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# THE BEHAVIOUR OF RADIUM IN SOIL AND IN URANIUM MINE-TAILINGS

# COMPORTEMENT DU RADIUM DANS LE SOL ET DANS LES RESIDUS DE MINES D'URANIUM

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Pinawa, Manitoba R0E 1L0
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## RÉSUMÉ

L'existence d'un certain nombre de déchets historiques a suscité le besoin de développer une stratégie d'évacuation des matériaux contaminés par le radium-226.

Ce rapport examine les propriétés radiologiques et chimiques pertinentes du radium, en particulier la solubilité de ses sels, sa capacité de produire un complexe, son comportement à l'adsorption et examine comment ces propriétés peuvent être comparées à celles des autres membres du groupe alcalino-terreux.

Le rapport traite des facteurs chimiques qui déterminent la mobilité du radium dans le sol ou l'eau souterraine. L'adsorption sur les argiles, les minéraux et la matière organique ainsi que la coprécipitation sont les processus principaux qui entravent la mobilité du radium. Le rapport examine les études de lixiviation dans le sol.

La plus grande source potentielle de radium dans l'environnement est la lixiviation des résidus de mines d'uranium. C'est pour cette raison qu'on examine la minéralogie des résidus de mines et les tentatives pour les lixivier. On compare les niveaux de radium des résidus lixiviés aux normes de niveaux de radium et on suggère des objectifs réalistes pour les méthodes de lixiviation.

On examine les techniques d'épuration du sol, d'immobilisation du radium et de traitement des eaux de rejet contenant du radium.

Finalement, on fait des recommandations pour une stratégie de lixiviation possible du sol contaminé par le radium et pour une recherche plus étendue pour mettre au point une stratégie d'évacuation.

L'Énergie Atomique du Canada, Limitée
Établissement de recherches nucléaires de Whiteshell
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## ABSTRACT

The existence of a number of historical wastes has prompted the need to develop a disposal strategy for material contaminated with radium-226.

This report reviews the pertinent radiological and chemical properties of radium, in particular the solubility of its salts, its ability to complex, its adsorption behaviour, and how these properties compare with those of the other members of the alkaline earth series.

Chemical factors that determine the mobility of radium in soil/groundwater environments are discussed. Adsorption on clays, minerals and organic matter, and coprecipitation are the main processes that inhibit radium mobility. Soil leaching studies are reviewed.

The largest potential source of radium in the environment is the leaching of uranium mine-tailings. Hence the mineralogy of mine-tailings and attempts to leach them are reviewed. Radium levels in leached residues are compared to the standards for radium levels, and realistic targets are suggested for leaching methods.

Techniques for scrubbing soil, immobilizing radium, and treating wastewater containing radium are reviewed.

Finally, recommendations are made for a possible leaching strategy for radium-contaminated soil, and for further research to develop an effective disposal strategy.

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# CONTENTS

# 1. INTRODUCTION

The question of dealing with low- and intermediate-level radioactive wastes has recently received increased attention in Canada [1,2]. These wastes arise from nuclear power stations, nuclear research establishments, nuclear fuel and radioisotope production facilities, uranium mining and milling operations, and from medical, research, and industrial organizations. A categorization of the sources, nature, volume, and estimated total radioactivity, of these wastes has been produced by James F. MacLaren Limited [3]. Disposal options exist, or are being developed, for most of the radioactive wastes presently being produced. However, a number of historical wastes exist, due to industrial processes some of which are now defunct, for which a disposal strategy does not exist. These wastes consist mainly of uranium and radium processing wastes and associated contaminated soils. For instance, the soil at several sites in Port Hope, Ontario, and at a site in Scarborough, Ontario [4], is contaminated with radium-226. In some places at Port Hope the wastes and soil are mixed with discarded equipment and municipal garbage.

In general the wastes are of large volume and widely dispersed. Besides radium the soils contain other long-lived radionuclides such as uranium and thorium. The specific activity is generally low, but a number of areas of relatively high specific activity have been identified. Table 1 shows $\gamma$-spectrometry data obtained at Chalk River Nuclear Laboratories (CRNL) for samples from the Port Hope area. For comparison, the radium-226 content of uranium mine-tailings is also shown (see also reference 5).

In the early stages of the Port Hope clean-up, contaminated soils adjacent to occupied property were taken to the waste management area at CRNL, with very little attention paid to alternative disposal or decontamination options. One option for the cleanup of such historic wastes is a soil decontamination process, which would avoid the need to establish new disposal sites. A suitable decontamination process must selectively extract uranium-series contaminants, in particular radium-226, since radioactive decay of the latter produces radioactive radon gas. Another option is to consolidate the wastes where they are, so as to reduce groundwater contamination and radon release to acceptable levels. Successful development of these options requires a detailed knowledge of the chemical properties of the contaminating radionuclides and how they are retained or released by the various components of the soil or waste form.

This report will concentrate on radium. A discussion of the radiological and chemical properties of radium will be given, followed by a review of the chemical factors governing the mobility of radium in soil/groundwater environments. This will include a section on soil leaching. Since tailings from uranium mining and milling operations are the largest potential source of radium contamination, a discussion of their nature and attempts to leach radium from them will be given. Finally, earlier attempts at extracting or immobilizing radium will be discussed. On the basis of this review, a number of recommendations will be made concerning possible solutions and further research.

## 2. STANDARDS

Before reviewing leaching processes and possible methods of decontaminating radium-bearing material, we must establish a residual level that can be considered harmless. The success or failure of a particular decontamination process can then be measured against this standard level.

The distribution of radium in nature has been reviewed by Ames and Rai [6] and more briefly by Sheppard [7]. The average radium content in rocks of North America and Europe varies from 1 pCi/g* for sedimentary shales and clays to $10^{-2}$ pCi/g for ultrabasic rocks. For soils the range is generally 0.1 to 1.0 pCi/g [8], but concentrations up to 4 pCi/g have been encountered in soils surrounding, but uncontaminated by, uranium

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*1 pCi/g ≡ 0.037 Bq/g.

milling operations in the United States [9]. The radium concentration in river water is usually between $10^{-1}$ and $10^{-2}$ pCi/$dm^3$ [10].

For contaminated soils and water it is probably unreasonable to expect to reattain these background levels. The International Commission on Radiological Protection has set 10 pCi/$dm^3$ as an upper limit for environmentally acceptable water [11], and this has been adopted as the Canadian federal standard [12,13]. Accordingly the Atomic Energy Control Board has suggested that this should be the goal of waste treatment technologies [14].

For mine effluents and public water supplies, Ontario and Saskatchewan have set an objective of 3 pCi/$dm^3$ of radium-226 in filtered (pore size = 1.2 μm) water [15]. A similar standard was established in 1962 by the U.S. Public Health Service and subsequently increased to 5 pCi/$dm^3$ by the Regulations on Radionuclides issued by the Environmental Protection Agency (EPA) in 1976 [16]. Thus targets of 10 pCi/$dm^3$ total and 3 pCi/$dm^3$ dissolved radium-226 were established for the treatment of uranium mine effluents by Moffett et al. [17] and Schmidt and Averill [18], respectively.

No data have been found on the maximum permissible concentration (MPC) in either mine-tailings or soils. However, according to Borrowman and Brooks [19] an MPC for radium-226 of ≈ 20 pCi/g is an acceptable target for both tailings and soils. This number is based on recommended levels for gypsum wall board and building materials in the United Kingdom [20] (25 pCi/g) and in the USSR [21] (20 pCi/g). According to Borrowman and Brooks, uranium mill tailings containing 20 pCi/g would have a net γ-radiation level of 0.05 mR/h measured three feet above the surface, a level not considered hazardous [22]. Thus, the attainment of a level of 20 pCi/g could be considered a measure of the efficacy of a particular waste treatment. Whether such a level can be achieved by leaching methods remains to be seen.

## 3. RADIOLOGICAL PROPERTIES OF RADIUM

The radiological properties of radium have been reviewed by Sheppard [7] and by Itzkovich and Ritcey [23].

