MODELING THE CONTROLS ON ACIDITY REMOVAL IN VERTICAL FLOW PONDS[1]

Arthur W. Rose[2]

Abstract. Previous evaluations of vertical flow ponds (VFP) have indicated that these passive treatment systems generally do not remove acidity at a rate greater than 35 g/m^{2}d (Rose, 2004). The reason for this empirical limit has not been clear. In this paper, the chemical processes in VFPs are modeled using the PHREEQC program to show that CO_2 concentrations are a key to acidity removal, and commonly set a limit approximating the above acidity removal rate.

The modeling results indicate that CO_2 generation in the compost layer can be critical in providing elevated levels of alkalinity in effluent at pH 5.5 and above. The increased P_{CO2} greatly increases the potential amount of $CaCO_3$ dissolved from the limestone layer. For example, for a simple H_2SO_4 influent solution at pH 3.5 in equilibrium with open-air CO_2 ($10^{-3.5}$ atm.), reaction with $CaCO_3$ in a closed system generates only about 27 mg/L ($CaCO_3$) of potential acidity removal at pH 7. If Fe^{2+} in this influent exceeds 15 mg/L, the effluent at pH 7 will still be net acid. Reactions leading to increased CO_2 and acidity removal include 1) consumption of dissolved O_2 by compost (potential acidity removal 45 mg/L), 2) reduction of ferric iron (potential acidity removal 60 mg/L for 50 mg/L Fe^{3+}), and 3) SO_4 reduction and precipitation of FeS (potential acidity removal about 113 mg/L for 24 mg/L SO_4 reduced). Higher SO_4 removal or precipitation of Al lead to still higher CO_2 and acidity removal. If the influent P_{CO2} is $10^{-1.5}$ instead of $10^{-3.5}$, the acidity removed is much higher, about 150 mg/L compared to 27 mg/L for the low-CO_2 case. At typical flow rates of 0.1 L/m^2/d, an acidity removal of 113 mg/L is equivalent to about 16 g/m^2/d. If 100 mg/L SO_4 is reduced, as at many systems, then 320 mg/L acidity is removed, equivalent to a rate of 46 g/m^2/d. For strongly acidic systems, the influent pH, Fe, P_{CO2} and degree of SO_4 reduction, along with extent of $CaCO_3$ dissolution, are key factors limiting acidity removal.

Comparison of VFP influent and effluent chemistry with the modeling results indicates that typical VFPs generate only enough CO_2 in their compost layers to remove about 35-40 g/m^2/d of acidity. At higher loadings, effluent alkalinity is insufficient to neutralize all the acidity from the dissolved Fe^{2+}. Provision of a compost layer with enough retention time to accomplish SO_4-reduction as well as O_2 consumption and Fe^{3+} reduction can greatly increase the effectiveness of systems. The modeling method used here can be used to estimate acidity removal in design of a system, though extent of SO_4 reduction remains difficult to estimate.

Additional Key Words: acid mine drainage, passive treatment, limestone dissolution.

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Introduction

Vertical Flow Ponds (VFPs, or SAPS, Successive Alkalinity Producing Systems) are a major method for passively treating net acid mine drainage (Hedin et al., 1994). Rose and Dietz (2002) and Rose (2004) compiled data from a large number of VFPs and showed that, empirically, most systems were limited to an acidity removal rate of 35 to 40 $g/m^2/d$. At influent loadings higher than this, the effluent was generally still net acid, in spite of apparent retention times in limestone of several days. This removal rate has been used to design the size of VFPs in recent years, but the reason for this limit has never been clear. The purpose of this paper is to discuss the reasons for this limitation, and the implications of the limiting processes.

The approach is to first model the chemistry of the reaction of various simple AMD solutions with compost and limestone; then extend the modeling to data from real sites. The modeled acidity removal for the effluents is converted into acidity removal per unit area ($g/m^2/day$) using a typical flow rate per unit area. The implications of the results for performance and design of systems are then examined.

Chemical Processes in Vertical Flow Ponds

In a typical VFP, a layer of compost overlies a layer of limestone. AMD flows downward through the compost and into the limestone. Perforated underdrain pipes conduct the water back out to an oxidation-settling pond. In some systems, limestone and compost are mixed in a single layer and the system is called a sulfate-reducing bioreactor. Most VFPs are preceded by a pond to remove suspended sediment, and in some cases to oxidize and precipitate Fe.

Ideally, a VFP should generate effluent that is net alkaline (negative acidity). If the effluent pH exceeds about 6.5, the acidity from H^+, Al, and Fe^{3+} will be negligible, because the latter solutes have negligible solubility at pH 6.5. However, considerable acidity in the form of Fe^{2+} and Mn can be present. In order to have net alkaline effluent, alkalinity as HCO_3^- must exceed the acidity of Fe^{2+} and Mn. Therefore, generation of HCO_3^- (alkalinity) is essential for most VFPs with high-Fe influent.

As indicated in reaction (1), dissolved CO_2 (equivalent to H_2CO_3) converts to HCO_3^- (alkalinity) as pH increases.

$$CO_2\,(aq) + H_2O = H_2CO_3 = HCO_3^- + H^+ \qquad (1)$$

Figure 1 illustrates the gradual change in ratio from 99% dissolved CO_2 (equivalent to H_2CO_3) at pH 4.35 to 50% HCO_3^- at pH 6.35 to 99% HCO_3^- at pH 8.35. If the influent acid solution is high in dissolved CO_2, then there is the potential for high alkalinity, by conversion of the CO_2 to HCO_3^- as pH increases because of limestone reaction (i.e., reaction (1) goes to the right). Any CO_2 released by limestone dissolution adds to the HCO_3^-. Conversely, if dissolved CO_2 is low, the alkalinity of the neutralized solution cannot be as high, because CO_2-species come only from the $CaCO_3$.

