Restoration of Acid Drainage

W Geller, M Koschorreck, M Schultze, and K Wendt-Potthoff, UFZ-Helmholtz Centre for Environmental Research, Magdeburg, Germany

Introduction

Acid drainage (AD) originates from geogenic sources after sulfidic minerals have been oxidized to sulfuric acid and metal hydroxides. This process may also arise from mining on metal ores or coal, from agricultural use of sulfidic soils, or naturally from weathering of pyritic seams and soils. Volcanic activities may be sources of AD, too. The often extremely metal-loaded ADs cause severe impacts on fresh waters and coastal waters, and the respective aquatic organisms and ecosystems. The contaminated waters cannot be used for fishery, aquaculture, irrigation, and supply for drinking water.

Acid drainage from mining activities is a serious environmental problem worldwide. The total extent of polluted rivers and streams in the United States was estimated to 19 000 km and 730 km^2 of lake and reservoir areas. In the United Kingdom, the mine drainages are affecting river stretches of ~600 km – an equivalent estimate for Europe leads to ~5000 km. Contaminations coming from natural causes appear as unavoidable, for example the acidification of Rio Tinto by weathering of the Pyrite Belt in Southern Spain, or of river contaminations at active volcanoes. Despite their sometimes dangerous metal content, waters of volcanic origin are used in some countries for irrigation of agricultural areas. Sulfidic soils exist in coastal areas and estuaries worldwide, and they are known to lead to acidic sulfate soils after lowering the water table, with drainage water problems similar to acid mine drainage (e.g., Bangladesh, South-East Asia, Australia, and Finland).

This article is a short survey of the current state of the restoration measures aiming to make AD-water neutral and to eliminate toxic metals, aluminum, and iron.

Processes Controlling Acid Drainage (AD, AMD)

Definitions and Dimensions

Acid mine drainage (AMD) is the special type of AD resulting from mining. The term acid rock drainage (ARD) is often used as a synonym.

The terms alkalinity and acidity are defined differently. Acidity can be measured directly by titration, usually with a solution of 0.01 N sodium hydroxide, resulting in a measure of [mmol l^{-1}], or [meq l^{-1}]. Acidity can be calculated from the major acidic chemical components of water (Fe, Al, Mn [mg l^{-1}], and pH) in the range of pH 2–5 by the following equation:

$$\mathrm{Acid_{calc}[meq\ l^{-1}]} = 2^*\mathrm{Fe}^{2+;}/56 + 3^*\mathrm{Fe}^{3+}/56 + 3^*\mathrm{Al}/27 + 2^*\mathrm{Mn}/55 + 1000^*10^{-\mathrm{pH}} \qquad [1]$$

According to U.S. standards, acidity is measured by the amount of $CaCO_3$ to be added for reaching neutrality. The dimension [meq l^{-1}] can be converted to [mg $CaCO_3$ l^{-1}] by the factor 50:

$$\mathrm{Acidity[meq\ l^{-1}]} \times 50 = [\mathrm{mg\ CaCO_3\ l^{-1}}] \qquad [2]$$

Acidification by Oxidation of Metal Sulfides

Sulfidic ores or the pyrite components of the removed overburden of coal are exposed to oxygen during the mining process, and the sulfides are oxidized. The most important and most acidifying process is the oxidation of pyrite resulting in sulfuric acid, ferrous iron, and H$^+$-ions (eqns [3]–[6]). The given actual state of the system should not be considered alone by thermodynamic equilibrium calculations. The multistep reactions occur in a heterogeneous system and are usually mediated and kinetically controlled by catalytic activities of iron and sulfur bacteria. Once they are formed, the acids are stable as long as the system is aerobic.

$$\mathrm{FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+} \qquad [3]$$

$$\mathrm{Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O} \qquad [4]$$

$$\mathrm{Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+} \qquad [5]$$

$$\mathrm{FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+} \qquad [6]$$

Since acidity is increasing by oxidation, the titration of (anaerobic) samples should be done after hot chemical oxidation of Fe and Mn with peroxide to measure the full acidification potential (= hot acidity).

Accompanying the geogenic acidification, further problems arise beyond low pH and high acidity:

- the oxidation of sulfides leads to rising concentrations of dissolved solids, and
- particularly that of sulfate in the drainage waters.
- many of the mobilized metals are toxic.

Characteristics of Acid Drainage

The content of total dissolved solids of acid waters increases from about 50 mg l^{-1} at pH 5 in rain-acidic soft waters to 100 g l^{-1} at pH 0 in extremely acidic brines of volcanic springs. The spectrum of dissolved elements depends on the kind and concentration of the involved mineral acids, and the composition of the thereby dissolved rock or minerals. There are four major types of acid drainages (AD) from different geogenic sources (Table 1). The AD-waters from acid sulfate soils (ASS) and coal mining both show acidities up to 20–25 meq l^{-1} and sulfate concentrations to 2 g l^{-1}. The waters from ore mining and from volcanic sources can reach higher values by one order of magnitude.

1. AD from abandoned underground workings, overburden and dumps of coal mining, both deep and surface mining of hard coal and lignite. The acidity is released by oxidation of iron sulfide minerals, usually pyrite.
2. AD from abandoned underground workings, waste rock dumps, and tailings from mining of sulfidic ores, the dumps of which contain a geologically given spectrum of elements, that is left back after extracting the wanted metals.
3. AD from acid sulfate soils (ASS) have the same mineral source, iron sulfides that have been formed under anaerobic conditions after reduction of iron and sulfate in estuaries, coastal lagoons, and in wetlands of river floodplains. The acidity is set free by oxidation, after lowering the ground water by drainage and aeration of these soils.
4. AD from volcanic sources. Here, several mineral acids (SO_2, HCl, HF) are set free in hot areas, that completely dissolve the given rock, thereby releasing the full spectrum of metals and nonmetallic elements.

Untreated AD has been operationally defined by two basic types. The first type has oxic water, low pH, and high acidity. The second type appears in anoxic water, typically groundwater, and has higher pH values, combined with a hidden, potential acidity, which becomes apparent if the water is aerated. Thereby, this 2nd type AD is converted to 1st type AD. Although the pH values of AD mainly range between 2 and 4, negative pH values of −2.5 were found in old adits in Iron Mountain, California.

Source Control: Avoidance and Mitigation of AMD by Operating Mines

The avoidance of AMD is applied in modern mining and is based on two approaches.

1. Dosing of alkaline substances (e.g., limestone, lime, dolomite, soda ash, ashes of power plants) during deposition is applied in modern mining and results in minimizing the flux of metals and acidity. Mixed deposition with calcium bearing substances may limit the sulfate concentration in the drainage by precipitation of gypsum. The remaining sulfate concentrations, however, are still high (<1500 mg l^{-1}) because of the solubility of gypsum.
2. Minimizing the flow of effluent water and to immobilize the oxidation products are further suitable approaches to decrease the export of products of pyrite oxidation. Limiting the availability of oxidants (e.g., oxygen, ferric iron) is, therefore, an often used approach. Capping of pyritic material with reducing organic matter is used as well as the capping with water. Accordingly, pyritic materials were deposited on lake bottoms and impoundments under a permanent water cover (subhydric deposition). The rapid filling of underground mines or residual voids of open cast mines is based on the same idea.

