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22 Ways of Controlling Acid by Ecotechnology

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22.1 Introduction

Geogenic acidification results from the oxidation of sulfidic minerals that had been stable for millennia because of anaerobic conditions in the underground. The geochemical process is microbially intensified and therefore a natural process. However, it is also man-made, because the sulfidic minerals are oxidized as a consequence of aeration due to mining activities. Open-cast lignite mining starts with the dewatering of the overburden, of the lignite and of the uppermost layers below the coal. Pyrite and marcasite are then in contact with atmospheric oxygen instead of anaerobic groundwater. The acidity results from the oxidation of sulfur and iron and from the hydrolysis of iron (see also Evangelou, this Vol.). Bodies of water become acidified when the sulfuric acid and iron(II)-sulfate are leached and transported into the lake by the groundwater. In the case of refilling with groundwater, the resulting mining lakes are acidic, with pH between 2 and 3. Their water is brown because of the high content of dissolved iron hydroxide. The low pH is strongly buffered by iron. Other heavy metals formerly present in the overburden are dissolved and contaminate the lake water. Living conditions differ widely from those in natural lakes in Germany.

The general question of whether to do something against this acidity or not is a matter of water policy. One has to take into account:

- Demands of the society (local and governmental)
- Options for lake utilization
- Quality demands of the users in question
- Protection of the natural environment
- Structure and function of the ecosystems

A number of relatively small acidic lakes have existed for many decades. They have been and will be excellent sites for field research on the very extreme habitats and natural successions as well as natural neutralization processes. For large mining lakes – say 10 km^2 in area or more – the aim only should be a usable lake. In acidic lakes water-oriented recreational activities are restricted to water sports not involving body contact with the water. Fish do not survive at pH < 5, so fishing of any kind is excluded.

As mentioned above, the acidic water is strongly buffered and neutralization is complicated. Nevertheless, with occasional exceptions, in general the aim is a neutral lake where fish life is possible. The following recommendations are derived from experiences with land and water reclamation in the brown-coal region of East Germany, from limnological observations of existing mining lakes and from international literature on acid mine drainage. In this state-of-the-art report further research fields are defined.

22.2 Prophylactic Measures During the Mining Process

To minimize acid formation at the outset, some inhibitory measures should be taken during the mining process:

- Minimization of dewatering before excavation in volume and time.
- Deposition of sulfur-rich overburden material in the deepest part of the mining hole with little water exchange.
- Inhibition of the acid-forming metabolism of the *Thiobacilli* by treating the refuse piles with bactericides (Kleinmann et al. 1981; Onysko et al. 1984).
- Refilling of the dewatered subsurface and heaps after coal extraction as soon as possible.
- The shape of the lakes and their orientation with respect to the groundwater flow are important factors for the water quality. Elongation of mining lakes in the groundwater flow direction should be avoided. Such lakes are steps in the slope of the groundwater table and pull groundwater from above together with the acidity (Luckner et al. 1995).
- The final state of the mining activity and therefore the lake should preferably be such that the inflowing groundwater stems from the undisturbed rocks and not from the oxidized heaps.

22.3 Measures to Counteract Acidity in the Drainage Basin

The recultivation of the landscape should include measures to stop the acidification process at underground level and the migration of acid together with dissolved heavy metals. Iron, stemming from pyrite (FeS_2), is most important. It buffers the water at low pH between 2 and 3. Rules for good farming practice, forestry and fishery are known from acid rain research and experience. The landscape and its groundwater hydrology should look and function like or ecologically better than that before mining:

- Neutralizing fertilization with lime, dolomite powder (forestry), alkaline ashes, etc. to enhance the revegetation is also helpful in improving water quality (see also Katzur and Liebner, this Vol.). Liming dose is usually 2–4 t ha^{-1} (carbonate content 95–98%) and thus has an acid neutralization capacity (ANC) of about 40–80 kmol ha^{-1} (Kreutzer 1994).
- The groundwater table has to be kept high; fluctuations should be avoided. The result is to minimize aeration, acidification and heavy-metal migration.
- Evaporation and transpiration losses should be high. This reduces formation and throughflow of the groundwater.
- On the other hand, a higher air moisture in wetlands allows water condensation and thus a stabilization of the water in the subsoil.
- The vegetation cover should be close, if possible continuously during the whole year.
- Infiltration of appreciable amounts of carbon from organic fertilizer, such as dung, liquid manure and sewage sludge, and from harvest residues is useful to consume oxygen in the subsurface.
- Because nitrification produces acidity, ammonia fertilizer should be avoided and all N fertilizer has to be applied in nitrate form (Kelly 1994).
- The monocultural pine forests predominant before mining should be replaced by mixed forests with a large proportion of deciduous trees, creating a humus-rich topsoil.
- Long growth periods and restriction of wood-harvesting decrease the acid-forming cation export from the area.
- Clear cutting of large stands of trees must be avoided (Kreutzer 1994).
- One option for using the recultivated land is to build fish ponds, especially those for intensive fish cultivation with pellet feeding of carp. The sealing of the surface against atmosphere and oxygen is beneficial, as is the trickling of organic compounds into the ground, where they stimulate oxygen consumption.
- Another option for neutralizing land use is the establishment of wetlands. Wetlands are good habitats for sulfur-reducing bacteria. The product of desulfurication in an iron-containing environment is black

