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PASSIVE SYSTEMS FOR TREATING ACID MINE DRAINAGE: A GENERAL REVIEW

Abstract: *The environmental effects of acid mine drainage can be devastating. Acidity destroys vegetation, accelerates erosion, and increases the susceptibility of fish to disease while dissolved and precipitated metals contaminate soils and render water supplies unsuitable for human consumption. Treatment of acid mine drainage is a challenge because of its persistent nature. Once initiated, acid mine drainage can continue for decades and often long after active mining operations have ceased. Traditional treatment methods based on neutralization with alkaline reagents are not perfect solution for the problem, because they require continual supervision and a substantial investment in resources. Variations in local conditions require treatments tailored to individual sites. Recently, passive treatment systems have been proposed and implemented as low-cost, long-term treatment options. This review summarize literature data about many different types of acid mine drainage problems and passive systems for treating acid mine drainage. The paper also presents applications of passive systems for treatment and bioremediation of acid mine drainages.*

Key words: acid mine drainage, passive treatment technology, constructed wetlands, bioremediation.

INTRODUCTION TO ACID MINE DRAINAGE

Acidic drainage is a natural process that becomes accelerated and intensified by mining. When rock is exposed to weathering, it will release minerals as it comes into equilibrium with its environment [1]. Any dissolved metal leached from the rock will hydrolyze when it comes into contact with water, and will produce acid [1]. However, the primary metal related to acid mine drainage is iron. Combined with sulfate and/or sulfide, iron can cause real problems [1]. When acid mine drainage enters natural waterways, changes in pH and the formation of voluminous precipitates of metal hydroxides can devastate fish populations and other aquatic life (Figure 1).

In brief, the major cause is the accelerated oxidation of iron pyrite (FeS_2) and other sulphidic minerals resulting from the exposure of these minerals to both oxygen and water, as a consequence of the mining and processing of metal ores and coals. Many metals occur primarily as sulfide ores (zinc in sphalerite), and these tend to be associated with pyrite, which is the most abundant sulfide mineral on the planet. Coal deposits contain arable (generally 1–20%) amounts of “pyritic-sulfur” (a generic term that includes other iron sulfide minerals such as marcasite) as well as organic sulfur [2].

Pyrite oxidation is a multistep process involving an oxygen-independent reaction (ferric iron attack on the mineral) and oxygen-dependent reactions (reoxidation of ferrous iron to ferric and oxidation of reduced sulfur compounds produced as intermediates in the process, ultimately to sulfate).

Figure 1. *Mixing of acid mine drainage (right) with a natural stream resulting in the formation of voluminous precipitates [3]*

$$4FeS_2+15O_2+14H_2O \rightarrow 4Fe(OH)_3+8SO_4^{2-}+16H^+ \quad (1)$$

The regeneration of ferric iron (which is reduced to ferrous on reaction with pyrite) is the key reaction in promoting the ongoing oxidation of the mineral. At pH values above 4, this may be mediated chemically or biologically (by iron-oxidising bacteria such as *Gallionella ferruginea*), while below pH 4, abiotic iron oxidation is negligible [4], and the activities of moderately and extremely acidophilic iron-oxidising bacteria have a pivotal role in the genesis of acid mine drainage [5].

Acid mine drainage may form in underground workings of deep mines, although this is generally of minor importance when a mine is in active production and water tables are kept artificially low by pumping. However, when mines are closed and abandoned, and the pumps turned off, the rebound of the water table can lead to contaminated groundwater being discharged. Since the water that refills the mine dissolves any acidic salts that have built up on the pore spaces of the exposed walls and ceilings of underground chambers, this initial drainage water tends to be more potentially polluting (in terms of acidity and metal content) than acid mine drainage that is discharged subsequently [6]. Acidic metal-rich waters may also form in spoil heaps and mineral tailings. Due to the more disaggregated (and more concentrated) nature of the acid-generating minerals in these waste materials, acid mine drainage that flows from them may be more aggressive than that which discharges from the mine itself. Another important consideration here is the potential long-term pollution problem, as production of acid mine drainage may continue for many years after mines are closed. Although the generic term “acid mine drainage” is used frequently to describe mine water discharges, the pH of these waters may be above 6, particularly at the point of discharge (where dissolved oxygen concentrations are frequently very low).

Net acidity in acid mine drainage needs to be offset against any alkalinity present; this is chiefly in the form of bicarbonate (HCO_3^-) deriving from the dissolution of basic minerals (e.g., calcium carbonate), though biological processes may also generate alkalinity in acid mine drainage streams.

