

# Acid Drainage from Mines

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The drainage of waters from abandoned coal and metal mines is often acidic with an elevated heavy metal content. Interaction between this acid mine drainage and the environment can cause gross pollution. Whilst temporary engineered remediation can lessen the impact, complete amelioration is only possible using active and/or passive treatment systems. Active technologies are costly as they often include the controlled addition of chemicals which can produce a contaminated effluent that requires additional treatment. The study of natural marshland within mining areas has led to the development of using constructed wetlands as a potential treatment option. The chemistry of acid mine drainage often requires the use of aerobic (mine water oxidation) and anaerobic (sulphate reduction) systems and commonly utilizes some form of pretreatment system. The science of wetland treatment processes is still not fully understood and as a consequence the full potential of the technology has yet to be realized. There is evidence, however, that the use of passive treatment is a realistic and cost-effective remedial method for acid mine drainage.

KEY WORDS: Acid mine drainage, pollution, treatment systems, wetland treatment processes.

**W**ATERS WHICH DRAIN NATURALLY from abandoned mine workings are often characterized by a low pH and alkalinity with elevated concentrations of metals (e.g. iron, manganese and aluminium). These waters, commonly referred to as acid mine drainage, are not new, their occurrence having been recorded back as far as Roman times (Wildeman *et al.*, 1991). The extraction of sub-surface coal and metalliferous deposits has left a legacy of underground workings and exposure of wallrock to the surrounding environs. It is the interaction between the wallrock and oxygenated water which causes the generation of acid mine drainage. These processes have been dealt with comprehensively elsewhere (Johnson and Thornton, 1987; Argall and Brawner, 1979; Robb, 1994) and it is not the intention of this paper to review such processes.

When acid mine waters mix with surface waters there is the potential for gross pollution. An orange ochre (ferric hydroxide precipitate) may blanket the river, estuary or sea bed killing aquatic flora which can lead to disruption of the food chain. The quality of the resulting surface water can also render water abstractions useless. A number of such cases have been documented in recent years (e.g. the pollution of Restronguet Creek by the Wheal Jane Mine) and the plan to close many of the coal mines in the United Kingdom has led to much publicity:

## **Rivers at risk from flooded mines**

British Coal is opposing demands from the National Rivers Authority that it should continue to pump water from the Durham Coalfield. The companies' refusal could lead to massive pollution of the River Wear.

*New Scientist*, 19.02.94: 10

## **Pouring coal on troubled waters**

Spare a thought for the forgotten casualty; besides the jobless miners and their devastated communities, the rivers will suffer from poisoning by toxic pollution pouring from the abandoned mine workings.

*The Times*, 10.12.93: suppl.

## **Mine closure a time bomb, says Trust**

The latest closures of coal mines represents an environmental time bomb, says a report from the environmental research group, the Clean River Trust.

*Water Bulletin*, 3.12.93: 585

## **Abandoned pits pose threat to environment**

Abandoned coal mines can pose a massive threat to the environment for which there is no legal redress.

*The Daily Telegraph*, 8.4.94: 22

## **Concern over possible mine water pollution**

Planned mine closures by British Coal have prompted fears of water pollution as underground pumping operations may cease upon closure of the

mines. Acidic, metal rich, iron ore bearing water could, it is feared, seep out of mines and eventually contaminate the water table.

*Waste Management Today*, 1994: 21–22

The National Rivers Authority recognized (1994) a total of 96 discharges from abandoned mine workings into the rivers in England and Wales which when combined with discharges from working mines cause significant pollution to 198 kilometres of natural watercourses.

#### *Characteristics of acid mine drainage*

The nature of acid mine drainage varies significantly between and within different areas. It is this variation which makes both the prediction and treatment of a mine discharge very difficult. This is shown by Table I which lists the analyses of some key determinands within drainage from different sources.

Scrutiny of Table I shows that the discharges are acidic with a variety of heavy metal content, the latter being related to the environment in which the drainage was developed. Coal mine drainage, such as those identified in the Durham and Ayrshire Coalfields, typically contain elevated concentrations of iron, manganese, sulphate and aluminium. Drainage from metal mining, however, (e.g. the Cornish Tin Mines) can in addition, also contain relatively high levels of zinc, copper, arsenic, cadmium and lead.

