Remediation of Acid Mine Drain

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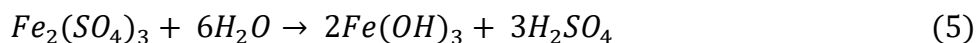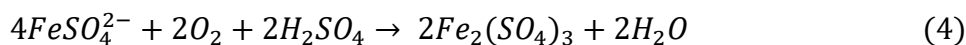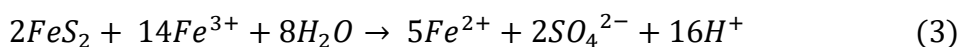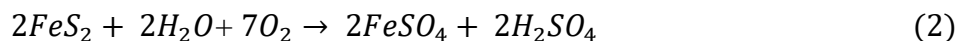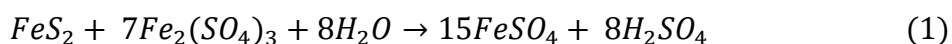[d]Department of Mechanical Engineering, VEC, Ambikapur

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Abstract

Acid mine drainage (AMD) is a significant environmental issue resulting from the discharge of acidic mine water in mining sites. The oxidation of sulfide minerals, particularly pyrite, during mining operations leads to the generation of Acid Mine Drainage (AMD) characterized by low pH and high concentrations of dissolved metals. AMD poses a severe threat to water quality and ecosystems due to its detrimental effects on surface and groundwater. This review paper provides a comprehensive overview of the processes involved in AMD contaminated with heavy metals and explores remediation strategies for polluted soils and groundwater. The complex reactions of metal sulfide oxidation, hydrolysis, and precipitation in AMD create challenges for its treatment. Traditional methods such as membrane filtration, adsorption, chemical precipitation, advanced oxidation processes, and ion exchange have limitations in terms of cost, scalability, and sustainability. The importance of effective AMD management is underscored by the potential hazards posed by elevated heavy metal concentrations to the environment and human health. The paper emphasizes the need for cost-effective and sustainable remediation strategies to mitigate the environmental impacts of AMD and ensure the protection of ecosystems and human well-being.

Introduction

Water pollution is a pressing environmental concern, with the discharge of acidic mine water emerging as a major source of contamination in mining sites. The generation of wastewater during mining operations significantly contributes to water pollution in the industry, particularly through the creation of Acid Mine Drainage (AMD) (Johnson et al., 2005; Lee et al., 2013). The oxidation of iron sulfide, particularly pyrite, found in active mining operations, abandoned mines, and mining waste, leads to the formation of acidic water, posing a significant threat to surface water quality and overall environmental well-being (Yadav et al., 2015).

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$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \rightarrow 15FeSO_4 + 8H_2SO_4 \qquad (1)$$

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (2)$$

$$2FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 5Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \qquad (3)$$

$$4FeSO_4^{2-} + 2O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (4)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (5)$$

AMD is formed when sulfide minerals, such as pyrite, present in rocks are exposed to air and water, either naturally or through human activities and subsequent microbial activities (Taylor, 2005). This process results in a decrease in water pH and the dissolution of metals like aluminum, iron, copper, manganese, and zinc, which further contribute to water acidity (Singh et al., 1985). The global issue of acid rock drainage/acid mine drainage has adverse effects on both ground and surface water, leading to acidification and the presence of toxic heavy metals (Mills, 2016).

Mining activities generate significant waste products, and the management of waste materials is a critical concern for the mining industry worldwide. Metal sulfides, such as pyrite ($FeS2$), are commonly associated with valuable metallic minerals. When these minerals, along with pyrite and pyrrhotite, are present, the oxidation of iron-sulfur minerals can result in the production of sulfuric acid and ferric ions (Mills, 2016).

In the case of iron and manganese, these metals are usually present in their reduced ionic stages ($Fe2+$ and $Mn2+$) in anoxic AMD. These reduced forms are more stable at higher pH levels than their fully oxidized counterparts ($Fe3+$ and $Mn4+$) (Skousen et al., 2011). The acidity in AMD encompasses both proton acidity (hydrogen ion concentration) and metal acidity (combined concentration of soluble metals, notably iron, aluminum, and manganese that produce protons when they hydrolyze) (Sheoran et al., 2010). Net acidity in AMD needs to be offset by any present alkalinity, often in the form of bicarbonate derived from the dissolution of basic minerals (e.g., calcium carbonate), and biological processes can also generate alkalinity in AMD (Johnson et al., 2005).

The release of acidic mine drainage, laden with heavy metals, into effluent drainages poses significant environmental degradation concerns and necessitates effective and cost-efficient abatement and treatment methods. One such approach is neutralization through alkaline reagent mixing, aeration, and removal of precipitates (Singh & Rawat, 1985).

This review paper aims to examine the processes involved in AMD contaminated with heavy metals and explore remediation strategies for polluted soils and groundwater. Elevated concentrations of

heavy metals resulting from AMD can pose potential hazards to the environment and human health when they exceed normal levels. In extreme conditions, heavy metals present in AMD can bioaccumulate through the food chain, posing a significant threat to animals, plants, and humans. However, treating AMD can be complex and costly, especially when management strategies are ineffective (Chen et al., 2021).

The complexity of metal oxidation, hydrolysis, and precipitation in AMD, driven by low pH and high metal loads, underscores the challenges associated with its treatment (Skousen et al., 2017). For both active and passive treatment methods of AMD, it is crucial to raise pH levels and remove dissolved metal concentrations, thereby reducing solution acidity and increasing alkalinity.

$$4\text{Fe}S_2 \text{ (s)} + 15O_2 + 14H_2O \ \text{-----}\rightarrow\ 4\text{Fe }(OH)_3\text{(s)} + 8SO_4^{2-} + 16H^+ \qquad (6)$$
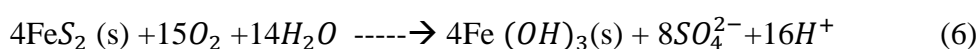
Statutory norms for AMD discharge

For the protection of the environment, it is recommended to prioritize the minimization of acid mine drainage (AMD) generation. If the generation of AMD cannot be prevented, it should be collected and appropriately treated. The National Pollutant Discharge Elimination System (NPDES) in the United States has established permissible effluent standards for coal mine drainage, outlined in the U.S. Code of Federal Regulations (2008). Adhering to these standards is crucial for ensuring that discharged effluents from coal mines meet the required environmental criteria. By focusing on both the prevention and proper management of AMD, we can significantly reduce its harmful impacts on ecosystems and water quality.

Table 1. Permissible effluent standard by NPDES.

Parameter	One day maximum (mg/L)	30 days average (mg/L)
Total iron	7.0	3.5
Total Manganese	4.0	2.0
Total Suspended Solids	70	35
pH	6-9	6-9

The Government of India, through the Central Pollution Control Board, has established standards for the discharge of industrial effluents under the Environment (Protection) Act of 1986. According to these standards, the maximum permitted concentration of iron in effluents is 3 mg/L, while the maximum permitted concentration of manganese is 2 mg/L. The pH range allowed for discharge is

between 5.5 and 9. Therefore, it is necessary to treat acid mine drainage (AMD) to remove dissolved metals and increase the pH level before discharging it into streams or rivers.

