FACTORS AFFECTING PERFORMANCE OF SUCCESSIVE ALKALINITY-PRODUCING SYSTEMS [1]

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Abstract: Successive Alkalinity-Producing Systems (SAPS) have proven to be a successful technology for renovating acidic mine drainage (AMD). This study was conducted to serve as a basis for development of guidelines to aid in the design of future systems. Performance of field systems and laboratory columns were monitored and modeled. The field study examined eight SAPS systems located in Virginia and West Virginia. Monthly performance data were collected on each system for periods of 2 to 5 years. The laboratory SAPS columns were operated for 13 months to measure the water chemistry changes as the AMD flowed down through the columns. All SAPS systems demonstrated an ability to generate alkalinity and/or neutralize acidity. Analysis of water-chemistry data collected from the field systems revealed significant correlations between alkalinity production and the natural log of residence time, influent total iron, and influent non-Mn acidity. The laboratory column study revealed seasonal variations in dissolved oxygen removal below the organic compost layer of these systems. During the colder months, sub-compost dissolved oxygen levels did not reach the 1 mg/l maximum concentration that is recommended to prevent limestone armoring. These studies revealed several concepts that can be used to guide SAPS system design: Alkalinity production appears to increase in response to residence time as a log-normal function; alkalinity production tends to vary in response to influent acidity; and a compost-residence time may be an important design element in order to achieve oxygen removal necessary for optimizing SAPS system performance.

Additional Key Words: acidic mine drainage, passive treatment, alkalinity.

Introduction

The evolution of passive treatment systems for renovating acidic mine drainage (AMD) has resulted in a collection of specialized systems that are each designed to treat a specific type of drainage. The Successive Alkalinity-Producing System (SAPS) is one of the latest results of this process (figure 1.). The SAPS is capable of treating highly acidic AMD containing elevated concentrations of iron, aluminum, and dissolved oxygen (Kepler and McCleary, 1994). The fundamental principle behind the function of the SAPS is to generate a sufficient quantity of alkalinity to neutralize the influent acidity. This results in an increase in pH, and allows for the removal of the acid soluble metals via the formation of insoluble oxyhydroxide complexes.

Some of the earliest known systems of this type were constructed in 1988 and 1990 (Hendricks, 1991; Duddleston et al., 1993). Kepler and McCleary (1994) documented similar systems in Pennsylvania and coined the term SAPS as they are now known. Previous studies of SAPS performance indicated an ability for

these systems to remove acidity ranged from an average of 51 $g \cdot d^{-1} \cdot m^{-2}$ (Narin et al. 1999), to 61.8 $g \cdot d^{-1} \cdot m^{-2}$ of acidity (Dietz and Stidinger, 1996). Kepler and McCleary (1994) reported acidity removal potential between 150-300 mg/l. What is unclear from these studies, however, is how acid neutralization is affected by influent AMD chemistry and system design.

Design guidelines available in published literature call for a limestone layer of 60 – 90 cm (2 – 3 ft.) in depth, an organic compost layer (preferably spent mushroom compost) of 15 – 45 cm (0.5 –1.5 ft.), and a 0.9 - 1.5 m (3 – 5 ft.) deep body of water above the organic layer. A limestone residence time of 12 – 15 hours is regarded as adequate for achieving maximum alkalinity generation, based on studies of the performance of ALDs (Skovran and Clouser, 1998; Kepler and McCleary, 1994). These guidelines originate from the early observations of several systems. If residence time in the limestone were an essential factor to system performance, a volumetric basis for the limestone layer design would also be a logical basis for system design. Such design guidelines would allow for the manipulation of system
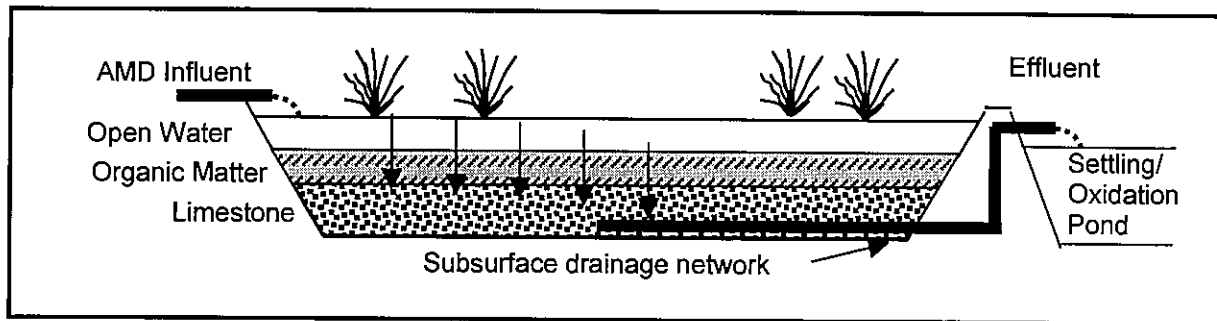
Figure 1. Generalized design elements of the SAPS passive treatment system. Drawing not to scale.

