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WATER POLLUTION (S SENGUPTA, SECTION EDITOR)

Remediation of Acid Mine Drainage-Impacted Water

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Abstract The formation of acid mine drainage (AMD), a highly acidic and metal-rich solution, is the biggest environmental concern associated with coal and mineral mining. Once produced, AMD can severely impact the surrounding ecosystem due to its acidity, metal toxicity, sedimentation and other deleterious properties. Hence, implementations of effective post-mining management practices are necessary to control AMD pollution. Due to the existence of a number of federal and state regulations, it is necessary for private and government agencies to come up with various AMD treatment and/or control technologies. This review describes some of the widely used AMD remediation technologies in terms of their general working principles, advantages and shortcomings. AMD treatment technologies can be divided into two major categories, namely prevention and remediation. Prevention techniques mainly focus on inhibiting AMD formation reactions by controlling the source. Remediation techniques focus on the treatment of already produced AMD before their discharge into water bodies. Remediation technologies can be further divided into two broad categories: active and passive. Due to high cost and intensive labor requirements for maintenance of active treatment technologies, passive treatments are widely used all over the world. Besides the conventional passive treatment technologies such as constructed wetlands, anaerobic sulfate-reducing bioreactors, anoxic limestone drains, open limestone channels, limestone leach beds and slag leach beds, this paper also describes emerging passive treatment technologies such as phytoremediation. More intensive research is needed to develop an efficient and cost-effective AMD treatment technology, which can sustain persistent and long-term AMD load.

Keywords Acid mine drainage (AMD) · Active AMD treatment · Passive AMD treatment · Phytoremediation

Introduction

While coal and mineral mining is an important revenue-generating industry, several environmental consequences are associated with it. The formation of a metal-rich acid solution known as acid mine drainage (AMD) is a major environmental problem associated with mining operations. Once exposed to AMD, the quality of adjacent surface water degrades drastically and eventually becomes unsuitable for sustaining biodiversity. Additionally, soils exposed to AMD become structurally unstable and highly prone to erosion [1–4]. Mostly, AMD is produced due to the oxidation of pyrite (FeS_2). In the presence of oxygen and water, pyrite oxidizes to form Fe^{2+}, SO_4^{2-} and H^+ ions [5].

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

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The produced Fe^{2+} ion then reacts with O_2 to form Fe^{3+}. This reaction is facilitated by the sulfur-oxidizing bacteria (*Thiobacillus thiooxidans*, *Thiobacillus ferooxidans*) as they utilize the produced energy from this reaction for their metabolism.

$$Fe^{2+} + 0.25\,O_2 + H^+ \rightarrow Fe^{3+} + 0.5\,H_2O \quad (2)$$

In addition, the produced Fe^{3+} further oxidizes pyrite to form Fe^{2+}, SO_4^{2-} and H^+ ions.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

The abiotic rate of pyrite oxidation by Fe^{3+} is much higher than oxidation by O_2 and water. Due to the production of H^+ ions, the pH of the whole system drops drastically and becomes highly acidic. If the pH of the system remains over 3.5–4.0 standard units, Fe^{3+} precipitates in the form of $Fe(OH)_3$. The yellow-orange colored precipitation of iron hydroxide is known as "yellow boy."

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

The overall stoichiometric pyrite oxidation reaction can be written as [5]:

$$FeS_2 + 3.75\,O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ + \text{heat} \quad (5)$$

Due to high acidity, the mobility of the metals in the environment increases significantly. Extensively acidic pH (as low as 2–4 standard units) coupled with metals toxicity can elicit severe impacts on aquatic biodiversity [6–12]. Abandoned mine sites often accelerate the AMD generation process and may require decades of proper management practices to reclaim. The adverse environmental impacts of AMD can exist forever if not addressed. The current number of abandoned mines in the USA is estimated to be more than 557,000 [13], many of which are active sources of AMD. Approximately 15,000 to 23,000 km of streams are currently impacted by AMD in the USA [2, 4, 11, 14, 15], which also represents a direct threat to human health. Due to its complex nature and wide array of consequences, AMD is termed a "multiheaded beast" [13], and taming this beast is a challenging task. According the US Forest Service (2005), the estimated cost of cleaning up AMD-impacted sites on National Forest System (NFS) land is around \$4 billion. Between the years 1998 and 2003 around \$310 million was spent on AMD-impacted NFS land clean-up services [13]. Currently, several AMD prevention and remediation technologies are in effect at various AMD-impacted sites. The objective of this paper is to review the commonly used AMD treatment technologies based on their working principles and efficiency.

AMD Treatment Technologies

AMD treatment technologies can be divided into two major categories: (1) prevention or source control techniques and (2) remediation techniques. While the former focuses on prevention of AMD generation and migration by controlling its source, the later focuses more on the mitigational measurements of produced AMD.