Although this relationship between heavy metal content and drainage source is relatively distinct in the UK, elsewhere this is not the case. Coal mine drainage in the USA, for example, can contain a variety of heavy metals, whereas the lignite mines in West Germany produce an acidic drainage with a low metal content.

The aim of this paper is to discuss the various options available for amelioration of acid mine waters, involving consideration of temporary remedial methods and full treatment using both active and passive systems.

#### *Temporary remedial methods*

If mine waters emit from a point source then it is possible that civil engineering methods may be employed to lessen the impact of pollution in receiving watercourses. For example, if the mine discharge is near the coast it may be feasible for the ferric-rich mine waters to be transferred via a pipeline for discharge and dilution at sea. The construction of a pipeline will require a high initial capital expenditure and commonly is an uneconomic option.

Experiences at Dalquharran Mine, Ayrshire, have led to a holding dam being constructed over the mine discharge which contains the mine waters flowing from the old workings. In the adjacent Water of Girvan there is an automatic flow gauge which monitors the stage and hence the volume of flow in the river. The flow gauge is connected to an automatic valve at the holding tank. When flows in the river are high (greater dilution potential) the valve at the holding tank opens to allow flow from the dam. When flows in the river decrease the valve then shuts. In theory this arrangement should work well, limiting pollution in the Water of Girvan yet discharging the mine waters. However, the Water of Girvan has a rapid response to rainfall and peak flows in the river may occur within hours of a storm, in comparison flow from the mine does not peak until one or even two days after the rainfall event (Robb, 1992). Thus when the peak flow from the mine occurs the valve in the stilling dam will have shut as the peak flow has passed in the Water of Girvan and mine waters will be stored. It should be noted that the construction of the dam has decreased the pollution in the river, although after particularly prolonged wet periods the dam can be overtopped resulting in pollution of the Water of Girvan.

If the pumps that maintain dry workings while the mines are operational are kept working after mine abandonment then there will be no groundwater rebound and, therefore, no risk from acid mine water generation. The costs, however, of maintaining the pumps may make this option unfeasible in an abandoned mine. One possible solution which would

TABLE I  
*Chemical variation within acid mine drainage*

	<i>pH</i>	<i>SO<sub>4</sub></i>	<i>Fe</i>	<i>Mn</i>	<i>Cu</i>	<i>As</i>	<i>Pb</i>	<i>Cd</i>	<i>Al</i>
Cornwall <sup>1</sup>	3.5	1500	300	20	10	15	0.1	0.1	60
Durham <sup>2</sup>	4.1	1358	75	4.8	0.2	0.0	0.01		4.2
Ayrshire <sup>3</sup>	4.1	6000	1200						10
Illinois <sup>4</sup>	3.0	1300	57	6.444					37

All units mg/l except pH.

Notes: <sup>1</sup> Data from National Rivers Authority (Southwestern Region), 1994

<sup>2</sup> Data from Younger and Bradley, 1994

<sup>3</sup> Data from Robb, 1994

<sup>4</sup> Data from Wildeman *et al.*, 1991

minimize the costs of pumping would be to allow partial recovery of groundwater levels in the mine workings to a level near that, but below where a discharge at the surface would occur. Water levels in the workings can then be monitored and maintained, with the use of pumps, at the required level. This would, however, require a detailed knowledge of the extent of the mine workings and an ability to infer the hydraulic regime from these. Commonly, owing to the prolonged development of mine fields, there are limited available plans showing the full extent of workings. Also owing to the complex flow patterns which may develop in mine workings it is very difficult accurately to predict the size and location of a discharge. In addition geological change in the workings (i.e. collapse) may initiate a new flow regime.

Even if it is possible to predict the location and control the discharge of mine waters from abandoned workings, by pumping, the costs for treating the water before discharge may make this option unfeasible.

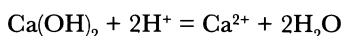
The preventative measures outlined above do not provide a solution to the pollution potential from an abandoned mine, they may, however, be used to limit its impact. The treatment of the polluted waters requires a different approach and can be achieved using active or passive methods.

#### *Active treatment*

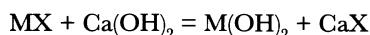
Active treatment methods incorporate the use of mechanized procedures which are dependent upon being continuously monitored and maintained.

