

OVERVIEW OF PASSIVE SYSTEMS FOR TREATING ACID MINE DRAINAGE

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Introduction

Active chemical treatment of AMD to remove metals and acidity is often an expensive, long term liability. In recent years, a variety of passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated mine waters. The primary passive technologies include constructed wetlands, anoxic limestone drains (ALD), successive alkalinity producing systems (SAPS), limestone ponds, and open limestone channels (OLC).

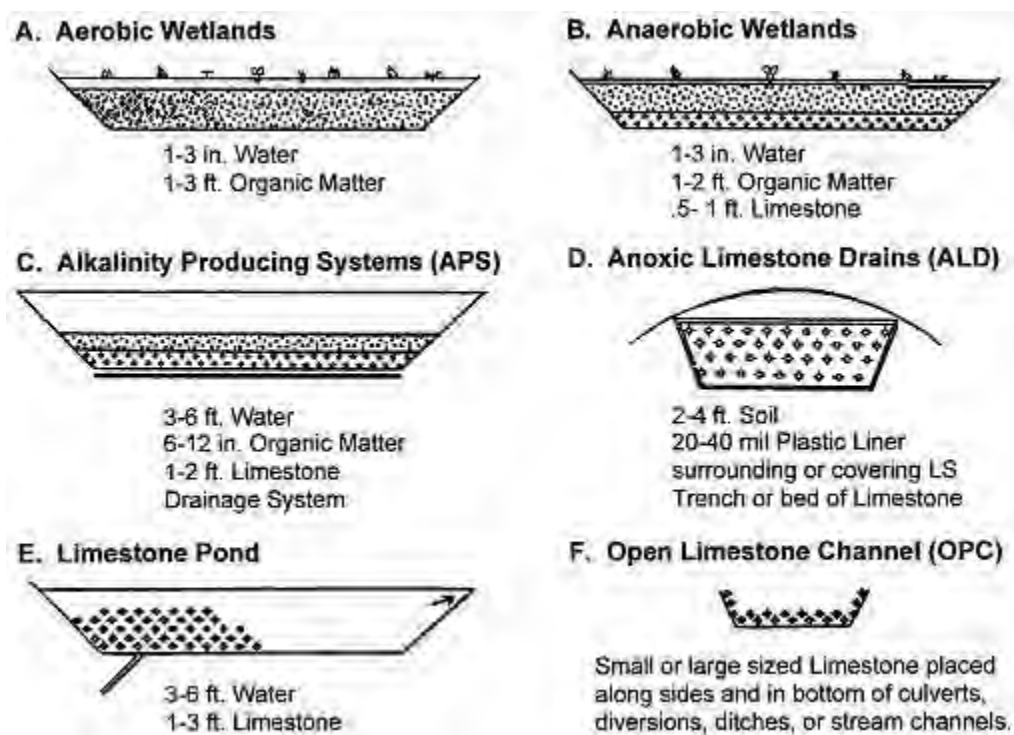


Figure 1. Schematic diagram of passive treatment systems to treat AMD.

Natural wetlands are characterized by water-saturated soils or sediments with supporting vegetation adapted to reducing conditions in their rhizosphere. Constructed wetlands are man-made ecosystems that mimic their natural counterparts. Often they consist of shallow excavations filled with a flooded gravel, soil, and organic matter to support wetland plants, such as *Typha*, *Juncus*, and *Scirpus* sp. Treatment depends on dynamic biogeochemical interactions as contaminated water travels through the constructed wetland. ALDs are abiotic systems consisting of buried limestone cells that passively generate bicarbonate alkalinity as anoxic water flows through. SAPS combine treatment concepts from both wetlands and ALDs. Oxygenated water is pre-treated by organic matter removing O_2 and Fe^{+3} , and then the anoxic water flows through an ALD at the base of the system. Limestone ponds are ponds built over the upwelling of a seep and the seep is covered with limestone for treatment. OLCs are surface channels or ditches filled with limestone. Armoring of the limestone with Fe hydroxides decreases limestone dissolution by 20 to 50%, so longer channels and more

limestone is required for water treatment.

At their present stage of development, none of the passive systems can be reliably implemented as a single permanent solution for most AMD problems to meet effluent limits. Relative to chemical treatment, passive systems require longer retention times and greater space, provide less certain treatment efficiency, and are subject to failure in the long term. However, a great many passive systems have realized successful short-term implementation in the field and have substantially reduced water treatment costs at many mine sites (Faulkner and Skousen 1994). Current research seeks to understand the dynamically complex chemical and biological mechanisms that occur within passive systems and which are responsible for AMD treatment.

Selection of an appropriate passive system is based on water chemistry, flow rate and local topography and site characteristics Hyman and Watzlaf 1995), and refinements in design are ongoing. Figure 1 (adapted from Hedin and Nairn 1994) summarizes current thinking on the appropriate type of passive system for various conditions. In general, aerobic wetlands can treat net alkaline water, ALDs can treat water of low Al, Fe³⁺, and DO, and SAPS, anaerobic wetlands and OLCs can treat net acidic water with higher Al, Fe³⁺, and DO. As scientists and practitioners improve treatment predictability and longevity of passive systems, they will be able to treat the more difficult waters of high acidity and high Al content.

