The Effects of Weathering and Diagenetic Processes on the Geochemical Stability of Uranium Mill Tailings

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Abstract. In the present study, a detailed examination of tailings cores and pore waters, kinetic column test work and geochemical modelling was combined with results from earlier studies to examine the key processes governing the geochemical stability of the Ranger tailings. Conclusions drawn from the work clearly demonstrates that the solid state speciation and mobility of metals and radionuclides in the tailings pile are governed by the processes of oxidative dissolution of sulfide minerals, weathering of phyllosilicates and organic matter diagenesis.

Introduction

In response to growing community concerns and increasing government regulation, mining companies are placing a greater emphasis on mine waste management to ensure that potentially harmful substances are safely stored in a manner that permits the restoration of post mining land uses. These wastes principally comprise waste rock arising from mining operations and tailings produced from the milling process. The milling process is designed to separate the ore (economic mineralisation) from gangue minerals, the latter often comprising of acid forming sulfides, radionuclides and toxic metals/metalloids such as lead, copper, mercury, cadmium, arsenic and selenium.

In the generation of tailings, the physicochemical properties (particle size, moisture content, chemical composition) of the host rock are altered by the action of comminution (mechanical crushing and grinding) and concentration which invariably requires lixiviants (such as acid, cyanide or oxidants) and other process chemicals. As a consequence the gangue minerals that comprise the tailings are much more susceptible to erosion and chemical weathering which, if not controlled, can lead to the release of harmful quantities of contaminants (far in excess of those released from the original ore body) into the environment. Therefore, the security of tailings disposal, particularly in the long-term and effective rehabilitation of tailings repositories are vital attributes of mine planning.

The principal objectives of decommissioning and rehabilitation of tailings storage facilities (TSFs), particularly above ground TSFs, are well known and according to the International Commission on Large Dams (ICOLD, 1996), include:

- Stabilisation of the impoundment - involving consideration of long-term stability, seismology, erosion protection and drainage systems;
- Hydrology - long-term assessment of catchment runoff, diversion arrangements and risk of breaching during heavy rainfall events;
- Contamination - leachate control or containment, surface and seepage water quality;
- Aesthetic or visual impact;
- After use or final land-use considerations; and
- Safety - public accessibility and inherent dangers, long-term surveillance and monitoring.

However, despite national and international standards/guidelines on tailings management there are still disastrous failures and long-term or chronic environmental impacts arising from TSFs. The most recent and notable catastrophic dam failures include Marcopper in the Philippines (1996), Merrienpruitt in South Africa (Wagener, 1997), the Las Frailes incident in Spain (1998) and Baia Mare in Romania (2000). All of these incidents involved a failure that resulted in the immediate release of large quantities of tailings and/or effluent into local rivers and nearby communities.

To allay community concerns prudent design, planning and management of TSFs for both operation and closure require a systematic risk-based approach to identify potential hazards, controls and mitigating measures. Fundamental to this assessment and planning process is a detailed understanding of the mineralogical characteristics and geochemical mechanisms that control the long-term evolution of the tailings and possible transfer of contaminants from the storage facility to the environment. Only through a thorough understanding of these mechanisms will it be possible to improve the certainty of environmental impact assessment and, in so doing, better define the requirements for the safe operation and ultimate long-term closure of TSFs.

Australia, like many other developed countries, has a history of rehabilitation of uranium mill tailings that shows an evolutionary approach in techniques and standards from the minimalistic strategies of the 1950’s, through the post closure planning era of the 1980's, to the holistic life of mine planning of the present time (Waggitt, 1994).

Cost effective design and safe management of uranium mill tailings can only be achieved if the risks to human health and the environment are recognised and understood at the time of mine planning. The application of environmental geochemistry is essential in the early phase of mine planning as it provides a systematic means of understanding the interactions at the tailings solid-water interface. These reactions are fundamental to the evolution of tailings pore waters and the rate of re-distribution and hence fate of contaminants within the tailings pile. At the macro level, this information is required to assess the long-term integrity of the proposed or existing TSF and its ability to prevent impacts on the beneficial values (ecological, human health) of surface and ground waters.

The paucity of integrated geotechnical/geochemical assessment protocols combined with the community's demand for greater environmental stewardship and conservation, provides a unique research opportunity to study the role of environmental geochemistry in the initial impact assessment of uranium mill tailings and for their subsequent long-term management and disposal.

For these reasons, the Ranger uranium mine was chosen as an ideal site for researching the effects of weathering and diagenesis on the long-term geochemical stability of uranium mill tailings. More specifically, we set out to demonstrate that the solid state speciation and mobility of metals and radionuclides in the tailings pile are governed by the processes of oxidative dissolution of sulfide minerals, weathering of phyllosilicates and organic matter diagenesis. Combined, these processes lead to the formation of authigenic minerals which control the solubility of pore water constituents and the long-term geochemical evolution of the tailings pile.

The Ranger Mine Project

Energy Resources of Australia Limited (ERA) owns and operates the Ranger Mine. The Ranger Mine and associated leases (Fig. 1) occupy a combined project area of approximately 79 km^2 enclosing some nine radiometric anomalies. Although the project area is excluded from Kakadu National Park, it does lie on Aboriginal land and hence is leased from the local Traditional Owners. To the north and adjoining the Ranger Project Area (RPA), is the 73 km^2 Jabiluka Project Area which is also leased by ERA. Fig. 2 shows the areal extent of both the Jabiluka and Ranger mine sites.

The Ranger operations consist of two ore bodies, Ranger #1 and #3 that are mined by open pit methods. Total reserves were estimated at 166 300 tonnes of U_3O_8 (Savory, 1994). Processing of ore from Ranger #1 commenced in October 1981 and was continuously mined until 1994 when the economic ore was depleted. Ore is currently sourced from the Ranger #3 pit which has a projected mine life of 13 years that will end in 2008.

Fordham (1993) after Eupene et al. (1975) succinctly summarized the mine geology as being dominated by intense chloritisation with variable lithology. Rock types within the ore body include mica-quartz-feldspar schists subjected to varying degrees of chloritisation, magnesium or dolomitic carbonates, carbonaceous schists, gneisses, dolerites and pegmatites. The primary ore mineral in Ranger #1 is uraninite ($UO_2(s)$). Secondary uranium minerals such as torbenite ($Cu(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$) and saleeite ($Mg(UO_2)_2(PO_4)_2 \cdot 8H_2O$) are enriched in a 20 m thick lateritic ore zone (Savory, 1994).