The nature of acid mine drainage has meant that traditional treatment processes have involved aeration, precipitation of oxyhydroxides/hydroxides, settling and filtering. Such treatment systems are relatively ineffective for acid mine drainage treatment as the acid pH often ensures that the oxidation kinetics are too slow. The addition of a chemical to raise the pH of the drainage will increase the precipitation kinetics of the metals as insoluble hydroxides. The chemicals used normally include calcium hydroxide (lime), sodium hydroxide (caustic soda) or magnesium hydroxide. The neutralization and complex formation reactions between lime and the acidic drainage are shown below:

- i) Lime neutralizes the acidity (hydrogen ions).



- ii) Lime complexes the metal (M) as a hydroxide, where X represents any metal ligand such as sulphate.



Experience has shown that a relatively small amount of lime is required to raise the pH of the mine water and the majority of the lime added is used to form

the heavy metal hydroxides. Following the reactions outlined, facility has to be made for the collection of the volume of sludge produced by the treatment. This sludge typically contains a variety of metal hydroxides, some calcium sulphate and unreacted lime (since lime has a solubility of about 1.0g/l).

Whilst the addition of chemicals is an effective treatment method, the cost of building and operating a chemical treatment plant can be relatively high. This, coupled with the fees for the disposal of metal-liferous sludge can substantially increase the running costs of the remedial scheme.

It is theoretically possible to use a variety of different active treatment options such as dissolved air flotation, ion exchange and others used in the water treatment field. The use of such treatment techniques can be complicated by the high metal loadings (drainage flow x metal concentration) within the mine water drainage and this combined with the costs of running such a treatment system often precludes their use.

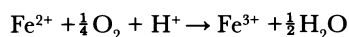
#### *Passive treatment*

Passive remedial action utilizes processes similar to those used in active treatment, although the application methodology is somewhat different, in that passive systems employ independent treatment systems which require a minimum of maintenance.

There have been several studies of naturally occurring bogs or marshland which were subjected to the influx of acid mine drainage (e.g. Weider and Lang, 1984). This research provided the insight into the use of such systems for the treatment of acid mine drainage. Development of these early studies was carried out by the US Bureau of Mines (Brodie, 1991) in attempts to treat waters issuing from abandoned coal mines. Further research and the study of natural wetland systems (Wildeman *et al.*, 1991; Hedin *et al.*, 1994) has firmly established the use of constructed wetlands for the treatment of acid mine drainage generated from coal and metal mining.

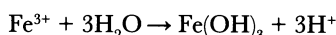
Successful treatment of acid mine drainage from coal and metal mines requires the consideration of aerobic and anaerobic wetland processes. The following discussion describes both systems and considers their use for the treatment of all metals likely to be found within the drainage.

*Aerobic wetland treatment* Drainage within deep abandoned mine workings is commonly oxygen-deficient with reducing conditions often being prevalent. As a consequence the iron within the acidic mine water is predominantly in the ferrous (iron II) state, although some ferric (iron III) iron will also be present. Upon exposure to the surface the ferrous form will oxidize to ferric form:

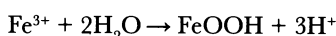


The rate of iron oxidation is controlled by the pH of the mine water. Below ground and at acid pH levels (pH 2.0 – 3.0) the oxidation of the mine water is controlled by bacteria and is relatively slow, the oxidation taking a number of days. At more alkaline pH levels (>pH 5.0), and in the presence of air, the oxidation is not bacterially controlled and can take a matter of minutes. Aerobic wetland systems are designed to encourage the oxidation process and are consequently relatively shallow (about 0.3m deep), vegetated and with surface flow predominating (Fig. 1).

As ferrous iron is converted to ferric iron in the wetland, a hydrolysis reaction takes place which causes the precipitation of ferric hydroxide or oxyhydroxide:



or



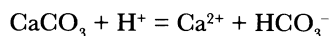
Therefore, by encouraging oxidation processes, iron will be removed in the aerobic wetland by ferric hydroxide precipitation causing the build up of the characteristic red ochre often observed at acid mine drainage sites. A consequence of this reaction is the production of acidity (hydrogen ions), which lowers the pH of the mine water. This can reduce the oxidation rate (as outlined above) and cause distress to plants growing in the aerobic cell. Plants such as reeds (i.e. *Typha latifolia* and *Phragmites australis*) are encouraged to grow as they pass oxygen through their root system causing aeration of the substrate. It is, therefore, desirable to add alkalinity to the mine

water to prevent the pH falling and hence ensuring that an optimum removal rate of iron is maintained.

