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Science of Acid Mine Drainage and Passive Treatment

What is Acid Mine Drainage (AMD)?

Drainage flowing from or caused by surface mining, deep mining or coal refuse piles that is typically highly acidic with elevated levels of dissolved metals.

How is AMD formed?

Basic AMD Chemistry

There are four commonly accepted chemical reactions that represent the chemistry of pyrite weathering to form AMD. An overall summary reaction is as follows:

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3\downarrow + 8\,H_2SO_4$$
Pyrite + Oxygen + Water → "Yellowboy" + Sulfuric Acid

The first reaction in the weathering of pyrite includes the oxidation of pyrite by oxygen. Sulfur is oxidized to sulfate and ferrous iron is released. This reaction generates two moles of acidity for each mole of pyrite oxidized.

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+$$
Pyrite + Oxygen + Water → Ferrous Iron + Sulfate + Acidity

The second reaction involves the conversion of ferrous iron to ferric iron. The conversion of ferrous iron to ferric iron consumes one mole of acidity. Certain bacteria increase the rate of oxidation from ferrous to ferric iron. This reaction rate is pH dependant with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5. This reaction is refered to as the "rate determining step" in the overall acid-generating sequence.

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O$$
Ferrous Iron + Oxygen + Acidity → Ferric Iron + Water

The third reaction which may occur is the hydrolysis of iron. Hydrolysis is a reaction which splits the water molecule. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependant. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.

$$4\,Fe^{3+} + 12\,H_2O \rightarrow 4\,Fe(OH)_3\downarrow + 12\,H^+$$
Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

The fourth reaction is the oxidation of additional pyrite by ferric iron. The ferric iron is generated in reaction steps 1 and 2. This is the cyclic and self propagating part of the overall reaction and takes place very rapidly and continues until either ferric iron or pyrite is depleted. Note that in this reaction iron is the oxidizing agent, not oxygen.

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$$
Pyrite + Ferric Iron + Water → Ferrous Iron + Sulfate + Acidity

Treatment of AMD

In 1968, Pennsylvania instituted strict effluent discharge limitations on mine operations. Many mining companies used chemical treatment methods to meet these new effluent limits. In these chemical treatment systems, the acidity is buffered by the addition of alkaline chemicals such as calcium carbonate, sodium hydroxide, sodium bicarbonate or anhydrous ammonia. These chemicals raise the pH to acceptable levels and decrease the solubility of dissolved metals. Precipitates form that are settled from the solution. But these chemicals are expensive and the treatment system requires additional costs associated with operation and maintenance as well as the disposal of metal-laden sludges.

Passive Treatment of AMD

As early as 1978, many variations of AMD passive treatment systems were studied by

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numerous organizations on the laboratory bench-testing level. During the last 15 years, passive treatment systems have been implemented on full-scale sites throughout the United States with promising results. The concept behind passive treatment is to allow the naturally occurring chemical and biological reactions that aid in AMD treatment to occur in the controlled environment of the treatment system, and not in the receiving water body.

Passive treatment conceptually offers many advantages over conventional active treatment systems. The use of chemical addition and energy consuming treatment processes are virtually eliminated with passive treatment systems. Also, the operation and maintenance requirements of passive systems are considerably less than active treatment systems.

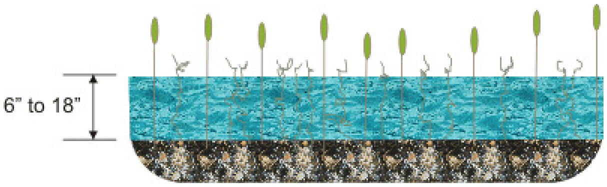
The first passive technology involved the use of natural Sphagnum wetlands that could improve the water quality of AMD without causing other detrimental impacts on the ecosystem. Although this concept had its limitations, it spawned research and development into other passive treatment technologies that did not follow the natural wetland paradigm.

