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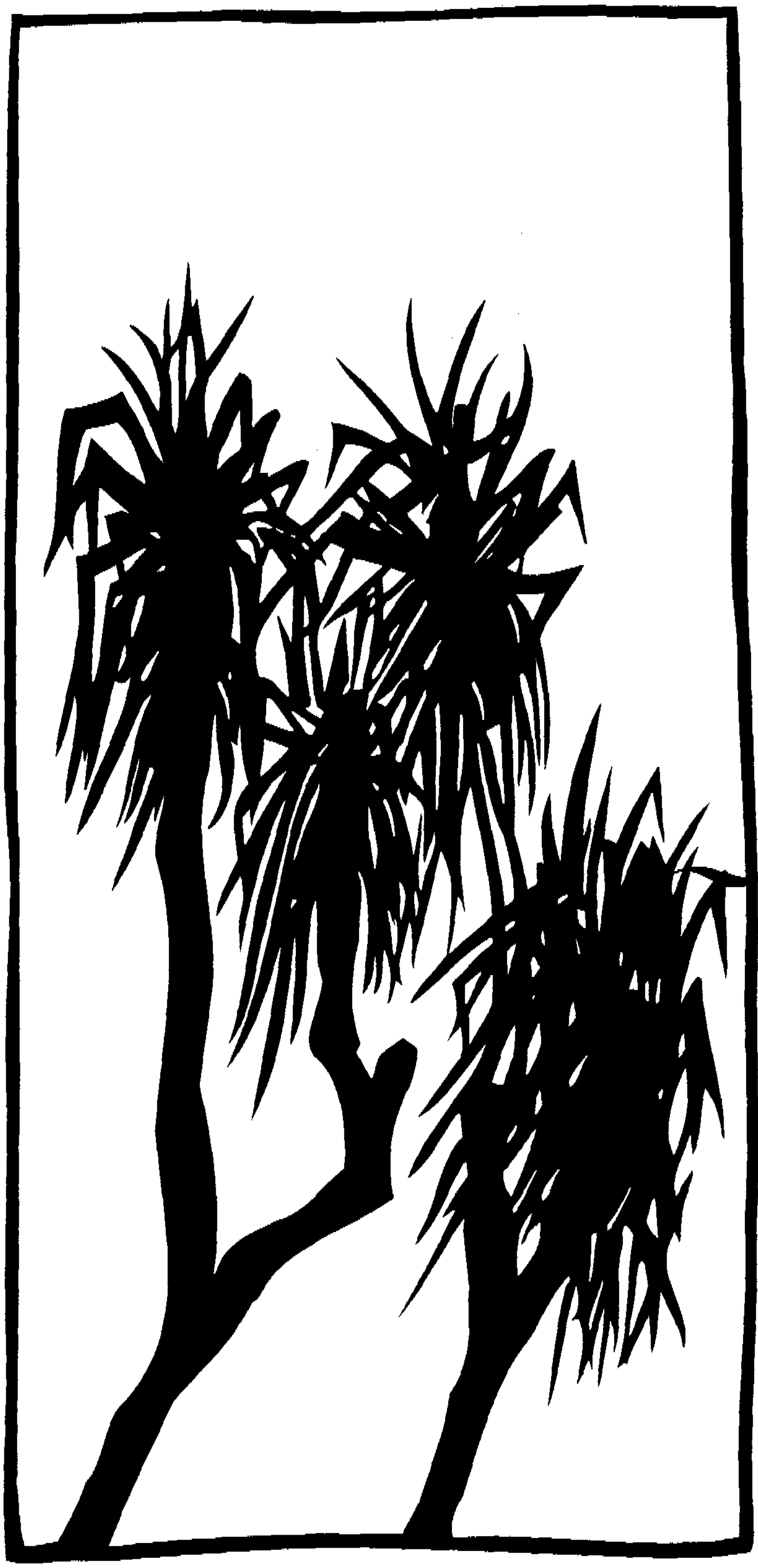

