PASSIVE TREATMENT OF ACID MINE DRAINAGE IN DOWN-FLOW LIMESTONE SYSTEMS[1]

by

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Abstract. Passive down-flow systems, consisting of compost and/or limestone layers, may be well suited for treatment of acidic mine drainage containing ferric iron and/or aluminum. Two columns were constructed and operated in the laboratory. The first column simulated a downward, vertical-flow anaerobic wetland, also referred to as successive alkalinity-producing systems (SAPS), and has received mine drainage for 97 weeks. The 0.16-m diameter column was vertically oriented and (from bottom to top) consisted of a 0.30-m thick layer of limestone, a 0.76-m thick layer of spent mushroom compost, and 0.91 m of free standing water. Water flowed vertically downward through the system. A second column, filled with only limestone, received water from the same source as the first column. This limestone column contained a 1.06-m thick layer of limestone and 0.91 m of free standing water and has received water for 55 weeks. Actual acid mine drainage (pH = 3.1, acidity = 200 mg/L (as $CaCO_3$), SO_4^{2-} = 600 mg/L, Total Fe = 10 mg/L, Mn = 14 mg/L, and Al = 18 mg/L) was collected every two weeks from a nearby abandoned deep mine and applied to these columns at a rate of 3.8 mL/min. For the compost/limestone column, effluent pH remained above 6.2 (6.2-7.9); however, pH at a depth of 0.38 m in the compost (halfway) dropped to < 4 after 28 weeks (net acidic). At the bottom of the compost, pH remained > 4.5 for all 97 weeks. Alkalinity was generated by a combination of limestone dissolution and sulfate reduction. Over the 97 week period, the column generated an average of 330 mg/L of alkalinity, mostly due to limestone dissolution. Bacterial sulfate reduction displayed an ever decreasing trend, initially accounting for more than 200 mg/L of alkalinity and after 40 weeks only accounting for about 50 mg/L. The column has removed virtually all of the iron and aluminum. Manganese was initially removed, then released (adsorption/desorption). For the limestone column, pH of the effluent remained about 7.0 throughout the 55 weeks of operation. Alkalinity was generated on a consistent basis by limestone dissolution and averaged 316 mg/L. Virtually all of the iron, aluminum, and manganese was removed within the limestone.

Additional Key Words: compost wetlands, sulfate reduction.

Introduction

Passive treatment of mine drainage has evolved from crude, generically applied wetlands to more specific unit operations designed for the particular quality of the mine water. Net alkaline water can be treated using aerobic wetlands that are sized based on metal loadings. Net acidic water that does not contain ferric iron or aluminum can be converted to net alkaline water using anoxic limestone drains (ALDs). While a significant amount of mine drainage can be successfully treated using these methods, water quality at many sites is not appropriate for these methods (i.e., contains ferric iron and/or aluminum). This water quality is more problematic for passive treatment techniques. Aluminum has been documented to significantly lower the permeability of ALDs and cause failure of the system (Watzlaf 1996). Ferric iron may cause similar reductions in permeability as well as armor the limestone, thereby reducing dissolution rates. Anaerobic wetlands may be used to treat net acidic, Al- or Fe^{3+}-bearing water, however, these wetlands require relatively large areas. One square meter of wetland can neutralize only 5 g of acidity per day (Hedin et al. 1994). The substrates of these systems usually contain organic matter and limestone. Alkalinity is generated by limestone dissolution and sulfate reduction. Transport of this alkalinity to the mainly surficially flowing water is by diffusion. Practitioners have attempted several wetland designs to force the water horizontally and vertically (up or down) through the organic matter and

limestone layers of these systems. Down-flow systems have seemed to be the most successful and have typically consisted of compost (usually spent mushroom compost which contains about 10% calcium carbonate, by weight) and limestone layers, and have been termed successive alkalinity-producing systems (SAPS) or vertical-flow anaerobic wetlands (Kepler and McCleary 1994). These systems are designed to have 1 m of standing water, a layer of compost 0.15 - 0.50 m thick, and a layer of limestone 0.3-1.0 m thick. A perforated pipe drainage system is placed at the bottom of the limestone layer. The compost-layer adds some alkalinity (by a combination of calcite dissolution and sulfate reduction), removes dissolved oxygen, reduces ferric iron to ferrous iron, and removes aluminum. Additionally, the compost may lower concentrations of other trace metals, such as cobalt, nickel, and zinc. The limestone layer adds additional alkalinity. These systems have been found to remove about ten times more acidity per unit area (50 $gd^{-1}m^{-2}$) than conventional anaerobic wetlands (Watzlaf and Hyman 1995, Watzlaf and Pappas 1996, Dietz and Stidinger 1996).

Methods

Compost/Limestone Column

Figure 1 shows a schematic of the laboratory-scale compost/limestone column. The column was 0.16 m in diameter and contained a 0.3 m thick layer of limestone, 0.76 m thick layer of spent mushroom compost, and 0.91 m layer of free-standing water. Actual field sites have been designed with thinner compost layers and thicker limestone layers, however, this test was designed to specifically investigate the compost layer. Sampling ports were positioned at the top, middle, and bottom of the compost layer. Each port was constructed by placing a rubber stopper in a hole drilled in the side of the column. A piece of stainless steel tubing was pushed through a hole in the rubber stopper and terminated near the center of the column. The outside end of the ports were fitted with a three-way valve to facilitate sampling with a syringe. No leakage was observed from any port. Mine water was collected at an abandoned, partially-sealed, underground mine located in Butler County, PA, transported to the laboratory, and applied to the column at a rate of 3.8 mL/min. Fresh mine water was collected every 2-3 weeks. Samples of influent and effluent were taken weekly. Samples from ports 1, 2, and 3 were taken about every other week. Acidified samples were filtered (0.2 μm) prior to acidification with HCl. Metals were analyzed by ICAP, and pH,

acidity, and alkalinity were measured using standard methods. The chemistry of the mine water changed during transport and storage. Iron concentrations were lowered, pH was lowered, and dissolved oxygen increased. These changes would naturally occur in the field if some type of holding or equalization pond was used. This paper reports the results of 97 weeks of operation.
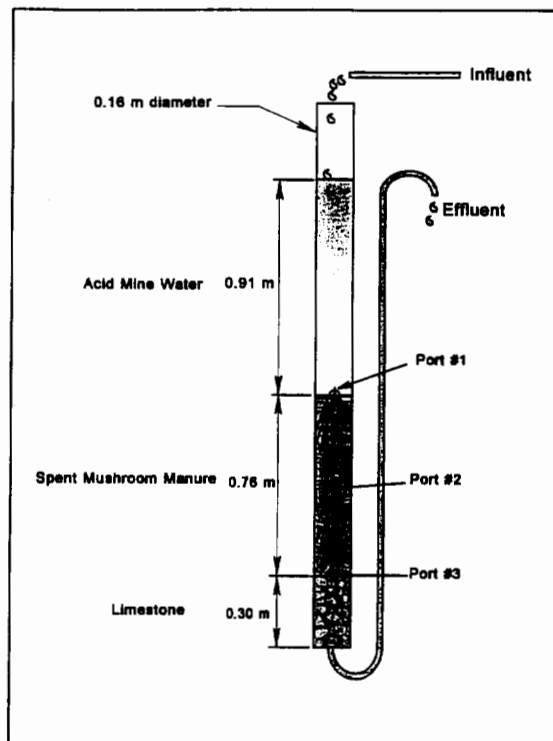

Figure 1. Schematic of Compost/Limestone column.

