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Acid mine drainage: Challenges and opportunities

Geoffrey S. Simate *, Sehliselo Ndlovu

School of Chemical and Metallurgical Engineering, University of the Witwatersrand, P/Bag 3, Wits 2050, Johannesburg, South Africa

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ABSTRACT

Acid mine drainage (AMD) or acid rock drainage (ARD) is considered as one of the main pollutants of water in many countries that have historic or current mining activities. Its generation, release, mobility, and attenuation involves complex processes governed by a combination of physical, chemical, and biological factors. In general, AMD is produced by the oxidative dissolution of sulphide minerals. This paper reviews the current state-of-the-art of AMD. It critically analyses the work performed in recent years on its occurrence, effects (on human health, plant life and aquatic species), and summarizes the remediation approaches taken so far to overcome the problem of AMD. The challenges faced in tackling the remediation of AMD have also been considered. Commercially developed projects that are either in operation, being piloted or under evaluation have also been discussed. Finally, the paper speculates on future directions or opportunities that deserve exploration.

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* Corresponding author. Tel.: +27 11 717 7570/76 112 6959; fax: +27 11 717 7599.
E-mail addresses: simateg@yahoo.com, simateg@gmail.com (G.S. Simate).

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Introduction

The problem of sulphide oxidation and the associated acid mine drainage (AMD) or acid rock drainage (ARD) has been a major focus of research over the last 50 years [1]. The term AMD is commonly used (than ARD) because the process occurs mainly at mining sites. It occurs in both operating and abandoned polymetallic sulphide mining sites [2,3] – in tunnels, mine workings, open pits, waste rock piles, and mill tailings [2–4]. Although the chemistry of AMD generation is straightforward, the final product is a function of the geology of the mining region, presence of microorganisms, temperature and also of the availability of water and oxygen [5]. These factors are highly variable from one region to another, and, for this reason, the prediction, prevention, containment and treatment of AMD must be considered carefully and with great specificity [5]. The causes of AMD are not only limited to the mining industry, but can also occur where sulphide materials are exposed, e.g. in highway and tunnel construction and other deep excavations [6–8]. In other words, any activity that disturbs mineralized materials can lead to AMD. The AMD is a strong acidic wastewater rich in high concentrations of dissolved ferrous and non-ferrous metal sulphates, and salts [9,10] and if AMD is left untreated, it can contaminate ground and surface watercourses, damaging the health of plants, humans, wildlife, and aquatic species [10,11]. Consequently, the development of cost-effective and sustainable remediation solutions for the AMD problem has been the subject of extensive research [12]. However, despite AMD being pinpointed as a looming problem as early as the 1970s, the simple cleaning processes available and the many parties with powerful incentives to act, such as government to non-governmental organizations to mining companies, no single party has produced the required combination of scale, resources and credibility to deal with the problem.

This paper reviews the current state-of-the-art of AMD. It describes the work performed in recent years on its occurrence, effects, and summarizes the control and remediation approaches taken so far to overcome the problem of AMD, the challenges faced and speculates on future directions or opportunities that deserve exploration. Accordingly, the paper is organized as follows: a background of the occurrence of AMD is presented first, followed by its effects on human health, plant life, and aquatic species. The paper then discusses some of the control and remediation strategies followed by a discussion of industrially useful materials generated from AMD. Commercially developed projects that are either in operation, being piloted or under evaluation have also been discussed. Finally, the paper explores the prospective future opportunities that may be available for treating AMD by integration of various conventional and non-conventional processes.

Occurrence of acid mine drainage

General overview

The main cause of AMD is the oxidation of sulphide minerals (Table 1) such as pyrite (FeS_2) as a result of exposure of these minerals to both oxygen and water [2,13], and microorganisms [14]. Although this process occurs naturally, mining activities accelerate the process of AMD generation because such activities increase the exposure of sulphide minerals to air, water, and microorganisms [15]. Thus, AMD is prominent in both operating and inactive or abandoned mining sites – in underground tunnels and shafts, open pits, waste rock piles, and mill tailings [4]. Though AMD is less important when the mine is in active production because the water tables are kept low by pumping, it is severe in closed and abandoned mines where pumps are turned off resulting in the rebound of water tables [2].

The process of AMD generation is extremely complex since it involves chemical, biological, and electrochemical reactions which vary with environmental conditions [8]. To start with, sulphide minerals in ore deposits are formed under reducing conditions in

Table 1
Some important metal sulphides with pyrite and marcasite being the predominant acid producers [7].

Metal sulphide	Chemical formula
Pyrite	FeS_2
Marcasite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Chalcocite	Cu_2S
Covelite	CuS
Chalcopyrite	$CuFeS_2$
Molybdenite	MoS_2
Millerite	NiS
Galena	PbS
Sphalerite	ZnS
Arsenopyrite	$FeAsS$

the absence of oxygen [16]. When exposed to atmospheric oxygen or oxygenated waters due to mining, mineral processing, excavation, or other earthmoving processes, sulphide minerals can become unstable and oxidize [16].

Usually the process of AMD production is well illustrated by considering the reactions during the oxidation of pyrite (FeS_2), which is one of the most common sulphide minerals [15,17,18]. As shown in Fig. 1, the oxidation of pyrite can follow several pathways [14,19,20] involving surface interactions with dissolved O_2, Fe^{3+}, and other mineral catalysts such as MnO_2 [4].

According to Akcil and Koldas [15], the first most important reaction is the oxidation of the pyrite (or sulphide) into dissolved iron, sulphate and hydrogen (Eq. (1)). However, the rate of pyrite oxidation and the resulting acid production is dependent on solid-phase compositional variables and microbial activities, as well as availability of oxygen and water [21].

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

The presence of sulphate in mine waste drainage is typically the first indicator of sulphide mineral oxidation [21]. In a sufficiently oxidizing environment (dependent on O_2 concentration, pH greater than 3.5 and bacterial activity), ferrous iron released in Eq. (1) may be oxidized to ferric iron, according to the following reaction [4,15]:

$$4Fe^{2+} + O_2 + 4H^+ \leftrightarrow 4Fe^{3+} + 2H_2O \tag{2}$$

If oxygen is low, Reaction (2) will not occur until the pH reaches 8.5 [22]. In general, under many conditions, Reaction (2) is the rate-limiting step in pyrite oxidation because the conversion of ferrous to ferric is slow at pH values below 5 under abiotic conditions [7].

At pH values between 2.3 and 3.5, ferric iron formed in Reaction (2) may precipitate as $Fe(OH)_3$ (and to a lesser degree as jarosite, $H_3OFe_3(SO_4)_2(OH)_6$), leaving little Fe^{3+} in solution while simultaneously lowering the pH [4,15].

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 \downarrow + 3H^+ \tag{3}$$

If pH is less than 2, ferric hydrolysis products like $Fe(OH)_3$ are not stable and Fe^{3+} remains in solution [1]. Nevertheless, any remaining Fe^{3+} from Eq. (2) that does not precipitate into $Fe(OH)_3$ (or jarosite) from solution through Eq. (3) may be used to oxidize additional pyrite, according to the following reaction [15]:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

As seen from Reaction (4) the oxidation of pyrite by ferric iron results in a further decrease in pH [23].

While oxygen is a primary oxidant, the ferric iron (Fe^{3+}) resulting from the oxidation of ferrous iron is now recognized as a more potent oxidant than oxygen even at circumneutral pH [8]. In fact, below pH of about 3, the oxidation of pyrite by ferric iron is about 10–100 times faster than by oxygen [1,24] thus making the oxidation of pyrite by ferric ions the dominant reaction [23]. Luther [25] attributed this observation to the more efficient electron transfer of Fe^{3+} compared to oxygen. This molecular orbital study by Luther [25] is consistent with pyrite oxidation data obtained by McKibben and Barnes [26] and Moses et al. [27].

When ferrous iron is produced (Eq. (4)) and sufficient dissolved oxygen is present the cycle of Reactions (2) and (3) is propagated until the supply of ferric iron or pyrite is exhausted [28]. However, even without dissolved oxygen, Reaction (4) will continue to completion and the water will show elevated levels of ferrous iron [28].

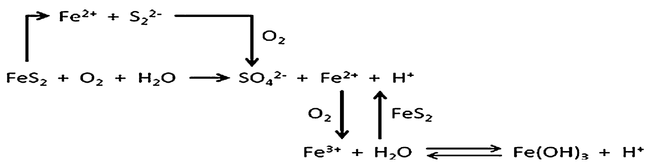

Fig. 1. Model for the oxidation of pyrite [14,19,20].

Accordingly, from the discussion above, the formation of AMD may be considered to take place in three major steps [1,29]:

(1) Oxidation of iron sulphide (Eq. (1)), and enhanced oxidation of sulphide minerals by ferric iron (Eq. (4))
(2) Oxidation of ferrous iron (Eq. (2)), and
(3) Hydrolysis and precipitation of ferric iron and other minerals (Eq. (3))

It must be noted that in naturally acidic systems, Reactions (2) and (4) can be significantly accelerated by the presence of acidophilic bacteria such as *Thiobacillus ferroxidans* [23,30]. This bacterium and several other species thought to be involved in pyrite weathering are widespread in the environment. *Thiobacillus ferroxidans* has been shown to increase iron conversion rate by a factor of hundreds to as much as a million [4,23].

Previously, the oxidation (or leaching) mechanism of sulphide bearing minerals by bacteria was thought of as comprising of two (or three) different mechanisms [31–33]. Firstly, the direct mechanism which assumes that bacteria attach onto the mineral particle surfaces, and directly oxidize iron and sulphur moieties in the mineral by biological means to release metal ions in solution (Eq. (5)). The second mechanism, the indirect mechanism, is assumed to involve the bacteria in solution oxidizing ferrous iron to ferric iron and elemental sulphur to sulphate ions (Eqs. (6) and (7), respectively). Thereafter, the generated ferric iron leaches the sulphide mineral (Eq. (8)).

$$MS_x + (2X - 0.5)O_2 + H_2O \overset{\text{bacteria}}{\rightarrow} M^{x+} + XSO_4^{2-} + 2H^+ \tag{5}$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \overset{\text{bacteria}}{\rightarrow} 2Fe^{3+} + H_2O \tag{6}$$

$$S^0 + 1.5O_2 + H_2O \overset{\text{bacteria}}{\rightarrow} SO_4^{2-} + 2H^+ \tag{7}$$

$$MS_x + Fe^{3+} \overset{\text{Chemical}}{\rightarrow} M^{x+} + XS^0 + Fe^{2+} \tag{8}$$

where *M* is a metal, and *X* is a whole number.