Alkalinity can be added to the aerobic system in two different ways. The first involves the use of organic matter as a growth substrate for the propagation of reeds in the aerobic cells. The growing reeds will pass oxygen through the organic substrate which will produce carbon dioxide. The gas dissolves in the mine water and will consume hydrogen ions, add alkalinity and raise the pH.

The amount of alkalinity produced is controlled by the solubility of carbon dioxide in the mine water. As the gas is only slightly soluble in water and the rate of production is less than that of iron precipitation, another method for the passive addition of alkalinity is required. One such method involves the use of an anoxic limestone drain.

**Anoxic Limestone Drains (ALD)** This method involves the pre-treatment of mine water through a drain consisting of crushed limestone which is buried in the ground and sealed from air (Fig. 2). The mine water reacts with the surfaces of the limestone to dissolve carbonate which consumes hydrogen ions (i.e. reduces the acidity) and adds alkalinity to the mine water:



The process must be kept anoxic to ensure that ferric hydroxide does not precipitate within the drain. This will cause armouring of the limestone surfaces which reduces the efficiency of the alkalinity production. If the mine water does contain elevated dissolved oxygen (>2mg/l) armouring will probably occur. In addition if the iron is predominantly in the ferric

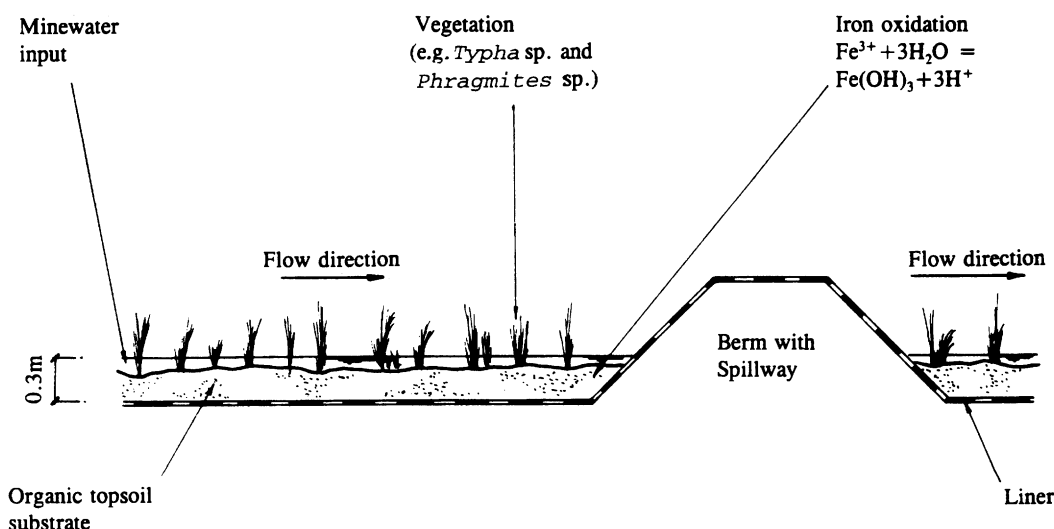


Fig. 1. Section through an aerobic wetland

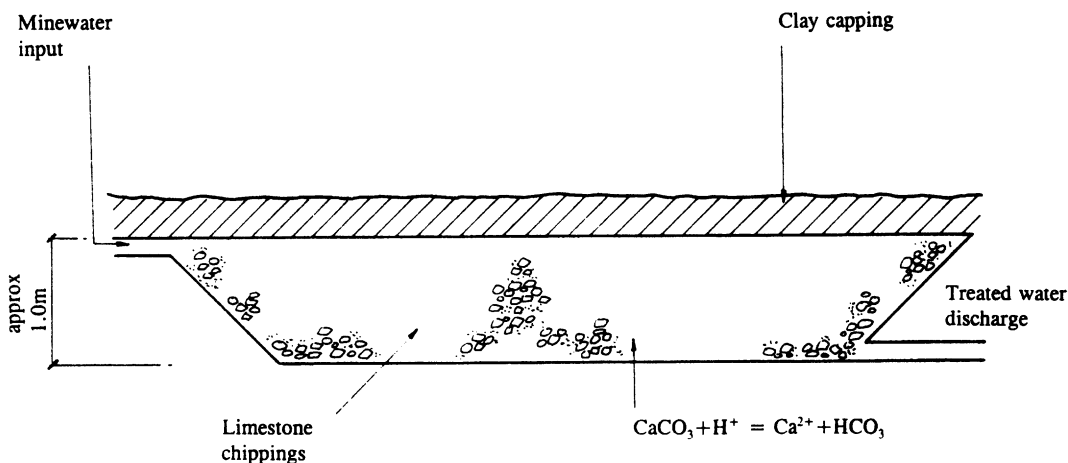


Fig. 2. Section through an Anoxic Limestone Drain (ALD)

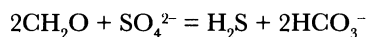
(Fe<sup>3+</sup>) form this will armour the limestone irrespective of the levels of dissolved oxygen. Studies carried out by the Mine Land Reclamation Centre in the USA, have indicated that an anoxic slurry pond can be used to remove dissolved oxygen from the mine water. This pond will strip the oxygen from the water and could induce reducing conditions. The latter point is important as this will potentially ensure that the iron will be in the ferrous state prior to its introduction into the ALD. This should, in turn, prevent the surfaces of the limestone from becoming armoured.

The use of an ALD or pre-treatment will inevitably produce hydroxide sludge at a faster rate in the wetland than without one. This means that whilst the area of aerobic wetland required is less with an ALD, it probably requires either a collection trench for the sludge or the deepening of the first aerobic cell.

