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RESEARCH ARTICLE

Acid mine drainage: electrochemical approaches to prevention and remediation of acidity and toxic metals

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Abstract Acid mine drainage (AMD), caused by biological oxidation of sulfide minerals in the presence of air and water, is a significant environmental problem because of its acidity and the presence of high concentrations of iron and solubilized toxic metal ions. The focus of this review is to consider the prospects for electrochemical technologies for either prevention or remediation of AMD, with physicochemical technologies mentioned for comparison.

Keywords Acid mine drainage · Electrochemical technologies · Soluble toxic metals · Prospects for implementation · Electrochemical neutralization

1 Introduction and chemistry of AMD

Acid mine drainage (AMD) is a significant environmental problem in the mining industry. Many metals of industrial importance occur as sulfides, but economically extractable ores, e.g., those of Cu, Ni, and Zn, often contain only 1–5 % of the desired sulfide, together with much greater amounts of iron pyrite (FeS_2). The valuable metal sulfides are separated by flotation after the ore is crushed into fine particles, typically <1 mm in diameter. The residues of sulfide-bearing "waste rock" and "tailings" are susceptible to chemical, microbial, and electrochemical oxidation in the presence of water and air (Eq. 1) [1–8].

$$FeS_2(s) + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad (1)$$

AMD formation is promoted by the large surface area of the particles, especially when tailings are left uncovered. Acidification can also occur within mine workings or around an open-pit mine often leading, in the latter case, to an acidified artificial lake. The total extent of acid production at a particular site is governed by the chemical composition and amount of the mined rock mass, the geology and hydrology of the site, and waste disposal routines [9, 10]. Modern mining operations attempt to prevent acidification, but AMD is endemic at older and abandoned mines. At least 23,000 km of streams and rivers, involving hundreds of thousands of sites, have been reported to be degraded by AMD in the US alone [11, 12].

Various microorganisms, notably *Acidithiobacillus ferrooxidans* (formerly *Thiobacillus ferrooxidans* [13]) catalyze oxidation of sulfides [14–19]. *Acidithiobacillus* species are aerobic autotrophs active over wide ranges of temperature and pH; indeed, active AMD is produced even in the permafrost regions of northern Canada [20–23]. *Acidithiobacillus ferrooxidans* thrives in the low pH and relatively low oxygen environments characteristic of abandoned mines and low-permeability tailings piles. Its multilayered cell wall allows it to maintain an approximately neutral internal pH even in extremely acidic external environments.

Acidification at the mineral surface results in a leachate with pH 2, and concomitant solubilization of iron and other metals in the tailings, some of which are toxic [24–26]. Extreme low pH values <0 have been recorded at the Iron Mountain site in California due to evaporation of water [27–32].

Subsequent oxidation of Fe(II) to Fe(III) (Eq. 2) occurs biologically and chemically. Admixture with uncontaminated water raises the pH of a typical AMD seepage as it migrates from its point of origin. This dramatically

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increases the rate of chemical oxidation of Fe^{2+} to Fe^{3+} by atmospheric oxygen (Eq. 3). Soluble Fe(III) can also oxidize pyrite to form more acid, along with sulfate and iron(II) (Eq. 4). Above pH 4, Fe^{3+} precipitates as $Fe(OH)_3$ or FeOOH (Eq. 5) [33], giving an unsightly gelatinous orange layer ("yellowboy") that smothers bottom-dwelling plant and animal life downstream of the AMD source.

$$Fe^{2+} + {}^{1}\!/\!{}_{4}O_2 + H^+ \rightarrow Fe^{3+} + {}^{1}\!/\!{}_{2}H_2O \quad (2)$$

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2 p(O_2) \quad (3)$$

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

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (5)$$

This review focuses on electrochemical approaches for the prevention, control, or treatment of AMD. Physicochemical technologies are introduced only briefly for comparison, because they have been extensively reviewed elsewhere [3, 34–39]. Prevention is the ideal option because it avoids the release of acid and metals into the environment. "Control" implies mitigation of acid formation and metal solubilization by amendment of the tailings body to control locally formed acid from seeping off-site. "Treatment" is the remediation of pre-formed AMD.

An advantage often cited for electrolytic technologies is the low cost of electricity (provided that the site needing remediation has access to the grid): at 8 ¢ per kWh, the cost of electrons is 0.5 ¢ per mol when the potential drop across the cell is 2 V. However, electrolytic processes are only economic when high current efficiencies can be achieved (i.e., most of the electrical energy is used to promote the desired chemical change) and the electrodes are durable, inexpensive, and not inactivated by fouling–deposition of insulating solids on their surfaces. Electrolytic remediation is inherently "green" provided that there is no need to "add a chemical to remove a chemical" because only electrons are used for oxidation and reduction. In the case of AMD, there is no need for an added supporting electrolyte to carry charge because AMD is inherently conductive. However, we must stress at the outset that no electrolytic technologies have yet supplanted their conventional counterparts in full-scale applications.

2 AMD prevention and control

2.1 Physico-chemical methods

Prevention of AMD requires the elimination of at least one of the four inputs of Eq. (1): sulfide minerals, air, water, and bacteria. No satisfactory methods have been developed for bacterial inhibition. In laboratory studies, bactericides have been shown to prevent acid formation from sulfide-bearing minerals. Anionic surfactants, such as sodium dodecyl sulfate (SDS) and alkyl- and aralkyl-sulfonates, kill bacteria by promoting transport of H^+ into the cell, disrupting homeostasis [40] but full bacterial control is rarely achievable [41, 42]. In addition, water-soluble surfactants leach away quickly [43] and are also toxic to aquatic organisms in general [44, 45]. Other ideas include using environmentally friendly surfactants [46] or natural sources of antioxidants, such as polyphenols to inhibit the growth of *A. ferrooxidans* [47, 48], but these materials are rarely available at AMD-impacted sites.