Natural Wetlands

Huntsman et al. (1978) and Wieder and Lang (1982) first noted amelioration of AMD following passage through naturally occurring *Sphagnum* bogs in Ohio and West Virginia. Studies by Brooks et al. (1985), Samuel et al. (1988), and Sencindiver and Bhumbra (1988) documented similar phenomena in *Typha* wetlands. Although evidence suggests that some wetland plants show long term adaptation to low pH and high metal concentrations, AMD eventually degrades the quality of natural wetlands, which is contrary to federal laws designed for wetland protection and enhancement. Such regulations do not govern use of artificially constructed wetlands for water treatment, leading to the suggestion that these engineered systems might provide low cost, low maintenance treatment of AMD (Kleinmann 1991). Over a thousand wetlands have since been constructed to receive AMD from both active mines and abandoned mine lands.

Constructed Wetlands

Mechanisms of metal retention within wetlands listed in their order of importance include: 1) formation and precipitation of metal hydroxides, 2) formation of metal sulfides, 3) organic complexation reactions, 4) exchange with other cations on negatively-charged sites, and 5) direct uptake by living plants. Other mechanisms include neutralization by carbonates, attachment to substrate materials, adsorption and exchange of metals onto algal mats, and microbial dissimilatory reduction of Fe hydroxides and sulfate.

The way in which a wetland is constructed ultimately affects how water treatment occurs. Two construction styles currently predominate: 1) "aerobic" wetlands consisting of *Typha* and other wetland vegetation planted in shallow (<30 cm), relatively impermeable sediments comprised of soil, clay or mine spoil, and 2) "anaerobic" wetlands consisting of *Typha* and other wetland vegetation planted into deep (>30 cm), permeable sediments comprised of soil, peat moss, spent mushroom compost, sawdust, straw/manure, hay bales, or a variety of other organic mixtures, which are often underlain or admixed with limestone. In aerobic wetlands, treatment is dominated by processes in the shallow surface layer. In anaerobic wetlands, treatment involves major interactions within the substrate.

Aerobic wetlands are generally used to collect water and provide residence time and aeration so metals in the water can precipitate. The water in this case usually has net alkalinity. Iron and Mn precipitate as they oxidize, and the precipitates are retained in the wetland or downstream. Wetland species are planted in these systems for aesthetics and to add some organic matter. Wetland plants encourage more uniform flow and thus more effective wetland area.

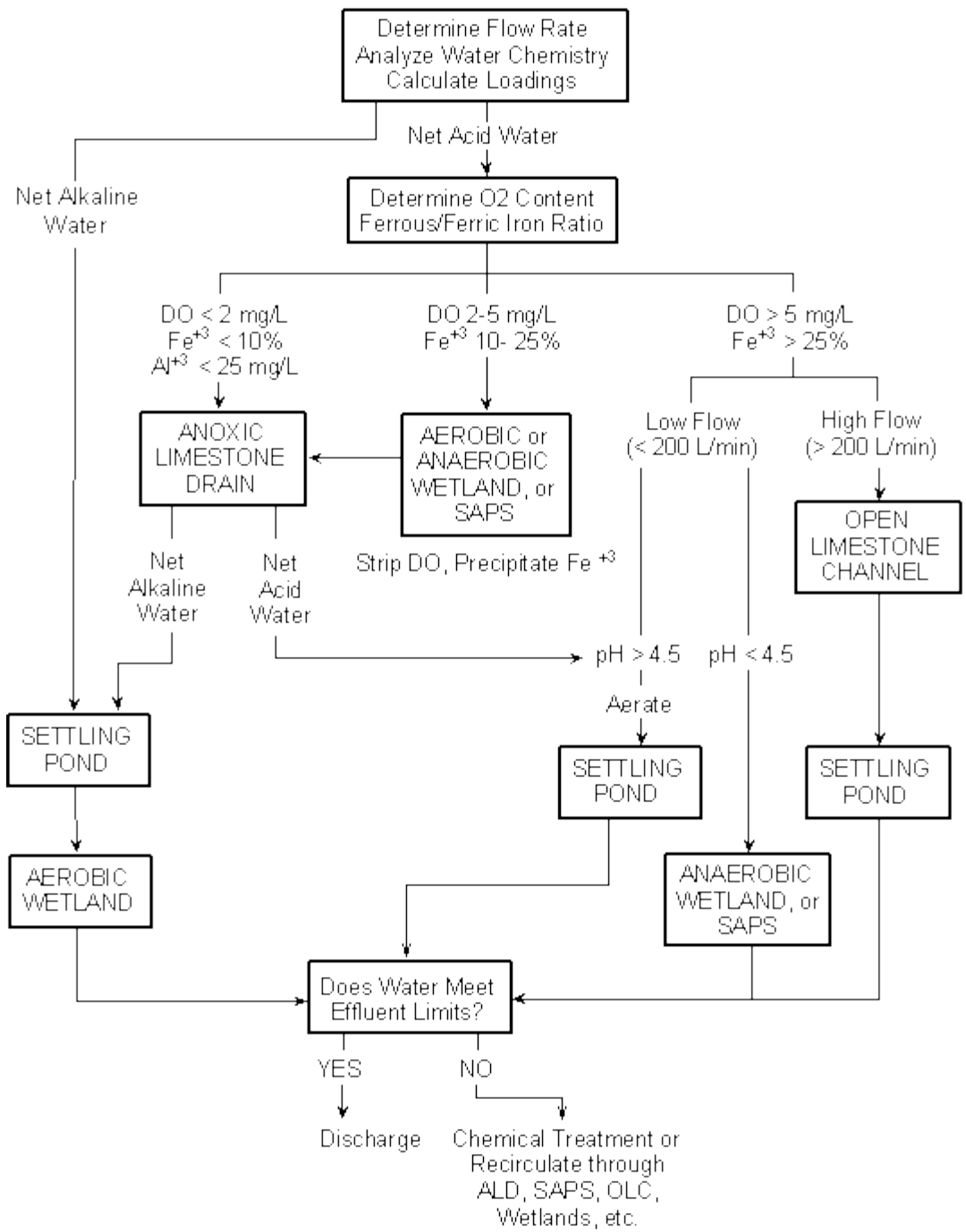


Figure 2. Flowchart for selecting a passive AMD treatment system based on water chemistry and flow (adapted from Hedin et al. 1994).