The soluble yield of radionuclides from fresh Ranger tailings

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THE SOLUBLE YIELD OF RADIONUCLIDES FROM FRESH RANGER TAILINGS

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Abstract

Keywords: Ranger tailings, soluble radionuclide component, gypsum, readsorption

Experiments were performed whereby fresh Ranger tailings samples were mixed with high-purity water to assess the quantity of contained radionuclides that were solubilised by this process, as a function of time. It is proposed that the gypsum ($CaSO_4.2H_2O$) content of tailings, produced by liming, may entrain a substantial fraction of the radionuclide burden. Because gypsum is sparingly soluble in water (about 2 g/L), coprecipitated radionuclides may be mobilised if gypsum were subsequently dissolved, for example if exposed tailings had egress to the environment at some future time.

To assess whether remobilisation by dissolution would be transient rather than permanent because of rapid readsorption to the mineral matrix of the tailings, two dissolution experiments were performed where sufficient tailings were added to water to provide a saturated solution of gypsum. When this was achieved, no further net dissolution of gypsum (and hence net mobilisation of radionuclides) would occur, and the subsequent solution-phase radioactivity would be determined by adsorption rather than dissolution.

The present results imply that net mobilisation of radionuclides occurs over a two hour period in the case of progressive dissolution of gypsum (undersaturation) whereas in the case of saturation being rapidly achieved, net loss of soluble radionuclides is observed over a two hour period.

Introduction

Most of the tailings produced by the Ranger Uranium mine are currently stored in an above-grade impoundment, the tailings dam. However, Environmental Regulation 29 governing the operation of the mine specifies that, as part of final site rehabilitation, the tailings be relocated to the pit from which ore has been removed. There is a provision under this regulation for the tailings to be finally impounded at the current site if it can be demonstrated that the environment would be *'no less well protected'* by this option.

The structural life of the present tailings dam is about 200 years, with a high probability that the tails would be essentially quantitatively contained for 1000 years. However, it is inevitable that an above-grade final repository would eventually erode, and almost certain that this would ultimately lead to tailings dispersal in Magela Creek and some of its tributaries.

A recent model predicts, given certain assumptions being realised, that a critical group of inhabitants downstream from a breached tailings impoundment may receive a radiation dose in excess of that currently permissible for a member of the public (Akber 1993).

This model depends, in part, on the work of Wasson *et al.* (1993), which makes predictions concerning the deposition sites of erosion products from a hypothetical tailings-impoundment breach, as a function of particle size. The Akber model assumes a distribution of radionuclides according to particle size. It concludes, with use of the Wasson sedimentological predictions, that radionuclides may be chiefly deposited in a relatively small area at the southern end of the Magela floodplain.

However, the possibility that a significant fraction of the radionuclide burden may be incorporated in a relatively soluble fraction of limed tailings, specifically the gypsum phase, has not been explicitly considered. Snodgrass *et al.* (1982) have investigated limed tailings of similar mineralogy to those at Ranger and have concluded that about 95% of ^{226}Ra, ^{210}Po and ^{210}Pb may be leached during the milling process. They conclude that this leached fraction may then be largely distributed in gypsum and jarosite phases in limed tailings. The latter mineral, which is formed during milling but is not stable at pH > 2, is postulated as being generated *in situ* by oxidation of residual pyrite. There is much less pyrite in Ranger tailings than those of the Snodgrass, *et al.* study (~0.2% *cf* ~5%), so radionuclides may be distributed mainly between gypsum and ferric hydroxyoxides (a jarosite hydrolysis product) at Ranger. Supportive evidence for hydroxyoxides acting as an adsorbant medium exists in an association which has been observed between iron and ^{226}Ra concentrations in Ranger tailings dam pore water (leGras 1992).

If a substantial fraction of the radionuclide contents of Ranger tailings is in readily-solubilised forms, then the dispersal model for these tailings components may need to be reviewed. In particular, radionuclides in solution, or adsorbed to colloid-size particles are likely to travel farther and be more widely dispersed than those attached to clay-size particles or larger.