Most technical approaches to AMD prevention focus on exclusion of air from pyrite sources. Underground mine sealing can limit AMD formation at abandoned underground mines by restricting both the access of air into the mine, and the flow of water within and from the mine. Dry seals are barriers across a mine entrance where water does not drain. They are cheap, easy to build, and can be effective for long periods of time [49, 50], being constructed with concrete blocks, masonry, or concrete. These materials can be amended with fly ash or flue gas desulfurization (FGD) sludge, whose alkalinity helps to neutralize any acidic seepage. Wet seals, constructed from concrete blocks that have holes or pipes inserted in them to permit water flow but exclude air, can be used when water flow through the mine is unavoidable. However, they are prone to clogging, and often ineffective for long-term use. An alternative is the construction of a water-tight dam capable of resisting the maximum hydrostatic head that may develop in the flooded mine complex [49, 50].

Several preventative technologies have been developed to exclude air from finely divided sulfidic mineral tailings. Subaqueous tailings disposal can be used to inhibit AMD when hydraulic pressure converts abandoned pit mines into artificial lakes, provided both that the inflow of oxygenated water is low enough to maintain the deep lake anoxic [51], and that spring and fall turnover does not cause significant reoxygenation [52, 53]. The proposal of submarine disposal of tailings [54] risks resuspension of the tailings by tidal action [55] and contamination of fishing grounds with toxic metals [56, 57].

Above-ground covers also aim to exclude air from tailings piles [58]. In "dry" disposal, the reactive waste is situated entirely above the water table; "perched" layers are partly above and partly below the water table; at an "elevated" water table the reactive waste lies entirely below the water table and is thus waterlogged. All types of covers must be able to maintain water saturation and minimize oxygen diffusion for long periods, usually by providing a sealing layer over the tailings [51], to control erosion and provide improved esthetic appearance of the site if the cover can support sustainable vegetation [59]. Alkaline inorganic media, such as calcareous minerals, such as FGD sludge and pulverized steel-making slags, combine air exclusion with pH control [49]. Organic barriers (natural soil, sewage sludge, compost, straw, peat, wood waste, and paper mill sludge) also scavenge oxygen before it reaches the sulfide layer by promoting the growth of aerobic organisms, but tend to have limited useful life. However, none of these methods inhibit AMD formation completely [60].

The intentional formation of natural hard pans of ferricrete (iron-rich cement), silcrete (silica-rich cement), gypcrete (gypsum-cemented zone), or calcrete (calcite-cemented zone) restricts the flow of both water and oxygen. Full-scale implementation of this technology at two Australian mines inhibited AMD generation by 10–1000× [61].

Microencapsulation involves excluding air by coating tailings particles chemically. Drawbacks include the cost of treatment chemicals, incomplete coating of the particles, and the long-term stability of the chemical coating in highly acidic environments. Organic coatings, in particular, are costly and have poor long-term stability because they can act as a carbon source for microorganisms. Some examples, studied only at laboratory scale, include lipids [62–67], polyethylene polyamines [68–70], benzene-1,3-diamidoethanethiol (BDET) [71, 72], fatty acids [73–75], silanes [76, 77], and humic acid [78–81].

Inorganic approaches to coating involve formation of a highly insoluble iron phosphate, by oxidizing Fe(II) on the surface of the tailings particles (e.g., with H_2O_2, NaClO, or $KMnO_4$) in the presence of a phosphate (NaH_2PO_4, KH_2PO_4, phosphate fertilizer, phosphorite rock) and a buffer (CH_3COONa) [82–89] to prevent contact between pyrite and water and oxygen. While successful at the lab scale, the method suffers from short-term effectiveness in the field. Coating pyrite with silica has also been considered because the solubility of silica is less pH-dependent than that of phosphates [86, 90, 91] but the technique tends to be excessively complex and expensive [92]. Carrier-microencapsulation (CME) involves coating pyrite with a thin layer of metal oxide or hydroxide based on titanium [93] or silicon [94–96] oxides using catechol solution as a carrier. The CME coating was found effective in controlling pH drop during a one-month laboratory experiment even in the presence of iron-oxidizing bacteria.

Desulfurization employs froth flotation to produce a "high-sulfur" concentrate and a "low-sulfur" residue that can be used as an inert cover to protect the main tailings body from acidification [38, 97]. The key to desulfurization is the use of a hydrophobic "collector" (e.g., potassium amyl xanthate, with or without an "activator' of $CuSO_4$) that has high affinity for pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$, $x < 0.125$), which are preferentially concentrated into the froth [98, 99]. Desulfurization is unsuited to alkaline (cyanide-containing) tailings because the affinity of pyrite for the xanthate decreases in alkaline solution [100]. Desulfurized tailings from Doyon gold mine, Rouyn-Noranda, Quebec, reduced the release of zinc and copper to the leachates by >87 and 98 %, respectively, and lowered the oxygen flux available to reactive tailings up to 96 % [101, 102]. Desulfurized tailings have been used as a soil supplement to inhibit acid generation, and hence metal release, in the context of protecting browsing ruminants from metal uptake in plants [103]. However, the sulfur content of desulfurized tailings and the water table level are critical factors in reducing available oxygen through consumption and saturation, and frequently affords only modest efficacy [104].

2.2 In situ electrochemical prevention of AMD

Chesworth et al. [105, 106] first reported an electrochemical procedure involving cathodic protection of an ore body, as an alternative to preventing access by air. The cathode of the electrochemical cell is the tailings pile (or an exposed seam of pyrite), which must be partially submerged. A steel rod forms the electrical contact to the pyrite in the case of a seam, or a grid of metal mesh or graphite in the case of a tailings pile. An external circuit connects the cathode to the anode (scrap iron), which is submerged in the water body to be protected, which acts as its own supporting electrolyte. The process relies on long residence times of the water within the seam or mass.