iron sulfide. This may be found in anaerobic parts of wet topsoils and especially between the rhizomes of the reed. In the USA, constructed wetlands have been proved to be service ecosystems for abatement of acidity in drainage waters from mining heaps (Hedin 1989; Kleinmann et al., this Vol.). Fish ponds and wetlands have had a long tradition in the Lusatian lignite district, East Germany, which should be continued now after mining.

All the measures recommended for drainage basins are at the same time part of the concept of a sustainable development of the landscape (Ripl et al. 1992):

1. Minimizing the groundwater throughflow.
2. Decreasing the coupled transport of substances.
3. Enhancing evaporation from the vegetation cover.
4. Enrichment of soils with organic substances to increase the binding capacity for water and other materials.

The post-mining landscape is much higher in relief than before and the groundwater table cannot reach the surface of higher heaps. These oxidized parts are sources for reacidification. Harmful, because intensifying the acidification, are fluctuations of groundwater and lake water tables. By these means new acid is produced and transported, together with acid-soluble heavy metals. The use of mining lakes for water storage therefore may be endangered by the acidity of the surroundings. Water table changes in this case are the operational normality. Evidently, the only way to avoid pyrite oxidation is to refill the overburden with water. The diffusion coefficient of oxygen in a water-filled heap is about 1/10,000 of that for an aerated one.

22.4 Neutralizing In-Lake Quality Management

22.4.1 Abatement of Acidification During Filling

Where there is danger of geogenic acidification, the possibility of filling with surface water has to be tested at an early stage. Criteria include the availability of water in quantity and quality as well as the costs of necessary pipelines, pumping stations, inlet and outlet buildings and sometimes surface water treatment plants. Natural elimination mechanisms such as incorporation, degradation, sedimentation, etc. may achieve the same quality targets in a longer time but without costs. There is a risk

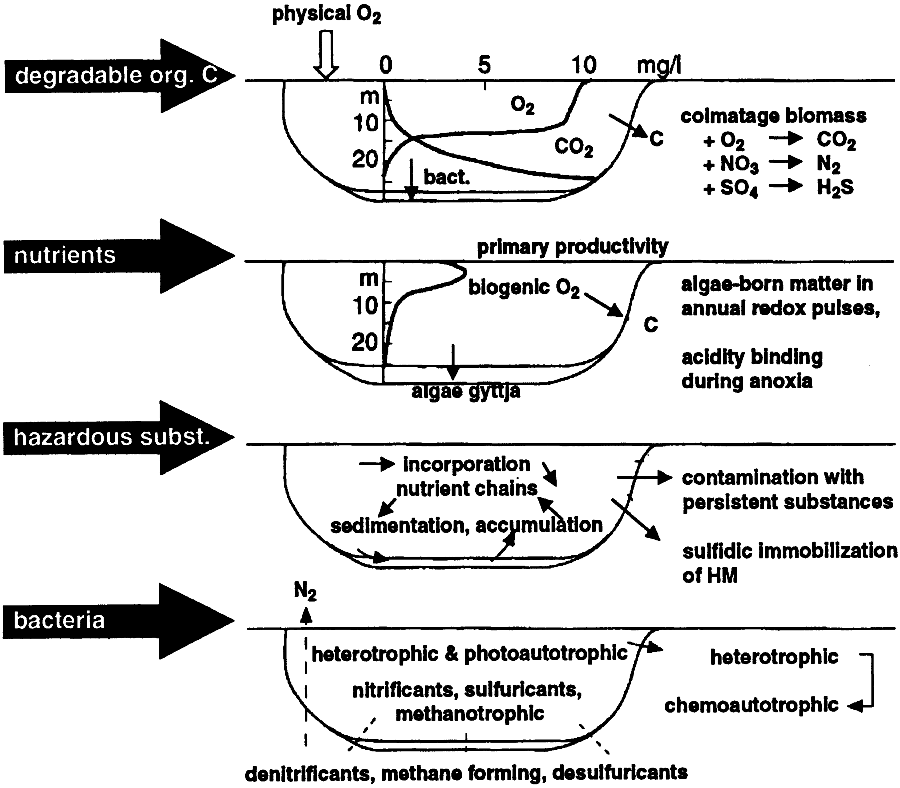


Fig. 22.1. Loading of a mining lake with contaminated surface waters and the most important consequences. *HM* Heavy metals. (After Glässer and Klapper 1992)

