FINAL REPORT

PROJECT No. 5 of the Mount Lyell Remediation
Research and Demonstration Program

Characterisation and impact assessment of mine tailings in the King River system and delta, Western Tasmania.

by

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EXECUTIVE SUMMARY

Ninety-seven million tonnes (Mt) of mine tailings and 1.4 Mt of slag have been deposited into the Queen and King River systems over the past 78 years. The sediments are rich in sulphide minerals, mainly pyrite (iron-sulphide), and are derived from the Mount Lyell copper mine. This material is currently residing in overbank, river bottom and delta deposits associated with the King River. The sediments and their pore waters contain potentially dangerous concentrations of metals and acid that are toxic to aquatic life in the King River and Macquarie Harbour. In order to quantify the impact of the sediments on water quality in the river and harbour, an integrated program of field, analytical and computer modelling work is used to estimate the fluxes of elements and acid between the sediments and the water.

Field work consisted of installing mini-piezometers (groundwater monitoring devices), measuring hydraulic head and water chemistry, and sampling sediment, groundwater and surface water for later chemical analysis. Two types of sediment bank were identified: high mounded banks upstream and relatively low flat-topped banks downstream. Two examples of each type of bank, as well as specific locations on the north and south lobes of the King River delta were targeted for study. Sediment and water samples were examined and their compositions were measured using a combination of techniques. Fluxes of fluid, elements and acid are calculated using computer modelling of fluid flow, the hydraulic parameters measured in the field and water compositions measured in the laboratory. Computer modelling also indicates which minerals and processes are controlling the compositions of the groundwater in the sediments.

The tailings contain rock, crystal and slag fragments, generally ranging in size from 0.01 mm to 0.2 mm, as well as variable proportions of organic debris from natural sources in the King River catchment. Minerals in the rock and crystal fragments are dominated by common silicate, oxide and sulphide minerals. Sulphide minerals are the source of many of the heavy metals. The slag is also enriched in trace metals such as zinc, cobalt, nickel and lead, and may be a significant source of some metals because of its high reactivity with water. Tailings in the delta contain 5-7 % by weight of pyrite and about 0.16 % by weight of copper, while the sediment banks are estimated to contain 2-3 % by weight of pyrite and 0.085 % by weight of copper.

The upper layers of the tailings sediment are not saturated with water, and this permits infiltration by air. Acid production in the tailings is initiated by the reaction of sulphide minerals with atmospheric oxygen. For example, the upper 1.5 m of the delta containing about 4.4 Mt of tailings is undersaturated with water, and is the most significant source of acid and metals, at least from the delta sediments. Preliminary estimates indicate that almost complete oxidation of pyrite in permanently unsaturated tailings takes place in one to four years. Interaction between the products of sulphide oxidation and water produces sulphuric acid, and a range of soluble heavy metals. The oxidation of aqueous iron compounds at, and above the water table, results in further acidity and widespread formation of iron-oxide precipitates which coat most of the sediment grains.

The composition of groundwater in the tailings is highly variable, and steep chemical gradients are present at the water table in the delta. Groundwater varies from highly acid to near-neutral (pH = 2.54 to 7.1) and is enriched in copper, iron, aluminium, manganese, silicon and arsenic, with some samples also showing elevated concentrations of nickel, zinc, cobalt, lead, selenium and mercury. Groundwater in the banks is generally more acid and oxidised than groundwater in the delta. The north lobe of the delta contains the most reduced and near-neutral-pH groundwater. Much of the variation in groundwater chemistry is attributed to differences in the sulphide and organic content of the tailings, and other local controls on redox conditions. The activity of sulphate-reducing (and possibly methane generating) bacteria at the tidal interface on the delta appears to be important in lowering metal and acid concentrations in delta groundwater discharged to the harbour.

The groundwater chemistry is controlled by interaction between groundwater and sediment. Some elements appear to be controlled by mineral solubility and equilibrium processes, for example, silicon by amorphous or microcrystalline silica, and iron by the iron-oxide coatings on mineral grains. Other elements are present in the groundwater in concentrations much higher than mineral solubility suggests. For example, the concentrations of aluminium are orders-of-magnitude higher than calculated solubilities for aluminium-bearing minerals. One possible explanation is that aluminium is out of equilibrium with the minerals in the sediments. The sources for many other elements in the water are identified, although the processes which control their aqueous concentrations are not always clear.

Element and acid fluxes from the tailings to surface water are calculated using a combination of groundwater modelling, measured water compositions and estimated discharge areas. The hydraulic conductivity of tailings deposits in the sediment banks and delta is high. Groundwater fluxes are approximately 20, 40 and 50 litres/day/square metre for the high mounded sediment banks, relatively low flat-topped banks and delta, respectively. Examples of copper and acid fluxes into the King River and Macquarie Harbour are 4.5 kg copper/day and 155 kg sulphuric acid equivalent/day. Additional fluxes into the river and harbour water result from episodic rain and flood events, where water flushes through and over the sediments. Although these fluxes are difficult to estimate accurately, they are thought to be broadly similar in magnitude to those from groundwater sources. The contribution of metals and acid from the river bottom sediments that include slag is unknown. Using these estimates, it is concluded that the King River and Macquarie Harbour currently receive an average daily addition of approximately 10 kg of copper and about 300 kg of sulphuric acid equivalent from the sediment banks and delta. Such a release is likely to have significant ecological consequences in a pristine river system; however, in the King River system this represents only 1-5 % by weight of the total quantity of metal and acid entering the Queen and King river systems from the Mount Lyell lease site. These figures are considered to be reliable unless the estimated contribution from episodic rainfall events is much higher. Furthermore, if high concentrations of metals and acid are produced from short-lived flushing events, their environmental impact may be quite significant. Priority should be given to the remediation of acid drainage from the Mount Lyell lease site and understanding the effects of periodic rainfall events.

Based on current hydrogeological parameters and groundwater chemistry, the mass loadings recorded from groundwater discharge and surface water runoff are predicted to continue for thousands to tens of thousands of years.

Any physical disturbance of the tailings which involves oxidation will have the potential to significantly lower the pH and raise the metal content of the associated leachate. It is evident that high concentrations of copper, iron, aluminium, silicon, manganese, zinc, cobalt and nickel can be readily mobilised from oxidised tailings material by acidic fluids, and that such fluids are routinely generated by natural infiltration processes. Under some circumstances, however, it may be possible to relocate a portion of the tailings from one subaqueous site to another without exacerbating metal or acid release.

The installation of low permeability, reactive substrates (clay + calcium/magnesium carbonate + organic matter) on the sediment banks prior to revegetation is predicted to assist with decreasing groundwater discharges, decreasing surface water / tailings interaction, and developing sustainable revegetation programmes. Enhancing and extending naturally occurring bioremediation processes in the delta is considered to be one of the most cost-effective methods for improving the quality of groundwater discharges from the delta. This may be achieved by inundating dry sediment with water and providing organic matter to promote the growth of sulphate reducing bacteria.

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PREAMBLE

The water quality and associated ecology of the Queen and King rivers and the Macquarie Harbour in Western Tasmania has been adversely affected by mining activities at Queenstown over the past 100 years (Figure 1). Acidic and metal polluted drainage generated by groundwater and surface water flow through oxidised sulphide-bearing rock, and the disposal of sulphidic tailings to the Queen River since 1916 have been the principal processes implicated in this environmental degradation. Widespread and severe erosion exacerbated by deforestation and locally derived acid rain, as well as the disposal of sewage and municipal solid waste to the Queen River over part of its mining history, have contributed additional stress to the receiving environment. An estimated 95 million tonnes of sulphidic tailings, 1.4 million tonnes of smelter slag and approximately 10 million tonnes of top soil were disposed of to the Queen-King river system between 1916 and 1994 (Locher, 1995).

Figure 1 Location Plan showing the King River Catchment below Lake Burbury

Tailings and slag material were by-products from copper-rich volcanogenic massive-sulphide deposits at Mount Lyell. While several discrete styles of mineralisation have been identified in the Lyell Mineral Field (Solomon, 1989), the majority of the ore is pyrite-chalcopyrite dominated, and hosted by strongly deformed and brecciated, quartz-sericite-chlorite±carbonate altered felsic volcanic rocks of Cambrian age.

Disposed into the East Queen River at Queenstown, the unwanted sand to mud sized residue from the copper pre-concentration process and smelting activities has migrated down the Queen and King rivers and has accumulated as (i) subaerial overbank deposits on the King River, (ii) subaqueous bottom sediments in the King River, and (iii) largely subaqueous deltaic deposits at the mouth of the King River in the Macquarie Harbour. Estimates from Locher (1995) indicate that some 10 Mt of this material is currently located in the King River bed, roughly 3.4 Mt is stored in the King River banks, and much of the remainder has accumulated in the King River Delta.

Overbank sediment deposits on the King River were deposited during storm events and range from 6 metres above river level for the banks upstream, to less than 0.5 metres near the delta. With the construction and operation of the John Butters hydro-electric power station on the Upper King River (Figure 1) since October 1991, the influence of storm events on fluvial process has been significantly dampened, and the once periodic inundation of the elevated sediment banks is now unlikely.

The subaerial portion of the King River Delta currently covers approximately 2.5 square kilometres and is bisected by a shallow channel through which the King River continues to flow. The maximum elevation across the subaerial delta at low tide is approximately 1.5-2.0 metres, and a portion of the area is routinely inundated by generally unpredictable barometric tides in the Macquarie Harbour. Tidal influences routinely effect 30-50 cm water level rises over the delta, but complete inundation is reported by residents of Strahan to occur more than once per year. Operation of the John Butters Power Station has significantly reduced the incidence of widespread inundation of the subaerial delta. Tailings in the delta is largely comprised of fine to coarse sand, with a partially cemented crust developed irregularly which appears to account for the more elevated sections. Key detrital components include siliceous rock fragments containing muscovite, chlorite and sulphides, sulphidic fragments, quartz vein material, carbonate, clay, organic debris and slag. The main sulphide minerals in the tailings include pyrite, chalcopyrite, bornite, sphalerite, galena, tennantite and tetrahedrite (Hince, 1993).

The ubiquitous orange colouration of surficial tailings material in overbank and delta deposits reflects extensive chemical modification by oxidation, but the detailed chemical processes and long term environmental impacts of the tailings accumulations are unknown. The contribution of these deposits to the release of acid and heavy metal concentrations to surface water has not been accurately determined.

The purpose of this study is to characterise the mineralogy and chemistry of the tailings material currently in storage in various fluvial environments in the Queen and King rivers and associated delta, and to describe the potential of these tailings to cause further environmental impacts by the release of metals and acid. The effects of these mine wastes on water quality is compared to other key sources of water pollution entering the Macquarie Harbour (eg. the Mount Lyell Mining Lease). Such data permits the current and future acid and metal generating capacity of the tailings to be quantified, and appropriate management strategies to be devised.

Achieving these aims requires data on the speciation of environmentally significant metals in solid and aqueous phases. Metals fixed as solid phases may occur in primary crystal phases, as secondary amorphous or crystalline precipitates, or as compounds adsorbed onto pre-existing solid matter. In order to predict the flux of metals and acid into surface water, a broad understanding of groundwater chemistry, hydrogeology and mineralogy of the tailings accumulations is required. Selective sampling of sediments and their pore water, in collaboration with the collection of fundamental hydrogeological, chemical and mass balance data have provided the necessary framework to determine the processes and magnitude of acid and metal release. Fluid fluxes based on measured and modelled hydrogeological data are used in conjunction with analytical data on groundwater chemistry to calculate metal and acid release over unit areas for selected fluvial and deltaic settings. Channel cross-sections provided by Locher (1995) and calculations of the perimeters of banks and delta by photo-analysis permit estimation of discharge areas, thereby permitting rates of discharge of metal enriched water to be derived. With estimated current discharge rates and a knowledge of the average composition of the tailings, predictions of the future impact of these deposits can be made. Geochemical modelling and leach tests have assisted with an understanding of the fate of aqueous components as they discharge to surface waters, and the likely environmental impacts if the tailings are physically disturbed. Key field observations and an understanding of acid generating processes have assisted with the formulation of potential remedial strategies.

PREVIOUS WORK

The feasibility of exploiting the sulphidic tailings deposit in the King River Delta for their sulphur and metal content has been examined by a number of companies. The Mount Lyell Mining and Railway Company Limited (MLMRCL) instigated an evaluation of the King River Delta between 1969 and 1972. They reported an average Cu content of 0.16%, and estimated that 300000 t of pyrite (4-7 wt.%) were present in the top 1.5 m of exposed delta (Hince, 1993). More recent exploration by Cottesloe Corporation (1987 to 1993) evaluated the tailings as a potential resource for sulphur, copper, gold, iron, cobalt, silver, barium, lead, zinc and molybdenum. Cottesloe calculated that the delta contained 5-7 Mt of pyrite, with sulphur being the primary asset. The inshore portion of the delta was estimated to contain 7.0 Mt of tailings which includes 0.5 Mt of pyrite concentrate, containing 200000 t of S, 3000 t of copper, 400000 kg of cobalt, and 400 kg of silver/gold. Reported copper grades averaged 1000-2000 ppm, and appeared to decrease away from the mouth of the river in a broadly concentric fashion. In the coarser grained oxidised crust on the delta, the copper sulphides were found to be largely bound together with other (secondary) material.

Auger drilling by Cottesloe (1987-1993) indicated that potentially economic components in the delta sediments are unevenly distributed, but tend to be segregated into the finer-grained, higher density portion of the tailings. Concentrations of cobalt, gold, barium, iron and sulphur all increase with decreases in the sediment particle size, and significant upgrading of the tailings could be achieved by rejecting the coarser half of the delta's inshore sediment. The composition and concentration of sulphide minerals in a typical tailings sample was reported as 5.57% pyrite, 0.21% chalcopyrite, 0.13% covellite, 0.11% sphalerite and 0.04% galena, and limonite coatings were recorded around grains of pyrite and chalcopyrite. Combined mineralogical and chemical analyses indicated that cobalt and sulphur occur chiefly in pyrite. Iron not present in pyrite occurs largely in limonite, siderite and magnetite. Gold was predicted to occur partially in its native state, with copper partly in chalcopyrite, and barium exclusively in barite. Cottesloe (1987-1993) estimated that 55% of the copper in the delta appears to be secondary, occurring as thin films of what was thought to be covellite/chalcocite on both sulphide and non-sulphide grains throughout the delta.

Five technical reports on matters pertinent to water quality, the impact of tailings and acid rock drainage (ARD) management strategies were produced by Environmental Geochemistry International (EGI) from 1991 to 1993 for the MLMRCL. This work indicated that most ARD has a low pH and contains elevated concentrations of Cu, Fe, Al, Mn and SO_4. EGI (1991a) identified and quantified the major individual sources of ARD and aqueous copper entering the King and Queen river catchments. It was concluded that some 580 tonnes of soluble copper was entering the Queen River annually. An order-of-magnitude less soluble copper was recorded entering the King River catchment from Comstock and Linda Creeks. Based on a tailings discharge rate of 200 litres/second, EGI (1991a) estimated that, in 1991, 1650 tonnes of copper was being disposed to the Queen River per year.

EGI (1991b) conducted a series of laboratory tests to examine the chemical consequences of mixing ARD and unpolluted river water (West Queen River) with or without fresh mine tailings, in an effort to simulate various operating scenarios at the Mount Lyell mine. Trials utilising mixtures of the three components demonstrated that the solubility of aluminium and copper was lower than predicted by dilution. Copper solubility appeared to be controlled by adsorption rather than precipitation reactions, with an estimated 130 mg of copper being adsorbed per kilogram of tailings. Lime (CaO) co-disposed with tailings appeared to be slowly dissolving during the process of mixing with ARD. Initially iron behaved as a conservative element during mixing and dilution, and must have been in its 2+ oxidation state. 62% of iron remained in solution after high degrees of mixing and dilution. Experiments with mixtures of ARD and unpolluted West Queen River showed that most elements behaved as would be predicted by quantitative dilution, except for the precipitation of some Fe.

EGI (199b, 1993) concluded that the combined effects of neutralisation and adsorption by the tailings and dilution by the King River provide significant control on the concentrations of heavy metals entering Macquarie Harbour. A geochemical-surface water flow numerical model (RIVCHEM) developed to evaluate the impact of acid mine drainage inputs from the Mount Lyell site also predicted that a significant portion of aqueous copper would be adsorbed onto tailings particles, and further suggested that all manganese remains soluble, most iron precipitates as ferrihydrite and most aluminium remains soluble (EGI, 1993).

During 1991, 4-5000 tonnes/day of fresh tailings were being co-disposed with calcium oxide at a rate of approximately 12 t $CaCO_3$ equivalent/day. The short term Acid Neutralising Capacity (ANC) of this mixture, which was predicted by EGI (1991b) to be due to the calcium oxide, was 1.5 kg $CaCO_3$ equivalent/t tailings, and the long term ANC was calculated at 13.3 kg $CaCO_3$ equivalent/t tailings, and assumed to be related to gangue minerals such as carbonates and oxides. EGI (1991b) predicted that tailings at mine discharge displayed a Net Acid Generation (NAG) in the order of 22 kg H_2SO_4 equivalent/t tailings. A relatively slow reaction time during the NAG tests suggested that the sulphides are likely to be slow to oxidise naturally.

Preliminary calculations (EGI, 1991b) suggested that acid contributions to surface water from the subaerial tailings banks on the King River are 2-3 orders of magnitude less than the acid input from ARD sources at the Mount Lyell mine leases. EGI (1991b) estimated that acid release from material in bank storage is between 0.03 and 0.45 t of H_2SO_4 equivalent/day. These figures were based on a total surface area of between 0.3 and 0.5 km^2, an exposure depth of 3 cm and a sulphide oxidation rate of 0.5 to 5 g of pyrite/kg/year for tailings containing a few percent pyrite. This input compares to a figure of approximately 30 t of H_2SO_4 equivalent/day discharged directly from the Mount Lyell mine leases.

A brief study of the King River Delta sediments was conducted by EGI (1991c), to evaluate the acid forming potential of selected samples, and provide a preliminary indication of the mineralogical association of copper within the sediments. They determined that the delta had an exposed surface area of about 2.0 sq. km, and that the uppermost 10 cm of tailings is highly oxidised, and strongly acid generating when mixed with water (EGI, 1992). Beneath the oxidised surface layer, residual sulphides were reported to be stable, albeit reactive if oxidised. EGI (1992) regarded the delta as a potential long-term source of acid and copper to the Macquarie Harbour, and as unlikely to be colonised by vegetation.

The delta tailings were described as generally orange-brown and highly oxidised at the surface (0-10 cm), and grey and relatively un-oxidised beneath the water table (0 to 85 cm). The pH of natural pore water was measured at near neutral. A general increase in sulphur was reported with depth in the delta sediments, due to a decrease in oxidation, but significant natural variability in total sulphur was observed (average $\approx$2 wt.% sulphur in fresh tailings, with one sample up to 5.5 wt.% S). Bulk chemical data indicated that copper, iron and manganese were significantly depleted in the surface 10 cm, and this was attributed to sulphide oxidation and leaching.

The Acid Neutralising Capacity (ANC) of tailings below the water table was approximately 50% of the ANC for fresh tailings, and the Net Acid Generation (NAG) procedure clearly demonstrated that sulphides in the tailings are reactive. EGI (1991c) concluded that sulphide oxidation was continuing at depth in the delta, and that physical disturbance would likely accelerate oxidation, and lead to the production of acid leachate. Based on extraction tests, EGI (1991c) suggested that most of the residual copper in the delta sediments occurs as sulphides, and predicted that, if oxidised and partially oxidised delta sediments were disrupted and deposited on the harbour floor, no major release of copper would occur.

Locher (1995) examined sediment transport in the King River, and provides a comprehensive physical framework for understanding river geomorphology and important baseline information regarding volumes and locations of sediment in storage in the King River system and delta. Her study showed that the banks of the King River can be up to 100 m wide and a maximum of 5 m in height above low water level. Locher estimated that they contain 3.4 Mt of tailings, and proposed that they developed in height and surface expression from existing levee banks. Locher determined the median grainsize of the tailings throughout the history of disposal to be approximately 75 µm, with slag averaging 160 µm. A specific gravity of 2.9 was recorded for fresh tailings, and 2.7 for material in the sediment banks. Locher found copper to be an excellent indicator of mine derived versus natural sediments (between 100 and 2500 ppm for tailings against natural background concentrations of 6 to 29 ppm).

Locher (1995) established that mine wastes have raised the river bed level by 5 m for much of the lower King River, and approximately 7.3 to 10 Mt of sediment are stored in the King River bed. She determined that more than 80% of the estimated total bank sediments are stored between the Quarter Mile Bridge and Teepookana Bridge whilst greater than 80% of the estimated total bottom sediments are stored below the Teepookana Bridge.

According to Strahan historian Harry McDermott, the King River had a delta before mining activities commenced (Locher, 1995). The delta has expanded gradually, and the growth of the subaerial portion as determined from photographs dated 1953, 1974 and 1984, is presented in EGI (1991c). The vast majority of the tailings are believed to have been carried to the delta and the harbour floor (Locher, 1995).

Hince (1993) conducted a physical and chemical evaluation of the tailings within the King River and delta, and provided insight into the distribution, mode of occurrence and behaviour of contained heavy metals. His work focussed on the development of a chemical leach procedure to assist determination of metal speciation in solid phases and evaluation of aqueous metal mobility. Hince determined that quartz and aluminosilicates comprised ≥70% of the tailings, with sericite, biotite and chlorite comprising the bulk of the latter component. Pyrite (≤5%), magnetite (1-2%), rutile and an orange iron-bearing precipitate make up the remaining significant phases. Non-oxidised tailings samples contain 3-7% sulphur, and oxidised samples contain about 0.2%. Hg concentrations in sediment samples varied between 0.03 µg/g and 0.11 µg/g, and no trends were observed with depth. Hince (1993) also recorded the following anthropogenic contributions to the tailings mixture: methyl isobutyl carbinol, sodium isopropyl xanthate, and alkyl dithionocarbamate.

Three series of sequential and single-step extraction procedures were conducted on a range of oxidised and non-oxidised tailings samples to establish metal speciation. Hince (1993) concluded that the most suitable procedure consisted of a four-part single-step extraction process, utilising (i) water to recover soluble secondary phases, (ii) pH buffered hydroxylamine hydrochloride to extract metals adsorbed onto or included within iron and/or manganese-oxide bearing secondary precipitates, (iii) hydrogen peroxide to oxidise and dissolve sulphides, and (iv) hot, concentrated nitric acid to release metals associated with silicates.

In addition, Hince (1993) conducted simulated leach tests on subaerial and subaqueous tailings with deionised water and filtered Haulage Creek water. He concluded that exposed tailings have the capacity to release large quantities of acid as well as Cu, Zn, Fe and Mn, and that subaqueous tailings have the potential to be a sink for heavy metal accumulation. Further tests were recommended for subaqueous sediments stored under flowing water.

Examination of the geological literature for the Mount Lyell deposit has provided a broad mineralogical characterisation of all possible "primary" mineral assemblages likely to be present in the tailings. Silicates include quartz (SiO_2), muscovite($(KAl_3Si_3O_{410}(OH,F)_2)$), chlorite ($(Fe,Mg)_6Al_4Si_4O_{10}(OH)_8$), biotite ($K(Fe,Mg)_3Al_3Si_3O_{10}(OH,F)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$), epidote ($Ca_2FeAl_2Si_3O_{12}(OH)$), zircon ($ZrSiO_4$), sphene ($CaTiSiO_5$), fuchsite (chromian muscovite) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), and sulphides comprise pyrite (FeS_2), chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), tetrahedrite ($Cu_{12}Sb_4S_{13}$), tennantite ($Cu_{12}As_4S_{13}$), sphalerite (ZnS), enargite (Cu_3AsS_4), argentite (Ag_2S), galena (PbS), molybdenite (MoS_2), hexastannite (Cu_2FeSnS_4), arsenopyrite (FeAsS), digenite (Cu_2S), mawsonite ($Cu_6Fe_2SnS_8$), pyrrhotite (FeS), stromeyerite (AgCuS), linneaite (Co_3S_4), betechtinite ($Pb_2(Cu,Fe)_{21}S_{15}$) and bournonite ($PbCuSbS_3$). Carbonate minerals are widespread in some ore types, with siderite ($FeCO_3$) and dolomite ($(Ca,Mg(CO_3))$) being most common. Accessory phases include magnetite (Fe_3O_4), chromite ($FeCr_2O_4$), hematite (Fe_2O_3), goethite (FeO.OH), ilmenite ($FeTiO_3$), rutile (TiO_2), limonite ($FeOH.nH_2O$), barite ($BaSO_4$), anhydrite ($CaSO_4$), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$, fluorite (CaF_2) and monazite ($(Ce,La,Th)PO_4$), and rare to trace amounts of native copper, metallic gold and electrum (Au-Ag alloy) have been reported.

The ecological impact of ARD on Macquarie Harbour has received little attention until recently. Acid drainage from the King River has been implicated as a potential contributing factor in a number of significant fish losses incurred by a fish farm in the Macquarie harbour (Wood 1991). If ARD is proven to be a key issue in local fish kills, we may conclude that periodic flushing "events" have a more significant short-term impact on the ecology of the harbour than those caused by sustained but lower level acid/metal release.

