Draft Final Report

R&D Project 360

The Use of Constructed Wetlands to Ameliorate Metal-Rich Mine Waters: Stage 1
Review of Existing Literature

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1. SUMMARY

Man-made constructed wetlands have been used extensively and successfully to treat municipal sewage and drainage from coal mines. They offer potential for treatment of metal-contaminated mine drainage (MCMD) from metalliferous mines.

MCMD is generally formed when sulphide ores become exposed to oxygen and water, conditions favourable to their oxidation by bacteria such as *Thiobacillus ferrooxidans*. MCMD may be strongly acid and may contain high concentrations of a range of heavy metals.

If MCMD pollutes watercourses, aquatic life may be threatened. Pollution of rivers by MCMD generation is a problem worldwide. In the UK the situation is typified by pollution from remote, long-abandoned metalliferous mine sites. The MCMD may be draining from the mine workings themselves or from tailings.

Constructed potential wetlands offer a cheaper solution than other techniques for MCMD treatment, with lower construction, operation and maintenance costs and good long-term treatment prospects.

A constructed wetland normally consists of a lined basin, filled with an organic substrate such as mushroom compost, in which 'emergent' wetland plants have been established. MCMD enters at the upstream end and emerges treated from the downstream. Flow may be confined to the substrate or surface water may be present.

Processes of metal removal in wetlands are not well understood. Microbially-mediated processes of metal-oxidation and sulphate-reduction have potential to lock the metals up in the substrate as oxides and sulphides. Some wetland plant species supply oxygen and organic matter to the substrate to assist these processes.

Several case studies of constructed wetlands are discussed in detail. Effective removal of cadmium, copper, lead, manganese and zinc has been observed. From these, and from the literature reviewed, design and construction suggestions have been made.

* The use of small 'cells' arranged in a combination parallel and serial configuration is advantageous.

* Theoretical design equations are available but their usefulness is restricted. Empirical design suggestions may be of more use.

* Organic substrates of composted materials may be best although some people maintain that substrate-choice affects wetland performance minimally.

* 'Emergent' wetland plants such as *Typha latifolia* and *Phragmites communis* are used most often. The use of mosses, such as *Sphagnum* species has serious drawbacks.
* Care should be taken to provide a uniform distribution of influent MCMD, to control flow path within each cell and to maintain a low surface flow velocity.

* The use of liners, to isolate wetland components from groundwater, is essential.

* Locally available natural materials can be used successfully in wetland construction.

* Entire plants, rhizome cuttings or tubers of some wetland plant species can be transplanted successfully.

* Maintenance requirements tend to be minimal.

Pilot-scale research in the field into the optimum combination of substrate type and plants species to suit the situation in the UK is desirable before full-scale constructed wetlands are built.

Keywords: wetlands, metals, mines, water, water treatment.
2. INTRODUCTION

This report is an applied review of the existing literature on the use of wetlands to treat metal-contaminated mine drainage (MCMD) from metalliferous mines, with special consideration of the situation in the United Kingdom. The review covers the following:

* metal-contaminated mine drainage, its composition and formation
* the scale of the pollution problems caused by MCMD
* conventional, non-wetland, MCMD treatment methods
* the merits and demerits of wetlands over other treatment methods
* the components of a wetland that may function to ameliorate MCMD
* the state of knowledge on the metal-removing process occurring
* case studies of wetlands treating MCMD from metal mines
* design and construction suggestions

Finally, discussion focuses on the applicability of MCMD treatment using wetlands to the situation in the UK.
3. WHAT IS METAL-CONTAMINATED MINE DRAINAGE?

Metal-contaminated mine drainage (MCMD) is formed when sulphide containing minerals are exposed to water and oxygen. MCMD may contain high levels of heavy metals and sulphate ions and may be but is not always, strongly acid. Some examples of MCMD chemical composition are given in Table 3.1.

Sulphide minerals are ubiquitous and a large number have been implicated in the generation of MCMD (Table 3.2). These minerals are primarily found under a mantle of soil and often beneath the water table (BCAMD Task Force, 1989). In such a situation, the generation of MCMD is very slow and an insignificant effect on the environment will result. Human activities, including mining, result in the exposure of these minerals to air and water and hence the generation of MCMD.

The generation of MCMD is a chemical/microbiological process. The pathway for the generation of MCMD from pyrite (FeS₂) has received most study. A general consensus has been reached. The oxidation of pyrite is considered the main source of acidity in mine spoils (Grube et al. 1971). The following discussion is based on BCAMD Task Force (1989), Kleinmann and Erickson (1987), Pulford (1991) and Wildeman and Laudon (1988). The reactions are:

\[
\text{FeS}_{2(s)} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+ \tag{3.1}
\]

\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \tag{3.2}
\]

\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_{3(s)} + 3 \text{H}^+ \tag{3.3}
\]

\[
\text{FeS}_{2(s)} + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \tag{3.4}
\]

Pyrite is oxidized by two oxidizing agents - oxygen, as a gas or dissolved in water, and ferric iron (Fe³⁺) ions.

Equation 3.1 represents the oxidation of pyrite by oxygen. This step results in an increase in acidity. If the environment surrounding the pyrite is sufficiently oxidizing, ferric ions are generated (equation 3.2).

Above pH 2.3 - 3.5, ferric ions are not stable in water; they form ferric hydroxide (equation 3.3) which lowers pH further. Ferric hydroxide is very insoluble, so few Fe³⁺ ions are left in solution.
Table 3.1 Chemical constituents of example metal-contaminated mine drainage.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>A(3)</th>
<th>B(2)</th>
<th>C(1)</th>
<th>D(2)</th>
<th>E(4)</th>
<th>F(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>18</td>
<td>-</td>
<td>15</td>
<td>50</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>As</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>0.03</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>1.6</td>
<td>43</td>
<td>6</td>
<td>-</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>50</td>
<td>-</td>
<td>50</td>
<td>50-300</td>
<td>144</td>
<td>2.9</td>
</tr>
<tr>
<td>Pb</td>
<td>0.01</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Mn</td>
<td>32</td>
<td>-</td>
<td>20</td>
<td>20-300</td>
<td>7</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>32</td>
<td>25</td>
<td>-</td>
<td>28</td>
<td>3.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2100</td>
<td>-</td>
<td>-</td>
<td>20-2000</td>
<td>1000</td>
<td>33</td>
</tr>
<tr>
<td>pH</td>
<td>2.6</td>
<td>7</td>
<td>3.6</td>
<td>3.0-5.5</td>
<td>2.7</td>
<td>7.5</td>
</tr>
</tbody>
</table>

All concentrations in mg/l.

Mine Sites:
A Big Five Tunnel, Colorado, USA (Abandoned precious metal mine)
B Britannia Mine, British Columbia, Canada (Abandoned copper mine)
C Pennsylvania Mine, Colorado, USA (Abandoned gold/silver mine)
D Typical coal mine drainage
E Parys Mountain, Anglesey, UK (Abandoned copper mine)
F Hafna Mine, Gwynedd, UK (Abandoned lead/zinc mine)

Adapted from (1) Emerick et al. (1988), (2) Ritcey (1989), (3) Wildeman and Laudon (1989) and (4) research carried out by Richards, Moorehead and Laing Ltd.
Table 3.2 Common sulphide minerals implicated in the production of metal-contaminated mine drainage.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>Aqueous end products of complete oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous FeS</td>
<td>Fe(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Arsenopyrite FeAsS</td>
<td>Fe(^{3+}), AsO(_4)(^{3-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Bornite Cu(_2)FeS(_4)</td>
<td>Cu(^{2+}), Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Bravolite (Ni,Fe)S(_2)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>* Chalcocite Cu(_2)S</td>
<td>Cu(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Chalcopyrite CuFeS(_2)</td>
<td>Cu(^{2+}), Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Cinnabar HgS</td>
<td>Hg(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Cobaltite CoAsS</td>
<td>Co(^{2+}), AsO(_4)(^{3-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Covellite CuS</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>* Enargite Cu(_9)(As, Sb)(_2)S(_4)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>* Galena PbS</td>
<td>Pb(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Mackinawite FeS</td>
<td>Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Marcasite FeS(_2)</td>
<td>Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Marmatite (Zn,Fe)S</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>* Millerite NiS</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>* Molybdenite MoS(_2)</td>
<td>MoO(_4)(^{2-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Niccolite NiAs</td>
<td>Ni(^{2+}), AsO(_4)(^{3-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Orpiment As(_2)S(_3)</td>
<td>AsO(_4)(^{3-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Pentlandite (Fe,Ni)(_2)S(_4)</td>
<td>Fe(^{3+}), Ni(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Pyrite FeS(_2)</td>
<td>Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>* Pyrrhotite Fe(_{1-x})S</td>
<td>Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Realgar AsS</td>
<td>AsO(_4)(^{3-}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Smythite, Greigite FeS(_4)</td>
<td>Fe(^{3+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Sphalerite ZnS</td>
<td>Zn(^{2+}), SO(_4)(^{2-}), H(^+)</td>
<td></td>
</tr>
<tr>
<td>Stannite Cu(_9)FeSnS(_4)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tetrahedrite Cu(_{32})(Sb,As)(<em>2)S(</em>{13})</td>
<td>Cu(^{2+}), SbO(^{3+}), AsO(_4)(^{3-})</td>
<td></td>
</tr>
<tr>
<td>Violarite (Ni,Fe)S(_4)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Known to be oxidized by *Thiobacillus ferrooxidans*.
* Known to be oxidized by iron-oxidizing bacteria.

Adapted from BCAMD Task Force (1989), Gama Xavier (1990) and Ritcey (1989).
Any Fe\(^{3+}\) ions remaining in solution are free to oxidize pyrite (equation 3.4). Further acidity is generated by this reaction. Since ferric ions are stable below pH 2.3 and are thus not removed by precipitation, this step is significant in the production of very acid MCMD.

Thus, the overall reaction can be written:

\[
\text{FeS}_2 + \frac{13}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{SO}_4^{2-} + 4 \text{H}^+ \quad (3.5)
\]

if the pH is greater than 2.3, or, if the situation is more acid than pH 2.3:

\[
\text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{13}{2} \text{Fe}^{3+} + \frac{17}{4} \text{H}_2\text{O} \rightarrow \frac{15}{2} \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + \frac{17}{2} \text{H}^+ \quad (3.6)
\]

Key features of this pathway are as follows:

* Weathering of pyrite is by oxidation, oxygen gas from outside the deposit being the ultimate oxidant.

* Oxidation generates acidity.

* The oxidation of Fe\(^{2+}\) (equation 3.2) is the slow step.

* Once Fe\(^{3+}\) ions have been produced by weathering, these rapidly oxidize pyrite further unless they are removed by precipitation.

* Iron-oxidizing microorganisms, such as *Thiobacillus ferrooxidans*, can significantly increase the rate of pyrite oxidation, especially by mediating the oxidation of Fe\(^{2+}\) (equation 3.2). This reaction can be sped by a factor of 1,000,000 times and the overall acid generation increased by up to 20x. These bacteria tend to be most active between pH 2 and 4 (Filion *et al.* 1990).


There is a dearth of information on how MCMD is produced in the absence of pyrite. Little research has been carried out on the pathways of oxidation of other sulphide minerals. Table 3.2 lists the ultimate products of oxidation for some of these.