The third mechanism, indirect contact mechanism, assumes that the bacteria attach themselves onto the mineral particle surfaces and excrete polymers forming an exopolymeric layer [34]. The bacteria subsequently oxidize ferrous iron to ferric iron within this exopolymeric layer, and the generated ferric iron leaches the mineral within this compartment (Eqs. (6) and (8), respectively).

Currently, as shown in Fig. 2, the two postulated 'indirect' mechanisms with no evidence for a 'direct' enzymatically mediated process are termed the thiosulphate mechanism and the polysulphide mechanism [35–37]. The thiosulphate mechanism involves solely the chemical reaction of ferric iron with acid-insoluble metal sulphides (FeS_2, MoS_2 and WS_2) producing thiosulphate [37]. Thiosulphate which is unstable in acidic liquors, particularly in the presence of ferric iron, reacts further with ferric iron in a series of reactions via tetrathionate ($S_4O_6^{2-}$), disulphane-monosulphonic acid ($HSSSO_3^-$) and thionate with the final product being sulphate [38]. The polysulphide reaction mechanism involves the attack of acid soluble sulphides (ZnS, NiS, CoS, $CuFeS_2$ and PbS) by ferric iron and protons. The proton mediated dissolution forms free metal ions and hydrogen sulphide (Eq. (9)) and the hydrogen sulphide formed is microbially oxidized to sulphuric acid (Eq. (10)) [13].

$$MS_x + 2XH^+ \overset{\text{chemical}}{\rightarrow} M^{x+} + XH_2S \tag{9}$$

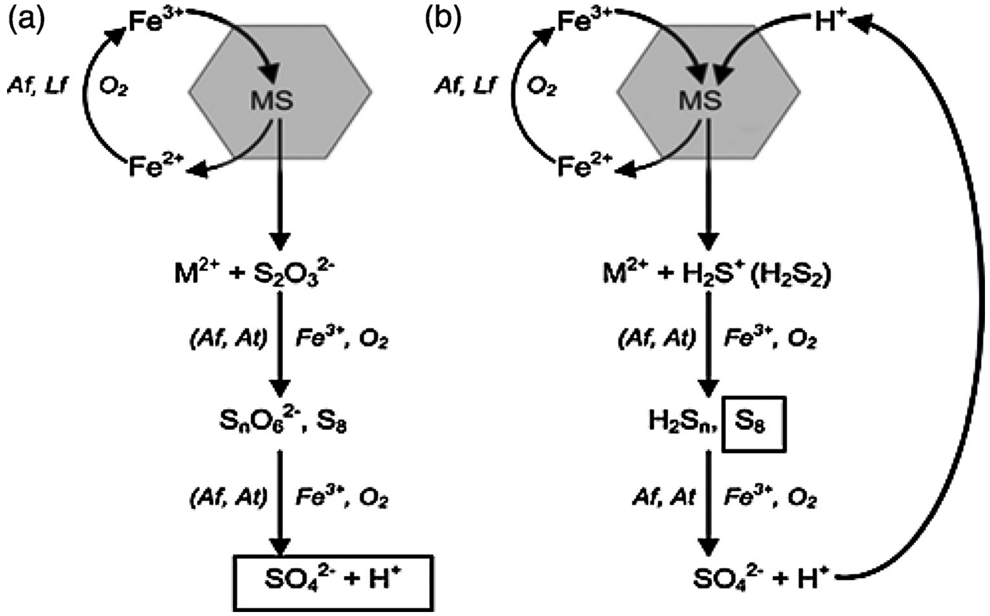

Fig. 2. Hypothetical scheme for the oxidation of pyrite or metal sulphide by iron- and sulphur-oxidizing acidophilic bacteria producing sulphuric acid [37,38].

$$H_2S + 2O_2 \overset{\text{bacteria}}{\rightarrow} H_2SO_4 \tag{10}$$

where x is a whole number.

The metal attack by ferric iron forms ferrous iron and polysulphide (Eq. (11)). Polysulphides are a general class of compounds in which sulphur is polymerized and reduced, generally of the form H_2S_x ($x > 2$) with typical value of x not being more than 6 [39]. The polysulphide is oxidized by ferric iron producing elemental sulphur (Eq. (12)). The sulphur produced is reasonably stable under experimental and environmental conditions and can only be degraded to sulphuric acid (Eq. (13)) by sulphur oxidizing microbes such as *Acidithiobacillus thiooxidans* [37]. The sulphuric acid formed enhances the dissolution of sulphide metals by proton attack [13].

$$MS_x + Fe^{3+} + 2H^+ \overset{\text{Chemical}}{\rightarrow} M^{x+} + H_2S_x + Fe^{2+} \tag{11}$$

$$H_2S_x + 2Fe^{3+} \overset{\text{Chemical}}{\rightarrow} 0.125XS_8 + 2Fe^{2+} + 2H^+ \tag{12}$$

$$0.125S_8 + 1.5O_2 + H_2O \overset{\text{bacteria}}{\rightarrow} SO_4^{2-} + 2H^+ \tag{13}$$

The role of the bacteria in both the thiosulphate and polysulphide mechanisms is to regenerate the ferric iron and protons consumed by the leach reactions [35].

While the principal sulphide mineral in mine wastes is pyrite, other sulphide minerals are also susceptible to oxidation releasing elements such as aluminium, arsenic, cadmium, cobalt, copper, mercury, nickel, lead, and zinc to the water flowing through the mine waste [4]. However, not all sulphide minerals generate acidity when being oxidized [16]. As a general rule, iron sulphides (pyrite, marcasite, pyrrhotite), sulphides with metal/sulphur molar ratios <1, and sulphosalts (e.g. enargite) generate acid when they react with oxygen and water. Sulphides with metal/sulphur molar ratios = 1 (e.g. sphalerite, galena, chalcopyrite) tend not to produce acidity when oxygen is the oxidant [16]. However, when aqueous ferric iron is the oxidant, all sulphides are capable of generating acidity. Therefore, the quantities of iron sulphide present in an ore deposit or mine waste plays a crucial role in determining the characteristics of the mine drainage [16]. It must also be noted that the oxidation rates vary amongst sulphide minerals, and it is often reported that reactivity decreases in the order marcasite → pyrrhotite → sphalerite–galena → pyrite–arsenopyrite → chalcopyrite → magnetite [1,21,40–42].

Given below are summaries of oxidation reactions of some of the sulphide minerals as given by Blowes et al. [4] and Dold [1]:

Oxidation of pyrrhotite ($Fe_{(1-x)}S$)

Pyrrhotite dissolution can proceed through oxidative or non-oxidative reactions [4]. Dissolved oxygen and Fe^{3+} can be important oxidants of pyrrhotite. When oxygen is the primary oxidant, the overall reaction may be written as

$$Fe_{(1-x)}S + \left(2 - \frac{x}{2}\right)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + 2SO_4^{2-} + 2xH^+ \tag{14}$$

The stoichiometry of pyrrhotite affects the relative production of acid [1]. At one extreme, if $x = 0$ and the formula is FeS, no H^+ will be produced in the oxidation reaction; at the other extreme, the maximum amount of acid will be produced by the iron-deficient Fe_7S_8 phase [1].

Non-oxidative dissolution of pyrrhotite occurs in acidic solutions when predominant S^{2-} surface species are exposed; and the reaction occurs as follows [4]:

$$Fe_{(1-x)}S_{(s)} + 2H^+ \rightarrow (1-x)Fe^{2+} + H_2S \tag{15}$$

Oxidation of chalcopyrite ($CuFeS_2$)

Complete oxidation of chalcopyrite without acid production may be written as [1]:

$$CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2\,SO_4^{2-} \tag{16}$$

The oxidation of chalcopyrite in the presence of ferric ions under acidic conditions can be expressed as [4],

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \tag{17}$$

Oxidation of arsenopyrite (FeAsS)

Arsenopyrite (FeAsS) may be oxidized by the following reaction path:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4SO_4^{2-} + 4H_2AsO_4^- + 4H^+ \quad (18)$$

Combined with ferrous iron oxidation and ferrihydrate precipitation, the overall arsenopyrite oxidation reaction can be written as follows:

$$2FeAsS + 5O_2 + 12H_2O \rightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 2H_2AsO_4^- + 14H^+ \quad (19)$$

If ferric iron is the oxidant, the oxidation rate of arsenopyrite is similar to the oxidation rate of pyrite [1]. If oxygen is the oxidant, the oxidation rate of arsenopyrite is lower than that of pyrite [1,43].

Oxidation of sphalerite (ZnS) and galena (PbS)

The common result of the wet oxidation of sphalerite is dissolved Zn, and sulphite, while that of galena is secondary anglesite ($PbSO_4$) in equilibrium with a Pb^{2+} and SO_4^{2-}solution according to the following equations [1]:

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-} \quad (20)$$

$$PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-} \quad (21)$$

Effects of acid mine drainage

As can be seen from the previous section, the oxidation of sulphidic minerals (such as pyrite) promotes the creation of sulphuric acid which subsequently promotes the release of a whole range of metals. As a result, AMD contains high concentrations of acid and dissolved metals. When this toxic mixture flows into groundwater, streams and rivers, it gives rise to several environmental problems. AMD is toxic to aquatic organisms, destroys ecosystems, corrodes infrastructure, and taints water in regions where freshwater is already in short supply [18,44]. This section presents and discusses the effects of AMD with respect to human health, plant life, and aquatic life.

Human health

In order for humans to be affected by the pollutants in AMD, they first need to be exposed to the pollutants. Currently, very little is known about how much risk there is of human exposure and if that exposure can cause human health. However, what is known is that many of the components and pollutants in AMD are dangerous to humans [45].

Effect of heavy metals

AMD contain a variety of dissolved heavy metals. Heavy metals, termed as elements with atomic density greater than 6 g/cm^3 [46,47] or conventionally defined as elements with metallic properties and an atomic number greater than 20 [48], have serious implications on human health due to their acute and long term toxicity [49]. In fact any toxic metal may be called heavy metal, irrespective of its atomic mass or density [50].

