

Minerals, Metals and the Environment II



The Institution of
Mining and Metallurgy

Minerals, metals and the environment II

Papers presented at the 'Minerals, metals and the environment II' conference,
organized by the Institution of Mining and Metallurgy
and held in Prague
from 3 to 6 September, 1996



The Institution of Mining and Metallurgy

Chemical Modelling as a Management Tool for Water Pollution Control

D. Limpitlaw

*Department of Mining Engineering, University of the Witwatersrand,
Johannesburg, South Africa*

Abstract

Many defunct collieries in South Africa have become environmental liabilities. In a colliery currently being re-mined by opencast methods, the coal seam was originally extracted using bord and pillar mining. Depressions in the seam floor have facilitated the formation of large underground water bodies. This water has become acidic and contaminated by heavy metals. Mine water is treated by a liming plant and then released into evaporation pans. Seepage from the pans enters a natural wetland. The de-watering of old workings ahead of mining periodically subjects the liming plant to large quantities of low quality water, and a nett export of salts such as sulphate occurs. As the mine is situated in a sensitive river catchment, this pollution is unacceptable.

An independent water sampling programme indicated that the wetland reduces pollution to a limited degree and that the liming plant treats water inconsistently. A chemical speciation program developed by the US Environmental Protection Agency was used to analyse effluent from the liming plant and wetland. The nature of precipitates at equilibrium was used as an indicator of water quality. Liming plant effluent water was found to vary greatly due to the conditions prevalent in the different water bodies. The liming plant and wetland were periodically subjected to pollution loads beyond the wetland's assimilative capacity, resulting in failure of the system. Despite this, the software provided evidence of the wetland's pollution-ameliorating potential, enabling mine personnel not trained as chemists to understand the chemical implications of pollutants present in acid mine drainage.

The paper contains a case study from the South African coal mining industry and concludes with recommendations on the management of this wetland which may be applicable to similar situations elsewhere.

Introduction

Coal mining in South Africa has been conducted since the turn of the century. Old underground operations mined by hand-got methods were abandoned once the seam could no longer be economically exploited. These collieries represent environmental liabilities due to the occurrence of sinkholes, underground fires and acid seepage. Often the only viable way to rehabilitate these mines is to completely re-mine the remnant coal and pillars by opencast means. In one such colliery the economically exploitable limits of a shallow coal deposit were reached in

the early sixties, causing the underground mine to close. The highly fractured state of the roof caused the workings to fill with water rapidly, forming several large underground water bodies. Within one decade of closure, the mining company constructed evaporation pans to dispose of the effluent.

Pyrite (FeS_2), present in the coal and associated strata oxidised to form soluble hydrous iron sulphates and sulphuric acid, which are characteristic of acid mine drainage (AMD) (Caruccio & Geidel, 1978). An absence of calcite made the coal attractive to the export market, but prevented *in situ* neutralisation of this drainage. This lack of neutralisation capacity within the coal deposit, coupled with the predominance of acid soils in the area, has led to AMD pollution of local rivers. When the evaporation pans proved insufficient to ameliorate AMD, a liming plant was erected to treat water before release into the pans.

Three decades later improvements in technology allowed re-mining of the seams by opencast dragline methods. This has necessitated de-watering of the underground acid lakes. The liming plant previously treated acid water seeping under gravity from the old workings. This was water from the surface of the stratified underground water bodies. Poor quality water occurred at deeper levels in the water bodies. During de-watering, this poor quality water was pumped to the liming plant for treatment. The additional load on the plant resulted in weakly buffered water being released to the evaporation pans. Contaminated sediments in the pans (from their previous use as an acid water disposal facility) and seepage from a coal dump (q.v. figure 1) resulted in the re-acidification of liming plant water.

In the last year (1995), the linings of the evaporation pans have begun to allow large volumes of acid water to flow into a natural wetland occurring downstream.

Wetlands

Wetlands are distinctive tracts of land that exhibit one or more of the following characteristics:

- the water table is at or above the land surface long enough to promote the formation of undrained hydric soils,
- the existence of reducing conditions within the soils,
- impeded drainage,
- support of distinctive plant and animal communities,
- water is the dominant factor determining both the development of soils and wetland biota, (Rogers *et al.*, 1985; Kusler *et al.*, 1994).

As water flows through a wetland system, it undergoes a series of quality alterations brought about by complex interactions between the water and vegetation, soils and rock. Processes which promote these alterations include weathering, mineralisation, microbial decomposition, aeration, ion exchange and nutrient uptake (Begg, 1986). Wetland biogeochemical processes which improve water quality are assisted by hydrological factors.

Wetlands perform optimally as passive treatment systems where influent water has a pH value in excess of 6.0 and contains nett alkalinity (Nairn *et al.*, 1991). It is currently thought that the dominant metal removal processes include the oxidation of iron and manganese together with the hydrolysis of these and other metals such as aluminium (Nairn *et al.*, 1991).

As wetlands most often form in areas of low relief, they intercept run-off and sub-surface flow from several quarters. A strong dilution effect is often present and, in addition to biogeochemical processes, this usually acts to improve water quality.

Sampling

In 1994, the Department of Mining Engineering at the University of the Witwatersrand began an intensive study of this wetland and other components of the system.

Sampling of surface water qualities in the wetland, tributary streams, the liming plant and evaporation pans was conducted for a period of twelve months. Two sets of samples were taken at monthly intervals at sites established throughout the system. The first sample was analysed in the field for pH value, electrical conductivity (EC) oxidation/reduction potential (Eh) and dissolved oxygen (DO). The second sample was sent to a laboratory for analysis. Analyses were made for *inter alia*, sulphate, heavy metals, ammonia and nitrate.