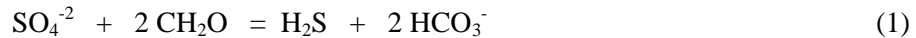


Because of their extensive water surface and slow flow, aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn hydroxides. The extent of metal removal depends on dissolved metal concentrations, dissolved oxygen content, pH and net alkalinity of the mine water, the presence of active microbial biomass, and detention time of the water in the wetland. The pH and net acidity/alkalinity of the water are particularly important because pH influences both the solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis. Metal hydrolysis produces H^+ , but alkalinity in the water buffers the pH and allows metal precipitation to continue. Inorganic oxidation reaction rates decrease a hundred-fold with each unit drop in pH, but microbial oxidation may increase these. Following Fe oxidation, abiotic hydrolysis reactions precipitate Fe hydroxides. Therefore, aerobic wetlands are best used with water that contains net alkalinity to neutralize metal acidity. Abiotic Mn oxidation occurs at pH >8 while microorganisms are thought to catalyze this reaction at pH >6 (Wildeman et al. 1991). Manganese oxidation occurs more slowly than Fe and is sensitive to the presence of Fe^{2+} , which will prevent or reverse Mn oxidation. Consequently in aerobic net alkaline water, Fe and Mn precipitate sequentially, not simultaneously, with the practical result that Mn precipitation occurs (if at all) mainly in the later stages of wetland flow systems, after all Fe is precipitated.

Brodie and co-workers at the Tennessee Valley Authority (TVA) have reported extensively on their use of aerobic wetlands to treat AMD (Brodie 1993). A typical staged design might include an anoxic limestone drain (ALD, see next section) to passively add alkalinity to the source AMD, a settling basin to hold precipitated Fe flocs, followed by two or three aerobic wetland cells to sequentially remove additional Fe and Mn. Nine TVA wetlands receive moderate quality AMD (pH range of 4.1 to 6.3; total Fe <70 mg/L; total Mn <17 mg/L; total Al <30 mg/L; net alkalinity 35 to 300 mg/L as $CaCO_3$), which require no further post-system treatment of water exiting the wetlands. Four TVA wetlands treat water with high Fe (>170 mg/L) and no net alkalinity. Two of these systems require NaOH treatment to comply with NPDES effluent limits, while two others use ALDs for further treatment of the effluent. A final TVA wetland system receives low Fe (<0.7 mg/L) and Mn (5.3 mg/L) and is ineffective in Mn removal. Based on their experience with these systems since 1985, Brodie (1993) suggests that staged aerobic wetland systems can accommodate Fe loads of up to 21 grams/ m^2 /day even in the absence of excess alkalinity. Manganese loads up to 2 grams/ m^2 /day can be accommodated, if alkalinity is present.

Analysis of 73 sites in Pennsylvania suggested that constructed wetlands are the best available technology for many postmining ground water seeps, particularly those of moderate pH (Hellier et al. 1994). However, those sites with net acidic discharges have a much lower successful treatment efficiency. For example, the Rougeux #1 site has a flow of 5.2 gpm and influent chemistry of 2.9 pH, 445 mg/L acidity as $CaCO_3$, Fe 45 mg/L, Mn 70 mg/L, and Al 24 mg/L. After flowing through a two-celled aerobic wetland, pH increased to 3.2, acidity was decreased by 43%, Fe by 50%, Mn by 17%, and Al by 83%. The wetland cost about \$15/ m^2 to build in 1992 and was severely undersized. Although there is improvement in the water, the wetland effluent did not conform to effluent limits. Two other wetlands constructed on the site show similar results.

Anaerobic wetlands encourage water passage through organic rich substrates, which contribute significantly to treatment. The wetland substrate may contain a layer of limestone in the bottom of the wetland or may mix the limestone among the organic matter. Wetland plants are transplanted into the organic substrate. These systems are used when the water has net acidity, so alkalinity must be generated in the wetland and introduced to the net acid water before dissolved metals will precipitate. The alkalinity can be generated in an anaerobic wetland system in two ways (Hedin and Nairn 1990). Certain bacteria, Desulfovibrio and Desulfotomaculum, can utilize the organic substrate (CH₂O, a generic symbol for organic carbon) as a carbon source and sulfate as an electron acceptor for growth. In the bacterial conversion of sulfate to hydrogen sulfide, bicarbonate alkalinity is produced:



Alkalinity can also be generated as the limestone under the organic material reacts with acidity in the wetland:



The limestone continues to react when kept in an anaerobic environment because ferrous iron is relatively soluble at pH 7 in anoxic water and ferrous hydroxide does not form and coat the limestone. If ferrous iron is oxidized, forming ferric iron, then the ferric iron can hydrolyze and form ferric hydroxide, which then coats limestone when pH is above 3.0. Bacterial sulfate reduction and limestone dissolution produce water with higher pH and add bicarbonate alkalinity for metal removal.