MCMD production can continue, if conditions are suitable, until all sulphide ore has been oxidized. This may take thousands of years.

The products of oxidation may be immediately flushed away by mine or surface water, or may accumulate in the rock prior to being flushed.

Low pH water is capable of mobilizing heavy metals from surrounding minerals.
which need not be sulphide ores, alternatively the contaminated water may encounter acid-consuming minerals such as calcite. As the pH is raised, metal ions become less soluble so the degree of contamination will be reduced. The acid-consuming capacity in a particular situation is finite.

The pH and metal content of the MCMD in a particular situation will depend on the relative amounts of sulphide and acid-consuming minerals present, and the balance between the processes of sulphide-oxidation and acid consumption. In a 'worst-case' situation, where considerable amounts of pyrite are present, once all the neutralizing mineral has been reacted, the resulting MCMD may have a pH of 2-3 and be highly contaminated with a range of metals.

Factors influencing acidity and degree of contamination of the MCMD include (Ritcey, 1989):

* sulphide grain size and surface area
* porosity and permeability of the deposit
* nature of gangue materials
* nature of sulphide ore
* nature of acid-consuming minerals
* various environmental factors influencing the activity of the iron-oxidizing bacteria.

Acidic micro-environments may occur around sulphide grains, even if sufficient acid-neutralizing capacity exists to maintain the bulk water at neutral or alkaline pH. In this situation there may still be significant metal contamination of the surface or mine water.

The term metal-contaminated mine drainage has been adopted for this review to indicate that while 'Acid Mine Drainage' will be metal-contaminated, MCMD may not be acid.
4. WHAT IS A WETLAND?

It is difficult to give a precise definition of 'wetland'. One working definition adopted is "land in which the water table is at or above the ground surface for long enough each year to maintain saturated soil conditions and the related vegetation" (Reed et al. 1988).

A wetland is an 'ecotone' or 'edge habitat' between dry land and deep water. The United States Fish and Wildlife Service defines an area as wetland by requiring it to meet one or more of three conditions (from Hammer and Bastian 1989):

* Areas supporting predominantly hydrophytes (aquatic plants), at least periodically.

* Areas having predominantly undrained hydric soil (wet enough for long enough to produce anaerobic conditions that limit the types of plants that can grow there).

* Areas with non-soil substrate (for example rock or gravel) that are saturated or covered by shallow water at some time during the growing season.

The hydrophytes may be submergents, requiring complete immersion (e.g. pondweeds), floating (e.g. chickweed), emergents rooted in sediment yet having most of their plant material above the water surface (e.g. Typha species), mosses, shrubs or trees (Kleinmann et al. 1986).

Components of a natural or constructed wetland include:

* substrate

* plants that are adapted to water-saturated anaerobic substrates

* the water column, which may be in or above the surface of the substrate

* invertebrates and vertebrates (very few, in wetlands receiving MCMD owing to the elevated metal levels and acidity)

* algae

* aerobic and anaerobic microbial populations

Constructed wetlands can be of two main types, subsurface flow (SSF) or surface flow (SF) depending on whether they are designed to confine water flow to the substrate or not. This distinction is discussed further in Section 10.1.1.
5. THE SCALE OF THE PROBLEMS CAUSED BY MCMD

Metal mining in the UK was an important industry throughout the eighteenth and nineteenth century. Lead, zinc, tin and copper were the principle metals extracted. Gold, silver and arsenic were mined to a lesser extent. The main orefields were located throughout southwest, central and northern England, mid and north Wales and Scotland; the main areas of metal mining are shown in Figure 5.1. The great period of British metal ore production, was between the 1840's and 1890's with few mines remaining in commercial production after 1940. For a history of mining in Wales see Bick (1976). In 1989, there were two tin mines operating in Cornwall and intermittent gold production in very small quantities from mines in Wales. However, prospecting continues today and there is one gold mine, at Cononish in Scotland, poised to go into commercial production.

Thus metal mines in the UK are almost invariably abandoned. They have been located near watercourses to make use of water power and in general there has been no reclamation of spoil during their operation.

Problems of water pollution vary from region to region, depending on the nature of the mineralisation (lode material high in calcium causes fewer problems) and the nature of the county rock (limestone areas are less affected). The profile of water pollution from mines varies from region to region, also. In Wales, MCMD seriously affects rivers that would otherwise be pristine, whereas in more industrialized areas, such pollution will have a lower profile.

In the USA, MCMD from surface coal mines is a major problem in the large coal belt. In Canada, the problem of MCMD is typified by pollution from large, opencast metal mines in very remote locations.

MCMD causes widespread and serious water pollution problems and is reckoned by some to be the most serious environmental impact of the mining industry (Gama Xavier 1990). In general, MCMD can ruin fisheries and recreational lakes, damage structures, increase the cost of municipal water treatment, degrade the value of land and lower the potential of an area for tourism (Ziemkiewicz 1990).

There are reckoned to be 2000 ha of land despoiled by mining in Wales (Johnson et al. 1977). The National Stream Survey carried out by the United States Environmental Protection Agency estimated that there were 4600 km of watercourses in the United States that were acidic due to the effects of MCMD and 5800 km that were strongly impacted, but not rendered acidic (Herrick et al. 1990). One estimate (Pichtel et al. 1989) is that there are 1.3 million hectares of abandoned mine lands requiring reclamation in the humid region of the United States.

The scale of the problems caused by MCMD can be illustrated by consideration of the event at the Wheal Jane mine in Cornwall on 13 January 1992 and the impacts of the Cwmystwyth and Cwmrheidol mines in mid-Wales.
Figure 5.1 Distribution of metalliferous mine sites in Great Britain. Courtesy Professor G. D. Barri Jones.
The event at the Wheal Jane mine in January 1992 polluted the river Carnon and the Fal estuary in Cornwall with high levels of copper, zinc, nickel, arsenic, cadmium and iron, sufficient to turn the river and estuary a rusty red colour. This account is derived from NRA South West, Public Relations (1992):

In March 1991 operations ceased at the Wheal Jane tin mine, the last operating mine in the Carnon Valley. The pumps draining the mine were removed and the workings began to fill with water, contaminated by its passage through the workings with acidity and heavy metals including copper, zinc, nickel, arsenic, cadmium and iron. In November 1991, this water reached the surface and began to discharge. This discharge was treated by pumping to the tailings dam and adding lime. Water backed up and emerged untreated from other outlets and, when pumping was stopped for technical reasons in January 1992, an underground collapse lead to a large escape of MCMD into the River Carnon. Pumping and treatment in the tailings dam was quickly resumed, but does not represent an economic long-term solution.

Peak heavy metal concentrations recorded included 450 mg/l zinc and 600 μg/l cadmium in the river and 32.5 mg/l zinc in the estuary.

Animal life in the river was already sparse due to metal pollution by mining from diffuse sources, so no major mortalities were noted. No significant accumulations of heavy metals were noted in oysters from the estuary, but normal metal levels in shellfish in the region are high, also because of historic mining activity.

The Cwmystwyth mine complex has been estimated to release 90 kg/day of zinc into the Ystwyth river (Cremer and Warner Ltd 1974). During the summer drainage from the mine results in a ten-fold increase in zinc concentrations in the river and a three-fold increase in the winter (Rogers and Laidlow 1991).

The Cremer and Warner report notes that salmon spawning is unsuccessful if mean yearly zinc concentrations exceeds 0.3 mg/l and that fish are absent in waters where the 95 percentile of zinc concentration exceeds 1 mg/l. EEC limits for the protection of salmonid fish, at the low water hardness encountered in the Ystwyth, are less than 0.03 mg/l (Gardiner and Mance 1984). Peak zinc concentrations during storms in excess of 0.8 mg/l have been noted in the river (Rogers and Laidlow 1991) as have average concentrations of 0.5 mg/l (Cremer and Warner Ltd 1974). Thus it is obvious that MCMD is heavily impacting on the fishery.

The Cwmrheidol mine is thought to have less of an effect on the adjacent watercourse. The main contaminant is zinc; levels are raised by some 200% during the summer and some 50% during the winter (Rogers and Laidlaw 1991). The CEGB installed a limestone bed filter to treat drainage from the main adits but this has proved relatively ineffective at removing zinc for two reasons. Firstly, the limestone quickly becomes 'armoured' with precipitated iron hydroxides rendering it chemically inactive.
Secondly, some 50% of the mine water is thought to by-pass the filter. (Milne et al. 1987). Zinc levels in the Rheidol below the mine are lower than in the Ystwyth (average concentrations around 0.2 mg/l, 95 percentile around 0.3 mg/l, Cremer and Warner Ltd 1974), but zinc will still heavily impact on aquatic fauna, on the basis of comparison with EEC limits for fish and other freshwater life (Gardiner and Mance 1984).

A study of the Nant Gwydir, in the Conwy catchment (Neville Jones 1990) attributed the absence of any forms of aquatic macroinvertebrates along a length of the river to pollution by the Parc Mine complex. These macroinvertebrates are a crucial link in the food chain and predatory fish would not be expected in their absence. Factors implicated include high zinc concentration (0.8 - 2.0 mg/l), the presence of ferric hydroxide deposits and the presence of a continuous supply of fine suspended matter.
6. NON-WETLAND TECHNIQUES

There are a wide range of techniques for treatment and control of metal-rich mine waters which do not involve wetlands. Choice from this range will depend on factors including:

- whether the mine is operating or disused
- the volume and chemistry of the mine waters
- whether waters are issuing from adits or surface waters are being contaminated by mining waste
- various site-specific factors
- economic factors.

It is possible to group these techniques into

- those controlling generation of MCMD
- those controlling migration of MCMD
- those involving collection and treatment of MCMD.

Of these, the first set of techniques is considered to be the best solution but the third set is most widely practised world wide.

Most research on such measures has taken place in the United States and Canada. General techniques are presented first, then the techniques used in the UK are discussed.

Techniques controlling generation of MCMD generally work on the basis of restricting the supply of oxygen and/or water to pyritic ores or by inhibiting the bacteria that catalyse the oxidation of the sulphide ores. Water saturated soil or bog covers and water inundation can be used for surface waste (Barton-Bridges and Robertson 1989, Kleinmann and Erickson 1987). Inundation of mine workings with water may also be successful. When an abandoned coal mine was left to flood naturally, acidity production fell by 75% (Kleinemann 1991). This technique is risky in that if inundation is not total, increased MCMD production may result. Maps of old abandoned workings are usually incomplete or inaccurate so assessing whether workings can be successfully flooded is difficult.

Phosphate minerals can be used to coat pyrite particles, rendering them inactive (Ziemkiewicz 1990) but this technique is limited to currently operating mines and is expensive. Bactericides, such as anionic detergents and food preservatives can reduce MCMD production by inhibiting *Thiobacillus ferrooxidans*. Bactericides have been used successfully for surface waste (Onysko et al. 1984, Sobek et al. 1990) in
operating and disused mines. Ponds have also been treated (Davison and Jones 1990). Bactericides do not lend themselves to the prevention of MCMD production from underground workings. Attempts to inject alkaline chemicals into mine workings and wastes (Kleinmann and Erickson 1987, Skousen et al. 1987) have been unsuccessful.

