**Costelloe, Marina (2003) *Environmental review of the Mary Kathleen uranium mine.* Masters (Research) thesis, James Cook University.**

# Chapter 4 Tailings dam and evaporation ponds

## 4.1 Introduction

Tailings impoundments may represent serious environmental mine site problems (Nordstrom 1977; Alpers and Blowes, 1994; Morin and Hutt, 1997; Jambor and Blowes, 1998; Nordstrom and Alpers, 1999). Sulphide oxidation, and associated acid generation, as well as the solution and precipitation processes of heavy metals are potential problems within tailings dams. In addition metalloids as dissolved species, insoluble and potentially soluble solid forms also exist within tailings dams and also raise environmental concerns. Uranium tailings seepage also has the potential for radionuclide migration into aquifers or surface seepage points (Landa and Gray, 1995; Landa, 1999; Morin et al., 1988). Tailings repositories are required to have an engineered long structural life, ensuring the tailings are isolated from the environment (East et al., 1994). To adequately manage tailings from uranium mines, effective containment of solid and liquid wastes, minimal leaching by rain or surface water, and attenuation of gamma-radiation is required (Ward et al., 1984).

This chapter reports on the Mary Kathleen tailing area and seepage from the tailings dam toe. The main objective of this chapter is to document the current environmental status of the rehabilitated tailings dam and compare these results to previous environmental studies undertaken in the 1980s. The nature of exposed tailings will be established by determining their composition and radioactivity. The nature and magnitude of contamination and radioactivity from the seepage toe will be investigated by analysing seepage chemistry, seepage precipitates and pond sediments.

## 4.2 Description

### 4.2.1 Location and origins of tailings dam area and evaporation pond spillways

The ore was processed in the treatment plant using radiometric sorting, crushing and grinding, acid leaching, solvent extraction, precipitation and calcination. Reagents used at Mary Kathleen were manganese and iron oxide; sulphuric acid (leaching) and ammonia were used to extract uranium and hence these chemicals exist at elevated levels within the tailings. During both operating phases, tailings and acidic effluent slurries were pumped 1.5 km from the plant to the tailings retention dam (Ward and Cox, 1985). The tailings settled out in the retention area and the decanted acidic effluent gravitated to unlined evaporation ponds below the dam wall (Flanagan et al., 1983). The dam (Figure 4.1) was constructed using a rolled earthfill and metasedimentary waste rock wall across a narrow section of a natural valley, with surrounding hills forming the sides of the dam (Ward and Cox, 1985). Secondary embankments were constructed from mine waste (Ward et al., 1984). The tailings retention area covered 28.5 hectares and provided storage for 7 million tonnes of tailings (MKU, 1986).

The tailings disposal system was designed to confine all liquid wastes, however, seepage from the tailings dam was evident during the mining phase. Seepage areas were found to follow zones of major fracture in bedrock (Flanagan et al., 1983). Piezometers, boreholes and pumps were installed on seepage paths downstream of the ponds (Figure 4.2) to monitor the water table and seepage flows and to collect the seepage water and return it, via a collection pond, to the mine and treatment plant for operational use (Ward et al., 1983). Pumps were also installed in the creek bed downstream of the area to transfer groundwater trapped in the aquifer, close to the rock bar (EP8), to the collection pond.

Figure 4.1. Cross section of tailings dam at Mary Kathleen. (modified from MINENCO 1986)

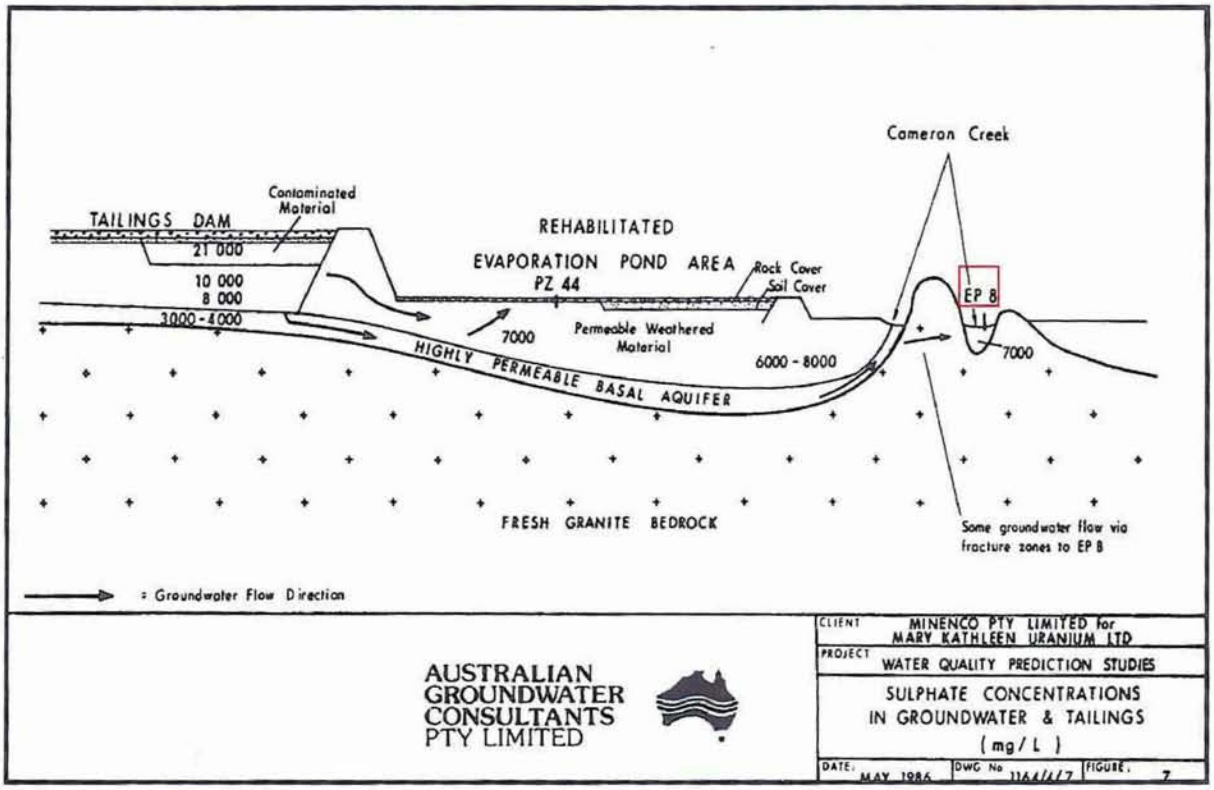


Figure 4.2. Mary Kathleen tailings dam environmental sampling points

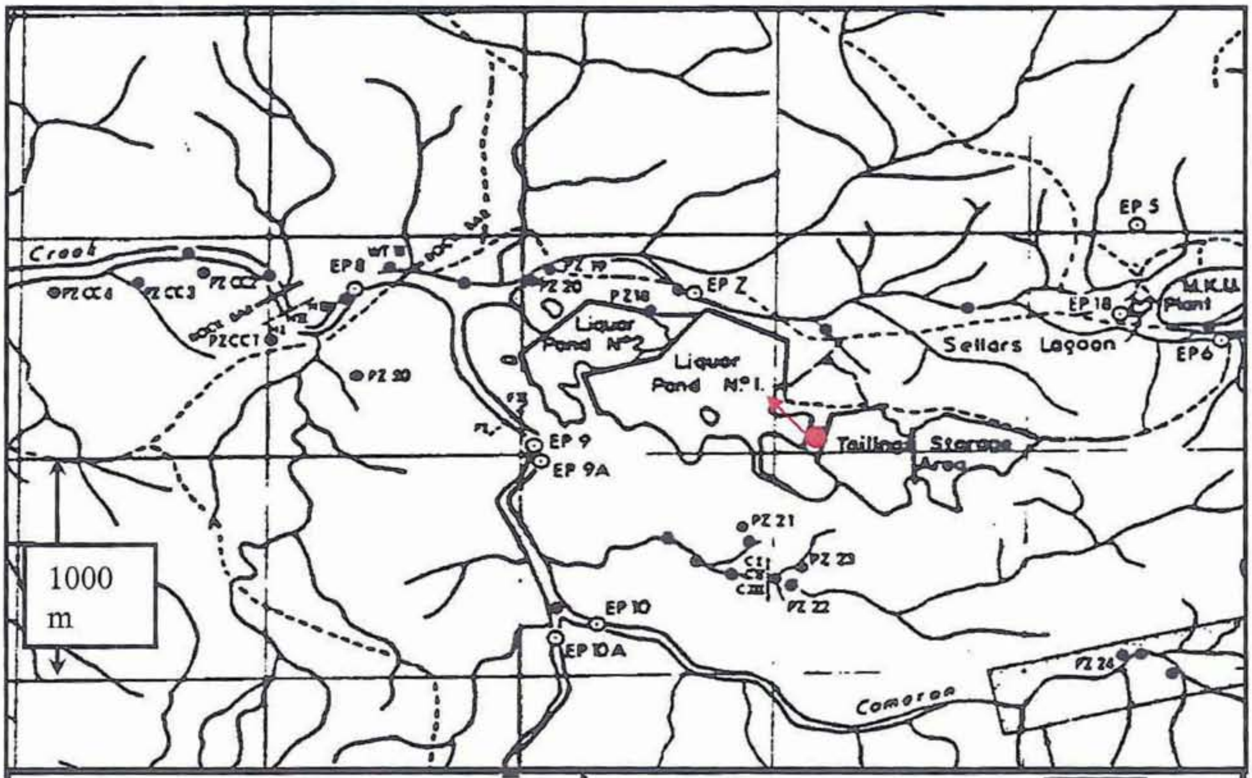


Figure 4.2. Mary Kathleen tailings dam environmental sampling points
(Modified from MINENCO 1166/2 1986)