Radium is a naturally occurring radioactive element. All isotopes ($^{206}$Ra to $^{230}$Ra) are radioactive. Since most of the wastes considered here are produced by treatment of uranium ores, the most important isotope is $^{226}$Ra. Radium-226 is formed when $^{230}$Th emits an α-particle. Radium-226 decays (half-life 1620 a) to the gas $^{222}$Rn. The $^{238}$U decay scheme is shown in Figure 1. Both $^{226}$Ra and its daughter, $^{222}$Rn, present radiological hazards; $^{226}$Ra from its ability to replace calcium in bone structures, and $^{222}$Rn by retention in the lungs in the form of $^{210}$Pb and $^{210}$Po.

## 4. CHEMISTRY OF RADIUM

Both Sheppard [7] and Itzkovich and Ritcey [23] reviewed briefly the chemistry of radium. Here, it is considered in greater detail, and compared to that of the other alkaline earth cations. Discussion will concentrate on those properties expected to exert a major influence on the leachability and mobility of radium. More general discussions of radium properties, including analytical methods, are given in references 24 to 27.

Radium is an alkaline earth element and, like the other Group IIA members, exhibits only the +2 oxidation state. The general properties of this group have been reviewed [28,29].

### 4.1 SOLUBILITIES

The radium salts of the strong acids HCl and $HNO_3$ are soluble (Table 2). In general, this is the case for the other alkaline earth cations (e.g. $BaCl_2$, Table 2). Table 3 gives the solubilities of sulphate, carbonate and phosphate salts. The relative order of solubility varies with the anion. For sulphates, the solubility decreases in the order

$$Ca^{2+} > Sr^{2+} \gg Ba^{2+} > Ra^{2+} .$$

In general the solubilities of the oxyanion salts are low and the alkaline earth cations should precipitate in the presence of large concentrations of the anions. The close similarity in the solubilities of $RaSO_4$ and $BaSO_4$ should be noted.

## 4.2 ION SIZE

Table 4 gives ionic crystal and hydrated ion radii for the alkaline earth cations. The crystal radius increases and the hydrated radius decreases from $Be^{2+}$ to $Ra^{2+}$. The final column in Table 4 gives the charge/crystal radius ratio. In the case of $Be^{2+}$ the high charge density on the ion promotes hydrolysis of beryllium salts in aqueous solution. This high charge density confers distinct properties on $Be^{2+}$ compared to the other cations, none of which show any tendency to hydrolyze. Consequently, $Be^{2+}$ will not generally be included in discussions of the properties of the alkaline earth elements.

## 4.3 COMPLEX FORMATION

As expected, the tendency to form complexes decreases as cation size increases. This is not so obvious for complexation with inorganic anions, Table 5, but is more so with organic ligands, Table 6. Complexation by inorganic anions is generally weak compared to complexation by organic acids, with radium showing the least tendency to form complexes. The smaller-than-expected complexation constant for $Mg^{2+}$ with EDTA is due to steric crowding, the small $Mg^{2+}$ ion having difficulty accommodating the four carboxylate groups.

## 4.4 THERMOCHEMICAL AND ELECTROCHEMICAL PROPERTIES

Thermochemical data have been published for radium and several radium salts [35,36], and compiled by Riese [37]. The data tabulated by Riese are taken from a number of previous sources, and have not been checked for compatibility with the values of the thermodynamic parameters listed in Tables 2, 3, 5 and 6. The electrochemical behaviour of radium has been reviewed by Toshima [38].

## 4.5 ADSORPTION

Adsorption and ion-exchange processes will be particularly important in determining the rate of radium transport in any groundwater/soil system. Such processes are extremely complicated in the "real" environment, and will be discussed in Chapter 5. In this section a few fundamental aspects of the adsorption process will be discussed.

If only electrostatic factors were important, then all the alkaline earth cations should have the same tendency to absorb or ion-exchange. However, there is a well-defined selectivity or affinity series, which has been derived theoretically by Eisenmann [39]. He considered the consequences of the assumption that cation-exchange equilibria are dominated by (a) coulombic interactions between cations (in various states of hydration) and the fixed groups of the exchanger material, and (b) ionic hydration effects caused by ion-dipole interactions with water molecules. When ionic hydration effects predominate, ions of smaller hydrated radius tend to displace ions of larger hydrated radius, and the affinity series for adsorption (or ion exchange) can be written (see Table 4)

$$\mathrm{Cs}^{+} > \mathrm{K}^{+} > \mathrm{Na}^{+} > \mathrm{Li}^{+}$$

$$\mathrm{Ra}^{2+} > \mathrm{Ba}^{2+} > \mathrm{Sr}^{2+} \sim \mathrm{Ca}^{2+} > \mathrm{Mg}^{2+} > \mathrm{Be}^{2+} .$$

Although $\mathrm{Ra}^{2+}$ was not considered by Eisenmann, its small hydrated radius (Table 4) would place it at the head of the affinity series, as indicated. If coulombic interactions between cation and exchange site predominate, then the selectivity is reversed.

### 4.6 SUMMARY

Where measured, the chemical properties of radium fit nicely into the alkaline earth series. Hence, the behaviour of radium, under conditions where its properties have not been defined, can often be inferred from its position in the alkaline earth series, and to a first approximation it will generally behave in a manner similar to barium. Table 7 summarizes trends for several important properties.

## 5. RADIUM MOBILITY IN, AND RETENTION BY, SOILS

Two major geochemical processes can retard transport of cationic species, relative to groundwater flow, in a porous medium such as soil:

(i) Adsorption wherein the cations are attracted to a surface (generally colloidal) by electrical and chemical processes. The colloids may be clay minerals, hydrous metal oxides or hydroxides, or organic matter.

(ii) Precipitation, or coprecipitation, as part of an amorphous or crystalline solid.

The nature and strength of such interactions with geological media will not only determine the rate at which the species (radium in this case) is transported through soil, but will also have a major impact on chemical processes designed to remove (leach) the particular radionuclide from the soil. Therefore, if a chemical decontamination technique is to be developed for soils, a thorough understanding of the nature and strength of these geochemical interactions is required.

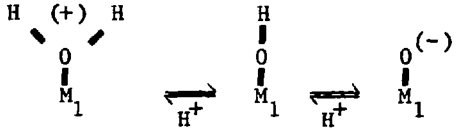
In this section the nature of these geochemical processes will be briefly reviewed, experimental data for $^{226}$Ra adsorption by different mechanisms, and transport in different media, will be presented, and finally the leaching of $^{226}$Ra from soils will be discussed.

## 5.1 ADSORPTION ON METAL OXIDES

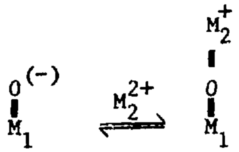
In aqueous solution, the surfaces of metal oxides, hydroxides and hydrous oxides are covered with hydroxyl groups capable of showing weakly acidic behaviour. For pH values above the point of zero charge ($pH_{pzc}$), the surface will be negatively charged. This charge will increase with pH and electrolyte concentration, and is neutralized by adsorption of cations. Compilations of points of zero charge have been given by Parks [40] and by Kinniburgh and Jackson [41].

For simple 1:1 electrolytes, cation adsorption is generally independent of the cation. This is not so for divalent cations. Cation adsorption often involves specific interactions with the surface, and in some cases takes place even when the surfaces have a net positive surface charge. A rapid increase in divalent cation adsorption generally occurs over a narrow pH range and often starts at $pH < pH_{pzc}$. In these cases, adsorption is usually better correlated with the hydrolysis properties of the adsorbing ion than with the charge properties of the solid. This is particularly true for strongly hydrolyzable cations, and the adsorption process is often viewed as an exchange of $M^{2+}$ for $H^+$ from the acidic surface OH groups. This can be envisaged as the coordination of dissolved metal ions with deprotonated surface hydroxyl groups, i.e.

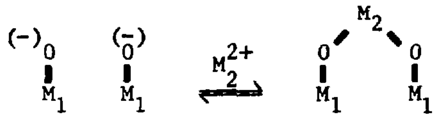
(a)



(b)



(c)



((b) and (c) represent two different modes of surface coordination).