Carpenter et al. (1991) provided an excellent base of fundamental chemical and biochemical data on the Macquarie Harbour water and sediments. One conclusion of particular relevance to this study is the identification of significant bacterial populations in harbour sediments. Similar microbial biomasses were reported from three sediment samples analysed, but differences in the relative abundance of phospholipid-derived fatty acids at each site indicated variable microbial community structures. Significant populations of anaerobic bacteria were present in sediments near the mouth of the King River, and biomarkers for sulphate reducing bacteria were present in all samples.

FIELD WORK

Introduction

Thirty-four person days of field work were conducted on the King River delta and sediment bank deposits between the 28th of July and the 3rd of August, 1995. The field component consisted of the following facets:

- Installing and surveying mini-piezometers in key locations within the delta and sediment bank deposits.
- Sampling groundwater from the piezometers and selected surface water.
- Determining field chemical parameters for groundwater samples from piezometers (pH, Eh, Conductivity).
- Filtering and acidifying groundwater samples from the piezometers for trace metal analysis.
- Measuring groundwater levels and water level recovery rates in piezometers to establish hydrogeological conditions.
- Drill testing and geological logging at selected locations.

- Determining field chemical parameters (pH, Eh, EC) for groundwater and surface water from numerous localities (eg. traverses on delta).
- Extensive shallow auguring (0.1-1.5 m) for geological samples and hydrogeological data.
- Limited surveying to assist with mass balance calculations based on aerial photo analysis.

Sediment Sampling

Introduction

Tailings sediment samples were collected from four types of deposit. These are:

(i) Sediment from the King River Delta (Plate 1).

(ii) Sediment from banks along the King River, which can be broadly divided into (a) mounded banks above Teepookana (Plate 2), and (b) lower relief banks downstream (Plates 3 and 4).

(iii) Sediment from the bed of the King River.

Plate 1 View from the north-west margin of the south lobe of the delta

Plate 2 View of the downstream end of Bank N

Plate 3 View of Bank H looking downstream

Plate 4 View of Bank D looking upstream

Grab samples from surface and near-surface environments were obtained by shovel, and hand augers permitted sediments from as deep as 1.5 m to be retrieved. Sonic drilling techniques enabled partial sediment recovery from as deep as 7.5 m, and percussion drilling permitted sampling from around the cutting head. All of these techniques resulted in significant physical disruption of tailings material. Samples from water saturated zones were collected with their pore water to minimise chemical modification during storage. River bottom samples were stored in 50 ml LDPE screw-top bottles and other sediment samples were collected in 250 ml screw-top LDPE bottles. Samples were transferred to large insulated coolers after each day's field work.

Drilling

Banks / Delta

Two holes were drilled in tailings material; one in the delta (DEL-C1: between DEL-WS7 and DEL-WS8) was terminated at 5.5 m (Figure 2 and Plate 5), and the other in bank R (R-C1: 10 m south of R-WS2) was completed to a depth of 7.45 metres (Figures 3 and 4). A hand-held sonic drill rig fitted with a self-locking tool for recovering sediment cores was employed to assist with continuous sampling. The unconsolidated sediment was logged and sampled. Sample numbers and descriptions are included in Appendix 1, and geological logs for the drillholes are included in Appendix 2.

Figure 2 Location of surface sampling traverse lines and drillhole on the King River Delta

Plate 5 View of the installation of DEL-C1 on the north lobe of the delta

Plate 6 Vertical profile through part of the unsaturated zone in Bank H

Figure 3 Location and designation of the King River sediment banks

Figure 4 Piezometer locations on the King River sediment banks

River Bottom

Sampling of river bottom sediment was coordinated by Helen Locher (MLRRDP-Project 4) using the sonic drilling equipment located on a small barge. Seven holes were completed at 5 sites in the King River, and station locations are indicated on Figure 5. Fifty-eight subsamples of this material stored in 50 ml LDPE bottles were made available to this study group for mineralogical and chemical evaluation. Brief sample descriptions are provided in Appendix 1.

Figure 5 Location of drillholes by Helen Locher (After Locher, 1995)

Auger and Grab Samples

Sixty-five samples of tailings material were collected over a range of depths from both mounded and flat overbank deposits and the delta using shovel and hand augers. Some additional grab samples were retrieved from the base of the piezometer drillholes from the cutting head of a hand-held percussion drill rig. These samples were recovered from proximal to the monitoring zone, to permit comparison between water chemistry and mineralogical analysis. Sample location information is provided on Figures 2 and 4, and Appendix 1.

Hydrogeology

Groundwater Monitoring Network

A suite of temporary mini-piezometers were installed in a range of fluvial and deltaic settings in sediment banks and the delta. These were designed to provide groundwater samples and water level and recovery data from discrete locations. These data are essential to determine hydraulic gradients, hydraulic conductivity and groundwater flux through the saturated sediments towards the river or harbour. Piezometers were installed in banks R, N, H, and D along the north side of the King River and in both the north and south lobes of the delta. On each bank, at least 2 piezometers were located perpendicular to the river in order to determine groundwater flow rates towards the river, the most likely receptor of groundwater. A transect of monitoring bores was completed perpendicular to the tidal interface on the

North Delta, and on the South Delta, two transects were completed, one perpendicular to the tidal interface and the other perpendicular to the King River channel. At most sites, at least one location was instrumented with two piezometers completed at different depths to provide information on vertical hydraulic gradients and changes in groundwater chemistry with depth. In total, thirty-five piezometers were installed in the tailings deposits: five in Bank R, four in Bank N, four in Bank H, three in Bank D, nine in the north delta lobe and ten in the south delta lobe. Sediment bank locations are provided on Figure 3, and piezometer locations are provided on Figures 4 and 6.

Figure 6 Piezometer locations on the King River Delta

Piezometer Design, Construction and Installation

The piezometers were designed to be temporary, allowing a large number to be easily installed. Piezometers on the higher sediment banks (Banks R, N, and H) were installed using a hand-held percussion drill with a 40 mm cutting head. This method smears the cuttings along the upper portion of the borehole, above the groundwater monitoring zone. The piezometers installed in these boreholes were constructed from 6 m lengths of 25 mm internal diameter (ID), Class 12 PVC, the bottom 25 cm of which was slotted by a hacksaw. The slotted interval was covered with 100 μm nylon sieve mesh which was attached to the base plug and extended 30 cm above it. After the well screen and casing was lowered in the open borehole, the saturated sediments tended to collapse around the piezometer, and open annular space in the unsaturated zone was backfilled with cuttings from the borehole. The piezometer was capped and a slot made below the cap to equalise atmospheric pressure across the PVC wall. Construction details for the 25 mm piezometers are shown in Figure 7.

Figure 7 Design of Piezometers

Piezometers in the shallowest bank (Bank D) and the north and south lobes of the delta were installed manually using a combination of auguring and hand driving. Where possible, piezometers were installed by driving a piece of 50 mm ID PVC casing to the desired final depth of the well. Piezometers were then lowered into the casing and the casing was extracted. In these locations, piezometers were constructed of 3 m lengths of 40 mm ID, Class 9 PVC. The lower 25 cm were slotted by hand, and, like the 25 mm ID piezometers, the slotted interval was covered with 100 μm nylon sieve mesh. Piezometers were backfilled when necessary, however, in most cases, the water table was sufficiently close to the surface that the saturated sediments collapsed around the borehole. Excess lengths of pipe were trimmed with a hacksaw, the piezometer capped, and a slot made below the cap to equalise atmospheric pressure across the PVC wall. Construction details for the 40 mm piezometers are shown in Figure 7.

Piezometer Monitoring

Groundwater levels were measured in each borehole using an electric down-hole water-level tape. These levels were measured relative to the surface water (ie. King River or Macquarie Harbour) levels at each site at the time of water sample collection, allowing hydraulic gradients relative to the nearest surface-water body to be calculated. Water levels were also measured after sampling so that hydraulic conductivity values could be estimated for each borehole. Surveying was conducted with chain, compass and spirit level.

Piezometer installation and monitoring parameters are presented in Table 1, and cross sections of the piezometers from the banks and delta are displayed in Figures 8 to 18. Piezometers accessed groundwater in the sediment bank deposits and delta from 50 to 700 cm below the ground surface.

Table 1 Field data from piezometers.

Figure 8 Cross section of Bank R showing piezometers.

Figure 9 Cross section of Bank N showing piezometers.

Figure 10 Cross section of Bank N showing piezometers.

Figure 11 Cross section of Bank H showing piezometers.

Figure 12 Cross section of Bank D showing piezometers.

Figure 13 Longitudinal section of Bank D showing piezometers.

Figure 14 Cross section of South Delta Lobe showing piezometers perpendicular to river.

Figure 15 Cross section of South Delta Lobe showing piezometers perpendicular to harbour

Figure 16 Miscellaneous piezometers from the South Delta Lobe.

Figure 17 Cross section of North Delta Lobe showing piezometers perpendicular to harbour

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Figure 18 Cross section of North Delta Lobe showing piezometers near harbour.

Table 2 Groundwater and surface water chemistry - Field and laboratory parameters.

Groundwater and Surface Water Sampling and Field Analysis

Twenty-four to forty-eight hours after installation of the piezometers, groundwater was extracted from each well and discarded to remove potential contamination introduced during construction and emplacement, and to ensure the collection of a representative groundwater sample.

A 15 mm outside diameter (OD), PVC jerk pump was employed to recover groundwater samples from the 25 mm ID piezometers, and 25 mm OD open-tube PVC bailers were used for the 40 mm ID piezometers. These instruments were flushed/washed with the local groundwater prior to sampling. Wherever possible, 1000 ml of groundwater was taken from each piezometer and stored in two 500 ml LDPE screw-top bottles which had been thoroughly rinsed with the incoming sample. EC, pH and Eh readings were taken in the field on one of the 500 ml aliquot's while the other was divided in two subsamples. The first consisted of a 250 ml sample of unfiltered groundwater stored in an acid-washed HDPE screw-top bottle. The second sample was delivered in stages into the top of a 60 ml syringe containing a Sartorius silica pre-filter and Sartorius millipore 0.45 µm filter in series, and filtered into another 250 ml, acid-washed HDPE screw-top bottle. Acidification requirements were determined on the basis of field pH readings and sample volume (normally 250 ml), and the required volume of reagent grade 1.0 M HNO3 was added by syringe to the filtered sample, after an equivalent volume of sample was quantitatively removed. Details of sample numbers, volumes, pH, EC, Eh, and acid additions are provided in Table 2. Groundwater sample numbers are derived directly from their associated piezometer (ie. DEL-WS8-UU and DEL-WS8-AF represent the Unfiltered-Unacidified and Acidified-Filtered groundwater samples from the delta piezometer DEL-WS8).

All water samples were transferred directly to a large-volume insulated cooler in the field and stored at low temperatures. Samples were maintained at temperatures close to or below their initial temperature until delivered to the laboratory.

Forty filtered/acidified and unfiltered/unacidified groundwater and surface water samples were collected and submitted to Amdel for analysis. Three harbour water samples were taken proximal to piezometers (DEL-WS25 next to DEL-WS2, DEL-WS42 next to DEL-WS12, and DEL-WS45 next to DEL-WS15 during high tide), at the same time as the piezometers were sampled. Samples DEL-WS22 and DEL-WS29 represent duplicates of samples DEL-WS2 and DEL-WS1 respectively, and were taken for BOD analysis and to assist evaluation of laboratory analytical precision.

Measurement of pH, EC and Eh for groundwater at the water table in the delta was conducted along traverse lines over the delta by excavating shallow holes and inserting the probes into the resulting pools of water. The location of the traverses is shown on Figure 2 and results are displayed on Figures 19, 20 and 21. Traverses were designed to coincide with the location of piezometers to permit comparison between surficial and deeper groundwater.

Figure 19 pH of the upper layer of groundwater in the King River Delta.

Figure 20 Electrical conductivity of the upper layer of groundwater in the King River Delta.

Figure 21 Redox potential of the upper layer of groundwater in the King River Delta.

Field Analytical Procedures

A TPS meter and an Ionode Intermediate Junction, epoxy body, glass bulb pH electrode (IJ40) was used to measure the pH of water samples from piezometers, excavations and spot surface water locations. Prior to measurement, the electrode was calibrated using pH 6.88 and pH 4.01 buffer solutions at a similar temperature to the water samples. The same meter and an Ionode ORP electrode were used to measure Eh. Zobells solution was used as a standard: Eh readings of Zobells solution were consistently within ±20 mV of the expected Eh value. A TPS meter and electrical conductivity probe was used to measure electrical conductivity (EC, mS) in each of the samples. Water temperature was measured with a mercury bulb thermometer and the EC probe was calibrated for temperature against a standard solution of KCl.

LABORATORY ANALYTICAL WORK

Water Chemistry

The HDPE bottles containing the groundwater samples were transported in the large-volume, insulated coolers packed with ice. Sufficient ice was used to ensure that some was still present when opening the coolers after transit. Samples were sent to the NATA-registered Amdel laboratory in Adelaide.

All samples were analysed for pH and EC. Acidified samples were analysed for Na, K, Ca, Mg, Cl, SO_4, P and metals and unacidified samples were measured for nitrate, bicarbonate and a selected suite of metals. The metals measured were: As, Sn, Mo, Cr, Zn, Cd, Pb, Ba, Co, Fe, B, Si, Mn, V, Cu, Ag, La, Ni, Y, Al and Sr. For seven of the acidified samples, Se, Sb, Tl and Hg were also measured. Water chemistry results are included in Table 3.

Table 3 Groundwater and surface water chemistry - Analytical results

Sediment Chemistry AND MINERALOGY

Preparation Procedures

Sediment samples were transferred from their insulated field container to a refrigerator, and maintained at 4°C. In order to minimise exposure of sulphide material to air, ≈100g representative subsamples of eighty moist to saturated sediments were placed into plastic Petrie dishes and stored in vacuum desiccators. The samples were dried over a 7-10 day period by maintaining very low internal pressures. Samples that resisted complete dehydration were installed into an oven at 50°C whilst still in the desiccator, and under vacuum. Sediment required for microscopy, XRD analysis, bulk chemical analysis, SEM work and leach tests were all taken from the vacuum-dried subsamples.

Bulk Chemical Analysis

Approximately 20-30 g batches of eighty vacuum-dried sediment samples were dispatched to Amdel (Adelaide) for analysis in 50 ml HDPE screw-top bottles (Table 4). Sediments were subjected to acid digestion and analysed by ICP for Na, K, Ca, Mg, P, Cu, Fe, Mn, Zn, Pb, As, Ni, Cd, Co, Cr, V, Ag, Sn, Mo, Bi and by S. Results for the sediment chemistry are presented in Table 4.

Table 4 Sediment chemistry

Microscopy

Approximately 5-10 g of twenty vacuum-dried samples (Table 4) were placed into circular PVC moulds connected to a glass slide by double-sided tape. Epoxy resin stained with blue dye was poured into the moulds, and the samples returned to a desiccator and placed under vacuum for a few minutes. The desiccator was returned to atmospheric pressure and the epoxy resin left to set for 12 hours. Single polished thin sections were prepared under oil from the consolidated mounts, and the sections were stored with a film of oil to prevent oxidation. A Leitz binocular microscope with facilities for reflected and transmitted light work was utilised for examination.

XRD

10-20 grams of fourteen representative sediments (Table 4) were finely ground under acetone in an agate mortar and pestle. Samples were submitted to the Physics Department at Monash University and analysed using a Scintag Powder Diffractometer with a solid-state Ge detector, and a Cu Kα radiation source. Eleven samples were analysed by conventional X-ray diffraction techniques with 2-100° 2θ scans. Unoriented and 2 μm oriented preparations of three clay-rich samples were subjected to glycolation, and heat treatment to 250°C, 400°C and 550°C. Scans for the clay-bearing samples were routinely 2-70° 2θ. Results are included in the section on mineralogy, and spectra are presented in Appendix 3.

Electron Microprobe Analysis

Two samples, DT-1 and KR-1, were prepared for analysis by microprobe techniques, to further clarify the composition of detrital components Polished sections of these two samples were cleaned in ethanol, carbon coated and analysed in an ARL-SEMQ II probe utilising standardless EDS techniques at the Earth Science Department, Monash University. Analysis was conducted at an accelerating voltage of 15kV and with a nominal beam current of 15 mA. The beam current was adjusted when necessary to maintain an X-ray count of close to 2200/sec, for which the EDS detector and a configuration file had been calibrated. Standardless microprobe analysis is a rapid quasi-quantitative method for determining atomic ratios of a selected suite of elements, and output includes normalised mass proportions of these components as elements or oxides. Loss on ignition (LOI) is not incorporated into the analysis, and therefore the method can only be considered to be semi-quantitative for hydrous or CO_2-bearing assemblages. A configuration file was generated to account for peak overlaps with the elements Na, K, Ca, Mg, K, Si, Al, Fe, Ti, Cr, Mn, Cu, Zn, Ni and S. Probe results are provided in Appendix 4.

A Jeol Superprobe located at CSIRO (Division of Minerals) in Port Melbourne was used to conduct Back Scattered Electron and X-ray mapping of detrital grain boundaries. Analysis was conducted at 15 kV and a beam current of 15 mA, over 400 x 400 or 500 x 600 step areas, with a step increment of 0.5 μm and 100 ms dwell times at each point. Spectrometers were set to detect Fe, S, Cu, Si and Ca.

In Lens Field Emission SEM

Access to an In Lens Field Emission Scanning Electron Microscope (IFESEM; CSIRO Port Melbourne) was secured to assist with detailed evaluation of the chemistry and morphology of surface features and coatings on detrital tailings grains.

Six representative samples of vacuum-dried unconsolidated sediment from DT-1, KR-1, DEL-S9, DEL-WS5-S, DEL-WS12-S and D-S-8 were provided to CSIRO technicians. Samples were removed from their vacuum desiccator, and 10-20 grains were scattered onto a brass mount. A few drops of isopropanol were applied to assist adherence of the grains, and the mount was vacuum dried in a desiccator. The dry sample was coated with a conductive layer of Pt, since this was not expected to interfere significantly with predicted components of the sample. Samples were subjected to accelerating voltage ranging from 15kV to 2 kV, depending on the competing needs of high resolution and reasonably comprehensive semi-quantitative analytical data. The IFESEM was fitted with a thin window EDS detector capable of identifying all elements down to and including Li. Spectral data are provided in Appendix 5 and photomicrographs in Plates 17 to 31.

Leach Tests

Introduction

Two single-stage leach tests with water and dilute sulphuric acid were designed to help assess the likely hydrogeochemical consequences of flushing sulphidic tailings sediments with rain, river or harbour water. A third single-stage extraction test with ammonium acetate was conducted to determine the concentration of metals adsorbed onto grain surfaces. The presence and apparent reactivity of silicate slag in many samples suggested that conventional sequential extraction tests would be of limited use, since the behaviour of variably altered slag in a range of extraction media is unknown. This conclusion appears to be supported by the results. Samples from saturated and unsaturated settings were chosen (Table 4) and submitted to Amdel (Melbourne).

Deionised Water and Dilute Sulphuric Acid

20 gram portions of tailings material from each sample were mixed separately with distilled / deionised water and 0.01 M sulphuric acid (pH ≈ 2.0) in a solid:fluid weight ratio of 1:2. Gentle agitation of the mixtures was continuous for 48 hours. The leachate was removed from contact with the sediment, filtered through a 0.45 μm filter and analysed for Cu, Fe, Mn, Al, Si, As, Sn, Mo, Cr, Zn, Cd, Pb, Ba, Co, B, V, Ag, La, Ni, Y and Sr by ICP-ES with detection limits of 0.01 μg/l. Sulphate was analysed by Ion Chromatography. Analytical results are in Tables 5 and 7. The pH and EC of the leachate was measured five minutes after initial mixing, after 1 and 2 hours, and thereafter on a regular basis. The data for pH and EC are displayed in Tables 6 and 8.

Table 5 Analytical results from distilled water leach

Table 6 pH and EC results from the distilled water leach

Table 7 Analytical results from dilute sulphuric acid leach

Table 8 pH and EC results from the dilute sulphuric acid leach

Ammonium Acetate

5 gram batches of tailings material from each sample were added to 1.0 M ammonium acetate (NH_4OAc) solution in a solid:fluid weight ratio of 1:10 (ref. Kersten and Forstner, 1989). Gentle agitation of the mixtures was continuous for 24 hours. The leachate was removed from contact with the sediment , filtered through a 0.45 µm filter and analysed for Cu, Fe, Mn, Al, Si, As, Sn, Mo, Cr, Zn, Cd, Pb, Ba, Co, B, V, Ag, La, Ni, Y and Sr by ICP-ES with detection limits of 0.01 µg/l. Sulphate was measured by Ion Chromatography. Analytical results are in Table 9. The pH, EC and Eh of the leachate was measured five minutes after initial mixing, after 15 minutes, and at 2 hour intervals thereafter. The plots of pH, EC and Eh against time are displayed in Table 10.

Table 9 Analytical results from ammonium acetate leach

Table 10 pH, EC and Eh results from the ammonium acetate leach

RESULTS

General

Most recent studies of tailings focus on engineered impoundments, and direct comparison between hydrogeochemical processes in such settings and in an active fluvial-deltaic system is difficult. Tailings from the Mount Lyell copper mine are subject to relatively unique processes, such as short and medium-term cyclical drying/wetting, flushing, oxidation, nutrient addition and bacterial modification.

The redox interface between largely oxidised and largely unoxidised sulphidic tailings material is difficult to locate in the field, and appears to have little direct relationship with the current water table. This can be attributed to the following factors;

(i) Fresh sulphidic material, highly oxidised tailings and original sediments are often similarly coated with orange, secondary iron-oxides, and hence display an oxidised appearance.

(ii) Long-term changes in groundwater levels are predicted to have resulted from factors such as operation of the John Butters Power Station, thereby disrupting pre-existing groundwater levels.

(iii) Seasonal, tidal and dam-related river level fluctuations result in significant short-term changes in groundwater levels.

(iv) The sporadic distribution of organic matter and associated anaerobic bacterial activity often results in sulphide precipitation in previously oxidised zones.

For the purposes of this report the tailings are referred to as either saturated or unsaturated, rather than oxidised and unoxidised. While river bed sediments are essentially always saturated, tailings in the banks and delta may be broadly divided into saturated and unsaturated zones. During the winter months, much of the unsaturated tailings are likely to be permanently moist. The classification of tailings based on pore water content is complicated by perched water tables which result from discontinuous clay-rich horizons at various levels in both the sediment banks and delta. The clay layers permit sufficient water to be retained in overlying sediments to prevent significant oxidation of pyrite locally. Plate 6 displays an example of this phenomenon on Bank H. Largely fresh sulphidic material is visible more than 1.5 metres above the present water table, and is surrounded on all sides by sulphide depleted sediment.

Crusted portions of the tailings deposits are believed to represent coarser grained accumulations that have been cemented by metal-oxide rich precipitates. While most surficial tailings deposits display metal-oxide bearing coatings, a coarser grainsize appears to facilitate local lithification by oxides. The distribution of both small and large crusted sections of tailings in both the sediment bank deposits and delta confirms this observation. For example, crusts often develop immediately proximal to dead trees / logs in their downstream shadows on sediment banks, and around log jams / vegetation on the delta. Such settings permit the development of localised low-energy zones which facilitate the deposition of relatively coarse grained sediment.

Morphology and Geology of the Delta

The subaerial King River Delta consists of a broad expanse of low relief, highly oxidised tailings material with irregularly distributed and partially buried logs and occasional anthropogenic waste (Plates 1, 5 and 6). The delta displays a maximum relief of approximately 2.0 m above the harbour water during an average low tide, but the majority exhibits relief of less than 1.0 meter. Typical tidal variations produce vertical water level rises on the order of 30-50 cm, and under low tide conditions the subaerial surface area of the delta is approximately 2.5 square kilometres. Anecdotal evidence indicates that rises in water level up to approximately 1.0 m may occur more than once per year. During these peak flow events, much of the delta is inundated.

The delta is bisected by a narrow channel through which the King River flows (Figure 2), and quasi-perennial and shallow ephemeral channels traverse the surface of both the north and south lobes. These lesser waterways are instrumental in conveying overflowing river water and incident rainfall off the delta toward the harbour.

The north and south portions of the delta appear to display broadly different physical and, therefore, chemical characteristics. In general terms the north delta is comprised of finer grained material than the south, and therefore includes a higher proportion of finer grained sand, clay and organic debris. The physical differences in the delta deposits may be attributed to the relative energetics of lateral transport of sediment at the head of the developing delta. The north lobe of the delta appears to be significantly more sheltered in terms of lateral transport than the south lobe, and hence finer grained fractions have a greater opportunity to settle out. These gross physical/chemical differences are reflected in the groundwater chemistry (see below).

Large sections of the delta, in particular the southern lobe, appear to have accumulated by progressive foreset development during flood events, and these deposits appear to control its gross structure. These foresets are visible due to planation during successive flood events (Plate 7), and display current directions radiating away from the mouth of the King River. Highly irregular relief comprising chaotically distributed megascopic foresets established during peak flow will be sporadically filled with finer grained, horizontally stratified components during the waning phase of a flood event. Successive flood events will remove portions of the earlier deposits. Consequently, the detailed internal structure of the delta is predicted to be extremely complex and locally highly variable in terms of grainsize, composition and the orientation, scale and anisotropy of internal layering. A widespread distinctive laminated horizon identified by EGI (1991c) was not confirmed by this study and, although coherent horizontal stratification is sometimes evident on the scale of metres (especially on the north lobe), it is considered unlikely to be more continuous.

