Wetland Use in Acid Mine Drainage Remediation

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ABSTRACT

There are estimates that 557,000 abandoned mines exist in the U.S. (Costello 2003), mostly coal mines in the western portion of the country. Many of these mines have no wastewater control features and become flooded over time. The ensuing highly acidic (pH~3) wastewater is laden with toxic heavy metals (Gibert et al. 2004). One method used to treat acid mine drainage is to divert water through wetlands. In wetlands, increasing pH and alkalinity influences heavy metal concentrations, while microbial and plant activity mineralizes contaminants to form precipitates. Different approaches can be taken to neutralize and remove targeted heavy metals, from aerobic wetlands for iron, anaerobic wetlands for other sulfides and metals, and using lime to influence pH and alkalinity.

KEYWORDS

Acid Mine Drainage (AMD), Remediation, Wetlands, Mine-Water Chemistry

INTRODUCTION: ACID MINE DRAINAGE

Abandoned and active mines are a major pollution concern. "In 1989, it was estimated that ca. 19,300 km of streams and rivers, and ca. 72,000 ha of lakes and reservoirs worldwide had been seriously damaged by mine effluents..." (Johnson and Hallberg 2005a). The U.S. Forest Service estimates that there are between 20,000 and 50,000 mines actively producing acid drainage in the western U.S. that affects between 8,000 and 16,000km of streams (Schlesinger 2002), while estimates from the Mineral Policy Center project that there are 557,000 abandoned mines in the U.S. (Costello 2003). The waters draining from these mines are often acidic and contain elevated concentrations of heavy metals (iron, aluminum, and magnesium) and metalloids (arsenic).

Active mines are only a minor concern compared to abandoned mines. Active mines may be deep and well below the water table, but pumping water out of the mine or lowering the water table keeps the water pollution to minimal levels. Once mines are abandoned and pumping ceases, the water table rises. Contaminated groundwater is then able to discharge from the mine, compounding the pollution problems. Some case studies included in this paper are the Wheal Jane mine, which in 1992 had 50,000m³ of acid mine drainage (AMD) released into the environment (Hallberg and Johnson 2005a), as well as mines in Korea and India.

In deep mining, large tunnels and slopes were cut down to coal deposits (Earth Conservancy, 2000). These mines usually have remnants of coal veins that were left to

support the mine structure. Mine openings and outfalls are two primary sources of AMD leaving mines. Outfalls are points of overflow from deep mines and are caused by holes that were drilled into the mine structure to relieve water accumulation when the mine was active. Another source of AMD is derived from culm banks that consist of separated rock and coal removed from the mine. Culm banks are generally stored outdoors exposed to precipitation, which develops into AMD.

Mine – Water Chemistry

The chemical composition of AMD can be complex, often depending on the geological formations found in the mine. Treating AMD is pivotal on what pollutants compositions are found in the waste stream. The following section details a few of the main heavy metals found in AMD.

Pyrite

The oxidation of iron pyrite (FeS₂) is one of the major sources of pollution. Pyrite is the world's most abundant sulfide mineral, and is present with most sulfide ores. The concentrations of pyrite in coal deposits are generally between 1-20 % (Johnson and Hallberg 2005a). Equation 1 shows a condensed formula for the reaction that occurs, which actually takes place over 4 steps.

$$4 \operatorname{FeS}_2 + 15 \operatorname{O}_2 + 14 \operatorname{H}_20 \rightarrow 4 \operatorname{Fe}(\operatorname{OH})_3 + 8 \operatorname{SO}_4^{2-} + 16 \operatorname{H}^+$$
(1)

Acidity

Acidic mine waters are typically caused by the oxidative dissolution of sulfide minerals, such as pyrite. The generation of free protons from the hydrolysis of metals, (Equation 2-5) causes a mineral acidity to develop (Hallberg and Johnson 2005a, Costello 2003). The acidic nature of mine wastes is also dependent on chemical concentrations in the area. Due to that, AMD covers a wide scope of toxic concentrations and pH levels.