The system was claimed both to inhibit the formation of AMD and to remediate the acidity already present—i.e., it represents both prevention and treatment simultaneously. As a prevention technology, it is a galvanic cell whose EMF polarizes the cathode (pyrite) so as to oppose its oxidation by air, and also decrease bacterial viability. However, the anode reaction involves oxidation of iron, which therefore acts sacrificially. The sacrificial property of the iron was enhanced by operating the cell electrolytically with an external DC supply. This method removes acidity in the pond via proton reduction at the cathode; the polarization of the pyrite cathode simultaneously inhibits further acid production. However, cathodic removal of H^+ is balanced stoichiometrically by dissolution of iron to Fe^{2+} at the anode, requiring replacement of the sacrificial anode. The cell was self-maintaining, with its own internal feedback system, depending on the acidity of the influent: an increase in pH lowered the cell potential and hence the current, while a decrease in pH had the opposite effect. Besides scavenging other potentially harmful metals from solution, the precipitate of iron(III) hydroxide also physically seals the seam or mass of pyrite against further oxidation [107–109].

Shelp et al. [110, 111] undertook a laboratory test of this concept using a block of massive sulfide/graphite rock from Sherman open-pit iron mine (Temagami, Ontario) as the cathode, scrap iron as the sacrificial anode, and acidic leachate collected from the mine site as the electrolyte. The resulting galvanic cell generated sufficient voltage and current to raise the pH of acid leachate from 3.0 to a maintenance value of 5.5; the initial EMF of 870 mV decreased to 292 mV during the 45 day-study while the current decreased from 4.9 to 3.5 mA, thus inhibiting the oxidation of sulfide minerals. Potentially toxic elements, such as Al, Cd, Co, Cu, Ni were removed from solution by sorption to a relatively stable Fe/Al sulfate precipitate.

Among other metals employed as sacrificial anodes in this experimental arrangement, zinc was superior to iron; the pH increased from 3.0 to a maintenance value of 6.7 over a 32-month period, and concentrations of toxic metals decreased to environmentally acceptable levels. However, the price of zinc would deter its use in AMD amelioration. Aluminum offered only a modest increase in pH from 3.17 to a plateau of 4.4 and failed to show a significant decrease of metal concentrations other than copper [112].

In an attempt to demonstrate the feasibility of extending this process from sulfide bedrock to tailings, Lin et al. [113, 114] carried out a bench-scale study with tailings from the 5 ha Falconbridge Hardy Mine Tailings Management Facility (Sudbury, Ontario). This deposit consists mainly of pyrrhotite overlain with 2–2.5 m of glacial fluvial sands and gravel [115, 116]. It behaves as a single semiconductor with electrochemical reactions occurring at the outer surface of the tailings body rather than on the surfaces of individual sulfide particles. Anodes were installed in the overburden at the 1.2 ha test area, with electrical contact to the tailings body (cathode), with DC power supplied through a rectifier. Oxygen was reduced in situ at the negatively polarized tailing/electrolyte interface, with the applied current density controlled by the rate of oxygen diffusion to the tailings, inhibiting the oxidation of sulfide minerals and release of metal ions.

In a promising variant of this approach, the whole electrochemical cell acted as a physical cover for the sulfidic tailings body, with the anode placed in the electrolyte of the cell above the cathode [117, 118]. Both anodes and cathodes were embedded in a water-retaining material, such as inorganic clay, silt, till, sand or gravel, or organic wood waste, wood chips, peat, animal, or municipal waste. The cathode, where oxygen reduction occurred, comprised either steel rods or mesh, or a layer of granular electrically conductive material, such as graphite, covering the entire body of tailings. As above, the electrochemical cell could operate either galvanically (with sacrificial anodes of iron, aluminum or magnesium) or electrolytically (with a chemically inert anode). The galvanic variant was demonstrated at the MSE Technology Applications, Inc site in Butte, Montana, with sacrificial Mg anodes and steel mesh cathode. Compared with untreated controls, the electrochemical cells retained total sulfur and pyritic sulfur at higher levels, but without significant trends in leachate sulfate, total sulfate, or pH [119].

A conceptual method, involving construction of a permeable layer of a mixture of particles of sulfide mineral in close contact with grains of a more electropositive material, has been described [120]. The protective layer comprises an ensemble of miniature galvanic cells in which particles of sulfide are cathodes and the other material (e.g., particles of iron) form sacrificial anodes. Electrical conductivity is achieved by contact between the grains of the different materials. The objective is to deoxygenate the water as it migrates into the tailings body, while simultaneously forming a protective coating of iron hydroxide on the pyrite grains.

3 AMD treatment methods

Remediation is required if formation of AMD has already occurred or is unpreventable, but does not prevent further acidification at the AMD source. The key consideration is to achieve an effluent stream that can be safely discharged to the environment, at the lowest cost. Treatment modalities may be directed towards removal of any or all of the following agents: acidity, sulfate, iron, or other (toxic) metal ions.

3.1 Chemical neutralization of AMD and chemical precipitation of heavy metals

Any suitable base can be used stoichiometrically to react with the acid formed during AMD. In the so-called active systems [121, 122] the neutralizing agent, oxidants, flocculants, and coagulants are often added simultaneously. The choice of base is determined mainly by what is conveniently, cheaply, and locally available. Bases include calcium carbonate (limestone), calcium hydroxide (hydrated lime), calcium oxide (pebble quicklime), sodium carbonate (soda ash), sodium hydroxide (caustic soda), and ammonium hydroxide [36, 49, 123–125]. Powdered limestone is cheap [$1 US (in 2005) per kmol of hydroxide equivalent], readily available, easy to apply, virtually non-toxic, and causes no handling or storage problems [126]. Hydrated lime ($4), soda ash ($21), caustic soda ($31), and ammonia ($8), are all more expensive and hence are used only in niche applications [125]. Basic by-products from pulp and steel mills [127, 128], coal-fired power plants

[129, 130], or quicklime manufacturing [131] can also be used.