   Since ferric iron is often the main oxidant in pyrite oxidation, the treatment of pyritic material by phosphate was found to be successful. Ferric

Table 1 Typical ranges of most important parameters of acid drainage, derived from data on water with pH<6

Source of AD	*Coal/lignite mining*	*Ore mining*	*Acid sulfate soils*	*Volcanic waters*
pH value	2.8–5.0	2.3–4.0	2.9–4.1	0.9–4.5
Acidity (meq l^{-1})	1–25	5–450	0.3–20	0.3–500
Sulfate (mg l^{-1})	400–2500	1000–20 000	150–1500	100–12 000
Iron (mg l^{-1})	5–350	25–7500	0.5–40	0.1–150
Aluminum (mg l^{-1})	1–40	20–1000	5–150	1–500
Comments:	Heavy metals and arsenic may reach high concentrations (g l^{-1})		Acids HCl or HF may be more important than sulfuric acid	
	Water of underground origin tends to be anoxic with pH 4–6.			

phosphate is precipitating, binding the oxidant ferric iron on one hand, and forming coatings on the pyritic surfaces which mitigate the further attack of oxidants and bacteria (microencapsulation).

The Restoration of Acid Drainage

Beyond the avoidance and mitigation of AMD by measures of source control the problems of acid drainage can be approached with restoration technologies:

1. Water treatment plants: active or passive technologies to remove contaminants in acid drainages.
2. In situ treatment of acid ground water and pit lake management, which is necessary to avoid or to remediate acidification and metal loadings appearing in flooded mining voids after surface mining.

To avoid or remediate the damage and impacts of acid drainage, the restoration of AD-water aims:

- to neutralize the water to pH values between 6 and 8;
- to eliminate toxic metals like Ni, Cu, Cd, etc., and to decrease dissolved aluminum and ferric/ferrous iron. Dissolved iron is not toxic, but it is causing ochreous precipitations after mixing with neutral fresh or sea water, thereby degrading impacted ecosystems in the receiving waters.
- to decrease the concentration of sulfate below the human threshold for taste and health (250–500 mg l^{-1}), and below the levels for corrosion problems.

The Basic Processes and Treatments for Restoration of AD

The processes that can be used for restoration measures are based on

- chemical treatment with alkaline substances,
- physical treatment with membranes, ion-exchange, or electrolysis,
- biological reduction and removal of ferric iron, toxic metals, and sulfate.

Chemical neutralization and oxidation of metals After aeration of AD and addition of alkaline substances (e.g., limestone, lime, sodium hydroxide, soda, ashes) neutral pH is reached. The pH change leads to the precipitation of hydroxides. Iron and sulfur are the usually dominating elements of AD. The stability of the respective minerals and precipitates depends on both pH value (Figure 1) and redox potential (Eh-value, Figure 2). In Figure 2, the process of chemical neutralization after aeration is indicated as the shift from [A] to [X]. Although neutralization should change only the pH but not the Eh, one will find results in the range around [X] because of the removal of the previously dominating redox couple Fe^{3+}/Fe^{2+} as ferric iron hydroxide. The dominating redox system after neutralization of aerated water is O_2-H_2O_2-H_2O. Aluminum and other metals are also removed from the water as (co-)precipitated hydroxides. Anoxic waters, if neutralized, would change from [B] to [Y], retaining their highly soluble ferrous iron. Therefore, the earlier mentioned aeration is necessary to oxidize the iron, and no precipitation will happen until oxidizing agent is added to the water.

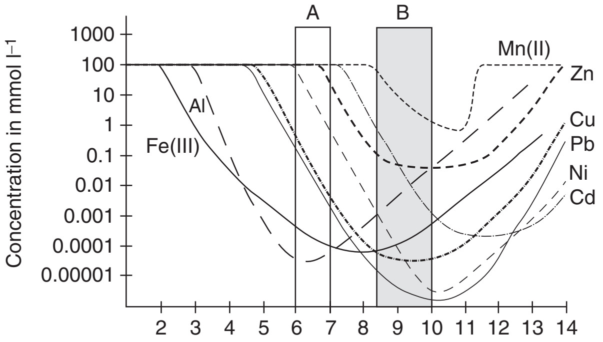

Figure 1 Remaining concentration of metals with increasing pH values of AD (adapted from 1.); assumptions: equilibrium with respective metal hydroxides; maximum concentration of each metal 100 mmol l^{-1}; based on calculations with Wateq4f. The vertical rectangular fields indicate the pH values expected after passive treatment with (a) organic matter (sulphate reduction) or calcite or both and (b) caustic magnesia. With permission from 1. Cortina JL, Lagreca I, de Pablo J, Cama J, and Ayora C (2003) Passive in situ remediation of metal-polluted water with caustic magnesia: Evidence from column experiments. *Environmental Science and Technology* 37: 1971–1977.

Nickel, zinc, and manganese require pH values above neutral to precipitate as hydroxides (Figure 1). This has to be kept in mind when selecting the alkaline substances for chemical treatment if these metals are the dominating ones.

Using calcium bearing alkaline reactant (e.g., limestone or lime), sulfate is precipitated as gypsum ($CaSO_4$), and its concentration is limited by the saturation level (~1500 mg l^{-1}). Aiming at lower levels of sulfate, further processes have to be included in the overall treatment approach. Generally, the chemical neutralization of AD produces high quantities of voluminous sludge that is rich in gypsum and often contaminated with heavy metals. Such sludge must be dewatered and safely disposed of at considerable costs.

Anaerobic processes for reduction of sulfate and metals

Anaerobic processes in the range of positive Eh-values Passive AD treatment in anaerobic wetlands

