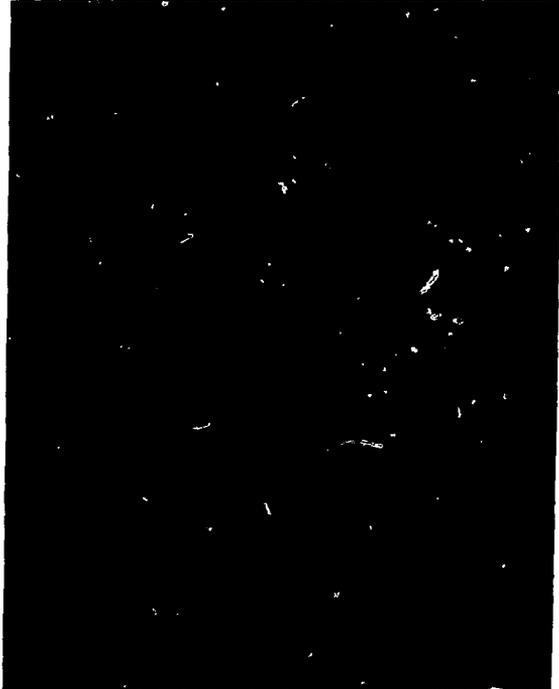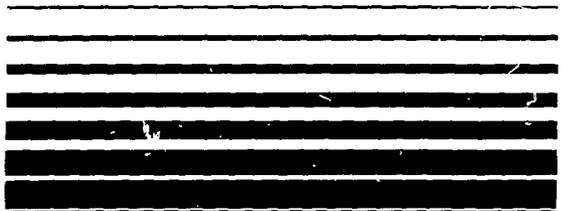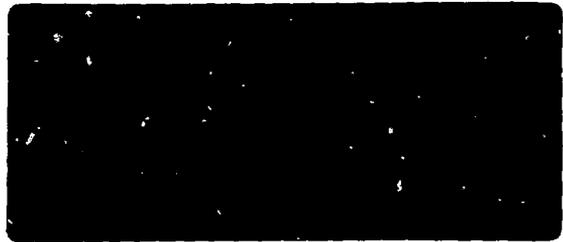# Report Rapport

Atomic Energy
Control Board

Commission de contrôle
de l'énergie atomique

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PLACEMENT OF RADIUM/BARIUM
SLUDGES IN TAILINGS AREAS

by

K.L. Murphy
G.E. Multamaki

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A Report prepared for the
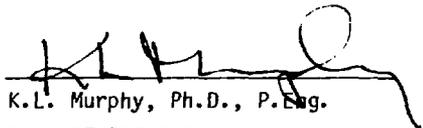Atomic Energy Control Board

by

International Environmental
Consultants Ltd.

31 March 1980

PLACEMENT OF RADIUM/BARIUM
SLUDGE IN TAILINGS AREAS

A Report for

ATOMIC ENERGY CONTROL BOARD
OTTAWA, ONTARIO

31 March 1980

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Les opinions exprimées dans ce rapport sont celles des auteurs et n'engagent pas la Commission de contrôle de l'énergie atomique.

The opinions expressed in this report are those of the authors and do not necessarily reflect those of the Atomic Energy Control Board.

ABSTRACT

Current technology for the removal of radium from uranium mining and milling effluents involves the addition of barium chloride to precipitate the radium as radium/barium sulphate. The precipitate is allowed to settle in sedimentation basins prior to discharge of the effluent. The sedimentation basins are not suitable for final disposal of the sludge thus other acceptable means must be found. Placement of the sludges in the tailings area has been proposed.

The geochemical environment of fresh tailings areas was characterized as an acidic, oxidized surface zone underlain by an alkaline, reduced zone comprising the rest of the tailings. It was predicted that this acidic oxidizing zone would become larger as pyrite is oxidized to sulphuric acid, and the alkaline minerals are leached from the tailings. The increased acidity would solubilize uranium, thorium, heavy metals and, with the depletion of soluble sulphate, would solubilize radium.

The quantity of sludge produced was estimated to be several orders of magnitude less than the quantity of tailings for any milling operation thus, the quantity of additional radium added to the tailings area would be small relative to the radium in the tailings.

To confirm whether sludge addition affected radionuclide solubilization, Laboratory leaching tests were conducted on slurries of acid leach tailings, and sludge tailings mixtures. Radium in the $(Ra,Ba)SO_4$ sludge was at least as stable as radium in the tailings and the sludge was capable of adsorbing radium released from the tailings. The addition of sludge did not affect uranium and thorium solubilization.

From these results, it appears that the placement of $(Ra,Ba)SO_4$ sludge in tailings areas would not adversely affect the stability of radionuclides in the tailings or sludge.

RESUME

A l'heure actuelle, la technique d'enlèvement du radium des effluents
d'extraction et de broyage de l'uranium s'effectue en ajoutant du chlorure
de baryum afin de précipiter le radium qui devient ainsi un sulfate de
radium/baryum. On laisse ensuite reposer le précipité dans des bassins de
sédimentation avant d'en faire disparaître les effluents. Etant donné que
les bassins de sédimentation ne se prêtent pas à l'évacuation définitive
de la boue, il faut donc trouver d'autres moyens convenables. On a proposé
de placer des boues dans la zone de dépôt des résidus.

L'environnement géochimique des zones de résidus frais se caractérise par
l'acidité et l'oxydation de la surface, au-dessous de laquelle se trouve
une zone alcaline réduite qui comprend le reste des résidus. On croyait que
cette zone acide et oxydée augmenterait à mesure que la pyrite s'oxyde et
devient de l'acide sulfurique et que les minéraux alcalins sont lessivés
des résidus. L'acidité accrue rendrait solubles l'uranium, le thorium et
les métaux lourds et, de concert avec la diminution des sulfates solubles,
le radium.

On a calculé que la quantité de boue produite serait inférieure de quelques
ordres de grandeur à la quantité de résidus provenant du broyage et qu'ainsi
la quantité additionnelle de radium ajoutée à la zone des résidus serait
faible, en comparaison avec le radium qui se trouve dans les résidus.

Afin de déterminer si l'addition de boue touche la solubilité des radionuclides,
des essais de lixiviation en laboratoire ont été effectués sur des pulpes de
résidus de lixiviation acide, et sur des mélanges de boue et de résidus.
Le radium contenu dans la boue de $(Ra,Ba)SO_4$ était au moins aussi stable
que celui qui se trouve dans les résidus et la boue pouvait absorber le radium
émis par les résidus. L'addition de boue n'a touché en rien la solubilisation
de l'uranium et du thorium.

Ces résultats indiquent que le fait d'ajouter de la boue de $(Ra,Ba)SO_4$ dans les
zones de résidus n'influerait pas de façon négative sur la stabilité des
radionuclides dans les résidus ou dans la boue.

PROJECT: 2079.1
PLACEMENT OF RADIUM/BARIUM
SLUDGE IN TAILINGS AREAS

ATOMIC ENERGY CONTROL BOARD
OTTAWA, ONTARIO

DATE: 31 MARCH 1980

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ACKNOWLEDGEMENTS

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1.0   SUMMARY

Current technology for the removal of radium from uranium mining and milling effluents involves the addition of barium chloride to precipitate the radium as radium/barium sulphate. The precipitate is allowed to settle in sedimentation basins prior to discharge of the effluent.

Since the Atomic Energy Control Board (AECB) considers the sedimentation basins as storage areas, adequate sites must be provided for the sludges. Placement of the sludges in the tailings area has been considered. However, no quantitative data exist concerning the effect on physical and chemical conditions in the tailings, on radium resolubilization or on the quantity of additional radium which would be released to the environment. AECB retained IEC International Environmental Consultants Ltd. (IEC) to undertake a technical assessment of the implications of utilizing tailings areas as a disposal site to assist AECB in developing policy on the disposal of sedimentation basin sludges. IEC's findings are briefly outlined below.

The quantity of (Ra, Ba) SO_4 sludge produced is several orders of magnitude less than the quantity of tailings for any milling operation. Further, the quantity of radium in the sludge is small relative to radium in the tailings. Consequently, the placement of the sludge would be of concern only if radium and other radionuclides are more readily leached from the sludge or if the presence of the sludge increases leaching from the tailings.

Based upon geochemical considerations and information regarding ore milling processes it was predicted that the geochemical environment of fresh tailings areas could be characterized as an acidic oxidized surface zone underlain by an alkaline, reduced zone comprising the rest of the tailings. This acidic oxidizing zone can become larger as pyrite is oxidized to sulphuric acid, and the alkaline minerals are leached from the tailings. The increased acidity and oxygen availability will solubilize uranium, thorium, heavy metals and, with the depletion of soluble sulphate, it will solubilize radium.

To confirm these predictions on the effect of sludge addition on radium, thorium and uranium solubilization, IEC conducted laboratory leaching tests on slurries of tailings and sludge-tailings mixtures from the acid leach process. Samples of the slurry decant were adjusted to simulate the predicted geochemical conditions for the tailings areas. The results indicated that radium in the (Ra, Ba) SO_4 sludge was at least as stable as radium in the tailings and that the sludge was capable of adsorbing radium released from the tailings. The addition of sludge did not effect uranium and thorium solubilization.

From these results, it appears that the placement of (Ra, Ba) SO_4 sludge in tailings areas would not adversely affect the stability of radionuclides in the tailings or sludge.

2.0   INTRODUCTION

In the recovery of uranium from ore deposits, large quantities of waste tailings are produced by Canadian mine/mill complexes. These tailings are conveyed to impoundment areas in slurry form. After settling, the supernatant is discharged to the environment together with runoff from precipitation on the tailings basin. Currently, all operating uranium mines in Canada employ barium chloride treatment to control the release of dissolved radium to the aquatic environment. The dissolved radium in the tailings decant is precipitated with barium chloride as $(Ra, Ba) SO_4$. Following precipitation the precipitate is settled in ponds or lakes. In some instances settling tanks have replaced ponds and flocculants have been added to aid settling.

Since AECB does not consider the precipitation ponds to be suitable for final disposal of these sludges, acceptable sites must be found. Options which have been suggested for sludge management include underground placement either in worked out mine areas ,or in special chambers, or placement in the tailings areas. Conceptually, the latter alternative is attractive and probably would minimize sludge handling. This alternative would be subject to the AECB policy which requires that upon abandonment, radioactive releases from a tailings area must be within present regulatory limits, and that treatment to meet these limits should not be required in perpetuity. No quantitative data exist concerning either the effect of physical and chemical conditions in the tailings on resolubilization of radium from precipitated sludges or the fraction of this additional radium which would be released. IEC International Environmental Consultants Ltd. were retained by the Atomic Energy Control Board to examine the implications of placing radium/barium sludge in tailings areas as background information for the development of regulatory policy by AECB.

