

Acid mine drainage remediation options: a review

D. Barrie Johnson*, Kevin B. Hallberg

School of Biological Sciences, University of Wales, Bangor LL57 2UW, UK

Abstract

Acid mine drainage (AMD) causes environmental pollution that affects many countries having historic or current mining industries. Preventing the formation or the migration of AMD from its source is generally considered to be the preferable option, although this is not feasible in many locations, and in such cases, it is necessary to collect, treat, and discharge mine water. There are various options available for remediating AMD, which may be divided into those that use either chemical or biological mechanisms to neutralise AMD and remove metals from solution. Both abiotic and biological systems include those that are classed as “active” (i.e., require continuous inputs of resources to sustain the process) or “passive” (i.e., require relatively little resource input once in operation). This review describes the current abiotic and bioremediative strategies that are currently used to mitigate AMD and compares the strengths and weaknesses of each. New and emerging technologies are also described. In addition, the factors that currently influence the selection of a remediation system, and how these criteria may change in the future, are discussed.

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1. Acid mine drainage: nature of the problem

Acidic sulfur-rich wastewaters are the by-products of a variety of industrial operations such as galvanic processing and the scrubbing of flue gases at power plants (Johnson, 2000). The major producer of such effluents is, however, the mining industry. Waters draining active and, in particular, abandoned mines and mine wastes are often net acidic (sometimes extremely so). Such waters typically pose an addi-

tional risk to the environment by the fact that they often contain elevated concentrations of metals (iron, aluminium and manganese, and possibly other heavy metals) and metalloids (of which arsenic is generally of greatest concern). In 1989, it was estimated that ca. 19,300 km of streams and rivers, and ca. 72,000 ha of lakes and reservoirs worldwide had been seriously damaged by mine effluents, although the true scale of the environmental pollution caused by mine water discharges is difficult to assess accurately.

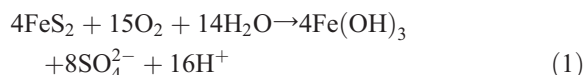
The origin of acidic metal-rich mine drainage waters has been described in detail elsewhere (e.g., Johnson, 2003). In brief, the major cause is the accelerated oxidation of iron pyrite (FeS_2) and other

* Corresponding author. Tel.: +44 1248 382358; fax: +44 1248 370731.

E-mail address: d.b.johnson@bangor.ac.uk (D.B. Johnson).

sulphidic minerals resulting from the exposure of these minerals to both oxygen and water, as a consequence of the mining and processing of metal ores and coals. Many metals occur chiefly as sulfide ores (e.g., zinc in sphalerite), and these tend to be associated with pyrite, which is the most abundant sulfide mineral on the planet. Likewise, coal deposits contain variable (generally 1–20%) amounts of “pyritic-sulfur” (a generic term that includes other iron sulfide minerals such as marcasite) as well as organic sulfur.

The often-quoted equation (Eq. (1)) summarising the complete process of pyrite oxidation is somewhat misleading in that (i) the primary oxidant involved in pyrite oxidation in most situations is ferric iron rather than molecular oxygen (Evangelou, 1995), and (ii) pyrite oxidation is a multistep process involving an oxygen-independent reaction (ferric iron attack on the mineral) and oxygen-dependent reactions (reoxidation of ferrous iron to ferric and oxidation of reduced sulfur compounds produced as intermediates in the process, ultimately to sulfate).



The regeneration of ferric iron (which is reduced to ferrous on reaction with pyrite) is the key reaction in promoting the ongoing oxidation of the mineral. At pH values above 4, this may be mediated chemically or biologically (by iron-oxidising bacteria such as *Gallionella ferruginea*), while below pH 4, abiotic iron oxidation is negligible (Stumm and Morgan, 1981), and the activities of moderately and extremely acidophilic iron-oxidising bacteria have a pivotal role in the genesis of acid mine drainage (Johnson and Hallberg, 2003).

Acid mine drainage (AMD) may form in underground workings (groundwaters) of deep mines, although this is generally of minor importance when a mine is in active production and water tables are kept artificially low by pumping. However, when mines are closed and abandoned, and the pumps turned off, the rebound of the water table can lead to contaminated groundwater being discharged, sometimes in a catastrophic event such as the one that happened at the Wheal Jane mine in 1992 when a range of contaminants entered the environment (Younger et al., 2004; Neal et al., 2004). Since as