With regards to humans and animals, the danger of heavy metal pollutants in water lies in two aspects of their impact [47]. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. In general, the toxicity or poisoning of heavy metals results from the disruption of metabolic functions. Heavy metals disrupt the metabolic functions in two ways [50]: (1) they accumulate in vital organs and glands such as the heart, brain, kidneys, bone and liver where they disrupt their important functions, and (2) they inhibit the absorption, interfere with or displace the vital nutritional minerals from their original place, thereby, hindering their biological functions.

A summary of some of the heavy metals and their effects on human health together with permissible limits is presented in Table 2 [50–52].

Effect of low pH

There is an indirect, but devastating effect of high acidity in AMD. Drainage water from the AMD is initially clear, but turns a vivid orange colour as it becomes neutralized because of the precipitation of iron oxides and hydroxides [53]. This precipitate, often called ochre, is very fine and can deposit and imbed on the river, stream or ocean bed thus cementing substrates [22]. Thus, small animals that used to feed on the bottom of the river or stream or ocean (benthic organisms) can no longer feed and so are depleted [22]. Because these animals are at the bottom of the aquatic food chain, this has impacts higher up the food chain into fish. So, even if the acidity and heavy metals are neutralized, AMD still affects humans and wildlife a long way down stream because of these indirect effects.

Plant life

Effect of heavy metals

Contamination of soil by heavy metals is a critical environmental concern due to their potential adverse ecological effects [54]. High concentrations and/or certain mixtures of heavy metals in plant tissues can affect plant growth in different manners [46]. In general, plants experience oxidative stress upon exposure to heavy metals that leads to cellular damage and disturbance of cellular ionic homeostasis [50,54]; thus disrupting the physiology and morphology of plants [46]. Table 3 is a summary of the main effects of some of the heavy metals on plants [46,47,54].

Table 2
Heavy metals and their effects on human health together with permissible limits [50–52].

Heavy metal	Effect	Permissible level (mg/L)
Arsenic	Bronchitis, dermatitis, poisoning	0.02
Cadmium	Renal dysfunction, lung disease, lung cancer, bone defects, increased blood pressure, kidney damage, bronchitis, bone marrow cancer, gastrointestinal disorder	0.06
Lead	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness, liver, kidney, and gastrointestinal damage, acute or chronic damage to the nervous system, epilepticus	0.10
Manganese	Inhalation or contact causes damage to nervous central system	0.26
Mercury	Damage to the nervous system, protoplasm poisoning, spontaneous abortion, minor physiological changes, tremors, gingivitis, acrodynia characterized by pink hands and feet	0.01
Zinc	Damage to nervous membrane	15.0
Chromium	Damage to the nervous system, fatigue, irritability	0.05
Copper	Anaemia, liver and kidney damage, stomach and intestinal irritation	0.10

Table 3
Main effects of heavy metals on plants [46,47,54].

Heavy metal	Effects
Cadmium	Decreases seed germination, lipid content, and plant growth; induces phytochelatins production
Lead	Reduces chlorophyll production and plant growth; increases superoxide dismutase
Nickel	Reduces seed germination, dry mass accumulation, protein production, chlorophylls and enzymes; increases free amino acids
Mercury	Decreases photosynthetic activity, water uptake and antioxidant enzymes; accumulates phenol and proline
Zinc	Reduces Ni toxicity and seed germination; increases plant growth and ATP/chlorophyll ratio
Chromium	Decreases enzyme activity and plant growth; produces membrane damage, chlorosis and root damage
Copper	Inhibits photosynthesis, plant growth and reproductive process; decreases thylakoid surface area

Effect of low pH

Plants need a proper balance of macro and micronutrients in the soil and thus the soil pH has an important influence on the availability of nutrients and on the growth of different kinds of plants [55]. For example, when the soil pH is low; nitrogen, phosphorus and potassium are tied up in the soil and not available to plants. Calcium and magnesium, which are essential plant nutrients, may be absent or deficient in low pH soils. At low pH, toxic elements such as aluminium, iron and manganese are also released from soil particles, thus increasing their toxicity [55,56]. Furthermore, if soil pH is low, the activity of soil organisms that break down organic matter is reduced. Proper soil pH increases microorganism activity which produces improved soil tilth, aeration and drainage. This is turn allows for better use of nutrients, increased root development, and drought tolerance [55].

Aquatic life

Effect of heavy metals

Aquatic organisms, such as fish, accumulate heavy metals directly from contaminated water and indirectly via the food chain [57]. Since heavy metals are highly persistent, and toxic even in trace amounts, they can potentially induce severe oxidative stress in aquatic organisms [58]. Cadmium, copper, lead, and zinc are metals of particular concern because of their severe toxicity to aquatic life. Acute exposure (short-term, high concentration) of these metals can kill organisms directly, whereas chronic exposure (long-term, low concentration) can result in either mortality or non-lethal effects such as stunted growth, reduced reproduction, deformities, or lesions [59]. Table 4 shows the levels of metals recommended for the protection of aquatic life [51].

Effect of low pH

The pH of waters is important to aquatic life because it affects the normal physiological functions of aquatic organisms, including the exchange of ions with the water and respiration [60]. Such important physiological processes operate normally in most aquatic biota under a relatively wide pH range (e.g. 6–9 pH). In fact most of the freshwater lakes, streams, and ponds have a natural pH in the range of 6–8 [61]. When the ambient pH exceeds the range physiologically tolerated by aquatic organisms it can result in numerous sub-lethal effects (e.g. diminished growth rates) and even mortality [60]. Table 5 is a summary of the effects of pH on aquatic life [62]. As can be seen from Table 5, there is no definitive pH range within which all freshwater aquatic life is unharmed and outside which adverse impacts occur [60]. Rather, there is a gradual “deterioration” in acceptability as pH values become further removed from the normal range [60]; particularly when the pH of most aquatic systems falls below 6 and especially below 5 [61].

Table 4
Aquatic life protection standards [51].

Heavy metal	Permissible level (ppb)
Aluminium	5 if pH < 6.5, 100 if pH > 6.5
Arsenic	5 (FW), 12.5 (SW)
Cadmium	0.017 (FW), 0.12 (SW)
Lead	1–7 Depending on water hardness
Nickel	25–150 Depending on water hardness
Manganese	None
Mercury	0.1
Zinc	30 FW
Chromium	Cr^{6+}: 1 (FW), 1.5 (SW); Cr^{3+}: 8.9 (FW), 56 (SW)
Copper	2–4 Depending on water hardness
Selenium	1

FW: freshwater; SW: saltwater.

As the pH approaches 5, non-desirable species of plankton and mosses may begin to invade, and populations of fish such as smallmouth bass disappear; below a pH of 5, fish populations begin to disappear, the bottom is covered with undecayed material, and mosses may dominate near shore areas. Below a pH of 4.5, the water is essentially devoid of fish [61]. However, some aquatic organisms (e.g. certain species of algae) have been found to live at pH 2 and lower; and others at pH 10 and higher [60,61]. Nevertheless, there are few such organisms, and their extreme tolerances are not reflective of the pH tolerated by the majority of organisms occurring in a given aquatic ecosystem [60,61]. In summary, pH of 5–9 is the safe range for freshwater fish and for maximum productivity, the pH should be maintained between 6.5 and 8.5 [60].

Control and treatment of acid mine drainage

As environmental effects regarding AMD became more visible over the years, a lot of research has been dedicated to the development of remediation techniques – source control and migration control [2]. Source control techniques are directed towards controlling the formation of AMD at source [12,63]. They are based on the removal of oxygen and/or water from the system [2,7,64]. As shown by Reactions (1) and (4), oxygen and water are two of the three principal reactants [7]. For example removing water before it contacts pyritic material by pumping may be done to minimize the formation of acidic products. Alternatively, the control and prevention methods which aim to eliminate sulphide oxidation can be achieved by separating sulphide minerals from the waste [64]. Table 6 shows various source control techniques that have been evaluated to prevent or minimize the generation of AMD [2,64]. Despite several years of research, attempts to prevent AMD generation have proven to be practically extremely difficult [65]. Therefore, due to practical difficulties involved in preventing the formation of AMD at sources, migration controls have been the major counteracting measures for AMD [2,66].

Migration control techniques are directed towards treatment of the resulting drainage [12,63]. These techniques can be divided into two broad categories – active and passive treatments [2]. However, a more useful classification is between those remediation technologies that rely on biological activities and those that do not [2]. As can be seen from Fig. 3, within the two classes, there are

Table 5
Effect of pH on aquatic life [62].

pH	Effect
3.5–3.0	Toxic to most fish; some plants and invertebrates can survive such as the water bug, water boatmen and white mosses
4.0–3.5	Lethal to salmonids
4.5–4.0	Harmful to salmonids, tench, bream, roach, goldfish and the common carp; all stock of fish disappear because embryos fail to mature at this level
5.0–4.5	Harmful to salmonid eggs, fry and the common carp; the lake is usually considered dead and a "wet desert"; it is unable to support a variety of life
6.0–5.0	Critical pH level, when the ecology of the lake changes greatly; the number and variety of species begin to change; salmon, roach and minnow begin to become less diverse; less diversity in algae, zooplankton, aquatic insects, insect larvae; rainbow trout do not occur and molluscs become rare; there is a great decline in salmonid fishing; the fungi and bacteria that are important in organic matter decomposition are not tolerant so the organic matter degrades more slowly and valuable nutrients are trapped at the bed and are not released back into the ecosystem; most of the green algae and diatoms (siliceous phytoplankton) that are normally present disappear. The reduction in green plants allows light to penetrate further so acid lakes seem crystal clear and blue; snails and phytoplankton disappear
9.0–6.5	Harmless to most fish
9.5–9.0	Harmful to salmonids, harmful to perch if persistent
10.0–9.5	Slowly lethal to salmonids
11.0–10.5	Lethal to salmonids, carp, tench, goldfish and pike
11.5–11.0	Lethal to all fish

processes that may be described as either active or passive. While the former is more appropriate to be used in mines under operation where fast remediation of enormous amounts of water is needed, the latter is a more realistic solution when AMD remediation has to be achieved in abandoned mine sites where the absence of any accountable entity and the remote location require the use of a long lasting, low cost and environmentally sustainable treatment option with no artificial energy requirements [67]. These remediation techniques have been extensively documented elsewhere [2,7,22,29,63,68,69], thus are not discussed in detail in this paper. However, these techniques are very expensive and unsuitable in the long term. For example, conventional liming leads to the creation of unstable secondary wastes while passive approaches are plagued by hydraulic problems, particularly clogging due to precipitation of metals which interfere with the biological and microbiological activities [29]. Therefore, the next section discusses state-of-the-art technologies for recovery of metals, water, sulphuric acid and/or sulphate from AMD; thus generating industrially useful material.