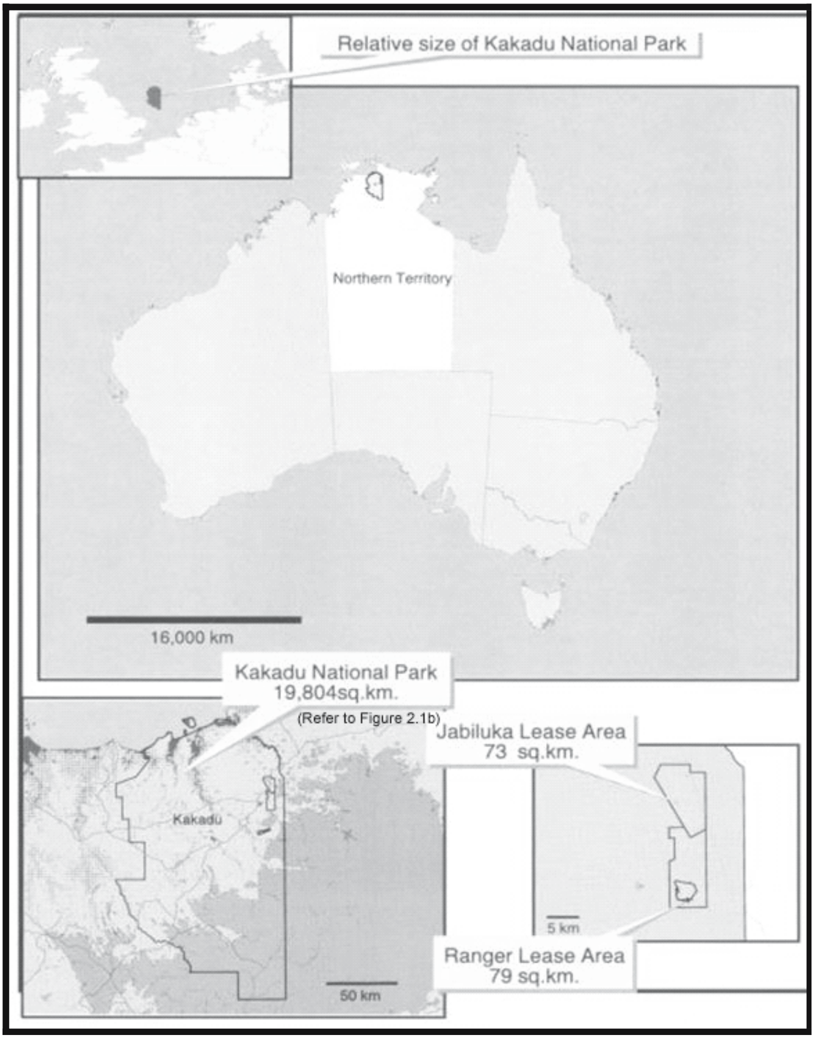


Fig. 1. Relative sizes and location of Kakadu National Park, Jabiluka and Ranger Mine leases.

Almost 50% of the gangue is magnesium chlorite, with an additional 40% comprising quartz and sericite. Petrographic analyses (Savory, 1994) show that ore minerals invariably occur within a matrix of fine compact chlorite. The primary ore also contains galena, localized pyrite, smaller quantities of finer chalcopyrite, dolomite, apatite, rutile and hematite.

Tailings management incorporates a 107 ha tailings dam and the Ranger #1 (or Pit #1) void (Fig. 2). The tailings dam has a capacity of 15 Mm^3 and currently stores approximately 13 Mm^3 of Ranger #1 tailings at an overall density of 1.09 t/m^3. Tailings are no longer pumped to the dam, as it is used to evaporate excess process water. Since December 1996, tailings from the milling of Ranger #3 ore and the remaining stockpiled Ranger #1 ore have been deposited into the Pit #1 void. At the end of mine life, the closure plan requires that all tailings be transferred to the Pit #1 and #3 voids for final storage. Thus, the site of the existing tailings dam will be rehabilitated and restored such that the land can be incorporated back into Kakadu National Park. Careful design of the pit repositories and isolation of the tailings from surface and ground waters will be essential for the long-term protection of Kakadu's World Heritage values.

The tailings dam is a 1 km^2 ring dyke or turkey's nest impoundment located 500 m due west of the Ranger #1 pit. It lies across the head of a shallow valley which once formed the headwaters of Coonjimba Creek as shown in Fig. 2 (Sinclair, 1992).

The main minerals in the solid phase of the tailings at Ranger are quartz, chlorite, muscovite and gypsum. Large particles of hematite have been observed by SEM, and other minerals found in minor amounts are pyrite, chalcopyrite, galena, uraninite and brannerite (Fordham, 1993). Sulfur speciation is predominated by acid-soluble sulfates (Fordham, 1993).

Lime was used to neutralise acid tailings, usually to a pH just above neutral. Magnesite was also used as an alternative to lime (Fordham and Beech, 1989). The deposition of acid tailings was also trialled to improve settled density (Fordham and Beech, 1989; Richards and Peter, 1990; Fordham et al., 1992; Fordham, 1993; Fordham et al., 1993).

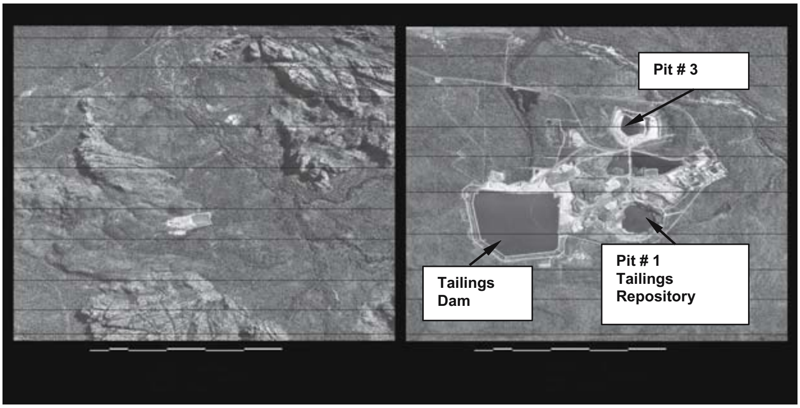


Fig. 2. Aerial view of Jabiluka (left) and Ranger (right) Mine sites.