PASSIVE TREATMENTS TECHNOLOGIES

Passive treatment can be defined as any technology that takes advantage of chemical and biological processes that occur in nature, to upgrade contaminated water. Passive treatment systems were initially considered attractive to treat acid mine drainage (AMD) due to their expected lower costs of construction, operation and maintenance, and their ability to operate at remote locations with limited operational requirements.

Passive treatment systems for acid mine drainage use the chemical, biological and physical removal processes that occur naturally in the environment to modify the influent characteristics and ameliorate any associated environmental impacts. The major processes include:

- Chemical processes: oxidation, reduction, coagulation, adsorption, absorption, hydrolysis, precipitation;
- Physical processes: gravity, aeration, dilution;
- Biological processes: biosorption, biomineralization, bioreduction, alkalinity generation.

The primary passive technologies include constructed treatment wetlands (aerobic and anaerobic), anoxic limestone drains, successive alkalinity producing systems, limestone ponds, and open limestone channels.

Each of these technologies are described briefly below, and discussed in detail within the sections that follow.

Significant biological processes

The basis of bioremediation of acid mine drainage derives from the abilities of some microorganisms to generate alkalinity and immobilize metals, thereby essentially reversing the reactions responsible for the genesis of AMD.

Microbiological processes that generate net alkalinity are mostly reductive processes and include denitrification, methanogenesis, sulfate reduction, iron and manganese reduction. Ammonification (the production of ammonium from nitrogen-containing organic compounds) is also an alkali-generating process. Due to the relative scarcity of the necessary materials, some of these processes tend to be of minor importance in acid mine drainage (AMD)-impacted environments [2].

Ferric iron and sulfate tend to be highly abundant in acid mine drainage, alkali genesis resulting from the reduction of these two species has a potentially major significance in acid mine drainage impacted waters. Photosynthetic microorganisms, by consuming a weak base (bicarbonate) and producing a strong base (hydroxyl ions), also generate net alkalinity (Equation (2)) [2].

$$6\ HCO_3^-\ (aq) + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6\ OH^- \quad (2)$$

While the reduction of soluble ferric iron does not decrease solution acidity, the reduction of solid phase (crystalline and amorphous) ferric iron compounds does, as indicated in Equation (3), where e^- represents an electron donor, which is generally supplied by an organic substrate [2].

$$Fe\ (OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad (3)$$

Bacteria that catalyze the dissimilatory reduction of sulfate to sulfide generate alkalinity by transforming a strong acid into a relatively weak acid -hydrogen sulfide as indicated in Equation (4) [2].

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2CO_3 \quad (4)$$

Besides the ameliorative effect on acid mine drainage brought about by the resulting increase in pH, the reduction of sulfate is an important mechanism for removing toxic metals from acid mine drainage, since many of them (e.g., zinc, copper and cadmium) form highly insoluble sulfides (e.g., Equation (2)).

$$Zn^{2+} + H_2S \rightarrow ZnS + 2H^+ \quad (5)$$

Biological oxidation of ferrous iron to ferric is the other major metal immobilizing process that occurs in aerobic wetlands and bioreactors [2].

The majority of bioremediation options for acid mine drainage are passive systems, and of these, only constructed wetlands and compost bioreactors have so far been used in full-scale treatment systems. The major advantages of passive bioremediation systems are their relatively low maintenance costs, and the fact that the solid-phase products of water treatment are retained within the wetland sediments.

On the downside, they are often relatively expensive to install and may require more land area than is available or suitable, their performance is less predictable than chemical treatment systems, and the long-term fate and stability of the deposits that accumulate within them are uncertain [2].

Constructed Treatment Wetlands

Wetlands can reduce acid mine drainage through physical, chemical, and biological processes. The physical processes, such as filtration and sedimentation, are important in removing particulate metals. The chemical and biological processes remove dissolved metals. Wetlands mainly remove metals through adsorption to organic substrates, and through bacteria. Because plant uptake accounts for only about 10% of the metal removal, plants are considered optional [2]. Acid mine drainage should not be routed into a natural wetland for treatment. Instead, a wetland should be constructed to meet the needs of acid mine drainage treatment. A natural wetland may or may not meet those needs, and may cause more problems than it solves. In addition, it is illegal to intentionally pollute a wetland.

Two types of wetlands are used for acid mine drainage treatment: aerobic and anaerobic.

Figure 2. *Aerobic wetlands [7]*

Aerobic wetlands are generally constructed to treat acid mine waters that are net alkaline. This is because the main remediative reaction that occurs within them is the oxidation of ferrous iron and subsequent hydrolysis of the ferric iron produced, which is a net acid generating reaction (Equation (6) and (7)) [2].