Limestone Column

The limestone column was constructed the same as the compost/limestone column except without the compost. The column was 0.16 m in diameter and contained a 1.06 m thick layer of limestone and 0.91 m layer of free-standing water. Sampling ports were positioned at the top of the limestone and 0.38 m and 0.76 m below the top of the limestone (the same vertical positions as the compost/limestone column). Mine water was collected at the same abandoned underground mine, transported to the laboratory, and applied to the column at a rate of 3.8 mL/min. Fresh mine water was collected every 2-3 weeks. Samples of influent and effluent were taken weekly. Samples from ports 1, 2, and 3 were taken about every other week. Acidified samples were filtered (0.2 mm) prior to acidification with HCl. Metals were analyzed by ICAP, and pH, acidity, and alkalinity were measured

using standard methods.

This column was constructed after the compost/limestone column to determine the necessity of the compost. This paper reports the results of 55 weeks of operation. Because these columns were fairly large-scale, only one column of each treatment was operated. While replicate columns may have resulted in more robust conclusions, handling the large volume of water necessary for replication was beyond our allotted resources.

Results and Discussion

Compost/Limestone Column

Figure 2 shows the pH at the influent, effluent, and the three ports. The pH at port 2 remained above 6.0 for only 20 weeks, followed by a rapid drop to less than 4.0 after 29 weeks as the calcium carbonate was depleted from the upper half of the compost layer. The pH at the bottom of the compost (port 3) started at 7.0 and fell to 5.0 after 97 weeks.

Alkalinity was produced in the column by both limestone dissolution and sulfate reduction. Figure 3 shows the alkalinity produced by the entire compost/limestone column by 1) limestone ($CaCO_3$) dissolution (based on increases in Ca, where 1 mg/L increase in Ca stoichiometrically yields 2.497 mg/L of alkalinity as $CaCO_3$), 2) sulfate reduction (based on decreases in SO_4^{2-}, where 1 mg/L decrease in SO_4^{2-} stoichiometrically yields 1.042 mg/L of alkalinity as $CaCO_3$), 3) the "calculated sum" of these two, and 4) the "actual" change (based on decreases in net acidity). The majority of the alkalinity was produced by limestone dissolution, typically about two times the alkalinity than could be accounted for by sulfate reduction. Sulfate reduction decreased over time as the pH within the compost layer declined. At pH values less than 4, sulfate reducing and fermentative bacteria are less active. The fermentative bacteria break down complex carbon sources into the simpler carbon compounds that the sulfate reducing bacteria require. Alkalinity due to sulfate reduction went from about 200 mg/L to 100 mg/L in the first 16 weeks. In weeks 1 through 48, alkalinity due to sulfate reduction averaged 109 mg/L and in weeks 48 through 97, only 29 mg/L.

Figure 4 shows that most of the limestone dissolution occurred within the mushroom compost, which is about 10% $CaCO_3$ (note that negative acidity values indicate net alkaline conditions). However, within 24 weeks, conditions at port 2 were net acidic.

Based on water quality at port 3 and the effluent, the limestone layer has yet to contribute significant alkalinity.

Fe and Mn are not intended to be removed in SAPS systems, however, figures 5 and 6 show that iron and manganese were removed. Fe removal was probably due to a combination of adsorption and precipitation as hydroxides and sulfides. Mn was initially removed then released, presumably due to adsorption and desorption. Ideally, iron and manganese would be removed in an aerobic wetland following the SAPS.

Aluminum is typically removed from mine drainage at pH values between 4 and 5. At pH 4, aluminum is quite soluble, over 100 mg/L may be dissolved in the mine water. At pH values over 5, however, the solubility of aluminum drops significantly, typically to less than 1 mg/L. Aluminum was initially removed prior to port 2 (figure 7), where the pH remained above 5 for 22 weeks (see figure 2). As the pH at port 2 dropped below 5 in week 23, Al concentrations began to increase. By week 32, aluminum concentrations at port 2 were not significantly different than the influent concentrations. The pH at port 3 dropped to about 5 in week 93 (see figure 2). At that time, soluble aluminum concentrations began to increase. It appeared as if Al was moving in a front through the compost layer, successively precipitating and dissolving with the changing pH conditions. After the aluminum front passed by port 3, we were unsure of the effect the limestone layer would have. This prompted construction of the second column containing only limestone.

Table 1 displays the average influent and effluent water quality for the 97 weeks of operation of the compost/limestone column.

Laboratory Limestone Column

The pH values at the influent, effluent, and the three ports over the 55 weeks of operation are shown in figure 8. The pH of the effluent remained above 6.0, with most of the pH increase occurring in the top third of the column. The pH averaged 3.15 at the influent, 3.27 at port 1, 6.53 at port 2, 6.68 at port 3, and 7.09 at the effluent. No significant decline in pH was observed at any of the ports.