Plate 7 Typical surface expression of foresets on the south lobe of the delta

Plate 8 View looking up the King River on Bank H

In addition to typical silicate- and sulphide-bearing tailings sediment, the delta contains a small but common component of slag, numerous thin layers (<1 mm to 30 mm) of leaf-litter dominated organic debris, irregularly distributed buried and exposed logs, and a minor component of miscellaneous refuse (eg. tyres, cardboard, cans, bottles). Animal bones are not uncommon, and occasionally display a thin surficial, green precipitate that appears to be malachite (copper carbonate).

Wind erosion is reportedly significant during the dry summer months, and small aeolian dunes at the back of the north delta are evidence of this effect. The dunes indicate that wind-borne tailings transport is dominantly to the east. Widespread evaporative crusts developed in local depressions on top of the delta would have the effect of minimising wind-borne transport of tailings and acid-forming material, but significant quantities of unconsolidated surficial sand could be mobilised. The effect of the evaporative crust on retarding recharge to the delta from precipitation is unknown, but could be significant.

Morphology and Geology of River Banks

The majority of sediment contained in the King River overbank deposits is unsaturated, extensively oxidised and dominantly comprised of mine tailings. Based on field and petrographic evidence, the grainsize of tailings material appears to increase downstream, with the delta hosting the coarsest grained debris.

Excavations in the downstream end of Bank M (Locher, 1995; photo's 4.7 and 4.8) revealed that the sediment banks have a strongly layered internal structure resembling a broad, open antiform, with its axis running along the central portion of the bank. These deposits appear to have evolved by progressive draping of sediment onto this geometry. Although lateral continuity of layers for more than tens of metres is unlikely, well developed stratification and shallow dips away from the spine of the bank are predicted to be common features. The downstream ends of each of the four banks examined in this project were distinctly clay-rich, and this is likely to be a common feature of all such deposits.

Puddles, ponds, small lagoons, creeks and swampy ground characterise the landward side of many sediment bank deposits (Plates 8 and 9). These areas often develop permanent or intermittent creeks, and contain highly acid to near neutral flows, depending on local catchments and the internal structure of the banks. Given the moderate to high hydraulic conductivity of the tailings material and relatively low water table, semi-permanent bodies of water situated on the banks (eg Bank H) are direct evidence of (shallow) subsurface aquitards (ie clay dominated layers). Preliminary observations suggest that the internal structure of the banks has significant implications for surface runoff and groundwater discharge, and may exacerbate the rapid release of acid and metals. For instance, the geometry of near-surface clay horizons act to preclude the deep penetration of some precipitation. These discontinuous aquitards permit partial infiltration and then facilitate rapid discharge and accumulation of incident rainfall to shallow pools on the banks. Subsequent evaporation and concentration of acid and metals is likely to be common prior to a surface flushing event which will deliver short-lived but high-volume pulses of acidic surface leachate to the receiving environment (Plate 10).

Plate 9 View of fresh sulphidic tailings on the surface of Bank D

Plate 10 View of the downstream end of Bank H during a period of heavy rainfall

Organic debris comprising buried logs and abundant leaf litter is irregularly distributed throughout the banks. Drilling on banks R and H encountered large logs at several metres depth, and required relocation of piezometers.

Field observations indicate that release of acid and metals from delta and banks will be in the form of quasi-continuous seepage from the saturated tailings accumulations and periodic surficial flushing by rainfall events. The short-term storm / flood runoff events could be producing the most damaging ecological impacts through punctuated release of accumulated/concentrated acid and metals from the surface of the banks and delta.

King River - Bottom Sediments

River bottom sediments provided by Locher (Project 4; Map 5) reveal a predominance of slag and coarse grained sulphidic sediments. The relatively high density of this material has restricted its distribution to the river bottom and the upper portion of the delta. Since the disposal of slag only commenced in 1972, much of it resides in the upper part of the river bottom sequence (Locher, 1995), and the upper 2 metres of the delta.

The occurrence of the slag-rich tailings appears to be fundamental to the formation of the “hardpan” in the base of the King River, and similar cementation processes in other crusted tailings material.

Microbial Activity

Carpenter et al. (1991) identified significant populations of anaerobic bacteria in harbour sediments near the mouth of the King River, and reported that these contained biomarkers indicating the presence of sulphate reducing bacteria. Gaseous emissions from numerous, small point sources were observed on both lobes of the delta (particularly the north) in the tidal interface zone (Plate 11). Field-based flame tests indicated the presence of methane at a few of these sites. This suggests that methanogenic bacteria are flourishing locally at least.

Plate 11 View of the discrete occurrence of a gaseous emission from the delta

Plate 12 View of groundwater seepage from the delta

A strong odour of H_2S was detected in groundwater samples on banks N and H and from the south lobe of the delta (tidal zone) from relatively acid groundwater samples. This gas is likely to have been generated by sulphate reducing bacteria. Elevated concentrations of HS^- are predicted to be present in other less acid water associated with subsurface organic debris and microbial activity. The anomalously low aqueous sulphate concentrations (representing total soluble sulphur) in groundwater samples DEL-WS1, DEL-WD1 and DEL-WS2 are interpreted to reflect microbial sulphate reduction, and pyrite precipitation. $BOD_{(5)}$ analyses (ie. five day biochemical oxygen demand) of relatively reduced groundwater from DEL-WS1 and DEL-WS2 returned results of 21 mg/l and 8 mg/l respectively, supporting the presence of significant bacterial activity.

In the delta, the distribution of subsurface organic debris (leaf litter, wood debris and organic refuse) is highly irregular, and varies laterally on the scale of metres, and vertically on the scale of centimetres. The distribution of subaqueous organic material appears to have a fundamental control on bacterial activity and therefore on groundwater chemistry. Based on the distribution of ultra fine grained biogenic pyrite (framboids) in the delta, sulphate reducing bacteria appear to be widespread proximal to subaqueous organic debris. With more organic debris in the north delta, the groundwater chemistry is generally less acid, and aqueous metal concentrations are generally lower, particularly in the tidal interface zone where sediments are permanently saturated. Biogenic pyrite was also observed on subaqueous organic debris in the sediment banks.

Physical disruption of saturated tailings (eg. excavating, auguring, drilling, installing piezometers) often resulted in the visible release of biogenic pyrite to the water column. Almost complete oxidation of such biogenic pyrite over a period of a few days is believed to be responsible for significant variations between field and laboratory pH and conductivity measurements in some (relatively reduced, unfiltered / unacidified) groundwater samples. Laboratory pH measurements were more acid, EC measurements were higher, and yet dissolved iron concentrations were dominated by ferrous iron. These results indicate that the oxidation of ferrous to ferric iron was not responsible for these changes, and that the dissolution of some acid producing component was implicated.

From these observations we can conclude that natural bioremediation is currently active in both the banks and the delta, and is locally (at least) very effective in lowering the concentrations of acid and metals in groundwater.

Pyrite Oxidation Rate

Relatively rare, thin blankets (1-20 cm) of fresh sulphide-rich tailings are irregularly distributed over the lower portions of some banks and parts of the north delta proximal to the river. Their distribution indicates that deposition occurred after the dam became operational and the mine was closed. It is concluded that they represent river bottom sediments that have been remobilised during peak flow events (ie. 1-2 times / year). Anecdotal evidence indicates that the most recent of such events occurred during August-September 1994. This suggests that significant oxidation of pyritic tailings material takes more than 12 months.

Trace amounts of detrital pyrite trapped in standing dead trees, preserved by the moist, reducing conditions, have been observed on bank R at a level that indicates pre-dam flood transport. Since negligible deposition or erosion of tailings from the top or landward side of bank R is indicated since operation of the power station, and petrographic work indicates little or no fresh pyrite remains on the surface of this sediment bank, it would appear that virtually complete oxidation has taken less than four years.

Samples of fresh pyrite-rich tailings taken from the river edge of the downstream end of Bank N have been placed on top of the bank to assist with a more accurate evaluation of pyrite oxidation rates. Samples were placed in depressions in large logs as well as in plastic containers with porous bases at the beginning of August, 1995.

Hydrology

The banks and delta receive an average annual rainfall of 1800 to 2200 mm (Figure 22). Runoff plus infiltration for the banks and delta is predicted to be close to 70-80%, with a recharge estimated at about 20%. Evapotranspiration will be negligible at present, but may be locally as high as 10%. Some proportion of the runoff and infiltration is ponded on the surface of the banks and delta, and is concentrated by evaporation.

Figure 22 Regional annual rainfall for the study area

Groundwater in the delta appears to be derived from on-shore groundwater sources, and from surface infiltration by rain, river and harbour water. The majority of the delta exhibits less than 1.5 m of relief relative to the average harbour water level, and depth to groundwater in the delta is usually less than 50 cm. Groundwater levels respond rapidly to rainfall, tidal influences and river level changes caused by operation of the power station. Proximal to the tidal interface zone the direction of the hydraulic gradient depends on tidal conditions, and significant variations in river flow conditions are predicted to have a similar effect. Significant seepage from the delta can be observed in the tidal zone at low tide, and groundwater reacts with the atmosphere to produce what are likely to be iron-bearing precipitates (Plate 12).

Groundwater in the sediment banks appears to be derived primarily from infiltration by rainfall and from surface drainage, with lesser contributions from river-margin groundwater sources and local input from the King River. Extensive groundwater seepage from the banks during low flow conditions is evident in photo 5.5 from Locher (1995).

DIMENSIONS OF TAILINGS DEPOSITS

Photographic enlargements of the sediment banks and delta were prepared from Tasmap's 1988 colour aerial photographic coverage of the central west coast of Tasmania. The principal photographs were from Run 26W, frames 1123-144 and 1123-145 at an initial scale of 1:42000. Black and white scaled enlargements were scanned and the digital images analysed to establish the area and perimeter of individual tailings deposits. Field measurements along selected banks and the delta using a chain were conducted to minimise errors introduced by photographic edge distortions. Image analysis determinations of the surface area of each bank and the delta, and the perimeter of each deposit along the King River or Macquarie Harbour are provided in Table 11.

Table 11 Dimensions of tailings deposits

The maximum depth of tailings material in each of the banks studied was determined from a combination of geological logging (auger and drill samples), petrographic work and bulk chemical analysis of sediment samples. When compared with visual techniques, the total Cu, S, Fe and As content of tailings samples appeared to provide a reasonable indication of the origin of the sedimentary material. When visual evaluation was unreliable, the bulk analysis was used to indicate a sample's origin. The following values generally provided a reliable indication of tailings-free sedimentary material: Cu ≤50 ppm, S ≤500 ppm, Fe ≤1.5%, and As <3 ppm.

Volumetric estimates of tailings contained in each surveyed bank were calculated on the maximum depth of tailings as determined from drillhole or piezometer sediment sample chemistry (ie. surface area x max. depth of tailings). Values for the maximum depth of tailings in unsurveyed banks were interpolated from available data. Tonnages of tailings contained in the sediment banks are based on a specific gravity of 1.6 for unsaturated material as determined by Locher (1995). Results are provided in Table 11.

Analytical Data

Hydrogeochemistry

Analyses of groundwater and surface water samples indicate that several elements have the potential to contribute to ecological problems. These primarily include Cu, Fe, Mn, Al, Si, As, Ni, Zn, Hg, Se, Pb and Co. Analytical results are provided in Table 3. The concentrations of key metals in groundwater in the sediment banks and delta are roughly an order of magnitude lower than those in surface drainage from the lease site. However, they are roughly an order of magnitude higher than those measured in the lower King River (MLMRCL data from sites 28 and 29; ref. Figure 23) in 1993 and 1994.

Figure 23 Location of regional water monitoring stations

Aqueous copper concentrations range from below detection limit (BDL) for near neutral groundwater samples from the tidal interface zone on the delta, to a maximum of 8.7 mg/l in highly acidic groundwater from Bank D. Aqueous Cu concentrations in the sediment banks generally increase down the river, with groundwater in the topographically lower banks and river margin of the delta hosting the highest concentrations.

Analytical differences between filtered and unfiltered water samples suggest that Cu is partially particulate (ie. >0.45µm) and partly dissolved (ie. <0.45µm). Fe in groundwater samples is almost totally soluble, and elevated concentrations (0.2 to ≈18.0 mg/l) are widespread in the delta and sediment bank deposits. These concentrations are dominated by ferrous species.

Si is largely soluble in groundwater samples, and dissolved concentrations range from 0.9 to 78 mg/l, with a majority of samples biased toward the higher concentrations. Concentrations of Al are relatively high under acidic conditions, and range from BDL to ≈23 mg/l. Despite locally high clay fractions in some tailings samples, there is little difference in Al concentrations between filtered and unfiltered samples. Aqueous Mn ranges from 0.5 to 22 mg/l, with most groundwater samples containing relatively high concentrations. Mn also appears to be almost exclusively in soluble form.

Concentrations of soluble As range from BDL to 0.33 mg/l, but are commonly near the upper value in both the delta and sediment bank deposits. While the As is sometimes largely particulate, in other samples it is dominantly soluble. The As values are often several times higher than ANZECC guidelines for the protection of aquatic ecosystems. Soluble Ni concentrations in groundwater are sporadically elevated, and range from BDL to 1.02 mg/l. The Ni is dominantly in soluble form in water samples. Aqueous Zn concentrations are relatively high in the sediment banks deposits and acidic delta samples, and range from BDL to 5.03 mg/l. Zn is largely in a soluble form in groundwater samples. Cd appears to be largely soluble in groundwater samples, and displays elevated concentrations in acidic portions of the north delta (0.04 to 0.13 mg/l). Pb is largely in soluble form in groundwater samples, and ranges from BDL up to 0.19 mg/l. Elevated Pb concentrations are rare and are largely confined to the north delta in the more acidic samples. High Co concentrations in largely soluble form are found in most of the acidic groundwater in the delta, and range from BDL to ≈2.0 mg/l.

Se, Hg, Sb and Tl analyses were only conducted on a suite of seven groundwater samples. As predicted by EGI (1991c), Se concentrations are relatively high for some samples (eg. DEL-WS2: 106 µg/l). Although the limited results were highly variable, the distribution of Se suggests that elevated aqueous concentrations may be favoured by reducing and near-neutral conditions. ANZECC guidelines for the protection of aquatic ecosystems provide a recommended criteria for total Se in fresh water of 1-10µg/l. Concentration ranges for Hg were also variable, with a single high of 9.4 µg/l in groundwater within bank D. Sb and Tl concentrations were uniformly low, with values for Sb ranging from BDL to 2.0 µg/l, and for Tl from BDL to 3.3 µg/l. Aqueous Ag concentrations are BDL for all groundwater samples.

Detectable bicarbonate concentrations were recorded in four reduced groundwater samples from the delta in the tidal interface zone (1-87 mg/l). These values are believed to reflect the influence of microbial activity, but are likely to have been significantly lowered by exsolution of CO_2 during transport to the laboratory. Loss of H_2S gas is also likely to have lowered total sulphur concentrations in samples where a strong odour was detected (ie. DEL-WS12, DEL-WD12 and N-W3 and H-WD2).

Nitrate was detected in groundwater samples on both the banks and delta. Concentrations are generally low and range from BDL to 23.6 mg/l. The unpredictable pattern of nitrate concentrations suggests that it is strongly influenced by the haphazard distribution of organic debris. Harbour water samples (DEL-WS25, DEL-WS45, DEL-WS42) contained between 0.4 and 565 mg/l nitrate, indicating that some nutrients could be supplied to groundwater in the delta by brackish harbour water. Ammonia and nitrite were not analysed, but should be included in future work, especially for highly reduced groundwater samples (eg. tidal zone on delta). All of the groundwater samples from piezometers on the north lobe of the delta were analysed for phosphorous, to identify potential limiting factors for the growth of bacterial populations. Analysis was conducted on filtered / acidified samples, and a single on-scale reading of 0.2 mg/l was obtained in DEL-WD1. This is regarded as relatively high for soluble phosphorous, and being in the tidal zone may reflect contributions from the harbour water.

Chloride concentrations range from BDL to 4380 mg/l, and are significantly elevated in the delta groundwater. Na, Ca, Mg and SO_4 are similarly elevated in delta groundwater samples relative to sediment bank deposits, indicating the likely interaction of sea water in the delta. This is predicted to be the result of periodic inundation of the delta by harbour (brackish) water. This process appears to be responsible for significant differences in the chemistry of the delta groundwater relative to the sediment bank deposits. For example, periodic inundation is likely to be responsible for a net increase in sulphate, chloride and nutrients in groundwater in the delta. Despite this chemical signature of periodic inundation of the delta, K is conspicuously low in all but the three most reduced (ie. sulphate poor) delta groundwater samples. This suggests that K is being removed by mineral saturation reactions (eg. jarosite).

In the delta, reduced, near neutral groundwater samples associated with organic-rich material and bacterial activity generally display the lowest aqueous metal and acid concentrations, although Fe, Si, Mn and As remain elevated. This observation highlights the importance of naturally occurring bioremediation as a crucial process in controlling water quality.

The chemistry of groundwater in the banks and delta is highly variable, and appears to be at least partly controlled by local differences in tailings composition, particularly the organic and clay content. Data for pH, EC and Eh were recorded for the water table (upper 10 cm of groundwater) along selected traverses on the delta (Maps 7 to 9 and Tables 2 and 3). Groundwater varies from highly oxidised (530 mV) and acidic (pH=2.54) to near neutral (pH=7.10) and relatively highly reduced (-57 mV). Field measurements also revealed low (400 µs/cm) to very high electrical conductivities (≈30000 µs/cm), with the higher values reflecting interaction of brackish harbour water with the delta sediments (eg. DEL-WS1, DEL-WD1, DEL-WS2, DEL-WS3, DEL-WS15). No consistent variation in groundwater chemistry was noted with distance from the harbour water, in either pH, EC or Eh. Significant increases in the EC of groundwater at the water table were noted to be empirically related to the local abundance of clay material, possibly indicating enhanced cation exchange.

The chemistry of groundwater in the south lobe of the delta is less variable and more acid than in the north lobe, probably reflecting a lower organic content and less microbial activity in the former. These results clearly indicate that pore water in the delta is not always near neutral, as suggested by EGI (1991c). Furthermore, this study has demonstrated that despite a paucity of sulphides in the upper 10 cm of the delta tailings that there is significant acid forming capacity in these sediments.

Acid Generation

Groundwater at the water table in the delta displayed distinct differences to deeper groundwater as measured from nearby piezometers (Maps 7 to 9 and Table 2). The upper layer of groundwater is generally highly acid, with the magnitude of pH increases with depth being dependent on local tailings composition. Increases of 2-3 pH units were recorded from the water table to deep (1-1.5 metres) groundwater in the north lobe of the delta (eg. DEL-WS8; 3.93 to 6.5 over 120 cm). The groundwater at the water table in the north lobe also displays significantly lower conductivity values than deeper groundwater from piezometers. Increases in EC on the order of 2-5 times are recorded with depth (eg. DEL-WS8; 700 µs/cm to 3800 µs/cm over 120 cm). These changes are also associated with progressively reducing conditions with depth (eg. DEL-WS8; 256 mV to -2 mV over 120 cm). Similar trends in pH and Eh are also evident in the south lobe, but no field EC readings were taken from groundwater from the piezometers.

Chemical differences between the water table and deeper groundwater suggests that acid production in the upper layer of groundwater in the delta may be controlled by processes other than direct sulphide oxidation. Similar conclusions can be drawn from data in EGI(1991c) on the chemistry of groundwater from the delta. Their results indicate that in the laboratory the pH of pore-water becomes slightly more acid over time, while the EC decreases significantly. In addition, it is evident from the study by EGI (1991c) that surface layers in the delta contain more acid-generating material than less oxidised, deeper material, and that the relatively rapid decrease in the pH of extract water (not in contact with sediment) over 2 days suggests that some reduced aqueous iron and/or sulphur species are highly reactive.

Despite an apparent paucity of pyrite, there is abundant acid forming material in the upper few centimetres of the tailings material in both the delta and the river banks. Rainwater accumulating in puddles on the surface of the delta exhibits pH values in the range of 2.9 to 3.5 within seconds to minutes, and surface and near-surface runoff from the tailings banks behaves similarly. This acidity is probably enhanced by periodic dissolution of acid forming material by rainwater, and subsequent evaporation in disconnected pools on both banks and delta. When the pools combine to form runoff during heavy and persistent rainfall, short-term acid contributions to the river and harbour are significant.

The migration of groundwater containing acid forming material in the form of reduced aqueous species, and its subsequent near-surface oxidation is consistent with chemical gradients observed in groundwater, and the latent acidity of surficial tailings during rainfall events (refer to Discussion - Acid Production).

Sediment Mineralogy and Mineral Chemistry

General

Sedimentary deposits in the King River and delta are comprised of pre-mine siliceous detritus and overlying siliceous and sulphidic tailings residue from the copper concentration process at the Mount Lyell mine. Both the sediment banks and delta are dominated by tailings material. Pre-mine and tailings sediment in the overbank deposits, and the upper 1-4 metres of the delta are coated with a thin veneer of orange iron oxyhydroxide.

Pre-Mine Sediments

Petrographic data on original sedimentary material were compiled from R-C1-730-745, R-C1-580-600 and DEL-C1-420-550. Pre-mine sediments are comprised of subangular to subrounded silt and fine to coarse-grained sandy detritus containing silicic volcanics (25 vol.%), vein quartz (25 vol.%), microcrystalline silica (15 vol.%), metasedimentary rock fragments (25 vol.%), assorted accessory crystal components (3-7 vol.%) and miscellaneous organic debris (1-5 vol.%). Volcanic detritus is almost exclusively silicic, and can include partially resorbed, euhedral quartz phenocrysts, patches of microcrystalline silica, and subordinate muscovite. Vein quartz fragments display crack-seal, space-filling and mosaic textures, and are generally barren. Microcrystalline quartz fragments probably represent volcanic debris, but a metasedimentary origin is also possible. Deformed meta-sedimentary material such as sericite-chlorite±quartz±epidote schists, siltstones, sandstones and quartzites are present. Accessory crystal components include fine to coarse grained clinopyroxene (trace to 5 vol.%), variably weathered k-feldspar and/or plagioclase (trace to 2 vol.%), fine to medium grained anhedral magnetite (trace to 1%), fine to coarse grained ilmenite (trace to 1%), subhedral to anhedral fine grained zircon (trace to 1%), and traces of variably retrogressed hornblende, chromite and spinel. Fragments of carbonate and primary sulphides were conspicuously absent from these samples, but rare biogenic pyrite framboids and rims of biogenic pyrite on iron and/or carbon-rich grains were found in DEL-C1-420-550. This sample indicates that there is a mass transfer of metals from the tailings downward into earlier sediments, and that caution should be exercised when using chemical parameters such as bulk Cu or S concentrations to clarify sedimentary origin.

Mine Tailings

The tailings sediment comprises rock and vein fragments from highly altered and mineralised sections of the Cambrian Mount Read Volcanics. At Mount Lyell the volcanics are dominated by felsic to mafic lavas, breccias, lapilli tuffs and volcaniclastics, and the overlying sequence includes siltstone and conglomerate (Solomon, 1989). Much of the copper mineralisation is syngenetic in origin, and developed by exhalative hydrothermal processes on or near a Cambrian seafloor. Secondary assemblages developed during ore formation include quartz, chlorite, sericite, carbonate, and sulphides. The deposits have been subjected to multiple phases of deformation and upper greenschist facies regional metamorphism (Solomon, 1989). Metamorphic assemblages include biotite, chlorite, K-feldspar, epidote, albite, sphene and carbonate.

The grainsize of tailings disposed to the East Queen River over the life of the mine ranges from <1 µm to ≈1000 µm, with median values ranging from 10-80 µm (Locher, 1995).

Tailings

Tailings sediments comprise fragments of ore gangue, vein quartz, felsic volcanics, metasedimentary material and slag, and assorted crystal components in highly variable proportions. The following relative abundances in detrital components was determined from the petrographic study:

DETRITAL COMPONENTS	**VOL.%**
Rock Fragments	
Gangue	40-80
Felsic Volcanics	0-10
Metasedimentary	1-10
Vein Quartz	1-15
Slag	0-60
Crystal Components	
Pyrite (FeS_2)	0-10
Chlorite ($(Fe,Mg)_6Al_4Si_4O_{10}(OH)_8$)	0-3
Muscovite ($KAl_3Si_3O_{10}(OH,F)_2$)	0-3
Carbonate ($MeCO_3$)	0-5
Magnetite (Fe_3O_4)	0-3
Ilmenite ($FeTiO_3$)	0-1
Chromite ($FeCr_2O_4$)	0-Trace
Zircon ($ZrSiO_4$)	0-Trace
Organic Matter	1-5 %

Fragments of ore gangue are quartz-rich rocks containing varying proportions of fine to coarse grained foliated to decussate aggregates of chlorite (chamosite; Appendices 3 and 4, analyses A4.43 to A4.48) and white mica (muscovite-2M; Appendix 3), as well as euhedral to subhedral pyrite±chalcopyrite crystals (Plate 13). Other sulphides including sphalerite, galena, and bornite are also observed occasionally in these fragments. Fine to coarse grained, euhedral to subhedral carbonate crystals (often Mn-rich siderite; Appendix 4, analyses A4.34 to A4.42) are occasionally distributed throughout the gangue fragments. In some situations, sulphides and carbonates are completely encased by a silicate matrix, and in other cases are exposed to fluid interaction along fragment boundaries. Some of the gangue fragments are coarse grained aggregates or crystals of chlorite, with lesser chlorite+muscovite or muscovite alone.

