SUCCESSIVE ALKALINITY-PRODUCING SYSTEMS (SAPS) FOR THE TREATMENT OF ACIDIC MINE DRAINAGE[1]

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Abstract: Constructed wetland treatment system effectiveness has been limited by the alkalinity-producing, or acidity-neutralizing, capabilities of the systems. Anoxic limestone drains (ALD's) have allowed for the treatment of approximately 300 mg/L net acidic mine drainage, but current design guidance precludes using successive ALD's to generate alkalinity in excess of 300 mg/L because of concerns with dissolved oxygen. "Compost" wetlands designed to promote bacterially mediated sulfate reduction are suggested as a means of generating alkalinity required in excess of that produced by ALD's. Compost wetlands create two basic needs of sulfate reducing bacteria; anoxic conditions resulting from the inherent oxygen demand of the organic substrate, and quasi-circumneutral pH values resulting from the dissolution of the carbonate fraction of the compost. However, sulfate reduction treatment area needs are generally in excess of area availability and/or cost effectiveness. Second generation alkalinity-producing systems demonstrate that a combination of existing treatment mechanisms has the potential to overcome current design concerns and effectively treat acidic waters ad infinitum. Successive alkalinity-producing systems (SAPS) combine ALD technology with sulfate reduction mechanisms. SAPS promote vertical flow through rich organic wetland substrates into limestone beds beneath the organic compost, discharging the pore waters. SAPS allow for conservative wetland treatment sizing calculations to be made as a rate function based on pH and alkalinity values and associated contaminant loadings. SAPS potentially decrease treatment area requirements and have the further potential to generate alkalinity in excess of acidity regardless of acidity concentrations.

Additional Key Words: acid mine drainage, passive alkalinity generation, anoxic limestone dissolution.

Introduction

Ferrous iron (Fe^{2+}) is the most common and typically most abundant contaminant found in coal mine drainage. The oxidation and subsequent hydrolysis of Fe^{2+} is the single greatest contributor to the production of mineral acidity associated with coal mine drainage and is the basis of the commonly used term, acid mine drainage (AMD). Any water containing Fe^{2+} is considered to contain a proportional amount of mineral acidity, although a more broad based characterization of the same water may or may not justify the qualifying term of AMD.

Coal mine drainage may be characterized as net acidic, or as net alkaline. Net acidic mine drainage lacks adequate buffering capacity to neutralize the entire complement of protons produced (in this example) by the oxidation and hydrolysis of Fe^{2+}. Net alkaline mine drainage contains sufficient neutralizing potential, generally as bicarbonate (HCO_3^-), to accept any proton acidity generated by the described reactions. Manganese and aluminum are also common mineral-acidity-producing components of coal mine drainage and require consideration in the balancing of net acidic versus net alkaline discharges.

Any coal mine drainage treatment scenario must be predicated on the ultimate neutralization of acidity, resulting from naturally net alkaline drainage, or from the active addition or passive generation of alkaline substances. Constructed wetlands can passively generate alkalinity through either dissimilatory sulfate reduction, carbonate dissolution, or a combination of these two processes. Much attention has been directed toward the functioning of these two processes within the substrate of constructed wetlands (Hedin et al. 1988, McIntire and Edenborn 1990), although a shifting emphasis is being placed on more direct passive alkalinity generation in anoxic limestone drains (ALD's) (Brodie et al. 1991, Skousen and Faulkner 1992).

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ALD's promote carbonate dissolution by placing a relatively large source of carbonate material; e.g., $CaCO_3$, in the flow path of AMD. ALD's are designed to maintain and promote anoxic conditions, and produce alkalinity as HCO_3^-. As AMD exits an ALD and is exposed to atmospheric oxygen, iron oxidation and hydrolysis reactions occur until the entire complement of iron is removed from the discharge, or until the neutralizing potential of the discharge is utilized (the drainage remains net acidic) and the pH of the flow decreases to a level inhibiting further iron precipitation.

