

PASSIVE TREATMENT OF LOW-PH, FERRIC IRON-DOMINATED ACID ROCK DRAINAGE IN A VERTICAL FLOW WETLAND I: ACIDITY NEUTRALIZATION AND ALKALINITY GENERATION¹

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Abstract. Passive treatment of acid rock drainage (ARD) is typically limited by the chemistry of the ARD. Anaerobic, ferrous iron-dominated ARD can be treated directly with limestone in an anoxic limestone drain (ALD), but alkalinity generation is limited because the high pH (5 – 6) reduces limestone solubility. Oxygenated, ferrous iron-dominated ARD cannot be treated directly with limestone due to the potential for armoring by iron oxyhydroxide precipitates. Vertical flow wetlands that rely on biological processes are typically employed. Reducing and alkalinity producing systems (RAPS) are one type of VFW that requires biological pretreatment of ARD to remove oxygen. The biological pretreatment typically adds alkalinity to the ARD, limiting the alkalinity generated in the RAPS via limestone dissolution by lower the solubility of limestone. The low pH (< 3) of oxygenated, ferric iron-dominated ARD is prohibitive to the biological processes typically required for effective passive treatment. In this study, highly oxidized (i.e., 99% Fe³⁺), low-pH (2.4), ARD is treated with a VFW system amended with fine-grained (1.2 mm) limestone-buffered organic substrate (LBOS). Nearly 100% of the influent acidity (averaged >1300 mg·L⁻¹) is neutralized in the LBOS with an average 600 mg·L⁻¹ of additional alkalinity measured in the effluent; total alkalinity generated in the LBOS averages > 1800 mg·L⁻¹. Limestone dissolution accounts for 80 – 95% of the total alkalinity generated in the system. Limestone dissolution is very rapid and occurs in a thin (2 – 5 cm) dissolution front that advances as the limestone is depleted. Armoring due to iron oxyhydroxide precipitates apparently does not limit limestone dissolution, as limestone consumption above the dissolution front is nearly complete with greater than 85% of the limestone removed; limestone below the front is apparently unaffected. Sizing recommendations are made based on the influent acidity load and the volume of limestone in the LBOS.

Additional Key Words: limestone-buffered organic substrate, limestone dissolution, armoring, biological oxidation of organic matter, anaerobic wetland

Introduction

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Passive treatment of acid rock drainage (ARD) is often limited by the ability of treatment systems to produce adequate alkalinity to buffer mineral and proton acidity present in the ARD (Hedin et al., 1994a). Passive alkalinity addition generally requires an anaerobic environment and is accomplished through two distinct mechanisms: biological oxidation of organic matter and reaction of ARD with an alkalinity-generating material. Hence, the limitations on alkalinity production are a function of the passive systems ability to promote these two mechanisms.

While numerous microbially-catalyzed reactions occur in passive systems, sulfate reduction, mediated by sulfate reducing bacteria (Widdel, 1988), is primarily responsible for pH neutralization and sulfate and toxic metals removal (Gusek, 1998; Machemer and Wildeman, 1992; McIntire and Edenborn, 1990). Because sulfate reducing bacteria are generally accepted to be inactive at pH <5 (Widdel, 1988), biologic alkalinity generation is generally limited to influent ARD with pH >4. Calcitic limestone (greater than 90% calcite, CaCO_3) is by far the most common alkalinity-generating material used in passive treatment. In general, limestone dissolution is self-buffering, providing a pH of about 8 (Barton and Vatanatham, 1976; Rose, 1999), making it is essentially impossible to over treat the ARD. Due to the rapid autooxidation of ferrous iron and low solubility of ferric iron at near-neutral pH, the presence of oxygen and ferric iron in ARD results in the armoring and passivation of limestone. Thus, direct treatment of ARD with limestone is limited by the presence of ferric iron and/or oxygen (e.g., Sterner et al., 1998).

The limitations placed on biologic alkalinity generation (i.e., pH) and limestone dissolution (i.e., ferric iron and oxygen) permit division of net acidic ARD into groups according to treatment options based on oxidation state. In most cases, ARD is ferrous iron-dominated, because ferric iron is relatively insoluble at pH greater than about 3.5 (Rose and Cravotta, 1998). Empirical evidence suggests that ferric iron generally does not occur in ARD with pH >4 (Hedin et al., 1994a). At pH less than about 3 (the exact value depending on iron and sulfate content), major amounts of dissolved ferric iron can be present (Hedin et al., 1994a; Rose and Cravotta, 1998). Near-neutral, iron-bearing ARD (pH 5 – 6) is normally relatively reduced, while more acidic ARD is more oxidized (Rose and Cravotta, 1998). Consequently, there are three general types of net acidic ARD: reduced, high pH (>6), ferrous iron-dominated ARD; oxygenated,

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moderate pH (4 – 6), ferrous-iron dominated ARD; and low pH (<3), ferric iron-dominated ARD.

Reduced, ferrous iron-dominated ARD, the only type of net acidic ARD appropriate for direct contact with limestone (i.e. $<1 \text{ mg}\cdot\text{L}^{-1} \text{ Al}^{+3}, \text{ Fe}^{+3}, \text{ or O}_2$), is commonly treated using anoxic limestone drains (ALDs, Turner and McCoy, 1990). Calculated increases in bicarbonate alkalinity due to measured increases in pH accounts for generally $< 1 \text{ mg}\cdot\text{L}^{-1}$ alkalinity (Hedin et al., 1994b), suggesting that for treatment of reduced, ferrous iron-dominated ARD, initial pH is relatively unimportant in determining the final alkalinity. The principle bicarbonate-producing process in ALDs is the reaction of calcite with carbonic acid (Hedin et al., 1994b). Hence, the presence of high pCO_2 in the influent ARD will enhance the alkalinity generating potential by increasing the equilibrium concentrations of alkalinity (Hem, 1985) and by increasing the rate of limestone dissolution (Plummer et al., 1979). However, even under very high pCO_2 , the concentrations of alkalinity that develop in ALDs rarely exceeds $350 \text{ mg}\cdot\text{L}^{-1} \text{ CaCO}_3$ equivalents (Hedin et al., 1994b; Watzlaf and Hyman, 1995; Watzlaf et al., 2000).

Although ARD with pH <3 is not uncommon, the majority of net acidic ARD exposed at the surface commonly has pH 4 – 6 (e.g. Hedin et al., 1994a; Rose and Cravotta, 1998) and is dominated by ferrous iron. Consequently, for most surface ARD, dissolved oxygen is the only impediment to direct treatment of ARD with limestone. Vertical flow wetlands (VFW) are commonly employed to overcome the limitations of oxygenated ARD (e.g. Gusek, 1998; Kepler and McCleary, 1994; Watzlaf, 1997; Watzlaf et al., 2000; Wildeman et al., 1993). Vertical flow wetlands are constructed in layers, typically comprised of organic material (e.g. compost) overlying a limestone drain, designed to be continually flooded and anaerobic, and engineered so that the flow of ARD is directed down through the layers (Kepler and McCleary, 1994). Reducing and alkalinity producing systems (RAPS) are a common variation of VFW typically employed with passive treatment systems designed for coal-related ARD (e.g. Watzlaf, 1997). Appropriately named, the principle behind the RAPS design is that the microorganisms within the organic layer remove dissolved oxygen before alkalinity is generated in the drain (Kepler and McCleary, 1994). Although biological alkalinity generation is commonly observed, most RAPS rely solely on limestone dissolution for alkalinity generation (Nairn et al., 2000). However, biological alkalinity generation can effect the amount of limestone dissolution both negatively, by raising the ARD pH before it reaches the limestone drain, and positively, by generating carbon dioxide and effectively raising the pCO_2 of the ARD. Hence, it is the pCO_2 generated in

the RAPS organic layer that likely controls the rate and amount of limestone dissolution in the drain.

