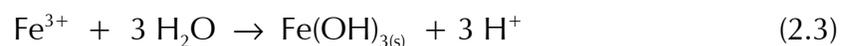
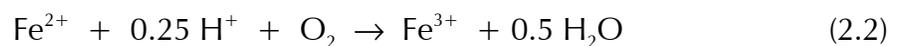
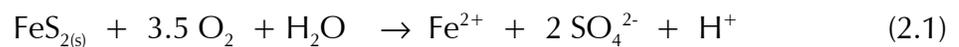


Chapter II

Literature Review

Acidic Mine Drainage

Acidic mine drainage (AMD) is a serious environmental pollutant of particular importance in the coal mining regions of the Eastern United States (Herlihy et al., 1990). AMD occurs as a result of the oxidation of the sulfidic minerals associated with coal deposits when they are exposed to oxygen and water during the mining process. The most common of these minerals is pyrite (FeS_2), which is responsible for producing the majority of AMD (Rose and Cravotta, 1998). The sequential stoichiometric process for AMD formation is commonly defined using the following reactions (Stumm and Morgan, 1981):

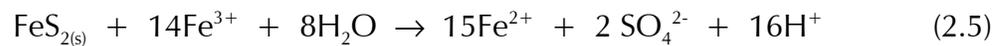


The process is initiated with the oxidation of pyrite and the release of ferrous iron, sulfate, and acidity (Eq. 2.1). Ferrous iron then undergoes oxidation forming ferric iron (Eq. 2.2). Finally, ferric iron is hydrolyzed, forming insoluble ferric

hydroxide and releasing additional acidity (Eq. 2.3). Summing these equations demonstrates the acid-producing nature of pyrite oxidation in that for each mole of FeS_2 that is oxidized, four moles of acidity (H^+) are generated (Eq. 2.4) (Rose and Cravotta., 1998).



The process of AMD generation is spontaneous and naturally occurring, but it is greatly hastened in the presence of *Thiobacillus sp.* bacteria which facilitate the oxidation of sulfur (Eq.2.1) and iron (Eq.2.2) (Kleinmann et al., 1981). Pyrite oxidation is also catalyzed in the presence of Fe^{3+} , generating 16 moles of acidity per mole of FeS_2 oxidized (Eq. 2.5)



Since the oxidation of pyrite results in the production of Fe^{3+} , it creates an autocatalytic effect which serves to accelerate the production of AMD (Rimstidt, 1998). The combination of these processes is represented graphically in Figure 2.1.

The resulting drainage from the pyrite oxidation process is characterized as having high acidity, low pH, and elevated concentrations of sulfate, manganese, and iron (Table 2.1). It is important to note that the acidity that is associated with AMD is primarily mineral acidity rather than proton acidity (Hedin et al., 1994a). The mineral acidity reflects the total proton generation potential after all of the metals in solution are hydrolyzed. The process of iron hydrolysis forms insoluble Fe(OH)_3 , which produces the characteristic reddish-brown color commonly referred to as “yellow boy”.

