# A Review on the Use of Constructed Wetlands for the Treatment of Acid Mine Drainage

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# 12.1 What is Acid Mine Drainage?

Acid mine drainage (AMD) or acid rock drainage (ARD) is an environmental pollutant that is associated with mining activities. The production of AMD is actually a natural occurrence but mining activities have, however, accelerated this process, resulting in negative impacts to the environment [1–3].

In a natural environment small amounts of acid are produced when sulfide ore is exposed to an oxidizing environment and this occurs through the natural weathering of rocks that enclose sulfide. Subsequently, naturally occurring processes neutralize the acid, with surrounding alkaline rocks providing the most alkalinity [1]. These neutralization processes (shown below) include dissolution of carbonate substrates like calcite and dolomite [equations (12.1), (12.2)]; reduction of iron hydroxides within sediment [equation (12.3)]; and dissimilatory sulfate reduction [equation (12.4)]. All of these processes collectively consume protons and produce alkalinity, thereby reducing AMD impact. Mining of sulfide ore has fractured large amounts of these sulfide-containing rocks and this has led to the exposure of roots-rock surfaces. This consequently leads to the production of large quantities of AMD. In addition to this, these naturally occurring processes have been become unbalanced and as such, natural buffering sources become less and less available [2].

$$CaCO_3 + 2 H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$
 (12.1)

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + HCO_3^-$$
 (12.2)

$$3 \text{ Fe}(OH)_3 + H^+ \rightarrow \text{ Fe}_3(OH)_8 + H_2O$$
 (12.3)

$$SO_4^{2-} + 2 CH_2O \rightarrow H_2S + 2 HCO_3^{-}$$
 (12.4)

In a mining environment, AMD generation begins with the mining of sulfide ore and continues to generate, even after the mine is closed or abandoned [4, 5]. Initially AMD is formed in the groundwater of an active mine; however the rate of AMD generation is slow as the water level is kept to a minimum for dewatering, through the use of pumps. When the mine is shut down however, pumping

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operations cease, leading to groundwater levels rising and eventual flooding of the mine [6]. The rate of AMD generation thereby rapidly increases and the groundwater eventually leaches into surface waters and waterways [7].

Chemically, AMD is formed from the exposure of sulfide ore minerals to water and oxygen. Oxidizing bacteria also play a role in this generation and typically act as catalysts. Once the ore is exposed, sulfate and heavy metals such iron, copper, lead, nickel, manganese, cadmium, aluminium and zinc are leached and solubilize into the water [4, 6, 8]. In Johannesburg, the ore body is uraniferous, and this has resulted in the mobilization of uranium into the aquatic environment. Tutu et al. [9] found uranium in open, accessible surface waters in excess of 70 mg/L in certain instances. In general, the concentration of sulfate and other contaminants in the water is highly variable as a consequence of ore body heterogeneity. Thus, depending on the characteristics of the mine, the drainage generally has a low pH, high salinity and high concentrations of heavy metals. It should be noted that mine drainage can also be neutral or alkaline depending on the pH and that these waters may also have significant environmental impacts. They are not considered further here.

There are four well-known equations that describe the formation of AMD and they are expressed in terms of pyrite, as it is the most common sulfide mineral mined. For other sulfide-containing minerals the stoichiometry and reaction rates differ slightly. The generation of AMD begins through the oxidation of pyrite to ferrous iron and sulfate [equation (12.5)]. Through the action of iron-oxidizing bacteria, ferrous iron is oxidized to ferric iron [equation (12.6)]. This oxidation can also occur when Fe<sup>2+</sup> travels to surface waters such as rivers and dams, where the pH is relatively higher i.e. pH > 5 [1]. Ferric iron then spontaneously reacts with water to form ferric hydroxide [equation (12.7)] and this is the orange-red precipitate seen in AMD, also known as yellow boy. Excess Fe<sup>3+</sup> acts as an additional and secondary reducing agent for pyrite [equation (12.8)]. Equations (12.5), (12.7) and (12.8) release a substantial amount of acidity into the water, which characterizes AMD as acidic. The overall process results in sulfuric acid and ferric hydroxide being produced [equation (12.9)].