Plate 13 Reflected light photomicrograph of sample DT-1

Plate 14 Reflected light photomicrograph of sample DT-1

Other rock fragments include mica-schists and quartz-mica schists, and these either represent foliated gangue or metasedimentary material. Sandstone and siltstone detritus is relatively rare. Schistose rocks include chlorite, chlorite+sericite, and muscovite+quartz ±chlorite varieties, and can include accessory phases such as carbonate, biotite, magnetite, rutile, ilmenite, zircon, sphene, epidote and pyrite. Altered silicic volcanic fragments are dominated by microcrystalline quartz, with minor retrogressed feldspar phenocrysts and varying proportions of sericite. Quartz vein fragments displaying fibrous crack-seal, irregular mosaic, granoblastic and open-space growth textures are common. Accessory sulphide components within the vein material are rare, but can include pyrite±chalcopyrite.

Slag represents slightly in excess of 1% of the total volume of mine waste disposed of to the Queen River, and appears to be almost exclusively restricted to the river bottom and upper delta deposits. In the upper sections of the river bottom sediment pile, the slag comprises at least 40-50 vol.%, but probably averages from 1-3 vol.% in the upper 1-2 m of the delta. The slag is a grey-brown-black, subrounded to subangular glassy product derived from the smelting of copper ore. Microprobe analyses of anhydrous slag indicate that it is largely a Fe-Cu sulphide saturated iron-silicate glass, containing lesser proportions of Al, Mg and K (Appendix 4, analyses A4.1 to A4.7). Chemical data in Table 4 highlights the iron-rich nature of the slag, and clearly demonstrates that it is also relatively enriched in Zn, Cu, Co, Pb, Mo and Cr (refer section of Leach Tests). Fracturing to produce characteristically cuspate margins and cuspate shards, the slag generally contains significant proportions (2-5 vol.%) of rounded, immiscible sulphide-melt inclusions (Fe-Cu-S; Appendix 4, analyses A4.16, A4.25 to A4.28, and Plate 14) and rare euhedral crystals with the morphological and optical properties of olivine. Based on the chemistry of the slag, this phase is probably fayalite (Fe_2SiO_4). The anhydrous slag composition (Appendix 4, analyses A4.1 to A4.7) provides a general indication of the bulk chemistry of fresh tailings material.

Post depositional modification of the slag is widespread, particularly in samples that are at least partially subaerial, and can be intense in places (KR-1 below). Alteration commences with hydration of the outer layers of the slag. Microprobe data indicate that this involves a major depletion of iron. This is supported by the development of intense red staining on the inside of plastic bottles containing water-saturated slag-rich samples, and the formation of "hardpan" layers (see below). Modification proceeds by the development of concentric zones of hydration layers, which often mimic the initially cuspate borders of the slag fragments. When a Cu-Fe-sulphide melt blebs are encountered during slag hydration, the alteration front progresses around the sulphides, leaving unaltered blebs surrounded by concentric hydrated layers (Plate 14). Some time later, the sulphides succumb to oxidation and disappear (Plate 14). Plate 18 displays a cross section through the finely layered hydrated shell of a slag fragment. Microprobe data indicate that slag hydration and Fe depletion is accompanied by losses of Ca, Mg and K, and relative increases in Si, Al, S, Ti, Cu and Zn (Appendix 4 and analyses A4.9 to A4.15 and A4.19 to A4.22).

Pyrite varies from coarse grained (50-100 µm) angular detritus (Plate 13) to ultra-fine grained (<0.1µm) framboidal crystals of biogenic origin forming circular clusters and grain coatings (Plate 15). Primary pyrite occurs as both individual crystals and as a common component of gangue rock fragments. Rounded and irregular inclusions of chalcopyrite are not uncommon in pyrite. Chalcopyrite rarely occurs as discrete grains, and is usually associated with gangue-bearing rock fragments, commonly containing quartz+chlorite+pyrite±muscovite. Subordinate sulphides often intimately associated with chalcopyrite include sphalerite, sometimes galena and rarely bornite. Magnetite is occasionally found adjacent to chalcopyrite.

Plate 15 Reflected light photomicrograph of sample DEL-WS3-S

Plate 16 Reflected light photomicrograph of sample DEL-WS3-S

Plate 17 IFESEM photomicrograph of sample DT-1

Plate 18 IFESEM photomicrograph of sample DEL-WS12-S

Plate 19 IFESEM photomicrograph of sample DT-1

Plate 20 IFESEM photomicrograph of sample DT-1

Plate 21 IFESEM photomicrograph of sample DEL-S9

Plate 22 IFESEM photomicrograph of sample DEL-WS5-S

Plate 23 IFESEM photomicrograph of sample DEL-WS12-S

Plate 24 IFESEM photomicrograph of sample DEL-WS12-S

Plate 25 IFESEM photomicrograph of sample D-S-8

Plate 26 IFESEM photomicrograph of sample DEL-WS5-S

Plate 27 IFESEM photomicrograph of sample DEL-WS5-S

Plate 28 IFESEM photomicrograph of sample DEL-WS12-S

Plate 29 IFESEM photomicrograph of sample DEL-WS12-S

Plate 30 IFESEM photomicrograph of sample DEL-WS12-S

Plate 31 IFESEM photomicrograph of sample DEL-WS12-S

Plate 32 Back Scattered Electron and X-Ray mapping image from microprobe analysis

Plate 33 X-Ray mapping image from microprobe analysis

Large discrete crystal fragments of carbonate are widespread throughout saturated tailings. Limited analytical work indicates a predominance of Mn-rich siderite (Appendix 4 and analyses A4.34 to A4.42). A range of accessory crystal components are observed, sometimes associated with a small proportion of country rock, but generally as discrete crystals. These include magnetite, ilmenite, chromite, zircon, spinel and hematite.

All of the tailings samples examined contained organic debris, ranging from pollen, seeds, leaf litter and wood fragments. The organic content of tailings varies significantly (<1 vol.% to >10 vol.%), but is estimated to average ≤1 vol.%. SEM work revealed the presence of amorphous carbon material providing a weak binding medium for grains of sediment from water saturated, reduced samples. This substance may be the product of microbial activity on decayed plant matter, and may provide the substrate for biogenic pyrite precipitation (see below).

Although significant chemical degradation of the tailings is occurring, little evidence of these changes is evident in most grains. Signs of alteration and dissolution are scant, presumably due to relatively high rates of fluid flow and rapid dissolution, but there is a clear indication of secondary precipitation. The widespread orange iron-oxide coating is the best evidence of chemical modification. Grains in unsaturated tailings, particularly those in slag-rich samples, generally display thicker iron-oxide coatings than in saturated samples. The distribution of the iron-oxide coatings is a direct reflection of the maximum extent of oxidation of reduced groundwater, and has no direct relationship to the extent of sulphide oxidation. For example, almost 2 m of pre-mine sediments on Bank R are iron stained.

Saturated Tailings

Most of the detrital pyrite (and other sulphides) in saturated tailings deposits appears very fresh. Progressive destruction / dissolution of pyrite is generally only evident in the highly reduced, water saturated samples where the dissolution process has been reversed and preserved by biogenic sulphide precipitation. It most saturated samples, oxidation appears to be focussed on the margins of pyrite grains, and groundwater flow rates appear to be too rapid to preserve degraded rims or sulphate by-products.

Small quantities (trace to 1 vol.%) of framboidal biogenic pyrite are evident in several of the more reduced, organic-rich, water saturated sediment samples (eg. DEL-WS12-S, DEL-WD8-S, DEL-WS3-S, DEL-C1-420-550, R-C1-250-280). Biogenic pyrite occurs as circular concentrations of framboids, and as thin veneers lining the margins of silicate-bearing rock and sulphide fragments which are initially coated with amorphous organic matter (Plate 15). Biogenic pyrite is also observed lining and disseminated throughout organic fragments (leaf litter and wood). The organic coating on grains appears to be providing a reduced substrate for sulphide deposition. Rare examples of biogenic chalcopyrite can be seen in DEL-WS12-S and DEL-WS3-S, where delicate botryoidal growth habits are preserved on the margins of silicate grains (Plate 16).

Crystal fragments of carbonate minerals were observed in water saturated samples, but were absent from the unsaturated zone. Despite being in contact with relatively acid groundwater, carbonate was still present in many saturated samples, but appeared to have undergone complete dissolution in nearby unsaturated zones.

Geological logging of river bottom sediments conducted by Locher (1995) indicated an abundance of slag, and this was supported by recent drill samples collected by Locher (Project 4) and examined in this study (Appendix 1 and Figure 5). One polished section was prepared from this material from upstream of the Teepookana Bridge (Sample KR-1; Figure 24). KR-1 represents a “hardpan” or strongly cemented slag-rich layer that develops on the upper surface of the river bottom sediments. The distribution of this layer as mapped by Locher (1995) is shown in Figure 24. The KR-1 hardpan is comprised of 35-40 vol.% slag, 40-45 vol.% siliceous gangue rock fragments, 5-10 vol.% vein quartz grains, and roughly 5% coarse, fresh pyrite±chalcopyrite grains. Other accessory crystal components (total ≤5%) include siderite (manganese-rich solid solution), magnetite, ilmenite and zircon. Most detritus is coated with a relatively thick layer of iron-oxide. The role of this coating around carbonate grains for inhibiting acid neutralisation is unknown, but may be important.

Figure 24 Surface characteristics of the King River Bed

The cementation process appears to result from the mobilisation of iron from the slag and its precipitation as iron-oxide around grain boundaries (Plates 13 and 14). This has been facilitated by the increase in molar volume associated with progressive hydration of slag fragments (Plate 14), which dramatically reduces porosity. Additional data on the process accompanying slag hydration were provided by Back Scattered Electron (BSE) and X-ray mapping techniques. X-ray maps across the hydrated rim of three slag grains identified some elemental depletions and enrichments associated with hydration (Plates 32 and 33). The delicate banding in the hydrated rim is comprised of zones of silica, iron and copper enrichment with X-ray statistics indicating a strong association between Fe and S in the grain in Plate 32, and between Cu and S in the grain in Plate 33. More work would be required to determine the specific environmental processes controlling chemical episodes preserved in the rims. However, the distribution of hardpan layers in the King River bed, the distribution and degree of slag hydration, the chemical changes accompanying hydration, and the chemical reactions revealed in saturated river bottom samples all suggest that oxidation is the key factor in alteration and partial dissolution of the slag, as well as in the formation of the hardpan. Successive wetting and drying episodes may also play some role, but no clear evidence for such processes is evident in the unbroken concentrically zoned hydration layers surrounding slag fragments, and it is unlikely that the hardpan is ever unsaturated. Sufficient oxygen may be available from turbulent river water during low flow periods to cause oxidation.

Unsaturated Tailings

Petrographic work confirmed field observations from panned concentrates that although highly depleted, minor to trace amounts of fresh pyrite and chalcopyrite are often still present in near-surface unsaturated tailings material both in the banks and delta. Relatively thick coatings of iron-oxide are observed around some of these sulphides in unsaturated samples (Plate 13). It is not known to what extent these coatings inhibit sulphide dissolution, but results from leach tests suggest that they may be ineffective in this regard (Tables 5 and 7; Sample DT-1).

Limited chemical data in Table 4 indicates a general depletion of Cu and S in the bank sediments relative to the delta, supporting the likelihood of higher rates of leaching from the unsaturated bank deposits.

Secondary Phases

XRD analysis of Fe-rich samples (ie. DT-1, KR-1) failed to clarify the nature of the iron-oxide precipitate coating most sediment grains. Numerous iron-oxide, iron-sulphate and related hydrates were evaluated, but the only likely assemblage (goethite) consistent with the spectral data has peaks overlapping with other silicate minerals. X-ray spectra from EDS analysis on the IFESEM also indicated that the precipitate was dominated by Fe and O. From these data it may be concluded that the orange precipitate is likely to be predominantly goethite.

All unbroken grains examined by IFESEM were coated with an iron-oxide precipitate (?goethite). While the form and extent of the goethite precipitate varies, the crystal habit is largely as thin bladed aggregates less than 1 µm in length (Plates 19 to 26). Almost all X-ray spectra recorded from these iron-oxide surface coatings identified smaller but additional persistent peaks for Cu and C (Appendix 5; all spectra). No discrete Cu±Fe±O±C bearing phases were identified visually. The relative proportion of the Fe, O, Cu and C peaks varied significantly, but Cu and C peaks were qualitatively noted to be higher from sediment samples from saturated and reduced settings (eg. DEL-WS12-S). Peak counts for Cu and C were observed to accumulate rapidly during the initial seconds of analysis, and taper off during the remaining portion of the 100 second count time. This appeared to indicate that the Cu±Fe±O±C material was a thin surface coating that was largely removed by beam damage early during analysis. Accelerating voltages were lowered to test this hypothesis, and the intensity of Cu and C peaks were qualitatively noted to rise. The Cu±Fe±O±C material is believed to represent one or more surficial secondary phases, with the most obvious possibilities including a Cu±Fe carbonate (eg. malachite), a Cu±Fe oxide (eg. cuprous ferrite) intermixed with amorphous organic matter, or an adsorbed Cu±Fe bearing organo-metallic complex.

Secondary calcite was detected overgrowing goethite in some samples from saturated settings (Plate 27), and this may be attributed to reaction of lime (CaO) derived from tailings processing with CO_2 from bacterial activity.

Although no distinctive clay morphologies or diagnostic spectra were recorded, subordinate peaks for Al, Si, Ca, Na and Mg were often recorded from thick goethite surface coatings (Plate 20, Spectra A5.2), suggesting intimate admixtures with accessory secondary clays.

The desiccation cracks evident in Plates 17, 19 and 20 are believed to be artefacts of the sample preparation procedure, since little evidence for extensive fracturing of the iron-oxide coatings of silicate or slag fragments was evident from petrographic work. This process may have significant implications for processes which result in drying of the tailings material. Dehydration fracturing of the carapace of grains may accelerate fluid infiltration and further reaction (refer to the Leach Tests).

Grain coatings and intergranular cement of amorphous, structure less carbon was noted from IFESEM work on samples from water saturated, reduced settings in the delta. This material may be one of the products of bacterial activity.

In thin section and under the IFESEM, pyrite grains were often found to be strongly pitted. Examples of such pits are provided in Plates 28 and 29. The cores of these pits (large and small) were identified as being dominated by iron-oxides, with the suggestion of minor sulphur (ie. sulphates) indicated from X-ray spectra (Appendix 5, A5.8). It is possible that the oxidation of pyrite commences in these small holes, and progresses outwards. This is supported by the thinly layered rim of iron-oxide developed on the outer margin of one of these pits (Plate 30) adjacent to fresh pyrite.

Leach Tests

General

Five vacuum-dried sediment samples were subjected to three single-step leach tests. Samples KR-1, DEL-WS12-S and DEL-WS3-S were taken from water saturated environments, the first from the bed of the King River, and the latter two from the delta. Samples DT-1 and H-S7 were collected from unsaturated zones on the delta and Bank H, respectively. Analytical results are presented in Tables 5 to 10.

Distilled Water

Single-step leach tests using distilled water on sediments from saturated and unsaturated environments demonstrated unequivocally that high concentrations of acid and metals can be released from tailings material that has been subjected to drying (± minor oxidation) by interaction with rainwater (Tables 5 and 6). The following observations can be made:

- Interaction between all of the tailings sediment and distilled water generated significant acid immediately. The lowest pH was generated by samples from unsaturated environments.

- The pH of all leachates increased slightly over time, in conjunction with a significant rise in the EC. These results may indicate the influence of acid consuming dissolution reactions.

- Aqueous sulphate concentrations are not directly proportional to leachate acidity, suggesting that other processes may be responsible for at least some of the latent acidity in tailings material (refer to Discussion).

- The highest concentrations of most metals were derived from the slag-rich samples KR-1 (≈40 vol.% slag) and DT-1 (≈15-20 vol.% slag), strongly supporting observations regarding the high reactivity of the slag.

- Very high Cu and Zn concentrations were extracted from KR-1 (5.5, 24 mg/l) and DEL-WS3-S (6.5, 5.6 mg/l)

- Very high concentrations of Si, Fe and Al were extracted from all samples except DEL-WS12-S.

- Some of the elevated metals in leachate samples were not identified as significant in groundwater. For example, relatively high concentrations of Zn (up to 24 mg/l), Co (up to 16 mg/l) and Ni (3 mg/l) were recorded. These results are believed to be partly attributable to the high proportion of slag in some samples, as well as variations in redox conditions between the natural and artificial leaching processes.

- The highest Fe concentrations were associated with the most acid leachates, being derived from the two samples from unsaturated settings. At the pH indicated in Table 6, the high Fe concentrations in most leachates (up to 30 mg/l) suggest the predominance of ferrous aqueous species.

- The highest Mn concentrations are associated with sediments from saturated environments, and may reflect rapid dissolution of residual manganiferous siderite (carbonate) which is not present in most unsaturated sediment samples.

- The highest EC readings were found in water saturated samples from the delta. It is most likely that relatively salt-rich pore water trapped in original samples is responsible.

Dilute Sulphuric Acid

Similar trends recorded for the water leach tests were found with dilute sulphuric acid extractions. Results in Tables 7 and 8 show that:

- Very high concentrations of metals can be mobilised by low pH fluids, in particular Fe, Si, Al, Cu, Zn, Co, Mn and Ni.

- As would be expected, dilute acid is more effective at dissolving metals than water, although some inconsistencies were observed. Higher Co, Zn and Ni concentrations in leachate from the water tests compared to the acid leachates suggests that sediment samples in the latter trials contained lower abundances of slag. This may be due to density separation of samples in transit and incomplete mixing at the laboratory.

- The pH of all leachates increased significantly over time, in conjunction with a general decrease in the EC. It is possible that the precipitation of iron-oxide in association with acid consuming reactions may be partly responsible for this trend.

- The lowest pH values were generated by samples from unsaturated environments, reflecting the trends observed with the water leaches.

- The highest concentrations of Cu, Zn and Co were again derived from the slag-rich sample KR-1.

- The highest Mn concentrations remain strongly associated with sediments from saturated environments.

- Similar iron concentrations (26 mg/l) were observed from all samples except DEL-WS12-S, and these values were broadly comparable with those from the water leaches. Aqueous Al values were significantly higher than for the water leach, often by a factor of 10.

Ammonium Acetate

Ammonium acetate was used as a cation exchange extractant, designed to displace metals that were adsorbed to grain surfaces. Aqueous concentrations from this series of leaches cannot be directly compared to the water and acid leaches since the solid:fluid weight ratio was 5 times lower. Results in Tables 9 and 10 indicate that:

- Very little metal, including copper, occurs as adsorbed species on grain surfaces. Expressed as the proportion of total copper in the samples, the adsorbed component in the leach samples varies from 0.01 to 0.57 wt.%. Similar ranges were evident for Mn, Co, and Zn (0.1 to 4 wt.%).

- The largest concentration of adsorbed Cu, Zn, Co and Ni were mobilised from the slag-rich saturated sample KR-1. It is not known whether this can attributed to adsorption processes alone, since the reactivity of altered slag with the extractant has not been established.

- The pH, EC and Eh of the leachate remained essentially constant throughout for all samples except H-S7, where some elevated EC values were recorded.

- The results for Cu suggest that the Cu±Fe±O±C matter on grain surfaces identified from IFESEM work is likely to be a precipitate, rather than an adsorbed compound.

Sources of Metals in Groundwater

The source of aqueous copper is mainly detrital chalcopyrite (≈ 85-95 wt.%) and surface coatings of Cu±Fe±O±C precipitates on detrital grains (≈1-10 wt.%). The proportions are based on the assumption that all Cu released during acid leaches was from surficial Cu-bearing precipitates. Lesser contributions may be from Cu-Fe sulphide blebs in slag fragments, copper in silicate slag, and minor amounts in accessory primary sulphides and biogenic chalcopyrite.

Iron probably comes from chlorite, pyrite, siderite, goethite, chalcopyrite, Cu-Fe sulphide blebs in slag fragments, (iron-silicate) slag and magnetite. Smaller contributions may come from other sulphides such as sphalerite, as well as ilmenite and chromite. Goethite, chlorite, magnetite, sphalerite, ilmenite and chromite are unlikely to contribute significantly to soluble iron concentrations, but water chemistry is predicted to be strongly influenced by the other assemblages.

Aluminium is present in silicates such as chlorite, muscovite, pyrophyllite, biotite, feldspar, spinel and slag. Since the most Al-rich groundwater is found in the banks, slag is not a primary source. Alteration of chlorite and possibly muscovite are implicated in the elevated concentrations of aqueous aluminium in groundwater from both the banks and delta.

Sulphur occurs in a wide range of assemblages, including pyrite, chalcopyrite, sphalerite, galena, sulphide phases in slag, sulphur in the slag, bornite (covellite and chalcocite) and barite. With the exception of barite, sphalerite and galena, all of these phases will contribute significantly to aqueous sulphur concentrations. Brackish harbour water may also be a source of sulphur (sulphate ions) to groundwater in the delta.

The vast majority of manganese is hosted by manganiferous siderite (oligonite (Fe,Mn(CO_3)); solid solution between siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$), with minor contributions from slag, and possible additions from trace concentrations in pyrite. The relatively high aqueous concentrations of manganese are believed to be primarily due to the low pH of groundwater and surface water, and the high solubility of carbonates under acid conditions.

Cobalt, nickel and arsenic are predicted to be largely present as trace components in pyrite, and will be released during pyrite oxidation. Cobalt and nickel are also found in elevated concentrations in slag, from which they may be readily released. Cadmium is probably present as a trace substitute for zinc in sphalerite, and the chromium in chromite and, to a lesser extent, fuchsite (chromium-muscovite). The low solubility of these elements is likely to influence aqueous metal concentrations. Zinc occurs principally in sphalerite, and lead is dominantly in galena, although significant contributions from slag are possible. Neither sphalerite nor galena appear to be as soluble as pyrite, and therefore aqueous zinc and lead concentrations in groundwater are relatively low.

Barium will be present primarily in barite and as a trace element in feldspar. While barite is largely insoluble, feldspar will be reasonably reactive in acidic environments.

Selenium is a common trace element in chalcopyrite is this is probably its primary source. Aqueous selenium concentrations appear to be influenced by redox state, with reducing conditions favouring enhanced solubilities. This may be an artefact of a limited data set. The sources of mercury, antimony and thallium in groundwater are unknown, but are assumed to be tailings related.

The major component of the tailings is silica, which is derived from quartz, assorted aluminosilicates (chlorite, muscovite, biotite, feldspar) and slag. In general, Si concentrations in groundwater are close to saturation with respect to microcrystalline quartz (refer to geochemical modelling). Sodium, potassium and chloride in groundwater are largely supplied by brackish harbour water. Calcium and magnesium are also largely from harbour water, with lesser contributions from carbonates (eg. calcite, dolomite and siderite), lime and possibly chlorite.

MODELLING

Hydrogeology

Parameters for Groundwater Flow Modelling

Hydraulic conductivity values were calculated from water level recovery tests performed on many of the piezometers after sampling. Data from Banks R, N, and H were analysed using the Hvorslev recovery test method for an unconfined, partially-penetrating well (Hvorslev, 1951). The hydraulic conductivity of the sediments around each well was assumed to be isotropic for the purpose of the Hvorslev analysis (Table 12). In Bank D and the north and south lobes of the delta, where recovery rates of water levels were too rapid to measure by hand, a minimum hydraulic conductivity value was estimated based on the amount of groundwater removed and a recovery time of about 20 seconds. Results and equations used are included in Table 12. Data used to determine the value T_o for each Hvorslev analysis are included in Table 13 and Figure 25.

Table 12 Hydraulic conductivity values

Table 13 Slug test calculations

Figure 25 Graphical analysis of hydraulic head for the delta and banks

Hydraulic conductivity values of sediments in the higher banks, Banks H, N, and R were significantly lower ($K = 7x10^{-8}$ to $1x10^{-6}$ m/s; Table 12) than those estimated for sediments further downstream, Bank D and the north and south lobes of the delta ($K \approx 1x10^{-4}$ m/s; Table 12). Some of the variation in hydraulic conductivity values measured in the higher banks is probably due to smearing of clay particles in the monitoring interval during drilling. This would reduce the apparent hydraulic conductivity of the sediments immediately surrounding the boreholes. Since the average grain size of sediments appears to increase downstream, the general trend of increasing hydraulic conductivity values from the higher banks ($K \approx 10^{-6}$ m/s) to the lower banks and the delta ($K \approx 10^{-4}$ m/s) indicated by more rapid water level recovery rates is reasonable. The effective porosity of all sediments was estimated to be 35% (0.35), a value typical of many unconsolidated silt and sand-rich deposits.

Groundwater levels were measured in each piezometer before sampling. Since these were measured relative to the nearest river or harbour surface water level at the same time, the levels could be used to calculate horizontal and vertical hydraulic gradients between individual piezometers and between the piezometers and the river or harbour (Figures 26 to 32).