Anaerobic wetlands promote metal oxidation and hydrolysis in aerobic surface layers, but also rely on subsurface chemical and microbial reduction reactions to precipitate metals and neutralize acid. The water infiltrates through a thick permeable organic subsurface sediment and becomes anaerobic due to high



biological oxygen demand. Several treatment mechanisms are enhanced in anaerobic wetlands compared to aerobic wetlands, including formation and precipitation of metal sulfides, metal exchange and complexation reactions, microbially generated alkalinity due to reduction reactions, and continuous formation of carbonate alkalinity due to limestone dissolution under anoxic conditions. Since anaerobic wetlands produce alkalinity, their use can be extended to poor quality, net acidic, low pH, high Fe, and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are likely to be of critical importance to long term AMD treatment. However, Wieder (1992) documents that the mechanism and efficiency of AMD treatment varies seasonally and with wetland age. Like their aerobic counterparts, anaerobic wetlands are most successful when used to treat small AMD flows of moderate water quality. At present, the sizing value for Fe removal in these wetlands is 10 grams/m²/day (Hedin and Nairn 1992).

Case Studies:

Sorption onto organic materials (such as peats and soils) decreased Fe from 32 mg/L to 5 mg/L (84%), Mn from 15 to 14 mg/L (7%), and total suspended solids from 32 to 12 mg/L (63%), but eventually all sorption sites on substrate materials are exhausted by continual introduction of metals in acid water (Brodie et

al. 1988). Kleinmann et al. (1991) suggested adsorption of metals by organic substrates may compensate for limited initial biological activity during the first few months of operation in a new wetland system. A field study, which examined five wetland substrate types over a 25-month period, also demonstrated that organic substrates were saturated after only one to seven months of AMD input at 9 to 17 mg Fe per gram substrate (Wieder 1993). Although some natural inputs of organic matter occur annually at plant senescence, the adsorption capacity of a wetland is limited by saturation of all exchange sites. Substantial artificial inputs of organic matter have been used as a successful strategy to temporarily renew this adsorption capacity, following an observed decline in wetland performance (Eger and Melchert 1992, Haffner 1992, Stark et al. 1995).

Insoluble precipitates such as hydroxides, carbonates, and sulfides represent a major sink for metal retention in wetlands. About 50 to 70% of the total Fe removed from AMD by wetlands is found as ferric hydroxides (Henrot and Wieder 1990, Calabrese et al. 1991, Wieder 1992). Ferric hydroxide formation depends both on the availability of dissolved oxygen and on the initial oxidation state of Fe in the AMD. Wieder (1993) reported significant retention of ferric hydroxides in surface sediments of anaerobic wetlands.

Up to 30% of the Fe retained in wetlands may be found as ferrous iron and may be combined with sulfides (Calabrese et al. 1991, McIntyre and Edenborn 1990, Wieder 1992). Iron mono and disulfides form as a result of H₂S formation by microbial sulfate reduction in the presence of an oxidizable carbon source. In addition to its metal removal potential, sulfate reduction consumes acid and raises water pH (Hedin and Nairn 1992, Rabenhorst et al. 1992).

Long term retention of Fe sulfides and Fe hydroxides in a wetland is not well understood. Under continued anoxic conditions and in the absence of soluble Fe³⁺, pyrite should remain stable. Calabrese et al. (1994) changed the influent of their anaerobic wetland from AMD to freshwater with no concomitant export of Fe²⁺. The effluent pH was >6 due to continued limestone dissolution.

Some workers have indicated that wetland systems can be seeded with specially designed and selected microorganisms (Davison 1993, Phillips et al. 1994) to introduce or re-establish microbial activity. However, experiments utilizing appropriate controls have not established the efficacy of this approach (Calabrese et al. 1994). Experience with bioremediation of other wastes suggests that selection and enrichment of naturally occurring microbial populations is a superior, more cost-effective approach (Alexander 1993).

In constructed wetlands, higher plants serve several purposes including: substrate consolidation, metal accumulation, adsorption of metal precipitates, stimulation of microbial processes, wildlife habitat, and aesthetics. Wetland plant species vary in their ability to accumulate metals (Fernandes and Henriques 1990). Some reports document elevated tissue concentrations (Spratt and Wieder 1988), while others show little metal accumulation (Folsom et al. 1981). On an annual basis, uptake by *Typha* accounted for less than 1% of the Fe removed by volunteer wetlands treating AMD (Sencindiver and Bhumbla 1988).

Several studies report on the effects of different plant species in wetlands. Early in the development of treating AMD with constructed wetlands, *Sphagnum* was the predominant wetland species. *Sphagnum* has a well documented capacity to accumulate Fe (Gerber et al. 1985, Wenerick et al. 1989). However, Spratt and Wieder (1988) found that saturation of *Sphagnum* moss with Fe could occur within one growing season. Some have indicated that metal retention over the long term is limited in some wetlands because organic matter inputs by wetland plants are limited (Kleinmann 1990). Many of the original constructed wetlands were vegetated with *Sphagnum* but few remained effective. Cattails (*Typha*) have been found to have a greater environmental tolerance than *Sphagnum* moss (Samuel et al. 1988). One of the reasons is that cattails do not accumulate metals into their tissues through uptake. Algae and a few other wetland species have also received attention due to the observation that enhanced metal removal was associated with algal blooms (Hedin 1989, Kepler 1988, Pesavento and Stark 1986, Phillips et al. 1994). In Colorado, algal mixtures were found to aerobically remove Mn from mine drainage (Duggan et al. 1992), presumably due to elevated pH resulting from algal growth and the extra oxygen generated photosynthetically by the algae. Probably the most important role that wetland plants serve in AMD treatment systems may be their ability to stimulate microbial processes. Kleinmann et al. (1991) explain that plants provide sites for microbial attachment, release oxygen from their roots, and supply organic matter for heterotrophs.