Prevention or Source Control Technologies

Safe disposal and storage of post-mining overburdens and tailings play a vital role in AMD control. Several source-controlling techniques are available to prevent AMD formation. As pyrite-bearing mine wastes produce AMD in the presence of water and oxygen, one way to prevent AMD production is the exclusion of either one or both of them from the system. Co-disposal of pyritic materials along with some benign material (waste rock, limestone) is the most common practice to reduce AMD production from mine waste [16–18]. The mixing of large waste rocks with fine tailings is practiced sometimes which possesses higher moisture content and hence reduce oxygen penetration through mine wastes [16]. Depending upon the neutralization potential (NP) of the soil type, pyritic wastes are mixed with alkaline amendments such as limestone to reduce acidity of the overall system [17, 19–21]. Besides limestone, materials such as fluidized bed combustion (FBC) ash and Kiln dust with higher NP (20–70 %) are also used as alkaline amendments. In addition to their ability to increase the net alkalinity of the system, these materials also transform into a cement-like hard substance which acts as a barrier and stabilization material [17, 22–24]. Flooding/sealing of underground mines [18], underwater storage of mine tailings and land-based storage in sealed waste heaps are some of the commonly used techniques to prevent AMD migration to local water bodies [25]. The diversion of surface and groundwater from acid-producing pyritic waste piles is another important AMD prevention approach. Diversion ditches, grout barriers and slurry walls are some of the techniques used to control water migration through mine spoils [16, 17, 26]. Encapsulation, capping and sealing of sulfidic mine sites with non-sulfidic topsoil layer [16, 27] are often used to reduce water penetration (rainfall and runoff) through mine spoils. Single- (for semi-arid regions) or multi-layer (for high-rainfall regions) soil covers are used for encapsulation. The capping materials consist of a clay layer to prevent oxygen penetration and an alkaline layer to provide a hard capsulated barrier to prevent water from reaching the waste piles. A coarse layer is often present to drain the infiltrated water [16, 28]. A vegetative top layer provides stabilization to the overall system and retains moisture [16, 29–31]. As sulfur-oxidizing bacteria play a vital role in the AMD generation process, the use of bactericides such as anionic surfactants is also a common practice. The bactericides, which are often applied as liquid amendment or spray, can control the AMD formation only for a limited time period [16, 17]. The major disadvantage of these expensive preventive technologies is their ineffectiveness in the long-term. Most of these techniques have failed to protect the environment against long and persistent AMD pollution.

Remediation Technologies

AMD remediation technologies can be divided into two categories: active treatment and passive treatment.

Active Treatment Technology

The responsibility to clean-up abandoned mine sites is borne by both private operators and government agencies. A number of federal and state laws such as the National Historic Preservation Act of 1966, the Clean Air Act of 1972, the Endangered Species Act of 1973 and the Surface Mining Control and Reclamation Act of 1977 are currently in effect in the USA to regulate the standards of the post-mining water discharges into the surrounding ecosystems [13, 17]. The US Forest Service even has the authority to administer the Comprehensive Environmental Response Compensation and Liability Act of 1980 on National Forest System lands through an Executive Order (No. 12580) passed in 1987 [13]. The addition of various acid-neutralizing and metal-precipitating chemical agents into AMD water is a common practice to meet the effluent discharge limits within a short time span. A wide range of chemical agents such as limestone ($CaCO_3$), hydrated lime ($Ca(OH)_2$), caustic soda (NaOH), soda ash (Na_2CO_3), calcium oxide (CaO), anhydrous ammonia (NH_3), magnesium oxide (MgO) and magnesium hydroxide ($Mg(OH)_2$) are being used during the active treatment of AMD water worldwide [17, 18]. The efficiency of each of the chemicals depends on factors such as the site specificity (seasonal variation), daily AMD load and metal concentration. Hence, the selection of appropriate chemical agent is very important for the success of the treatment process.

One of the major advantages of the active treatment process is that unlike the passive treatment facilities, it does not require any additional space or construction. Furthermore, the active treatment process is fast and effective in removing acidity and metals. The other advantage of the active treatment technique is the lower cost associated with handling and disposal of sludge in comparison to passive treatment techniques [32]. Although the active treatment process has several advantages, it is not favored due to its limitations. The major disadvantage of the active treatment process is that it requires a continuous supply of chemicals and energy to perform efficiently. Costly chemicals and engaging sufficient man power to maintain the system increases the overall cost of this technology significantly. The efficiency of these systems is completely dependent on its regular maintenance and chemical supply, which makes it difficult to control for most of the remotely located abandoned mine sites. The efficiency and cost of the systems also vary with the type of neutralizing agent used. Limestone is inexpensive but less soluble in water and hence less effective than the other chemical agents. Chemicals such as hydrated lime are also inexpensive but ineffective if higher pH (~9) is required for precipitation of metals like Mn [17, 33]. Although NaOH is approximately 1.5 times more effective than lime, NaOH is almost nine times more expensive [18]. Due to their extremely hazardous nature, chemical agents such as NaOH and anhydrous ammonia need special attention during handling. Also, the use of excessive ammonia can create problems such as nitrification and denitrification in receiving water bodies [17, 34].