AMD treatment methods can be broadly classified into two categories: active treatment and passive treatment.

Active treatment involves the mechanical addition of alkaline chemicals (reagents) to raise the pH and facilitate the precipitation of metals. Although active treatment methods are more expensive, and complex compared to passive treatment methods, they can be highly effective in treating AMD. Some examples of active treatment methods include:

Active Treatment methods	
Ion Exchange	Reverse Osmosis (RO)
Fluidized Bed Reactor	Rotating Cylindrical treatment
Biological Reduction	Zero valent ions
Ceramic microfiltration	Electro- Cogulation

Passive Treatment: Passive treatment methods rely on natural alkaline reagents, biological processes, and microbial actions to maintain the balance of biotic and abiotic factors within controlled microbiological-chemical reactors, typically without the need for powered mechanical additions (Seervi et al., 2017). These methods have the advantage of low operational and maintenance requirements, as well as minimal technical expertise for operation (Seervi et al., 2017). The selection of an appropriate passive treatment system depends on factors such as the local topography, site characteristics, water chemistry, and flow rate of the discharged water (Yadav & Jamal, 2016). Numerous passive systems have been designed for treating AMD by harnessing naturally occurring biological and chemical processes, without the use of hazardous chemicals. Passive treatment methods offer sustainable and environmentally friendly approaches to AMD remediation. By leveraging natural processes, these methods can effectively reduce the concentrations of dissolved metals and adjust the pH of AMD before its discharge into water bodies. Proper selection and design of passive treatment systems are essential for optimizing their performance based on the specific characteristics of the site. Some examples of passive treatment methods include:

Passive Treatment Methods	
Limestone Dissolution	Anoxic limestone Drain (ALD)

Open Limestone Channel (OLC)	Constructed Wetland
Successive Alkalinity Producing system (SAPS)	Biological Treatment Process
Sulfide Reducing Bio-Reactor (SRBR)	Alkaline leach bed.
Adsorption technology: industrial waste	Diversion Wall

History of passive treatment:

Huntsman et al. (1978) at Wright State University conducted studies on water with pH 2.5 and observed that as the water flowed through a boggy area, the pH increased to 4.5, and the concentrations of metals such as iron, manganese, calcium, sulfate, and magnesium decreased. The presence of an alkaline reagent, limestone, located downstream, effectively raised the pH. Similarly, researchers from West Virginia University studied a natural wetland dominated by Sphagnum moss and found no adverse ecological damage within 20 to 50 meters of the influent. The pH of the water ranged between 3.05 to 3.55 and 5.45 to 6.05, and the concentrations of sulfide and iron decreased (Wiedar and Lang, 1982).

Constructed wetlands have shown potential for intentional treatment of coal mine drainage. In the late 1980s, two new approaches were developed to extend the treatment capabilities of wetlands to more acidic water. The first approach involved a wetland constructed by US Bureau of Mines researchers, which successfully neutralized the water and precipitated iron as sulfide. However, it was found that an aerobic and anaerobic system was necessary for effective iron removal (Zipper et al., 2005).

The other approach involved adding reagents to acidic water in an anoxic environment before allowing it to flow into a settling pond or wetland system. This resulted in the coating or "armoring" of the system with iron hydroxide. This system, known as a Sequential Alkalinity Producing System (SAPS), is also referred to as a vertical flow pond, vertical flow wetland, or vertical flow system. Aluminum is still retained in this system (Kepler and McCleary, 1997). A detailed process is discussed in the figure 1.

While passive treatment methods have long-term potential, their effectiveness can be challenging to maintain due to the need for regular maintenance, armoring, and the potential failure of alkaline reagents. Failure of these systems can undermine confidence in their effectiveness. It has been observed that undersized or improperly designed systems are more prone to failure (Simmons et al., 2002).
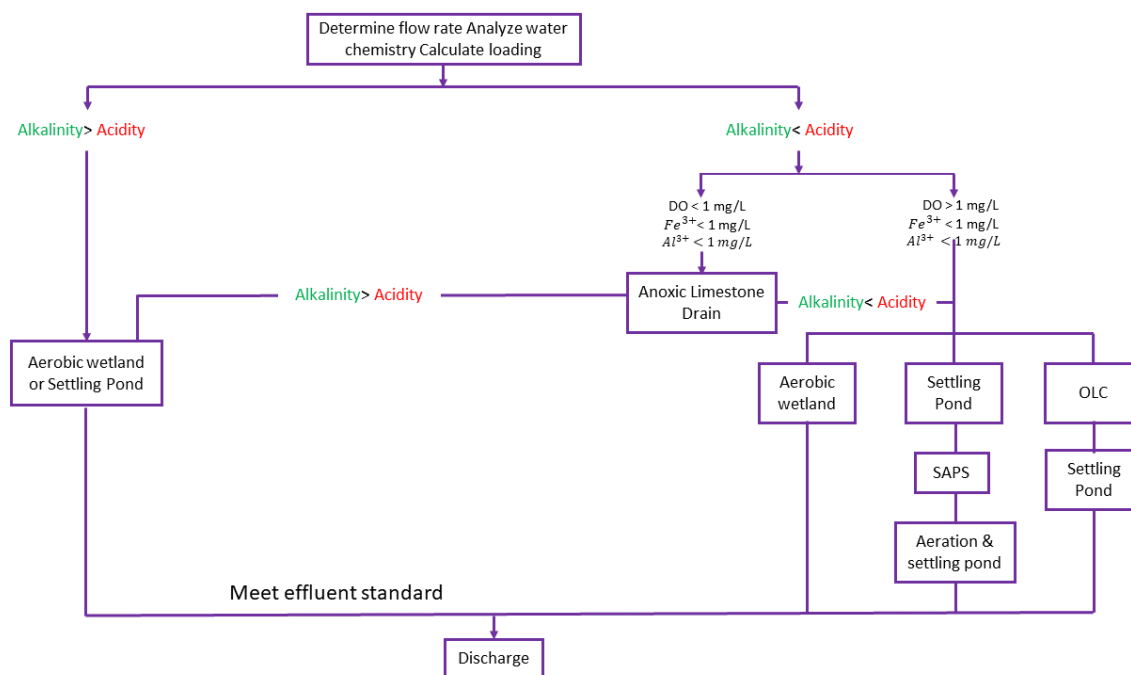
Figure 1: selection of Passive treatment methods based on water chemistry and flow rate. (Hedin et al., 1992, Skousen et al., 2000)

Different passive treatment is discussed below in details.

