over the delta. The location of the traverses is shown on figure 2 and results are displayed on figures 19 to 21. Traverses were designed to coincide with the location of piezometers to permit comparison between surficial and deeper groundwater.

Field analytical procedures

A TPS meter and an Ionode Intermediate Junction, epoxy body, glass bulb pH electrode (IJ40) were 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. Redox potential (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, µS/cm) in each of the samples. The EC probe was calibrated for temperature against a standard solution of KCl. Water temperature was measured with a mercury bulb thermometer.

4 Laboratory analytical work

4.1 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.

4.2 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, ≈100 g representative subsamples of 80 moist to saturated sediments were placed into plastic Petric dishes and stored in vacuum desiccators. The samples were dried over a 7 to 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 to 30 g batches of 80 vacuum-dried sediment samples were dispatched to Amdel (Adelaide) for analysis in 50 mL HDPE screw-top bottles. 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 S.

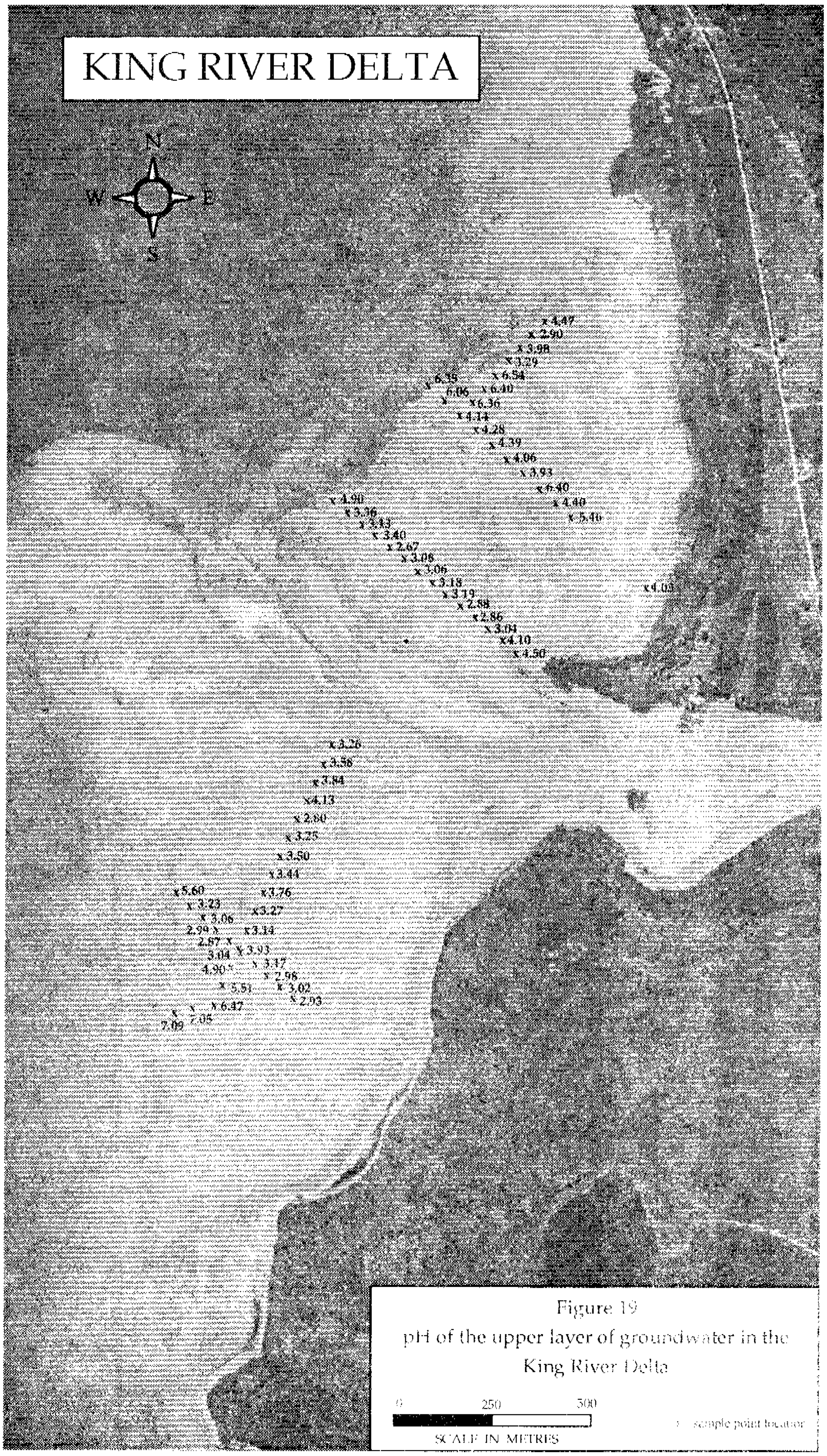

Figure 19

pH of the upper layer of groundwater in the King River Delta

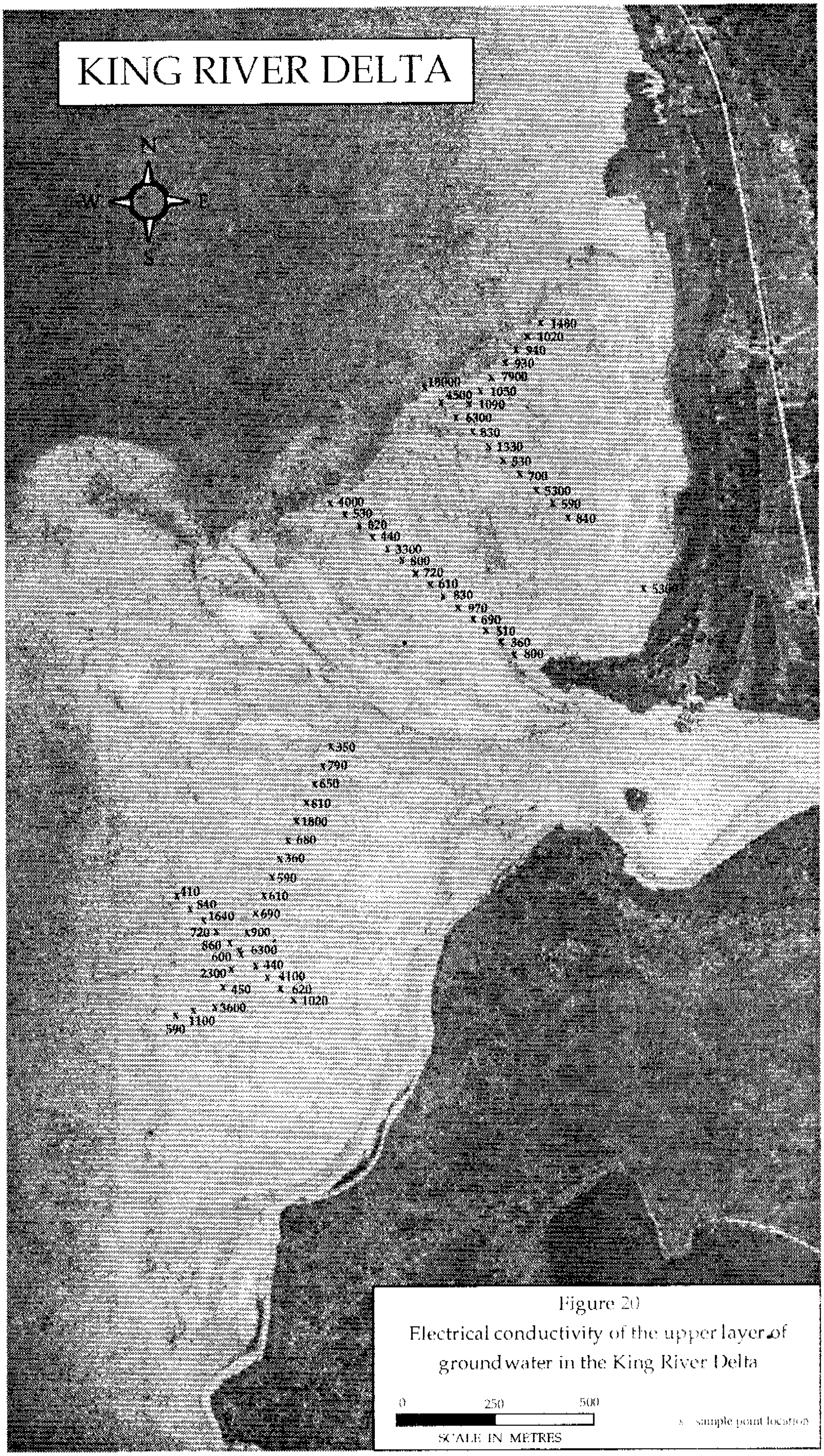

Figure 20

Electrical conductivity of the upper layer of ground water in the King River Delta

