# SUCCESSIVE ALKALINITY-PRODUCING SYSTEMS (SAPS)[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 where greater than 300 mg/L of alkalinity is required. "Compost" wetlands designed to promote bacterially mediated sulfate reduction are suggested as a means of generating alkalinity in these instances, but compost wetland needs are generally in excess of area availability and/or cost effectiveness. Second generation alkalinity-producing systems have proven that a combination of existing treatment mechanisms can overcome current design concerns and effectively treat acidic waters ad infinitum. Successive alkalinity-producing systems **(SAPS)** combine ALD technology with sulfate reduction mechanisms; promoting a vertical flow through organic substrates, into limestone beds, and ultimately discharging the pore waters. SAPS allow for conservative wetland treatment sizing calculations to be made as a rate function based on pH, alkalinity values, and associated contaminant loadings; and significantly decrease treatment area requirements.

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

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## Introduction

Appalachia's coal mining impacted waterways are now realizing their first real opportunity for biological recovery. The widespread utilization of wetland treatment systems in the early 1980's ushered in this potential, but these first efforts routinely fell short of expectations. Reviews such as those by Wieder (1989) inappropriately evaluated passive treatment system efficacy against a set of somewhat arbitrary standards established by the 1972 Federal Clean Water Act, and served to impede the development of the technology within the private sector. Wieder's evaluations failed to recognize that these initial wetlands functioned to within the limits of their design; i.e., the improvements realized in water quality were actually predictable and complete.

There can be little debate that since their introduction over a decade ago, passive treatment systems have become increasingly effective in abating acid mine drainage (AMD). These successes have led to an ever growing number of private/public watershed restoration endeavors, and a greater acceptance of passive treatment by the environmental regulatory community. With this acceptance has come a need to permit and review; and therefore, the necessity of a design guidance document.

The most widely used document of this type was published by the U.S. Bureau of Mines (BOM) in 1994; providing excellent design guidance if used in the manner it was intended. However, this same work is also serving to limit the continued development of passive treatment technology in that the regulatory community hesitates to consider applications outside of the relatively small set of design criteria established in the document. It is critical to understand that (likely without exception) every wetland treatment system evaluated by the BOM was constructed to treat a discharge outside the realm of accepted treatability at the time of construction; yet these very systems have become the design standards for today's efforts.

Additionally, 10 of the 13 wetlands evaluated in the development of the document were constructed in or prior to 1989, with the remaining three constructed between 1990 and 1992. The earliest designs were based on a completely different knowledge base than we have available today; and in actuality, it is these systems that have provided us with the ability to implement ever more successful designs. High flows, high acidities (> 300 mg/L), and aluminum are viewed by many as serious impediments to passive treatment success. These parameters must be addressed via passive means if the goals of stream restoration are to be met. It is counterproductive to the restoration effort to limit today's treatment needs by the works of up to a decade ago; rather than using this knowledge in a manner to advance the potentials of passive treatment.

This introduction provides the premise for the following paper; i.e., that we cannot advance passive treatment technology without addressing water quality problems outside the currently accepted range of treatment. The success of effective acid mine drainage treatment is in essence totally contingent upon acidity neutralization and/or alkalinity generation. The early passive treatment work provided for today's Successive Alkalinity Producing Systems (SAPS), which have been producing alkalinity for over four years under conditions not consistent with the BOM's recommendations. We will explain the basic mechanisms of SAPS' treatment technology along with an overview of several functioning SAPS in an attempt to broaden the base of design guidance decisions.

## Background

Net acidic coal mine drainage lacks adequate buffering capacity to neutralize the entire complement of protons produced by (typically) the oxidation and hydrolysis of iron and/or aluminum and/or manganese. Constructed wetlands can passively generate alkalinity through either dissimilatory sulfate reduction, carbonate dissolution, or a combination of these two processes. Efforts were directed towards sulfate reduction in the late 1980's (Hedin et al. 1988, McIntire and Edenborn 1990); although today the emphasis is shifting towards limestone dissolution. This mechanism is typically carried out within anoxic limestone drains (ALD's) (Brodie et al. 1991, Hedin et al. 1994, Sterner and Skousen (this proceeding), although recent work by Ziemkiewicz (this proceeding) indicates that open limestone trenches may play an important treatment role as well.

