Degassing CO_2 from mine water: implications for treatment of circumneutral drainage

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Abstract This paper presents the results of investigation of the effects of CO_2 degassing on the chemistry of both net acid and net alkaline circumneutral mine drainage. Batch studies were carried out to mechanically aerate and degas the waters at a number of sites across the UK which resulted in large changes in concentrations of dissolved iron, alkalinity, dissolved CO_2, and pH. In the case of the net alkaline waters pH was raised by nearly 2 points over the course of the experiment. A simplistic model for CO_2 degassing was constructed in order to assess $d[CO_2]/dt$ over the initial stages of degassing. CO_2 concentrations were shown to decrease sharply over the first few minutes of the experiments. The results of this study have implications for the design of both passive and active mine water treatment schemes. The highly pH dependent nature of iron oxidation rates means that stripping CO_2 and thereby raising (or stabilising) pH can reduce residence times needed for Fe(II) oxidation and also reduce the cost of chemical dosing where it is required.

Key Words alkalinity, acidity, CO_2 degassing, pH

Introduction

It is widely accepted that control of pH is critical in the remediation of ferruginous mine drainage since rate of Fe(II) oxidation is highly pH dependent, with an increase in pH of one unit resulting in a 100 fold increase in oxidation rate (Equations 1 and 2; Liang 1993). Raising pH can therefore reduce the residence time required for iron oxidation in a treatment system from days or weeks to just a few minutes.

$$-\frac{d[Fe^{2+}]}{dt} = \frac{k_1[Fe^{2+}]P_{O_2}}{[H^+]^2} \qquad (1)$$

$$pH = -\log_{10}[H]^+ \qquad (2)$$

Circumneutral mine drainage, whether net-acid or net-alkaline often contains significant amounts of dissolved CO_2, far in excess of concentrations that would be observed at atmospheric equilibrium. This excess CO_2 contributes to the overall acidity of the system and can be removed by mechanical aeration and degassing to produce measureable changes in pH in the waters in question (Kirby *et al.* 2009).

Treatment of net alkaline waters often includes an aeration cascade to increase dissolved oxygen followed by a settling lagoon or wetland. For net acid sites pH is often raised by the addition of chemicals such as calcium or sodium hydroxide or by the inclusion of an alkalinity generating step such as a limestone drain prior to removal of Fe(III) hydroxide precipitates. It is uncommon to find cascades or mechanical aeration steps included in such treatment schemes specifically designed for the stripping of excess CO_2. Reducing the concentration of dissolved CO_2 however, can measurably reduce the acidity of a mine water and can have a large impact on the chemical consumption of an active treatment plant.

Methods

Experimental procedure: Analytical grade HNO_3 from Fisher Scientific was used as received. High purity 18 MΩ deionised water was used for the preparation of solutions in the laboratory. All syringe filters used were 0.8/0.2µm Acrodisc PF with Supor membrane. A submersible Whale® Water Systems self-venting pump powered by a 12 V car battery was used for mechanical agitation (leading to aeration and CO_2 degassing), as shown in Fig. 1. Approximately 10 L of fresh mine-water was collected and agitated. pH, temperature, and dissolved oxygen (DO) were measured and logged every 10 seconds throughout using two hand held Hanna combination meters HI-9828. Both meters were calibrated according to manufacturer's instructions prior to experimentation.

Two 15 mL samples of the mine water were taken at the beginning and end of each experiment and acidified with 4 drops of 20% HNO_3. One of the samples was passed through a syringe filter prior to acidification to remove Fe(III) particulates and was taken to be representative of dissolved Fe(II) (note the HNO_3 had demonstrably not caused appreciable oxidation of Fe(II)). All Fe samples were then analysed by a Perkin Elmer Optima 2100DV ICP-OES previously calibrated using standard solutions.

Alkalinity was determined using a Hach digital titator with a 1.6 N H_2SO_4 cartridge. 100 mL samples of fresh mine water were titrated using a bromocresol green-methyl red indicator. The end point was determined as a colour change from green to pink. Titrations were carried out in duplicate and in triplicate where the first two readings differed by more than 5 mg/L $CaCO_3$ equivalent.