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (12.5)

$$Fe^{2+1}/_4O_2 + H^+ \rightarrow Fe^{3+} + 1/_2H_2O$$
 (12.6)

$$Fe^{3+} + 3 H_2O \rightarrow Fe(OH)_3 + 3 H^+$$
 (12.7)

$$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^+$$
 (12.8)

$$FeS_2 + 3.75 O_2 + 3.5 H_2O \leftrightarrow Fe(OH)_3 + 2 SO_4^{2-} + 4 H^+$$
 (12.9)

(Iron sulfide + Oxygen + Water ↔ Ferric hydroxide + aqueous sulfuric acid)

The initial oxidation step of other common sulfide minerals such as arsenopyrite [equation (12.10)], chalcopyrite [equation (12.11)] and sphalerite [equation (12.12)] are shown below:

$$4\text{FeAsS} + 13\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}_2\text{AsO}_4^{-} + 4\text{H}^+$$
 (12.10)

$$2\text{CuFeS}_2 + 4\text{O}_2 \rightarrow 2\text{Cu}^{2+} + \text{Fe}^{2+} + \text{SO}_4^{2-}$$
 (12.11)

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$
 (12.12)

#### Sources of AMD 12.2

AMD is produced within and around mining areas. These typically include abandoned and active mines, both of which can be open-pit or underground [5, 10]. Secondary sources of AMD include

Mineral	Chemical formula
Arsenopyrite	FeS <sub>2</sub> .FeAs
Bornite	$\mathrm{CuFeS}_4$
Chalcocite	Cu <sub>2</sub> S
Chalcopyrite	CuFeS
Covellite	CuS
Galena	PbS
Gold sulfide	$Au_2S$
Millerite	NiS
Mobybdenite	$MoS_2$
Pyrite	$FeS_2$
Pyrrhhdite	$Fe_{11}S_{12}$
Sphalerite	ZnS

Table 12.1 Mineral sources of sulfide which can contribute to acidic mine water

mine waste dumps, ore stockpiles, tailings dumps, tailings dams, haul roads, quarries and sludge ponds [6, 10, 11]. The nature of AMD from these secondary sources may be more aggressive than the drainage water due to factors such as particle size, surface area, amorphosity, homogeneity and disaggregation [12].

Any sulfide-containing mineral is classified as a potential source of AMD [4, 11]. Generally speaking, the most common metal sulfide associated with AMD is pyrite. Metal concentrations, however vary according to the characteristics of the mine and thus other metals may be more significant [1]. Particularly for South Africa where the coal and gold mining industries are extensive, pyrite especially contributes massively to the formation of AMD. A list of other sulfide based minerals, all of which could potentially contribute to AMD is presented in Table 12.1.

# 12.3 Environmental and Social Impacts of AMD

# 12.3.1 Environmental Impacts

There has been increased public awareness on the environmental hazards associated with AMD. AMD is globally considered to be one of the most hazardous forms of water pollution and has significant environmental impact [4, 11]. The Environmental Protection Agency (EPA) considers it to be "second only to global warming and ozone depletion" in terms of ecological risk.

The impacts of AMD on the environment and ecosystems have been widely reported [13–16]. It is a multifactor pollutant that affects the environment chemically, biologically, ecologically and physically (Figure 12.1). The toxicity of metals, high sulfate concentrations (and consequent high salinity), total dissolved solids, low pH and high acidity of AMD all play a role in negatively impacting the environment as well as life. Owing to this multifarious nature of AMD, food chains and ecosystems collapse at much higher rates than if it were a single pollutant. The ultimate result is the irreversible destruction of habitats and the death of organisms in both terrestrial and aquatic habitats [11].

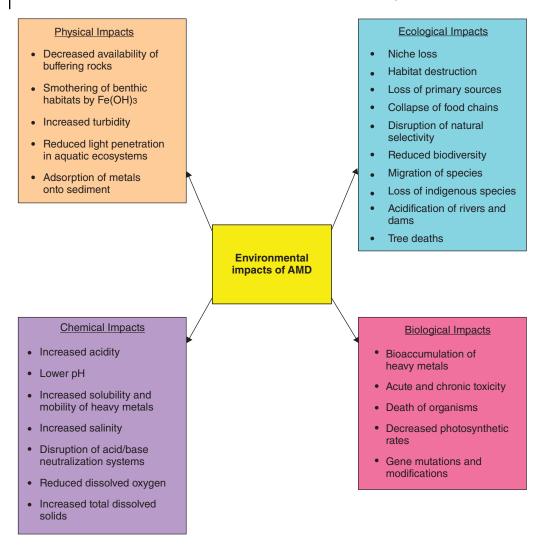


Figure 12.1 The physical, chemical, biological and ecological impacts of AMD.