the water that refills the mine dissolves any acidic salts that have built up on the pore spaces of the exposed walls and ceilings of underground chambers, this initial drainage water tends to be more potentially polluting (in terms of acidity and metal content) than AMD that is discharged subsequently (Clarke, 1995). Acidic metal-rich waters may also form in spoil heaps and mineral tailings, essentially by the same biologically driven reactions as in mine shafts and adits. Due to the more disaggregated (and more concentrated, in the case of tailings) nature of the acid-generating minerals in these waste materials, AMD that flows from them may be more aggressive than that which discharges from the mine itself. Another important consideration here is the potential long-term pollution problem, as production of AMD may continue for many years after mines are closed and tailing dams are decommissioned. Although the generic term acid mine drainage (or “acid rock drainage”) is used frequently to describe mine water discharges, the pH of these waters may be above 6, particularly at the point of discharge (where dissolved oxygen concentrations are frequently very low). In the case of iron and manganese, these metals are generally present in their reduced (Fe^{2+} and Mn^{2+}) ionic states in anoxic AMD, and these forms of the metals are much more stable at higher pH than the fully oxidised (Fe^{3+} and Mn^{4+}) ions. Some AMD streams remain neutral-to-alkaline, although others show a marked decline in pH as they oxygenate. This is because the total (or “net”) acidity derives both from “proton acidity” (i.e., hydrogen ion concentration) and “mineral acidity” (the combined concentration of soluble metals, notably iron, aluminium, and manganese, that produce protons when they hydrolyse). Net acidity in AMD needs to be offset against any alkalinity present; this is chiefly in the form of bicarbonate (HCO_3^-) deriving from the dissolution of basic minerals (e.g., calcium carbonate), though, as noted below, biological processes may also generate alkalinity in AMD streams.

2. “Source control” vs. “migration control” options

Given the axiom that “prevention is better than cure”, it is generally preferable, although not always pragmatic, to preclude the formation of AMD in the

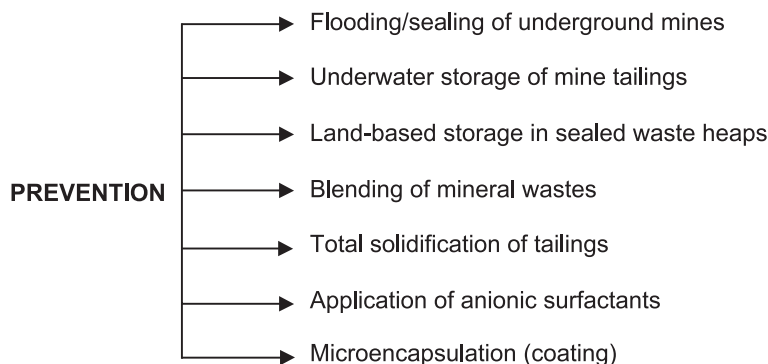


Fig. 1. Various approaches that have been evaluated to prevent or minimise the generation of mine drainage waters.

first instance. Such techniques are known collectively as “source control” measures (Fig. 1) and will be described only briefly.

In as much as both oxygen and water are required to perpetuate the formation of AMD, it follows that by excluding either (or both) of these, it should be possible to prevent or minimise AMD production. One way in which this may be achieved is by flooding and sealing abandoned deep mines. The dissolved oxygen (DO_2) present in the flooding waters (ca. 8–9 mg/l) will be consumed by mineral-oxidising (and other) micro-organisms present, and replenishment of DO_2 by mass transfer and diffusion will be impeded by sealing of the mine. However, this is only effective where the location of all shafts and adits is known and where influx of oxygen-containing water does not occur.

Underwater storage has been used for disposing and storing mine tailings that are potentially acid-producing (Li et al., 1997). Again, the objective is to prevent contact between the minerals and dissolved oxygen. Shallow water covers may be used, and their

effectiveness may be improved by covering the tailings with a layer of sediment or organic material, which has the dual benefit of limiting oxygen ingress and affording some protection against resuspension of the tailings due to the actions of wind and waves. Dry covers used for surface storage of reactive mineral spoils may also incorporate an organic layer (Fig. 2). The “sealing layer” that covers the spoil is usually constructed from clay, although in areas of the world that experience acute wet and dry seasons, drying and cracking of the cover can render it less effective than in temperate zones (Swanson et al., 1997).

Another suggested approach for minimising AMD production is to blend acid-generating and acid-consuming materials, producing environmentally benign composites (Mehling et al., 1997). A variant on this theme is to add solid-phase phosphates (such as apatite) to pyritic mine waste in order to precipitate iron (III) as ferric phosphate, thereby reducing its potential to act as an oxidant of sulfide minerals. However, inhibition of pyrite oxidation using this