### 4.2.2. Initial rehabilitation and modifications to rehabilitation

When mining ceased in 1982 all contaminated equipment and soil from the treatment plant area and evaporation ponds were buried in the tailings dam. Table 4.1 is a brief summary of the closure and rehabilitation of the evaporation ponds and tailings storage areas.

Table 4.1. Chronology of rehabilitation of tailings and evaporation ponds.

(Summarised from MKU, 1986).

| | |
|---|---|
| **1982** | |
| SEPTEMBER | Cessation of mining activities. |
| OCTOBER | Cessation of treatment plant operations. |
| NOVEMBER | Additional evaporation ponds established. |
| **1983.** | |
| JUNE | Clean-up of evaporation pond evaporite layer commenced. |
| JULY | Placement of clay/soil/evaporite material, from base of evaporation ponds, on top of lower tailings section. Strengthening of north wall of tailings dam initiated. |
| SEPTEMBER | Clean up of the creek and collection ponds to the south and west of the treatment plant commenced. |
| OCTOBER | Cameron Creek clean-up completed. |
| **1984.** | |
| FEBRUARY | Controlled discharge of evaporation pond liquid to Cameron Creek. |
| MARCH | Completion of soil/clay layer placement on upper tailings section. Commencement of one metre waste rock cover on upper south tailing section. |
| APRIL | Completion of outer cove of north wall, tailings area. |
| MAY | Completion of waste rock layer placement on upper south tailings section. Commencement of outer cover placement on east wall, tailings area. Relinquishment of certain leases initiated. |
| JUNE | Placement of waste rock cover in upper north tailings area commenced. |
| AUGUST | Additional monitoring piezometers installed - tailings and evaporation ponds. |
| SEPTEMBER | Clean-up of Pond 1 completed. Sections of Pond 1 reflooded to maximise evaporation area. Removal of slimes, evaporite and contaminated ground from Pond 2 area initiated. Evaporation pond liquid volume: 267,000 cubic metres. |
| OCTOBER | Further investigations into the evaporation ponds area cover design undertaken. |
| **1985** | |
| JANUARY | Pond 2 clean-up. Rock cover placement in upper north tailings area. Infiltration trenches clean-up. Contouring of Pond 2 area commenced. |
| FEBRUARY | Placement of waste rock cove in Pond 1 commenced. Placement of soil cover in Pond 2 commenced. |

| | |
|---|---|
| MARCH | Placement of waste rock cover in Pond 2 commenced. Remaining evaporation pond liquid transferred to the north section of the tailings area. Liquid volume: 50,000 cubic metres. |
| APRIL | Clean-up of subsidiary evaporation areas in Ponds 1 and 2 commenced. |
| MAY | Clean-up of subsidiary evaporation areas completed and cover placement commenced. Review of the impact of site operations and rehabilitation works on the water quality in Cameron Creek initiated. |
| JULY | Treatment of final liquid volume on tailings area with fine limestone. |
| AUGUST | Residues from limestone treatment of liquid in tailings area commenced. |
| SEPTEMBER | Surrender of leases external to site area and access road completed. Placement of waste rock cover on lower section of tailings area commenced. |
| OCTOBER | Placement of soil cover in tailings area completed. Placement of waste rock cover in evaporation ponds area completed. |
| NOVEMBER | Placement of waste rock cover on lower section of tailings area completed. Final site clean-up activities completed. Clean-up workforce leaves site. |
| DECEMBER | Cessation of seepage water collection. |

**1986**

Post- rehabilitation monitoring programme.

---

Constraints were made on future land use including controls on building construction in the tailings/evaporation, dumps and mine areas as a precaution against possible exposure to radon daughters (Ward and Cox, 1985).

### 4.2.3. Contamination/Seepage predictions from closure plan

Surface seepage from the tailings dam was reported to be due to the percolation of waters derived from rehabilitation activities in the lower north section of the tailings dam, where soil from the treatment plant, dredged water from the evaporation ponds and the last remaining quantities of liquor were disposed of by evaporation in small ponds (MINENCO, 1985). Chemical compositions of water samples from the seepage and surface sample locations (evaporation ponds) from the final water quality report (1986) are detailed in Appendix 10. The following analytical parameters were collected between July 1985 to April 1986 and were included in the final report: pH, TDS, $SO_4$, Cl, $CO_3$, $HCO_3$, Na, Ca, Mg, K, Al, Mn, Fe, U, Th, Pb, Cu, Zn, Cr, Ni, Cd, Mo, Ra226, Th230, Pb210, Po210, gross α and gross β. Manganese, iron and sulphate were closely monitored because they were added during processing as reagents which were then pumped into the Mary Kathleen tailings dam.

Seepage from the tailings storage area into the aquifer was expected to decline from 230 $m^3$/day in 1985 to 50 $m^3$/day in 2005 to 2025 and 30 $m^3$/day in the long term (MINENCO, 1985).

Dry season TDS was expected to be less than 4000 mg/L after 1995 and less than 3000 mg/L after 2020. Reported discussions with site personnel and an investigation of records indicate that there was no red/brown iron precipitation at the toe of the tailings dam or in seepage waters prior to 1983 (MINENCO, 1985).

A rainfall event of 4 mm in 1986 (14th April) was monitored in detail (MINENCO, 1986). Seepage flow and a water sample were collected. Flow volumes and water chemistry are given in Table 4.2.

Table 4.2. Seepage flow and water quality 1986 (modified from MINENCO 1985)

| Date | Flow (m3/day) |
|---|---|
| 10/04/86 | 5 |
| 14/04/86 | 92 |
| 16/04/86 | 29.1 |
| 21/04/86 | 0 |
| 29/04/86 | 0 |

The water quality details for the 14th April 1986 are as follows (mg/L)

| Seepage area | pH | TDS | Cl | $SO_4$ | U | Mn | Fe |
|---|---|---|---|---|---|---|---|
|  | 6.85 | 14,700 | - | 9030 | 0.02 | 525 | 0.20 |

Geochemical plumes of $SO_4$, Cl and Mn were recognised in the subsurface during the rehabilitation program (MINENCO, 1986). Sulphate contamination of the groundwater system was documented and abundant salts precipitated in the local creek beds during rehabilitation. There was no indication of elevated levels or for the mobilisation of other elements including uranium (Flanagan et al., 1983).

Hydrogeological studies (Flanagan et al., 1983; MKU, 1986; MINENCO, 1986) of the tailings area at the time of rehabilitation led to the following conclusions:
a) seepage from the tailings dam will be contained within the local catchment areas and is neutralised by the alkaline soils and aquifer to a quality which meets the standards of stockwater;
b) the movement of heavy metals and radionuclides is severely retarded by the soils and aquifer;
c) there is no evidence that uranium or any of its daughters moving from the waste disposal area now or in the future;
d) sulphate is the main contaminant in the groundwater system, however, there does not appear to be any potential problem associated with long term accumulation of salts in stream beds affected by contaminated groundwater;
e) the recently formed iron rich precipitates and existing salts should be effectively flushed out of the drainage system during the normal surface flow;
f) vegetation growth on the surface of the area should assist in increasing evapo-transpirational loss and reduce the effects of long term infiltration.