Long term successful treatment by a staged anaerobic wetland has also been reported for slightly net

acidic water (Fe 89 mg/L; net acidity 40 mg/L as CaCO₃) at the Simco constructed wetland near Coshocton, OH (Stark et al. 1994). The wetland, built in 1985, has improved in treatment efficiency over time, not requiring any chemical treatment since 1990. The density of cattail shoots has increased to a current density of 17 shoots/m². Success at the Simco wetland is attributed to the presence of moderate mine water quality (near neutral pH and Fe <100 mg/L), sound wetland design, periodic site maintenance, and high vegetative cover.

Five anaerobic wetland systems in WV receiving 4 to 98 L/min of net acid water (110 to 2400 mg/L as CaCO₃ and Fe from 10 to 376 mg/L) reduced acidity by 3 to 76% and Fe concentrations by 62 to 80% (Faulkner and Skousen 1994). These wetlands were generally much smaller in area than that recommended by early formulas published by the U.S. Bureau of Mines (Hedin 1989) based on iron loads. For example, one of these wetlands, Keister, reduced the acidity of a 17-L/min flow from 252 to 59 mg/L as CaCO₃ (76% reduction) and increased pH from 3.1 to 5.4. Iron was reduced from 23 to 9 mg/L (62%), Mn from 23 to 20 mg/L (11%), and Al from 27 to 13 mg/L (52%). The Pierce wetland used an organic substrate over limestone and treated a 98-L/min flow. Influent pH was 3.3, acidity was 118 mg/L as CaCO₃, Fe of 10 mg/L, Mn of 8 mg/L, and Al of 9 mg/L. Outflow pH was 4.4, acidity was reduced to 57 mg/L as CaCO₃ (52%), Fe decreased to 2 mg/L (80%), Mn was reduced by 11%, and Al by 25%.

A wetland system consisting of six wetland cells (total area of 2500 m²) and a sedimentation basin each received a small flow (5 L/min) of AMD with pH of 3.0, acidity of 217 mg/L as CaCO₃, Fe of 27 mg/L, Al of 12 mg/L, and Mn of 2 mg/L (Hellier 1996). At this site in PA, the effluent after passing through the wetland was raised to pH 5.1, and the water contained a net acidity of 16 mg/L as CaCO₃, with about 46% iron removal, and 56% Al removal.

A 1022 m² surface flow wetland was constructed in KY to treat 37 L/min of AMD with a pH of 3.3, acidity of 2280 mg/L as CaCO₃, Fe of 962 mg/L, Mn of 11 mg/L, and Al of 14 mg/L (Karathanasis and Barton 1997). After construction in 1989, metal concentrations in the effluent were reduced during the first six months of treatment, however, the system failed thereafter due to insufficient wetland area and metal overloading. In 1995, a two-phase renovation project began incorporating the use of an ALD, and a series of anaerobic drains that promote vertical flow through limestone beds overlain by organic compost (much like a SAPS). Results to date indicate a pH of 6.4, slightly net alkaline water (15 mg/L as CaCO₃), Fe reduction of 96%, Mn removal of 50%, and Al by 100%.

A large anaerobic wetland located at Douglas, WV treated a 1000-L/min flow effectively for one year (Cliff et al. 1996). The influent pH was 3.0, with acidity of about 500 mg/L as CaCO₃, Fe of 30 mg/L, and Al of 40 mg/L. An average net alkalinity of 127 mg/L as CaCO₃ was realized in the effluent water. Four years after installation, the original acidity of 500 mg/L as CaCO₃ is being reduced to between 250 to 300 mg/L as CaCO₃. It has remained at this level of treatment for the past two years.

Anoxic Limestone Drains

Anoxic limestone drains (ALD) are buried cells or trenches of limestone into which anoxic water is introduced. The limestone dissolves in the acid water, raises pH, and adds alkalinity. Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe⁺² does not precipitate as Fe(OH)₂ at pH <6.0.

ALDs were first described by the Tennessee Division of Water Pollution Control (TDWPC) (Turner and McCoy 1990). TVA subsequently observed that AMD seeping through a coal refuse dam was being treated passively by limestone contained in an old haul road buried under the dam. Once the water containing excess alkalinity reached aerobic conditions at the ground surface, the metals oxidized and precipitated while the water remained near pH 6 (Brodie et al. 1990). TVA and TDWPC began building ALDs in 1989. Originally, ALDs were used for pre-treatment of water flowing into constructed wetlands. Brodie (1993) reported that ALDs improved the capability of wetlands to meet effluent limitations without chemical treatment. Since 1990, ALDs have also been constructed as stand-alone systems, particularly where AMD discharges from deep mine portals.