Limestone dissolution - The pH of Acid Mine Drainage (AMD) can be increased by adding alkaline minerals such as calcite (CaCO3) or dolomite (CaMgCO3), or by introducing the water to higher pH sources like saltwater. This causes metallic ions such as Fe3+, Cu2+, Pb2+, and As3+ to precipitate out (Mills, 2016). Carbonate dissolution, which occurs due to the higher concentration of bicarbonates in anoxic mine water, is a major source of bicarbonate in many anoxic environments (watzlaf et al., 2004). Limestone dissolution by mine water enhances the pH under closed environments, leading to the development of anoxic limestone treatment systems (Turner and McCoy, 1990). These systems, known as anoxic limestone drains (ALDs), involve burying limestone to allow contact with atmospheric oxygen. Under oxic conditions (presence of oxygen), limestone dissolution may be enhanced by the active generation of acidity through ferric iron and aluminum hydrolysis (Hater et al., 2013). High-Ca limestone with over 90% CaCO3 is preferred for passive treatment due to its higher solubility compared to impure limestone or dolomite limestone (Zipper et al., 2011).

$$CaCO_3^+ + H^+ \rightarrow Ca^{2+} + HCO^{3-}$$
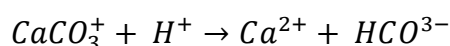
While lime neutralization is a cost-effective process for heavy metal removal from AMD, it produces a voluminous, hard-to-settle sludge laden with metals (Masifana et al., 2018). Lime neutralization involves neutralizing acid mine drainage, and most trace elements tend to

precipitate as the pH is raised (Singh et al., 1985). For the treatment of low concentrations of ferrous iron in the range of pH 6.5 to 8.0, the water can be directed to a settling chamber to precipitate metals (Akcil et al., 2006). Lime is less effective at increasing the pH to treat high ferrous iron water, and the application method is more complex compared to using lime.

$$4Ca(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 \rightarrow 4CaSO_4 + 2Fe(OH)_3 + 2H_2O$$
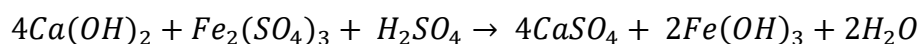
Lime dissolution involves dissolving limestone by contact with acidic water (AMD), which increases the pH and promotes sedimentation and precipitation of metals. The efficiency of this process depends on water retention time, flow rate, and metal load. Lime dissolution is a cost-efficient method for removing metals like Fe and Al through dissolution and precipitation, but its effectiveness is limited for Mn removal.

RBR: (Sulfide Reducing Bio-Reactor) - Biotic passive treatment systems (BPTS) are well-designed closed ecological systems that rely on microbial processes to reduce acidity and dissolved heavy metal concentrations. Aerobic and anaerobic wetlands and bioreactors play a crucial role in these systems. Sulfide-reducing bioreactors (SRB) are particularly effective in microbially reducing sulfate to sulfide, generating alkalinity, and precipitating dissolved metals as insoluble solids. SRB activity consumes protons present in acidic water, producing alkalinity (Sheoran et al., 2010).

Sulfate removal can be achieved through the use of H2S, a strong reducing agent. The sustainability of sulfide-reducing systems depends on the availability of carbon sources, such as lipids, proteins, sugars, organic acids, cellulose/hemicelluloses, and lignin. These components must be hydrolyzed before they can be utilized by the microbial community. The pH range required for optimal performance is 5-8 (Sheoran et al., 2011).

Anaerobic processes involving sulfate-reducing bacteria (SRB) utilize sulfate as an electron acceptor, resulting in the formation of hydrogen sulfide, an increase in water pH, and the precipitation of heavy metal sulfides. SRB also produce bicarbonate, which further increases the pH (Rodríguez et al., 2009). The degradation of sulfate by SRB produces H2S gas, which is injected into the precipitating reactor, reacts with metals, and forms metal sulfides that precipitate at the reactor's bottom (Ighalo et al., 2021). Bacterial activity and dissolved oxygen (DO) increase the pH of the water (Misindi et al., 2018).

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Bioreactors are sometimes affected by bed compaction, leading to reduced permeability and short circuiting. To mitigate this issue, materials like gravel, coarse sand, walnut shells, and wood chips are added to minimize compaction and maintain permeability (Skousen et al., 2017).

SAPS (Successive Alkalinity Producing System)- Sequential Alkalinity Producing Systems (SAPS) are widely used in the passive treatment of acid mine drainage (AMD) to neutralize acidity, remove sulfides, and precipitate metals. SRB activity is crucial for metal removal and pH increase, utilizing various organic carbon sources (Patel et al., 2019). The anaerobic environment, which reduces Fe^{3+} to Fe^{2+}, hinders iron hydroxide precipitation (Jage et al., 2001). Fe and Al precipitate an organic layer in SAPS to maintain low dissolved oxygen (<1 mg/L) and prevent limestone armoring (Zipper et al., 2011).

Effluents from SAPS are discharged into settling ponds for acid neutralization and metal precipitation before final discharge. Vertical flow systems with a 15-hour retention time can treat 20 g/m2/day (Skousen et al., 2010). The use of limestone layers in SAPS with hydraulic retention times of 1-2 days is economically viable for reducing acidity and increasing pH (Lee et al., 2013). SAPS often incorporate buried cells containing large amounts of limestone to stimulate metal precipitation by reducing acidity. They can be combined with drains for better control and management (Skousen et al., 2000). Drained water from SAPS is often directed to sedimentation ponds or aerobic wetlands to collect and retain hydroxide precipitates (Johnson and Hallberg, 2005).

SAPS represent a combination of ALD and wetland methods, addressing limitations of both. They are effective in removing Al and Fe and increasing pH up to 7.5 with a suitable hydraulic retention time (HRT) of 15-16 days, but their efficiency for Mn removal is <10% (Patel et al., 2018; 2019). pH plays a crucial role in heavy metal removal, with iron being removed most effectively at pH 3.5, while partial removal of Zn and Cu occurs (Rodríguez et al., 2009). Hou et al., (2019) reported the oxidation of Fe^{2+} to Fe^{3+} through aeration and hydrogen peroxide, followed by pH adjustment and precipitation of $Fe(OH)_3$ through flocculation and separation.

Studies by Kepler et al. (1994) demonstrated the effectiveness of SAPS in increasing alkalinity, decreasing acidity, and reducing iron levels. Jage (2000) found that the net alkalinity generation in SAPS is proportional to the log of residence time. Skousen & Zimkiewicz (2005) observed the reduction of acidity concentration and acid load in Vertical Flow Wetlands (VFW), with

acid removal rates ranging from 2 to 17 g/m2/day. Bhattacharya et al. (2007, 2008) conducted tests and evaluations of SAPS performance, highlighting the decrease in sulfate reduction and dissolved organic carbon over time in coal mines.

Anoxic limestone drains (ALD)- Anoxic Limestone Drains (ALDs) involve passing acidic water through buried limestone cells or trenches, effectively raising pH levels and increasing alkalinity (Lee et al., 2013; Skousen et al., 2000). ALDs have higher rates of limestone dissolution due to increased carbon dioxide partial pressure in the drain. However, they may not be suitable for flow with high concentrations of ferric iron and aluminum, as the accumulation of hydroxide precipitates can lead to clogging and failure (Cravotta, 2006; Johnson and Hallberg, 2005).