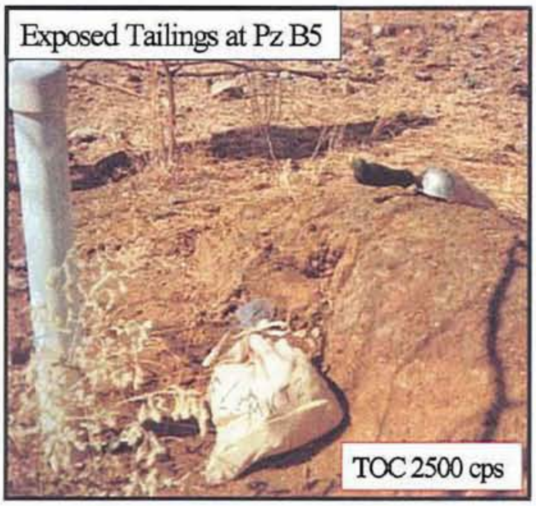
## 4.3 Tailings storage surface area

The study of the tailings area focussed on two areas (Figure 4.2), the surface of the tailings dam and the seepage at the tailings dam toe. Vegetation and tailings samples were taken from the tailings dam surface. Water, Fe-rich precipitates and mineral efflorescence samples were collected from the seepage area.

### 4.3.1 Tailings

Tailings samples were taken near Piezometer 16 (MKT1 395806 E 7708073 N), Piezometer B5 (MKT2, Figure 4.3) and from a small gully near the NW corner of the tailings dam (MKT3). Tailings exposed at these former two areas cover approximately 1m x 1m and occur where the installation of piezometers in the 1980s caused minor spills. Tailings are very fine grained as processing reduced 55% of the ore to less than 75 μm (MKU, 1982).

Figure 4.3. Photograph of tailings spill at Piezometer B5 (Photographed 10-10-1999).



### 4.3.2 Mineralogy

The tailings comprise primary gangue minerals including quartz, garnet, clinopyroxene, plagioclase, chlorite, sericite, epidote, scapolite and chalcopyrite as well as the secondary phases gypsum and jarosite. Tailings mineralogy was determined XRD analysis (Appendix 1). Exposed tailings are acidic and have high a conductivity (Table 4.3).

Table 4.3. pH and conductivity of surface tailings spill samples.

| Sample Name | pH | Conductivity (uS/cm) |
|---|---|---|
| MKT1 | 4.5 | 1400 |
| MKT2 | 4.9 | 955 |
| MKT3 | 4.2 | 1000 |

### 4.3.3 Geochemistry

Tailings materials have major (> 1 %wt) concentrations of Ca and Fe and minor (> 1000 ppm) concentrations of S, Ce, La, Mg, Mn, Na and P (Table 4.4). Low U concentrations (< 100ppm) are, as expected, due to the removal of U during the extraction process.

Table 4.4. Major (wt%) and trace element (ppm) tailings spill geochemistry.

| | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | V | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | ppm | | | | | | | | | | | | | | | |
| MKT1 | 15.7 | 9.78 | 0.5 | 0.7 | 0.4 | 148 | 725 | 7510 | 356 | 7510 | 2320 | 16 | 5210 | 257 | 6390 | 11 | 250 | 43 | 101 | 58 | 15 |
| MKT2 | 17.4 | 10.3 | 0.2 | 0.7 | 0.3 | 169 | 117 | 9560 | 250 | 9560 | 2550 | 14 | 4510 | 201 | 2060 | 0 | 248 | 62 | 103 | 68 | 14 |
| MKT3 | 2.8 | 14 | 1.7 | 0.4 | 0.9 | 36 | 645 | 895 | 113 | 1150 | 587 | 7 | 2100 | 133 | 51710 | 78 | 152 | 7 | 87 | 22 | 31 |

It is assumed that most of the Cu, Ni, Ce, and La are held in primary ore minerals (e.g. chalcopyrite, allanite) as well as secondary phases formed during and after tailings disposal (e.g. Fe-oxyhydroxides, gypsum and other sulphates).

MKT1 and MKT2 show similar geochemical signatures with elevated values of Ca, As, Ce, La, Cu and Mn (Table 4.4). MKT3 has significantly higher amounts of Fe and S and much lower REE and U. In the north of the tailings dam (site of MKT3), soil from the treatment plant, dredged water from the evaporation ponds and the last remaining quantities of liquor were disposed of by evaporation in small ponds. Hence, sample MKT3 may represent a mixture of tailings, evaporative salts and contaminated soil.

### 4.3.4 Vegetation

The tailings area is covered with grass, a few small bushes and very few trees. Two vegetation samples (MKV33 & MKV34) were taken from Piezometer 16 (MKT1) and one sample (MKV39) from the evaporation pond area. Vegetation collected on tailings partially accumulate Mn, Ce and La. MKV39 sampled from MKS12 where white abundant efflorescences were observed, contain high Na, Mg, S, Th and Zn (Table 4.5).

Table 4.5. Major (wt%) and trace element (ppm) geochemistry of ashed tailings vegetation samples

| | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | V | Y | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | ppm | | | | | | | | | | | | | | | | |
| *Aerva javanica* (kapok bush) | | | | | | | | | | | | | | | | | | | | | | |
| MKV33 | 18 | 1.3 | 2 | 5.1 | 1 | 28 | 130 | 1690 | 135 | 1090 | 1930 | 31 | 11710 | 40 | 21410 | 267 | 35 | 16 | 17 | 10 | 518 | MKT1 |
| *Enneapogon lindleyanus* | | | | | | | | | | | | | | | | | | | | | | |
| MKV34 | 6.7 | 2.4 | 1.7 | 0.9 | 0.3 | 38 | 180 | 2530 | 142 | 1620 | 1030 | 88 | 3920 | 67 | 15710 | 43 | 48 | 13 | 28 | 13 | 330 | MKT1 |
| *Cynodon dactylon* | | | | | | | | | | | | | | | | | | | | | | |
| MKV39 | 4.3 | 0.5 | 2.8 | 6 | 7.3 | 6 | 68 | 23 | 166 | 19 | 562 | 44 | 4970 | 8 | 59710 | 336 | 349 | 3 | 16 | 4 | 1460 | MKSS13 |

MKV39 accumulates 47 times the concentration of Zn than is present in the substrate, whereas MKV34 and MKV39 accumulate 6 times the concentration of Ni than present in the substrate. MKT1 contains high As (148 ppm), Ce (7510 ppm), La (7510 ppm), Mn (2320 ppm) and Pb (257 ppm) this is reflected in the geochemistry of vegetation sampled at this site.

Table 4.6. Major (wt%) and trace element (ppm) geochemistry of ashed *Amaranthaceae Aerva javanica* (kapok bush) sampled from the open pit, West tip, tailings dam surface and background.

| | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | V | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | ppm | | | | | | | | | | | | | | | |
| Background sample | | | | | | | | | | | | | | | | | | | | | |
| MKV13 | 19.8 | 0.9 | 2.6 | 6 | 0.2 | 8 | 650 | 30 | 90 | 20 | 570 | 24 | 10400 | 5 | 9450 | 323 | 2 | 3 | 26 | 4 | 47 |
| Open pit samples | | | | | | | | | | | | | | | | | | | | | |
| MKV5 | 20.6 | 3.1 | 3.6 | 4 | 0.4 | 17 | 254 | 347 | 786 | 236 | 1760 | 247 | 15200 | 15 | 16300 | 270 | 11 | 10 | 28 | 13 | 410 |
| MKV6 | 21.9 | 2.4 | 2.4 | 5 | 0.2 | 19 | 81 | 216 | 477 | 164 | 327 | 117 | 7700 | 12 | 20010 | 272 | 6 | 7 | 22 | 7 | 177 |
| MKV14 | 20.2 | 2.9 | 1.9 | 4 | 0.5 | 16 | 14 | 737 | 208 | 497 | 540 | 42 | 5640 | 34 | 15300 | 147 | 15 | 153 | 27 | 10 | 54 |
| MKV21 | 23.1 | 1 | 2.2 | 5 | 0.1 | 14 | 34 | 436 | 285 | 300 | 905 | 186 | 9690 | 12 | 11700 | 201 | 8 | 151 | 14 | 9 | 728 |
| MKV42 | 18.8 | 2.3 | 1.5 | 4 | 0.7 | 11 | 239 | 366 | 181 | 245 | 740 | 34 | 6720 | 22 | 14410 | 313 | 15 | 71 | 58 | 18 | 311 |
| West Tip sample | | | | | | | | | | | | | | | | | | | | | |
| MKV26 | 17 | 2.1 | 2.8 | 3 | 0.3 | 12 | 245 | 307 | 176 | 221 | 903 | 84 | 11800 | 13 | 9380 | 122 | 13 | 58 | 31 | 18 | 543 |
| Tailings dam surface sample | | | | | | | | | | | | | | | | | | | | | |
| MKV33 | 18 | 1.3 | 2 | 5 | 1 | 28 | 130 | 1690 | 135 | 1090 | 1930 | 31 | 11710 | 40 | 21410 | 267 | 35 | 16 | 17 | 10 | 518 |