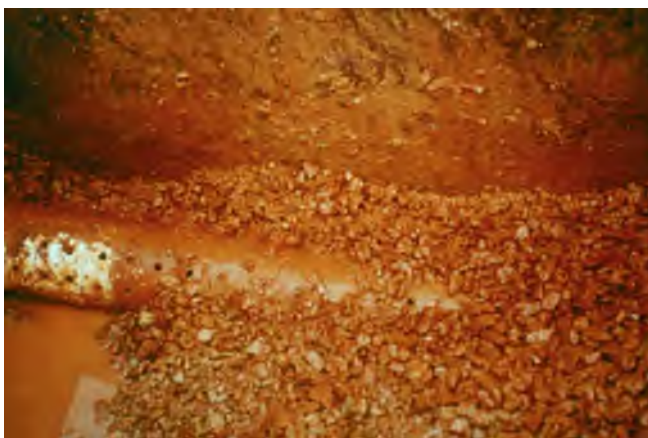
Longevity of treatment is a concern for ALDs, especially in terms of water flow through the limestone. If appreciable dissolved Fe³⁺ and Al³⁺ are present, clogging of limestone pores with precipitated Al and Fe

hydroxides has been observed (Faulkner and Skousen 1994, Watzlaf et al. 1994). For waters with high sulfate (>1,500 mg/L), gypsum (CaSO₄) may also precipitate (Nairn et al. 1991). For an accepted design, no Fe³⁺, dissolved oxygen (DO), or Al³⁺ should be present in the AMD. Selection of the appropriate water and environmental conditions is critical for long term alkalinity generation in an ALD. The maximum alkalinity that ALDs may generate is about 300 mg/L as CaCO₃, although the specific level varies with water chemistry and contact time (Watzlaf and Hedin 1993).

Faulkner and Skousen (1994) reported both successes and failures among 11 ALDs treating mine water in WV. In all cases, water pH was raised after ALD treatment, but three of the sites had pH values <5.0, indicating that the ALDs were not fully functioning or that the acid concentrations and flow velocities were too high for effective treatment. Water acidity in these drains, varying from 170 to 2200 mg/L as CaCO₃, decreased 50 to 80%, but Fe and Al concentrations in the outflow also decreased. Ferric iron and Al³⁺ precipitated as hydroxides in the drains. With Fe and Al decreases in outflow water, some coating or clogging of limestone is occurring inside the ALD.

At the Brandy Camp site in PA, an ALD was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the ALD, the effluent had a pH of 6.0, net alkalinity of 10 mg/L as CaCO₃, Fe of 50 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. Most of the Fe and Mn passed through this system and precipitated in subsequent wetlands, while Al was precipitated inside the drain.

Since many sources of AMD have mixed amounts of Fe³⁺ and Fe²⁺ and some DO, utilization of an ALD under these conditions is not recommended. Current research involves pre-treating AMD by passing the water through a submerged organic substrate to strip oxygen from the water and to convert Fe³⁺ to Fe²⁺. The pre-treated water is then introduced into an underlying bed of limestone (see section 5.4; Kepler and McCleary 1994, Skousen, 1995). Like wetlands, ALDs may be a solution for treating specific types of AMD or for a



finite period after which the system must be replenished or replaced.

Limestone has also been placed in 60-cm corrugated pipe and installed underground, and water is introduced into the pipe. Septic tanks have also been filled with limestone and AMD introduced into the tank. These applications have been used on steep slopes in lieu of buried cells or trenches, and on sites that have poor access and small water quality problems (Faulkner and Skousen 1995).

Successive Alkalinity Producing Systems

Successive alkalinity producing systems (SAPS) combine the use of an ALD and an organic substrate into one system (Kepler and McCleary 1994). Oxygen concentrations in AMD are often a design limitation for ALDs. In situations where DO concentrations are >1 mg/L, the oxygen must be removed from the water before introduction into an anoxic limestone bed. In a SAPS, acid water is ponded from 1 to 3 m over 0.2 to 0.3 m of an organic compost, which is underlain by 0.5 to 1 m of limestone. Below the limestone is a series of drainage pipes that convey the water into an aerobic pond where metals are precipitated. The hydraulic head drives ponded water through the anaerobic organic compost, where oxygen is consumed and ferric iron is reduced to ferrous iron. Sulfate reduction and Fe sulfide precipitation can also occur in the compost. Water with high metal loads can be passed through additional SAPS to reduce high acidity. Iron and Al clogging of limestone and pipes can be removed by flushing the system (Kepler and McCleary 1997). Data are still being gathered on the ability of SAPS to treat high Al water. Kepler and McCleary (1997) describe success with periodic flushing of Al precipitates from drainage pipes. One SAPS cited by them treat AMD containing 41 mg/L Al. However, Brodie (personal communication, 1997) described a SAPS receiving >40 mg/L Al at the Augusta Lake site in Indiana being plugged with Al precipitates after 20 months despite flushing. Successful SAPS have used mushroom compost, while other types of organic material have problems



with plugging. Many possible variations in composition and thickness of organic matter, including the addition of limestone, desirability of promoting sulfate reduction, flow rates through organic matter, time schedule for replacement or addition of new organic matter, and precipitation of siderite in the limestone remain to be investigated.

Kepler and McCleary (1994) reported on initial successes for three SAPS in PA. The Howe Bridge SAPS reduced acidity from 320 mg/L to 93 mg/L as CaCO₃, and removed 2 mg/L ferric iron. The REM SAPS decreased acidity from 173 to 88 mg/L as CaCO₃, and exported more ferrous iron than entered. The Schnepf Road SAPS decreased acidity from 84 to 5 mg/L as CaCO₃, but removed all 19 mg/L ferric iron, with only 1 mg/L ferrous iron exiting the wetland.