Generation of industrially useful materials from acid mine drainage

While there is a wide range of technologies available for treating AMD before discharge, the sustainability of any remediation system is a factor that is becoming increasingly critical in decision making [2]. Many traditional processes for the treatment of acid mine water generally give rise to new waste streams that require further treatment or disposal. These residues and emissions contain the elements and compounds removed from the mine drainage and the additives and supplements dosed during the treatment processes. These streams can be in the form of sludge, brines, and spent media or emissions (e.g. gases). Besides iron (20–30%), the sludge produced also contains hundreds of toxic elements (in ppm) such as arsenic, cadmium, chromium, copper, manganese, nickel, and lead, and therefore, must itself be treated as a hazardous waste. No consideration of mine drainage treatment technologies is complete without an understanding of these residues and emissions. The management of these residues is, however, quite challenging and generally requires careful consideration and planning. Therefore, a paradigm shift has taken place in the processing of the hazardous components of AMD and management of residues arising from the remediation processes. Focus is not only on merely neutralizing acid mine water, but also on the development of near zero waste processes through the recovery of water and other useful and commercially exploitable by-products from both the acidic water and the resulting residues. In other words, significant attention has now been directed towards recovery of industrially useful materials.

As already stated, AMD is characterized by elevated concentrations of acid and dissolved metals which can be extracted as valuable products. These valuable products could then be used to offset the cost of treatment. When the value of treated water and by-products exceeds the cost of treatment, it is feasible to create enterprises that will provide economic benefits while dealing with the environmental problem.

In general, the incentives driving the recovery of by-products include the following:

Table 6
Source control measures [2,64].

Control measure	Description
Control of water migration	Water is intercepted and diverted away to prevent it from passing through the waste materials with the potential to form AMD
Flooding/sealing of underground mines	Sealing mine to prevent water and air infiltration
Underwater storage of mine tailings	Because oxygen has a very low solubility and a diffusion rate through water almost four orders of magnitude less than in air oxidation of reactive wastes can be minimized by deposing and storing sulphide-bearing waste under water
Land-based storage in sealed waste heaps	Dry covers, caps and seals (incorporating an organic layer) used to isolate or encapsulate sulphide-bearing waste thus limiting the access of either oxygen or water, or both
Blending of mineral wastes	Blending acid generating and acid consuming materials
Application of anionic surfactants	Use of anionic surfactants as bactericide inhibit bacterial activity that catalyse the conversion of ferrous iron and, subsequently, prevent acid generation
Coating of certain mine wastes	Coating involves the leaching of waste with a phosphate solution containing hydrogen peroxide. Hydrogen peroxide oxidizes the surface portion of the pyrite and releases iron oxides so that phosphate precipitation forms a passive surface coating

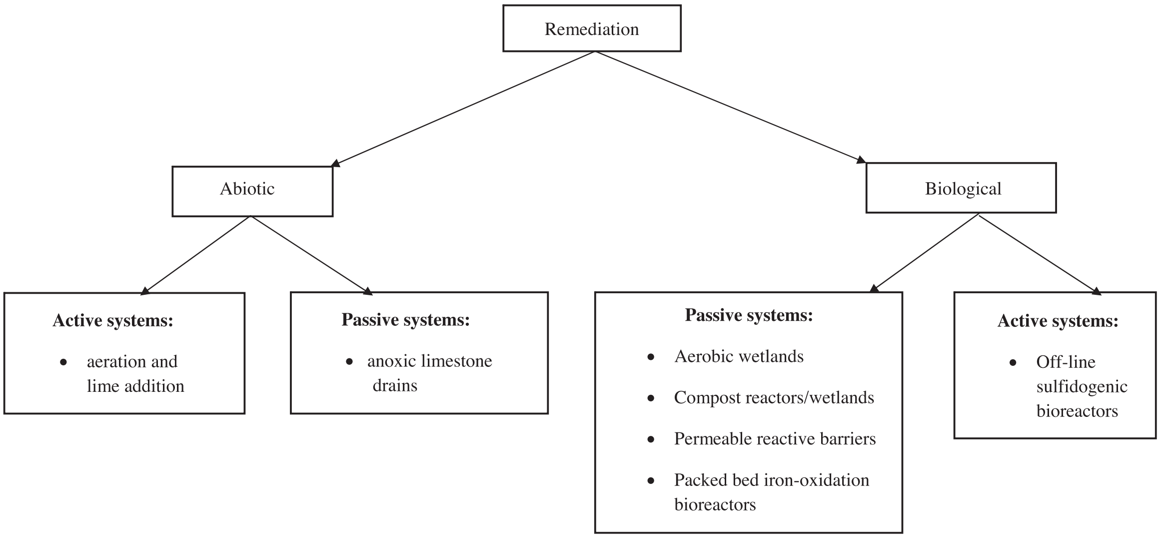

Fig. 3. Abiotic and biological remediation technologies for acid mine drainage waters [12].

- Reduction of waste sludge and brine products, which require perpetual handling and disposal with associated long-term environmental liabilities.
- Generation of a revenue stream to partly or fully offset the ongoing treatment costs.
- Contribution to the long-term sustainability of mine water treatment projects.

As stated above, significant attention should now be directed towards recovery of industrially useful materials. Therefore, the recovery of useful products from the treatment process waste streams may include the following:

- Recovery of metals.
- Recovery of saleable products, such as sulphur, sulphuric acid or sulphate.
- Production of electricity.
- Alkali recovery, such as $CaCO_3$.
- Building and construction related materials, such as gypsum and cement.
- Agricultural use (e.g. fertilizer).
- Adsorbents used in municipal and industrial wastewater treatment.
- Pigments (e.g. ferrihydrite) [150].

Some of the above mentioned products are discussed in the following sections.

Recovery of metals

Current techniques that have been used to treat heavy metal wastewater include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods [70]. However, AMD is characterized by varying compositions of heavy metals depending on the originating mineral deposit type [3], thus the commercial benefit of the dissolved metals can only be realized if they are selectively extracted and/or concentrated.

Selective precipitation

The most generally applied treatment of AMD involves the addition of alkaline reagents to increase the pH and precipitate the dissolved metals as hydroxides [71], followed by the collection and processing, and, typically, burial of sludge which contains toxic metals [72]. Although this treatment can provide effective remediation, it has the disadvantages of high operational costs and problems related to the disposal of the bulky sludge that is produced [2,7,71,73,74], and the other problem is that selective extraction is very difficult. A more sustainable option should be based on the recovery and reuse of heavy metals. The use of sulphide not only allows producing effluents with metal concentrations in the order of magnitude of ppm and ppb, but also gives the possibility of precipitation at low pH and selective precipitation for metal reuse [74]. Sulphide precipitation can be effected using either solid (FeS, CaS), aqueous (Na_2S, NaHS, NH_4S) or gaseous sulphide sources (H_2S) [75]. There is also the possibility of using the degeneration reaction of sodium thiosulphate ($Na_2S_2O_3$) as a source of sulphide for metal precipitation [75].

Using discrete chemical and biological stages, Macingova and Luptakova [10] selectively removed Fe, Cu, Al, Zn and Mn from AMD in a selective sequential precipitation (SSP) process. In this process, iron was completely removed in two steps by oxidizing ferrous iron using hydrogen followed by precipitation using sodium hydroxide [10]. In the initial stage, a partial precipitation of iron was achieved due to decrease in pH during iron oxidation. In the biological stage, sulphite-reducing bacteria was used to produce hydrogen sulphide that was later transported to the contactor filled with AMD (in the chemical stage) where precipitation of metal sulphide occurred. After filtration of precipitate, the filtrate pH was adjusted to higher value using sodium hydroxide. The pH adjustment simultaneously precipitated metal hydroxide. After filtration of metal hydroxide precipitate, the filtrate was returned to the contactor and the whole process was repeated at the higher pH value. Table 7 shows the results obtained [10]. As can be seen from the table, selective recovery of various metal precipitates was achieved.

In a study by Sampaio et al. [74], Cu was continuously and selectively precipitated from Zn using Na_2S. Selective precipitation was based on the control of pS ($=-\log[S^{2-}]$) and pH. Here, having the solubility product defined as $K_{SP} = (Me^{2+})(S^{2-})$, it means that different sulphide concentrations (S^{2-} potentials) are required to

Table 7
Conditions and results of selective sequential precipitation process [10].

Step	1	2	3	4	5	6
pH	2.8	3.7	3.7	5.0	5.0	9.5
Reagent	H_2O_2	NaOH	H_2S	NaOH	H_2S	NaOH
Removed metals	Fe	Fe	Cu	Al, Zn	Zn	Mn
Proportion (%)	99.99	99.99	99.99	98.94:1.06	99.99	99.99

precipitate different metals. Therefore, the addition of sulphide to selectively precipitate heavy metals can be controlled using an ion selective electrode for sulphide (S^{2-}), a so called pS electrode [74]. In this study, selective precipitation of copper from zinc was achieved at pS and pH of 25 and 3, respectively.

Several precipitating agents have also been developed in the last few years for chemically and selectively precipitating divalent and univalent heavy metals from water and effluents [76]. Selective metal precipitating agents include dithiocarbamate [77], Thio-Red [77] and dipropyl dithiophosphate [78]. The principal advantages of using metal precipitant agents are [76]: (1) the formation of metal compounds which have a very low solubility, and (2) the lesser production of metallic residue in comparison to the production of metallic sludge using common chemicals, like sodium hydroxyde or lime. However, the high cost of these reagents inhibits their use for different industrial applications [76,79].

