

Overview of AMD Treatment Technologies

Contaminated mine waters are treated with active and passive technologies. Active technologies typically involve industrial chemicals, mechanical equipment, electricity, and regular operational oversight. Passive technologies utilize natural materials, natural chemical and biological processes, and require infrequent operational oversight. Passive treatment is a preferred first-consideration for mine water remediation because, compared to active alternatives, it can have significantly lower routine and long-term operation and maintenance (O&M) requirements. The following sections describe passive and active treatment technologies that could be applicable to the Upper Two Lick Creek AMD problems. The discussion is intended to identify appropriate treatment technologies. The design and sizing of treatment systems can be completed using AMDTreat (<https://www.osmre.gov/programs/reclaiming-abandoned-mine-lands/amdtreat>) or recommendations by a consulting engineer.

1. Passive Treatment

A variety of passive treatment technologies exist, and the appropriate technology is based on mine water chemistry. Photo 1 is a decision tree that is used to identify appropriate passive technologies based on water chemistry and effluent targets. Once the appropriate technologies have been selected, sizing the of the technology is based on flow and loading rates.

For passive treatment purposes, mine water chemistry is divided into alkaline and acid mine water:

Alkaline mine water has $\text{pH} > 6$ and contains more alkalinity than acidity. These net alkaline waters are often reported by laboratories as having negative hot acidity. The primary contaminant of alkaline mine water is ferrous iron with manganese as a secondary contaminant. Aluminum is sparingly soluble at $\text{pH} 6-8$ and so is typically not a problem with alkaline mine waters. Alkaline Fe-contaminated discharges commonly occur from flooded underground mines with carbonate overburdens and from surface mines with a net alkaline overburden (natural or through amendments).

The treatment of alkaline mine waters does not require the addition of alkalinity. The primary focus of their treatment is the creation of oxic conditions that promote the oxidation and precipitation of Fe and Mn.

Acid mine water contains more acidity than alkalinity. The acidity is primarily due to dissolved Fe and Al and to a lesser degree from low pH and Mn. The treatment of acidic waters requires the addition of alkalinity. The two sources of alkalinity in passive systems are limestone containing calcite (CaCO_3) and organic substrates. The dissolution of calcite raises pH and generates alkalinity. The anaerobic decomposition of organic substrate by microbes generates alkalinity and hydrogen sulfide (H_2S) which will precipitate divalent metals (Fe, Zn, Cu, Cd, etc.). Depending on the treatment, the effluent of the alkalinity-generating unit may require further treatment to remove residual metals, H_2S , and dissolved organic carbon.

Selection of Appropriate Passive Treatment Technology:

1.1 Alkaline Water Containing Fe – Settling ponds and wetlands

The removal of Fe from net alkaline waters is achieved through oxidation and settling. The standard passive technology is oxidation/settling ponds followed by constructed wetlands. The ponds remove and store Fe solids and the constructed wetlands remove residual Fe. The oxidation of Fe requires dissolved oxygen which is typically provided through waterfalls, weirs, and air-water exchange at the pond surface.

1.2 Alkaline Water Containing Mn – Wetland or aggregate bed

The removal of Mn from net alkaline waters is achieved through oxidation and precipitation. Ferrous iron (Fe⁺²) interferes with Mn oxidation, so the treatment requires prior removal of Fe²⁺. The Mn removal process is microbial and is enhanced by substrate on which the microbes can attach. Constructed wetlands provide organic substrate and can be used to remove Mn. Aggregate is an effective substrate for microbial attachment and Mn removal. In situations where treatment of Mn is specifically targeted (i.e. NPDES permit) an oxic aggregate bed is the most efficient and reliable method for Mn treatment.

1.3 Acidic Water Containing Fe and Mn

1.3.1 Anoxic Limestone Drain

In some coal-producing regions, mine water discharges are characterized by pH 5-7 with alkalinity but are net acidic because of high concentrations of Fe⁺² and Mn. If treated with only aerobic technologies, Fe will be decreased through oxidation and precipitation, but the alkalinity will be consumed and a low pH discharge will result. The simplest treatment of these waters is an anoxic limestone drain (ALD). The mine water is collected and piped into a buried bed of limestone aggregate. The collection and construction must maintain anoxic conditions. Flow through the bed generates additional alkalinity but does not remove Fe or Mn due to anoxic conditions. The effluent from the ALD is alkaline and the removal of Fe and Mn is accomplished with aerobic treatment (see alkaline water containing Fe and Mn above). When properly designed and installed, ALDs provide decades of treatment benefits with minimal O&M.