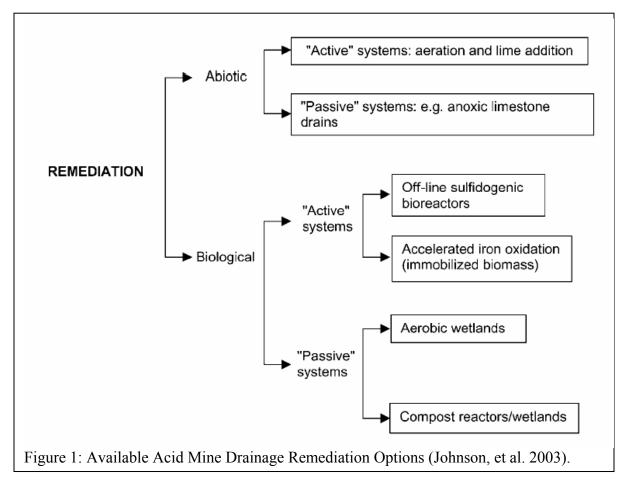
$Al^{3+} + 3 H_2O \rightarrow Al(OH)_3 + 3H^+$	(2)
$Fe^{+3} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$	(3)
$\operatorname{Fe}^{+2} + 0.25 \operatorname{O}_2(\operatorname{aq}) + 2.5 \operatorname{H}_2\operatorname{O} \longleftrightarrow \operatorname{Fe}(\operatorname{OH})_3 + 2\operatorname{H}^+$	(4)
$Mn^{+2} + 0.25 O_2(aq) + 2.5 H_2O \leftrightarrow Mn(OH)_3 + 2H^+$	(5)

There are also a variety of other reactions that contribute to the creation AMD, such as Equations 6-11 (Costello 2003).

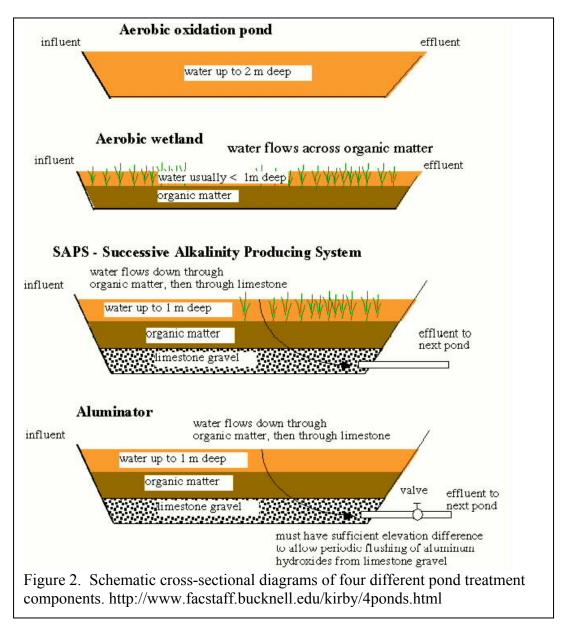
Sphalerite: $ZnS(s) + 2O_2(aq) \rightarrow Zn^{+2} + SO_4^{-2}$	(6)
Galena: $PbS(s) + 2O_2(aq) \rightarrow Pb^{+2} + SO_4^{-2}$	(7)
Millerite: NiS(s) + 2O ₂ (aq) \rightarrow Ni ⁺² + SO ₄ ⁻²	(8)
Greenockite: $CdS(s) + 2O_2(aq) \rightarrow Cd^{+2} + SO_4^{-2}$	(9)
Covellite: $CuS(s) + 2O_2(aq) \rightarrow Cu^{+2} + SO_4^{-2}$	(10)
Chalcopyrite: $CuFeS_2(s) + 4O_2(aq) \rightarrow Cu^{+2} + Fe^{+2} + SO_4^{-2}$	(11)

WASEWATER TREATMENT BY WETLANDS

Due to the large area of some abandoned mines, inhibiting the formation and release of waste drainage is impractical. That observation means that wastewater must be treated after it leaves the mine (Hallberg and Johnson 2005a). There are several active and passive methods being explored to treat AMD (see figure 1). The more cost intensive active systems include adding lime, aeration, off-line sulfidogenic bioreactors. Active treatment methods generally accrue more financial costs due to constant operation and maintenance fees (chemicals, mechanical systems) (Costello 2003). Passive systems include using anoxic limestone drains, aerobic wetlands, compost reactors, permeable reactive barriers, and packed bed iron-oxidation bioreactors. Wetlands have become a favorable option in comparison to other treatment methods because of the wetland is relatively self-sustaining once established, and wetlands are cheaper than active treatment systems.