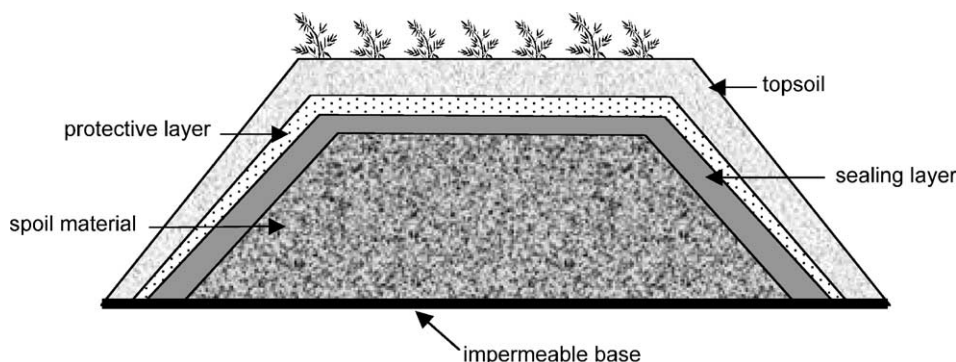


Fig. 2. Layout of a “dry cover” for minimising production of mine spoil effluents.

approach may only be temporary, due to the process of “armouring” of the added phosphate minerals (Evangelou, 1998). Application of soluble phosphate (together with hydrogen peroxide) is one of the “coating technologies” that has been developed by Evangelou et al. (described in Evangelou, 1998). The peroxide oxidises pyrite, producing ferric iron, which reacts with the phosphate to produce a surface protective coating of ferric phosphate. An alternative technique involving the formation of an iron oxide/silica coating on pyrite surfaces has also been described (Evangelou, 1998).

Finally, in as much as lithotrophic (“rock eating”) iron- and sulfur-oxidising bacteria have a pivotal role in generating AMD, various laboratory- and field-scale tests using biocides have been carried out to inhibit their activities in mineral spoils and tailings. This has generally involved the application of anionic surfactants such as sodium dodecyl sulfate (SDS), which are highly toxic to this group of microorganisms. However, the effectiveness of biocide applications has been found to be highly variable affording,

at best, only short-term control of the problem and requiring repeated applications of the chemicals (e.g., Loos et al., 1989).

Given the practical difficulties entailed in inhibiting the formation of AMD at source, often, the only alternative is to minimise the impact that this polluting water has on receiving streams and rivers, and the wider environment; such an approach involves “migration control” measures. Quite often, these have been divided into “active” and “passive” processes, the former generally (though not exclusively) referring to the continuous application of alkaline materials to neutralise acidic mine waters and precipitate metals, and the latter to the use of natural and constructed wetland ecosystems. Passive systems have the advantage of requiring relatively little maintenance (and recurring costs) than active systems, although they may be expensive and/or impractical to set up in the first place. In reality, all “passive” treatment technologies require a certain amount of maintenance costs. A more useful subdivision is between those remediation technologies that rely on biological activities and

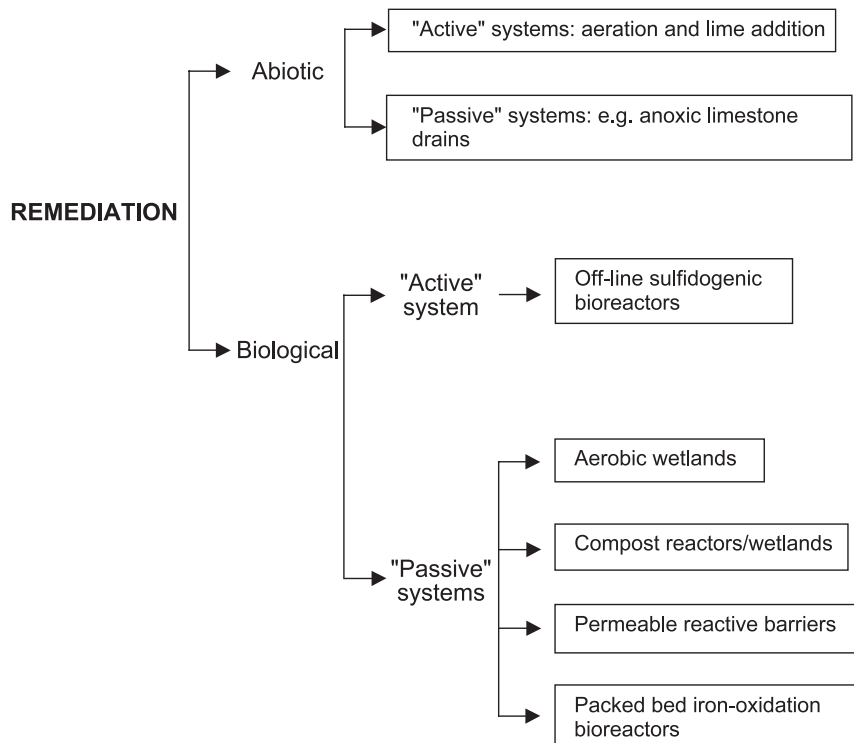


Fig. 3. Biological and abiotic strategies for remediating acid mine drainage waters.

those that do not. Within these major groups, there are processes that may be described as either “active” or “passive” (Fig. 3).