depth in areas where space is limited in order to achieve the recommended residence time, and thus, desired treatment goals. Moreover, since limestone-dissolution kinetics are affected by acidity, pH, and dissolved metal concentrations (Hedin and Watzlaf, 1994), influent AMD chemistry should factor into determining the optimal residence time for a specific situation. This research attempts to define these relationships by studying the long-term performance of SAPS systems in the field and a laboratory column experiment.

Field Study

Site Selection

Eight SAPS were identified in Virginia and West Virginia. As a requirement, each system had to be of the basic system design as illustrated in Figure 1, with a limestone layer, overlying bed of mulch, and a subsurface drainage network. In addition, each SAPS had to receive a net acidic influent as these systems are not intended for treating net alkaline discharges.

Methods

Construction and materials data were determined from field measurements, as-built drawings, and personal communication with design engineers. Monthly water samples were collected from each SAPS cell influent and effluent points. Sample collection and analyses were performed by private testing laboratories contracted by thesystem operators. Flow was measured in the field using a calibrated bucket and stopwatch, while pH was measured in the field using a calibrated field probe. Total alkalinity was measured by titrating 50ml of raw sample with 0.1$\underline{N}$ H_2SO_4 to pH 4.6. Total acidity was determined by boiling 50ml of raw sample with 1ml of 30% H_2O_2 and titrating to pH 8.3 with 0.02$\underline{N}$

NaOH (APHA, 1985). Concentrations of Fe and Mn were measured for acidified samples using inductively coupled argon plasma spectroscopy (ICP). Sulfate was determined using either ion chromatography or ICP. Researchers visited the systems over a two-year period to observe system performance and determine that sampling and analysis were being conducted in an appropriate manner. The theoretical retention time (t_r) in hours for each of the systems was estimated using the equation:

$$t_r = 4.403 \cdot V_{ls} \; V_v \, Q^{-1}$$

where,

V_{ls} = Volume of limestone (m^3)
V_v = Bulk void volume expressed as a decimal
Q = Volume of flow into the system (GPM)

Results and Discussion

<u>System Design</u> All systems were constructed using high calcium limestone (>90% $CaCO_3$) aggregate between 4 to 6 inches in diameter. System sizes ranged from 22.3 m^2 (240 ft^2) to 662.18 m^2 (7128 ft^2). Limestone layers depths ranged from 0.46 m (18 in.) to 0.76 m (30 in.). Organic matter depth and composition varied greatly due to the individual operator's preference, desire for experimentation, and availability of organic materials. All SAPS were planted with either cattails (*Typha sp.*), or bulrushes (*Scirpus sp.*). The average construction cost was approximately $29,000.

<u>Water Quality</u> Water quality data were collected on a monthly basis for a period of 24 months or longer. Due to periods of drought during this study, some sampling events recorded no flow. These samples were eliminated from the data set due to inability to relate water chemistry to SAPS residence

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Table 1. Average influent water quality parameters for the eight SAPS systems. Numbers in parentheses represent the range of data for a given parameter.