Passive Treatment Technology

Passive AMD treatment technologies can be classified into two groups: conventional and emerging technologies. The conventional passive treatment technologies such as constructed wetlands and anaerobic sulfate-reducing bioreactors have been used for a long time. Emerging technologies such as phytoremediation are also being investigated for efficient AMD remediation.

Conventional Passive Treatment Technology

1. Constructed Wetlands

Constructed wetlands are one of the most commonly used passive AMD treatment technologies. There are two types of wetlands: aerobic and anaerobic. Aerobic wetlands are shallow water bodies (<30 cm in depth), which provide sufficient retention time to oxidize and precipitate subsequent metal hydroxides. Wetland plants such as *Typha* sp., *Juncus* sp. and *Scirpus* sp. regulate the water flow, stabilize and accumulate the metal precipitates, maintain the microbial population and increase the aesthetic value of the contaminated site [18, 35]. Wetland plants involve two major mechanisms to remove heavy metals from AMD: phytoextraction and rizhofiltration. In phytoextraction, metal-hyperaccumulating plants uptake metals from wetland substrate and store them in their root and/or shoot. In rhizofiltration, plants absorb, adsorb or precipitate metals in the root zones (rhizosphere) [36–41]. The studies often reported that the amount of metal retention inside the wetland cells is higher than the metal uptake in the plant tissues [40, 42]. Plants such as *Typha latifolia*, *Scirpus validus*, *Phragmites australis* and *Oryza sativa* form plaques in their root epidermis by producing metal oxide and hydroxide precipitates that prevent the translocation of metals in the plant tissues [40, 43–45]. Although formation of Fe oxide and hydroxide plaques in plant root zones is more common, Al and Mn plaques are also reported by researchers [40, 44]. Aerobic wetlands are more efficient in removing Fe, Al and Mn in comparison to other metals. The Fe retention rate in aerobic wetlands can vary from 0.13 to 96 % of the initial Fe load [40, 42, 46, 47]. Wetland plants such as *T. latifolia*, *Lemna minor*, *Nuphar variegatum* and *Potamogeton epihydrus* can remove 29–56 % of the initial Al load [48]. High Mn retention (~76 %) is also demonstrated by plants such as *Desmostachya bipinnata* [47]. Both Al and Fe are mainly stored in the root zone, but the distribution of Mn is often noticed in the entire plant body. High acidity removal (43 %) and an increase of the pH from 2.9 to 7.1 are also observed inside the aerobic wetlands [47, 49]. The efficiency of wetlands in treating AMD depends on factors such as the seasonal variations, the acidity and metal load and the dissolve or soluble metal concentration gradient [40, 42, 50, 51].

Cost-effectiveness is one of the major advantages of aerobic wetlands. The cost of aerobic wetlands ranges from $23 to $7, 000/t/year in terms of removal of 0.1 to 27 t/year of acidity over a 20-year life span [35]. The amount of metal retention is always higher than metal extraction in aerobic wetlands. Studies showed that aerobic wetlands possess high retention capacity for different metals such as 69 kg Al/year, 8089 kg Fe/year and 130 kg Mn/year [40, 46]. The efficiency of the aerobic wetland systems decreases if the influent water has a pH<5. Hence, aerobic wetlands are always associated with other passive treatment systems such as anoxic limestone drains (ALDs) or vertical flow wetlands (VFWs) and receive net alkaline AMD water from them [18, 35, 49, 52]. Aerobic wetlands cannot remove sulfate [42] and are less effective when metal concentrations are very high in the system [40, 42].