‘Cold’ acidity titrations were also carried out using a Hach digital titator with 1.6 N NaOH cartridge. Samples were titrated to an end point of pH 8.4 measured using the pH module on a Hanna combination meter HI-9828. It should be noted that it was very difficult to get agreement between different titrations as both CO_2 degassing and iron oxidation and precipitation occur on the same timescale as the titration.

In order to overcome the difficulties encountered with the ‘cold’ acidity titration an additional ‘hot titration’ (AWWA, 1999) was carried out in the field to determine net acidity/alkalinity. Initially 100 mL of fresh mine water was taken and titrated to pH 4 using a Hach digital titator with a 1.6 N H_2SO_4 cartridge. Three drops of 30% H_2O_2 were then added. The sample was heated to boiling point and boiled for 2 minutes using a camping stove. The sample was then allowed to cool before titration to pH 8.4 again using the Hach digital titrator with a 1.6 N NaOH cartridge. Net acidity or alkalinity was then determined according to the difference between the quantities of acid and alkali consumed during the procedure.

Site descriptions

The sites investigated are located across the UK. Blenkinsop and Dawdon are situated in the north of England while Tan-y-Garn and Six Bells are located in south Wales.

Blenkinsop: The treatment scheme at Blenkinsop was designed as a preventative measure upon closure of the mine in 2002. Prior to the commissioning of the treatment scheme in 2005 predictions of iron concentrations of around 100 mg/L were expected for up to 11 years before settling down to 10—20 mg/L. In fact the first flush saw levels of 1000 mg/L of iron which to date have reduced to around 140mg/L. The water which was originally highly net-acid is now borderline net-acid with metal acidity and carbonate alkalinity almost in parity. The water is pumped from 20m below the shaft top and passed initially through a Newton aerator to begin the oxidation process. The flow of water then is split between two parallel settling ponds before flowing through two reed beds in series. Due to the higher than expected levels of iron encountered, a lime-dosing system has been employed to treat the mine water.

***Figure 1** experimental setup for batch-wise mechanical aeration.*

Tan-y-Garn: The experimental Tan-y-Garn treatment scheme was commissioned in January 2006, using a reducing alkalinity producing system (RAPS) which was the first of its kind to be used by the UK Coal Authority in the treatment of mine water. The scheme is entirely passive being gravity fed and comprising a series of three settling ponds and one wetland for the removal of Fe(III) precipitates after the RAPS. The flow rate on site is low being circa 3 L/s and varies considerably with high rainfall and drought events. Influent iron concentration has remained fairly constant since the site was commissioned at around 50 mg/L.

Dawdon: The primary objective for developing this active treatment plant (commissioned in 2009) was to prevent contamination of the East Durham Aquifer in the North of England, which provides drinking water to a number of nearby towns. The water being treated contains high levels of dissolved salt, with chloride concentrations of up to 40,000 milligrams per litre, approximately twice that of sea water. The contaminated mine water is pumped to control levels within the old workings to some depth below sea level. Water is then transferred from the mine shaft to the treatment plant via an 850m pipeline. The heavy contamination and salinity of the mine water required a bespoke process design to be developed. Initially there is a degassing stage followed by lime dosing. Recirculation of hydrated ferric oxide (HFO) solids between the treatment tanks results in the formation of high density sludge. Finally, the water is passed through a clarifier with the overall process reducing the iron levels in the water from 160 mg/L to less than 1mg/L. The treated effluent is eventually discharged out to sea via twin directionally drilled outfalls.

