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

7 Discussion

7.1 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 to 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 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:

$$FeS_2 + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad \text{Reaction 1}$$

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:

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

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:

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

The combination of the reactions 1 to 3 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:

$$Fe(OH)_3 = FeO(OH) + H_2O \qquad \text{Reaction 4}$$

Water coming into contact with the oxidised surface layers of sediment in the delta and banks becomes quite acidic (pH 2.5 to 3). Although this process is not understood, it may be due to hydrogen ions being liberated from the iron oxyhydroxide coatings. Goethite/lepidocrocite (FeOOH) 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 with 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 is important, as acid re-enters the groundwater. 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:

- regular lowering of the water table enhances drying and oxidation of the sediments;
- 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
- regular lowering of the river dramatically increases the horizontal hydraulic gradient of groundwater in the sediment banks, thereby increasing discharge rates.

7.2 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:

- groundwater discharge from the banks and delta;
- surface runoff from the banks and delta; and
- 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 released 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:

- groundwater flux data from hydrogeological modelling;
- groundwater chemical data (table 3):
- estimates of the depth of the discharge face from channel cross sections (Locher 1995); and
- the length of individual discharge zones as determined by airial photo analysis (tables 12 and 14).

Based on hydrogeological modelling, the groundwater flux from Banks R to H were estimated at 20 L/d/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 L/d/m^2 based on the higher hydraulic conductivities in Bank D, and the depth of the discharge faces were estimated to be 3 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 L/d/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 1, 2). 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 (MLMRCL site 14, see figure 23) collated from data supplied by the MLMRCL (McQuade CV, Johnston JF & Innes SM 1996).

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 to 6 mg/L, which is 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 be 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

Table 14 Mass transfer calculations

Location	Perimeter along river bank (m)	Perimeter along harbour (m)	Average depth of discharge face (m)	Average groundwater flux to river (l/day/m2)	Average groundwater flux to harbour (l/day/m2)	Groundwater discharge to river (l/day)	Groundwater discharge to harbour (l/day)	Cu in groundwater near river (mg/l)	Cu in groundwater near harbour (mg/l)	Cu input to river from banks and delta (kg/day)	Cu input to harbour from delta (kg/day)	Acid in groundwater near river (mg/l H2SO4)	Acid in groundwater near harbour (mg/l H2SO4)	Acid input to river from banks and delta (kg H2SO4 / day)	Acid input to harbour from delta (kg H2SO4 / day)
Bank A	686		2.5	40		6.86E+04		4.00		0.27		300		20.58	
Bank B	1128		2.5	40		1.13E+05		5.00		0.56		300		33.84	
Bank C	361		2.5	40		3.61E+04		6.00		0.22		300		10.83	
Bank D	**925**		2.5	40		**9.25E+04**		**6.26**		**0.58**		**127.56**		**11.80**	
Bank E	505		2.5	40		5.05E+04		6.00		0.30		200		10.10	
Bank F	652		2.5	40		6.52E+04		4.00		0.26		100		6.52	
Bank G	660		3	20		3.96E+04		2.00		0.08		100		3.96	
Bank H	**679**		**3**	20		**4.07E+04**		**1.78**		**0.07**		**44.52**		**1.81**	
Bank I	153		3	20		9.18E+03		1.50		0.01		100		0.92	
Bank J	503		3	20		3.02E+04		1.50		0.05		100		3.02	
Bank K	243		3	20		1.46E+04		1.50		0.02		100		1.46	
Bank L	689		3	20		4.13E+04		1.50		0.06		100		4.13	
Bank M	606		4	20		4.85E+04		1.50		0.07		100		4.85	
Bank N	**501**		**4**	20		**4.01E+04**		**0.89**		**0.04**		**48.72**		**1.95**	
Bank O	699		4	20		5.59E+04		1.50		0.08		100		5.59	
Bank P	379		4	20		3.03E+04		1.50		0.05		100		3.03	
Bank Q	634		4	20		5.07E+04		1.50		0.08		100		5.07	
Bank R	**763**		**4**	20		**6.10E+04**		**1.59**		**0.10**		**36.77**		**2.24**	
Delta North	**1393**	**1564**	**2.5**	**50**	**50**	**1.74E+05**	**3.91E+05**	2.60	0.3	**0.45**	**0.12**	31.92	**24.61**	**5.56**	**4.28**
Delta South	**1515**	**2239**	**2.5**	**50**	**50**	**1.89E+05**	**5.60E+05**	**2.60**	0.3	**0.49**	**0.17**	31.92	**24.63**	**6.04**	**4.66**
Delta Island	1073		2.5	50		1.34E+05		3.00		0.40		31.92		4.28	
TOTAL	**14747**	**3803**				**1.39E+06**	**9.51E+05**			**4.25**	**0.29**			**147.60**	**8.95**

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 to 5% of that added to the Queen River from the Mount Lyell lease site. Metal and acid loadings of 3.3 t of Cu and 114 t of H_2SO_4 equivalent/yr to the King River and Macquarie Harbour from the tailings are small compared with 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.

