Treatment and Utilisation of Hilton Mine Water

By B. M. CHAPMAN,[1] D. R. JONES,[1] R. F. JUNG,[1] C. J. JONES,[2] O. KADLETZ[2] and J. W. S. TEAGUE[2]

ABSTRACT

A study of the passive treatment system for Hilton minewater revealed that it consists of four main process steps. The water, which contains soluble and particulate iron and zinc and is supersaturated with CO_2, is pumped to the surface and then passes through a degassing unit into settling ponds where larger particles of iron hydroxide, containing some adsorbed zinc, can settle out. The still turbid supernatant is pumped to the top of a hill, from where it is allowed to trickle in a broad sheet, releasing CO_2, towards an earthen channel in the valley below. Consequently the pH rises from around 6 to 7.5. This in turn promotes further decrease in the concentration of soluble zinc by increased adsorption of zinc on to iron hydroxide particles. The channel then transports the water to the third process in the system - a 53 ML pond acting primarily as a flocculation-sedimentation basin. The clarified water overflows into a second channel, downstream of the pond, which constitutes the fourth process in the system. Here, copious quantities of filamentous algae further reduce zinc concentrations to acceptable levels before the water is collected for recycle into mine operations. The work reported here represents a detailed study of this system and describes the optimisation of the operation of each of the individual steps involved.

INTRODUCTION

Mt Isa Mines Ltd is presently developing production capacity from its new Hilton Mine, a large lead-zinc-silver ore-body about 20km north of Mt Isa. Over the last few years the dewatering flow has increased from about 2000 to 6000 cu m/day. In summary, the minewater containing Fe and Zn is pumped to the surface and is combined in a system of settling ponds with the discharge known as 0-50 water which is being pumped directly from an aquifer in the vicinity (see Fig. 1). The resulting mixture contains a large quantity of flocculated iron hydroxide precipitate which partially settles out in these ponds before the supernatant is pumped to an outlet at the top of a nearby

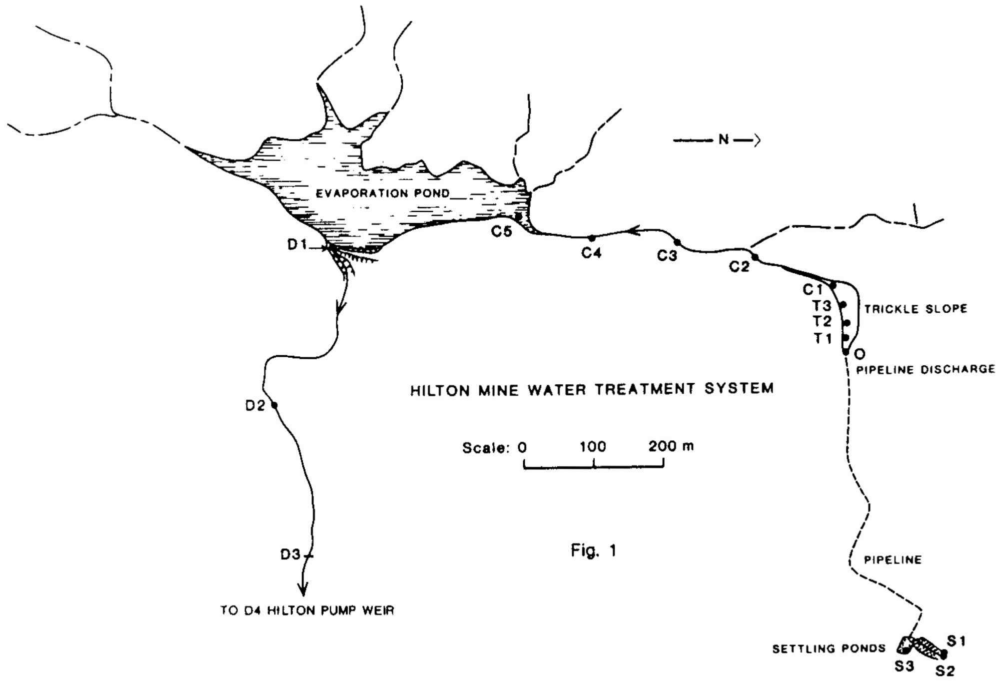

Fig. 1

hill. After leaving this outlet the water is allowed to flow freely down the hillside about 50m into an earthen channel leading to an impoundment known as the "Evaporation Pond" with a volume of 53 Ml. The resulting stream is about 400m long and the depth varies between 60 and 500mm. The depth of the evaporation pond is about 1.25m average and its surface area is 4.2 hectares. After leaving the Evaporation Pond the water travels 1.4 km along a downstream channel to the Hilton Pump Weir where it is pumped to Mt Isa for use in mine operations.