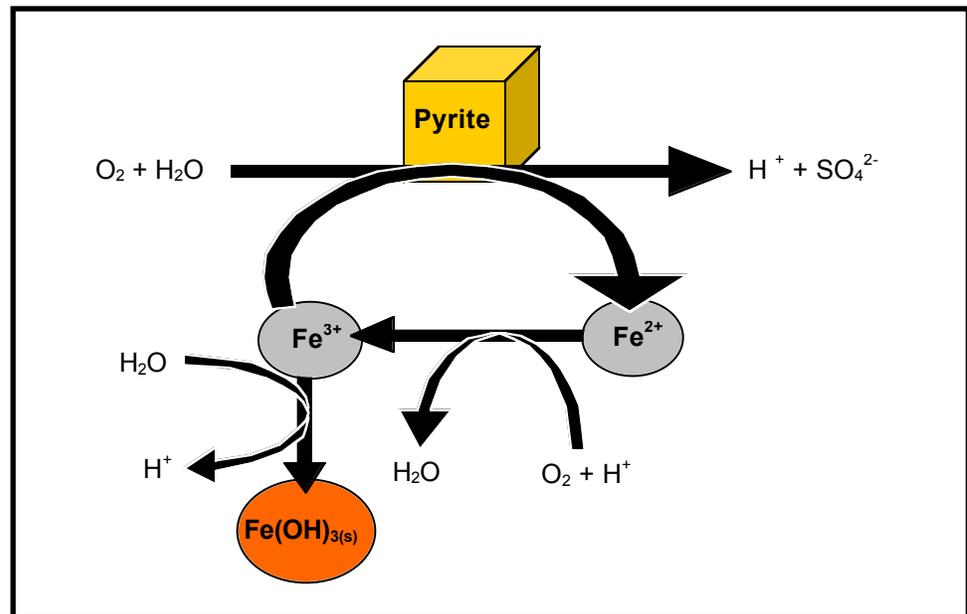


Figure 2.1. Theoretical model of the pyrite oxidation process. (Rimstidt, 1997).

Table 2.1 Range of average water quality parameters for ten acidic mine drainage discharges in western Pennsylvania (Hedin et al., 1994a)

Parameter	Concentration Range (mg/L)
Total Iron	89 - 473
Total Manganese	9 - 130
Sulfate	1128 - 2495
pH	2.6 - 6.3
Acidity (mg/l as CaCO ₃)	75-929 ¹

¹CaCO₃ equivalent

When AMD reaches a receiving stream, it often threatens local aquatic life and domestic drinking water supplies (Manyin et al. 1997). The toxicity of the drainage varies as a function of the pH and the concentrations of dissolved metals (Earle and Callaghan, 1998). The physical deposition of iron oxides in the streambed is also believed to harm the benthic macroinvertebrate communities by coating the substrate and suffocating the organisms (Slater, 1996). Kleinmann, (1989) estimated that in the United States alone, over 20,000 km of streams and rivers and over 72,000 hectares of lakes and reservoirs have been adversely impacted by AMD.

AMD Remediation Regulations

With the passage of the Surface Mining Control and Reclamation Act (SMCRA) in 1977, Congress placed active coal mines and related facilities under the jurisdiction of the National Pollutant Discharge Elimination System (NPDES) established by the Clean Water Act (CWA). The resulting regulations required each mine operator to obtain an NPDES permit before discharging any water into a receiving stream and to ensure that such discharge meets water quality standards as defined by the individual permit. Current technology-based standards for active coal mines effluent concentrations are listed in Table 2.2. These standards may be altered by regulatory agency if necessary to protect water quality in the receiving stream to the degree required by the CWA.

It has been estimated that the United States mining industry spends over \$1 million per day to treat AMD in order to comply with these standards (Kleinmann, 1989). Since the generation of AMD does not normally end with cessation of mining activities, this treatment often continues in order to comply with the terms of the NPDES permit.

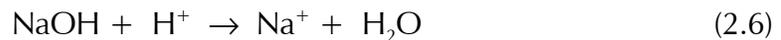
Table 2.2 Federal NPDES effluent limitations for coal mine drainage (U.S. CFR, 1993).

Parameter	One Day Maximum (mg/L)	30 Day Average (mg/L)
Total Iron	7.0	3.5
Total Manganese	4.0	2.0
Total Suspended Solids	70	35
pH (std. units)	6 - 9	6 - 9

NPDES permits are only required for post-SMCRA mining operations, however. Not covered by these regulations are thousands of AMD seeps resulting from mining activities abandoned prior to the passing of the SMCRA. Such sites are scattered throughout the Appalachian region and are major contributors to the problem of AMD contamination (Kleinmann, 1989). Some of these areas are reclaimed by private watershed groups or through programs such as Abandoned Mine Lands Fund or EPA's non-point source abatement 319 grants, but the majority continue to pollute the streams of the Appalachian region unabated. This fact has caused a growing concern over the protection of AMD impacted watersheds which has resulted in a push for improved and expanded methods for controlling and treating AMD.

Active Treatment

Current methods used to treat AMD can be divided into two categories: active treatment and passive treatment. Active treatment typically involves the addition of caustic chemicals such as sodium hydroxide (NaOH) (Eq. 2.6), or ammonia (NH₃) (Eq. 2.7) to mine waters in an effort to raise the pH of the water (Skousen et al., 1998).