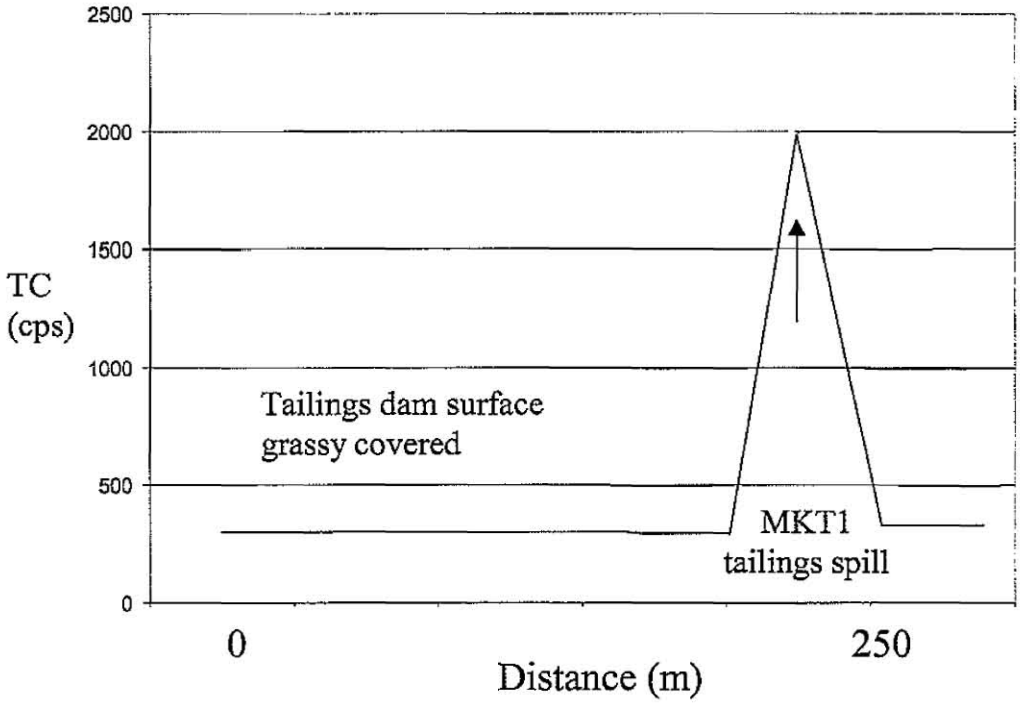
The *Amaranthaceae Aerva javanica* sample taken from the surface of the tailings dam has distinctly higher As, Ce, La, Th and elevated Mn, Pb, S and Zn values than other *Amaranthaceae Aerva javanica* sampled in and around the mine site (Table 4.6).

### 4.3.5 Radiometrics

The tailings gamma-ray survey was designed to estimate dose rates, surface contamination and confirm known and unknown radiation sources on top of the tailings area. Spot readings were taken on the surface of the tailings dam. All radiometric data were tabulated and assessed for data quality (Appendix 3).

Tailings surface total count readings along traverse 9 averaged 300 cps which is below acceptable background levels (Figure 4.4). Elevated readings were recorded at the MKT1 sample site. Elevated radiation levels (up to 2500cps) were also recorded at 2 other small isolated areas (MKT2, MKT3). As previously discussed, these areas are the result of minor tailings spills.

Figure 4.4. Tailings dam surface total count (cps) traverse, including a brief description of surface features.



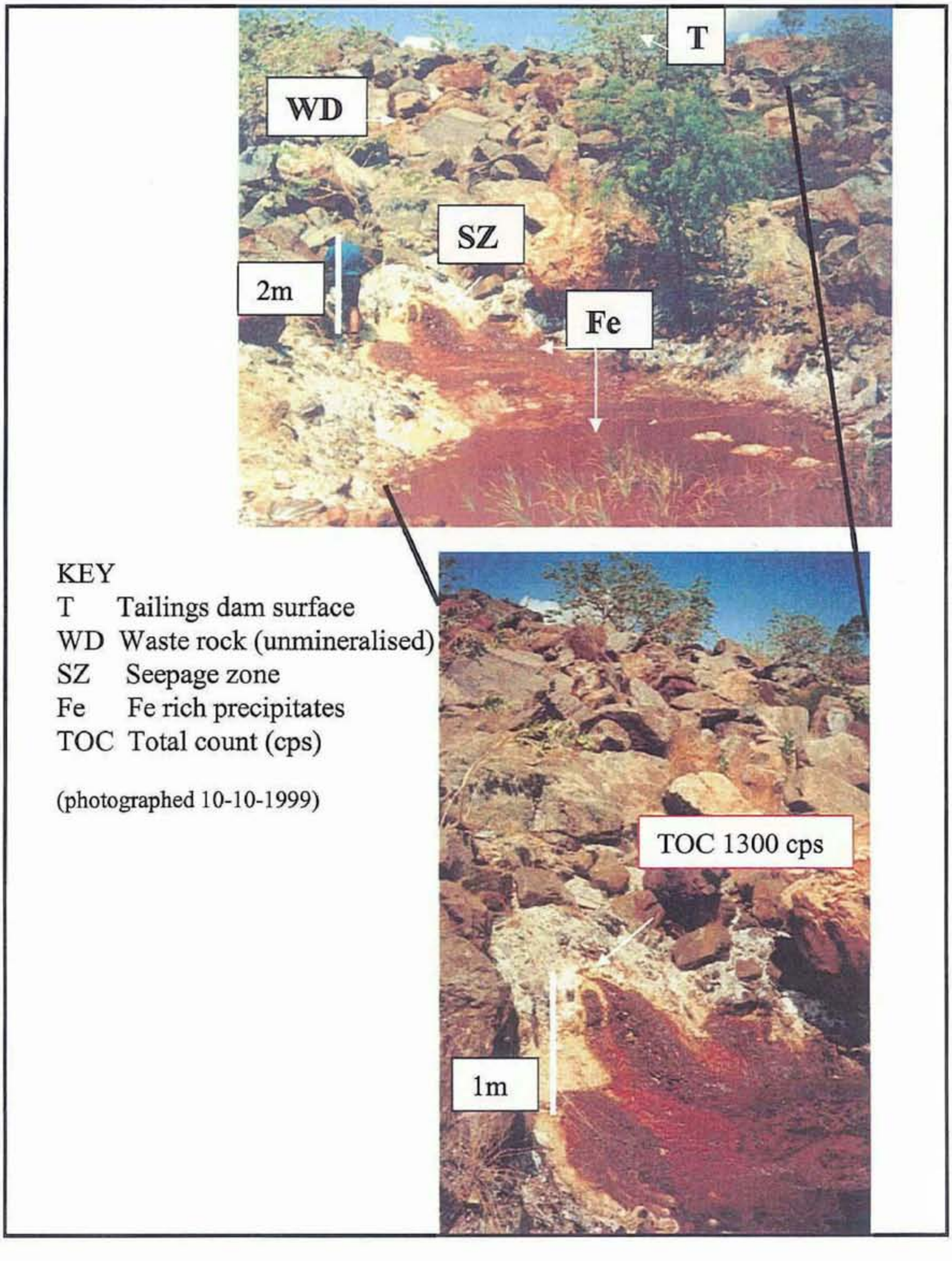
Unmineralised waste rock materials were used to construct the dry cover and surface readings (300 cps) are similar to those of soil covered waste dumps present at the mine site. Overall, the dam cover appears to attenuate radiation from underlying tailings.