Techniques controlling migration of MCMD can be very successful. BCAMD Task Force (1989) proposed an integrated programme of general civil engineering measures, involving diversion of surface water, ground water interception, infiltration control and waste placement methods. Such measures, coupled with revegetation, may reduce acid production by 50% (Kleinmann and Erickson 1987).

Waste placement 'high and dry' can be used successfully in operating mines (Meek 1991) and in the reclamation of abandoned mines. The use of cover materials to reduce rainwater infiltration is discussed in detail in BCAMD Task Force (1989). Such materials include top soil, bentonite clays, compost and tertiary-treated sewage sludge, also synthetic materials (plastic liners, concretes, cements, asphalts and tars). The merits of these are discussed in Pulford (1991).

Stream and river sealing can be used if significant point-source infiltration of water into mine workings can be shown. Concrete can be used (Carvalho et al 1990) as can polyurethane grout (Ackman and Jones 1991). In general, however, entry of water into mine workings is diffuse.

Collection and treatment of MCMD should generally be considered as a last resort, but may be used in conjunction with methods controlling generation and migration. A discrete flow of MCMD is necessary, so techniques lend themselves to the treatment of adit drainage.

Tried and tested methods involve alkaline addition, to neutralize the acidity and cause metals to be precipitated. Alkalis used include limestone, ammonia, caustic soda, soda ash and hydrated lime. BCAMD Task Force (1989) and Skousen (1991) discuss the merits of each and give practical details. Such measures entail large running costs and considerable capital expenditure. Precipitates must be disposed of and treatment may need to be carried out for many years.

The In-Line System (ILS) described in Ackman and Kleinmann (1991) offers savings in alkali requirements through better mixing of alkali and MCMD. An experimental electrolytic treatment has been tested in the laboratory (Ziemkiewicz 1990).

Passive alkaline addition usually involves percolation through limestone bed filters or limestone-lined channels. Generally these lose effectiveness quickly since precipitated hydroxides 'armour' the limestone making it chemically less active. Thus limestone must be regularly replaced.
The UK situation (Palmer 1989, 1990) involves abandoned mines almost exclusively. Reclamation methods which impact on water quality include:

- covering of surface waste in situ with uncontaminated capping material
- concentration of waste in one place prior to capping
- revegetation with metal tolerant plants
- excavation, removal and disposal off-site
- on-site reprocessing
- reducing discrete water inputs to mine workings

The first three of these have been practised in the UK. The fourth has been little used owing to the large quantities of waste and the costs of disposal of such waste to landfill. On-site reprocessing has been considered at some sites, but not recently carried out successfully. As noted before, water inputs to mine workings are typically diffuse. The use of a polyethylene membrane between capping material and waste, to further reduce water infiltration, is becoming more common. Passive limestone beds have been used to treat water during reclamation schemes but are of little use in the long term.
7. DEVELOPMENT OF WETLAND TECHNIQUES AND THEIR ADVANTAGES AND DISADVANTAGES

Interest in the use of wetlands to treat mine drainage followed two independent studies of natural wetlands, undertaken to determine the effect that coal mine drainage was having on wetland vegetation. Both studies demonstrated no adverse effect on the vegetation, rather an improvement in water quality downstream of the wetland was noted (Kleinmann and Erickson 1987).

Huntsman et al. (1978) studied an area of *Sphagnum recurvum* receiving coal mine drainage at pH 2.5. Concentrations of iron, magnesium, sulphate, calcium and manganese all decreased during the passage through the bog, and pH increased to 4.6. The final effluent pH was 6-7, downstream of a natural crop of limestone.

Wieder et al. (1982) studied another area of *Sphagnum*-dominated wetland, the Tub Run Bog in northern West Virginia. Coal mine drainage entered the bog at pH 3-3.5, with sulphate and iron concentrations of 250 mg/l and 70 mg/l respectively. After 20-50 m of flow through the bog, effluent water quality was equal or superior to, that of nearby streams unaffected by mine drainage, at pH 5.5 with 5-15 mg/l sulphate and less than 2 mg/l iron concentrations.

Pilot-scale tests were carried out following these observations (e.g. Kleinmann et al. 1983). Full-scale field trials followed, using constructed bogs, with *Sphagnum* and other mosses as dominant plants, to treat drainage from coal mines. These were not all that successful; *Sphagnum* is relatively intolerant to iron and not viable in conditions of fluctuating water depth. Experience with these trials, has led to the use of wetlands dominated by emergent plants, commonly cattails (*Typha latifolia)*.

Constructed wetlands offer many advantages over other treatment technologies, as summarized by BCAMD Task Force (1989) and Howard et al. (1989b):

* wetland systems can adapt to very acid (pH of 2.5) MCMD with elevated metal content
* capital costs are relatively low
* operational and maintenance costs are low
* systems are generally self-maintaining and require little or no operator supervision
* systems provide additional environmental benefits such as wildlife habitat and flood control
lower requirements for supervision mean that wetland systems may be the only option for remote, abandoned mine sites subject to climatic extremes, as typical of many sites in Wales and Colorado

the ability of constructed wetlands to improve water quality is well documented in the USA.

There are disadvantages over other treatment technologies (BCAMD Task Force 1989, Hammer and Bastian 1989)

* earth moving requirements may be great for mountainous terrain and thus capital costs are elevated

* land area requirements can be large, with up to 50m² required per m³ per day flow

* treatment during winter is impaired - low temperatures slow biological reaction, freezing lowers water depth and prevents aeration and mixing of the water by the wind

* impacts on wildlife are still unknown

* operating experience is lacking

* constructed wetlands take time to become established; during this time treatment efficiency may be low

Constructed wetlands offer several advantages over natural wetlands to treat MCMD.

* It is rare that a natural wetland suitable to be engineered to treat MCMD, will be located sufficiently close to the mining area.

* A far higher degree of control can be exercised over flow patterns, loading rates, plant density and other hydraulic, vegetational and morphological factors. Much can be learnt from consideration of how these factors relate to the metal-removal ability of natural wetlands receiving MCMD and it may be easier to put these lessons into practice with a wetland constructed from scratch.

* There are a variety of ecological and aesthetic arguments against polluting an existing natural wetland. These arguments are to some extent enshrined in law, for example under United Kingdom and United States law a wetland is considered as part of the receiving water course and a permit is required for discharge.
8. PROCESSES OF METAL REMOVAL IN WETLANDS

8.1 Introduction

Figure 8.1 illustrates the process of metal removal that may take place in a wetland. Since this is a relatively new field, the various removal mechanisms, the relationship between them and their relative importance are not well understood.

Studies have so far concentrated on wetlands treating MCMD from coal mines. Iron and manganese are the major contaminants in such MCMD. As a result, removal mechanisms for other metals are less well understood.

Iron and manganese are not chemically 'special cases' and good removal efficiencies for other metals have been observed in the case studies (Section 9.2) so cautious extrapolation of removal mechanisms for other metals may be justified.

For the purpose of further discussion, the wetland is considered as having three main components: the vegetation, the water column and the substrate. Algae are considered with vegetation, microbial activity with the substrate.

8.2 Vegetation

Wetland vegetation may facilitate metal removal by direct means:

* Direct filtration of particulate matter. Sphagnum species are good at retaining metal hydroxide particles that have precipitated out of solution, owing to the high surface area of the plant within the water column

* By adsorption and cation exchange

* Through direct uptake of heavy metals

and by indirect means:

* By providing attachment sites for bacteria within the water column

* Decaying plant matter forms a source of organic material for metal-oxidizing bacteria in the aerobic zone of the substrate and sulphate-reducing bacteria in the anaerobic zone

* By oxygenation of the substrate

The indirect functions are thought to be the most important (Hammer and Bastian 1989). Further information on the processes of direct uptake, adsorption and cation exchange and oxygenation of the substrate is given below.
Figure 8.1 Processes of metal removal that may occur in a wetland (from Kleinmann and Girts 1986).
8.2.1 Adsorption and cation exchange

Adsorption involves the binding of particles or dissolved substances in solution to sites on the surface of the plant matter. In a cation exchange reaction positively-charged metal ions in solution bind to negatively-charged sites on the surface of the plant matter. The attractive force for cation exchange is electrostatic and the size of this force depends on a wide range of factors. A cation in solution will displace a cation bound to a site on the surface if the electrostatic attraction of the site for the dissolved cation exceeds that for the bound cation, hence the term 'cation exchange'.

The cation exchange capacity (CEC) of a material is a measure of the number of binding sites per unit mass or volume. *Sphagnum* species have a higher CEC than other wetland plants such as *Typha* due in part to their high surface area to volume ratio.

The cation exchange properties have been attributed to carboxyl functional groups (-COOH) in the humic acids of peats and pectic compounds in plant cellular tissue (Howard *et al.* 1989b). The CEC of *Sphagnum* is the same whether the plant is alive or dead. Howard *et al.* (1989b) investigated the CECs of a range of forest products such as charcoal and leaf litter.

Wieder (1990) found the CEC of *Sphagnum* peat to be higher than that of sawdust and he determined general rules for cation selectivity. He concluded that cation exchange in wetlands will be minor for those cations likely to form insoluble precipitates (*e.g.* manganese, iron) but may not be minor for others (*e.g.* copper, nickel, zinc, cadmium and lead).

Cation exchange does not represent a long-term method for MCMD treatment since all cation exchange sites quickly become occupied by heavy metals and cation exchange binding is a reversible process. For recently established wetlands, however, cation exchange may be an important mechanism whilst unoccupied cation exchange sites exist.

8.2.2 Direct uptake

*Sphagnum* species have a well established ability for direct uptake of iron (see *e.g.* Gerber *et al.* 1985) but except in low flows of MCMD with low ion concentrations (Fe$^{2+}$ < 10 mg/l) iron accumulation becomes sufficient to kill the plant within a single growing season (Spratt and Wieder 1988). Uptake may be sufficient to 'petrify' the plant (Kleinmann 1990).

*Typha* species are more tolerant of iron as they do not accumulate the metal to toxic levels (Sencindiver and Bhumbla 1988). As a consequence of this, the role of *Typha* plants as a sink of iron is thought negligible.
One study (Sencindiver and Bhumbla 1988) calculated that only 0.3% of the annual iron loading was taken up by the plants in a constructed wetland receiving MCMD with 10 mg/l iron. Another (Eger and Lapakko 1988) calculated that direct uptake by plants was responsible for 1% of the nickel removal capability for a natural wetland receiving MCMD from a copper/nickel mine. Taylor and Crowder (1983a) studied metal uptake by *Typha latifolia* in detail. In plants exposed to soils with a high copper and nickel content, these metals were largely excluded from the above ground parts of the plant, but accumulated in the root stock. Iron and manganese were accumulated by above and below ground parts. Leaf tissue metal levels for *Typha latifolia* plants exposed to high levels of heavy metals may reach 460 μg/g of nickel and 130 μg/g copper (Taylor and Crowder 1983b), 190 μg/g copper and 240 μg/g zinc (Zhang *et al.* 1990). Root tissue levels of 440 μg/g lead have also been noted (Lan *et al.* 1990).

Direct uptake is an active process, requiring the plant to be alive, in contrast to cation exchange. Plant matter may liberate its heavy metal content when decomposing.