ALDs aim to increase pH, reduce acidity, and lower metal loads by facilitating the oxidation of ferrous iron and precipitation of ferric hydroxide. Short-term performance of ALDs can be effective in the presence of significant concentrations of ferric iron and aluminum (Johnson et al., 2005). ALD effluent typically ranges from pH 6 to 7.5, requiring a hydraulic retention time (HRT) of 14-15 hours (Yadav et al., 2016). Optimum alkalinity generation occurs within the range of 150-300 mg/L (as $CaCO_3$) after 14 to 23 hours of retention time (Zipper et al., 2011). ALDs consist of limestone-filled trenches where acidic water is directed to produce carbonate alkalinity through dissolution (Zipper et al., 2011). ALDs can be used as pre-treatment for AMD before passing the water through a passive treatment unit (Skousen et al., 2011).

The limitation of ALDs is the clogging of metal hydroxides when the pH reaches 4.5 or higher, especially in the presence of significant concentrations of O_2, Al, or Fe^{3+} (Zipper et al., 2011). Successful ALDs can avoid clogging by ensuring that Al, Fe^{3+}, and dissolved O_2 concentrations in the influent water are less than specified limits. Skousen et al. (2011) suggest that ALDs can be effective for AMD with dissolved O_2 up to 2 mg/L, Al up to 25 mg/L, and less than 10% of total Fe in the Fe^{3+} form. Metal removal is essential to prevent bed clogging and premature failure. Clogging and permeability issues have been reported, leading to premature failure of ALDs (Coatzlaf, 2000). ALDs require at least 15 hours of retention time and are effective in increasing limestone dissolution (Lee et al., 2013).

ALDs are modified lime dissolution methods that operate under anoxic conditions. The efficiency of ALDs depends on limestone armoring, HRT, geographical conditions, and temperatures. Manganese removal can occur in ALDs, but only after iron removal, and it is more effective at higher temperatures with a larger required area compared to iron removal.

Metal removal is necessary to prevent clogging and reduced ALD lifespan by decreasing permeability and calcite dissolution. ALDs are not effective in removing aluminum due to its insolubility at pH 4.5 and 8.5. Some cases have reported premature failure of ALDs due to clogging and jamming caused by retained materials (Coatzlaf, 2000). ALDs can remove approximately 70-80% of iron, less than 40% of aluminum, and have limited effectiveness in reducing manganese (Skousen, 2005; Johnson, 2005; Zipper, 2011). Skousen et al. (2011) highlighted the effectiveness of ALDs in reducing iron concentrations in AMD by approximately 90%.

Open limestone channel- The open limestone channel (OLC) is a widely used and simple method for treating acid mine drainage (AMD) with low metal content and high dissolved oxygen (DO). It serves as an open-air alternative to the anoxic limestone drain (ALD), where the AMD flows over a certain distance while being lined with high-Ca limestone (Zipper et al., 2011). OLCs are most effective on slopes steeper than 20% or when periodic high flows dislodge iron (Fe) armoring on the limestone (Zipper et al., 2011). The slope of the channel directly affects the success of OLCs. If the slope exceeds 10 degrees, water can pass through the limestone layer too quickly, impeding neutralization (Taylor et al., 2005). Conversely, if the gradient is too low, metal precipitation around limestone particles can reduce the neutralizing capacity and affect flow characteristics.

OLCs are capable of removing approximately 70% of Fe, 40-50% of Al, and 10-20% of Mn (Skousen et al., 2011). They can raise the pH of water up to a maximum range of 7.5-8.0. AMD flows through open sloping channels where it gets neutralized within a pH range of 6 to 8 (Zipper et al., 2005). OLCs have been successful in treating acidity levels ranging from 4 to 205 mg/L, with removal rates of 0.03 to 19 mg/L per meter of channel length and neutralization rates of 30-60% (Ziemkiewicz and Brant, 1997). These open channels or ditches lined with limestone introduce alkalinity to acid water (Skousen et al., 2000). OLCs are commonly used for AMD conveyance as they provide a practical means of transportation. Optimal performance is achieved on slopes exceeding 20% to maintain flow velocities that keep precipitates in suspension, preventing armoring of limestone surfaces (Skousen et al., 2000). Armoring reduces the dissolution rate of limestone to 20% of its unarmored rate (Skousen et al., 2000).

The mechanism of OLCs involves the precipitation of metals and is dependent on the flow rate and slope angle. However, their effectiveness in metals removal decreases when the concentration of aluminum (Al) is high (Skousen et al., 2000).

Biological process- Microorganisms have the ability to bioremediate acid mine drainage (AMD) by generating alkalinity and immobilizing metals, effectively reversing the processes that lead to AMD formation. Microbial processes that generate net alkalinity include denitrification, methanogenesis, sulfate reduction, and iron and manganese reduction. Reduction of ferric iron and sulfate, which are abundant in AMD, can have a significant impact on AMD-impacted waters. While the reduction of soluble ferric iron does not directly decrease acidity, biological sulfate reduction by sulfate-reducing bacteria converts sulfate to sulfide. The biogenic sulfide can then precipitate the heavy metals present in mine drainage (Pratinthong et al., 2021).

Increasing the pH from 5 to 6 and removing sulfide can achieve approximately 85% removal, leading to permanent removal of sulfide and metals, production of less hazardous water, and the potential for metal recovery. The optimal efficiency is typically achieved at a dosage of 25 g/L, and temperature plays a crucial role, with a range of 15-40°C showing high efficiency. However, biological treatment methods exhibit low effectiveness for manganese (Mn) removal (Patel et al., 2016; Skousen et al., 2011).

The process of biological treatment involves the use of microorganisms, followed by sedimentation of biological sludge and eventually the emptying of the reactor (Costa et al., 2017). However, biological sulfate reduction has some drawbacks, including slow process kinetics, the requirement for organic matter, and an increase in dissolved organic content in the treated effluent.

Biological treatment of AMD is a slow process compared to other techniques, as it relies on biochemically-mediated processes within living organisms. Longer retention times are necessary to achieve effective pollutant reduction. Monitoring and maintaining pH and temperature are crucial for practical applications involving large volumes of water, as performance can be compromised or halted if not properly controlled (Ighalo et al., 2021). The oxidation of ferrous iron to ferric iron at low pH and the rate of precipitation at low pH are influenced by bacterial activity and dissolved oxygen levels (Silva, 2011).

Aerobic wetlands- It works on the oxic nature, it is best suited to low metal load and low DO to attain oxic, it is generally implemented to provide residence time so that aeration can occur and metal can precipitate. Aerobic wetlands are practical for treating water that has net alkalinity (Cravotta 2006; Johnson and Hallberg 2005; Skousen et al., 2000). AeWs provide residence time for Fe oxidation, hydrolysis, and settling of the metal hydroxide (Skousen et al.,

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2017). Aerobic wetlands are generally constructed to treat mine waters in anoxic with help of microbial activities to attain net alkaline. This is because the main premeditative reaction that occurs within them is the oxidation of ferrous iron and subsequent hydrolysis of the ferric iron produced. (Skousen et al., 2017)

It is shallow ponds usually design to precipitation of metal oxide or hydroxide by proving the aeration and suitable residence time (Yadav et al., 2016). In USA metal sludge 30-40mm and many studies from Pennsylvania and USA 3.2-4.4 cm.