ALDs should not be installed to treat waters with Al, ferric iron (Fe⁺³), or dissolved oxygen (DO) because these conditions result in the formation of solids that will plug the limestone aggregate. Dissolved Al and Fe³⁺ form hydroxide solids at pH 6-8, irrespective of the presence of anoxic conditions. If DO and ferrous iron are present, Fe will oxidize and form oxyhydroxide solids within the aggregate.

The amount of alkalinity generated by an ALD is limited by calcite solubility equilibria. Generally, ALDs discharge at least 150 mg/L alkalinity which is sufficient to neutralize the acidity produced by the oxidation and hydrolysis of 80 mg/L Fe. However, for discharges with greater than 80 mg/L Fe, the ALD pre-treatment may not produce a net alkaline discharge. In these cases, additional alkalinity generation features are required (see below).

1.3.2 Oxic Limestone Drain

An oxic limestone drain is a bed of limestone aggregate that is open to the atmosphere. OLDs allow Al, Fe, and Mn precipitation to occur within the aggregate bed. The short-term result is typically an alkaline discharge with pH 6-7 and low concentrations of metals. The drawback of the OLD is the accumulation of Al, Fe, and Mn solids that decrease limestone permeability and reactivity. This results in a decline in treatment effectiveness that necessitates rehabilitation or replacement of the limestone. The problem of solids accumulation in OLDs can be mitigated in several ways.

1. Oxic Limestone Channel (OLC). The limestone can be installed in steep channels (minimum 20% slope) that create water velocities that are sufficient to carry some of the solids to the bottom of the channel. OLCs typically raise pH and decrease concentrations for acidity, Fe and Al but do not create an effluent with neutral pH and low concentrations of metals. The effluent if the OLC typically requires further treatment.

2. Ramp Oxic Limestone Bed. For beds with horizontal flow through the aggregate, the stone can be installed in the shape of a ramp. As limestone in beginning of the bed becomes plugged, water will flow up the ramp and into un-plugged aggregate. This design provides a method of naturally mitigating permeability losses. The effluent of a Ramp OLB can be good quality and suitable for discharge.

3. Drainable Oxic Limestone Bed. Aggregate beds can be constructed with a flushing system that removes a portion of the solids when the bed is rapidly drained empty. Automated flushing devices are available that operate based on water level in the bed (siphon) or a specified time interval (Agridrain SDS). The routine effluent from a drainable oxic limestone bed can be good quality and suitable for discharge. The water produced during flushing events contains high concentrations of solids and must be settled in a settling pond.

Eventually the limestone aggregate in oxic limestone beds must be rehabilitated and/or replaced. The Fe and Al solids in OLBs can be readily removed by stirring in water. Rehabilitation can range from stirring, which moves the solids to the bottom of the bed, to washing with removal of the high TSS water. The frequency of rehabilitation depends on the design and concerns about the effluent quality. Generally, a rehabilitation schedule of every 3-7 years should be assumed.

1.3.3 Vertical Flow Pond

A vertical flow pond treats acidic water contaminated with Fe and Al through a combination of microbial activity and limestone dissolution. A variety of designs exist. The commonly used design consists of a layer of limestone aggregate overlain with a layer of alkaline organic substrate overlain with standing water. The limestone aggregate and organic matter layers may also be mixed into a single layer. The mine water enters at the surface and flows vertically down through the layers to a distributed collection system placed at the bottom of the limestone layer. The collected water is discharged through a water level control structure that determines the water elevation in the pond.

VFPs are also called SAPS (successive alkalinity producing systems) and RAPS (reducing and alkalinity producing system). The depths of the organic and limestone layers differs between

systems. Bioreactors and “Jennings” systems contain predominantly organic substrate, which is intended to promote microbial activity, especially bacterial sulfate reduction.

There are few limits on the influent quality of the VFPs. The technology has been very effective in treating mine waters with low pH and elevated concentrations of Al and Fe. When properly designed and installed, VFPs discharge alkaline water with pH 7-8 and less than 1 mg/L Al. Removal of Fe is variable, with most systems removing 10-30 mg/L Fe. Little Mn removal occurs. The effluent of VFPs commonly contains reduced sulfur compounds and dissolved organic carbon which requires aerobic treatment (pond or wetland).

Over time the organic substrate in VFPs becomes less permeable and reactive due to the precipitation of Fe and Al solids and will need to be replaced. The frequency of replacement depends on the design but is generally every 10-15 years.

2. Active Treatment

Active mine water treatment involves the addition of industrial chemicals and use of mechanical devices to promote neutralization and metal removal. Active systems generally provide faster treatment than passive systems and so have smaller footprints. The sludge produced in active system is less dense than passive systems and requires more frequent management.