System	n	Flow (gpm)	Residence time (h)	pH[1] (su)	Fe (mg/l)	Mn (mg/l)	Sulfate (mg/l)	Alkalinity[2] (mg/l)	Acidity[2] (mg/l)
BEL1	11	50.0	3.6	4.6	0.53	2.32	517	0.1	105.2
		(20.0 - 80.0)	(2.2 - 8.9)	(3.7 - 4.9)	(0.23 - 0.99)	(1.81 - 3.24)	(216 - 914)	(1.0 - 0.0)	(56.0 - 176.0)
BEL2	11	48.6	14.3	5.0	0.64	2.18	569	1.6	51.8
		(20.0 - 80.0)	(6.8 - 27.2)	(4.6 - 6.0)	(0.16 - 3.53)	(1.46 - 3.14)	(210 - 974)	(0.0 - 9.0)	(17.0 - 134.0)
LLC2	16	26.7	16.3	4.4	0.87	50.30	734	0.6	182.9
		(5.0 - 55.0)	(4.7 - 52.3)	(3.4 - 6.3)	(0.24-10.66)	(14.0 - 95.0)	(90.6 - 2025)	(0.0 - 4.0)	(62.0- 287.0)
LLC3	16	26.7	20.1	4.6	1.70	48.84	739	1.4	131.1
		(5.0 - 55.0)	(5.9 - 64.7)	(3.4 - 7.6)	(0.27 - 6.37)	(15.0 - 98.0)	(64.5 - 1688)	(0.0 - 12.0)	(8.0 - 260.0)
LLC4	16	26.4	11.8	5.0	1.68	46.36	670	2.7	119.9
		(5.0 -55.0)	(3.1 - 34.4)	(4.3 - 6.4)	(0.38 - 4.47)	(4.26 - 92.0)	(23.1 - 1531)	(0.0 - 48.0)	(42.0 - 302.0)
PMAC	48	1.0	625.2	4.40	121.66	10.34	1153	2.0	196.2
		(0.08 - 5.0)	(32.9 - 2191.1)	(3.1 - 5.8)	(12.0 - 356.0)	(3.61 - 27.0)	(300 - 3120)	(0.0 - 38.0)	(6.0 - 585.0)
USC1	19	18.0	89.79	4.0	1.07	35.10	686	0.1	256.2
		(2.0 - 40.0)	(26.6 - 531.5)	(3.6 - 4.4)	(0.44 - 1.82)	(12.0 - 137.0)	(90 - 2019)	(0.0 - 1.0)	(86.0 - 382.0)
USC2	19	18.3	50.3	5.1	0.75	19.33	540	28.5	72.2
		(2.0 - 40.0)	(15.2 - 303.9)	(4.5 - 6.5)	(0.19 - 2.18)	(4.41 - 39.0)	(121 - 1395)	(0.0 - 142.0)	(0.0 - 218.0)

[1] Value represents median
[2] CaCO₃ equivalent

Table 2. Average effluent water quality parameters for the eight SAPS. Numbers in parentheses represent the range of data for a given parameter.

System	n	pH[1] (su)	Fe (mg/l)	Mn (mg/l)	Sulfate (mg/l)	Alkalinity[2] (mg/l)	Acidity[2] (mg/l)	Net Alkalinity Generated[2] (mg/l)
BEL1	11	5.0	0.64	2.18	569	1.6	51.8	54.8
		(4.6 - 6.0)	(0.16 - 3.53)	(1.46 - 3.14)	(210 - 974)	(0.0 - 9.0)	(17.0 - 134.0)	(30.0 - 96.0)
BEL2	11	6.2	0.38	2.14	541	42.5	5.0	87.7
		(5.6 - 6.7)	(0.10 - 1.05)	(0.19 - 3.64)	(198 - 1086)	(2.0 - 146.0)	(0.0 - 22.0)	(26.0 - 190)
LLC2	16	4.6	1.7	48.8	739	1.4	131.1	52.6
		(3.4 - 7.6)	(0.27 - 6.37)	(15.00 - 98.0)	(64 - 1688)	(0.0 - 12.0)	(8.0 - 260.0)	(-12.0 - 170.0)
LLC3	16	5.0	1.68	46.4	670	2.7	119.9	12.5
		(4.3 - 6.4)	(0.38 - 4.47)	(4.26 - 92.0)	(23.1 - 1531)	(0.0 - 48.0)	(42.0 - 302.0)	(-131.0 - 184.0)
LLC4	16	5.8	2.33	43.2	651	19.9	49.7	87.4
		(4.8 - 6.9)	(0.67 - 5.12)	(7.13 - 64.0)	(43.1 - 1382)	(0.0 - 73.0)	(0.0 - 138.0)	(-50.0 - 313.0)
PMAC	48	6.5	15.45	10.3	1107	153.1	2.8	343.3
		(5.64 - 7.7)	(1.58 - 89.0)	(4.06 - 28.0)	(35.0 - 2880)	(33.0 - 258.0)	(0.0 - 49.0)	(130.0 - 673.0)
USC1	19	4.7	1.16	31.6	508	8.0	195.8	68.3
		(4.2 - 6.2)	(0.51 - 2.51)	(8.4 - 124.0)	(94.0 - 1457)	(0.0 - 124.0)	(0.0 - 472.0)	(-276.0 - 438.0)
USC2	19	6.0	0.68	16.0	283	54.0	0.0	48.0
		(4.6 - 6.7)	(0.22 - 2.06)	(6.9 - 38.9)	(140 - 1380)	(0.0 - 160.0)	(-200.0 - 160.0)	(-336.0 - 200.0)