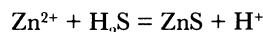
Once the iron has been removed using an aerobic wetland the remaining metals (i.e. zinc, copper, cadmium, lead and mercury) may require removal. This can be achieved using an anaerobic wetland system.

**Anaerobic wetland systems** Whilst the aerobic wetland uses oxygenation processes within a surface flowing system, anaerobic systems are quite different. These require the mine water to flow through a body (normally around one metre thick) of organic material under anaerobic conditions (Fig. 3). Mine water has high levels of sulphate (see Table I) and it is this which is consumed to remove the metals in the wetland. The organic material, can be locally derived and might include spent mushroom compost, different manures and sawdust. The organic material

must, however, contain sulphate-reducing bacteria (*Desulfovibrio* sp.). These reduce the sulphate in the mine water to produce hydrogen sulphide gas and dissolved alkalinity:



The resulting hydrogen sulphide will then react with the heavy metals within the mine water and cause their precipitation as heavy metal sulphides:



It can be seen that the above reaction produces acidity, however, the sulphate-reducing reaction produces more alkalinity (one mole excess over the proton acidity produced) and hence a net alkaline condition prevails. This provides additional buffering within the anaerobic wetland which is necessary as the bacteria present will not flourish at pH levels below 5.5.

This production of alkalinity by sulphate-reducing bacteria might be considered as a pre-treatment for an aerobic system, should an anoxic limestone drain fail. The anoxic slurry pond, which was originally designed as a pre-treatment for the ALD (i.e. for oxygen removal), will contain sulphate reducing bacteria and hence has the capacity for the anaerobic production of alkalinity. Recent studies in the USA have shown that this system can be used as part of a wetland treatment system (NMLRC, 1993), although its use as an alkalinity generator has yet to be tested. It is understood (Haddon, 1994) that an anoxic slurry pre-treatment system has been incorporated into the Wheal Jane Mine remedial scheme.

It is very important to maintain anaerobic conditions throughout the wetland cell. The growth of reeds