Figure 26 Bank R - hydraulic gradient and fluxes

Figure 27 Bank N -hydraulic gradient and fluxes

Figure 28 Bank H - hydraulic gradient and fluxes

Figure 29 Bank D - hydraulic gradient and fluxes

Figure 30 South lobe of delta - hydraulic gradient and fluxes perpendicular to river

Figure 31 South lobe of delta - hydraulic gradient and fluxes perpendicular to harbour

Figure 32 North lobe of delta - hydraulic gradient and fluxes perpendicular to harbour

Overall, groundwater flow in the sediment banks was towards the river. Horizontal hydraulic gradients in the sediments banks were lowest in Bank R (0.007-0.06 m/m towards the river; Figure 26) and Bank D (0.006-0.02 m/m towards the river; Figure 29), and highest in Bank N (0.06-0.14 m/m towards the river; Figure 27) and Bank H (0.01-0.08 m/m towards the river; Figure 28). Horizontal hydraulic gradients away from the river were measured in one piezometer in Bank R and one piezometer in Bank D. These piezometers were near the river bank and the hydraulic gradient reversal probably indicates a lag in water level response in the piezometer to changing river levels rather than indicating hydraulic conditions in the sediment banks in general.

Horizontal hydraulic gradients between the south lobe of the delta and the river ranged from 0.001-0.006 m/m towards the river (Figure 30) indicating the potential for groundwater flow from the delta to the river. However, hydraulic gradients from the south lobe towards the harbour were very low and variable, ranging from -10^{-3} to 10^{-4} m/m (Figure 31) indicating only minimal potential for flow under these tidal conditions. Water levels in the transect of piezometers on the north lobe of the delta indicated that, under rising tide conditions, groundwater flow in the north lobe was still towards the harbour, with horizontal hydraulic gradients typically in the 0.001-0.003 m/m range. Under conditions in the field, water at the harbour / delta interface was often largely fresh (ie. river water with relatively low EC values), and therefore the density differences due to saline harbour water are likely to be minimal.

Approaches to Modelling

Two approaches were used to calculate groundwater flow rates and chemical fluxes within the saturated zone of the sediment banks and delta to the King River and Macquarie Harbour. These approaches included 1-dimensional steady-state groundwater flow modelling based on Darcy's Law and 2-dimensional steady-state groundwater flow and solute transport modelling using the numerical model FLOTRANS (Guiger et al., 1995).

Darcy Flow Modelling

The 1-D form of Darcy's Law (Eqn. i) was used to estimate the Darcy flux from sediment banks R, N, H, and D to the King River (Figures 26 to 29), from the south lobe of the delta to the King River (Figure 30) and from the north and south lobes of the delta to Macquarie Harbour (Figures 31 and 32).

$$q_l = -K\frac{dh}{dl} \qquad \text{(i)}$$

where: q_l = Darcy flux or specific discharge (m/s)

K = hydraulic conductivity (m/s)

dh/dl = hydraulic gradient (m/m) where l = x (horizontal gradient) or

l = y (vertical gradient)

Hydraulic conductivity values measured or estimated from water level responses (Table_12) were used as field-measured hydraulic gradients (Figures 26 to 32). For Banks R, N, H, and D, the resulting Darcy flux values were used to estimate water fluxes from the sediment banks into the river across a 1 m wide (bank length) by 2 m long (river bottom) discharge face (Figures 26 to 30). A discharge face of 1m wide by 1 m long was assumed for the contact of the King river and Macquarie Harbour with the delta.

The average linear velocity of groundwater between individual wells and between the banks or delta and the harbour was estimated using Equation ii. These values could then be used to estimate travel times of groundwater within the sediment banks and delta.

$$\bar{v}_l = \frac{q_l}{n} \qquad \text{(ii)}$$

where:

v_l = average linear velocity of groundwater (m/s)

q_l = Darcy flux or specific discharge (m/s)

n = effective porosity

Two-Dimensional Steady-State Groundwater Flow and Solute Transport Modelling

The numerical model FLOTRANS (Guiger et al., 1995) was used to model 2-dimensional, cross-sectional, steady-state groundwater flow and solute-transport between Bank H and the river and between the south lobe of the delta and the river. The model is based on the following 2-D groundwater flow equation (Eqn. iii) and the 2-D advection dispersion equation (Eqn. iv).

$$\frac{\partial h}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial h}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) = 0 \qquad \text{(iii)}$$

$$\frac{D_{xx}}{R}\frac{\partial^2 C}{\partial x^2}+\frac{D_{yy}}{R}\frac{\partial^2 C}{\partial y^2}-\frac{\bar{v}_{xx}}{R}\frac{\partial C}{\partial x}-\frac{\bar{v}_{yy}}{R}\frac{\partial C}{\partial y}=\frac{\partial C}{\partial t} \qquad \text{(iv)}$$

where: K_{xx} = horizontal hydraulic conductivity (m/s)

K_{yy} = vertical horizontal hydraulic conductivity (m/s)

R = retardation factor (1 + (ρb /n) K_d)

h = hydraulic head (m)

C = solute concentration in groundwater (g/m^3 = mg/l)

D_{xx} = hydrodynamic dispersion coefficient (parallel to x) (m^2/s)

D_{yy} = hydrodynamic dispersion coefficient (parallel to y) (m^2/s)

v_{xx} = average horizontal linear velocity of groundwater (m/s)

v_{yy} = average vertical linear velocity of groundwater (m/s)

n = effective porosity

ρb = bulk density of saturated porous medium (g/m^3)

K_d = distribution coefficient (solid vs aqueous concentration)

Similar boundary conditions were used for each of the problems modelled with FLOTRANS. In each case, the boundary furthest from the river was assumed to be a no-flow boundary, as was the base of the modelled domain. The top of the model domain was defined as a constant flux boundary, with a recharge rate of 0.002 m/d, approximately 20% of annual precipitation. The boundary at the contact between surface water and groundwater was a constant head boundary extending for 1 or 2 m into the King River.

In each case, hydraulic conductivity was assumed to be isotropic and homogeneous within the domain. Initially these values were based on field estimates but they were later refined during calibration and sensitivity analyses. Sensitivity analyses were performed in conjunction with calibration steps primarily to determine the effects of varying hydraulic conductivity values and recharge rates on the resulting configuration of the water table.

Solute transport modelling in Bank H and the south lobe of the delta perpendicular to the King River was based on the final “best-fit” 2-D groundwater flow models (Appendix 6, Figures A6.1 and A6.5). In both cases, a constant concentration of solute (50 mg/l) was maintained at the water table boundary and the solute was assumed to behave conservatively within the flow system (ie. non reactive, retardation factor (R) = 1). The initial solute concentration in the domain was set at 0 mg/l. The solute transport models were run for 4000 days (Bank H) and 1000 days (south lobe). Results of the 2-D groundwater flow and solute transport modelling are included in Appendix 6.

For both Bank H and the south delta, the groundwater flow models were relatively insensitive to varying recharge rates from about 10-50% of precipitation, however, the best fit for both models was found with a recharge rate of 0.002 m/d. The recharge rate was assumed to be constant between the banks and the delta. The flow models were, however, extremely sensitive to variations in hydraulic conductivity.

Bank H

Using the average of the field measured values for hydraulic conductivity in Bank H (K = 1×10^{-7} m/s), the water table rose several metres over measured hydraulic head values. Only when hydraulic conductivity was increased to about 5×10^{-6} m/s was the mounding of the water table minimised, and hydraulic head values close to those measured in the field were reproduced (Appendix 6, Figure A6.1). The increased value for hydraulic conductivity is not difficult to reconcile if we consider that smearing of clays may have occurred during borehole drilling. However, it does indicate that hydraulic conductivity values for the high sediment banks (Banks R, N, and H) are probably about an order of magnitude greater than those calculated from the 1-D Darcy Flow modelling (Figures 26 to 28).

Fluxes from Bank H to the river, calculated from the 2-D groundwater flow model, are on the order of 40 litres/day per linear metre of sediment bank (Appendix 6, Figure A6.2). As in the 1-D Darcy flux model, discharge was assumed to occur over a discharge face of 2 m^2. Fluxes from the 2-D modelling are about 2 orders of magnitude greater than those calculated from the simple 1-D Darcy flux model (≈0.5 litres/day), however, if the calculated Darcy fluxes are corrected to account for the higher hydraulic conductivity of the sediment bank, the fluxes from the 1-D (25 litres/day) and 2-D modelling (40 litres/day) are similar.

The average linear groundwater velocity calculated from the 2-D modelling was 9.7×10^{-2} m/d in Bank H (Appendix 6, Figure A6.3). Based on this value, the average residence time of groundwater with a 15 m travel path through the saturated zone would be on the order of 6 months and that with a 30 m travel path would be over 1 year.

Solute transport modelling at Bank H indicates that solute concentrations near to the river edge (eg. in piezometer H-W1) would attain steady state conditions after about 1 to 1.5 years (Appendix 6, Figure A6.4) and that it would take only a month or two after entering the groundwater flow system for a conservative solute to begin discharging to the river.

South Lobe of Delta - Perpendicular to the King River

In the south lobe of the delta, the estimated hydraulic conductivity value of 1×10^{-4} m/s (12 m/d) and the assumed recharge rate of 0.002 m/d produced a reasonable fit to the hydraulic head measured in the piezometers perpendicular to the King River (Appendix 6, Figure A6.5).

Fluxes from the south lobe of the delta to the river, calculated from the 2-D groundwater flow model, are on the order of 100 litres/day per linear metre of delta/river interface (Appendix 6, Figure A6.6). Discharge in the 2-D model was assumed to occur over a discharge face of 5 m^2 whereas discharge in the Darcy flux model was assumed to occur over 1 m^2. Fluxes calculated from the 1-D Darcy flux model ranged from about 20-50 litres/day, which if taken over a 5 m^2 discharge area would range from 100-250 litres/day. Again, the fluxes calculated from the 1-D and 2-D modelling are similar and indicate significant discharge from the delta to the river under the conditions present during monitoring.

The average linear groundwater velocity calculated from the 2-D modelling was 8.1×10^{-2} m/d in the south lobe of the delta (Appendix 6, Figure A6.7). Based on this value, the average residence time of groundwater with a 50 m travel path through the saturated zone would be on the order of 2 years and that with a 100 m travel path would be at least 3 to 5 years.

Solute transport modelling indicates that solute concentrations at a piezometer located in the delta about 15 m from the river bank (eg. DEL-WS9) would attain steady state conditions after about 1.5 to 2 years (Appendix 6, Figure A6.8) whereas concentrations about 60 m from the river bank would take about 2.5 to 3 years to reach steady state conditions.

Conclusions from Hydrogeological Modelling

The major conclusions drawn from the 1-D and 2-D groundwater flow modelling and the 2-D solute transport modelling are:

- Calculated hydraulic conductivity values in the higher banks (Banks R, N, and H) are probably 10 to 50 times too low. This is most probably due to smearing of clays in the sediments during piezometer installation. More realistic hydraulic conductivity values for these sediments banks are likely to be on the order of 10^{-6} m/s.

- Hydraulic conductivity values are higher in the lowest sediment bank (Bank D) and the north and south lobes of the delta. Based on water level recovery times, the hydraulic conductivity of these sediments is likely to be on the order of 10^{-4} m/s.

- Groundwater flux from Bank H to the King River is estimated to be between 25 and 40 litres/day/linear metre. The discharge face was assumed to extend 2 m into the King River. It is considered likely that groundwater fluxes from banks N and R, and intervening banks, would be similar to those determined for bank H.

- Groundwater flux from the south lobe of the delta to the King River is estimated to be between 100 and 250 litres/day/linear metre over a discharge face assumed to extend 5 m under water. This area may be excessive, and groundwater discharge to the river would decline proportionally as the discharge face is reduced. If the discharge face extended only 1 m under water, the fluxes would be on the order of 20-50 litres/day/linear metre.

- Groundwater fluxes from the delta to the harbour were estimated only from the 1-D Darcy Flux modelling. The calculated fluxes were highly variable because of the large range of hydraulic gradients measured along the north and south delta transects. For the north delta, fluxes ranged from 10 to 90 litres/day/m^2 into the harbour, whereas in the south delta, hydraulic gradients indicated that water was flowing into the delta from the harbour at fluxes of up to 70 litres/day/m^2.

All of the modelling results presented above assume steady state conditions, however, water levels in the King River and Macquarie Harbour fluctuate significantly in response to power station requirements and storm and tidal influences. Therefore, the calculated fluxes are only valid for the conditions at the time of monitoring, but they indicate that there is the potential for significant groundwater flow to occur from the sediment banks and the delta to the King River and Macquarie Harbour. These fluxes provide the basis from which to estimate loading of contaminants from the tailings-rich sediments to these water bodies.

Detailed monitoring to provide time-series data showing the response of hydraulic head in the sediment banks and delta to changing river and harbour levels throughout the year would be required to calculate groundwater fluxes under different hydraulic conditions.

Geochemistry

Introduction

The geochemistry of the groundwater and sediment was modelled for several reasons:

(i) test the quality of the analytical data for groundwater samples,

(ii) identify the predominant aqueous species in the groundwater,

(iii) predict the saturation states of minerals, and

(iv) provide insight into whether equilibrium models are sufficient to model the interaction between sediment and groundwater in the banks and delta.

The modelling package chosen was MINTEQA2 and it was used to calculate distributions of aqueous species and mineral saturation indices using the measured groundwater compositions. MINTEQA2 was chosen over others (eg. EQ3NR/EQ6, SOLVEQ/CHILLER, THERMO) because it has a more extensive database of mineral and aqueous species likely to be important in sulphidic mine tailings. MINTEQA2 is a combination of the programs MINEQL (mathematical methods and computer code) and WATEQ (database of thermodynamic properties for mineral, aqueous and gaseous species). It was developed by the United States Environmental Protection Agency and IBM-PC versions are freely available on the World Wide Web.

Several pieces of information are necessary as input to the program. Temperature was input as 10°C for all runs because the ambient temperature during sampling in the field was usually 9°C to 11°C. Input values of pH and Eh were those measured in the field for each sample. Element or aqueous species concentrations in mg/l were input after adjusting for dilution during acidification and recalculation to species appropriate for MINTEQA2 (eg. As is input as H_3AsO_3 and/or H_3AsO_4). There are many options available with MINTEQA2; however, the most straightforward calculations were chosen in order to be able to interpret the results more reliably. Ionic strength was calculated from the modelled distribution of species, inorganic carbon (alkalinity) was not specified, mineral species were not allowed to react (dissolve, precipitate, adsorb/desorb) in any of the model calculations and the Davies equation was used to estimate activity coefficients for aqueous species. It was necessary to specify redox couples for elements with variable valence states, so the program would include all appropriate minerals and aqueous species in its calculations. This was problematic in some cases as the program would not always converge within the maximum number of iterations (200). Nitrogen and vanadium were problem elements. Co-, Sn-, Mo- and La-bearing species are not present in the MINTEQA2 database. Adsorption models were not included because of time constraints and the results of the leach tests provide evidence that adsorption is negligible in the sediment analysed.

Calculations were made for most of the analysed groundwater samples, except for a few that lacked field-measured pH and Eh. For each sample, a distribution of aqueous species and mineral saturation indices for all minerals within the database were calculated. An example output file is shown in Appendix 7. The results are summarised below.

Quality of the Analytical Data for Groundwater Samples

The quality of the analytical data was tested by calculating charge balances from the measured groundwater compositions and calculated distribution of species. The charge balance is expressed as:

$$\left[\frac{\sum anions - \sum cations}{\sum anions + \sum cations}\right] \times 100 \qquad \text{(v)}$$

In all cases, there was a calculated excess negative charge, ranging from <1% up to 89%. There is no obvious reason for the excess of anions; however, there is a rough correlation with measured sulphate concentration and pH. Large charge imbalances are usually associated with high sulphate concentrations and low pH.

The most likely source of uncertainty is the sulphate concentrations. The other major anion, chloride, was reanalysed by AMDEL after initial calculations showed charge imbalances. The results for chloride (Table 3) are considered to be reliable. Measured metal concentrations in unacidified and acidified, filtered samples were usually similar, also indicating reliability. Errors in the concentrations of major cations (Na, K, Ca, Mg) are unlikely to be high enough (up to an order of magnitude) to explain charge imbalances. The sulphur concentrations are given in terms of sulphate, and it is possible that the sulphur existed as species with other valence states (eg. S(IV), S(-II)). Calculations were made using Eh measured in the field. If the actual values were lower (more reduced conditions) or the groundwater were not at equilibrium, then it is possible that some of the sulphur was present as sulphite or sulphide, leading to improved charge balances. The amount of sulphate necessary to be present as sulphide to give charge balance was calculated to be <1% to approximately 95%, depending on the sample.

Predominant Aqueous Species

Metals can exist in water as many aqueous species and the type(s) of species can affect mineral solubility, adsorption/desorption behaviour and possibility bioavailability. The predicted predominant aqueous species are given below for the metals measured and detected in the groundwater samples. The species included in the database are listed in brackets after each element. Only a selected set of elements are discussed.

Aluminium

(Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3(aq)$, $Al(OH)_4^-$, $Al(SO_4)^+$, $Al(SO_4)_2^-$)

The predicted predominant aqueous species of aluminium depend on pH and sulphate concentration. The aluminium hydroxide species are predicted to predominate in most cases, except for high sulphate concentration, low pH samples such as in Bank D, where about 80% of the aqueous aluminium is present as Al-sulphate species.

Arsenic

($H_4AsO_3^+$, H_3AsO_3(aq), $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-},
H_3AsO_4(aq), $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-})

In the north side of the delta samples the predominant aqueous species is predicted to H_3AsO_3(aq); however, in the banks (D, H, N and R) and the more oxidised samples of the south side of the delta, the predominant species is $H_2AsO_4^-$ or in some cases near equal concentrations of reduced and oxidised arsenic species.

Cadmium

(Cd^{2+}, Cd-chlorides, Cd-hydroxides, Cd-sulphates, Cd-sulphides)

The speciation of cadmium is dependent on pH, chlorinity and sulphate, sulphide and total cadmium concentrations. No one species of cadmium is predicted to predominate over all samples. Mixtures of Cd^{2+}, Cd-chloride and Cd-sulphate species are predicted to be present, depending on the sample.

Chromium

(Cr^{2+}, Cr^{3+}, Cr-hydroxides, Cr-chlorides, Cr-sulphates, Cr-nitrate, Na-chromate)

Chromium was not detected in many samples, and most of them were unfiltered and unacidified. In sample 3 from Bank D (D-W3; filtered and acidified), the highest measured Eh, the predominant chromium species was predicted to be Cr^{3+}.

Cobalt

(Co^{2+}, $Co(OH)^+$, Co^{3+})

Cobalt species are not included in the MINTEQA2 database; however, calculations with EQ3NR for sample DEL-WS9 predict that Co^{2+} is the predominant aqueous species.

Copper

(Cu^+, Cu^{2+}, Cu(I)-chlorides, Cu(II)-chlorides, - hydroxides, -sulphate, -bisulphide)

The speciation of aqueous copper is controlled by pH, redox, chlorinity and sulphate, sulphide and total copper concentrations. Copper was not detected in the groundwater samples from the north side of the delta. The predominant copper species predicted in the groundwater samples from the south side of the delta are mostly Cu^{2+} and $CuSO_4$(aq), although in one sample (DEL-WS17) $CuCl_2^-$ and Cu^+ were predicted to predominate. In all of the copper-containing samples from the sediment banks (D, H, N, R), Cu^{2+} and $CuSO_4$(aq) were predicted to predominate, although Cu^+ may be an important aqueous copper species in the more reduced samples (eg. Bank N; sample N-W2).

Iron

(Fe^{2+}, Fe^{3+}, Fe(II)-sulphides and Fe(II)- and Fe(III)-chlorides, -hydroxides, and -sulphates)

Despite the many possible aqueous species for iron, the predominant ones were invariably predicted to be Fe^{2+} and $FeSO_4$(aq), for both sides of the delta and all banks studied.

Lead

(Pb^{2+}, Pb-chlorides, -sulphides, -sulphates)

Aqueous lead is predicted to be distributed amongst several species, but Pb^{2+} and $PbSO_4$(aq) made up more than 50% of the total lead in all cases.

Mercury

(Hg^{+}, Hg_4^{2+}, Hg-chlorides, -hydroxides, -sulphides and -sulphate)

Mercury concentrations were measured in seven samples and detected in four: North side of the delta (sample DEL-WS9), south side of the delta (sample DEL-WS14), Bank D (sample D-W3) and Bank R (sample R-WD1). In all samples Hg(aq) was predicted to predominate, although in the sample from Bank D, $HgCl_2$(aq) may be important.

Selenium

(HSe^{-}, $HSeO_3^{-}$, SeO_4^{2-}, Se(-II)-, Se(IV)- and Se(VI)-metal species, as well as protonated and deprotonated derivatives of the non-metal species)

Selenium concentrations were measured in seven samples, and detected in five. In a sample from the north side of the delta (sample DEL-WS2), HSe^{-} was the predominant species, but in all other samples from the north and south side of the delta and Bank H, $HSeO_3^{-}$ was predicted to be the predominant species.

Zinc

(Zn^{2+}, Zn-chlorides, -hydroxides, -bisulphides, -sulphates, -bicarbonates, -selenate)

In all samples, Zn^{2+} and Zn-sulphate species were predicted to predominate, with the exception of DEL-WS2 (north side of the delta), in which Zn^{2+} and $ZnCl^{+}$ were predicted to predominate.

Mineral Saturation States

Mineral saturation states were calculated as part of the output from MINTEQA2. They are useful for indicating what minerals might be dissolving or precipitating into or from the groundwater, or controlling the groundwater composition. The calculations are based on an equilibrium model, so the results are only an indication, as kinetic factors may inhibit approach to equilibrium.

North Lobe of the Delta

The minerals which are commonly close to saturation (saturation index = log (Q/K) = 0±1) are: $Al(OH)_3$ (amorphous), chalcedony, cristobalite, hydrapatite (in P-bearing groundwater), amorphous silica, vivianite (Fe-phosphate), $ZnSiO_3$, wairakite, goethite/lepidocrocite, calcite/magnesite (in carbonate-bearing groundwater), talc, leucite, celestite, gypsum/anhydrite, Fe-vanadate and SbO_2 (in Sb-bearing groundwater).

The minerals which are commonly supersaturated (saturation index > 1) are: Barium, Ba-arsenate, ferrous-hydroxychloride, magnetite/hematite, cuprous-ferrite, quartz, aluminium-hydroxysulphate, alunite, diaspore, halloysite, leonhardite, albite/K-feldspar, pyrophyllite, muscovite, laumontite, montmorillonite and Na-, K-, Mg- and Ca-nontronite. In particular, the nontronite minerals were usually supersaturated by 10 to 20 orders of magnitude (10 < saturation index < 20). In addition, some of the clay minerals (eg. halloysite, leonhardite, muscovite (sericite), pyrophyllite, laumontite) were also predicted to be supersaturated by up to 10 orders of magnitude or more. The sulphate-bearing minerals may not be supersaturated, or at least as much as predicted, due to the uncertainty in the predicted concentrations/activities of sulphate aqueous species.

South Lobe of the Delta

In the south side of the delta, the minerals which are close to saturation (index = 0±1 log unit) are: Aluminium hydroxysulphate, boehmite, goethite/lepidocrocite, iron hydroxychloride, gypsum, amorphous silica, selenium metal (in Se-bearing groundwater), Fe-vanadate, and in some cases, gibbsite, diaspore, anhydrite, albite, laumontite, cuprite, cupricferrite, barium arsenate. The biggest difference relative to the samples from the north side of the delta is that aluminium-bearing minerals were less saturated/supersaturated in the south side of the delta.

The minerals predicted to be supersaturated were similar to those predicted in the north lobe of the delta. The most supersaturated minerals were the nontronite and clay minerals. Other silicates, eg. feldspar, were undersaturated in general.

Bank D

The predicted saturated and supersaturated minerals are much the same as in the south lobe of the delta. The magnitude of saturation is much less (up to 10 log units for the nontronite species), with Fe-bearing, clay and other silicate minerals being less supersaturated or undersaturated. Cuprous ferrite is near saturation and cupric ferrite is well undersaturated, in contrast to the copper-bearing groundwater of the delta. The sampled groundwater are all unsaturated with respect to goethite/lepidocrocite, again in contrast to the delta groundwater. This reflects the much lower pH (2.5-3.0) in Bank D, compared to those measured in the delta (5.5 < pH < 7.1).

Bank H

Predictions of mineral saturation indices were similar to Bank D, except for copper-sulphide minerals which were close to saturation or supersaturated. Sample H-WS2 had a higher pH (5.7) than the 3 other samples from Bank H, and this is reflected in aluminium-bearing minerals being saturated to supersaturated.

Bank N

Sample N-W1 was predicted to be supersaturated with many Al-, Fe- and Cu-bearing minerals, but the other 3 groundwater samples from bank N were similar with respect to mineral saturation as samples from Banks D and H.

Bank R

Most minerals were predicted to be undersaturated in the groundwater samples from bank R. Exceptions were cuprous ferrite, barite, nontronite minerals and pyrophyllite.

