

Chemical Characteristics and Prediction Capability GENERAL REPORT

By C. H. KIDD

1.0 INTRODUCTION

Seven papers have been reviewed and in this session. Broadly they can be grouped into three categories as follows:-

A Chemical Characterisation of Mine Waters

- Miller & Murray - Prediction of Time Dependent Factors in Acid Mine Drainage
- Jeffrey et. al. - Sulphide Oxidation in Pyritic Overburden; A Controlled Leach Column Study
- Sheridan et. al. - The Effect of Ore Type, Depth, and Leach Time on Cyanide Species in Column Tests using NaCN Leach Solutions

B Mine Water Treatment/Management

- Gilchrist & Hunt - The Recovery of Water from a Colloidally Stable Kimberlite Suspension
- Chapman, et. al. - Treatment and Utilisation of Hilton Mine Water

C Prediction of Impacts

- Kiss-Mate C. - Numerical Simulation of Chemical and Nuclear Contamination Transport in Aquifers and its Possible Application for the Control of Environmental Impacts due to Mining Activity.
- Wilk Z. et. al. - A zinc-Lead Ore Mine Water Contamination by Paper Factor Fluid Waste

2.0 MILLER S AND MURRAY G

"Prediction of Time Dependent Factors in Acid Mine Drainage"

The paper of Miller and Murray is the first of three papers which address the problem of predicting the quality of mine drainage from laboratory studies of the waste and ore. This type of work is very important part of permitting new mining projects in places where there is strict environmental regulations such as in Victoria and New South Wales in Australia, New Zealand, Canada and the United States. With the worldwide trend to the "polluter pays" it is essential that all miners recognise the value of this work as they are likely to have to bear the costs of having to clean up future problems and possibly, their past mistakes. The cost of clean up is clearly illustrated in Miller and Murray's paper where they quote the figure of \$C1.5 billion for the expected cost of rehabilitation of reactive mine wastes in Canada.

Miller & Murray briefly describe the processes involved in the generation of acid mine drainage and go on to outline the key factors in identifying and predicting time dependent changes in acid mine drainage (AMD).

AMD forms from oxidation of sulphide minerals, the most common of which is pyrite (Fe S_2), which are integral part of most base and precious metal deposits and coal deposits. The authors describe three main stages in the generation of AMD as follows:-

Stage 1 Chemical and/or biological oxidation of sulphides which slowly produce acid. Acid is neutralised by carbonate minerals and therefore there is little (if any) decrease in pH but the total dissolved salts may increase. The length of this stage may be from 1 to 20 years and monitoring pH will not identify whether sulphide oxidation is occurring.

Stage 2 The neutralising minerals are consumed and pH falls leading to multiplication of acidophillic bacteria

Stage 3 Once pH is below about 3.5 bacterially catalysed sulphide oxidation becomes effective. The rate of AMD generation increases and it is limited only by the concentration of ferric ion which is dependent on the availability of oxygen.

Miller and Murray outline the acid-base accounting method for screening materials to determine their acid forming potential (NAPP) by subtracting the acid neutralising capacity (ANC) from the total sulphur content; in addition the pH and electrical conductivity of saturated paste extracts are measured.

However, the authors have extended the method by classifying materials into four main types and they present a new approach to presenting the data graphically. Their four material types are:-

Acid Forming	pH<4 ; NAPP>0
Potentially Acid Forming	pH>4 ; NAPP>0
Non Acid Forming	pH>4 ; NAPP≤0
Barren	essentially devoid of sulphur

The material of most concern is the potentially acid forming (PAF) because it represents a potential long term problem, the timing of which is difficult to quantify. The period before the onset of acid generation is the lag period, the length of which is governed primarily by the acid neutralising capacity.

The authors stress the importance of applying the acid base accounting to individual samples and not composites, because of the variability that commonly occurs between and even within material types. Once the wastes have been grouped according to the above classification, then representative samples of each group, particularly the range of PAF can be selected for leaching trials to determine the time dependent changes in AMD.