Since the solubility of most metals in solution is much lower at near neutral pH, the metals form insoluble complexes (typically oxyhydroxides) and precipitate out of solution (Snoeyink and Jenkins, 1980). Active treatment processes are very effective in achieving this, but are usually expensive due to the need to construct and maintain a treatment facility, and to continually purchase chemical reagent. Estimated annual costs for treating one, 100 GPM discharge can range from \$9,000

to \$22,000 depending on the water quality, and the chemicals used (Skousen et al., 1990). Questions have also been raised about the potential harm of using such strong chemicals. Sodium hydroxide treatment generates high concentrations of Na^+ (Eq. 2.6), which increases the salinity of the receiving stream and can potentially harm sensitive organisms (Campbell, 1990). In addition, the ammonium ion (NH_4^+) that is generated from ammonia treatment is able to deprotonate, lowering the stream's pH and releasing ammonia, which is toxic to aquatic life (Skousen and Ziemkiewicz, 1995) (reverse reaction of Eq. 2.7).

Passive Treatment

Passive treatment systems rely on natural chemical and biological processes to renovate AMD. They are typically modeled after natural wetlands with design modifications directed toward meeting specific treatment goals. Initial work into the effectiveness of these systems began in the late 1970s with two separate investigations of natural *Sphagnum sp.* peat wetlands that were receiving AMD (Hedin et al., 1994a; Weider, 1982). These systems were able to adjust pH and lower iron concentrations without any obvious deterioration of the wetland itself. This discovery inspired the development of artificial wetland treatment systems specifically for the treatment of AMD. Unfortunately, the replication of natural wetlands proved quite difficult and treatment performance declined rapidly with the accumulation of toxic metals in the peat under high loading rates (Hedin et al., 1994a). Despite these early failures, the potential of the wetland design for the passive treatment of AMD was recognized and new designs were developed.

One of the first designs put into wide use was a shallow (± 0.3 m), surface flow wetland planted with cattails (*Typha sp.*) (Skousen et al., 1998; Hedin et al., 1994a). Substrates for these wetlands varied from natural soils to composted organic matter. These "aerobic" wetlands, as they were termed, aerated the mine waters as they

flowed among the planted vegetation. This allowed for the oxidation of ferrous iron and its subsequent deposition as an oxyhydroxide (Eqs. 2.2 & 2.3). These designs proved capable of removing iron, with reported removal rates of up to 21 g/day/m² (Hedin et al., 1994a). Manganese concentrations, however, were still relatively unchanged and the pH in many cases actually decreased due to the generation of proton acidity resulting from the process of iron hydrolysis (Skousen, 1997; Robinson, 1995).

Modifications of the aerobic wetland design were made to enhance pH adjustment and increase metal precipitation. These included the addition a bed of high calcium limestone beneath an organic substrate (Hedin et al., 1994a). This design encouraged the generation of bicarbonate alkalinity by both anaerobic microbial sulfate reduction and limestone dissolution (Eqs. 2.8 & 2.9), The bicarbonate that is generated neutralizes the acidity of the AMD, thereby raising the pH (Eq. 2.10), and increasing the precipitation of acid soluble metals.



The organic matter in these systems serves as an additional sink for metals in solution by adsorbing them onto active exchange sites (Skousen et al., 1997). While the capacity of this mechanism to remove metals is finite, it does serve as a significant removal process during the early stages of use until the microbial populations establish themselves (Watzlaf, 1997). The placement of the limestone below the organic matter serves to ensure its dissolution in an anoxic, reducing environment created by the high oxygen demand of fermentative bacteria present at the surface of the organic layer. This condition is critical to the longevity of these systems because in the presence of oxygen, ferric iron precipitates on the limestone surface and

severely limits its dissolution: a process known as “armoring”. In an anoxic environment, the ferrous form of iron predominates and does not interfere with the limestone dissolution (Hedin et al., 1994a; Watzlaf, 1997).

These wetlands, referred to as “anaerobic” wetlands, were capable of removing significant quantities of iron. Hedin et al. (1994a) reported mean iron removal rates of up to 42.7 g/day/m², but these systems were still limited in their ability to adjust pH and lower manganese concentrations. The primary limiting factor to their effectiveness was the slow mixing of the alkaline substrate water with the acidic surface water (Kepler and McCleary, 1994). Attempts to compensate for this slow diffusion usually resulted in the construction of very large wetlands to provide for long retention times (Skousen et al., 1997). This demand on land area became a major impediment to the increased use of these systems by mine operators with limited space for wetland construction (Robinson, 1995).