because of unwanted contaminants in the rivers in question, e.g. oxygen-consuming organics, plant nutrients, hazardous substances and unwanted bacteria including pathogens. Behaviour, metabolisms and pathways of matter have to be investigated in advance (see Fig. 22.1; Glässer and Klapper 1992).

The large running waters in and around the mining districts in East Germany contain neutral water buffered by hydrogen carbonate. The salt content is generally lower than that of groundwaters in the coal region. With surface water added, the water table in the mining hole may be kept higher than the groundwater level in the surroundings. The flow direction will be from the lake into the dewatered underground spaces. The infiltration of degradable substances during this first filling is advantageous with respect to the abatement of acidification. Under anoxic conditions, the acidification process may be stopped and eventually turned into the contrary – iron immobilized in sulfidic form. The third

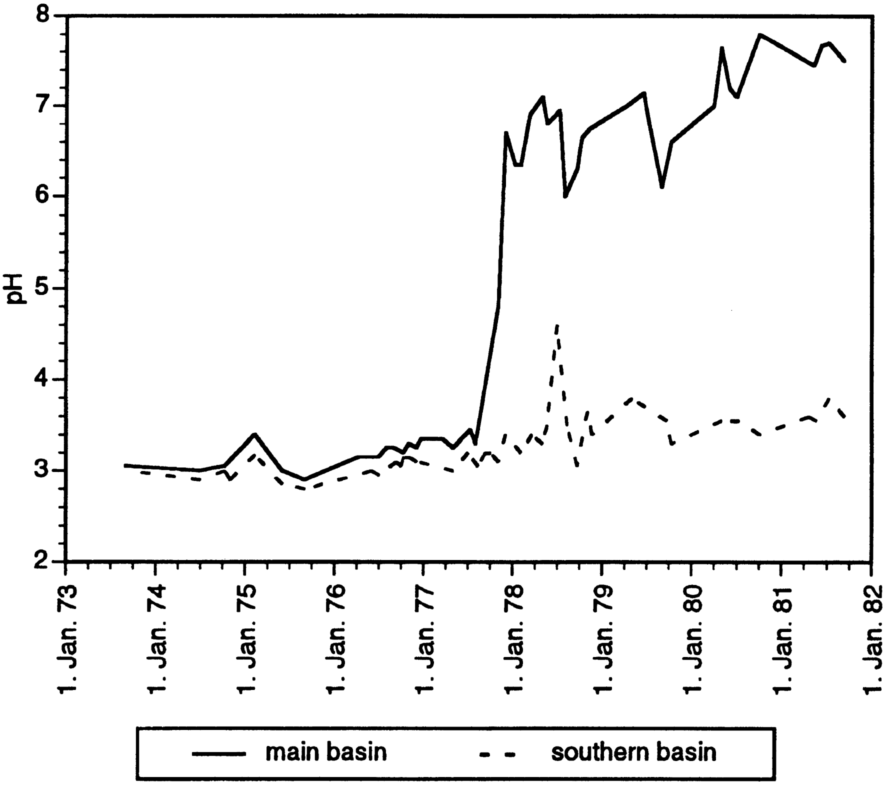


Fig. 22.2. Spatial distribution of pH values in Senftenberger See 1973–1981. A throughflow of Schwarze Elster River water exists since 1976. The water in the main basin is effectively exchanged, in contrast to the southern partial basin, being separated by an island and macrophyte stands. (After Puetz et al. 1991, cited in Benndorf 1994)

acidification step, the hydrolysis of iron sulfate to hydroxide, may be suppressed in this way.

The addition or throughflow of surface water in an already filled acidic lake causes two processes that counteract acidification. Firstly, a part of the acidic lake water is replaced by neutral river water. Secondly, a distinct neutralization results from carbonate hardness. The ANC of the surface water is consumed by the iron (and aluminium) buffer of the acid lake water. When the iron buffer is overcome, the pH shifts to the bicarbonate buffering system, i.e. into the pH range from 6 to 8. An impressive example was given at the mining lake Senftenberger See. For neutralizing purposes, 1.2 times the volume was replaced by river water from the river Schwarze Elster. The change in the pH value of the lake water looks like a titration curve (see Fig. 22.2). To avoid unwanted loading and decay of water quality, the addition of surface water should be limited to the amount necessary for neutralizing. ANC should be thoroughly monitored. Reacidification may occur when the buffering capacity is low.