3.0 · STUDY APPROACH

This study is a preliminary evaluation of radium/barium sludge placement in tailings areas. The study does not provide detailed site-specific information, but rather identifies the important parameters and information required for site-specific field studies. Investigations have been based on existing information and only a modest experimental program was included to supplement existing data.

The implications of sludge placement were restricted to consideration of possible increases in the quantity of radionuclides escaping to the environment through either groundwater or surface water. The types of tailings and effluent treatment systems currently operating in Canada were considered.

A relatively short geological time frame of up to several hundred years was selected. If sludge placement does not result in significant additional radium releases within this time frame, then the relatively small additional amount of radium contributed by the sludge will be of little consequence.

Site visits were made to the facilities of Eldorado Nuclear Ltd. at Uranium City, Saskatchewan, Gulf Minerals Ltd. at Rabbit Lake, Saskatchewan and Agnew Lake Mines Ltd. at Agnew Lake, Ontario to gain familiarity with the effluent treatment and tailings systems and to obtain basic information on each system. As IEC was familiar with the effluent treatment and tailings systems of Rio Algom and Denison Mines Ltd., at Elliott Lake, Ontario and Madawaska Mines Ltd., near Bancroft, Ontario site vists were not required. With the permission of the mines additional information was subsequently obtained from AECB files in Ottawa.

Information on the leachability of radium from tailings and from sludge was obtained from the literature. In addition, IEC was permitted access to unpublished data from ongoing leaching experiments at the Wastewater Technology Centre of Environment Canada.

Within the scope of this study, it was not possible to consider the consequences of sludge placement at the specific individual facilities. The environmental conditions to which tailings and sludge would be exposed over the long term were predicted on the basis of geochemical considerations and information obtained from individual facilities on ore type processing. The mobilization of radium under these conditions was predicted qualitatively. Laboratory experiments were used to confirm relative radium dissolution from sludge and sludge-tailings mixtures under the predicted environmental conditions.

To introduce the geochemical considerations and discussion of radionuclide mobilization in Section 5, background information on the quantity and characteristics of radionuclides in tailings and sludge is presented in Section 4.

4.0   BACKGROUND

Three geologically distinct uranium ore types are mined in Canada: quartz pebble conglomerates at Elliot Lake, pegmatite deposits in the Bancroft area of Ontario and the vein deposits of North Saskatchewan. The chemical composition of each ore type varies significantly both with respect to uranium mineralization and the associated gangue minerals. Therefore, a variety of milling and extraction techniques are used for uranium recovery and the physical and chemical nature of uranium tailings piles are site-specific.

The high degree of variation of radionuclide content in the original ore-bodies results from the differential mobilities of uranium and thorium. North Saskatchewan vein deposits have almost no thorium-232, while pegmatite and conglomerate deposits in Ontario contain significant concentrations of thorium-232 (0.2-0.5%) and uranium-238 (0.1-0.3%). At radiogenic equilibrium appreciable activity associated with their daughter products exist.

4.1   Radium in Orebodies

Of the 16 isotopes of radium, radium-226 is of concern due to its radiotoxicity and long half life of 1,620 years. Radium-226 is one product in the uranium-238 decay series. Its immediate precursor is thorium-230. No known stable radium minerals exist. The activity ratio of radium-226 at radioactive equilibrium with uranium-238 is 3.5×10^{-7}. Thus a uranium mineral having 10^3 ppm U would contain only 3.5×10^{-4} ppm Ra, too insignificant to be termed a radium mineral.

Radium has a relatively simple chemistry. Only the divalent state is known. Insoluble inorganic radium compounds include the sulphate and carbonate salts while the chloride, bromide, nitrate and hydroxide salts are reasonably soluble.[1, 2] As an alkaline earth element it most closely follows the aqueous chemistry of barium although radium salts are less soluble than analagous barium salts. The solubilities of uranium and radium salts are similar and are higher than thorium salts.[3] An exception is thorium sulphate which is moderately soluble under acidic conditions.[4] Of the alkaline earth metals, radium shows the least tendency to form organic complexes, although 1:1 complexes with citric, tartaric and succinic acids occur at a pH of approximately 7.[5]

Complex and competing ion effects are important when considering the behaviour of radium in aqueous systems. High salinity enhances ion enrichment caused by the competition and exchange between ions in solution and ions adsorbed on particle surfaces and the specific ions strongly affect radium dissolution. The greater the chemical affinity of an element to radium, the greater the enhancement of leaching ($Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > K^+ > Na^+$).[6] Other factors that affect dissolution are temperature, dissolved gases, oxidation potential and pH.

4.2   Effect of Mill Processing

Radium balances for three types of mills: acid leach with resin-in-pulp ion exchange, acid leach with solvent extraction, and alkaline leach, are presented in Table 4.1.[7] More radium is dissolved in the alkaline leach process than in the acid leach. It must be noted that other studies have reported soluble radium in acid leach circuits up to an order of magnitude higher than shown in Table 4.1, and it is possible analytical methods account for this discrepancy. However, the data in Table 4.1 are consistent with other data showing a higher specific activity for the slimes fraction.

TABLE 4.1   FATE OF RADIUM IN MILLING PROCESSES

	Acid Leach RIP		Acid Leach SX		Alkaline Leach	
	mg/d	(%)	mg/d	(%)	mg/d	(%)
Incoming Ra-226 (Ore)	300	(100)	146	(100)	739	(100)
Ra-226 dissolved in Process	2	(0.7)	0.56	(0.4)	20	(3)
Outgoing Ra-226						
Tailings						
Sands	81	(27)	26	(18)		
Slimes	225	(75)	116	(82)	719	(97)
Dissolved	0.36	(0.12)	0.45	(0.31)	∿ 0	∿ (0)
Yellowcake	0.15	(0.05)	0.025	(0.02)	20	(3)

Note: Percentages do not total 100% exactly.

[1]Data from Tsivoglou and O'Connell (1962)

In tests simulating acid leach processing[8] soluble radium of less than 0.03 percent was reported in comparison to the 0.4 to 0.7 percent of the radium-226 reported by Tsivoglou and O'Connell (Table 4.1). A further study reported a range of 3 to 5 percent for the radium-226 in solution.[9]

The distribution of radium-226 in a typical acid leach circuit from Elliot Lake indicated an activity of 335 pCi/g in the ore and a level of 328 pCi/g or 98% of the original activity level in the limed tails.[10] It was stated that radium was dissolved in the leaching process but was immediately reprecipitated as a sulphate. The maximum activity level for radium-226 in solution was 7,000 pCi/L and occurred following the leaching step. The activity of the yellowcake was less than 100 pCi/g.

In the alkaline leach circuit at the Beaverlodge Mill of Eldorado Nuclear Ltd., where pyrite is floated and treated in a separate acid leach circuit, virtually all of the radium entering the mill remained with the tailings.[11] Less than 2% reached the acid leach circuit and only about 0.5 % reached the precipitation circuit. An activity level of only 80 pCi/g was reported in the yellowcake. At any station, the dissolved radium was less than 1.5% of the total present in the system. Within the leach circuit the specific activity of the minus 75 um solids was twice that of the plus 75 um fraction. These values remained at approximately 400 and 200 pCi/g respectively through to the primary Dorrclone which separates coarse tailings for backfill.

Chemical transformations of radium in the mill could significantly affect radium behaviour in tailings piles. None of the studies reviewed from the literature established the quantity of radium that dissolved during mill leaching and was immediately reprecipiated or readsorbed. If the dissolution reaction was rate controlling, the concentration in solution would remain low.

4.3   Other Radionuclides in Orebodies

Radium-226 has traditionally been used as the indicator of radiological hazard in uranium mining effluents.   Orebody radionuclides other than radium-226 include the decay products of both the uranium-238 and uranium-235 decay chains.   In some ores, thorium-232 and its decay products will be present.   The radionuclides are shown in Table 4.2 in decreasing order of radiotoxicity.

TABLE 4.2 MPC_W FOR ISOTOPES IN DECREASING ORDER OF RADIOTOXICITY

Isotope		MPC_W pCi/L*
radium	- 226	10(3**)
lead	- 210	100
polonium	- 210	700
thorium	- 230	2,000
thorium	- 234	20,000
uranium	- 234	30,000
uranium	- 238	40,000
bismuth	- 210	40,000

* MPC_W value is the maximum permissable concentration in water for individual members of the public (1/10 ICRP value for continuous occupational exposure)

**   Drinking Water Quality Objectives, Ministry of the Environment 1978.

Little is known about the behavior of either lead-210 or polonium-210 in the milling process.[12]   Neutralization of tailings slurries prior to discharge is assumed to reduce the level of soluble lead-210 to acceptable values. Concentrations of lead-210 from 1 to 8 pCi/L were reported for the final discharge from the Elliott Lake tailings area.[13]   As long as tailings decants remain alkaline (as they will during mine/mill operation) lead-210 should remain at low levels in the decant and should not be concentrated in the sludge.

Thorium is rendered virtually insoluble by neutralization in the mill.[12] Again, as long as the tailings decant remains alkaline the thorium would not be solubilized. Uranium is removed in the mill with an efficiency of at least 90%. The remaining uranium in the tailings will remain insoluble accept at low pH.[12]

No data were obtained from the literature for bismuth-210, however its half life is very short.

Other radionuclides are not expected in significant concentrations and have not been considered.

4.4   Residual Radium-226 in Tailings and Sludge

Between 95% and 100% of the incoming radium in the ore is conveyed to the tailings areas with approximately 75% of the radium present in the slimes. The form and concentration of radium-226 will be different in tailings, tailings decant, and sludge for the acid and alkaline leach mill process.

4.4.1   Radium in Acid Leach Tailings and Sludge

The radium-226 activity level of approximately 330 pCi/g in the limed tailings is equivalent to 330 µg radium-226 per tonne of tailings.[10] Measured radium-226 in the tailings decant was approximately 800 pCi/L[10] which would represent 4.9 µg of radium-226 in solution per tonne of tailings discharged to the tailings area (milling rate = 4700 t/d).

The ratio of radium-226 in the tailings to radium-226 precipitated in the sludge is 67:1 assuming 100% precipitation of radium from solution. The quantity of sludge produced in precipitating radium can be calculated from the quantity of $BaCl_2$ (11 mg/L as Ba Cl_2) added to the tailings decant (4000 gpm), on the assumption that all the barium precipitates as (Ra, Ba) SO_4, and the weight of radium-226 incorporated into the sludge is insignificant. This means that the sludge would have an activity level of approximately 65,000 pCi/g. The weight ratio of tailings to sludge is about 13,000 to 1. These calculations are summarized in Table 4.3 on the next page.