For this purpose it is necessary to maintain a given standard of water quality which is achieved by the self-purification processes operating within this passive treatment system. These promote a progressive reduction in metal levels as the water passes through the system. The present study was intended to identify the specific processes involved to allow them to be optimised and to ascertain whether they would continue to operate satisfactorily into the foreseeable future.

EXPERIMENTAL

Three series of investigations were undertaken and will be considered under separate headings. The first was a study to determine the hydrodynamic flow patterns for water discharged into the evaporation pond. This pond effectively decouples the upstream portion of the treatment system from the lower section because of its reservoir effect. The second was a survey to assess the degree of attenuation of metal levels, both soluble and particulate, in the flowing waters throughout the system. Concurrent with this, an analysis was undertaken of the surficial sediments all the way from the settling ponds to the overflow of the evaporation pond. The third was a detailed investigation of the channel downstream from the evaporation pond to establish the relative importance of biotic activity compared with abiotic processes on metal attenuation.

Sites

For the field work it was essential to establish a convenient grid of sampling sites along the trickle slope (section 1) and the channel leading to the pond (section 2), in the pond itself (section 3), and in the channel between the dam overflow and the Hilton Pump Weir (section 4). Within each of the sections 1,2 and 4 a series of roughly equidistant sampling sites was chosen (see Fig. 1). The four (including the discharge outlet 0 of the pipe on the hill) in section 1 were designated 0, and T1 to T3. Five sites, C1 to C5 were chosen in section 2 and four, D1 to D4 (including the pond overflow D1 and the Hilton Pump Weir D4), in section 4.

In the pond a total of 36 sites were chosen in such a way as to give a fairly even coverage of the area and as far as possible were arranged in the form of transects across its surface. 150 mm spherical polystyrene marker buoys, identified by either a Roman or Greek letter, were anchored at the required locations to mark these sites.

HYDRODYNAMICS OF EVAPORATION POND

In order to establish the major flow patterns for incoming mine water into the evaporation pond a volume of 20 L of Rhodamine concentrate (0.84 M) was released into the channel from a site 35m upstream of C5 near the pond inflow. This was injected over a period of 3 mins commencing at 9 am on 12 October 1985. From the network of marker buoys on the pond it was possible, from a photographic record of events, to plot fairly accurately the progress of the pulse front. Water samples were taken regularly on the surface and at depth from strategic locations. Since the volume of the pond was known to be about 53 ML and the flow-rate into it between 3-5 kL/day it was therefore expected that the peak of the pulse would take of the order of 10-15 days to cross the pond.

Results and Discussion

The dye pulse entered the pond by channeling through the western side of the reed bed at its inlet end. Once in the pond the leading edge of the very intense red pulse spread much more rapidly than anticipated. In addition this edge appeared to have a very sharp front. Closer inspection from the sampling canoe revealed that the dye cloud was confined to the top 100-200 mm of the water column. The progress of the dye pulse across the pond can be seen from the contours of its leading edge which are plotted in Fig. 2 for approximately equal intervals of time.