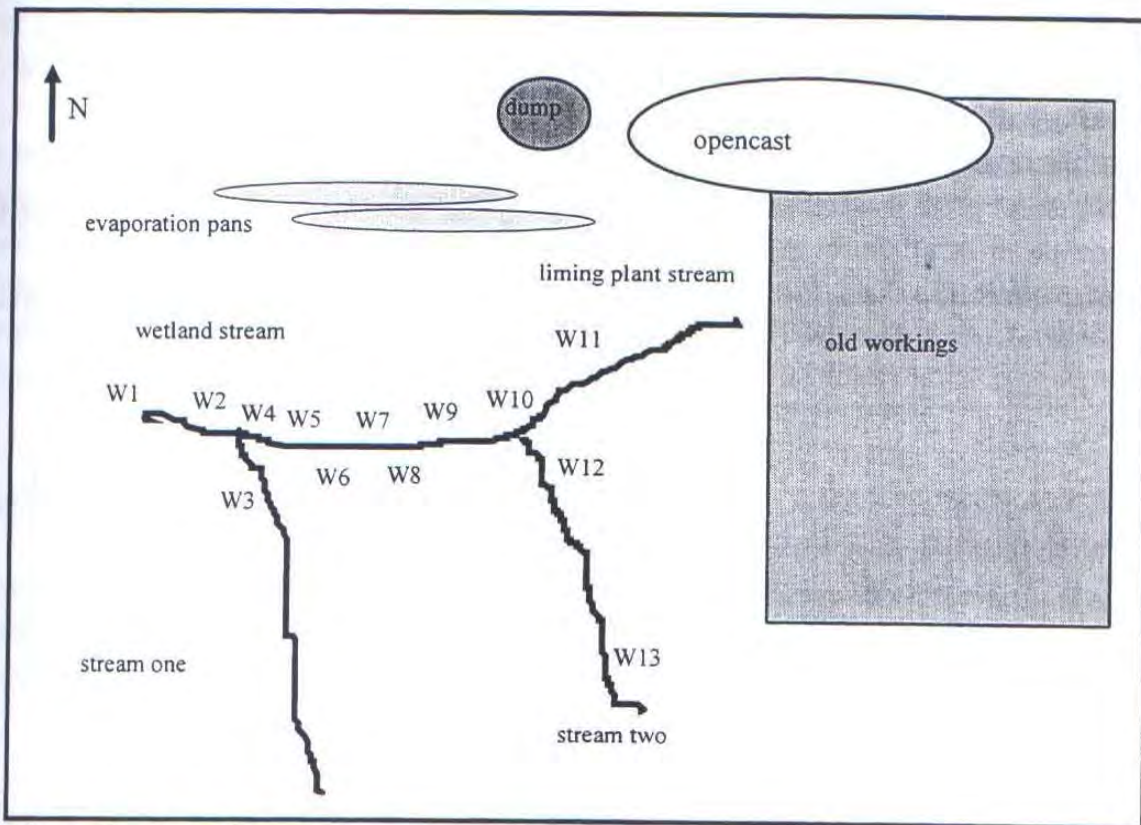


Figure 1. Area layout.

The water sampling sites are identified by a 'W' preceding a number. Sites are numbered consecutively upstream, regardless of which water course they occur in.

Polluted water sources were identified around the upper reaches of the liming plant stream where effluent seeps from the evaporation pans, in the upper reaches of stream two, where water seeps out of the old workings, and half-way along the wetland, where a seep transports water along an impermeable dwyka tillite from the floor of the coal.

Initial analysis of sampling results indicated that little improvement in water qualities resulted from wetland action. Data acquired via satellite and through vegetation sampling indicated that significant changes occurred in wetland vegetation along the axis of the system.

Chemical Speciation Modelling

To quantify changes in water quality in the wetland, water data were analysed using MINTEQA2, a chemical speciation model developed by the US Environmental Protection Agency (EPA). This is an equilibrium model and does not take reaction kinetics into account.

Using averaged values for the full sampling period at each site, the model predicted the state of the determinants at equilibrium. Important assumptions made during modelling are:

- super-saturated solids precipitate,
- water temperature: 15°C¹,
- water is exposed to the atmosphere.

This model was interpreted as if water collected at each point was removed from the wetland and stored until equilibrium was reached. Lower quantities of mineral precipitation at a downstream point indicate that some process has acted upstream to reduce concentrations of chemicals required to precipitate this mineral.

Several simulations were run:

- run 1: modelling of chemical data only,
- run 2: dissolved organic matter (DOM) included in simulation,
- run 3: DOM and an adsorption surface included in simulation,
- run 4: modelling of chemical data with DOM and with the suppression of diaspore, boehmite and gibbsite,
- run 5: diaspore, boehmite and gibbsite suppressed with the inclusion of DOM and the adsorption surface.

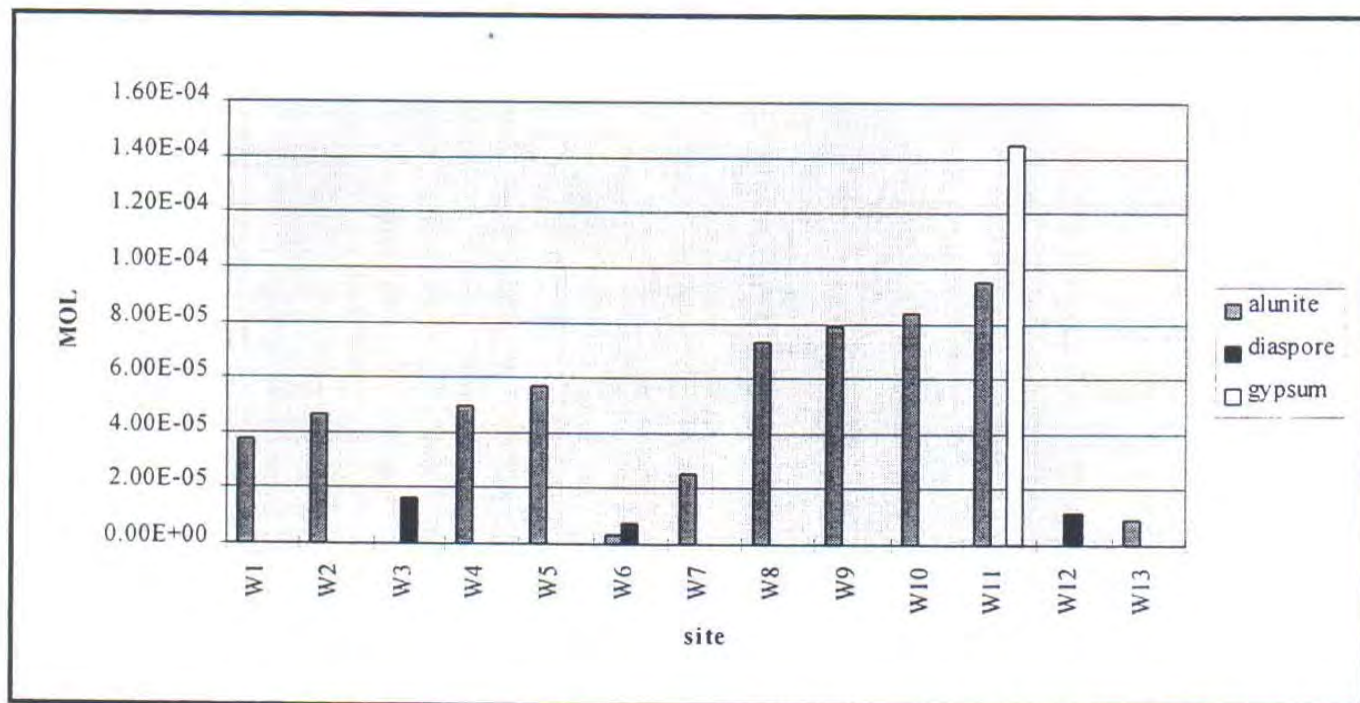


Figure 2. The effect of wetland action on water quality as modelled with MINTEQA2 (run 1).