Acidity is neutralized and alkalinity generated by several processes. An obvious one is reaction with limestone. However, as is shown below, the amount of alkalinity generated by reaction with limestone is strongly dependent on the CO_2-pH conditions of the water contacting the limestone.

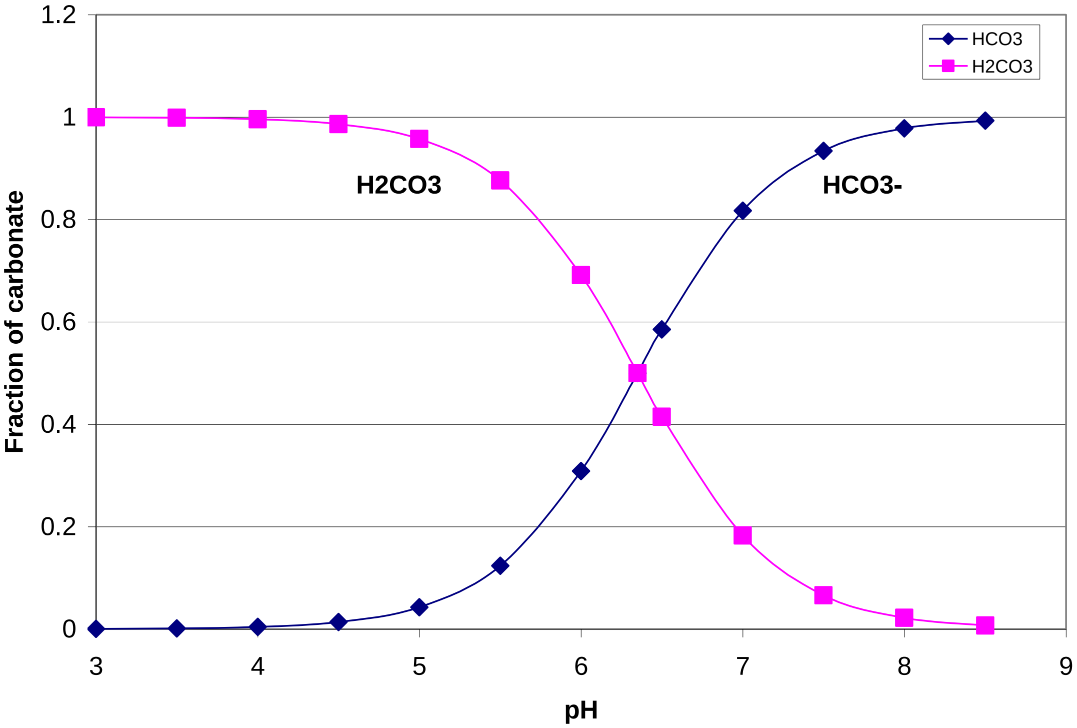

Figure 1. Proportions of total carbonate species as H_2CO_3 vs. HCO_3^- as a function of pH at 25°C.

In terms of CO_2, it has many sources. If influent water is at equilibrium with CO_2 in air, the $P_{CO2} = 10^{-3.5}$ atm. A P_{CO2} level at approximately this value is expected if the influent water cascades down a slope or spends significant time exposed to air in the ponds (pre-VFP and VFP). In contrast, if the influent water emerges from an underground mine or from groundwater, the P_{CO2} may be considerably higher, perhaps $10^{-0.5}$ to $10^{-1.5}$ atm., though this value will decrease on exposure to air. Additional CO_2 is added in the compost layer by several processes, as discussed below, to generate much higher P_{CO2}. The extent and effectiveness of these processes are critical in determining the acidity-alkalinity relations of effluent from a VFP.

A main intent of the compost layer is to consume all dissolved O_2 from the water and to reduce dissolved ferric (Fe^{3+}) to ferrous (Fe^{2+}). The chemical reactions are approximately as follows:

$$O_2(aq) + CH_2O \text{ (compost)} = CO_2(aq) + H_2O \qquad (2)$$

$$4Fe^{3+} + CH_2O \text{ (compost)} + H_2O = 4Fe^{2+} + CO_2 (aq) + 4H^+ \qquad (3)$$

The CH_2O is a representation of the approximate composition of the organic matter in the compost. As indicated in these equations, CO_2 species are a product of both reactions. The exact mix and concentration of CO_2 species depends on the pH and P_{CO2}. The CO_2 species will be dominantly a combination of CO_2 (aq) and H_2CO_3 at pH less than 6.35, and HCO_3^- at higher pH (Fig. 1). The above redox reactions are mediated by bacteria that derive energy and probably organic compounds from the reactions. The above reactions probably occur in sequence, reaction (2) proceeding largely to completion before reaction (3) can become important. Some consumption of organic matter is processed to cell constituents and not directly to CO_2.

A third process in the compost is sulfate reduction, utilizing the SO_4 in AMD:

$$SO_4^{2-} + 2CH_2O + 2H^+ = 2\ CO_2(aq) + H_2S + 2\ H_2O \qquad (4)$$

This reaction is also conducted by bacteria, and occurs only when all O_2 and Fe^{3+}have been reduced. Again, consumption of organic matter leads to generation of CO_2 as a product, and the reaction consumes H^+.