The dye was confined to the top 200 mm of the water column throughout the day and the visual observations were confirmed by quantitative depth sampling. The data obtained demonstrated a distinct stratification in both the concentration and temperature profiles and indicated an intimate association between both phenomena. It was obvious that the warm water discharged from the mine retained its heat by direct solar radiation and contact with the sunlit hillside of the trickle slope. On reaching the pond it flowed out in a thin surface layer over the relatively colder lower layers. Changes in wind direction caused this surficial dye front to be moved backwards and forwards by many tens of meters across the pond within the space of a few minutes. This behaviour is clearly apparent in the dyefront

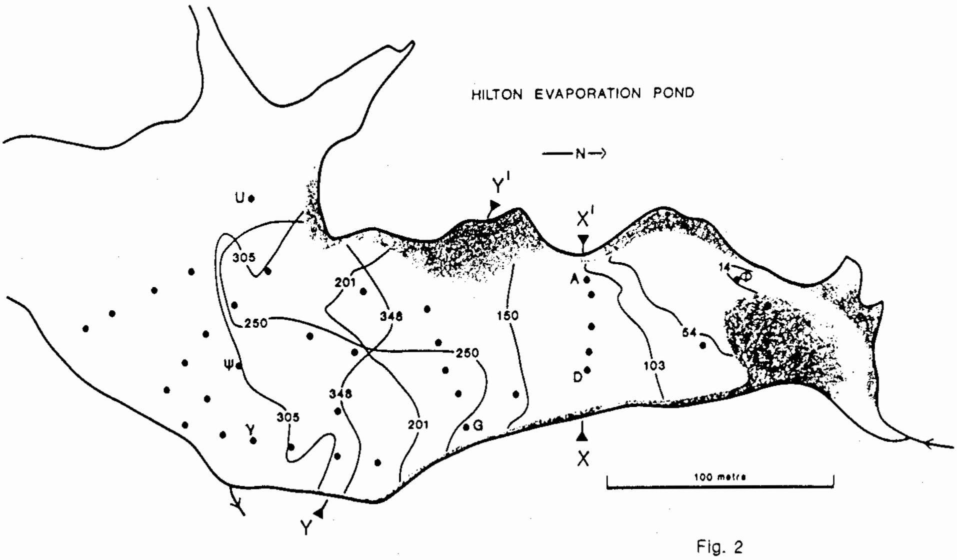

Fig. 2

contours shown in Fig. 2. This wind-induced movement allowed the dye to travel quickly to relative backwaters in the pond which otherwise would not have been expected to receive significant quantities of dye so early.

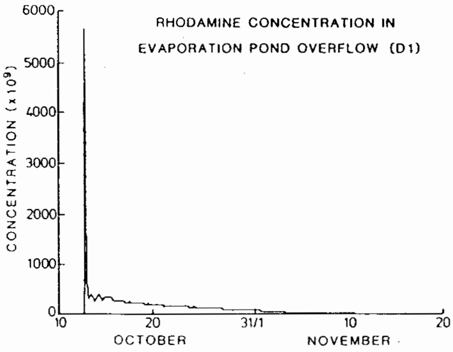

Fig. 3

By mid-afternoon on the day of release it was obvious that the leading edge of the pulse Rhodamine would soon be discharging from the pond and regular sampling at the overflow D1 was commenced. However, presumably because the prevailing wind was generally blowing the surface layer back upstream, no significant quantity of dye was discharged during daylight hours. However, after sunset, the wind dropped and the dye-laden surface layer which had been backed-up in a wedge towards the leeward inlet end quickly spread out over the surface and discharged a highly concentrated spike of Rhodamine over the outlet (see Fig. 3). It is clear then that from the point of view of water treatment, wind direction can be both favourable or unfavourable. If it is blown back upstream it can be delayed from discharging for some time as was observed here. On the other hand, if it is blown downstream, the short-circuiting of the pond can be accelerated so the retention time is only a few hours.

During darkness, in the absence of insolation to maintain the thermal stratification, the originally warmer surface layers rapidly lost heat by radiation and evaporation and their increased density allowed mixing with the bulk waters below, resulting in a relatively even spreading of the dye through the water column by next morning. Except at the northern inlet end of the pond where fresh dye-free mine water had been entering, the horizontal mixing in the pond was also fairly even because of the wind factors mentioned previously.

The most important aspect of the results obtained in this experiment was the demonstration that, during the day, the retention pond could be severely short-circuited through diurnal thermal stratification leading to considerable quantities of raw "untreated" mine water being discharged within a few hours after entering the pond. This would result in a reduction in the time available for the treatment processes including adsorption, degassing and particle settling.