Integrated Study Program

Within the present study, an integrated research program was developed to characterise the key equilibrium and kinetic processes that control the long-term geochemical evolution and fate of contaminants such as evaporites (Mg/Ca sulfate salts), radionuclides (uranium and radium-226) and trace metals (Cu, Pb, Cd, Ni and Co) within the Ranger tailings pile.

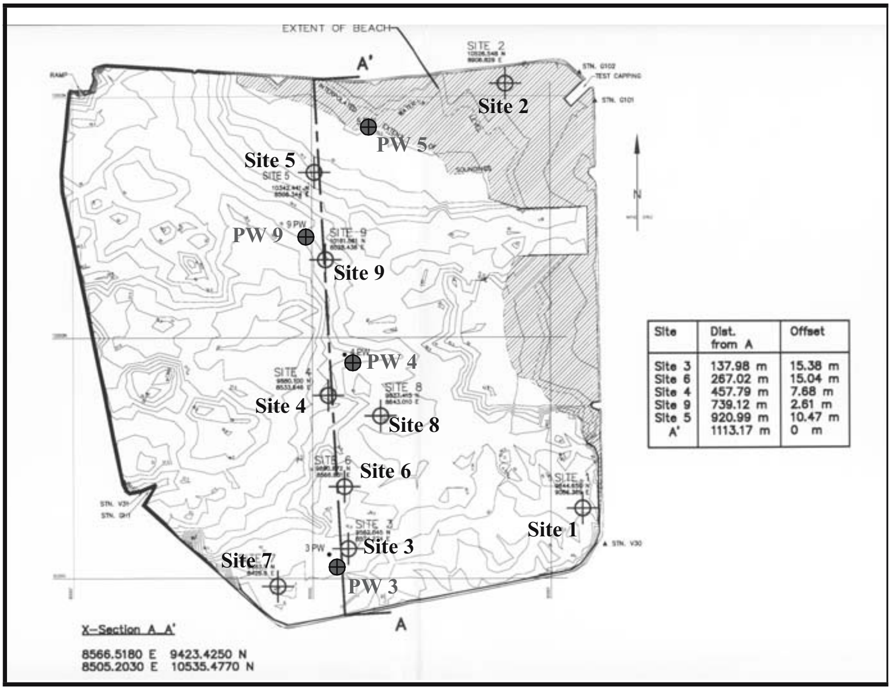
Specific activities undertaken within the study included:

- A critique of contemporary international research on the application of environmental geochemistry for assessing the risks and long-term closure requirements of tailings storage facility;
- Mineralogical and geochemical characterisation of fresh (run of mill) and aged (permanently stored) uranium mill tailings;
- Establishment of tailings depth profiles within the tailings storage facility for the *in situ* measurement of pore water chemistry;
- An assessment of the solid state speciation or partitioning of radionuclides within the tailings solids;
- Establishment of large scale laboratory kinetic leach columns to simulate the long-term geochemical evolution of the tailings pile and to identify mechanisms responsible for the solubility and release of radionuclides and accessory minerals into the receiving environment; and
- Development of a geochemical model that combines both equilibrium and kinetic processes to predict the chemical mass balance and long-term evolution of tailings pore waters.

The study attempted to highlight the important geochemical features of uranium mill tailings that either have positive and/or detrimental implications for their long-term management. Acquisition of such knowledge will assist in the development of appropriate controls and contingency measures to ensure that problematic drainage or seepage losses do not impact on the beneficial uses (human health and ecological) of regional surface and ground waters.

Field Investigations

Two sampling campaigns were conducted in the tailings dam, one in January 1998 to collect undisturbed tailings cores and the second in June 1999 to install and collect in-situ porewater samples. Data obtained from these campaigns allowed for a detailed evaluation of vertical and lateral hydrogeological and hydrochemical profiles within the tailings impoundment. Sample locations for both campaigns are shown in Fig. 3. Vertical cross-sections of core profiles are shown in Fig. 4.



Site	Dist. from A	Offset
Site 3	137.98 m	15.38 m
Site 6	267.02 m	15.04 m
Site 4	457.79 m	7.68 m
Site 9	739.12 m	2.61 m
Site 5	920.99 m	10.47 m
A'	1113.17 m	0 m

Fig. 3. Tailings dam sample profile locations.

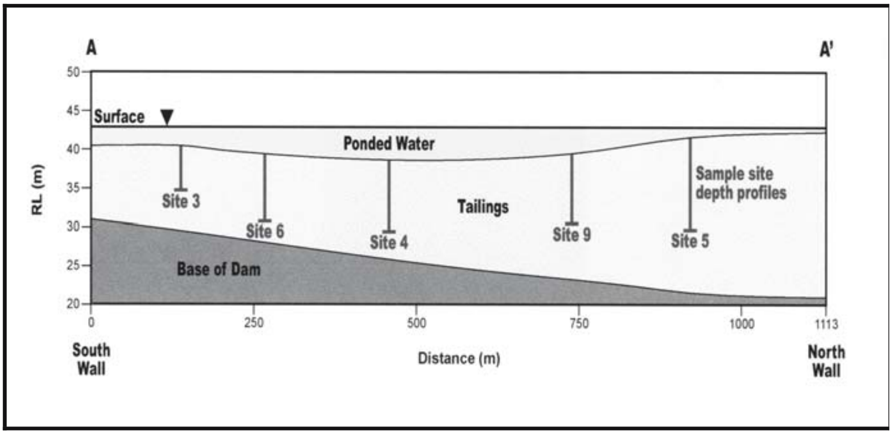


Fig. 4. Cross section A-A' tailings core profiles (January, 1998).

Tailings and Mill Chemistry

Markos (1979) has described the geochemical reactions that occur in a typical sulfuric acid-leach/tailings neutralisation uranium mill, resulting from the interaction of the acid-lixiviant and the uraniferous ore. Importantly, ferric ion (Fe^{3+}) is required in the leach solution to achieve rapid and complete oxidation of tetravalent uranium. Uraninite ($UO_2(s)$) is the principal uranium mineral:

$$UO_2(s) + 2Fe^{3+} \leftrightarrow UO_2^{2+} + 2Fe^{2+} \qquad (1)$$

The addition of an oxidant, such as pyrolusite (MnO_2) or sodium chlorate ($NaClO_3$), in sufficient quantity ensures that iron is present predominantly as Fe^{3+}. The second part of the leaching oxidation process is the addition of dilute sulfuric acid to control the pH at around 1.8. At this pH, the sulfuric acid ionizes to sulfate, bisulfate and hydrogen ion. Acid is not consumed directly by dissolution of UO_2 but is required to oxidise iron from the ferrous to ferric valency state. In addition to uranium, the oxidation process also causes the dissolution of gangue minerals (carbonates and aluminosilicates) and accessory metal/metalloid sulfides.