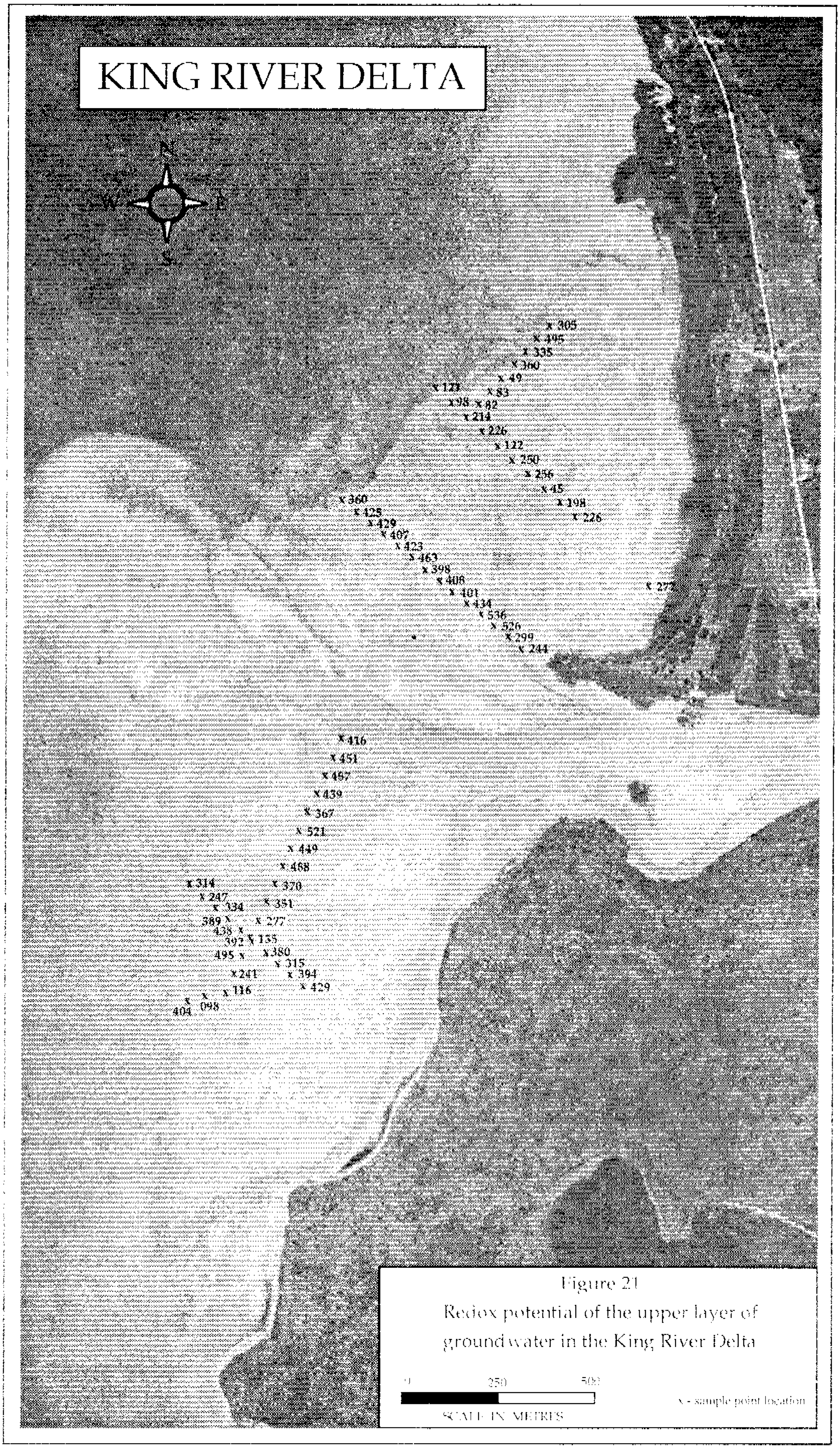

Figure 21

Redox potential of the upper layer of groundwater in the King River Delta

Microscopy

Approximately 5 to 10 g of 20 vacuum-dried samples 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 used for examination.

XRD

Approximately 10 to 20 g of 14 representative sediments 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° to 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 analysed with 2° to 70° 2θ scans. 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 15 kV 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/s, 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

Detailed evaluation of the chemistry and morphology of surface features and coatings on detrital tailings grains was conducted using an In Lens Field Emission Scanning Electron Microscope (IFESEM, CSIRO Port Melbourne).

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 to 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 2 to 15 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.

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 and submitted to Amdel (Melbourne).

Deionised water and dilute sulphuric acid

Twenty 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. The mixtures were gently agitated continuously 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. 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.

Ammonium acetate

Five 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 (Kersten & Forstner 1989). Gentle agitation of the mixtures was continuous for 24 hours. The leachate was 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. The pH, EC and Eh of the leachate was measured five minutes after initial mixing, after 15 minutes, and at 2 hour intervals thereafter.

5 Results

5.1 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.