ALD's have a finite potential to produce alkalinity that cannot exceed equilibrium with available CO_2; i.e., any increase in CO_2 leads directly to an increase in HCO_3^- (Stumm and Morgan 1970). Proton acidity (H_3O^+) is also converted to alkalinity in ALD's, leading to increased pH values. ALD's must be designed large enough to detain the flows to be treated for a period sufficient for the above reactions to occur (the hydration of CO_2 is a relatively slow process), but there is little empirical evidence that beyond a certain detention time, alkalinity concentrations can be increased (Hedin et al. 1993). The generation of 300 mg/L of alkalinity is considered to be the maximum capability of current ALD design, and although greater alkalinity concentrations have been reported, the median alkalinity production of operating ALD's is likely less than 300 mg/L (personal observations).

Dissolved oxygen and ferric iron (Fe^{3+}) are considered to be the two factors limiting the broader utilization of ALD's. Dissolved oxygen concentrations in the contaminated discharge should preferably be less than 1 mg/L to prevent the oxidation of ferrous to ferric iron, which can armor limestone and limit any further dissolution of the stone. Ferric iron can also be present in flows with pH values less than 3.5, even with low dissolved oxygen concentrations, again presenting armoring concerns. Aluminum presents an additional concern in that aluminum hydroxide formation is strictly pH dependent and can occur within an ALD in the absence of oxygen. Aluminum hydroxides do not appear to armor stone in the fashion of ferric hydroxides, but concerns over physical plugging of the available void space within the stone exist.

ALD implementation has been generally relegated to point of discharge mine flows meeting these guidelines. Mine drainage exposed to atmospheric oxygen typically exceeds 1 mg/L of dissolved oxygen; for this reason, the assumption has been that ALD's cannot be constructed in succession where there is an intermediate aerobic treatment step (Hedin et al. 1993). This assumption has limited attempts to passively treat discharges requiring alkaline additions in excess of net 300 mg/L.

Wetlands referred to as compost wetlands, designed to generate HCO_3^- through sulfate reduction, are recommended to provide additional alkalinity in these instances. Compost wetlands are amenable to further alkalinity generation because they create two basic needs of sulfate reducing bacteria; anoxic conditions as a result of the inherent oxygen demand of the organic matter, and quasi-circumneutral pH values as a result of the dissolution of the carbonate fraction of the compost. However, bacterially mediated sulfate reduction treatment area needs are generally in excess of area availability and/or cost effectiveness, based on the rate and seasonal production of alkalinity generation.

The oxygen demand associated with the bacterial decomposition of organic rich waters is well documented and exaggerated at the water-sediment interface (Stumm and Morgan 1970). It is equally well documented that the underlying described sediments become anoxic, resulting in the reduction of oxidized metals and a shift to anaerobic bacterial metabolism (Wetzel 1975). It is both readily conceivable and well documented that the biogeochemical cycling of nutrients is strongly controlled by oxidation-reduction states that are in turn strongly mediated by bacterial metabolism. Sulfate-reducing sediments in wetlands are always associated with atmospheric oxygen in the sense that they underlie open water and require organic carbon as an energy source. It is a logical progression to investigate the potential development of limestone dissolution zones beneath reduced organic zones.

We will document in this paper that oxygen concentrations are a design consideration rather than a limiting factor to utilizing the benefits of limestone dissolution in passive treatment systems, and that limestone dissolution is already an integral function of many passive treatment systems constructed in open environments. We will report that limestone dissolution after the fashion of ALD's can be and has been incorporated into passive treatment systems after the subject mine drainage has been exposed to the open atmosphere. We will also suggest that successive alkalinity-producing systems (SAPS) can significantly reduce the currently accepted area treatment needs of passive treatment systems. SAPS technology represents another phase in the evolution of passive treatment systems (fig. 1).

The aerobic wetland shown in "A" is an emergent marsh, surface flow system. The compost wetlands referenced in "B" and "C" are also surface flow systems, additionally dependent on anaerobic treatment utilizing microbial sulfate reduction. Relatively large surface areas are required to even theoretically meet the effluent quality depicted in these two scenarios. The SAPS treatment pictured in "D" combines aerobic an anaerobic treatment in vertical flow systems, potentially requiring significantly less area to achieve the goals of "B" and "C".

Site Descriptions

Three passive treatment systems were evaluated for this study. The wetlands are all located in Jefferson County, PA roughly 10 km northwest of the town of Brookville. The Howe Bridge system was constructed in October 1991 and modified in July 1993, the REM system was built in September 1989 and modified in March 1992, and the Schnepp Road system was constructed in July 1992. The Howe Bridge system treats two artesian flow, abandoned gas well discharges, while the REM and Schnepp Road systems treat abandoned deep mine flows.