In the Senftenberger See, in 1995 the water level was lowered for operational purposes. The pH decreased immediately, because of groundwater inflow, with the consequence of a fish-kill. The lake should be in a bypass to a stream. Acidity then may be controlled by the carbonate hardness and amount of the surface water added. Another option for control during the filling process is the utilization of treated groundwater from the active mine industry. For example, water treatment plants exist in the large power plants Schwarze Pumpe, Vetschau and Lübbenau in Lusatia. Mining water treatment plants are situated in Burgneudorf, Rainitza and Lichterfeld; these employ liming and separation of iron hydroxide. It is planned to treat two-thirds of the filling water in these facilities (Luckner et al. 1995). In cases with low acidification potential in the surrounding rock layers, a decision to do nothing and to wait the years necessary until all acidity is removed might also be a rational option.

22.4.2 Abatement of Acidification by In-Lake Measures

In-lake liming has been used in many soft water lakes impaired by acid rain. Throughout 1988, about 5000 surface waters were treated in the operational liming program conducted by the Swedish government (Nyberg 1989, cited in Olem 1991). Successful lake liming by different application technologies has been reported in Canada, USA and Norway, among others, as a suitable neutralizing measure for lakes with low ionic content. These lakes are quite different from the mining lakes with hard waters. They are buffered by iron in a lower pH range. A rough estimate of the limestone demand for the neutralization of the acidic mining lakes of the Lusatian district comes to about 235,000 t limestone powder. This would have to be distributed over a large number of lakes by a potential liming campaign (Schultze and Geller 1996). The neutralizing chemistry is shown in Chapter 3. For mining lakes, chemical alkalization is generally possible but expensive because of the high alkalinity demand. Today, worldwide attention is focused on the biological production of alkalinity – desulfurication and pyrite formation – that is, a reversal of the process of pyrite oxidation. Pyrite oxidation and reduction of sulfate to pyrite are shown in the following equation:

$$\begin{aligned} 2FeS_2 + 7O_2 + 2H_2O &\rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ + 7C \\ &\rightarrow 2FeS_2 + 7CO_2 + 2H_2O\,. \end{aligned}$$

To remove sulfuric acid by desulfurication is a relatively cheap method, but only applicable under anaerobic conditions. Denitrification of nitrate also produces alkalinity, but it is not as important because the nitrate concentrations are low. Such an anaerobic environment is found in the deep water of stratified eutrophic lakes. In oligotrophic or mesotrophic lakes, anaerobiosis occurs only in the monimolimnia of the meromictic types. In these deep water bodies, which do not take part in any mixing for many years, the oxygen demand accumulates.

After depletion of dissolved oxygen, the heterotrophic degradation of organic matter is continued with the help of nitrate- and sulfate-oxygen. This sulfate reduction is a desirable process as it eliminates sulfuric acid. Pyrite oxidation produces a high concentration of iron. Therefore the end product is not hydrogen sulfide but iron sulfide. This is insoluble and settles as black mud. Other (toxic) metals are also transferred in their insoluble sulfidic form. This immobilization seems to be an important step from the extreme environment of acidic to more nearly natural neutral lakes.

The living conditions required by the heterotrophic sulfate-respiring bacteria must be investigated in order to design an ecotechnology (Wendt–Potthoff and Neu, this Vol.). At first, observations from nature should be evaluated. Further ideas may be gained from technological solutions for denitrification and desulfurication in drinking-water treatment (Fichtner 1983; Klapper 1991; Brettschneider and Pöpel 1992). Environmental conditions which have to be realized for sulfate respiration within an ecotechnology are:

- Exclusion of dissolved (and nitrate-) oxygen
- Presence of degradable organic substrate
- Biologically inert or organic materials as supporting structures or biofilm carriers
- High content of sulfate (and iron)
- Initial microhabitats with $pH > 4$

The neutralized water needs reaeration after desulfurication to become a fish habitat.

Most acidic mining lakes are oligoproductive in the early stages of their development. The oxygen demand of sedimenting and degrading algae is not high enough for oxygen depletion (see for example Fig. 22.3, mining lake Koschen). A similar productivity but very small hypolimnion volume is producing oxygen depletion and the first signs of alkalization near the bottom in mining lake 117 near Lauchhammer. The lake treatment plant Laubusch is heavily loaded with domestic sewage. Deep water is strongly anaerobic and neutralized up to the hydrogen carbonate range.