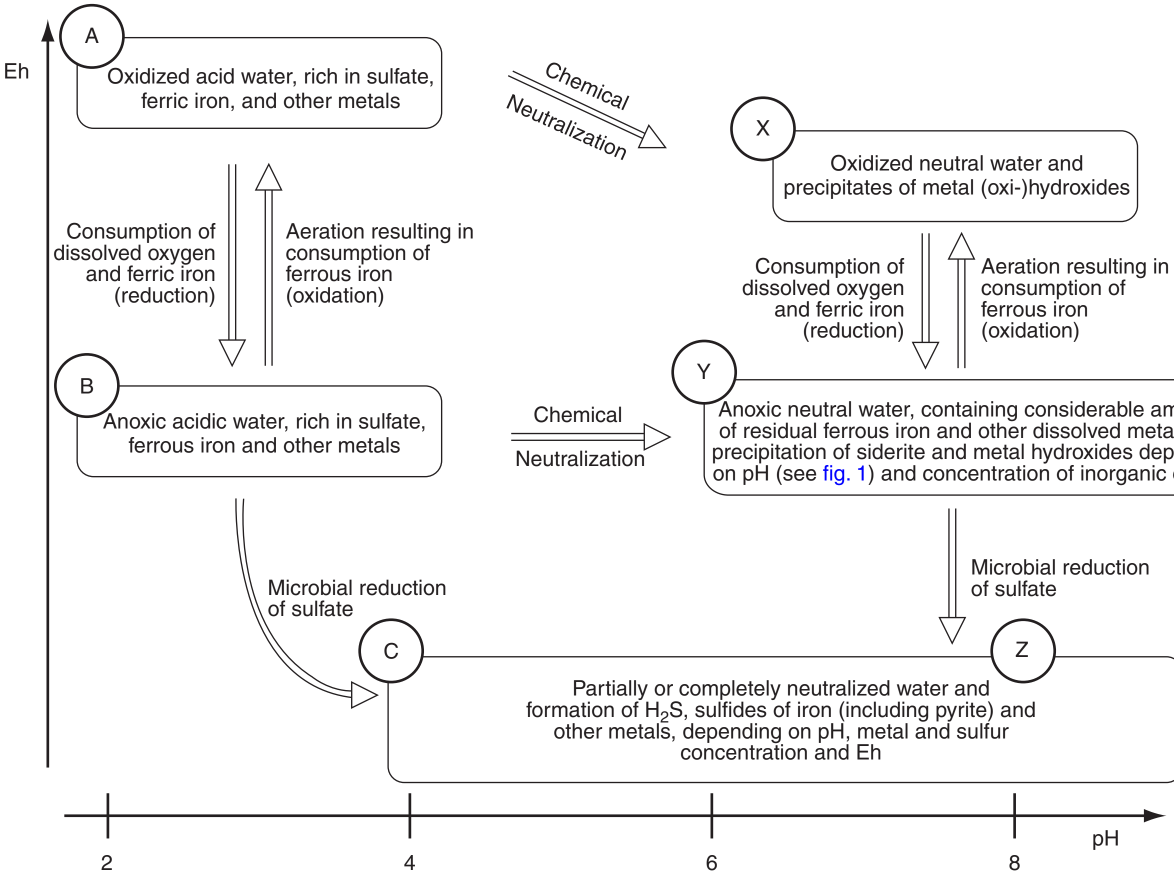

Figure 2 Conceptual stability diagram of iron-species and pyrite, vs. pH. Pyrite – one of the most common iron sulfide minerals in the Earth's crust, chemically FeS_2; Siderite – ferrous iron carbonate, frequently formed in sedimentary environments rich in ferrous iron and carbondioxide, chemically $FeCO_3$. The reduction and oxidation reactions of Fe and S are usually mediated by iron and sulfur bacteria. The reduction of Fe(III) to Fe(II) and sulfate to sulfide ([B] to [C]) occurs with negative Eh, precipitation of iron sulfides with neutral conditions ([C] to [Z]), only.

and most compost bioreactors typically proceeds in the broad range of Eh vs. pH between [A], [B], and [Y] in Figure 2. The average result is often a decrease of acidity and metals in the out-flowing water, leaving open questions about the details of involved chemical reactions (precipitation of hydroxides or sulfides, sorption mechanisms). Heterogeneous spatial distributions may be described with a mosaic of co-existing spaces with higher and with lower Eh-values. Many wetland systems use a final step with aeration of the treated water (polishing pond), leading to oxidation of remaining reduced metals and their subsequent precipitation (shift from [Y] to [X] in Figure 2). This final polishing step consumes a part of the alkalinity produced in the previous anaerobic step.

Anaerobic sulfate reduction at negative Eh-values The process of metal-sulfide oxidation is reversible with anaerobic conditions. The acids are eliminated by the reduction of sulfate and metals, and subsequent precipitation of iron sulfide and other metal sulfides (shift from [A] to [C] to [Z] in Figure 2). The reactions are driven by iron and sulfate-reducing bacteria, which need organic substances $[CH_2O]$ as sources of carbon or energy:

$$SO_4^{2-} + 2[CH_2O] \rightarrow H_2S + 2HCO_3^- \qquad [7]$$

$$H_2S + Me^{2+} \rightarrow MeS(s) + 2H^+ \qquad [8]$$

The precipitation of sulfides results in decreased concentrations of sulfate. The water remains neutral, if the precipitated metal sulfides are irreversibly buried in the sediment. It is a pre-requisite for the long-term success that reoxidation can be avoided.

State-of-the-art techniques for treatment of acid drainage Passive treatment is the deliberate improvement of water quality using only naturally

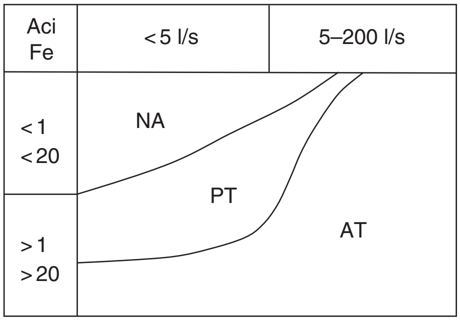

Figure 3 Suitability of monitored natural attenuation (NA), passive treatment (PT), and active treatment (AT) options for remediation of polluted mine waters, expressed as functions of the magnitude of AD-flow ($l\ s^{-1}$) and intensity of contamination of mine water discharges: Acidity (meq l^{-1}), Fe (mg l^{-1}). From ERMITE-Consortium: Younger PL and Wolkersdorfer Ch. (eds.) (2004) Mining impacts on the fresh water environment: Technical and managerial guidelines for catchments scale management. *Mine Water and the Environment* 23 (1, Suppl.): 1–80. From Younger PL (2002) Mine water pollution from Kernow to Kwazulu-Natal: Geochemical remedial options and their selection in practice. Geosciences in south-west England. *Proceedings of the Ussher Society* 10: 255–266. http://cvrm.ist.utl.pt/events/conferences/pdf/ScottSimpsonLecture2002.pdf

available energy sources in systems that require only infrequent maintenance to operate effectively over the entire system design life (Definition by: PIRAMID, 2003).

Active treatment plants are more expensive to build and to run, but they reach the high efficiencies needed for big volumes of strongly acidified water. Both levels of treatment may include chemical and different biological processes, often arranged in sequence.

The suitability of chemical or biological processes in the passive treatment or in their active modifications depends on the magnitude of flows and the concentrations to be treated. Only dilute waters may be left to monitored natural attenuation without any treatment (see Figure 3). Small flows of low-concentrated AD can be handled with passive treatments, whereas big flow volumes with high-concentrated loads of acidity need active treatment plants. Flows of more than $5\ l\ s^{-1}$ and concentrations higher than $1\ meq\ l^{-1}$ of acidity are considered as high and need more than the low-flow and low-cost passive treatment.