Six Bells: Mine water is extracted via a borehole driven 216m into the ground at a point where an underground roadway intercepts the disused mine workings. Despite relatively low influent Fe concentrations and high alkalinity it was decided to install an active treatment plant at this site due to sizing constraints. The water is initially pumped into a hydrogen peroxide dosing system before flowing into two parallel settlement lagoons measuring 1540m^2 each. The water then flows into a wetland area before being released into a nearby river. Pumping commenced in January 2002, the first flush of water found to contain 250 mg/L iron. After a period of four months the Fe concentration in the water had reduced to 45mg/L with further reduction to 20mg/L by 2010. The final effluent from the treatment system contains circa 1 mg/L Fe.

Results and discussion

The sites studied using mechanical aeration and degassing can be split into two groups in terms of their behaviour regarding changing pH and concentrations of dissolved carbonate species. These groups are characterised by their determination as net-acid (or borderline net acid) and net-alkaline. Values of alkalinity and acidity were determined using several different techniques the results of which are shown in Table 1. Measurements were taken pre- and post-agitation and it can be seen that the differences between these measurements was significant (up to 427 mg/L $CaCO_3$ equivalent). The final classification of a site as net-acid or net-alkaline was based on the results of hot peroxide titrations (Kirby and Cravotta 2005) which ensured that all CO_2 had been removed and all Fe(II) oxidised. It can be seen that the results of ‘cold’ acidity and alkalinity measurements made after 2 hours of aeration fit much more closely with the results from the hot peroxide titrations. This highlights the effect of large quantities of dissolved CO_2 on the measured acidity of the water. In the case of the water at Dawdon, degassing actually changes the classification from net-acid to net-alkaline.

The main impact of the high concentrations of dissolved CO_2 is the reduction in pH of the emerging mine water compared to samples with the same alkalinity at atmospheric equilibrium. Figure 2 shows the changes in pH measured at two of the sites over the course of the degassing experiments as CO_2 concentration decreases. The shapes of these curves are characteristic of the changes in pH observed at net-acid and net-alkaline sites and are explained in detail below.

Net-acid and borderline net-acid sites

For all of the sites that were net (or borderline) acid the initial pH values were below pH 6. It can be seen that pH rose quickly within the first 10 minutes of aeration indicating the degassing of dissolved CO_2. The pH peaked at all net acid sites between 6.3 - 6.5 before decreasing again. The characteristic shapes of the curves can be explained by the changing chemistry of the system over time.

1. Initial increase in pH corresponds to rapid CO_2 degassing.
2. As rate of CO_2 degassing slows rate of increase of pH also slows.

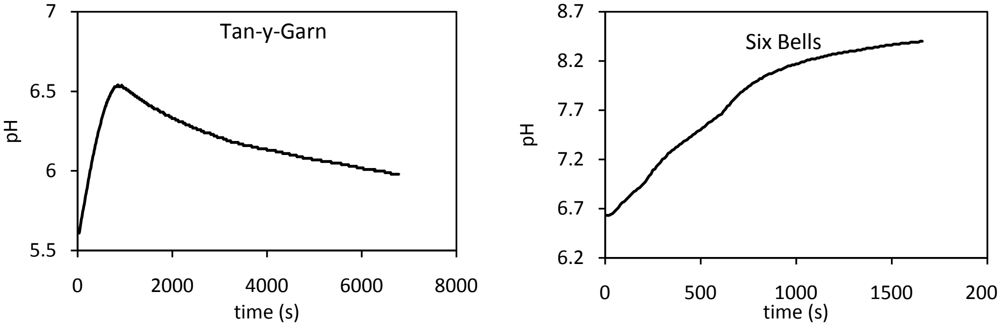

Figure 2 *Typical changes in pH recorded during batch-wise mechanical aeration experiments.*

Table 1 *Average values for acidity, alkalinity measurements pre and post aeration, compared to the hot peroxide titration (mg/L $CaCO_3$ equivalent) with post aeration Fe(II) (mg/L).*

	Pre-aeration			**Post-aeration**				
Site	**Acid**	**Alk**	**Difference**	**Acid**	**Alk**	**Difference**	**Fe(II)**	**Hot peroxide**
Blenkinsop	449	264	185 net acid	22	36	14 net alk	5.75	44 net acid
Tan-y-Garn	181	57	124 net acid	17	1	16 net acid	4.3	19 net acid
Dawdon	479	425	54 net acid	121[a]	276	153 net alk	0.06	195 net alk
Six Bells	251	749	498 net alk	0	625	625 net alk	0.05	615 net alk

[a] On the day of the Dawdon trial there were problems with the battery used to drive the aeration pump. The relatively high remaining acidity is a result of incomplete CO_2 degassing.