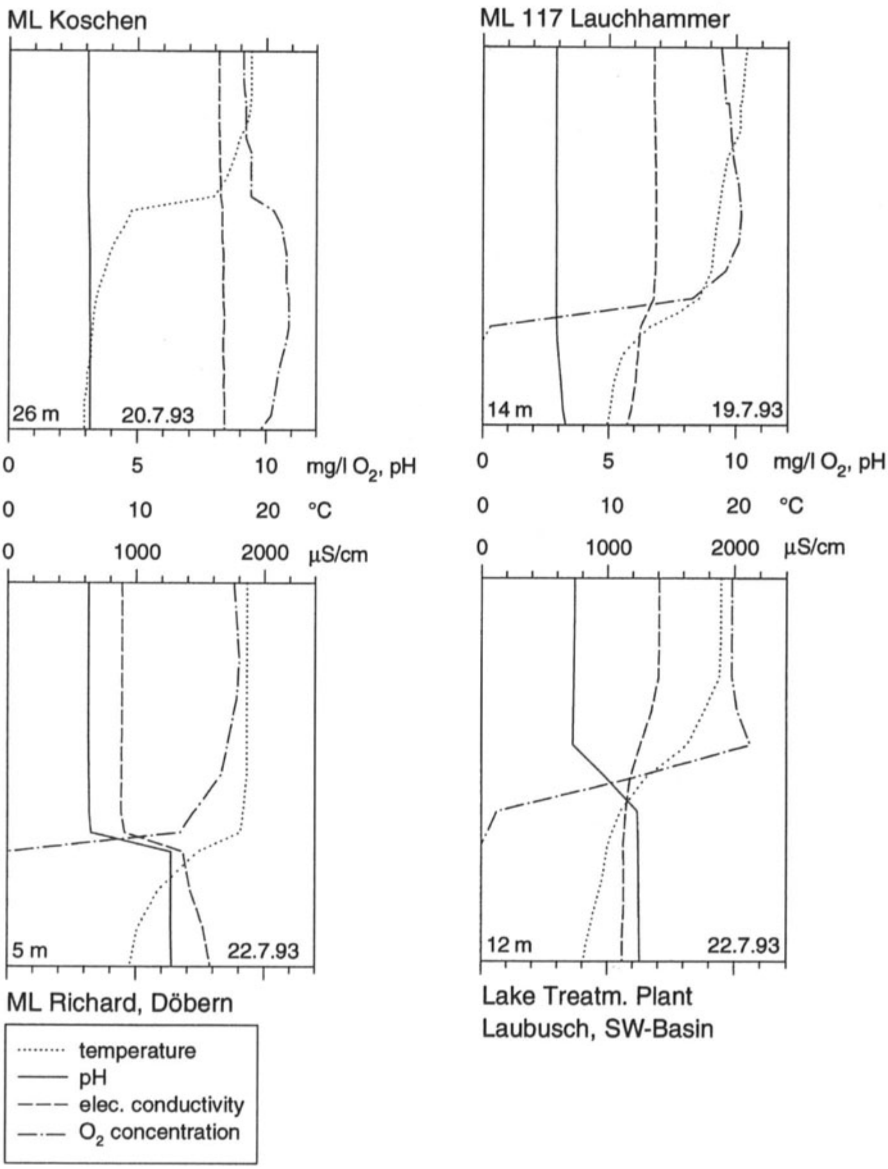


Fig. 22.3. Geogenic acidic mining lakes (*ML*) in Lusatia

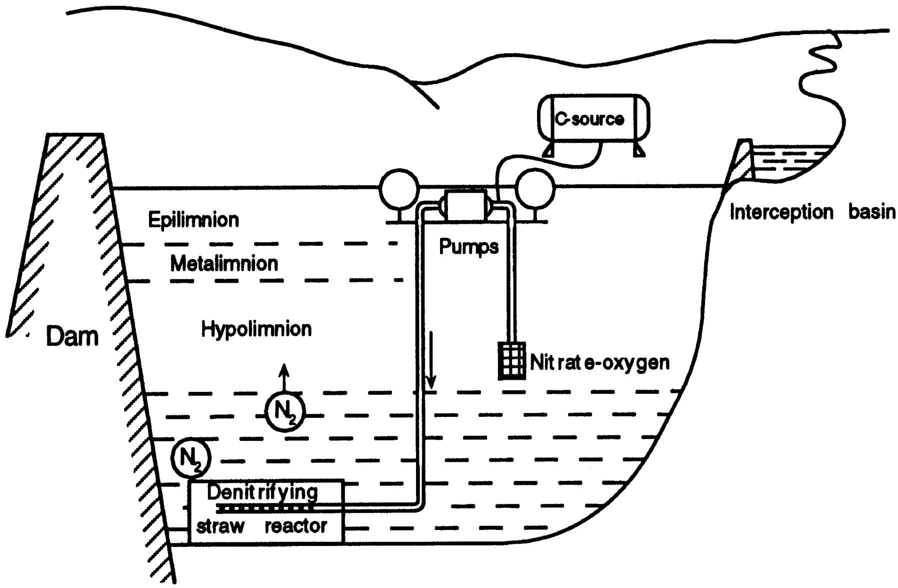
The precipitation of iron sulfide results in decreasing conductivity in the deep layers.