Aerobic wetlands have proven effective in many situations to remove of Fe (60-95%) from solution, they fail to adequately remove Mn, commonly less than 10% of Mn is predicated (Taylor et al., 2005). Mn oxidation occurs more slowly than Fe oxidation, and is sensitive to the presence of $\llbracket Fe \rrbracket^{2+}$, which will inhibit or reverse Mn oxidation (Wildeman et al.,1993; Luan et al., 2012). The pre-treated effluent enters into a typical aerobic wetland system planted with Typha sp. To aid wetland performance.

In Aerobic Wetland the oxidation of ferrous iron occurs and Mn oxidation is slower than Fe and Al oxidation, removal of metals showing slower water flow. Aerobic wetland oxidation of metals, hydrolysis, and precipitation with contact of oxic nature best way to removal efficiency of Fe is 60-95% and suited to increase pH value up to 6.5 but Mn removal is very low compare to other metals (Skousen et al., 2011). Taylor et al. (2005) reported most of metals are precipitated by increasing the pH of AMD and for that process many passive treatments used in Aerobic wetland Fe precipitation shows good results in between 60-95% removal of Fe. Metal removal was successful AeWs where the influent water pH was >6 (Skousen and Ziemkiewicz, 2005). Removal rates were 10–20 g m−2 day−1 for Fe and 0.5– 1.0 g m−2 day−1 for Mn (Hedin et al. 1994). AeWs remove metals by slowing the rate of water flow and allowing for oxidation and bacterial activity. As $\llbracket Fe \rrbracket^{2+}$ is oxidized, the resulting $\llbracket Fe \rrbracket^{3+}$ precipitates as ferric hydroxide in these structures as long as the pH is 3.5 or above. These processes also help to settle other metals that co-precipitate with the Fe (Skousen et al., 2017).

Anaerobic wetland- Anaerobic wetlands (AnWs) are a modified version of natural aerobic wetlands where vegetation is grown above the water to create an anoxic environment. Typha and other wetland vegetation are typically planted in deep (>30 cm), permeable substrates composed of soil mixed with organic materials like peat moss, spent mushroom compost, sawdust, straw/manure, or hay bales (Skousen et al., 2017). AnWs consist of a layer of organic

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matter (0.30-0.60 m) over a bed (0.15-0.30 m) (Yadav et al., 2016). These wetlands facilitate microbial processes under anoxic conditions, particularly the reduction of sulfates when sulfates and biodegradable organics are present (Zipper et al., 2011).

AnWs have been developed as an improved wetland system suitable for highly acidic acid mine drainage (AMD) (Skousen et al., 2017). Limestone may be added to the organic material in the substrate to enhance alkalinity generation and create favorable conditions for microbial activity (Hedin et al., 1994; Ziemkiewicz et al., 2005). AnWs often have pond depths exceeding 1 foot (Lee et al., 2003).

The removal efficiencies achieved in AnWs under anoxic conditions include 70-90% for iron, 90% for aluminum, pH increase above 6, and a decrease in acidity by 70-90%. However, the removal of manganese is generally low (Skousen et al., 2006). Wetland systems, including AnWs, have been recognized for their ability to improve water quality by reducing oxygen demand, phosphates, suspended solids, and metals through physical, chemical, and biological processes (Sheoran, 2006; Johnson and Hallberg, 2005). Constructed wetlands are considered easier to operate and maintain compared to conventional mechanical systems, providing a controlled and manipulable environment (Sheoran et al., 2006). Studies conducted in South Korea suggest that a retention time of 1 to 2 days is appropriate and cost-effective for wetland systems (Lee, 2003).

In the aerobic conditions typically found in surface waters, iron, aluminum, and manganese precipitate as oxides and hydroxides. Ferrous iron oxidizes to ferric iron, primarily forming iron oxy-hydroxides. The rate of iron precipitation at low pH depends on the activity of iron-oxidizing bacteria, which also catalyze pyrite oxidation (Silva et al., 2012).

Limestone diversion walls- In limestone diversion walls (LDW) methods, the limestone aggregate is filled in constructed wall and vigorous mixing of AMD is done. LDW methods is suitable in hilly topographical area with availability of 10 m hydraulic head. LDW was developed in Sweden for acidity removal from acid rain (Yadav & Jamal,2017; Patel et al., 2018).

Behaviours of Metal during AMD treatment

Acid mine drainage (AMD) water from coal mines is characterized by low pH and high concentrations of sulfate and metals, including Fe, Mn, Al, and Zn (Chai et al., 2020). In highly acidic water, heavy metals tend to be more soluble and enter the solution through secondary

reactions involving iron sulfate, sulfuric acid, and various compounds present in mines or streams such as clay, limestone, sandstone, sulfide, and organic substances (Geochem, 2006). These reactions explain the presence of metals like Ca, Mg, Na, K, Fe, Al, Mn, and silicates in mine drainage. The high concentrations of heavy metals in AMD are toxic to microorganisms, leading to slow bacterial growth and a decrease in sulfate reduction (Patel et al., 2018).

Iron is the most common contaminant in coal mine drainage. It can be removed through oxidation and precipitation processes. Bacterial activity and abiotic reactions play a role in oxidizing ferrous iron (Fe2+) to ferric iron (Fe3+). The pH level affects iron removal, with pH values below 3 limiting solid formation. Iron removal is limited between pH 3 and 6, while pH levels above 6 allow for greater iron removal. Treatment systems involving neutralization and aeration can help remove iron by precipitating it as ferric hydroxides.

Aluminum's solubility is primarily determined by pH. At pH 4 or below, aluminum hydroxide (Al(OH)3) remains highly soluble. However, precipitation of aluminum occurs at pH greater than 4, typically around pH 4.5 or above. Manganese removal is challenging due to its high solubility. The oxidation and precipitation of manganese require a pH greater than 6, usually occurring after most of the iron has already precipitated. Effective removal of manganese often requires a pH above 9 or 10, which is highly alkaline.

Zinc and copper removal from acid mine drainage (AMD) can be achieved through neutralization and precipitation processes. Increasing the pH to around 6-7 can decrease the solubility of zinc and copper, allowing them to precipitate as metal hydroxides. Sorption onto precipitated metal oxides can also contribute to zinc removal. Sulfide and sulfate in AMD are challenging to remove. Sulfide oxidation results in the production of AMD, while sulfate removal depends on pH variation and can involve processes such as precipitation, absorption, and ettringite formation.