In the limestone, H^+ and CO_2 (H_2CO_3) react with calcite to neutralize the solution and generate alkalinity (HCO_3^-):

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2(aq) + H_2O \text{ at pH} < 6.4\ (25^oC) \qquad (5)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \text{ at pH} > 6.4 \qquad (6)$$

$$CO_2 + CaCO_3 + H_2O = Ca^{2+} + 2\ HCO_3^- \qquad (7)$$

As indicated by these reactions, CO_2 can be either a reactant or a product at this stage. The complete result can best be calculated from a speciation model of the system.

Modeling of Chemical Reactions in Vertical Flow Ponds

An illuminating set of calculations is to model the amount of calcite dissolution and alkalinity generation as a function of initial pH, P_{CO2}, Fe, Al and sulfate reduction. These initial calculations assume the minimum P_{CO2} of $10^{-3.5}$ atm, as expected for water exposed to air in the two influent ponds of typical systems. Using the PHREEQC program (Parkhurst, 1995), a pH 3.5 H_2SO_4 solution in equilibrium with P_{CO2} of air ($10^{-3.5}$ atm), reacted to pH 7 with calcite in a closed system at 10°C, removes only 27 mg/L acidity (expressed as $CaCO_3$). The endpoint of pH 7 is chosen because VFPs rarely develop effluent with higher pH. An acidity value of 27 mg/L as $CaCO_3$ is equivalent to the acidity represented by 15 mg/L Fe^{2+}. Therefore, a VFP with no compost and receiving an air-equilibrated influent could produce net alkaline water only if the influent Fe^{2+} was less than 15 mg/L (even if problems with $Fe(OH)_3$ precipitation are neglected). About half of the removed acidity in this case is due to pH increase, and about half due to generation of HCO_3^-.

Results of calculations for several other situations are illustrated in Fig. 2. The influent is assumed to have a defined P_{CO2} (usually equilibrated with air at $10^{-3.5}$), and varying pH and concentrations of Fe. This solution is then is reacted with organic matter (compost), and finally with limestone. Amounts of organic matter are varied to allow differing levels of Fe^{3+} and SO_4

reduction. The results are shown as Acidity Removed (mg/L $CaCO_3$) = influent acidity minus effluent acidity at pH 7. Acidity is calculated as

$$A = 50000*(2m_{Fe2+} + 3m_{Fe3+} + 10^{-pH} – m_{HCO3-}) \qquad (8)$$

where A is acidity in mg/L as $CaCO_3$, and m indicates moral concentration. In later calculations, if Al is present, it is included as $3m_{Al}$. All acidity values are expressed as $CaCO_3$ (50 mg/L $CaCO_3$ = 1 meq H^+). Note also that acidity is a net acidity which includes the effect of any alkalinity, as seen in eq. (8) (Cravotta and Kirby, 2004). All calculations are for 10^oC, which is an approximate annual average groundwater temperature for Pennsylvania. Note, however, that actual temperatures vary seasonally with large decreases in organic reaction rates in winter, as discussed later.

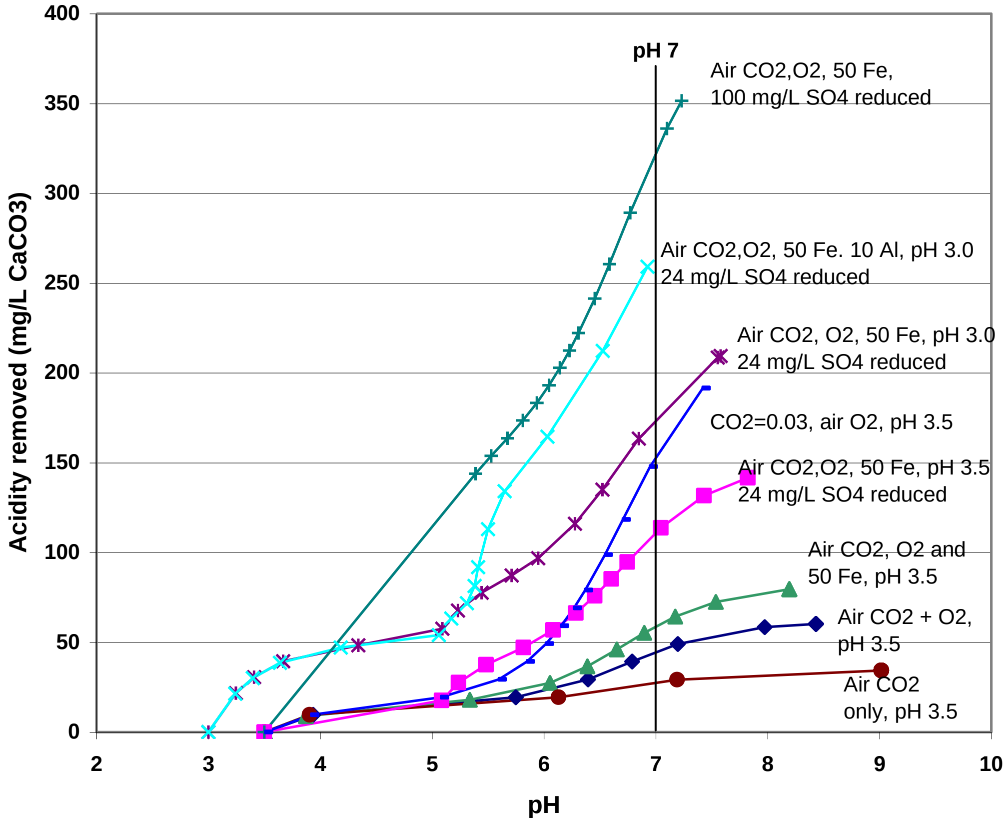

Figure 2. Results of calculated acidity removal for pH 3.5 and 3.0 solutions reacted with organic matter and $CaCO_3$, showing the large range of possible acidity removal depending on the influent chemistry and degree of SO_4 reduction.

