, particularly where alkali dosing is employed as part of the treatment train.

The data collected by IMC Consulting Engineers Ltd (2003) are, however, preliminary. It is now the intention to collect further data relating to pCO_2 in coal and metal mine waters around the UK, with a view to more accurately deriving pCO_2 values. We also intend to directly measure dissolved CO_2 concentrations in these mine waters, in order to compare directly measured and derived values. In this way, in the future we hope to be able to make recommendations as to how to optimize treatment to address elevated pCO_2 in mine waters. For example, if there are simple means by which elevated pCO_2 levels can be reduced (e.g. simple aeration), with a consequent effect on the net acidity of any given discharge, this may significantly influence subsequent choices regarding the particular treatment technology. In other cases (e.g. the Wheal Jane treatment system, above), it may be possible to substantially reduce chemical reagent costs by rapidly degassing CO_2 prior to dosing.

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