The chief disadvantage of neutralization technologies is the precipitation of Fe(III) through oxidation of Fe(II) with either atmospheric oxygen (Eq. 2) or other oxidants. This gives a highly aqueous (95–98 % water), multi-constituent sludge that is difficult and expensive to dewater, because of the need for thickening and flocculating agents [49, 53, 132]. From limestone, the sludge comprises iron hydroxocarbonates, unreacted neutralizing agent, gypsum $CaSO_4{\cdot}2H_2O$, and toxic metals, such as Cd, Pb, Cu, Ni, or Cr that are partly co-precipitated. Approximately one ton of sludge (dry weight) is formed per ton of limestone (Eq. 6).

$$\begin{aligned}&FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O\\&\quad\rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2(g)\end{aligned}\tag{6}$$

Sludge density and settleability can be improved by seeding the solution, often by recycling the fine solids back into the reactor tank. Magnetized magnetite (Fe_3O_4) seed crystals have been used experimentally to produce a magnetically active sludge that co-precipitated Cu, Zn, and Mn. Rapid separation from the aqueous phase using a magnetic separator gave a final effluent with metal concentrations below the limits set for drinking water [133].

Anoxic limestone drains (ALD) constitute a passive in situ technology to isolate acid neutralization from iron oxidation and precipitation. They comprise cells or trenches of limestone that are covered to prevent the ingress of air, through which the AMD flows, affording an effluent at pH ~ 6, with subsequent oxidation of iron and sludge precipitation [35, 50, 125]. Many studies of ALDs have been performed from bench to field scale [134–138]. Drawbacks to the long-term use of ALDs include clogging with particulate matter and hydroxide precipitates. For example, $Al(OH)_3$ has minimum solubility near pH 6, and $Fe(OH)_3$ would form if the ALD was not completely anoxic (Eq. 2). The ALD must have sufficient capacity to neutralize all the acidity of the AMD even at peak flow volumes, and since the consumption of limestone is stoichiometric, its life-span is inevitably finite [49, 121].

Metals are precipitated with basic anions whose metal salts have small K_{sp} values, notably carbonates, hydroxides, and sulfides. All such salts become more soluble at low pH, and so metal removal is a by-product of chemical neutralization. $Ca(OH)_2$ and NaOH precipitate metals, such as Cu, Ni, Zn, Cd, Pb as hydroxides $M(OH)_2$ above pH 7; limestone and soda ash yield hydroxocarbonate precipitates. All these generate large volumes of relatively low density sludges that are hard to dewater [139–143]; also, certain complexing agents inhibit metal hydroxide precipitation [144].

Sulfides of heavy metals are usually highly insoluble and easier to dewater than hydroxocarbonates [144], leading to highly efficient metal removal over a wider pH range than hydroxide precipitation. Sulfide precipitants include solid (FeS, CaS), aqueous (Na_2S, NaHS, NH_4HS), and gaseous (H_2S) [145, 146]—although H_2S is both highly odorous and highly toxic. The process has been used in the context of AMD [147–149] including at commercial scale (ChemSulfide by BioteQ, Canada). In “active biological treatment” H_2S is generated biologically by sulfate-reducing bacteria (SRB) under anaerobic conditions in circum-neutral pH water. The process has been applied to AMD at pilot scale [150] and also commercially by ThioTeq (Paques, Nederland) and BioSulfide (BioteQ, Canada) [151].

In principle, heavy metals can also be precipitated by chelation. Trimercaptotriazine (TMT), Thio-Red potassium/sodium thiocarbonate (STC), and HMP-2000 sodium dimethyldithiocarbamate (SDTC) failed to remove divalent metals to meet US EPA standards [152]. In a laboratory study, MetX (disodium 1,3-benzenediamidoethanethiol), whose salts with soft Lewis acid metals are insoluble over a wide pH range, was used to remove metals from AMD at a coal mine in Pikeville, Kentucky [152, 153]. However, cost of the ligand is an obstacle to treating the vast volumes of AMD present at many sites, besides the question of the ultimate disposal of these precipitates. A successful niche application has been reported in which a solid aminobisphosphonate scavenged uranium (completely) and scandium (98 %) from water samples at Finnish mines by trapping the metal ions inside channels in this material without prior pH adjustment [154, 155].

3.2 Electrochemical neutralization of AMD

Electrolytic technologies applied to AMD remediation are seen as alternatives to chemical neutralization and precipitation. Conceptual advantages of electrochemical “acid neutralization” include (1) eventual formation of a sludge that is easier to dewater and less voluminous than that produced by chemical neutralization; (2) co-precipitation of most other (toxic) metals from the AMD, including arsenic; (3) in some variants, the formation of sulfuric acid as an exportable by-product from the anolyte, in place of importing a basic neutralizing agent (although recognizing the unfortunately low value of this commodity).

The essence of these approaches is some variation of electrochemical splitting of water, usually in an anion-exchanging divided cell using AMD as the catholyte and an uncontaminated solution, such as dilute sulfuric acid as the anolyte. The net result is the transfer of sulfuric acid from the catholyte (where H^+ is reduced to H_2) to the anode compartment (where water is oxidized to O_2 and H^+); migration of SO_4^{2-} into the anolyte maintains charge neutrality. Subsequently, the pH-adjusted catholyte can be aerated to oxidize Fe(II) to Fe(III), which precipitates. The catholyte must remain anoxic during electrolysis in order to avoid cathode fouling by iron; for this reason electrolysis of 'aged' AMD that already contains high levels of Fe(III) is probably impractical.

In the first report of electrolysis of a (synthetic) AMD, Tyco Laboratories (1972) [156] electrolyzed a solution containing iron(II) and sulfuric acid in an undivided cell with carbon anode and polished 316 stainless steel cathode. The objective was to provide an electrochemical alternative for the oxidation of Fe^{2+} (Eq. 7) to the relatively slow process of air oxidation (in acidic solution) or more expensive chemical oxidants, such as hydrogen peroxide or ozone, with remediation of acidity by reduction of H^+ to hydrogen gas (Eq. 8).