Designing a passive treatment system for AMD requires the understanding of mine water chemistry, available treatment techniques and experience. Analytical sampling of the AMD is extremely important in the selection of appropriate treatment technologies.

Passive AMD Treatment Technologies

Aerobic Wetland:

An aerobic wetland consists of a large surface area pond with horizontal surface flow. The pond may be planted with cattails and other wetland species. Aerobic wetlands can only effectively treat water that is net alkaline. In aerobic wetland systems, metals are precipitated through oxidation reactions to form oxides and hydroxides. This process is more efficient when the influent pH is greater than 5.5. Aeration prior to the wetland, via riffles and falls, increases the efficiency of the oxidation process and therefore the precipitation process. Iron concentrations are efficiently reduced in this system but the pH is further lowered by the oxidation reactions.



Typical Section of an
Aerobic Wetland

A typical aerobic wetland will have a water depth of 6 to 18 inches. Variations in water depth within the wetland cell may be beneficial for performance and longevity. Although shallow water zones freeze more quickly in winter, they enhance oxygenation and oxidizing reactions and precipitation. Deeper water zones provide storage areas for precipitates but decrease vegetative diversity.

Aerobic wetlands are sized based on the criteria developed by the now defunct U.S. Bureau of Mines for abandoned mined lands (AML) and compliance. AML criteria for aerobic wetland sizing is as follows:

Minimum wetland size (ac) = [Fe loading (lb/day) ÷ 180 (lb/ac/day)] +
[Mn loading (lb/day) ÷ 9 (lb/ac/day)] +
[Acidity (lb/day) ÷ 60 (lb/day/acre)]

To calculate loading rates (lb/day), take the flow rate (gpm) x concentration (mg/l) x 0.012.

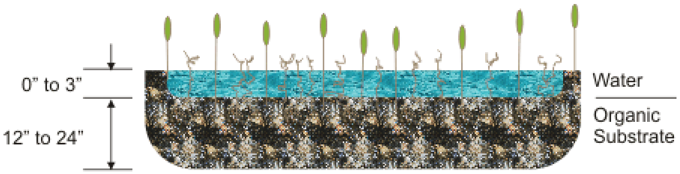
The factor of 0.012 converts gallons per minute and milligrams per liter to pounds per day as follows:

lb/day = (gal/min)(mg/l)(3.8 l /gal)(g/1000 mg)(lb/454 g)(60 min/hr)(24 hours/day)

Compliance criteria are suggested for wetlands that have to meet a specific National Pollution Discharge Elimination System (NPDES) effluent limitation. Compliance criteria are more conservative than AML criteria and results in wetlands that are approximately twice as large.

Compost or Anaerobic Wetland

Compost wetlands, or anaerobic wetlands as they are sometimes called, consist of a large pond with a lower layer of organic substrate. The flow is horizontal within the substrate layer of the basin. Piling the compost a little higher than the free water surface can encourage the flow within the substrate. Typically, the compost layer is made from spent mushroom compost that contains about 10 percent calcium carbonate. Other compost materials include peat moss, wood chips, sawdust or hay. A typical compost wetland will have 12 to 24 inches of organic substrate and be planted with cattails or other emergent vegetation. The vegetation helps stabilize the substrate and provides additional organic materials to perpetuate the sulfate reduction reactions.



Typical Section of an Anaerobic or Compost Wetland

Anaerobic wetlands are used to treat AMD from active mine discharges to meet established effluent requirements. Generally, the design of these wetlands is conservative and can treat discharges that contain dissolved oxygen, Fe^{3+}, Al^{3+} or acidity less than 300 mg/l. When treating discharges from abandoned mines the goal is to reduce the pollution to levels that will restore the receiving stream. In these cases, wetlands can accept discharges with an acidity in the 500 mg/l range.