Initially, raw data was fed into the model with no allowance for organic complexation and without the presence of an adsorption surface. Results of the first run (figure 2) clearly show changes in water quality as water flows through the wetland. Improvement in water quality

¹ Actual water temperature ranges from 5°C in winter to over 20°C in summer.

between the upper reaches of stream two (W13) and the lower reaches (W12), just before the stream enters the wetland, was indicated by surface water sampling and by remotely sensed data². The chemical equilibrium model shows that different precipitates may be expected at W13 and W12. At W13, the mineral alunite precipitates. This is a hydrous potassium aluminium sulphate ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) produced through the alteration of rocks rich in alkalic acid by sulphate-rich water (Macdonald Encyclopaedia of Rocks & Minerals, 1989). Downstream, at W12, precipitation of the mineral diaspore is indicated by the model. Diaspore is associated with boehmite and gibbsite. It is an aluminium hydroxide ($\text{AlO}(\text{OH})$) which is stable under metamorphic conditions and therefore unlikely to precipitate from wetland waters. A kinetic model would probably predict the formation of an amorphous form of aluminium hydroxide (Fey, pers. comm. 1995). This aside, the model clearly supports the notion of chemical alteration of water between W13 and W12.

At W11, stream two intersects water in the liming plant stream. The vastly different chemistry of this water is indicated by the large amounts of gypsum and alunite that precipitate. Gypsum is a hydrated calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and is associated with water that has been limed. It precipitates at no other point in the wetland. This indicates that water chemistry is altered as water flows through the wetland. With exception of anomalies at W6 and W7 (the site of a seep) and W3 (a sample point in stream one), alunite precipitation decreases linearly downstream.

The water encountered at sites W6 and W7 differs appreciably from water at other points in the system. The water sampling programme highlighted this fact and supported the notion of a seep. Alunite precipitation at both of these sampling points is reduced and diaspore is predicted as a precipitate at W6. No alunite precipitates from water at W3. Diaspore is predicted as the precipitate from water in stream one. This suggests that the presence of diaspore is an indicator of less polluted water in the wetland.

Characteristics of waters encountered in the wetland

The first simulation indicated that water in the wetland system was not homogenous and that waters from different sources differ in their chemical composition. Using averaged sampling data, characteristic ratios of major determinants were plotted.

² Using data from Landsat, a transformed vegetation index image was created. This identified areas of plant stress and showed that stress decreased downstream in stream two until its confluence with the wetland, where another pollution source was intercepted.

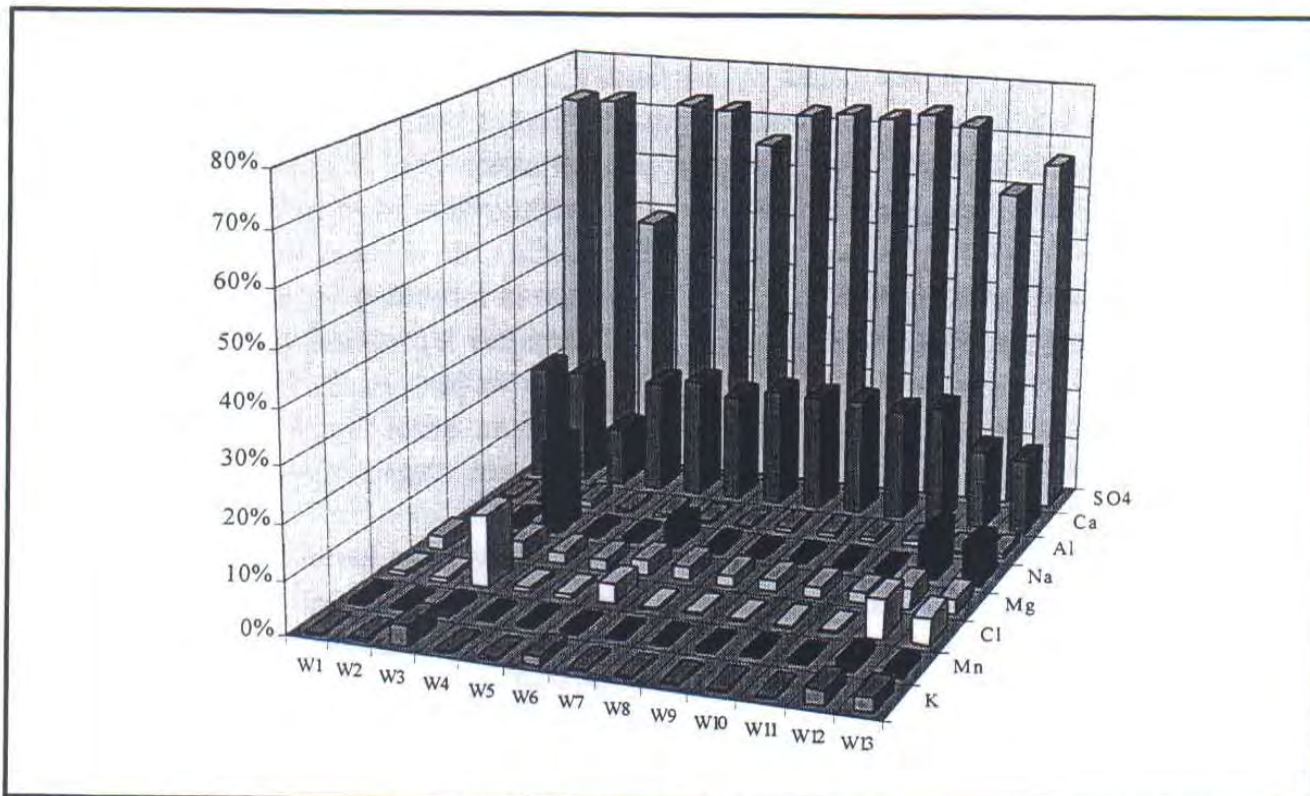


Figure 3. Contribution to total pollution load by the major determinants in wetland waters.

In figure 3, four characteristic ratios were identified:

- stream two water (e.g. W12),
- wetland water (e.g. W9),
- seep water (W6) and
- stream one water (W3).

Figure 3 indicates that other sources of water, such as stream one and the seep at W6, have little effect on the characteristic composition of water in the wetland. This suggests that any improvement in water quality is not due to dilution.

Dissolved Organic Matter

To refine model predictions, dissolved organic matter (DOM) was added as a component. In natural systems organic matter is present in surface waters. The common-sense notion that this matter must influence water chemistry is supported in the literature (Kerr, unpublished data; Perdue & Serkiz, 1987, 1988 in Allison *et al.*, 1991; Susetyo *et al.*, 1990 in Allison *et al.*, 1991) and is included in the geochemical database attached to the MINTEQA2 model. The DOM used in this simulation is based on log K values for the complexation of trace metals by organic matter in the Suwannee River, Fargo, Georgia, USA³. Although the DOM in the wetland is not likely to be the same as that in the Suwannee River, the inclusion of any organic matter is likely to improve the simulation of reality.

The effect of organic matter on precipitation is shown in figure 4. As in the first run, precipitation of solids decreases linearly downstream. The most notable difference occurs at the sites where diaspore precipitation is predicted. Alunite no longer forms at W13, but is replaced

³ This DOM has a site density of 5.0×10^{-4} moles of sites per gram of organic matter (Allison *et al.*, 1991)

by diaspore precipitation. The amount of diaspore precipitated at W12 is appreciably less than at W13. Gypsum precipitation at W11 is reduced and the amount of alunite precipitated in the rest of the system is marginally greater than for the no-organic matter scenario. DOM has an effect on both equilibrium pH values and the amount of solid precipitated. This must be borne in mind when interpreting model results.