Among the negative environmental impacts presented in Figure 12.1, the most significant and visible impact of AMD is the smothering of metal precipitates on the water surface. This poses significant impacts to water habitats in that it reduces the penetration of sunlight, creates turbidity and lessens the diffusion of oxygen. This makes it difficult for photosynthetic organisms to thrive and can lead to the loss of autotrophic sources, thereby disrupting food chains. In benthic habitats soil is smothered with precipitates and heavy metals adsorb onto the sediment. All of these limits vegetation speciation and reduces biodiversity.

Acid/base neutralizing processes also become disturbed as buffering sources such as carbonate rocks become less available owing to their excessive neutralization of AMD. In particular bicarbonate

and carbonate sources get broken down to carbon dioxide and water as a result of the low pH. This also affects photosynthesis as many plants use bicarbonate as an inorganic carbon source [17]. The heavy metals in AMD can also have disastrous effects on organisms. Depending on the concentration and toxicity of the metal, organisms may bioaccumulate the metal [18], which can cause acute and chronic toxicity or at the worst, sudden death can occur.

# 12.3.2 Social Impacts of AMD

AMD is discharged or leached into dams and rivers, which can further contaminate public water systems. Communities residing in the vicinity of sulfidic ore mines are most affected and threatened by AMD. AMD contaminated water cannot be utilized for potable or domestic purposes as it does not meet the required water quality standards [7]. AMD thus poses a significant threat to humans, not only in terms of toxicity but also in terms of water supply. In developing countries, it is estimated that billions of people will face water scarcity by the year 2050 [19] and if AMD is not controlled or treated, this risk will be exacerbated.

Economically, AMD also has significant impacts. Owing to the acidic nature of AMD, it is highly corrosive and can corrode most iron-based structures [20]. In functional mines AMD-contaminated water cannot be re-used as it increases the level of toxicity in a mine, which can lead to disastrous effects. As such the operating costs of pumping and using potable water are high. AMD also limits the use of downstream waterways, affecting industries such as fishing, agriculture, irrigation and recreation [7]. In addition, Johannesburg, the economic hub of Africa is the site of an estimated AMD discharge which will exceed 250 mega liters per day, which has to be treated. This costs the South African fiscus in excess of US50 million per year, just for pH neutralization using lime. It is estimated that this cost will increase to treat the AMD to legislative limits [21]. Thus, effective, cheap remedial techniques are required to prevent the economic benefits from mining being eroded through protracted clean-up.

# 12.4 Remediation of AMD

There are various physical, chemical and biological mechanisms by which AMD can be treated. These are summarized in Table 12.2. They are categorized as physical, chemical or biological. All three of these mechanisms can be employed individually or in combination in both active or passive systems.

Physical	Chemical	Biological
Adsorption	pH control	Dissimilatory sulfate reduction
Absorption	Complexation	Action of oxidizing bacteria
Sedimentation	Oxidation/reduction	
Flocculation	Chelation	
Crystallization	Electrochemical	
Filtration Nanofiltration	Ion exchange Precipitation	

Table 12.2 Physical, chemical and biological mechanisms of AMD treatment (modified from [20])

AMD remediation is generally classified as active or passive. Active systems are highly effective and can treat the AMD to almost any desired purity. Active processes include using alkali precipitation, reverse osmosis, ion exchange and active bioremediation (typically within reactors). Most active processes have a fairly small surface footprint, but are instead complex, costly, require continuous chemical feed and rely on well trained technical personnel to operate and maintain. In addition, as the purity of the treated AMD is increased, the level of technology required increases exponentially.

Whilst highly technical solutions might well be applicable in many locations, especially in the developed world or at active mine sites, following closure of a mine site the feasibility of an active processes diminishes rapidly as skilled personnel move elsewhere. In the developing world, in particular, there may be no skilled technical expertise anywhere following closure of the mine, and thus if ongoing treatment is required, it is generally preferable to utilize passive treatment techniques. Constructed wetlands (CWs) are obvious passive remediation technologies.