Figure 9 shows that all of the alkalinity production can be attributed to limestone dissolution,
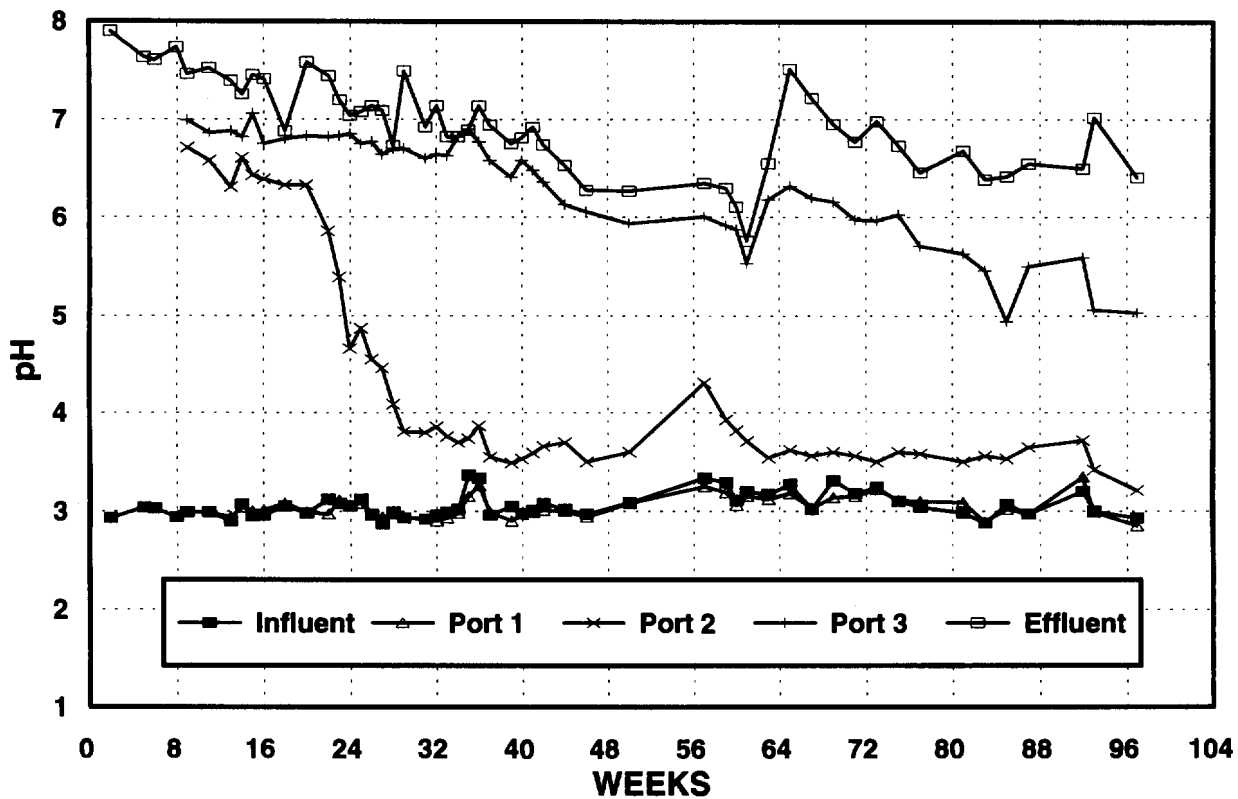
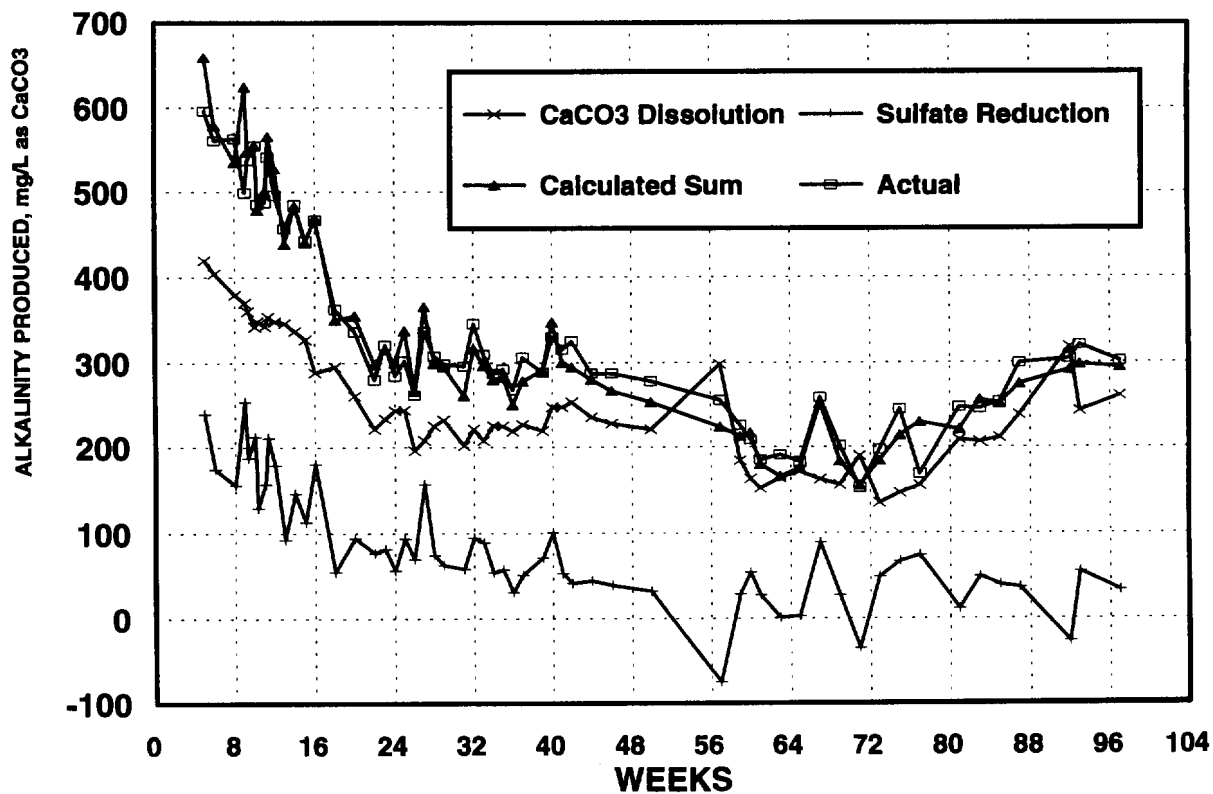Figure 2. Compost/Limestone column - pH vs. time.

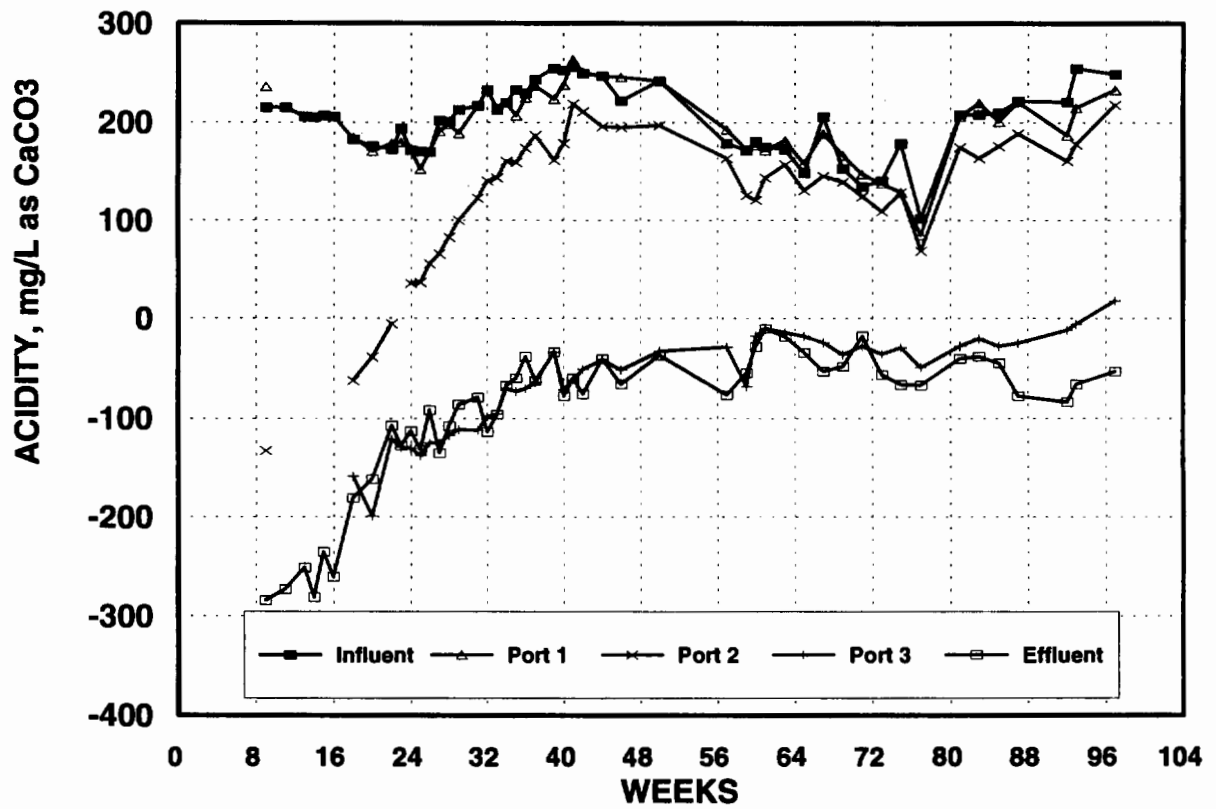Figure 3. Compost/Limestone column - alkalinity production vs. time.