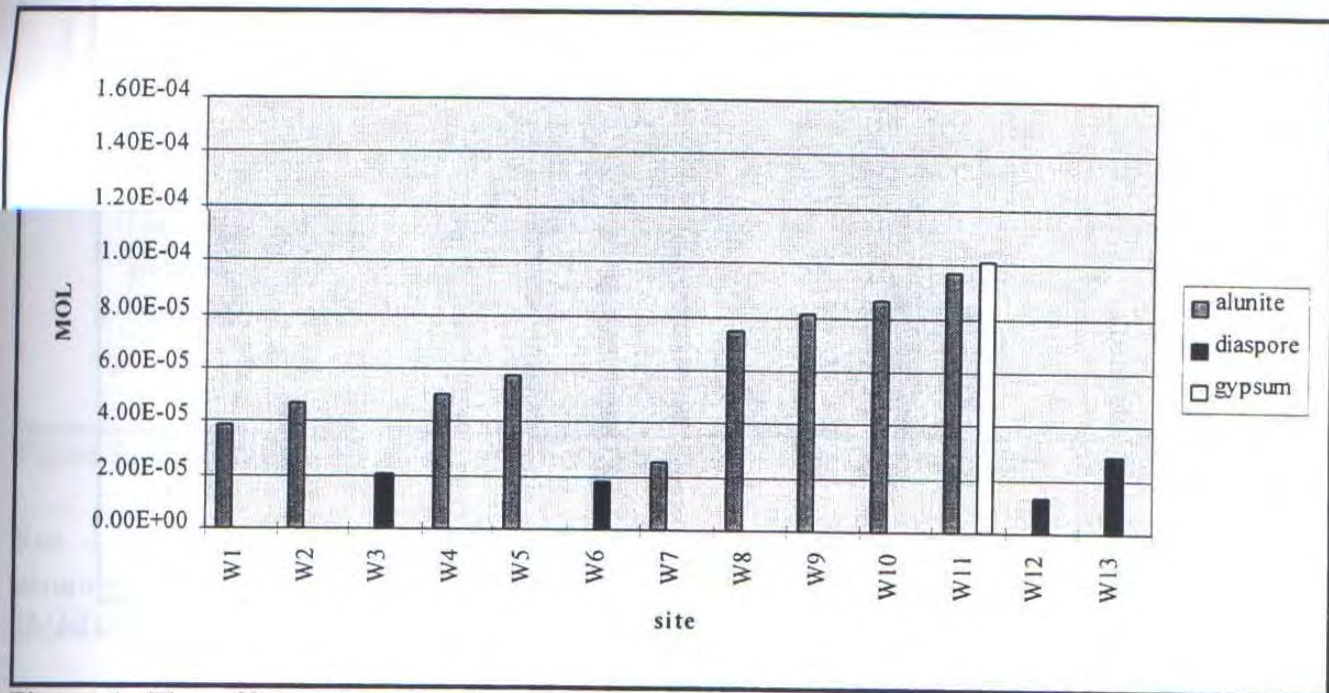


Figure 4. The effect of wetland action on water quality as modelled with MINTEQA2 using DOM as a component of wetland waters (run 2).

Kerr (pers. comm. 1994) advocates the use of MINTEQA2's adsorption surface model when attempting to simulate wetland systems. In run 3 MINTEQA2's diffuse layer model⁴ was applied to the wetland data (in the presence of DOM). As a result, only diaspore was predicted as a precipitate at all sites. The amount of solid matter precipitated increased from a maximum of 1.01×10^{-4} moles, predicted in run 2, to 7.71×10^{-4} moles.

For each run, the pH value at equilibrium was computed. Values for run 1 (raw data) and run 2 (DOM) appear to coincide with values reported by the sampling programme. pH values reported for run 3 (adsorption & DOM) are difficult to reconcile with the measured values.

Diaspore is unlikely to form under the conditions encountered in the wetland as it is stable under metamorphic conditions. For this reason, the mineral was excluded from the mass balance and prevented from precipitating. This practice was used by Kerr (unpublished) to determine the state of solids in a wetland when MINTEQA2 predicted an unlikely form. Run 4 included DOM and prevented the precipitation of diaspore, boehmite and gibbsite (figure 5). Consequently, alunite precipitated at all sampling sites. The amount of alunite precipitated follows trends identified in earlier runs. At sites where no alunite precipitated previously, small quantities were predicted.

The final run (run 5 - q.v. figure 6) using averaged data entailed the suppression of the three minerals mentioned above and the inclusion of DOM and the adsorption surface. The result was the precipitation of two new minerals (hercynite and $\text{Al}_4(\text{OH})_{10}\text{SO}_4$) at most sites and

⁴ with an area of $600 \text{ m}^2/\text{g}$, a concentration of 3.422 g/l and two types of adsorption site (high energy $1.922 \times 10^{-4} \text{ mol/l}$; low energy $7.690 \times 10^{-3} \text{ mol/l}$).

equilibrium pH values similar to the those obtained in run 3. The use of the adsorption surface does not appear to be justified on the grounds of irreconcilable pH values - water with zero alkalinity and 200 mg/l acidity is unlikely to move to pH 7 at equilibrium.