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \, (\text{anode}) \tag{7}$$

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2(g) \, (\text{cathode}) \tag{8}$$

$$\text{Net reaction: } Fe^{2+} + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\, H_2(g) \tag{9}$$

Because the ideal stoichiometry of Eq. 9 does not conform to Eq. (1), where $c(H^+) > c(Fe^{2+})$, complete reduction of H^+ would require oxidation of water at the anode (Eq. 10). In addition, the use of an undivided cell allowed unwanted reduction processes at the cathode (Eqs. 11 and 12).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{10}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$

$$Fe^{2+} + e^- \rightarrow Fe^0 \tag{12}$$

Stiller [157] used a sacrificial iron anode and a pyrite cathode in a galvanic cell that was divided with a sand barrier. The reduction of H^+ to H_2 at the cathode complemented the dissolution of iron to Fe^{2+}, which could be oxidized to Fe^{3+} by atmospheric oxygen outside the cell. In essence, this proposal involves the stoichiometric replacement of $2H^+$ by one Fe^{2+}; at a commercial scale, the cost and amount of iron would be prohibitive. Treharne and Wright [158] electrolyzed AMD from a mine exit in Lake Hope, Ohio, with a sand barrier to separate the catholyte and anolyte. Their concept was to pre-oxidize the AMD, which had metal content of 500–1000 ppm and pH 2.5, with ozone (produced from the oxygen formed at the anode). The AMD flowed sequentially from the anode compartment, where the acidity increased to pH 0.6, into the cathode compartment, where the pH increased by reduction of H^+ to H_2 (Eq. 8), with precipitation of Fe(III). However, competing reduction of Fe^{3+} to Fe^{2+} (Eq. 11) could not be suppressed completely. The treated water (at pH 6–8) had an iron content <1 ppm after passage through a sand filter to remove solids. It was suggested (but not proven) that the hydrogen evolved by Eq. 8 could be used to reduce the iron hydroxide precipitate to high iron content filings that could be extracted magnetically.

Several authors have combined water splitting with chemical neutralization of the anolyte, precipitating sulfate as $CaSO_4$ and recognizing that the two precipitates ($CaSO_4$ from the anolyte and FeOOH from the catholyte) are easier to dewater than the combined sludge produced by direct neutralization of AMD. The concept was demonstrated in control experiments with iron-free solutions and an anion-selective membrane to facilitate the migration of sulfate ions from the catholyte to the anolyte, where a recirculating lime slurry neutralized H^+ and precipitated ${SO_4}^{2-}$ [159, 160]. Friedrich and Knappnik [161] applied this concept to aged AMD from an open cast mine with pH 2.8 that principally contained Fe(III), Al(III), and sulfate. They used ceramic diaphragms or ion exchange membranes, an iron cathode, and a Pt–Ir-coated titanium anode. Fe(III) precipitated as the pH in the catholyte increased to 7.3, where it settled to the bottom of the cell (at high current densities metallic iron was also deposited). As an alternative to chemical neutralization of the anolyte, it was suggested that oxidation of sodium chloride might be used as the anode reaction, with the objective of selling chlorine as a by-product. However, the decreasing market for chlorine mitigates against this possibility.

Instead of pre-oxidizing iron, as done by Treharne and Wright [158], an alternative is to increase the pH of a catholyte electrochemically and then sparge with air to oxidize Fe(II) and hence precipitate Fe(III). This approach was used with a dimensionally stable anode (DSA) composed of $Ti/IrO_2–Ta_2O_5$, and cathodes of stainless steel, platinum, or reticulated vitreous carbon [162, 163]. In synthetic AMD, copper and nickel were partly removed by electrodeposition at the cathode; complete removal required precipitation of their hydroxides at high pH, along with anodic oxidation of water. The foregoing method was applied to aged AMD from nickel mining at the Clarabell Mine Tailing Area in Copper Cliff, Ontario, Canada [163]. More than >99 % of the iron was precipitated as the pH of the catholyte increased above pH 4, but mostly within the cell. Subsequently, Wang et al. [164, 165] applied this approach to the removal of arsenic from AMD, taking advantage of the strong chemisorption of inorganic arsenic to precipitates of iron(III) hydroxide [166–168].

3.3 Electrodialysis and electrokinetics

Electrodialysis (ED) involves the migration of ionic species through an ion-permeable membrane under the influence of an electric field rather than electrochemical processes of oxidation or reduction. It can thus be used to separate and pre-concentrate the ionic constituents of AMD, but it is inherently difficult to avoid long treatment times. The electrical charge balance in the cathode and anode compartments is maintained by electrolysis of water, affording OH^- and H^+ respectively. Typically a ‘stack’ of anion exchange (AEM) and cation exchange membranes (CEM) is arranged alternately with the format [Cathode − $[\text{CEM-AEM}]_n$ − Anode].

In the context of AMD, ED is limited by the need for a clean feed, free of particulate matter in order not to foul the membranes. With respect to the metal cations, the result of ED is a concentrated solution that could be considered for electrowinning or other treatment, and a diluate of reclaimed water. Buzzi et al. [169] electrodialyzed AMD having pH 2.4–4.5 from coal mining in Criciuma/SC Brazil, at laboratory scale, using a five compartment cell and electrodes composed of $70TiO_2$: $30RuO_2$. AMD was fed into the central compartment of the cell; all other compartments were initially filled with aqueous Na_2SO_4. Although >97 % of metal cations and sulfate anions were removed from the AMD compartment with little net pH change, the AMD became distributed among five streams; also, iron precipitates formed at the surface of CEM, unless a pretreatment step was included to remove iron. Recently, Marti-Calatayud et al. [170] recovered sulfuric acid from a synthetic AMD containing 0.02 M $Fe_2(SO_4)_3$ at pH 1.68, using a three-compartment ED cell separated by one CEM and one AEM: Fe(III) precipitated at the cathode.