A key assumption in the preceding calculations is that the influent to the VFP has P_{CO2} equilibrated with open air. A calculation for water influent to the compost layer with higher P_{CO2} of $10^{-1.5}$ atm (0.03 atm) at pH 3.5 shows a much higher acidity removal of about 150 mg/L $CaCO_3$ at pH 7. Influent water of this character might be relevant for a system receiving water from a flooded underground mine or a groundwater outflow, with limited residence time in ponds before flowing into the compost. The marked difference in acidity removal indicates that the influent P_{CO2} level is a crucial variable. More data are needed on the P_{CO2} or Total Inorganic Carbon of water influent to the compost layer of VFPs.

Table 1 summarizes the results of the calculations shown in Fig. 2. As indicated above, a pH 3.5 solution of H_2SO_4 equilibrated with air CO_2 ($10^{-3.5}$ atm.) and then reacted with limestone to pH 7 removes about 27 mg/L (as $CaCO_3$) of acidity.

The influent water at essentially all VFPs contains dissolved O_2 because the pond surface is in contact with air, leading to absorption of O_2 at the water surface. Reduction of this dissolved O_2 in the compost leads to generation of CO_2 (eq. 2). The equilibrium concentration of dissolved O_2 is about 10 mg/L but varies somewhat with temperature. Note that anoxic limestone drains should not contain Fe^{3+} and do not generally contain any dissolved O_2.

If the dissolved O_2 initially in equilibrium with air (~10 mg/L dissolved O_2) is chemically reduced by 0.00028 moles of C (eq. 1), then P_{CO2} entering limestone is higher ($10^{-2.26}$) and the Acidity Removed at pH 7 increases from 27 to 45 mg/L $CaCO_3$.

Table 1. Results of acidity removal calculations

Influent					Reduction Step		Effluent[1]	
pH	log P_{CO2}	log P_{O2}	Fe mg/L	Al mg/L	C added M/L	log P_{CO2}	Acidity rem. mg/L CaCO3	
3.5	-3.5	0	0	0	0	-3.5	27	No reduction
3.5	-3.5	-0.68	0	0	0.00028	-2.26	45	Reduce O2 only
3.5	-3.5	-0.68	50	0	0.0005	-2.02	60	Reduce Fe to ferrous
3.5	-3.5	-0.68	50	0	0.001	-1.78	113	Reduce 24 mg/L SO_4
3.5	-3.5	-0.68	50	0	0.00258	-1.35	320	Reduce 100 mg/L SO4
3.0	-1.5	-0.68	0	0	0	-3.5	150	High influent CO2
3.0	-3.5	-0.68	50	0	0.001	-1.74	165	Reduce 24 mg/L SO4
3.0	-3.5	-0.68	50	10	0.001	-1.72	260	Reduce 24 mg/L SO4

[1] Eflfuent at pH 7

If 50 mg/L Fe^{2+} is present along with enough SO_4 to balance charge, the equilibration with air oxidizes Fe^{2+} to Fe^{3+}. If an additional 0.00022 moles/L of C are used to reduce Fe^{3+} back to Fe^{2+} in the compost, the acidity removed at pH 7 is 60 mg/L. Note that at pH 7, the (net) acidity of this solution is about 45 mg/L ($CaCO_3$). The effect of 50 mg/L Fe^{2+} (90 mg/L acidity) exceeds the 45 mg/L of alkalinity as HCO_3^-. At higher influent Fe concentrations, the effluent acidity increases further because the CO_2 effects are inadequate to generate enough alkalinity to balance the Fe acidity. Note also that in the calculation, all influent Fe is effectively Fe^{3+}, which is not commonly true in real systems.

If 0.001 moles of C are provided, so that O_2, 50 mg/L Fe^{3+} and 24 mg/L of SO_4 are reduced to generate still more CO_2 ($P_{CO2} = 10^{-1.78}$), the acidity removed is 113 mg/L at pH 7. In this step, FeS precipitates to remove about 28% of the Fe from solution. Effluent acidity at pH 7 is close to zero; i.e., the alkalinity effects of SO_4 reduction are barely adequate to remove enough Fe to bring the net acidity to zero.

At pH of about 3.3 and lower, the pH has a significant effect on acidity removal. Greater amounts of $CaCO_3$ dissolution are required to neutralize the solution, leading to higher dissolved CO_2 and then higher HCO_3^- in the neutralized effluent. Also, low pH allows higher amounts of Fe^{3+} in the influent water, leading to more CO_2 generated by reduction to Fe^{2+}. Figure 2 shows a calculation for influent at pH 3 but otherwise the same as a previous case (log P_{CO2} = -3.5, 50 mg/L Fe, 0.001 moles C/L). The acidity removal is 170 mg/L compared with 113 mg/L for the previous case.