TABLE 4.3   Estimated Radium-226 in Tailings and Sludge

	Radium-226 in Tailings pCi/g	Radium-226 in Tailings Decant pCi/L	Radium-226 in Sludge pCi/g	Quantity of Tailings / Quantity of Sludge
Acid Leach	330	800	65,000	13,000 / 1
Alkaline Leach	1000	70	940	7,200 / 1

4.4.2 Radium in Alkaline Leach Tailings and Sludge

Alkaline leach tailings contain approximately 1000 pCi/g radium-226 at the point of discharge to the tailings area.[14] This is equivalent to 1000 µg radium-226 per tonne of tailings. Measured radium-226 in the tailings decant was approximately 70 pCi/L which represents 0.13 µg of radium-226 per tonne of tailings discharged (milling rate = 800 t/d).

The ratio of radium-226 in the tailings to radium-226 in the sludge is about 7600:1 assuming 100% precipitation of radium from solution. Again the quantity of sludge produced in precipitating radium can be calculated from the quantity of $BaCl_2$ added to the tailings decant (72 kg/d), assuming all the barium precipitates as (Ra, Ba) (CO_3, SO_4) and the weight of radium-226 incorporated into the sludge is insignificant. This means that the sludge would have an activity level of approximately 940 pCi/g. The weight ratio of tailings to sludge is about 7200:1. These calculations also are summarized in Table 4.3.

5.0   SOLUBILIZATION AND MOBILIZATION OF RADIUM AND OTHER RADIONUCLIDES

Two factors are important in predicting the implications of sludge placement: the relative amounts of radium in sludge and tailings, and the chemical differences between radium in sludge and tailings which could affect the mobility of the radium in either. In Section 4 it was established that the the quantity of radium in the sludge is much less than in tailings. Consequently, sludge would only be a problem if it is readily mobilized or causes mobilization of radium in the tailings. The factors affecting radium solubilization in sludge and tailings and the probable geochemical environments to which sludge and tailings will be subjected have been examined to predict radium mobilization. Behaviour of sludge and tailings in these environments is predicted from available literature.

5.1   Factors Affecting Solubilization of Radium and Other Radionuclides

The physical and chemical factors affecting the dissolution of radium and other radionuclides from tailings and sludges are those which affect solubilization in general. Increasing surface area and temperature will enhance dissolution, as will increases in the liquid:solid ratio. Both pH and Eh affect the basic chemistry of the system, and thus will influence leaching. The chemical form of the radionuclide is important. Radium which remains within the ore matrix would be expected to behave differently from radium which has been liberated from the ore and reprecipitated in the mill circuit. Both the ionic strength and the presence of specific cations and anions in leaching solutions may be expected to have an effect. High sulphate concentrations will inhibit the dissolution of radium. In addition, certain organic reagents used in milling may complex radionuclides.

Because of the complex chemical form of tailings, it is not possible to predict from fundamental considerations the dissolution of radium under various conditions. A number of recent investigations have examined the solubilization of radium from tailings, but basic information on the solubility of radium compounds is limited, and the behaviour of (Ra, Ba) SO_4 sludges has received little attention.

## 5.1.1 Solubilization from Tailings

Most of the solubilization experiments have been static laboratory stirred leaching tests. Some tests have been performed with the specific objective of developing mill processes to extract radium and have employed high salt concentrations which would not be expected to occur in tailings piles.

Several physical variables have been shown to have minor effects on radium solubilization. It was found that the percentage of radium-226 extracted did not vary significantly with tailings particle size, although the equilibrium radium-226 concentration in solution was highest for the smallest diameter particles which contained more radium initially.[8, 15] Variations in stirring speed over a wide range had no detectable effect on the rate of radium leaching. Increases in temperature over the range 5 to 45°C increased the extent of leaching slightly, while in the range of 25°C to 70°C increased temperature augmented the removal of radium from unwashed tailings, but decreased the removal from washed tailings by a factor of two.[8, 15]

Enhanced extraction of radium has been reported with increasing liquid: solid ratios. Using acid leach tailings which had been washed previously with demineralized water and then dried, the percentage of radium leached with demineralized water increased almost linearly with liquid: solid ratios up to 60:1 (Figure 5.1). This is analogous to the dissolution of a sparingly soluble salt such as barium sulphate in water. With solid $BaSO_4$ present, barium ions in solution will be at equilibrium and hence the percentage of the barium which dissolves will be proportional to the liquid: solid ratio.

FIGURE 5·1

EFFECT OF LIQUID : SOLID RATIO ON
LEACHING OF Ra-226
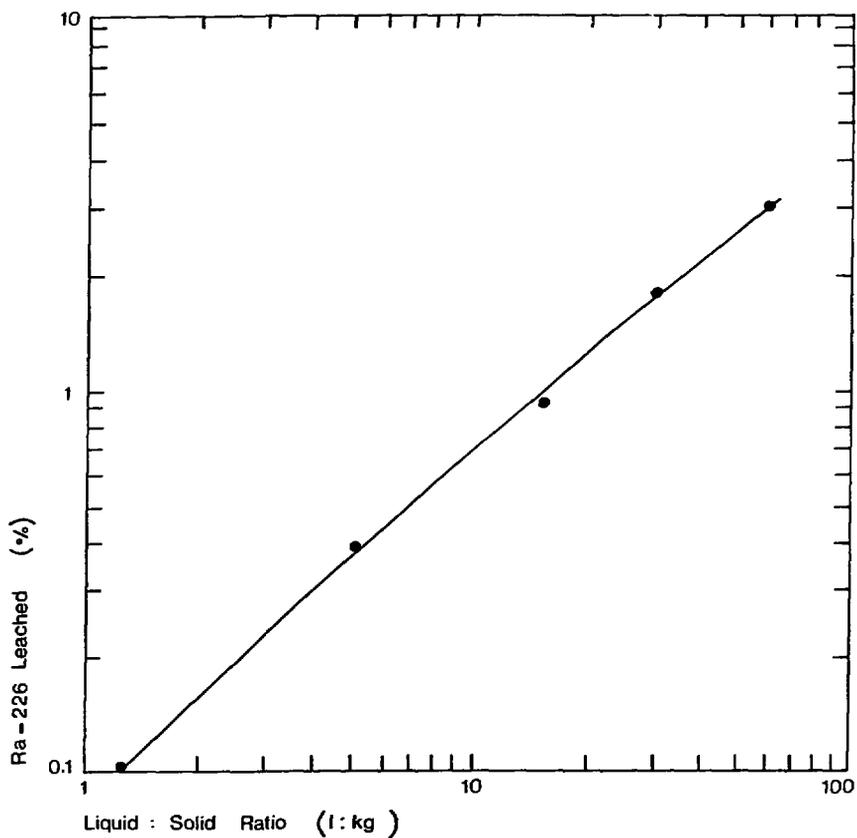
After Levins et al (1978)

It was suggested that this analogy should apply to radium although mixed sulphates of other alkaline earth elements may reduce the concentration of radium in solution. Lysimeter studies showed higher activity levels in leachate at high flow rates indicating that more radium was being extracted.[16] The increased flow rate through the lysimeter is equivalent to increasing the liquid:solid ratio in a static slurry test.

Figure 5.2 indicates the pH of the tailings slurry solution had a marked effect on the dissolution of radium, particularly at high liquid: solid ratios and low sulphate concentrations.[8] When the pH was reduced below the initial value of 5.1 through addition of acid the percentage of radium leached increased. Less radium was leached by sulphuric acid than by hydrochloric or nitric acids. Sulphuric acid decreased the concentration of radium-226 in solution below pH 3. Similiarly, radium dissolution decreased by more than an order of magnitude at pH values above 8.

A further study reported that below pH 2.5 the amount of radium leached increased dramatically.[17] This was pastulated to be related to bulk dissolution of some critical component of the tailings such as an iron oxide. Apparently conflicting results were obtained using 1M KCl. The percentage extraction varied by less than a factor of 2 over the pH range 1 to 13.[15] For $CaCl_2$, decreasing the pH from 10 to 1 increased extraction by a factor of 3 approximately.

The effect of salt concentration on radium leached from low sulphate tailings is presented in Figure 5.3.[8] Sodium chloride and sodium nitrate concentrations greater than 200 mg/L Cl^- and 300 mg/L NO_3^{2-} substantially increased the amount of radium leached. It was postulated that the effect of salt concentration could be due either to a decrease in adsorptive properties of tailings at high ionic strengths and/or displacement of adsorbed radium by other cations. However, sodium sulphate concentrations had little effect on the amount leached, probably due to lower radium solubility in a sulphate solution. When pitchblende tailings were leached using solutions of ammonium chloride, potassium nitrate and sodium nitrate the amount of radium dissolved was directly proportional to leach solution concentrations.[17]
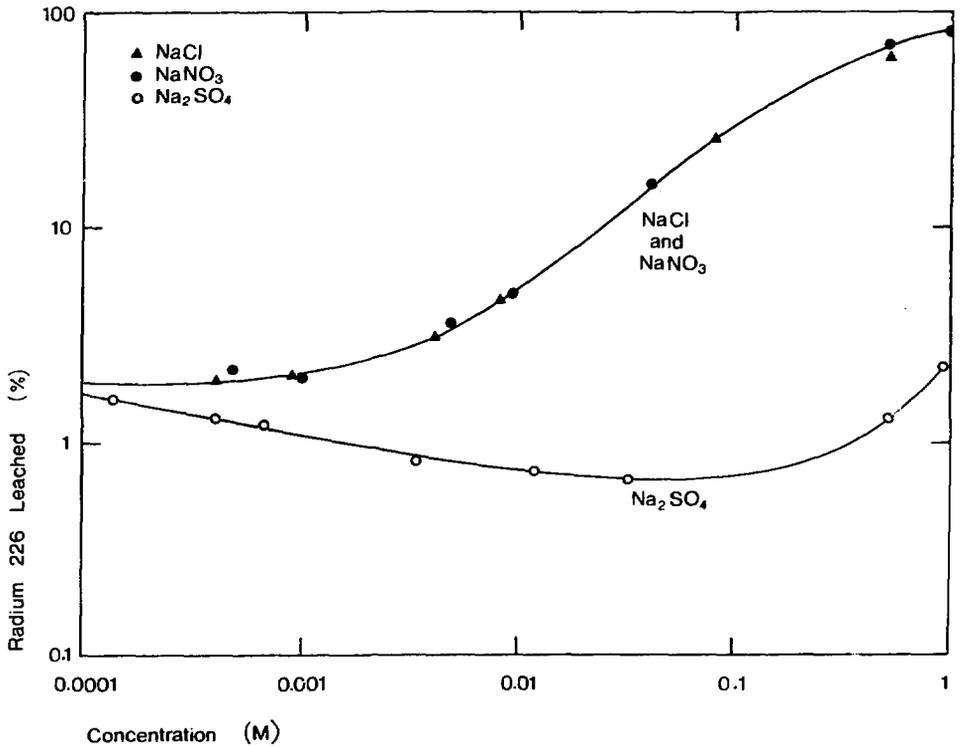
FIGURE 5·2

