CHEMICAL ANALYSIS OF CORES OBTAINED FROM A VERTICAL FLOW POND[1]

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Abstract: The vertical flow pond at Jennings Environmental Education Center, Butler County, PA, was constructed in 1997. After five years of operation, the system continued to produce alkalinity and remove iron and aluminum, but the flow rate through the system has continuous declined. To determine the type and pattern of chemical distribution throughout the system, 9 cores were obtained and analyzed for iron, manganese, aluminum, silica, sulfate, calcium and trace metal concentrations. Iron precipitates accumulated in the upper 7-10 cm of the spent mushroom compost and limestone mixture with the majority of aluminum precipitate accumulation occurring between 10 and 20 cm below the surface of the media. Although there was sufficient $CaCO_3$ in the substrate to continue to provide alkaline addition, the accumulation of metals in the upper 10 cm of the substrate has reduced the permeability of the substrate.

Additional Key Words: iron, aluminum, silica, spent mushroom compost, limestone, permeability

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Introduction

During the last decade, vertical flow ponds (VFPs), a.k.a. vertical flow wetlands (VFWs), and sequential alkalinity producing systems (SAPS) have been used to treat acid mine drainage (AMD), but the mechanisms operating within these systems are not completely understood. Based on the initial design of these systems proposed by Kepler and McCleary (1994), VFPs provide alkaline addition through limestone dissolution and sulfate reduction, resulting in the precipitation of iron and aluminum in the substrate. Brenner (2001a,b) reported that VFPs are effective in removing over 90% of the iron and aluminum, but they are not effective in manganese removal. Demchak (1998) indicated that the efficiency of some of these systems is seasonal, especially as the systems aged. Iron removal began to decline after 18-24 months due to a reduced limestone availability and metal accumulation in the substrate and similar results were reported for scale model systems (Brenner 2001a,b; Brenner et al. 2002). When these scale models were dissected, iron precipitates had accumulated in the upper third of the substrate and in the second year of operation, there was a decline in both the amount of alkaline addition and metal removal to a reduced limestone availability and metal accumulation in the substrate and similar results were reported for scale model systems (Brenner 2001a,b; Brenner et al. 2002). When these scale models were dissected, iron precipitates had accumulated in the upper third of the substrate and in the second year of operation, there was a decline in both the amount of alkaline addition and metal removal.

In the summer of 1997, a vertical flow pond was constructed to treat an acid mine discharge at the Jennings Environmental Education Center, Butler County, Pennsylvania. The system consisted of a 30 cm layer of river gravel, overlain by 75 cm of spent mushroom compost (300 tons) amended with 380 tons of AASHTO #9 (1.68 x 16 mesh) limestone aggregate. The pond was designed to maintain a maximum of 80 cm of water over the substrate, but in order to adjust the water level in the pond; an adjustable discharge pipe was installed that was based on the elevation of the emergency spillway. During the first two years of operation (1997-1999), the vertical flow pond was effective, adding alkalinity (196 mg/L) and removing iron (56 to 8 mg/l) and aluminum (19 to <1 mg/L). The system was only effective in removing manganese during the first five months of operation. Overall the system only removed 1 mg of manganese and in at least two samples, manganese was actually released from the system (which may be related to changes in pH, redox conditions or adsorption/desorption operating within the system). Within two years following construction, the system appeared to exhibit variations in discharges, suggestive of plugging or that short circulating was occurring within the vertical flow pond. In June, 2000, a series of dye tests completed on the Jenning's VFP along with two VFPs at other sites confirmed that there was a reduction in permeability most likely due to the accumulation of iron and aluminum precipitates in all three systems. As a result of these studies, it was decided to core the Jennings VFP to determine the pattern of metal accumulation throughout the system.

Methods

In August 2002, nine evenly spaced cores were removed from the VFP at the Jennings Environmental Education center using 2.5 cm PVC pipes. The exact location of each core was surveyed and mapped as to its location in the VFP. Once a core was removed, it was logged into three distinct zones (A, B, C) based on its visual appearance, and photographed (Figure 1). A sample was removed from each zone (total of 27 samples) and transported to an analytical chemistry laboratory for analysis. The samples were dried and passed through a series of sieves to separate limestone and substrate fragments from the metal precipitates. The final pan samples were analyzed for iron, manganese, aluminum, silica, calcium and trace metal concentrations using x-ray fluorescence. The concentration of each chemical compound was expressed as g/100g. Once these analyses were completed, chemical speciation was determined for a representative core by x-ray diffraction. To determine the loss on ignition (L.O.I.) as representative of the volatile organics in each zone, a known weight of sample was place in a Muffle furnace at 950 C for 2hrs and expressed as a percent of sample weight. Sulfate concentrations were analyzed using the Gravimetric methodology with the ignition of the residue (Standard Methods 4500 SO_4 C). The remainder of the core was sealed and frozen for additional analyses at a later date.