3. Abiotic remediation strategies

3.1. Active technologies

The most widespread method used to mitigate acidic effluents is an active treatment process involving addition of a chemical-neutralising agent (Coulton et al., 2003b). Addition of an alkaline material to AMD will raise its pH, accelerate the rate of chemical oxidation of ferrous iron (for which active aeration, or addition of a chemical oxidising agent such as hydrogen peroxide, is also necessary), and cause many of the metals present in solution to precipitate as hydroxides and carbonates. The result is the production of an iron-rich sludge that may also contain various other metals, depending on the chemistry of the mine water treated. Various neutralising reagents have been used, including lime (calcium oxide), slaked lime, calcium carbonate, sodium carbonate, sodium hydroxide, and magnesium oxide and hydroxide. These vary in cost and effectiveness; for example, sodium hydroxide is some 1.5 times as effective but is about nine times the cost of lime. Some removal of sulfate (as gypsum) is achieved when calcium-containing neutralising reagents are used. Although active chemical treatment can provide effective remediation of AMD, it has the disadvantages of high operating costs and problems with disposal of the bulky sludge that is produced.

While active chemical treatment is in its basic concept a low technology approach to AMD remediation, there have been a variety of refinements aimed at improving the efficiency of the process and reducing the problems associated with the bulky sludges produced. For example, multiple-stepped addition of reagents accompanied by pH control can result in the selective removal of some AMD components such as arsenic and molybdenum (Aube and Payant, 1997). Various flocculating reagents may be used to promote aggregation of precipitates, thereby aiding their removal in settling ponds. The iron-rich sludge produced by alkali addition is highly voluminous and water-rich, typically containing only 2–4% solids. Modifications to the technique, involving partial

recycling of sludge into lime-holding tanks can produce a sludge that contains ca. 20% solids, which further improves to ca. 50% solids on dewatering (e.g., Coulton et al., 2003a). The major advantage of a “high-density sludge” process is that costs of disposal and storage of the final product are greatly reduced.

3.2. Passive technology

An alternative approach for addition of alkalinity to AMD is the use of anoxic limestone drains (“ALD”; Kleinmann et al., 1998). The objective with these systems is to add alkali to AMD while maintaining the iron in its reduced form to avoid the oxidation of ferrous iron and precipitation of ferric hydroxide on the limestone (“armouring”), which otherwise severely reduces the effectiveness of the neutralising agent. Within the drain, the partial pressure of carbon dioxide is increased, accelerating the rate of limestone dissolution and consequently increasing the concentration of alkalinity, which may reach up to 275 mg/l compared to an open system which, in equilibrium, would produce only 50–60 mg alkalinity/l (Kleinmann et al., 1998). Inasmuch as, in theory, ALDs require minimum maintenance once constructed, their use is considered to be a passive approach to mine water treatment. In an ALD, mine water is constrained to flow through a bed of limestone gravel held within a drain that is impervious to both air and water (generally constructed of a plastic bottom liner and a clay cover). The dimensions of the drain vary from narrow (0.6–1.0 m) to wide (10–20 m) diameter, typically ca. 1.5-m deep and ca. 30 m in length.

Although anoxic limestone drains produce alkalinity at a lower cost than constructed compost wetlands, they are not suitable for treating all AMD waters. In situations where the AMD contains significant concentrations of ferric iron or aluminium, the short-term performance of anoxic limestone drains may be good, but the build up of hydroxide precipitates gradually decreases drain permeability, which may cause failure of the drain within 6 months of construction. Problems also occur where ALDs are used to treat aerated mine waters; passage of AMD through an anoxic pond prior to the anoxic limestone drain may be necessary to lower dissolved oxygen concentrations to levels required to prevent iron oxidation. Another potential drawback is that the formation of

ferrous carbonate and manganous carbonate gels within ALDs may cause the incongruent dissolution of the limestone gravel (Evangelou, 1998).

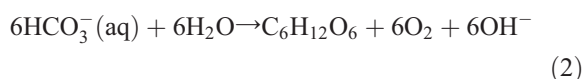
ALDs are generally used as one component in a passive treatment system, in association with aerobic and/or compost wetlands. Addition of ALDs to constructed wetlands that have been performing poorly has been reported to cause dramatic improvements in the quality of waters draining these systems (Kleinmann et al., 1998).

4. Biological remediation strategies

4.1. Significant biological processes

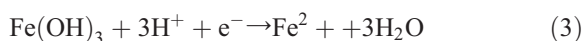
The basis of bioremediation of AMD derives from the abilities of some microorganisms to generate alkalinity and immobilise metals, thereby essentially reversing the reactions responsible for the genesis of AMD. While in aerobic wetlands constructed to treat AMD, macrophytes such as *Typha* and *Phragmites* spp. are the most obvious forms of life present, their direct roles in improving water quality have been questioned (Johnson and Hallberg, 2002).