The pH level plays a crucial role in metal removal, as it affects precipitation and solubility. Low pH inhibits sulfide reduction and increases metal solubility. pH control is effective for precipitating many heavy metals, but some may be unaffected. Factors like temperature, hydraulic retention time, acidity of metals, alkalinity, and oxygen concentration also influence metal removal in AMD treatment processes.

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Table1: Removal of trace metal by pH control.

Metals	Removal pH (Dissolution)	Source
Fe	3-6 (oxidation step), pH > 6 removal 10-20 mg/l	Johnson et al 2011
	pH< 3.5 dissolved to Ferric, pH-3 40% concentration Removal	Watzlaf et al., 2004
Al	Dissolved at pH- 3.5 or less. pH 5-8 less effective	Hedin 1994)
	pH< 4	Silva et al., 2005
Mn	pH>8	Lora 2011,
	pH<8 slow oxidation	Morgan 1981
	pH> 11	Silva et al., 2005
	pH > 7.5-8 start precipitation	Yadav et al., 2016
	pH > 9-10	Watzlaf 2004
Zn	pH > 6.5	Skousen et al., 2017
	pH> 5.6	Hater et al., 2014
Cu	pH > 9	Altameemi et al., 2012

Temperature: Temperature affects the dissolution, adoption, and precipitation of metals. An increase from 20 to 32°C improves sulfide reduction reactions, but temperatures above 40°C decrease bacterial activity. Water solubility also depends on temperature, with reactions decreasing by over 50% at temperatures below 10°C compared to 20°C.

Hydraulic Retention Time (HRT): HRT balances flow rate and removal efficiency. Shorter HRT may allow sufficient time for sulfate-reducing bacteria (SRB) activity to neutralize acidity and precipitate metals, but it can also wash out biomass and increase dissolved oxygen input. A 60-hour retention time is sufficient to remove dissolved oxygen below 1 mg/L even at low temperatures. HRT of 1-2 days is appropriate and economical for limestone layers, but longer HRT can reduce porosity and permeability of reactive mixtures.

Acidity: Acidity in mine water comes from dissolved metals like iron, aluminum, and manganese, as well as free protons at low pH. Acidity can be estimated based on pH and concentrations of dissolved metals. It is generally expressed as a mass or loading of equivalent calcium carbonate ($CaCO_3$). Alkalinity, on the other hand, is a measure of a water's ability to neutralize acid additions and is commonly provided by alkaline materials like limestone.

Alkalinity: Alkalinity can be generated, and protons neutralized by adding alkaline materials, such as limestone (CaCO3). Mine water with pH above 4.5 and acid neutralizing capacity is considered to contain alkalinity. Dissolved carbonates (HCO3- and CO32-) are the main source of alkalinity, but other compounds like hydroxyl ions, silicates, borates, organic lignite, phosphates, and ammonia can also contribute. Water can have both acidity and alkalinity, and their net balance determines whether it is net alkaline or net acidic.

Table: 2 Solubility and saturation pH of different chemicals (Taylor, 2005)

Neutralization material	Saturation pH	Solubility (mg/L) in cold water
Limestone ($CaCO_3$)	8-9.4	14
Dolomite ($CaMg(CO_3)_2$	8-9.5	10-300
Magnesite $MgCO_3$)	9.5-10	60-100
Caustic Soda (NaOH)	14	450,000
Ammonia (NH_3)	9.2	900,000
Soda Ash (Na_2CO_3)	11.6	75,000
Caustic magnesia (MgO)	9.5-10.8	1-50
Hydrated lime ($Ca(OH)_2$)	12.4	1,3000-1,850

Mechanism of metal removal:

Mine water contains high concentrations of iron, manganese, aluminum, sulfate (SO4), calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na), with iron, manganese, and aluminum being more abundant compared to other metals. Various chemical and biological processes can be employed to remove iron, manganese, and aluminum from coal mine drainage, with the specific process depending on the metal and influenced by pH and oxidation-reduction potential (Eh). The pH has a significant impact, as most elements (except Cd and Cu) are negatively correlated with pH, while all metals show a strong positive correlation with sulfate (SO4) concentration. Metal removal from acid mine drainage (AMD) involves mechanisms such as sorption, coprecipitation, and exchange with precipitated iron, manganese, organic materials, and soil-like materials. Sorption to organic materials is important for aluminum and divalent transition metals, while sorption to precipitated iron, manganese, and even limestone surfaces can contribute to the removal of trace metals from the water.

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Reduction: Chemical and microbial processes differ in anaerobic and aerobic environments. In anaerobic conditions where oxygen is absent, metals like Fe(II) and Mn(II) do not oxidize, and their hydroxides, such as Fe(OH)2 and Mn(OH)2, do not form (Waztlaf et al., 2006).

The dissolution of metals as sulfide compounds depends on pH and the solubility product of the specific metal sulfide. Metal sulfides form in the order of CuS, PbS, ZnS, and CdS based on their solubility. FeS is one of the last metal sulfides to form, and MnS is the most soluble. The reduction of manganese is typically associated with the reduction of iron (Muhammad et al., 2015).

In the case of coal mine drainage, metal contamination is usually limited to iron, manganese, and aluminum, along with hydrogen sulfide produced by bacterial activity (Taylor et al., 2005). Sulfate reduction is primarily influenced by dissolved iron concentration, while aluminum does not form sulfide compounds. The high solubility of MnS makes it difficult to remove from acid mine drainage (AMD) (Skousen et al., 2011). Precipitating active heavy metals present in the water helps reduce metal concentration and acidity, thereby improving water quality through metal removal (Johnson et al., 2010).

Adsorption: Adsorption is a promising and preferred technique for treating acid mine drainage (AMD), where solute particles are transferred from the aqueous phase onto adsorbent solid surfaces. This process utilizes active sites on the adsorbent to remove contaminants from the wastewater. Coprecipitation, which involves impurities adsorbing onto nuclei or crystals during solid phase precipitation, is another effective co-removal process. Control measures such as pH adjustment and oxidation states of species can enhance the adsorption process. Activated carbon has been identified as a potential adsorbent for heavy metal removal, although limited research has been conducted on its use for inorganic removal. Different adsorbents, including organic, clay/earth-based materials, activated carbon/biochar, zeolites, and fly ash, have been classified based on their primary constituents. Copper adsorption, for example, was found to be highest at pH 9, 25°C, and a specific metal ion concentration (Altameemi et al., 2012) (Hashem et al., 2021; Ighalo et al., 2021).

Sulphate Reduction: In an anaerobic environment containing an organic substrate, bacterial sulphate reduction can occur, affecting the water chemistry of acidic mine water. During this process, bacteria oxidize organic compounds using sulfate as a terminal electron acceptor, resulting in the release of hydrogen sulfide and bicarbonate. The absence of oxygen and the presence of organic substrates lead to anoxic conditions and a lack of oxidized forms of iron

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and manganese. Sulfate-reducing bacteria are most active in lower pH drainage, as their activity decreases when the water pH exceeds 5 (Skousen et al., 2011). Alkalinity generation involves reducing sulfite to sulfide in the presence of an electron donor (Costa et al., 2017, Waztlaf et al., 2004).