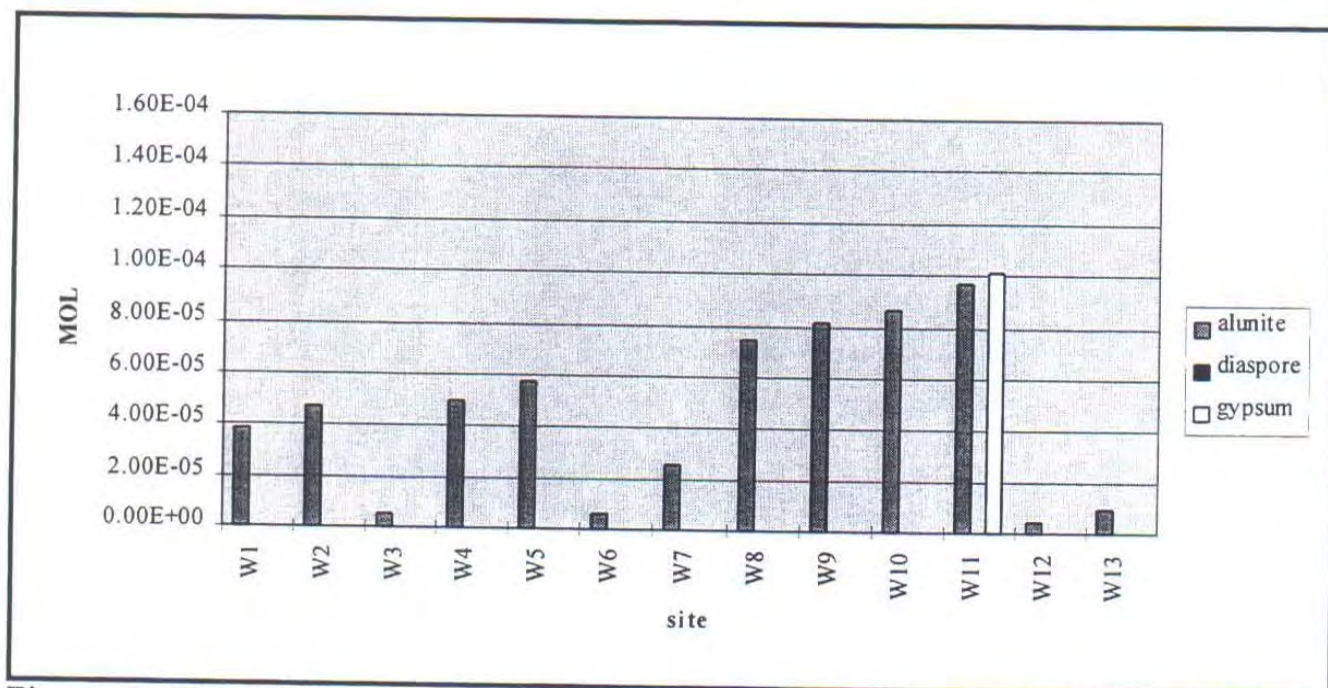


Figure 5. The effect of wetland action on water quality as modelled with MINTEQA2, suppressing the precipitation of diaspore, boehmite and gibbsite (run 4).

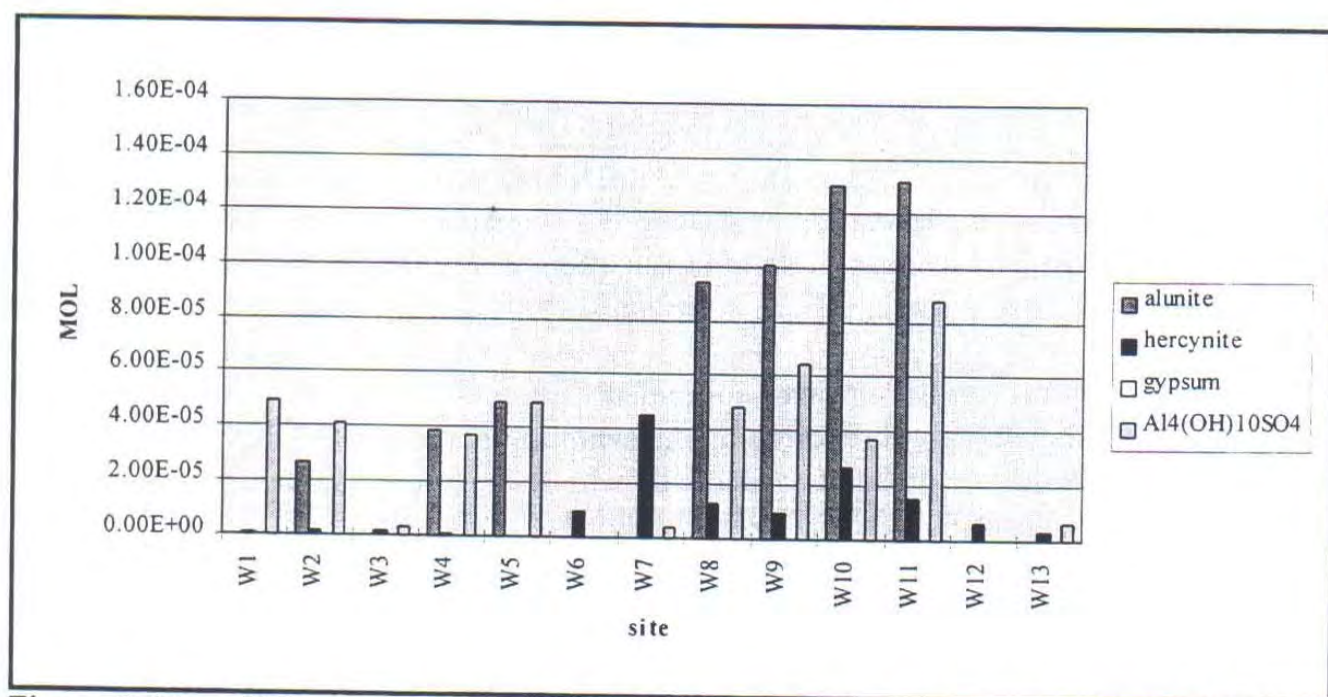


Figure 6. The effect of wetland action on water quality as modelled with MINTEQA2 using an adsorption surface and suppressing the precipitation of diaspore, boehmite and gibbsite (run 5).

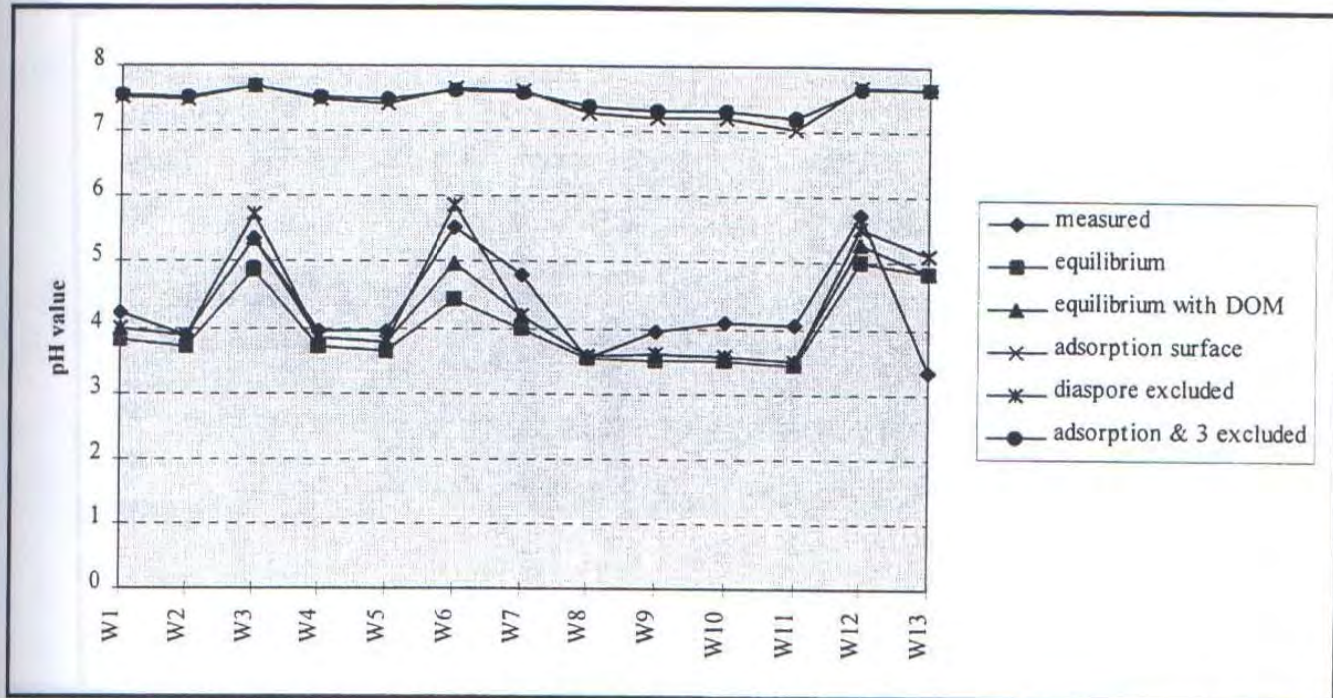


Figure 7. Equilibrium pH values predicted by MINTEQA2 contrasted with actual sample values.