ALD's are designed to place a relatively large source of carbonate material; e.g., $CaCO_3$, in the flow path of AMD. The systems 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 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 $CO_2$ (Stumm. and Morgan 1970), and are routinely considered to have a maximum potential of generating 300 mg/L of alkalinity.

Dissolved oxygen, ferric iron ($Fe^{3+}$), and aluminum are considered to be the primary factors limiting the broader utilization of ALD's. All of these factors have led to concerns with armoring and or physical plugging of the ALD's, and while failed ALD's exist, it is likely that many of these failures can be more directly attributed to physical design features and only indirectly to mine drainage chemistry. However, ALD implementation has been generally relegated to point of discharge mine flows exhibiting less than 1 mg/L of the three stated parameters, thereby limiting 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 generally recommended to provide alkalinity when faced with any of the above scenarios. Compost wetlands are amenable to 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 this source of alkalinity.

SAPS technology evolved from a combination of these two technologies. Oxygen concentrations are a design consideration rather than a limiting factor in utilizing the benefits of limestone dissolution in passive treatment systems; as supported by the dependence of limestone within the organic matter of sulfate reducing wetlands. Additionally, the oxygen demand associated with the bacterial decomposition of organic rich waters; i.e., compost wetlands, is well documented (Stumm and Morgan 1970, Wetzel 1975). It was a logical progression to investigate the potential development of limestone dissolution zones beneath reduced organic zones.

## Site Descriptions

Four SAPS will be discussed in this evaluation. All four systems are located in Jefferson County, Pennsylvania within the Mill Creek (Clarion River Basin) watershed. The Howe Bridge SAPS was constructed in October of 1991, the REM SAPS was built in March of 1992, the Schnepp Road system was constructed in July of 1992, and the Filson SAPS was completed in August of 1994. The Howe Bridge system treats two artesian flow, abandoned gas well discharges, the REM and Schnepp Road systems treat abandoned deep mine flows, and the Filson project collects untreated surface mine discharges.

Each wetland treatment system incorporates an ALD at the point of AMD discharge, followed by an aerobic treatment area, a SAPS, and then additional anoxic and/or aerobic treatment components. An overview of the dimensions and composition of the four study SAPS is provided in Table 1. A typical cross-sectional view of a SAPS treatment component is shown in Figure 1.

Table 1. SAPS dimensions and materials.

| Identification | Surface Area (m) | Free-Standing Water (m) | Substrate Composition[1] |
|---|---|---|---|
| Howe Bridge..... | 25 x 60 | 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 |
| Filson................ | 20 x 55 | 1.8 | 45 cm compost, 60 cm limestone |

[1] Spent mushroom compost , limestone (minimum 90% CaCO3) at 1.3 to 1.9 cm diameter.

## Methods

Each **SAPS** has been evaluated regularly since its construction, so that 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, 1 0-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".



Figure 1. Typical cross-sectional view of a successive alkalinity producing system (SAPS) treatment component.