The first attempts of using wetlands for AMD were in 1984, when Wieder and Lang detected that AMD that flowed through a bog was cleaner (Kalin 2004, Johnson et al. 2002). Further trials using bogs proved to less successful, but they did present evidence that microbial activity plays an active part in mineralizing metals into stable compounds and adding alkalinity to wastewater.



Aerobic Wetlands

Aerobic wetlands are primarily used when iron is the main contaminant. Aerobic wetlands also require net alkaline waters that are able to buffer an increase in hydrogen ions released from metal hydrolysis reactions. Aerobic wetlands generally are shallow and include plant to immobilize heavy metals (see figure 2). The main drawback to aerobic wetlands is that over time the accumulation of precipitate will severely limit their

remediation abilities. Periodic removal of precipitates is necessary, either through flushing the area or dredging (Costello 2003).

Anaerobic – Compost Reactors with Wetlands

"When waters are net acidic, the pH must be raised and ideally the waters will be bought to net alkaline conditions. When iron and aluminum are the main contaminants then alkaline addition followed by an aerobic settling pond is often used to precipitate metals and raise pH. The most common wetland application for hard rock mines aims to establish sulfate-reducing bacteria under anaerobic conditions and, as a result of the bacteria's metabolic needs, metals are precipitated as sulfides," (Costello 2003).

Anaerobic wetlands generally are accompanied by some form of bioreactor or chemical addition in order to control the pH and alkalinity.

Bioreactors

Passive bioreactors are defined as lined trenches and pits containing a mixture of organic matter and/or alkaline agent. Some examples of bioreactor fillings include compost, cobbles, animal waste, food processing waste, and crushed lime. The purpose of bioreactors is to adjust the pH of the AMD and to establish desired microorganisms (Costello 2003, Hallberg and Johnson 2005b).

Chemical Additions

Another approach used to increase the alkalinity in AMD wetland systems is the addition of lime into the system (see figure 2 for two examples of lime addition). The addition of lime (calcium carbonate) raises the pH of the wastewater by reacting with hydronion ions (Equations 12 & 13). Lime also adds alkalinity to the water by producing bicarbonate ions (Costello 2003, Younger et al., 2002). One option is to use an anoxic limestone drain that adds alkali to the AMD but does not oxidize ferrous iron to form precipitates (Johnson and Hallberg 2005a). It is important to limit iron precipitates on the limestone because the iron will dramatically decrease the effectiveness of the limestone.

$CaCO_3 + 2H \rightarrow Ca^2 + H_2O + CO_2$	(12)
$CaCO_3 + H_2CO_3 \rightarrow Ca^{+2} + 2HCO_3^{-1}$	(13)

Other chemicals that can be used to increase alkalinity include hydrated lime (calcium hydroxide), soda ash (sodium carbonate), caustic soda (sodium hydroxide), and ammonia (Costello 2003).

Microbial Activities

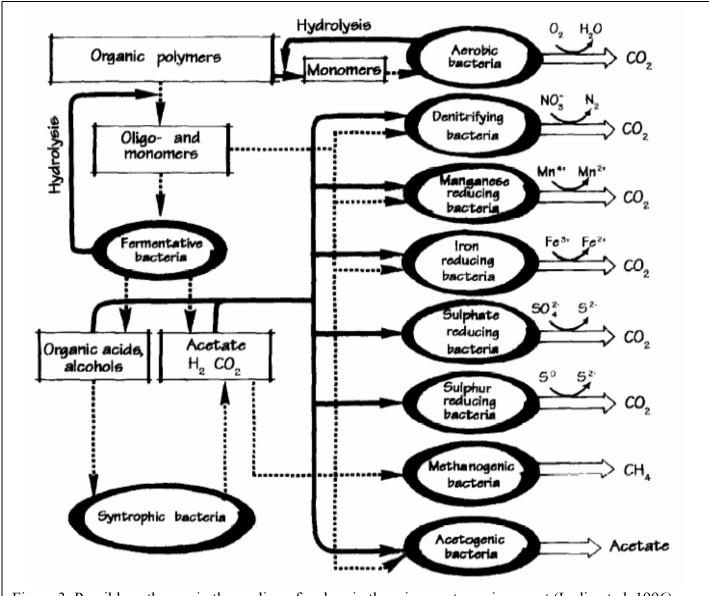


Figure 3: Possible pathways in the cycling of carbon in the mine waste environment (Ledin et al. 1996).