## 4.4 Tailings seepage area

### 4.4.1 Seepage Chemistry

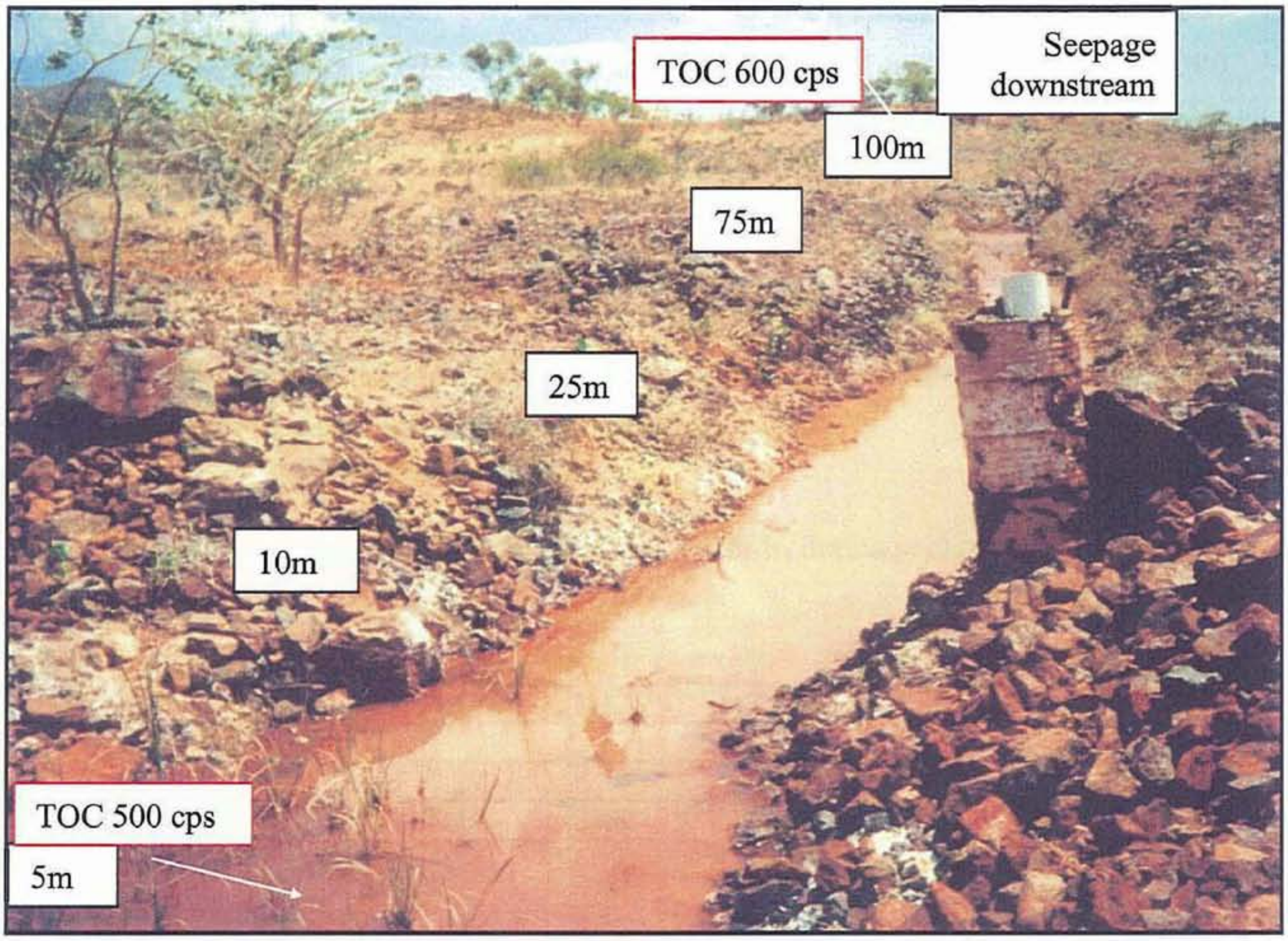
Tailings water seeps from the base of the tailings dam and flows toward the former evaporation ponds (Figure 4.4a and 4.4b).

Figure 4.4a. Photograph of tailings seepage area (395878 E 7708353 N)



(photographed 10-10-1999)

Figure 4.4b Photograph of tailings seepage drainage area (Photographed 10-10-1999)



The seepage water is acidic (pH 5.7), saline (0.31 %) and radioactive (TC 1300 cps) with low dissolved oxygen (2.6 mg/L) and emanates at a rate of approximately 0.5 L/s. Field water quality measurements from the seepage point toward the evaporation pond area are listed in Table 4.6.

Table 4.6. Seepage water quality (in field measurements)

| Sample | Location of water quality checks | pH | Dissolved Oxygen (mg/L) | Temp. (°C) | Salinity (%) | TC (cps) |
|---|---|---|---|---|---|---|
| MKW4 | Seepage point (395878 E 7708353 N) | 5.7 | 2.6 | 25.7 | 0.3 | 1300 |
| MKW10 | Tailings seepage zone | 5.9 | 3.3 | 34 | 0.3 | |
| MKW11 | Downstream 10m (stagnant pond) | 6.4 | 3.4 | 32.5 | 0.3 | 500 |
| MKW12 | Downstream 30m (shallow) | 6.6 | 3.63 | 30.8 | 0.3 | |
| MKW13 | Downstream 70m (shallow) | 7.0 | 6.24 | 32.5 | 0.3 | |
| MKW5 | Downstream 100 m (395902 E 7708410 N) | 6.6 | 5 | 26.2 | 0.3 | 600 |
| MKW6 | Pond - evap ponds area (396317 E 7709224 N) | 8.1 | 7.8 | 23.6 | 1.0 | |

Continuing downstream (Figure 4.4b), surface waters from the drainage trench and in the evaporation ponds have higher pH, dissolved oxygen, and salinity values than at the seepage point. Seepage waters are radioactive with total count readings at 1300 (background TOC for this site is 400 cps).

Water chemistry measurements shows that seepage waters (MKW4) have high Fe, Mg, Ni, and Zn levels (Table 4.7). Water collected from the drainage channel (MKW5) and small evaporation pond (MKW6) has higher cation (Na, Ca, Mg), anion ($SO_4$, Cl, $HCO_3$) and Al, Cu, Mo, U values than the seepage water.

Table 4.7. Analysis of seepage water (MKW4) water in drainage channel (MKW5) and evaporation pond water (MKW6)

| Parameter | MKW4 | MKW5 | MKW6 |
|---|---|---|---|
| | | | |
| pH | 5.89 | 6.78 | 8.29 |
| Conductivity (µS/cm) | 8800 | 5580 | 40000 |
| Total Hardness (mg $CaCO_3$/L) | 3190 | 3850 | 11800 |
| Total Alkalinity (mg $CaCO_3$/L) | 93.5 | 248 | 618 |
| Total Dissolved Solids (mg/L) | 6080 | 5875 | 20700 |
| | | | |
| Sodium (mg/L) | 215 | 230 | 2400 |
| Potassium (mg/L) | 70 | 60 | 14.1 |
| Calcium (mg/L) | 512 | 546 | 600 |
| Magnesium (mg/L) | 465 | 603 | 2500 |
| Sulphate (mg/L) | 4200 | 3930 | 14000 |
| Chloride (mg/L) | 48.5 | 243 | 790 |
| Bicarbonate (mg/L) | 114 | 302 | 770 |
| Carbonate (mg/L) | <1 | <1 | <1 |
| Aluminium (µg/L) | <3 | <3 | 154 |
| Arsenic (µg/L) | <50* | <50 | <50 |
| Barium (µg/L) | 16 | 18 | 10 |
| Copper (µg/L) | <5 | <5 | 18 |
| Iron (mg/L) | 250 | 49 | 7.56 |
| Manganese (mg/L) | 328 | 119 | 0.19 |
| Molybdenum (µg/L) | <0.5 | 1 | 5 |
| Nickel (µg/L) | 167 | 76 | 17 |
| Uranium (µg/L) | 303 | 423 | 5090 |
| Zinc (µg/L) | 56 | 49 | 34 |

* -higher reporting limit due to high sample salinity

Progressive chemical changes in the analysed surface waters are due to (a) evaporation of surface waters in ponded areas and the concentration of soluble elements and compounds (e.g. alkalis, sulphate, chloride, bicarbonate, uranium); and (b) the formation of Fe-rich flocculants at the seepage point and in the drainage channel and the associated fixation of trace elements in the Fe-rich precipitates (Table 4.8).

Analysis of MKW6 alkaline (pH 8.29) and comparably low Fe (7.56 mg/L) evaporation pond water indicates the iron in seepage waters has oxidised and precipitated as an iron sulphate. This indicates that uranium remains soluble and is most likely present as the highly soluble uranium $(6^{+})$ $UO_2^{2+}$ ion in alkaline waters collected from the evaporation ponds.