Each wetland treatment system incorporates an ALD at the point of AMD discharge, followed by an aerobic treatment area, and then additional anoxic and aerobic treatment components. The performance of the ALD's in these systems is reported elsewhere in these proceedings (Hedin and Watzlaf). (The Howe Bridge, REM, and Schnepp Road ALD's were constructed with a greater cross-sectional area than typical ALD designs, averaging 7 m in width and roughly 1.5 m in depth.) This study focuses on the ability to create effective anoxic limestone dissolution treatment components for AMD abatement in open atmospheres. An overview of the dimensions and composition of the three study SAPS is provided in table 1. A typical cross-sectional view of a SAPS treatment component is shown in figure 2.

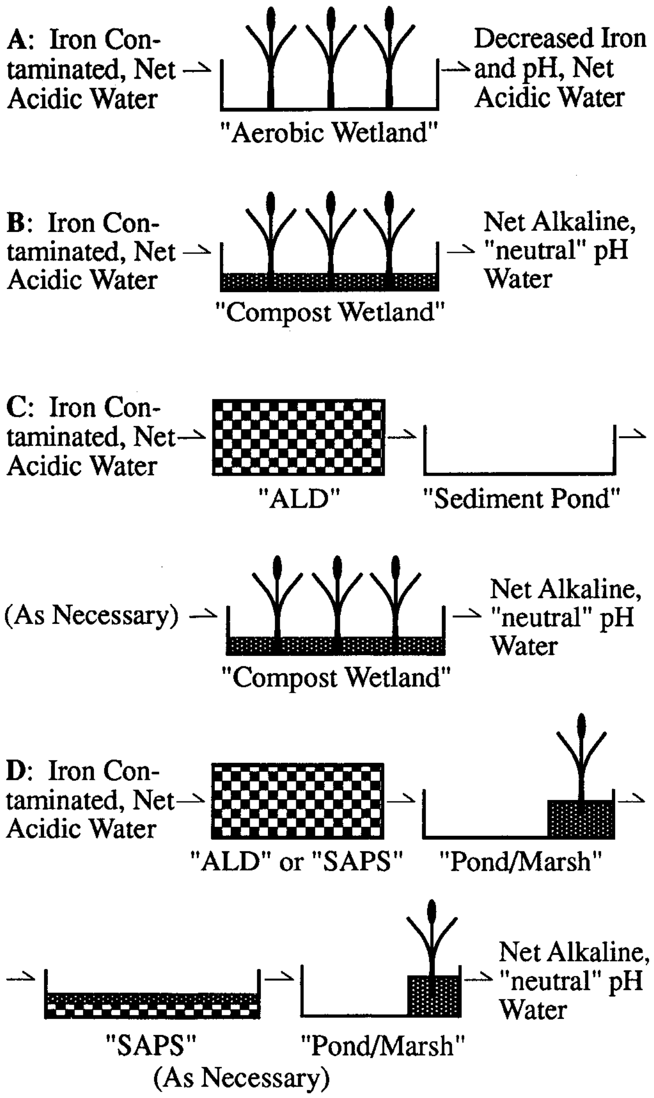

Figure 1. Evolution of passive, wetland treatment technology.

Table 1. Study SAPS treatment component dimensions and materials.

Location	Surface dimensions, m	Freestanding water, m	Substrate composition[1]
Howe Bridge......	60 x 25	1.9	45 cm compost, 45 cm limestone
REM.................	10 x 15	1.6	45 cm compost, 60 cm limestone
Schnepp Road....	10 x 20	1.8	45 cm compost, 60 cm limestone

[1] Spent compost from mushroom industry, limestone (minimum 90% $CaCO_3$) at 1.3 to 1.9 cm diameter.

