TREATMENT OF ACID ROCK DRAINAGE (ARD) WITH A LIMESTONE BUFFERED ORGANIC SUBSTRATE (LBOS) IN A VERTICAL FLOW CONSTRUCTED TREATMENT WETLAND[1]

by

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Abstract. A limestone buffered organic substrate (LBOS) is added as a component to a typical vertical flow constructed treatment wetland, thereby raising the neutralization potential (NP) of the organic substrate. Acid neutralization and metal removal both occur in the upper few centimeters of the substrate, resulting in the development of a migrating pH boundary. As the buffering capacity in the upper portion of the LBOS is spent, the pH boundary migrates downward and neutralization occurs at a deeper substrate depth.

Additional Key Words: passive alkalinity generation, metal removal processes.

Introduction

The treatment of acid rock drainage (ARD) is accomplished through chemical and biological processes that decrease metal concentrations and acidity. Although metal solubility is pH- and/or redox (Eh)-controlled, depending on the metal, treatment is commonly achieved through alkalinity addition to neutralize acidity and raise pH. Alkalinity addition has traditionally been accomplished through the "active" addition of alkaline reagents (e.g., sodium hydroxide), which may then be mechanically mixed and aerated. Although these active treatment systems can be expensive to maintain and operate, they are generally highly effective.

Due to the high cost of implementing active treatment, researchers over the past two decades have focused on "passive" technologies for alkalinity addition and metal precipitation. Passive alkalinity addition is accomplished by reaction of ARD with an alkalinity-generating material (e.g., limestone) and through the biological oxidation of organic matter. For successful remediation of most ARD chemistries, the redox-state of the ARD must be reduced during contact with the alkalinity generating material. Passive systems generally rely on microorganisms within an organic layer (e.g., mushroom compost) to reduce the ARD through the oxidation of the organic matter.

The vertical flow constructed treatment wetland is a common design that employs an organic layer overlying a limestone drain. ARD passes vertically through the organic layer and is reduced, then passes through the limestone drain and is neutralized. The reduced, neutralized ARD continues to an oxidation pond where metals precipitate as the water is oxygenated. These systems are reported to generate up to 300 mg/L of alkalinity with a minimum of 12 hours of retention time, limiting them to the concentration and volume of acidity that can be effectively treated.

In this paper, we present a modification to the classic vertical-flow treatment-wetland system that increases the passive generation of alkalinity by an order of magnitude thus facilitating efficient metal removal. By adding a limestone-buffered organic substrate (LBOS) in place of the typical organic substrate, alkalinity is generated in the entire volume of substrate rather than in the restricted volume of a limestone drain. Metal removal occurs in a thin zone of the LBOS. This zone migrates down through the LBOS as the neutralizing capacity is consumed creating a pH migration front.

Materials and Methods

Eight plastic tanks (92 cm diameter by 122 cm tall) were used to simulate vertical flow wetland cells. The tanks were filled with a 92 cm of LBOS overlying a 15 cm coarse limestone drain. ARD was collected as runoff from a coal storage facility on the Savannah River Site, Aiken, S.C. and delivered continuously to the top of the tanks from December 1998 to December 2000. The effluent drained from the bottom of the tanks through standpipes such that a 15 cm column of

[1] Paper presented at the 2001 National Meeting of the American Society of Surface Mining and Reclamation, Albuquerque, New Mexico, June 3-7, 2001. Pub. by ASSMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2001 pp 326-327
DOI: 10.21000/JASMR01010326

https://doi.org/10.21000/JASMR01010326

ARD was maintained over the LBOS and flow through the system was driven by gravity. The eight tanks were treated as replicates receiving the same ARD at approximately the same flow rate (20 mL/min. average).

The LBOS was made by volumetrically mixing 25% limestone screenings (sand size) with 75% organic material (mostly composted stable waste). The LBOS has a paste pH of 7.6, an average neutralization potential (NP) of 52.9% $CaCO_3$ equivalents, and a cation exchange capacity of 83.3 meq/100 gram.