[1] Value represents median
[2] CaCO₃ equivalent

time. Samples collected during the first year of operation were also eliminated; other researchers have observed over-performance by young systems that is not typical of long term performance (Skovran and Clouser, 1998).

Residence time was calculated using an estimated limestone bulk void volume of 50%, and the influent flow rate on the day of sampling. Average residence times for the eight SAPS ranged from 3.6 hours to 26 days (Table 1). All sampling events recorded AMD influents that would not meet NPDES discharge limits for at least one criterion.

Changes in water quality resulting from SAPS treatment are shown in Table 2. All eight systems raised pH consistently. Iron removal varied for systems receiving low iron loadings. On sampling events when the total iron concentration exceeded 2mg/l, iron removal was usually observed. Manganese removal was nominal. On all net-acidic sampling events, acidity was neutralized and/or alkalinity was generated. For the purposes of this research, net alkalinity generation is defined as the sum of the reduction in acidity and the increase in alkalinity.

Data Analysis

All data collected from the eight systems, a total of 156 sampling events, were pooled for analysis. Some observations were then eliminated based on several criteria, reducing the number of eligible samples to 135. Three samples were eliminated due to low flows that resulted in theoretical residence times of greater than 120 days. Five samples were eliminated because they failed to generate at least 5 mg/l as $CaCO_3$ of net alkalinity. Thirteen samples were eliminated because the influent water chemistry was net-alkaline.

Initial analysis was through development of a Pearson's correlation coefficient (r) matrix. All available influent parameters (pH, total Fe, total Mn, sulfate, and total acidity) were included in this procedure, as well as net alkalinity generation. In addition, a second acidity value was calculated to represent that portion of total acidity that is not derived from manganese oxidation ($Acid_{Fe,Al,pH}$, or non-Mn acidity). This adjusted acidity value reflects acidity derived from iron, aluminum, and pH that is assumed to be neutralized by a SAPS system, and is calculated by rearranging the formula derived for calculating the acidity typical coal mine drainages (eq. 1) to achieve the new acidity calculation (eq. 2) (adapted from Hedin et al., 1994; Rose and Cravotta, 1998)

$$Acid_{Total} = 50(2Fe^{2+}/56 + 3Fe^{3+}/56 \qquad (1)$$
$$+ 3Al/27 + 2Mn/55 + 1000(10^{-pH}))$$

$$Acid_{Total} - 1.818Mn = Acid_{Fe,Al,pH} \qquad (2)$$

The natural logarithms of each of these parameters were also included to determine if non-linear relationships exist.

The natural log of the residence time explains the greatest amount of variation in net alkalinity generation (r = 0.7414) (Figure 2), indicating that alkalinity generation occurs most rapidly within the first several hours of AMD-limestone contact and that additional residence time yields decreasing gains in alkalinity.

Total iron showed strong positive linear (Figure 3) and logarithmic correlations with net alkalinity generation. Non-manganese acidity proved to be a stronger indicator of alkalinity generation than total acidity (Figure 4). These findings indicate that residence time and influent water quality affect SAPS performance.

Additional analyses are also being conducted, but those results are not yet available. A validation data set of field-performance data from five SAPS systems in western Pennsylvania was obtained to determine if these relationships were valid on SAPS located elsewhere.