Electrokinetic (EK) decontamination of mine tailings and tailings-impacted soils and groundwater involves the application of a low intensity electrical current through a porous matrix saturated with an electrolyte solution. Metal cations are attracted electrostatically to the cathode, but current density must be optimized for every application, as exemplified by the removal of lead from synthetically contaminated sandy soils (98.5 sand and 1.5 % clay) from the mining district of Zimapan, Hidalgo State, Mexico, at a current density of 0.024 mA cm^{-2} [171]. In the electrokinetic removal of arsenate at the Ylöjärvi mine in Finland, the competing anions oxalate and (especially) phosphate inhibited arsenic removal significantly [172]. Ryu et al. [173] achieved a two-fold reduction in energy usage by using a pulsed electric field for the electrokinetic remediation of a sample of surface soil from the abandoned Sambo mine at Youngduk, Republic of Korea, where the contaminating metals (Zn and Cd) were strongly bound to the soil matrix. EK has also been applied to 20-year-old copper mine tailings from the El Teniente smelter in Chile, VI region, using bipolar stainless steel electrodes to shorten the copper migration pathway and increase the effective conductivity of the acidified tailings [174]. Copper was precipitated as $Cu(OH)_2$ or deposited as Cu^0 on the cathodes (sulfuric acidified tailings, 20 V applied and 8-day treatment). The use of a pulsed variable electric field coupled with reversal of polarity gave sustained improvement in removal of copper, specific energy consumption, and current efficiency compared with conventional EK [175–179].

Electrokinetic technology has been improved by the introduction of ion exchange membranes to promote the migration of Cu^{2+} from the soil to the electrodes. In laboratory studies, with rather short path-length cell, dry tailings from the El Teniente copper mine samples were converted to a pulp at pH 2 by addition of sulfuric or citric acid. The removal efficiency improved at higher liquid-to-solid (L/S) ratios, by increasing the voltage, and by lowering the pH [180–184]. The mobility of the metal ions in the matrix could be enhanced by using a pulsed sinusoidal electric field and periodic polarity reversal [185, 186]. Aged tailings (>20 years) required stronger acid and longer pretreatment to liberate copper ions from the matrix [187, 188].

3.4 Electrocoagulation

Sacrificial metal anodes have been used to stimulate electrolytic metal precipitation in undivided cells. Electrocoagulation is achieved by co-precipitation of the sacrificial metal (Eq. 13) and the metals present in the AMD due to the increase of pH due to cathodic reduction of H^+ (Eq. 14). The drawback to all these technologies is the high cost of the sacrificial metal anodes.

$$\text{Anode: (e.g.) } Fe(s) \rightarrow Fe^{2+} + 2e^- \quad (13)$$

$$\text{Cathode: } H^+ + e^- \rightarrow {}^1\!/\!{}_2H_2 \text{ or } H_2O + e^- \rightarrow {}^1\!/\!{}_2H_2 + OH^- \quad (14)$$

Jenke and Diebold [189] used sacrificial steel, zinc, and lead anodes to treat both synthetic AMD and acidic waste solutions produced at the Butte, Montana operation of the Anaconda Mining Company. Metal hydroxide precipitates (from both the AMD and the sacrificial anodes) were formed in high pH zones near the cathode, even when the bulk pH was too low to stabilize the precipitates thermodynamically. At a sacrificial steel anode, with the final pH 4.7, Al and Cu precipitated quantitatively as well as 90 % of Zn. Manganese and magnesium were also precipitated when Zn anodes were used. Sacrificial Pb anodes were not useful for precipitating sulfate as $PbSO_4$, because the precipitate fouled the cathode. Smit [190] used sacrificial zinc anodes in an undivided cell to increase the pH of AMD and simultaneously precipitate sulfates and phosphates as zinc-hydroxo complexes. A claim was made for electrolytic recovery and reuse of the zinc anode, but this would seem to be very costly. Smith and Sloan [191] co-precipitated Zn, Al, Fe, Ni, Mn, Mg, Cd, and Cu from AMD using aluminum or iron as sacrificial anodes. Periodic polarity reversal was used to avoid cathode fouling and to promote even wearing of the electrodes, along with injection of air to promote oxidation of Fe(II).

Electrocoagulation using iron or aluminum anodes was used to treat AMD at the Bor-Drivelj-Cerovo copper mining and smelting complex in Serbia. The AMD had pH 2.63, heavy metals up to 610 mg/L, and sulfate up to 12 g/L. After pretreatment with CaO to raise the pH to 7, electrocoagulation removed >99 % of the heavy metals and >70 % of sulfate, to produce an effluent that could be discharged safely to the environment [192, 193]. Sacrificial aluminum anodes were used in a continuous filter press reactor to lower the concentration of arsenic from 24 to 1.8 μg/L and that of sulfate from > 35,000 μg/L by half, in a pH 7 mine drainage from Guanajuato Mexico, using current densities of 4 and 6 mA/cm^2 [194–196].

Kumarasinghe et al. [197] combined electrocoagulation with aluminum anodes followed by ultrafiltration for the removal of Cu, Pb, and Cd. Oncel et al. [198] compared chemical precipitation using NaOH with electrocoagulation for remediation of AMD from an abandoned coal mine in Turkey. The chemical method gave >99 % removal of Fe, Al, Zn, Si, Pb, Cr, and As at a final pH of 8; Ca (33 %), Sr (38 %) and B (25 %) were partly removed at pH 10. Electrocoagulation with iron electrodes achieved >99.9 % removal of these elements within 40 min at current density 50 mA/cm^2, with the final effluent having pH near 7. Electrocoagulation was the cheaper method 1.98 €/m^3 compared with 4.5 3 €/m^3 (pH 8) and 6.62 €/m^3 (pH 10) for chemical precipitation because of the large volumes of NaOH needed.