Miller and Murray go on to describe the current methods of assessing AMD generation. These involve leaching either in accelerated batch reactors, columns or field trials. The authors favour leaching coarse material (<25 mm) in columns with simulated rainfall because they allow the determination of short term leachate composition, the lag period, and the reactivity of the sulphides. Batch reactors are used to demonstrate the ability to generate acid and support bacterially catalysed oxidation.

While the authors stress repeatedly throughout their paper, the uncertainties involved in quantitative predictions of the lag period and composition of leachates. They have not addressed how this can be dealt with particularly where the regulatory authorities are seeking a set of numbers on which to regulate the discharge quality. As far as the reporter is aware, part of the reason for the uncertainty with the predictions is due to the fact that application of this type of study is relatively new. It was developed in the coal industry only about 10 years ago and applied to base metal mining projects only over the past five or six years. Therefore, there are few projects worldwide in which the methods have been applied at the outset and the waste dump seepage monitored subsequently to confirm the time dependent changes in AMD. Perhaps some of the uncertainty will disappear over the next 5 to 10 years as monitoring data becomes available

from more projects where acid-base analysis has been carried out of the outset.

The paper is an important contribution, however the reporter believes it could have been greatly improved by inclusion of a good case history to illustrate the use of the technique and some of the pitfalls, such as sampling.

3.0 JEFFREY J.J., LAWSON R.T., SARBUTT J.V. AND BOWDLER R.J.

"Sulphide Oxidation in Pyritic Overburden
A Controlled Leach Column Study"

In this paper the authors describe the results of a long term study of oxidation and leaching characteristics of sulphidic mine spoil under conditions typically encountered in the field. They delve further into some the factors that control time dependent changes in the generation of acid mine drainage that Miller and Murray briefly touched on.

The authors present the results of a column leaching experiment which ran for 5 years and in which the environment was controlled to closely simulate the field conditions of Woodlawn Mine in New South Wales from where the material originated. Their Table 1 provides information on the composition of the materials used in the study. Of note are the total sulphur content (2.18%) and the pH (3.9 - 4.2), but there is no information provided on the acid neutralising capacity. The latter is indirectly referred to several times in the paper, but not quantified, which limits the comparison with other materials studied elsewhere, such as by Miller & Murray.

Another shortfall in the presentation of the results is the lack of detail given for the first 12 months, the period during which bacterially catalysed oxidation commenced. Some of this data could readily have been included in a graphical form.

The main conclusions the authors is reached from the study were:-

1. The leaching characteristics cannot be properly assessed by short-term, benchtop leach tests, because the latter are not sensitive to factors that regulate weathering in the field situation. This conclusion is similar to statements by Miller and Murray. While this is strictly true in the reporters experience shorter term tests are generally the only practical approach in the six months to two years time frame normally available before preparing evidence for statutory approvals.
2. The capacity for oxygen to diffuse into the waste material is probably the major factor limiting oxidation of sulphides. This was demonstrated by examination of pore gas concentrations which showed a linear decrease in oxygen concentrations above the reacting front. The apparent diffusion coefficient for oxygen in the top 150 cm of the column was more than an order of magnitude less the diffusion coefficient for oxygen in air. The authors attributed this low apparent diffusion coefficient to the low air-filled porosity of the overburden, which was typically less than 0.09 compared with a total porosity estimated to be 0.27.
3. The distribution of particle sizes in the waste will influence the length of time leaching continues, and therefore, study materials should at least roughly correspond with that in the waste dumps. The authors attributed the drop off in metal concentrations to the completion of oxidation of finer sized fractions in their sample. They estimated that at least 80% of the surface area of Woodlawn overburden was due to material of less than 2 mm, yet this material contributed only 37% by total weight. It is not clear whether this percentage allows for the boulder sizes, which were excluded from the sample at the outset.