One factor affecting net alkalinity generation but not addressed by this analysis is the generation of bicarbonate alkalinity via microbial sulfate reduction.

Column Study

In an effort to further understand the function of the SAPS systems, a series of nine columns were constructed and tested at Virginia Tech's Whitethorn Farm. These columns were designed to vertical scale of field SAPS systems and were constructed using 3/4" high calcium limestone (94.0% $CaCO_3$), and composted hardwood bark mulch (Figure 5.).

Methods

A solution of synthetic AMD, prepared to standardize influent chemistry, was passed through the columns at flow rates such that limestone residence times of 15, 30, and 60 hours were achieved; each flow-rate was replicated three times. Temperature varied
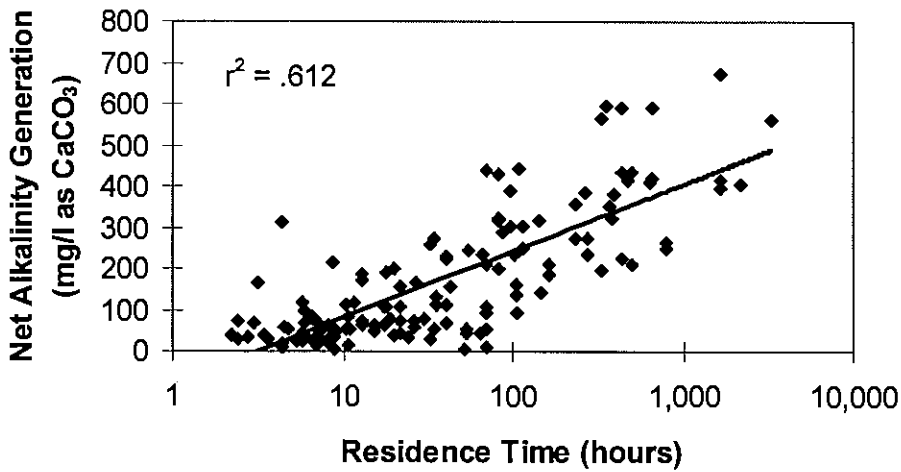
Figure 2. Relationship between residence time and net alkalinity generation for the eight SAPS systems. Net alkalinity is expressed as $CaCO_3$ equivalent. n = 135
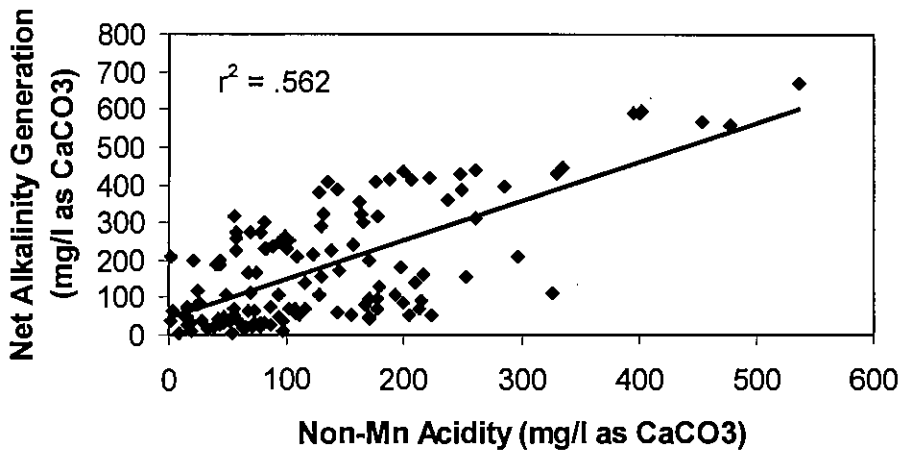