#### 12.4.1 **Constructed Wetlands**

CWs were first described and documented in the early 1960s where the quality of wastewater was improved through the use of natural sphagnum moss wetlands [22, 23] and this eventually stimulated the idea of wetlands being used to neutralize AMD [24]. Considerable research expanded on this idea and after five decades, CWs have now been globally implemented at many mine sites for the treatment of AMD [25].

# 12.4.1.1 Constructed Wetland Configuration Types

CWs are classified in terms of hydrology, although some sources do classify them according to macrophyte type [26]. In terms of hydrology there are two types of CWs:

- 1) Surface flow wetlands
- 2) Sub-surface flow wetlands which include:
  - Horizontal sub-surface flow
  - Vertical sub-surface flow.

Since AMD characteristics and CW designs and configurations are highly variable, the use of CWs for treating AMD is presented chronologically from the 1990s to the present. The use of CWs for treating AMD prior to 1990 is excluded from this analysis as it can be found elsewhere in literature. Also, the work described here is not necessarily exhaustive, and there may be documented use of CWs for treating AMD which are not discussed here. In general, however, the mechanisms described will be similar.

# 12.4.1.2 Mechanism by which CWs Remediate Most AMD/ARD

There are three main components to AMD: acidity (and pH), sulfate, and (heavy) metals. Sulfate is primarily removed through the process of dissimilatory sulfate reduction, which occurs in the anaerobic regions of the CW. In the anaerobic zone, a hydrocarbon, together with the sulfate are reacted with a resultant sulfide and carbonate [27–29]. The reaction is shown as Equation (12.13):

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^{-}$$
 (12.13)

In this reaction CH<sub>2</sub>O represents organic matter. Thus, the pH starts to increase as alkalinity is generated. The CW may also contain a source of alkalinity, such as being constructed from dolomite,

which may also increase the pH. The rise in pH is due to the consumption of protons within the system. This can be due to a reaction that consumes protons (such as oxidation). Indeed, if the initial pH is especially low, fermentations that produce weak acids are also able to increase the pH. As the pH increases, many of the metals in solution precipitate, provided the pH does not increase too far (in which case some may solubilize again).

The solubility of most metals and the chemistry of their precipitates at different pH values are shown in their unique Pourbaix diagrams, which are freely available in literature. For example, iron has a very well described Pourbaix diagram, which clearly shows how by pH 7 that most forms of iron are insoluble. Thus, heavy and other metals tend to precipitate. In the presence of  $H_2S$  and free alkalinity, the soluble metals are also able to precipitate as metal sulfides, which are insoluble. In this instance, the cycle will be complete, and the cause of the AMD, which is typically a sulfide mineral, will be present again. Provided it remains within an anaerobic environment, it will remain in this stable, benign form. The formula for this reaction is given by equation (12.14) [27].

$$M^{2+} + H_2S + 2CH_2O \rightarrow MS + 2H_2O + 2CO_2$$
 (12.14)

Whilst this description is accurate on a macro-scale, there is still very little known about what happens at the micro-scale level, and more specifically about the interaction between the roots, the microbes within the roots and the CW matrix, and the AMD. Notwithstanding this, CWs have been successfully used for treating AMD for more than 30 years. In the next section, the performance of these wetlands is discussed. The section will be presented chronologically, since the lessons learned at some sites were incorporated in later systems.

## 12.4.1.3 Constructed Wetlands for Treating AMD Prior to 2000

Prior to 2000, a number of CWs were constructed for the treatment of AMD, and those described here were constructed primarily in North America and the UK. In the UK, a pilot-scale CW was designed and constructed for the Wheal Jane Mine in Cornwall [27]. Wheal Jane was formally abandoned in 1991, and in 1992, an adit plug failed, causing a large-scale release of AMD. Passive systems were considered appropriate and the final system included an aerobic reed bed, primarily designed for iron and arsenic removal. Hamilton et al. [27] describe their results on a pilot-scale system, with flow rates of between 0.1 and 0.6 L/s. These aerobic reed beds were successful in removing iron; however during ferric iron hydrolysis, acidity was generated, and this caused a decrease in the pH, despite the purpose of wetlands being to neutralize pH and remove iron.