4. Rates of release of iron or other metals may not necessarily relate to sulphide oxidation, since secondary mineral formation may occur in material below the oxidation zone. The authors concluded there was a high probability that after 5 years the iron concentrations were being controlled by an equilibrium of leachate Fe with jarosite ($KFe_3(SO_4)_2(OH)_6$) and that this was also responsible for buffering the pH at about 3.3 despite an apparent reduction in oxidation of sulphides (as evidenced by the decline in Cd, Cu and Zn). The absence of Pb in the leachate despite galena (PbS) in the waste material was attributed to formation of the virtually insoluble $Pb^{2+}SO_4$.

5. In their final concluding remark the authors state that if the physical and chemical environment within reacting material are quantified by use of selected sensors and probes then thermodynamic principles can be utilised to predict long-term leaching patterns. While this may be theoretically possible, the reporter wonders as to the practicality of this remark in the real world outside the research laboratory.

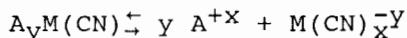
In their experiments, the authors maintained their column in a damp condition by daily application of water and controlled the temperature within a narrow range (20-23°C). It is not stated how closely these conditions would reflect those in a dump at Woodlawn Mine, where the rainfall is intermittent and the temperature may range from 0° to 40°C. Perhaps the wetting and drying, combined with the heating and cooling could lead to greater oxygen ingress into the dump and increased oxidation.

4.0 SHERIDAN J.P., HENDRIX J.L., NELSON J.H.

"The Effect of Ore Type, Depth, and Leach Time on Cyanide Species in Column Tests Using NaCN Leach Solutions"

This paper presents the results of column leaching studies of three different ore types using sodium cyanide solution. Although not specifically stated, the aims of the study appear to have been to provide information on the types of cyanide compounds, their probable distributions, and their mobility in precious metal mill tailings impoundments.

The authors firstly describe the chemistry of cyanide. They note that cyanide occurs as simple cyanides, for example NaCN, and complex metal cyanides of the general formula of $A_yM(CN)_x$ where A is often an alkali metal but may be a transition metal, y is the number of A ions, M is a transition metal such as Fe^{2+} , Fe^{3+} or Cu^{+1} and x is the number of cyanide groups. Many of the complex metal cyanides are insoluble but some ionise to release a soluble $M(CN)_x$ group according to the following general reaction:



Many of these complex metal cyanide ions undergo stepwise formation and dissociation, the extent of which depends upon pH, temperature, and free CN^- concentration.

In their paper the authors concentrate on iron and copper complexes. They state that photodecomposition of the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ ions is the most important mechanism for the release of toxic free cyanide into the environment. The reason for this statement is not given in the text but the reporter assumes it is because iron cyanide complexes are the most common forms found in tailings pore fluids and seepage. No similar explanation is given for copper complexes but the reporter assumes it is also a common form.

The paper outlines the experimental procedures used in the study. Details of the chemical composition of the three ores studied are

given in their Table 1, but no information is included on the mineral forms present in the samples. The metallurgical protocol including the grind, the addition of CaO for pH adjustment and the concentrations of NaCN are all noted. It is not stated whether the solution recirculated through the columns or simply passed through once; It appears to the reporter that the latter was adopted. It is not clear why this procedure was adopted since it hardly represents the real processes that go on deep in a tailings impoundment where the supply of NaCN is limited.

The leach results are presented in their Table (II) which compares the overall cyanide material balance for NaCN leaching. Two figures are presented, one which shows the variation of $\text{Fe}(\text{CN})_6^{4-}$ with time, and the other of CN_{wad} with time.

Conspicuously absent is the lack of results of variations of species with depth although there is some suggestion in the text, particularly in the case of the copper complexes, that the information was collected and was of some interest.

The authors conclude that cyanide speciation within tailings is definitely related to ore mineralogy yet there is no information on ore mineralogy in the paper itself; The only information that is given is that the ore types differ. The reporter presumes information in the mineralogy was stated in the masters thesis on which the paper is based.