The work described in this report was designed to estimate the quantity of ^{238}U-series radionuclides mobilised to the solution phase by stirring fresh tailings with deionised water. The experiments were conducted in two parts:

- the ratio of tailings to water was adjusted such that the aqueous phase would never attain saturation with respect to gypsum ($CaSO_4.2H_2O$). In this way there would be a progressive transfer of any gypsum-entrained radionuclides to solution as the sparingly-soluble salt dissolved;
- the ratio of tailings to water was adjusted such that gypsum saturation would be attained rapidly. Under these conditions any gypsum-entrained radionuclides would rapidly be solubilised to the extent that the gypsum dissolved. However, because no net gypsum is dissolved after the initial saturation, no net solubilisation of radionuclides should occur; hence changes in soluble radionuclide concentrations should reflect adsorption of species onto the mineral surfaces of the tailings.

Experimental

A 20 L bucket of fresh tailings slurry was obtained from ERA and stored sealed in a fume cupboard. To minimise handling of the tailings, a calibration was performed whereby a volume of tailings was pumped into a tared, graduated beaker using a small electric pump. The mass of tailings was measured and its density calculated using the volume estimated from the beaker graduations (density = mass/volume). The density of tailings slurry arrived at from these measurements was 1.55 ± 0.03 t/m^3 (n = 4).

Fordham (1993) has estimated that the proportion of gypsum in the tailings dam is about 5% on a dry mass basis. This accords with an estimate calculated from the mass of calcium oxide used as a neutralant since milling commenced (Supervising Scientist 1982-1996) of 4.5%, which would be supplemented by Ca already present in the ore. On this basis, a dry mass of about 47 g of dry tailings (66 g of wet tailings given a conversion factor of 1.4) in 1 L of water should yield a saturated solution of gypsum.

For the experiment where saturation with gypsum was intended, approximately 300 g of tailings were pumped into each of four weighed 2 L polyethylene beakers. These were placed on magnetic stirrers and 1 L of high-purity water added to each. The experiment was performed at room temperature, approximately 25° C. One of the four beakers was removed for processing at intervals of 1 minute, 2 hours, 4 hours and six hours. This involved filtering the slurry through a 0.45 μm membrane filter (Nuclepore) and then coprecipitating the dissolved radionuclides with a iron/manganese hydroxyoxide mixture generated *in situ* (Paulka and Akber, internal method). No attempt was made to quantitatively recover the filtrate, due to excessively long filtration times, and the need to ensure that the residual tailings were not sucked dry. An aliquot of the filtrate was reserved for determination of Mg, Ca and SO_4^{2-} by ion chromatography (leGras 1993).

The consecutive variation of the *double precipitation method* involves bubbling air through an acidified filtrate, followed by addition of 20 mL of 0.2 M of potassium permanganate solution, then by pH adjustment to 8.0 using concentrated ammonia solution. Then 50 mL of 0.3M manganese chloride solution is added and the precipitate filtered using a Whatman #42 paper after settling is complete. The pH of the filtrate is adjusted to between 5 and 6 and 50 mL of 0.16M ferric chloride solution added. After pH adjustment to 8 using concentrated ammonia solution, the precipitate is filtered using a Whatman #42 paper. The two precipitates (with papers) are dried overnight at 110° C and then ashed at 400° C overnight in a muffle furnace.

The experiment where insufficient tailings were used to achieve gypsum saturation was performed in the same way, except a smaller tailings mass was added to each 2 L beaker.

The experimental details are presented in Tables 1 and 2.