Another recently developed method for heavy metal removal based on chelating precipitants is termed CH collector method. This is simply a solid material which binds heavy metals to its surface [80]. Typically, such chelating precipitants contain groups with replaceable hydrogen atoms such as carboxyl (—COOH), hydroxyl (—OH), mercapto (—SH) or sulphonic (—SO_3H) groups, together with functional groups of basic character, such as amino (—NH_2), amino (cyclic) (—NH—), carbonyl or thio keto with which the reacting metal is coordinated to form a four, five or six member ring. This invention is unique in that ion channels are formed inside the material in which metal ions are collected from the solution [80]. The collection of the heavy metal ions does not require a separate precipitation step or any adjustments to the solution's pH. Unlike traditional methods, the CH collector method also allows the recovery of metals occurring in very small concentrations. The new method enabled the complete removal of uranium from the water collected from a Finnish mine [80]. The study showed that there was no need to pre-treat the water even though it contained high concentrations of other metals. The efficiency of the method was also tested on scandium and it was removed from waste water with 98% recovery [80].

Selective adsorption

While a wide number of techniques have been studied and/or are being used for the removal of heavy metals from aqueous solutions, adsorption has evolved as the preferred method [81,82]. Most of the adsorbents used in these studies are highly porous materials, providing adequate surface area for adsorption [83]. However, the existence of intraparticle diffusion may lead to the decrease in the adsorption rate and available capacity, especially for macromolecules [83]. With the advent of nanotechnology, various types of nanomaterials with large surface area and small diffusion resistance have been developed and are now receiving considerable attention in water treatment [83–86]. For example, nanoscale iron particles have been established as effective reductants and catalysts for a variety of contaminants including heavy metals [86]. Iron nanoparticles possess the advantages of large surface area, high number of surface active sites, and high magnetic properties, which lead to high adsorption efficiency, high removal rate of contaminants, and easy and rapid separation of adsorbent from solution via magnetic field [83]. In addition, it is possible that after magnetic separation by the external magnetic field, the harmful components can be removed from the magnetic particles, which can be reused [83,87,88].

The adsorption studies by Hu et al. [83] showed that the nanoscale maghemite (γ-Fe_2O_3) synthesized using a sol–gel method was very effective for selective removal of Cr(VI), Cu(II), and Ni(II) from wastewaters. The removal efficiency was highly pH dependent, which also governed the selective adsorption of metals from the solution. The optimal pH for the selective removal of Cr, Cu, and Ni was found to be 2.5, 6.5, and 8.5, respectively. Regeneration and readsorption studies demonstrated that the maghemite nanoparticles could be recovered efficiently for the re-adsorption of the metal ions, and metals could be highly concentrated for recycling.

Several studies have also been carried out to assess the technical feasibility of various kinds of raw and surface oxidized carbon nanotubes (CNTs) for sorption of various metals from aqueous solutions [81]. CNTs are carbon nanomaterials that were re-discovered by Iijima [89]. These materials have shown exceptional adsorption capabilities and high adsorption efficiencies for various organic pollutants [90], inorganic pollutants [91] and heavy metals [92–94]. The CNTs are particularly attractive as sorbents because, on the basis of mass, they have larger surface areas than bulk particles, and that they can be functionalized with various chemical groups to increase their affinity towards target compounds [84,85,95]. The CNTs also have small size, and are hollow with layered structures [96], which are important attributes for adsorption.

The studies have shown that the sorption capacities of metal ions by raw CNTs are very low, but significantly increased after oxidization by HNO_3, NaOCl, and $KMnO_4$ solutions [81]. In fact, this is one other advantage of CNTs in that they can be functionalized (or oxidized) with various kinds of chemical agents depending on the adsorption objective. The removal efficiency was also highly pH dependent, thus governing the selective adsorption of metals from the solution. The sorption/desorption studies showed that CNTs could be regenerated and reused consecutively several times without significant loss in adsorbent capacity signifying its appropriateness for commercial application. Therefore, the superior sorption capacity and effective desorption of heavy metal ions suggest that the CNTs are promising sorbents for environmental protection applications [81].

Selective ion exchange

Ion exchange may be defined as the exchange of ions between the substrate and surrounding medium [97]. In comparison to the other methods, ion exchange is technologically simple and enables efficient removal of even traces of impurities from solutions, and is particularly useful when it is necessary to treat large volumes of diluted solutions [98]. In other words, the technique is designed to remove traces of ionic impurities from water and process streams and give a product of desired quality [97]. Depending on the type of functional groups of exchanging certain ions, the ion exchangers may be classified as strongly acidic, e.g. sulphonate —SO_3H; weakly acidic e.g. carboxylate –COOH; strongly basic, e.g. quaternary ammonium – N^+R_3; and weakly basic, e.g. tertiary and secondary amine –N^+R_2H and –N^+RH_2 [97]. There are also amphoteric exchangers, which depending on the pH of the solution may exchange either cations or anions. These ion exchangers are also called bipolar electrolyte exchange resins (BEE) or zwitterionic ion exchangers [97,99].

Some of the metals which have been recovered and purified on an industrial scale by means of ion exchange include [97]: uranium, thorium, rare earth elements (REEs), gold, silver, platinum group metals (PGM), chromium, copper, zinc, nickel, cobalt and tungsten. Selected few heavy metals have been discussed below.

Studies on recovery of Cu(II) ions have shown that due to low pH values of wastewaters ($pH < 2$), conventional chelating ion exchangers of iminodiacetate and aminophosphonic functional groups practically do not adsorb Cu(II) ions. Special chelating ion exchangers characterized by much greater affinity for Cu(II) than for other metal ions have been used instead [100–102]. For example, Cu(II) ions can be removed from less acidic solutions ($pH > 1.5$) using Dowex XFS-4196 chelating ion exchanger which can be easily regenerated by means of sulphuric acid of a concentration of 100 g H_2SO_4 dm^{-3} [98]. Amphoteric ion exchange fibres can also be applied for removal of Cu(II) ions from acidic wastewaters. Various other types of ion exchangers have also been applied for selective removal of Cu(II) ions [103–105].

A mixture of nickel and vanadium from industrial wastewaters formed during gas desulphurization has been treated in stages. To remove nickel and vanadium ions, the industrial wastewaters must be oxidized, pH adjusted within the range 5–10 and then it must be passed through the chelating ion exchanger bed [98]. Ni(II) ions are adsorbed in the ion exchanger and pH of the solution takes values smaller than 5. The obtained solution from Ni(II) ion exchanger would again be introduced into the bed of another chelating ion exchanger in order to remove vanadium ions [100,101]. Regeneration of ion exchanger beds resulted in concentrated solutions of nickel and vanadium ions. Carboxylic ion exchangers have also exhibited great selectivity for Ni(II) ions [98]. For example, macroporous carboxylic cation exchanger Wofatit CA-20 in the sodium form has been applied for selective Ni(II) ions removal from washings formed during the nickel plating [106].

On account of its high toxicity, lead content in water and industrial wastewaters must be reduced to a minimum within the ppb level [98], thus several ion exchange studies have been carried out to remove Pb(II) ions. Of significant importance is the simultaneous removal of Pb(II) and Cd(II) ions as well as organic ligands using anion exchangers of various types [107,108]. Some results showed that the anion-exchangers of weakly basic functional groups are characterized by higher affinity for the complexes of Pb(II) and Cd(II) with EDTA than strongly basic anion exchangers and that the anion-exchangers of polyacrylic skeleton are characterized by greater affinity for the above mentioned complexes than the anion-exchangers of the same type of polystyrene skeleton [98]. Other studies have shown that higher selectivity, great exchangeability as well as reversibility of the sorption–elution process towards Pb(II) ions are characteristics of the sulphine cation exchanger exhibiting-SO_4^{2-} groups [109]. On the other hand, chelating ion exchanger with iminodiacetate functional groups, Lewatit TP-207, has been recommended by the Bayer Company for selective removal of metal ions, particularly of Pb(II) ions [110].

Recovery of water

The removal of heavy metals from AMD using the technologies discussed in the previous sections, simultaneously recovers water. However, the processes have several disadvantages which include pH dependence, which means that the removal of the mixture of heavy metals cannot be achieved at a single pH level. Therefore, it is imperative that other technologies which are not pH dependent such as electrodialysis, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and membrane distillation, are persuade.

Electrodialysis

Amongst the different membrane technologies, electrodialysis has been tested and proven to be an effective technology for water recovery [111–114]. Electrodialysis is a membrane separation process based on the selective migration of aqueous ions through ion-exchange membrane as a result of an electrical driving force [115]. The transport direction and rate of each ion depends on its charge, mobility, solution conductivity, relative concentrations, applied voltage, etc. Electrodialysis is considered as a clean technology which does not require the addition of chemicals; can be operated in continuous mode and allows the obtaining of profitable by-products [117].

Recent study has shown that electrodialysis is suitable for recovering water from AMD, with contaminant removal efficiencies that are greater than 97% [19]. Precipitation of iron at the surface of the cation-exchange membrane which resulted in blockage of the membrane through the scaling phenomenon was found to reduce the efficiency of the processes. However, prior iron removal would prevent a continuous increase in the membrane voltage, thus improving process efficiency [19].

The recovery of water has also been studied in other acidic systems containing various metals [111,113,114,116]. In all these studies, electrodialysis has been found to be an effective method for water recovery. In fact, membrane modules on average have a water recovery rate ranging from 50% to 80% [118]. However, the only major disadvantage is that membrane technologies can be very expensive in applications where the wastewater contains elevated hardness and sulphate near gypsum saturation [118]. The high cost of operation is due to the large reagent requirement for upstream pretreatments, high power demand, and expensive disposal options for the concentrated brine solution produced by membranes. At a time when responsible energy and environmental practices are under the spotlight, technologies with high energy use and that produce a large volume of wastewater are becoming less appealing.

Membrane distillation

A five-decade old technique which is currently being explored for various applications such as desalination, water and wastewater treatment, removal of volatile organic compounds, and food processing is membrane distillation [119–122]. This process is a combination of the conventional distillation and membrane separation processes [123]. Membrane distillation processes have several configurations which are as follows [124]: (1) direct contact membrane distillation (DCMD), (2) air gap membrane distillation (AGMD), (3) sweeping gas membrane distillation (SGMD), and (4) vacuum membrane distillation (VMD). Amongst these configurations, DCMD, is the most widely used because it is convenient to set up, consumes relatively low energy, and gives high water flux [124].