Run 4 is thus the most realistic simulation of conditions in the wetland. Based on the assumptions stated above, this model has provided evidence that water is chemically altered as it flows through the wetland.

Liming Plant

One of the major variables controlling the long term viability of the wetland as a passive pollution treatment system is the liming plant. This system commonly treats 14 Ml of AMD per day. In order to avoid acidification of limed water in the evaporation pans, the mine has proposed releasing limed water directly into the wetland. The South African Department of Water Affairs and Forestry requires evidence of the stability of the limed effluent before permission will be granted. If the limed water is intrinsically unstable and is likely to become acidic, it should not be released into the wetland. MINTEQA2 was used to determine the equilibrium pH value of the liming plant effluent. When this value is compared to the measured value, it is possible to estimate (qualitatively) the intrinsic stability of the water.

The investigation showed that liming plant water is not stable (q.v. figure 8), but that the equilibrium pH value was not necessarily lower than the measured value. During the months (November 1994 - March 1995) where excessive volumes (>14 Ml/day) were required to be treated due to the de-watering of underground water bodies, the liming plant effluent became more acid with time. If the liming plant effluent is to be discharged directly into the wetland, strict control of lime added and water volumes treated is necessary.

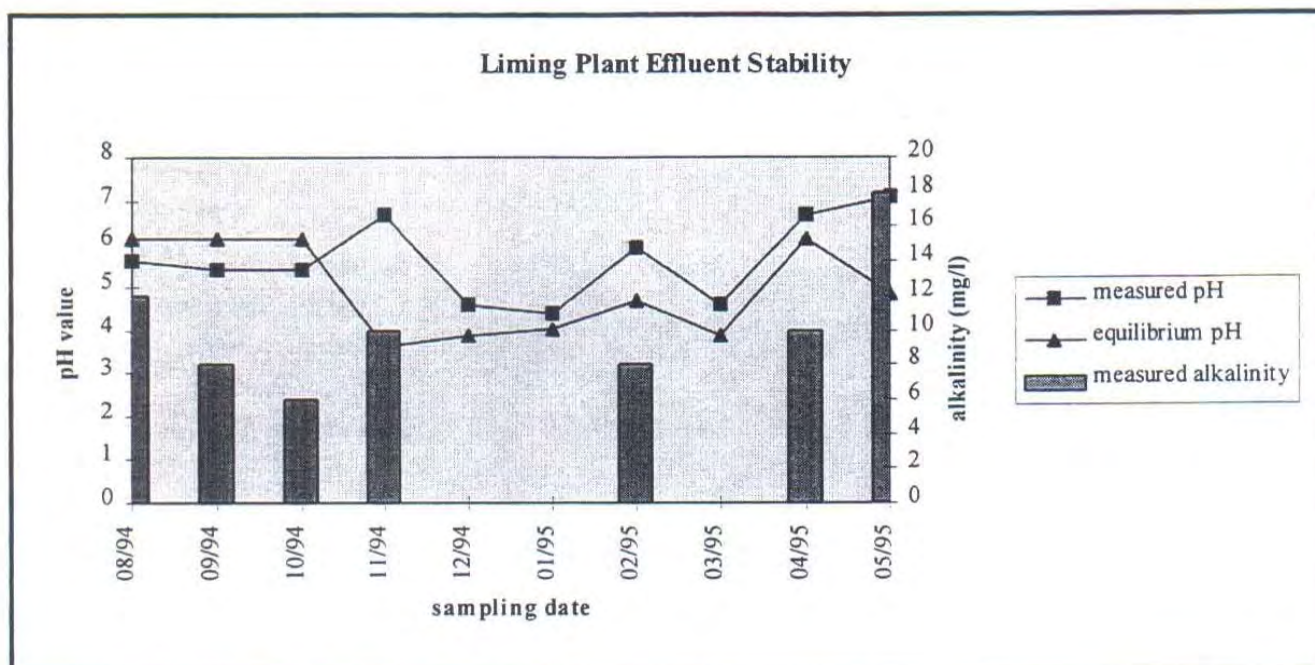


Figure 8. Stability of liming plant effluent.

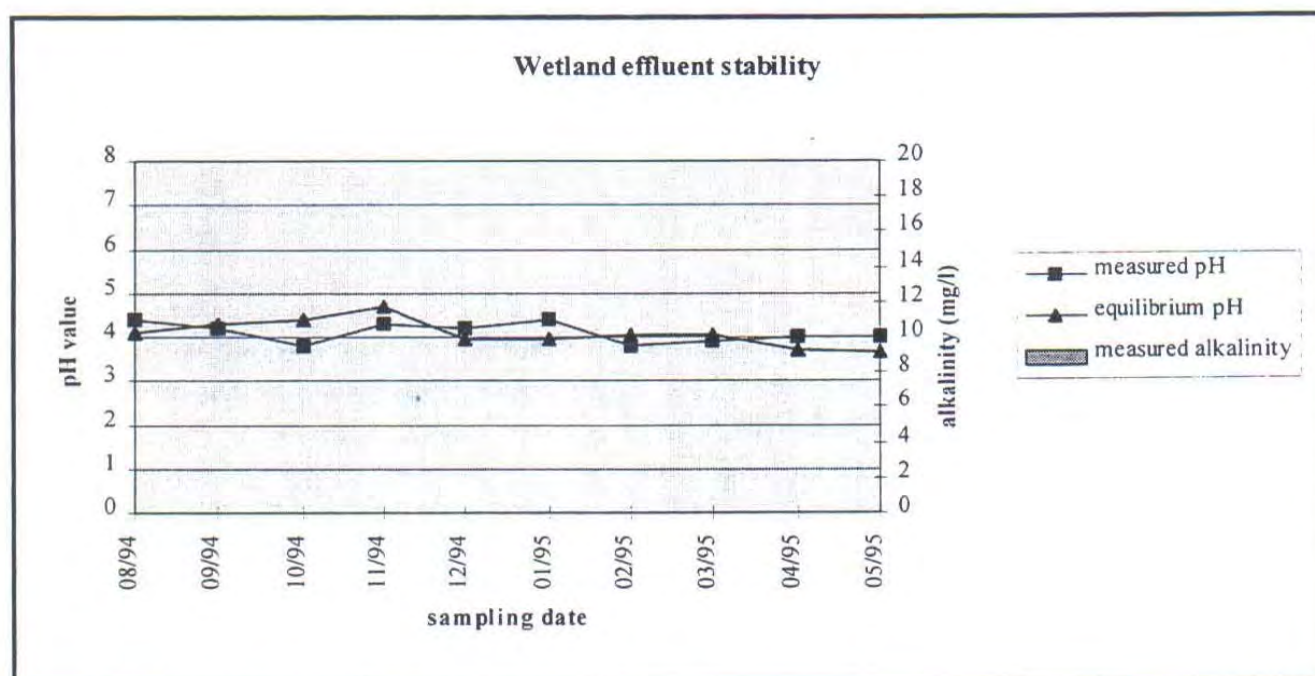


Figure 9. Stability of wetland effluent (W1).