Green rusts are metastable compounds having the general formula $[\mathrm{Fe}^{\mathrm{II}}_{(6-x)}\mathrm{Fe}^{\mathrm{III}}_{x}(\mathrm{OH})^{x+}_{12}].[\mathrm{A}^{x-}_{x/n}].y\mathrm{H_2O}$, where A is an n-valent anion, such as $\mathrm{Cl^-}$, $\mathrm{CO_3^{2-}}$, or $\mathrm{SO_4^{2-}}$. Electrocoagulation has been used to produce green rusts and hence to precipitate iron from AMD [199, 200] although they can also occur naturally in AMD [201, 202]. Other metal ions can substitute for either the bivalent or the trivalent iron in green rusts, which have been used at the laboratory scale for removal of metals, such as Fe, Al, and Cu from real AMD sampled from four sites in the UK [203].

3.5 Electrowinning technologies

Electrowinning refers to cathodic deposition of metals from an aqueous solution (hydrometallurgy) as an alternative to conventional smelting technologies. Some tailings ponds contain millions of tons of potentially valuable metals besides iron. Nordstrom [6] has tabulated metal concentrations in several US mine waters, including the notorious Iron Mountain site in California, where concentrations of iron, zinc, and copper are 111, 24, and 5 grams per liter. These concentrations suggest that metal recovery might be a significant economic offset to remediation, possibly in tandem with preconcentration methods to enhance the viability of the electrowinning step.

Copper is an obvious target for electrowinning technology, as it is both valuable and less electropositive than $\mathrm{H^+}$ (E° ($\mathrm{Cu^{2+}}$) = +0.34 V), but the major interference is the presence of Fe(III). Clarke et al. [204] reported the electrochemical deposition of copper from AMD from the Berkeley Pit, Butte, Montana, and from the Penn Mine, Camanche Reservoir, California by deposition as a fine powder onto rotating cylinder electrodes; recovery of Zn, Fe, and Mn required prior removal of sulfate from solution and separation, for example by electrochemical ion exchange followed by electrodialysis. Laboratory scale experiments using this combined technology along with chemical oxidation of $\mathrm{Fe^{2+}}$ and pH adjustment gave 99.9 % removal of copper and 99 % of zinc, iron, and aluminum, the latter as $\mathrm{Al_2O_3}$, with minimal residual concentrations of toxic metals (As, Cd, Co, etc.) in the final effluent.

High recovery (over 99.9 %) of copper was also observed by Hatfield et al. [205] using simulated mine drainage water (pH 2.6, 150 ppm $\mathrm{Cu^{2+}}$) and a vertical flow-through cell containing a carbon felt cathode. However, the presence of Fe(III) was found to cause significant inhibition of the electrodeposition of copper from real AMD collected from Berkeley mine drainage pit in Butte, Montana [206]. Fe(II) did not inhibit electrodeposition of copper, but Fe(III) (E° ($\mathrm{Fe^{3+}/Fe^{2+}}$) = + 0.77 V compared with E° ($\mathrm{Cu^{2+}/Cu^0}$) = + 0.34 V) caused reoxidation (corrosion) of the copper deposit. Although iron could be removed as ferric oxides/hydroxides by aeration at pH 4–5 with >90 % retention of copper, the process was not considered commercially viable. Earlier, Loutfy and Bharucha [207] suggested reducing Fe(III) to Fe(II) (which does not inhibit copper deposition) by using copper powder or sulfur dioxide before electrodeposition of copper. Similar considerations underlie the approach of Paidar et al. [208] who used deaeration (to avoid oxidation of Fe(II)) prior to electrodeposition of copper from a mine drainage having pH 3.5 from Priest's Creek, Storwartz, Roros, Norway. Although this was a favorable case, in that the concentration of iron was only 10 ppm, but the current efficiency for copper was only 20 % due to its low initial concentration of 2 ppm.

A particularly favorable example for recovering copper from AMD was reported by Gorgievski et al. [209]. AMD from the former Cerovo copper mine in RTB Bor, Serbia, contains up to 1.55 g/L of copper at pH 3.4–3.6 with exceptionally low iron content (<10 ppm).

Electrodeposition of copper was achieved in a recirculating batch cell with a stainless steel grid anode and either porous copper sheet or carbon felt as cathode. The current efficiency was initially 80–100 % but decreased rapidly as $c(Cu^{2+}) < 0.3$ g/L.

Luptakova et al. [148] and Ubaldini et al. [210] electrolyzed a synthetic AMD whose composition was matched to that of the abandoned and flooded Smolnik mine in Slovakia, and respectively, a lead and zinc mine located in Tunel Kingsmill outlet of the Rio Yauli Peru using a Pt mesh cathode and Pt wire anode under potentiostatic conditions. Although simultaneous deposition of Zn at the cathode (99 % current efficiency) and MnO_2 at the anode (94 % current efficiency) was achieved, the process required preliminary removal of iron and aluminum by oxidation and precipitation to prevent electrode fouling..5

3.6 Fuel cells in the context of AMD

Cheng et al. [211, 212] have developed a fuel cell based on the chemistry of Eq. 15 in which the fuels are AMD and atmospheric oxygen.

$$Fe^{2+} + {}^{1}\!/\!{}_{4}O_2 + 2{}^{1}\!/\!{}_{2}H_2O = Fe(OH)_3(s) + 2H^+ \qquad (15)$$

Reaction 15 is mildly favorable thermodynamically under standard conditions ($\Delta G^0 = -27.15$ kJ per mol Fe)

$$\text{Anode:}\ Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^- \qquad (16)$$

$$\text{Cathode:}\ 1/4O_2 + H^+ + e^- = 1/2H_2O \qquad (17)$$

Using a carbon cloth anode, Pt-impregnated carbon cloth as the cathode, and separation with an anion exchange membrane, the cell generated a maximum power density of 290 mW/m^2 with current efficiency >97 %. Optimal power production was achieved at pH 6.3 and ferrous iron was completely removed by conversion to insoluble ferric iron in the anode chamber. The system has been modeled kinetically by Song et al. [213] and by Sun et al. [214], who described an air–cathode fuel cell to use the ferrous iron from a synthetic AMD for the fabrication of heterogeneous electro-Fenton catalysts [215, 216]. However, it is difficult to imagine implementation of such technologies at field scale, not least because of problems of electrode fouling by solid materials in the influent and the production of iron hydroxide precipitates during the process.