Figure 3. Relationship between influent iron concentration and net alkalinity generation for the eight SAPS systems. Net alkalinity is expressed as $CaCO_3$ equivalent. n = 135
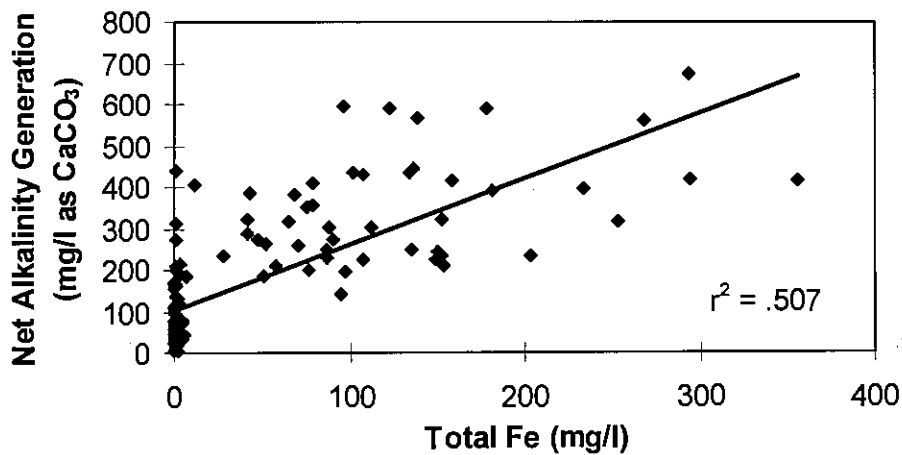

Figure 4. Relationship between non-manganese acidity and net alkalinity generation for the eight SAPS systems. Net alkalinity is expressed as $CaCO_3$ equivalent. n = 135

with ambient fluctuations. Influent and effluent water samples were taken and analyzed in the same manner as the field samples. Sampling ports were located in the organic compost layer and at the compost / limestone interface to monitor vertical changes in water chemistry.

Results and Discussion

We began operating the system in December, 1998; the first samples were collected in January, 1999. Influent AMD averaged 22.26 mg/l total iron, 7.59 mg/l total manganese, 288.1 mg/l total acidity, and 0 mg/l total alkalinity. The median pH was 2.61. All columns were able to neutralize all influent acidity and maintain an alkaline effluent of at least 140mg/l on all sampling events. Residence time was shown to have no significant correlation with net alkalinity generation (r^2=-0.1601). This may be a result of the young age of the columns and the greater reactive surface area of the smaller diameter limestone; all columns were performing to near-maximum capability. Net alkalinity generation was correleated total iron (r^2=0.5228) and non-manganese acidity (r^2=0.9672) as in the field study.

Significant trends in dissolved oxygen (DO) concentrations were observed as the AMD moved down the columns. DO concentrations of greater than 1 mg/l in iron rich waters are known to promote armoring of limestone with ferric hydroxides which will limit the effective lifetime of the system (Skousen et al., 1998). Analysis of samples taken from the port at the base of the compost layer indicate that shorter residence times, coupled with low temperatures, prevent the removal of oxygen to 1 mg/l levels (Figure 5). We interpret this observation to be a result of the lower biological activity of fermentative bacteria, and higher solubility of O_2, at lower temperatures. The low pH the influent AMD also limits biological activity; further hindering oxygen removal.

The columns that maintained a limestone residence time of 60 hours were unique in their ability to remove oxygen to less than 1 mg/l regardless of temperature. The organic matter of these columns was determined by specific yield analysis to contain 2.831 of void space. This translates into a organic matter residence time of 22.82 hours. Recommendations for SAPS system sizing should include residence times for the design the organic mulch layer to ensure long term performance. This figure is considered to be conservative due the relatively low biochemical oxygen demand of the bark mulch. Other materials such as composed manure and spent mushroom compost may require shorter residence times given the bioavailability of those materials
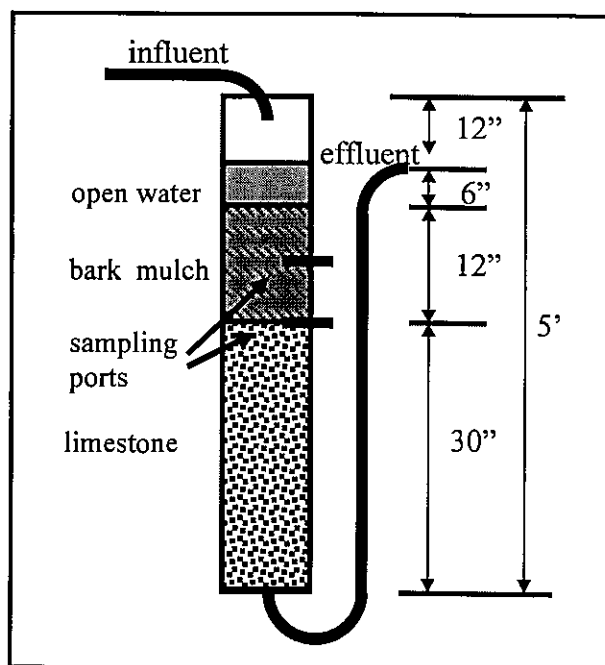