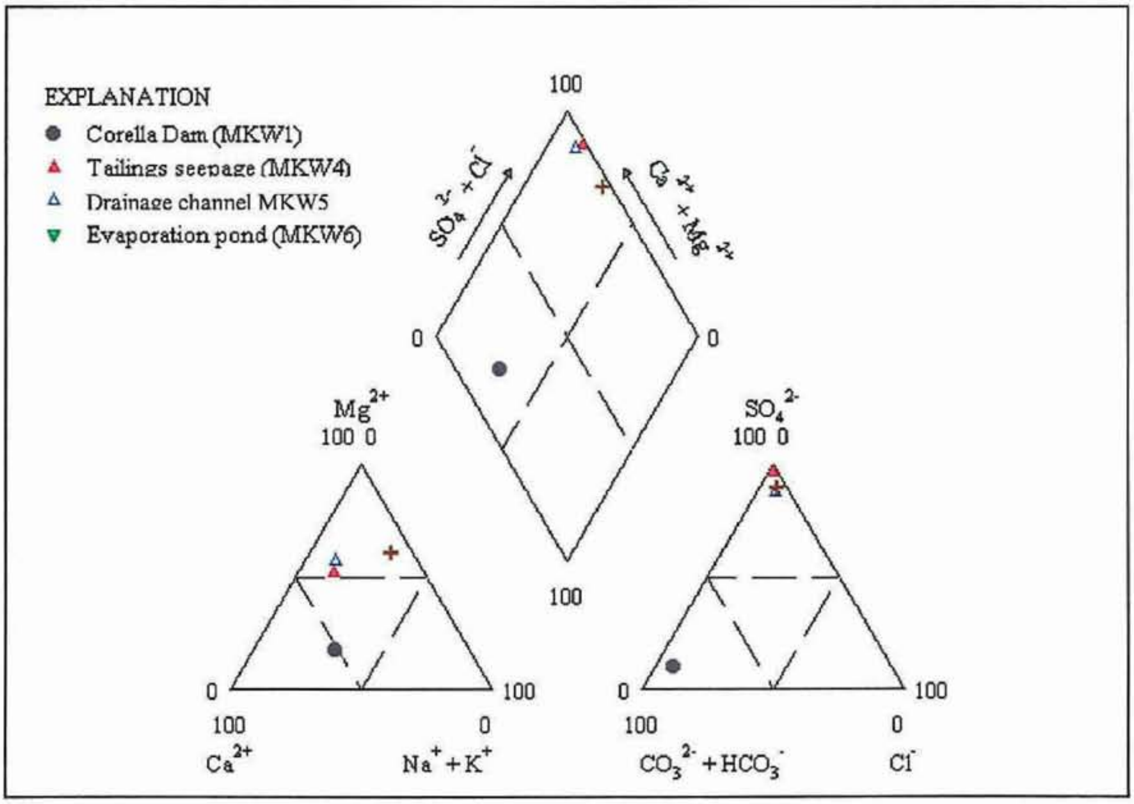
Table 4.8. Selected water geochemistry parameters from the seepage zone and drainage channel indicating concentration changes.

| Seepage zone | | Drainage channel |
|---|---|---|
| U 303 µg/L | ↗ | U 423 µg/L |
| Fe 250000 µg/L | ↘ | Fe 49000 µg/L |
| Mn 328000 µg/L | ↘ | Mn 1190 µg/L |
| TDS 6080 mg/L | ↘ | TDS 5872 mg/L |
| $S0_4$ 4200 mg/L | ↘ | $S0_4$ 3930 mg/L |

TDS levels between 5875 and 20700 mg/L can cause loss of production and a decline in animal condition should cattle drink this water (ANZECC, 2000). U exceeds the recommended water quality quidelines (low risk) for live stock drinking water by two times in MKW5 and twenty times in MKW6 (ANZECC, 2000). Sulphate levels above 2000 mg/L may cause chronic or acute health problems in stock. However, cattle are unlikely to drink this water since the salinity and manganese will make it distasteful.

The Piper diagram (Figure 4.5) shows that seepage waters are relatively enriched in $Mg^{2+}$ and $SO_4^{2-}$ compared to background waters. The sulphate-rich composition reflects its origin in the dissolution of magnesium, calcium and sulphate minerals and oxidation of sulphides. Evaporation pond water is not only enriched in $SO_4^{2-}$, but also in $Na^+$+$K^+$.

Figure 4.5. Piper diagram illustrating the chemistry of Corella Dam, tailings seepage and evaporation pond waters.



### 4.4.2 Seepage precipitates

Abundant Fe-rich flocculants and gelatinous Fe-rich precipitates are present at the seepage point, in the drainage channel and to a lesser degree in the evaporation ponds. Red iron rich precipitates were sampled from the seepage point and at regularly spaced intervals down stream. White mineral efflorescences are also present in the seepage and drainage areas (Appendix 2).

#### 4.4.2.1 Iron rich precipitate mineralogy and geochemistry

The Fe-rich gelatinous wet sediments were labeled in the field as MKE38-44 and MKSS16-18. Samples MKE38-44 were sieved to 2 mm - 63μm and samples MKSS16-18 were sieved into two fractions 2 mm - 63μm and < 63μm and submitted to ALS for

geochemical analysis. Dried seepage samples have elevated total count readings (MKSS16; 181 cps, MKSS17; 179 cps, MKSS18; 168 cps).

The iron rich sediments inspected by XRD analysis comprise major amounts of amorphous Fe-oxyhydroxides and minor quantities of bassanite ($CaSO_4\ 0.5H_2O$), gypsum ($CaSO_4.2H_2O$), epsomite ($MgSO_4$), copiapite ($(Fe,Mg)Fe_4(SO_4)_6(OH)_2.20H_2O$), jarosite ($KFe^{3+}{}_3(SO_4)_2(OH)_6$), hexahydrite ($MgSO_4.6H_2O$), and schwertmannite ($Fe_8O_8(SO_4)(OH)_6$).

The formation of acid and iron sulphates occurs by the following chemical steps:

$$FeS_{2\ (pyrite)} + 3O_2 + 2H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 4H^+$$

$$2FeS_2 + 2H_2O + 7O_2 + 2CaCO_3 \rightarrow 2FeSO_4 \text{ (ferrous sulphate)} + 2CaSO_4.2H_2O \text{ (gypsum)} + 2CO_2$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \text{ (sulphuric acid)} \rightarrow 2Fe_2(SO_4)_3 \text{ (ferric sulphate)} + 2H_2O$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 \text{ (ferric hydroxide)} + 3H_2SO_4$$

Iron precipitates when it is the ferric oxidation state (iron III) in the form of iron hydroxide $Fe(OH)_3$, as an iron rich sediment at a pH greater than 5.5 by the following reaction:

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

The precipitates display significant enrichment (i.e > 15 wt%) of Fe, major (i.e. > 1 wt%) concentrations of Ca and S, minor contents (i.e. > 1000 ppm) of Ce, La, K, Mg, Mn, and Na and elevated (i.e. > 100 ppm) contents of P, Sr, U and commonly As (Table 4.9).

Table 4.9. Major (wt%) and trace element (ppm) geochemistry of seepage zone iron precipitates.