The authors second conclusion is also difficult to deduce from the results presented in the paper. They conclude that the $\text{Fe}(\text{CN})_6^{4-}$ ion is the most abundant cyanide species in column leaching studies when iron is present in sufficient quantities in the ore. However, comparison of the percentages of $\text{Fe}(\text{CN})_6^{4-}$ in Table II with the abundance of iron in the solids (Table I) shows that in the oxide ore about 7.6% of CN is $\text{Fe}(\text{CN})_6^{4-}$ compared with about 86% in both the sulfidic and carbonaceous ores. But on examination of Table 1, The oxidised ore has a greater amount of iron (2.6%) than the carbonaceous ore (1.4%). To the reporter the results as presented, do not support the authors conclusion. Conclusions 3, 4 and 5 summarise what was observed. No possible

explanations for these observations are presented in paper. These conclusions are somewhat misleading to reporter, as one assumes that they refer to the effluent solutions from the columns. This being so, then the conclusion that $\text{Cu}(\text{CN})_4^{3-}$ levels in the carbonaceous ore is intermediate between the oxidised and sulfidic ores contradicts the information presented in Table II where $\text{Cu}(\text{CN})_4^{3-}$ is reported as 0.0% for carbonaceous ore compared with 0.2% oxidic ore.

Conclusion 6 is not fully supported by data presented in the paper.

In summary, the information presented in this paper is of considerable interest and importance to the understanding of cyanide speciation in seepage from precious metal tailings, but insufficient results have been presented in the paper to enable readers to reach the same conclusions as the authors.

5.0 GILCHRIST I.C.R., HUNT M.S.

"The Recovery of Water from a Colloidally Stable Kimberlite Suspension"

This paper describes a breakthrough in solving the problem of how to recover clear recycle water from water used to wash Kimberlite ore prior to crushing in order to remove adhered fine clay particles. The problem arises because the clay forms a colloidally stable suspension and because being a water short area it is critical to recover water from the tailings for washing.

The authors describe the properties of the clay slimes. The particle size are ultra-fine; 75% passing 10 micron and 20% passing 1 micron. About 50-60% of the solids is saponite which is a smectite (swelling clay), 10-20% talc and minor amounts of chlorite, illite and quartz. Saponite is obtained by substitution of some Si^{4+} ions in the outer layers by Al^{3+} , which leaves a net negative charge on the lattice that may be neutralised by cations such as Na^+ and Ca^{2+} . This imparts strong negative electrostatic charge on the particles, which with

a -45mV mean zeta-potential, is sufficient to provide colloidal stability to the suspension.

The authors outlines the results of testwork on methods recovering the water including coagulation, flocculation and coagulation/flocculation. The testwork indicated that coagulation was not a viable route since syneresis (i.e the spontaneous separation of the liquid with shrinkage of the gel) was not achieved for any of the coagulant salts or pH ranges studied. Anionic polymers were the most effective at reducing flocculation despite the contradictory polarity, which the authors note is a characteristic of all the de Beers Kimberlite mines. Despite success with a two stage process and reasonably low cost reagents, flocculation was rejected on the grounds that the water recovery was low.

The authors report that four stage coagulation/flocculation was the optimum process to produce clear water. This consisted of adding lime (coagulant), then an anionic flocculant followed by another dose of lime and then flocculant again. The two stage lime addition was necessary to avoid gelation and a two stage flocculant addition was necessary to provide an expressible floc for Montan PA97S was found to be the best of 11 anionic flocculants tested. This is a very high molecular weight medium charge polymer. Magnesium sulphate was also an effective coagulant but was more expensive.

Pilot-plant scale testing indicated that sludge compaction and expression were the two most promising methods of dewatering the sludge. The authors go on to discuss how it is proposed to incorporate a clarification step into the water reticulation circuit. An isolated washing circuit was elected because of improved scrubbing efficiencies and because the properties of the slimes would not change seasonally.

The clarified water is extremely hard and scaling is a potential problem. The design of the transport and disposal facilities of the fine sludge is only addressed briefly as the method selected will depend to a large degree on the properties of the sludge

which will in turn depend on the dewatering method selected from the full-scale trials currently in progress.