One method used to reduce wetland size was with the pre-treatment of the AMD using anoxic limestone drains (ALDs). ALDs are limestone-filled trenches that can rapidly produce bicarbonate alkalinity via limestone dissolution. They are installed at the point of discharge to capture the AMD subterraneously and then capped with clay or compacted soil to prevent contact with oxygen (Hedin and Watzlaf, 1994). The acidic water flowing through trench dissolves the limestone and releases bicarbonate alkalinity. The effluent is then discharged into a settling pond to allow for the acid neutralization, pH adjustment, and metal precipitation processes. These systems have demonstrated the ability to raise the alkalinity and/or neutralize acidity by as much as 300 mg/L as CaCO₃ requiring a retention time in the ALD of only 14 - 23 hours (Hedin and Watzlaf, 1994, Hedin et al., 1994a). ALD pretreatment of AMD allows for the construction of smaller, more effective treatment

systems due to the decreased metal loadings and increased pH of the ALD effluent discharged into them.

ALDs, however, are not capable of treating all types of discharges. Significant concentrations of aluminum and ferric iron (> 1 mg/l) can eventually clog the ALD with the precipitation of metal-hydroxides once a pH of about 4.5 is reached (Hedin et al., 1994a). ALD systems will also fail if the influent contains elevated dissolved oxygen (> 1 mg/L) because of the problem with limestone armoring. This also prohibits the recycling of mine waters through a second ALD to further improve water quality.

Successive Alkalinity-Producing Systems (SAPS) are the latest generation of passive treatment systems for acidic mine drainage. They combine the mechanism of anaerobic wetland alkalinity production with the efficiency of the ALDs and attempt to compensate for some of the inherent limitations of both (Kepler and McCleary, 1994). The design of SAPS is similar to that of the anaerobic wetland, but a drainage system in the limestone layer is added to discharge the water from the bottom rather than from the surface. This eliminates the alkalinity diffusion problem common to anaerobic wetlands by forcing the entire volume of water through the bed of limestone and thus reducing the need for large wetlands. Anoxic conditions in the limestone layer are ensured by the high oxygen demand of the overlying organic matter. The final effluent is discharged into a settling pond to allow for the neutralization and precipitation processes.

With the advent of the SAPS design, the efficient treatment oxygenated mine waters became possible without the need for large land areas. For more severe AMD discharges, several systems can be linked in series to generate alkalinity successively until the treatment goals are reached. These systems are also able to overcome the

clogging problem in the limestone layer with the use of a valved flushing pipe. This pipe is located at a lower elevation than the effluent pipe in order to utilize the head pressure of the water to rapidly flush out the system. Opening this valve removes the loose metal hydroxide floc from the limestone layer and discharges it into the settling pond (Kepler and McCleary, 1997, Kepler, 1999).

The construction of passive treatment systems using the SAPS design began in the late 1980s with systems in Galax, Virginia (Hendricks, 1991). Later, and through independent invention, Kepler and McCleary (1994), documented similar systems in Pennsylvania and coined the term SAPS as they have now come to be known. These systems ranged in size from 150 - 3100 m² with limestone layers of 0.30 - 0.60 m and compost layers ranging from 0.30 - 0.45 m. Studies of SAPS performance indicated an ability for these systems to remove acidity ranged from an average of 51 g/d/m² (Narin et al. 1999), to 61.8 g/d/m² of acidity (Dietz and Stidinger, 1996). Kepler and McCleary 1994, reported acidity removal potential between 150-300 mg/l. What is unclear from these studies, however, is how acid neutralization is affected by influent AMD chemistry and system design.

Current design guidelines call for a limestone layer of 0.60 – 0.90 m (2 – 3 ft.) in depth, a organic layer (preferably spent mushroom compost) of 0.15 – 0.45 m (0.5 – 1.5 ft.) deep, and 0.90 - 1.5 m (3 – 5 ft.) deep body of water above the organic layer. In addition, a residence time in the limestone layer of between 12 – 15 hours is regarded as adequate for achieving maximum alkalinity generation based on studies of the performance of ALDs (Skovran and Clouser, 1998; Kepler and McCleary, 1994).