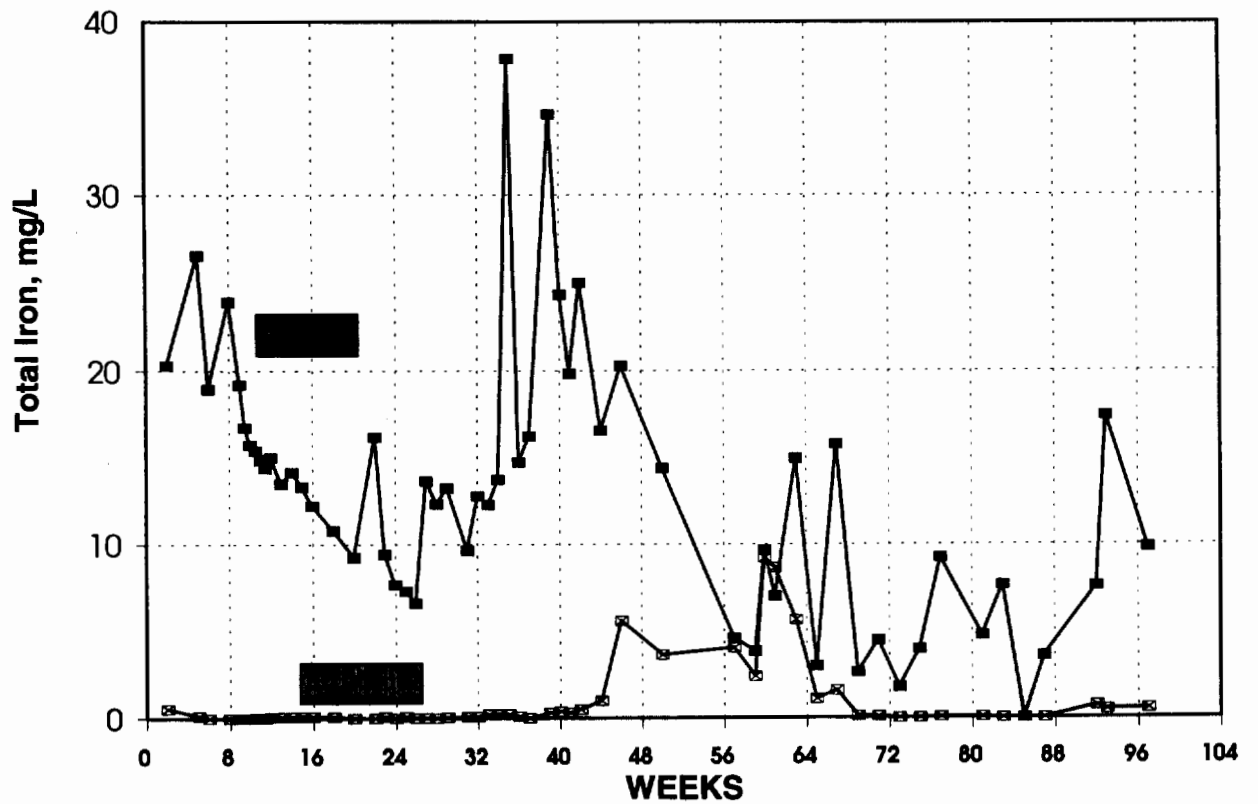Figure 4. Compost/Limestone column - acidity vs. time.

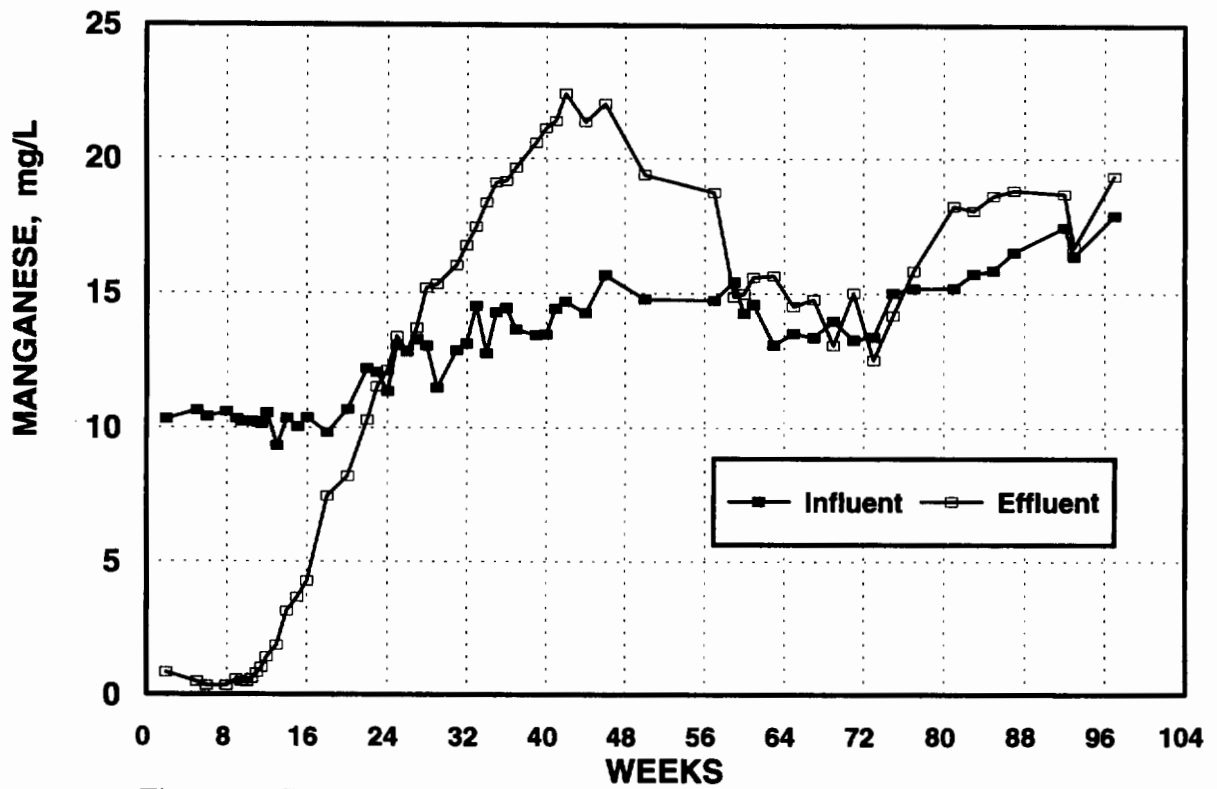Figure 5. Compost/Limestone column - total iron vs. time.