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (6)$$

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe\,(OH)_3 + 12H^+ \quad (7)$$

If there is failing alkalinity in the mine water to prevent a significant fall in pH as a result of these reactions, this may be amended by the incorporation of, for example, an anoxic limestone drains. In order to maintain oxidizing conditions, aerobic wetlands are relatively shallow systems that operate by surface flow. Macrophytes are planted for aesthetic reasons to regulate water flow (e.g., to prevent channeling) and to filter and stabilize the accumulating ferric precipitates. They also provide additional surface area for precipitation of solid phase ferric iron compounds and minerals. In addition, by causing oxygen flow from aerial parts to their root systems, some aquatic plants may accelerate the rate of ferrous iron oxidation.

The aerobic wetlands collect water and provide residence time. Anaerobic wetlands generally contain a layer of limestone on the bottom.

When mine water contains dissolved oxygen (DO), ferric iron, or aluminum, or is net acidic, construction of an anaerobic wetland is recommended [2]. The limestone in an anaerobic wetland will raise the pH and decrease the residence time required to treat acid mine drainage. If dissolved oxygen, ferric iron, or aluminum is present, the limestone can become armored, limiting its effectiveness. In such cases, the limestone needs to be placed so that it is anaerobic to prevent armoring.

The processes going on at the bottom of the wetland are what make the wetland so effective at treating mine water. Both types of artificial wetland have a constructed substrate that will pull out most of the minerals and elevate the pH [2]. The two best materials to use for the substrate are fairly fresh municipal compost or cow manure mixed with hay. Other types of substrate material include mushroom compost, log yard waste, and peat moss [2].

Two problems must be recognized when using wetlands for remediation. Due to seasonal variation, the acid removal rate is not consistent. No design corrections are available now to solve this problem. Also, the rates of acid reduction/metal removal will decrease over time as the substrate becomes filled with metals. However, if the input flows are low and periodic maintenance is performed, wetlands can provide long-term treatment of mine drainage [2].

For wetlands to remove metals, the mine water needs to be held for 20 to 40 hours. If the mine water pH is below 5, the residence time should be 40 hours. If the pH is nearly neutral, the mine water needs approximately 20 hours of residence time. The final design and construction decisions will be based on the flow rate to be treated, the loading rates of the metals, and the space available.

Anaerobic Wetlands/Compost Bioreactors

In contrast to aerobic wetlands, the key reactions that occur in compost bioreactors used to mitigate acid mine drainage are anaerobic.

The term "compost bioreactor" is a preferable generic term to describe such systems, as in some installations, they are enclosed entirely below ground level and do not support any macrophytes, so that they should not be described as "wetlands". Indeed, whether or not macrophytes are used in constructed compost ecosystems is often down to aesthetic considerations alone.

Penetrating plant roots may cause the ingress of oxygen into the anaerobic zones, which is detrimental to reductive processes. The microbial catalyzed reactions that occur in compost bioreactors generate net alkalinity and biogenic sulfide, and therefore, these systems may be used to treat mine waters that are net acidic and metal-rich, such as acid mine drainage from abandoned metal mines. Again, in contrast to aerobic wetlands, the reductive reactions that occur within compost wetlands are driven by electron donors that derive from the organic matrix of the compost itself.

Figure 3. *Anaerobic wetlands [8]*

The choice of bulky organic materials used vary according to local availability as well as their proven effectiveness, although generally, the composts are prepared by mixing relatively biodegradable materials (e.g., cow or horse manure, or mushroom compost) with more recalcitrant materials (e.g., sawdust, peat, or straw). The slow biodegradation of the latter is presumed to act as a long-term provision of appropriate substrates (and ammonium) for the indigenous iron- and sulfate-reducing bacteria (FRB and SRB) that are generally considered to have the major roles in AMD remediation in compost bioreactors. However, there are few quantitative data on the relative significance of iron and sulfate reduction in compost wetlands [2], and virtually, nothing is known about how the microbiology of these systems changes as the ecosystem ages, especially with regard to substrate provision. Besides biologically mediated processes, AMD quality in compost wetlands is improved by filtration of suspended and colloidal materials and adsorption of metals by the organic matrix.