Methods

Each wetland has been evaluated regularly since its construction. The reported data reflect temporal and spatial characterizations of the treatment processes examined. Chemical and physical analyses were made directly in the field and in the authors' laboratory facilities. Field pH and Eh determinations and temperatures were made with an Orion model 250A meter and an Orion temperature compensating pH triode. Alkalinity was determined directly in the field with the same meter using an Orion total alkalinity test kit. Sample acidity was determined in the laboratory by boiling with hydrogen peroxide and titration to pH 8.3 using a Fisher ACCUMET model 230A pH/Ion meter. Alkalinity and acidity are reported in milligrams per liter as $CaCO_3$ equivalents. Dissolved oxygen was determined directly in the field with a YSI model 50B temperature compensating dissolved oxygen meter and polarographic probe. Total iron and ferrous iron were determined using the 1,10-phenanthroline method with a Milton Roy Co. Spectronic 20 D spectrophotometer. Manganese was determined by the periodate oxidation method, aluminum by the aluminon method, and sulfate by the barium sulfate turbidmetric method, all using the referenced spectrophotometer. Calcium was directly titrated by the EDTA titration method. All analyses follow Standard Methods for the Examination of Water and Wastewater (American Public Health Association 1985). Flows were determined by "bucket and stopwatch".

This study also utilizes data collected by the U.S. Bureau of Mines (BOM) Pittsburgh Research Center . Iron, manganese, aluminum, magnesium, and calcium were determined in the BOM laboratory in 0.45-*u*m membrane filtered and acidified samples using inductively-coupled argon plasma spectroscopy. Ferrous iron was determined by the BOM on acidified samples following the potassium dichromate method, and sulfate was determined through reactions with barium chloride and thorin as an endpoint indicator (Hedin et al., in press). Field pH and alkalinity were determined as above.

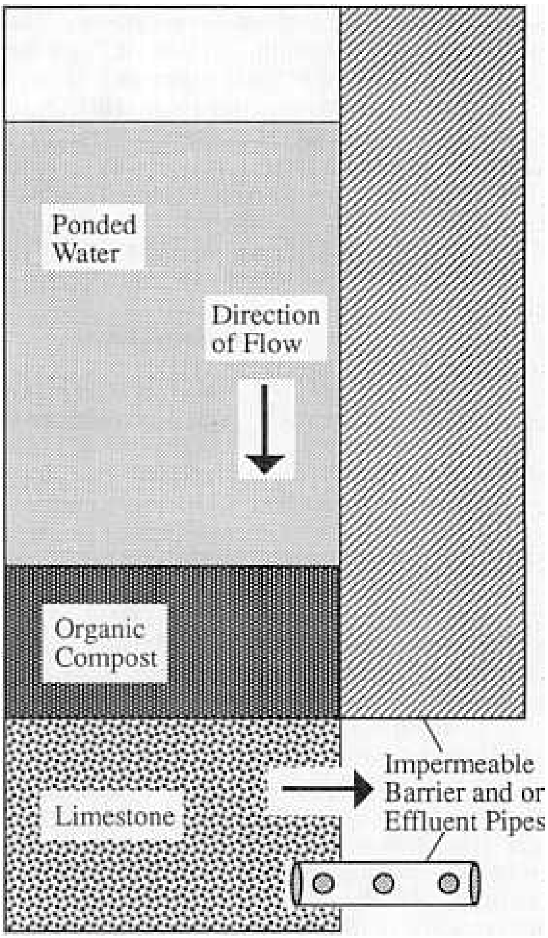

Figure 2. Typical cross-sectional view of a successive alkalinity producing system (SAPS) treatment component.

Results

The study results are predicated on several basic principles and assumptions. Increases in alkalinity and/or decreases in acidity are considered to be equal for these discussions. Any measured increase in calcium concentration between two sample locations is assumed to be proportionally related to alkalinity production, as in equation 1. This fraction of alkalinity will be referred to throughout this study as "calcium alkalinity".

$$H_2CO_3 + CaCO_3 \text{ ----> } Ca^{2+} + 2HCO_3^- \qquad (1)$$

Alkalinity production associated with sulfate reduction can similarly be determined directly by decreases in sulfate concentrations between two points, as in equation 2.

$$2CH_2O + SO_4^{2-} \text{ ----> } H_2S + 2HCO_3^- \qquad (2)$$

Sulfate, however, can also coprecipitate with ferric hydroxides and is prone to more analytical variation (less accurate measure) than many parameters. More weight is therefore placed on net changes in acidity associated with limestone dissolution for this study.