Microbiological processes that generate net alkalinity are mostly reductive processes and include denitrification, methanogenesis, sulfate reduction, and iron and manganese reduction. Ammonification (the production of ammonium from nitrogen-containing organic compounds) is also an alkali-generating process. Due to the relative scarcity of the necessary materials (e.g., nitrate), some of these processes tend to be of minor importance in AMD-impacted environments. However, inasmuch as both ferric iron and sulfate tend to be highly abundant in AMD, alkali genesis resulting from the reduction of these two species has a potentially major significance in AMD-impacted waters. Photosynthetic microorganisms, by consuming a weak base (bicarbonate) and producing a strong base (hydroxyl ions), also generate net alkalinity (Eq. (2)).

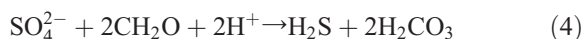


While the reduction of soluble ferric iron does not decrease solution acidity, the reduction of solid phase

(crystalline and amorphous) ferric iron compounds does, as indicated in Eq. (3), where e^- represents an electron donor, which is generally supplied by an organic substrate.



Bacteria that catalyse the dissimilatory reduction of sulfate to sulfide generate alkalinity by transforming a strong acid (sulfuric) into a relatively weak acid (hydrogen sulfide; Eq. (4)).



Besides the ameliorative effect on AMD brought about by the resulting increase in pH, the reduction of sulfate is an important mechanism for removing toxic metals from AMD, since as many (e.g., zinc, copper and cadmium) form highly insoluble sulfides (e.g., Eq. (5)).



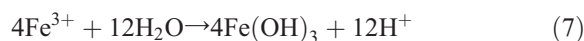
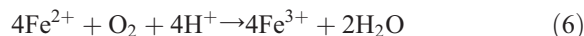
Biological oxidation of ferrous iron to ferric (which is highly insoluble above pH 2.5) is the other major metal-immobilising process that occurs in aerobic wetlands and bioreactors, as described in Sections 4.2 and 4.6.

As shown in Fig. 3, the majority of bioremediation options for AMD are passive systems, and of these, only constructed wetlands and compost bioreactors have so far been used in full-scale treatment systems. The major advantages of passive bioremediation systems are their relatively low maintenance costs, and the fact that the solid-phase products of water treatment are retained within the wetland sediments. On the downside, they are often relatively expensive to install and may require more land area than is available or suitable, their performance is less predictable than chemical treatment systems, and the long-term fate and stability of the deposits that accumulate within them are uncertain (Johnson and Hallberg, 2002).

4.2. Passive biological systems: aerobic wetlands

Aerobic wetlands are generally constructed to treat mine waters that are net alkaline. This is because the main remedative reaction that occurs within them is the oxidation of ferrous iron and subsequent hydrol-

ysis of the ferric iron produced, which is a net acid-generating reaction (Eqs. (6) and (7)).



If there is insufficient alkalinity in the mine water to prevent a significant fall in pH as a result of these reactions, this may be amended by the incorporation of, for example, an anoxic limestone drain (see above). In order to maintain oxidising conditions, aerobic wetlands are relatively shallow systems that operate by surface flow. Macrophytes are planted for aesthetic reasons to regulate water flow (e.g., to prevent channelling) and to filter and stabilise the accumulating ferric precipitates (ochre). They also provide additional surface area for precipitation of solid phase ferric iron compounds and minerals. In addition, by causing oxygen flow from aerial parts to their root systems, some aquatic plants may accelerate the rate of ferrous iron oxidation.

There has been some debate as to whether iron oxidation in aerobic wetlands is exclusively abiotic or accelerated, at least in part, by microorganisms. The Eq. (8) that describes the rate of ferrous iron oxidation in aqueous environments, as postulated by Stumm and Morgan (1981), indicates that both oxygen concentration and pH are important parameters in dictating how quickly iron oxidises.

$$\frac{d[\text{Fe}^{2+}]}{dt} = \frac{k[\text{O}_2] \cdot [\text{Fe}^{2+}]}{[\text{H}^+]^2} \quad (8)$$

However, as noted by Stumm and Morgan (1981) and illustrated in Fig. 4, at pH values of <4, the rate of iron oxidation is effectively independent of pH. Inasmuch as most aerobic wetlands operate at near-neutral pH, it follows that chemical oxidation of ferrous iron will proceed rapidly, although the presence of neutrophilic iron-oxidising bacteria, that live at the interface of aerobic and anaerobic zones (e.g., *Gallionella ferruginea*) and those that break down organically complexed iron (such as *Leptothrix* spp.), does imply that there, these contribute to iron oxidation in these passive systems (D.B. Johnson, unpublished data).