The ratio p (number of protons released per cation adsorbed) tends to change from solid to solid. In general the alkaline earth cations exhibit lower values, and are less strongly adsorbed, than the more hydrolyzable transition metal ions ($Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ni^{2+}$). This observation leads to the postulate that the tendency for a particular divalent cation to adsorb is directly related to its ability to displace protons from the surface, or, alternatively, that more strongly adsorbed ions tend to hydrolyze more readily [42]. In fact the adsorbed species may be in a more hydrolyzed state than that of the cation in aqueous solution. Thus studies of the adsorption of $Ba^{2+}$ on vitreous silica and $^{226}Ra^{2+}$ on $\alpha$-$SiO_2$ [37] suggest that at high pH (> $pH_{pzc}$) some of the adsorbed cation is in the form $BaOH^+$ and $^{226}RaOH^+$, respectively. For $^{226}Ra^{2+}$ adsorption on quartz, the data were fitted to the surface complexation model of Davis et al. [43,44], the best fit being obtained by assuming that both $^{226}Ra^{2+}$ and $^{226}RaOH^+$ are present at high pH.

The pH at which divalent cation adsorption becomes significant varies with the particular cation and solid involved, the solid:solution ratio, the specific surface area of the solid, the total cation concentration, and the concentration of other interacting species. Consequently it is difficult to generalize. For adsorption of alkaline earth cations on $\delta$-$MnO_2$, p increases with increasing atomic number [45], i.e. $Mg^{2+}$, p = 0.05 to 0.25; $Ca^{2+}$, 0.12 to 0.35; $Sr^{2+}$, 0.45; $Ba^{2+}$, 0.50 and the selectivity sequence for adsorption is

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} .$$

Given the position of $Ra^{2+}$ in the alkaline earth cation series and the trend in its chemical properties one would expect $Ra^{2+}$ to be at least as strongly adsorbed as $Ba^{2+}$. However, the sequence is reversed for adsorption on $\alpha$-$Fe_2O_3$ [46], indicating that coulombic interactions predominate over ionic hydration effects (see Section 4.5).

Since the selectivity sequence varies from oxide to oxide and is often inconsistent within the alkaline earth series, it is generally not possible to be sure of the behaviour of $Ra^{2+}$ compared to that of the other alkaline earths. There have been very few studies of $Ra^{2+}$ adsorption on metal oxides. Two exceptions are the work of Riese [37] on $Ra^{2+}$ adsorption on quartz ($\alpha$-$SiO_2$), and the work of Ames et al. [47] on adsorption on amorphous ferric oxyhydroxide (FeOOH). The quartz sorbent was assumed to be a single-site amphoteric surface, in keeping with the general view of mineral oxides. Radium adsorption was found to increase for pH > 3, and, in the absence of competing ions such as $Ca^{2+}$, about 90% of the radium (initially 1000 $pCi/dm^3$) was adsorbed at pH 8 to 9. Adsorption was observed below the point of zero charge ($pH_{pzc} \sim 3$) and arbitrarily attributed to residual negatively charged sites. The presence of $Ca^{2+}$ ($10^{-3}$ to $10^{-4}$ $mol \cdot dm^{-3}$) was found to strongly inhibit $Ra^{2+}$ adsorption, especially at alkaline pH values. The data were treated using the thermodynamic model of James and Healy [48] and the complexation site-binding model of Davis et al. [43,44]. Both models fitted the data for pH > 4 to 5, with the latter model also good for adsorption in the presence of competing ions such as $Ca^{2+}$, especially at alkaline pH values.

For adsorption onto amorphous ferric oxyhydroxide [47], the data fit a Freundlich isotherm. The amount of $^{226}Ra$ adsorbed was inversely proportional to the total concentration of alkaline earth cations but independent of whether the accompanying anion was $Cl^-$ or $HCO_3^-$.

## 5.2 ADSORPTION ON CLAY MINERALS

The clay minerals are hydrous aluminosilicates formed by sequential stacking of sheets with an octahedral lattice ($Al^{3+}$ cations in sixfold coordination with $OH^-$ anions) and sheets with a tetrahedral lattice ($Si^{4+}$ cations in fourfold coordination with $O_2^-$ anions). Most clays have a negative surface charge due to nonstoichiometric isomorphous substitution of cations within the structure, i.e. $Al^{3+}$ for $Si^{4+}$ in tetrahedral sheets, and $Mg^{2+}$ for $Al^{3+}$ in octahedral sheets. The extent of substitution controls the surface charge and hence the amount of cation adsorption, as opposed to adsorption on metal oxides, which is controlled by $H^+$ or $OH^-$ adsorption from solution (see Section 5.1). Consequently, the term cation exchange is more commonly used than cation adsorption.

For simple two-layer (i.e. TOTO...)* clays like kaolinite, which exhibit very little isomorphous substitution, the most reactive ion-exchange sites are located along the edge of the kaolinite crystal [49]. This is shown schematically in Figure 2A. Clays such as illite, vermiculite and montmorillonite are three-layer (i.e. TOTTOT...) structures. For montmorillonites, water and hydrated cations can enter the space between the unit cells and cause expansion, so that montmorillonites do not have a fixed dimension along this axis. Because of this variable spacing, the interlayer cations can be of diverse hydrated radii. Pommer [50] has shown that these interlayer cations are less strongly held than edge cations, and consequently are more readily ion-exchanged, i.e. adsorption in the inner-layer is basically electrostatic and reversible, whereas adsorption at edge sites is more localized (chemisorption) and correspondingly irreversible. Hence cation adsorption at edge sites will be more difficult, but once adsorbed, a cation will be more difficult to remove. The situation is shown schematically in Figure 2B, and Table 8 lists the ion-exchange capacities for a number of clays [51,52].

Other factors being equal, cations of higher valence tend to replace those of lower valence, and are more difficult to replace when already adsorbed. Thus trace amounts of divalent cations can often be adsorbed from solutions containing a large excess of monovalent cations. For cations of the same valence, the ion with the smaller hydrated radius will be more strongly adsorbed. Thus, for the alkaline earth cations,

$$Ba^{2+} > Sr^{2+} \sim Ca^{2+} > Mg^{2+} .$$

Radium, which has the smallest hydrated radius of the alkaline earth cations (Table 4), would be expected to be the most strongly adsorbed and, once adsorbed, the most difficult to displace. It should preferentially adsorb at interlayer sites in three-layer clays, which can accommodate ions of diverse hydrated radii. If $Ra^{2+}$ is originally adsorbed at

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* T - Tetrahedral Unit
O - Octahedral Unit

edge sites (a possibility with mine-tailings that have undergone vigorous treatment with strong acids), it would be expected to be very difficult to release by ion exchange.

Only one comprehensive study of radium adsorption on a clay, that of Riese [37] on kaolinite, appears to have been done. He assumed that kaolinite could be represented by a mixture of two distinct adsorption sites, SiOH and AlOH sites; and that the surface charge was due primarily to surface ionization and complexation reactions. Surface charge due to isomorphous substitution in the clay lattice was neglected since the measured cation exchange capacities were low at moderately acidic pH. Adsorption rose as the pH was increased above 2, with about 90% of the radium (initially 1000 pCi/dm$^3$) being adsorbed at pH 8 to 9. Adsorption was also observed below the pH$_{pzc}$ and was attributed to minor isomorphous substitution in the clay lattice, possibly caused by slight incongruent dissolution at acidic pH or by lattice substitution of trace constituents. The presence of Ca$^{2+}$ strongly inhibits $^{226}$Ra$^{2+}$ adsorption and favors desorption, especially at alkaline pH values. The complexation site-binding model accurately models the competitive effects of Ca$^{2+}$ and $^{226}$Ra$^{2+}$ adsorption. The model was fitted assuming two reactions for radium adsorption:

$$\mathrm{SOH} + {}^{226}\mathrm{Ra}^{2+} \rightleftharpoons \mathrm{SO}^{-} - {}^{226}\mathrm{Ra}^{2+} + \mathrm{H}^{+}$$

$$\mathrm{SOH} + {}^{226}\mathrm{Ra}^{2+} + \mathrm{H_2O} \rightleftharpoons \mathrm{SO}^{-} - {}^{226}\mathrm{RaOH}^{+} + 2\mathrm{H}^{+} .$$

where S denotes an adsorption site on the surface. The species, $^{226}$RaOH$^+$, was of minor importance but improved the model fit at alkaline pH.