### 8.2.3 Oxygenation of the substrate

Many wetland plants have the ability to transport oxygen to the substrate, as illustrated in Figure 8.2. These plants tend to be 'emergents' and include *Typha* species (cattail), *Phragmites communis* (common reed), *Juncus* species (rush), *Scirpus* species (clubrush) and *Carex* species (sedges) (Reed *et al.* 1989). Structural and physiological adaptations include the presence of aerenchyma tissues and lacunae, which function as support structures, store gases to provide buoyancy and are involved in the transport of oxygen to the substrate (Gruntenspergen *et al.* 1989). The process of 'thermoosmosis' is thought responsible for this transport (see Grosse 1989 for an explanation); the driving force is a temperature difference with plant leaves being warmer than surroundings. Volumes of air transported between 40 ml/hr (*Nymphoides peltata*) and 3.5 l/hr (*Victoria amazonica*) are reported for a 2-3°C temperature difference (Grosse 1989).

An oxidized zone around the plant roots (the 'rhizosphere') results. The importance of this to metal removal is discussed in Section 8.4 'Substrate'. Oxidation of Fe²⁺ and Mn²⁺ ions in the rhizosphere has been reported for many wetland plants including *Typha latifolia* and *Phalaris* species (Good and Patrick 1987) and 'plaques' of iron oxyhydroxides noted on *Typha* roots (Kleinmann 1990). Plaques of other metals have not been noted since studies of this nature have been confined to coal mine drainage wetlands.

Michaud and Richardson (1989) compare the rate of oxygen release from the roots of five wetland plants. Descending order of oxygen release per unit mass was found to be *Typha latifolia*, *Juncus effusus*, *Sparganium americanum*, *Eleocharis quadranguta* and *Scirpus cyperinus*. However, the calculations did not take into account growth characteristics such as stand density, oxygen transfer per unit substrate area would be a better measure.
Figure 8.2 Wetland plants have the unique ability to transport oxygen to support their roots growing in anaerobic substrates (from Hammer and Bastian 1989).
8.2.4 Algae

Algae are widespread in MCMD. They may occur attached to vegetation or substrate or free in the water and may have the capacity to remove metals from the MCMD. Many species are able to tolerate high heavy metal levels and strongly acid conditions and since the aquatic insects that feed on them are less tolerant, algae have a competitive advantage. Interest in algae for MCMD treatment stems from the observation that algal blooms have been associated with a reduction in concentrations of dissolved manganese.

Stevens et al. (1989) note the presence of filamentous algae with rust-coloured and dark brown encrustations in MCMD from coal mining. These were found to contain iron and manganese salts. Gyure et al. (1987) found a dense 0.1 m-thick layer of algae growing in an MCMD-fed lake at pH 2.7. The growth of this layer appeared to be nutrient-limited rather than acidity-limited.

One species of alga, *Cyanidium caldarium*, has been studied in detail in the laboratory. In acid waters of pH 2-5, Alig et al. (1991) observed binding of copper and cadmium onto the cell surface. Live cells accumulated more heavy metals. Cadmium was preferentially accumulated, up to 17 mg/g dry weight of cells. Copper accumulations of up to 7 mg/g dry weight were observed. Lucido and Iwasaki (1991) grew the alga on simulated copper/nickel mine drainage. Copper was accumulated to 19 mg/g dry weight. Bioadsorption and precipitation onto the cell wall were proposed as mechanisms of metal removal.

One study (Kepler 1988) presents preliminary results for a full-scale field study, using both algae ponds and ponds planted with emergent marsh vegetation, to treat MCMD from an abandoned coal mine. A significant removal of iron and manganese has been observed by the combination treatment.

Unfortunately, algal biomass in wetland systems is generally low, so the contribution of algae to metal removal will be small (Kleinmann 1990).

Attempts have been made to increase algal biomass production by periodic fertilization. Results have been inconclusive due in part to the abiotic metal-removal reactions that occur when phosphate is added to the MCMD.

8.3 Water

The effectiveness of a wetland to treat MCMD will depend on the effectiveness with which metal contaminants and acidity are removed from the water column. The ultimate fate of any removed contaminants will be in the substrate or the vegetative matter.
Processes affecting the concentration of the metal in the water of the wetland include:

* Dilution
* Evaporation
* Complex formation
* Microbially-catalysed oxidation and hydrolysis
* Precipitation

Dilution is the simplest method. Wetlands tend to be found at a low point in the relief, so additional water inputs from surface drainage or precipitation will act to dilute the MCMD. Additional water inputs may contain alkalinity and thus raise pH.

Evaporation from the water surface will increase the concentration of metals, lower the residence time and thus reduce treatment effectiveness.

Dissolved metals may form complexes with suspended matter, including decaying organic matter from the wetland plants. These complexes may subsequently settle to the substrate.

Bacteria, free-living or attached to sites or suspended matter or vegetation, are thought to catalyse oxidation and hydrolysis of dissolved iron, causing it to precipitate. This is thought to be the most important iron-removing mechanism in wetlands as they are currently being constructed. Manganese-oxidizing bacteria have also been identified in wetlands; bacteria oxidizing other metals are likely to be present but are as yet unidentified.

Precipitation of iron hydroxides and oxyhydroxides can cause other metal ions, especially manganese, to become precipitated. The other ions may adsorb onto the surface of the precipitating oxides or hydroxides (Jones 1978). This phenomenon is known as 'coprecipitation'.

Neutralization of the MCMD by any available alkalinity will cause metal ions to precipitate. Above pH 5, dissolved aluminium will hydrolyse and precipitate. Ferric iron (Fe³⁺) precipitates as 'yellow boy' (ferric oxyhydroxide) above pH 5.5 (Skousen 1991) in the absence of microbial interventions.

8.4 Substrate

The substrate of a constructed or natural wetland will have a general organic soil ecosystem as described by Sikora and Keeney (1983); an upper aerobic portion is underlain by a lower anaerobic layer with a thin transitional layer between the two.
In the anaerobic layer, metabolic action of microorganisms leads to anaerobic conditions with characteristic redox potentials and the predominance of reduced forms of carbon, nitrogen, phosphorous, manganese, iron and other elements. Large vertical gradients of oxygen, temperature and redox potential characterise the upper, aerobic layer suggesting that it is chemically dynamic, as does the amount of decaying organic matter present.

The aerobic layer tends to be thin, restricted by the high resistance of the substrate to oxygen diffusion and the high demand for oxygen in this layer (Good and Patrick 1987).

Bacteriological investigations (e.g. Batal et al. 1987) have shown that iron- and manganese-oxidizing bacteria are present in the aerobic zone and sulphate-reducing bacteria are present in the anaerobic zone.

General methods of metal-removal in the substrate include direct mechanisms:

* cation exchange and adsorption
* physical filtration

and indirect ones:

* providing physical support for wetland plants
* providing attachment surfaces for microbial populations including sulphate-reducing and metal-oxidizing bacteria.

*Sphagnum* moss may be considered part of the vegetation or part of the substrate, depending on the situation. Dead *Sphagnum* (peat) substrate will have some of the metal-removing functions above: filtration, provision of attachment sites, and cation exchange capacity.

Cation exchange capacity tends to become saturated in wetlands treating MCMD. Studies of natural wetlands that have been receiving elevated metals concentrations for many years note the presence of sulphide and oxide deposits within the substrate (e.g. Lett and Fletcher 1980).

For these reasons, it is generally accepted that the microbially-mediated processes of metal-oxidation and sulphate-reduction represent the only long-term metal removal mechanism in constructed wetlands. These processes are not currently fully understood.
Microbially-mediated iron-oxidation, followed by subsequent precipitation of iron oxyhydroxides as the familiar orange sludge 'yellow boy', is considered by some workers to be the most important iron-removal mechanism in wetlands. *Thiobacillus ferrooxidans*, the bacterium implicated in the production of MCMD from many sulphide ores, is known to catalyse the oxidation of Fe$^{2+}$ at pH less than 3.5, as follows (Batal et al. 1989):

\[
4 \text{Fe}^{2+} + \text{O}_2 + 10 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 + 8 \text{H}^+ \quad (8.1)
\]

Other bacteria have been isolated capable of iron oxidation at pH values closer to neutral (7.0) (Batal et al. 1989).

Manganese oxidizing bacteria have been isolated, but their activity tends to be low if the pH is less than 6.0 (Kleinmann 1990). Manganese oxidation may occur as follows (Batal et al. 1989):

\[
\text{Mn}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2 \text{H}^+ \quad (8.2)
\]

Note that acidity is produced by these oxidation reactions.

Limited results but similar chemistries suggest possible removal of nickel, copper, lead, zinc, silver and gold by similar mechanisms. (Watson et al. 1989).

Microbially-mediated sulphate-reduction (SR) consumes sulphate ions and produces hydrogen sulphide and alkalinity in the form of the bicarbonate ion as follows (Hedin et al. 1989).

\[
\text{SO}_4^{2-} + 2 \text{CH}_2\text{O}^- \rightarrow \text{H}_2\text{S} + 2 \text{HCO}_3^- \quad (8.3)
\]

Where 'CH$_2$O' represents a simple organic molecule, for example acetate. The hydrogen sulphide is released as a gas, whereupon it ionizes to give sulphide ions (S$^2$). These react with a range of heavy metal ions to produce metal sulphide precipitates *e.g.* pyrite, FeS$_2$, iron monosulphide FeS, chalcopyrite CuFeS$_2$.

In marine systems, SR is the primary process by which carbon is 'mineralized' but in freshwaters the process is usually restricted by the availability of sulphate ions (Herlihy and Mills 1985). Marine SR is usually restricted by the availability of organic matter (Hedin et al. 1989). In wetland systems receiving MCMD, neither sulphate or organic matter availability should be restrictive, hence SR has good potential as a metal-removing mechanism.
Although precipitation of metals such as iron as oxides, following microbially-mediated oxidation, is thought the most important removal mechanism in wetlands, there are many reasons why precipitation as sulphides is a more desirable way to immobilize metals. (Herlihy and Mills 1985, Hedin et al. 1988):

* sulphate-reduction generates alkalinity, so will help to neutralize acidity
* sulphide precipitates are denser than oxide precipitates
* sulphides may be more stable, and less vulnerable to resolubilization
* sulphides are precipitated within the organic sediments and so are less vulnerable to disruption by sudden surges in flow.

Several workers (Belin et al. 1991, Dvorak et al. 1991, Hammack and Edenborn 1991) have evaluated the potential of sulphate-reducing bacteria to remove metals from simulated MCMD in laboratory-scale studies. Experimental systems comprise barrels or columns filled with mushroom compost, inoculated with bacteria such as Desulfovibrio. Successful treatment of cadmium, iron, manganese, nickel and zinc has been observed. The effect of cation exchange was discounted by appropriate experimental procedures. Treatment efficiency is shown in Table 8.1. Removal figures indicate both the variability and potential utility of sulphate-reduction.

Wetland plants may have a three-fold effect on enhancing these microbially-mediated processes. Firstly, aerobic metal oxidation can occur in the rhizosphere created by oxygen transmission to the roots. Secondly, carbohydrates and other organic compounds exuded by the roots together with decaying plant material, provide a carbon source for sulphate-reducing bacteria. Thirdly, as effective pyrite formation is known to require alternative anaerobic conditions and limited aeration (Faulkner and Richardson 1989), the oxygenation of the substrate by the plant roots provides an extensive region where anaerobic and aerobic conditions are adjoining. These conditions may be advantageous for precipitation of other metal sulphides.