To summarise, the groundwater in the banks were unsaturated or less supersaturated with respect to many minerals, compared to the groundwater in the delta. The low profile banks (D and H) were closer to the delta groundwater than those of the high profile banks (N and R). The most likely reason for the differences is the groundwater in the banks is normally more acid and oxidised.

Controls on Groundwater Composition

The modelling indicates that groundwater compositions are controlled by a complex set of minerals and processes. Some elements appear to be controlled by mineral solubilities and equilibrium processes, while others are controlled either by unknown minerals or kinetic reactions.

There are two elements that may be controlled by mineral solubilities and equilibrium processes: Si and Fe. Both elements may not be directly important to water quality, but they can affect the precipitation or dissolution of other more toxic elements, eg. Cu incorporated into copper-iron minerals and Al incorporated into aluminium-silicate minerals. Aqueous silica is predicted to be close to saturation with amorphous silica. This is consistent with petrographic observations of microcrystalline silica in many sediment samples. Aqueous iron in many samples is close to saturation with goethite/lepidocrocite. One of these phases likely comprises much of the iron coatings observed on detrital mineral grains. Other iron-bearing minerals are either supersaturated or undersaturated, eg. magnetite and hematite are predicted to be supersaturated and pyrite and other iron sulphides are highly undersaturated. The iron sulphides may not be so undersaturated if the model estimates of aqueous sulphide/sulphate ratios are too low or the measured redox potentials (Eh) are too high.

Many elements are supersaturated with respect to one or more minerals. Groundwater are predicted to be supersaturated with respect to copper, with a cuprous ferrite solid phase predicted to precipitate. This is consistent with the observation (IFESEM/EDS analysis; Appendix 5) that copper is present in the iron oxide mineral coatings (Appendix 5).

DISCUSSION

Acid Production

The variations in chemistry between deep and shallow groundwater in the delta is thought to be related to oxidation of the upper layer of groundwater (10-15 cm) by diffusion of oxygen from the atmosphere. Oxidation of aqueous ferrous iron will initiate precipitation of ferric oxyhydroxides, thereby producing acid. Decreases in aqueous metal concentrations (ie. EC) will result from precipitation of iron-oxyhydroxides. Similar processes are expected to be occurring in the sediment banks. Oxidation of ferrous iron and precipitation of ferric oxyhydroxides not only describes the widespread iron-oxide staining and gradients in the groundwater chemistry, but may also explain the widespread acidity of some tailings-rich sediments that do not appear to contain significant amounts of pyrite or ferrous sulphate.

The general process of sulphide oxidation and acid production may be represented by the following equilibria based on pyrite oxidation and dissolution. Detrital pyrite in the tailings deposits is sporadically or continuously exposed to oxygen from the air, and decomposes to ferrous iron, sulphate and acid according to the following simplified reaction:

$$FeS_2 + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$
(vi)

Much of the groundwater in the delta and banks contains high ferrous iron concentrations, suggesting that this reaction is currently proceeding. As groundwater levels fluctuate, ferrous ions can be transported, for example, to higher levels in the delta. As the groundwater retreats, pores and grain surfaces will remain surrounded with groundwater containing the ferrous iron in the unsaturated zone. Oxidation of the iron in this residual water may be represented by the reaction:

$$Fe^{2+} + 0.25\ O_2 + H^+ = Fe^{3+} + 0.5\ H_2O \qquad \text{(vii)}$$

This reaction is slow, but may be catalysed by bacterial activity. High concentrations of ferric iron are unstable and the iron will tend to precipitate, eg., as ferric hydroxide:

$$Fe^{3+} + 3\ H_2O = Fe(OH)_3(s) + 3\ H^+ \qquad \text{(viii)}$$

The combination of the reactions (vi) - (viii) produces 4 moles of acid for every mole of pyrite.

Partial dehydration of ferric hydroxide generates the ubiquitous orange Fe-oxide coatings over grain surfaces throughout the tailings deposits and pre-mine sediments:

$$Fe(OH)_3 = FeOOH + H_2O \qquad \text{(ix)}$$

Water coming into contact with the oxidised surface layers of sediment in the delta and banks become quite acidic (pH = 2.5-3). Although this process is not understood, it may be due to hydrogen ions being liberated from the iron oxyhydroxide coatings. FeOOH (goethite/lepidocrocite) likely precipitates as water evaporates from pore spaces leaving H^+ trapped or adsorbed onto ferric oxyhydroxide films. Later near-neutral rainfall displaces some of the H^+ into solution forming acid water on contact. The water would be expected to have a low EC compared to the initial groundwater, due to the highly oxidised nature of the new solution and the low solubility of ferric oxyhydroxides at pH higher than approximately 2. There are other oxidation reactions that may be instrumental in lowering pH, eg., those that involve gaseous and aqueous species such as H_2S, CH_4, HS^-, and NH_4^+. No associated decrease in EC would be expected from such reactions.

If these acid-forming reactions are occurring in the subaerial tailings sediments, the variations in groundwater elevation for the mass transfer of acid and metals (as acid re-enters the groundwater) is important. In addition, the precipitation reactions will tend to reduce the porosity and permeability of surficial tailings deposits, particularly in the delta. Permeability decreases due to iron-oxide precipitation/cementation may be partly responsible for the flooding of farmland at the mouth of the King River.

Periodic and rapid rises and falls of the river system due to operation of the dam on the King River could be contributing to a more rapid acid-generation cycle and more rapid flushing of acid out of the sediment banks. This is likely for several reasons:

(i) regular lowering of the water table enhances drying and oxidation of the sediments,

(ii) rapid water table level fluctuations facilitate the transfer of aqueous ferrous ions into the upper, oxidised portions of sediment banks where further acid is generated, and

(iii) regular lowering of the river dramatically increases the horizontal hydraulic gradient of groundwater in the sediment banks, thereby increasing discharge rates.

Current Impact of Tailings on Water Quality

Contributions of metals and acid from stored tailings to the King River and Macquarie Harbour may be estimated from three categories of data:

(i) groundwater discharge from the banks and delta,

(ii) surface runoff from the banks and delta, and

(iii) interaction between the groundwater / river water and the river bottom sediments.

Quantitative estimates of loadings from groundwater discharge are presented below; however, they do not reflect the transient nature of water flow in the banks, river and delta. Continuous monitoring data would be necessary to properly evaluate the effect of episodic surface runoff during prolonged rainfall events. The reactivity of slag-rich material, and the potential of river bottom sediments to contribute significantly to acid and metal pollution was recognised during the course of this study. Although the leach tests indicate that high concentrations of metals and acid can be provided by slag-rich material, the extent of periodic oxidation and/or drying of the river bed sediments is unknown. Further work is required to estimate their influence on water quality.

Metal and Acid Fluxes from Groundwater Discharge

Metal and acid transfer from tailings deposits to surface water is calculated using: (i) groundwater flux data from hydrogeological modelling, (ii) groundwater chemical data (Table 3), (iii) estimates of the depth of the discharge face from channel cross sections (Locher, 1995), and (iv) the length of individual discharge zones as determined by airphoto analysis (Tables 11 and 14).

Table 14 Mass transfer calculations

Based on hydrogeological modelling, the groundwater flux from banks R to H were estimated at 20 litres/day/m^2, with the depths of discharge faces ranging from 4 m at Bank R to 3 m at Bank H. Fluxes for banks G to A were estimated at 40 litres/day/m^2 based on the higher hydraulic conductivities in Bank D, and the depth of the discharge faces were estimated to be 3 m to 2.5 m at the mouth of the King River. Average values for groundwater fluxes to the river and harbour from both the north and south lobes of the delta were estimated at 50 litres/day/m^2. The depth of the discharge face for groundwater to the river was set at 2.5 m and to the harbour at 5.0 m. These values represent reasonable upper estimates for the hydrogeological regime. Discharge volumes compared well with infiltration volumes, based on estimates of surface area, annual rainfall data (Figure 22) and 20% recharge to groundwater.

Average metal and acid concentrations for groundwater in the banks and delta were calculated from measured groundwater compositions. Copper values, for example, were based on averages of measured data for a specific setting, where samples with copper concentrations below detection were assigned to be 0.01 mg/l. The acid budget was based on average H^+ ion concentrations from field pH measurements, plus an additional 2 moles of H^+ for every mole of Fe in solution (reactions (vi) and (vii) above). For banks where no water compositions are available, estimates were based on interpolation between the closest data sets.

Key results of the mass transfer calculations are shown in Table 14. It is estimated that daily groundwater discharges from the sediment banks and delta are responsible for transporting about 4.5 kg of Cu, 155 kg of H_2SO_4 equivalent, 40 kg of Fe, 13 kg of Al, 31 kg of Mn, 0.3 kg of As and 133 kg of Si into the King River and Macquarie Harbour. These estimates assume no reaction with sediments. The calculated fluxes for metals and acid are approximately two orders of magnitude less than those calculated from median chemical and flow data for the Queen River at Queenstown (Site 14) collated from data supplied by the MLMRCL (Supervising Scientist, 1996a).

One of the key factors minimising metal and acid release from groundwater discharge at present is the natural bioremediation currently active in the delta. Metal and acid concentrations from reduced groundwater in the delta are the lowest recorded. Assuming a scenario where biological activity in the delta ceased due to lack of nutrients or a catastrophic extinction, the copper concentration of groundwater may rise to an average of 4-6 mg/l (greater than an order-of-magnitude increase). Under current hydrogeological conditions, this situation would roughly double the total daily copper load from tailings groundwater discharge, and would have a similar effect on acid and other metals.

Metal and Acid Fluxes from Surface Runoff

It is difficult to estimate the contribution of metals and acid from surface runoff from the banks and delta. Based on comparison of pH and EC values for ponded water, surface runoff and groundwater, and assuming approximately 70% of precipitation runs off:

- The mass of pollutants contributed from surface runoff from the banks is expected to be equivalent or significantly less than that from groundwater discharge from the banks.

- The supply of metal and acid from surface runoff from the delta is predicted to equivalent or significantly higher than that provided by groundwater discharge from the delta.

It may be reasonable to assume that mass contributions to acid and metal pollution from the stored tailings material generated from sustained groundwater discharges and episodic surface runoff are roughly equivalent. The relative mass contributions from these two sources, however, is likely to be less important than the rates of delivery. Groundwater discharge involves low rates of application relative to episodic surface flushing events, and immediate environmental impact from the latter is predicted to be greater than from ongoing seepage.

Conclusions on Metal and Acid Fluxes

The input of metals and acid from groundwater (± river water) percolation through slag-rich river bottom sediments has not been estimated, because of insufficient data. The results of leach tests indicate that metals, in particular Cu, Zn, Co and Ni, can be released from slag-rich sediments.

The total mass of metal and acid generated from groundwater and surface water interacting with the tailings is approximately 1-5% of that added to the Queen river from the Mount Lyell lease site. Metal and acid loadings of 3.3 tonnes of Cu and 114 tonnes of H_2SO_4 equivalent per year to the King River and Macquarie Harbour from the tailings are small compared to those released from the Mount Lyell lease site; however, the short-lived episodes of water pollution produced by surface flushing of the banks and delta may be critical to local water quality. These episodes are expected to supply sporadic, large volume pulses of low-strength but highly acid leachate to river and harbour water, and may have a significant impact on aquatic ecosystems.

Predicted Impact of Tailings on Water Quality

The estimated fluxes of metals and acid currently supplied to surface water by groundwater discharge probably represent near-maximum values. Given the concentration and availability of fresh sulphides and slag, and assuming a similar hydrogeological regime, existing pollution levels are predicted to continue for thousands of years. Although some pyrite and chalcopyrite (≈1-10%) will be effectively inaccessible to fluids due to encasement in quartz or siliceous rock fragments, the majority is predicted to be available for extraction by groundwater. Furthermore, while some reduction in permeability is possible from precipitation reactions, complete cementation is unlikely.

Between 1969 and 1972 the MLMRCL estimated that approximately 300000 t of pyrite was present in the top 1.5 m of exposed delta (4.36 Mt), and that the sediment had an average copper content of 0.16%

(Hince, 1993). Based on these figures, the delta sediment has an Acid Producing Potential (APP) strictly from pyrite of 112 kg H_2SO_4 equivalent/t, which is within the range measured for delta sediments by EGI (1991c). The upper 1.5 metres of the delta has the potential to generate 490000 tonnes of H_2SO_4 equivalent (2 moles H_2SO_4 for 1 mole pyrite) and 7000 tonnes of copper. Much of this material will be available for leaching by groundwater, and assuming calculated discharge rates will take 12000 years to mobilise the copper and over 50000 years to extract all of the acid.

Assuming an average pyrite concentration of 2 wt.% and a copper content of 0.085 wt.% in the sediment banks, based on the bulk chemistry and petrographic work, the 2.73 Mt of tailings in storage (Table 11) contain roughly 55000 tonnes of pyrite and 2300 tonnes of copper. This material has an APP from pyrite of 33 kg H_2SO_4 equivalent/t, which represents a total of 89000 tonnes of H_2SO_4 equivalent. Based on current discharge rates from the sediment banks, groundwater will take 1860 years to extract all of the available acid, and almost 2200 years to leach the copper.

The differences between the banks and the delta reflect more rapid oxidation in the sediment banks, and the substantial influence of bioremediation in the delta.

Predicted Impact of Severe Drought

Periods of extreme drought will be associated with a general lowering of the water level in the King River, and decreases in both infiltration and runoff from both the banks and delta. These changes are predicted to significantly lower the water table and decrease the horizontal hydraulic gradient of groundwater, especially in the river banks. Such changes will inevitably result in lower groundwater fluxes, and thereby a decrease in the release of acid and metals to surface water.

An unusually depressed groundwater table will facilitate the widespread oxidation of sulphidic material that is routinely saturated, and restrict the distribution of bacterial remediation. Furthermore, zones of perched groundwater are also likely to contract or disappear, adding to the amount of sulphide available for oxidation. Hence while periods of drought are predicted to be related to decreases in surface water pollution from the banks and delta, oxidation processes accompanying the drying event will be strongly acid generating.

Drought-breaking rains are predicted to generate short to medium term pulses of relatively high-strength, acid and metal-rich leachate from both groundwater sources and surface water runoff.

Predicted Impact of Physical Disturbance

General

The leach tests provide the best indication of the effects of physically disturbing the tailings sediments. The sample collection and preparation procedure for the leach tests was roughly equivalent to exhuming, drying and at least partially oxidising saturated and unsaturated tailings material. Physical disturbance which involved subjecting the tailings to drying, oxidation and subsequent leaching could be reasonably assessed in view of these results (Tables 5 to 10). Given that leach tests were conducted on samples that were vacuum dried and vacuum stored, highly oxidised samples of once saturated tailings material would be expected to generate higher concentrations of metals and acid than indicated in the leach tests.

Any disturbance to tailings which accelerates oxidation will exacerbate metal and acid generation. Material of particular concern in this regard includes tailings with high concentrations of highly reactive biogenic sulphides, or slag-rich samples. Disturbance of tailings which involves interaction with more acid fluids or higher fluid fluxes will also have a negative impact on water quality. Physical disturbances which avoid further oxidation, pH decreases and increases in fluid interaction are unlikely to significantly affect metal and acid release from tailings. This means that, under controlled circumstances, it may be possible to mobilise portions of the tailings without increasing short-term metal releases. Removal of sediment from one subaqueous site and immediate deposition into another (at similar pH's) without significant oxidation during transfer is not predicted to cause a significant increase in metal and acid release. Such a process may have other deleterious impacts such as raising turbidity, but increases in metal release are unlikely.

Erosion

The impact of erosional processes (eg. sediment bank slumping, flood events, wind erosion, surface runoff) on the release of metals and acid from the tailings deposits is difficult to determine, quantify or anticipate. In general, such processes are predicted to have a minor influence on a) the total mass of sulphidic sediment available for leaching, and b) water quality. This conclusion is based on several factors:

(i) The strong influence of the John Butters power station on reducing the magnitude and frequency of flood events in the King River.

(ii) The relatively high porosity and permeability of the sediment banks tends to minimise runoff.

(iii) The widespread (and ongoing) development of weak lithification and crusts in the tailings banks and delta will have the effect of consolidating sediment deposits.

(iv) The dominant wind direction is predicted to displace but not remove significant volumes sediment from the delta.

(v) The development of vegetation on the mounded banks will have a stabilising effect.

(vi) The density contrast between silicate and sulphide grains suggests that transport of sediment via wind erosion may favour removal of the inert silicate component.

(vii) Flood episodes are likely to generate the most significant erosion of tailings sediment. Addition of such sediment to surface water will therefore be at a maximum when associated dilution reaches its peak. The overall effect on water quality is likely to be minimal.

(viii) Difficult access to the King River from the Macquarie Harbour for pleasure craft may minimise anthropogenic erosive processes.

Acid Neutralisation

The largest contribution to acid neutralisation in groundwater appears to be from bacterial sources. The near-neutral pH's from groundwater in the delta are attributed largely to bacterial sulphate reduction. Essentially no free carbonate remains in unsaturated tailings, and initial indications are that available carbonate in saturated tailings may be largely siderite. Dissolution of siderite will be acid generating, and produce elevated aqueous Mn concentrations. The abundance and distribution of secondary carbonate (Plate 27) is unknown, but is believed to be negligible.

Implications of Study for Revegetation

The delta is effectively devoid of vegetation, with only rare communities of grasses observed at the tidal interface on the north delta. In general the sediment banks are poorly vegetated, with the major evidence of previous growth being numerous tree stumps. The smaller tree stumps, often displaying bases in tailings material, indicate that growth was very commonly initiated within tailings material. The density, diversity and age of living trees on the sediment banks appears to increase up stream. This is thought to be related to three key factors:

(i) new sulphidic tailings are periodically deposited on the lower relief banks, thereby replenishing the supply of acidity and metals,

(ii) typical fluctuations in the water table in the banks are effective in bringing acidity and latent acidity (aqueous Fe^{2+}) into the root zone of plants in the lower banks, and

(iii) the higher relief of the upstream banks means that trees have longer to become established before their root zone enters the zone of influence of acid groundwater.

These observations suggest that in the short-term, revegetation with large trees is unlikely to be successful on the banks (especially the lower banks) until long-term reductions in acid production can be achieved. This conclusion is supported by a stand of reasonably mature Blackwoods *(Acacia Melanoxylon)* near the northern end of Bank R (≈20 m south of piezometer R-WD2). It is estimated that these trees were growing for 10-15 years in oxidised tailings, and based on the decomposition of timber and the relative height of surviving members, most have only died within the last 5 years. The distribution of sediment around their bases suggests that inundation with recent sediment was not responsible for their demise.

POTENTIAL REMEDIAL MEASURES

The mass transfer of metal and acid to surface water depends on several key issues:

(i) sulphide (pyrite) ±slag oxidation rates,

(ii) groundwater fluxes, which are in turn related to hydraulic conductivities and hydraulic gradients,

(iii) the volume, composition and rate of release of surface runoff,

(iv) the rate of groundwater level fluctuations (wetting / drying episodes), and

(v) the acid neutralising capacity of tailings.

The challenge is to develop cost-effective, efficient and sustainable remediation strategies that address one or more of these issues. The surface area:height ratio and hydrogeological regime of problematic sediments in the delta (upper 1.5 m) and those in the banks is quite different, and potential remedial techniques will need to address these differences.

Sediment Banks

In the banks, reductions in acid and metal release from the tailings can be achieved by vigorous revegetation of appropriate (eg., initially shallow-rooted) species on a substrate comprising clay (≈75-80%) + calcium / magnesium carbonate (≈10%) + organic debris/mulch (≈10%). To a limited extent this is occurring naturally on the downstream end of some of the banks. A strategy involving a relatively thin cover (eg., 5-30 cm) of such material would have the combined effect of:

(i) lowering groundwater recharge,

(ii) enhancing runoff while minimising interaction between surface water and tailings,

(iii) enhancing water loss through evapotranspiration,

(iv) partially treating infiltration (acting as a chemical barrier) prior to entering the saturated zone,

(v) acting as a self-sealing system in the event of unavoidable acid production,

(vi) ultimately lowering the water table and thereby reducing horizontal hydraulic gradients and groundwater discharge rates, and

(vii) dampening groundwater level fluctuations by lowering recharge.

The full effect of such an approach may not be evident for decades or longer, since cyclical die-back (postulated above) may be an essential part of the (natural remediation) process of building-up organic debris on the banks. A build-up of organic debris is likely to be an integral part of the feedback loop for enhancing additional plant growth and further water loss through evapotranspiration.

Delta

Minimising infiltration and interaction between surface runoff and tailings from the delta is impractical. Given the topography, tidal influences and highly acid nature of the upper part of the delta tailings, the potential for significantly enhancing water losses through evapotranspiration is minimal, since there is unlikely to be widespread colonisation of the delta by any vegetation. Furthermore, although there are several potential methods for manipulating and/or treating groundwater fluxes from the delta, they are likely to be expensive and would require periodic maintenance and ongoing monitoring.

As with the banks, the recommended remedial strategy is an extension of natural processes currently operating within the tailings. Sulphate-reducing bacterial activity at the tidal interface zone on the delta is believed to be responsible for significantly lowering metal and acid release to the harbour. It is recommended that optimum conditions for the growth of these bacteria are established, and that such conditions are encouraged more widely throughout the delta. This strategy relies on altering the chemistry of the tailings and associated groundwater via biological processes, and may not necessarily include manipulating fluid fluxes or degree of fluid-mineral interaction. Preliminary indications are that the following factors would be required:

(i) increase the surface area of permanently saturated tailings, by creating local depressions in the delta,

(ii) add organic debris to the depressions to provide a local source of C, N and P.

Non-disruptive techniques for engineering depressions will need to be developed, and may be prohibitively expensive on a large scale. One approach may involve (mechanical) compaction of selected sections of the tidal interface, which would saturate exposed tailings and simultaneously lower hydraulic conductivity.

Improved groundwater and surface water quality and minimising wind erosion could be expected to result from enhancing naturally occurring bioremediation. In effect, the delta may be encouraged to develop some of the characteristics of a mangrove environment. Further consideration will need to be given to the logistics of creating local depressions, the effect of increased anaerobic bacterial activity on the local ecology and the long-term impact of this approach on the visual amenity of the delta.

Considerations for Future Work

Field work was conducted over a seven-day period during winter and was directed at obtaining single groundwater samples and measurements of hydrogeological parameters from each piezometer. The data obtained represent a snap-shot in time from a complex, dynamic and evolving hydrogeochemical system. Significant progress has been made in identifying and quantifying the fundamental processes operating in the banks and delta. Future studies should consider the implications of the results from this and other studies prior to planning further work.

Rapid changes in river water levels due to the controlled release of water from the dam associated with the John Butters Power Station, and unpredictable variations in harbour water levels due to the effect of meteorological conditions on tides, have undoubtedly influenced the horizontal hydraulic gradients measured from piezometers. In addition, recharge rates to groundwater in both the banks and delta are likely to be strongly influenced by rainfall. Consequently, hydrogeochemical monitoring studies conducted over longer periods than this study would be more helpful for resolving the influence of seasonal variations in groundwater flow and composition and the impact of short-lived episodes of rainfall and flooding.

Analytical results suggest that the installation of piezometers facilitated degassing (eg., H_2S, CO_2, CH_4) of reduced groundwater which may have had some influence on the groundwater chemistry prior to sampling. Gas loss during transit, and post-sampling oxidation of ultra-fine grained biogenic sulphides in (filtered) water and sediment samples, appears to have occurred to some extent in as little as 3-4 days in highly reduced samples. Such processes can affect the results of aqueous chemical and mineralogical analysis, and steps should be taken to minimise the effect. More rigorous attempts to record ambient redox conditions (possibly in the field), and preserve representative redox-pair ratios in aqueous and sediment samples are recommended for future hydrogeochemical studies. Groundwater and surface water analyses, especially from the delta, should include sulphide, sulphite and sulphate, as well as ammonia, nitrite and nitrate.

The internal lining of LDPE bottles containing water-saturated slag-rich material turned deep red after 2-3 weeks, presumably due to leaching of iron from slag, and precipitation of iron-oxide material via the diffusion of oxygen through the bottles. The reactivity of the slag was not predicted and should be considered in future work. Methods for securing physically undisturbed sediment samples, as well as preventing oxidation, should be devised to assist with identification of delicate and reactive secondary assemblages.

CONCLUSIONS

Ninety-seven million tonnes of sulphidic tailings and 1.4 Mt of slag (Locher, 1995) derived from Cambrian volcanogenic massive sulphide mineralisation from the Mount Lyell copper mine were disposed to the Queen and King River systems between 1916 and 1994. 2.73 Mt are currently stored in sediment banks on the King River, about 10 Mt are stored in the base of the river (Locher, 1995) and approximately 85 Mt have accumulated in the King River delta. The upper 1.5 m of the subaerial delta contains 4.36 Mt of tailings. Sediment deposits contain water saturated to unsaturated material, and both types are acid generating. Tailings in the delta contain 5-7 wt.% pyrite and about 0.16 wt.% Cu, while the sediment banks are estimated to contain 2-3 wt.% pyrite and 0.085 wt.% Cu. Groundwater discharges and surface water runoff from the sediment banks and delta are currently contributing metals and acid to the King River and Macquarie Harbour.