EFFECT OF pH ON LEACHABILITY OF Ra-226
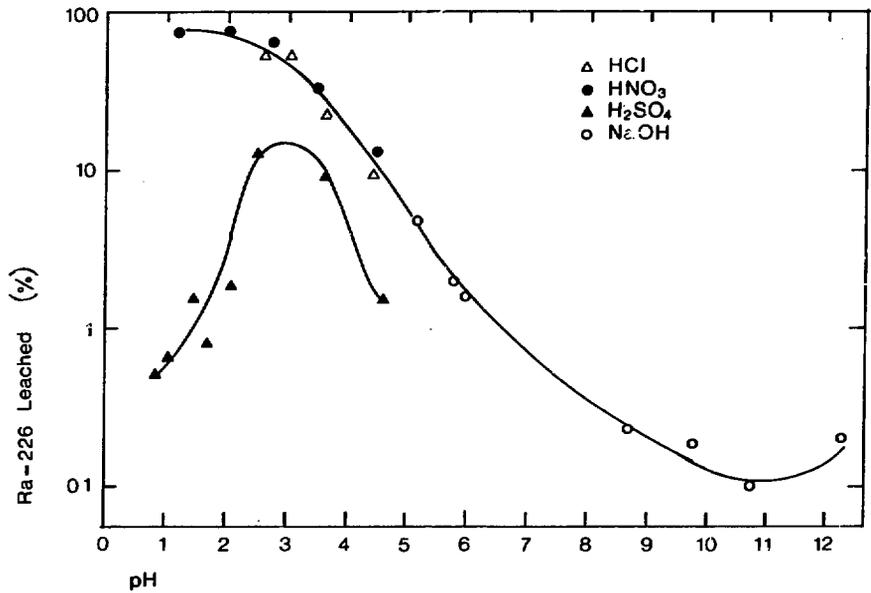
After Levins et al (1978)

FIGURE 5·3

EFFECT OF CONCENTRATION OF
SODIUM SALTS ON LEACHABILITY
OF Ra-226

Levins et al 1978

The effects of specific cations also have been examined. One study indicated increases in calcium and magnesium ion concentration increased the amount of radium leached.[8] With barium, the amount of radium leached increased rapidly with increases in barium concentration up to approximately 140 mg/L and further increases in barium had no effect. It was postulated that the overall process consisted of rapid equilibrium adsorption of barium on the particle surface, solid state interchange between a barium ion on the surface and a radium ion in the crystal lattice, and release of the radium from the surface. With solid state diffusion suggested as the rate controlling step, it is inferred that the radium is incorporated or enclosed in the crystal lattice and not simply adsorbed on the surface. This model was assumed to be applicable to other metal ions such as calcium and magnesium.

Washing the tailings with water at a liquid:solid ratio of 10:1 removed 93 percent of the sulphate in the tailings, decreasing the concentration from 6 g/L to 0.4 g/l. Only a small amount of the radium was removed during the water wash. Five sequential washings of acid leach tailings with demineralized water leached less than one percent of the radium.[8] The wash greatly increased the amount of radium released in subsequent leaching with various salt solutions. Sulphate salts have been demonstrated to reduce leaching of radium. The addition of 1000 mg/L SO_4^{2-}, decreased the amount of radium leached by approximately 50 percent.

Various workers have examined the time required for radium leaching. It was found that extraction with both organic and inorganic extractants occurred within the first 15 minutes,[18] while another study reported that 50 percent of the amount leached in 3 hours with ammonium nitrate occurred within the first 30 minutes.[17] With demineralized water a maximum amount solubilized in 15 minutes.

Decreased solubilization at longer times was attributed to $RaSO_4$ precipitation as the sulphate concentration increased with time. Maximum radium removal from unwashed tailings with potassium chloride required 2 hours leaching while removal from washed tailings was complete after 15 minutes and was more efficient.[15]

Generally, increased solubilization of radium from tailings occurs with increasing liquid:solid ratio, decreasing pH and the presence of various cations and anions while soluble sulphate reduces radium solubilization. Most of the total radium solubilized from the tailings is leached in less than one hour.

5.1.2 Solubilization From Sludge

There is less information available regarding solubilization of radium sulphate and radium/barium sulphate sludge than there is regarding solubilization of radium from tailings. Further, there is little information in the chemical literature concerning the solubility of barium sulphate.

Several values for $RaSO_4$ solubility can be found in the literature. Perhaps the most reliable value is 2.1×10^{-4} g per 100 cc of water at $20°C$[19] although a value of 2×10^{-6} g per 100 cc of water at $25°C$ is also quoted.[20] These solubility values correspond to activity levels of 15×10^8 pCi/L and 14×10^6 pCi/L respectively.

Data regarding the solubility of $BaSO_4$, the closest analog to radium sulphate, is of interest because $BaSO_4$ is the major component of the sludge. The solubility of $BaSO_4$ doubles as temperature increases from 0° to 20°C. Solubility is inversely proportional to very high concentrations of H_2SO_4, and is increased by high concentrations of hydrochloric and nitric acid.[19]

A preliminary investigation of the stability of radium/barium sulphate was conducted over the pH range 2 to 10 in the presence of barium sulphate concentrations up to 1500 mg/L.[21] Test solutions were allowed to equilibrate with the sludge at a liquid:solid ratio of 30:1 for a period of one week without stirring. Generally, the release of radium is lowest when the overlying sulphate concentration was 800 mg/L but no overall trend with respect to pH could be discerned. The maxium radium concentration in solution was approximately 35 pCi/L, representing solubilization of 0.005% of the radium. Additional tests showed that Desulfovibrio vulgaris metabolized the sludge and increased the rate of radium release under anaerobic conditions.

Lysimeter tests were conducted with tailings and sludge at two water flow rates.[16] Control lysimeters contained abandoned tailings while in the other lysimeters 11% of the tailings by weight was replaced by an equivalent weight of radium/barium sulphate sludge. The sludge was mixed with tailings in the top portion of the lysimeter. In interpreting the results, it is necessary to estimate the relative initial activites of the lysimeters with and without sludge added. Although initial activity levels of radium-226 in the tailings and sludge were not recorded, it is reasonable to assume values of approximately 300 pCi/g and conservatively 20,000 pCi/g for tailings and sludge respectively. On this basis the initial activity in the lysimeters containing sludge was approximately 8 times greater than for tailings alone. Thus if the rate of release of radium from sludge and tailings are equal, leachate activity levels should be approximately a factor 8 higher for the lysimeters containing sludge.

For tailings plus sludge, reported radium-226 activity levels in leachate were at most a factor of 3 above levels for tailings alone. There was no increase in lead-210 levels when sludge was present, but thorium-230 levels increased by 3 orders of magnitude in the early stages of leaching. Increased water application rates increased the amount of radium released from both tailings and sludge. Other tests using simulated settling ponds to evaluate chemical fixation of the radium/barium sulphate sludge found chemical fixation reduced the radium-226 activity level in the effluent from 3 - 9 pCi/L to less than 1 pCi/L.[16]

The information available suggests that barium sulphate sludge should be relatively stable chemically. Experiments have not shown large releases of radium from the sludge.

5.1.3 Physical Factors Affecting Solubilization

Although the chemical form of radium in uranium mill tailings has not been established precisely, radium probably occurs both in the adsorbed state and as a principal constituent of a mineral precipitate or a co-precipitate. In adsorption, the concentration in the solution and solid phases approach equilibrium rapidly. The concentration in the solution phase is dependent upon the selectivity coefficient for the exchange reaction and the concentrations of the competing cations. For chemical precipitation or co-precipitation, the concentrations in solution are dependent upon the solubility product for the reaction and the concentrations of reactants and reaction products. In order for the release of radium to the solution phase to continue, the products of dissolution (including radium) must be removed from the reaction site. This implies that the water flux through the tailings can be a major factor affecting solubilization. The increased dissolution with increasing water flux is supported by the results of the liquid:solid ratio experiments discussed previously.

Although experimental evidence of a similar release for radium/barium sulphate sludges is lacking, the same trends would be expected as most radium probably occurs as a co-precipitate in the sludge and the concentration of radium in solution would depend upon the solubility product of the precipitate. It should be noted that the concentration in the solution phase would be relatively independent of the flux. Factors influencing the solution flux will be considered in Section 5.2, which deals with mobilization.

The effect of particle size on the soluble concentration of radium in tailings effluent is difficult to predict. Smaller particle sizes with larger surface areas would increase rates of dissolution. Although grain size and surface area can affect the geochemical reactions directly, possibly the greatest effect would be on the water flux. As the grain size decreases, the hydraulic conductivity decreases, resulting in lower flux through the tailings. However, since the equilibrium times in the previous batch experiments of 0.5 to 1.0 hour are considerably less than the residence time of water in the tailings, radium in solution would be in equilibrium with the solid phase and relatively independent of the rate of dissolution.

The large surface area associated with fine-grained materials also would result in higher exchange capacities in these materials. Ion exchange theory indicates that the concentration in the solution phase increases as the ion exchange capacity of the solid phase increases. Thus, if exchange is the primary mechanism of radium retention, higher solution concentrations could be expected with fine grained materials.

A major factor in the solubilization of radium in tailings is the possible acid conditions generated as a result of pyrite oxidation. Physical factors affecting oxygen migration within the tailings will have an indirect yet pronounced effect on radium release to the solution phase. The principal mechanism for oxygen migration into the tailings is probably diffusion and advection in the gas phase. Advection in the solution phase would appear to be of lesser significance. Low rates of oxygen migration would be associated with fine textured materials, and materials at a high water content.[22]

5.2   Factors Affecting Mobilization of Radionuclides

Although, the quantity of radium present as radium/barium sulphate sludge from a particular mining operation has been demonstrated to be small in comparison to the total quantity of radium in the tailings generated by the same operation, the concentration of radium in the sludge material could represent an environmental hazard.

Mechanisms of transport include both wind and water. Water transport would occur as a result of overland flow during runoff while wind erosion would occur as a result of wind action on the surface desiccating and detaching particles. The importance of these processes depends upon the physical setting of the tailings and the method of applying the sludge.

Overland flow and subsequent erosion and transport of sludge material would be determined by the water balance of the tailings. The potential for erosion and runoff would be reduced if surface runoff from lands adjacent to the tailings area was diverted around the tailings and the surface of the tailings was permeable or vegetated. Tailings situated in low precipitation areas or where individual precipitation events tend to be of low intensity have a reduced potential for surface runoff. Wind velocity and the orientation of the tailings surface with respect to the prevailing winds affect the wind mobilization of sludge materials on the tailings surface.

Surface transport of sludges can be readily overcome by placing the sludge at depths where they would be isolated from the surface environment. Furthermore, since the radium content of the sludge will remain relatively high, the sludge should be placed in areas where erosion will be minimized.