2.1 Sodium Hydroxide

Sodium hydroxide (NaOH) is a highly alkaline reagent that is added to AMD to raise pH to precipitate metals. It is provided in liquid form which is stored in a tank on-site and added to the mine water using valves or pumps. Metal solids typically accumulate in a settling pond. When properly sized and operated, the effluent of the setting ponds can be discharged. Sludge in the settling ponds must be removed, typically on an annual schedule.

The high pH conditions created with NaOH are suitable for treatment of Al, Fe, and Mn. It is possible to overtreat and discharge water to pH > 10, which can be problematic depending on the quality of the receiving stream. NaOH treatment is generally not cost-effective on AML sites due to high reagent and operator costs.

2.2 Lime and Lime Slurry

Lime (CaO) is the most inexpensive manufactured alkaline chemical. When delivered in a dry form, it is either added directly to mine water or mixed with water to create a slurry $\text{Ca}(\text{OH})_2$ that is then added to the mine water. Managing an on-site mixing process is difficult so pre-mixed lime slurry has become an attractive alternative. The lime slurry is delivered by tanker trucks and stored on site in a tank that is continuously mixed to maintain the slurry. The reagent is added to the mine water using pumps. The slurry/mine water mixture is sent to setting ponds where metal solids precipitate. When properly sized and operated, the effluent of the settling ponds can be discharged. Sludge in the settling ponds must be removed, typically on an annual schedule.

Alternatively, lime or lime slurry can be added directly into acidic streams to raise pH and precipitate Fe and Al. Metals solids will accumulate in the stream channel.

2.3 Hydrogen Peroxide

Hydrogen peroxide (H₂O₂) is a power oxidizing reagent that is added to AMD to oxidize dissolved Fe. It is provided in liquid form which is stored in a tank on-site and added to the mine water using valves or pumps. Metal solids typically accumulate in a settling pond. When properly sized and operated, the effluent of the setting ponds can be discharged. Sludge in the settling ponds must be removed, typically on an annual schedule.

Hydrogen peroxide is only appropriate for treatment of alkaline mine water because it does not add alkalinity. Additionally, it will not oxidize dissolved Mn. Therefore, it is only appropriate to remove Fe from alkaline mine water.

3. Hybrid and Innovative Treatment Technologies

A combination of active and passive technologies can be effective for speeding metal removal reactions and thus reducing treatment system sizes. The removal of Fe from alkaline waters can be limited by pH and dissolved oxygen concentrations. Both can be increased through mechanical aeration. While aerators typically require electricity, the cost of the hybrid system can be substantially less than one using only chemical technologies.

Lime slurry systems generally operate at pH 8-10, which can be ineffective for Mn removal. Instead of using additional chemicals to promote Mn removal, it can be cost-effective to treat the settling pond effluent with a wetland or oxic aggregate bed.

Research into innovative mine water treatment technologies is ongoing. A recent EPA-sponsored project showed that the alkalinity production by ALDs could be enhanced by adding gaseous CO₂ to the influent mine water. This technology would be applicable to discharges with high (> 100 mg/L) ferrous iron concentrations. The cost-effectiveness of the technology has not been established.

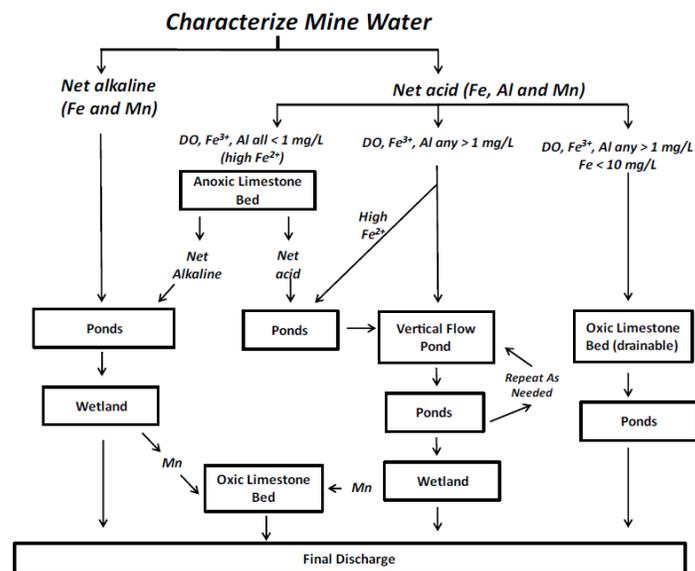


Photo 1: Passive Treatment decision tree