The physical construction of the study sites does not allow for direct and/or accurate measurement of flow at all sample locations. While significant perturbations to the treatment systems are not known for these sites, water gains and losses do occur. The effects of these gains and losses have been compensated for through the measurement of magnesium, a conservative ion in wetland treatment systems. The effluent magnesium concentrations for this study have been divided by the influent magnesium values to determine a reasonable dilution-concentration factor. The effluent parameters have been "corrected" by dividing the effluent concentrations by the applicable dilution-concentration factors. The dilution-concentration factors were typically slightly less than 1 and had a minor effect on the reported data. The purpose of this study is to report treatment principles and trends. Treatment comparisons are not made between the systems, so concentrations rather than loadings (as in grams per day) were used. Passive treatment based on biological mechanisms decreases with decreasing temperatures. The emphasis of this study has been placed on winter treatment data to provide a conservative and accurate assessment of SAPS applicability.

Table 2 displays the increases in alkalinity and concurrent decreases in acidity attributable to $CaCO_3$ dissolution in the Howe Bridge SAPS for two consecutive winters. Data from two consecutive summer samples have been included to demonstrate the seasonal effectiveness of the biological component of alkalinity production through microbially mediated sulfate reduction. Table 3 displays the means and ranges of other measured parameters within the Howe Bridge SAPS for the same sample dates.

Periodic measurements of dissolved oxygen in the Howe Bridge SAPS consistently displayed values less than 0.2 mg/L in the effluent, while the influent concentrations ranged between 5 and 10 mg/L. The entire complement of iron in the effluent is reduced, indicating that armoring of the limestone within the SAPS should not be of concern. Measurements of Eh at the effluent discharge pipe were generally less than 20 millivolts, subject to atmospheric interference. The discharge pipe of this system has never accumulated any typically orange ferric hydroxide precipitates, while the exposed surface area of the SAPS component is characteristically orange. The discharge pipe does accumulate black deposits of iron monosulfides, which are converted to ferric hydroxides when exposed to oxygen.

Table 2. Alkalinity produced and acidity removed through limestone dissolution, Howe Bridge SAPS, January 23, 1992 through July 27, 1993.

Sample Date	Calcium Alkalinity[1]	Acidity[1] Removed	% Removal Attributable to Calcium Alkalinity
January 23, 1992.....	174.5	207	84
February 21, 1992...	134.8	202	67
July 15, 1992...........	174.5	366	48
January 18, 1993.....	125.0	134	93
February 22, 1993...	90.3	118	77
July 27, 1993...........	148.0	344	43

[1] Alkalinity and acidity are presented as mg/L of $CaCO_3$ equivalent.

The chemistry of the influent sample changes dramatically over a course of 3 to 10 m and is not totally representative of the level of treatment occurring within the Howe Bridge SAPS. The influent sample location is at the discharge point of a settling pond and provides a convenient sampling station. The AMD falls roughly 1 m over a rock spillway to a shallow aerobic wetland (compost substrate) that is approximately 20 m wide by 30 m long and sparsely planted with *Typha latifolia.* The remaining alkalinity in the reported influent sample is utilized by the precipitation of an additional amount of iron at the base of the spillway and within the shallow marsh area, with a consistent chemistry at the actual SAPS surface of zero alkalinity and a pH of roughly 3.0. This observed decrease in pH is a common phenomenon that has limited the passive treatment of decidedly net acidic discharges, so it is significant to note that the SAPS discharge of this water reflects a pH of about 6.0.

Table 4 displays the increases in alkalinity and concurrent decreases in acidity attributable to $CaCO_3$ dissolution in the REM SAPS over the course of 1 yr. Seasonal variations resulting from microbially mediated sulfate reduction are not nearly as evident in this SAPS as at Howe Bridge, possibly because of the much smaller relative treatment area at REM. Table 5 presents the means and ranges of other measured parameters within the REM SAPS for these same sample dates.

Table 3. Influent-effluent water quality, Howe Bridge SAPS, January 23, 1992 through July 27, 1993, effluent corrected for dilution-concentration.

	(Influent)			(Effluent)		
Parameter[1]	n	Mean	Range	n	Mean	Range
pH, s.u...........	6	NA	3.29 - 6.14	6	NA	5.84 - 6.49
Acidity..........	6	321.0	207 - 396	6[2]	92.6	0 - 278.8
Calcium.........	6	182.4	136.0 - 230.8	6	230.2	192.2 - 279.4
Magnesium....	6	94.8	67.1 - 114.6	6	99.8	77.8 - 123.6
Sulfate...........	6	1,189	875 -1,407	6	1,033	621 -1,258
Fe^{2+}..............	6	193.0	149 - 231	6	102.0	47.7 - 159.0
Fe^{3+}..............	6	1.6	0 - 9.6	6	0	0

NA Not applicable.