Tailings material is comprised of rock, crystal and slag fragments, generally ranging in size from 10-200 µm, as well as variable proportions of organic debris contributed from natural sources in the King River catchment. The rock component includes ore gangue, felsic volcanics, vein quartz and metasediments. Gangue fragments predominate and are comprised of quartz, chlorite (chamosite), muscovite, minor siderite (commonly manganiferous), and sulphides including pyrite, chalcopyrite, sphalerite and galena. Felsic volcanics are dominated by microcrystalline quartz, and metasediments are usually comprised of variable proportions of quartz, chlorite and muscovite. The crystal component comprises pyrite, chlorite, muscovite, carbonate, magnetite, ilmenite, chromite and zircon. Slag is a sulphur- and copper-saturated iron-rich, silicate glass with inclusions of a Cu-Fe sulphide and an iron-silicate crystal phase (fayalite). The slag is also relatively enriched in trace metal components such as Zn, Co, Ni and Pb.

Acid production in the tailings is initiated by sulphide oxidation, principally pyrite. Preliminary estimates indicate that almost complete oxidation of pyrite in permanently unsaturated tailings can take place in between one and four years. The oxidation of aqueous ferrous species at, and above the water table, is instrumental in the widespread formation of iron-oxide precipitates which coat most detrital components. The precipitation of iron-oxide, likely to be goethite, is considered to make a significant addition to acid generation. The goethite is invariably intermixed with subordinate amounts of Cu±Fe±O±C, possibly representing an additional phase such as cuprous ferrite.

The composition of groundwater in the tailings is highly variable, and steep chemical gradients have been identified at the water table in the delta. Groundwater varies from highly acid to near-neutral (pH = 2.54 to 7.1) and is variably enriched in Cu, Fe, Al, Mn, Si and As, with some samples also showing elevated concentrations of Ni, Zn, Co, Pb, Se and Hg. Groundwater from the banks is generally more acid and oxidised than groundwater from the delta, and the north lobe of the delta displays the most reduced and near-neutral groundwater compositions. Much of the variation in groundwater chemistry can be attributed to differences in the sulphide and organic content of the tailings, and other local controls on redox conditions. The influence of sulphate-reducing bacteria at the tidal interface on the delta appears to be very important in lowering metal and acid concentrations in groundwater discharged to the harbour.

Cu in groundwater and surface is principally derived from chalcopyrite, surface precipitates around detrital grains (eg. cuprous ferrite), Cu-Fe sulphides in slag and Cu in the silicate matrix of the slag. Contributions of adsorbed copper to the total budget are probably less than 2%. Sources of iron most likely to contribute significantly to soluble iron concentrations include pyrite, siderite, chalcopyrite and slag. The majority of Mn is found in siderite and widespread dissolution of this component from the unsaturated tailings is probably responsible for high aqueous concentrations. Al is largely present in layer silicates, and is probably primarily derived by dissolution of chlorite and muscovite.

The groundwater chemistry is partly controlled by mineral solubility and equilibrium processes (eg. Fe and Si), and partly by kinetic factors or the solubility of unidentified minerals (eg. Al). For the metals examined, adsorption usually accounts for less than 1 wt.% of the total mass in sediment samples, suggesting that groundwater chemistry is dominated by pH and redox dependent dissolution and precipitation reactions.

The widespread development of hydration rims around slag fragments highlight the reactivity of the glass under oxidising conditions. Analytical results indicate that elevated concentrations of Cu, Fe, Si and Mn, and atypically high contributions of Co, Zn and Ni may be associated with alteration and leaching of slag.

The hydraulic conductivity of tailings deposits in the sediment banks and delta is high, and ranges from K≈10-6 m/s to 10-4 m/s, with the latter values representing the topographically lower banks and delta. Groundwater fluxes calculated from measured hydraulic gradients and hydrogeological modelling indicate values of 20, 40 and 50 litres/day/m2 for mounded sediment banks, flat banks and the delta respectively. In conjunction with the groundwater chemistry, these figures show that groundwater discharges from the banks and delta are responsible for mobilising approximately 4.5 kg of Cu and 155 kg of H_2SO_4 equivalent per day into the King River and Macquarie Harbour. The contribution of acid and metal from surface water runoff is predicted to be significant from the delta, but less important from the banks. Surface runoff from the banks and delta is estimated to contribute similar loads of acid and metals to those provided by groundwater sources, but these will be delivered in episodic and potentially more damaging flushing events. The mass transfers of metals and acid from groundwater percolation through (slag-rich) King River bottom sediments in unknown.

The King River and Macquarie Harbour currently receives an average daily addition of ≈10 kg of Cu and ≈300 kg of H_2SO_4 equivalent from groundwater discharges and surface water runoff from the sediment banks and delta. Such a release is predicted to have significant ecological consequences in a pristine river system. In the King River system, however, this mass of metals and acid represents only 1-5 wt.% of the total mass of metal and acid entering the Queen and King river systems from the Mount Lyell lease site. On these grounds, it is clear that priority should be given to the remediation of acid drainage from the Mount Lyell lease site, and evaluation of the effects of periodic flushing events.

Based on current hydrogeological parameters and groundwater chemistry, the mass loadings recorded from groundwater discharge and surface water runoff are predicted to continue for thousands to tens of thousands of years.

Any physical disturbance of the tailings which involves oxidation will have the potential to significantly lower the pH and raise the metal content of the associated leachate. It is evident that large concentrations of Cu, Fe, Al, Si, Mn, Zn, Co, and Ni can be readily mobilised from oxidised tailings material by acidic fluids, and that such fluids are routinely generated by natural infiltration processes.

The installation of low permeability, reactive substrates (clay + carbonate + organic matter) on the banks prior to revegetation, is predicted to assist with decreasing groundwater discharges, decreasing surface water / tailings interaction and developing sustainable revegetation programmes. Enhancing and extending naturally occurring bioremediation processes in the delta is considered to be one of the most cost-effective methods for improving the quality of groundwater discharges from the delta.

RECOMMENDATIONS

- Groundwater discharges and surface runoff from tailings in the King River banks and delta are estimated to be responsible for only 1-5 wt.% of the total mass of metals and acid entering the King River system and Macquarie Harbour. Under these circumstances, it is recommended that efforts to improve water quality focus on drainage from the Mount Lyell lease site.

- Leach tests indicate that even rainwater can release significant concentrations of metal and acid from oxidised tailings, and hence any physical disruption of tailings material that involves oxidation is not recommended.

- Continuous monitoring studies are recommended to fully understand the influences of controlled river level fluctuations, irregular tides and episodic rainfall events on the discharge of groundwater and surface water runoff from the banks and delta. Surface drainage, in particular, requires thorough evaluation, due to its potential to deliver significant pulses of acid material.

- The reactivity of slag material under a range of redox conditions needs to be quantified. In addition, it is potentially very important to evaluate the likely metal and acid contribution of slag-rich river bottom sediments to the King River.

- The composition of leachate draining from the remaining slag stockpile at Queenstown needs to be evaluated in view of the results outlined here. Remedial activity may be warranted.

- Continue to characterise the mineralogy and acid generating capacity of the tailings. This work should include quantifying the residual sulphide content of tailings material, particularly from the banks. Detailed XRD and SEM work on undisturbed samples is required to fully characterise the nature of acid forming secondary assemblages and surface precipitates. Such data could assist with the development and implementation of remedial strategies.

- Quantitative studies on sulphide oxidation rates are necessary to improve predictions of the rates of acid production and metal release. Studies should examine fresh sulphidic tailings, iron-oxide coated sulphide-bearing tailings (saturated and unsaturated settings), and material containing biogenic sulphides.

- Additional groundwater sampling should be undertaken. While the groundwater chemistry from the banks was broadly consistent, significant variations in the chemistry of groundwater in the delta indicate the need for more work. Greater emphasis should be placed on the analysis of Se and Hg in water samples in future studies.

Implementation of the remedial strategies outlined below are recommended when the metal and acid released from tailings in the banks, delta and river bottom is roughly equal in magnitude to that issuing from the Mount Lyell lease site. The following approaches are proposed to facilitate long-term, cost-effective and sustainable improvements in the quality of water in the King River and Macquarie Harbour:

- Conduct a detailed botanical survey on the nature, distribution, density, age and status of (native) vegetation on the King River sediment banks, to clarify the processes involved in the ongoing die-back.

- Establish trials on the application of a clay+limestone+organic substrate to revegetation plots, and quantify its influence on groundwater recharge, hydraulic gradients and groundwater quality, as well as the proportion and quality of runoff.

- Conduct a detailed characterisation of bacterial activity in delta and banks, with emphasis on quantifying its current contribution to controlling the concentrations of metals and acid in groundwater and surface water. Results should include an evaluation of the limiting factors on bacterial activity, and predict the potential for bioremediation to improve groundwater and surface water quality on a larger scale, in both the banks and delta.

- Pending the results of the characterisation of bacterial activity, controlled, small-scale bioremediation trials should be established on the north delta.

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APPENDIX 1 - Sediment Sample Descriptions and Locations

APPENDIX 2 - Geological sections of drillholes

APPENDIX 3 - Spectra from XRD Analysis

APPENDIX 4 - Analytical data from Microprobe Analysis

Analysis A4.1

31-October-95 17:15

Spectrum ID = Anhydrous Slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 27016 Y= 12119

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.27	0.0044		0.407
MgO	1.47	0.0057		0.301
Al2O3	6.51	0.0267		0.550
SiO2	29.42	0.1247		1.050
SO4	3.37	0.0136		0.380
K2O	0.39	0.0037		0.094
CaO	3.14	0.0267		0.290
TiO2	0.66	0.0045		0.188
Cr2O3	0.43	0.0036		0.161
MnO	0.03	0.0002		0.047
FeO	52.04	0.4394		2.161
CuO	1.02	0.0083		0.436
ZnO	0.04	0.0003		0.102
NiO	0.21	0.0017		0.160
Total	100.0			

Analysis A4.2

31-October-95 17:17

Spectrum ID = Anhydrous Slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 27016 Y= 12119

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.72	0.0025		0.119
MgO	1.55	0.0061		0.120
Al2O3	6.58	0.0270		0.215
SiO2	29.2	0.1236		0.406
SO4	3.81	0.0154		0.157
K2O	0.47	0.0044		0.040
CaO	3.22	0.0273		0.114
TiO2	0.59	0.0040		0.069
Cr2O3	0.21	0.0017		0.043
MnO	0.05	0.0004		0.025
FeO	53.21	0.4473		0.849
CuO	0.32	0.0026		0.095
ZnO	0.0	0.0000		0.000
NiO	0.08	0.0007		0.039
Total	100.0			

Analysis A4.3
31-October-95 17:17
Spectrum ID = Anhydrous Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 27016 Y= 12119
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.72	0.0025		0.119
MgO	1.55	0.0060		0.120
Al2O3	6.58	0.0270		0.215
SiO2	29.2	0.1236		0.406
SO4	3.81	0.0154		0.157
Cl	0.0	0.0000		0.000
K2O	0.47	0.0044		0.040
CaO	3.22	0.0273		0.114
TiO2	0.59	0.0040		0.069
Cr2O3	0.21	0.0017		0.043
MnO	0.05	0.0004		0.025

FeO	53.21	0.4473		0.849
CuO	0.32	0.0026		0.095
ZnO	0.0	0.0000		0.000
NiO	0.08	0.0007		0.039
Total	100.0			

Analysis A4.4
31-October-95 17:28
Spectrum ID = Anhydrous Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 27079 Y= 12354
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.77	0.0027		0.124
MgO	1.54	0.0060		0.120
Al2O3	6.48	0.0265		0.213
SiO2	28.86	0.1220		0.404
SO4	4.1	0.0165		0.162
Cl	0.0	0.0000		0.000
K2O	0.47	0.0044		0.040
CaO	3.18	0.0269		0.113
TiO2	0.67	0.0045		0.074
Cr2O3	0.04	0.0003		0.019
MnO	0.0	0.0000		0.000
FeO	52.91	0.4452		0.846
CuO	0.57	0.0046		0.126
ZnO	0.26	0.0021		0.100
NiO	0.16	0.0013		0.054
Total	100.0			

Analysis A4.5
31-October-95 19:16
Spectrum ID = Central Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5

X= 24499 Y= 10881

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.2	0.0043		0.152
MgO	1.73	0.0069		0.125
Al2O3	6.96	0.0290		0.218
SiO2	31.38	0.1344		0.417
SO4	3.88	0.0157		0.158
Cl	0.0	0.0000		0.000
K2O	0.49	0.0046		0.041
CaO	2.25	0.0192		0.095
TiO2	0.56	0.0038		0.067
Cr2O3	0.0	0.0000		0.000
MnO	0.1	0.0009		0.034
FeO	50.57	0.4292		0.822
CuO	0.74	0.0060		0.143
ZnO	0.0	0.0000		0.000
NiO	0.13	0.0011		0.049
Total	100.0			

Analysis A4.6

31-October-95 19:15

Spectrum ID = Central Slag (KR-1) - As for analysis above but expressed in terms of the metals.

Livetime = 100.

kV= 15

Angle= 52.5

X= 24499 Y= 10881

Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.89	0.0043	2.47800	0.112
Mg	1.04	0.0069	2.73739	0.075
Al	3.68	0.0290	8.73558	0.116
Si	14.66	0.1344	33.42875	0.195
S	1.55	0.0157	3.10102	0.063
Cl	0.0	0.0000	0.00000	0.000
K	0.41	0.0046	0.66946	0.034
Ca	1.61	0.0192	2.57170	0.068

Ti	0.33	0.0038	0.44500	0.040
Cr	0.0	0.0000	0.00000	0.000
Mn	0.08	0.0009	0.09255	0.027
Fe	39.31	0.4292	45.03160	0.639
Cu	0.59	0.0060	0.59641	0.114
Zn	0.0	0.0000	0.00000	0.000
Ni	0.1	0.0011	0.11255	0.039
O	35.73			
Total	100.0			

Analysis A4.7
31-October-95 18:25
Spectrum ID = Middle of Slag Fragment (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 19006 Y= 13210
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.57	0.0019		0.109
MgO	1.22	0.0046		0.108
Al2O3	4.98	0.0199		0.189
SiO2	27.18	0.1133		0.395
SO4	4.3	0.0173		0.167
Cl	0.0	0.0000		0.000
K2O	0.22	0.0021		0.028
CaO	3.18	0.0268		0.114
TiO2	0.36	0.0024		0.054
Cr2O3	0.0	0.0000		0.000
MnO	0.0	0.0000		0.000
FeO	56.31	0.4708		0.877
CuO	0.87	0.0069		0.157
ZnO	0.72	0.0058		0.168
NiO	0.08	0.0006		0.038
Total	100.0			

Analysis A4.8
31-October-95 18:33

Spectrum ID = Outer Edge of Slag (KR-1) - Iron-oxide rich rim.

Livetime = 100.

kV= 15

Angle= 52.5

X= 18946 Y= 13094

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.15	0.0032		0.207
MgO	0.43	0.0014		0.085
Al2O3	2.11	0.0074		0.162
SiO2	9.53	0.0360		0.302
SO4	0.21	0.0008		0.046
Cl	0.0	0.0000		0.000
K2O	0.29	0.0027		0.039
CaO	0.97	0.0081		0.078
TiO2	0.08	0.0005		0.030
Cr2O3	0.0	0.0000		0.000
MnO	1.55	0.0122		0.169
FeO	83.24	0.6723		1.332
CuO	0.32	0.0025		0.120
ZnO	0.0	0.0000		0.000
NiO	0.12	0.0009		0.059
Total	100.0			

Analysis A4.9

31-October-95 17:32

Spectrum ID = Inner Laminated Edge of Slag-1 (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 27064 Y= 12420

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.78	0.0032		0.125
MgO	1.36	0.0061		0.115
Al2O3	13.29	0.0610		0.316
SiO2	41.25	0.1844		0.514

SO4	5.21	0.0211		0.201
Cl	0.0	0.0000		0.000
K2O	0.14	0.0013		0.023
CaO	0.61	0.0052		0.054
TiO2	0.85	0.0058		0.091
Cr2O3	0.03	0.0002		0.017
MnO	0.02	0.0001		0.015
FeO	33.39	0.2890		0.726
CuO	2.45	0.0204		0.283
ZnO	0.64	0.0053		0.169
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.10
31-October-95 17:44
Spectrum ID = Inner Edge Slag -2 (KR-1)
Livetime = 35.92
kV= 15
Angle= 52.5
X= 14882 Y= 16841
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.88	0.0031		0.114
MgO	1.43	0.0057		0.099
Al2O3	6.42	0.0267		0.183
SiO2	31.55	0.1348		0.365
SO4	3.67	0.0148		0.134
Cl	0.02	0.0003		0.008
K2O	0.48	0.0045		0.035
CaO	3.25	0.0275		0.100
TiO2	0.59	0.0040		0.060
Cr2O3	0.04	0.0003		0.016
MnO	0.0	0.0000		0.000
FeO	51.27	0.4316		0.724
CuO	0.39	0.0032		0.091
ZnO	0.0	0.0000		0.000
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.11

31-October-95 17:40

Spectrum ID = Middle Portion of Laminated Edge of Slag-1 (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 14762 Y= 16841

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.9	0.0031		0.134
MgO	1.43	0.0056		0.116
Al2O3	6.24	0.0258		0.210
SiO2	30.9	0.1316		0.420
SO4	3.54	0.0143		0.152
Cl	0.02	0.0002		0.008
K2O	0.45	0.0042		0.039
CaO	3.32	0.0281		0.117
TiO2	0.55	0.0037		0.067
Cr2O3	0.1	0.0008		0.031
MnO	0.02	0.0002		0.015
FeO	52.18	0.4389		0.847
CuO	0.29	0.0023		0.090
ZnO	0.07	0.0006		0.052
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.12

31-October-95 17:45

Spectrum ID = Middle Edge Slag -2 (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 14908 Y= 16841

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.48	0.0019		0.184

MgO	1.25	0.0055		0.205
Al2O3	10.76	0.0484		0.528
SiO2	38.87	0.1729		0.920
SO4	8.26	0.0334		0.464
Cl	0.0	0.0000		0.000
K2O	0.09	0.0009		0.035
CaO	0.04	0.0004		0.027
TiO2	0.65	0.0044		0.146
Cr2O3	0.25	0.0021		0.096
MnO	0.0	0.0000		0.000
FeO	38.14	0.3257		1.436
CuO	0.57	0.0047		0.252
ZnO	0.63	0.0052		0.313
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.13

31-October-95 17:47

Spectrum ID = Middle Edge Slag -2 (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 14908 Y= 16841

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.0	0.0040		0.142
MgO	1.19	0.0052		0.108
Al2O3	10.86	0.0490		0.286
SiO2	38.97	0.1739		0.497
SO4	7.97	0.0323		0.246
Cl	0.0	0.0000		0.000
K2O	0.14	0.0013		0.023
CaO	0.07	0.0006		0.018
TiO2	0.67	0.0046		0.080
Cr2O3	0.12	0.0010		0.036
MnO	0.0	0.0000		0.000
FeO	38.2	0.3269		0.777
CuO	0.69	0.0057		0.150

ZnO	0.12	0.0010	0.073
NiO	0.0	0.0000	0.000
Total	100.0		

Analysis A4.14

31-October-95 17:52

Spectrum ID = Outer Edge Slag -2 (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 14879 Y= 16874

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM% +/- 2 SIGMA
Na2O	0.87	0.0034	0.136
MgO	1.01	0.0043	0.102
Al2O3	10.58	0.0470	0.288
SiO2	39.35	0.1738	0.508
SO4	4.49	0.0182	0.187
Cl	0.0	0.0000	0.000
K2O	0.11	0.0011	0.022
CaO	0.18	0.0016	0.030
TiO2	0.84	0.0058	0.090
Cr2O3	0.18	0.0015	0.044
MnO	0.08	0.0006	0.033
FeO	40.99	0.3516	0.813
CuO	0.99	0.0082	0.182
ZnO	0.17	0.0014	0.088
NiO	0.15	0.0013	0.058
Total	100.0		

Analysis A4.15

31-October-95 18:22

Spectrum ID = Middle Portion of Hydrated Rim of Slag - (KR-1)

Livetime = 48.97

kV= 15

Angle= 52.5

X= 18986 Y= 13210

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.31	0.0117		0.152
MgO	13.56	0.0722		0.261
Al2O3	28.48	0.1388		0.353
SiO2	26.4	0.1161		0.326
SO4	0.15	0.0007		0.026
Cl	0.05	0.0005		0.010
K2O	0.07	0.0008		0.013
CaO	0.04	0.0004		0.011
TiO2	0.0	0.0000		0.000
Cr2O3	0.04	0.0004		0.016
MnO	0.02	0.0002		0.013
FeO	28.53	0.2683		0.507
CuO	0.11	0.0010		0.045
ZnO	0.24	0.0022		0.079
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.16
31-October-95 18:29
Spectrum ID = Sulphide in Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 18861 Y= 13171
Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.0	0.0000	0.00000	0.000
Mg	0.0	0.0000	0.00000	0.000
Al	0.04	0.0003	0.12145	0.011
Si	0.11	0.0009	0.30677	0.015
S	15.75	0.1564	38.13853	0.165
Cl	0.0	0.0000	0.00000	0.000
K	0.0	0.0000	0.00517	0.002
Ca	0.0	0.0000	0.00000	0.000
Ti	0.02	0.0002	0.02876	0.008
Cr	0.02	0.0002	0.03242	0.010

Mn	0.0	0.0000	0.00000	0.000
Fe	18.77	0.2005	26.09427	0.364
Cu	28.4	0.2738	34.70924	0.663
Zn	0.47	0.0046	0.56337	0.101
Ni	0.0	0.0000	0.00000	0.000
O	36.41			
Total	100.0			

Analysis A4.17
31-October-95 19:08
Spectrum ID = Iron oxide residue from slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 26416 Y= 13975
Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	1.04	0.0040	3.04546	0.169
Mg	0.64	0.0035	1.76954	0.081
Al	4.6	0.0311	11.53667	0.175
Si	0.93	0.0075	2.23921	0.066
S	2.26	0.0226	4.76295	0.096
Cl	0.28	0.0028	0.52730	0.036
K	0.04	0.0005	0.07221	0.014
Ca	0.16	0.0018	0.26315	0.027
Ti	0.0	0.0000	0.00000	0.000
Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	61.91	0.6540	74.90614	1.023
Cu	0.53	0.0052	0.56413	0.139
Zn	0.17	0.0017	0.18033	0.094
Ni	0.12	0.0012	0.13290	0.053
O	27.33			
Total	100.0			

Analysis A4.18
31-October-95 19:08
Spectrum ID = Iron oxide residue from slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 26416 Y= 13975

Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	1.04	0.0040	3.04546	0.169
Mg	0.64	0.0035	1.76954	0.081
Al	4.6	0.0311	11.53667	0.175
Si	0.93	0.0075	2.23921	0.066
S	2.26	0.0226	4.76295	0.096
Cl	0.28	0.0028	0.52730	0.036
K	0.04	0.0005	0.07221	0.014
Ca	0.16	0.0018	0.26315	0.027
Ti	0.0	0.0000	0.00000	0.000
Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	61.91	0.6540	74.90614	1.023
Cu	0.53	0.0052	0.56413	0.139
Zn	0.17	0.0017	0.18033	0.094
Ni	0.12	0.0012	0.13290	0.053
O	27.33			
Total	100.0			

Analysis A4.19

31-October-95 19:27

Spectrum ID = Middle Edge Hydrous Slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 23619 Y= 10521

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.85	0.0034		0.131
MgO	1.01	0.0045		0.099
Al2O3	10.58	0.0480		0.281
SiO2	40.01	0.1792		0.502

SO4	8.62	0.0349		0.256
Cl	0.07	0.0007		0.016
K2O	0.07	0.0006		0.016
CaO	0.09	0.0007		0.020
TiO2	0.94	0.0064		0.095
Cr2O3	0.03	0.0003		0.019
MnO	0.0	0.0000		0.000
FeO	36.72	0.3131		0.762
CuO	0.75	0.0062		0.157
ZnO	0.05	0.0004		0.046
NiO	0.2	0.0017		0.065
Total	100.0			

Analysis A4.20

31-October-95 20:10

Spectrum ID = Hydrous banded Slag (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 31368 Y= 41966

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	3.52	0.0176		0.240
MgO	0.9	0.0046		0.088
Al2O3	8.26	0.0416		0.239
SiO2	73.55	0.3510		0.667
SO4	2.55	0.0094		0.147
Cl	0.04	0.0004		0.013
K2O	0.12	0.0010		0.023
CaO	0.04	0.0003		0.015
TiO2	1.01	0.0063		0.104
Cr2O3	0.04	0.0003		0.021
MnO	0.0	0.0000		0.005
FeO	9.56	0.0763		0.406
CuO	0.2	0.0015		0.084
ZnO	0.13	0.0010		0.079
NiO	0.08	0.0006		0.043
Total	100.0			

Analysis A4.21

31-October-95 20:32

Spectrum ID = Hydrous banded Slag (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 29334 Y= 41497

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.6	0.0029		0.174
MgO	0.44	0.0023		0.107
Al2O3	6.92	0.0348		0.380
SiO2	84.27	0.3983		1.246
SO4	1.64	0.0057		0.210
Cl	0.19	0.0017		0.049
K2O	0.0	0.0000		0.000
CaO	0.0	0.0000		0.000
TiO2	0.66	0.0039		0.150
Cr2O3	0.0	0.0000		0.000
MnO	0.11	0.0008		0.071
FeO	4.83	0.0366		0.515
CuO	0.0	0.0000		0.000
ZnO	0.0	0.0000		0.000
NiO	0.35	0.0027		0.162
Total	100.0			