Treatment of Acid Drainage by Active Systems

Chemical treatment plants The chemical neutralization of AD is the simplest treatment and can be applied at all scales of flow and acidity (Table 2). For high flows and high concentrations, the addition of lime or limestone after oxidation of all components is the conventional and cheapest treatment. It is applied in technical plants comparable to the technology of ordinary wastewater treatment. The size of active treatments ranges from laboratory experiments (a few liters), to pilot scale experiments (some m^3), and to full-scale technical plants ($100\ m^3$ and more). The AD-waters are neutralized with hydraulic residence times (HRT) from 10 min to 8 h. The sulfate concentrations can be decreased by liming below the solubility limits of gypsum. Additional precipitations, using Barium or Aluminium, are able to reach the quality levels of potable and industrial water.

Using lime, $Ca(OH)_2$, or $Mg(OH)_2$, the pH raises to very high levels (10–12), facilitating the precipitation of nickel, zinc, and other heavy metals. By adding aluminum hydroxide or related compounds, the concentration of sulfate can be decreased to less than $100\ mg\ l^{-1}$. In both procedures, the highly alkaline water has, in a final step, to be adjusted to neutrality with addition of $CO_2(g)$.

The density of the large volumes of formed sludge of metal hydroxides is usually low. It can be increased by recycling limestone sludge from the final step, back to the first step of the treatment (High Density Sludge (HDS) technology).

The process of neutralizing AD with lime(stone) is necessary as a pretreatment for the physical treatments and some of the biological reactor systems.

Physical treatment plants The physical treatments for AD utilize membrane-bound processes, reverse osmosis, nanofiltration, or electrodialysis, achieving drinking water quality. Comparable to desalination plants, these treatments separate the AD into low-concentrated fresh water and highly concentrated brines as waste products. The process of reverse osmosis is driving the passage of water through the membrane by high pressure, leaving behind the concentrated salts. In the electrodialysis the dissolved ions are forced in an electric field to pass a membrane assembly. Details of the treatments are accessible from http://www.usbr.gov/pmts/water/reports.html.

Other physical treatments use electrolysis or ion-exchange to separate dissolved metals from waste AD. Electrolysis can be applied to convert sulfate into elemental sulfur. The relatively sophisticated physical treatments may be considered as emerging technologies that are useful to reach additional aims, such as the production of drinking water or the separation of valuable metals from AMD. The physical treatments actually are technically developed to experimental or pilot scale, the main problem being the optimization of energy efficiency.

Table 2 Chemical processes to treat AMD in active and passive treatment plants

Process technology and sites	*Used reactive material, source of AMD*	*Results of treatment*
Chemical treatment plants		
CaCO3 neutralization[3] (Navigation site coalmine, Witbank, South-Africa)	Limestone (CaCO3) powder AMD-source: synthetic discard leachate	AMD neutralized despite high levels of Fe(II); Fe(II), Fe(III), and aluminum removed; sulfate lowered. Inflow: pH 1.8; 8.34 g l^{-1}SO$_4^{2-}$; 2.5 g l^{-1} Fe Outflow: pH 6.6; 1.97 g l^{-1}SO$_4^{2-}$; $<$0.056 g l^{-1} Fe
Grubenwasserreinigungsanlage (mine water treatment plant) (Vattenfall Europe, Mine Nochten/Tzschelln, Spree River, East-Germany)[9]	Biological/chemical Fe(II) oxidation, aeration; lime (Ca(OH)$_2$) AMD-groundwater of lignite surface mining	Treated flow: 86 400 m^3 d^{-1} Inflow: pH 4–5; Fe 700 mg l^{-1} Outflow: pH 6.5–8.5; Fe $<$ 1 mg l^{-1}
High-density-sludge (HDS) process[2,5] (Navigation site coalmine, Witbank, South-Africa)	Limestone (CaCO$_3$), lime (Ca(OH)$_2$), CO$_2$-gas AMD-source: active mine drainage and tailings	Inflow: pH 2.1; about 3 g l^{-1}SO$_4^{2-}$ Outflow: pH 8.5, about 1.1 g l^{-1}SO$_4^{2-}$ HRT: 4.2 h
HDS process[8] (Wheal Jane treatment plant, Cornwall, UK)	AMD of decommissioned mine	Treated flow: 864 m^3 d^{-1} Inflow: pH 3.8; Fe 160 mg l^{-1} Outflow: pH 9; Fe 1.3 mg l^{-1}
SAVIM (ettringite) process/Cost effective sulphate removal (CESR)[2] (∼20 European plants)	Lime (Ca(OH)$_2$, Al(OH)$_3$, CO$_2$-gas AMD of different mines	Inflow: ∼0.6–3.35 g l^{-1} SO$_4^{2-}$, Outflow options: Effluent quality: 0.5 g l^{-1}SO$_4^{2-}$ Potable water: 0.2 g l^{-1}SO$_4^{2-}$ Industrial water: 0.05 g l^{-1}SO$_4^{2-}$
Same treatment[2]	Berkeley Pit water	Inflow: pH 2.8; 8.73 g l^{-1} , Outflow: 0.015 g l^{-1}SO$_4^{2-}$
Pulsed bed CO$_2$ treatment[7]; Prototype column reactor (USGS; Toby Creek PA)	Limestone sand with 30 s/30 s to 10 s/50 s pulsed influent AMD; addition of CO$_2$ to accelerate limestone dissolution, CO$_2$ recycling. Field tests with AMD from different mines	Treated flow: 3.6 m^3 h^{-1} Inflow: pH 3.9–4.8; acidity 2.5–6.8 meq l^{-1}; Outflow: pH 6.2–6.3; acidity 0.2–1.3 meq l^{-1}; precipitation of Fe(OH)3 and Al(OH)$_3$ no removal of Fe(II) and Mn(II); short HRT $<$ 10 min

Continued

Table 2 Continued

Process technology and sites	*Used reactive material, source of AMD*	*Results of treatment*
Barium sulfide process[2,4]; Pilot scale study (Crown mines; CSIR, South Africa)	Lime pretreatment; BaS treatment and sulfate removal as $BaSO_4$; H_2S stripping by CO_2-gas; H_2S-gas converted to S^0 with Fe(III); CO_2 stripping and $CaCO_3$ precipit.; recovery of BaS from $BaSO_4$ by thermal reduction with coal.	During lime treatment SO_4^{2-} lowered from 2.8 to 1.25 g l^{-1}; precipitation of metal hydroxides; after BaS treatment and removal of $BaSO_4$:SO_4^{2-} <0.2 g l^{-1}; pH 1.6–7.2
Oxidation of ferrous iron in aeration tank with geotextile and other support media[6] (Navigation site coalmine, Witbank, South Africa)	Addition of nutrients, CO^2, air flow; control of pH and temperature; support media.	Inflow: 4.5–5 g l^{-1} Fe(II); pH 2.0 Fe(II) oxidation rates: 9.5–27.6 g Fe l^{-1} d^{-1}
	AMD-source: Toe Seep Dam Navigation mine	Optimum conditions: *T*: 29 °C; pH 2.0; Fe(II): 16 g l^{-1} HRT: 8 h
(Semi-)Passive treatments: aerobic metal removal		
Surface-catalyzed oxidation of ferrous iron (SCOOFI)[8] (Scotland)	For example, trickle filter media for aeration HRT: ~2 min(!)	Inflow: Fe $<$ 50 mg l^{-1}
Oxic open limestone drain (OLD)[8]	AMD-source: HRT: 2–3 h	Inflow: Fe, Al 10–20 mg l^{-1}, <1.8 meq l^{-1} acidity