[1] Acidity is presented as mg/L of $CaCO_3$ equivalent; all other values are in mg/L.

[2] n = 3 < 10 mg/L readings, calculated as zeroes.

Periodic measurements of dissolved oxygen at this system also consistently displayed values less than 0.2 mg/L in the effluent, and concentrations ranging between 5.0 and 10 mg/L in the influent. The majority of iron at the effluent point is reduced, although a measurable amount of ferric iron remains, raising design concerns with potential armoring of the limestone. This SAPS component was designed with the capability to regulate water levels, and the system was completely drained and the substrate examined in November 1993. The surface of the organic substrate had accumulated up to 5 cm of iron hydroxides, but these precipitates did not extend to any degree into the compost substrate, and examination of the limestone over its entire depth did not indicate any armoring of the limestone. The measurable ferric iron found in the effluent may result from a complexing of soluble ferric iron with humic derivatives common to the rich organic compost substrate (Shapiro 1957), or may be the result of the analytical method in that ferric iron is measured indirectly.

As a demonstration of the potential effectiveness of SAPS technology, we have included data from the aerobic treatment system immediately upflow of the REM SAPS (table 6). This treatment component carries 10 cm of water above a 30 cm compost substrate and is densely vegetated with *Typha latifolia*. This marsh component has 50% more surface

Table 4. Alkalinity produced and acidity removed through limestone dissolution, REM SAPS, July 15, 1992 through July 13, 1993.

Sample Date	Calcium Alkalinity[1]	Acidity[1] Removed	% Removal Attributable to Calcium Alkalinity
July 15, 1992...........	78.8	83.5	94
August 19, 1992......	66.8	89.9	74
January 18, 1993.....	78.6	81.1	97
February 8, 1993.....	71.5	89.5	80
March 4, 1993..........	80.2	82.0	98
May 4, 1993.............	108.7	90.8	120
July 13, 1993............	74.7	79.1	82

[1] Alkalinity and acidity are presented as mg/L of $CaCO_3$ equivalent.

treatment area than the associated SAPS treatment unit, yet removes approximately 85% less acidity than the SAPS on a mean basis for these sample dates. The surface of the compost in this area is coated with up to 10 cm of ferric hydroxide, while the compost is black and rich in hydrogen sulfide odor when disturbed. The presence and dissolution of limestone within the anoxic compost (the compost contains approximately 10% limestone by weight) is an important treatment factor in wetlands dependent on alkalinity generation through sulfate reduction. Sulfate reducing bacteria, with *Desulfovibrio* being the most ubiquitous in AMD affected areas, are not effective at pH values less than 5.0 (Postgate 1984). However, the relatively small decrease in acidity here suggests that there is limited potential for mixing of the substrate pore waters with the discharging surface waters.

Table 5. Influent-effluent water quality, REM SAPS, July 15, 1992 through July 13, 1993, effluent corrected for dilution-concentration.

	(Influent)			(Effluent)		
Parameter[1]	n	Mean	Range	n	Mean	Range
pH, s.u..........	7	NA	2.97 - 3.30	7	NA	3.61 - 4.22
Acidity..........	7	173.0	146 - 208	7	87.9	65 - 117
Calcium.........	7	187.5	171.0 - 209.7	7	213.7	196.8 - 243.6
Magnesium....	4	94.2	80.8 - 110.0	4	95.8	84.4 - 107.0
Sulfate..........	7	1,008	895 -1,029	7	972	883 -1,203
Fe^{2+}..............	7	2.5	0.8 - 5.4	6	14.7	3.6 - 31.7
Fe^{3+}..............	7	21.3	13.6 - 30.5	6	1.8	0 - 5.6

NA Not applicable.

[1] Acidity is presented as mg/L of $CaCO_3$ equivalent; all other values are in mg/L.

Table 6. Influent-effluent water quality, REM "Compost Wetland", July 15, 1992 through July 13, 1993, effluent corrected for dilution-concentration.