Kepler and McCleary (1997) reported the use of SAPs in OH, PA, and WV. In all cases, Al in AMD precipitated in their systems. Their drainage design incorporates a flushing system called the 'Aluminator.' This allows for the precipitated Al to be flushed from the pipes thereby maintaining hydraulic conductivity through the limestone and pipes. One SAPS, Buckeye, received 3 L/min of very acid water (pH of 4.0, acidity of 1989 mg/L as CaCO₃), Fe of 1005 mg/L, and Al of 41 mg/L. Over a two-year period, the effluent had a pH of 5.9, net acidity concentration of about 1000 mg/L, Fe of 866 mg/L, and <1 mg/L Al. A second site, Greendale, treated a 25-L/min flow, and increased the pH from 2.8 to 6.5, changed the water from a net acid water (925 mg/L as CaCO₃) to a net alkaline water (150 mg/L as CaCO₃), Fe from 40 to 35 mg/L, and Al from 140 to <1 mg/L.

At the Brandy Camp site in PA, a SAPS was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the SAPS, the effluent had a pH of 7.1, net alkalinity of 115 mg/L as CaCO₃, Fe of 3 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. The system effectively increased alkalinity, but retained most of the Fe and Al inside the system. Longevity of treatment is a major concern for ALDs, especially in terms of water flow through the limestone. Eventual clogging of the limestone pore spaces with precipitated Al and Fe hydroxides, and gypsum (CaSO₄) is predicted (Nairn et al. 1991). For optimum performance, no Fe⁺³, dissolved oxygen (DO), or Al should be present in the AMD. Selection of the appropriate water and environmental conditions is critical for long-term alkalinity generation in an ALD.

Limestone Ponds

Limestone ponds are a new passive treatment idea in which a pond is constructed on the upwelling of an AMD seep or underground water discharge point. Limestone is placed in the bottom of the pond and the water flows upward through the limestone (Faulkner and Skousen 1995). Based on the topography of the area and the geometry of the discharge zone, the water can be from 1 to 3 m deep, containing 0.3 to 1 m of limestone immediately overlying the seep. The pond is sized and designed to retain the water for 1 or 2 days for limestone dissolution, and to keep the seep and limestone under water. Like ALDs, this system is recommended for low DO water containing no Fe³⁺ and Al³⁺. However, the advantage of this system is that the operator can observe if limestone coating is occurring because the system is not buried. If coating occurs, the limestone in the pond can be periodically disturbed with a backhoe to either uncover the limestone from precipitates or to knock or scrape off the precipitates. If the limestone is exhausted by dissolution and acid neutralization, then more limestone can be added to the pond over the seep. Three limestone ponds have been installed but no information is available on their treatment.



Open Limestone Channels

Open limestone channels (OLCs) introduce alkalinity to acid water in open channels or ditches lined with limestone (Ziemkiewicz et al. 1994). Acid water is introduced to the channel and the AMD is treated by limestone dissolution. Past assumptions have held that armored limestone (limestone covered or coated with Fe or Al hydroxides) ceased to dissolve, but experiments show that coated limestone continues to dissolve at 20% the rates of unarmored limestone (Pearson and McDonnell 1975). Recent work has demonstrated that the rate for armored limestone may be even higher (Ziemkiewicz et al. 1997). The length of the channel and the channel gradient, which affects turbulence and the buildup of coatings, are design factors that can be varied for optimum performance. Optimum performance is attained on slopes exceeding 20%, where flow velocities keep precipitates in suspension, and clean precipitates from limestone surfaces. In appropriate situations, OLCs are being implemented for long term treatment. Utilizing OLCs with other passive systems can maximize treatment and metal removal.

Among the questions still to be investigated are the behavior of OLCs in waters of different pH and high heavy metal loads (like metal mine drainage), possible interactions of slope with water chemistry, and the possible importance of limestone purity.



Ziemkiewicz et al. (1997) found armored limestone in a series of laboratory experiments was 50 to 90% as effective as unarmored limestone in neutralizing acid. Seven OLCs in the field reduced acidity in AMD by 4 to 205 mg/L as CaCO_3 , at rates of 0.03 to 19 mg/L per meter of channel length. The highest removal rates were with channels on slopes of 45 to 60% and for AMD with acidity of 500 to 2600 mg/L as CaCO_3 . For example, the Eichleberger OLC was 49 m long on a slope of 20%, and received about 378 L/min of 510 mg/L acidity as CaCO_3 . After flowing down the channel, the acidity was decreased to 325 mg/L as CaCO_3 (36% decrease). The PA Game Commission OLC was only 11 m in length on a 45% slope, and received 484 L/min

of 330 mg/L acidity as CaCO₃. The water acidity at the end of the channel was 125 mg/L as CaCO₃ (62% decrease).

Three OLCs were installed in the Casselman River Restoration project (Ziemkiewicz and Brant 1996). One OLC, 400 m long on a 8% slope, received 60 L/min of pH 2.7 water, 1290 mg/L as CaCO₃ acidity, 622 mg/L Fe, 49 mg/L Mn, and 158 mg/L Al. The effluent pH over a two year period was 2.9, acidity was 884 mg/L as CaCO₃ (31% decrease), Fe was 210 mg/L (66% removal), Mn was 42 mg/L (14% decrease), and Al was 103 mg/L (35% decrease).

At the Brandy Camp site in PA, a 15-m-long OLC on a 10% slope was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier, case study 1997). After passage through the OLC, the effluent had a pH of 4.8, net acidity of 50 mg/L as CaCO₃, Fe of 17 mg/L, Mn of 8 mg/L, and Al of 3 mg/L. The OLC removed 72% of the Fe and about 20% of the Mn and Al from the water.