Accordingly, as with an ALD and based on empirical evidence (Watzlaf et al., 2000), RAPS receiving moderate pH, ferrous iron-dominated ARD directly (as opposed to receiving ARD effluent from an upstream RAPS) can only generate up to approximately $450 \text{ mg}\cdot\text{L}^{-1}$ net alkalinity as CaCO_3 (i.e., the sum of influent acidity neutralized + measured effluent alkalinity). Moreover, where RAPS are used in succession, the rate of net alkalinity addition for the first RAPS is about 40 to $60 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$, while the rate for the second RAPS falls off to about 30 to 50 % of the rate of the first system (Watzlaf et al., 2000). This progressive decline in RAPS performance can be attributed to the fact that the water entering the second RAPS unit is closer to calcite equilibrium than the original ARD; influent pH and calcium of the second RAPS unit is always higher (Watzlaf pers. comm., 2001). The amount of alkalinity RAPS can generate is limited by two contradictory factors: the influent water quality's effect on calcite solubility and the biological productivity of the substrate. Since calcite solubility increases with decreasing pH (Plummer et al., 1979), limestone dissolution in a RAPS is favored by lower pH influent. In general, alkalinity generation in a RAPS increases in response to increasing levels of acidity-related influent water-chemistry parameters (e.g. Fe, non-Mn acidity, Jage et al., 2000). However, at low pH and/or temperature, the influent ARD limits biological activity, hindering oxygen removal, biologic alkalinity generation, and ferric iron reduction (Jage et al., 2000).

Consequently, RAPS are not well designed to treat low pH (<3), ferric iron-dominated ARD. Low pH can easily overwhelm microbial populations in the organic matter and ferric iron can passivate the limestone drain through armoring. For RAPS to be effective, the pH in the organic layer must be maintained at microbially tolerable levels. Buffering the organic layer has been suggested (Hedin et al., 1994a; Watzlaf, 1997). However, with ferric iron-dominated ARD, raising the pH will decrease the solubility of iron oxyhydroxides, resulting in precipitation and a concomitant decrease in pH below levels suitable for biogenic alkalinity generation. This cycle of raising the pH through the neutralizing capacity of the substrate and lowering the pH through precipitation will continue very rapidly until all of the acidity is neutralized, all of the neutralization potential is consumed, or all of the limestone is passivated by armoring precipitates (e.g. Sterner et al., 1998). Thus, alkalinity generation in a RAPS receiving low pH, ferric iron-dominated ARD relies solely on the neutralization potential (e.g., limestone content)

of the organic substrate to raise the pH. The availability of the neutralization potential, in turn, will depend on the extent of limestone dissolution in the presence of ferric iron.

Most RAPS built in the Appalachian coal regions are constructed using a mushroom-compost substrate with a low neutralization potential ($<10\%$ CaCO_3 equivalents by weight) (e.g. Watzlaf, 1997). Several researchers (Dvorak et al., 1992; Hedin et al., 1994a; Hellier, 1996; Watzlaf, 1997) have suggested the incorporation of additional limestone to bolster the buffering capacity of the organic substrate, while others (e.g., Skousen et al., 1998; Zipper and Jage, 2001) recommend against mixing organic-layer materials with limestone, due to the potential for metal oxyhydroxide precipitates occluding porosity. Watzlaf (1997) found that alkalinity generation occurs along a sharp reaction front in the compost layer of a RAPS-type VFW column study receiving low pH, ferric iron-dominated ARD. All of the alkalinity generated in this system resulted from the neutralization potential of the organic layer; the limestone drain did not contribute significant alkalinity (Watzlaf, 1997). The dissolution front advanced through the compost layer as the substrate's buffering capacity ($<10\%$ CaCO_3 equivalents by weight) was consumed (Thomas et al., 1999; Watzlaf, 1997). There was no indication that limestone dissolution or permeability was effected by ferric iron precipitates in the organic substrate, however influent iron ($10 \text{ mg}\cdot\text{L}^{-1}$) and aluminum ($18 \text{ mg}\cdot\text{L}^{-1}$) concentrations were low and within limits for direct contact with limestone (e.g. $< 25 \text{ mg}\cdot\text{L}^{-1}$, Sterner et al., 1998).

In this paper, the mechanisms and limitations of alkalinity generation in the organic layer of a RAPS-type vertical flow wetland (VFW) treatment system receiving low pH, ferric iron-dominated ARD are discussed. Limestone screenings (1.2 mm nominal grain size) have been added to the organic layer in an effort to boost the neutralization potential and maximize alkalinity generation. Evidence is provided which demonstrates that sizing criteria and system longevity can be based on the neutralization potential of the organic substrate and independent of the contaminant-loading rate.

Materials and Methods

Substrate

A limestone buffered organic substrate (LBOS) was made by mixing 25% limestone screenings with 75% organic material by volume. The screenings were high calcium limestone (91.5% by weight CaCO_3 as reported by the quarry) with a nominal grain size of 1.23 mm; greater than 80% of the screenings were between 0.59 and 4.76 mm. The density of the LBOS mixture was determined by weighing a known volume of the LBOS at field moisture (before ARD was passed through the substrate).

Experimental System

Eight plastic tanks (92 cm diameter by 122 cm tall) were used to simulate VFWs. Each tank was filled with 92 cm of LBOS overlying 15 cm of coarse (#57) limestone. The ARD used in this experiment was drawn from a coal pile retention basin (CPRB) that collects runoff from a nearby coal storage pile at the Department of Energy (DOE) Savannah River Site (SRS), near Aiken, S.C., USA. The ARD was delivered continuously to the top of the tanks for two years. The flow rate was set such that the average acidity loading rate of $50 \text{ g acidity} \cdot \text{d}^{-1} \cdot \text{m}^{-2}$; the recommended acidity loading rate for a RAPS-type VFW (e.g., Watzlaf and Hyman, 1995). The effluent drained from the bottom of the tanks through standpipes such that a 15-cm column of ARD was maintained over the LBOS.

Water Sampling and Analysis

The influent and effluent was sampled weekly for two years. Tank effluent was sampled from a port installed on the effluent pipe at ground level. Fine-scale pore water samples were collected using a vacuum-operated pore-water extractor (i.e., swamp suckers or swampers, (Winger and Lasier, 1991) and acrylic pore-water diffusion samplers (i.e., peepers, Carignan, 1984; Carignan et al., 1985; Hesslein, 1976). Two tanks were sampled with the swampers, each in three different locations. At each location, pore water was drawn from the LBOS at three different depth intervals (1.5, 7.5- and 15-cm deep). A single sample of the influent ARD water column above the LBOS was taken from each tank. Peeper samples were collected once from a single tank. Peepers were constructed with a total of seven sampling horizons in the vertical profile. Each horizon had three replicate wells, each 3 cm in diameter with a volume of

approximately 3 mL. Wells within a horizon and wells between horizons were spaced approximately 5 cm apart on center. Each peeper was inserted in the LBOS such that the first two wells were in the water column above the LBOS with the bottom edge of the second well positioned at the substrate-water interface. The remaining five wells provided a pore water profile of the upper 25 cm of the LBOS. The peepers were left to equilibrate for at least two weeks and no longer than three weeks.