Migration of contaminants in solution in a porous medium will result from advection, dispersion and chemical reactions of the contaminant. Advection is movement of the solute as a result of the bulk movement of the solution phase. Neglecting dispersion and chemical reactions, the velocity of the solute will be equal to that of the solution phase. Advective transport is influenced by direction of flow, the solution flux (or velocity) and the concentration of the solute in solution.

Within tailings, precise flow directions are very difficult to predict. In a heterogeneous medium the greatest water flux occurs in zones of highest hydraulic conductivity producing a complex three dimensional pattern of converging and diverging flow lines. Differential settling rates of the fine and coarse constituents of tailings, and the periodic movement of the effluent pipe give rise to an extremely complex stratigraphy. At a constant saturated volumetric moisture content of 0.4, the hydraulic conductivity between the coarse and fine constituents of tailings has been shown to vary by more than four orders of magnitude.[22] Water would tend to be diverted around lenses or deposits of fines, reducing the rates of dissolution and mobilization of radium in these deposits.

Tailings areas generally are constructed above the natural water table, therefore, the direction of water flux from process water or precipitation entering the tailings would be vertically downward.

The flux of water through the tailings depends upon the quantity of water and the hydraulic properties of the tailings. During operation of the tailings area, natural precipitation would be supplemented by the process water. Hydraulic conductivities are estimated to range from approximately 10^{-2} cm/sec for the coarse fraction of tailings to about 10^{-6} cm/sec or less for the fines. Under a unit hydraulic gradient, infiltration fluxes range between 300 and 0.3 m/yr. As precipitation in current uranium mining areas of Canada does not exceed 0.75 m/yr with normal evaporation losses, the flux of waters into the tailings would be controlled by water availability rather than the hydraulic properties of the tailings.

During closure and abandonment of the site, infiltration of water and thus the solution flux through the tailings could be further reduced by vegetation and application of cover material. Considering the relatively small volumes of sludge, no significant effect on solution flux through the tailings would be expected. The extent to which the solution flux would affect contaminant transport from the sludge would depend upon the method of sludge placement. If placed in fine textured zones, advective transport would be substantially reduced.

Solute dispersion occurs in response to concentration gradients and velocity variation, and results in the occurrence of a mixed zone at the front of a contaminant plume. Although dispersion in the heterogeneous environment of a tailings area would be large compared to that expected for a homogeneous medium, it can probably be regarded as a second-order effect on radium migration in comparison to advection and geochemical processes. The principal role of dispersion probably is in the diffusion of contaminants from fine-textured lenses into the main advective stream in the coarser zones.

Geochemical processes are expected to be the major factor controlling the migration of radium and other radionuclides out of the tailings. The concentration of radium or other leachates in solution leaving the base of the tailings would change with the geochemical conditions. Ion exchange and precipitation or co-precipitation are the principal geochemical reactions affecting radium migration. Where precipitation is the principal geochemical process, and the precipitated phase is present, the maximum concentration in solution will be that predicted by the solubility product for the reaction.

The physical flow characteristics may have a substantial indirect influence on contaminant mobilization. The migration of oxygen is influenced by the thickness and porosity of cover materials or the unsaturated flow properties of the tailings. The presence of oxygen will accelerate pyrite oxidation which in turn increases contaminant mobilization through production of an acidic environment. Considering the small volume of sludges added, any changes in physical characteristics would be minimal. Any influence on the chemical characteristics of leachate leaving the tailings would be confined to the influence of the sludge on the geochemical processes.

The transport of contaminants in hydrogeologic environments outside the tailings area would proceed subject to the same processes discussed above, with the velocity of the contaminants being controlled principally by geochemical retardation. Radium migration rates in a wide range of natural geological materials have been reported as 6×10^{-3} times the average linear pore water velocity.[23] In studies of radium migration in a sandy aquifer adjacent to the Nordic tailings area at Elliott Lake,[24] a sulphate plume was found to extend to a distance of about 400 m from the tailings while the radium plume extended a distance of only 15 m. Apparently the radium was migrating at a velocity of about 3×10^{-2} times that of the water. The mechanisms of radium retardation were not identified although it was shown that the migration rates were highest in regions where the pH was less than 5.

The mobilization of radium depends primarily on the geochemical processes operating in the tailings area. These processes would not be significantly affected by the addition of small quantities of radium/barium sulphate sludge. Therefore, there is no reason to expect that this addition will substantially affect the concentration of contaminants in groundwaters adjacent to the tailings or the rate of migration of contaminants away from the tailings.

5.3   Predicted Radionuclide Solubilization

In order to assess the environmental impact of uranium tailings piles one must examine tailings geochemistry, biochemistry, the process materials they contain and the role of surface and groundwater as reaction media.   The important reactions are those which operate under natural geochemical cycles, either as primary processes which create uranium ore deposits or as secondary dispersion and concentration processes which alter parent deposits.

The solubility and transport of radionuclides into the environment is controlled by physical as well as chemical factors.   In the aquatic environment, fluctuations in factors such as pH, Eh, dissolved gas content (CO_2, O_2, H_2S), temperature, ionic strength, particulate and biota loads are interrelated with the basic chemical nature of the element itself. Solubilized radionuclides may form colloids, be incorporated into bottom sediments, be taken up by organisms, or be adsorbed on organic and inorganic suspended material (Figure 5.4).[25]   Changes in water chemistry may create disequilibrium conditions that significantly alter the radionuclide content of any particular phase.   Chemical mobilities determine the solubility and transport of radionuclides in the tailings leachate.

A major factor influencing changes in the geochemical environment is the flux of oxygen into the tailings.   As oxygen moves more slowly through water, the water table depth and its seasonal fluctuations are of importance.   Slowly dropping water levels with minimal water table fluctuation will cause changes from reducing to oxidizing conditions over a narrow range of depth.   Wide fluctuations will result in a wider zone of change.

FIGURE 5.4

TRANSPORT PATHWAYS IN AQUATIC SYSTEMS

Eisenbud (1973)
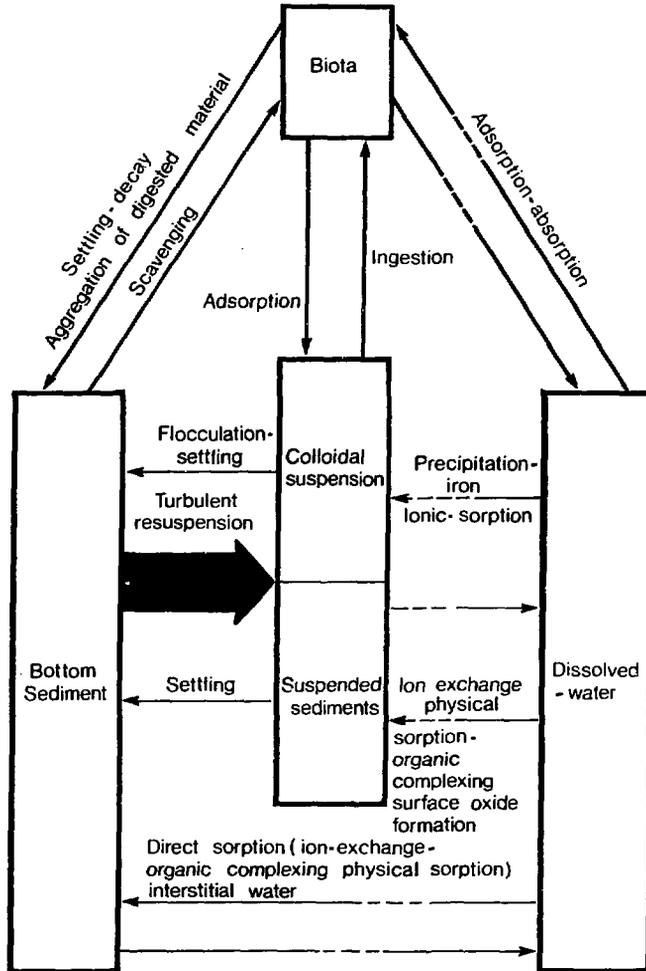
Because of gravitational separation of fine and coarse fractions and the relocation of the point of tailings discharge, tailings piles are not homogeneous. The stratigraphy of the system is complex, with the various stratigraphic units being characterized by differing permeabilities, porosities and mineralogies.

The long term geochemical environment for acid leach and alkaline leach tailings will be different because they possess considerably different chemical characteristics.

5.3.1 Acid Leach Tailings With Pyrite

The fate of uranium daughter radionuclides during milling has not been documented clearly. It is likely that they are solubilized along with rare earths and heavy metals. Moreover, solubilized radium in the mill circuit likely reacts immediately with sulphate ions and then it precipitates as colloidal complexes and/or adsorbs onto the finely powdered tailings gangue. Most of the radium (>80%) is associated with the -200 mesh fraction (slimes) and particularly with pyrite fines.[26-29] In the mill circuit the pyrite surface is oxidized due to the high temperature and oxygen fugacity producing a monolayer of iron sulphate on the iron sulphide fines where radium ions could be adsorbed readily.

The mineral jarosite $[KFe_3(SO_4)_2 (OH)_6]$ is precipitated in the mill acid leach circuit, and gypsum $(CaSO_4.2H_2O)$ is formed during neutralization of mill effluent with lime prior to discharge to the tailings. The quantity of jarosite and gypsum in current tailings areas is estimated to be 0.3 and 3.7% by weight respectively based on the available quantities of iron and calcium. Radium-226 levels of 80,000 pCi/g and 7,000 pCi/g for jarosite in old tailings and gypsum in current tailings have been reported.[28] Data are not yet available to indicate whether the radium is cation substituted within the jarosite and gypsum lattices, or is ionic radium and/or colloidal radium sulphate co-precipitated or adsorbed onto these sulphate compounds. This will have an important influence on the relative mobility of radium-226 in the tailings pile.

About 60% of the thorium was found to be dissolved from the ore within the mill.[30]   It likely exists as $Th(SO_4)_2$.   When the acid leach solution is neutralized by lime, thorium would precipitate as insoluble $Th(OH)_4$ along with other heavy metals and rare earths.   The solubility of thorium is pH dependent; at pH 4 it is >100 ppm while at pH 7 it drops to   <0.1 ppm.[11]   Thorium present as the highly refractive mineral monazite is probably not attacked significantly in the mill.

Uranium exists in solution in the hexavalent state as the uranyl species $(UO_2)^{2+}$.   The uranyl ion is highly soluble in oxidizing solutions and is transported as carbonate, sulphate, phosphate, hydroxide, chloride and fluoride complexes.[32-35]   These soluble uranyl complexes may precipitate under strong reducing conditions caused by bacteria or organic debris. Although the U (IV) ion is of low solubility, it is readily oxidized to the highly mobile U (VI).   It is suspected that except under strongly reducing conditions, uranyl ions not recovered in the mill would be flushed out of the tailings system with the initial release of interstitial water.   Uranium present in tailings as resistate minerals will leach at an undetermined but low rate under both acidic and basic conditions.