A second major remediative process that occurs in aerobic wetlands receiving AMD is the removal of

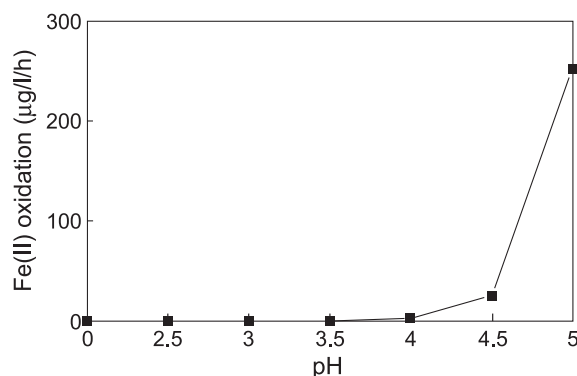


Fig. 4. Abiotic ferrous iron oxidation as a function of pH, calculated from Stumm and Morgan (1981) for an aqueous solution of 10 mM ferrous iron containing 8 mg O₂/l.

arsenic, originating primarily from the oxidative dissolution of arsenopyrite (FeAsS) present in mine waste materials. Soluble arsenic, which is present mostly as anionic As (V) (AsO₄³⁻) in mine waters, may be removed mainly by adsorption onto positively charged ferric iron colloids and, in theory, by the formation of scorodite (FeAsO₄). Interestingly, novel strains of *Thiomonas*-like bacteria that oxidise arsenic (III) to arsenic (V), as well as oxidising ferrous iron and reduced sulfur compounds, have been isolated from mine waters (Battaglia-Brunet et al., 2002; Coupland et al., 2003). These bacteria probably contribute to removal of arsenic in these waters and have potential for use in fixed bed bioreactor systems similar to those described in Section 4.6 for the oxidation and precipitation of iron.

4.3. Passive biological systems: anaerobic wetlands/compost bioreactors

In contrast to aerobic wetlands, the key reactions that occur in compost bioreactors used to mitigate AMD are anaerobic. The term “compost bioreactor” is a preferable generic term to describe such systems, as in some installations (such as those at the Wheal Jane site), they are enclosed entirely below ground level and do not support any macrophytes, so that they should not be described as “wetlands”. Indeed, whether or not macrophytes are used in constructed compost ecosystems is often down to aesthetic considerations alone. Penetrating plant roots may cause the ingress of oxygen into the anaerobic zones, which is detrimental to reductive processes.

The microbially catalysed reactions that occur in compost bioreactors generate net alkalinity and biogenic sulfide (Eq. (4); Section 4.1), and therefore, these systems may be used to treat mine waters that are net acidic and metal-rich, such as AMD from abandoned metal mines. Again, in contrast to aerobic wetlands, the reductive reactions that occur within compost wetlands are driven by electron donors that derive from the organic matrix of the compost itself. The choice of bulky organic materials used vary according to local availability as well as their proven effectiveness, although generally, the composts are prepared by mixing relatively biodegradable materials (e.g., cow or horse manure, or mushroom compost) with more recalcitrant materials (e.g., sawdust, peat, or straw). The slow biodegradation of the latter is presumed to act as a long-term provision of appropriate substrates (and ammonium) for the indigenous iron- and sulfate-reducing bacteria (FRB and SRB) that are generally considered to have the major roles in AMD remediation in compost bioreactors. However, there are few quantitative data on the relative significance of iron and sulfate reduction in compost wetlands (Vile and Wieder, 1993), and virtually, nothing is known about how the microbiology of these systems changes as the ecosystem ages, especially with regard to substrate provision. Besides biologically mediated processes, AMD quality in compost wetlands is improved by filtration of suspended and colloidal materials and adsorption of metals by the organic matrix.

An important engineering variant on the basic compost bioreactor theme is the reducing and alkalinity producing system (RAPS) layout (Younger et al., 2003), which is also referred to as successive alkalinity producing system (SAPS; Kepler and McCleary, 1994). In this type of system (Fig. 5), AMD flow moves downwards through a layer of

compost (to remove dissolved oxygen and to promote the reduction of iron and sulfate) and then through a limestone gravel bed (to add additional alkalinity, as in ALDs). Usually, water draining a RAPS flows into a sedimentation pond, and/or an aerobic wetland, to precipitate and retain iron hydroxides.