Bioremediation

Bioremediation of soil and water involves the use of microorganisms to convert contaminants to less harmful species in order to remediate contaminated sites (Alexander 1993). Microorganisms can aid or accelerate metal oxidation reactions and cause metal hydroxide precipitation. Other organisms can promote metal reduction and aid in the formation and precipitation of metal sulfides. Reduction processes can raise pH, generate alkalinity, and remove metals from AMD solutions. In most cases, bioremediation of AMD has occurred in designed systems like anaerobic wetlands where oxidation and reduction reactions are augmented by special organic substrates and limestone. In a few cases, substrates have been incorporated into spoils to aid in in-situ treatment of water by the use of indigenous microorganisms.

A mixture of organic materials (sawdust and sewage sludge) was emplaced into a mine spoil backfill to stimulate microbial growth and generate an anoxic environment through sulfate reduction. The results of the organic matter injection process caused no change in water pH, about a 20% decrease in acidity (1500 to 1160 mg/L as CaCO₃, and a similar decrease in Fe, Mn, and Al. The results indicate that the process works, but improvements in organic material injection and the establishment of a reliable saturated zone in the backfill are needed for maximum development (Rose et al. 1996).

The Lambda Bio-Carb process is a bioremediation system utilizing site-indigenous, mixed microorganism cultures selected for maximum effectiveness (Davison 1993). On a field site in PA using this bioremediation process, Fe in AMD was decreased from 18 mg/L to < 1 mg/L, Mn declined from 7 mg/L to 2 mg/L, and pH increased from around 6.0 to 8.0.

The Pyrolusite process uses selected groups of microorganisms growing on limestone to oxidize Fe and Mn into their insoluble metal oxides (Vail and Riley 1997). On a field site in PA using a limestone bed inoculated with microorganisms, Fe was decreased from 25 mg/L to < 1 mg/L, Mn went from about 25 mg/L to < 1 mg/L, while pH and alkalinity in the effluent were increased.



Diversion Wells

The diversion well is a simple device initially developed for treatment of stream acidity caused by acid rain in Norway and Sweden (Arnold 1991). It has been adopted for AMD treatment in the eastern USA. A typical diversion well consists of a cylinder or vertical tank of metal or concrete, 1.5-1.8 m in diameter and 2-2.5 m in depth, filled with sand-sized limestone. This well may be erected in or beside a stream or may be sunk into the ground by a stream. A large pipe, 20-30 cm in diameter, enters vertically down the center of the well and ends shortly above the bottom. Water is fed to the pipe from an upstream dam or deep mine portal with a hydraulic head of at least 2.5 m (height of well). The water flows down the pipe, exits the pipe near the bottom of the well, then flows up through the limestone in the well, thereby fluidizing the bed of limestone in the well. The flow rate must be rapid enough to agitate the bed of limestone particles. The acid water dissolves the limestone for alkalinity generation, and metal flocs produced by hydrolysis and neutralization reactions are flushed through the system by water flow out the top of the well. The churning action of the fluidized limestone also aids in limestone dissolution and helps remove Fe oxide coatings so that fresh limestone surfaces are always exposed. Metal flocs suspended in the water are precipitated in a downstream pond.



Arnold (1991) used diversion wells for AMD treatment in PA and reports that three wells increased pH from 4.5 to 6.5, with corresponding decreases in acidity. For example, one diversion well located at Lick Creek treats about 1000 L/min of slightly acid water. After passing through the diversion well, the pH changes from 4.5 to 5.9 and the net acid water (8 mg/L as CaCO_3) changes to net alkaline water (6 mg/L as CaCO_3). Similar results are found for several other sites in PA.

Diversion wells have also been constructed in the Casselman River Restoration Project (Ziemkiewicz and Brant 1996). This large diversion well has a retention time of about 15 min for a 360-L/min flow of moderately acid water. The diversion well reduces the acidity from 314 to 264 mg/L as CaCO_3 , Fe from 83 to 80 mg/L, and Al from 24 to 20 mg/L.

At the Galt site in WV, a diversion well changes a 20-L/min flow from a pH of 3.1 to 5.5, acidity from 278 to 86 mg/L as CaCO_3 , Fe from 15 to 2 mg/L, and Al from 25 to 11 mg/L (Faulkner and Skousen 1995).

Limestone Sand Treatment

Sand-sized limestone may also be directly dumped into AMD streams at various locations in watersheds. The sand is picked up by the streamflow and redistributed downstream, furnishing neutralization of acid as the stream moves the limestone through the streambed. The limestone in the streambed reacts with the acid in the stream, causing neutralization. Coating of limestone particles with Fe oxides can occur, but the agitation and scouring of limestone by the streamflow keep fresh surfaces available for reaction.

The WV Division of Environmental Protection treats 41 sites in the Middle Fork River, including the

headwaters of 27 tributaries (Zurbuch 1996). The first year's full treatment was based on four times the annual acid load for non-AMD impacted streams and two times the load for AMD tributaries. During subsequent years, limestone sand application will be an amount equal to the annual acid load, or about 2,000 tons/yr. About 8,000 tons of limestone were deposited among the 41 sites in 1995. Water pH has been maintained above 6.0 for several miles downstream of the treatment sites. The anticipated precipitate coating of the limestone was not observed. It is predicted that treating the river with limestone sand will be necessary three times a year to maintain water quality for fish populations.



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