Resolubilization of metals from the sediment gives cause for concern. To provide long-term treatment of MCMD, immobilization must be permanent and the wetlands must not become a source of contamination at a later stage. Acidic, aerobic conditions can cause resolubilization of iron monosulphide (FeS) but pyrite (FeS₂) is acid-resistant. If the wetland is designed to quickly immobilize iron as pyrite, the danger of remobilization will be limited (Hedin et al. 1989).
Table 8.1 Treatment efficiency of laboratory-scale sulphate-reduction systems

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<td>Flow rate, l/day</td>
<td>3</td>
<td>79</td>
<td>100</td>
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<tr>
<td>Volume of compost, l</td>
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<td>624</td>
<td>3038</td>
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<td>Influent concentration of stated metals, mg/l</td>
<td>Zn 750</td>
<td>Fe 67</td>
<td>Cd 0.29</td>
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<td>Mn 24</td>
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<td>Ni 0.85</td>
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<td>Zn 302</td>
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<td>Effluent concentration of stated metals, mg/l</td>
<td>Zn &lt;1</td>
<td>Fe &lt;0.2</td>
<td>Cd &lt;0.005</td>
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<td>Zn 0.42</td>
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<td>Treatment efficiency, %</td>
<td>Zn &gt;99</td>
<td>Fe &gt;99</td>
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<td>Zn &gt;99</td>
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<td>Treatment efficiency, mg/day/litre of compost</td>
<td>Zn 150</td>
<td>Fe 8.5</td>
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<td>Zn 10</td>
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* Carbon source added to feed
9. CONSTRUCTED WETLANDS TO TREAT MCMD FROM METAL MINES

9.1 Introduction

The information in the literature on the use of constructed wetlands to treat MCMD from metal mines is sparse. Much has been written on the use of wetlands to treat sewage and coal mine drainage; some of this literature will have general applicability. There are also reports detailing the use of wetlands to treat metal-processing wastes (Masters 1988, 1989), landfill leachate (Staubitz et al. 1989), aluminium-rich runoff from highway construction (Wieder et al. 1988) and urban runoff (Meiorin 1989).

The objectives of wetland treatment of MCMD from metal mines will be site-specific, depending on factors such as the 'strength' of the MCMD, in terms of acidity and metal concentrations, the nature of the receiving water course and the legislation encountered. In some situations wetlands may represent a complete treatment system, in others a 'biological polishing' of relatively uncontaminated effluent or a pre-treatment stage before chemical treatment.

In the UK, for abandoned metalliferous mines, use as a complete treatment is most likely to be considered.

In general, a constructed wetland will consist of a basin, constructed of natural materials of low permeability or a pit, lined with materials such as butyl rubber. Some form of influent distribution structure will be installed, as will some form of effluent collection system. Flow control mechanisms and high-flow bypass structures will be likely. A substrate of gravel, peat, soil or decomposed organic matter will be present. In this, wetland plants, usually emergents such as *Typha latifolia*, will be planted. Water level will usually be controlled to saturate the substrate and provide 0.1 - 0.5 m of standing water.

9.2 Case studies

There are several examples in the literature of natural wetlands engineered to receive MCMD and may be thus termed 'constructed' by virtue of engineered effluent collection or influent distribution structures. (e.g. Eger and Lapakko 1989, Emerick et al. 1988). Emerick et al. (1988) used a pre-existing sedge wetland, dominated by *Carex aquatilis* to treat MCMD from an abandoned gold/silver mine. Owing to the low hydraulic conductivity of the wetland (10^{-3} - 10^{-4} cm/sec) it possessed only a limited ability to accommodate drainage from the mine and the experiment was terminated.

There is potential to engineer improved treatment in natural wetlands already receiving MCMD. The engineering of unpolluted natural wetlands to receive MCMD is subject to the legislative, aesthetic and practical restrictions discussed in Section 7.
9.2.1 Big Five Tunnel, Colorado, USA. (Abandoned precious metal mine)

The Big Five Tunnel site wetland was constructed as a pilot treatment system on an EPA superfund site in the Idaho Springs - Central City metal-mining area in Colorado, USA. This discussion is based on reports in Chappell et al. 1988, Howard et al. 1989a, Howard et al. 1989c, Wildeman and Laudon 1988, Wildeman et al. 1988 and Wildeman et al. 1990.

All inputs to the system, with the exception of precipitation, and all outputs are controlled. Drainage flow is nearly constant throughout the year. Three cells of 19m$^2$ each were constructed. Each cell can be fed MCMD independently and was filled to a depth of 1m with substrate. The substrate in cell A was fresh, unused, mushroom compost (derived from about 50% animal wastes, 50% barley mash wastes from a local brewery). Cell B contained a mixture of peat, manure and decomposed wood products and Cell C contained 0.10-0.15 m of limestone overlain with the organic mixture used in Cell B.

Influent MCMD was distributed using a perforated pipe above a 'rock box' occupying the full depth and width of the wetland and filled with 0.10-0.15 m diameter washed river rock, retained by a plastic fence.

The construction was considered straightforward and local materials were used. Local wetland vegetation was transplanted to the site. Cattails and sedges (*Typha laxifolia, Carex utriculata, Carex aquatilis*) were chosen. Selection was easy but transplanting represented a significant investment in labour and equipment.

Substantial metal removal was observed during the first winter, despite vegetation being planted in September, at the onset of dormancy. Cation exchange, adsorption or microbial-mediated processes were considered responsible.

After several seasons, the mechanical portions of the system were still in good working order although the rock box inlet structures had become partially blocked with precipitated metal hydroxides.

Iron hydroxide precipitates were observed throughout the system. Algae were observed to have colonised Cell A only. September transplanting of wetland vegetation did not work well. Iron-oxidizing and sulphate-reducing bacteria were observed to have colonized the wetland. An area of 19m$^2$ was sufficient to maintain a self-contained eco-system.

Manganese removal has been observed to be slight, although copper removal has generally been near 100%. Iron and zinc removals have been up to 60% and 100% respectively. Sulphate removal of 10% was noted for Cell A only, suggesting some microbial sulphate-reduction for this cell. Removal of 53% of influent aluminium, 66% of cadmium and 69% of chromium was also noted for Cell A.
Cell A gave the best metal removal. With less than 1.5 l/min flow, consistently good results for copper, iron and zinc removal have been obtained. Concentrations of these metals at this flow correspond to loading rates of 100 mg/day copper, 1000 mg/day iron and 4000 mg/day zinc. Iron and zinc removal varies inversely with flow rate but copper removal does not, suggesting that complexing with organic matter may be important for copper removal. Metal mass-removal rates (mg/day/m²) were slightly greater in summer than in winter.

9.2.2 Red Lake, Ontario, Canada. (Abandoned copper/zinc concentrator)

A process which the authors term 'ecological engineering' has been undertaken on the site of an abandoned copper/zinc concentrator in northern Ontario (Kalin 1988, Kalin et al. 1989a, Kalin et al. 1989b).

Ecological engineering measures are based on ecological study of the natural recovery processes occurring on tailings sites and are designed to achieve a maintenance-free 'walk away' solution.

A 'decant pond', limed during mining operations, is fed MCMD generated by the tailings. Some 760,000 tonnes of tailings are present and these contain about 41% pyrite and 4.1% pyrrhotite.

The measures are designed to create an ecosystem consisting of three main components: microbial sulphate-reduction, cattail cover to provide organic matter for the sulphate-reducing bacteria and maintain reducing conditions in the sediment and periphytic algae to relegate metals to the sediment.

Hand and mechanically transplanted cattails (Typha latifolia) were established on the beaches of the pond and artificial islands of cattails were created. A log boom was established across the pond to limit disruption of the islands by wind action.

Inert building materials placed in the pond provided excellent support for the growth of periphytic algae, as did the cattail roots. Some species of this algae were observed to be enriched in zinc, copper and iron; concentrations were 10x higher than in the sediment.

This periphytic algae will transport metals to the sediment as they die or are sloughed off by wave action. Upon decomposition, the algae will help maintain the reducing conditions necessary for sulphate-reduction. Metals liberated by the decomposing algae should be precipitated as sulphides.

A body of water known as Boomerang Lake, on the same site, was receiving an acid-and metal-contaminated plume of groundwater through seepage of a tailings dam. Measures incorporated here have included the building of an interception trench such that the plume feeds a polishing pond, planted with Typha latifolia. In the lake itself.
log booms were used to retain brushwood as a support for the growth of periphytic algae. Also, a submerged aquatic moss was employed for its ability to carpet the sediment and prevent oxygen infiltration. In these ways, sulphate-reduction was encouraged and metal translocated from water column to sediment.

The measures detailed here represent the first attempt at this sort of solution. Water quality, as the final arbiter of success, was observed to have improved 'promisingly' two years after the measures had been implemented.

9.2.3 Guangdong, Region, China. (Operating lead/zinc mine)

A very large (87,500 m²) constructed wetland is being used to treat a large volume of flow (350 l/sec) of wastewater from a lead/zinc mine in China (Lan et al. 1990). The wetland is divided into shallow 'aquatic treatment areas', which have been colonized by wetland plants, and deeper 'stabilization areas'. Mean depths of these areas are 0.1 m and 2.5 m respectively. Cattails are the dominant vegetation. Stands were planted by the dual inlets in 1983. The plants covered 55% of the wetland area in 1990. Also present are Phragmites communis, Paspalum conjugatun, Cyperus malacensis and Eleocharis plantagineiformis.

The climate of the region is subtropical, with typical winter and summer temperatures of -5°C and 40°C respectively.

The wetland increases the dissolved oxygen concentration of the mine water three fold, reduces suspended solids levels by 99% and reduces lead, zinc and cadmium concentrations by 80-95% from initial values of 1.6, 1.9 and 0.022 mg/l respectively.

An indirect benefit of the improved water quality has been a considerable reduction in the compensation payments made by the mine to farmers and occupiers of the surrounding land, contaminated by the mine. Payments had totalled US$ 0.5 million before the wetland was constructed.

9.2.4 Buick Mine/Mill Complex, Missouri, USA. (Operating lead mine and mill)

A series of artificial meanders has been used to treat water from a mine/mill complex in Missouri, USA (Erten et al. 1988, Wixon and Davies 1985).

The meanders accept water from the combined tailings pond for the complex and discharge, after a final sedimentation pond, into the receiving water course. They are around 1 m deep and have a total length of 5 km.

The mine water is naturally hard (500 mg/l calcium carbonate) and alkaline, so dissolved metal concentrations are relatively low for such a complex. Concentrations of metals in the water entering the meanders are 12 mg/l zinc, 2 mg/l manganese,
0.005 mg/l copper and 0.05 mg/l lead. Algal blooms periodically occupy the entire series of meanders. The processes of algal adsorption and uptake, sedimentation and adsorption/uptake by aquatic vegetation are thought to remove metals in this system.

Metal removal figures quoted include 25% of the lead, 99% of the zinc, 33% of the copper and 95% of the manganese. pH increases from 6.5 to 8.0. An effluent with metal concentrations well within drinking water standards results.