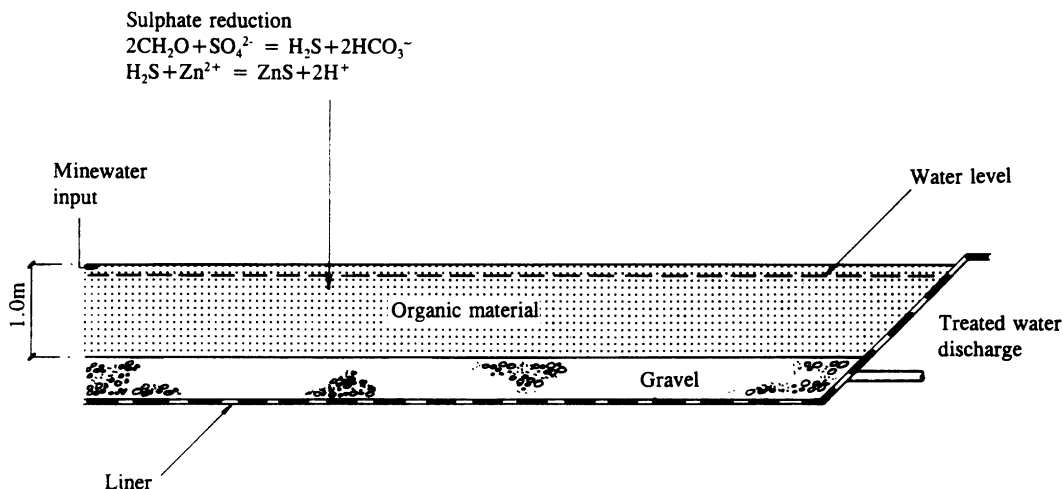
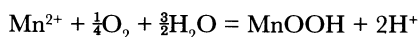


Fig. 3. Section through an anaerobic wetland

and ponding/flooding should, unlike the aerobic cells, be actively discouraged as this will pass oxygen into the organic substrate destroying the anaerobic condition. There will also be a problem with competing aerobic and anaerobic micro-environments which will ultimately reduce the effectiveness of the treatment system. This could explain the lack of success of the early combined wetlands designed in the USA (Gusek, pers. comm., 1993).

#### Manganese and aluminium removal

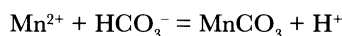
Inspection of Table I reveals the presence of two metals, namely manganese and aluminium, remains to be addressed. Manganese can undergo oxidation and hydrolysis in an aerobic wetland producing precipitates of manganese oxyhydroxides:



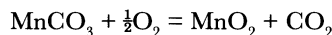
Although the reaction is theoretically possible, there is no natural mechanism that rapidly oxidizes manganese under acidic conditions and hence the amount of acid added (i.e. by the release of hydrogen ions) will be minimal (Hedin *et al.*, 1994). In fact the aerobic wetland used for iron removal will remove little or no manganese either by oxidation, particularly at lower pH levels, or other processes such as adsorption onto iron hydroxide surfaces. Removal within an anaerobic system is possible. The solubility product of manganese sulphide is, however, considerably higher than other metal sulphides found in mine water and the sulphide will only form if the other metals are present in minor amounts. The evidence indicates that a separate passive treatment is required for the removal of manganese.

The removal of manganese is most likely in an aer-

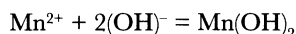
obic system, under alkaline conditions, where manganese can be removed by the following mechanisms:



and



To ensure these removal mechanisms operate at a fast enough rate pH values greater than 6.0 must be present. Also, should the pH reach levels above 10.6, manganese hydroxide will precipitate:



Studies have shown that certain types of algae, in particular those which contain cyanobacteria, remove appreciable amounts of manganese in an aerobic environment where they are attached to the surfaces of rocks. The algae create a micro-environment with the rock which is believed to have an elevated pH. This alkaline micro-environment causes manganese to precipitate by one of the mechanisms outlined above. It is, therefore, likely that a constructed rock filter (Fig. 4) will remove appreciable levels of manganese.

Aluminium, like ferric iron, will form metal hydroxides should the treated waters exceed pH 4.5, without requiring the presence of oxygen. This can present problems with ALD performance as, although iron can be transformed to the soluble ferrous form by using a pre-treatment system, aluminium cannot. Aluminium hydroxide precipitation causes the plugging of ALDs and whilst the armouring can be relatively easily removed by flushing, this demonstrates that elevated aluminium can be a problem in the passive treatment system.