Machemer et al. [29] described the design and optimization of the wetland constructed at the Big Five Tunnel, in Idaho Springs, Colorado. The CW consisted of five cells, some of which were vegetated, some not. Significant quantities of organic matter such as mushroom compost and animal manure were placed on the cells. The system overall was able to raise the pH from 3 to 6, and effectively removed iron, nickel and nitrate. It was, however, not successful at removing much more than 15% of the sulfate.

Mitsch and Wise [30] describe the use of a 0.39 ha CW for the treatment of AMD in a stream in South Eastern Ohio, USA. The CW was constructed as a 9-cell system, with plants grown in organic matrices such as mushroom compost and manure. There was a combination of surface and subsurface flow systems described. This system had little effect on acidity or pH, although 80% of the iron was removed, and 33% of the aluminium was removed. They also found very little sulfate reduction within the CW. An important finding was that plants have little to do with the retention of metals, despite the fact that they have elevated levels of metals within their tissues. Groudeva and

Groudev [31] conducted research on remediating AMD from a uranium mine using a passive system which included an aerobic wetland. Their AMD feed had a pH of 3.2, sulfate approaching 1.9 g/L, 700 g/L of iron, 44 g/L of copper, uranium and radium with a combined  $\beta$ -radioactivity of 3.85B q/L. The aerobic CW portion of this passive system removed 28% of the sulfate, 40% of the iron, 20% of the copper, 60% of the zinc and almost 40% of the radioactivity.

The predominant trends in this period before 2000, were thus towards mimicking natural wetland systems which were known to remediate AMD somewhat and to apply "ecological engineering approaches to decommissioning" [32]. The fundamental mechanisms of remediation were known, and if sulfate reduction was required a carbon source was added to the CW.

# 12.4.1.4 Constructed Wetlands for Treating AMD Between 2001 and 2010

The literature gathered for this period can be broadly divided into two categories:

- 1) Papers describing the performance of constructed wetlands and exploring the mechanism of remediation in greater detail; and
- 2) Reflexive papers considering the limitations of existing CWs treating AMD.

A selection of these findings is discussed here.

## 12.4.1.4.1 Descriptive Papers

There was considerable effort towards understanding the microbial processes occurring within CWs during this period. Kosolapov et al. [33] describe the contribution of microbial processes to removing metals in carbon-deficient effluents being treated by CWs. They discuss the role of biosorption, specifically that it is a mechanism by which metals are able to be removed; however that unless the biomass is removed, the effect is short-term due to the short life-cycle of microorganisms. They describe the main process being through precipitation as a metal sulfide and further discuss the role of reduction or oxidation of different metals into insoluble states.

Reduction is an important mechanism for some priority metals such as U(VI), Cr(VI) and others, which can be reduced to a valencies of IV or III. This mechanism is in some instances very important, since trivalent chromium is much less toxic than hexavalent chromium, and U(IV) is much less mobile. The removal of Fe(II) in contrast was described as being removed through abiotic processes through the oxidation of Fe(II) to Fe(III) which reacts with water to form a hydroxide which is insoluble. In this work, they also discuss that CWs cause biological methylation of certain metals such as mercury. This is an anaerobic process and occurs naturally within CWs. In certain locations, such as Johannesburg, there is considerable mercury contamination of the environment due to informal gold mining [34] and this must be considered as part of the design of any system.

Nelson et al. [35] discussed the removal of metals by CW systems treating metal rich water in North Carolina, and specifically in this case they had elevated levels of mercury, copper, zinc and lead. Whilst at this site, the water being treated was not AMD, and was therefore not acidic; it was able to remove more than 80% of copper and mercury, and they noted that the systems were shallow and primarily aerobic, which explains the high removal of mercury (rather than methylation). Manganese, as described by Hallberg and Johnson [7], is also difficult to remove within a wetland system. It is difficult to oxidize Mn(II) to Mn(IV) which is the insoluble form. This typically requires pH > 8 and does not typically form an insoluble sulfide. Thus, CWs may be less useful as a treatment technology if Mn removal is a priority.