Figure 1: Photograph of sample cores after removal from the vertical flow pond.

Results and Discussion

The upper A zone was red-brown and varied in depth from 4.5 to 10.5 cm (mean 7.9 ± 0.58 cm) while the middle B was light gray with depths varying from 4.2 cm to 50.7 cm (mean 24.6 ± 4.75 cm. The lower C zone was dark gray to black with a distinct sulfide odor and varied in depth from 2.8 to 57.6 cm (mean 22.7 ± 6.97 cm). These variations in depth of three zones were probably a result of the mushroom and limestone not being thoroughly mixed and/or the uneven settling of the material over time. Although the volatile organics varied from 59.14% to 71.53% (Ave. 65.01 ± 2.91%), there was not a significant difference ($P > 0.20$) in the organic content among the different cores (Table 1), but the mean volatile organics was significantly higher in the A zone (70.63 ± 6.95%) than it was in either the B (62.81 ± 5.63%) ($P<0.05$) or the C zone (61.59 ± 9.02%), but there was not a significant different in the volatile organics between the B and C zones.

Table 1 Comparison of the percent volatile organics (L.O. I.) among the different cores or among the different zones in cores from a vertical flow pond in Butler County, Pennsylvania.

			Zones		
Core	A	B	C	Mean	SE
1	76.17	67.35	55.46	66.83	4.25
2	67.50	58.82	58.75	61.69	1.18
3	70.23	58.68	59.45	62.79	3.73
4	72.59	62.37	67.28	67.41	2.96
5	70.31	66.30	66.86	67.82	1.80
6	5.21	69.25	70.13	71.53	1.34
7	69.53	61.29	61.31	64.04	2.24
8	60.96	58.90	57.55	59.14	1.00
9	73.18	62.32	57.49	64.33	4.65
Mean	70.63	62.32	61.59	65.01	2.91
SE	6.95	5.63	9.02		

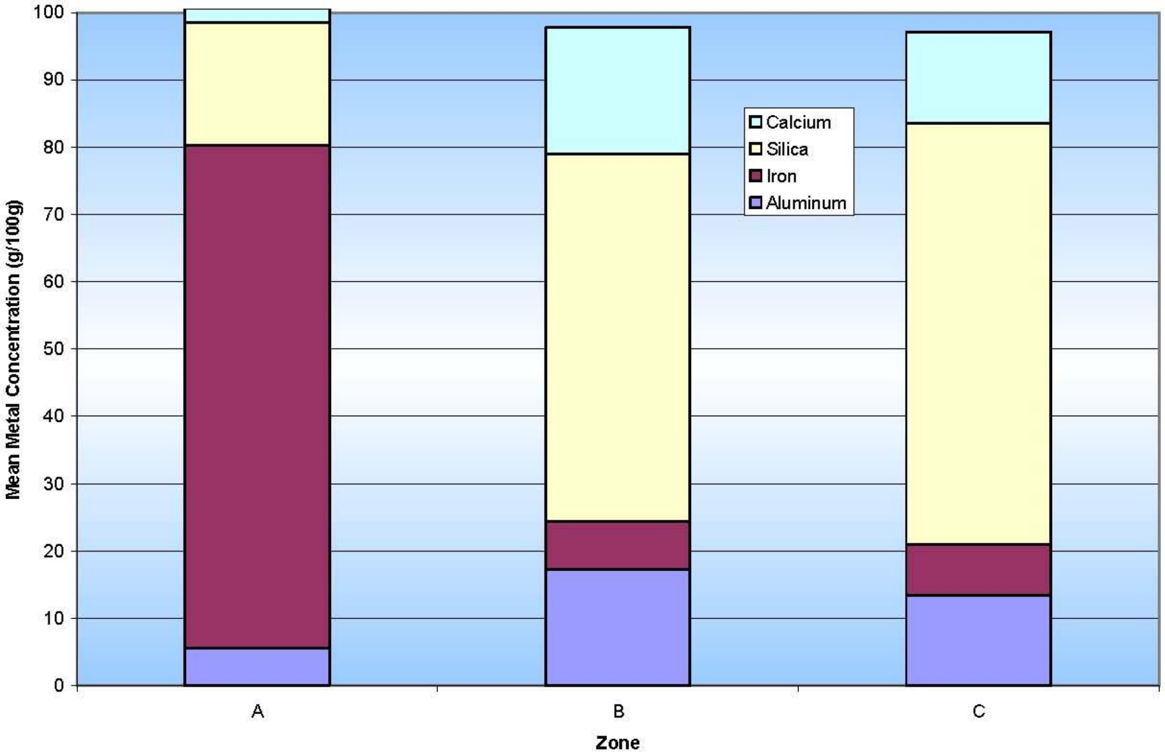

Figure 2: Mean concentrations of the four major chemical fractions within the three zones of the cores.