Influent, effluent, and swamper pore water samples were analyzed for temperature, pH, acidity/alkalinity, sulfate, iron (Fe_T and Fe^{+2}), and dissolved metal content (Al, Fe, Mn, and Ca). Sulfide was also analyzed in the effluent and swamper samples. Due to the small sample volume, only temperature, pH, alkalinity, and dissolved metal content could be collected using the peepers. Flow through each tank was measured at the effluent using a graduated cylinder and a stopwatch. Temperature and pH were measured in the field. Unfiltered samples were analyzed for acidity and alkalinity by laboratory titration following standard methods (e.g., APHA, 1998). There was no difference between filtered and unfiltered acidity or alkalinity replicates. All samples for dissolved metal analysis were filtered with a 0.45 μm filter and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6000, Perkin-Elmer Corporation, Norwalk, CT) using the QA/QC protocols outlined in EPA method 200.8. Only the major elements iron, aluminum, manganese, and calcium are reported in this paper. Samples collected for iron speciation were filtered (0.1 μm), acidified, and stored in brown amber bottles at 4°C. Iron speciation was determined following a colorimetric FerroZine technique (To et al., 1999) that complexes ferrous iron. Samples for dissolved sulfide were filtered (0.45 μm) and analyzed in the field using a CHEMetrics™ sulfide test kit. Samples for dissolved sulfate were filtered (0.22 μm) into a glass vial containing silver phosphate (50 mg) such that no headspace remained. The lack of headspace prevented exsolution and oxidation of dissolved sulfide, while dissolved silver phosphate reacted to remove the sulfide as silver sulfide. Dissolved sulfate was determined by filtering the precipitated silver sulfide and then analyzing the filtrate by standard BaCl gravimetric methods (APHA, 1998).

Substrate Sampling and Analysis

A total of seventeen 5-cm diameter substrate cores were taken from five different tanks for total calcium analyses. Six cores were taken from two tanks (two sets of triplicate cores) six months before the completion of the project. The additional, eleven cores were taken at the end

of the project, including triplicate cores from the same two tanks previously sampled, replicates from two additional tanks, and a single core was taken from the final tank. The cores were divided into three subsamples (approximately 3-5 cm in length) based on three distinct color zonations (Thomas and Romanek, 2002). Samples for total calcium analyses were air-dried and ground to a fine powder with a cryogenic grinder. Approximately 0.5 g of each powdered sample was digested with 10mL of 50% trace-metal grade HNO_3 plus a few drops of 30% H_2O_2 at 105°C. The digest was diluted to a final volume of 50 mL with deionized water before analysis by inductively coupled plasma optical emission spectrometry (ICP-OES, Elan 4300DV, Perkin-Elmer Corporation, Norwalk, CT).

At the completion of the project, a total of five 2.5-cm substrate cores were taken from the top 30 cm of each tank for neutralization potential (NP) analysis (40 cores total from 8 tanks). The cores were divided into three subsamples based on distinct color zonations (Thomas and Romanek, 2002). Each subsample was lyophilized and ground with a cryogenic grinder to a fine powder. The uppermost color zonation was the most intensely studied with a total of 51 subsamples analyzed. Thirteen samples were selected randomly for NP analysis from the subsamples of each of the other two zones. Several methods exist to test the neutralization potential (NP) of a soil (e.g. Skousen et al., 1997), however they are all subtle variations of the original NP method of Sobek et al. (1978). The general Sobek method calls for the digestion of a dried sample (1-2 gm) with a known quantity (50 mL) and strength (0.5 N) of hydrochloric acid. The solution is then back-titrated with a base (NaOH) of known strength (0.5 N) to pH 7.0, thus determining the neutralizing content of the sample (Skousen et al., 1997; Sobek et al., 1978).

Total calcium and NP were determined on dried samples of the initial substrate to provide baseline data. Subsamples were collected from individual tanks during construction at several different depths as the tanks were filled. Each set of subsamples from an individual tank was air-dried, homogenized, ground cryogenically, and treated like the rest of the samples.

Results

Influent Water Chemistry and Loading Rates

The influent was low pH (2.4), ferric iron-dominated ARD. Primary contaminants were iron (average = 142 $\text{mg}\cdot\text{L}^{-1}$), aluminum (average = 84 $\text{mg}\cdot\text{L}^{-1}$), acidity (average = 1304 $\text{mg}\cdot\text{L}^{-1}$ as CaCO_3 equivalents), and sulfate (average = 1521 $\text{mg}\cdot\text{L}^{-1}$). Manganese was consistently low

averaging $4 \text{ mg}\cdot\text{L}^{-1}$ and thus contributed very little to the total acidity. The pH (average = 2.4) was consistent for the length of the project with little variation. Ferric iron averaged 96% of the influent ARD total iron. Historic data indicate that the ARD is typically oxidized and highly acidic in nature (pH<3; e.g., Anderson, 1990; oxygen is near saturation, Millings, 1999; and iron is >95% ferric, Anderson et al., 1991). A summary of the average influent ARD water chemistry is presented in Table 1, the range is presented in parentheses below the average value.

The final average surface-area acidity loading was $58 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$ with a range between tank averages of 44 to $76 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$ (Table 2). Recommended surface-area loading rates for RAPS is $50 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$ (e.g., Demchak et al., 2001; Watzlaf and Hyman, 1995). For any individual tank occasional high flow rates resulted in acidity loading rates as high as $975 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-2}$ (Table 2) without any significant reduction in the effluent alkalinity. Total acidity load averaged 18.6 Kg CaCO_3 equivalents over the course of the study with range of 15.9 to 27.2 Kg CaCO_3 equivalents (Table 2).

Effluent Water Chemistry

Metal removal. The average and range of the effluent chemistry for the eight individual tanks studied is summarized in Table 1. The average for all eight tanks presented in this section is calculated from the individual tank averages (bottom of Table 1). The average dissolved iron ($15 \text{ mg}\cdot\text{L}^{-1}$) in the effluent showed a ten-fold decrease from average influent concentrations, while average aluminum was consistently removed below $0.2 \text{ mg}\cdot\text{L}^{-1}$ (Table 1). Effluent manganese concentrations are equal to and occasionally higher than the influent ARD (Table 1).