Sulfate reduction has a potentially large effect on generation of CO_2 and resulting acidity removal. If the influent solution has the same characteristics as above (pH 3.5, log P_{CO2} -3.5, Fe^{3+} = 50 mg/L, and enough C to reduce 100 mg/L SO_4 as well as O_2 and Fe^{3+}), the acidity removed at pH 7 is 320 mg/L, and about 140 mg/L of this removal occurs in the compost layer, where pH is increased to greater than 5.

These results clearly show that CO_2 generated in the compost layer can have a major effect on alkalinity generation and acidity removal in VFPs. In particular, sulfate reduction in the compost zone can greatly increase the P_{CO2} and the acidity removed compared to situations where only dissolved O_2 and Fe^{3+} are removed. Increasing amounts of sulfate reduction generate increasing amounts of CO_2 and result in increased dissolution of limestone.

A final step of acidity removal occurs during precipitation of Al by neutralization of the H^+ generated in this process:

$$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+ \tag{9}$$

In SO_4-rich AMD, this reaction happens mainly at pH above 5. If neutralization by $CaCO_3$ proceeds beyond this pH in a Al-bearing solution, appreciable additional acidity is removed as $Al(OH)_3$ or other Al phases such as Al hydroxysulfate are precipitated and the resulting H^+ neutralized. A calculation for removal of 10 mg/L Al as $Al(OH)_3$ is shown on Fig. 2, leading to 265 mg/L acidity removal. Note that if the Al phase is an Al hydroxysulfate, as found by Thomas and Romanek (2001), the acidity removal (Al^{3+} removal) is a combination of H^+ consumption plus precipitation of an "acid salt" that remains in the system and may be liberated at a future time.

Of course, the Al precipitate tends to coat the limestone and inhibit neutralization, so Al precipitation is a mixed blessing. Rose (2004) found that Al concentrations less than 20 mg/L had limited effects on VFP performance over periods of a few years, but higher concentrations led to plugging and failure of VFPs. However, in at least the first year or two of operation, Al precipitation can be a major mechanism of acidity removal. In sulfate-reducing bioreactors, the Al precipitation may continue for a much longer time.

Conversion of Acidity Removal to Removal Rate in g/m^2/d

The above modeling indicates that the potential amount of acidity removed in many VFP systems may be limited by CO_2 generation in the compost layer. Reactions generating CO_2 in the compost layer all involve reduction by organic matter, but the amount of CO_2 depends on the species that are reduced (O_2, Fe^{3+}, SO_4) and the extent to which reduction proceeds. A comparison with observed acidity removal rates in g/m^2/d is desirable.

The acidity removal rate in g/m^2/d can be estimated from the flow rate per unit area (L/d/m^2) and the acidity removal (mg/L $CaCO_3$). Data from Tables 1 and 3 in Rose (2004) indicate that flow rates in successful VFPs are commonly 0.05 to 0.15 L/min/m^2, so 0.1 L/min/m^2 is taken as typical (Fig. 3). Given the above figure of 45 mg/L for acidity removal for the case of only dissolved O_2 and CO_2, then the acidity removal rate is 45 mg/L x 0.1 L/min/m^2 x 1440 min/day x 0.001 g/mg = 6.5 g/m^2/d. This rate is only 25% of the 35 g/m^2/d suggested by Rose (2004). This calculation assumes complete equilibration of the inflowing water with O_2 in air, and calcite dissolution to pH 7, so in many cases the rate may be lower.

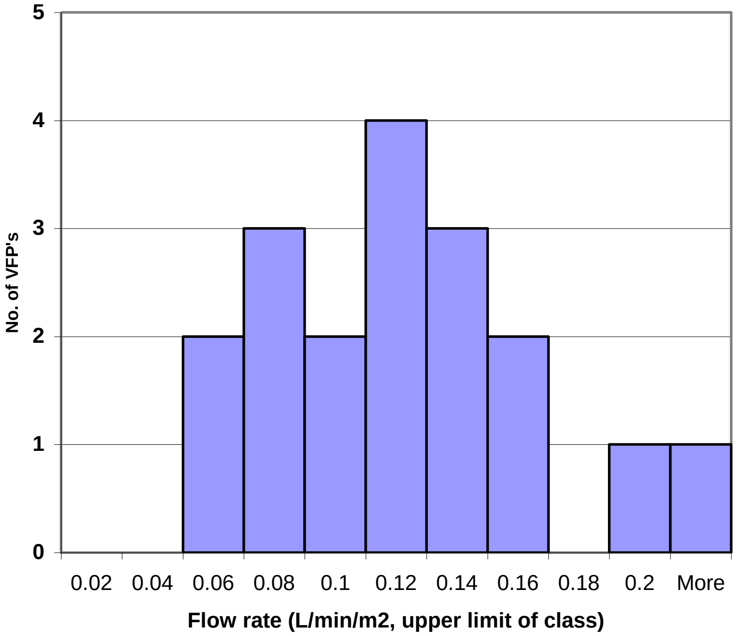

Figure 3. Frequency distribution of flow rates in L/min/m^2 for VFPs of Rose and Dietz (2002)

The acidity removed to pH 7 by reduction of 50 mg/L Fe^{3+} plus dissolved O_2 starting at pH 3.5 is about 60 mg/L $CaCO_3$. Note that 50 mg/L Fe^{3+} is somewhat supersaturated at pH 3.5, so it exaggerates the likely effect at this pH. Assuming flow of 0.1 L/min/m^2, this corresponds to a rate of 8 g/m^2/d, still small compared to 35 g/m^2/d.