Iron precipitates were concentrated in the A zone of the cores with a mean concentration of 74.64 ± 3.74 g/100 g, which differed significantly from the mean of 7.03 ± 1.09 gm/100 gm and 7.51 ± 0.48 g/100 g in the B and C zones of the cores, respectively ($P < 0.001$) (Figure 2). Based X-ray diffraction, a portion of the iron precipitate was iron oxide (Fe_2O_3), but an iron hydroxide $(FeOH)_3$ fraction may also be present in an amorphous state that cannot be detected by X-ray diffraction. The existence of Fe_2O_3 precipitate in the substrate corresponds with the results reported by Wieder and Lang (1986) that 93% of accumulation in AMD treatment wetlands was in oxidized forms. The mean aluminum concentrations were higher in the B zone (17.31 ± 2.06 g/100 g) and C (13.39 ± 1.43 g/100 g) zones than it was the A (5.64±0.98 g/ 100 g) ($P < 0.001$), but there was not a significant difference in aluminum concentrations between the B and C zones. These aluminum precipitates are most likely aluminum hydroxides ($Al(OH)_3$) that occur in an amorphous state and their chemical composition could not be determined by X-ray diffraction. Silica oxide (SiO_2) concentrations increased significantly throughout the cores from a mean of 18.23 ± 2.03 g/100 g in the A zone to a mean of 54.68 ± 4.01 g/100 g and 62.66 ± 1.69 g/100 g, in the B and C zones, respectively (P <0.001). However, there was a significant correlation between aluminum and silica concentrations at all three levels of the cores (Figure 3). The aluminum-silica ratio was similar in the A (1:3.23) and B (1:3.16) zones, but it increased to 1:4.70 in the C zone. These results suggest that both aluminum and silica migrated through the substrate concentrating in the lower levels of the VFP, but silica appeared to migrate more rapidly in the lower levels of the substrate. Manganese concentrations did not vary significantly among the three zones (P > 0.10) and was a minor component in all three zones varying from a mean of 0.012 ± 0.003 g/ 100 g in the A zone to means of 0.153 ± 0.0509 g/100 g and 0.300 ± 0.10 g/100 g in the B and C zones, respectively. Other chemical compounds present the core samples occurred in concentrations less than 3 g/100 g per sample included chromium (Cr_2O_3), phosphorus (P_2O_5), thallium (TiO) and nickel (NiO) and the combined total of all these compounds was 9.04 g/100 g in zone A and 23.98 g/100 g and 29.86 g /100 g in zones B and C, respectively. The increase in these compounds in zone B and C was primarily due to an increase in P_2O_5 (∑12.98 g/ 100 g in B and ∑19.34 g/100 g in C) and TiO (∑10.96 in B and ∑10.96 g/100 g in C) concentrations, but in all three zones Cr_2O_3 and NiO comprised less than 2% of these four compounds.

The original concept of VFPs was that the organic compost would provide a carbon source for bacterial sulfate reduction. In theory, the reduction of sulfates to sulfides results in the formation of iron precipitates as either FeS or FeS_2 and elemental sulfur along with neutralizing mineral acidity and generating bicarbonate alkalinity. Duplicate Samples obtained from this VFP from 1997-1999 and analyzed by two different laboratories produced varying results. The results reported by the Pennsylvania Department of Environmental Protection (PA DEP) indicated that sulfate concentrations in effluent increased by an average of 113 mg/L, whereas the U.S. Department of Energy Laboratory (DOE) laboratory reported an average sulfate reduction of 35 mg/L over the same three-year period (Jennings Water Quality Improvement Coalition, 1999). In the current study, sulfate concentrations did not vary significantly (P > 0.10) among the three zones (A-4.85 ± 0.98, B-2.45 ± 0.48, C-2.98 ± 0.68) and sulfides were not detected in any of the cores suggesting that little if any sulfate reduction was occurring within the VFP. The sulfide odor detected in zone C when the cores were removed was most likely a result of anaerobic decomposition of the organic substrate in zone C and not sulfate reduction.

Calcium carbonate ($CaCO_3$) (as determined by X-ray diffraction) concentrations were significantly less in the A zone (2.18 ± 0.85 g/100 g) than in either the B (18.73 ± 2.86 g/100 g) or C (13.53 ± 1.30) zones ($P < 0.001$), but there was not a significant difference in $CaCO_3$ concentrations between the B and C zones ($P > 0.10$) (Figure 1). The loss of $CaCO_3$ in the A zone may have been a result of dissolution and/or settling of the limestone over the life of the system. Based on the amount of $CaCO_3$ in the B and C zones, there appears to be sufficient acidic buffering capacity remaining in the system.