## 5.3 ADSORPTION BY ORGANIC MATTER

According to Schnitzer and Khan [53], the organic matter found in soils and sediments is of two types - humic and non-humic. The humic component is stable to microbial attack and represents a significant fraction of the organic matter in most soils and waters.

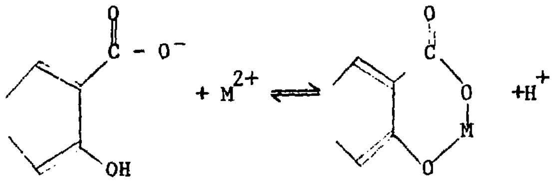
Humic substances may be described as polymers (300 to 30 000 molecular weight) containing phenolic hydroxylic groups and carboxylic groups with a small number of aliphatic OH groups. Based on their solubility in alkaline and acid solutions, the humic substances are usually divided into three fractions:

(1) humic acid, which is soluble in alkaline solution but is precipitated by acidification;

(2) fulvic acid, which is the humic fraction that remains soluble in an aqueous acidified solution (i.e. soluble over the whole pH range);

(3) humin, the fraction that cannot be extracted from soils by either acids or basic solutions.

Humic and fulvic acids are polyelectrolytic weak acids that tend to form complexes with metal ions. The extent of complex formation depends on the tendency of the ligating groups to replace $H^+$ with $M^{2+}$:



Consequently the ability of these acids to form metal ion complexes depends on both the acid-base behaviour and metal-ion binding tendency of the polymeric base [54]. The stabilities of metal-humic complexes are generally higher than those of the corresponding complexes with inorganic anions [55]. This would be expected to hold true of the alkaline earth cations in view of the relative stabilities of their inorganic complexes (Table 5), and those organic complexes formed with agents containing carboxylic acid groups (Table 6). This does not necessarily mean that humic acids will always solubilize divalent cations in aqueous environments, since humates can form negatively charged colloids that coagulate and precipitate in the presence of, for example, $Ca^{2+}$ and $Mg^{2+}$ [54]. The other alkaline earth cations would be expected to do the same.

Marshall [56] has summarized several investigations on the affinity series of cations with respect to humic substances. For crude humic acid (peat) the affinity series

$$Ba^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > K^{+} > Na^{+} > Li^{+}$$

was obtained. On the basis of this series, $Ra^{2+}$ would be expected to be the most strongly adsorbed of the alkaline earth cations, although this is by no means certain given the position of $Sr^{2+}$ in the series.

According to Titayeva [57], $Ra^{2+}$ is readily extracted from natural waters by peat, and appears to be associated with the insoluble organic material (humins). Work by Rusanova [58] indicated that the soil horizons enriched in organic matter accumulate (i.e. immobilize) radium from the groundwater, and Nathwani and Phillips [59] claimed that organic matter and clays were the dominant soil constituents contributing to $^{226}Ra^{2+}$ adsorption. It appears to be a general observation for the alkaline earth cations that an increase in organic content of soils or sand leads to increased sorption and immobilization. This has been demonstrated, particularly for $^{90}Sr^{2+}$ [60,61] and Grisak and Jackson [62] have concluded that $^{226}Ra^{2+}$ will behave like $Sr^{2+}$. The effect has been quantified by Prokhorov [60] who observed a decrease in the diffusion coefficient of $^{90}Sr^{2+}$ from quartz sand from $1.1 \times 10^{-6}$ $cm^2/s$ to $1.0 \times 10^{-8}$ $cm^2/s$ upon addition of humic acids, indicating a significant decrease in mobility.

## 5.4 PRECIPITATION AND COPRECIPITATION

As well as by adsorption, cations may be removed from solution by either direct precipitation or isomorphous substitution with an ion of similar size in a crystal that is forming (coprecipitation) or that has previously formed (replacement). Such processes would cause a significant decrease in cation transport in the particular environment. Cation adsorption can eventually lead, via surface hydrolysis, to the precipitation of a metal hydroxide/oxide on the sorbent surface, providing the cation concentration and pH are high enough. This precipitation mechanism will be important for hydrolyzable cations such as the transition metals, but not for the alkaline earth cations, which, with the exception of $Be^{2+}$, have little tendency to hydrolyze (see Section 4.2). Alkaline earth cations are more likely to precipitate with groundwater anions with which they form insoluble salts; the data in Table 3 suggest that precipitation as carbonates, phosphates, and sulphates (particularly $Ba^{2+}$ and $Ra^{2+}$) could lead to their immobilization.

The replacement of one cation in a crystal lattice by another is common in the creation of distinct mineral species. In general the cations should have similar ionic radii (within 15%), charge values that do not differ by more than a unit, and similar covalent character. The new solid must be more stable (less soluble) than the original solid, i.e. thermodynamics must favour the transformation in the specific environment.

Two pairs of alkaline earth cations that satisfy these requirements are $Ca^{2+}$ and $Sr^{2+}$, and $Ba^{2+}$ and $Ra^{2+}$ (see Tables 3 and 4). Consequently, it is not surprising to find the replacement of $Ca^{2+}$ by $Sr^{2+}$ in $CaCO_3$, or $Ba^{2+}$ by $Ra^{2+}$ in $BaSO_4$. Coprecipitation of $^{226}Ra^{2+}$ with $BaSO_4$ is a common method of immobilizing (temporarily) $^{226}Ra^{2+}$ in uranium mine-tailings. Routson [63] reported that in the presence of substantial amounts of phosphate, calcite ($CaCO_3$) was replaced by apatite $Ca_5(PO_4)_3OH$, with $^{90}Sr^{2+}$ replacing some of the calcium. Other replacement reactions have been summarized by Ames and Rai [6]. They include the replacement of $Ca^{2+}$ by $Ba^{2+}$ in both $CaCO_3$ (calcite) and $CaSO_4 \cdot 2H_2O$ (gypsum). Also Brown et al. [64] have shown that $Ba^{2+}$ can replace $Ca^{2+}$ in apatite.

There is considerable evidence that $Ra^{2+}$ can replace alkaline earth and other cations in insoluble salts. As mentioned above, the prime example is the coprecipitation of $^{226}Ra^{2+}$ with $Ba^{2+}$ in $Ba(Ra)SO_4$. Processing uranium ores with sulphuric acid produces gypsum and jarosite ($(K,Na)Fe_3(SO_4)_2(OH)_6$), and $^{226}Ra^{2+}$ tends to be associated with both (up to 80,000 pCi/g with jarosite [65]). Although the $^{226}Ra^{2+}$ is commonly claimed to be adsorbed, it seems more probable, considering the low solubility of

$^{226}RaSO_4$ (Table 3), that it is incorporated in the lattices in place of $Ca^{2+}$ and $K^+$. Granger et al. [66,67] showed that $^{226}Ra^{2+}$ that had migrated out of uranium ores at Ambrosia Lake, New Mexico, was partly reconcentrated in barite ($BaSO_4$) and cryptomelane ($KMn^{2+}Mn^{4+}_{7.25}O_{16}\cdot H_2O$), replacing $Ba^{2+}$ and $Mn^{2+}$ respectively. Replacement of $Ca^{2+}$ by $^{226}Ra^{2+}$ in apatite has been proposed as a method of immobilizing Ra [64].

## 5.5 GENERAL DISCUSSION

In a soil system it is very difficult to determine which of the above processes (Sections 5.1 to 5.4) is dominant. The reasons for this are many. The composition of the soil may not be uniform, and factors such as soil texture and water-content will be important. Also, mineral oxides, clays and humic substances do not occur independently in soils. Metal oxides are commonly adsorbed or precipitated on clay surfaces, thereby changing their cation-exchange capacities. Humic substances have a strong tendency to adsorb on hydrous oxides, clays, and other surfaces. This is envisaged as a ligand exchange process,

$$R - \overset{O}{C} - O^- + HOM \rightleftharpoons R - \overset{O}{C} - OM \quad + OH^-$$

(where M denotes a metal ion species that is part of the hydrous oxide). These processes occur at adsorption sites on the oxides, and exert a major impact on cation adsorption.