The small mining lake Richard near Döbern is iron-meromictic. Because of a very high content of dissolved iron the conductivity in the monimolimnion is high. Of special interest is the neutralization in the anaerobic part of the lake. Nitrate elimination needs environmental preconditions very similar to those for sulfate respiration and offers ideas for technology. In California, USA, small but deep ponds were covered and supplied with methanol as carbon source. Eight days at 22 °C or 15 days at 16 °C were required to reduce the nitrate concentration from 20 to 2 mg/l with 65 mg methanol /l. An open pond had not reached the desired level after 20 days (Brown 1971; Jones 1971; Sword 1971). The cheapest organic substrates are wastes such as liquid manure, pre-treated domestic sewage, molasses and industrial wastes. In experiments on sulfate elimination for drinking-water purposes, whey, sucrose, sodium lactate and ethanol were investigated. The latter performed best. In the other substrates, the desulfuricants were overgrown by acetogenic bacteria, which lowered the pH by producing organic acids (Brettschneider and Pöpel 1992).

Another example of an anaerobic ecotechnology which has worked well was developed for heterotrophic nitrate dissimilation in the reservoir Zeulenroda, in the former GDR. It was accomplished in the hypolimnion of the main storage basin, which is normally still aerobic, even at the end of the summer stagnation (see Fig. 22.4). Rape straw was selected as the supporting surface for denitrifying bacteria, serving simultaneously as a slowly decomposing carbon source.

A total of 13,000 straw bales were packed tightly into a steel cage measuring 20 × 60 × 1.5 m. Three layers were encased in an outer covering of wire mesh. On the lowest layer a herringbone-pattern drain system was created which distributed the nitrate-rich water together with decomposing substrate. This substrate consisted of a mixture of lower fatty acids and was a waste product of paraffin oxidation. At first the dissolved oxygen was consumed, after which the nitrate oxygen was utilized. In the first stage the decomposition resulted in the formation of nitrite. This was further reduced to nitrogen gas after complete disappearance of nitrate. In this way it was possible to discharge nitrate-free water from the hypolimnion into a non-impounded river segment. There it can become saturated with oxygen before it reaches the terminal barrage with its raw water intake (Klapper 1991).

Natural processes of acidification and alkalinization are quite different in different lake environments. Polymictic lakes and those filled mainly with groundwater may remain acidic and oligoproductive for decades. In



$$C_{12}H_{12}O_{12} + 8\,NO_3^- \longrightarrow 4\,N_2\uparrow + 12\,CO_2 + 11\,H_2O$$

Fig. 22.4. Schematic diagram of heterotrophic nitrate dissimilation in the hypolimnion of a reservoir. (After Klapper 1991)

deeper, stratified lakes and those filled with nutrient-rich surface water, alkalinization can take place in the deep water and in the surrounding groundwater as well (see Fig. 22.5).

Many of the mining lakes have critical depths and the neutralizing processes are interrupted when stratification breaks down. In this case it is useful to shorten the fetch of the wind by artificial barriers, which divide the surface into some shorter segments; by this means the mixing depth is decreased. From an ecological point of view natural materials should be preferred, e.g. floating reed installed across the lake (see Fig. 22.6).

For research purposes, lake volumes can be partitioned by introducing enclosures or limnocorrals. Standing waters generally are protected by law against nutrient input. A controlled addition of nutrients or organic substrates for controlling acidity goes against the commonly accepted water policy and should be used only temporarily to stimulate alkalinization processes. As a long-term goal, the water quality in a nearly natural mining lake should correspond to its hydrography. Deep lakes will be kept oligotrophic or mesotrophic, shallow ones more or less eutrophic. The finished neutralization will be accompanied by flocculation of iron hydroxide together with phosphorus. Macrophyte stands will assist this