The wetland acts to increase the stability of water before it leaves the mine property. This assertion is supported by comparing the precipitated solids predicted by MINTEQA2 (figures 10 & 11 have purposely been plotted at the same scale - see figure 12 for detail obscured in figure 11).

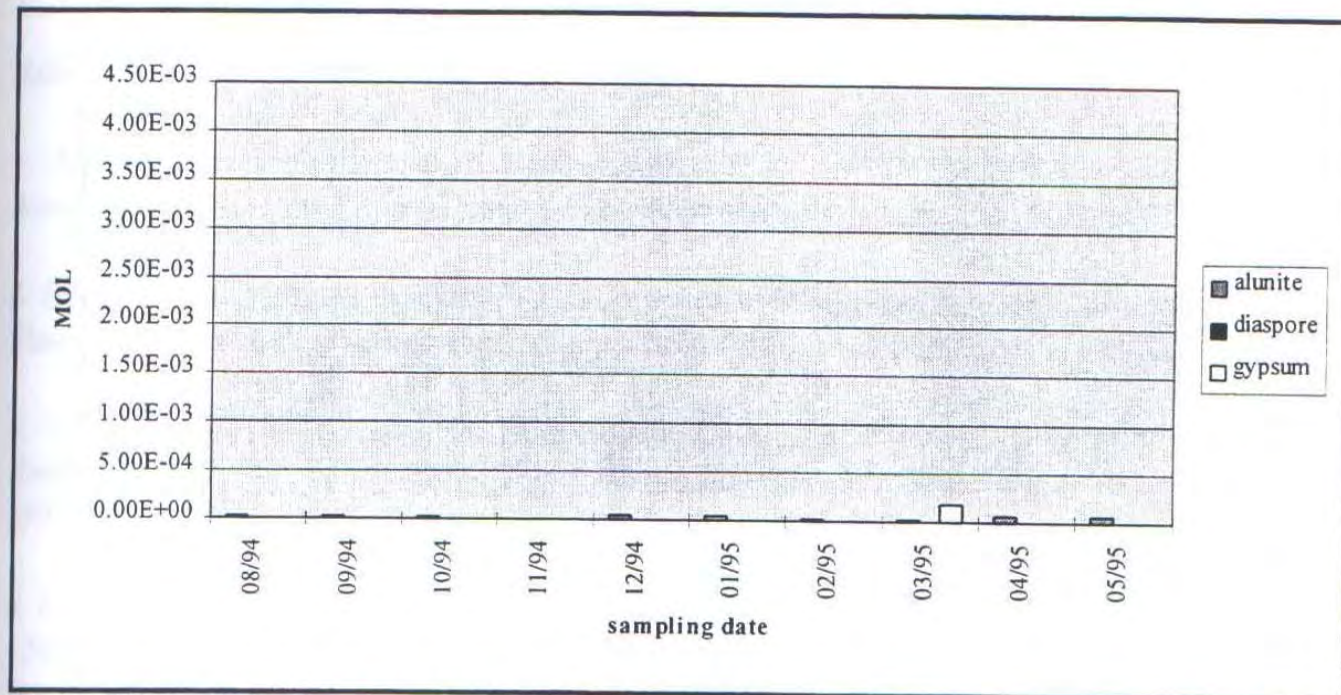


Figure 10. Precipitation from wetland effluent (W1).

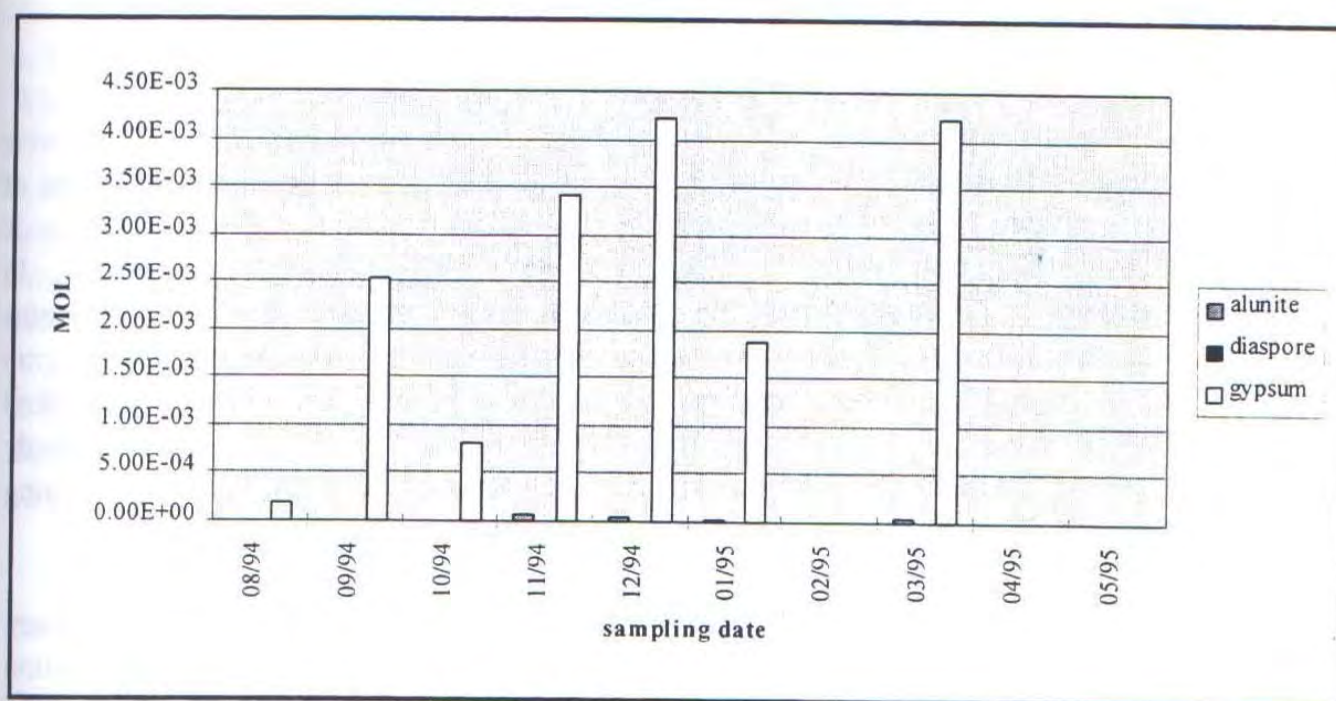


Figure 11. Precipitation from liming plant effluent.