Influent/effluent water samples were collected weekly between April 1999 and December 2000 and monitored for pH, temperature, acidity, alkalinity, metals, sulfate, and sulfide. Pore water was sampled weekly between April 2000 and October 2000 from ports installed at 23, 46, 69, and 92 centimeters deep in the LBOS. Sediment cores were taken in June and November 2000 for mineralogical investigations.

Results

The eight tank replicates exhibited similar behavior and response to changing influent chemistry and environmental conditions (e.g., temperature) and therefore tank effluent data are given as an average of all eight tanks (table 1). On average the tanks exhibited an 88% reduction of iron and a greater than 99% reduction of aluminum in the effluent relative to the influent ARD. Furthermore, pore water data indicate that the majority of this removal occurs in the upper 23 cm of the LBOS.

Table 1. Average influent/effluent chemistry with total concentration range given in parentheses. All concentrations are given in mg/L. Acidity and alkalinity are given as mg/L $CaCO_3$ equivalents.

	Influent (ARD)	Tank Effluent
pH	2.47 (1.79 – 3.18)	6.43 (5.94 – 6.78)
Fe	122 (20 – 237)	15 (0.5 – 54)
Al	69 (8.5 – 274)	0.05 (0 – 1.18)
Mn	3.6 (1.0 – 8.4)	4.6 (0 – 8.8)
Acidity	1024 (364 – 2149)	0
Alkalinity	0	628 (438 – 1449)
Sulfate	1530 (926 – 3385)	1152 (20 – 2732)
Sulfide	0	17 (0 – 300)

The influent acidity is likewise neutralized within the upper 23 cm of the LBOS. Alkalinity increases sharply in the upper 23 cm of substrate and increases only slightly in the remaining 69 cm of LBOS and 15 cm of limestone drain. Therefore approximately 1500 mg/L of alkalinity is generated in the upper 23 cm of the LBOS (neutralization of 1000 mg/L $CaCO_3$ equivalents acidity plus the generation of additional 500 mg/L $CaCO_3$ alkalinity). The pH is generally less than 4.5 in the upper 23 cm and near the effluent pH of 6.5 immediately below.

Petrographic analyses (e.g., electron microprobe, x-ray diffraction) of the sediment cores show that a mineralogical layering occurs in the LBOS. The upper portion (10 cm) of the substrate is dominated by iron oxyhrydroxides, depleted of limestone screenings and the NP averages 6.3% $CaCO_3$ equivalents. Below approximately 10 cm, the substrate is black with fine-grained acid-volatile sulfides and framboidal pyrite. Fine pristine limestone grains are abundant and the NP is the same as the initial substrate (53% $CaCO_3$ equivalents). The boundary between these two zones is dominated by aluminum precipitates (oxyhydroxides and sulfates) and ragged limestone grains exhibiting progressive replacement by $CaSO_4$. Framboidal pyrite, as well as minor iron oxyhydroxide, is also present.

Discussion

Previous studies have shown that a migrating pH boundary develops in vertical flow treatment wetlands as the NP of the organic substrate is consumed. Based on mineralogy, we explain the development of this pH boundary as follows. As the acidic (low pH), metal-rich ARD comes in contact with the LBOS, the acidity is neutralized through reaction with the limestone screenings (ragged and replaced limestone grains found at boundary). This causes an increase in pH and a subsequent precipitation of iron and aluminum as oxyhydroxides. Eventually the limestone in this upper portion of the LBOS is consumed, allowing the ARD to penetrate deeper into the substrate. Aluminum compounds are dissolved from the upper portion of the substrate as the pH drops and re-precipitated at the boundary as the pH rises again. Reducing conditions develop in the LBOS as the migration boundary moves below the sediment-water interface, allowing for bacterial sulfate-reduction. Ferric iron from the ARD reacts with biogenic sulfide to produce the abundant pyrite framboids found concentrated just below the migration boundary. The high alkalinity levels are the result of fine-grained, widely dispersed limestone screenings equilibrating with the ARD and from the biological oxidation of organic matter. Because neutralization occurs in progressive layers within the substrate over time, we propose that sizing and longevity of the LBOS is a function of the LBOS volume, the LBOS NP, and the acid loading rate.