Unlike other membrane separation processes which are driven by absolute pressure difference (e.g. reverse osmosis, nanofiltration and microfiltration) or an electrical potential gradient (e.g. electrodialysis) or concentration gradient (e.g. dialysis), membrane distillation is a thermally driven separation process that utilizes hydrophobic and microporous membranes as a contactor [125]. The driving force in the membrane distillation is the vapour pressure difference induced by the temperature difference across the hydrophobic membrane [119]. In other words, the temperature difference existing across the membrane results in a vapour pressure difference, thus vapour molecules are transported from the high vapour pressure side to the low vapour pressure side through the pores of the membrane [122]. The hydrophobicity of the membrane prevents the transport of liquid across the pores of the partition while water vapour can be transported from the warm side, condensing at the cold surface [124]. Since the separation mechanism is based on the vapour/liquid equilibrium, it means that the component with the highest partial pressure will exhibit the highest permeation rate [122]. Moreover, mass transfer in membrane distillation is controlled by three basic mechanisms – Knudsen diffusion, Poiseuille flow (viscous flow) and molecular diffusion [119].

Compared with other separation processes, membrane distillation has several important advantages: a 100% complete rejection of dissolved-non-volatile components; lower operating pressure than pressure-driven membrane processes; reduced vapour space compared to conventional distillation; low energy consumption; and low operating temperature [122]. Low operating temperatures (considerably below boiling point) of a feed enables the utilization of waste heat as a preferable energy source. In fact, this technology can be integrated with alternative (or renewable) energy sources such as solar, wind, wave, geothermal, or waste energy recovery system [122,123].

Recently, membrane distillation has been used to recover water and concentrate acid and metal values from mining wastewater and process solutions [124]. The influence of acid concentration and the presence of inorganic salts in the feed were investigated using DCMD for three different synthetic solutions: (A) 0.5 M H_2SO_4, (B) 0.5 M H_2SO_4 + 0.2 M NaCl, and (C) 0.5 M H_2SO_4 + 0.2 M Na_2SO_4 + 0.2 M NaCl. The flow rate of both hot and cold sides of the module was 900 mL/min with the feed temperature of 60 °C and the cold water temperature of 20 °C. The test work showed that fluxes remained reasonably stable, within the range of 20–31 kg/m^2/h for all experiments. In the study, both water vapour and gaseous hydrochloric acid were transported across the membrane in solution (B) and (C), whereas sulphuric acid was retained in all experiments. The final concentration of sulphuric acid in the three feed solutions increased from 0.5 to 2.45 M, 2.40 M and 2.95 M, respectively. The sulphate and sodium separation efficiencies were over 99.9% and overall water recovery exceeded 80%, indicating that DCMD was successfully used for recovering fresh water and concentrating the acid in the solutions. Solvent extraction was then used to recover the acid and metal values in the concentrated solution.

Recovery of sulphuric acid

AMD is predominantly acidic due to high concentrations of sulphuric acid. As a result, the presence of acid renders it highly corrosive and polluting in nature [111]. The hazards associated with low pH values have already been discussed (see section: effects of acid mine drainage). Therefore, there is a need to develop a system to recover acid from AMD. Previously, methods which include thermal decomposition [126], electrolytic precipitation/deposition [127,128], ion exchange [129,130], diffusion dialysis [131], electrodialysis [117,132] and solvent extraction [133–135], have been utilized to recover various acids for reuse or disposal. Amongst these methods, electrodialysis has an added advantage because the recovered acid is usually at a significantly high concentration so that the subsequent purification (if necessary) via other techniques is relatively inexpensive [136].

Martí-Calatayud et al. [117] studied the recovery of sulphuric acid from AMD using an electrodialysis cell with three compartments. The results showed that the recovery of sulphuric acid from AMD can be achieved by means of an electrodialysis cell. Significant increases in the sulphuric acid concentration were obtained with the proposed scheme consisting of a three-compartment electrodialysis cell with cation-exchange membrane (CEM) and anion-exchange membrane (AEM). Wisniewski et al. [137] investigated the separation of mineral acids from spent solutions of acid and iron salts obtained in the course of conventional electrodialysis. The results showed that electrodialysis is able to recover and concentrate hydrochloric and sulphuric acids further from the acid and iron salt concentrates produced in the course of conventional electrodialysis.

However, the application of electrodialysis on a large scale for the extraction of sulphuric acid from acid mine water has not been tested. It is also important to note that this process would be more economically viable for acidic waters that have very high sulphate ion content. Therefore, it cannot be applied arbitrarily, but only for acidic water sourced from environments of high sulphur content such as coal beds.

Similarly as discussed in section: membrane distillation, membrane distillation process can be used to recover or concentrate sulphuric acid. Moreover, Tomaszewska [22] used membrane distillation to recover hydrochloric acid from spent pickling liquors containing residual acid.

Simultaneous removal of metals and production of electricity

Microbial fuel cells (MFCs) have emerged in recent years as a promising yet challenging technology for converting organic waste including low-strength wastewaters and lignocellulosic biomass into electricity through the metabolic activity of the microorganisms [138,139]. An MFC is considered to be a promising and sustainable technology that would meet increasing energy needs, especially when using wastewaters as substrates [140,141]. Since it results in the production of electricity and clean water as final products, it may offset the operational costs of wastewater treatment plants [140]. Recent studies by Cheng et al. [142,143] show the development of an AMD fuel cell, based on fuel cell technology, which is capable of abiotic electricity generation from synthetic AMD solutions. Test works conducted using synthetic solutions of similar composition and constituent as typical AMD solutions have shown that the device (AMD fuel cell) can efficiently remove dissolved iron from the solution while also generating electricity at power levels similar to conventional MFCs. Though the power and current yields are still relatively low, improvements in the fuel cell technology will possibly lead to more efficient power generation in the future.

Cyclic electrowinning/precipitation method

Recently, a method termed cyclic electrowinning/precipitation (CEP) which combines precipitation and electrowinning was developed [144]. In this method, the concentration of metal cations is increased in the first stage followed by electrowinning to recover and separate the metals from waste water in the second stage. Basically, the operations are as follows: In the first unit the metal laden water is fed into a tank in which an acid (e.g. H_2SO_4) or a base (e.g. NaOH) is added to change the water pH effectively separating the water from the metal precipitate which settles at the bottom. The clear water is siphoned off and more contaminated water is brought in. The pH swing is applied again first re-dissolving the precipitate and the re-precipitating all the metals, thus increasing the metal concentration each time [144]. This process is repeated until the concentration of the metal cations has reached a point where electrowinning can be efficiently employed. When that point is reached it is taken to a second device called a spouted particulate electrode, where metal cations are converted to stable metal solids so that they can be removed [144]. The tested heavy metals were cadmium, copper and nickel. The results showed that cadmium, copper and nickel were reduced to 1.50, 0.23 and 0.37 ppm, respectively, way below the maximum contamination levels established by the EPA [144]. The main advantage of this processes is that sludge is continuously formed and re-dissolved within the system so that none is left as an environmental contaminant.

Other useful products and applications

The active treatment of AMD involves the addition of alkaline reagents such as limestone or slaked lime to increase the pH and precipitate the dissolved metals as hydroxides [2,145], a technology that involves huge material and transportation costs [2]. In general about 1 t of sludge (dry-weight basis) is formed per tonne of limestone used, and the sludge has high water content (95–98%) making it difficult to dewater [146]. The other challenges involving AMD sludge are the volumes generated and the long term chemical stability [147]. Furthermore, sludge treatment and disposal costs over the lifetime of a treatment facility may be almost an order of magnitude higher than the capital costs and the costs of the neutralization chemicals [146]. In summary, although active treatment can provide effective remediation, it has the disadvantages of high operational costs and sludge disposal problems. Therefore, in recent years, due to several disadvantages of AMD treatment as stated above, concerted effort has been made to investigate the potential use of the sludge which would otherwise be disposed of to landfill at significant costs. The section below looks at some of the applications of the AMD treatment sludge.

Production of iron pigments

Studies have shown that the sludge obtained from AMD can be considered for the production of inorganic pigments [148–150], and magnetic particles like ferrites [151]. To produce commercially usable iron oxides as raw material for production of pigments, additives to ceramics, etc., treatment of AMD using a two-step selective precipitation process was developed [150]. The two step process that uses magnesium oxide and sodium hydroxide, results in the ferrous and ferric oxyhydroxide sludge that can be thermally transformed to basic ferric pigment. A study by Hedin [150], however, indicated that while the end product was of high quality, processing associated with costs made the materials more costly to produce than mined oxides although this may be offset when considering the high cost of hydrous ferric oxide disposal. Marcello et al. [149] investigated the use of hydrous ferric oxides from active coal mine drainage treatment as pigment within ceramic tile glaze. Favourable results occurred when the ferrous hydrous oxides was blended with an industrial standard pigment.

Research by Cheng et al. [142,143] has also shown that fuel cell technologies cannot only be used for simultaneous AMD treatment and power generation, but also to generate iron oxide particles having sizes appropriate for use as pigments and other applications. As already discussed in section: simultaneous removal of metals and production of electricity, a fuel cell called an AMD fuel cell based on an MFC was developed and used during the process. During treatment, ferrous iron was oxidized in the anode chamber under anoxic conditions, while oxygen was reduced to water at the cathode. Ferrous iron was completely removed through oxidation to insoluble ferric iron, and precipitated at the bottom of the anode chamber. The particle diameter of the iron oxides could be controlled by varying the conditions in the fuel cell, especially current density, pH and initial ferrous iron concentration. Upon drying, the iron oxide particles were then transformed to goethite (α-FeOOH).

Building and construction related materials

Many of the constituents in sludge are the same as those used in cement manufacturing. For example, calcite, gypsum, silica, Al, Fe and Mn are common raw materials for cement. Therefore, the components that make up AMD treatment sludge such as gypsum, calcite and ferrihydrite can be utilized as raw materials in the manufacturing of construction materials and other products. Levlin [152] indicated that in order to avoid waste disposal, inorganic components in sludge can be used for the production of building materials. Research by Lubarski et al. [153] found that the high aluminium content of sludge produced from the treatment of acidic drainage at some coal and gold mines could be used for the production of aluminous cement. Other studies have suggested that sludge can replace up to as much as 30% Portland cement in blended cement [154]. In this option, the utilization of sludge reduces mining of raw materials for production of building material.