Process Optimisation

In order to prevent this short-circuiting it was decided to install an impervious "curtain" across the pond at the XX' transect shown in Fig. 2. The curtain is held up by a boom and weighted at the base, but in the deeper parts of the pond it does not reach completely to the bottom. Its role is to hold back the buoyant warm inflowing waters and the floating surface particulate scum preventing them spreading rapidly across the pond surface. They are eventually forced under the base of the curtain causing mixing to occur with the deeper and cooler waters on the other side of the curtain. The resulting increase in residence time of the inflow has allowed a greater degree of settling and reaction to occur. This has also caused the flow to change from that of a mixed reactor (following the overnight mixing) more towards plug flow which provides more efficient treatment.

The curtain was installed in mid 1985 and was very effective in preventing the surface skimming of particulate-laden water. However, a release of tracer dye during a subsequent field trip showed that the 1 m depth of the curtain was not quite sufficient to ensure optimum vertical mixing in the water column. Accordingly a second curtain, extending to 2 m below the surface, was constructed some distance downstream of the first at transect YY' in Fig. 2. This combination of two curtains has proved very effective in improving the flocculation-sedimentation role of the pond.

WATER CHEMISTRY

Nett removal of heavy metals from a water column can only occur via processes involving chemical reactions. Since the long term stability of the treatment system is critically dependent on the sensitivity of these processes to changes in the chemical environment (for example, pH and redox potential) it was essential to identify the most important ones.

If an upstream source of heavy metals has been discharging for a long time, a steady-state will ultimately be reached where all of the original surface sites on the stream bed are in adsorption/desorption equilibrium with the concentrations of cations and anions in the water column (1,2). Under these circumstances, although adsorption processes on to the bed sediments can no longer give rise to metal attenuation there still exist three mechanisms which are available for species attenuation: (1) precipitation of solids, (2) adsorption of dissolved species on to newly-formed solids or (3) adsorption on to existing suspended materials (such as clays). For attenuation in any of these cases the solids referred to must subsequently sediment. Because it had already been in operation for several years this passive treatment system, as far as the Hilton Pump Weir, was expected to have reached such a steady-state.

Water samples were taken from level 4 in the mine, from the settling ponds at the surface and from the surface stream down to the Hilton Pump Weir. Sediment samples from the primary settling ponds to the Hilton Pump Weir (site D4), were collected to provide the necessary data to establish the removal mechanisms for the metals of interest.

Results and Discussion

Analyses were carried out for both particulate and dissolved forms of the cations and anions in the water samples. Since the behaviour of the dissolved fraction of each component as a function of distance downstream can indicate whether or not nett removal is occurring the dissolved concentration data for sites 0 to D4 are plotted in Fig. 4 on a logarithmic scale. The CO_2 concentrations shown were calculated from the measured HCO_3^- and pH values using the appropriate equilibrium constant expression.

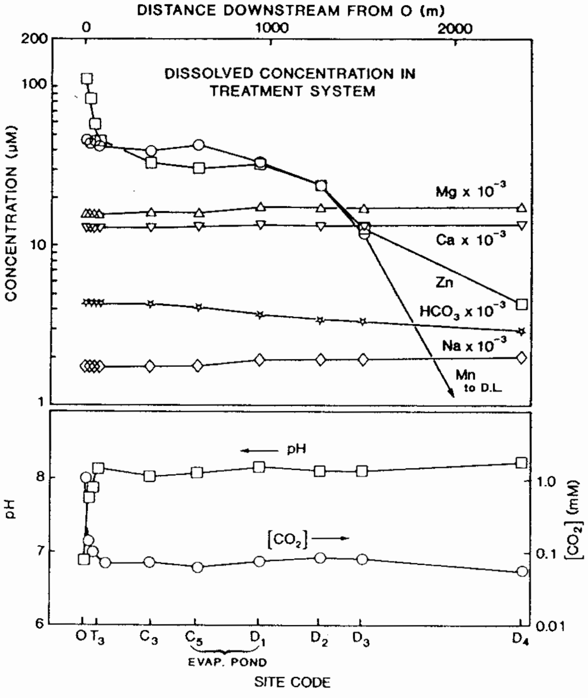

Fig. 4

Because of the arid environment there were no diluting inflows to complicate the interpretation of Fig. 4 which shows the levels of major cations were almost constant throughout the system. However, a prominent feature of Fig. 4 is the correlation between CO_2 loss from solution and removal of soluble zinc. Eighty six percent of the CO_2 is lost in the first 23 m downstream from 0. This is responsible for the increase in pH from 6.89 to 7.74 (the HCO_3^- concentration does not change significantly). Major amounts of Zn and CO_2 are lost between Sites 0 and C5 whereas the level of Mn decreases only slightly.