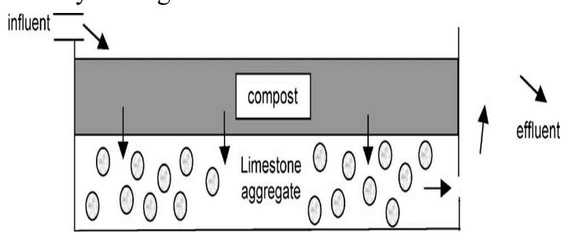

Figure 4. *Schematic layout of a reducing and alkalinity producing system (RAPS). Water flowing through the compost layer is stripped of dissolved oxygen, while both this layer and the underlying limestone add alkalinity to the acid mine drainage [2]*

An important engineering variant on the basic compost bioreactor theme is the reducing and alkalinity producing system (RAPS) layout [9], which is also referred to as successive alkalinity producing system (SAPS [2]). In this type of system (Fig. 4), AMD flow moves downwards through a layer of compost (to remove dissolved oxygen and to promote the reduction of iron and sulfate) and then through a limestone gravel bed (to add additional alkalinity, as in ALDs). Usually, water draining a RAPS flows into a sedimentation pond, and/or an aerobic wetland, to precipitate and retain iron hydroxides.

Figure 5 presents simple schematic diagram which illustrates the type of treatment wetlands used for mine waters where are:

A – Aerobic wetlands where emergent macrophites are planted in a thin gravel substrate for net-alkaline mine waters;

B – Compost wetlands for acid mine waters where head is limiting;

C – RAPS for acid mine waters where there is sufficient head. An alternative design of RAPS can incorporate a fully mixed layer of compost and limestone [10].

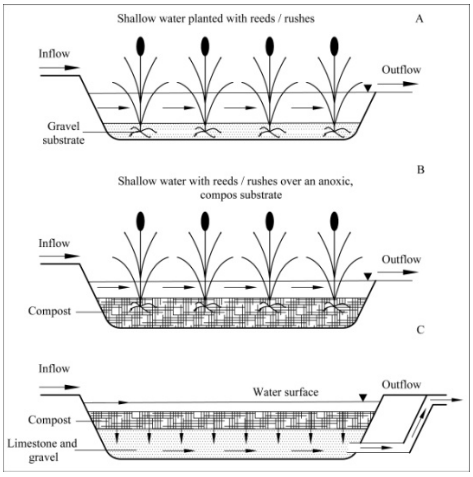

Figure 5. *Types of treatment wetlands [10]*

Passive bioremediation systems that utilize a combination of aerobic and anaerobic wetlands have been used for full-scale treatment of acid mine drainage. An example is the "Acid Reduction Using Microbiology (ARUM)" system [2]. This system comprises of two oxidation cells within which, iron is oxidized and precipitated; beyond these, acid mine drainage passes first through a holding cell, and then through two "ARUM" cells within which, alkali and sulfide are generated. The organic materials that promote sulfate reduction in the ARUM cells originate from floating macrophytes (e.g., cattails). The ARUM systems have been shown to be effective in treating acid mine drainage in high latitude and subtropical locations [2].

Anoxic limestone drains

Anoxic Limestone Drains (ALD's) are trenches of buried limestone into which mine water is diverted (Figure 6). Often the limestone is covered in plastic and buried to limit the amount of oxygen in the system [9].

ALD's also allow carbon dioxide to build up in the system. This is a benefit because higher levels of carbon dioxide allow more alkalinity to be added to the acid mine drainage [9]. The acid mine drainage must meet specific parameters for the ALD to work properly. The DO, ferric iron, and aluminum should be under 1mg/L; if they are not, the risk of premature failure increases [9].

In theory, an ALD that will last for 30 years requires 30 tons of baseball-sized limestone for each gallon per minute of flow [9]. Because the oldest operating ALD's are only 7 years old, no one knows if the limestone will actually last for 30 years.

Regardless, the ALD must be large enough to detain the mine water for about 14 hours to allow the reactions to occur. If possible, the water should be aerated as soon as it leaves the ALD and be directed to an aerobic pond or wetland.

Figure 6. *Anoxic limestone drain [9]*

Alkalinity Producing Systems

Alkalinity-Producing Systems (APS) are a combination of an ALD and an anaerobic wetland. The limitations that dissolved oxygen places on ALD design can be eliminated in an APS by combining open water and a substrate with a high organic content overlying a limestone treatment zone. The APS design provides a relatively sound assurance that the acid mine drainage contacting the limestone will be anoxic. In designing an APS system, the sizing calculations can be based upon the pH and buffering capacity of the acid mine drainage [9]. The initial component of an APS system is generally a settling pond. The pond allows the mine water to use up its alkalinity buffer and remove some of the metals. When the water goes through the APS, the water is further neutralized and more of the metals are removed.