Nyquist and Gregor [36] discuss a CW used to treat Kristineberg Mine tailings at very high latitude. In their study system, AMD entered into the CW with a pH of 2.65 and the CW was found to have almost no impact on the AMD, except for approximately 30% removal of the copper. The pH was unchanged as were most other metals including iron. Unfortunately, there is no satisfactory reason in this paper as to why this wetland failed; however the residence time according to the authors would range from 60 to 120 hours and it is may be that this is insufficient for treating AMD, especially within a cold climate environment. Notwithstanding these limitations, CWs are effective sinks for many metal species.

During this period, considerable attention was paid to the microbiology of sulfate reduction within CWs. Hallberg and Johnson [37] continued research on the Wheal Jane CW with a microbiological study on the CW ecosystem. They found acidophilic iron oxidizing bacteria, and over the course of their study, heterotrophic acidophiles emerged as the dominant group of bacteria, sometimes accounting for as much as 25% of the total enumerable microbial population. Riefler et al. [38] reported that in the CW that they were studying, in Ohio, USA, they found that the sludge within their system contained more than  $6 \times 10^6$  sulfate-reducing bacteria cells (SRBs) per gram of sludge. The system was also effective at removing iron and aluminium.

Kuschk et al. [39] conducted field research to assess the effectiveness of CWs treating the acidity within AMD. They compared subsurface flow, surface flow and hydroponic systems with unplanted systems. Their findings showed that the planted surface flow appeared most effective, removing 80% of acidity, and increasing the pH from 3.3 to greater than 4.5. Using the same experimental apparatus, Wiessner et al. [40] assessed the effectiveness of the different CWs to remove iron and zinc. They found that a maximum of 97% of the iron and 77% of the zinc was removed, but that rainfall events remobilized some of the metals accumulated within the systems.

Koschorreck [41] prepared a mini-review of microbial sulfate reduction at low pH, typically the conditions to be found within CWs treating AMD. It was established that DSR can occur at pH < 5 and that the inhibitory effects on this process included  $H_2S$  and certain organic acids. Metal sulfide precipitation was also noted to have an inhibitory effect, especially if in competition with iron-reducing bacteria. He concludes that there is not always a reasonable explanation for why sulfate reduction does not occur in low pH environments, especially one like that described by Nyquist and Gregor [36].

#### 12.4.1.4.2 Reflexive Papers

Following the emergence of CWs as a treatment technology thought to be suitable for post-mining AMD treatment (as a result of their low maintenance requirements) in the 1980s and 1990s, by the next decade there were a number of researchers who reflected on the efficacy of CWs as a remediation technology. Hallberg and Johnson [42], following much research on the Wheal Jane wetland, noted the following limitations with the use of CWs for treating AMD.

- Passive AMD remediation techniques allow for very little system control and are subject to seasonal and other variabilities (such as rainfall).
- There were insufficient data for accurate assessment of sizing and performance of CWs, and this is a problem which is still relevant today [43].
- CWs are sometimes ineffective when used in isolation.
- CWs sometimes fail catastrophically.
- The role of the macrophytes (at that time) was not fully resolved.
- Manganese removal was not always effective.

Further, they importantly conclude that the biogeochemistry and microbiology of the systems is highly complex and that there is limited understanding of these processes.

Wiseman and Edwards [44] considered the use of CWs for treating coalmine AMD in Wales in the 1990s. The systems they monitored were effectively able to remove in excess of 80% of the iron in the feed; however, the authors are clear to note that the system required maintenance, which must be costed for in the design phase. Whitehead and Neal [45] briefly discuss the long-term conclusions arising from the Wheal Jane wetland. They point out that the sludges which accumulate within the CW are toxic and hazardous; thus care needs to be taken during maintenance or refurbishment of any CW treating AMD for disposal of wastes. In environments where AMD is enriched in uranium, this problem is further amplified as a host of international regulations considering the handling and transport of radioactive substances would need to be considered.