3. Rising pH causes increasingly rapid Fe(II) oxidation and precipitation which consumes alkalinity and causes pH to fall again.

Net-alkaline sites

The shapes of the curves for pH change in net alkaline waters are very different to those observed for net acid waters. The pH rises continuously throughout the experiment with CO_2 degassing as there is sufficient alkalinity present to neutralise any acidity generated by the formation of Fe(III) hydroxides. It is worth noting the final pH at Six Bells of 8.3 which would give near instantaneous Fe(II) oxidation.

The fact that the pattern of the pH changes observed remains consistent across different sites with similar chemistry implies that this method of aeration with pH monitoring can serve as a useful guide in the assessment of mine water discharges. As has been noted above, measurements of acidity and alkalinity can vary widely and the accuracy of the measurements is highly dependent on the skill and experience of the individual carrying out the work. By contrast, provided that the pH meter used is working correctly the degassing method with pH logging is a very straightforward way in which to assess a discharge, with far less likely hood of the introduction of operator error. The measurements for Fe(II) concentration taken at the end of the degassing experiments also give a useful indication as to the potential iron removal efficiencies that could be achieved without chemical dosing. It can be seen that for these circumneutral net acid waters final iron concentrations can be brought close to 5 mg/L with 2 hours aeration alone.

Having observed such significant changes in pH it was decided to attempt to model CO_2 degassing in these systems. A simple model was constructed based on changes in Fe(II) concentration and pH over time. The model assumed that after oxidation, precipitation of Fe(III) hydroxides was instantaneous and that alkalinity was consumed stoichiometrically according to Equation 3. This method has been used previously by Kirby *et al.* (2009).

$$Fe^{2+} + CO_3^{2-} + 2\tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightarrow Fe(OH) \qquad (3)$$

Changes in Fe(II) concentration over time were calculated (at 10 second intervals) using a 4th order Runge Kutta (RK4) method and values of k_1 (the rate constant for homogeneous iron oxidation) as described by Geroni and Sapsford (2011). The corresponding changes in alkalinity were then calculated at 10 second time intervals. Concentrations of Fe(II) and alkalinity, together with logged values for pH, temperature and DO were then input into PHREEQCi in spreadsheet mode to produce the values for dissolved CO_2. Examples of the outputs typical of net acid and net alkaline sites are shown in Figure 3.

The data highlights the differences in Fe(II) oxidation rates between the different sites, with near complete Fe(II) oxidation in around 10 minutes at Six Bells compared to around 8 mg/L Fe(II) remaining after 100 mins at Tan-y-Garn. The TDIC output from PHREEQCi follows closely changes in alkalinity and it can also be seen that this is completely consumed for the net-acid site whereas (as expected) it remains high for net-alkaline conditions. The only real similarity between the two types of sites was in the rate of CO_2 degassing. In all cases it was rapid over the first 5—10 minutes, after which point the rate slowed significantly. This corresponds with the peak in pH observed under net-acid conditions between 10—15 minutes after aeration commenced. For the net alkaline systems dissolved CO_2 did not reach equilibrium with the atmosphere over the time scale of the experiments for any of the waters investigated suggesting that further degassing would have led to even greater increases in pH.

The reduction of TDIC and dissolved CO_2 to zero under net-acid conditions underlines the oversimplification of the system by the assumptions made in this way of modelling. However the model does provide a useful guide as to the changes that could be expected in similar systems over the initial stages of aeration and degassing.