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 and will be referred to throughout this study as "calcium alkalinity". Alkalinity production associated with sulfate reduction can similarly be determined directly by decreases in sulfate concentrations between two points; although
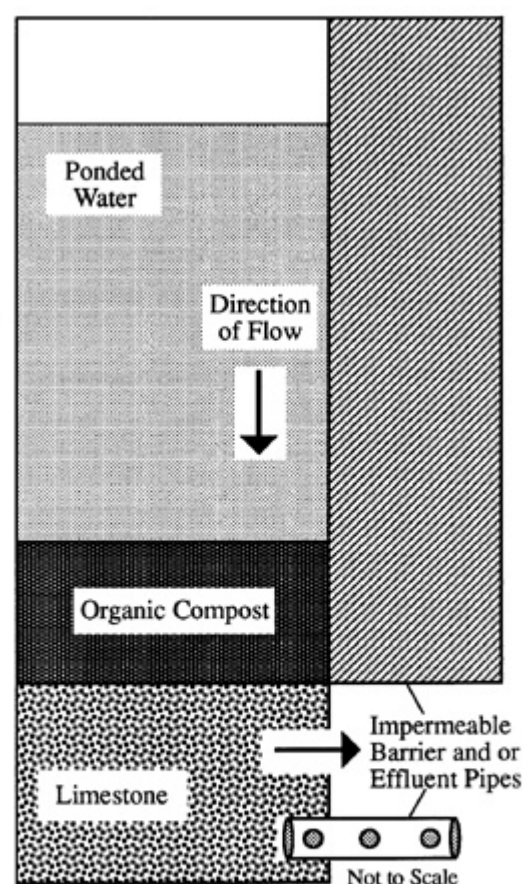
sulfate can also coprecipitate with ferric hydroxides and is prone to more analytical variation (less accurate measure) than many parameters. More weight is therefore placed on net changes in acidity associated with limestone dissolution for this study.

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 were considered through the measurement of magnesium, a conservative ion in wetland treatment systems. Dilution/concentration factors utilizing magnesium were typically slightly less than 1; thereby having a negligible 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 have been used. Passive treatment based on biological mechanisms decreases with decreasing temperatures, so the emphasis of this study has been placed on winter treatment data to provide a conservative and accurate assessment of SAPS applicability. Reported data is for the SAPS component of the treatment systems only.

## Results

Table 2. displays the increases in alkalinity and concurrent decreases in acidity related to $CaCO_3$ dissolution in the Howe Bridge SAPS for four consecutive winters and three consecutive summers. noted seasonal variation is directly attributable to the biological component of alkalinity production through sulfate reduction during the warmer months. The influent pH typically ranges between 2.8 and 3.5 s.u., and discharges between 5.3 and 6.3 s.u. dependent on flow rate. Experiments at this site with variable flow rates have clearly indicated that the degree of alkalinity production and discharge pH values are dependent on AMD residence time within the SAPS; with the lower values expressed at lower residence times.

Table 2. Alkalinity produced and acidity removed through limestone dissolution[1], Howe Bridge SAPS, January 23, 1992 through January 26, 1995.

| Sample Date | Calcium Alkalinity | Acidity Removed | % Removal Attributable to Calcium Alkalinity |
|---|---|---|---|
| 01/23/92 | 174 | 207 | 84 |
| 07/15/92 | 174 | 366 | 48 |
| 01/18/93 | 125 | 134 | 93 |
| 07/27/93 | 148 | 344 | 43 |
| 01/20/94 | 136 | 162 | 84 |
| 07/29/94 | 145 | 328 | 44 |
| 01/26/95 | 141 | 156 | 90 |

[1] alkalinity & acidity as mg/L, $CaCO_3$ equivalent

Table 3. displays the increases in alkalinity and concurrent decreases in acidity attributable to $CaCO_3$ dissolution in the **REM SAPS** over the course of three consecutive summers and two consecutive winters. Seasonal variations resulting from microbially

Table 3. Alkalinity produced and acidity removed through limestone dissolution[1], REM SAPS, August 19, 1992 through August 12, 1994.

| Sample Date | Calcium Alkalinity | Acidity Removed | % Removal Attributable to Calcium Alkalinity |
|---|---|---|---|
| 08/19/92 | 67 | 90 | 74 |
| 01/18/93 | 79 | 81 | 98 |
| 07/13/93 | 75 | 79 | 95 |
| 01/20/94 | 70 | 73 | 96 |
| 08/12/94 | 66 | 87 | 76 |

[1] alkalinity & acidity as mg/L, $CaCO_3$ equivalent

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. The influent pH here typically ranges between 3.0 and 3.3 s.u., and discharges between 3.6 and 4.3 s.u.