Adsorbents in industrial wastewater treatment

Standard treatment technology for the removal of impurities such as phosphorus from municipal wastewater involves dosing of the wastewater with coagulants such as alum, ferric chloride or lime [155,156], but the costs of these reagent chemicals often make their use impractical or uneconomic for low concentrations and high volumes often encountered in many wastewaters. Therefore, it is necessary that alternative coagulants are sought. Given the wide range of studies that successfully removed phosphorous from wastewaters using iron and/or aluminium hydroxide sludges, Wei et al. [151] hypothesized that the AMD sludge containing a mixture of iron and aluminium hydroxide precipitates would be a suitable medium for the adsorption of dissolved orthophosphate from solution. In other words, sludges produced by the neutralization of AMD could be especially appropriate for phosphorus sequestration as it is composed primarily of aluminium and iron hydrous oxides, the same chemical forms produced when alum or ferric chloride is added to wastewater at near neutral pH. In addition, research by Sibrell et al. [157] and Sibrell and Tucker [158] has shown that dried AMD sludge, or residuals can be used as a low-cost adsorbent to efficiently remove phosphorus from agricultural and municipal wastewaters. The phosphorus that has been adsorbed by the AMD sludge can later be stripped from the sludge and recycled into fertilizer; and the mine drainage sludge can be regenerated and reused for a number of additional applications.

Studies by Edwards and Benjamin [159] have also shown that the iron ferrihydrite component of AMD sludge from lime treatment plants can be used as a highly effective adsorbent for the removal of metals from water streams. Similarly metal hydroxide sludge has also been used to remove carcinogenic dyes from wastewater [160].

Review of commercially developed projects

This section discusses projects that are either in operation, being piloted or under evaluation.

CSIR ABC (alkali–barium–calcium) process

This precipitation process developed by CSIR (South Africa) uses barium hydroxide to precipitate dissolved sulphate from AMD. It consists of the following 3 stages: pre-treatment, treatment with barium carbonate and the waste processing stage as shown in Fig. 4 [161]. In the pre-treatment stage the feed water is treated with lime and CaS to remove free acid and metals. During this stage, the sulphate content is lowered from about 4500 mg/L to about 1250 mg/L [161]. In the water treatment stage, $BaCO_3$ is added into the water producing barium sulphate as the solid waste and clean water. The water treatment stage is integrated with a sludge processing stage to recover the alkali, barium and calcium (ABC) from the sludge through reduction in a coal-fired kiln. In this process, good quality water containing less than 100 mg/L of sulphate is obtained in a cost effective way from polluted mine water [161]. This process is a strong candidate for cost-effective treatment of mine water. However, the major limitation of this technology is the amount of sludge produced which is expensive to dispose. High capital and operating costs associated with the thermal reduction of waste to produce CaS, gypsum and other solids for disposal also make the technology less cost-effective.

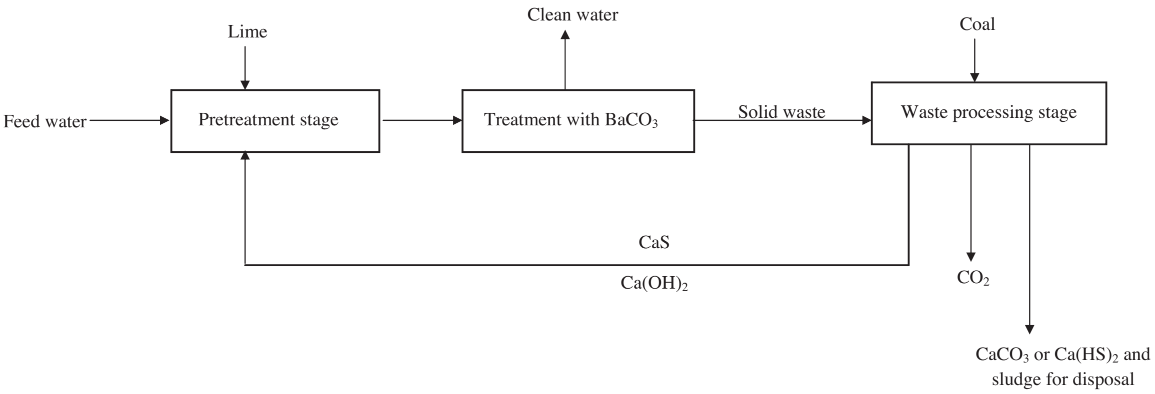

Fig. 4. Process flow diagram for the CSIR-ABC process [161].

SAVMIN process

This process was developed by Mintek (South Africa) to treat polluted mine water [162,163]. Fig. 5 shows the process flow diagram, and the main process stages are as given below [162,163].

Stage 1 – Metal precipitation: using lime, the pH of the feed water is raised to between 12.0 and 12.3 to precipitate metals (trace) and magnesium.

Stage 2 – Gypsum ‘de-supersaturation’: using gypsum seed crystals, gypsum is precipitated from the supersaturated solution and removed.

Stage 3 – Ettringite precipitation: using aluminium hydroxide, dissolved calcium and sulphate are removed from the solution by the precipitation of ettringite (a calcium–aluminium sulphate mineral).

Stages 4 and 5 – Recycling of aluminium hydroxide: using sulphuric acid, the ettringite slurry from stage 3 is decomposed at pH 6.5 in a solution supersaturated with gypsum (no precipitation). The resulting aluminium hydroxide is recycled to the third stage and the solution supersaturated with gypsum is contacted with seed crystals (stage 2) to precipitate and remove gypsum. The remaining solution saturated with gypsum is recycled.

Stage 6 – Carbonation and calcite precipitation: using carbon dioxide, the pH of the solution from the third process stage (pH 11.2–12.4) is lowered to precipitate and remove calcite.

The end products of the SAVMIN process are potable water and a number of potentially saleable by-products (metal hydroxides, gypsum and calcite). One of the major advantages of SAVMIN process is that high quality products can be obtained [163]. A major disadvantage of this process is the vast amount of the sludge produced which is expensive to dispose [163,164].

SPARRO process

This is a membrane desalination process which was designed to treat calcium sulphite scaling mine water. The process was developed in the late 1970s by Resources Conservation Company in Seattle, USA [165]. The SPARRO technology can treat most waste waters and produces good quality water at variable water recoveries. However, the main disadvantage is that the life of membranes is greatly reduced (due to fouling) because of the quality of the feed water [164]. Compared to the conventional reverse osmosis technology, the membrane life in SPARRO process has been improved by introducing the use of a pump system, independent gypsum seed control and other design configurations [166,167], but is still not ideal. Any improvement to the membrane performance is expected to increase the economic viability of the SPARRO treatment process.

GYP-CIX process

This is a continuous fluidized bed ion-exchange process that effectively removes calcium and sulphate from water that is saturated with gypsum [168]. The process consists of two stages of operation [168]. Firstly, cations are removed in a multi stage continuous loading train, using cation exchange resins. The second operation is the removal of the anion in another multistage loading train using anion exchange resins. Sulphuric

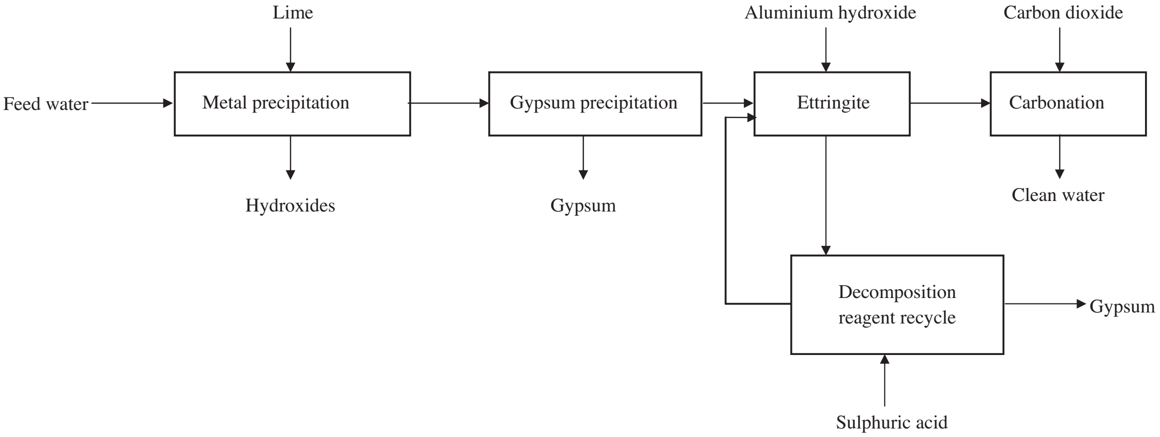

Fig. 5. SAVMIN process flow diagram [162,163].

acid is used to regenerate the cation exchange resin while lime slurry is used for anion resin regeneration. In both cases, the waste produced is brine slurry containing precipitated calcium sulphate and water of re-usable quality [168]. The main advantages of this process are the use of low cost chemicals and high water recoveries [168]. However, its main disadvantage is the large volume of gypsum sludge produced during the regeneration of the ion-exchange resins which presents challenges in terms of its disposal [164].

THIOPAQ process

This is a biotechnological process which uses two distinct microbiological populations and stages [169]; (i) conversion of sulphate to sulphide by using hydrogen gas (from the conversion of ethanol/butanol to acetate and hydrogen) as the electron donor and precipitation of metal sulphides, and (ii) conversion of any excess hydrogen sulphide produced to elemental sulphur, using sulphide-oxidizing bacteria. In this way sulphate is removed from AMD to produce water of re-usable quality. This process has lost attractiveness over the years due to an increase in the price of ethanol and butanol which are energy sources for the process [169].

The Rhodes BioSURE process

This is a South African invented biological treatment that has been used at Grootvlei by East Rand Water Care Company (ERWAT). It was developed by the Environmental Biotechnology Group (EBRU) of Rhodes University [170]. The process removes acidic sulphate using free waste stock, such as sewage sludge, instead of expensive carbon and electron donor sources (such as ethanol and hydrogen). This makes it significantly cheaper than other similar alternatives. This technology is restricted by the availability of sewage sludge or other organic wastes used as carbon and energy sources; however, it has the advantage of providing an option for the co-disposal of sewage sludge, reducing the costs of landfill solid waste [171].

TUT MBA (magnesium–barium–alkali) process

This process is an improvement on the CSIR-ABC process. It is a more feasible option than the ABC process as $Ba(OH)_2$ is used for two functions simultaneously; (i) sulphate removal by means of $BaSO_4$-precipitation, and (ii) magnesium removal by $Mg(OH)_2$-precipitation [174].