Microorganisms fulfill important roles in the creation and remediation of AMD. In regards to microorganisms causing AMD, the activities of acidophilic microorganisms in abandoned mines causes an increase in oxidation reactions. "Many of the microbial processes that can change metal mobility occur in drainage water from mine waste," (Costello 2003). In the case of bioremediation of AMD, microorganisms can also cause metal to become immobilized and generate alkali (see figure 3 for possible metabolic pathways).

Acidophilic microorganisms generally favor the environmental conditions seen in AMD, and the iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* tend to flourish in mine waters (Hallberg and Johnson 2005a). Once acidophilic bacteria are established, there is the possibility that they will increase chemical reactions involved in acid mine drainage, compounding the problem (Costello, 2003). Iron-oxidizing bacteria can precipitate ferric iron out of the AMD to improve water conditions.

"In terms of the operation of the treatment system, it is important to note that the presence of these versatile microbes in the water will compromise such a treatment system should any ferrous iron be present in these effluents as well. The iron-oxidizing *Thiomonas* will catalyze the oxidation of the ferrous iron to ferric iron. The subsequent hydrolysis of the ferric iron will generate more acidity, essentially leading to a reversal of the whole AMD remediation process" (Hallberg and Johnson 2005a).

Bacteria, such as species of *Thiomonas*, are able to oxidize reduced sulfur compounds as well as oxidize ferrous iron in aerobic conditions (Hallberg and Johnson 2005a). Plant Activities

Plant Activity – Phytoremediation

Phytoremediation is defined "the use of green plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants," (Costello 2003). There are several factors that must be addressed when studying the effectiveness of plants in AMD treatment. Ideal plants must be hardy; able to tolerate low nutrient levels, be resistant to weather shifts, and uptake more contaminants than normal plants. Determining acceptable plants for use in AMD remediation becomes difficult because of the specific characteristics displayed by plant species. There are 300 documented species that are capable of hyperaccumulating nickel, 26 cobalt, 24 copper, 19 selenium, 16 zinc, 11 manganese, 1 thallium, and 1 cadmium (Brooks et al. 1998, Costello 2003).

The use of phytoremediation is generally accompanied by other forms of treatment, such as bioreactors. Plant activity must be monitored to assure the system is effective and to determine the spread of immobilized contaminants. The initial uptake of heavy metals is sometimes associated with soil parameters more than plant types (Bogan and Sullivan 2003). As the soil becomes saturated, heavy metal seepage will minimize the effects of phytoremediation. Another negative aspect of using plants for AMD treatment is that caution must be taken to avoid animal consumption of contaminated vegetation (Costello 2003, Sheoran and Sheoran 2005, Collins et al. 2004).

Conclusion

Wetlands have proven to be effective in treating AMD in ideal conditions. While the source of pollution remains un-dealt with, the spread of pollution remains contained to the soil and plant life in the treatment system.

"....we are still not addressing the origins of the problem, that is, reaction rates and the contaminant generating process. Treatment approaches must be assessed for their effectiveness on appropriate time scales if we are to find truly sustainable solutions. There is no doubt that passive treatment systems and/or constructed wetlands effectively reduce organic water pollution. But when the run-off from mining wastes flow through wetlands, the deposition of metals onto adsorption sites can overload them, leading to system failure and wetland destruction" (Kalin 2004).

Fluctuations in source water (flooding, droughts) and the eventual buildup of precipitates lead to lower AMD remediation and are negative aspects of using wetlands. Wetlands also are ineffective in areas with rocky soils and steep slopes. Close proximity to floods and large land requirements negatively impact wetland use. Yet the cost of using active treatment methods as opposed to passive treatments is not practical due to the nature of the problem. The majority of mines producing AMD in the U.S. currently have inefficient treatment systems, making active treatment financial improbable.

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