Contact time (min)	Tailings mass (g)	Filtrate volume (mL)	Initial aqueous volume (mL)$^{\nabla}$	Mass of ashed mixed oxide (g)
1	319	744	1083	9.592
120	349	735	1087	9.573
240	342	732	1090	9.619
360	341	656	1088	9.567

∇: assumes that 40% of the tailings slurry volume was water

Table 1. Details for the 'gypsum saturated' tailings shakeout experiment

Contact time (min)	Tailings mass (g)	Filtrate volume (mL)	Initial aqueous volume (mL)$^{\nabla}$	Mass of ashed mixed oxide (g)
1	73.1	864	1019	9.863
120	64.1	949	1017	9.865
240	62.7	938	1016	9.864
360	93.5	728	1024	10.088

∇: assumes that 40% of the tailings slurry volume was water

Table 2. Details for the 'gypsum unsaturated' tailings shakeout experiment

Portions of the ashed mixed oxides were cast in polyester resin for determination of ^{238}U-series radionuclides by γ-ray spectroscopy (Pfitzner 1994). Only samples stirred for 1 minute and two hours for both the 'saturated' and 'unsaturated' experiments were determined in this way. The experimental details are presented in Table 3.

Sample	Mass of mixed oxide (g)	Mass of mixed oxide in resin cast (g)	γ-ray spectroscopy count time (s)
saturated/1 minute	9.592	1.740	89 523
saturated/2 hours	9.573	1.708	83 207
unsaturated/1 minute	9.863	1.540	82 576
unsaturated/2 hours	9.865	1.733	86 818

Table 3. Details for γ-ray spectrometric measurement of tailings shakeout samples

Results and Discussion

Solubilisation of gypsum

The solubility of gypsum at 25° C is 2.1 g/L (Aylward and Findlay 1974), which corresponds to 12.2 mM. The data in Tables 4 and 5 present the concentrations of individual species in the shakeout experiments, derived from ion chromatography.

Contact time (min)	$[SO_4^{2-}]$ (mM)	[Mg] (mM)	[Ca] (mM)
1	43.6	26.5	12.0
120	46.8	29.2	12.6
240	46.6	29.2	12.5
360	47.4	30.0	12.4

Table 4. Molar concentrations of common ions in 'gypsum saturated' tailings shakeout experiment

Contact time (min)	$[SO_4^{2-}]$ (mM)	[Mg] (mM)	[Ca] (mM)
1	14.0	7.4	4.8
120	12.2	6.3	4.2
240	12.0	6.0	4.4
360	19.9	8.1	9.6

Table 5. Molar concentrations of common ions in 'gypsum unsaturated' tailings shakout experiment

These results demonstrate that saturation with gypsum was established quickly in the experiment where an excess of tailings was used. Indeed, these solutions are formally supersaturated, the solubility product for $CaSO_4$ being 7.1 x 10^{-5} M^2 (Lide 1995), while the ion products range from 5.2-5.9 x 10^{-4} M^2. This discrepancy is probably due mainly to the presence of undissociated $CaSO_4$ ($CaSO_4^0$) in the solution of relatively high ionic strength. $CaSO_4^0$ does not contribute to the thermodynamic formulation of the solubility product (Lide 1995). Where undersaturation was expected, this is observed, but the rate of dissolution is not rapid compared with the time scale of observations. This finding is obscured in Table 5 by differences in tailings mass between beakers. The data contained in Table 6 are presented in terms of mass dissolved per gram of tailings, and therefore adjust for mass differences.

On the basis that gypsum comprises 5% of tailings, about 20% of the available gypsum was dissolved during elutriation for the 'gypsum saturated' experiment. This compares with 30%-

35% of available gypsum dissolved for the 'gypsum unsaturated' experiment at 1 and 120 minutes, rising to about 50% after 6 hours. This illustrates the relative slowness of gypsum dissolution, even under unsaturated conditions. The rapid initial dissolution of gypsum for both experiments may reflect an amorphous or highly disseminated phase that is rapidly solubilised. The much slower subsequent rate for the 'gypsum unsaturated' experiment may indicate a larger proportion of gypsum that is either crystalline or stongly adsorbed, and hence more slowly dissolved. Therefore, the preparation of a thoroughly washed tailings sample may require a more extended procedure that would be suggested by 'typical' dissolution kinetics.