An important parameter that quantifies the amount of adsorption or ion exchange, without specifying the detailed nature of the system, is the distribution coefficient,

$$K_d = M_i/[M_i]$$

where $M_i$ is the concentration of surface species in mol/kg of suspended solid oxide, and $[M_i]$ is the concentration of species i in solution ($mol/dm^3$). This parameter has been used to measure the amount of radium adsorbed by a number of naturally occurring materials including tuff and soils from Utah and California [6]. Distribution coefficients were generally found to be large (> 200 and often > 400 $dm^3/g$) indicating strong adsorption.

A number of influences on the interactions of radioactive wastes with soils have been investigated by Fowler et al. [68] in a general review. They investigated degrees of retention for various isotopes of Pu and U and also for $^{241}Am$ and $^{137}Cs$, and found that $^{137}Cs$ was generally strongly adsorbed whereas the other isotopes were not strongly adsorbed. The relatively low retention of Pu, U and Am was claimed to be due to hydrolysis and complexation (with $CO_3^{2-}$) reactions that gave negatively charged species incapable of adsorbing (ion exchange) onto the negatively charged soil particles. Cesium, being unhydrolyzed, was positively charged and consequently ion exchangable. Radium-226 would be expected to behave like $^{137}Cs^+$, since hydrolysis and complexation reactions to produce negatively charged species (i.e. with $SO_4^{2-}$, $CO_3^{2-}$, $PO_4^{3-}$) are unlikely (Table 5). Occlusion of radionuclides during $CaCO_3$ precipitation was also found to be a major mode of retention and, as discussed above (Section 5.4), $^{226}Ra^{2+}$ should also be retained in media containing high carbonate concentrations.

## 5.6 SOIL LEACHING STUDIES

On the basis of previous discussion, one would expect $^{226}Ra^{2+}$ to be strongly adsorbed in most soil environments, and consequently difficult to leach (mobilize) except in very aggressive solutions. This is borne out by the few soil-leaching studies that have been performed. Thus, Nathwani and Phillips [34,59] studied leaching of $^{226}Ra^{2+}$ from Port Hope soils under two conditions, both expected with naturally infiltrating waters, i.e. $CO_2$-saturated (pH $\approx$5.5) and $SO_2$-saturated (pH $\approx$ 3.5) water. They found that leaching was significantly affected by changes in soil texture and leachant acidity. Thus, maximum concentrations in the leachate were achieved for the coarser and intermediate size fractions, and in the more acidic leachant. Over short periods (30 to 45 d) the leaching process could be approximated by Fick's law of diffusion, yielding diffusion coefficients for radium in the range $5 \times 10^{-11}$ to $10^{-13}$ $cm^2/d$. These coefficients provide a basis for estimating the extent of $Ra^{2+}$ leaching over longer time periods, although it would be necessary to establish that diffusion control was maintained. Using such an extrapolation, Nathwani and Phillips [59] estimated that ≈ 0.1% of the $^{226}Ra^{2+}$ would be leached, from an initial concentration between 1500 and 5000 pCi/g, over a five-year period.

Radium-226 was found to be exchangable by sufficiently large concentrations of $NH_4^+$, $K^+$ and $H^+$ [55], but non-exchangeable by these ions in the presence of $Ca^{2+}$. This was arbitrarily attributed to a structural change in the soil. This agreed with the findings of Verkovskaja et al. [69], who found that the amount of exchangable $^{226}Ra^{2+}$ was inversely proportional to the concentration of $Ca^{2+}$ and $Mg^{2+}$.

## 6. RADIUM IN URANIUM MINE-TAILINGS

The largest potential source of $^{226}Ra^{2+}$ in the environment is uranium mine-tailings. Consequently a great deal of attention has been paid to treating them in order to remove mobile radionuclides, in particular $^{226}Ra^{2+}$, thereby reducing the radiological hazard.

### 6.1 ORE MINERALOGY

The process used to extract uranium from its ores depends to a large extent on the ore mineralogy. Two commercial processes, one based on a sulphuric acid leach and the other on an alkaline carbonate leach, have been described in detail by Itzkovich and Ritcey [23]. The sulphuric acid process is used for Elliott Lake ore, which contains 0.05 to 0.10% uranium, mainly in the minerals brannerite and uraninite (see Table 9). The associated material is mostly quartz, with small amounts of feldspars, sericite ($(KAl_3Si_{10}(OH)_2)$) and chlorite ($((Mg,Fe,Mn)_6(AlSi_3)O_{10}(OH)_8)$). About 5% pyrite is present, together with monazite and traces of other minerals. The Saskatchewan ores contain from 1 to 3% uranium and are treated using the alkaline carbonate process. The main mineral is pitchblende ($UO_2 \cdot UO_3$), with some coffinite ($U(Si)_4)_{1-x}(OH)_{4x}$) and brannerite. Associated minerals include sulphides, arsenides and sulpharsenides containing iron, copper, nickel, lead, zinc, arsenic, antimony and minor amounts of molybdenum and vanadium. The remainder is mainly quartz, sericite and chlorite.

During milling a small amount of $^{226}Ra^{2+}$ dissolves, but the majority remains in the leach residue. Current tailings are treated with lime to bring the pH up to 10.5 before disposal to the tailings ponds. The overflows from the ponds are then sent to radium-settling basins where barium chloride is added to precipitate the $^{226}Ra^{2+}$ as a coprecipitate with barium, $Ba(Ra)SO_4$. The overflows from these settling ponds are then discharged to surrounding streams and lakes. The precipitation reduces the level of dissolved $^{226}Ra^{2+}$ from 200-800 $pCi/dm^3$ to around 2-8 $pCi/dm^3$ [70].

## 6.2 TAILINGS MINERALOGY

An understanding of the composition of tailings is the first stage in understanding how $^{226}Ra^{2+}$ is attached and, consequently, what kind of process is required to remove it or, alternatively, to fix it in place. As discussed in Section 5, radium will react in several specific ways with a variety of materials. Where it resides in the tailings, and the strength of its attachment to various solids, will depend very strongly on the system chemistry and mineralogy.

Several studies of tailings mineralogy have been performed [71-73] and the $^{226}Ra^{2+}$ distribution discussed [70]. In general, tailings contain the following minerals:

(a) Quartz comprises > 70% of tailings sands and 20 to 60% of tailings fines [71];

(b) Clays, such as illite and kaolinite, are found in tailings fines (10 to 30%);

(c) Feldspars are a major constituent of fines;

(d) Other usual minerals include: calcite, barite, chlorapatite, and $\alpha$-hematite;

(e) In sulphuric acid leached tailings, gypsum and jarosite are observed.

The constituents of Elliott Lake mine-tailings are given in Table 9.

## 6.3 DISTRIBUTION OF RADIUM

Skeaff [70] studied the distribution of $^{226}Ra^{2+}$, as a function of particle size, in Canadian mill tailings, and has shown that up to 90% of the $^{226}Ra^{2+}$ is concentrated in material smaller than 200 mesh. Similar observations have been made by Borrowman and Brooks [19] for tailings from Salt Lake City, Utah, and Grants, New Mexico, and by Wiles [74] for tailings from Beaverlodge, Saskatchewan.

Much less is known about which minerals are associated with the $^{226}Ra^{2+}$. Coprecipitation with barium to yield a mixed barite precipitate is well known, but there is evidence that $^{226}Ra^{2+}$ is associated with other sulphate-containing minerals in tailings from the sulphuric acid leach process. Thus Moffett et al. [65] report that, in Elliott Lake mill tailings, a large amount of $^{226}Ra^{2+}$ is adsorbed on a jarosite-type carrier to a level of 80 000 pCi/g. Also Kaiman [72,73] claims that $^{226}Ra^{2+}$ is predominantly associated with gypsum in fresh tailings, but with jarosite in weathered tailings. Radium has a very low sulphate solubility, and the above evidence suggests that it initially coprecipitates with $Ca^{2+}$ in gypsum, but eventually redistributes, possibly by dissolution of the gypsum and incorporation into jarosite.