Challenges and future scope

Prevention and Treatment of AMD: The prevention, treatment, and metals recovery processes for acid mine drainage (AMD) still offer significant prospects for development in terms of theory, processes, equipment, and the research of new approaches and technologies. Prevention technologies aim to limit the formation of AMD at the source, while effective management of solid waste materials generated by industries can also contribute to preventing AMD formation and facilitating waste disposal. Bacterial activity can inhibit microbial activity and reduce AMD formation, although its effectiveness can be influenced by environmental and climatic conditions. Oxygen barriers have been widely used to prevent AMD formation, but their efficacy can be compromised by climate change impacts. Passive treatment technologies show promise, particularly in pure pyrite systems, but their stability and sustainability in complex environments remain unclear. Utilizing mine waste, such as in filling goaf areas or as construction materials, can help reduce AMD formation and provide economic benefits.

Metals Recovery: Recovering and reusing valuable minerals is an effective and sustainable approach to AMD treatment, as it can offset the treatment costs. Various treatment technologies are available, including limestone neutralization, constructed wetlands, sulfate-reducing bioreactors, adsorption, and membrane technologies. However, these technologies require long-term treatment and monitoring until the source of AMD is depleted, leading to increased treatment costs. Metals removal from AMD differs for each metal, with methods generally effective for removing Fe and Al through oxidation and precipitation. However, Mn removal poses challenges due to its high solubility. Constructed wetlands, anoxic limestone drains (ALDs), and Subsurface Flow Anaerobic Passives Systems (SAPS) have shown promise in removing Fe and Al, with SAPS being cost-efficient and effective. Further research is needed to improve Mn removal, potentially by incorporating fly ash and steel slag beds into SAPS as oxidation beds. It's important to address the limitations of these beds, such as the production of toxic sludge by-products. Additionally, the generation of alkalinity increases with net acidity loading in all systems.

Discussion

Acid mine drainage (AMD) poses significant environmental challenges, but there are various prevention, treatment, and metals recovery approaches that can be employed to mitigate its impacts. The adsorption technique shows promise as a preferred method for AMD treatment, with adsorbent materials effectively removing contaminants from wastewater. Coprecipitation and adsorption processes can co-remove impurities during the precipitation of solids from solution. pH control and oxidation states of species play a crucial role in controlling AMD through coprecipitation. Activated carbon has shown potential as an adsorbent for heavy metal removal.

Sulfate reduction processes, facilitated by bacterial activity, can help reduce AMD formation by oxidizing organic compounds using sulfate as a terminal electron acceptor. However, the activity of sulfate-reducing bacteria is significantly influenced by pH, and their effectiveness is more pronounced in lower pH drainage. Oxygen barriers have been widely used to prevent AMD formation, but their effectiveness can be affected by climate change and other environmental factors. Passive treatment technologies, such as constructed wetlands, show promise in AMD treatment, but further research is needed to assess their stability and sustainability in complex environments.

The recovery and reuse of mine waste present a valuable opportunity for AMD control. By utilizing mine waste in various applications, such as filling goaf areas or producing construction materials, the formation of AMD can be reduced, while also providing economic benefits. Treatment technologies, including limestone neutralization, constructed wetlands, sulfate-reducing bioreactors, adsorption, and membrane technologies, offer direct methods for reducing metals in water and mitigating the generation of AMD. However, these technologies often require long-term treatment and monitoring until the source of AMD is depleted, leading to increased costs.

Metals recovery and reuse offer effective and sustainable approaches to AMD treatment, as they can offset treatment costs by extracting valuable minerals. Multidisciplinary partnerships between organizations, institutions, industries, and the public play a crucial role in addressing the challenges and opportunities associated with AMD treatment, including issues, treatment planning, funding, and remediation.

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References:

1. Aoyagi T, Hamai T, Hori T, Sato Y, Kobayashi M, Sato Y, Inaba T, Ogata A, Habe H, Sakata T, (2017), Hydraulic retention time and pH affect the performance and microbial communities of passive bioreactor for treatment of acid mine drainage, AMB Express.

2. Altameemi I A, Thurya M (2012), A simple method for treatment of waste water containing Cu and Zn ions using sorption on dried concoplus leave, Journal of Basrah Researches ((Sciences)) Vol.(39). No.(2) .A (2012)

3. Bilai M, Ihsanullah I, Younas M, Hassan Shah M. (2021), Recent advances in application of low-cost adsorbent for the removal of heavy metals from water: a critical review, separation and purification technology 278.

4. Bhattacharya J, Yim G J, Woo ji S, Lee H S and Cheong Y W. (2007), 'SAPS' influent and effluent geochemical parameter related to AMD pollution control: A case study water in mining environment Cagliari Italy. 27, 12-19.

5. Bhattacharya J B, Ji S W, Lee H S, Cheong Y W, Yim G J, Min J S, and Choi Y S, (2008), Treatment of acidic coal mine drainage: design and operational challenges of successive alkalinity producing system, mine water environment 12-19.

6. Choudhary R P, Sheoran A S (2012), Performance of single substrate in sulphate reducing bioreactor for the treatment of acid mine drainage minerals engineering 29-35.

7. Calugaru Iuliana Laura, Thomas Genty, Neculita m, (2021), Treatment of manganese, in the presence or absence of iron, in acid and neutral mine drainage using raw vs half-calcined dolomite, mineral engineering 160.

8. Chen Guan, Ye Yicheng, Yao Nan, Nanyan Hu, Jie Zhang, Yang Huang, (2021), A critical review of prevention, treatment, reuse, and resource recovery from acid mine drainage, journal of cleaner production 329.

9. Dev S, Roy S, Bhattacharya J (2017), Optimization of the operation of packed bed bioreactor to improve the sulfate and metal removal from acid mine drainage journal of environment management 135-144.

10. Esmaeili A, Mobbini M, Eslami H (2019), Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies, Applied water science 9:97.

11. Gaikward R.W., Gupta D V (2008), Review on removal of heavy metals from acid mine drainage.

12. Hedina B C, Hedin R S , Capoa R C, Stewart B W (2020), Critical metal recovery potential of Appalachian acid mine drainage treatment solids, international journal of coal geology 231, 103610.

13. Idaszkin Y L, Carol E, De Pilar A M (2017), Mechanism of removal and retention of heavy metals from the acid mine drainage to coastal wetland in the Patagonian marsh chromosphere 183, 361-370.

14. Ighalo Joshua O., Setyo Budi Kurniawanc, Kingsley O. Iwuozord, Chukwunonso O. Aniagora, Oluwaseun J. Ajalaf, Stephen N. Obaa, Felicitas U. Iwuchukwua, Shabnam Ahmadih, Chinenye Adaobi Igwegbe (2021), a review of treatment technologies for the mitigation of the toxic environmental effects of acid mine drainage (AMD), process safety and environment protection, 157.

15. Johnson D B, Hallberg K B, (2005), Acid Mine Drainage remediation options: A review. Science of the total environment 338, 3-5.