Contact time (min)	[SO_4^{2-}] (mg/g slurry)	[Mg] (mg/g slurry)	[Ca] (mg/g slurry)
1	18.8	2.50	2.70
120	18.6	2.43	2.70
240	18.7	2.35	2.87
360	21.0	2.15	4.19

Table 6. Mass-adjusted dissolution of common ions in 'gypsum unsaturated' experiment

It is evident that the dissolution of gypsum is a relatively slow process, of comparable time scale to contact time. Conversely, the concentration of Mg per gram of tailings declines with longer elutriation time. This may indicate re-equilibration of Mg at ion exchange sites exposed by gypsum dissolution. Exchange sites on tailings mineral surfaces may have been occluded by gypsum and occupied by Ca ions. Initial slurry Mg contents would have been mainly in solution, with some Mg occupying ion exchange sites. Figure 1 shows the mass-adjusted concentration of Mg and Ca as a function of time for the 'gypsum unsaturated' experiment.

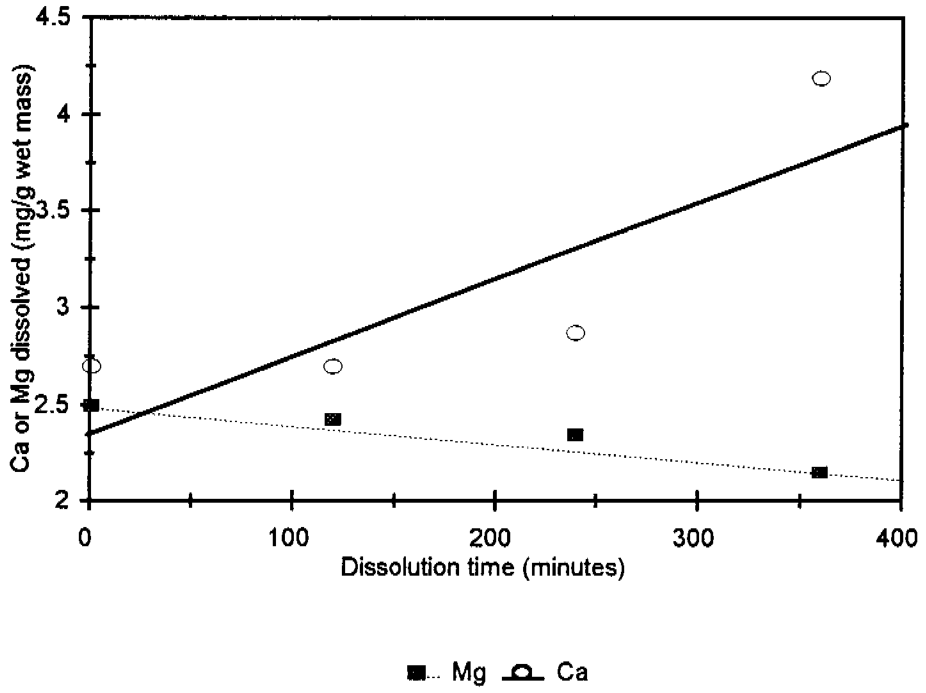

Figure 1. Mass of Ca and Mg released per gram of tailings slurry with time

Solubilisation of ^{238}U-series radionuclides

As previously described, four mixed oxide samples were cast in polyester resin and determined for selected radionuclides using γ-ray spectroscopy. Only the ^{238}U-series isotopes determined are discussed in this report. All unadjusted radionuclide measurements are recorded in Appendix 1. Different masses of tailings were used for each elutriation experiment, and each of these generated a different mass of mixed oxide coprecipitate, from a different filtrate volume. Because of these factors a calculation is required to convert the unadjusted activity (per gram of mixed oxide) of each radionuclide to the activity per gram of tailings. The relevant equation is:

$$A_{tails} = (A_{meas} \times M_{oxide} \times V_{init})/(M_{tails} \times V_{filt})$$

Where A_{tails} is the activity solubilised per gram of tailings slurry, A_{meas} is the measured activity (per gram of mixed oxide), M_{oxide} is the total mass of mixed oxide M_{tails} is the mass of tailings slurry in the beaker, V_{init} is the initial aqueous volume and V_{filt} is the filtrate volume.