Of the other minerals in tailings, the incorporation of $^{226}Ra^{2+}$ into calcite and chlorapatite is also a strong possibility. Apatite minerals appear to form readily from calcite [63] in the presence of substantial amounts of phosphate (produced by the leaching of monazite). Fyfe [75] has shown that $Ba^{2+}$ can readily replace $Ca^{2+}$ in the apatite lattice and that the resulting mineral only slowly redissolves when leached with acid. Radium-226 would be expected to adsorb onto the clay materials (Section 5.2) and onto quartz particles [37]. In fact, Seeley [76] has suggested that in the presence of large amounts of sulphate, precipitation of $RaSO_4$ onto quartz (sand) particles will occur. Figure 3 lists reactions that could occur during sulphuric acid leaching, and subsequent treatment, of the tailings.

In summary we would expect to find the $^{226}Ra^{2+}$ associated predominantly with sulphate solids (e.g. barium sulphate, gypsum, jarosite), in the form of coprecipitates. Also the precipitation of $RaSO_4$ or $Ba(Ra)SO_4$ or $Ca(Ra)SO_4 \cdot 2H_2O$ on the surface of mineral particles is a strong possibility. The remaining $^{226}Ra^{2+}$ would be expected to adsorb onto clay surfaces.

These conclusions are very general. The relative importance of the various deposits is expected to be site dependent varying with the local mineralogy, which would account for some of the variability in the leaching data to be discussed.

## 6.4 LEACHING OF TAILINGS

Much effort has been put into the study of $^{226}Ra^{2+}$ leaching from uranium mine-tailings. The leaching approaches can be separated into four categories: water washing, and leaching with solutions of salts, acids, and chelating agents, respectively. The results are summarized in Tables 10 to 13 [5,19,76-86].

Significant discrepancies exist in reported results, and care must be taken in interpreting these differences. Levins et al. [77] suggest that the various methods of radium analysis are a possible cause of these disagreements. Despite these uncertainties a discussion of the leaching data is merited.

### 6.4.1 Leaching With Water

Radium-226 leaching in distilled water was generally very inefficient, Table 10, the best result (40% removal) being achieved when a very small solid to liquid weight ratio (S/L = 0.0001) was used [78] (Table 10A). The dependence of leaching efficiency on S/L is a general phenomenon. Shearer and Lee [78] also observed that the S/L effect was greater for tailings than for sediments washed down river from the tailings pile. Also they observed that the solid to liquid ratio was greater for waste solids from the acid leach process than for tailings from the alkaline leach process. These observations suggest that the leaching efficiency is limited by the sulphate concentration in the leaching solution. Significant amounts of sulphate in a readily soluble form must exist in the tailings (from the acid leach process). The larger the volume of water used, the lower the sulphate concentration and the more radium leached. This was confirmed by Levins et al. [77] who simultaneously followed $^{226}Ra^{2+}$ and sulphate release, and demonstrated an inverse correlation between the two.

The 40% leaching efficiency observed for Colorado tailings indicates that a significant portion of the $^{226}Ra^{2+}$ is weakly adsorbed or associated with a moderately soluble sulphate. For Elliott Lake tailings the amount leached in distilled water was much lower, i.e. 7.9% after 68 d at S/L = 0.0005 [79].

### 6.4.2 Salt Leaching

For salt leaching the nature of the salt cation is very important, as is the nature and concentration of the anion, especially if it be sulphate.

Shearer and Lee [78] found that, for river sediments, the amount of $^{226}Ra^{2+}$ leached varied with the nature of the salt cation, decreasing in the order

$$Ba^{2+} > Sr^{2+} > Ca^{2+} \approx Mg^{2+} \approx K^{+} \approx Na^{+}$$

for $10^{-2}$ mol•dm$^{-3}$ chloride solutions (Table 11G). The chloride ion would not be expected to influence results, since the chlorides of all the cations, $Ra^{2+}$ included, are highly soluble. Also, the amount of $^{226}Ra^{2+}$ released increased as $Ba^{2+}$ concentration increased. For mine-tailings prewashed with $H_2O$ to remove sulphate, 30 to 40% of the $^{226}Ra^{2+}$ could be leached by treatment with $BaCl_2$. Silver and coworkers [80,81] also obtained much better $^{226}Ra^{2+}$ release after a prewash with $H_2O$. Orders of cation effectiveness similar to those of Shearer and Lee were observed by Seeley [76] and Wiles [74], the latter for Saskatchewan tailings produced by the alkaline carbonate process. However, Havlik et al. [83] found an almost inverse order for the leaching of Czechoslovakian tailings pond sediments. They attributed this to the presence of sulphate, which caused reprecipitation of the $^{226}Ra^{2+}$, especially with $Ba^{2+}$, as a mixed sulphate.

Obviously, when sulphate is present, $^{226}Ra^{2+}$ release is difficult and favoured only in the presence of cations that do not form insoluble sulphates (e.g. $K^+$, $Na^+$). When sulphate is present the percentage leached is directly proportional to the $K_{sp}$ values for the sulphates of $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ (see Tables 3 and 11G). When $^{226}Ra^{2+}$ is not reprecipitated as a sulphate, the amount leached by the various cations is in the order expected from the absorbability of the cations. On the basis of the generally observed selectivity sequence for cation exchange (see Section 4.5), $Ba^{2+}$ would be expected to exchange most readily with $^{226}Ra^{2+}$, as observed.

In the absence of sulphate, between 30% and 75% of the $^{226}Ra^{2+}$ can generally be ion exchanged by washing with 1.0 mol•dm$^{-3}$ salt solution, Table 11. If multiple leaching stages are used, then leaching efficiencies > 90% can be achieved (Table 11A,D,G). The highest efficiency, 94%, was achieved by Seeley [76] when leaching slimes solids (from Ambrosia Lake, New Mexico) in 1.0 mol•dm$^{-3}$ NaCl + 0.1 mol•cm$^{-3}$ HCl, using four 30 min stages of countercurrent leaching, plus two water washes; the residual concentration was 198 pCi/g. For the leaching of tailings pond sediments from Bytiz, Czechoslovakia, Havlik et al. [83] achieved 100% $^{226}Ra^{2+}$ removal with a 1-h leach with 1 mol•dm$^{-3}$ KCl. However, these sediments were initially extremely low in $^{226}Ra^{2+}$ 14 pCi/g, Table 11H) and cannot be taken as generally representative.

Leaching has been attempted with salts containing anions other than $Cl^-$: these include $NO_3^-$, $HSO_4^-$, $CO_3^{2-}$, $HCO_3^-$, $H_2PO_4^-$, $PO_4^{3-}$, and hexametaphosphate. Generally poor leaching efficiencies are achieved. This is not surprising for phosphate and carbonate which form fairly insoluble salts with the alkaline earth cations, Table 3. The one leaching experiment using $NO_3^-$ (Table 11E) indicates that this anion probably does not inhibit $^{226}Ra^{2+}$ leaching. Some success was achieved using hexametaphosphate solutions (Table 11C) [85].

### 6.4.3 Acid Leaching

Acid leaching has been attempted with HCl, $HNO_3$ and $H_2SO_4$ solutions. Very limited success was achieved with $H_2SO_4$ due to precipitation of $^{226}RaSO_4$ [77]. With HCl and $HNO_3$, good leaching efficiencies can be achieved for pH < 3. Generally acid concentrations greater than 1.0 $mol \cdot dm^{-3}$ have been used and efficiencies are generally better than for salt leaching. The results are collected in Table 12.

For acid leaching, temperature is important, and generally two or three stages are required to achieve > 90% removal. The most efficient leach was achieved by Seeley [76] using 3 $mol \cdot dm^{-3}$ $HNO_3$ at 85°C and a solid to liquid ratio of 0.25. By employing up to three, 1-h stages, over 97% of the $^{226}Ra^{2+}$ was removed from slimes solids (3300 pCi/g initial) and sand tailings (150 pCi/g) from Ambrosia Lake, New Mexico (Table 12A). A 92% leach was achieved after three 30 min stages with 1.5 $mol \cdot dm^{-3}$ HCl at 60°C and a solid to liquid ratio of 0.25 (Table 12B). Nitric acid leaching, followed by a further leach with either $H_3PO_4$, $Ba(NO_3)_2$, $H_2O$ or HF, was generally less efficient than multi-stage leaching with $HNO_3$ alone.