4.4. Passive biological systems: composite aerobic and anaerobic “wetlands”

Passive bioremediation systems that utilise a combination of aerobic and anaerobic wetlands have been used for full-scale treatment of AMD. An example is the “Acid Reduction Using Microbiology (ARUM)” system (Kalin et al., 1991). This system comprises of two oxidation cells within which, iron is oxidised and precipitated; beyond these, AMD passes first through a holding cell, and then through two “ARUM” cells within which, alkali and sulfide are generated. The organic materials that promote sulfate reduction in the ARUM cells originate from floating macrophytes (e.g., cattails). The ARUM systems have been shown to be effective in treating AMD in high latitude and subtropical locations (Kalin and Chaves, 2001). The passive treatment plant at the Wheal Jane site is also a composite system.

4.5. Passive biological systems: permeable reactive barriers

Permeable reactive barriers (PRBs) are being used increasingly to treat a wide range of polluted groundwaters. Those that have been installed to bioremediate AMD operate on the same basic principles as compost bioreactors, described in Section 4.3 (Benner et al., 1997). Construction of PRBs involves digging of a trench or pit in the flow path of contaminated groundwater, filling the void with reactive materials

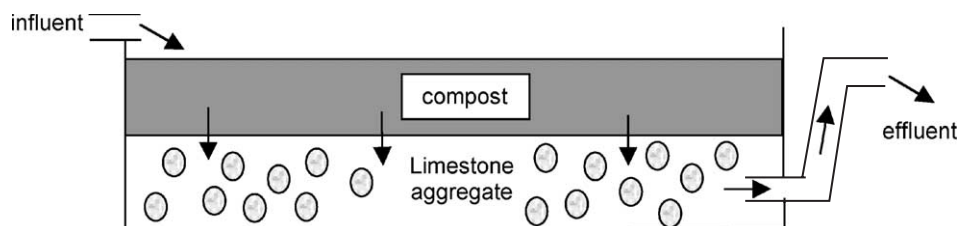


Fig. 5. Schematic layout of a reducing and alkalinity producing system (RAPS), redrawn after Younger et al. (2003). Water flowing through the compost layer is stripped of dissolved oxygen, while both this layer and the underlying limestone add alkalinity to the AMD.

(a mixture of organic solids and possibly limestone gravel) that are sufficiently permeable to allow unimpeded flow of the groundwater, and landscaping of the disturbed surface. Reductive microbiological processes within the PRB generate alkalinity (which is further enhanced by dissolution of limestone and/or other basic minerals) and remove metals as sulfides, hydroxides, and carbonates. The largest PRB yet constructed has been installed to remediate extremely acidic groundwater emanating from a large pyritic shale waste dump in Shilbottle, northeast England (Younger et al., 2003). The PRB is 180-m long, 3-m deep, and 2-m wide and consists of a mixture of composted horse manure and straw (25%), composted green waste (25%), and limestone (50%).

4.6. Passive biological systems: iron-oxidising bioreactors

The oxidation of ferrous iron to ferric in acidic (pH<4) mine waters is greatly accelerated by iron-oxidising prokaryotes (bacteria and archaea), many of which are autotrophic (i.e., like green plants, they fix inorganic carbon and have minimum nutritional requirements). The most well-studied of these bacteria is *Acidithiobacillus ferrooxidans*, an obligate acidophile that also oxidises a variety of reduced inorganic sulfur compounds. The rate-limiting factor in biological iron oxidation is often the numbers of iron-oxidising bacteria present, and several research groups have sought to address this by immobilising *At. ferrooxidans* onto a solid matrix, forming the basis of packed bed reactors or biological contactors. Iron oxidation rates of up to 3.3 g/l/h have been recorded in packed bed bioreactors (Long et al., 2003). Research in this area has concentrated on the perceived advantages (or otherwise) of different support media for the bacteria and have focussed exclusively on a single species of iron oxidiser *At. ferrooxidans*. This is somewhat unfortunate, as it is now known that a considerable biodiversity of ferrous iron-oxidising prokaryotes exists (Hallberg and Johnson, 2001), each having different affinities for ferrous iron, temperature and pH optima, etc. It would be anticipated that different species of iron oxidisers would be more appropriate to some situations than others, e.g., moderately acidophilic *Thiomonas* spp. to accelerate iron oxidation in mine waters of pH above

3. Biological considerations, rather than immobilisation strategies, might therefore be more important in optimising iron oxidation in packed bed bioreactors.

5. Active biological systems: sulfidogenic bioreactors

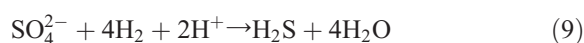
Off-line sulfidogenic bioreactors represent a radically different approach for remediating AMD (Johnson, 2000; Boonstra et al., 1999). These engineered systems have three potential advantages over passive biological remediation: (i) their performance is more predictable and readily controlled; (ii) they allow heavy metals, such as copper and zinc, present in AMD to be selectively recovered and reused; and (iii) concentrations of sulfate in processed waters may be significantly lowered. On the negative side, the construction and operational costs of these systems are considerable.