	(Influent)			(Effluent)		
Parameter[1]	n	Mean	Range	n	Mean	Range
pH, s.u..........	7	NA	3.02 - 3.32	7	NA	2.96 - 3.21
Acidity..........	7	207.4	161 - 234	7	195.4	163 - 228
Calcium.........	7	209.0	182.0 - 225.9	7	210.8	185.6 - 230.8
Magnesium....	4	106.6	92.5 - 120.0	4	98.3	86.2 - 113.0
Sulfate..........	7	1,180	963 -1,314	7	1,114	970 -1,313
Fe^{2+}..............	7	55.0	36.4 - 73.0	7	4.1	1.8 - 11.9
Fe^{3+}..............	7	8.5	2.0 - 17.1	7	26.0	15.7 - 32.3

NA Not applicable.

[1] Acidity is presented as mg/L of $CaCO_3$ equivalent; all other values are in mg/L.

The Schnepp Road SAPS also produces a significant measure of calcium alkalinity in an open environment (tables 7 and 8). The significant feature once again is that aerobic surface waters with dissolved oxygen values ranging from roughly 5 to 9 mg/L are made anoxic within the SAPS, discharging at measured values of 0.2 mg/L or less.

The results from these three SAPS indicate that the limitations dissolved oxygen places on ALD design can be eliminated in SAPS through the combined use of open water and high organic content substrate overlying a limestone treatment zone. The SAPS design provides a relatively sound assurance that the AMD contacting the limestone will be anoxic. SAPS design mimics natural lake biogeochemistry in much the same way that aerobic wetland treatment mimics natural marshes. The oxygen content of the hypolimnion, or deeper portion, of natural lakes rich in organic matter is rapidly depleted through bacterial respiration. Oxygen consumption is greatest at the sediment-water interface, and even in well aerated surface waters, oxygen does not generally diffuse more than several centimeters into the sediments of a standing body of water (Mortimer 1971).

Table 7. Alkalinity produced and acidity removed through limestone dissolution, Schnepp Road SAPS, July 26, 1992 through July 13, 1993.

Sample Date	Calcium Alkalinity[1]	Acidity[1] Removed	% Removal Attributable to Calcium Alkalinity
July 15, 1992...........	79.3	85	93
August 19, 1992......	76.2	84	91
January 18, 1993.....	70.1	69	102
July 13, 1993...........	79.3	75	106

[1] Alkalinity and acidity are presented as mg/L of $CaCO_3$ equivalent.

The oxygen demand, chemical and biological, per unit area of the SAPS substrate will determine the depth of penetration and the concentration of oxygen available to the sediments. These same assurances cannot necessarily be made for an ALD whose water supply may undergo periodic fluctuations in quality and/or dissolved oxygen concentrations within the associated mine pool or mine spoil. Additionally, with ferric iron converted to ferrous iron in the reducing zone of the sediment-water interface of the SAPS treatment area, a water chemistry consistent with present ALD design criteria is met. Table 9 compares the calcium alkalinity production realized at both the Howe Bridge SAPS and the Howe Bridge ALD for the same dates to emphasize both the potential of SAPS treatment and the consistency with ALD alkalinity generation.

Table 8. Influent-effluent water quality, Schnepp Road SAPS, July 15, 1992 through July 13, 1993, effluent corrected for dilution-concentration.

	(Influent)			(Effluent)		
Parameter[1]	n	Mean	Range	n	Mean	Range
pH, s.u...........	4	NA	5.86 - 6.20	4	NA	6.29 - 6.88
Acidity..........	4	83.5	69 - 102	4	5.2	0 - 18
Calcium.........	4	196.2	184 - 212	4	221.2	207 - 237
Sulfate...........	4	750	654 - 846	4	717	622 - 810
Fe^{2+}..............	4	1.6	0.4 - 3.6	4	1.0	0.6 - 1.2
Fe^{3+}..............	4	19.0	16.5 - 21.2	4	0.1	0 - 0.2

NA Not applicable.

[1] Acidity is presented as mg/L of $CaCO_3$ equivalent; all other values are in mg/L.

Variations in alkalinity production and pH adjustment within the three study SAPS are believed to be a function of detention time within the limestone treatment zones. Limestone dissolution in ALD's is viewed as a rate function with 12 hrs. currently purported as a minimum detention time for maximum alkalinity production (Hedin et al. 1993 and personal observations by the authors). The Howe Bridge SAPS approaches this detention time, while the REM and Schnepp Road SAPS have variable detention rates of 4 to 8 hrs.