Anaerobic wetlands are built with organic-rich substrates, which provide reducing conditions and neutralizing agents such as limestone. Often anaerobic wetlands are constructed underground and are devoid of vegetation. In this kind of a system, net acidity of AMD water is removed by the dissolution of limestone and the metabolism of iron- and sulfate-reducing bacteria. The organic-rich substrates are prepared by mixing of biodegradable products such as manure with straw, peat and sawdust. This mixture serves as a long-term food source for the indigenous anaerobic iron- and sulfate-reducing bacteria due to their slow biodegradation rates. A variety of manures such as chicken, cow and horse litter and mushroom compost are used as substrates for the microbial community [17, 18, 53, 54]. Sometimes, the anaerobic wetlands are engineered as the reducing and alkalinity-producing system (RAPS) [55] or as the successive alkalinity-producing system (SAPS) (where multiple RAPS are used) [56]. In this type of system, AMD first flows downward through a compost layer, which removes dissolve oxygen (DO) and facilitates iron and sulfate reduction. Subsequently, the AMD passes through a limestone and gravel bed, which adds alkalinity. To precipitate and retain the iron hydroxides, water from the RAPS system is channeled through a settling pond or aerobic wetland. In anaerobic wetlands, the sorption of metals occurs on the organic substrates through exchangeable or complexation reactions. Initially, 50–80 % of metal removal from the AMD inside the anaerobic wetland system takes place due to sorption, which decreases over time due to the substrate saturation [17, 57]. The retention of metals as of oxide, hydroxide, carbonate and sulfide precipitates also occurs in anaerobic wetlands. Unlike sorption reactions, precipitation of metals is not time-limited and depends on the density and volume of the wetland cells. The total Fe removed from AMD water by anaerobic wetland systems is dominated by Fe hydroxides (~50–70 %) and Fe sulfides (~30 %). Iron hydroxide often reduces to Fe^{2+} by anaerobic iron-reducing bacteria, and this reaction increases the pH of the system.

$$Fe(OH)_3 + 0.5\,H_2 \rightarrow Fe2^+ + 2OH^- + H_2O \qquad (6)$$

Anaerobic sulfate-reducing bacteria produce iron mono and disulfides while reducing the sulfate present in the AMD water. The reduction of sulfate also increases the pH of the system [17, 53, 58–60].

Anaerobic wetlands can remove approximately 0–67.9 t/year of net acidity and costs between $341 and $4762/t/year [35]. The removal of sulfate and increase in pH are some of the major advantages of the anaerobic wetlands. The anaerobic wetlands can also reduce the acidity and Fe concentration of the AMD water by 3–76 and 62–80 %, respectively [61]. The major disadvantage of the anaerobic wetlands is the decrease of its efficiency over time. The saturation of substrates occurs within a span of 1–7 months as most of the available exchangeable and complexation sites become saturated with metals. Sometimes, the addition of organic matter is required to revive the filtering efficiency of the wetland [17, 62–64]. The efficiency of the anaerobic wetlands also changes with seasonal variation and wetland age [17, 53]. The lifetime of the system can be severely affected if the plants above the ground penetrate the system's protective cover through their roots and introduce oxygen to the anaerobic layers [18].

A pilot passive treatment plant was constructed in 1994 at Wheal Jane Mine in Cornwall, England, for long-term AMD treatment. The project was unique because it employed both aerobic and anaerobic wetland facilities. After appropriate lime dosing, AMD water was allowed to pass through serious of anoxic cell, anoxic limestone drain, five aerobic cells, anaerobic cell and rock filter. Data show that this kind of hybrid system is capable of removing Fe and sulfate between 55 and

92 %, and 3 and 38 %, respectively. This system can also remove other metals such as Cd, Cu and Zn depending on the pretreatment and flow rate of the AMD [65].

2. Anaerobic Sulfate-Reducing Bioreactors

Anaerobic sulfate-reducing bioreactors are another type of widely used passive treatment technology, which involves sulfate-reducing bacteria to remediate AMD. Sulfate-reducing bacteria are a group of chemoorganotrophic and strictly anaerobic bacteria, which is primarily represented by the genera of *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum*.

Anaerobic sulfate-reducing bioreactors are made up of a thick layer of organic-rich materials mixed with limestone. An additional thin layer of limestone is also used under the organic layer, which provides the additional alkalinity and also supports the underlying drainage channels. The AMD passes vertically through the organic layer and limestone bed and is discharged through the drainage system. The organic layer serves as the substrate of sulfate-reducing bacteria. In this layer, sulfate-reducing bacteria reduce SO_4^{2-} to H_2S and oxidize organic matter (CH_2O) to bicarbonate ions (HCO_3^-) [66]. Sulfate-reducing bacteria use the energy produced in this reaction for their growth and development.

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (7)$$

The reaction of AMD with limestone causes limestone dissolution and produces HCO_3^- and Ca^{2+}.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (8)$$

The produced HCO_3^- further reacts with H^+ ions and produces CO_2 and water. Hence, the consumption of the H^+ ions results in the increase of the pH of the overall AMD water. At high pH, metals start to precipitate in the form of metal sulfides, oxides, hydroxides and carbonates.