The REM SAPS was designed with the capability to regulate water levels, and the system was completely drained and the substrate examined in November of 1993. The surface of the organic substrate had accumulated up to 5 cm of iron oxyhydroxides, but these precipitates did not extend into the compost substrate; and examination of the limestone over its entire depth did not indicate any armoring of the limestone.

The Schnepp Road SAPS also produces a significant measure of calcium alkalinity in an open environment as shown in Table 4. The influent pH here is roughly 5.6 to 5.8 s.u., with effluent values typically greater than 6.9 s.u. The consistency of calcium alkalinity production through the seasons is again evident.

The most recently constructed SAPS in this report, the "Filson" site, collects and treats both surface waters and subsurface discharges intercepted by the construction of the SAPS. This system treats the largest flow, at approximately 175 lpm, and has shown consistent values since start-up (Table 5.) Influent pH values vary between 3.5 and 4.5 s.u. and discharge between 6.3 and 6.6 s.u.

Periodic measurements of dissolved oxygen at each of the four SAPS have consistently displayed values of less than 0.2 mg/L in the effluents; while the influent concentrations have ranged between 5 and 10 mg/L. Effluent Eh values are generally less than 20 millivolts, subject to atmospheric interference during measurement. Essentially the entire complement of iron in each system enters the SAPS as $Fe^{3+}$ and discharges as $Fe^{2+}$, indicating that armoring of the limestone within the SAPS should not present a concern. The discharge pipes of these systems have never accumulated any typically orange ferric oxyhydroxide precipitates, while the exposed surface areas of the SAPS' components are characteristically orange.

Table 4. Alkalinity produced and acidity removed through limestone dissolution[1], Schnepp Road SAPS, July 15, 1992 through July 19, 1994.

| Sample Date | Calcium Alkalinity | Acidity Removed | % Removal Attributable to Calcium Alkalinity |
|---|---|---|---|
| 07/15/92 | 79 | 85 | 93 |
| 01/18/93 | 70 | 69 | 101 |
| 07/13/93 | 79 | 75 | 105 |
| 01/20/94 | 72 | 74 | 97 |
| 07/19/94 | 69 | 81 | 85 |

[1] alkalinity & acidity as mg/L, CaCO3 equivalent

Table 5. Alkalinity produced and acidity removed through limestone dissolution[1], Filson SAPS, August 26, 1994 through February 10, 1995.

| Sample Date | Calcium Alkalinity | Acidity Removed | % Removal Attributable to Calcium Alkalinity |
|---|---|---|---|
| 08/26/94 | 225 | 275 | 82 |
| 02/10/95 | 218 | 231 | 94 |

[1] alkalinity & acidity as mg/L, CaCO3 equivalent

Variations in alkalinity production and pH adjustment within the four study SAPS are in part a function of detention time within the limestone treatment zones. Limestone dissolution in ALD's is viewed as a rate function with 12 hours currently purported as a minimum detention time for optimum alkalinity production (Hedin et al. 1994 and personal observations). The Howe Bridge and Filson SAPS approach this detention time, while the REM and Schnepp Road SAPS have variable detention rates of 4 to 8 hours.

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 to continue "pushing" water downward and through the substrate material.

## Discussions and Conclusions

The results from these SAPS applications indicate that the limitations dissolved oxygen places on ALD design can be eliminated through the combined use of open water and high organic content substrate. 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.

Iron oxidation and hydrolysis reactions are strongly controlled by solution pH, buffered by alkalinity, 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.

Current passive treatment sizing criteria for iron are based on relatively area extensive, iron removal rates per given area. Treatment based on detention considerations as with the SAPS can be more cost effectively managed in open water ponds than in shallow marsh wetlands because of significant volume to area ratio advantages. Acidity neutralization of AMD (through the removal of iron) should therefore 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). These features in combination allow for SAPS based treatment to be less area intensive than commonly used sizing criteria.

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. 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 and will benefit the field as yet another building block in addressing the next tier of "untreatable" AMD.

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