Sulfidogenic bioreactors utilise the biogenic production of hydrogen sulfide to generate alkalinity and to remove metals as insoluble sulfides, which is one of the processes that occurs in compost bioreactors and PRBs. However, off-line sulfidogenic bioreactors are constructed and operated to optimise production of hydrogen sulfide. Inasmuch as the SRB currently used in these reactors are sensitive to even moderate acidity, the systems have to be engineered to protect the microorganisms from direct exposure to the inflowing AMD.

At least two technologies using off-line sulfidogenic bioreactors have been described: the Biosulfide and the Thiopaq processes. The Biosulfide system has two components, one biological and one chemical, which operate independently (Rowley et al., 1997). Raw AMD enters the chemical circuit where it comes into contact with hydrogen sulfide generated in the biological circuit. By careful manipulation of conditions (pH and sulfide concentration), selective separation of a particular metal sulfide is possible; this may then be removed from the partially processed water ahead of further treatment. Some of the treated AMD enters the biological circuit to provide the sulfate source in the bioreactor, which contains a mixed culture of SRB. For the process to run optimally, additional alkali may be required beyond that produced by the SRB, in which case, it is added

in chemical form. The Thiopaq system differs from the Biosulfide process in that it utilises two distinct microbiological populations and processes: (i) conversion of sulfate to sulfide by SRB and precipitation of metal sulfides and (ii) conversion of any excess hydrogen sulfide produced to elemental sulfur, using sulfide-oxidising bacteria. The Thiopaq process has been operating successfully in treating zinc-contaminated groundwater at the Budelco zinc refinery in the Netherlands since 1992. The zinc sulfide produced is fed into the refinery and is incorporated into the metallic zinc product from the plant. Application of this technology to AMD has also been demonstrated on a pilot-scale at the Kennecott Bingham Canyon copper mine in Utah, where >99% of copper present in a pH 2.6 waste stream was selectively recovered (Boonstra et al., 1999).

SRB are, in general, heterotrophic bacteria and, unlike the iron-oxidising acidophiles described earlier, require provision of organic material as carbon and energy sources. In the first sulfidogenic bioreactor set up at the Budelco refinery, this was provided in the form of ethanol. However, hydrogen may substitute as electron donor for sulfate reduction (Eq. (9)).



The use of hydrogen is advantageous because it is more economical to use for high sulfate loadings and results in lesser production of bacterial biomass. Hydrogen may conveniently be formed by cracking methanol or from natural gas. In both cases, carbon dioxide is also produced, and some SRB are able to fix this as their source of carbon (Boonstra et al., 1999).

6. Remediation options: factors in decision making

The choice of which option to use to remediate AMD is dictated by a number of economical and environmental factors. Sometimes the true environmental cost of a remediation system is not immediately apparent. One such cost is the amount of fossil fuel energy needed to transport liming materials, often long distances from source to mine sites (such as at the Wheal Jane mine in Cornwall, where the lime is transported several hundred kilometres from a site in

the midlands of England). Traditionally, large discharge volume mine waters have been treated by active chemical processing, particularly when the waters are acidic. The necessary land surface area and topographic problems may rule out passive biological systems in some situations. However, the mining industries are becoming increasingly attracted to the latter, as they avoid the high recurrent costs of lime addition and sludge disposal. The land areas (“footprints”) required for passive systems can, in theory, be made dramatically smaller by focussing on optimising biological processes, for example, packed bed bioreactors for removing iron from acidic mine waters, which are far more effective than aerobic wetlands. It does need to be recognised that, in reality, none of the remediation systems described in this review are maintenance-free; passive systems also require a certain amount of management and will eventually fill with accumulated ochre (aerobic wetlands) and sulfides (compost bioreactors). The long-term stabilities of these materials are uncertain, but since as they may contain toxic elements (arsenic, cadmium, etc.), their storage or disposal requires careful consideration.

The sustainability of any remediation system is a factor that is becoming increasingly critical in decision making. One of the problems here is that products of AMD remediation have not been perceived as a resource. However, this view may be changing. Recently an iron oxide sludge recovered from a drainage channel at an abandoned coal mine in Pennsylvania has been used to manufacture burnt sienna pigment in a commercially successful venture (Hedin, 2003), and base metals recovered by active biological treatment of AMD from metal mines provide some financial return on the investment and running costs of sulfidogenic bioreactors.

Ultimately, legislation is likely to become the dominant factor in determining which remediation system can be used in any situation. For example, it might become increasingly untenable to dispose of base metals in sludges and sediments (with all of the inherent storage problems) when there are technologies available for their recovery and recycling. Limits on the concentration of sulfate that can be discharged from processing plants may restrict the choice of a system to one that effectively removes sulfate as well as metals and acidity from mine waters. One certainty

is that the problem of what to do about the pollution threat posed by AMD will be with us for very many years to come.

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