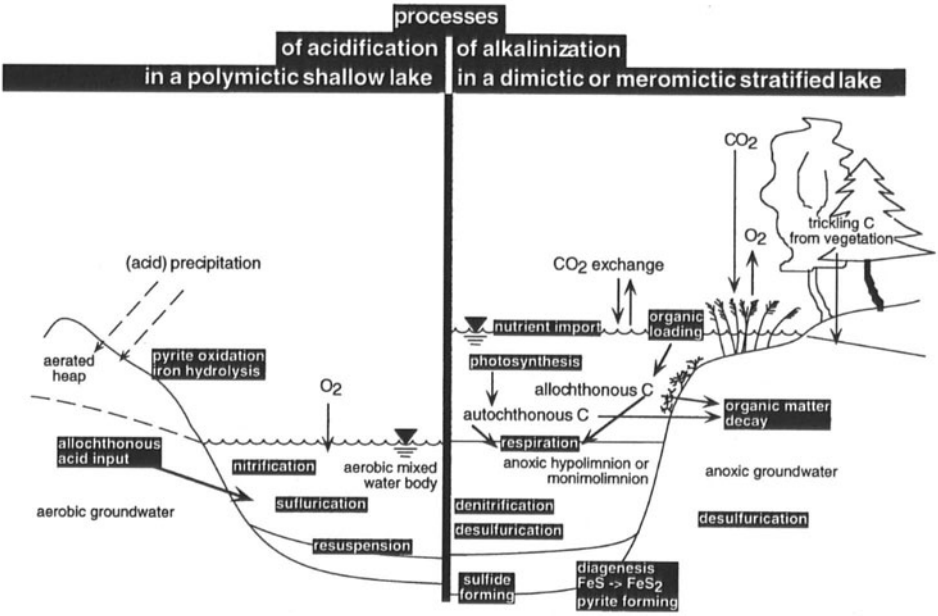


Fig. 22.5. Processes affecting acidity in shallow and in stratified water bodies

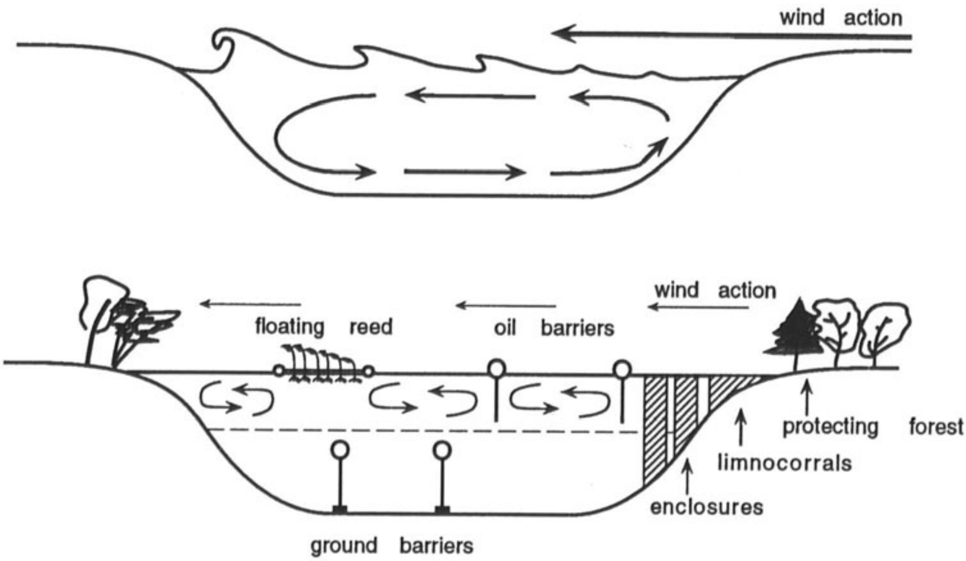


Fig. 22.6. Circulation and stability without and with barriers

Table 22.1. Ecotechnologies for recovery of acidic mining lakes

In situ (within the mining lake)	Whole lake anaerobic	Only very small bodies of water with high organic load; covered surface
	Anaerobic parts	Use of deep water for desulfurication Use of enclosures for research Stabilization of stratification Sediments as traps for sulfur and metals Addition of organic substrate Addition of nutrients and production of organics by controlled eutrophication
	In-lake placement of a throughflow reactor	Throughflow straw reactor positioned in the deep water and addition of organic substrate
Ex situ (before and between mining lakes)	Anaerobic treatment	Anoxic straw-filled trenches Anoxic limestone drains Closed subsoil reactor, filled with inert or degradable biofilm carriers; addition of C-substrate Infiltration ponds with compost bottom and drainage
	Aerobic treatment	Reed-bed treatment plants for combined purification of tailings and sewage Reaeration channels with limestone overflow barriers

process. They are suitable in different service ecosystems for polishing the water.