9.3 Discussion

The Big Five Tunnel site represents a good pilot-scale system for investigation of the treatment of MCMD from a defined source. The ecological engineering trials show some success for this integrated approach with broader objectives than the other case studies, namely a 'walk-away' no-maintenance solution to the problems of acute MCMD. The Chinese wetland is a simple, successful but very large treatment system for a large volume of mine drainage. The meanders are successful but influent metal concentrations are low. This last system will emulate the natural recuperative powers of rivers.

Results from the Big Five Tunnel site can be most closely applied to the UK situation for treatment of MCMD from adits. The ecological engineering trials are conducted on pre-existing contaminated lakes so do not directly relate to this situation. However, implementation of measures to provide a variety of different metal-removing components within a conventional constructed wetland warrants consideration. Such measures could include deeper water areas to allow for sedimentation, areas of brushwood to support periphytic algae and attempts to establish submerged aquatic moss.

The Chinese system may be inefficient; a smaller area, divided into cells through which the water progresses sequentially, may be a more efficient means of treating the mine effluent in this case. The flow rate of the MCMD was very large (360 l/sec), but the areal requirements, in terms of square metres of wetland per litre per minute flow of this system is close to that of the Big Five Tunnel site (4 m²/l/min and 12 m²/l/min respectively). Existing MCMD-polluted lakes and impoundments could be engineered relatively easily to approximate to the Chinese wetland.

Meanders may be a less efficient use of land than the other systems and other solutions are likely to provide better contact between wastewater, sediment and plants, hence better treatment.
Metals treated successfully in the case studies are:

Big Five Tunnel site: copper and zinc (90-100% removal), aluminium, cadmium, chromium and iron (about 60% removal)

Red Lake area: some success in terms of zinc removal but hard to quantify
( ecological engineering)

Guangdon, Region China: cadmium, lead and zinc (80-95% removal)

Buick mine/mill: manganese and zinc (90-100% removal)
(meanders) copper and lead (25-35% removal)

Sulphate-reduction was observed only in Cell A of the Big Five Tunnel site, which utilized mushroom compost as a substrate. Some 10% of influent sulphate was reduced.

Typha latifolia or Cattails have been used in all these case studies. Transplants are successful and the plants tend to become dominant over other species.

A summary of performance figures for two of the wetlands, the Big Five Tunnel and the Chinese study, is presented in Table 9.1.
Table 9.1 Performance figures for some of the case study wetlands.

<table>
<thead>
<tr>
<th>Performance criterion</th>
<th>Big Five Tunnel site</th>
<th>Guangdong Region, China</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flow rate</strong></td>
<td>1.5 l/min</td>
<td>350 l/sec</td>
</tr>
<tr>
<td><strong>Influent metal concentration, mg/l</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cadmium</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>copper</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>iron</td>
<td>37</td>
<td>-</td>
</tr>
<tr>
<td>lead</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>zinc</td>
<td>8</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Metal removal efficiency, mg/m²/day</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cadmium</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>copper</td>
<td>5.3</td>
<td>-</td>
</tr>
<tr>
<td>iron</td>
<td>53</td>
<td>-</td>
</tr>
<tr>
<td>lead</td>
<td>-</td>
<td>560</td>
</tr>
<tr>
<td>zinc</td>
<td>210</td>
<td>470</td>
</tr>
<tr>
<td><strong>Water treatment efficiency, m²/l/min</strong></td>
<td>12</td>
<td>4</td>
</tr>
</tbody>
</table>
10 DESIGN AND CONSTRUCTION

10.1 Theoretical and mechanical design

10.1.1 Introduction

The literature contains detailed theoretical design guidelines which tend to be based on experience with sewage treatment wetlands and empirical and mechanical guidelines, mostly from coal mine drainage treatment wetlands. Some of this literature is applicable to the design of wetlands to treat MCMD from metal mines, as is discussed below.

In this section, surface flow and subsurface flow wetlands are distinguished and theoretical and empirical design guidelines presented. Site-selection, and configuration are discussed, as are the choice of vegetation and substrate. Flow regime (water depth and velocity) is considered as is how to optimise the design for a range of other factors.

10.1.2 Surface flow and subsurface flow wetlands

The distinction between the two types of wetland is based on whether or not flow is confined to the substrate. This is determined by the hydraulic conductivity of the substrate and by water level. The terminology is confusing in that subsurface water flow is likely to occur in a SF wetland but at a much lower rate than surface flow.

Most wetlands constructed for MCMD treatment have been surface flow wetlands.

Of the two types, surface flow wetlands are simpler to design and construct and require simpler inlet distribution structures. 'Emergent' wetland vegetation is used in SF systems. A water depth can be selected that is optimum for the chosen wetland species. Invasive weeds are unlikely to become established in flooded conditions.

SF systems are, however, subject to ice-cover in cold climates. The effects of snow or ice-cover have been little studied but treatment efficiency will be lowered because effective water depth is reduced and hence retention time is reduced (Kadlec 1989). Some water storage facility may be necessary for the winter months.

Subsurface flow systems provide for greater contact between wastewater and substrate but are prone to clogging with precipitated metal hydroxides and may experience problems with invasive weeds. Design is more difficult and a constant flow rate is important to avoid breakthrough (resurgence of the water before the outlet). Influent distribution structures require closer attention as does choice of substrate.
10.1.3 Site-selection

Factors to be considered at the site-selection stage include (Brodie 1989, Reed et al. 1988)

* proximity to source of MCMD

* proximity to suitable discharge point

* land availability (knowledge of property ownership, restrictions placed by previous, current or future land uses, public opposition)

* hydrological factors (surface and groundwater flow patterns and water quality, drainage basin characteristics, implications for downstream users). A detailed water budget should be constructed as detailed in Section 10.1.4

* access factors (access for construction equipment and personnel, and for delivery of equipment and materials). Provision of long term right of access for maintenance necessary

* availability of utilities (electricity, if pumping required)

* geological considerations (character of surface materials and soils, depth of bedrock which must exceed excavation depth, availability of construction materials)

* topographic considerations (it must be possible to obtain a slope of 0-3% for the base of the wetland without extensive earthmoving). Topography also affects drainage and erosion potential, access and slope stability.

Information and techniques available include soil surveys, geological and topographic maps, aerial photographs, walkover surveys and site investigations, such as auguring, test pit digging, percolation tests and mapping.

10.1.4 Preliminary design considerations (Howard et al. 1989c)

These include the chemistry of the drainage and the hydrology of the area. Comparison of drainage chemistry with regulatory requirements will enable the assessment of the degree of treatment required and partially answer the question of whether wetland treatment is appropriate.

Possession of background information on mine drainage composition is crucial.

Good knowledge of the surface and groundwater hydrology is the key to success. A complete water budget for the site should be constructed, including investigation
of all inflows and outflows of surface water, rainfall, estimation of losses from evaporation and transpiration and subsurface losses and gains.

Other preliminary design considerations include the availability and cost of plants and substrate, the treatment efficiency of the available substrates and the long-term cost of the wetland compared to other treatment systems.

10.1.5 Configuration

To minimise the risk of hydraulic short-circuiting, and to provide operating flexibility, large wetlands are best divided into smaller 'cells'. The topography of a site will often suggest the use of cells also.

Cells may be arranged in series, in parallel or as a combination of the two, as shown in Figure 10.1. Parallel configurations allow for the assessment of different treatments and for backup, should one cell be unusable for any time. Easier uniform distribution of influent is possible in a parallel configuration because flow per unit cross sectional area of wetland will be lower. Serial configurations allow for a staged treatment with different wetlands treating different aspects of the contamination. In either type of configuration, failure of one cell should not cause failure of the system.

A modular design, incorporating both serial and parallel configurations, is the best configuration for any system and the only configuration for a large system (Howard et al. 1989c), combining the advantages of parallel and serial configurations.

Intercell connections can be used as re-aeration devices and may be lined with limestone rip-rap to partially neutralize acidity. If there is considerable hydraulic head between cells, intercell connections must dissipate the energy of the flow to avoid problems of erosion and precipitate resuspension in the next cell.

10.1.6 Size and shape

Size and shape of cells may be determined using theoretical design equations or empirical 'rules of thumb'.

Tentative theoretical design methods have been advanced for constructed wetlands. These tend to be based on reaction kinetics (SF and SSF systems) or on consideration of water flow through the substrate (SSF systems).
All constructed wetlands are attached-growth biological reactors and performance is based on first-order, plug-flow kinetics (Reed et al. 1988, Watson and Hobson 1989). Growth is 'attached' in that microbes grow on the surface of particles and roots. A 'trickling filter' used in sewage treatment is another example of an attached-growth biological reactor. First-order kinetics implies that the rate of change of concentration with time is proportional to the concentration. 'Plug-flow' implies that water entering the reactor flows as a coherent body along the length of the reactor and any two water molecules entering the reactor at the same time will eventually emerge together at the effluent. A simplified scheme is presented here, see Reed et al. 1988, Watson and Hobson 1989 and Watson et al. 1989 for more detail and Kadlec 1989 for guidance on deviation from the simple scheme.

The basic relationship is

\[
\frac{C_e}{C_o} = \exp\left(-K_t t\right)
\]  

(10.1)

where

- \(C_e\) = effluent concentration, mg/l
- \(C_o\) = influent concentration, mg/l
- \(K_t\) = temperature-dependent first order reaction rate constant, days\(^{-1}\)
- \(t\) = hydraulic residence time, days

Hydraulic resistance time can be defined as

\[
t = \frac{L \cdot w \cdot n \cdot d}{Q}
\]

(10.2)

where

- \(L\) = length of system, m
- \(w\) = width of system, m
- \(n\) = porosity of bed, as a decimal fraction
- \(d\) = depth of submergence, m
- \(Q\) = average flow through the system, m\(^3\)/s
Inflow

Figure 10.1 Wetland system configurations.

A. Parallel modules

B. Serial cells

C. Combination arrangement
Porosity is defined as

\[ n = \frac{V_v}{V} \]  

where \( V_v \) = the total volume of voids in the system  
\( V \) = the total volume

Typical values of \( n \) observed are between 86% and 98% for a surface flow system. Initial porosities are between 18% (coarse gravel substrate) and 45% (silt and clay substrate) for SSF. The porosity of the substrate will change considerably for an SSF system, as vegetation becomes established. Design must consider the eventual porosity.

For other derivations of these equations, see the references cited above.

Design of wetlands to treat MCMD on the basis of reaction kinetics should be approached with caution. There is little experience on the applicability of these equations to MCMD treatment and rate constants in the literature are derived from sewage treatment wetlands. The equations also relate to microbial activity and it is as yet unclear which metals are removed by such activity.

Subsurface flow can be expressed using Darcy's law for fine grained soils, sands and gravels or by Ergun's equation for 'clean' coarse gravels and rocks (Hobson 1989, Watson and Hobson 1989, Watson et al. 1989).

Darcy's law can be written

\[ Q = K_s A S \]  

where \( Q \) = flow per unit time, m³/day  
\( K_s \) = saturated hydraulic conductivity of a unit area of the medium perpendicular to the flow direction, m/day  
\( A \) = saturated cross-sectional area, m²  
\( S \) = hydraulic gradient of the system, or bed slope, as a decimal fraction.