Measurements (not shown) of particulate metal levels across the pond revealed that Fe and Zn decrease by factors of 40 and 12, respectively, from C5 to D1 and hence it is clear that the pond is acting as a sedimentation basin. Prior to the installation of the curtains the skimming of warm input water over the surface of the pond considerably reduced the efficiency of this process such that the entire surface of the pond and the lower portion of the channel to D4 was at times observed to be stained brown by what is now known to be stratified surface flow of particulate-laden water. It can also be demonstrated that, although soluble Zn levels decrease by only 10% across the pond, Mn drops by 30%. After the water leaves the evaporation pond Fig. 4 shows that the concentrations of soluble Zn and Mn decrease rapidly between D1 and D3 and that by D4, Mn concentrations are below detection limit (0.7 uM).

Although this diagram indicates that Zn and Mn are being chemically removed from solution, it provides only circumstantial evidence for the types of mechanisms which may be responsible. In order to obtain an idea of which solids, if any , might be precipitating, the saturation indices for a number of possible solids were calculated and plotted as a function of distance downstream. The saturation index (SI) is defined as the logarithm of the ratio of the activity product of the component ions of the solid in solution to the solubility product for the solid. Values greater than zero indicate supersaturation; values less than zero, undersaturation. Solubility products for freshly precipitated material are needed for this purpose as the use of those for aged crystalline solids could lead to an overestimate of the SI for the solid in the system which is being studied. Positive values of the SI do not necessarily indicate that a particular solid is actively precipitating since high degrees of supersaturation are possible if suitable nucleation sites are absent or if crystallation kinetics is slow or inhibited by the presence of certain chemical species. Since SI calculations will only give a guide to those solids which might be precipitating chemical and XRD analyses of the sediments are also required to provide further supporting evidence.

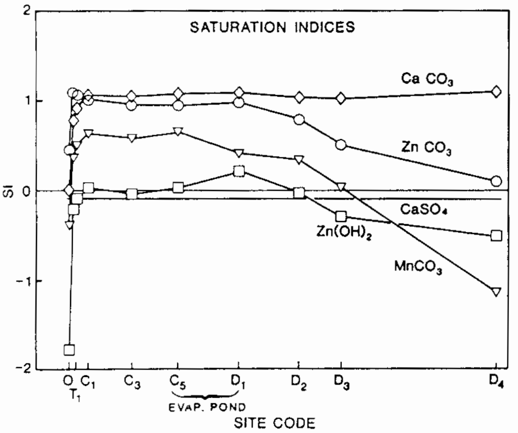

Fig. 5

Saturation indices, calculated by suppressing precipitation in the thermodynamic chemical equilibrium program MINEQL (3) are shown in Fig. 5. Following discharge of the water at 0, the SI's for $ZnCO_3$ and $MnCO_3$ rise rapidly and plateau at 1.05 and 0.61, respectively but fall off towards zero as D4 is approached. The SI for $Zn(OH)_2$ rises from -2 to 0 on the trickle slope whereas that for $CaSO_4$ (gypsum) remains constant at -0.05 over the whole system. These results imply that the concentration of zinc in solution may be controlled by the solubility of $ZnCO_3$. However, detailed analysis of the stream sediments is required before the actual phase which controls the removal of an element can be identified. For example, the zinc levels may be controlled by adsorption on to $Fe(OH)_3$ rather than by the precipitation of a solid whose solubility product has been exceeded. Indeed, studies on the uptake/release of zinc and other heavy metals on samples of iron-containing precipitate collected from the treatment system showed the adsorption of Zn (and Mn) is extremely sensitive to pH within the range 6.5 to 8.5 (see Fig. 6). This effect of pH is of critical importance in the initial settling tanks where the pH of the metal-bearing mine water is lowered when it mixes with 050 aquifer water supersaturated with CO_2 and hence the uptake of zinc on the freshly produced iron hydroxide precipitate would be inhibited. 050 water is thus reducing the efficiency of this part of the treatment process since the considerable scavenging capacity of the fresh iron-containing precipitate (most of which is lost to the remainder of the system due to gravity settling) is not being utilised.