Because acidic (pH 2) uranium tailings water is high in aqueous sulfate and near gypsum saturation, the addition of slaked lime ($Ca(OH)_2$) to neutralise the tailings to pH 7 to 8 initiates gypsum precipitation. The addition of lime also initiates the precipitation of a number of other secondary minerals as described by Morin (1983): ferrihydrite ($Fe(OH)_3$), gibbsite ($Al(OH)_3$), aluminosilicates ($Al_2Si_2O_5(OH)_4$) and amorphous silica ($SiO_2(am)$). The formation of these secondary minerals creates a highly reactive geochemical environment that affects the solubility of radionuclides and metals via direct precipitation-dissolution, co-precipitation and sorption processes.

The tailings also contain significant quantities of microbiologically reactive organic and nitrogen compounds. The presence of organic matter in the tailings is significant as several studies (Sholkovitz, 1973; Froelich et al. 1979; Van der Weijden, 1992; Postma and Jakobsen, 1996) on natural sediments show that post-depositional reactions are primarily fuelled by the microbially-mediated decomposition of organic matter.

Organic matter is the key to any biogeochemical consideration of sediment diagenesis, not only because it represents chemical potential energy capable of driving diagenetic reactions but also because it plays a critical role in cycling radionuclides and trace metals. This metal cycling occurs as a result of the redox couple that forms between the electron donor (organic matter) and an in-situ oxidant that accepts electrons from organic matter (Stumm and Morgan, 1996). The oxidation of organic matter proceeds via the reduction of various oxidants in their decreasing free energy yield per mole of organic carbon oxidised. Reactions releasing the highest free energy yield ($-\Delta G^{o}_{r}$) also produce the greatest available energy for bacterial utilisation.

The order of oxidation proceeds with the initial removal of dissolved oxygen followed by the reduction of nitrate, manganese(IV), uranium(VI), iron(III), molybdenum(VI) and sulfate, as is summarised in Table 1. These reactions best represent the key redox couples within the tailings pile and are well documented as being mediated by heterotrophic bacteria.

Of the 45 cores recovered from the tailings impoundment, six were selected as best representing the various lithogenic and authigenic phases observed along the 1 km long N-S sampling transect (see Figs. 3 and 4). These cores were subjected to a detailed physical, mineralogical, geochemical and analytical program, the results of which are only partially described in the following sections to demonstrate how organic matter diagenesis and authigenisis control the long-term geochemical stability of the tailings pile.

Table 1. Half cell reactions of oxidants present in the tailings pile and their associated free energies and electron activities.

Half Cell Reaction*	ΔGr kJ mol^{-1}	pε
Oxidation Reaction		
$CH_2O + H_2O \leftrightarrow HCO_3^- + 5H^+ + 4e^-$		
Reduction Reactions		
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	-474	13.76
$0.8NO_3^- + 4.8H^+ + 4e^- \leftrightarrow 0.4N_2 + 2.4H_2O$	-480	12.00
$2MnO_2 + 2HCO_3^- + 6H^+ + 4e^- \leftrightarrow 2MnCO_3 + 4H_2O$	-478	8.60
$4Fe(OH)_3 + 4HCO_3^- + 8H^+ + 4e^- \leftrightarrow 4FeCO_3 + 12H_2O$	-376	0.70
$2UO_2(SO_4)_2^{2-} + 4e^- \leftrightarrow 2UO_2(am) + 4SO_4^{2-}$	-56	0.17
$2UO_2(CO_3)_2^{2-} + 4H^+ + 4e^- \leftrightarrow 2UO_2(am) + 4HCO_3^-$	-146	0.11
$2MoO_4^{2-} + 8H^+ + 4e^- \leftrightarrow 2MoO_2 + 4H_2O$	-342	-1.86
$0.5SO_4^{2-} + 4.5H^+ + 4e^- \leftrightarrow 0.5HS^- + 2H_2O$	-96	-3.76

* Equations are representative of the following average porewater concentrations and conditions: $[U] = 1.7\times10^{-6}$ mol L^{-1}; $[NO_3^-] = 1.1\times10^{-3}$ mol L^{-1}; $[SO_4^{2-}] = 0.25$ mol L^{-1}; pH = 7; $[Mo] = 2.0\times10^{-6}$ mol L^{-1}; $[HCO_3^-] = 2.5\times10^{-4}$ mol L^{-1}; 25°C; 1 bar. ΔG_r and pε were calculated from thermodynamic data reported by Stumm and Morgan (1996) and Grenthe et al. (1992). CH_2O is used to represent organic matter.

Tailings Porewater Geochemistry

The major ion porewater profiles are vertically stratified in two distinctive geochemical zones: (a) an upper zone which extends from the surface of the tailings down to RL 35 m. This zone is characterised by high conductivity (> 25 mS/cm) and near neutral to slightly acidic pH water and (b) a lower zone which extends from the inflection point at RL 35 to the base of the dam. This zone is characterised by a 50% decrease in conductivity within a few metres of the inflection point and slightly basic pH water. Like the overlying tailings pond water, the major ion chemistry is characterised by magnesium, sulfate, calcium, manganese, and ammonia.