Sources

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Sulfate-reducing tank bioreactors Sulfate-reducing tank bioreactors require continuous flow of water and substrate supply, and offer a great degree of control (pH vs. Eh range [C] to [Z] in Figure 2). They are feasible to treat high water volumes, where sulfate is to be removed, or where metals are to be recovered from the drainage. Metal removal as sulfide generally works well in tank bioreactors, with the exception of manganese and arsenic. Microbial inocula for the reactors are usually taken from well-established preliminary setups of the same process, or from other sulfate reducing systems. In most cases the sulfate reducing bacteria are neutrophilic, applications of acidophilic consortia are rare but promising.

As acidic drainage is typically low in organic constituents, carbon and energy sources have to be added. On the basis of these sources, three main reactor types can be distinguished (Table 3): Reactors with complex/solid, with liquid, and with gaseous substrates, having different technical advantages and drawbacks. Full-scale technologies that are able to treat large volumes of AD with high efficiency were described as the THIOPAQ® and the BioSulphide™ processes. In reactors of the first type, the complex solid substrates also serve as a fixed bed for biofilm growth and metal precipitation. Cheap materials such as manure, spent mushroom compost, wood cuttings, sawdust, or straw are used. Flow is often low in these systems, and it may change with time because of compaction or degradation of the substrate or clogging by biomass. Available organic carbon is difficult to control in this type of reactor, and may be limiting the lifetime of the system.

The typical liquid organic substrates (electron donors) applied in sulfate reducing bioreactors are alcohols (ethanol, methanol, glycerol, waste of biodiesel production, which consists mainly of glycerol and methanol), organic acids (lactate, acetate), but molasses or whey are also used. Various reactor types operate with liquid substrates: fixed bed reactors, both with complex matrix and inert plastic, glass or crushed lava as a solid biofilm support, Up-flow Anaerobic Sludge Blanket (UASB), or Expanded Granular Sludge Blanket (EGSB) reactors. A further development of the UASB reactor is the so-called BEST (Bioreactor Enhanced by Separation Technology), which allows a better biomass retention when compared with that of the original design. Sulfate reducing bioreactors can also be gas-fed with H_2 and CO_2 as energy and carbon sources. A cheap source is synthesis gas, which is a mixture of H_2, CO_2 and CO. This process avoids high COD in the effluent and produces high-quality water. A novel modification of the technology is a membrane module bioreactor, in which the synthesis gas is circulated through pressurized gas-permeable polypropylene hollow fibers.

In general, liquid substrates work well for low to moderate sulfate loads, whereas gas-fed reactors become more economic for high loads. Bioreactors can be operated in a single-stage process, where the sulfate reducing microbial community may face acidic inflow and metal sulfides to accumulate within the reactor. In a separate step, the influent can be preneutralized, since low pH is critical for the sulfate reducing community. Alternatively, sulfate reduction can be separated from metal sulfide precipitation, as it is realized in the BioSulphide™ process (Table 3). Excess H_2S formed in sulfate-reducing bioreactors can either be recycled for metal precipitation, or it can be oxidized to elemental sulfur in an additional, aerobic reactor (THIOPAQ® process).

Treatment of Acid Drainage by Passive Systems

Passive treatment systems (Table 4) are designed to remedy AD-waters with flows of 5–5000 $m^3\,d^{-1}$, using surface areas of ponds, wetlands, or subsurface passages in a scale of 100–2000 m^2. The water flows through the passive systems with hydraulic residence times (HRT) of 1 day–1 month. The resulting treatment efficiencies are usually high for the elimination of iron, but often low for sulfate. Compared with single systems, the combined steps of successive chemical and biological treatments gave better results in some well documented cases (see references 2–4 in Table 4).

Passive chemical treatments and aerobic wetlands Low-flow/low-acidity waters can be restored by respective passive treatments like open or anoxic limestone channels or drains. Open limestone channels (OLC) use the acidity consuming dissolution of limestone. Their application is limited to very low loads of metals or to flow rates high enough to prevent rapid formation of reactivity-lowering precipitates on the limestone. Anoxic limestone drains (ALD) are typically air-tight covered trenches filled with limestone. ALD prevent the formation of iron precipitates by keeping iron in ferrous state because of the anoxic conditions. CO_2 resulting from the reaction of limestone with acidity enhances the further dissolution of limestone according to eqn [9]:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad [9]$$

Therefore, ALDs produce usually neutral water with very high bicarbonate alkalinity. High aluminum concentrations may result in a gradual decrease of performance because of precipitation of aluminum hydroxide.

In aerobic wetlands, dissolved metals are oxidized and precipitated as metal hydroxides or oxides.

Table 3 Biological tank reactors for AMD treatment

Bioreactors	*Volume (m^3)*	*Flow ($m^3 d^{-1}$)*	*HRT (d)*	*Temperature (°C)*	*Substrate*	*Inflow (pH)*	*Outflow*	*Inflow SO_4^{2-}*	*Outflow ($g\ l^{-1}$)*	*Inflow substracte*	*Outflow (COD $g\ l^{-1}$)*	*SRR (SO_4^{2-} $g\ l^{-1}\ d^{-1}$)*	*Source*
With solid substrates													
Upflow wet-substrate bioreactor	0.027	7.2–24.3	1–3.8		Manure	2.7	6.3–7.1	0.5				0.06–0.09	14
Pittsburgh system	0.6	0.08	5	10	Compost	3.2	6.4	1	0.83				3
Palmerton system	9	0.1	9–17	18–24	Compost	6.2	7.1	3	2.39				3
On-site SRB bioreactor	Very large	5760	4–5	Average 4.5	Manure/ straw	3.6 (3.3–7.5)	8.9						9, 15
With liquid substrates													
Electrolab P350	0.002			30	Glycerol	3.8		0.24	0.067	0.46	0.29		7
Bench scale reactor	0.013				Lact./ molasses	5.7–6.4	6.9–7.1	0.43–0.45	0.15–0.2	0.31-0.41	0.18-0.27		5
BCL Ni/Cu mine, Botswana	0.015	0.030	0.5	20–22	Ethanol	5.1	6.1	1.6	0.375	1.73	1.66	2.45	6
Ditto	0.015	0.030	0.5	20–22	Ethanol	4.3	7.0	2.1	1.14	1.74	1.1	1.92	6
Pilot plant reactor, crushed lava	3.9		0.18		Methanol	2.9	6.5	1.97	0.83			3.22	4
ViaSystems, pilot scale Thiopaq	7	24	0.3		Ethanol			0.84	0.4			3	10
In-lake reactor, plastic support	11.4	4.8	2.4	10–25	Methanol	2.6	>6	1.25	0.6			0.28	11
Full scale plant Thiopaq, S-Africa	105	192–384	0.2–0.4	17	Ethanol	7.2	7.7	2.2	0.2	0.69	0.22	12	8