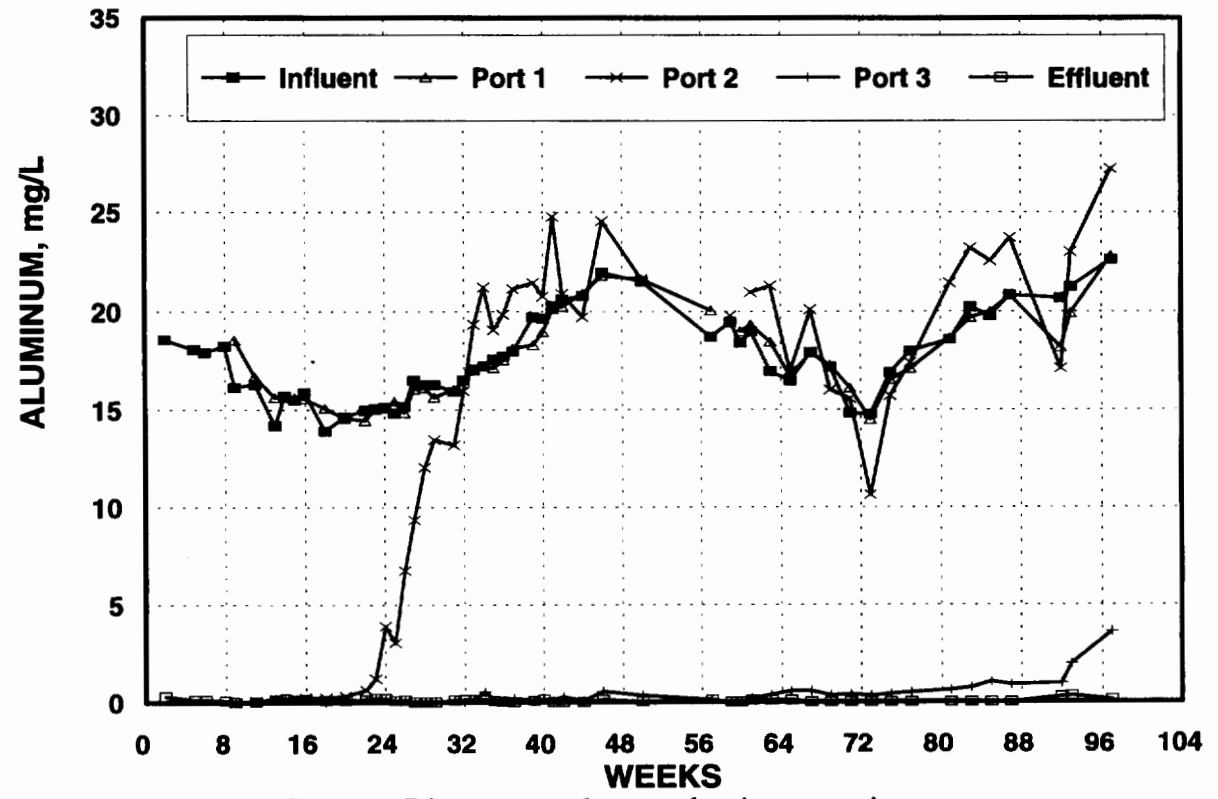Figure 6. Compost/Limestone column - manganese vs. time.

Figure 7. Compost/Limestone column - aluminum vs. time.

Table 1. Average water quality of compost/limestone column through 97 weeks and limestone column through 58 weeks. Results of the compost/limestone column through 57 weeks are also shown for comparison to limestone column. pH in standard units. All concentrations in mg/L. Alkalinity and net acidity in mg/L as $CaCO_3$. Negative acidity indicates net alkalinity.

| Parameter	Compost/Limestone through 97 weeks		Limestone through 58 weeks		Compost/Limestone through 57 weeks	
	Influent (n=58)	Effluent (n=57)	Influent (n=32)	Effluent (n=32)	Influent (n=39)	Effluent (n=40)
pH	3.05	6.99	3.14	7.09	3.02	7.16
Alkalinity	0	154	0	154	0	193
Net Acidity	208	-126	193	-123	218	-162
Ferrous Iron	1.9	0.47	4.2	<0.1	1.4	0.14
Total Iron	13.2	0.86	9.4	<0.1	15.9	0.47
Aluminum	17.6	<0.1	18.6	<0.1	17.1	<0.1
Manganese	13.0	12.7	14.7	2.3	12.1	11.1
Sulfate	605	528	622	624	599	500
Calcium	91.8	192	99.0	244	89.1	200
Magnesium	44.9	51.0	48.3	50.3	43.1	49.9
Sodium	3.1	3.5	3.2	3.4	3.1	3.4
Potassium	2.4	3.1	2.5	2.8	2.4	3.3
Anions/Cations	1.02	0.97	1.01	0.97	1.02	0.97
Flow, L/min	-	0.0038	-	0.0038	-	0.0038
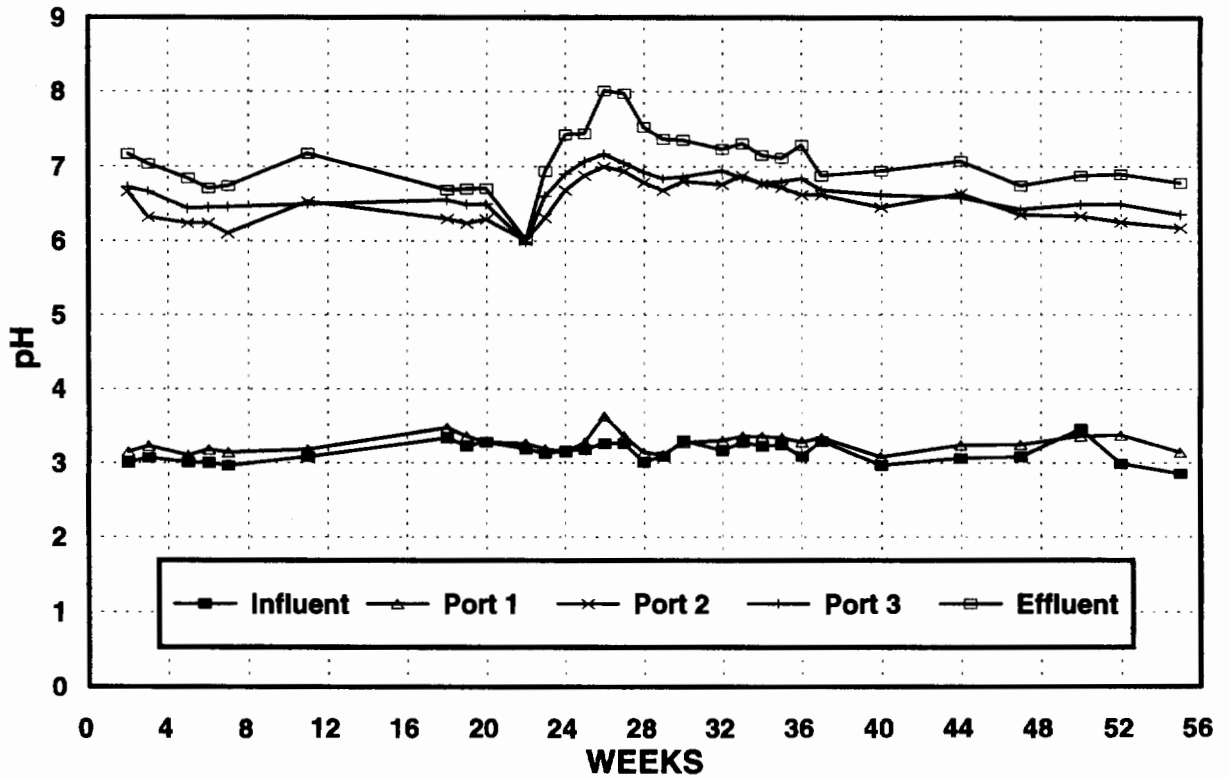
Figure 8. Limestone column - pH vs. time.
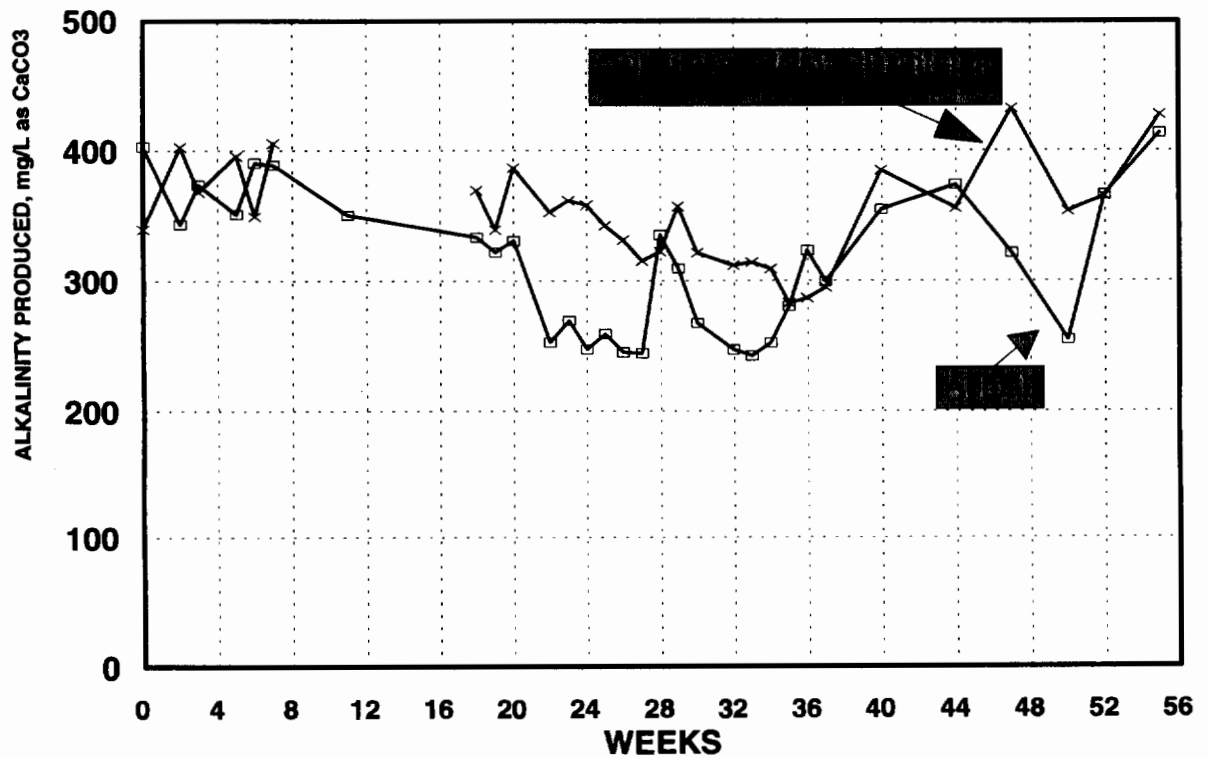
Figure 9. Limestone column - alkalinity production vs. time.