Conclusions

The results of these CO_2 degassing trials could play an important role in the design of semi-passive treatment systems. The inclusion of any aeration/degassing step up front of an active treatment plant for circumneutral water will reduce the rate of lime consumption which is likely to have a large cost benefit in the long term as the cost of transport and raw materials increases. In all of the sites investigated here (which are typical of coal mine drainage in the UK) an efficient aeration tank with sufficient residence time could completely eliminate the need for chemical dosing from marginally net acidic sites. In the case where only a few minutes residence time was available it would still be possible to remove between 30—50% of excess CO_2. A change in dissolved CO_2 of 120 mg/L corresponds to a reduction in the quantity of lime required to neutralise the associated carbonic acid of 202 mg/L. At a treatment site where the flow rate is 50 L/s this gives a reduction of 864 kg of lime per day. Not only is there an obvious benefit in economic terms as a reduction in the up-front purchase cost of the lime, but a lower concentration of dissolved $CaCO_3$ will result in less lime scale formation reducing maintenance costs and a reduced mass of

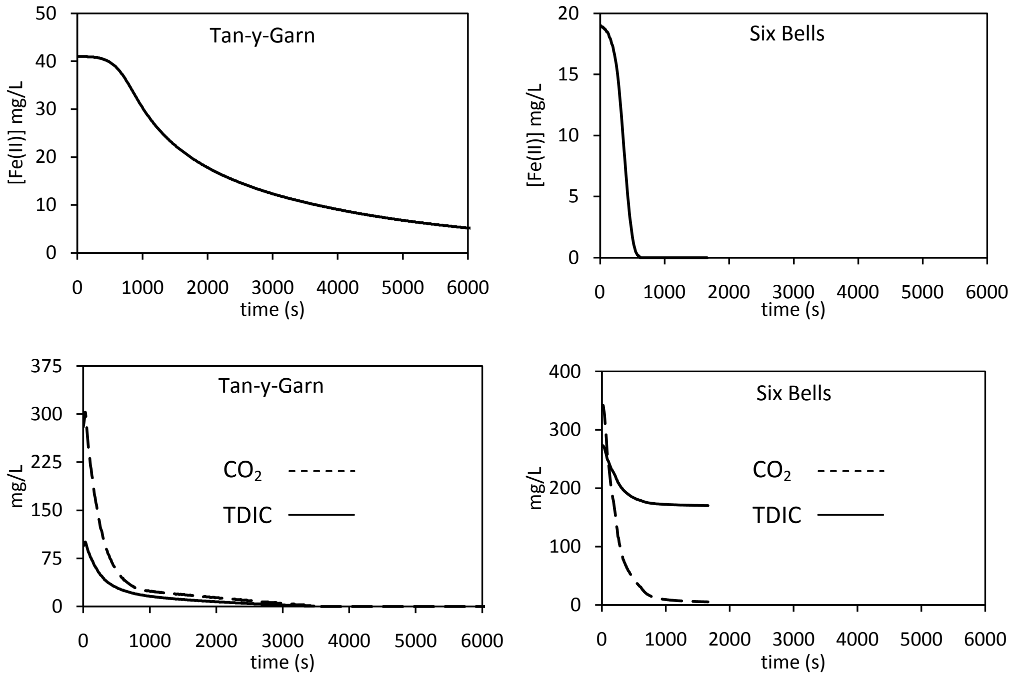

Figure 3 *Typical changes in concentration of Fe(II) and carbonate species with CO_2 degassing. Tan-y-Garn is representative of net acid sites with Six Bells showing net alkaline behaviour.*

sludge sent to landfill.

In the case of net alkaline sites, several minutes aeration (whether in a reaction vessel or by recirculation over an aeration cascade) could increase pH to a point where HFO settling rather than Fe(II) oxidation rate becomes the rate determining step for iron removal. This point is particularly important with relation to the Six Bells site discussed in this study. The current treatment system with hydrogen peroxide dosing could be completely replaced by a large aeration cascade that would increase pH above 7 meaning that the relatively small settling ponds would have sufficient residence time for Fe(II) oxidation.

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