Budelco, full scale Thiopaq		8400			Ethanol			1	<0.2			3	10
With gaseous substrates													
Pilot bioreactor, pozzolana	0.2	89–528	0.3–0.6	10–35	Acet./H_2/ CO_2		7.5–8.75	0.5	<0.003		0.09–0.12	0.024–1.92	1
Membrane bioreactor		36–144		25	H_2/CO_2			5.4	3.7–4.1				12
Kennecott, pilot scale Thiopaq	5	4.8	1	30–35	Ethl./ synth. Gas	7.0–7.5		30	<0.5				2, 13
Budelco, full scale Thiopaq	500	7200	1–3	30–35	Acet./ synth. Gas	7.0–7.5		5–10	0.6–1.2				2, 13

Abbreviations: acet. acetate, COD: chemical oxygen demand, ethl.: ethanol, HRT: hydraulic retention time, lact.: lactate, synth. gas: synthesis gas containing H_2, CO_2, and CO.

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Table 4 Performance of different passive technologies to treat AMD (typical values and examples)

	Aerobic wetland	*Compost wetland*	*RAPS*	*Underground SR reactor*	*ALD*
Technical information					
Flow (m^3 d^{-1})	10–1000	10–200	5–200	5–5000	70–200
Area (m^2)	200–2000	200–2000	100–1500	10–1000	ND
Res. time (d)	0.5–2.5	2–10	5–25	ND	0.2–1
Inflow quality					
pH	3–6.5	3–5	3–5	3	2.5–6
Acidity (meq l^{-1})	0–10	2–20	1–10	ND	2–30
Fe (mg l^{-1})	1–250	10–200	1–200	3–100	10–300
SO_4^{2-} (g l^{-1})	0.5–2	0.5–3	0.5–1	0.3–3	0.4–3
Treatment efficiency (%)					
Acidity	0–10	30–95	30–95	ND	30–100
Fe	50–98	50–95	50–90	70–99	0–90
SO_4^{2-}	ND	0–20	0–10	0–70	0–40
Removal rate					
Acidity (eq m^{-2} d^{-1})	0–0.4	0.1-0.5	0.2–1.3	ND	ND
Fe (g m^2 d^{-1})	1–10	1-50	2–20	0–6	ND
SO_4^{2-} (g m^2 d^{-1})	ND	0-20	0–10	0–70	ND
	ALD + aerobic wetland	ALD + RAPS	Aerobic + compost wetland	ALD + aerobic wetland + compost wetland	
	Review of 13 sites[1]	Jones Branch, USA[2]	Lick Run, USA[3]	Wheal Jane, UK[4]	
Technical information					
Flow (m^3 d^{-1})	1000 ± 1556	53	164 ± 27	17–34	
Area (m^2)	1417 ± 285	1022	3869	2850	
Inflow quality					
pH	5.3 ± 1	3.4	2.8	3.9	
Acidity (meq l^{-1})	ND	45	17	ND	
Fe (mg l^{-1})	50 ± 54	787	170	144	
SO_4^{2-} (g l^{-1})	ND	3	1.7	1.7	
Treatment efficiency (%)					
Acidity	ND	95	56	ND	
Fe	83 ± 28	95	84	99.5	
SO_4^{2}-	ND	55	23	30	
Removal rate					
Acidity (eq m^{-2} d^{-1})	ND	2.2	0.4	ND	
Fe (g m^2 d^{-1})	6.2 ± 11.7	39	6.1	1.3	
SO_4^{2-} (g m^2 d^{-1})	ND	87	16.4	4.5	

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ND = not determined

Aerobic wetlands are constructed to optimize the access of oxygen: shallow depth, cascades, etc. The processes of oxidation and precipitation of metals lower the pH, and the treated water may show decreased loads of metals.

The beneficial treatment effect of wetland plants like Typha is under discussion and might be restricted to facilitate sedimentation and to aesthetic reasons.

Automatic lime addition systems (Aquafix) are working in the field, their size has to be adapted to the considered water volumes.

Biological treatment in anaerobic wetlands Compost wetlands are surface flow wetlands filled with organic material like mushroom compost, sawdust, or manure, often mixed with limestone. The mineralization of the organic material provides anoxic conditions in the substrate, which enables both chemical neutralization by the limestone, and to a lesser extent, microbial sulfate reduction.

To force the water through the reductive material, vertical flow systems have been developed, called Reducing and Alkalinity-Producing System (RAPS) or Successive Alkaline Producing Systems (SAPS). These systems are surface inflow wetlands that are sealed against the groundwater and that are filled with layers of alkaline substances and organic material. The outflow of the water is through drainage tubes at the bottom of the wetland. Underground reactors are RAPS-like systems that have no open water on top, but are covered air-tight. Generally, the passive systems are not readily controlled, and the process conditions are usually poorly documented. In constructed wetlands the redox potential is usually above the limits that are necessary to drive the reduction of sulfate (Figure 2). Therefore, the systems predominantly produce precipitated hydroxides of iron and other metals as end-products. The performance of wetlands can be measured by treatment efficiencies, area-adjusted process rates, or first-order removals. When the performance of 142 different wetlands in the United States was checked, generally, their efficiency was neither related to the type of substrate used, nor to area, and loading rates. Alkalinity generation of RAPS type wetlands was depending on residence time and inflow acidity. Wetlands did not attenuate sulfate in the long term.

Selection of a suitable combination of passive treatment steps According to the limitations of the different types of passive treatment, the best combination of successive steps has to be selected for a given type of AD. Resulting from a project funded by the European Community, an engineering guideline for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters was developed (Figure 4). Experiences with pilot plants of passive wetlands made clear that in arrangements of successive treatment steps the whole process should start with an ALD followed by an anaerobic cell and aerated or open cells or 'polishing ponds.'

In Situ Treatment of Ground Water

Active treatment options for acidic ground water often fail or require enormous efforts (e.g., pumping).