It is likely that inorganic chemical precipitates within the tailings pile contain the majority of readily leachable toxic elements.   Of major concern is the stability of these precipitates, especially the sulphates and hydroxides.   Table 5.1 shows solubility products for the major species of interest.   Where suphides are present in the ore, the acid generating potential of the tailings threatens this stability.

TABLE 5.1   SOLUBILITY PRODUCTS FOR SPECIES OF INTEREST[37, 38, 39]

Element	- log Ksp
$FeSO_4$	2.0
$UO_2SO_4.3H_2O$	2.0
$Th(SO_4)_2$	4.0
$CaSO_4.2H_2O$	5.0
$PbSO_4$	7.7
$BaSO_4$	10
$RaSO_4$	12 - 14
$KFe_3(SO_4)_2 (OH)_6$	(Unknown)
$CaCO_3$	8.3
$BaCO_3$	8.8
$RaCO_3$	9.0
$FeCO_3$	10.5
$PbCO_3$	13.1
$Th(CO_3)_2$	(Unknown)
$Ra(OH)_2$	< 3.0
$Ba(OH)_2$	3.0
$Ca(OH)_2$	5.4
$Mn(OH)_2$	12.8
$Fe(OH)_2$	14.7
$Fe(OH)_3$	38.7
$Th(OH)_4$	39 - 44
$U(OH)_4$	45

The possible *future* behaviour of a hypothetical tailings pile is shown in Figure 5.5 based on the following assumptions:

1. The area has a positive net water balance and water tables are dropping. (Presently, tailings dumps are constructed above ground and therefore well above the district's natural water table. Upon abandonment the majority of water entering the tailings site is eliminated, causing the water table to drop gradually).

2. The tailings contain a significant quantity of sulphides and have been limed prior to discharge.

3. Surface tailings have been over-limed and fertilized so that a stable floral community exits.

4. Sorption and organo-metallic reactions are ignored as they will principally reflect flux and not the overall evolution of the system.

Figure 5.5 shows that as water tables fall, the presence of free oxygen (O_2) will expand the region of oxidizing conditions (positive Eh) downward. Oxidizing conditions enhance the acid generating capacity of the sulphides and create a strongly acidic leachate. The acidity produced will quickly neutralize the highly basic tailings (pH> 10) within the oxidized zone and the pH of the percolating water will drop rapidly to 1 or 2.

FIGURE 5.5

PREDICTED GEOCHEMICAL CONDITIONS IN ABANDONED ACID LEACH TAILINGS
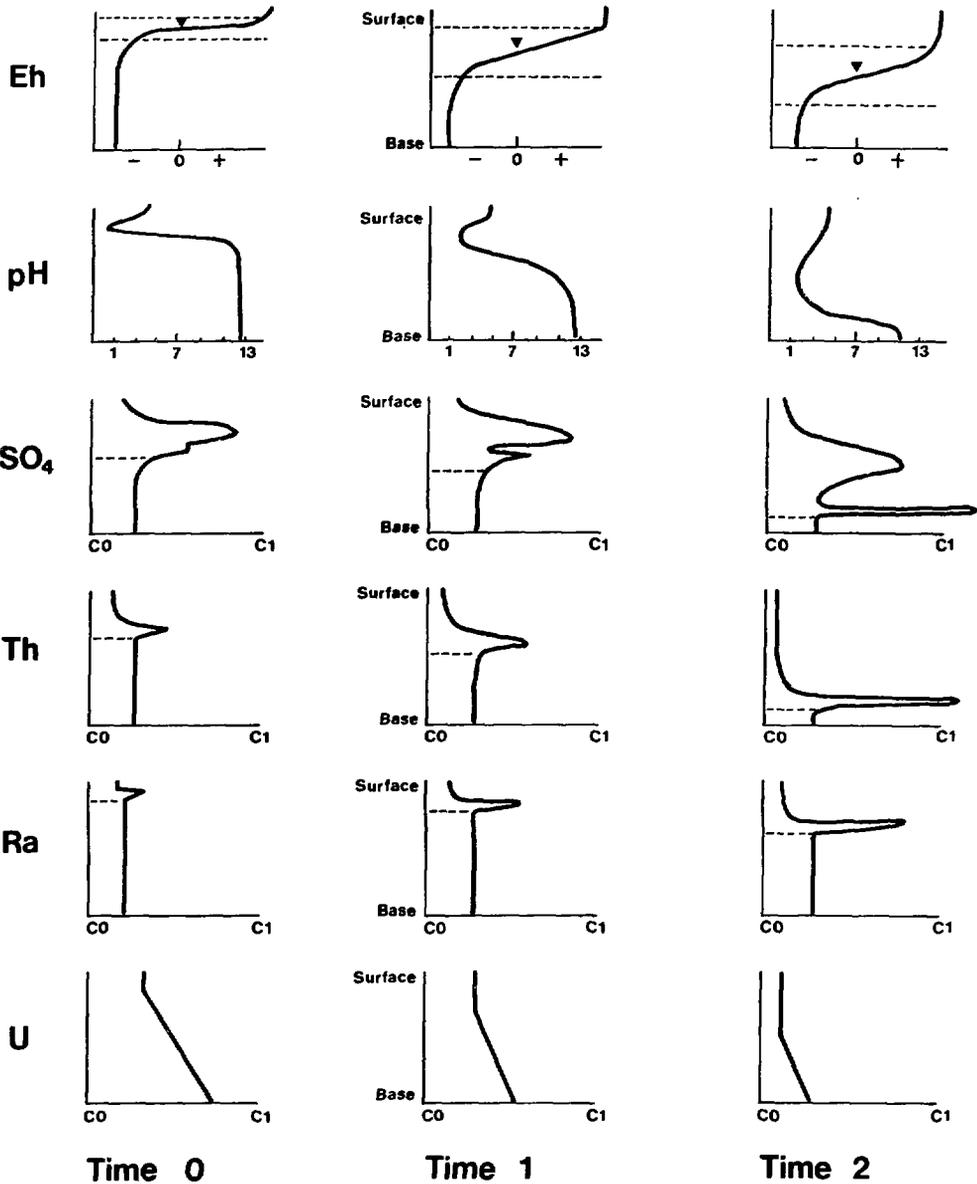
After Lush et al (1978)

The reactions responsible for this change can be expressed as:[37]

1) $FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

2) $Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2\ H_2O$

3) $Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+$

4) $FeS_2(s) + 14\ Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
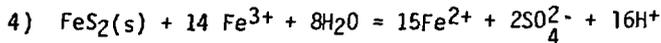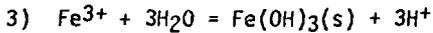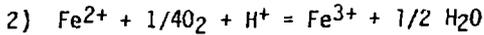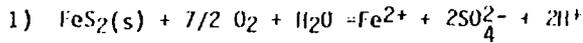
One mole of pyrite will lead to the release of four equivalents of acidity: 2 equivalents from $S_2(-II)$ oxidation and 2 from $Fe(II)$ oxidation. Any radium-226 adsorbed on or associated with the pyrite fines will be solubilized during oxidation.

The oxidizing bacteria <u>Metallogenium sp.</u> and <u>Thiobacillus thiooxidans</u> catalyze steps 1 and 4 in the above reaction sequence. In addition, the anaerobic bacteria <u>Desulfovibrio</u> is capable of metabolizing sulphate precipitates, thus releasing H_2S and metal cations into solution.[40]

The potential for leaching radionuclides from tailings is enhanced greatly if jarosite, gypsum and radium/barium sulphate sludge is metabolized in this manner. The growth of one or more species of bacteria in the tailings also creates a possible transport for radionuclides. Living bacteria and bacteria cell wall debris have been shown to concentrate elements from solution including heavy metals and radionuclides.[41, 42] Colloidal bacteria cell debris flushed from the tailings may be a major contributor of radioactive releases to the environment.

Sulphide oxidation probably occurs only in the top two feet of tailings fines and up to nine feet in coarse tailings.[28, 43] A high water table in these piles limits the downward diffusion of oxygen and reduces changes in redox potential. If and when the water level drops, oxidation will occur at greater depths, resulting in increased concentrations of sulphate, heavy metals and radionuclides. These reaction products will be carried downward, neutralizing lime and precipitating as gypsum, jarosite and other heavy metal sulphates and hydroxides. The jarosite precipitate, like pyrite may pose a duel threat to long term tailings stability. Upon dissolution, high radium-226 and ferric iron levels are released.

The following reactions indicate this sequence
(i) for lime addition:

5) $KFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + 4H_2O = 3Fe(OH)_3 + 2CaSO_4.2H_2O + KOH$
    jarosite)   (lime)   (gypsum)

(ii) limestone addition:
6) $KFe_3(SO_4)_2(OH)_6 + 2CaCO_3 + 6H_2O = 3Fe(OH)_3 + 2CaSO_4.2H_2O + KOH + 2CO_2$

note $2CO_2 + 4OH^- = 2CO_3^{2-} + 2H_2O$

Ferric iron is then available to catalyze the pyrite oxidation series shown previously (reactions 1 - 4).

Dissolution of precipitates such as jarosite and gypsum may also release toxic metals such as Pb, Ni, Zn, Cu and rare earths.

Figure 5.5 suggests that two distinct zones of sulphate concentrations will be generated: a free sulphate upper pulse and a precipitated metal sulphate lower pulse. The sulphate and hydrogen ions generated in the oxidizing zone will dissolve $Th(OH)_4$ precipitates. The soluble $Th(SO_4)_2$ species will migrate downwards, following the leading edge of the oxidizing boundary.

As the sulphate content of the tailings becomes depleted, radium will be mobilized and follow the trailing edge of the sulphate and thorium plug. It is suspected that much of the current radium leaching from acid leach uranium tailings is not ionic radium but is complexed/adsorbed on colloidal particulates.

The behaviour of the various species in Figure 5.5 may be summarized as follows:

Eh: Oxidizing conditions exist at and above the water table; reducing conditions (negative potential) exist below the water table. The dashed lines indicate possible fluctuations in the water table.

pH: The surface is buffered by lime/limestone, vegetation and fertilizers. Strongly acidic conditions exist at and above the water table due to the presence of oxygen and sulphides. Strongly alkaline conditions exist below the water table due to anaerobic conditions and the initially high pH of the tailings slurry.

SO_4: Sulphate is mobile under acidic conditions in the strongly oxidizing zone, producing the upper large "soluble" sulphate band. At the acidic zone front, soluble sulphate would precipitate as MSO_4 complexes, producing the narrow lower "total" sulphate band (M = Ca, Fe, etc).

Th: Thorium is solubilized in the zone of "soluble" sulphate and precipitated at the leading edge of the "total" sulphate zone.

Ra: Radium is solubilized in the oxidized zone of low pH and low sulphate and is precipitated at the trailing edge of the "soluble" sulphate zone where large quantities of sulphate exist.