Combined metal removal averaged 95% (Table 2) for the eight tanks with almost 90% of the total iron and 100% of the aluminum (Table 1) removed in the LBOS. Thomas and Romanek (2002) have demonstrated that the bulk of this removal occurs as iron oxyhydroxides and aluminum hydroxysulfates. Although sulfide minerals (greater than 95% as iron sulfide) are

Table 1. Influent and effluent water chemistry for the individual VFW tanks.^a

| | Flow (mL·min ⁻¹) | Temp (°C) | pH Std Units | Effluent Alkal. as mg·L ⁻¹ CaCO ₃ | Net Alkal. as mg·L ⁻¹ CaCO ₃ | Ca (mg·L ⁻¹) | Fe* (mg·L ⁻¹) | Al* (mg·L ⁻¹) | Mn (mg·L ⁻¹) | Sulfate (mg·L ⁻¹) | Sulfide (mg·L ⁻¹) |
|----------------------|---------------------------------|--------------|-----------------|---|--|-----------------------------|------------------------------|------------------------------|-----------------------------|----------------------------------|----------------------------------|
| Influent | | 22.9 | 2.4 | | -1304 [†] | 52 | 142 | 84 | 3.9 | 1521 | |
| ARD | | (6 to 36) | (1.6 to 3.0) | | (-2320 to -738) | (23 to 114) | (92 to 237) | (39 to 274) | (1.8 to 8.4) | (926 to 3385) | |
| Tank 2 | 17.9 | 22.8 | 6.48 | 657 | 1850 | 570 | 12.91 | 0.16 | 4.5 | 1248 | 1.2 |
| | (0 to 110) | (4 to 37) | (5.9 to 6.9) | (315 to 1575) | (1227 to 2997) | (268 to 807) | (0 to 40) | (0 to 9.3) | (1.5 to 7.2) | (696 to 1817) | (0 to 15) |
| Tank 10 | 18.8 | 23.8 | 6.42 | 588 | 1829 | 611 | 11.63 | 0.02 | 5.1 | 1275 | 3.2 |
| | (0 to 72) | (6 to 36) | (5.9 to 6.9) | (322 to 1102) | (1080 to 3040) | (371 to 1003) | (0.1 to 90) | (0 to 0.2) | (2.6 to 9.5) | (495 to 2732) | (0 to 20) |
| Tank 13 | 27.9 | 22.3 | 6.34 | 560 | 1771 | 610 | 32.79 | 0.07 | 4.8 | 1277 | 0.7 |
| | (0 to 380) | (4 to 34) | (5.5 to 6.9) | (295 to 974) | (1216 to 2926) | (392 to 921) | (0.6 to 123) | (0 to 4.2) | (1.1 to 11.5) | (876 to 1938) | (0 to 15) |
| Tank 24 | 23.1 | 22.5 | 6.40 | 606 | 1817 | 619 | 16.73 | 0.03 | 5.1 | 1273 | 4.0 |
| | (0 to 120) | (5 to 36) | (6.0 to 6.9) | (300 to 1326) | (1277 to 2943) | (373 to 888) | (0 to 120) | (0 to 0.4) | (1.4 to 11.5) | (541 to 2257) | (0 to 40) |
| Tank 30 | 21.1 | 22.7 | 6.42 | 620 | 1831 | 616 | 14.1 | 0.02 | 5.2 | 1302 | 1.6 |
| | (0 to 90) | (5 to 33) | (5.9 to 6.8) | (320 to 1425) | (1301 to 2964) | (380 to 943) | (0.01 to 76) | (0 to 0.3) | (1.9 to 12.2) | (678 to 2323) | (0.05 to 15) |
| Tank 36 | 23.3 | 22.0 | 6.33 | 607 | 1816 | 604 | 19.18 | 0.02 | 4.4 | 1186 | 2.8 |
| | (0 to 324) | (3 to 35) | (5.5 to 6.8) | (280 to 1139) | (1256 to 2964) | (372 to 853) | (0 to 58) | (0 to 0.3) | (1.2 to 8.5) | (627 to 2098) | (0 to 20) |
| Tank 39 | 21.3 | 21.9 | 6.5 | 652 | 1865 | 609 | 2.26 | 0.02 | 4.7 | 1113 | 9.4 |
| | (0 to 120) | (3 to 35) | (6.0 to 7.0) | (374 to 1546) | (1226 to 3070) | (398 to 915) | (0 to 11) | (0 to 0.2) | (1.8 to 10.3) | (263 to 1585) | (1 to 30) |
| Tank 44 | 15.8 | 21.7 | 6.50 | 663 | 1874 | 558 | 6.77 | 0.05 | 3.9 | 936 | 15.6 |
| | (0 to 130) | (4 to 35) | (5.2 to 7.1) | (340 to 1118) | (1204 to 3093) | (362 to 907) | (0 to 48) | (0 to 2.2) | (1.1 to 11) | (427 to 1569) | (0.1 to 50) |
| Average ^f | 21.2 | 22.5 | 6.42 | 619 | 1832 | 600 | 14.55 | 0.05 | 4.71 | 1201 | 4.8 |
| Min | 15.8 | 21.7 | 6.33 | 560 | 1771 | 558 | 2.26 | 0.02 | 3.90 | 936 | 0.7 |
| Max | 27.9 | 23.8 | 6.50 | 663 | 1874 | 619 | 32.79 | 0.16 | 5.20 | 1302 | 15.6 |

^a The top value is the tank average, the bottom set of numbers (in parenthesis) is the range over the two year study

[†] The DCPRB acidity is given as negative alkalinity where alkalinity = -(acidity)

* Values assigned zero were below detection limits of the ICP-MS

^f The overall average, min, max calculated from the individual tank averages

Table 2. Influent loading rates^a

| | Acidity Loading Rate g CaCO ₃ ·m ⁻² ·d ⁻¹ | Total Acid Load (Kg) | Iron Loading Rate g Fe·m ⁻² ·d ⁻¹ | Aluminum Loading Rate g Al·m ⁻² ·d ⁻¹ | Influent Combined Metals moles·m ⁻³ ·d ⁻¹ |
|----------------------|--|----------------------------|---|---|---|
| Tank 2A | 48.1 (0 to 245) | 15.9 | 5.5 (0 to 36) | 3.4 (0 to 25) | 0.26 (0 to 1.8) |
| Tank 10A | 51.1 (0 to 320) | 16.9 | 6.3 (0 to 30) | 3.7 (0 to 18) | 0.29 (0 to 1.3) |
| Tank 13A | 75.8 (0 to 974) | 27.2 | 9.0 (0 to 113) | 5.1 (0 to 65) | 0.40 (0 to 5.3) |
| Tank 24A | 66.7 (0 to 330) | 19.0 | 7.5 (0 to 37) | 4.4 (0 to 21) | 0.35 (0 to 1.7) |
| Tank 30A | 57.7 (0 to 245) | 16.4 | 6.4 (0 to 26) | 4.0 (0 to 16) | 0.31 (0 to 1.2) |
| Tank 36A | 60.3 (0 to 743) | 21.3 | 7.2 (0 to 107) | 4.1 (0 to 49) | 0.32 (0 to 4.6) |
| Tank 39A | 58.1 (0 to 297) | 16.0 | 6.7 (0 to 44) | 4.1 (0 to 31) | 0.31 (0 to 2.2) |
| Tank 44A | 44.3 (0 to 410) | 16.1 | 5.2 (0 to 39) | 2.9 (0 to 22) | 0.23 (0 to 1.8) |
| Average [†] | 57.8 | 18.6 | 6.7 | 4.0 | 0.31 |
| Min | 44.3 | 15.9 | 5.2 | 2.9 | 0.23 |
| Max | 75.8 | 27.2 | 9.0 | 5.1 | 0.40 |

^a The top value is the tank average, the bottom set of numbers (in parenthesis) is the range

[†] The overall average, min, max calculated from the individual tank averages

ubiquitous in the reduced portions of the LBOS, they are extremely fine grained and comprise an insignificant portion of the metals removed in the system (Thomas and Romanek, 2002).