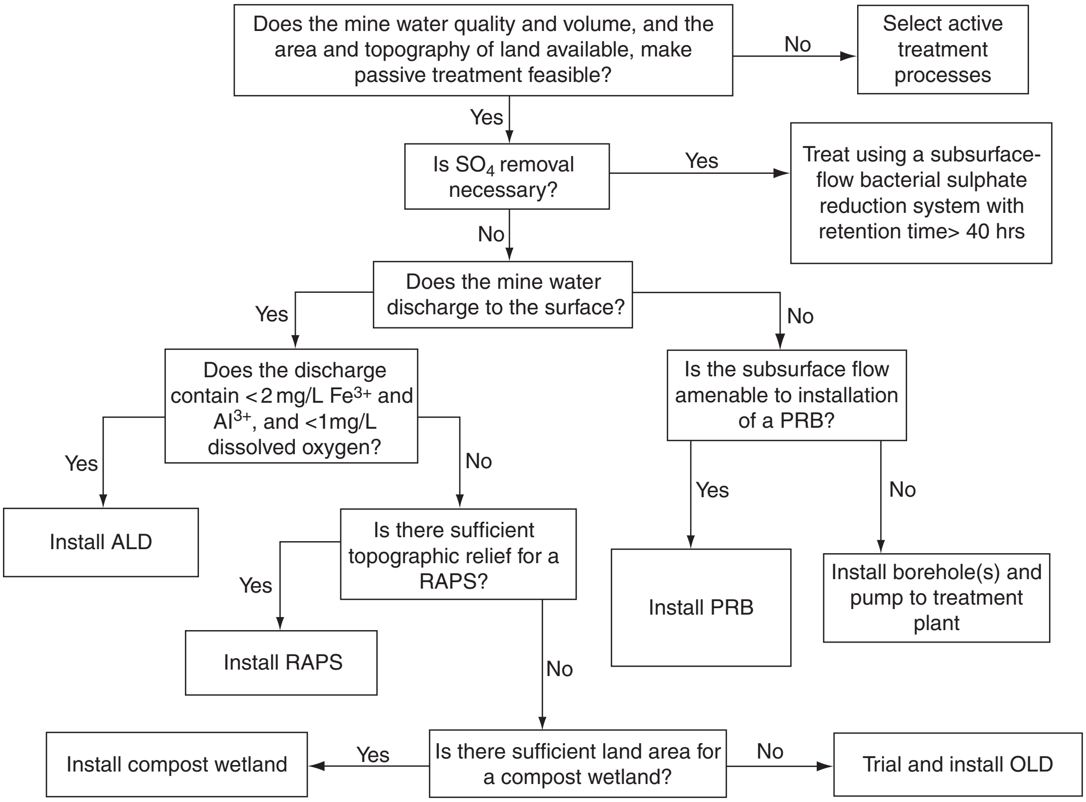

Figure 4 Flow chart for process selection for passive treatment of acidic mine drainage. From PIRAMID Consortium: Younger PL, Jarvis A, and Laine D (2003) *Engineering Guidelines for the Passive Remediation of Acidic and/or Metalliferous Mine Drainage and Similar Wastewaters*, 166pp. EU RTD-Project. Newcastle upon Tyne, UK: Newcastle University. http://www.ncl.ac.uk/piramid

Table 5 Examples of in situ treatment of AMD-impacted ground water by permeable reactive barriers

Sites	*Used reactive material+source of AMD*	*Results of treatment*
Reactive barriers		
Nickel Rim (Sudbury, Ontario, Canada)[5]	50% pea gravel, 20% municipal compost, 20% leaf compost, 10% wood chips AMD-source: abandoned mine tailings	Rate of sulphate reduction 25–116 mmol l^{-1} d^{-1} (varying seasonally and depending on detection method) Inflow: ~30 mmol l^{-1}, SO$_4^{2-}$,10 mmol l^{-1} Fe End of barrier: ~10 mmol l^{-1}, SO$_4^{2-}$, 2 mmol l^{-1} Fe
(British Columbia, Canada)[3]	84% pea gravel, 15% leaf compost, 1% limestone AMD-source: storage site for ore concentrates	Inflow: 3630 μg l^{-1} Cu, 15.3 μg l^{-1} Cd, 131 μg l^{-1} Ni, 2410 μg l^{-1} Zn In the barrier: 10.5 μg l^{-1} Cu, 0.2 μg l^{-1} Cd, 33 μg l^{-1} Ni, 136 μg l^{-1} Zn
Shilbottle (Northumberland, UK)[2]	50% limestone gravel (25 mm grain size), 25% composted horse manure and straw, 25% green waste compost AMD-source: coal spoil heap	Inflow: $>$6500 mg l^{-1} SO$_4^{2-}$, $>$300 mg l^{-1} Fe,$>$165 mg l^{-1} Mn, $>$100 mg l^{-1} Al, pH $<$ 4, $>$280 meq l^{-1} acidity Outflow of barrier (mean): pH 4, 10 meq l^{-1} acidity 50% Fe and 40% SO$_4^{2-}$ removed
Aznalcollar (Spain)[1]	3 modules	Inflow: 1 g l^{-1} SO$_4^{2-}$, 30 mg l^{-1} Cu, 30 mg l^{-1} Zn, pH 3-4
	1. 50% limestone, 30% municipal compost, 20% sewage sludge	Module 1: Failed due to hydraulic problems
	2. 50% limestone, 50% compost, small amount of zero-valent iron	Module 2 and 3: pH became near neutral, more than 90% of metals were removed, sulfate reduction was not significant
	3. 66% limestone, 33% compost	
	AMD-source: accidental tailings-spill in April 1998	
Injection of organics into the aquifer		
Southern shore of Lake Senftenberg[4] (Germany)	Methanol and nutrients AMD-source: aerated pyrite in Quaternary and Tertiary aquifers, aeration caused by dewatering of a neighbouring lignite mine	Inflow: 1600 mg l^{-1} SO$_4^{2-}$, 180 mg l^{-1} Fe, pH 4.3, 7.3 meq l^{-1} acidity Outflow of barrier (660-694 days of operation): 800 mg l^{-1} SO$_4^{2-}$, 10 mg l^{-1} Fe, pH 5.8, 1 meq l^{-1} alkalinity

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Reactive barriers provide alternative options to improve the ground water chemistry. Permeable Reactive Barriers (PRB) are constructed parts of aquifers, filled with mixtures of limestone, pea gravel, and diverse organic materials for AD treatment. The treatment by reactive barriers combines the same processes as described in the earlier sections: chemical neutralization, biological production of alkalinity, and retention of metals by precipitation of sulfides or (oxi-)hydroxides.

The filling mixtures fulfill two requirements: to provide a suitable substrate for the desired reactions, and to provide a suitable hydraulic conductivity over a long period (actual designs aim to 20 years). The hydraulic conductivity has to be high enough to keep the ground water passing the barrier on one hand, and to provide an appropriate reaction time inside the barrier on the other hand. The precipitation of metals, the gradual decay of the organic material, and the accumulation of gas after decay of organic material may change the hydraulic conditions in reactive barriers over their life time.

A different approach is the injection of liquid organics into the underground using the aquifer as reactor. A mixture of methanol and nutrients was successfully applied in field-scale tests to treat the AD ground water flowing into the pit Lake Senftenberg (Germany) (Table 5).