While the problem presented in this paper appears to be unique, to one particular kimberlite mine, the paper illustrates the importance of applying mineralogy and surface chemistry fundamentals to the solution of a severe solid/liquid separation problem. The reporter believes the methodology may have application elsewhere, where water recycling is critical.

6.0 CHAPMAN B.M., JONES D.R., JUNG R.F., JONES C.J.,
KADLETZ O. AND TEAGUE J.W.S

"Treatment and Utilisation of Hilton Mine Water"

This paper examines the specific self-purification processes involved in a passive water treatment system, which is being used to treat dewatering discharge from the Hilton Mine in Central Queensland before it is pumped to Mt Isa for use in the mine water supply.

About 6000 m³/day of water containing Fe and Zn is pumped from the new Hilton Mine, a large lead-zinc-silver ore body. This dewatering discharge is combined in a system of settling ponds with groundwater pumped directly from an aquifer in the vicinity. On mixing a large quantity of flocculated iron hydroxide precipitates and partially settles in these ponds before supernatant is pumped to the top of the hill where it is allowed to trickle down a slope and then to follow a stream channel to an impoundment known as the evaporation pond. A progressive reduction in metal levels has been observed.

The authors present the results of three series of investigations into the self purification process.

The first series of investigations concentrated on the hydrodynamics of the evaporation pond to determine what affect they could have on water quality. It was found that during the day, the retention pond could be severely short-circuited through diurnal stratification and wind effects thus reducing the time

fluctuation was due to photosynthetically induced pH changes in the water close to the algal filament.

7.0 CSABA KISS-MATE

"Numerical Simulation of Chemical and Nuclear Contamination Transport in Aquifers and its Possible Applications for the Control of Environmental Impacts due to Mining Activity"

This paper describes a numerical model developed in Hungary for simulation of flow, heat and solute transport in aquifers. While these are numerous models that simulate groundwater flow, heat transport and solute transport, there are few that the reporter is aware that combine all these features in one simulation package.

The authors have unfortunately spent much of their paper defining the theory and describing the workings of the model. Much of the theory of the heat flow, water flow and solute transport could have been left out as they are well described elsewhere. Similarly there is just not enough room in a paper of this nature to give satisfactorily describe the input and output parameter, boundary conditions.

The paper includes three example problems to illustrate the use of the model. Each uses a simple grid of node size 100 m x 100 m. Solute transport from a slug of contaminated is examined in the first example. In the second example a continuous source of contaminant is examined. While in the third example fresh or clean water is recharged into an aquifer containing brackish water and the improvement in quality throughout the aquifer is simulated. As far as the reporter can tell the temperature options were not used in the examples.

The authors present no comparisons with either analytical solutions or results from other recognised modelling codes.

From the material presented in the paper the reporter finds it difficult to evaluate whether the new model presents any advance

available for treatment processes such as degassing, adsorption and particle settling. A 2 m deep floating curtain was suspended across the pond to force buoyant warm inflowing water to sink and mix. The authors state that proved this very effective in improving the flocculation-sedimentation role of the pond but no information presented in the paper to demonstrate this.

The second series of investigations aimed to assess the degree of attenuation of metal levels both soluble and particulate in the flowing waters throughout the system. A plot of the dissolved concentrations of various cations and anions versus distance downstream from the discharge point at the top of the hills is presented. There is a high CO₂ loss and a substantial increase in pH over the first 23 m which is the trickle slope. Most of the zinc is lost over this section. The dissolved concentrations change little through the channel and evaporation pond sections, but there is a significant decline again in the lower portion of the channel below the evaporation pond. These latter declines are attributed largely to prolific growths of filamentous algae. Some particular Fe and Zn removal across the pond was noted.

A two day study was carried out to determine whether the algae are removing the metal from solution by metabolic uptake or passive adsorption on the cell structures. A diurnal variation was noted in Zn and Mn levels which their studies showed was due to an increase in pH in the water immediately over the algae during the day.