U: The behaviour of uranium is not known for certain. Most uranium is probably flushed from the tailings during initial dewatering. Some may be precipitated and/or adsorbed on tailings especially in the strongly reducing zone. The uranyl ion (UO_2^{2+}) species are very mobile and readily leached from the strongly acidic oxidizing zone.

Some of the field data and bench scale leaching studies support the hypothesis illustrated in Figure 5.5.[16, 44] Lysimeter studies have indicated that thorium levels remain relatively constant at high pH. As the pH declined this level rose passing through a maximum.

5.3.2 Acid Leach Tailings Without Pyrite

Sulphide minerals (primarily pyrite), oxygen fugacity and bacteria are chiefly responsible for the relatively quick conversion of alkaline (limed) tailings to acidic conditions. The solubility of most chemical species increases in acidic media, thus acid conditions greatly accelerate leach rates of stable and radioactive elements from tailings. The period for long term tailings evolution previously discussed (Figure 5.5) will be significantly altered if sulphide minerals are absent in the original ore body or are preconcentrated in the mill circuit. Pyrite fines have been shown to contain significant amounts of radium adsorbed during the milling operation. Preconcentration of pyrite and separate disposal would minimize the threats of acid generation and the release of adsorbed radium. If the tailings contain even small quantities of pyrite, eventual oxidation will generate acidity which will reduce alkaline conditions along the flow channels through the tailings. Accelerated leaching of radionuclides will occur along these channels. Pyrite content affects the flux from tailings but not the eventual final conditions in the system. Lower bleed rates extending over a longer time will give similiar equilibrium final conditions in tailings with a reduced pyrite content.

In the absence of pyrite, acidification of basic tailings can occur by other chemical processes. Acidic groundwater or rainfall could percolate through the tailings depleting the alkalinity.

5.3.3 Effect of Sludge Addition to Acid Leach Tailings

The addition of radium/barium sulphate sludge to acid leach tailings piles
may affect the release of radium from these piles. Since the amount of
sludge is very small in relation to the amount of tailings, its effect will
only be significant if the radium in the sludge is either more mobile than
the radium in the tailings or if the sludge addition alters the conditions
predicted in Figure 5.5 sufficiently to affect the mobility of the radium
already in the tailings.

A preliminary analysis of a $(Ra,Ba)SO_4$ sludge indicates it contains nearly
40% barium, high transition metal concentrations, uranium, rare earths and
radium (unpublished data). Large dissolved barium concentrations have been
shown to enhance the leaching of radium-226 from tailings and other
solids.[17, 45, 46] This leaching enhancement is thought to be an
exchange reaction, i.e.

8) Ba^{2+} + Ra^{2+} = Ba^{2+} + Ra^{2+}
     sol'n   solid   solid   sol'n
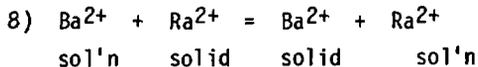
The dissolution of the sludge could increase sulphate and barium levels.
The presence of excess sulphate will increase the solubilization of thorium
as $Th(SO_4)_2$ and enhance the leach rate. Possibly, the barium exchange
mechanism and the dissolution of radium from sludge may increase radium
leach rates. The accompanying high sulphate levels however would tend to
inhibit radium solubilization.

Lysimeter studies performed at the Wastewater Technology Centre in
Burlington have indicated that leachate radium and thorium levels are
increased from tailings with $(Ra,Ba)SO_4$ sludge placed on top.[16] This
indicates that the upper layer of sludge contains a large amount of thorium
and/or the high SO_4^{2-} and Ba^{2+} content of the sludge catalyzes the
release of $Th(SO_4)_2$ and radium-226 from the tailings.

These lysimeter studies indicate the potential for increased levels of radium, thorium and other metals leaving the tailings area, although the quantity and location of the sludge employed does not represent a realistic model of sludge placement in tailings.

5.3.4 Alkaline Leach Tailings

The alkaline leach milling circuit produces tailings of a different composition than the acid leach cycle. In Canadian practice, a finer grind is used for the alkaline leach. A grind of 55% minus 325 mesh has been reported as typical for an alkaline leach mill whereas an acid leach circuit used a grind of 50% minus 200 mesh.[10, 14] Alkaline leach tailings will have a higher surface area per unit mass and a lower hydraulic conductivity. Other data indicate a lower uranium recovery for the alkaline leach process. Decant waters from alkaline mill tailings contain uranium concentrations up to 6 ppm, considerably higher than acid leach mill tailings. (See Table 5.2)

The tailings solids could contain significant quantities of precipitated and/or adsorbed colloidal inorganic metal hydroxides and carbonates. If the ore contains pyrite, a flotation circuit can be incorporated into an alkaline leach mill to remove the pyrite. The pyrite is discharged to the tailings, either homogeneously or in lenses, depending on whether discharge from the acid circuit is continuous or intermittent. This acidic effluent contributes sulphate to the otherwise carbonate complexed tailings area.

The quantity of radium actually dissolved from the ore in a carbonate leach mill has not been quantified but is probably similar to uranium dissolution and recovery. Since radium has low solubility in carbonate solutions, this liberated radium probably forms carbonate precipitates or is adsorbed immediately on other particles. Thus the majority of radium would be concentrated in the tailings fraction with the largest surface area, viz the slimes. This was substantiated in a recent study.[14] In this case the radium would be potentially mobile because of the large exposed surface area and sensitivity to changing chemical parameters such as pH and Eh.

TABLE 5.2   ALKALINE LEACH MILL DATA[14, 27]

| Constituent | Mine Water | Tailings | |
		Decant	Solids
pH	7.6	10	-
U	7	1 - 6	200
Th	0.03	0.05	<30++
Ra	8 pCi/L	70 pCi/L	1000 pCi/g
SO_4	400	250	-
Cl	2700	25	-

+   all concentration in ppm except pH(-log H) and radium-226 (as shown)

++   based on an ore with 0.003% ThO_2 content.

Since the solubility of thorium is quite low in alkaline carbonate leach solutions, most thorium in the ore would be discharged to the tailings unaltered. Any thorium dissolved in the mill would immediately precipitate as a hydroxide and would be discharged with the slime fraction of the tailings.

Radium levels in tailings decant waters from alkaline leached ores (70 pCi/L) are much lower than in corresponding acid leach tailings decant (800 pCi/L). Conglomerate and vein-type uranium ore bodies contain approximately similar radium-226 levels (1000 pCi/g). Tailings decant levels however, differ by an order of magnitude, indicating large chemical differences between acid and alkaline leach mill circuits. The much lower radium-226 levels in alkaline decants may indicate the poor leaching ability of strongly alkaline solutions and/or lower solubility of the $RaCO_3$ species.

It has been stated that carbonate leaching of uranium ore dissolves significantly more radium-226 than does acid leaching.[29] In alkaline mill circuits the levels of sulphide minerals and sulphate complexes (i.e. jarosite, gypsum) are very low or absent. This absence of adsorbing/precipitating sites may account for the apparent larger dissolved radium levels in the alkaline leach circuits. In one instance when the alkaline leach liquor solution was prelimed in the mill, the radium-226 values found in the resultant yellowcake decreased from greater than 1000 pCi/g to 50-80 pCi/g.[29]

As with the acid leach case, the long term mobility of radium-226 in the tailings will depend largely on whether oxidizing or reducing conditions are maintained. If the tailings were deposited in a deep lake, only limited oxidation would occur unless water levels were to be lowered. Accordingly, oxidizing and reducing conditions are considered separately.

5.3.5 Alkaline Leach Tailings Under Oxidizing Conditions

If water levels in the tailings eventually drop, oxidizing conditions will probably be produced as with acid leach tailings, if it is assumed some pyrite is present. Besides causing acidic conditions, the pyrite will contribute sulphate ions to the tailings. Alkaline leaching liquors contain large quantities of Na_2CO_3. If the original ore body contained 1% pyrite then the total potential acid generation under oxidizing conditions would be able to neutralize tailings leached using a liquor containing approximately 100 lbs Na_2CO_3 per tonne of ore.

Ores leached by the alkaline process contain substantially less than one percent pyrite. Lenses of above average grade pyrite may be formed by discharge from a special pyrite removal step. This may create localized highly acidic solutions allowing radionuclide mobilization downwards along flow channels. Total acidification of the tailings pile by oxidation of this quantity of pyrite alone is unrealistic.

Resistate thorium in the solid tailings would not leach unless acidic solutions were generated. Radium could be flushed as a carbonate species while uranium complexes will be quite mobile, except in the resistates. Percolation of natural waters through the alkaline reduced wastes would eventually decrease the pH and increase the Eh to produce oxidizing conditions which would allow metal hydroxide and carbonate complexes to be solubilized. At that time many of the variables discussed for acid leach tailings without pyrite may be involved in radionuclide mobilities.

Bacteria in the waste could play a significant role in element mobilities. The mill effluent contains appreciable sulphate ions (>200 ppm) and organic carbon, both essential to support sulphate-reducing anaerobic bacteria. Some radionuclides presently observed leaching from alkaline mill tailings could be bacteria catalyzed. These alkaline leach tailings lack a significant mill liquor precipitate, such as jarosite, or appreciable pyrite which provides a greater surface area for radium adsorption.

5.3.6 Alkaline Leach Tailings Under Reducing Conditions

Tailings covered by water may be in a reduced state as they are effectively isolated from the oxidizing atmosphere. Little chemical mobility would occur unless seepage rates through the tailings into ground waters became significant.

5.3.7 Effect of Sludge Addition to Alkaline Leach Tailings

Alkaline decant from carbonate leach tailings may contain approximately equal amounts of sulphate and carbonate ions. The addition of $BaCl_2$ would generate a radium/barium sludge of a mixed sulphate-carbonate nature. The amount of radium re-introduced to the tailings would be much smaller than in the acid leach tailings. Effects of incorporation of this sludge into tailings covered by water is not known. Effects in an oxidizing, above water environment are also unknown although the hypothesis discussed for acid leach tailings may generally apply.

5.4   Verification of Radionuclide Mobilization

A laboratory experimental program was carried out at the Wastewater Technology Centre at CCIW Burlington, Ontario, to examine radionuclide solubilization from sludge and tailings under the conditions predicted in Section 5.3.   This study was designed to support the prediction of radionuclide solubilization under changing chemical conditions in the tailings. Fresh tailings from the Elliot Lake area (acid leach process) and (Ra, Ba) SO_4 sludge from the WTC pilot scale filters were used for the experimental work. The details of the laboratory study are presented in Appendix I.