In the anaerobic sulfate-reducing system, the most common form is metal sulfide precipitation [67].

$$HS^- + M^{2+} \rightarrow MS + H^+ \quad (9)$$

In reaction [8], M^{2+} represents divalent metals such as Fe^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} and MS represents the produced metal sulfide. Metals can also precipitate in the form of hydroxide or carbonate [67].

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+ \quad (10)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (11)$$

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_3 + H^+ \quad (12)$$

Thus, sulfate-reducing bioreactors help in reducing acidity, metal and sulfate concentration of AMD water and improve the overall water quality. The efficiency of an anaerobic sulfate-reducing bioreactor depends on various factors. The amount of sulfate removed is dependent on the available surface area and hydraulic retention time (HRT), while the rate of sulfate removal is dependent on the initial sulfate concentration in AMD [68]. Studies have been conducted to test the efficiency of sulfate-reducing bacteria under various pH levels. Researchers found that pH in the range of 5–8 is best for optimum activity of the sulfate-reducing bacteria, as the inhibition of sulfate reduction and the increase in the solubility of metal sulfides occur at low pH [68–71]. Some studies also found that although at low pH (2.8–3.5) sulfate-reducing bacteria can survive due to their acid tolerance, their sulfate removal efficiency dropped to 14–35 % [70, 72]. Several studies have been conducted to characterize the sulfate-reducing bacterial community. Researchers found that the type of sulfate-reducing bacterial community change through time depending on the nature of the wastewater and the type of the food sources. Species such as *Desulfovibrio desulfuricans* and *Desulfobulbus rhabdoformis* are dominant in a sulfate-reducing bioreactor [73, 74]. Change of dominant bacterial community from iron oxidizing *Betaproteobacteria* in pre-treated AMD water to sulfur-oxidizing *Epsilonproteobacteria* and complex carbon degrading *Bacteroidetes* and *Firmicutes* phylums in post-treated water is also observed [75].

Studies have been conducted to evaluate the efficiency of the sulfate-reducing bioreactors. It is observed that the efficiency varies from 39 to 82 % removal of the initial SO_4^{2-} load (900–2981 mg/L) [72, 76–78]. Sulfate-reducing bioreactors exhibit a high metal removal ability, and they can remove 98–99 % of initial Cu [73, 74], 85–90 % of initial Fe [72, 74, 79] and 95–99 % of initial Al [72, 74] load from the AMD water. A net decrease in acidity and increase in pH of the influent AMD water can also be achieved through the bioreactors [70, 72, 75, 78].

The activity of sulfate-reducing bacteria is the rate-limiting factor of the anaerobic sulfate-reducing bioreactors. A near neutral pH, reducing environment, continuous supply of organic carbon and sulfate, solid support for microbial attachment and the formation and retention capacity of precipitated metal sulfides are some of the key factors of an efficient sulfate-reducing bioreactor. Extremely low pH (below 3.5) severely impacts the efficiency of the sulfate-reducing bacteria [70]. Low temperature also impacts the acclimatization of the sulfate-reducing bacteria significantly, but after acclimatization, they can be active and functional even in the cold climates (1–16 °C). A decrease in overall efficiency of sulfate-reducing bioreactors has been observed during the winter seasons [68, 80]. Despite their higher sulfate and metal removal efficiency, the sulfate-reducing bioreactors often fail to perform over long-term mainly due to the exhaustion of the substrates required for sustaining the sulfate-reducing bacterial community.

3. Other Commonly Used Passive Treatment Techniques

Anoxic limestone drains (ALD) are one of the commonly used passive AMD treatment systems. ALDs are typically 30 m long, 1.5 m deep and 0.6–20 m wide underground systems filled with limestone. Only anoxic water is introduced in the ALDs, which are impervious to air and water. In ALD, limestone reacts with AMD water and produces CO_2 which cannot escape from the system and raises the overall alkalinity [67]. Due to the anoxic condition, the iron remains in the reduced form inside the ALDs, and the formation and precipitation of iron hydroxide does not occur. The optimal performance of the ALD can be attained if the AMD channeled through it contains no ferric iron, aluminum or DO. The pH of ALD systems needs to be 6.0 because under more acidic conditions, metals like Fe and Al precipitate as hydroxides and form coats or armors on limestone [18]. Thus, iron hydroxide precipitation severely impacts the efficiency of the ALDs. ALDs can produce up to 275 mg/L of net alkalinity in comparison to 50–60 mg/L of net alkalinity produced by an open system in equilibrium [81]. A decrease of acidity by 50–80 % can be achieved through ALDs [17, 54]. The major drawback of ALD is its longevity. The presence of ferric iron and Al in AMD water can form hydroxide precipitates which reduce the permeability and efficiency of the ALD systems [82]. Typically, ALDs are used as a part of the hybrid passive treatment system in corporation with the aerobic and anaerobic wetlands [17, 18, 81].