Figure. 5 Cross-sectional view of the laboratory SAPS columns.

the design the organic mulch layer to ensure long term performance. This figure is considered to be conservative due the relatively low biochemical oxygen demand of the bark mulch. Other materials such as composed manure and spent mushroom compost may require shorter residence times given the bioavailability of those materials

Conclusions

Factors controlling generation of alkalinity by SAPS systems include residence time, temperature, and influent water chemistry. Our observations of field systems and laboratory columns lead us to the following statements:

- Residence time appears to affect alkalinity generation as a logarithmic function, indicating that alkalinity generation occurs most rapidly during the first few hours of anoxic water - $CaCO_3$ contact.

- The rate of alkalinity generation by SAPS systems increases in response to increasing Fe concentration and non-Mn acidity of influent waters.
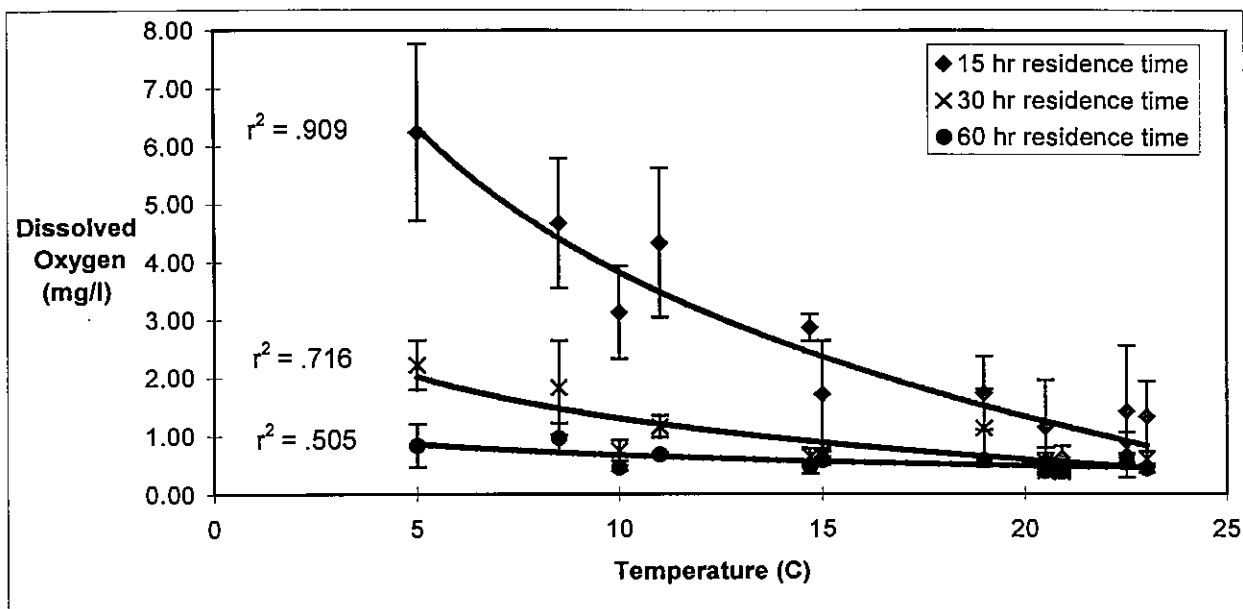
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Figure 5. Relationship between temperature and the average dissolved oxygen below the compost organic layer for the three set of columns. Vertical bars represent on standard deviation.

- The rate of alkalinity generation by SAPS systems may also affected by a seasonal armoring and de-armoring of the limestone in response to fluctuation in dissolved oxygen removal if the organic layer is of insufficient thickness to achieve adequate oxygen removal.

Acknowledgements

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