The adjusted activities for ^{238}U-series radionuclides are presented in Tables 7 and 8.

Radionuclide	1 minute contact time○	120 minute contact time○
^{238}U	0.10±0.022	0.035±0.016
^{234}Th	0.014±0.011	0.027±0.0089
^{230}Th	0.095±0.10	0.077±0.083
^{226}Ra	1.81±0.0053	1.04±0.0034
^{210}Pb	0.38±0.0086	0.35±0.0075

○: Activity units are becquerels of solubilised radionuclide per gram of tailings slurry; uncertainties are expressed as absolute errors

Table 7. Adjusted radionuclide activities for 'gypsum saturated' experiment

Radionuclide	1 minute contact time○	120 minute contact time○
^{238}U	0.40±0.070	0.64±0.088
^{234}Th	0.029±0.035	0.015±0.043
^{230}Th	0.067±0.26	0.44±0.31
^{226}Ra	4.5±0.015	7.8±0.023
^{210}Pb	0.67±0.027	1.2±0.032

○: Activity units are becquerels of solubilised radionuclide per gram of tailings slurry; uncertainties are expressed as absolute errors

Table 8. Adjusted radionuclide activities for 'gypsum unsaturated' experiment

These data show a trend, for most radionuclides, towards a reduction in activity (concentration) with time in the case of gypsum saturation, and an increase in concentration with time for the unsaturated experiment. These trends are more evident in Figures 2 and 3.

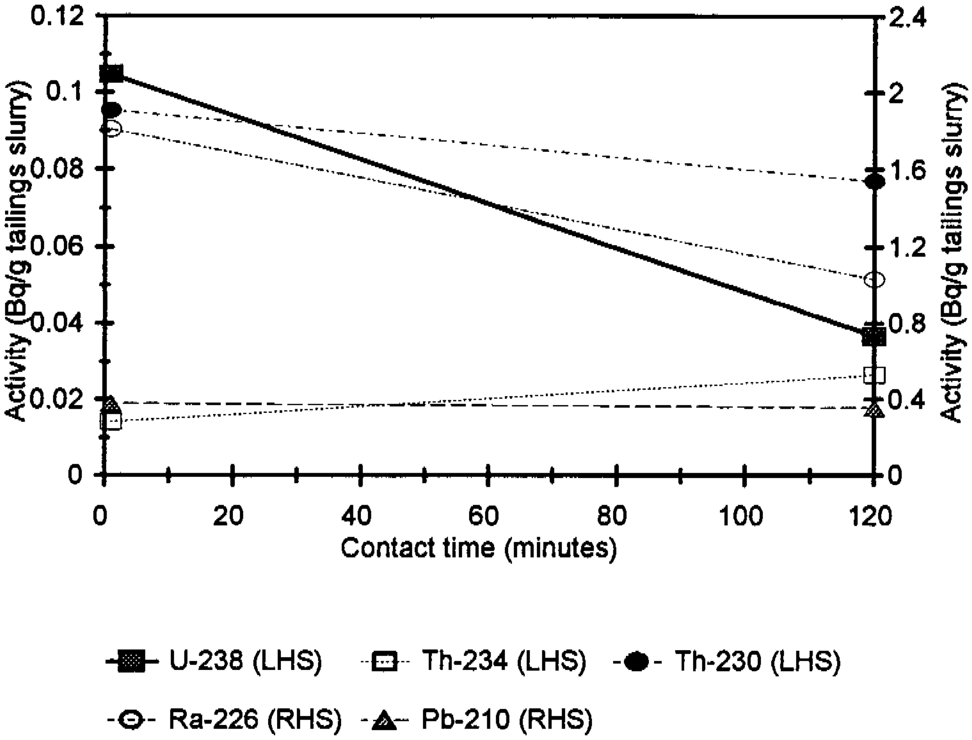

Figure 2. Activity trends for ^{238}U-series radionuclides in 'gypsum saturated' experiment