Tailings alone and two mixtures of tailings: sludge ratios approximately 50:1 and 500:1 by weight were slurried in deionized distilled water in a water: tailings ratio of 20:1 by weight. The tailings: sludge ratios were chosen to represent imperfect dispersed placement of sludge in tailings. The ratios 500:1 and 50:1 by weight represent approximately one and two orders of magnitude increases respectively in the actual ratio of sludge to tailings. The liquid-solid ratio (20:1) is within the standard range for slurry leaching test procedures. The quantities of sludge and tailings tested provide a worst case estimate of radionuclide solubilization (maximum leaching). The predicted changes in the geochemical environment of the tailings area were simulated by adjusting the pH and Eh conditions of slurry. Table 5.3 gives the physical, chemical and radiochemical analyses of filtered slurry samples. These results are only relative but do indicate the effect of sludge addition on leaching. The analytical results are presented for each tailings: sludge ratio for the same sequence of environmental conditions.

While the solubilization of uranium increased with decreasing pH and increasing Eh, the addition of sludge did not affect the quantity of uranium solubilized. Some of the inorganic precipitates (hydroxides, sulphates, carbonates) may release uranium, possibly as UO_2SO_4, when dissolved under acidic conditions. Typical acid leach tailings decant waters contain 50 to 150 ppb U, similar to the results for the second set of conditions in Table 5.3.

TABLE 5.3   IEC EXPERIMENTAL RESULTS

CONDITION	U ppb	Th-230 pCi/L	Ra-226 pCi/L	SO_4 mg/L	pH	Eh mv	Conductivity μmhos
Tailings Only							
1 Alkaline, high SO_4	7.56	74	403	950	9.1	+ 50	4545
2 Neutral, high SO_4	35.0	89	220	1480	6.8	115	5600
3 Acid, high SO_4	1500	7086	57	990	2.1	545	9100
4 Acid, low SO_4	26.0	79	1030	22	2.9	405	362
Tailings + 0.15 g Sludge							
1 Alkaline, high SO_4	0.91	56	208	1110	9.3	+ 10	4100
2 Neutral, high SO_4	28	46	84	1110	4.7	210	4600
3 Acid, high SO_4	1480	8599	66	1550	2.1	545	11520
4 Acid, low SC_4	16.6	59	505	11	3.2	390	164
Tailings + 1.5 g Sludge							
1 Alkaline, high SO_4	1.54	92	59	970	9.6	- 22	4100
2 Neutral, high SO_4	31.0	63	24	1120	4.3	+219	5700
3 Acid, high SO_4	1350	4831	49	920	2.1	540	10480
4 Acid, low SO_4	23.0	146	88	190	3.1	390	188

No changes in thorium-230 concentrations could be attributed to sludge addition, but a strong dependence on pH was observed. At a pH < 5, with high SO_4^{2-} levels, the precipitated $Th(OH)_4$ is solubilized to $Th(SO_4)_2$ as found under the third set of conditions. With low sulphate concentration and minimal $Th(OH_4)$ remaining in the tailings, the thorium-230 levels in the final decant were greatly reduced. These results support the hypothesis that thorium will become mobile at low pH and high sulphate concentrations as presented in Section 5.3.

Under all but one set of conditions, the quantity of radium-226 solubilized decreased with increasing amounts of sludge in the slurry. Under the third set of chemical conditions, the radium-226 levels were identical. The radium-226 levels under the first and last set of conditions for the tailings alone were approximately the same as in a typical acid leach tailings decant.

The sulphate concentrations were relatively independent of sludge addition. The decreasing pH and peroxide treatment removed easily soluble sulphate complexes ($CaSO_4$, $FeSO_4$) under the third set of conditions resulting in greatly reduced SO_4^{2-} levels in the last set of samples. The SO_4^{2-} levels under the first three sets of conditions were very similiar to measured values in acid leach tailings decant waters.

The conductivity was proportional to the dissolved species and pH in each sample and was relatively constant for each set of conditions. As most of the conductivity was due to sulphate ions, and the conductivity was not affected by sludge addition, there appears to be no preferential solubilization of the sludge.

The solubility product (Ksp) of $RaSO_4$ is about 10^{-14}. Ksp calculations using the measured radium-226 and SO_4^{2-} concentrations were quite close to this value. Values from the last two sets of conditions had lower calculated Ksp's since equilibrium conditions in the slurries were not attained. Although sludge addition did not affect SO_4^{2-} concentrations, the radium-226 levels for sludge-tailings mixtures were much lower than expected from $RaSO_4$ solubility calculations.

The change in chemical conditions from alkaline to acid (Condition 1 to Condition 3) resulted in increased levels of uranium and thorium in the slurry decant. In Section 5.3.1, it was predicted that both uranium and thorium would show greatly increased solubilization at low pH and high Eh. These slurry tests indicated that the predicted behavior is correct. High sulphate concentrations were present for all the first three test conditions as shown in Figure 5.5. These high sulphate levels increased the solubility of thorium as $Th(SO_4)_2$.

From Condition 3 to Condition 4, the slurry remained acidic but the sulphate concentration decreased by 1 to 2 orders of magnitude. This represents the predicted depletion of soluble sulphate species in the tailings (and sludge). With low sulphate concentrations present, the level of radium-226 was greater than under any of the previous conditions (1 to 3). In Section 5.1.1, literature sources indicated increased radium solubilization from tailings under acidic, low sulphate level conditions. Figure 5.5 and the accompanying text predicted increased radium solubilization at low pH after removal of the soluble sulphate from the tailings.

It is significant that the radium levels decreased with increased quantities of sludge in the slurry. It would appear that radium in the sludge was more stable than radium in the tailings and the sludge adsorbed radium released from the tailings.

The solubility product for $BaSO_4$ is approximately 10^{-10} therefore the barium concentration in a solution containing 1000 ppm SO_4^{2-} is 1.4 ppb. Under the fourth set of conditions, a sulphate concentration of 10 - 20 ppm would be in equilibrium with 0.13 to 0.07 ppm Ba^{2+}. This barium concentration is at least two orders of magnitude lower than the levels which caused significant Ba-Ra surface exchange as postulated in Section 5.1.1.

The thorium-230, radium-226 and SO_4^{2-} results are in close agreement with the predicted changes in Section 5.3. It is difficult to establish the significance of the uranium results, but they do not appear to conflict with the predictions.

Although these results may appear to conflict with the WTC lysimeter study results, the tailings: sludge ratio in the lysimeter was very large (8:1).[16] Further the method of water-solids contact was different. In the lysimeter tests, water was percolated through sludge placed on top of the tailings, resulting in increased radium and thorium levels in the effluent. In the IEC slurry tests, the sludge had the opportunity to adsorb radium released from the tailings. Also, the reduction of soluble sulphate and the depletion of easily soluble thorium in the solid phase under the final environmental conditions resulted in decreased thorium activity in the filtrate.

Madawaska Mines Ltd. is presently testing radium-226 leaching from tailings and two sludge-tailings systems (6760:1, tailings: sludge by dry weight). One system was a complete mixture of sludge and tailings while the second consisted of a layer of sludge surrounded by tailings. Each system was flushed with water for approximately ten weeks prior to sampling. Preliminary results are presented in Table 5.4.[47] The radium-226 levels were similar for all three systems and are the same as the IEC results under the third set of chemical conditions in Table 5.3. There are insufficient data to determine any trends in leachate radium levels in the Madawaska studies.

The apparent lack of problems with sludge addition to the tailings assumes that the predicted geochemical environment and laboratory tests adequately reflect the long term conditions in the tailings piles. The predictions of radionuclide solubilization under the changing chemical conditions in the tailings have been supported by the limited experimental program undertaken. The results of this program support the predictions of radionuclide solubilization in acid leach tailings.

TABLE 5.4   MADAWASKA MINES LEACHING STUDY RESULTS

Radium-226 in pCi/L

Sample Date	Jan. 7-11	14-18	21-25	28-Feb.1	4-8
Tailings	38	45	25	70	64
*Tailings/Sludge Mixture	40	47	59	60	52
*Tailings with Sludge Layer	32	27	27	47	68

* 6760:1 = Tailings: Sludge dry weight basis: each system was flushed with water for 10 weeks prior to sampling.

Solubilization and mobilization in alkaline leach tailings could be much different since the chemical form and mobility of the radionuclides is probably different. Most of the radium is present as a carbonate precipitate or is adsorbed on other carbonate and hydroxide precipitates. Thorium solubility is low in the alkaline leach solution and is discharged to the tailings unaltered. The precipitate produced from $BaCl_2$ treatment is probably a mixed sulphate-carbonate sludge rather than a sulphate sludge as in the treatment of acid leach tailings decant waters. Experimental study would be necessary to confirm the predicted solubilization in the alkaline leach tailings piles.

6.0   CONCLUSIONS

1. The placement of radium/barium sludge in tailings areas should not adversely affect the long term stability of the radionuclides in the tailings or sludge.

    This conclusion is supported by:

    a) The quantity of radium in the radium/barium sludge is much smaller than the quantity in the tailings and the total quantity of sludge produced in several orders of magnitude less than the amount of tailings produced.

    b) Radium in the sludge is at least as stable as radium in the tailings.

    c) Sludge incorporated into tailings adsorbs radium released from the tailings.

    d) The sludge does not affect the solubilization of uranium or thorium.

2. The radium/barium sludge should be well dispersed in the tailings and at sufficient depth to prevent wind transport of the sludge.

    Analysis of leachate from existing tailings areas should be undertaken to verify the predictions and the laboratory results. Corings of the tailings would be used to establish the geochemical conditions. Leachate samples from the various geochemical zones should be analyzed for radium, uranium and thorium.

    Laboratory and/or field studies should be undertaken to confirm the predictions made for alkaline leach tailings.

ACKNOWLEDGEMENTS

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APPENDIX 1

Laboratory Testing Procedure

APPENDIX I: LABORATORY TESTING PROCEDURE

Quantities used per test: fresh tailings 75 g
                           distilled water 1.5 L
                           RaBa sludge: tailings ratios
                           0:1; 1:500; 1:50 by weight

Procedure

1. Place tailings and sludge-tailings mixtures in a 2 L beaker and add
    distilled water to 1.5 L total volume.

2. Measure pH and adjust to 10.0 (Condition 1). Slurry tailings and
    sludge-tailings mixtures for 2.5 hours and then settle for 30 minutes.
    Filter the decant through a 0.45 um membrane filter and analyze for pH,
    Eh, conductivity, SO_4, Ra, U, Th.

3. Add distilled water to 1.5 L and adjust pH to 5.0 with 6N H_2SO_4
    (Condition 2). Slurry for 16 hours, then settle, filter and analyze as
    above.

4. Add 155 ml H_2O_2 and distilled water to volume and adjust the pH to
    4.0 with 6N H_2SO_4 (Condition 3). Slurry for 16 hours and decant for
    analysis as above.

5. Bring the volume to 1.5 L with distilled water and allow to settle for
    30 minutes. Measure pH and, if less than 3.5, discard. Repeat until
    pH >3.5 is achieved (Condition 4) and then slurry for 1 hour. Allow 30
    minutes settling and then filter the decant for analysis as above.