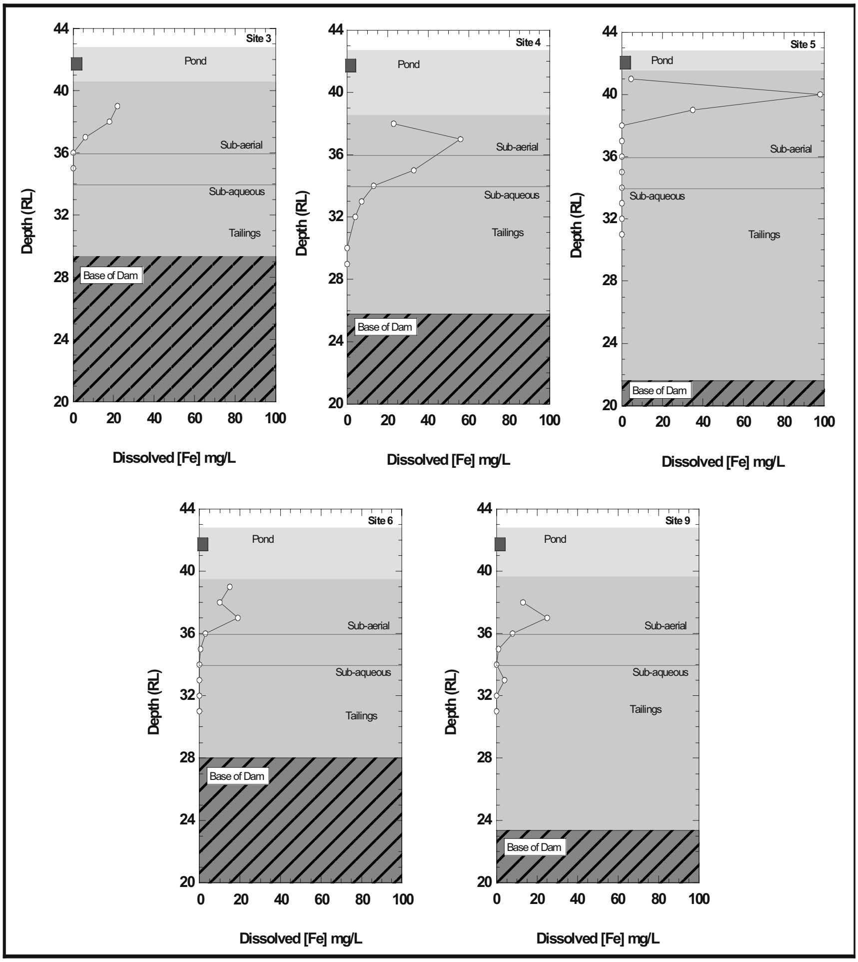


Fig. 5a. Porewater profiles for dissolved iron.

Porewater iron is a well known redox indicator and within the tailings pile, dissolved concentrations increase in the near surface sediments (1 m) up to about 100 mg/L (Fig. 5a). These elevated values are considerably higher than the water column value of 0.44 mg/L, and suggests that the high porewater inventory does not stem from the overlying pond water. Rather, these data suggest that the high dissolved Fe values are derived from reductive dissolution of Fe(III) oxides. Below the zone of Fe reduction (RL 35 m), Fe is removed from solution as authigenic sulfides in accordance with the redox zonation principles described by Froelich et al. (1979).

Porewater profiles for dissolved U (Fig. 5b) are variable and as such it is difficult to draw firm conclusions from the observed trends. In general, however, the U porewater profiles show a concentration minima coincident with Fe maxima (see Fig. 5a) in the near surface sediments (> RL 39 m). Below this horizon, U levels at

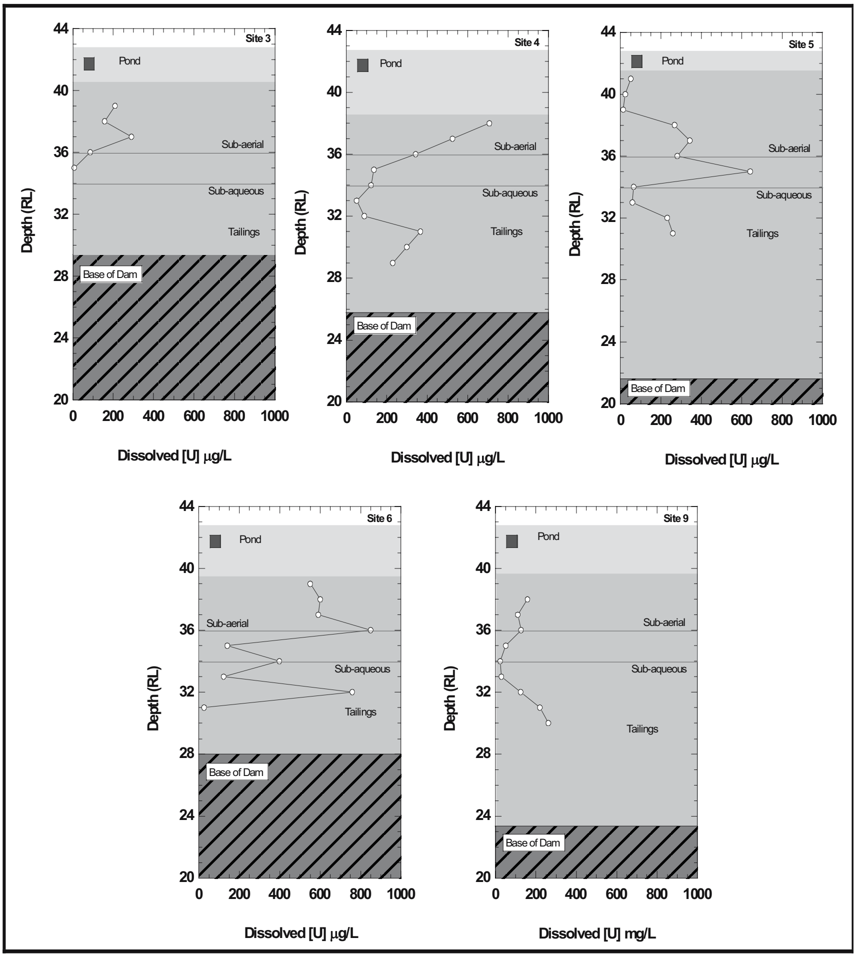


Fig. 5b. Porewater profiles for dissolved uranium.

most sites exhibit a concentration maximum (between RL 37 to 36 m) with values ranging from 180 to 800 µg/L. Within the constraints of available data, a second concentration peak is observed at RL 33 below which U levels significantly decrease (Sites 3 and 6) to around 1 µg/L. Such observations imply that U is associated with Fe(III) oxides and is redistributed following the reductive dissolution of Fe. The overlying pond water U concentrations were on the order of 50 µg/L (see Fig. 5b), which is well below the observed porewater maxima of around 800 µg/L. This suggests that U is being mobilised within the tailings pile via diagenetic processes rather than being supplied from the inventory of overlying pond water. Furthermore, the results of the solid state speciation test work confirm that 35 to 40% of the total U contained in the gel and fine grain tailings is associated with readily reducible phases such as amorphous Fe oxyhydroxides.