Sulfate removal and sulfide production. Sulfate removal averaged approximately 320 mg·L⁻¹ in the VFWs or about 20% of the ARD influent sulfate (Table 1). An average effluent sulfide value of 4.8 mg·L⁻¹ (Table 1) was recorded with a seasonal average range of 0.3 to 22 mg·L⁻¹. Effluent sulfide concentrations increased as the amount of sulfate removal increased, suggesting increases in removal were due to sulfate reduction.

Alkalinity generation. The VFWs consistently produced circumneutral (average pH=6.4) water with very little variation and the effluent was always net alkaline (Table 1). In Table 1,

Table 3. Effluent loading rates^a

| | Net Alkalinity Generated $\text{g CaCO}_3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ | Sulfate Reduction $\text{M} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ | Limestone Dissolved $\text{moles} \cdot \text{d}^{-1}$ | Effluent Combined Metals $\text{moles} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ | Combined Metals % removal |
|----------|--|--|--|---|---------------------------------|
| Tank 2A | 76 (2 to 478) | 0.35 (0 to 2.8) | 0.32 (0.01 to 2.1) | 0.01 (0 to 0.1) | 95.2% (88 to 100%) |
| Tank 10A | 78 (0 to 330) | 0.31 (0 to 1.9) | 0.35 (0 to 1.4) | 0.01 (0 to 0.04) | 95.8% (62 to 100%) |
| Tank 13A | 105 (3 to 1244) | 0.25 (0 to 1.6) | 0.60 (0 to 8.0) | 0.04 (0 to 0.6) | 88.4% (73 to 100%) |
| Tank 24A | 95 (0.1 to 427) | 0.33 (0 to 3.2) | 0.52 (0 to 2.7) | 0.02 (0 to 0.4) | 95.2% (73 to 100%) |
| Tank 30A | 84 (0.02 to 322) | 0.29 (0 to 1.8) | 0.46 (0 to 2.0) | 0.01 (0 to 0.1) | 95.2% (77 to 100%) |
| Tank 36A | 89 (0.01 to 988) | 0.27 (0 to 2.5) | 0.38 (0 to 5.6) | 0.02 (0 to 0.3) | 93.2% (84 to 100%) |
| Tank 39A | 100 (0.01 to 696) | 0.32 (0 to 1.5) | 0.51 (0 to 2.8) | 0.002 (0 to 0.02) | 99.3% (96 to 100%) |
| Tank 44A | 75 (3 to 477) | 0.26 (0 to 1.0) | 0.37 (0.01 to 2.7) | 0.01 (0 to 0.1) | 97.6% (85 to 100%) |
| Average | 87.8 | 0.30 | 0.44 | 0.02 | 95.0% |
| Min | 75.0 | 0.25 | 0.32 | 0.00 | 88.4% |
| Max | 105.0 | 0.35 | 0.60 | 0.04 | 99.3% |

^a The top value is the tank average, the bottom set of numbers (in parenthesis) is the range

[†] The overall average, min, max calculated from the individual tank averages

alkalinity is presented as the amount measured in the effluent and as the net amount generated by the VFWs. The alkalinity measured in the effluent averaged $619 \text{ mg} \cdot \text{L}^{-1} \text{ CaCO}_3$ equivalents, while the total alkalinity generated averaged $1832 \text{ mg} \cdot \text{L}^{-1} \text{ CaCO}_3$ equivalents. Net alkalinity generation averaged $88 \text{ g} \cdot \text{d}^{-1} \cdot \text{m}^{-2}$ (Table 3) and is much higher than previously reported values (e.g., Watzlaf et al., 2000). In fact, a maximum net alkalinity generation rate of almost $1250 \text{ g} \cdot \text{d}^{-1} \cdot \text{m}^{-2}$ was recorded for an individual tank (Table 3). This tank also had the highest range of acidity loading (Table 2).

Pore Water

Both swamper and peeper (Figure 1) data show the pH increases sharply above 23 cm. Alkalinity measured from the swamper pore water samples (Figure 1) also increases sharply

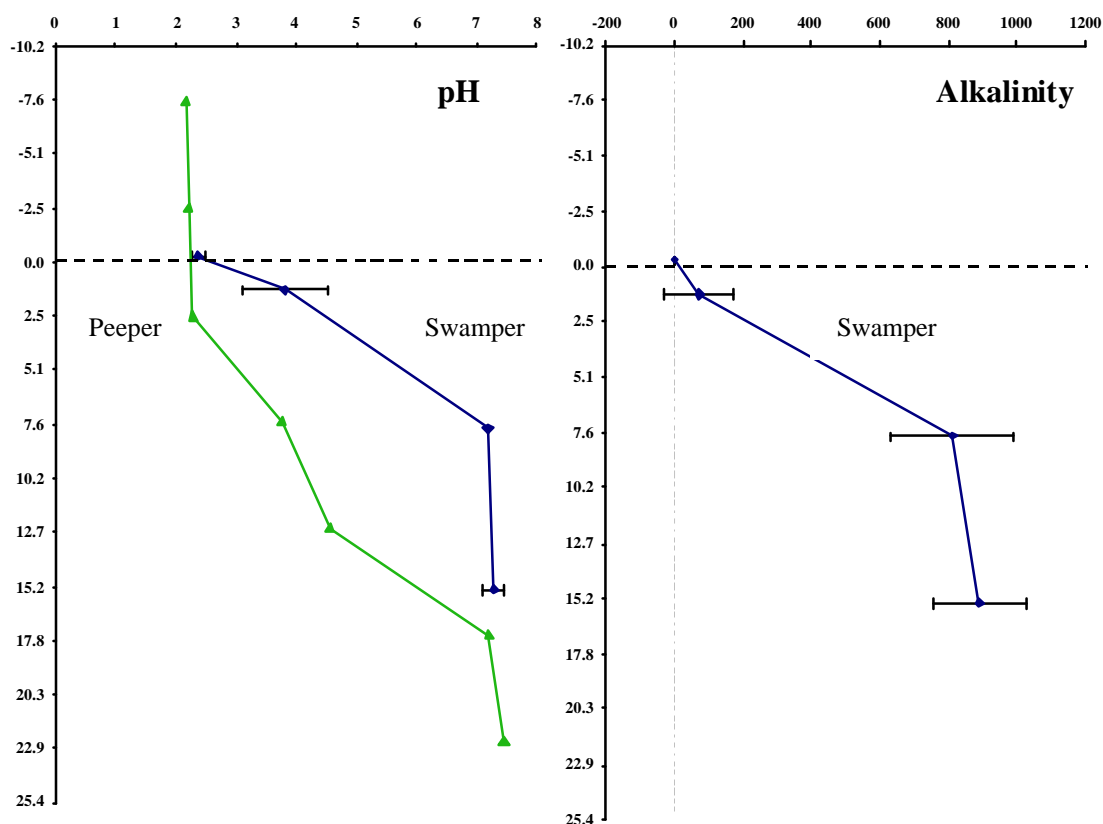


Figure 1. Pore water pH and alkalinity in the upper LBOS sampled with swamper and peepers (negative values represent samples from the ARD water-column overlying the LBOS).

reaching near maximum values by 7.5 cm. Alkalinity was not measured in the peeper samples. Although highly variable at any given depth, in general, the amount of dissolved calcium increases rapidly within the upper 12.5 cm of the LBOS (Figure 2). Calcium measured in the swamper samples just below the substrate-water interface is approximately double the influent concentration. Calcium concentrations nearly double again, approaching effluent values ($\sim 650 \text{ mg}\cdot\text{L}^{-1}$), by 7.5 cm deep (Figure 2). Pore water for calcium analysis was collected with the peepers several months after the swamper samples were collected. Peeper calcium levels show a similar trend of rapid increase. However, peeper calcium values peak 12.5 cm deep in the LBOS at values over $200 \text{ mg}\cdot\text{L}^{-1}$ greater than measured effluent concentrations ($\sim 500 \text{ mg}\cdot\text{L}^{-1}$). The amount of calcium rapidly drops to effluent concentrations over the next 10 cm (Figure 2).