Physical plugging of the limestone within the study SAPS has not presented any known hydraulic problems. The pressure exerted by the downward force of the freestanding pool above the substrate materials in the SAPS should actually reduce the risk of physical plugging as compared to waters flowing laterally through conventional ALD's or other subsurface treatment systems. Lateral flow systems are designed to maintain their entire flow beneath the surface and have historically failed because of substrate pore plugging with subsequent water mounding and a surface expression of the waters to be treated. The SAPS design, with adequate freeboard, allows for any build up of static head required (if any) to continue "pushing" water downward and through the substrate material. Additionally, the bottom discharge of a SAPS design in essence creates a treatment pond with a bottom or breastwork that leaks, further maintaining the integrity of the designed flow path.

Table 9. Alkalinity produced through limestone dissolution, Howe Bridge SAPS and ALD, January 23, 1992 through July 27, 1993.

Sample Date	Calcium Alkalinity SAPS[1]	Calcium Alkalinity ALD[1]
January 23, 1992......	174.5	179.5
February 21, 1992....	134.8	149.6
July 15, 1992............	174.5	163.6
January 18, 1993......	125.0	167.2
February 22, 1993....	90.3	164.1
July 27, 1993............	148.0	168.7

[1] Alkalinity is presented as mg/L of $CaCO_3$ equivalent.

Discussion and Conclusions

Most constructed wetlands of generic design to date have been limited in their effectiveness by the alkalinity-producing, or acidity-neutralizing, capabilities of the systems. Alkalinity generation for decidedly net acidic AMD based on microbially mediated sulfate reduction is simply not practical or cost effective. The ability to develop SAPS as alkalinity generating systems capable of producing an essentially infinite amount of alkalinity obviously broadens the scope of passive treatment.

Iron oxidation and hydrolysis reactions are strongly controlled by solution pH and dissolved oxygen. Rate constants for the formation of iron complexes increase from minutes and hours at circumneutral pH values, to months and years as pH values decrease below 4 (Sung and Morgan 1980, Stumm and Morgan 1970). The greater the buffering capacity of a given water, the greater the ability of that water to maintain a pH amenable to rapid metal removal. Adequate alkalinity must be made available in treatment situations to at least effectively neutralize the acid producing capabilities of the target metal contaminants. In that metal oxidation and hydrolysis reactions produce acidity, what is considered adequate alkalinity can be site specifically calculated from the sum equivalents of measured acid producing metals.

Current passive treatment sizing criteria for iron are based on an iron removal rate per given area. This method of sizing passive treatment systems applies a linear function (area) to a nonlinear function (removal rate). Iron removal is a function of area only as area relates to detention time and should be determined instead as a removal rate per rate limiting functions; i.e., pH and dissolved oxygen. Diffusion of oxygen into any given body of water can be assumed to be relatively constant for that body of water and can be determined and used as a constant for sizing considerations.

Sizing calculations can therefore be based upon the pH and buffering capacity of the AMD. Conservative a priori sizing calculations can be made for expected pH and alkalinity values, independent of whether those values are the result of ALD or SAPS origin. Iron, and therefore acidity, removal can and should occur within settling ponds designed to retain the flows for the period necessary to utilize the alkalinity buffer and decrease the pH to a range of 4.0 to 4.5. At this point, again through a priori calculations, SAPS can be implemented to the degree necessary to effectively neutralize the required amount of acidity for a given discharge.

Treatment based on detention can be more cost effectively managed in open water ponds than in constructed, shallow marsh wetlands because of obvious volume to area ratio advantages. Acidity neutralization of AMD (through the removal of iron) can be based on rate functions dependent on known levels of pH, alkalinity, and dissolved oxygen. Sizing calculations for iron removal and acidity neutralization therefore become a product of the contaminant loading, which is dependent on concentrations and flows (Kepler and McCleary, unpublished research).

SAPS provide a heretofore lacking component of effective AMD treatment based on existing and proven principles. Conventional *Typha* dominated wetland areas should be utilized between SAPS components to aid in suspended solids removal and to provide a sustainable supply of oxidizable organic matter to the SAPS units. Ongoing efforts are being directed towards maximizing detention time within the SAPS while minimizing the area necessary to utilize the alkalinity produced by the SAPS in the removal of target metals, particularly iron.

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