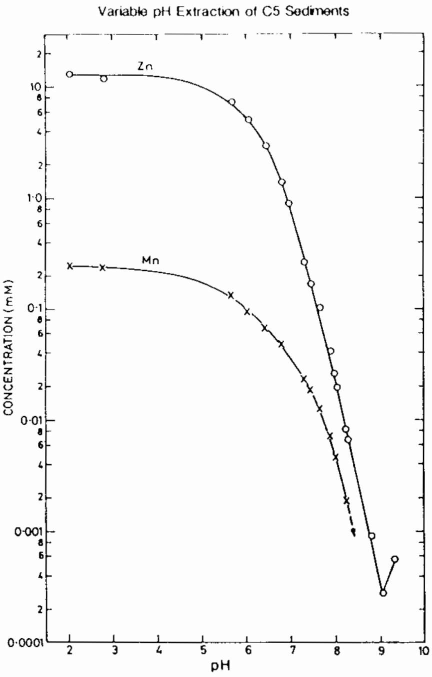

Fig. 6

Process Optimisation

The simplest way to overcome this problem was to raise the pH in the ponds by promoting rapid degassing of the dissolved CO_2. This was achieved by installing a compressed-air aerator tank just prior to discharge of the mine water into the settling tanks. An increase of between 0.5 to 1 pH units was achieved. To promote further degassing a splash plate was attached to the end of the discharge pipe at site 0 which caused the flow discharging on the top of hill to disperse into a spray of drops allowing further degassing, and a consequent increase in pH and reduction in soluble zinc levels.

ROLE OF BIOTA AND INORGANIC SEDIMENTS

Investigations in the field and in the laboratory have confirmed that the prolific growths of algae in the stream between the pond overflow and the Hilton Pump Weir are playing a major role in removing Zn and Mn from the water. Acid digests of algal samples collected from this section of the stream have shown that they contain large amounts of Fe, Zn and Mn. Selective extraction experiments with pH4 acetate buffer, 0.1 M hydroxylamine hydrochloride at pH 4 and ammonium oxalate indicate that a very high percentage of the total amount of these metals are located on the surface of the algal filaments. Approximately 70% of the Mn was present as manganese oxide which can only be dissolved at pH4 by treatment with a reducing agent. The remainder dissolved readily in a simple pH4 buffer. The algae might be removing metal from solution by metabolic uptake or passive adsorption on to cell structures. Alternatively, a microenvironmental increase in pH could be created as a result of photosynthesis where the locally higher pH, during periods of illumination, would favour the precipitation of Zn and Mn carbonates and the oxidation of Mn(II) to produce insoluble Mn(III)/Mn(IV) oxides.

Results and Discussion

A two day study was undertaken in which pH and temperature and the

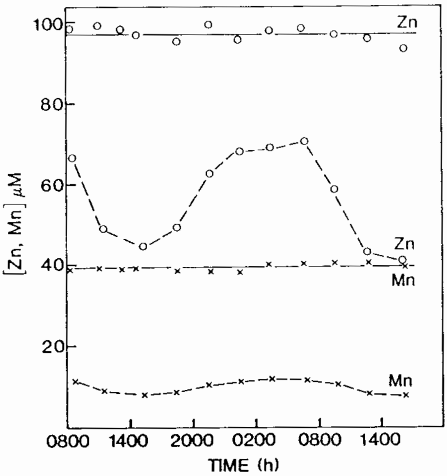

Fig. 7

levels of Zn and Mn at both the pond overflow and D3 were measured at regular intervals. The data for the metals are plotted against time in Fig. 7. It is obvious from this diagram that the concentrations of both Zn and Mn are considerably reduced (by factors of 2 and 4, respectively) in this section of the stream. Moreover, a diurnal variation occurs which does not originate in the evaporation pond but results from the passage of the water through the reach D1 to D3. Very intimate contact between the water and the algae occurs within the watercourse.