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as expected. Alkalinity generation was fairly consistent, averaging 316 mg/L and ranging from about 250 to 400 mg/L.

The net acidity/alkalinity graph displays the same results as pH; most of the alkalinity was generated in the upper third of the limestone layer (figure 10). The theoretical contact time of the water with this top third of the limestone is about 12 hours. Previous research studies have found that mine water reaches near maximum levels of alkalinity after 12 hours of contact in ALDs (Hedin and Watzlaf 1994).

Figure 11 shows the influent and effluent concentrations of iron. The influent iron concentrations were quite variable due to the transport and storage of the mine water, as well as some natural variation in mine water quality. Iron was removed in the upper third of the limestone. Storage of the mine water in the laboratory, as well as the 80 hours of retention time within the standing water layer in the column, enabled about half of the total iron to convert to the ferric form and allowed the water to become saturated with oxygen. Most of the iron, therefore, was probably removed as ferric hydroxides, which was consistent with observations of precipitates within the column.

Figure 12 shows that initially there was no manganese removal within the column. Manganese began to be removed at the effluent after 11 weeks, at port 3 after 18 weeks, at port 2 after 24 weeks. A black precipitate was deposited within the column that was very similar to precipitates that are observed in limestone-filled ditches that remove manganese. A possible explanation for this removal is biological manganese oxidation and precipitation as MnO_2. Other than the oxidation of manganese, the only other chemical oxygen demand on the mine water was that imposed by ferrous iron. The average influent ferrous iron concentration was 4.2, which would require less than 1 mg/L of dissolved oxygen to oxidize to ferric iron.

Aluminum concentrations were reduced to very low levels in the top third of the limestone (figure 13), which was consistent with the pH values (see figure 8). Precipitation of aluminum within ALDs is known to reduce the permeability to the point where the water completely bypasses the ALD. The difference between an ALD and this system is that the loading of aluminum per area perpendicular to the direction of flow is much less. The ALD that was constructed in the field to treat this water was loaded at

2100 g of Al/day/m^2 of area (perpendicular to the flow) and virtually ceased flowing within 6 months. The column in this study was loaded at 4.9 g of Al/day/m^2.

Comparison of Compost/Limestone and Limestone Systems

In addition to the 97-week water quality averages for the compost/limestone column, averages through 57 weeks are presented in Table 1 for comparison to the limestone column which has 58 weeks of water quality data. The two columns performed comparably related to changes in pH, iron, aluminum, magnesium, and sodium. Total and net alkalinity values averaged about 40 mg/L higher (25-30%) in the compost/limestone column, however, much of this can be attributed to significantly high alkalinity values in this column in the first 16 weeks (see figure 3). The average net alkalinity concentration of the effluent from weeks 18-58 for the limestone column was actually higher (122 mg/L) than the average for compost/limestone column (89 mg/L, weeks 18-57). Manganese was removed in the limestone column and not in the compost/limestone column, probably due to higher dissolved oxygen levels in the limestone column. Sulfate concentrations were unchanged in the limestone column and decreased about 100 mg/L in the compost/limestone column. Calcium levels were higher in limestone column. The added alkalinity from sulfate reduction in the compost/limestone column, to a certain extent, inhibited limestone dissolution by creating conditions closer to calcite saturation (Hedin et al. 1994).