Ergun's equation can be written

\[ \rho g S = 150 \frac{\mu V(1-\varepsilon)^2}{D_p^2 \varepsilon^2} + 1.75 \frac{\rho v^2 (1-\varepsilon)}{D_p \varepsilon} \]  

where \( \rho \) = density  
\( g \) = gravitational attraction  
\( S \) = hydraulic gradient  
\( \mu \) = viscosity  
\( \varepsilon \) = porosity  
\( D_p \) = particle diameter  
\( V \) = velocity = superficial velocity/\( \varepsilon \)
On the basis of experience with wetlands for sewage treatment, it is recommended that the unit flow velocity $Q/A$ does not exceed 8.6 m/day to avoid disrupting the substrate-root structure (Reed et al. 1988); this effects bed slope as follows:

$$S < \frac{8.6}{K_r}$$

(10.6)

where $S$ = hydraulic gradient/bed slope

$K_r$ = hydraulic conductivity

Reed et al. (1988) present a step-by-step approach to sizing a SSF wetland. Once substrate has been selected and depth chosen, equation 10.6 can be used to supply bed slope. Recommended bed slopes range from 1 to 8%. Darcy's law (equation 10.4) then supplies cross sectional area ($A$) and hence width. The length must be derived by prior experience or by consideration of reaction kinetics (equation 10.1) Reed et al. (1988) also present worked examples, for sewage treatment wetlands.

Uncertainties and qualifications cloud this theoretical approach. The hydraulic complexity of the situation (the effect of evapotranspiration, precipitation, snow and ice-cover) makes design difficult. Flow variation causes complications. Substrate porosity will vary considerably as vegetation becomes established.

There are many empirical design suggestions in the literature.

Empirical sizing guidance, from observations of coal mine drainage treatment wetlands, vary from 5 to 15 m$^2$ of wetland per litre/minute flow and from 4 grams of iron per day per square metre at pH 3 to 10 g Fe/d/m$^2$ at pH 4 (Hedin and Nairn 1990). Metal mine treatment case studies suggest 4-12 m$^2$/l/min (Table 9.1). One group (Hedin et al. 1989) suggests 50 m$^2$/l/min for wetlands designed to utilise sulphate-reduction.

Water depth in SF systems must allow for substantial deposition of metals. Depths are best if they vary, to allow a range of habitats, and thus treatment variation. Deep patches are good for wildlife and as recharge/refuge areas. A maximum average depth of 0.60 m is suggested, preferably 0.30-0.45 m, and at least 0.10 m in summer and 0.30 m in winter (Reed et al. 1988).

The United States Bureau of Mines suggests substrate comprising 0.05-0.10 m gravel and 0.30-0.45 m of compost for coal mine drainage treatment using SF systems.

If sulphate-reduction is to be incorporated, design should allow additional volume to account for reduced treatment efficiency during winter (the sulphate-reducing bacteria are less active). Additional volume is also needed for contingency and to allow for freezing of surface waters. Reasons for such 'over design' are discussed further in section 10.1.10.
10.1.7 Substrate

A variety of substrates have been used for the treatment of MCMD. These have included straw with *Sphagnum* peat, straw with clay, mushroom compost, forest litter and manure (Kleinmann and Girts 1987). Results from the Big Five Tunnel site suggest that a substrate of mushroom compost gives better metal removal than one of a mixture of peat, manure and decomposed wood products (Howard *et al.* 1989c). Successful laboratory-scale studies of sulphate-reduction to treat simulated MCMD (Belin *et al.* 1991, Dvorak *et al.* 1991, Hammack and Edenborn 1991) have used mushroom compost as a substrate.

Other studies (Brodie *et al.*, 1988, Stillings *et al.* 1988) suggest that substrate type is unimportant once the wetland has become established, which generally takes less than one year, indeed, any organic substrate can be used provided it is well composted (Kleinmann, R, US Bureau of Mines, personal communication). In remote locations, the overriding concern on choice of substrate may be local availability.

It may be advantageous to underlay the substrate with a layer of crushed limestone (Howard *et al.* 1989c). As the limestone is under anaerobic conditions, armouring by precipitated hydroxides will be low and significant neutralization of the MCMD should result. This layer will also improve hydraulic conductivity but care should be taken to avoid hydraulic short-circuiting.

Gravel can be incorporated into a substrate to increase permeability (Howard *et al.* 1989c).

The substrate should be analyzed prior to use to assess hydraulic conductivity, pH, buffering capacity, plant nutrient levels and microbial activity. Some workers consider that a near-neutral pH substrate enhances sulphate-reduction (Howard *et al.* 1989c). Initial hydraulic conductivities of between 0.1 and 0.001 cm/s have been suggested for SSF wetlands (Wood 1990), with a goal of 0.1 cm/s in the long term, after the plant roots have become established. High ammonia content may hinder the growth of vegetation (Howard *et al.* 1989c). For subsurface flow wetlands used in municipal water treatment, Darcy’s law (equation 10.4) has been used to select gravel size for gravel beds (Steiner and Freeman 1989). Particle size, hence hydraulic conductivity, may be varied with depth and along the wetland. This is easy to engineer with gravel, is practised in municipal SSF wetlands and may have applications for MCMD treatment wetlands; hydraulic conductivity in the inlet area can be increased to allow for precipitation of metal hydroxides.

The depth of substrate influences retention time in a SSF wetland. Other factors in the selection of depth include depth of root penetration, cost of substrate, climate and design for sulphate reduction. A maximum root penetration of 0.3 m has been observed for *Typha latifolia* and one of 0.6 m for *Phragmites* (Reed *et al.* 1988).
Sulphate-reduction potential can be enhanced by increasing the size of the anaerobic zone and increasing contact of the wastewater with this zone. The former can be accomplished with deeper substrates, 0.75 m or so (Hedin et al. 1989), the latter with appropriate inlet design.

In extreme cold climates, substrate depth may need to be increased further such that temperatures suitable for sulphate-reduction can be maintained all year round (3-5°C minimum, Howard et al. 1989c).

In a SSF wetland with an organic substrate, it may be advantageous to mound the substrate above the level of the influent water in the first part of the wetland to encourage the water to enter the substrate.

10.1.8 Vegetation

Most wetlands for MCMD treatment now use Typha latifolia, although early wetlands used Sphagnum species. Many factors influence this choice:

- **Tolerance to high metal concentrations.** Typha can tolerate high copper, nickel and zinc concentrations (Kleinmann 1990). Sphagnum species are relatively intolerant of iron (Spratt and Wieder 1988).

- **Effect of water level.** The use of Sphagnum species was abandoned due in part to their poor tolerance of fluctuating water levels. Sphagnum only tolerates inundation for a short while (Kleinmann et al. 1986). Typha may come to dominate if the standing water depth exceeds 0.15 m; as depth increases sedges (Carex species) give way to clubrushes (Scirpus species), clubrushes to Typha (Reed et al. 1988). Maximum depth and other physicochemical conditions for selected wetland plant species are given in Table 10.1.

- **Oxygen transfer capability.** Decreasing order of oxygen release per unit mass for five wetland plant species was found to be Typha latifolia, Juncus effusus, Sparganium americanum, Eleocharis quadrangula and Scirpus cyperinus (Michaud and Richardson 1989).

- **Root proliferation.** Phragmites and Scirpus species provide the greatest root proliferation while Typha species have limited root proliferation and overwintering capacity (Wood 1990).

- **Availability and transplantability.** Local species of vegetation, tolerant to environment and climate, are recommended. Typha, Phragmites, Juncus, Scirpus and Carex species are cosmopolitan in distribution (Reed et al. 1988). Typha are easy to transplant, Sphagnum and other mosses are not easy to obtain or transplant (Kleinmann et al. 1986).
**Soil requirements.** *Typha* will grow in a wide variety of media; sedges can be grown in silty clays (Reed et al. 1988).

**Availability of tolerant ecotypes.** Use of metal- and acid-tolerant ecotypes (populations within a particular species) of a particular wetland plant will enable stronger MCMD to be treated.

**Supply of organic matter to the substrate.** Some wetland plants e.g *Molinia* species die back in the winter thus supplying a large amount of matter to the substrate. This supply may increase the activity of sulphate-reducing bacteria.

**Diversity.** There is usually no need to reproduce natural wetland diversity in SF wetlands since *Typha*, *Typha* and *Phragmites* or *Typha* and *Scirpus* tend to come to dominate (Reed et al. 1988).

10.1.9 Inlet and outlet structures (Watson and Hobson 1989)

If a configuration involves parallel cells some form of flow splitting device will be needed. Valves are impractical because they would require regular adjustment. Flumes minimise clogging problems but weirs are less expensive and easily modified or replaced.

Inlet and outlet structures for surface flow wetlands are usually simple. Open-end pipes, channels and spillways are typically used. They should be sited to minimise hydraulic short-circuiting and sized to accommodate the maximum flow envisaged.

Inlet and outlet structures for substrate flow systems need more attention. Uniform flow distribution, across both width and depth of the bed, is important. Inlets can be uniformly spaced holes, slots, tees or serrations in pipes or channels across the width of the cell. Inlets above the bed allow for maintenance and adjustment and also provide aeration, but may be prone to freezing. Large, coarse gravel may be placed beneath inlets. Outlets may be perforated pipes buried in coarse gravel. Water level control can be provided by adjustable weirs or standpipes, rather than valves. Standpipes are simple, inexpensive and reliable.

The use of a 'rock box' inlet in the Big Five Tunnel site constructed wetland has been described earlier (Section 9.2.1).

Kleinmann *et al.* 1986 strongly advise the use of open channels rather than pipes for inlet and outlet structures since pipes almost invariably become blocked by precipitates.
Table 10.1 Physicochemical conditions for selected wetland plant species.

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Depth range, m</th>
<th>Salinity</th>
<th>Alkalinity, mg/l CaCO₃</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedges (Cyperus spp. and Carex spp.)</td>
<td>&lt; 0.30</td>
<td>freshwater</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rushes (Juncus spp.)</td>
<td>wet soil</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reedgrass (Phragmites australis)</td>
<td>-1 to +2</td>
<td>fresh or brackish water</td>
<td>0.5-298</td>
<td>3.7-9.0</td>
</tr>
<tr>
<td>River Bulrush (Scirpus fluviatilis)</td>
<td>&lt; 0.50</td>
<td>fresh or brackish water</td>
<td>30-220</td>
<td>7-9.1</td>
</tr>
<tr>
<td>Burread (Sparganium eurycarpum)</td>
<td>&lt; 1.20</td>
<td>freshwater</td>
<td>35-376</td>
<td>6.7-8.8</td>
</tr>
<tr>
<td>Cattail (Typha latifolia)</td>
<td>&lt; 0.30</td>
<td>fresh or brackish water</td>
<td>10-376</td>
<td>4.5-9.0</td>
</tr>
</tbody>
</table>

10.1.10 Flow regime

The flow path within each cell should be controlled to minimise hydraulic short-circuiting and hence maintain a sufficient contact time between MCMD and wetland. Large cells should be chambered, through the use of simple or subsurface dikes, logs, riprap baffles or hay bales. Hay bales are good in that they are cheap, relatively easy to adjust and provide a support for the growth of microbes, algae and plants.

Flow velocity within the cell should be carefully controlled. Too great a velocity leads to erosion and resuspension of precipitated matter, too low may lead to stagnation.

Kleinmann et al. 1986 suggest surface flow velocities of between 0.03 and 0.09 m/s. Cross dikes can be used to interrupt the flow if channelling occurs. Flow velocity can be controlled at the design stage. Careful design of intercell connections may be necessary as noted above (Section 10.1.5 'Configuration'). A dam or other influent storage facility may be used to restrict flow variations.