In vitro laboratory experiments have shown that the pH values in beakers containing the algae vary by as much as 1.5 pH units over a day/night cycle. In contrast, measurements of pH in the bulk flowing waters at D1 and D3 were the same (pH 7.7) to within experimental error. However, during a later field trip in February 1986 an experiment was carried out near the pond overflow, between sunset and sunrise on two consecutive days, to measure the pH close to an algal mat and to compare this with that for the bulk stream. At sunrise both the stream and the "algae" were at pH 7.95. As the sun rose the pH near the algae rose steadily to a maximum value of 8.6-8.8 whereas the bulk flowing water remained at 7.95. Samples of water from both areas were collected and later analysed. Over this time interval the water near the algae showed a dramatic decline in Zn and Mn concentrations which coincided with the pH rise. However, no reduction was observed in the main stream. Opportunities for intimate contact of the flowing water with the high pH algal microenvironment occur all of the way down to the Hilton Pump Weir (and beyond) and so by this point the bulk of the water is considerably depleted in Zn and Mn. As the sun was setting, the pH near the algae began to decline rapidly until, by nightfall, it had returned to its original baseline value.

Samples of the inorganic streambed sediment were collected 60m downstream of the pond overflow. Material was also collected from the banks of the stream at this point to provide a control for experiments designed to obtain some idea of the role that the sediments might play in removing Zn and Mn from the water. Samples of each of these solids were agitated with aliquots of evaporation pond water and the decrease in metal concentrations monitored. Both sediment types adsorbed Zn but only the material collected from the stream bed removed Mn. Bacteria are known to catalyse the oxidation of Mn(II) to Mn(IV) (4) but the addition of the biocide azide to the system did not inhibit the reduction in Mn levels. Consequently the reaction must be proceeding by an abiotic process. The only obvious difference between the two solids was that the substantial areas of that from the channel bed were covered with a soft black coating. Analysis of this material showed it to be primarily an amorphous form of manganese oxide with considerable quantities of associated Zn (Mn/Zn=4). Presumably this material was responsible for the ability of the sediment to remove Mn from solution since preformed Mn(IV) oxides are known to catalyse (5) the oxidation of initially adsorbed Mn(II). Consequently both inorganic and biological processes contribute to the reduction in Zn and Mn concentrations between the pond overflow and the Hilton Pump Weir. The large diurnal fluctuations observed at the latter site occur as a result of the photosynthetically induced pH changes in the water close to the algal filaments.

Process Optimisation

Although no modification has yet been attempted for this portion of the treatment system it is possible to increase the efficiency of metal removal by algae. By appropriate earthwork construction the algal biomass could be increased and the contact time and hydrodynamics of mass transfer with the flowing waters be optimised as has been carried out elsewhere (6).

REFERENCES

1. Chapman, B.M. and Jones, D.R. Simulation of metal transport in streams. In: Proc. ASCE Conf. on Environ. Eng., Boulder, Colorado: 635-642 (1983).

2. Chapman, B.M. and Jones, D.R. and Jung, R.F. Processes controlling metal ion attenuation in acid mine drainage streams. Geochim. Cosmochim. Acta 47: 1957-1973 (1983).

3. Westall, J.C., Zachary, J.L. and Morel, F.M.M. Technical Note 18. Water Quality Laboratory, Dept. of Civil Engineering, MIT, Cambridge, Massachussets (1976).

4. Diem, D. and Stumm, W. Is dissolved Mn^{2+} being oxidised by O_2 in absence of Mn-bacteria or surface catalysts ?. Geochim. Cosmochim. Acta 48: 1571-1573 (1984).

5. Hem, J.D. Redox processes at surfaces of manganese oxide and their effects on aqueous metal ions. Chem. Geol. 21: 199-218 (1978).

6. Gale, N.G. and Wixson, B.G. Control of heavy metals in lead industry effluents by algae and other aquatic vegetation, Proc. Int. Conf. on Management and Control of Heavy Metals in the Environment, London, Sept.1979, 580-582 (1979).