Summary

The depletion of calcium carbonate within the compost layer significantly decreased sulfate reduction activity. The pH throughout the compost layer is projected to be less than 4.5 after about two years of operation. It is unclear if any significant additional benefit will be derived from the compost after this two-year period. Data from a field down-flow compost/limestone system, however, indicate that sulfate reduction has continued for over 5 years. Results of these laboratory tests indicate that supplementing the compost with additional limestone should extend the duration of sulfate reduction by keeping the pH within the range where sulfate reduction actively occurs. For example, in the compost/limestone column, if a 50% (by volume) mix of compost and limestone had been used, there would be theoretically enough limestone to last for over 40 years (assuming a limestone dissolution of 250 mg/L).
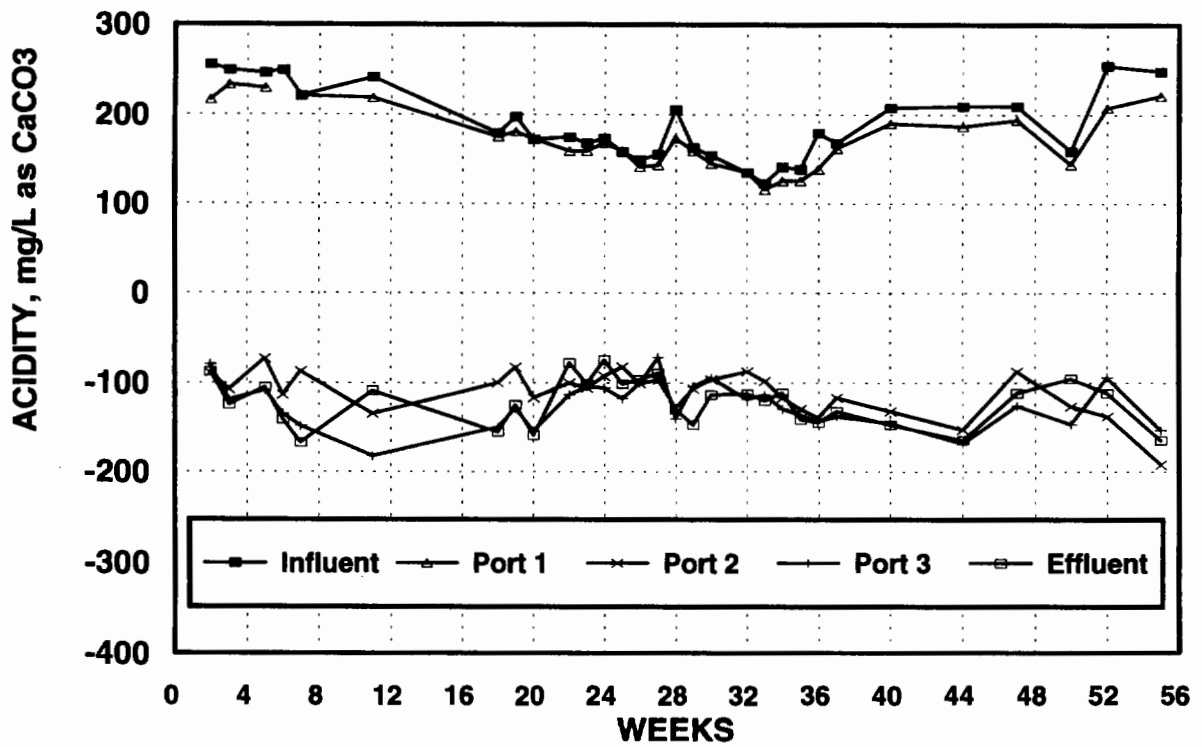
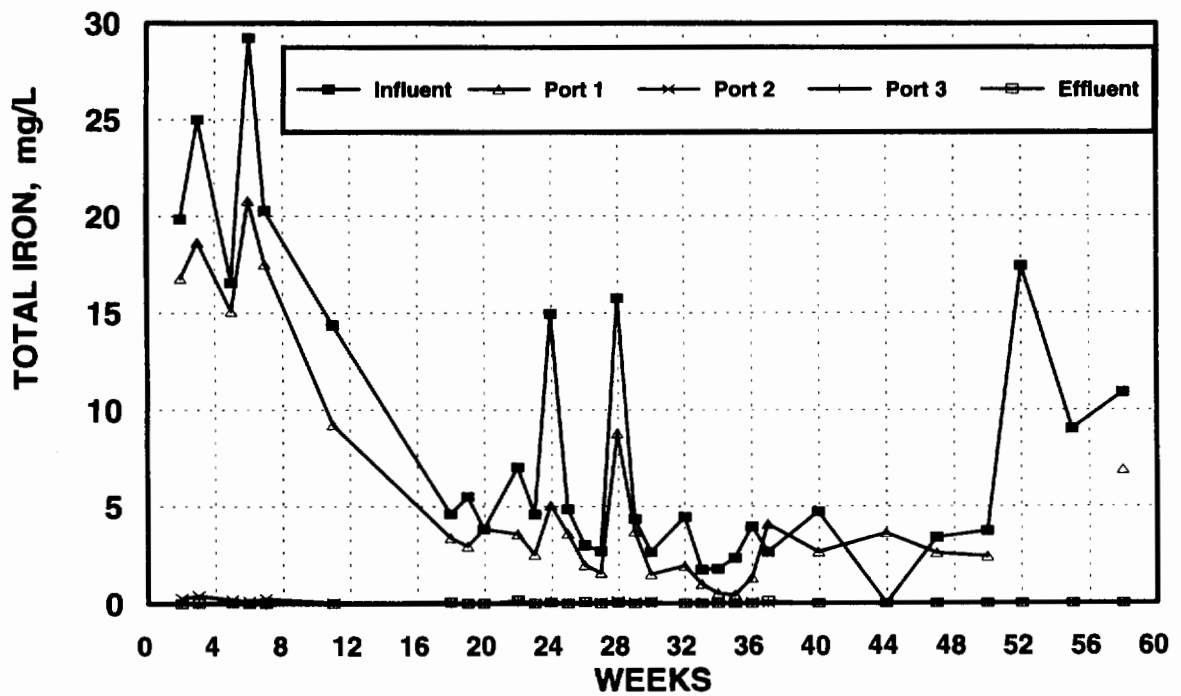Figure 10. Limestone column - acidity vs. time.
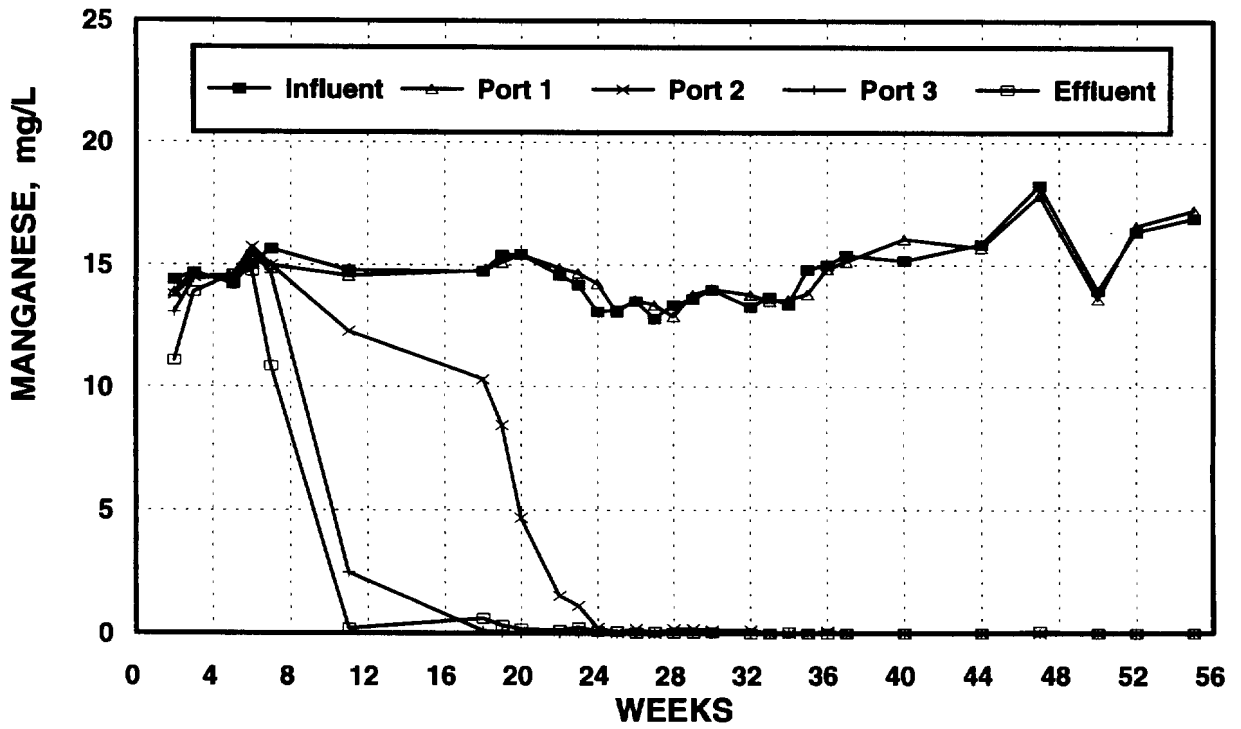