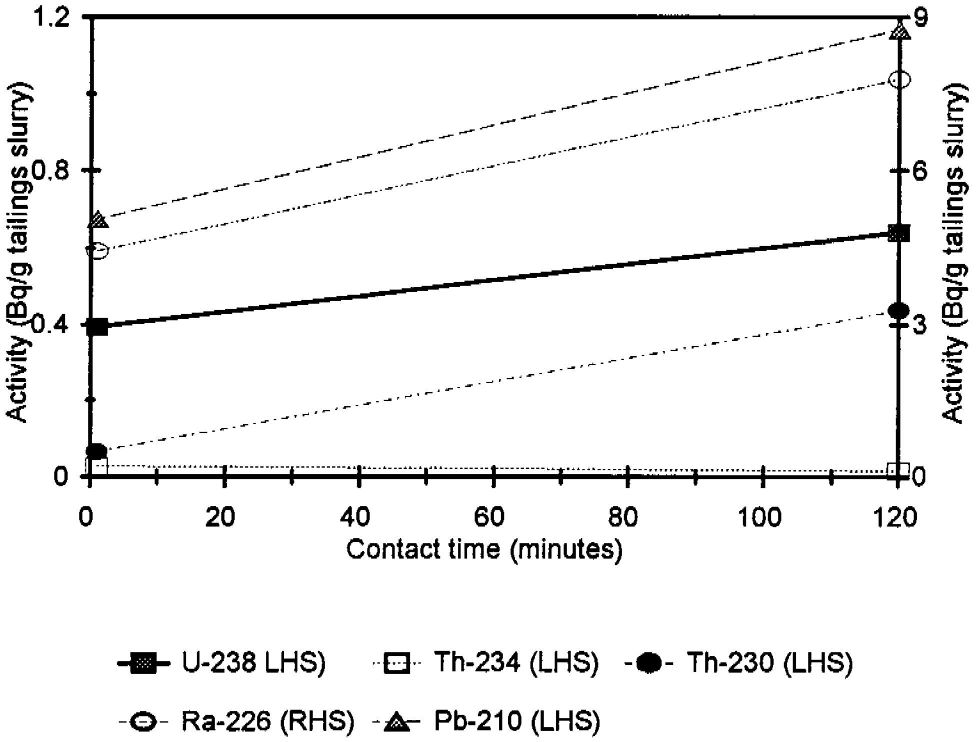

Figure 3. Activity trends for ^{238}U-series radionuclides in 'gypsum unsaturated' experiment

In the case of the 'gypsum saturated' experiment, ^{238}U, ^{226}Ra and ^{210}Pb had significantly different activity after 120 minutes, based on counting statistics. In each case the activity was *lower*. For the 'gypsum unsaturated' experiment, statistically significant time-related differences in activity were observed for ^{238}U, ^{234}Th, ^{226}Ra and ^{210}Pb. All isotopes had *higher* activity after 120 minutes except ^{234}Th, a nuclide of low activity and near the detection limit.

These findings are consistent with the idea that radionuclides such as ^{238}U, ^{226}Ra and ^{210}Pb are associated with the gypsum phase of tailings. In the case of tailings shakeout experiments where insufficient gypsum was available to provide a saturated solution, the slow dissolution of this sparingly soluble salt was mirrored by an increase in the soluble concentrations of these radioactive species.

It should be mentioned that these observations are also consistent with a slow re-equilibration of the ion-exchange complex as gypsum dissolves, resulting in the replacement of adsorbed radionuclides, all of which would be in cationic form, by Ca ions. However, the dissolution mechanism accords with literature precedent (Snodgrass *et al.* 1982). It also provides a better explanation for the observation that soluble activity *per gram of tailings slurry* is much greater for the unsaturated experiment. The major substantial difference between the two experiments, apart from the degree of saturation, was the *proportion* of available gypsum dissolved, especially the fraction that appears to dissolve more slowly. This may be identified with a more crystalline phase which in turn may provide the major repository for radionuclides.