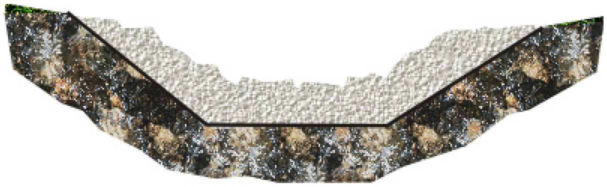
The compost wetland acts as a reducing wetland where the organic substrate promotes chemical and microbial processes that generate alkalinity and increase the pH. The compost removes any oxygen in the system. This allows sulfate to be reduced and also keeps the metals from oxidizing and armoring or coating the limestone present in the compost, thereby preventing its dissolution. Microbial respiration within the organic substrate reduces sulfates to water and hydrogen sulfide. The anoxic environment within the substrate also increases the dissolution of limestone.

Anaerobic wetlands are sized according to U.S. Bureau of Mines criteria for AML sites as follows:

Minimum wetland size (m^2) = acidity loading (g/day) ÷ 0.7

Open Limestone Channels

Open limestone channels may be the simplest passive treatment method. Open limestone channels are constructed in two ways. In the first method, a drainage ditch is constructed of limestone and AMD-contaminated water is collected by the ditch. The other method consists of placing limestone fragments directly in a contaminated stream. Dissolution of the limestone adds alkalinity to the water and raises the pH. Armoring or the coating of the limestone by $Fe(CO)_3$ and $Fe(OH)_3$ produced by neutralization reduces the generation of alkalinity, so large quantities of limestone are needed to ensure long-term success. High flow velocity and turbulence enhance the performance by keeping precipitates in suspension thereby reducing the armoring of the limestone. Open limestone channels are sized according to standard engineering practice using the Manning equation and providing additional freeboard. Impervious liners are sometimes used under the limestone to prevent infiltration of the AMD into the groundwater table.

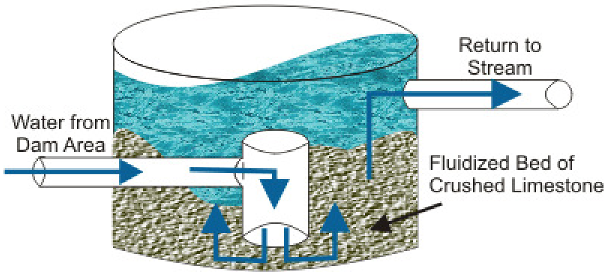


Cross Section of an Open Limestone Channel

Diversion Wells

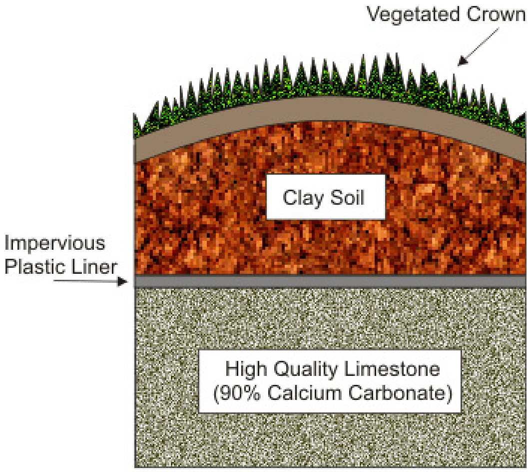
Diversion wells are another simple way of adding alkalinity to contaminated waters. Acidic water is conveyed by a pipe to a downstream "well" which contains crushed limestone aggregate. The hydraulic force of the pipe flow causes the limestone to turbulently mix and abrade into fine particles and prevent armoring. The water flows upward and overflows the "well" where it is diverted back into the stream. Diversion wells require frequent refilling with clean limestone to assure continued treatment.

Schematic View of a Diversion Well



Anoxic Limestone Drains (ALD)

An anoxic limestone drain (ALD) is a buried bed of limestone constructed to intercept subsurface mine water flows and prevent contact with atmospheric oxygen. Keeping oxygen out of the water prevents oxidation of metals and armoring of the limestone. The process of limestone dissolution generates alkalinity. The sole purpose of an ALD is to provide alkalinity thereby changing net acid water into net alkaline water. Retaining carbon dioxide in the drain can improve limestone dissolution and alkalinity generation.