Cross sectional diagrams of all of the described passive treatment systems are presented in figure 2.2.

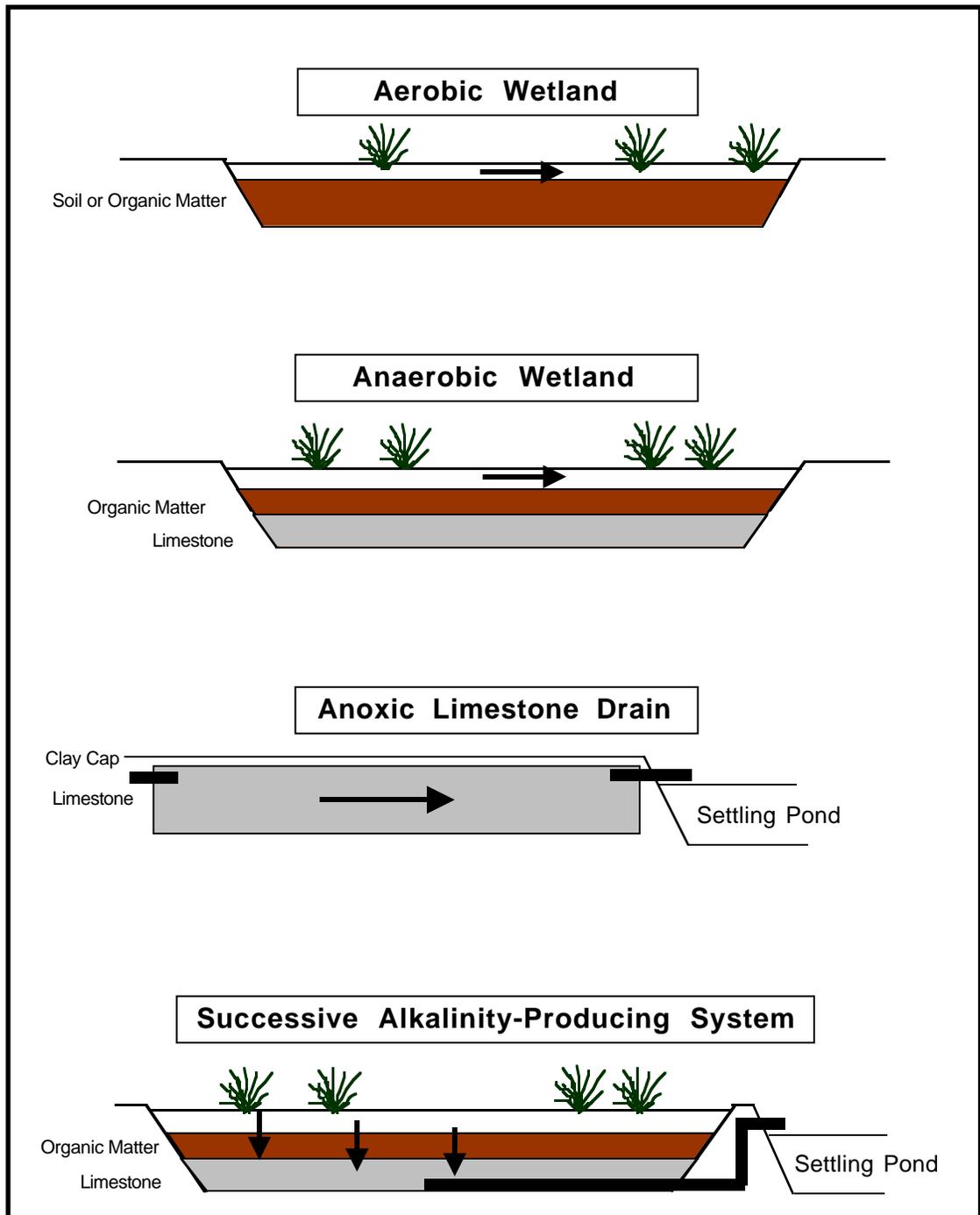


Figure 2.2. Cross sectional views of the four major passive treatment systems used in treating acidic mine drainage. Arrows represent predominant flow regime.