In the case of shakeout experiments that were saturated with gypsum, the time-dependence of radionuclide activity is opposite to that in experiments where gypsum is unsaturated and dissolves slowly. If potentially soluble radionuclides are associated with gypsum, then in a saturated solution of the latter no *net* dissolution of radionuclides should occur. The observed reduction in activities would then be due to losses of radionuclides from solution, probably mainly by adsorption to the suspended tailings, although some adsorption to the beaker walls may also occur.

Conclusions

The experiments described in this report are consistent with the literature prediction that uranium mine tailings containing gypsum may have a substantial fraction of their radionuclide burden associated with this sparingly soluble mineral.

If tailings are ever exposed, then solubilised radionuclides from gypsum dissolution may be dispersed more widely than had been assumed using alternative models. These models generally assumed that radionuclides were primarily associated with the silicate and oxide components of tailings, which would render them much less mobile.

It is assumed here that, in the case of exposed tailings, rainwater runoff would be the dominant mechanism for soluble radionuclide removal. Runoff would be unlikely to have a mean contact time on the tailings mass of more than a few hours. In addition, rainwater would probably quickly saturate with gypsum until erosion had depleted this mineral in the surface tailings deposits. If this were to happen, then a plausible outcome is the slow readsorption of radionuclides during passage over the tailings. However, the experiments described here suggest that readsorption may not be complete during the average residence time on exposed tailings. Some soluble radionuclides would then be transported to the fluvial system downstream from the rehabilitated mine site.

More elaborate experiments than those described would be necessary to determine the detailed behaviour of radionuclides dissolved from and in contact with tailings. However, due to the present uncertainties about the final repository of the tailings, and the difficulty in predicting the likely course of events over very long periods, further investigations of soluble radionuclides are not planned at this stage.

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Appendix 1. Unadjusted radionuclide activities for tailings shakeout experiments

Radionuclide	1 minute contact time○	120 minute contact time○
^{238}U	2.4 ± 0.5	0.90 ± 0.40
^{234}Th	0.33 ± 0.25	0.65 ± 0.22
^{230}Th	2.2 ± 2.3	1.9 ± 2.0
^{226}Ra	41 ± 0.1	25 ± 0.1
^{210}Pb	8.7 ± 0.2	8.8 ± 0.2
^{137}Cs	0.015 ± 0.018	0.016 ± 0.018
^{7}Be	0.12 ± 0.15	0.17 ± 0.13
^{228}Ra	0.18 ± 0.07	0.22 ± 0.06
^{228}Th	0.13 ± 0.07	0.16 ± 0.05
^{40}K	0.15 ± 0.21	0.30 ± 0.18
^{54}Mn	0.21 ± 0.03	0.23 ± 0.03

○: Activity units are becquerels per gram of mixed oxide; uncertainties are expressed as absolute errors

Table A1. Unadjusted radionuclide activities for 'gypsum saturated' experiment

Radionuclide	1 minute contact time○	120 minute contact time○
^{238}U	2.5 ± 0.4	3.9 ± 0.5
^{234}Th	0.18 ± 0.22	0.093 ± 0.26
^{230}Th	0.42 ± 1.6	2.7 ± 1.9
^{226}Ra	28 ± 0.1	47 ± 0.1
^{210}Pb	4.2 ± 0.2	7.1 ± 0.2
^{137}Cs	0.018 ± 0.019	0.001 ± 0.019
^{7}Be	0.35 ± 0.16	0.22 ± 0.17
^{228}Ra	0.27 ± 0.08	0.11 ± 0.07
^{228}Th	0.041 ± 0.051	0.11 ± 0.06
^{40}K	0.24 ± 0.20	0.050 ± 0.23
^{54}Mn	0.061 ± 0.027	0.043 ± 0.032

○: Activity units are becquerels per gram of mixed oxide; uncertainties are expressed as absolute errors

Table A2. Unadjusted radionuclide activities for 'gypsum unsaturated' experiment