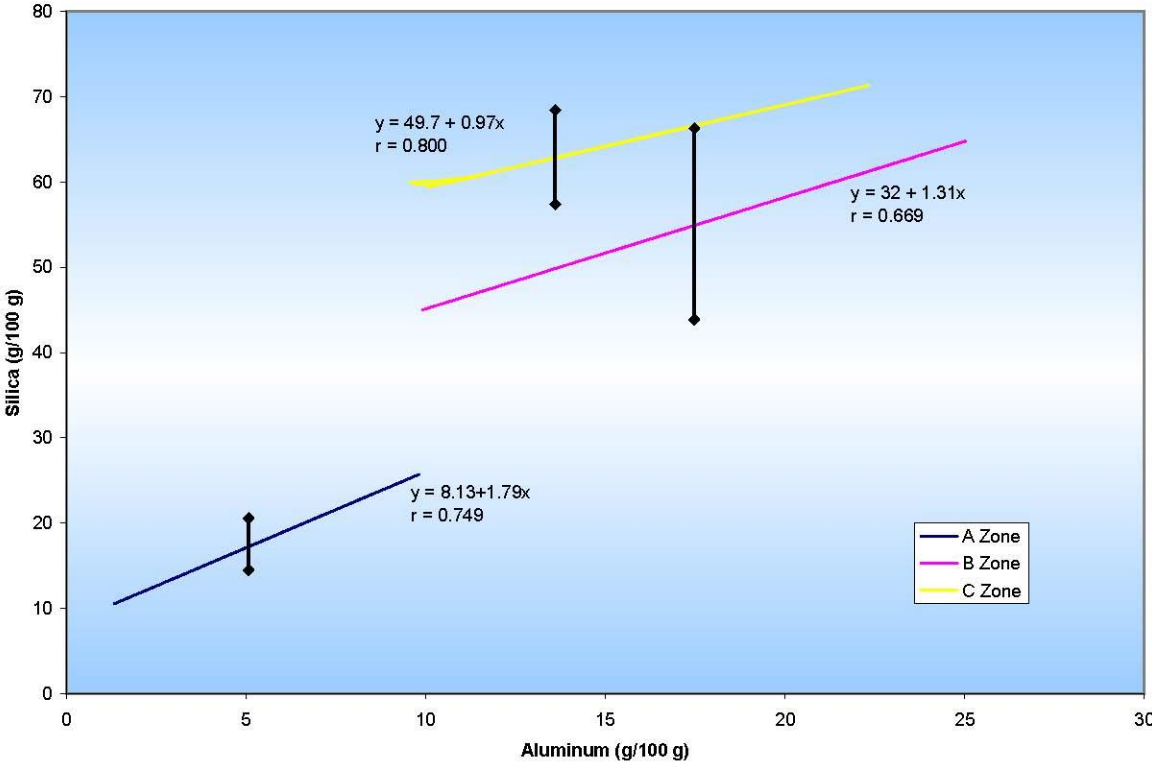

Figure 3: Least-square regression analysis indicating the correlation between aluminum and silica concentrations. The vertical lines represent the 95% conference intervals of the regression line.

Conclusions and Recommendations

Although the complete chemical analyses of the cores have not been completed, the results indicate that there was substantial amount of iron, aluminum, and silica accumulation in the VFP and that the accumulation of iron precipitates in the upper 7-10 cm (A zone) may reduce substrate permeability thereby reducing the efficiency of the system. By draining the VFP and mixing or removing the upper 7-10 cm of substrate the permeability of the system may be increased but this is most likely a temporary solution. Routine maintenance of the water distribution and discharge pipes may also extend the life of the system. Several VFPs of different designs are currently be evaluated to determine if there is a permanent solution to the plugging problems currently occurring in many VFPs. The correlation between aluminum and silica throughout the substrate suggests that these elements are derived from a common source, most likely the clays associated with the coal seams. Sulfate concentrations did not vary significantly among the different cores and in conjunction with the inconclusive sulfate analyses of the effluent obtained from different laboratories suggest that little if any sulfate reduction occurs in this VFP. It appears that the majority, if not all, acidity neutralization is a result of limestone dissolution and not sulfate reduction. The decline in $CaCO_3$ in the A zone may be a result of either the dissolution of limestone or settling over the life of the system, but based on the assumption that a substantial portion of the $CaCO_3$ represents limestone, there appears to be sufficient acid buffering capacity remaining in the system.

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