7.3 Predicted impact of tailings on water quality

The estimated fluxes of metals and acid currently released 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 to 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 300 000 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 m of the delta has the potential to generate 490 000 t of H_2SO_4 equivalent (2 moles H_2SO_4 for 1 mole pyrite) and 7000 t of copper. Much of this material will be available for leaching by groundwater, and assuming calculated discharge rates it will take 12 000 years to mobilise the copper and over 50 000 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 2) contain roughly 55 000 t of pyrite and 2300 t of copper. This material has an APP from pyrite of 33 kg H_2SO_4 equivalent/t, which represents a total of 89 000 t 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.

7.4 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 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.

7.5 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 6 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, 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, erosion related to flood events, wind erosion and 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 i) the total mass of sulphidic sediment available for leaching, and ii) water quality. This conclusion is based on the following:

- The strong influence of the John Butters Power Station on reducing the magnitude and frequency of flood events in the King River.
- The relatively high porosity and permeability of the sediment banks tends to minimise runoff.
- The widespread (and ongoing) development of weak lithification and crusts in the tailings banks and delta will have the effect of consolidating sediment deposits.
- The dominant wind direction is predicted to displace but not remove significant volumes of sediment from the delta.
- The development of vegetation on the mounded banks will have a stabilising effect.
- The density contrast between silicate and sulphide grains suggests that transport of sediment via wind erosion may favour removal of the inert silicate component.
- 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.
- Difficult access to the King River from Macquarie Harbour for pleasure craft may minimise anthropogenic erosive processes.

7.6 Acid neutralisation

The largest contribution to acid neutralisation in groundwater appears to be from bacterial sources. The near-neutral pH readings 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 29) is unknown, but is believed to be negligible.

7.7 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 lobe. 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 appear to increase upstream. This is thought to be related to three key factors:

- new sulphidic tailings are periodically deposited on the lower relief banks, thereby replenishing the supply of acidity and metals;
- 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
- the higher relief of the upstream banks means that trees have longer to become established before their root zone enters the zone of acid groundwater influence.

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 to 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.

7.8 Potential remedial measures

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

- sulphide (as pyrite, ± slag) oxidation rates;
- groundwater fluxes, which are in turn related to hydraulic conductivities and hydraulic gradients;
- the volume, composition and rate of release of surface runoff;
- the rate of groundwater level fluctuations (wetting/drying episodes); and
- 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 species (eg initially shallow-rooted) on a substrate comprising of ≈75 to 80% clay, ≈10% calcium/magnesium carbonate and ≈10% organic debris/mulch. 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 to 30 cm) of such material would have the combined effect of:

- lowering groundwater recharge;
- enhancing runoff while minimising interaction between surface water and tailings;
- enhancing water loss through evapotranspiration;
- partially treating infiltration (acting as a chemical barrier) prior to entering the saturated zone;
- acting as a self-sealing system in the event of unavoidable acid production;
- ultimately lowering the water table and thereby reducing horizontal hydraulic gradients and groundwater discharge rates; and
- 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, as postulated above, may be an essential part of the natural remediation process of building-up organic debris in 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:

- increase the surface area of permanently saturated tailings, by creating local depressions in the delta; and
- 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 reduced 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.

7.9 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/unfiltered water and sediment samples, appears to have occurred to some extent in as little as 3 to 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 to 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.

8 Conclusions

Ninety-seven Mt 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 River and King River systems between 1916 and 1994. Sediment banks on the King River currently contain 2.73 Mt sulphidic tailings, 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 to 7 wt% pyrite and about 0.16 wt% Cu, while the sediment banks are estimated to contain 2 to 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 to 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.

Copper in groundwater and surface-water 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. Aluminium 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 highlights 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 $K=10^{-6}$ 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 $L/d/m^2$ 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/d 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-water 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 is unknown.

The King River and Macquarie Harbour currently receive an average daily addition of $\approx$10 kg of Cu and $\approx$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 to 5 wt% of the total mass of metal and acid entering the Queen River 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 with carbonate with 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.

9 Recommendations

1. Groundwater discharges and surface runoff from tailings in the King River banks and delta are estimated to be responsible for only 1 to 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.

2. 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.

3. 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.

4. 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.

5. 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.

6. Characterisation of the mineralogy and acid generating capacity of the tailings should be continued. 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.

7. 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.

8. Additional groundwater sampling should be undertaken. Though 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 following remedial strategies are only recommended when the metal and acid released from tailings in the banks, delta and river bottom are of the same order of magnitude to that issuing from the Mount Lyell lease site:

1. 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.
2. Establish trials on the use of a clay+limestone+organic substrate for revegetation plots, and quantify its influence on groundwater recharge, hydraulic gradients and groundwater quality, as well as the proportion and quality of runoff.
3. Conduct a detailed characterisation of bacterial activity in the 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.
4. Pending the results of the characterisation of bacterial activity, controlled, small-scale bioremediation trials should be established on the north lobe of the delta.