Vertical flow wetlands (VFW) or permeable reactive barriers (PRB) are another type of passive AMD treatment system. In a VFW or PRB, AMD water flows through an organic-rich layer followed by a limestone bed before discharging through a drainage system. The VFW systems reduce ferric to ferrous iron and decrease the amount of DO. Sulfate reduction and Fe sulfide precipitation can take place in this system. A series of drainage pipes placed below the limestone layer carry the water to aerobic ponds where ferrous ions oxidize and precipitate [18, 55].

Limestone leach beds (LSB), slag leach beds (SLB) and open limestone channels (OLC) play a significant role in various AMD passive treatment systems. LSBs are ponds constructed to receive waters with little or no alkalinity and dissolved metals. These ponds are packed with limestone and designed to have retention time of at least 12 h. The limestone layer can be replenished when necessary. Alkalinity in this system can reach 75 mg/L [35]. In SLB ponds, a bed of steel slag fines is used to remediate AMD water, which need to be devoid of metals such as Fe, Al and Mn. This system can produce alkalinity up to 2000 mg/L, and the overall system is easy to replenish [35]. OLCs are open channels or trenches lined with limestone. In OLCs, limestone coated with Fe and Al hydroxides are used to decrease the limestone dissolution over time. The performances of the OLCs are dependent on different variables such as slopes, pH, flow velocity and thickness of the coating of limestone [35]. OLCs can remove 4–69 % of acidity, 72 % of Fe and 20 % of Mn and Al from AMD water [17, 35, 83]. OLCs are generally constructed with the combination of other passive treatment systems. The major advantage of OLC is its low-cost as it does not require any maintenance once constructed properly [17].

The construction of the passive treatment technologies depends on several factors such as characteristics of waste, flow rate, size of the construction area, local topography and environment. Figure 1 provides a decision-making tree for passive treatment systems based on the characteristics of the influent AMD water. Most of the time, the adaptation of a hybrid system is necessary to achieve the regulatory standards before discharging the AMD water into the local water bodies. The installation costs of the conventional passive treatment technologies are very expensive, and these systems also require a periodic monitoring and maintenance [84]. The passive treatment facilities also generate a considerable amount of sludge, and the removal and disposal cost of the sludge is also very high.

Emerging Passive Treatment Technology: Phytoremediation

Phytoremediation is an emerging passive AMD treatment technology. Researchers and remediation practitioners are evaluating phytoremediation-based alternatives because of the higher costs associated with conventional AMD remediation approaches. Phytoremediation can be applied to both AMD-impacted soil and water. As eroded AMD-impacted soils generally end up in surrounding water bodies and elevate the risk, remediation of both soil and water is very important. Phytoremediation of contaminated mine sites mainly involves two mechanisms: phytoextraction and phytostabilization. In the phytoextraction process, plants extract heavy metals from the contaminated sites and store the extracted metals in their biomass. On the other hand, phytostabilization provides a vegetative cover to highly erosion prone and heavily contaminated acid sulfate soils [36–39, 41]. Sometimes, due to the presence of heavy metals in high concentration, complete metal removal cannot be possible. In such conditions, phytostabilization immobilizes the metals and traps them in plant root zones, which minimizes the metal exposure to the surrounding ecosystems. The extensive root systems of the plants also protect the soils against erosion and leaching.

Several metal tolerant plant species have been used to remediate contaminated mine sites. Success of phytoremediation depends on the proper selection of the metal-hyperaccumulator plants. Hyperaccumulator plants generally accumulate metals in their aboveground biomass