Profiles of other trace metals (Co, Ni, Cu and Mo) which form insoluble metal sulfide minerals were also examined. The profiles of Co and Ni mirror the Fe profile (see Fig. 5a) and are consistent with the notion of sulfide formation below RL 37 m. Below this RL, the concentrations of Ni and Co decrease by an order of magnitude compared with their concentrations of > 100 µg/L in the upper oxic zone. The dissolved Cu distribution does not follow the same pattern. However, elevated levels of dissolved Cu can persist in sulfidic porewaters due to the formation of strong Cu-organic or polysulfide complexes which can maintain Cu in solution. Under conditions of low redox potential, Mo is believed to be reduced to the tetravalent state and then is coprecipitated with mackinawite ($FeS_{0.9}$) (Bertine, 1972).

Radium porewater profiles do not correlate well with either Sr or the expected geochemical analogue Ba. Such trends while inconsistent with other studies can perhaps be attributed to the presence of a non-barite host phase for Ra. Indeed, porewater concentrations of Ba are exceedingly low, with most values at or near the detection limit of 0.005 mg/L. The reductive dissolution of Ra-bearing barite or radiobarite, can result in the addition of substantial Ra to porewaters. In a uranium tailings impoundment in Canada, for example, the dissolution of radiobarite in reducing horizons resulted in elevated levels in porewaters of ca. 80 Bq/L (Martin et al. 2003). The relatively low Ra and Ba values measured in the porewaters at Ranger suggest that such processes are not occurring to any appreciable extent and that other mechanisms are controlling the mobility of Ra under the predicted reducing environment.

Kinetic Column Leach Studies

To evaluate the long-term geochemical stability of the tailings, it is necessary to understand the mechanisms responsible for controlling the release and subsequent transport of radionuclides and accessory metals/salts (collectively described as contaminants) into the environment. Laboratory scale leach columns were established as a means of assessing the leachability and kinetic behaviour of tailings under simulated weathering conditions.

Two parallel column experiments were conducted. The first column assessed the leaching characteristics of fresh tailings (“fresh tailings”) exposed to simulated rainfall events. These tailings are direct from the plant and representative of those that are currently being deposited into Pit #1. They are of a coarse grind and are neutralised to a pH of around 6. The second column was loaded with tailings (“aged tailings”) that were dredged from the tailings dam at a depth of 4 m below the tailings–pond water interface. These tailings are aged > 5 years, are fine grained and were deposited at a higher pH (6 to 8). They are representative of tailings that were originally deposited sub-aerially but from 1994 onwards were subsequently covered by water.

The design of the kinetic column study has attempted to account for climatic, hydrological, chemical and depositional parameters that have a significant influence on the in-situ weathering processes in the tailings. To achieve the desired design outcome, two columns were constructed for both the fresh and aged column studies. The upper column is designed with a high surface area per unit mass of tailings solids to ensure unsaturated leach conditions. The purpose of this column is to simulate leaching and exposure conditions similar to those that occur in the upper unsaturated zone (beaches) of the tailings dam. An understanding of unsaturated geochemical processes is necessary as the tailings were deposited sub-aerially over a ten year period (1986 to 1994). In the longer term, it is also conceivable that unsaturated zones may develop in the tailings repositories following final decommissioning and close-out. The lower column is completely encapsulated to maintain a constant state of water saturation and to prevent atmospheric contact. The purpose of this column is to simulate leaching conditions deep within the tailings dam and Pit #1 repositories where the tailings are stored below the water table and isolated from the atmosphere.

The columns were leached for a period of 520 days. During this period, there were 30 discrete leaching events in which 14.4 L of simulated rainwater was introduced into the upper unsaturated column via spray irrigation every 2.5 weeks (5.76 L/week).

Fig. 6a shows the pH elution trends for the aged unsaturated tailings over the 520 day (or 11.54 pore volumes) leaching period (the fresh tailings profile is similar). At the commencement of the leaching trial the pH of the fresh and aged tailings was 6.5 and 7, respectively. Within 1.12 pore volumes (≈ 2.8 months); the pH in each of the unsaturated columns had decreased by around 1 unit. Following this initial decline, the pH in the fresh unsaturated tailings formed two plateaus, one at 5 and another at 4.5 before declining to a final pH of 4 by the end of the leaching period. These successive pH plateaus are a likely indicator of the magnitude and reactivity of acid neutralising minerals such as aragonite and chlorite. Given that aragonite will react more rapidly than chlorite, it is conceivable that the first pH plateau, from pore volumes 1.12 to 5, represents the buffering associated with carbonate dissolution. This tenet is supported by the alkalinity trends, which show complete consumption of alkalinity in both the fresh and aged columns over the same elution period. Following the depletion of available aragonite/alkalinity, chlorite weathering reactions neutralise the acid generated from sulfide oxidation via the release of interlayer hydroxyl groups (brucite) as chlorite is altered to kaolinite.

In the saturated columns as a consequence of the various reduction reactions, alkalinity is generated by the oxidation of organic matter and, as such, tends to increase as successive oxidants are utilised by bacteria (Stumm and Morgan 1996). This trend is observed in Fig. 6b, where alkalinity increased in accord with the