In-Lake Measures at Acidic Pit Lakes

Pit lakes with extremely acidic water can be neutralized by large-scale liming as a conventional restoration technique. The traditional technology to treat acidic lakes by liming was already known from lakes that were acidified by acid rain or by industrial acid drainage. The 143-m deep, pre-alpine soft-water Lake Orta, Italy, was polluted by acidic industrial wastewater, and was finally neutralized with a suspension of 18 000 tons of powdered limestone. The world's largest liming program was conducted in Sweden over 20 years in rain-acidified areas and waters, where 200 000 tons of lime were spread every year. 6000 lakes were treated, and about half of the acidified area could be restored. Compared with rain-acidified soft waters, the acidities of acid mine lakes are one to two orders of magnitude stronger, but several lignite pit lakes in East Germany, and two ore mining lakes in Sweden and at the Gilt Edge Mine Superfund Site (USA) were also chemically treated (Table 6).

The long-term success of the chemical treatment, however, depends on the exchange rate of the lake water with ground water or other inflows from surrounding acidic dumps and rocks. If the autochthonous alkalinity that is produced by the lake's biota is larger than the rate of inflowing acidification, the initial treatment appears as a sustainable measure. The biological production of alkalinity is the sum of the processes that eliminate nitrate and sulfate from the system, and it was found in natural lakes to be in a range of 0.5–5 meq m^{-2} d^{-1}, as median values in low productive and in eutrophic lakes, respectively. These rates may also be expected in neutralized pit lakes with established ecosystems.

There are reports of high rates of biological sulfate reduction and gross production of alkalinity in the deep water of stratified lakes during the warm season. These effects, however, are usually disappearing with autumnal mixing of the water column. The input of atmospheric oxygen leads to re-oxidation of the reduced sulfur and iron species, i.e. the process is not sustainable in holomictic lakes.

Meromictic lakes have a permanent deep-water body, and treatments may have sustainable results, since meromixis is usually accompanied by some important consequences with respect to water quality: (1) often strong anoxia in the permanent deep-water body (monimolimnion), (2) enrichment of products of microbial decay in the monimolimnion, and therein, (3) occurrence of hydrogen sulfide and precipitation of metal sulfides. Unwanted substances can be enriched in the monimolimnion because of the very low exchange with the upper water layers. The 330-m deep pit lake in the former Island Copper Mine (Vancouver Island, Canada) was filled with sea water. By adding an overlay of fresh water, the lake was made meromictic. The whole pit lake is run as a big treatment plant for AMD to remove precipitated and adsorbed metals, thereby, with sedimenting plankton the deep-water body is used for subhydric deposition. A daily AMD average flow of about 11 840 m^3 d^{-1} was treated in the system. A similar, sustainable treatment might be applied in other meromictic pit lakes.

Perspectives

Beyond the given natural forms of AD, the anthropogenic main sources are the legacies from the well-known old and actual mining on sulfidic ores and on coal, and – increasingly noticed – from agricultural use of acid sulfate soils (ASS) in coastal and fluvial plains allover the world. Approaches to handle or solve the AD-problems have to face two different levels: (1) the development and amendment of old and new technical measures and the respective scientific background, and (2) the problems arising from unsuitable institutions and administration. The latter are a considerable problem where historic legacies of ephemeral mining are considered and where the

Table 6 Acidified lakes that were successfully treated by liming and/or sed for AMD treatment

Lake	*Volume (Mio m^3)*	*Acidity (meq l^{-1})*	*Chemical*	*pH-change*	*Source*
Lake Orta, Italy	1300	0.77	$CaCO_3$	3.9–6.8	1
Pit Lake Koschen, Germany	82	1.6	$CaCO_3$	3.0–3.3	3
Pit Lake Lohsa, Germany	44	2.9	$Ca(OH)_2$	2.7–5.4	3
Pit Lake Bockwitz, Germany	19	8.1	Na_2CO_3	2.7–5.4	3
Pit Lake Anchor Hill, South Dakota, USA	0.2		CaO, NaOH	3–7	4
Pit Lake Rävlidmyran, Sweden	0.53		$Ca(OH)_2$	3.7–7.5	5
Island Copper Mine Pit Lake	241		Fertilizer	Cu-, Zn-removal	2

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source territories are noncongruent with the affected river catchment areas.

The known approaches to treat acid drainages, mainly the methods of chemical and biological treatment, both active and passive ones, have to be further developed and combined. The best perspective for large amounts of AMD is the active remediation in treatment plants. Both chemical and biological treatments are basically known, but they should become more efficient. The combination of both approaches appears as promising.

Low-cost/low-maintenance solutions are needed for the ten-thousands of small sources of AMD. Here, the passive treatment methods, chemical and biological, aerobic and anaerobic ones, appear as the standard approaches in combinations that are to be adapted to the given case. A good perspective for the sustainable elimination of sulfur acidity is the passive biological treatment. There is an urgent need, however, for improvements of control and design of artificial wetlands and alkalinity producing systems to reach and to keep the Eh ranges that are needed to promote the microbiologically mediated reduction of iron and sulfate.

There are promising examples of successful large-scale treatments in the past. 6000 rain-acidified lakes in Scandinavia were restored by liming over 20 years. The heavily acidified soils of the Sudbury territory in Canada were neutralized with 1 kg lime per squaremeter. These successful examples should encourage respective measures for AD treatment, also in large scales.

Glossary

Acid drainage (AD) – Drainages with acidic water both from anthropogenic and from natural acid sources, such as from mining of coal, sulfidic ores, from aerated sulfide-containing soils, and from volcanic sources.

Acid mine drainage (AMD) – Mine drainage water acidified after oxidation of pyrite from mining of coal and sulfidic ores.

Acid rock drainage (ARD) – Drainage water acidified after oxidation of pyrite and other sulfide minerals at operating or abandoned mining sites or at naturally occurring outcrops of sulfide bearing geologic formations.

Acid sulfate soil (ASS) – Soils with sulfide content that release acidic and sulfate containing water after aeration by agriculture or lowered ground water.

Acidification – Change of water chemistry after input of acids by acid rain or acids from geogenic sources.

Anoxic limestone drain (ALD) – A covered bed for AMD flow and treatment filled with limestone for neutralization and organic matter to reach and maintain anaerobic conditions, to avoid armoring of the limestone surfaces by iron hydroxides.

Eutrophic lakes – Lakes with high levels of nutrients, that lead to high algal production, followed by high oxygen demand in the deep water with later decay of the produced organic matter.

Holomictic lakes – Lakes that are thermally stratified during the warm season and completely mixed from surface to the bottom after cooling of the water.

Meromictic lakes – Lakes that are permanently stratified with a deep water body of high density, usually because of high salt content in the deepest layer (monimolimnion).

Monimolimnion – The permanently stratified and usually anoxic deep-water body of meromictic lakes.

Permeable reactive barriers (PRB) – Constructed parts of aquifers, filled with mixtures of limestone, pea gravel, and diverse organic materials for the treatment of acidic ground water.

RAPS, SAPS – Reducing and Alkalinity-Producing System (RAPS) or Successive Alkaline Producing Systems (SAPS): artificial through-flow systems, that are protected against aeration and supplied with organic matter, in which alkalinity is produced by bacterial activities, reducing sulfate and metals.

See also: Acidification; Density Stratification and Stability; Mercury Pollution in Remote Freshwaters; Meromictic Lakes.

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