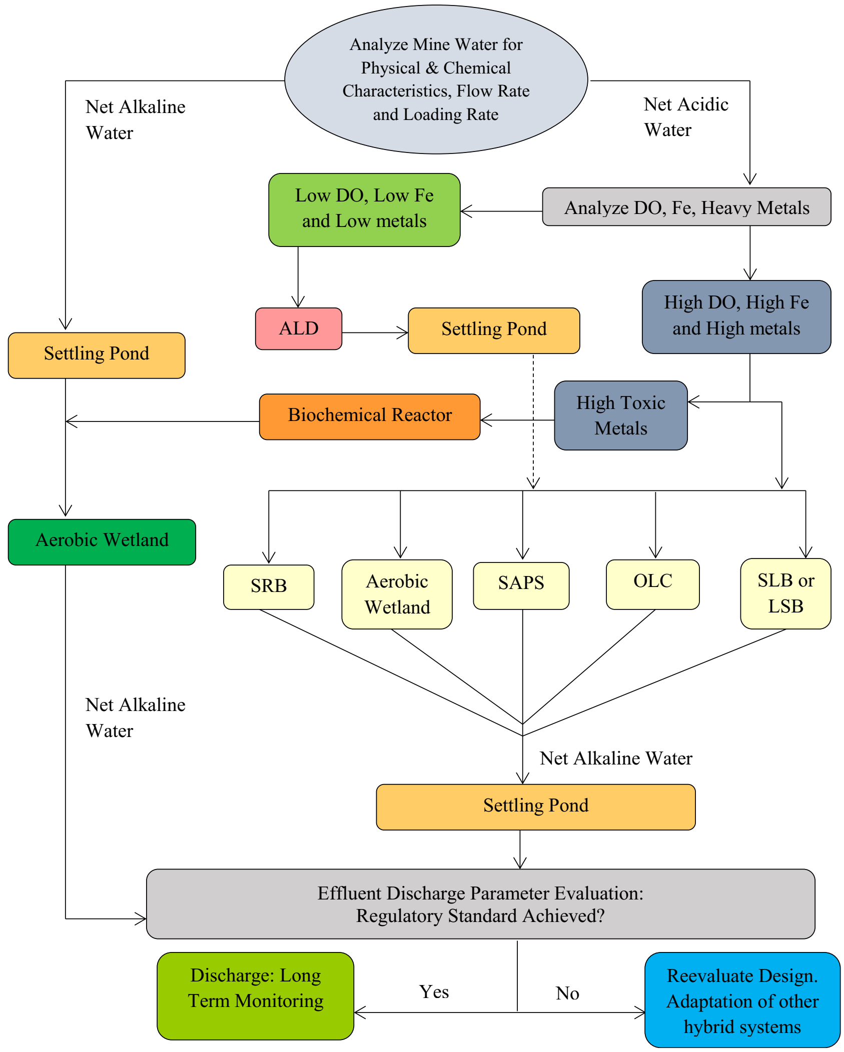

Fig. 1 Decision-making tree for the design of passive treatment system [Redrawn after 35, 84–86]

at a concentration that is 100-fold greater than the non-hyperaccumulator plants. Generally, these plants accumulate up to or more than 0.1 % of metals such as Cu, Pb, Cd, Cr, Ni and Co or 1 % of metals such as Zn and Mn in their dry biomass [36]. The high-accumulation factor (AF) and high-translocation factor (TF) are also some of the hyperaccumulation characteristics. More than 400 hyperaccumulator plant species belonging to families such as Brassicaceae, Asteraceae and Poaceae exist, which can be used in metal-contaminated mine sites [36, 41, 87]. Table 1 presents some of the most commonly used plants for remediation of AMD-impacted sites.

In China, a wide range of plant species (*Chrysopogon zizanioides*, *Sesbania rostrate*, *P. australis*, *Cyperus alternifolius*, *Leucaena leucocephala*, *Panicum repens*, *Gynura crepidiodes*, *Alocasia macrorrhiza* and *Chrysopogon aciculatus*) have been used to phytoremediate AMD water highly contaminated with Zn, Pb and SO_4^{2-} [91, 97, 98]. Plants like *C. alternifolius* and *C. zizanioides* possess very high-acid tolerance characteristics. An increase of pH from 2.4 to 7.5 and 80 % removal of its initial sulfate concentration are also noticed during the study [91]. In Australia, plant species like *Juncus usitatus*, *Lomandra longifolia*, *Cynodon dactylon*, *Pteridium esculentum*, *Acacia decurrens* and *Melaleuca alternifolia* are used for remediation of metals such as Fe, As, Cd, Cu, Pb and Zn from both AMD-impacted soil and water [90]. All of the plant species thrived well under the acidic conditions (pH ranged from 2.9 to 5.6), and species like *C. dactylon* can accumulate metals like Cd (14 mg/kg), Pb (658 mg/kg) and Zn (828 mg/kg) in its biomass. Species like *J. usitatus* and *L. longifolia* can also accumulate significant amount of Cd in their biomass (26 and 21 mg/kg, respectively). Another potential plant species for remediation of Cd- and Zn-contaminated mine sites is *Thlaspi caerulescens*. Studies reported that *T. caerulescens* can accumulate as high as 50–250 mg/kg Cd and 13,000–19,000 mg/kg Zn while growing in AMD-contaminated sites [87, 92]. Due to the low biomass production, *T. caerulescens* is not an ideal plant for phytoremediation. On the other hand, plants like *Cichorium intybus* L. and *C. dactylon* are potential phytoremediation