Some of these "constructed wetlands", "float reed" and „shore bioplateaus“ may be called well-tried and successful ecotechnologies. The recommended combinations of different ecotechnologies are summarized in Table 22.1. Further intensification is possible by a partial chemical alkalinization with lime, ashes, etc. The different conditions at each individual mining lake have to be checked by monitoring and limnological expertise in advance of filling. Additional investigations should be carried out as the lake fills and during the first succession stages of the young lake, until the water quality has stabilized. Ecological engineering may help to develop mining lakes as new sustainable ecosystems that have high human and ecological value. Sustainability has to function indefinitely through the design of the lake itself, with only a modest amount of human intervention (Mitsch 1993).

22.5 Conclusions

Acidity of geogenic origin released by mining activities is the most severe water quality problem in the lignite mining lakes in the former GDR. Only a few smaller examples of these extreme habitats should remain unaltered and be preserved for natural succession, in the interest of con-

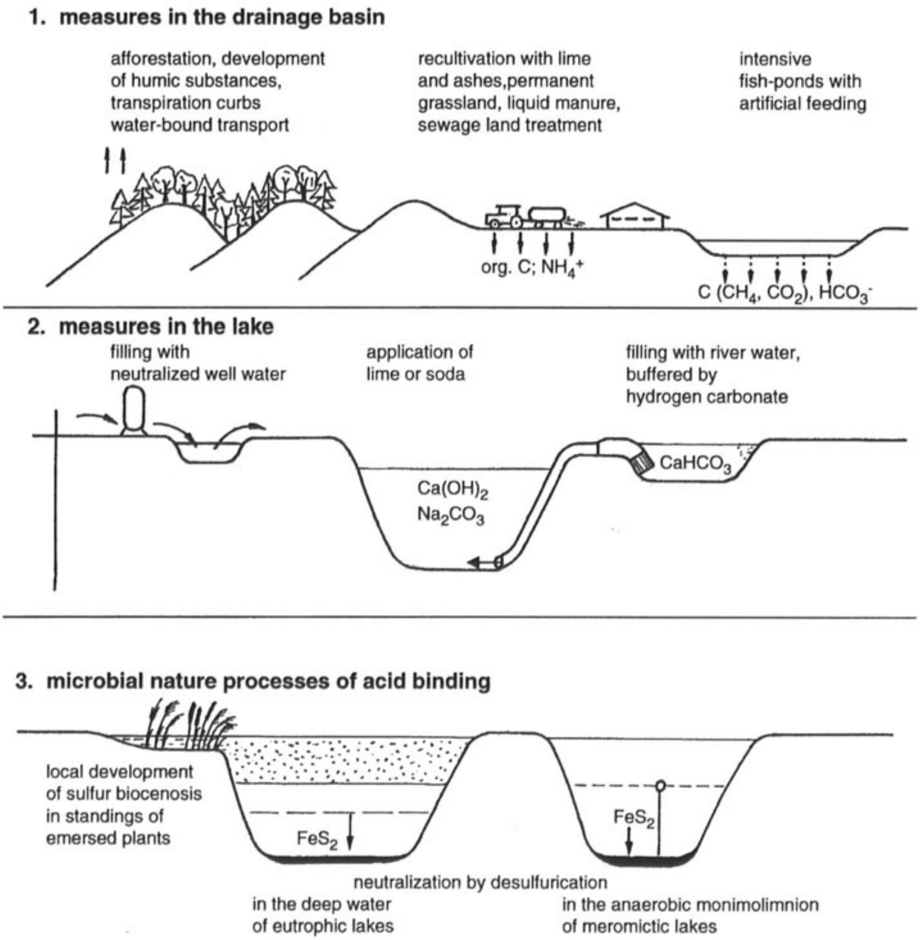


Fig. 22.7. Neutralization of geogenically acidified mining lakes. (Klapper and Schultze 1995)

servation and limnological research. In the majority of cases, water quality management has to be directed towards creating more nearly natural environments. Abatement of the acidification starts from sites of pyrite oxidation, includes the groundwater and acidity transport and concentrates on the mining lakes, where in-lake measures must be taken. Chemical neutralization is often not feasible because such large amounts of alkalizing agents are required. The large lakes are preferably filled with surface waters containing bicarbonate. The disadvantage of a higher trophic level has to be tolerated temporarily. Another neutralization alternative is the microbial process of acid binding desulfurication. There is an urgent need for research into ways to stimulate this strong anaerobic process. Further ecotechnological methods with limestone barriers, constructed wetlands, etc. are suitable for water polishing by aerobic flocculation of iron hydroxide (see Fig. 22.7).

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