| Sample | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | ppm | | | | | | | | | | | | | | |
| E sample (2mm-63 μm fraction) | | | | | | | | | | | | | | | | | | | | |
| MKE38 | 8.5 | 21.8 | 0.4 | 0.24 | 0.19 | 83 | 71 | 6840 | 62 | 3750 | 1120 | 8 | 195 | 27 | 60500 | 152 | 5 | 901 | 68 | 44 |
| MKE39 | 2.3 | 41.8 | 0.01 | 0.06 | 0.04 | 41 | <10 | 3760 | 8 | 1640 | 862 | <1 | 35 | 7 | 23410 | 50 | <0.1 | 1020 | 57 | 33 |
| MKE40 | 2 | 38.6 | 0.34 | 0.19 | 0.14 | 56 | 64 | 4890 | 21 | 2550 | 1510 | 7 | 159 | 12 | 14000 | 34 | 3 | 889 | 98 | 40 |
| MKE41 | 2.2 | 39 | 0.09 | 0.15 | 0.09 | 51 | 18 | 5070 | 19 | 2960 | 1580 | 10 | 95 | 9 | 18900 | 45 | 1 | 1010 | 43 | 41 |
| MKE42 | 1.3 | 39.7 | 0.01 | 0.15 | 0.09 | 21 | <10 | 3260 | <1 | 2190 | 1310 | <1 | 33 | <5 | 15210 | 40 | <0.1 | 599 | 22 | 33 |
| MKE43 | 1.6 | 37.4 | 0.02 | 0.23 | 0.09 | 93 | 23 | 4910 | <1 | 5070 | 3920 | 12 | 46 | 7 | 7190 | 133 | <0.1 | 206 | 69 | 51 |
| MKE44 | 6.6 | 15.9 | 0.87 | 1.08 | 0.53 | 102 | 150 | 6750 | 56 | 5810 | 8140 | 37 | 408 | 12 | 32210 | 274 | 11 | 199 | 70 | 65 |
| SS A sample ( 2mm-63 μm fraction) | | | | | | | | | | | | | | | | | | | | |
| MKSS18A | 5.9 | 31.4 | 0.1 | 0.1 | 0.1 | 124 | 17 | 10400 | 19 | 5290 | 1260 | 6 | 77 | 25 | 50110 | 125 | 1 | 1730 | 102 | 28 |
| MKSS17A | 1.2 | 43.5 | 0.1 | 0.2 | 0.1 | 54 | 33 | 3840 | 38 | 1800 | 1470 | 7 | 108 | 11 | 13610 | 25 | 3 | 986 | 60 | 39 |
| MKSS16A | 6.1 | 16.5 | 1.2 | 0.6 | 0.5 | 125 | 241 | 7090 | 50 | 6190 | 7020 | 39 | 441 | 19 | 36400 | 159 | 7 | 227 | 69 | 58 |
| SS B sample ( < 63 μm fraction) | | | | | | | | | | | | | | | | | | | | |
| MKSS18B | 1 | 42.3 | 0 | 0.1 | 0.1 | 146 | 11 | 11410 | 27 | 5690 | 1610 | 6 | 79 | 36 | 14510 | 27 | 1 | 2260 | 134 | 38 |
| MKSS17B | 0.3 | 46.8 | 0.1 | 0.2 | 0.1 | 38 | 17 | 4280 | 47 | 2000 | 1740 | 7 | 107 | 7 | 7890 | <10 | 2 | 1190 | 51 | 44 |
| MKSS16B | 1.4 | 34.8 | 0.1 | 0.4 | 0.2 | 158 | 45 | 12100 | 32 | 10300 | 9990 | 36 | 222 | 11 | 6200 | 96 | 4 | 380 | 122 | 69 |

ISQG-low and ISQG-high sediment quality guidelines (ANZECC, 2000) have been exceeded for As. ISQG-low sediment quality guidelines (ANZECC, 2000) have been exceeded for Ni (Appendix 8).

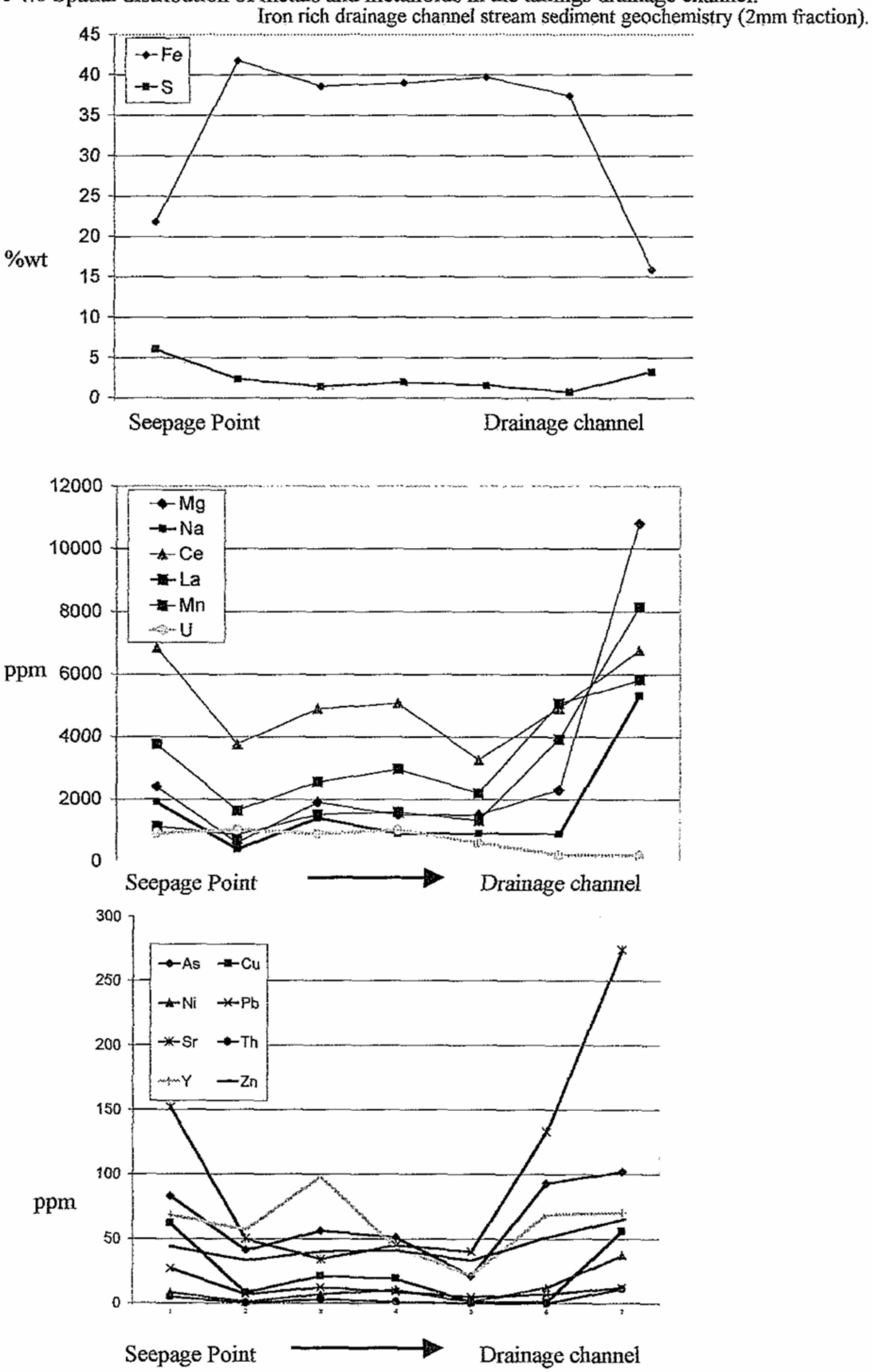
The coarser-grained fraction (63 µm – 2 mm) of the sampled Fe-rich precipitates displays higher Ba, Ca, K, Mg, P, S and Sr values and lower Ce, La, Fe, Mn, U, Y and Zn contents than the fine-grained fraction (< 63 µm). The oxygenation of $Fe^{2+}$ bearing seepage and surface waters causes the hydrolysis of dissolved $Fe^{2+}$ and leads to the precipitation of $Fe^{3+}$ phases. Co-precipitation and adsorption processes are likely responsible for the distinct metal (U, Y), metalloid (As) and rare earth element (Ce, La) enrichment of Fe-rich flocculants and sediments (Figure 4.6).

Organic carbon analysis shows very low organic matter within the tailings seepage precipitates (Table 4.10). The detected low organic carbon contents in the sediments are the result of low organic matter within the channel. The decay products of algae are one possible source of the small amounts recorded.

Table 4.10. Organic carbon analysis for five seepage samples (<63um fraction).

| Sample description. | $NonCO_3$-C % | Location |
|---|---|---|
| MKO12 (from MKE39) | 0.04 | seepage |
| MKO13 (from MKE40) | 0.07 | seepage |
| MKO14 (from MKE41) | 0.07 | seepage |
| MKO15 (from MKE42) | 0.08 | seepage |
| MKO16 (from MKE44) | 0.13 | seepage |

Figure 4.6 Spatial distribution of metals and metalloids in the tailings drainage channel.



#### 4.4.2.2 Sulphate efflorescences

Identified white mineral efflorescences (MKE19, MKE37) represent hydrous alkaline earth sulphates (e.g. bassanite, gypsum, epsomite) with minor admixtures of hydrous $Fe^{2+}$ sulphates (e.g. melanterite, rozenite) and hydrous $Fe^{3+}$ sulphates (possibly kornelite $Fe^{3+}{}_2(SO_4)_3{\cdot}7(H_2O)$, coquimbite $Fe^{3+}{}_2(SO_4)_3{\cdot}9(H_2O)$ ). MKE37 contains major (i.e. > 1 wt%) concentrations of Ca, Fe, Mg, Na and S and minor contents (i.e. > 1000 ppm) of Ce, K and La (Table 4.11). Compared to the Fe-rich precipitates, MKE37 has distinctly lower Fe, U, Ce and La concentrations because these elements have co-precipitated and adsorbed onto Fe-rich flocculants and sediments closer to the seepage source.