Analysis A4.22

31-October-95 20:35

Spectrum ID = Banding around Slag (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 28023 Y= 41575

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.01	0.0028		0.170

MgO	0.4	0.0013		0.073
Al2O3	2.94	0.0104		0.168
SiO2	6.14	0.0234		0.214
SO4	8.86	0.0351		0.263
Cl	0.08	0.0008		0.017
K2O	0.04	0.0004		0.013
CaO	0.0	0.0000		0.000
TiO2	0.0	0.0000		0.000
Cr2O3	0.0	0.0000		0.001
MnO	0.07	0.0006		0.032
FeO	80.04	0.6455		1.159
CuO	0.0	0.0000		0.000
ZnO	0.3	0.0023		0.120
NiO	0.12	0.0009		0.052
Total	100.0			

Analysis A4.23
31-October-95 20:44
Spectrum ID = Iron oxide surrounding banded slag (DT-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 18318 Y= 41821
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.98	0.0026		0.172
MgO	0.33	0.0010		0.067
Al2O3	0.69	0.0023		0.083
SiO2	2.41	0.0090		0.136
SO4	9.05	0.0355		0.268
Cl	0.04	0.0004		0.013
K2O	0.0	0.0000		0.000
CaO	0.11	0.0009		0.023
TiO2	0.02	0.0002		0.015
Cr2O3	0.0	0.0000		0.000
MnO	0.0	0.0000		0.000
FeO	85.83	0.6805		1.216
CuO	0.38	0.0028		0.116

ZnO	0.0	0.0000		0.000
NiO	0.17	0.0013		0.064
Total	100.0			

Analysis A4.24
31-October-95 19:19
Spectrum ID = Oxidised Sulphide Bleb in Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 24607 Y= 10911
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.0	0.0000		0.000
MgO	1.22	0.0053		0.970
Al2O3	2.45	0.0108		1.211
SiO2	22.11	0.0995		3.285
SO4	7.68	0.0323		2.091
Cl	20.34	0.2078		2.378
K2O	2.62	0.0223		0.947
CaO	6.63	0.0509		1.655
TiO2	7.35	0.0445		2.481
Cr2O3	0.0	0.0000		0.000
MnO	4.86	0.0372		2.377
FeO	24.54	0.1923		5.729
CuO	0.0	0.0000		0.000
ZnO	0.2	0.0015		0.864
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.25
31-October-95 19:23
Spectrum ID = Fresh Sulphide Bleb in Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 24626 Y= 10844
Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.0	0.0000	0.00000	0.000
Mg	0.0	0.0000	0.00000	0.000
Al	0.05	0.0003	0.13146	0.011
Si	0.24	0.0020	0.65887	0.021
S	17.11	0.1715	41.00777	0.172
Cl	0.0	0.0000	0.00000	0.000
K	0.05	0.0005	0.09560	0.010
Ca	0.05	0.0006	0.09997	0.010
Ti	0.03	0.0004	0.05451	0.011
Cr	0.02	0.0002	0.02422	0.009
Mn	0.0	0.0000	0.00000	0.000
Fe	25.4	0.2633	34.95206	0.430
Cu	18.69	0.1775	22.60538	0.543
Zn	0.31	0.0030	0.37016	0.083
Ni	0.0	0.0000	0.00000	0.000
O	38.05			
Total	100.0			

Analysis A4.26
31-October-95 17:58
Spectrum ID = Sulphide in Slag (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 12597 Y= 16960
Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.0	0.0000	0.00000	0.000
Mg	0.09	0.0005	0.27198	0.019
Al	0.13	0.0009	0.36661	0.019
Si	0.14	0.0012	0.39064	0.016
S	16.31	0.1628	39.18263	0.166
Cl	0.0	0.0000	0.00000	0.000
K	0.01	0.0001	0.01542	0.004
Ca	0.01	0.0001	0.01880	0.004
Ti	0.03	0.0004	0.05435	0.011

Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	22.66	0.2383	31.26563	0.399
Cu	23.05	0.2207	27.95708	0.594
Zn	0.37	0.0035	0.43682	0.089
Ni	0.03	0.0003	0.04001	0.017
O	37.17			
Total	100.0			

Analysis A4.27

31-October-95 17:59

Spectrum ID = Sulphide in Slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 12597 Y= 16960

Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.0	0.0000	0.00000	0.000
Mg	0.09	0.0005	0.27198	0.019
Al	0.13	0.0009	0.36661	0.019
Si	0.14	0.0012	0.39064	0.016
S	16.31	0.1628	39.18263	0.166
Cl	0.0	0.0000	0.00000	0.000
K	0.01	0.0001	0.01542	0.004
Ca	0.01	0.0001	0.01880	0.004
Ti	0.03	0.0004	0.05435	0.011
Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	22.66	0.2383	31.26563	0.399
Cu	23.05	0.2207	27.95708	0.594
Zn	0.37	0.0035	0.43682	0.089
Ni	0.03	0.0003	0.04001	0.017
O	37.17			
Total	100.0			

Analysis A4.28

31-October-95 17:59

Spectrum ID = Sulphide in Slag (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 12597 Y= 16960

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.0	0.0000		0.000
MgO	0.14	0.0005		0.032
Al2O3	0.24	0.0009		0.036
SiO2	0.3	0.0012		0.035
SO4	40.72	0.1628		0.415
Cl	0.0	0.0000		0.000
K2O	0.01	0.0001		0.005
CaO	0.01	0.0001		0.006
TiO2	0.06	0.0004		0.018
Cr2O3	0.0	0.0000		0.000
MnO	0.0	0.0000		0.000
FeO	29.16	0.2383		0.514
CuO	28.86	0.2207		0.744
ZnO	0.46	0.0035		0.111
NiO	0.04	0.0003		0.022
Total	100.0			

Analysis A4.29

31-October-95 18:05

Spectrum ID = Pyrite Crystal (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 14007 Y= 17645

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.11	0.0004		0.035
MgO	0.0	0.0000		0.003
Al2O3	0.06	0.0003		0.016
SiO2	0.06	0.0002		0.014

SO4	65.56	0.2689		0.480
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.05	0.0004		0.011
TiO2	0.07	0.0004		0.019
Cr2O3	0.0	0.0000		0.000
MnO	0.0	0.0000		0.000
FeO	33.84	0.2515		0.536
CuO	0.18	0.0013		0.056
ZnO	0.07	0.0005		0.041
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.30

31-October-95 18:09

Spectrum ID = Pyrite Crystal (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 13966 Y= 17657

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.0	0.0000		0.000
MgO	0.04	0.0002		0.015
Al2O3	0.08	0.0003		0.018
SiO2	0.09	0.0004		0.017
SO4	65.6	0.2690		0.478
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.0	0.0000		0.000
TiO2	0.01	0.0001		0.007
Cr2O3	0.0	0.0000		0.000
MnO	0.0	0.0000		0.000
FeO	33.95	0.2523		0.535
CuO	0.15	0.0011		0.051
ZnO	0.03	0.0002		0.028
NiO	0.04	0.0003		0.021
Total	100.0			

Analysis A4.31

31-October-95 18:09

Spectrum ID = Pyrite Crystal (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 13966 Y= 17657

Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na	0.0	0.0000	0.00000	0.000
Mg	0.03	0.0002	0.08050	0.009
Al	0.04	0.0003	0.12516	0.010
Si	0.04	0.0004	0.11838	0.008
S	26.27	0.2690	63.07289	0.192
Cl	0.0	0.0000	0.00000	0.000
K	0.0	0.0000	0.00000	0.000
Ca	0.0	0.0000	0.00000	0.000
Ti	0.01	0.0001	0.01013	0.004
Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	26.39	0.2523	36.37440	0.416
Cu	0.12	0.0011	0.14702	0.041
Zn	0.03	0.0002	0.03051	0.022
Ni	0.03	0.0003	0.04101	0.017
O	47.04			
Total	100.0			

Analysis A4.32

31-October-95 21:00

Spectrum ID = Chalcopyrite (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 8712 Y= 42144

Standardless

ELEMENT	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA

Na	0.0	0.0000	0.00000	0.000
Mg	0.0	0.0000	0.00000	0.000
Al	0.05	0.0003	0.14033	0.011
Si	0.06	0.0005	0.15548	0.010
S	19.03	0.1915	46.09668	0.175
Cl	0.0	0.0000	0.00000	0.000
K	0.0	0.0000	0.00000	0.000
Ca	0.04	0.0004	0.07246	0.009
Ti	0.03	0.0003	0.05079	0.010
Cr	0.0	0.0000	0.00000	0.000
Mn	0.0	0.0000	0.00000	0.000
Fe	18.96	0.1980	26.36465	0.360
Cu	21.99	0.2093	26.88139	0.571
Zn	0.17	0.0016	0.20540	0.060
Ni	0.02	0.0002	0.03281	0.016
O	39.65			
Total	100.0			

Analysis A4.33

31-October-95 22:36

Spectrum ID = Magnetite (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 23634 Y= 13949

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.77	0.0020		0.150
MgO	0.62	0.0019		0.091
Al2O3	1.45	0.0048		0.118
SiO2	0.71	0.0026		0.072
SO4	0.04	0.0002		0.017
Cl	0.0	0.0000		0.000
K2O	0.07	0.0006		0.017
CaO	0.08	0.0006		0.019
TiO2	1.58	0.0106		0.120
Cr2O3	0.18	0.0016		0.042

MnO	0.18	0.0014		0.051
FeO	93.99	0.7406		1.228
CuO	0.23	0.0017		0.087
ZnO	0.0	0.0000		0.000
NiO	0.1	0.0007		0.046
Total	100.0			

Analysis A4.34
31-October-95 22:02
Spectrum ID = Fe-rich Carbonate KR-1
Livetime = 100.
kV= 15
Angle= 52.5
X= 26049 Y= 11655
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.37	0.0073		0.306
MgO	16.58	0.0580		0.552
Al2O3	0.27	0.0009		0.063
SiO2	0.84	0.0032		0.096
SO4	0.06	0.0002		0.025
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.18	0.0016		0.035
TiO2	0.05	0.0004		0.026
Cr2O3	0.03	0.0003		0.020
MnO	4.04	0.0342		0.287
FeO	74.8	0.6447		1.325
CuO	0.1	0.0008		0.069
ZnO	0.49	0.0040		0.182
NiO	0.21	0.0018		0.083
Total	100.0			

Analysis A4.35
31-October-95 22:06
Spectrum ID = Fe-rich Carbonate KR-1
Livetime = 100.
kV= 15

Angle= 52.5

X= 25973 Y= 11636

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.71	0.0087		0.325
MgO	20.36	0.0739		0.611
Al2O3	0.3	0.0010		0.067
SiO2	0.67	0.0026		0.087
SO4	0.01	0.0001		0.012
Cl	0.08	0.0009		0.020
K2O	0.0	0.0000		0.000
CaO	0.25	0.0022		0.042
TiO2	0.07	0.0005		0.030
Cr2O3	0.0	0.0000		0.004
MnO	3.01	0.0259		0.249
FeO	71.81	0.6312		1.308
CuO	0.02	0.0002		0.035
ZnO	0.57	0.0048		0.198
NiO	0.13	0.0011		0.067
Total	100.0			

Analysis A4.36

31-October-95 22:09

Spectrum ID = Fe-rich Carbonate KR-1

Livetime = 100.

kV= 15

Angle= 52.5

X= 25878 Y= 11753

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	3.15	0.0102		0.352
MgO	20.91	0.0762		0.622
Al2O3	0.0	0.0000		0.000
SiO2	0.34	0.0013		0.062
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000

CaO	0.29	0.0026		0.045
TiO2	0.0	0.0000		0.000
Cr2O3	0.07	0.0007		0.032
MnO	3.53	0.0306		0.272
FeO	71.41	0.6295		1.313
CuO	0.0	0.0000		0.000
ZnO	0.18	0.0015		0.113
NiO	0.12	0.0010		0.063
Total	100.0			

Analysis A4.37
31-October-95 22:25
Spectrum ID = Carbonate in rock fragment KR-1
Livetime = 100.
kV= 15
Angle= 52.5
X= 11582 Y= 14585
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.42	0.0076		0.313
MgO	18.78	0.0667		0.596
Al2O3	0.0	0.0000		0.000
SiO2	0.48	0.0018		0.074
SO4	0.16	0.0007		0.043
Cl	0.0	0.0000		0.004
K2O	0.0	0.0000		0.000
CaO	0.18	0.0016		0.036
TiO2	0.0	0.0000		0.000
Cr2O3	0.0	0.0000		0.000
MnO	2.26	0.0193		0.218
FeO	75.35	0.6548		1.355
CuO	0.0	0.0000		0.000
ZnO	0.13	0.0011		0.095
NiO	0.24	0.0020		0.090
Total	100.0			

Analysis A4.38
31-October-95 22:02

Spectrum ID = Fe-rich Carbonate KR-1

Livetime = 100.

kV= 15

Angle= 52.5

X= 26049 Y= 11655

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.37	0.0073		0.306
MgO	16.58	0.0580		0.552
Al2O3	0.27	0.0009		0.063
SiO2	0.84	0.0032		0.096
SO4	0.06	0.0002		0.025
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.18	0.0016		0.035
TiO2	0.05	0.0004		0.026
Cr2O3	0.03	0.0003		0.020
MnO	4.04	0.0342		0.287
FeO	74.8	0.6447		1.325
CuO	0.1	0.0008		0.069
ZnO	0.49	0.0040		0.182
NiO	0.21	0.0018		0.083
Total	100.0			

Analysis A4.39

31-October-95 22:06

Spectrum ID = Fe-rich Carbonate KR-1

Livetime = 100.

kV= 15

Angle= 52.5

X= 25973 Y= 11636

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.71	0.0087		0.325
MgO	20.36	0.0739		0.611
Al2O3	0.3	0.0010		0.067
SiO2	0.67	0.0026		0.087

SO4	0.01	0.0001		0.012
Cl	0.08	0.0009		0.020
K2O	0.0	0.0000		0.000
CaO	0.25	0.0022		0.042
TiO2	0.07	0.0005		0.030
Cr2O3	0.0	0.0000		0.004
MnO	3.01	0.0259		0.249
FeO	71.81	0.6312		1.308
CuO	0.02	0.0002		0.035
ZnO	0.57	0.0048		0.198
NiO	0.13	0.0011		0.067
Total	100.0			

Analysis A4.40
31-October-95 22:09
Spectrum ID = Fe-rich Carbonate KR-1
Livetime = 100.
kV= 15
Angle= 52.5
X= 25878 Y= 11753
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	3.15	0.0102		0.352
MgO	20.91	0.0762		0.622
Al2O3	0.0	0.0000		0.000
SiO2	0.34	0.0013		0.062
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.29	0.0026		0.045
TiO2	0.0	0.0000		0.000
Cr2O3	0.07	0.0007		0.032
MnO	3.53	0.0306		0.272
FeO	71.41	0.6295		1.313
CuO	0.0	0.0000		0.000
ZnO	0.18	0.0015		0.113
NiO	0.12	0.0010		0.063
Total	100.0			

Analysis A4.41

31-October-95 22:25

Spectrum ID = Carbonate in rock fragment KR-1

Livetime = 100.

kV= 15

Angle= 52.5

X= 11582 Y= 14585

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.42	0.0076		0.313
MgO	18.78	0.0667		0.596
Al2O3	0.0	0.0000		0.000
SiO2	0.48	0.0018		0.074
SO4	0.16	0.0007		0.043
Cl	0.0	0.0000		0.004
K2O	0.0	0.0000		0.000
CaO	0.18	0.0016		0.036
TiO2	0.0	0.0000		0.000
Cr2O3	0.0	0.0000		0.000
MnO	2.26	0.0193		0.218
FeO	75.35	0.6548		1.355
CuO	0.0	0.0000		0.000
ZnO	0.13	0.0011		0.095
NiO	0.24	0.0020		0.090
Total	100.0			

Analysis A4.42

31-October-95 22:43

Spectrum ID = Carbonate in rock fragment (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 27654 Y= 10760

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.43	0.0074		0.312

MgO	11.54	0.0400		0.463
Al2O3	0.2	0.0007		0.054
SiO2	0.62	0.0024		0.083
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	2.3	0.0200		0.127
TiO2	0.32	0.0023		0.066
Cr2O3	0.08	0.0007		0.036
MnO	36.15	0.2976		0.870
FeO	46.33	0.3887		1.059
CuO	0.02	0.0002		0.035
ZnO	0.0	0.0000		0.000
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.43
31-October-95 18:17
Spectrum ID = Chlorite (KR-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 18943 Y= 15070
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.51	0.0129		0.200
MgO	13.74	0.0735		0.333
Al2O3	28.75	0.1404		0.449
SiO2	26.32	0.1158		0.413
SO4	0.08	0.0003		0.024
Cl	0.06	0.0006		0.014
K2O	0.06	0.0006		0.015
CaO	0.0	0.0000		0.001
TiO2	0.0	0.0000		0.000
Cr2O3	0.05	0.0004		0.022
MnO	0.05	0.0005		0.026
FeO	27.9	0.2631		0.634
CuO	0.01	0.0001		0.019

ZnO	0.48	0.0043		0.140
NiO	0.0	0.0000		0.008
Total	100.0			

Analysis A4.44

31-October-95 18:18

Spectrum ID = Chlorite (KR-1) - Analysis as above normalised to 88 wt.% to account for water.

kV= 15

Angle= 52.5

X= 18943 Y= 15070

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.26	0.0114		0.179
MgO	12.25	0.0647		0.297
Al2O3	25.28	0.1235		0.395
SiO2	22.81	0.1019		0.358
SO4	0.07	0.0003		0.020
Cl	0.05	0.0005		0.012
K2O	0.05	0.0005		0.013
CaO	0.0	0.0000		0.001
TiO2	0.0	0.0000		0.000
Cr2O3	0.04	0.0004		0.019
MnO	0.05	0.0004		0.023
FeO	24.72	0.2315		0.562
CuO	0.01	0.0001		0.013
ZnO	0.42	0.0038		0.124
NiO	0.0	0.0000		0.007
Total	88.0			

Analysis A4.45

31-October-95 19:32

Spectrum ID = Chlorite in rock fragment (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 21149 Y= 10967

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	2.15	0.0107		0.190
MgO	11.45	0.0598		0.309
Al2O3	29.27	0.1426		0.456
SiO2	26.35	0.1154		0.417
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.06	0.0006		0.014
CaO	0.09	0.0008		0.020
TiO2	0.01	0.0001		0.011
Cr2O3	0.0	0.0000		0.000
MnO	0.06	0.0006		0.028
FeO	30.52	0.2852		0.670
CuO	0.0	0.0000		0.000
ZnO	0.04	0.0004		0.041
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.46

31-October-95 19:32

Spectrum ID = Chlorite in rock fragment (KR-1). Normalised to 88 wt.% to account for the water content.

Livetime = 100.

kV= 15

Angle= 52.5

X= 21149 Y= 10967

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.93	0.0094		0.170
MgO	10.19	0.0526		0.275
Al2O3	25.76	0.1255		0.402
SiO2	22.86	0.1016		0.361
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.05	0.0005		0.013
CaO	0.08	0.0007		0.017
TiO2	0.01	0.0001		0.009
Cr2O3	0.0	0.0000		0.000

MnO	0.05	0.0005		0.025
FeO	27.04	0.2510		0.594
CuO	0.0	0.0000		0.000
ZnO	0.04	0.0003		0.037
NiO	0.0	0.0000		0.000
Total	88.0			

Analysis A4.47

31-October-95 21:18

Spectrum ID = Chlorite (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 20926 Y= 18106

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.74	0.0082		0.174
MgO	10.24	0.0517		0.297
Al2O3	28.33	0.1358		0.452
SiO2	25.72	0.1120		0.412
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.03	0.0003		0.012
TiO2	0.04	0.0003		0.019
Cr2O3	0.0	0.0000		0.000
MnO	0.32	0.0029		0.064
FeO	32.93	0.3068		0.696
CuO	0.16	0.0015		0.070
ZnO	0.49	0.0044		0.143
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.48

31-October-95 21:18

Spectrum ID = Chlorite (KR-1). Analysis as above normalised to 88 wt.% for water content.

Livetime = 100.

kV= 15

Angle= 52.5

X= 20926 Y= 18106

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.55	0.0072		0.155
MgO	9.09	0.0455		0.263
Al2O3	24.91	0.1195		0.397
SiO2	22.32	0.0986		0.357
SO4	0.0	0.0000		0.000
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000
CaO	0.03	0.0003		0.011
TiO2	0.04	0.0003		0.017
Cr2O3	0.0	0.0000		0.000
MnO	0.28	0.0026		0.056
FeO	29.2	0.2700		0.617
CuO	0.14	0.0013		0.062
ZnO	0.43	0.0039		0.127
NiO	0.0	0.0000		0.000
Total	88.0			

Analysis A4.49

31-October-95 20:14

Spectrum ID = Cement between Grains (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 31547 Y= 41440

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.73	0.0020		0.153
MgO	0.2	0.0006		0.054
Al2O3	0.78	0.0026		0.091
SiO2	2.27	0.0084		0.135
SO4	7.55	0.0294		0.251
Cl	0.0	0.0000		0.000
K2O	0.0	0.0000		0.000

CaO	0.04	0.0003		0.015
TiO2	0.02	0.0001		0.013
Cr2O3	0.09	0.0008		0.031
MnO	0.17	0.0013		0.051
FeO	87.38	0.6912		1.253
CuO	0.7	0.0053		0.162
ZnO	0.0	0.0000		0.000
NiO	0.07	0.0005		0.041
Total	100.0			

Analysis A4.50
31-October-95 20:18
Spectrum ID = Cement between Grains (DT-1)
Livetime = 100.
kV= 15
Angle= 52.5
X= 31088 Y= 41027
Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.8	0.0050		0.232
MgO	0.33	0.0010		0.067
Al2O3	1.81	0.0063		0.135
SiO2	3.32	0.0125		0.160
SO4	8.54	0.0338		0.261
Cl	0.1	0.0009		0.019
K2O	0.09	0.0008		0.020
CaO	0.03	0.0002		0.012
TiO2	0.09	0.0006		0.029
Cr2O3	0.08	0.0007		0.029
MnO	0.02	0.0002		0.019
FeO	83.41	0.6688		1.199
CuO	0.4	0.0030		0.120
ZnO	0.0	0.0000		0.000
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.51
31-October-95 20:21

Spectrum ID = Cement between Grains (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 30968 Y= 40938

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.77	0.0021		0.153
MgO	0.15	0.0005		0.045
Al2O3	1.08	0.0037		0.104
SiO2	2.12	0.0080		0.128
SO4	13.29	0.0524		0.326
Cl	0.0	0.0000		0.000
K2O	0.11	0.0010		0.022
CaO	0.04	0.0003		0.014
TiO2	0.0	0.0000		0.000
Cr2O3	0.0	0.0000		0.000
MnO	0.05	0.0004		0.028
FeO	82.21	0.6510		1.196
CuO	0.03	0.0002		0.034
ZnO	0.12	0.0009		0.079
NiO	0.02	0.0002		0.023
Total	100.0			

Analysis A4.52

31-October-95 20:24

Spectrum ID = Cement between grains (DT-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 32215 Y= 40824

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	0.92	0.0025		0.167
MgO	0.36	0.0011		0.070
Al2O3	1.85	0.0064		0.136
SiO2	2.19	0.0082		0.130

SO4	11.54	0.0456		0.305
Cl	0.1	0.0010		0.019
K2O	0.09	0.0008		0.019
CaO	0.05	0.0004		0.016
TiO2	0.21	0.0014		0.046
Cr2O3	0.26	0.0022		0.053
MnO	0.0	0.0000		0.000
FeO	82.23	0.6538		1.199
CuO	0.21	0.0016		0.088
ZnO	0.0	0.0000		0.000
NiO	0.0	0.0000		0.000
Total	100.0			

Analysis A4.53

31-October-95 20:55

Spectrum ID = Colliform matrix material to grains (KR-1)

Livetime = 100.

kV= 15

Angle= 52.5

X= 9195 Y= 42015

Standardless

OXIDE	WEIGHT %	K/RATIO	ATOM%	+/- 2 SIGMA
Na2O	1.46	0.0039		0.212
MgO	0.45	0.0014		0.080
Al2O3	0.72	0.0025		0.086
SiO2	2.95	0.0110		0.152
SO4	7.13	0.0280		0.240
Cl	0.05	0.0005		0.014
K2O	0.0	0.0000		0.000
CaO	0.14	0.0012		0.027
TiO2	0.05	0.0003		0.023
Cr2O3	0.03	0.0003		0.018
MnO	0.05	0.0004		0.026
FeO	86.08	0.6860		1.224
CuO	0.88	0.0067		0.179
ZnO	0.0	0.0000		0.000
NiO	0.0	0.0000		0.000

Total	100.0

APPENDIX 5 - Spectra from IFESEM Analysis

APPENDIX 6 - Hydrogeological Modelling

APPENDIX 7 - Geochemical Modelling

APPENDIX 8 - Bibliography

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