The adsorption properties of samples of stream-bed sediment were tested and it was found that the stream bed material adsorbed zinc more strongly than a control sample of sediment taken from the bank of the stream. Analysis of stream bed material showed it to be coated with a soft black coating of manganese dioxide which contained considerable quantities of zinc.

The authors conclude that both biological and inorganic processes contribute to the reduction in Zn and Mn. The large diurnal

over the numerous other simulation models that are now available commercially. Now are its applications for assessing the environmental impacts of mining clear from the examples given in the paper.

8.0 WILK, Z., ADAMCZYK, A.F., MOTYKA J & WITCZAK, S
A Zinc-Lead Ore Mine Water Contamination by a Paper
Factory Fluid Waste

In this paper the authors present a back-analysis study of the migration of contaminants within the cone of depression caused by large scale mine dewatering of karstic aquifers in Poland.

While the study does not involve prediction of water quality in mine discharges, it does provide useful information of the magnitude of the longitudinal dispersion coefficient for karstic limestone. This parameter is important for simulation of contaminant movement and the value derived in this study should prove useful to other workers predicting contaminant movement in aquifers in similar materials.

The authors present a concise description of the problem, the hydrogeological environment and their analytical approach.

The mine under study is a lead-zinc mine located in an area of karstic limestones and dolomites of Triassic Age in Southern Poland. The limestones form a high yielding aquifer which the authors refer to as the Triassic aquifer. Continuous dewatering is required in the mine and the pumping rates range from 2.3 to 3.5 m³/sec (i.e. 200,000 to 300,000 m³/day). This has resulted in the formation of a cone of depression that extends at least 5 km beyond the mine.

A pulp and paper mill is located about 4 km north of the mine. Waste sulfite liquors have seeped into the shallow Quaternary aquifers under the mill over a 50 year period contaminating the aquifer with residual lignosulphonate compounds. The authors note that the risk of contamination of the underlying Triassic aquifer due to vertical leakage induced by the dewatering was

recognised before the mine was developed almost 20 years ago.

The authors provide details of the hydraulic characteristics of the Triassic aquifer and present a map showing the quasi-steady-state cone of depression developed around the mine. The Triassic aquifer averages about 100 m thick, has an average hydraulic conductivity of 5.8×10^{-5} - 9.3×10^{-5} m/sec (5-8 m/day), and an average specific yield or drainage porosity of 0.035 (3.5%). Apparently, the aquifer exhibits a double porosity effect with the porous limestone blocks having a porosity between 10 and 20% while the interconnected fissure system has a porosity of 0.1%.

Also presented in the paper is a plot of the water quality of the mine discharge since the estimated time when the cone of depression formed under the paper mill. The arrival of the contamination is clearly evident and has the characteristics of a classical break-through curve.

To determine the longitudinal dispersion coefficient the authors assumed one dimensional flow was approximated which appears a reasonable assumption given the local conditions. They then fitted a normalised break-through curve to the actual water quality data. The curve was derived from nomograms prepared by another worker for generalised cases of one dimensional solute transport. To fit the curve it was necessary only to know the mean travel time which the authors calculated to be 1805 days from the observed data. By ignoring molecular diffusion, which is valid over these scales and flow velocities, the authors were able to determine that the longitudinal dispersion coefficient $\alpha L = 37.7$ m. They note this agrees reasonably well with another regional value of 60 m in the literature for similar limestones quoted elsewhere.

9.0 CONCLUSIONS

The first three papers in this theme have all provided useful contributions on characterising and predicting the quality of mine drainage. They have illustrated clearly some of the problems of ensuring that sampling and laboratory experiments are

representative of the field situation they are trying to simulate.

The second group of papers relate to treatment and management of mine waters. They do not involve a predictive component, but illustrate the methodology adopted to understanding treatment technologies at specific mines. The methodology could be used in predicting the results of similar treatment methods elsewhere.

The reporter believes that the third group of papers do not fairly represent the state of the art methods for predicting the impacts of mining on water quality. However, good case histories in which pre-mining predictions are compared with operational monitoring data are rare. This is an area which needs more attention in the future.