Reduction of 24 mg/L SO_4, plus 50 mg/L Fe^{3+} (including precipitation of FeS) and 10 mg/L dissolved O_2 leads to acidity reduction of 113 mg/L $CaCO_3$ at pH 7. This corresponds to 16 g/m^2/d at the 0.1 L/min/m^2 flow rate, about half the limiting rate of Rose and Dietz (2002) and Rose (2004).

Lowering the initial pH to 3.0 increases the acidity removal to 175 mg/L at pH 7, equivalent to 25 g/m^2/d, which is approaching the rate of many acidic systems.

If 10 mg/L Al is present with a starting pH of 3.0, then the acidity removed is about 265 mg/L and the rate is 38 g/m^2/d. This value is similar to the limit cited previously.

If 100 mg/L SO_4 is reduced, along with dissolved O_2 and 50 mg/L ferric iron, then the acidity removed is 320 mg/L and the rate is 46 $g/m^2/d$. The example shows the potential importance of extensive SO_4 reduction in acidity removal, and a potential for exceeding the 35 $g/m^2/d$ level.

The calculation with $P_{CO2} = 10^{-1.5}$ atm. showed 150 mg/L acidity removal, equivalent to 22 $g/m^2/day$, again indicating the important effect of influent CO_2.

The above modeling shows that a limit of approximately 35-40 $g/m^2/d$ is reasonable for relatively acid influent containing small to moderate levels of Al, if appreciable SO_4 reduction occurs. However, the calculations also show that the limit is dependent on the influent composition (pH, Fe, Al, P_{CO2}), on CO_2 generation in the compost layer and the extent of SO_4 reduction, as well as on the extent of reaction with limestone.

Calculated Acidity Removal at Vertical Flow Ponds

Calculations similar to those above have been made for data from several VFP systems, using the actual influent concentrations. Some of these systems have acidic effluent, indicating a limit in acidity removal. All modeling assumes an influent P_{CO2} at $10^{-3.5}$ atm. Results are displayed on Fig. 4.

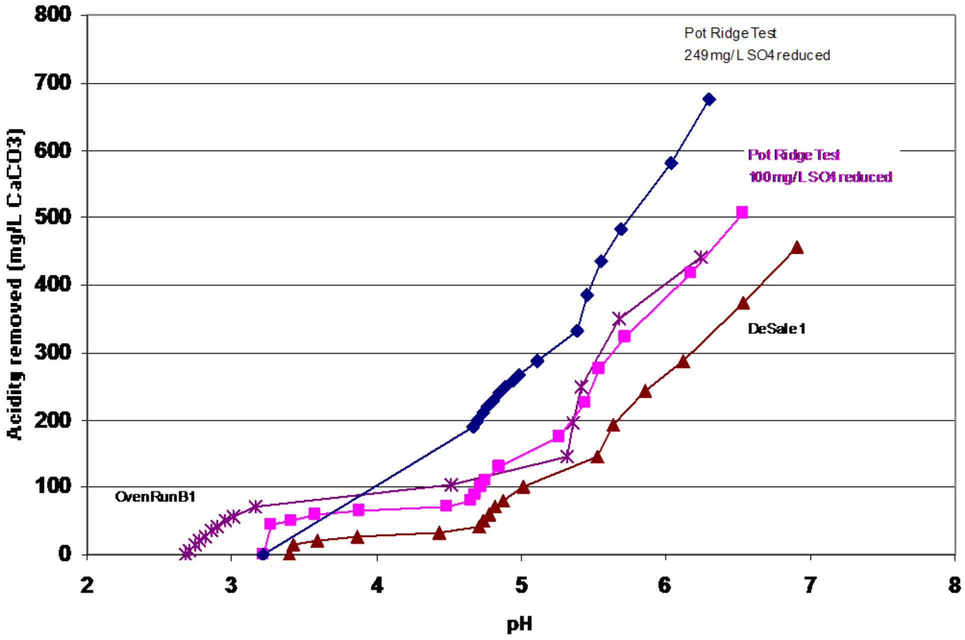

Figure 4. Examples of acidity removal modeling for several VFP systems.

At the Pot Ridge Test system (Rose et al., 2001), average influent has pH 3.21, 1071 mg/L SO_4, 135 mg/L total Fe, 22 mg/L Al, 109 mg/L Ca, 82 mg/L Mg and 28 mg/L Mn, with an acidity of 480 mg/L $CaCO_3$. Fe^{3+} solubility is calculated to be 45 mg/L, so this amount was assigned to Fe^{3+} and the remaining Fe to Fe^{2+}. Comparison of influent and effluent SO_4 indicates that a long-term average of 100 mg/L SO_4 has been reduced (though the amount varies seasonally, Rose et al., 2001). In the PHREEQC calculation, sufficient C is provided to reduce all the O_2 and Fe^{3+}, and 100 mg/L SO_4, and the resulting solution is reacted with increasing amounts of $CaCO_3$. The results on Fig. 4 indicate an initial jump to pH 3.27 and 44 mg/L acidity removed in the compost. This step represents the acidity removed by SO_4 reduction in the compost and by precipitation of appreciable Fe as FeS, counterbalanced by H^+ released by Fe^{3+} reduction to Fe^{2+}. No $CaCO_3$ dissolution occurs in this step, which is modeled to be entirely in the compost.