3.7 Bioelectrochemical systems

Bioelectrochemical systems (BESs) employ microorganisms to convert chemical energy from biodegradable waste into electrical energy. They are generally constructed of an anode and a cathode with options of being separated or of having various configurations depending on the task. Biodegradable materials, such as wastewater, are oxidized by microorganisms in the anode compartment and the flow of electrons generated can be used at the abiotic cathode for direct metal recovery (microbial fuel cells, MFC) or metal recovery with an external power supply supplement (microbial electrolysis cells, MEC), BESs with biotic cathodes have been also reported [217–219]. In the context of acid mine drainage, Lefebvre et al. [220] demonstrated at the lab scale the possibility of treating a synthetic AMD in the cathodic compartment of a microbial fuel cell. The anolyte, containing electrochemically active bacteria, included a complex (and expensive) mixture of nutrients, minerals, and vitamins to which sodium acetate was added as the carbon source and electron donor. Lefebvre et al. [221] used synthetic AMD comprising $FeCl_3$ at pH 2.4 as the catholyte, where the pH increased due to the $4e^-$ reduction of O_2 to water (the anolyte was kept anaerobic) Although Fe^{3+} was also reduced to Fe^{2+}, its concentration was maintained by the presence of O_2. Improved performance was obtained with membrane MFC; however, iron precipitated as the pH increased, causing irreversible damage to the membrane.

Luo et al. [222] demonstrated a microbial electrolysis cell (MEC) for simultaneous metal removal and hydrogen production from synthetic AMD solutions containing single and mixed metals and having a pH of 2.85; this was modeled on AMD from Dabaoshan mine, Guangdong Province, China. The MEC was a two-chamber reactor that employed a graphite brush anode and a cathode fabricated from carbon cloth with a platinum catalyst layer; these were separated by a bipolar membrane. The anodic medium contained sodium acetate, sodium mono- and di-hydrogen phosphates, ammonium and potassium chlorides, trace metals, and vitamins; the cathode chamber was filled with artificial AMD. A fixed voltage of 1.0 V was applied across the electrodes. In a single metal catholyte, Cu^{2+} was removed with 95 % efficiency after 24 h and >99 % after 42 h. Corresponding values for removal of Ni^{2+} were 87 % after 40 h and 97 % after 62 h, and 97 % for Fe^{2+} after 140 h operation. With mixed metals Cu^{2+} was first recovered at the cathode followed by Ni^{2+} and finally Fe^{2+}.

A microbial fuel cell for the remediation of sulfate using sulfate-reducing bacterium consortium in electroactive biofilm of zeolite has been reported by Angelov et al. [223]. However, despite intensive research directed towards wastewater treatment, power generation, bioremediation, desalination, and resource recovery, no-one has yet succeeded in demonstrating a BES at full scale with real waste water [224, 225].

4 Conclusions

The principal question under consideration is whether electrochemical methods can compete with conventional treatment methods for AMD. This review has considered several electrochemical approaches that have been advocated for AMD prevention or remediation, none of which has yet been implemented at full scale. With both the chemical and electrochemical approaches, many avenues have been explored in the laboratory that seem to have little prospect of being developed into full scale technologies.

Despite extensive experimentation, the attempts at prevention described in Sect. 2.2 still leave unanswered both technical and scientific questions. Technically, there is the difficulty of establishing the full electrical contact with the pyrite source, whether in the form of tailings (fine particles) or an inevitably fractured exposed seam. Scientifically, there remains doubt as to whether the cell that can be written as Eq. 18, truly operates as cathodic protection, or whether it is actually a galvanic cell in which the dissolving iron or other metal anode replaced H^+ stoichiometrically.

$$\mathrm{Fe} \mid \mathrm{Fe}^{2+}(\mathrm{aq}) \| \mathrm{H}^+ \mid \mathrm{H}_2/\mathrm{FeS}_2 \tag{18}$$

Considering treatment of AMD, there are four environmental detriments: (1) high acidity = low pH; (2) high iron concentrations; (3) high sulfate concentrations; (4) variable concentrations of other metals that may be toxic or a possible resource, depending on one's point of view. In rare cases, it may be possible to exploit AMD as a resource (e.g., copper) without attempting remediation, but if the objective is to render treated AMD acceptable for release to the wider environment, all four detriments must be addressed. It is difficult to imagine that a single technology could accomplish all these objectives at an acceptable cost, especially at legacy sites, the cost of whose remediation will fall on taxpayers. Complicating the matter is that most AMD sources exist at inaccessible locations, increasing the expense of conventional chemical treatments because of transportation costs, and of electrochemical processes because of remoteness from electrical power.

In terms of treatment technologies, electrolytic water splitting in a divided cell can be used to raise the pH of an AMD stream, while simultaneously increasing the acid concentration of the anolyte. Migration of the counter ion (sulfate) from the catholyte to the anolyte to restore charge balance results in the net transfer of sulfuric acid from the AMD (catholyte), to afford a "clean" sulfuric acid solution in the anolyte—or $CaSO_4$ could be produced by addition of lime. In principle, the effluent from the catholyte would then be suitable for air oxidation and precipitation of iron, which would incidentally co-precipitate much of the load of other metal ions. The advantage of this approach compared with chemical neutralization is a sludge that is less voluminous and more readily settlable. Unfortunately, there is unlikely to be a market for either gaseous hydrogen (from the catholyte) or moderately concentrated sulfuric acid (from the anolyte) at a remote location, although the acid could be used in hydrometallurgy if the mine is still operational. In this case also, opportunities may exist for the electrodeposition of valuable metals, notably copper, as an offset to the cost of remediation. Opportunities very likely exist for success with applications involving water splitting and electrowinning, also electrocoagulation and electrokinetic approaches.

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