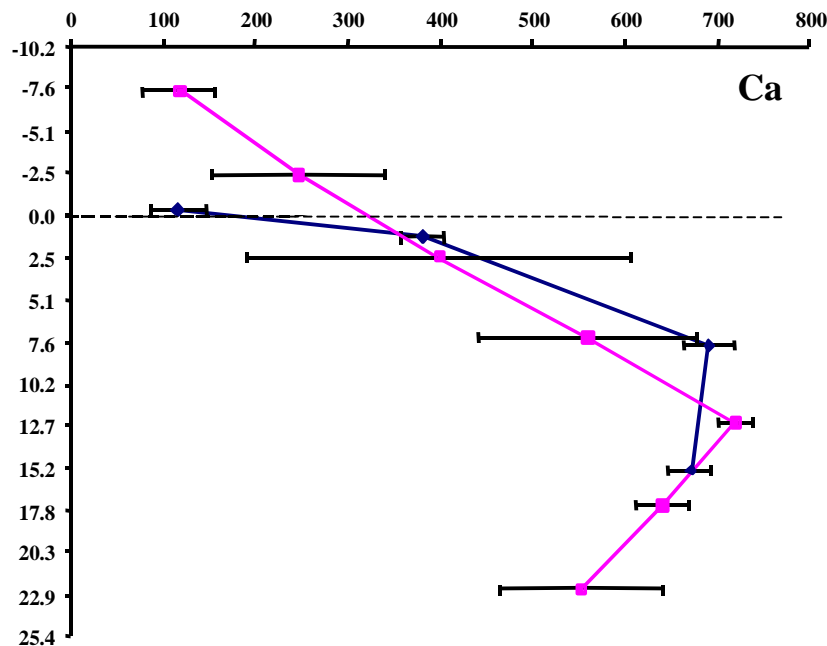


Figure 2. Pore water calcium in the upper LBOS sampled with swampers (pink squares) and peepers (blue diamonds). Negative values represent samples from the ARD water-column overlying the LBOS.

Substrate Analysis

The depletion of dissolved calcium in the pore water of the upper LBOS indicates that the source of calcium has been removed. Assuming that the limestone screenings are the main source of calcium in the LBOS, there are two possible mechanisms for removing the calcium source: dissolution or passivation (armoring) of the limestone. Substrate cores were taken from the top 30 cm of the LBOS in an effort to determine the degree of limestone dissolution.

The 30 cm substrate cores show a distinct color zonation due to mineralogical layering. The top approximately 5 cm of the cores is orange due to the prevalence of iron oxyhydroxides and hydroxysulfates (Thomas and Romanek, 2002). The remaining 25 cm of core material is largely the original brownish color of the substrate, however distinct zones of black iron sulfide are also present (Thomas and Romanek, 2002). The boundary between the oxide and sulfide zones is fairly sharp and demarcated by a thin transitional zone (about 2 – 5 cm) of white calcium and aluminum hydroxysulfate precipitates (Thomas and Romanek, 2002). The sharp increase in pH (Figure 1) occurs over a 5 cm interval coincident with the transitional zone of calcium and aluminum hydroxysulfate precipitates. The substrate cores were subdivided into sections for

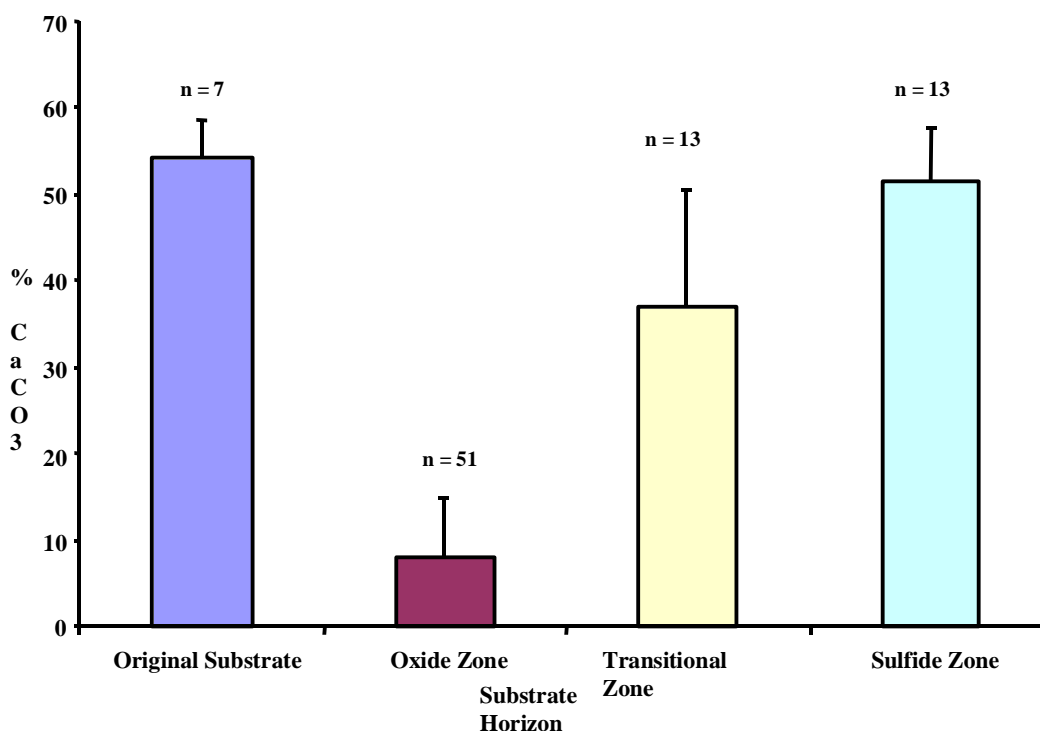


Figure 3. Neutralization potential of the original substrate and the three mineralogical zones identified in the upper LBOS. Values are reported as percent calcium carbonate by weight.

geochemical analyses based on the mineralogical zones: the iron oxide zone, the transitional hydroxysulfate zone, and the sulfide zone (see Thomas and Romanek, 2002 for details).