#### 12.4.1.5 Constructed Wetlands for Treating AMD from 2010 to the Present

In this period, the reporting of CWs treating AMD became global with the technologies having spread to Asia, Australia, Africa and the rest of Europe. De Matos and Zhang [46] report on the use of CWs for treating AMD to allow final discharge to natural ecosystems. The study was located in Spain and described two systems — a horizontal flow compost wetland followed by an anoxic limestone drain and a second system comprising a layered vertical flow system (with free water, organic material and limestone) followed by a series of aerobic wetlands. These systems treated different AMD streams, the first being designed for a more acidic AMD. In the first system, the pH was increased from 4 to 6.8; 90% of iron was removed but only 30% on manganese was removed. The second system removed 71% of iron, 80% of the aluminium present and 60% of the manganese.

Gikas et al. [47] considered the use of CWs for removing trace quantities of heavy metals. Using horizontal sub-surface flow CWs, with an artificially prepared feed of 2 mg/L of Cr, Pb and Fe, they obtained removals of greater than 87% for all three metals of concern. Guittonny-Philippe et al. [48] considered the use of CWs in removing pollution from industrial catchments. Specifically, the authors discuss the role of plants within CWs reporting a number of papers with conflicting results in this regard.

Sheridan et al. [21] reported on the use of a CW utilizing a charcoal matrix and one using a basic oxygen furnace slag matrix for treating AMD. In their study, they used two artificial AMD solutions both containing 6000 ppm of sulfate, 2000 ppm of iron and one with a pH of 4 and the with a pH of 4 and another with a pH of 1.35. Both the charcoal and the BOF CWs removed more than 75% of the sulfate and almost all iron. The pH was increased significantly in all cases. The authors point out that the mechanism of remediation, especially in the charcoal system was unknown.

Ji et al. [49] describe the use of a passive mine water treatment system which included a CW for treating AMD from the Ho-Nam Coal mine in Korea. Their findings show that the system was effective overall, but did not perform as designed or expected. Iron was removed prior to entering the CW. Other metals that were removed include aluminium, manganese, calcium and magnesium. Specifically, approximately 60% of the Mn was removed. This result is likely due to this CW being aerobic.

Panda et al. [50] prepared a mini-review on the bioremediation of acidic mine effluents with a specific focus on the role of the sulfidogenic microorganisms. They report that over 30 different bacteria (or strains thereof) and more than 25 archaea have been identified within AMD ecosystems, including CWs. The importance of understanding the microbiology and microbial ecosystems is explicitly described since the microbes (bacteria and archaea) are responsible for a large percentage of the removal of sulfate.

#### 12.5 Summary

It is tempting for consultants, consulting engineers, legislators and mines to use CWs as remediation technologies for AMD treatment or mine closure remediation. This is primarily due to the CWs looking pretty and natural (which is vastly different to most active mine sites); a lack of long-term costs (critically important given the longevity of most AMD sources) and the lack of continued ability to treat the AMD (often the mine has closed and only the legacy remains). The past 30 years of research quite clearly shows that it is still very difficult to design a CW to effect a specified remediation. There are rough rules of thumb which can be applied for design purposes. However the use of these rules of thumb in no way guarantees success. Even worse, the construction of a pilot-scale CW also does not guarantee success.

The heterogeneous nature of AMD also makes it very difficult to understand how a CW would react given a specific feed. It is much simpler to design CWs for urban/domestic effluent since the chemical constituents leaving any given wastewater treatment facility do not vary significantly. AMD, on the other hand, is as unique as the geochemical fingerprint associated with the ore body. Whilst most AMD contains iron and sulfate, the pH, the concentrations, the ratio of the concentrations and the presence of any other constituents will be vastly different. The synergistic and antagonistic effects of this chemical melange are not possible to predict, and thus research at each given site is required. Furthermore, to design a CW for treating AMD requires that the designer has an in-depth understanding of inorganic, redox and aquatic chemistry. As shown, some metals require oxidation to be immobilized, others require reduction, and these redox reactions may require very different pH values to occur. Thus, for adequate design, a CW may need a low pH zone, a high pH zone, an aerobic zone and an oxidative zone. Failure to understand the intersection of chemistry, redox and pH could take a dangerous AMD and cause extreme environmental toxicity and consequent damage (as in the case of the transformation of mercury to methylated mercury).

However, if careful analysis of the AMD is conducted, if the consulting engineers are able to communicate effectively in collaborative teams with geologists, microbiologists and chemists to understand the interplay between the system, the biogeochemistry and the microbiology, it is possible to design CWs for treating almost any AMD effectively to a specified limit.

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