On entering the limestone, the solution increases to pH 4.5 and 71 mg/L acidity was removed by $CaCO_3$ dissolution. A 3rd stage during which FeS is precipitated brings the pH to 5.3 and the acidity removed to 176. The FeS precipitation is driven by the increased pH from $CaCO_3$ dissolution, which decreases the solubility of FeS in the H_2S-bearing solution.

Above pH 5.3, acidity is removed during Al^{3+} precipitation as $Al(OH)_3$(am) and by generation of HCO_3^-. Precipitation of Al does not begin at lower pH because of strong Al complexing by SO_4. The acidity removed reaches approximately 400 mg/L at pH 6.0, which is the average observed pH of the system effluent. Concentration of HCO_3 reaches the equivalent of about 50 mg/L $CaCO_3$ alkalinity, and Al removal accounts for about 160 mg/L acidity removal. The observed acidity removal at Pot Ridge Test is 404 mg/L, and the acidity removal rate is 29 $g/m^2/d$, with a relatively low flow rate of 0.05 $L/min/m^2$.

To summarize, 34 mg/L of acidity removal occurs in the compost as a result of SO_4 reduction and FeS precipitation. Another 127 mg/L of acidity is removed by $CaCO_3$ dissolution, in part accompanied by precipitation of FeS. A final 230 mg/L of acidity removal is accompanied by Al precipitation and HCO_3 generation during $CaCO_3$ dissolution.

During summer and fall, SO_4 reduction at Pot Ridge Test is considerably more effective. On 9/27/98, the SO_4 decrease was 249 mg/L, from an influent of pH 2.68, Fe 172 mg/L, Al 29 mg/L, SO_4 1488 mg/L, and acidity 692 mg/L. Modeling this influent with enough C to accomplish 249 mg/L SO_4 loss shows a large initial neutralization in the compost to pH 4.67 and 189 mg/L acidity loss, mainly due to SO_4 reduction in the compost. On reaction with limestone, pH increases to 5.4 and acidity loss of 333 mg/L with partial loss of Fe as FeS. Above pH 5.4, Al starts to precipitate and HCO_3 becomes increasingly important. The effluent on this date closely matches the calculated effluent at pH 6.1 and acidity loss 600. This example shows the very large potential effect of SO_4 reduction.

Modeling of several other systems shows a range of characteristics. At DeSale 1, the influent AMD has pH 3.4, with 1510 mg/l SO_4, 137 mg/L Fe, 14 mg/L Al and 439 mg/L acidity. Data indicate about 80 mg/L SO_4-loss on average. Modeling this AMD shows a 13 mg/L decrease in acidity in the compost with little pH change because H^+ release on Fe^{3+} reduction approximately balance those of SO_4 reduction. Reaction with $CaCO_3$ then leads to an increase in pH to 4.7 at an acidity decrease of 50 mg/L, after which FeS starts to precipitate on continued $CaCO_3$ dissolution. At about pH 5.5, Al starts to precipitate, and accounts for about 75 mg/L acidity removal, with 262 mg/L represented by HCO_3 generation. The calculated acidity removal of about 450 mg/L at the observed effluent pH of 6.9 closely matches the observed acidity removal of 474 mg/L. Thus, this successful site derives most of its acidity removal from HCO_3 generation, and very little from SO_4 reduction.

At the Oven Run B site, extremely acid water (pH 2.87, SO_4 940 mg/L, Al 41 mg/L, Fe 68 mg/L and acidity 515 mg/L) flows into a large VFP. The available data indicate that effluent

SO_4 is consistently greater than influent SO_4. Possibly this indicates additional inflow into the bottom of the system, but modeling it with no SO_4 reduction indicates a gradual pH and acidity removed increase to about pH 4.5 and 100 mg/L acidity removal, with no initial jump as observed for systems reducing SO_4. Above pH 4.5, Al removal and HCO_3 generation contribute to acidity decrease. The system increased pH only to about 4.3, and removed only about 160 mg/L acidity.

Discussion

The preceding modeling indicates that the potential amount of acidity removed in a given VFP varies considerably and is limited by reactions in the compost as well as by reactions in the limestone layer. Influent CO_2 plus amounts of CO_2 generated in the compost by reduction of O_2, Fe^{3+} and SO_4 are important in generating adequate HCO_3^- in the effluent to balance Fe^{2+} and Mn^{2+} acidity. For systems with appreciable influent Fe, the effluent alkalinity must be adequate to neutralize precipitation of $Fe(OH)_3$ when the solution is aerated. Ideally, enough alkalinity should remain to neutralize dissolved Mn as well. The calculations show that for influent with high Fe, the effluent can have positive net alkalinity only if considerable sulfate reduction occurs in the system, or the influent CO_2 is high.

The discussion of Pot Ridge Test indicated that seasonal variation of sulfate reduction in the compost can be important. The seasonal increase of SO_4 reduction during summer and fall is illustrated by Fig. 6 and 7 in Rose et al. (2001). During winter, S was actually oxidized and released from the compost as SO_4, whereas in summer the SO_4 reduction reached several hundred mg/L. Similar seasonal changes are evident in data for the Penn Hills VFP supplied by Brent Means (Personal communication). Coincident loss of SO_4, decrease of acidity and increase of alkalinity occur during summer, with very little SO_4 reduction in winter. This pattern indicates that sulfate reduction may be ineffective during winter, with corresponding effects on acidity removal. However, at some systems the influent acidity also decreases during winter, thereby negating the effect on acidity removal. In any case, the possible seasonal effects must be taken into account.