HiPRO (high pressure reverse osmosis) process

This process was developed by Aveng Water. It is capable of consistently achieving greater than 97% water recovery [172]. The final products from this process are portable water, a liquid brine solution (less than 3% of the total feed) and solid waste. The solid waste products are saleable grades of calcium sulphate and less pure calcium sulphate and metal sulphates [172]. The main disadvantages of this process are that it produces waste brine and waste sludge which are expensive to dispose.

EARTH (environmental and remedial technology holdings) ion exchange process

This process uses ion exchange columns to recover uranium and sulphate ions from AMD [173]. The uranium bearing solutions could be sold to uranium processors. The sulphate ions recovered are reacted with ammonia gas to form 20% ammonium sulphate solution [173]. Metal cations are also recovered by use of cationic exchange resins, which are later eluted with nitric acid to form a mixed metal nitrate solution which can be sold. However, the feasibility of this technology is dependent on availability of a market for the products and stable prices [174].

Integration of processes and technologies

The threat of AMD to the environment will not be solved in the short to medium term, and is likely to persist for centuries to come. It will also not be solved by a single intervention. In addition, new processes developed have to include the sustainability factor. In this case the use of waste or byproducts from AMD becomes a very important alternative resource. It can be been seen from section: generation of industrially useful materials from acid mine drainage, that it is possible to recover heavy metals, water and acid from AMD. Furthermore, products that have commercial value such iron pigments and adsorbents, including building materials can also be generated from AMD. Thus treatment processes can be designed to produce an effluent and sludge of adequate quality to be recycled and reused for other applications. However, none of the methods seem to give good economics and high degree of energy efficiency when used individually. It is clear, therefore, that there is currently no commercial technology available to treat acid mine water 100% effectively. Hence the best way to working towards a sustainable solution of the AMD challenge is to take a business approach and consider the integration of existing technologies as well as technologies under development so as to come up with a

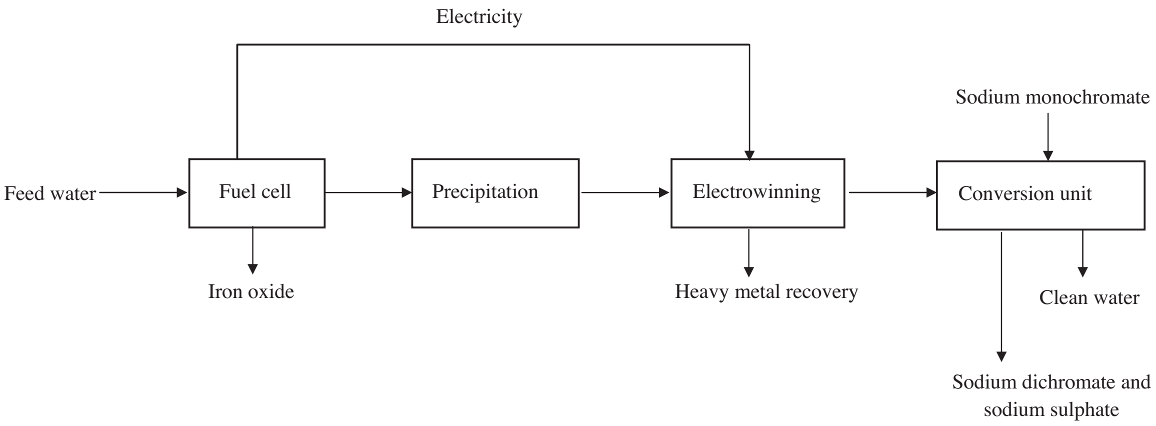

Fig. 6. First proposed integrated process.

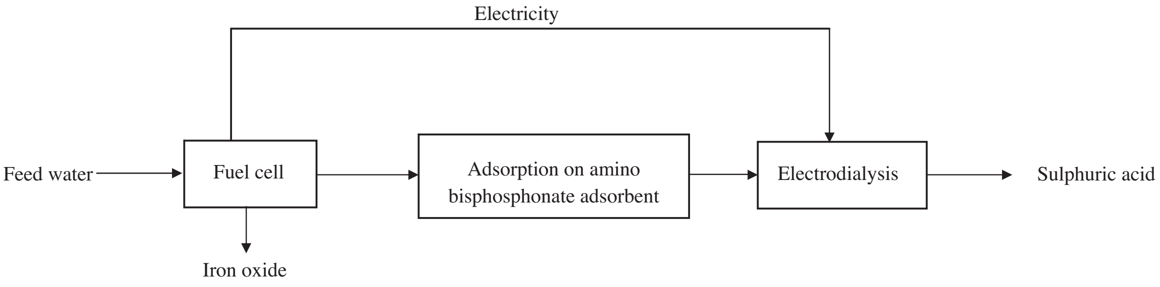

Fig. 7. Second proposed integrated process.

solution that has the potential to address the problem in a holistic and sustainable manner. In other words, coupling different processes together as two or three stage processes would be more appropriate. Such measures would possibly include the integration of both the active and passive water treatment systems. In fact, previous studies have shown that combinations of physico-chemical treatments may be able to partially or completely remove some organic and inorganic contaminants [175,176]. Furthermore, due to process integration, it can be seen from section: review of commercially developed projects, that most of the commercially developed processes can produce water of acceptable quality from AMD. However, there are several challenges associated with them. Technologies like CSIR-ABC, GYP-CIX, TUT-MBA and HiPRO processes produce heavy sludge which is expensive to dispose. Membrane technologies like SPARRO suffer from high operating costs as well as reduced membrane life due to fouling. While others like THIOPAQ and EARTH have high operating costs. EARTH is the only one that produces valuable by-products, but there is limited market for them. Therefore, in this section, different process combinations are proposed and discussed.

In view of the ever increasing demand for electricity, AMD fuel cells are recommended to be included in every integrated process. This would enable the treatment of AMD as well as production of useful products such as electricity and recoverable metals. The ever increasing need for clean, but scarce water also necessitates the coupling of AMD fuel cells to electrodialysis or even membrane filtration technologies (e.g. reverse osmosis). It must be noted, however, that fouling or deposition of solids on membrane filters is one of the main obstacles because it hinders the operation of the system in a constant and reliable way [177]. Nevertheless, the problem of fouling may be prevented by pretreating the effluent from the AMD fuel cell with AMD sludge.

The first proposed option will be to couple the AMD fuel cell with the CEP process. The first part may consist of the fuel cell where ferrous iron is completely removed through oxidation to insoluble Fe (III), forming a precipitate in the bottom of the anode chamber and on the anode electrode [142]. The iron contained in the precipitate or sludge could be marketed as a pigment for paint [150], cosmetics and possibly other uses. The electricity produced could be used to supplement the power in the electrowinning stage. The second part of the integrated process would consist of the CEP process. A pH swing (using NaOH or H_2S0_4) would be applied to the water coming from the fuel cell so as to precipitate the heavy metals such as cadmium, nickel, copper, etc. The precipitation and re-dissolution of metals would be repeated until the concentration of the heavy metals ($<$100 ppm) has reached a point where electrowinning can be efficiently done [144]. In electrowinning stage heavy metal ions will be converted using electric current to stable metal ions which can be recovered and separated from water. However, the metal barren solution still contains high amount of sulphate ions. The solution could be concentrated and then reacted with sodium monochromate (from roasting and leaching of chromite ore) to form a mixture of sodium dichromate and sodium sulphate. This mixture can then be recovered and separated from the water. Depending on the purity, the product can be marketed as a fertilizer or as a metal finish and other uses. The proposed integrated process flow diagram is shown in Fig. 6.

The second proposed integrated process will be to start off with an AMD fuel cell where iron would be precipitated as iron oxide at the anode. The metal-laden water will then be pumped to the adsorption circuit where the CH-collector would adsorb heavy metals directly from the wastewater [80]. The water now barren of metals is then pumped to electrodialysis circuit where a more pure form of sulphuric acid and other residual metals will be recovered [117,132]. The electrodialysis process efficiency is expected to be high as metals which might cause membrane fouling would have been removed in the fuel cell and by the collector. The products from this integrated process are expected to be iron oxide which could be sold as a pigment for paint [150], cosmetics and possibly other uses. The electricity produced from the fuel cell can act as a power source for electrodialysis. The sulphuric acid produced could be used in the leaching of metal ores. The basic flow diagram of the proposed process is shown in Fig. 7. The third proposed integrated process is shown in Fig. 8.

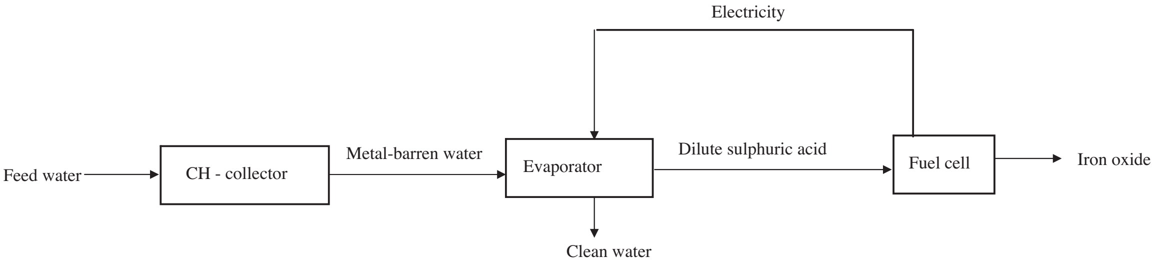

Fig. 8. Third proposed integrated process.

Summary and concluding remarks

This paper has shown without doubt that AMD has severe impacts on human life, aquatic species, can stunt terrestrial plant growth and harm wetlands, contaminate groundwater, raise water treatment costs, and damage concrete and metal structures [22]. In this review, a wide range of conventional and non-conventional processes for treating AMD have been presented. However, it has become clear that the threat of AMD to the environment will not be solved in the short to medium term, and is likely to persist for centuries to come. It will also not be solved by a single intervention, but will require the integrated implementation of a range of measures and processes. Undoubtedly, the review has shown that there is tremendous and urgent need for further research and innovation in order to develop new separation and purification technologies. For example, it is clear that most of the treatment processes developed so far give rise to new waste streams (e.g. brines and gypsum), and thus, there is need for an ongoing effort to develop new zero waste processes. Clearly most of the methods discussed in this review are not suitable for complete removal of heavy metals from mining waste water hence a combination of different technologies could go a long way in addressing challenges associated with AMD remediation.

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