Table 1 Plant species used for phytoremediation of AMD-impacted sites

Plant species	Family	Metals of concern	Advantage	Reference
Atriplex halimus L.	Amaranthaceae	Cd, Zn	Drought tolerant, Soil erosion prevention	[88]
Cichorium intybus	Asteraceae	Pb	Accumulation of Pb in biomass	[89]
Cynodon dactylon	Poaceae	Cd, Cu, Pb, Zn	Metal accumulation, vegetative cover	[89, 90]
Cyperus alternifolius	Cyperaceae	Cd, Cu, Mn, Pb, Zn	Acid tolerant	[91]
Thlaspi caerulescens	Brassicaceae	Cd, Zn	Hyperaccumulator for Cd and Zn	[87, 92]
Chrysopogon zizanioides	Poaceae	Al, As, Cd, Cu, Fe, Hg, Mn, Pb, Zn	Metal hyperaccumulator, acid tolerant, soil erosion prevention, soil stabilization	[91, 93–96]

candidates for Pb-contaminated mine sites. *C. intybus* and *C. dactylon* can accumulate as high as 800–1500 and 400–1200 mg/kg Pb in their biomass, respectively [89]. In a similar study, it is observed that *Atriplex halimus* L. can accumulate 830 and 440 mg/kg of Cd and Zn, respectively, in its biomass while growing on mine tailing under greenhouse condition [88]. Another commonly used plant species for mine site remediation is *C. zizanioides*, commonly known as vetiver grass. Due to their physiological characteristics and high tolerance of metals such as Al, Mn, Fe and Zn [95, 96] and heavy metals such as As, Pb, Hg and Cd, vetiver can be used efficiently to restore metal-contaminated sites [99]. Vetiver can tolerate Fe concentrations even up to 63,920 mg/kg [96]. Vetiver can remediate iron ore tailings contaminated with high concentration of metals such as Fe, Zn, Mn and Cu and can accumulate as high as 545–1197 mg/kg Fe, 302–531 mg/kg Zn, 415–648 mg/kg Mn and 13–66 mg/kg Cu in its root and shoot. High-mean translocation factors for Mn (0.86), Fe (0.71), Zn (0.69) and Cu (0.55) can be observed in vetiver's tissue [96]. Use of soil amendments like DTPA (diethylenetriamine pentaacetic acid) and compost mixture increases the metal uptake ability of vetiver. Vetiver possesses a massive root system, which can stabilize the erosion prone acid sulfate soil. So, planting vetiver on metal-contaminated mine soils can stabilize the soil and improve the overall soil quality [96, 98]. Once established, vetiver grass can grow on the acidic soils with continuous acidity production by sulfidic minerals [93]. In a study conducted in Queensland Australia, it was found that vetiver systems are able to control bank erosion while growing on acid sulfate soil [94]. The study showed that planting vetiver stabilized the edges of the channel and also promoted the establishment of other plants on the steep slopes, helping to prevent erosion and preventing the collapse of the highly acidic soil into the channel streams. Vetiver can trap sediments and pollutants from runoff water, which improves the overall water quality. The increase of pH and decrease of Fe concentration in water were also observed during the study [94].

Phytoremediation of AMD-impacted soil and water has shown positive results and fueled extensive research in this field worldwide. The major advantages of phytoremediation are that it is cost-effective and environment-friendly. The success of phytoremediation is primarily dependent on the plant availability of the metals. Due to factors such as soil properties, metal species, loading level and soil-ageing, the amount of plant available metal varies significantly. Several chemical agents and soil amendments such as EDTA (ethylenediaminetetraacetic acid), EDDS (ethylenediamine-*N*,*N*′-disuccinic acid), compost and DTPA have been applied to increase the plant available metal fraction in the soil. Most of the phytoremediation studies were performed in either under greenhouse conditions or in the field on a pilot scale. Hence, more extensive field-based research is required to optimize this emerging technique.

Conclusions

Remediation of AMD is a challenging proposition that is dependent on several factors such as the daily AMD load, flow rate, net acidity and metal concentration. The pre-mining analysis of the neutralization potential (NP) of soil through acid base accounting (ABA) helps to predict the nature of AMD and to adapt best AMD management practices. A number of AMD prevention and remediation technologies are being used worldwide to prevent AMD pollution in both active and abandoned mines. Long-term monitoring of the constructed systems is necessary as AMD pollution can exists for decades. Most of the conventional passive AMD remediation technologies are ineffective and/or expensive for long-term and persistent AMD load. Hence, a search for an effective, viable and sustainable AMD remediation technology is ongoing. Emerging passive treatment technologies such as phytoremediation have the potential to be successful and are attractive because of sustainability and cost-effective aspects of their implementation. However, most of the research in this area so far has been limited to greenhouse or pilot-scale field studies. Further long-term research is needed in order for this promising technology to be widely implemented in AMD-impacted areas.

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Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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