### 6.4.4 Leaching With Chelating Agents

Leaching efficiencies generally > 70% and often > 90% can be achieved by leaching with EDTA or DTPA (see Table 6). The results are summarized in Table 13. An efficiency of 94% was achieved leaching Ambrosia Lake tailings with 1.0 $mol \cdot dm^{-3}$ DTPA for 16 h at room temperature (Table 13C). Leaching with nitric acid at 70°C for 5 h with S/L = 0.1, followed by EDTA at 110°C for 24 h, gave a leaching efficiency of 97% (Table 13D).

### 6.4.5 Leaching Mechanisms

For leaching of tailings in water, both Wiles [74] and Nathwani and Phillips [79,87] observed an initial fast $^{226}Ra^{2+}$ ion release followed by a much slower release. They both attributed the fast release to chemical exchange. For the slower release, Wiles observed a $t^{1/2}$ time-dependence for the rate. Nathwani and Phillips fitted their release data to an expression derived to fit the rate at which an ion diffuses within a spherical particle. Thus the slow release at long times was thought to be controlled by intraparticle diffusion. The calculated values of the intraparticle diffusion coefficients ($\approx 10^{-13}$ $cm^2/h$) suggest that $^{226}Ra^{2+}$ trapped in the matrix will be released only very slowly.

Two models were proposed by Nathwani and Phillips to account for the two-stage desorption process. The aggregated tailings medium could be regarded as either (i) particles honeycombed with macropores and micropores or, (ii) a loose conglomeration of particles of varying size containing trapped $^{226}Ra^{2+}$. For (i), Radium-226 ions desorbing initially are those loosely held in the outer and larger pores. When these ions have desorbed, diffusion of $^{226}Ra^{2+}$ through the inner and smaller micropores within the aggregated medium controls the rate of release to solution.

This model offers a good explanation for the release of weakly adsorbed $^{226}Ra^{2+}$ that can be desorbed by water washing. The success of salt-leaching methods can be attributed to the ability of various cations to ion exchange with $^{226}Ra^{2+}$ relatively strongly adsorbed (possibly chemisorbed) at ion-exchange sites on clays, minerals, quartz and other materials. In the absence of anions, such as sulphate, that reprecipitate the $^{226}Ra^{2+}$, the ability of a cation to displace $^{226}Ra^{2+}$ from the surfaces of tailings components is in the order expected for cation adsorbabilities (see Section 4.5), and directly proportional to the cation concentration. This was particularly well demonstrated by the results of Wiles [74] for the leaching of tailings from Beaverlodge, Saskatchewan. He observed a first-order dependence of the leaching rate on cation concentration for $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$ and $Ca^{2+}$. For $Ba^{2+}$ the rate law resembled an adsorption isotherm, the rate being first order with respect to $Ba^{2+}$ for $[Ba^{2+}] < 10^{-3}$ mol·dm$^{-3}$ and independent of $[Ba^{2+}]$ for higher concentrations. The overall leaching reaction was envisaged to occur in three steps. An initial fast surface adsorption of $M^{2+}$ is followed by exchange between the $M^{2+}$ and $^{226}Ra^{2+}$ ions at some sites in the solid matrix. The final step is the release of $^{226}Ra^{2+}$ to solution, i.e.

$$M^{2+} \overset{K_1}{\rightleftharpoons} (M^{2+})_{surf}$$

$$(M^{2+})_{surf} + (^{226}Ra^{2+})_{matrix} \xrightarrow{k_2} (M^{2+})_{matrix} + (^{226}Ra^{2+})_{surf}$$

$$(^{226}Ra^{2+})_{surf} \xrightarrow{k_3} {}^{226}Ra^{2+}$$

This yields the rate law

$$R = \frac{d[Ra^{2+}]}{dt} = k_2NK_1[M^{2+}](1 + K_1[M^{2+}])^{-1}$$

where N is the total number of reactive surface sites, and the surface exchange reaction is assumed to be rate controlling (i.e. $k_3 \gg k_2$). For low $M^{2+}$ concentration this expression yields a leach rate that is first order with respect to cation concentration, whereas at high $[M^{2+}]$ the rate becomes independent of the cation concentration because the surface sites are saturated. Of the cations investigated by Wiles only $Ba^{2+}$ is sufficiently strongly adsorbed to saturate the surface sites.

Whether salt washing is capable of leaching $^{226}Ra^{2+}$ coprecipitated with sulphate (in $BaSO_4$, $CaSO_4 \cdot 2H_2O$ or $KFe_3(SO_4)_2(OH)_6$) or phosphate ($Ca_5(PO_4)_3Cl$), in tailings from the acid-leach process, is difficult to predict, since very little has been published on this aspect. Some dissolution of $BaSO_4$ has been observed in 1.0 mol·dm$^{-3}$ $CaCl_2$ [88]. Dissolution of the matrix is unlikely in neutral solution. However, work by McCready et al. [89] on the chemical stability of $Ba(Ra)SO_4$ precipitates indicates that a dynamic interchange of $SO_4^{2-}$ ions, accompanied by $^{226}Ra^{2+}$ and $Ba^{2+}$ release, occurs. A high solution concentration of $Ba^{2+}$ would be expected to accelerate the rate of release of $^{226}Ra^{2+}$ from these precipitates. A similar effect might be expected for $^{226}Ra^{2+}$ release from $CaSO_4 \cdot H_2O$ and $KFe_3(SO_4)_2(OH)_6$ in the presence of $Ca^{2+}$ and $K^+$. In the absence of published information it is difficult to assess the rate and extent of such processes.

In experiments with HCl and $HNO_3$, Wiles [74] observed a leach rate that was first order with respect to protons, for pH values about three or less. This suggested a similar chemical exchange mechanism to that he observed with simple salts. At higher concentrations ($pH \leq 2.5$) there is a higher order dependence and a much more rapid reaction. He concluded that this was related to the dissolution of the tailings matrix. A similar leaching enhancement for $pH < 3$ was observed by Levins et al. [77]. Dissolution of the tailings components would explain the generally higher leaching efficiency of acid solutions compared to salt solutions.

Oxide and mineral dissolution in acid solutions is a well-studied process [90,91]. Generally, matrix dissolution processes have a high activation energy [91] and require temperatures above 60°C to proceed at a significant rate. Consequently it is not surprising that efficient acid leaching processes have required high temperatures (Table 12). On the basis of the results in Tables 11 and 12 it is doubtful that acid leaching at low temperatures (25°C) would be any more successful than salt leaching, since matrix attack would be minimal. Acid attack of clay lattices has also been observed. Thus moderately acidic solutions ($pH \approx 3$) have been shown to cause partial structural disintegration of illites; strong acids leave only silicate residues [92-94]. Chelating agents such as EDTA and DTPA would be expected to facilitate ion exchange of $^{226}Ra^{2+}$, but also to attack oxide and mineral matrices [95,96].

Matrix attack by acids and chelating agents will lead to the release of "fixed" $^{226}Ra^{2+}$. Weakly adsorbed $^{226}Ra^{2+}$ in micropores will be more quickly released when the pores themselves are attacked and opened. Radium-226, which previously leached slowly due to slow intraparticle diffusion, will be released quickly by chemical or ion-exchange processes, and that portion "fixed" in clays, either by chemisorption or lattice substitution, will be released as the clay matrix is destroyed. Mineral dissolution will lead to the release of chemisorbed or incorporated $^{226}Ra^{2+}$. A significant amount of $Ba(Ra)SO_4$ dissolution is also to be expected in strong acid, as demonstrated by Benes et al. [88]. However, chelating agents were found to dissolve $BaSO_4$ much more readily than acids [88], and it is likely that dissolution of gypsum and jarosite, and the consequent release of $^{226}Ra^{2+}$, would occur most readily in EDTA and DTPA.