The results emphasize the significance of compost in the effectiveness of VFP systems. Some workers have considered compost to be a nuisance, but these results show that it can have very important effects in addition to just preventing $Fe(OH)_3$ coating of limestone. The compost must be thick enough that retention time in compost is adequate for all the reactions including SO_4-reduction to take place. Based on data from many systems (Rose and Dietz, 2002), a 30 cm layer of compost appears adequate for most conditions. A 15 cm thickness may be marginal, judging from results at Tangaskootack (Rose et al., 2004). However, for sites with high flow rate, high influent Fe^{3+} or where extensive SO_4 reduction is needed, a thicker layer of compost may be desirable.

At 0.1 $L/min/m^2$, 30 cm of compost, and 25% porosity in compost, the retention time in the compost is about 0.5 day. Apparently this retention time is adequate for reduction of O_2 and Fe^{3+} and appreciable SO_4 reduction. Note that compost reactions are sensitive to temperature, as well as pH and other chemical variables. Winter temperatures tend to cause lower performance than warmer periods, though this may be partly balanced by seasonal variation in influent chemistry. Addition of limestone to raise pH in the compost may have considerable effect on compost effectiveness, though some SO_4-reduction occurs in compost even in very acid influents. Further research is needed on these topics.

Modeling of the type described in this paper provides the potential for improved sizing and design of VFPs. Given a representative analysis of AMD to be treated, the compost reactions and the solution chemistry during progressive dissolution of limestone can be estimated. Table 2 provides an example of PHREEQC input for a calculation of the type performed here.

Unfortunately, the extent of SO_4-reduction is difficult to predict. A compilation of data for 9 successful systems indicates reduction of 25 to 100 mg/L of SO_4 over an annual period is typical, but most systems show high SO_4 reduction in summer and fall but low or negative reduction in winter and spring, as found at Pot Ridge Test (Rose et al., 2001). It would be conservative to assume a low rate of SO_4 reduction. In view of the potential importance of SO_4 reduction, considerable research and effort is needed to improve the capability of compost and methods for estimating reduction rates in compost.

Conclusions

1. Modeling the chemical processes in VFPs shows that the amount of acidity removed is limited in a complex manner by influent pH, P_{CO2}, Fe^{3+}, Al, and extent of SO_4-reduction, as well as extent of limestone dissolution.
2. If water at pH 3.5 enters the limestone layer containing only CO_2 from open air, the acidity removed in the VFP by $CaCO_3$ dissolution to pH 7 is limited to 27 mg/L, which is sufficient to neutralize only 15 mg/L Fe^{2+}. If the influent contains higher amounts of Fe^{2+} and Mn^{2+}, the effluent will be net acid.
3. CO_2 produced by reduction of O_2 and Fe^{3+} in the compost can add appreciably to acidity removal, to 45 and 60 mg/L, respectively.
4. SO_4-reduction is very effective in removing acidity and generating additional CO_2 that can provide net alkaline conditions in the final effluent, to levels of 320 mg/L acidity removed if 100 mg/L SO_4 is reduced.
5. Given the typical flow rates at VFPs of 0.1 $L/min/m^2$, VFPs with highly acid influent can remove acidity at rates of 25 to 45 $g/m^2/d$, as found empirically for many systems. However, at unusually low pH, or high levels of SO_4^- reduction or Al removal, higher removal rates can be attained, and in low-Fe systems with low SO_4 reduction, limiting removal rates can be much lower.
6. Compost is critical not only in reducing O_2 and Fe^{3+} in influent water, but also in generating CO_2 that is converted to HCO_3^- as pH in increased above 5.
7. A retention time in compost of about 0.5 days appears adequate to accomplish appreciable SO_4 reduction, at least during summer, but further research is needed to optimize this factor. Seasonal variation can be significant. Influents with high Fe^{3+} may require more compost.
8. The acidity removal of a given system can be estimated by modeling of the type used in this paper, though the degree of SO_4-reduction remains uncertain.

Table 2. Example of input to PHREEQC used in calculating acidity removal

```
TITLE Test of Pco2 effect on calcite neutralization.
SOLUTION 1  PRtest influent
       units   mg/L
       pH      3.21
       temp     10.0
       S(6)    1071        charge
      Al          22
      Fe(2)       90
      Fe(3)       45
      Ca          109
      Mg          82
      Mn          28
PHASES
      Fix_H+
                  H+ = H+
                  Log_k    0.0
EQUILIBRIUM_PHASES
       CO2(g)              -3.5       10.
      O2(g)                -0.68      10.
      Fix_H+               -3.21      H2SO4   10.0
SAVE Solution 1
END
USE Solution 1
REACTION 1   Reduce O2, Fe(3) and S with C
      C           1
      0.00286
SAVE Solution 2
END
USE Solution 2
REACTION 2  Add increments of CaCO3 to solution
      Calcite              1
      0.0       .0001      .0002  .0003  .0004          .0005     .0006     .0007     .0008    .001    .0015    .002    .0025
      .003      .004       .005
EQUILIBRIUM_PHASES
      Calcite              0.0        0
      FeS(ppt)0.0          0
      Al(OH)3(a)           0.0        0
SELECTED_OUTPUT
      -file                alkPRtest3.pun
      -totals              Ca         Fe(2)      Fe(3)      Al        Mn        S(6)
      -molalities          HCO3-
      -si                  CO2(g)  O2(g)   calcite
END
```

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