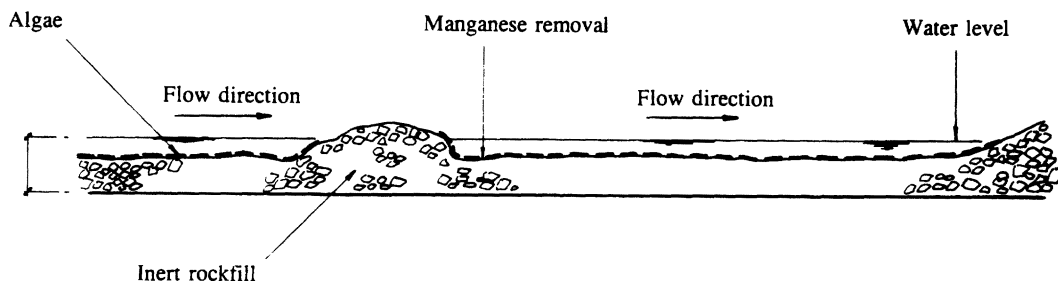
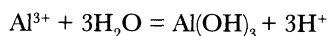


Fig. 4. Section through a rock filter

The elevated pH and alkalinity induced by the growth of some sulphate-reducing bacteria within an anoxic slurry pond might remove aluminium as a hydroxide:



It is also possible that aluminium will be removed by adsorption onto the surface of the organic matter present. The removal of aluminium might be accomplished by pre-treatment of the drainage using an anoxic slurry pond. Although this form of pre-treatment is, as yet unproven, the ability of the pond for the removal of oxygen and addition of alkalinity, makes its incorporation into a wetland treatment system potentially important.

#### *Problems associated with passive treatment and potential uses*

Whilst the use of constructed wetland treatment systems has been shown to be an effective method for the remediation of acid mine drainage (Brodie *et al.*, 1989; Wildeman and Laudon, 1989), research into the process and how it operates is still in its infancy. Constructed wetlands have, for example, only been operational for a few years in the USA and hence the effectiveness with time has yet to be assessed. The resilience of anoxic limestone drains has also yet to be tested. It is known that the neutralization process will involve the dissolution of limestone within the drain, the effects this has upon the structural integrity of the drain also requires consideration.

Another problem associated with the use of constructed wetlands is one of land availability. The size of the wetland treatment cells is governed by the metal loadings within the acid mine drainage (drainage flow rate  $\times$  heavy metal concentration). The metal loadings within some mine waters can be very high often requiring hectares of constructed wetlands for remedial action. It is these factors that require consideration of the land available and of what is the optimum treatment. It may be practical to only treat a proportion of the flow, which upon mixing with the untreated portion may provide sufficient dilution to allow the discharge of the combined

flow into the river system.

The relatively new science of using passive wetland treatment also means that the viability of using the same principles within other pollution treatment areas has yet to be tested. Waters with relatively high sulphate and heavy metal levels can potentially be treated using such techniques. Those areas where wetlands are being considered, and in some cases actually tested, include remedial treatment of domestic landfill leachate, run-off from roads and contaminated groundwater.

#### *Conclusions*

Civil engineering remedial measures can be incorporated to limit the potential consequences of a discharge from abandoned mine workings. Structures can be built to transfer mine waters to suitable discharge points or to hold polluting mine waters before controlled discharge. These measures unfortunately only provide a partial solution; they do not treat the polluting water.

Active treatment methods, such as liming, whilst successful at removing acidity and heavy metals, generally incur high initial capital expenditure (on plant) and material/running costs. The use of constructed wetlands (passive treatment) can also incur a high initial expenditure, although by comparison the running costs are much reduced.

Passive wetland systems have been used for the successful remedial action on acid mine drainage. The treatment system designed relies heavily upon the chemical characteristics of the drainage and can include the following:

- i) aerobic wetland – a surface flow system for the removal of iron.
- ii) anaerobic wetland – a subsurface flow system for the removal of zinc, copper, cadmium, lead and mercury.
- iii) a rock filter for the removal of manganese.

Pre-treatment of the mine water using anoxic limestone drains and anoxic slurry ponds can be extremely

beneficial, as their presence will often reduce the area of wetland required and remove other metals such as aluminium.

The wetland systems should be operated as separate sequential treatment cells and not combined. Combination often reduces the efficiency of the treatment.

The science of wetland treatment is still develop-

ing and a number of questions associated with the longevity of the systems and their potential, remain unanswered. Although all indications are that by considering all the aspects associated with the development of acid mine drainage, such as the hydrology, passive wetland schemes offer a relatively inexpensive method for the amelioration of acid mine drainage.

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