16. Jung S P , cheong Y, Yim G, Ji S, Kang H, (2013), Performance and bacterial communities of successive alkalinity- producing system (SAPSs) in passive treatment processes treating mine drainage differing in acidity and metal levels. Environment science pollution resources 3722-3732.

17. Kimos A. 2011, successive alkalinity- Producing system.

18. Klein R., Tischler J.S, Muhling M., and Schlomann M. (2013), Bioremediation of Mine Water, Biochem Eng BIotechnol 141, 109-172.

19. Kustula V., Witick A., and Merilainen J.J (2005), Successive alkalinity producing system for the tyreatment of acid sulphate soil runoff: preliminary result of field trial, agriculture and food science vol 14, 112-121.

20. Kefeni K K , Msagati A M T, Nkambule T T I, Mamba B B (2018), synthesis and application of hematite nanoparticles for acid mine drainage treatment journal of environment chemical engineering 6, 1865-1874.

21. Lee J Y, Khim J, Woo K, Ji W H. (2013), A full- scale successive alkalinity- producing passive system (SAPPS) for the treatment of Acid Mine Drainage, water air soil pollution 224:1656.

22. Lefticariu L., Walters E.V., Pugh C. W., and Bender K.S. (2015), Sulfate reducing bioreactor dependence on organic substrates for remediation of coal- generated acid mine drainage: Field experiment, Applied Geochemistry 63, 70-82.

Eur. Chem. Bull. **2023**,*12 issue 8), 5424-5447*

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23. Matthies R, Aplin A C, Jarvis A P (2010), Performance of a Passive treatment system for net acidic coal mine drainage over five year of operation, science of the total environment 408, 4877-488.

24. Muhammad S N, Kusin F M, Zahar M S M, Halimoon N, and Yusuf F M (2015), Passive treatment of acid mine drainage using mixed substrates: batch experiment, procedia environment science 30, 157-161.

25. Mills C 2016, An introduction to Acid mine drainage.

26. Mashifana,T, N Sithole (2018), Heavy Metals and Radioactivity Reduction from Acid Mine Drainage Lime Neutralized Sludge, Earth and Environmental Science, 120.

27. Nairn R W and Mercer M N, (2000), Alkalinity generation and metals retention in a successive alkalinity producing system. Mine water and the environment 124-133.

28. Neculita C M, Zagury G J, Bussiere B. (2008), Effectiveness of sulfate- reducing passive bioreactor for treating highly contaminated acid mine drainage: II Metal removal mechanisms and potential mobility, Applied Geochemistry 23, 3545-3560.

29. Neculita C M, Yim G J, Lee G, Ji S W, Jung J W, Park H S, Song H, (2011), Comparative effectiveness of mixed organic substrates to mushroom compost for treatment of mine drainage in passive bioreactors. Chemosphere 76-82.

30. Neculita C M, Zagury G J (2008), Biological treatment of highly contaminated acid mine drainage in batch reactor: long- term treatment and reactive mixture characterization, journal of Hazardous Materials 358-366.

31. Ouakibi O, Hakkou R, Mostafa and Benzaazoua (2014), Phosphate carbonated Wastes used as drains for acidic mine drainage passive treatment procedia engineering 407-414.

32. Olds W E, Tsang D C W, Weber P A, and Weisener C G (2013), Nickel and Zinc Removal from Acid Mine Drainage: Roles of Sludge Surface Area and Neutralising Agents, Journal of Mining, 5.

33. Patel M.D., and Jade R., (2019), Study of parameter affecting the performance of hybreid successive alkalinity producing system used for treatment of Acid Mine Drainage: an overview.

34. Qasem N A A, Mohambad R, Lawal D (2021), Removal of heavy metals from waste water: a comprehensive and critical review, clean water 4:36.

35. Rakotonimaro T V, Neculita G M, Bussiere B and Zagury G J, (2017), Comparative colomn testing of three reactive mixtures for the bio chemical treatment of iron- rich acid mine drainage, mineral engineering 111, 79-89.

36. Sato Y, Hamai T.,m Hori T., Habe H., Kobayashi M and Sakata T (2017), year-round performance of a passive sulfate-reducing bioreactor that uses rice bran as a an organic carbon source to treat Acid Mine Drainage, article on mine water environment.

37. Silva A M, Cunha E C, Silva F D R, Leao V A, (2012), Treatment of high manganese mine water with limestone and sodium carbonate journal of cleaner production 11-19.

38. Singh G and Rawat N S. (1985), Removal of trace element from Acid Mine Drainage, international general of mine water vol 4 ,17-21.

39. Sheoran A S, Sheoran V, Choudhary R P (2010), Bioremediation of acid- rock drainage by sulphate prokaryotes: A Review, mineral engineering 23, 1073-1100.

40. Song H, Yim G J, Ji S W, Nam I H, Neculita C M and Lee G, (2012), Performance of mixed organic substrates during treatment of acidic and moderate mine drainage in column bioreactor, journal of environment engineering 1077.

41. Siti Nurjaliah Muhammad, Faradiella Mohd Kusin, Mohd Syakirin Md Zahar Normala Halimoon and Ferdaus Mohamat Yusuf, (2015), Passive treatment of acid mine drainage using mixed substrates: batch experiments, Procedia Environmental Sciences 30, 157 – 16.

42. Houa S T, Cain J Y, Tana K Y. Xin H, Zhe W, Xin Y, (2019), Acid mine drainage treatment system for AMD in remediation of metal sulfide mines, China geology, 396-397.

43. Taylor J., Pape S., and Murphy N. (2005), A summary of passive and active technologies for acid and metalliferous Drainage (AMD). Fifth Australian workshop on acid drainage 29-31.

44. Trumm D, and Watts M (2010), Results of small-scale passive system trials to treat acid mine drainages, west coast Region, South Island, New Zealand, New Zealand journal of geology and geophysics vol 53 227-237.

45. Vasquez Y, Escobar M C, Neculita C M, Arbell Z, Roldan F (2016), Biochemical passive reactors for treatment of Acid Mine Drainage: Effects of hydraulic retention time on change in efficiency, composition of reactive mixture, and microbial activity. Chemosphere 153, 244-253.

46. Watzlaf G R, Schoroeder K L, Kleinmann R L.P., Kairies C.l., and Nairn R.W. (2004), The passive treatment of coal drainage.

47. Yadav H.L. and Jamal A. (2016), Treatment of Acid Mine Drainage: A general Review, article on International Advanced Research Journal in Science and technology vol3, issue 11.

48. Zagury G J, Kulnieks V I, Neculita C M (2006), Characterization and reactivity assem0ent of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment, chemosphere 64, 944-954.

49. Zipper C., Skousen J., and Jage C (2011), Passive treatment of Acid –Mine drainage, research journal of Virginia cooperative extension 460-133.

50. Jage C.R., Zipper CE, and Noble R, (2001), Factor affecting alkalinity generation by successive alkalinity producing system: regression analysis, A review journal on J Environ Qual 1015-1022.