Cross Section of an Anoxic Limestone Drain

An ALD can be considered a pretreatment step to increase alkalinity and raise pH before the water enters a constructed aerobic wetland. In the aerobic wetland, metals can be oxidized and precipitated. ALDs are limited to the amount of alkalinity they can generate based on solubility equilibrium reactions. Also, the effectiveness and longevity of an ALD can be substantially reduced if the AMD has high concentrations of ferric iron, dissolved oxygen or aluminum.

ALDs are sized based on the assumption that the drain will produce water between 275 and 300 mg/l of alkalinity. The amount of alkalinity generated is based on the solubility of the calcite within the limestone and the retention time within the ALD. Retention times of 14 to 15 hours are used as standard practice to balance construction costs and the efficiency of alkalinity generation. The overall equation to calculate the mass of limestone necessary for an ALD is as follows:

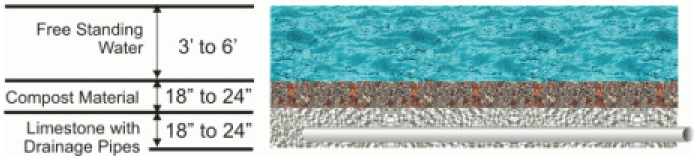
$$M = (Q\ r\ b\ td / Vv) + (Q\ C\ T / x)$$

Where M = mass of limestone in tons
Q = flow rate of AMD in cubic meters per day
r b = bulk density of the limestone in tons per cubic meter
td = retention time in days, 0.625 days is standard practice
Vv = bulk void ratio expressed as a decimal
C = effluent alkalinity concentration in tons per cubic meter
T = design life of the drain in days, typically 9,125days (25 years)
x = $CaCO_3$ content of the limestone as a decimal

Vertical Flow Reactors (VFR)

Vertical flow reactors (VFR) were conceived as a way to overcome the alkalinity producing limitations of ALD's and the large area requirements for compost wetlands. The VFR consists of a treatment cell with an underdrained limestone base topped with a layer of organic substrate and standing water. The water flows vertically through the compost and limestone and is collected and discharged through a system of pipes. The VFR increases alkalinity by limestone dissolution and bacterial sulfate reduction. Highly acidic waters can be treated by running the AMD through a series of VFRs. A settling pond and an aerobic wetland where metals are oxidized and precipitated typically follow a VFR plan.

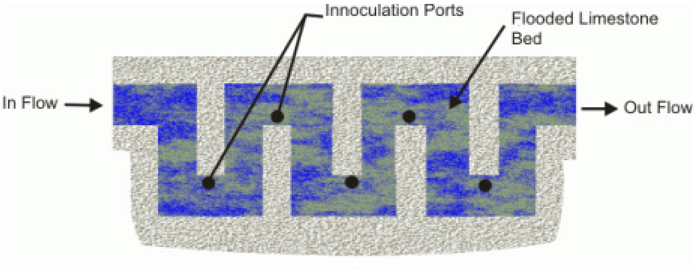
Typical Section of a Vertical Flow Wetland



VFRs are sized based on retention times required to produce the necessary alkalinity. Retention times of 12 to 15 hours are typically used for sizing VFRs and the amount of limestone necessary is calculated as shown above for ALDs.

Pyrolusite® Process

This patented process utilizes site-specific laboratory cultured microbes to remove iron, manganese and aluminum from AMD. The treatment process consists of a shallow bed of limestone aggregate inundated with AMD. After laboratory testing determines the proper combinations, the microorganisms are introduced to the limestone bed by inoculation ports located throughout the bed. The microorganisms grow on the surface of the limestone chips and oxidize the metal contaminants while etching away limestone, which in turn increases the alkalinity and raises the pH of the water. This process has been used on several sites in western Pennsylvania with promising results.



Plan View of a Pyrolusite Bed

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