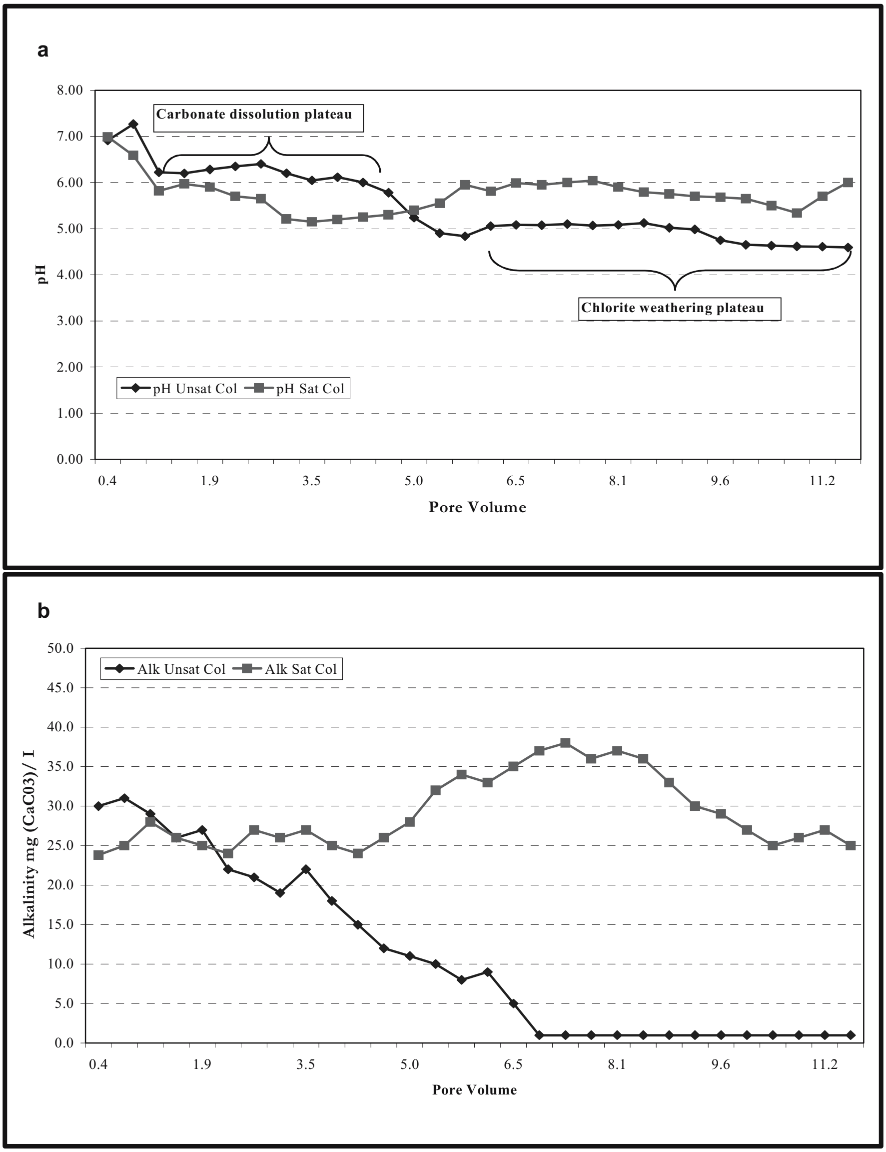


Fig. 6. Trends in (a) pH and (b) alkalinity for the aged tailings.

progression of the expected redox reaction sequence. More specifically, there was a noticeable increase in alkalinity (pore volume 6.5) at around the same time as Fe(III) reduction was at its peak.

A measure of the electrical conductivity (EC) of the column discharge provides an indication of the leaching of soluble salts from the unsaturated tailings. The initial leachate was highly saline with ECs of 24 and 17 mS/cm being measured for the fresh and aged unsaturated tailings, respectively. This salinity was mainly due to high concentrations of the major ions: SO_4^{2-}, Mg^{2+}, Mn^{2+}, Ca^{2+} and NH_4^+. After approximately 5 pore volumes of leachate had passed from both the fresh and aged columns, the EC had significantly decreased to around 5 mS/cm. A corresponding decrease was also observed in the concentrations of the major ions with the exception of calcium which remained relatively steady, ranging between 350–380 mg/L in the fresh unsaturated tailings and 450 mg/L in the aged unsaturated tailings (both being controlled by the solubility of gypsum).

The weathering of chlorite in acidic environments (unsaturated columns) will form secondary aluminosilicates such as kaolinite, amorphous SiO_2 phases and various Al-bearing secondary minerals. As a consequence, Al and $SiO_2(aq)$ are mobilised and their respective solubility governed by the newly formed secondary minerals. The dissolution of Al is coincident with a pH of ≤ 6 and closely follows the trend reported by Nordstrom (1982), in which Al-sulfate minerals such as basaluminite ($Al_4(OH)_{10}SO_4$), jurbanite ($AlOHSO_4$) and alunite ($KAl_3(SO_4)_2(OH)_6$) control the solubility of Al in acidic sulfate-rich waters. Dissolved silica is an important indicator for determining the solubility and equilibrium conditions pertaining to the formation of secondary silicate minerals. Silicon leachate concentrations (an indicator of $SiO_2(aq)$) remained relatively steady at 10 mg/L, then rapidly increased at the same juncture as alkalinity was exhausted and the pH decreased to around 4.8 (see Fig. 6).

Lead, Cu and Cd leachate concentrations for the unsaturated tailings were significantly higher than those observed for the saturated tailings. The elevated levels of Pb, Cu and Cd are clearly related to the oxidative dissolution of sulfide minerals.

The coincidence of U concentration minima and Fe maxima (Fig. 7a) in the saturated column reflects the onset of U reduction and removal from solution as a U(IV) authigenic mineral, presumably uraninite. These trends are consistent with studies by Lovely et al. (1991) and Gorby and Lovely (1992) who proposed that