The initial substrate has an average total calcium concentration of $217 \pm 12 \text{ g} \cdot \text{Kg}^{-1}$ ($529 \text{ g} \cdot \text{Kg}^{-1}$ as CaCO_3). Considering only the five tanks sampled in the fall 2000, the average total calcium concentration in the oxide zone (upper 5 cm) is two orders of magnitude less than the original substrate concentration at approximately $2.0 \text{ g} \cdot \text{Kg}^{-1}$ ($5 \text{ g} \cdot \text{Kg}^{-1}$ as CaCO_3). A little less than half of the original calcium has been removed from the transitional zone ($115 \text{ g} \cdot \text{Kg}^{-1}$ average, $287 \text{ g} \cdot \text{Kg}^{-1}$ as CaCO_3), while the sulfide zone has experienced a slight increase in calcium ($242 \text{ g} \cdot \text{Kg}^{-1}$, $604 \text{ g} \cdot \text{Kg}^{-1}$ as CaCO_3) relative to the original substrate. The removal of calcium from the oxide and transitional zones and the accumulation of calcium in the sulfide zone can be traced using the two tanks sampled in the early summer and again later in the fall of 2000. There is not a significant difference in the average calcium concentration of the oxide layer between the summer and fall samples; both are largely depleted of calcium. However, there is much greater variation in the early summer data. Calcium is removed from the transitional zone between the summer and fall sampling. The summer average ($200 \text{ g} \cdot \text{Kg}^{-1}$) of both tanks is slightly less than

the initial tank concentration, but drops significantly to $148 \text{ g} \cdot \text{Kg}^{-1}$ by the fall. The average total calcium concentration of the sulfide zone remains constant over time and slightly higher than the initial substrate concentration.

The average neutralization potential of the original substrate is $54.3 \pm 4.2 \%$ CaCO_3 (Figure 3). As anticipated, the NP results largely mimic the trends in total calcium (Figure 3). Expecting a wide degree of variation, the oxide zone was the most intensely sampled ($n=51$); it averaged an 85% reduction in CaCO_3 , but with little variation ($8.1 \pm 6.8 \%$ CaCO_3). There is an approximate 30% reduction in the average amount of CaCO_3 in the transitional zone ($37.0 \pm 13.6 \%$ CaCO_3) compared to the original substrate, but with greatly variability than the other zones. Results from the sulfide zone indicate that the substrate is largely unreacted ($51.3 \pm 6.2 \%$ CaCO_3).

Discussion

Designing a VFW system around a limestone-buffered organic substrate (LBOS) allows for the effective treatment of low-pH (<3), ferric iron-dominated ARD with very few limitations. Acid neutralization and alkalinity generation largely occurs within a narrow (2 - 5 cm), dynamic reaction boundary in the upper LBOS. This reaction boundary is a transitional zone of partially reacted limestone (32% reduction in NP) that grades into LBOS material (oxide zone) devoid of limestone (85% reduction in NP), above and LBOS with unreacted limestone (sulfide zone), below. From an alkalinity generation perspective, the oxide zone can be considered spent; there is no alkalinity generating material left and the pH is too low for sufficient biological oxidation of organic matter. In contrast, the unreacted sulfide zone represents the future neutralizing potential of the system. Almost all of the chemical change in the VFW occurs in and immediately adjacent to this transitional zone. Pore water chemistry (Figure 1 – 2) indicates that the pH, alkalinity, and calcium values in the oxide zone above the reaction boundary are similar to the influent ARD, while these parameters immediately below the reaction boundary approach the effluent values.

Thus, the alkalinity generating potential in a 2 – 5 cm thick zone of the LBOS is capable of outperforming typical RAPS-type VFWs at equivocal loading rates. While the average acidity loading rates (Table 2) were within the recommended range for a RAPS-type VFW ($50 \text{ g CaCO}_3 \cdot \text{d}^{-1} \cdot \text{m}^{-2}$; e.g. Watzlaf et al., 2000), loading rates as high as $974 \text{ g CaCO}_3 \cdot \text{d}^{-1} \cdot \text{m}^{-2}$ (Table 2)

were recorded without a significant impact on effluent alkalinity. In fact, effluent alkalinity concentrations less than 300 mg·L⁻¹ CaCO₃ equivalents were rarely ever recorded (Table 1). In addition to the average 619 mg·L⁻¹ CaCO₃ equivalents alkalinity measured in the effluent, all of the influent acidity was neutralized. Hence, the acid neutralizing potential of the LBOS (net alkalinity, Table 1) averaged 1832 mg·L⁻¹ CaCO₃ with values greater than 3,000 mg·L⁻¹ CaCO₃ measured. The maximum acid neutralization potential afforded by a RAPS is less than 450 mg·L⁻¹ CaCO₃ equivalents (Watzlaf et al., 2000); the minimum produced with the LBOS is greater than 1,000 mg·L⁻¹ CaCO₃ (Table 1). Previously reported rates of alkalinity addition from a single RAPS range between 40 to 60 g CaCO₃·d⁻¹·m⁻² (Watzlaf et al., 2000). The overall rate of net alkalinity generation in the LBOS averages 88 g CaCO₃·d⁻¹·m⁻² with individual tank averages over 100 g CaCO₃·d⁻¹·m⁻².

The LBOS-amended VFW is able to outperform a typical RAPS because the influent pH is low (<3), the limestone is very fine-grained, and the ARD is dominated by ferric iron (and aluminum). The low pH of the influent (~2.4) and fine grain-size of the limestone (~1.2 mm) increases the limestone dissolution rate by lowering the solubility and increasing the reactive surface area, respectively. More importantly, however, pore water data (Thomas and Romanek, 2002) indicate that dissolved iron and aluminum are removed concomitant with the rapid change in pH and sharp increase in alkalinity due to limestone dissolution at the reaction boundary. Details of the actual mechanisms of metal removal in the upper LBOS are presented elsewhere (Thomas and Romanek, 2002), but can be summarized in relation to acid neutralization as follows. The influent ARD reacts with limestone at the reaction boundary raising the pH > 6. This causes a sharp decrease in the solubility of ferric iron and aluminum solids. The precipitation of ferric iron oxyhydroxides and aluminum hydroxysulfates both generate three moles of acidity for every mole of metal precipitated, e.g.



The acidity is generated within close proximity to limestone, thus facilitating rapid neutralization. The ferric iron – aluminum hydrolysis and precipitation process is one of the key mechanisms of acid neutralization in the upper LBOS, because it essentially converts all of the mineral acidity to proton acidity (e.g., reaction 1) above the reaction boundary.

Armoring and Plugging Concerns

The trade-off in having the entire complement of mineral acidity neutralized at the reaction boundary is that the precipitates raise concerns for the long-term effectiveness of the LBOS. Two of the biggest concerns being armoring and subsequent passivation of limestone and reduced permeability due to plugging. Ferric iron and aluminum are traditionally the main limitation to using limestone for passive ARD treatment. Armoring by ferric iron rapidly passivates the limestone surface, rendering it ineffective. Limestone ghosts (i.e., the visible outline of a former crystal shape) outlined by ferric oxyhydroxide are ubiquitous in the oxide zone (Thomas and Romanek, 2002), indicating that armoring by ferric iron does occur, but the lack of any remnant limestone in the oxide zone suggests armoring does not result in passivation. This is likely due to the fine-grained size (1.2 mm) of the limestone screenings. Over the two years of the study, the LBOS did not show any signs of overall plugging or decrease in hydraulic connectivity, such as ponding of ARD over the LBOS. However, pulses in measured flow rate may be attributed to subtle short-term changes in the permeability of the substrate caused by dissolution and precipitation reactions that occur in the LBOS. One advantage to having fine-grained limestone evenly distributed throughout the LBOS is that, while primary porosity may be occluded with precipitates, secondary porosity is created as the limestone is dissolved. Furthermore, Demchak et al., (2001) noted that wood chips might decrease compaction by encouraging particle separation.