Limestone Ponds and Open Limestone Channels

Limestone ponds provide a solution for places that have room to treat acid mine drainage as it comes from a seep or spring [9]. Limestone is placed in the bottom of the pond and the water flows up through the limestone. The pond's size and design are based on the topography of the area and the water that emanates from the ground. The pond should retain the water for 1 to 2 days to enable the limestone to dissolve and to keep the seep and the limestone underwater. The pond should be built to hold 3 to 10 feet of water, to contain 1 to 3 feet of limestone at the bottom, and to keep the seep and limestone under water [5].

Figure 7. *Limestone ponds*

Limestone will become armored when exposed to oxygen in mine water, but several studies have shown that it still adds alkalinity to the water although at a reduced rate. As a result, open limestone channels can be effective if designed properly Open limestone channels are particularly useful in steep terrain where long channels are possible. They offer an acid mine drainage treatment opportunity where no other passive system is appropriate [5]. Since settlement basins will remove metals, they should be incorporated into the design.

The most successful channels have slopes steeper than 20% and use coarse limestone. Both the slope of the channel and the size of the limestone can minimize the settling of metals in suspension, preventing the channel from becoming plugged.

CONCLUSION

Acid mine drainage affects many sites and can be an incredibly difficult problem to solve. Unfortunately, there is no simple solution because mine sites vary so much and because site characteristics determine what can and cannot be done. It may be possible to use any of the above systems or a combination of them to create nearly pristine water.

The choice which option to use to remediate acid mine drainage is dictated by a number of economical and environmental factors. Sometimes the true environmental cost of a remediation system is not immediately apparent. One such cost is the amount of fossil fuel energy needed to transport liming materials, often long distances from source to mine sites.

Traditionally, large discharge volume mine waters have been treated by active chemical processing, particularly when the waters are acidic. The necessary land surface area and topographic problems may rule out passive biological systems in some situations. However, the mining industries are becoming increasingly attracted to the latter, as they avoid the high recurrent costs of lime addition and sludge disposal. The land areas ("footprints") required for passive could be made significantly smaller by focusing on optimizing biological processes, for example packed bed bioreactors for removing iron from acidic mine waters, which are far more effective than aerobic wetlands. It does need to be recognized that, in reality, none of the remediation systems described in this review are maintenance-free; passive systems also require a certain amount of management and will eventually fill with accumulated ochre (aerobic wetlands) and sulfides (compost bioreactors). The long-term stabilities of these materials are uncertain, but since as they may contain toxic elements (arsenic, cadmium, etc.), their storage or disposal requires careful consideration. Even if the acid mine drainage problem may not completely disappear, reducing it will go a long way toward solving it.

Legislation is likely to become the dominant factor in determining which remediation system can be used in any situation. For example, it might become increasingly untenable to dispose of base metals in sludge and sediments (with all of the inherent storage problems) when there are technologies available for their recovery and recycling. Limits on the concentration of sulfate that can be discharged from processing plants may restrict the choice of a system to one that effectively removes sulfate as well as metals and acidity from mine waters. It is obvious that the problem of the pollution threat posed by acid mine water will be present for very many years to come.

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BIOGRAPHY

Ana Luković was born in Niš, Serbia, in 1979. She graduated from University of Niš, Faculty of Occupational Safety, Department of Environmental Engineering, and completed her post graduate studies from University of Niš, Department of Environmental Engineering.

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PASIVNI SISTEMI ZA TRETMAN KISELIH RUDNIČKIH VODA: OPŠTI PREGLED

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Rezime: *Kisele rudničke vode mogu imati negativan uticaj na životnu sredinu. Naime, kiselost utištava vegetaciju, ubrzava eroziju zemljišta, povećava osetljivost riba na bolesti, dok rastvoreni metali u rudničkoj vodi zagađuju zemljište, čime se kontaminiraju i vodotoci. Tretman kiselih drenažnih voda iz rudnika predstavlja izazov zbog njihove agresivne prirode.Konvencionalne metode zasnovane na neutralizaciji, korišćenjem alkalnih reagenasa, zahtevaju kontinuirano praćenje procesa neutralizacije, kao i značajna ulaganja. Pasivni sitemi za tretman rudničkih voda su predloženi za implementaciju kao jeftinija i dugoročnija opcija.*

Rad sumira podatke iz postojeće literature o problemima koji su uzrokovani kiselim rudničkim vodama i različitim opcijama pasivnih sitema za bioremedijaciju i tretman ovih voda.

Ključne reči: kisele rudničke vode, tehnologije pasivnog tretmana, bioremedijacija, veštačke močvare.