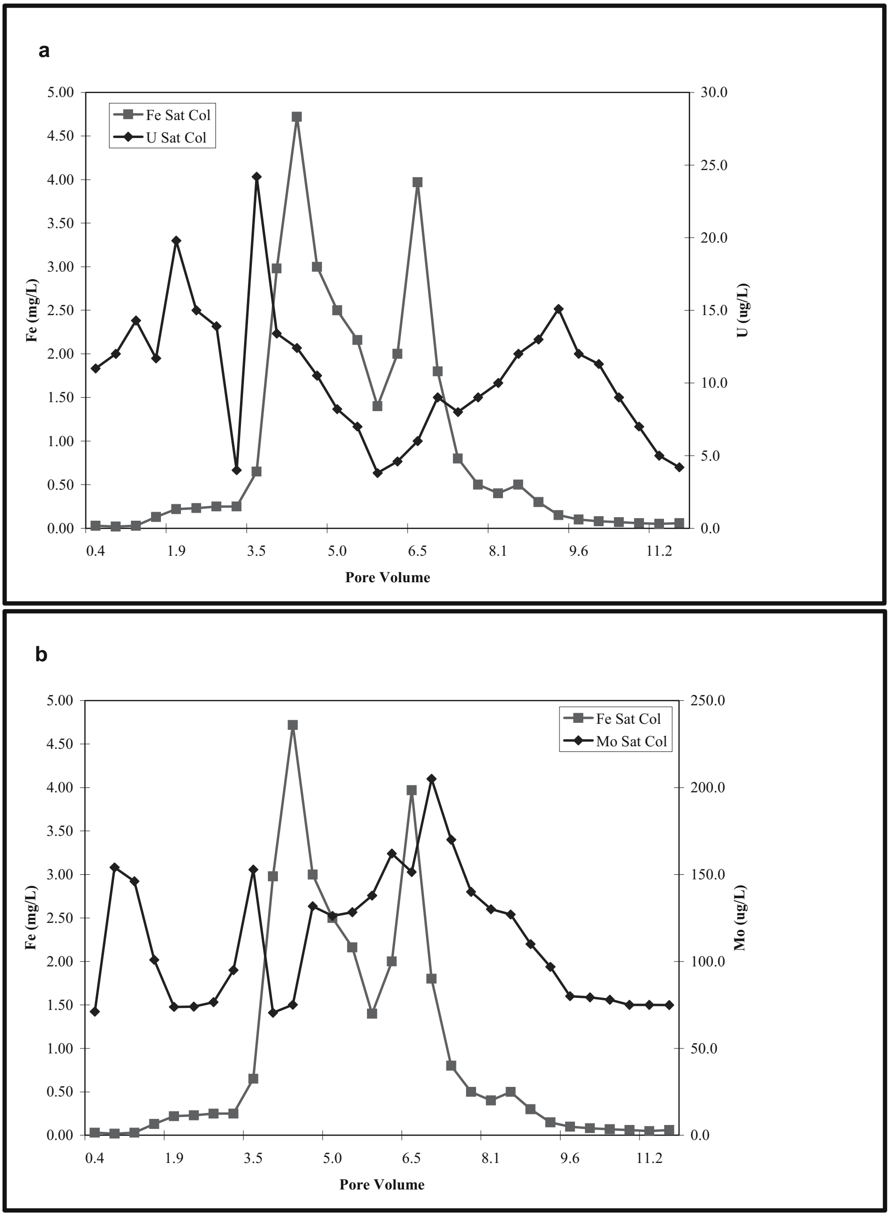


Fig. 7. Trends in (a) Fe and U and (b) Fe and Mo in aged tailings leachates.

dissimilatory Fe(III) reducing bacteria can also utilise U(VI) as an electron acceptor to derive energy for growth. As a consequence, U(VI) is reduced to U(IV) and subsequently precipitated as uraninite. The presence of dissimilatory bacteria in the columns explains the simultaneous reduction of U(VI) with Fe(III) as according to the predicted sequence of redox reactions described in Table 1, U(VI) reduction (pε 0.11-0.17) and subsequent precipitation as amorphous UO_2 was expected to occur after Fe(III) reduction at pε 0.7. The leachate concentrations of molybdenum (Fig. 7b) also closely approximate the reductive dissolution of Fe(III) oxides. The decrease in Mo concentrations from 9.6 pore volumes may suggest the onset of reducing conditions sufficient to remove Mo as insoluble molybdenite (MoS_2) or more likely as a co-precipitate with mackinawite (Bertine, 1972). Legeleux et al. (1994) reported that the reduction of Mo requires a strong reductant such as H_2S to precipitate molybdenite. This finding is also consistent with the redox sequence described in Table 1 in which Mo(VI) reduction (pε -1.86) is predicted to occur under strongly reducing conditions.

Geochemical Modelling

Geochemical models were used to simulate and confirm the hypothesised mechanisms described above. Models are a simplification of a much more complex natural system and as such, they can only be used to augment actual field and experimental data. This integrated approach provided valuable insight into the key equilibrium and quasi-steady-state reactions governing the long-term evolution of the tailings porewaters.

The kinetic model STEADYQL (Furrer et al., 1989, 1990) was used to predict the final leachate pH and solute concentrations for Fe, Al, Si and Cu following weathering of the two dominate phyllosilicate minerals (chlorite and muscovite) and the oxidative dissolution of pyrite and chalcopyrite in the unsaturated columns. The soluble reaction by-products from these kinetically controlled reactions were then allowed to equilibrate with respect the formation of authigenic phases such as kaolinite, ferrihydrite and chalcedony. The predicted values are compared with actual measurements to confirm the key geochemical processes governing the leachate/porewater chemistry of the unsaturated tailings. The predicted leachate pH and Fe, Al, Si and Cu concentrations are shown in Table 2 along with actual experimental data collected at the cessation of the 520-day leaching period. As a general statement, the predicted leachate values for pH, Fe, Al and Cu are in good agreement with the experimental data and in so doing, attest to the oxidative dissolution of metal sulfides and weathering of phyllosilicate minerals in the undersaturated tailings. Predicted silica concentrations are lower than actual leachate values but are of the correct magnitude expected for chlorite dissolution (Lowson et al., 2005). More specifically, the results presented in Table 2 confirm that leachates from the undersaturated tailings have a propensity to generate acid via the preferential oxidation of pyrite and chalcopyrite. In addition to the generation of acid, these reactions also result in the precipitation of Fe oxyhydroxides, presumably ferrihydrite, and the release of soluble Cu.

Equilibrium modelling, using the HARPHRQ code (Brown et al., 1991), indicated that elemental porewater concentrations were governed by various mineral phases. Alunite appears to be controlling the observed Al porewater concentrations. Barium is controlled by a poorly ordered micro-crystalline form of barite, as has previously been reported by Martin et al. (2003). The presence of such a phase was confirmed by SEM-EDX. Strontium, however, was found to be controlled by the solubility of strontianite ($SrCO_3$) rather than celestite ($SrSO_4$). Calcium and sulfate are clearly controlled by the solubility of gypsum, whereas iron is controlled by iron oxyhydroxide precipitation at shallow depths and mackinawite at lower depths. In the regions of the porewaters where alkalinity increases (see Fig. 6b), the solubility of Mn is controlled by rhodochrosite. Modelling of the saturated column leachates confirmed these findings.

Conclusions

Run of mill uranium tailings are a complex heterogeneous mixture of lithogenic (primary gangue minerals and weathering products) and secondary (components that form during milling) minerals, residual process chemicals and biogenic (products of biological activity) phases. Following transfer to the tailings storage facility, post depositional reactions alter the mineralogical and hydrochemical characteristics of the tailings solids and porewaters in accordance with weathering and diagenetic processes. These mechanisms will have a profound impact on the long-term geochemical stability of the tailings pile and as such will need to be taken into account in the design, management and closure of the final tailings repositories at the Ranger mine (Pits #1 and 3).

Table 2. Summary of predicted and actual leachate chemistry for unsaturated tailings.

Parameter	Predicted	Measured (fresh)	Measured (aged)
pH	4.3	4.02	4.6
Fe (3)	0.03	0.02	0.02
Al	0.32	3.00	0.29
Si (2)	8.45	30.00	19
Cu	0.40	0.80	0.05

(1) With the exception of pH, all concentrations are in mg/L
(2) Si solubility in the model is assumed to be controlled by kaolinite and chalcedony
(3) Fe is controlled by ferrihydrite

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