Figure 11. Limestone column - total iron vs. time.
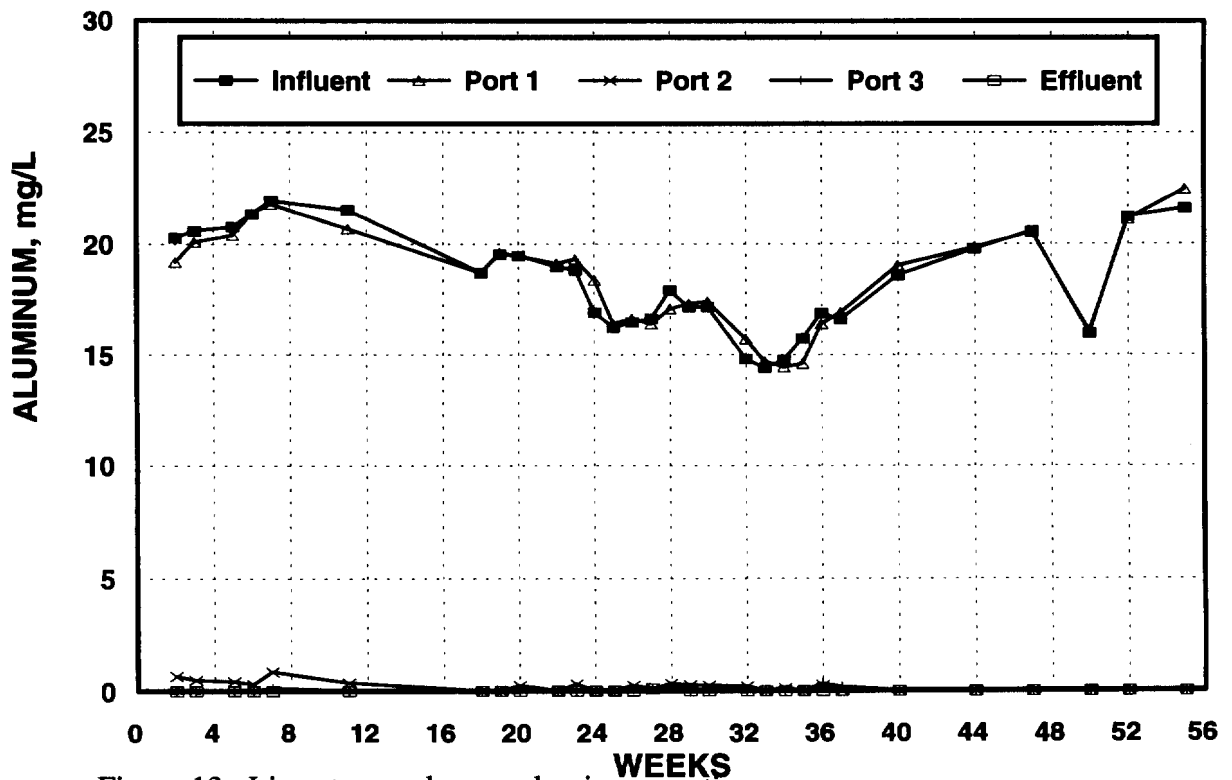
Figure 12. Limestone column - manganese vs. time.

Figure 13. Limestone column - aluminum vs. time.

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Precipitation of metal compounds within the compost or limestone may significantly reduce permeability. Currently, most field systems are incorporating the ability to utilize 1-2 m of head to compensate for any reduction in permeability. Since aluminum precipitates at pH values of 4-5, it should be removed in these systems. Iron and manganese, however, in their reduced forms (Fe^{2+} and Mn^{2+}) are soluble at pH 7.0. The compost layer is designed to reduce (or maintain) iron and manganese in their reduced states. If the mine water contains significant iron and manganese levels, the compost layer may prevent their precipitation within the system, and thereby slow the rate of permeability decrease. In addition, it may be advantageous to introduce the influent under the pond water surface, directly above the top of the compost to keep iron in the reduced state.

Acknowledgments

Literature Cited

Dietz, J. M. and D. M. Stidinger. 1996. Acidic mine drainage abatement in an anaerobic sub-surface flow wetland environment - case history of the treatment system at Corsica, PA. p. 531-540. In Proceedings of the American Society for Surface Mining and Reclamation Annual Meeting. (Knoxville, TN, May 15-20, 1996).
https://doi.org/10.21000/JASMR96010531

Hedin, R. S., G. R. Watzlaf, and R. W. Nairn. 1994. Passive treatment of acid mine drainage with limestone. Journal of Environmental Quality 23(6):1338-1345.
https://doi.org/10.2134/jeq1994.00472425002300060030x

Hedin, R. S. and G. R. Watzlaf. 1994. The effects of anoxic limestone drains on mine water chemistry. p. 185-194. In Proceedings of the International Land Reclamation and Mine Drainage Conference. (Pittsburgh, PA, April 24-29, 1994).
https://doi.org/10.21000/JASMR94010185

Kepler, D. A. and E. C. McCleary. 1994. Successive alkalinity-producing systems (SAPS) for the treatment of acidic mine drainage. p. 195-204. In Proceedings of the International Land Reclamation and Mine Drainage Conference. (Pittsburgh, PA, April 24-29, 1994).
https://doi.org/10.21000/JASMR94010195

Watzlaf, G. R. 1996. Effects of aluminum on anoxic limestone drains. In Proceeding of the West Virginia Acid Mine Drainage Task Force Meeting. (Morgantown, WV, In Press).

Watzlaf, G. R. and D. M. Hyman. 1995. Limitations of passive systems for the treatment of mine drainage. p. 186-199. In Proceedings of the National Association of Abandoned Mine Land Programs. (French Lick, IN, October 15-19, 1995).

Watzlaf G. R. and D. M. Pappas. 1996. Passive treatment of acid mine drainage in systems containing compost and limestone: laboratory and field results. p. 861. In Proceedings of the American Society for Surface Mining and Reclamation Annual Meeting. (Knoxville, TN, May 15-20, 1996).