Limitations and Longevity

At the loading rates employed in this study, the LBOS is not limited, but enhanced (e.g., net alkalinity generation increases), by increased acidity loading (see Thomas, 2002 for details). This is due to the fact that, at low pH, the rate of limestone dissolution is controlled by the transport of protons to the limestone surface (e.g., Plummer et al., 1979). Thus, increasing acidity load increases the rate of limestone dissolution. More importantly, because the LBOS is not dependent on microbial processes, low pH is not prohibitive to alkalinity generation. Due to the fine-grained nature of the LBOS, design limitations will likely result from hydraulic conductivity of the substrate and not the rate of limestone dissolution.

Plugging concerns notwithstanding, the longevity of the LBOS is solely a function of the amount of limestone (i.e., NP) in the original substrate and the predicted cumulative acidity load over the expected life of the system. The reaction boundary can be considered a diffuse, two-dimensional plane of minor thickness that progressively migrates through the LBOS as the limestone (NP) in the transitional zone is depleted. The rate of migration will depend on the rate of limestone dissolution, which is, in turn, dependent on the acidity loading rate. Comparing the total calcium concentrations from soil digests conducted on replicate cores taken five months apart, shows that total calcium levels are depleted in the transitional zone over time, while the calcium concentrations above and below remain unchanged.

As with the ALD approach, sizing of the LBOS depends on the length of time treatment is required, the cumulative acidity load over that time, and the NP of the organic substrate. For example, given the density ($0.741 \text{ g}\cdot\text{cm}^{-3}$) and the NP (54.3% CaCO_3 by weight) of the LBOS, there was approximately 13.2 Kg of limestone in the upper 5 cm oxide zone and a combined 26.4 Kg down through the transitional zone. The acidity load averaged 18.6 Kg CaCO_3 equivalents for all eight tanks with a range of 15.9 to 27.2 Kg CaCO_3 equivalents (Table 2). Thus, given the partial dissolution of limestone in the transitional zone and near complete dissolution in the oxide zone, the acidity load is roughly equal to the amount of limestone dissolved in any given tank. It is noteworthy that tank 13A, which received the highest acidity load (27.2 Kg CaCO_3 equivalents load), had a noticeably thicker oxide zone than other tanks (Thomas, 2002).

Although this sizing approach does not account for the production of biogenic alkalinity, it does give a minimum estimate of the life expectancy for anaerobic CTWs. Based on the total volume, density, and NP of the LBOS, each VFW has approximately 95 Kg of CaCO_3 (not including the limestone drain) and can treat an equivalent amount of acidity. Over the two years of this study, an average 18.6 Kg of acidity was neutralized in the LBOS (Table 2), suggesting that the LBOS would last over 10 years assuming the current acidity loading rate. Higher loading rates would merely shorten the system longevity. In systems where the acidity loading rate fluctuates widely, changes over time, or is generally not well constrained, the health of the LBOS may be evaluated at any given time by testing the NP of the LBOS at different depth intervals.

Conclusions and Recommendations

The LBOS-amended VFW is able to outperform the traditional RAPS design for two main reasons: the influent was low-pH (<3), ferric iron-dominated ($\text{Fe}^{+3} \gg \text{Fe}^{+2}$) ARD and the substrate was 54% by weight fine-grained (1.2 mm) limestone in an coarse-textured organic matrix made mostly of aged wood shavings. At very low pH (2-3), limestone dissolution is controlled by hydrogen ion activity and is limited by diffusion of protons to the limestone surface (e.g. Chou et al., 1989). Therefore, increasing the acidity loading rate results in an increase in net alkalinity generation. Due to the fine-grained nature of the LBOS, design limitations will likely result from hydraulic conductivity of the substrate and not the rate of limestone dissolution. Varying the organic matrix supporting the limestone may enhance hydraulic conductivity or replacing the organic material with very coarse sand or fine gravel may be an option, but has not been tested.

Low pH is not the only attribute of the influent ARD responsible for the LBOS success; ferric iron and aluminum hydrolysis and precipitation reactions are also crucial. Typical RAPS units are designed so that any ferric iron entering the organic substrate is converted to ferrous iron before entering the limestone drain (e.g. Kepler and McCleary, 1994); all of the iron is supposed to pass through the RAPS. This approach limits the alkalinity generating capacity of the system by prohibiting the conversion of mineral acidity to proton acidity. In the LBOS, the rapid abiotic precipitation of ferric oxyhydroxides is faster than the biological reduction of ferric iron, thus all of the mineral acidity is treated. If the ferrous component of the ARD had been larger, then the level of alkalinity attained could not have been realized.

The only major limitation is that a calcium sulfate and aluminum hydroxysulfate hardpan develops at the transitional zone (Thomas and Romanek, 2002). In the two years of this study the hardpan did not seem to occlude porosity enough to make a significant impact on the VFW hydrology. However, if a VFW system is designed to last 20 years, as is the rule of thumb for ALD sizing, then plugging and hydrologic short-circuiting constitute a major concern and warrant further investigation. If the hardpan presents a long-term plugging problem, periodic maintenance will be required to disrupt the layer. Flushing has been suggested for removal of iron and aluminum oxyhydroxide floc (e.g., Zipper and Jage, 2001) however, in the LBOS, the aluminum forms hydroxysulfates that are attached to surfaces and, thus, not amenable to flushing. The iron oxyhydroxides are also not likely to flush because they form above the

transitional zone. Small garden tillers have been used to mix fresh organic material into the upper portion of bioreactors (Gusek, pers. comm., 1998) and may be used in conjunction with flushing to help maintain hydraulic conductivity within the upper portion of LBOS. In less remote areas, it is recommended that the design employ a shallow LBOS layer with a thin limestone drain and a shorter life expectancy; periodic maintenance would involve replacing the LBOS layer when it is completely spent.

Current sizing recommendations for VFW systems are empirically based on the performance of existing VFW units. Since the focal mechanism for remediation in VFW systems has either been limestone dissolution (RAPS) or sulfate reduction (anaerobic bioreactor), life expectancies have been calculated based on the amount of limestone in the drain or the microbial sulfate reduction potential of the substrate. The neutralization potential and, until recently (e.g. Demchak et al., 2001), long-term reductive capacity (ability to maintain anoxia) of the organic layer in RAPS has been ignored in estimating the predicted life of the system. Likewise, where the volumetric approach of $0.3 \text{ moles metal} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$ sulfate reduction potential is beneficial in considering the microbial contribution to the wetland (Wildeman et al., 1993), it fails to consider abiotic reactions, which may compromise the substrate (e.g., consumption of the substrate's buffering capacity). The advantage of treating low-pH, ferric iron-dominated ARD with the LBOS is that treatment is, in general, independent of contaminant concentration in the influent ARD; sizing is based on the total capacity (total NP) of the LBOS. Higher contaminant loads result in faster consumption of the NP and, hence, shorter life of the system, but do not significantly affect the acid neutralizing capacity of the LBOS. The biological component of the LBOS, while beneficial, is not required for acidity neutralization; all of the alkalinity generated from the biological oxidation of organic matter comes after the influent acidity has been completely neutralized.

The reaction boundary can be considered a diffuse, two-dimensional plane of minor thickness that progressively migrates through the LBOS as the limestone (NP) in the transitional zone is depleted. The nature of acidity removal permits an evaluation of the remaining neutralization potential and the efficiency of acid consumption at any given time. Hence, the health of the LBOS may be evaluated and the longevity predicted by testing the NP of the LBOS at different depth intervals.

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