Table 4.11. Major (wt%) and trace element (ppm) geochemistry of MKE37 (2mm – 63μm fraction).

| | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | ppm | | | | | | | | | | | | | | |
| MKE37 | 15 | 1.8 | 1 | 2.1 | 2 | 27 | 47 | 1620 | 150 | 1010 | 615 | 33 | 231 | 17 | 139400 | 169 | 19 | 14 | 8 | 13 |

### 4.4.3 Stream and pond sediments

#### 4.4.3.1 Evaporation pond sediments

Evaporation pond sediments accumulate in a highly saline (up to 1.5 wt%), alkaline (up to pH 8.1) environment (MKW6). The sediments comprise variable amounts of sulphate salts (i.e. bassanite, bloedite, epsomite) and silicates (i.e. quartz, albite, chlorite, garnet, epidote, diopside, dickite). Most silicate phases likely represent clastic sediment particles whereas dickite may be an authigenic phase.

The fine-grained (< 63 μm) fraction of the pond sediments displays lower Ca, K and S values and higher Ce, Cu, Fe, La, Mg, Mn, Na, Ni, P, U and Zn contents than the coarser-grained (2 mm - 63 μm) fraction (Table 4.12).

Table 4.12. Major (wt%) and trace element (ppm) geochemistry of evaporation pond sediments.

| | Ca | Fe | K | Mg | Na | As | Ba | Ce | Cu | La | Mn | Ni | P | Pb | S | Sr | Th | U | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | | | | | | | | | | | | | | | | |
| A sample ( 2mm-63 μm fraction) | | | | | | | | | | | | | | | | | | | | |
| MKSS12A | 11 | 2 | 1.1 | 3 | 0.6 | 8 | 125 | 239 | 36 | 182 | 1190 | 18 | 409 | 6 | 63500 | 244 | 8 | 78 | 13 | 33 |
| MKSS13A | 10.3 | 2.3 | 2.4 | 2.2 | 1.3 | 8 | 165 | 124 | 101 | 75 | 1360 | 28 | 608 | 8 | 48300 | 372 | 11 | 217 | 16 | 59 |
| B sample ( < 63 μm fraction ) | | | | | | | | | | | | | | | | | | | | |
| MKSS12B | 4.6 | 4 | 0.9 | 6.4 | 1.4 | 21 | 122 | 480 | 94 | 358 | 2600 | 38 | 951 | 13 | 10900 | 60 | 18 | 197 | 25 | 83 |
| MKSS13B | 5.9 | 3.7 | 1.3 | 3.9 | 1.8 | 19 | 387 | 255 | 223 | 171 | 2290 | 53 | 1370 | 19 | 17700 | 145 | 21 | 342 | 31 | 110 |

Such elemental distributions are likely due the preferential partitioning of monovalent (K) and divalent cations (Ca, Sr) into coarse-grained alkali sulphates (i.e. bassanite, bloedite, epsomite) which occur as minor constituents in the evaporation pond sediments. These geochemical characteristics combined with the mineralogical data indicate that the geochemical signature of the evaporation pond sediments is the result of competing clastic and chemical sedimentation. Erosion of the surrounding soils most likely contributes clastic particles to the evaporation pond sediments.

ISQG-low sediment quality guidelines (ANZECC, 2000) have been exceeded for As, Cu and Ni in evaporation pond sediments (Appendix 8).

Organic carbon analysis (Table 4.13) shows low organic matter within the evaporation pond area in both sized fractions.

Table 4.13. Organic carbon analysis for MKSS12.

| Sample No. | Fraction | NonCO3-C % | Location |
|---|---|---|---|
| MKO22 (from MKSS12) | 2mm-63μm | 0.14 | seepage pond, N part of evap. ponds area |
| MKO23 (from MKSS12) | < 63μm | 0.2 | seepage pond, N part of evap. ponds area |

## 4.5 Discussion

### 4.5.1 Tailings processes

Chemical processes within a tailings repository alter the original mineralogy and pore water composition. Dissolved metals, and metalloids may: (a) persist in solution; (b) precipitate or coprecipitate by interacting with other components in the tailings; or (c) be adsorbed by tailings solids such as quartz, kaolinite, clays or amorphous substances (Landa and Gray, 1995; Landa, 1999). Contaminants from tailings liquids may leak from the tailings repository and impact on surface water quality. Radionuclides, heavy metals, and metalloids are mobilised from the tailings solids into tailings liquids through various processes (Landa and Gray, 1995; Zielinski et al., 1997): (a) sulphide oxidation and AMD development; (b) leaching by process chemicals; (c) acid leaching, reduction or reductive dissolution of Fe and Mn oxyhydroxides; (d) bacterial reduction; and (e) adsorption of alkalis onto clay minerals. It is undesirable that these radionuclides, metals and metalloids are released from the tailings repository into surface waters.

Elevated metal, metalloid and rare earth element concentrations in the seepage water could be due to a number of processes operating within the tailings dam. The dissolution of secondary sulphate salts in the saturated and unsaturated zone as well as the oxidation of sulphides in the unsaturated zone likely release contaminants to acid pore waters. Furthermore, bacterial reduction and reductive dissolution or reduction of Fe and Mn oxyhydroxides may occur in the saturated zone of the waste repository (Morin and Hutt, 1997; Nordstrom, 1977, 1982; Nordstrom et al., 1979). Prior to capping ferric ion precipitation in the tailings dam was noted by Ward et al. (1984). Reduction of ferric precipitates by only slightly oxygenated porewaters (DO: 2.6 mg/L) in the saturated zone may lead to the release of metals (Ce, Fe, La, Mn, Ni, U, Y, Zn), metalloids (As) and rare earth elements (Ce, La) into tailings liquids. Any residual sulphuric acid or sulphuric acid generated by sulphide oxidation in the tailings would leach tailings solids and act as a complexing agent for radionuclides, metals and rare earth elements. As a result, the contaminants would become mobilised from their host phases, and be dissolved in tailings waters and surface at the toe of the tailings dam embankment.

Since rehabilitation, the tailings liquids have developed to higher pH (5.8) and lower sulphate, chloride, TDS, Mn and U values. Furthermore, the sulphate concentration of the current seepage water (4.2 g/L) is below that of the discharge water from the former mill (21 g/L) and that of the tailings liquid sampled in 1984 before dry capping (24 g/L) (Ward et al., 1984). Flushing of mill water has occurred since the 1980s and hence sulphide oxidation and AMD generation have developed in the Mary Kathleen tailings repository.

### 4.5.2 Radionuclide movement

Radionuclides, may be mobilised from the tailings solids into tailings liquids through various processes (Landa and Gray, 1995; Zielinski et al., 1997). A distinct spatial distribution of metals and metalloids, has been recognised. Iron-rich precipitates with elevated gamma-radiation from the seepage point contain elevated As, Ba, Ce, La, Pb, Sr and U values. Hence, radionuclides are leached from the tailings repository into surface water seepages and adsorbed into Fe-rich precipitates at the seepage point. These radionuclides remain unidentified.

## 4.6 Summary

The study of the rehabilitated Mary Kathleen tailings repository has revealed that the multi-barrier dry cover is intact and that radiation levels are at background levels. Previous work predicted negligible release of elements and radionuclides from the tailings repository. However, today, metals (e.g. Fe, Mn, Pb, Th, U, Y), metalloids (As), rare earth elements (Ce, La), alkalis (Ca, Mg, Na, K, Sr, Ba), radionuclides and sulphate are mobilised from the dam into surface water, by seepages emanating at the toe of the tailings dam. The mobilisation is likely due to the oxidation of sulphide minerals, dissolution of sulphate salts and the reduction or reductive dissolution of Fe-oxyhydroxides within the tailings repository.

Fe-rich precipitate formation at the seepage point, in the drainage channel and the evaporation pond is due to oxygenation of $Fe^{2+}$ bearing seepage and surface waters. Oxygenation of tailings seepages upon discharge causes the hydrolysis of dissolved $Fe^{2+}$ and leads to the precipitation of $Fe^{3+}$ phases. Co-precipitation and adsorption processes are likely responsible for the distinct metal (U, Y), metalloid (As) and rare earth element (Ce, La) enrichment of Fe-rich flocculants and sediments. In contrast, alkalis (Ca, Ba, K, Mg, Na, Sr), Mn, sulphate and rare earth elements (Ce, La) remain in solution until pH neutralisation and evaporation lead to their precipitation in sulphate-rich (e.g. bassanite, bloedite, epsomite) evaporative sediments further downstream. The study highlights dry capping of Mary Kathleen uranium mill tailings did not prevent the mobilisation of numerous contaminants from the tailings dam into the surface environment.