Figure 10 and 11 do not indicate volumes of water treated by the liming plant. When large volumes have to be treated, the efficiency of the plant is reduced and the effect of this can be seen in the wetland water qualities. At W1, the final wetland sampling site, a small amount of precipitated solid is indicative of efficient pollution removal by the rest of the system. When large amounts of pollution are still present in the water at W1, greater precipitation can be expected at equilibrium. Thus, when gypsum, a mineral usually precipitated before W10, reaches W1, the system is barely functioning at all.

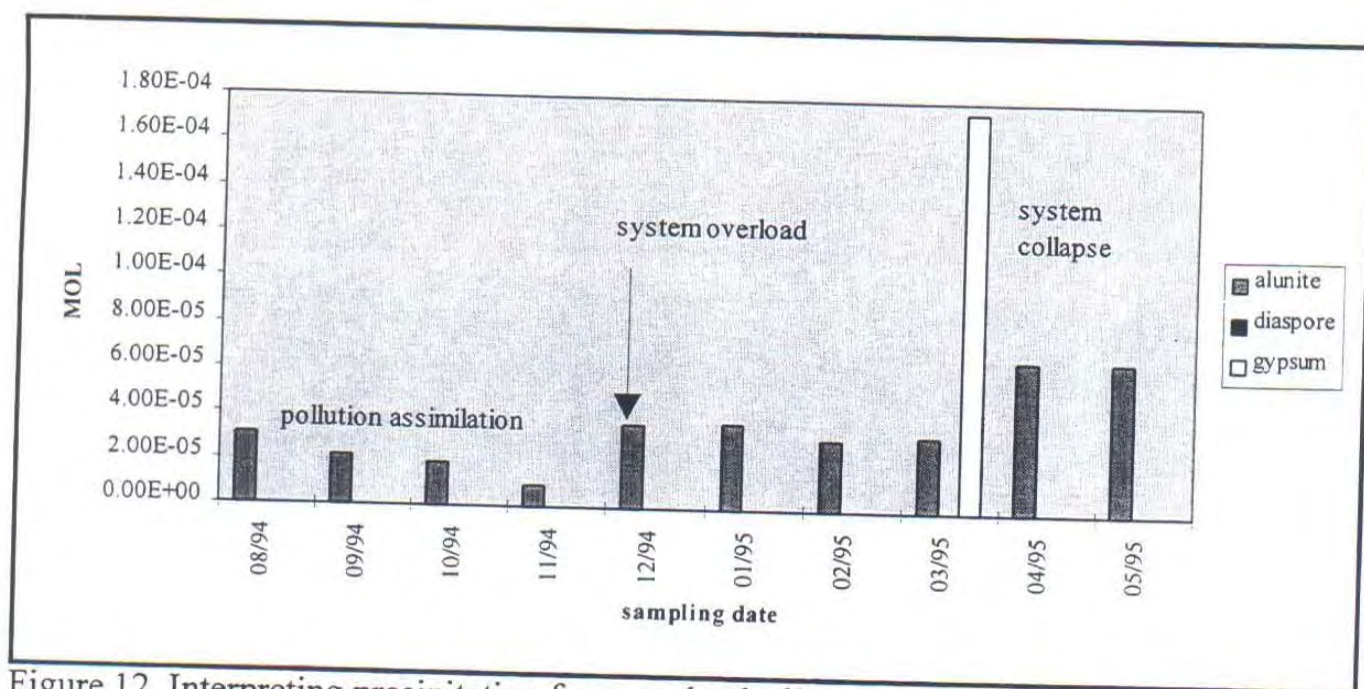


Figure 12. Interpreting precipitation from wetland effluent.

Conclusion

The wetland represents a valuable passive treatment resource which could continue to treat mine water long after mine closure in 2022. In order to realise this resource, effective management of the wetland must be instituted. The principal variable susceptible to anthropogenic influence is the liming plant. This installation was frequently overloaded during the period of study. In addition to this the quality of effluent leaving the plant was poorly monitored. These problems seem to arise due to the structure of the current monitoring system, which consists of grab samples taken at fixed intervals. These samples are analysed for pH value and a batch feed liming process is regulated according to the results of the analyses. The findings of this study support a suggestion by mine personnel to replace this system with a continuous feed liming process controlled by continuous monitors.

Wetlands function optimally at circumneutral pH values (Naim *et al.*, 1991), therefore, the efficacy of this wetland can be improved by increasing the pH value of influent water. The evaporation pans should be closed off to prevent the re-acidification of limed water. Circumneutral water from the liming plant should pass directly into the wetland and the acidic water which collects in the pans should be pumped to the liming plant for treatment. The wetland will thus not have to contend with high concentrations of acidity. This would reduce the stress on the key component of the passive treatment system - sulphate reducing bacteria in the sediment.

Despite the absence of wetland management, the wetland improves the quality of water passing through it. This improvement is currently insufficient to comply with discharge requirements set by the Department of Water Affairs and Forestry, but with improvements in wetland efficacy, major pollutants can be brought to below maximum permissible concentrations.

References

1. Allison J.D., Brown D.S. & Novo-Gradec K.J., *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems*, version 3.0 user's manual, US EPA, 1991, pp
2. Begg G. *The Wetlands of Natal - An Overview of their Extent, Role and Function* Natal Town Planning Report vol.68, Pietermaritzburg South Africa, 1986, pp 1 - 45, 87 - 114
3. Caruccio F.T. & Geidel G., Geochemical factors affecting coal mine drainage quality, *Reclamation of Drastically Disturbed Lands*, Chapter 8, (ASA-CSSA-SSSA), Madison, USA, 1978, 129 - 147.
4. Kusler J.A., Mitsch W.J. & Larson J.S., Wetlands, *Scientific American*, January 1994, pp 50D - 56.
5. Macdonald Encyclopaedia of Rocks and Minerals
6. Murray K. & Jooste M.M., *JESS Investigation into the Functioning of the Landau Wetland*, Witbank, 13 December, 1993, 88 pp (unpublished).
7. Nairn R.W., Hedin R.S. & Watzlaf G.R., A preliminary review of the use of anoxic limestone drains in the passive treatment of acid mine drainage, *Proceedings of the 12th Annual West Virginia Surface Mine Drainage Task Force Symposium*, Morgantown, West Virginia, April, 1991.
8. Rogers F.E.J., Rogers K.H. & Buzer J.S., *Wetlands for Wastewater Treatment with Special Reference to Municipal Wastewaters*, Witwatersrand University Press, Johannesburg, 1985, pp 1 - 20.

Personal Communication

1. Fey, M. Department of Geoscience, University of Cape Town
tel. +27-21-650-2903
fax. +27-21-650-3783
e-mail: fey@geology.uct.ac.za
2. Kerr, C. Department of Chemical Engineering, University of Durban
e-mail: kerr@che.und.ac.za
3. Murray, K. Watertek, Council for Scientific and Industrial Research, Pretoria.
tel. +27-12-841-2647
fax. +27-12-841-2647
e-mail: kmurray@watertek.csir.co.za