Redesign may be necessary if the wetland experiences flushing after significant rainfall/discharge events.

The facility for water depth control, using adjustable inlet and outlet structures, is important. Flooding of the surface can be used in a SSF wetland to control invasive weeds and possibly to encourage rhizome penetration (Hobson 1989). Seasonal changes in depth can counteract the effects of greater evapotranspiration in the summer and ice-cover in the winter. Seasonal changes in flow velocity may also be necessary (Huntsman et al. 1985).

10.1.11 Design optimisation (Girts and Knight 1989)

Some wetland water treatment systems have been designed to cope with 'average conditions', but require constant attention. Others have been designed to accommodate extremes of conditions expected during the operating lifespan. Experience shows that reliance on system resiliency is often better than reliance on operator intervention.

Optimisation of wetland design must provide the maximum treatment efficiency and capacity under all scenarios, minimize system costs, achieve the greatest possible flexibility and safeguard the long-term viability of the system.

'Over design' to cope with conditions more extreme than the average, must take into account predictable and probable perturbations. Predictable perturbations include low treatment during start-up periods and the effect of seasonal changes (high precipitation, high evapotranspiration, low temperature). Design for sulphate-
reduction will require a greater treatment volume to cope with reduced microbial activity during winter. Probable or unpredictable perturbations include record storm events, damage to the integrity of the structure or the loss of electrical power in certain cases.

Measures that may be used include designing for additional treatment capacity, allowing for recirculation, fail-safe structures such as overflows and standby chemical treatment capacity.

Some conventional treatment capacity is required in the United States where constructed wetlands are considered for use at operational mines.
10.2 **Construction**

10.2.1 **Construction plans**

Minimum contents for a construction plan for large wetlands for municipal wastewater treatment are given by Tomljanovich and Perez (1989). These may be used as the basis of a construction plan for MCMD treatment. The minimum contents are:

- site clearing limits
- access roads
- utilities (overhead and underground)
- erosion control measures
- location and boundaries of borrow areas
- trees and existing vegetation to be left undisturbed
- wildlife habitat enhancement structures
- dikes (location, crest width, length, evaluation, freeboard, upstream and downstream slopes)
- spillway location, elevation and type
- size, location, elevation and type of water control structures
- permeability requirements of substrate and dikes
- liners (type, location, specification)
- placement of substrate materials
- wetland base slope and tolerances
- species and spacing of vegetation to be planted
- liming and/or fertilizer requirements
- seeding, mulching, fertilizing and liming of dikes and disturbed land
- inlet and outlet distribution piping (type, location, elevation)
The level of detail will depend on size and complexity of the wetland, site characteristics and regulating requirements.

10.2.2 Preconstruction site activities

These should include marking and clearing the site, identifying any need for temporary diversion or pumping of water and identifying materials that can be reused (Tomljanovich and Perez 1989).

10.2.3 Construction details

Various authors (Howard et al. 1989c, Kleinmann et al. 1986, Reed et al. 1988, Steiner and Freeman 1989, Tomljanovich and Perez 1989) give useful details and suggestions for wetland construction:

Equipment

The correct type and size of construction equipment is critical. Equipment suitable for ground conditions should be used.

Liners

All components should be lined to isolate them from groundwater. A permeability of less than $10^6$ cm/sec is desired. Materials include compacted clay soils (0.15-0.25 m depth), bentonite, asphalt, butyl rubber and plastics. Bentonitic clays may not function correctly in MCMD. Synthetic liners are expensive and should be assessed for resistance to aqueous hydrogen sulphide (H$_2$S). If sheet materials are used, they should be smooth to prevent root attachment; growing tips may eventually stretch materials to breaking point. Liners should be strong and thick. If a sharp gravel substrate is to be used, a layer of sand may be needed between substrate and liner to prevent punctures. Liners should be below the maximum depth of root penetration.

Substrate material should be placed on the liner using light equipment to minimise substrate compaction and risk of liner puncture.

In severe climates, liners should be chosen carefully; a 0.76 mm thick Hypalon$^\text{a}$ (chlorosulphonated polyethylene) liner survived a hailstorm that shredded 0.25 mm polyethylene.
Dikes

Some dike seepage is usually acceptable, so on-site borrow materials are often appropriate. Dikes should be adequately compacted and sloped no steeper than 1 in 2. They tend to settle, so should be constructed with 0.45-0.75 m freeboard (the distance between crest and water level) which should provide 0.3 m freeboard long term. Vehicular access to dikes should be discouraged - crest widths should be insufficient and posts can be placed at each end. Dikes and disturbed areas should be revegetated immediately.

Inlets and outlets

Corrosion resistant coating should be used for pipes and sumps if pH < 5.0. The distribution system should avoid sharp bends or traps which allow for the accumulation of precipitates, should incorporate features allowing for clearing, should provide adjustable delivery of the MCMD and allow for modules to be bypassed. In cold climates, the distribution system should be insulated. One active and one reserve drain for each cell should be provided. In a research wetland, test wells should be installed to sample interstitial water.

Miscellaneous

The work area should be kept as dry as possible during construction. Design should be flexible enough to allow for field modification, for example, to account for new seeps discovered during construction. A polishing and treatment area after the wetland may be needed to comply with discharge laws during construction.

10.2.4 Vegetation establishment


Locally dominant species are best so vegetation available on site should be saved. Commercial nurseries may also be a source for plants. Recommended propagules are given in Table 10.2 for selected wetland plants.

Aerial seeding is possible but development from seed is slow. Seeding should take place in early spring.

Rhizomes and tubers should be collected in late autumn after shoot growth has stopped, or in early spring before extensive new growth. They should be cut into lengths containing 2-3 nodes, all vegetative matter should be removed and then they
should be placed into a moist medium (peat, sand) until planted. Rhizomes and tubers may be stored over winter at 2-14°C, treated with dilute bleach to reduce fungal injury.

The substrate can be saturated with tap water or MCMD free stream or lake water prior to planting to reduce stress on transplanted vegetation and rhizomes.

Rhizomes should be planted after the last frosts of spring and before the first frost of autumn. For *Typha latifolia*, 0.1 m long rhizome cuttings are recommended, containing at least one bud. These should be planted with one end about 40 mm below the surface of the medium and the other in the atmosphere. The bed should then be flooded to just below the surface until sufficient new growth has developed that the wetland can be put into operation.

With SSF wetlands, it may be necessary to wait until plant roots completely permeate the substrate before the wetland is put into operation. This may take up to 3 years, but generally takes under one year.

When transplanting whole *Typha latifolia* plants some 0.03 m² (48 in²) of the surrounding material should be taken. The plants should be dug out, not pulled up. Plants should be set in the wetland with stems upright and roots covered and in the humic substrate. Stems can either be cut to 0.2-0.3 m, such that a portion extends above the intended water level, or the stems can be broken over at the water level. In a SSF wetland, substrate should be mounded around the stems to avoid pooling.

Clumps of moss 0.2-0.3 m² should be transplanted and placed in a checkerboard pattern in the wetland.

*Typha* plants and rhizomes should be spaced at 1 m centres, clubrushes (*Scirpus species*) at about 1 m also, and reeds at about 0.5 m centres. Planting should stagger adjacent rows such that no straight water channels are present.

The use of walk-boards during hand planting will reduce compaction of the substrate.

In a wetland with a compost substrate and a limestone layer, sufficient nitrogen and calcium will be available, but fertilization with a little phosphorous and potassium may be necessary.

Costings should include an amount for contingency should vegetation fail to become established and replanting be necessary.
Table 10.2 Recommended propagules for selected wetland plant species.

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Recommended Propagule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedges (Cyperus spp. and Carex spp.)</td>
<td>tubers, rootstocks</td>
</tr>
<tr>
<td>Rushes (Juncus spp.)</td>
<td>transplants, rootstocks, seeds</td>
</tr>
<tr>
<td>Reedgrass (Phragmites australis)</td>
<td>rhizomes</td>
</tr>
<tr>
<td>River Bulrush (Scirpus fluviatilis)</td>
<td>transplants, rhizomes</td>
</tr>
<tr>
<td>Burread (Sparganium eurycarpum)</td>
<td>rhizomes</td>
</tr>
<tr>
<td>Cattail (Typha latifolia)</td>
<td>rootstocks, rhizomes</td>
</tr>
</tbody>
</table>


10.2.5 Maintenance

Kleinmann and Girts (1987) surveyed some twenty wetlands in the United States treating MCMD from coal mines. Maintenance procedures reported included replacing limestone ditch rip-rap, grading to limit surface runoff infiltration and establishing hay bale dikes to limit channelization. Maintenance was considered inexpensive and not time consuming.

Periodic clearing of inlet structures, to remove precipitates, may be necessary. Substrate and vegetation replacement may also be necessary (e.g. Masters 1989). Harvesting of emergent plant matter is not generally practised, organic matter returned to the substrate represents fuel for bacterial sulphate-reduction.
11. APPLICABILITY OF WETLAND TECHNIQUES IN THE UK

Constructed wetlands may represent the most feasible way of ameliorating MCMD from adits for one overriding reason: their low capital and operating costs. Although the Water Resources Act of 1991 states that those responsible for polluting rivers can be prosecuted and that the NRA can recover costs from the polluter, pollution from abandoned mines is specifically exempted (Hunt 1992). The scale of the problem and the number of sources of MCMD involved mean that a low cost solution is essential.

Other advantages of wetlands pertinent to their application to the typically remote sites in the UK include low labour requirements for operation and maintenance and the possibility of extensive use of on-site and local materials in construction, hence lower materials and transport costs.

The case studies have shown that successful removal of those heavy metals common in MCMD in the UK is possible and that wetlands can be constructed to withstand harsher climates than would be expected at UK metal mine sites.

There is considerable expertise in the UK with design, construction and operation of wetlands to treat municipal wastewater so a useful knowledge base is at hand.

For these reasons, constructed wetlands have great potential as a technique to treat MCMD from metalliferous mines in the United Kingdom.

With the current state of knowledge, full-scale field implementation of wetland treatment techniques would be unwise without pilot-scale trials to answer a range of questions:

1. What is the best substrate to use?
   Composted materials are readily obtainable. Those available on-site may include peat and forest litter. Tertiary-treated sewage sludge may represent a good, cheap, available substrate.

2. How might differences in geochemistry between the UK and the case study situations affect the performance of constructed wetlands?

3. How can sulphate-reduction processes be enhanced?
   Design modifications worthy of investigation include different inlet structures, substrate type and depth. The use of plants such as *Molinia* species, which provide a large amount of organic matter to the system when they die back, thus enhancing sulphate-reduction, but do not oxygenate the substrate, could be considered.
4. What is the best vegetation to use?
Little is known about the performance of Juncus species in constructed wetlands. These are a wetland plant typical of upland areas in the UK and they may survive the UK climate better, and be less vulnerable to strong winds than other plants such as Typha species and Phragmites communis. The role of metal-tolerance in plants in relation to wetland treatment is not well documented. In the UK metal-tolerant ecotypes of Deschampsia caespitosa are found in wetland situations receiving MCMD and may be a suitable plant material to use.
12. REFERENCES


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