Release of $^{226}Ra^{2+}$ from other sulphate lattices (e.g. $CaSO_4 \cdot 2H_2O$) has not been studied in detail. However, Seeley [76] investigated the release of $^{226}Ra^{2+}$ from $^{226}RaSO_4$ deposits on sand particles. He found that 98% of the $^{226}Ra^{2+}$ could be leached by 1.0 $mol \cdot dm^{-3}$ HCl. Coprecipitation of $BaSO_4$ decreased the leachability of $^{226}Ra^{2+}$, whereas coprecipitation with $CaSO_4$ increased it. This suggests that $^{226}Ra$ may be more readily leached from gypsum ($CaSO_4 \cdot 2H_2O$) than from $Ba(Ra)SO_4$.

Finally, there appears to be some $^{226}Ra^{2+}$ that cannot be leached by any of the above procedures. Roasting and leaching experiments by Ryon et al. [5] indicated that this $^{226}Ra$ was not associated with sulphates, clays (which can be destroyed by roasting), or residual uranium minerals. It is probably associated with highly insoluble refractory silicate of some kind.

### 6.4.6 Radium Levels In Leached Residues

With the exception of the results of Havlik et al. [83], which were performed on sediments containing only small amounts of $^{226}Ra^{2+}$, the lowest residual $^{226}Ra^{2+}$ level achieved was 4.5 pCi/g for the nitric acid leaching of sand tailings from Ambrosia Lake, New Mexico (Table 12A). In this case, also, the initial $^{226}Ra^{2+}$ level was relatively low (150 pCi/g).

A level of 4.5 pCi/g is well within the standard for building materials specified in Section 2. A more common procedure to obtain relatively low levels (30-50 pCi/g) involves a hot strong-acid leach followed by a leach with a chelating agent such as EDTA. Although this does not achieve the tentative standard specified in Section 2 (20 pCi/g), it appears to be a realistic lower limit to aim for.

For salt leaching, the lowest residual level of 63 pCi/g was achieved for multistage leaching of Australian mine-tailings in $5.0\ \mathrm{mol \cdot dm^{-3}}$ NaCl. On the basis of the results for salt leaching in Table 11, a reasonable aim for residual $^{226}Ra^{2+}$ is between 100 and 200 pCi/g depending on the initial $^{226}Ra^{2+}$. The higher the initial level the higher will be the residual level.

### 6.4.7 Bacterial Leaching

A possible means of leaching $^{226}Ra^{2+}$ from tailings, and perhaps also from soil environment, is through the bacterially catalyzed production of acidity. Thus microorganisms such as Thiobacillus ferrooxidan can catalyze the oxidation of mineral sulphides in the presence of oxygen, yielding sulphate and generating acidic conditions [97]. Such microorganisms have been isolated at Elliott Lake [80] where the tailings contain large amounts of pyrite (present in the original ore). Pyrite can be oxidized via the following reaction sequence [97]:

$$FeS_2 + 3O_2 + 2H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 4H^+$$

$$2Fe^{2+} + O_2 + 4H^+ \xrightarrow{\text{bacteria}} 2Fe^{3+} + 2H_2O$$

$$FeS_2 + 2Fe^{3+} \longrightarrow 3Fe^{2+} + 2S$$

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 4H^+ + 2SO_4^{2-} .$$

The acidic conditions produced would be expected to mobilize (leach) $^{226}Ra^{2+}$ by desorbing it from ion-exchange sites. Since sulphate is also produced, the $^{226}Ra^{2+}$ may be reprecipitated as sulphate.

Lysimeter studies on Elliott Lake tailings by Silver and Ritcey [80] showed that less $^{226}Ra^{2+}$ was mobilized in the presence of iron-oxidizing thiobacilli than when they were absent due to the low solubility of Ra in the presence of sulphate. However, groundwater monitoring conducted at tailings impoundments, both in the United States and Canada, showed that tailings-derived contaminants, including $^{226}Ra^{2+}$, have entered permeable geological deposits beneath the tailings, and are migrating in the groundwater [98-100]. The plumes extend several hundred metres or more from the impoundments. The tailings groundwater was found to be acidic, due to bacterially catalyzed oxidation of pyrite in the near surface tailings. Pyrite oxidation generally occurs within a few metres of the surface of the tailings, and the plumes gradually move downwards through the tailings, mobilizing $^{226}Ra^{2+}$ and high concentrations of iron, aluminum, heavy metals and other radionuclides. This acidic front travels at a rate much slower than the groundwater flow rate; this has been attributed to reactions that neutralize the acidity. These reactions have been summarized by Cherry et al. [101] and include calcite and siderite dissolution. Neutralization leads to the precipitation of minerals and amorphous compounds such as gypsum, amorphous silica, aluminosilicates, and possibly hydrous oxides of iron and manganese. Sampling and analysis [101] of this neutralization zone showed that the radionuclides, including $^{226}Ra^{2+}$, were removed by precipitation, coprecipitation and adsorption. Radium-226 therefore migrates at the rate of advance of the neutralization zone.

Other constituents of tailings appear to be susceptible to metabolism by bacteria. Thus McCready and co-workers [89] have shown that $Ba^{226}(Ra)SO_4$ precipitates are metabolized by sulphate-reducing organisms such as Desulfovibrio vulgaris, resulting in the dissolution of $BaSO_4$, production of $H_2S$ and the release of $^{226}Ra^{2+}$. Whether this is a significant mechanism for the mobilization of $^{226}Ra^{2+}$ is not known. However, it suggests that, over long periods, sulphate precipitates containing $^{226}Ra^{2+}$ may prove unstable, and $^{226}Ra^{2+}$ may be redistributed to other substances. Whether microorganisms can provide an efficient $^{226}Ra^{2+}$ leaching process has not been considered.

## 7. METHODS OF SCRUBBING OR IMMOBILIZING RADIUM

A number of leaching methods for removing radionuclides from soils and waste solids have been proposed and in many cases tested. Also, alternatives to waste-leaching, or scrubbing, methods have been developed, their aim being to immobilize $^{226}Ra^{2+}$ in a form that leaches so slowly that the groundwater will not have $^{226}Ra^{2+}$ levels in excess of the federal and provincial drinking water standards (see Section 2). Many of the techniques for $^{226}Ra^{2+}$ immobilization have been developed for mine-tailings, and may be difficult to adapt for soils.

Treatment of waste waters containing $^{226}Ra^{2+}$ has also received considerable attention, and some methods may prove applicable to the treatment of solutions used to leach radium-containing wastes. For such methods to be of value, they must produce a compact waste form suitable for disposal by methods used for the disposal of other radioactive wastes.

### 7.1 SOIL SCRUBBING METHODS

Four physical scrubbing processes were investigated for the removal of plutonium and americium from contaminated soils at Rocky Flats, U.S.A [102-105].

The first was a simple wet screening process with NaOH at pH = 11. The $Na^+$ and $OH^-$ ions help disperse the clay particles to yield a colloidal suspension. The $OH^-$ ions attach to the clay, yielding negatively charged particles that repel each other. The +35 mesh (> 420 μ) fraction was decontaminated to < 15 pCi/g, and could be returned to the environment. The remaining 30 to 40% remained active and would require permanent disposal.

The second method was attrition scrubbing using a high-pH detergent (Calgon) solution. The soil was scrubbed four times in a rotary-type attrition scrubber. More than 99% of the activity was removed with the fines, which comprised ≈ 20% of the soil.

Attrition scrubbing at low pH employed a solution of 2% $HNO_3$, 0.2% HF, 2% pine oil and 5% Calgon. Typically 84% of the soil could be decontaminated to < 3 pCi/g.

The fourth process took advantage of the anionic surface of the clay particles. A cationic flotation agent, such as an amine, was used to float the clay material in a conventional flotation process.

The scrubbing process at high pH was developed to pilot plant scale, and demonstrated to achieve the goal of 15 pCi/g, for ≈ 88% of the soil volume.

Horton and Albenesius [106] performed laboratory experiments to test the feasibility of separating Pu-contaminated soils (from the Savannah River Plant burial grounds) into Pu-rich and depleted fractions. By a process of water scrubbing and washing, they separated a clay-silt fraction containing ~ 95% of the Pu, but comprising only one-third of the total soil.

## 7.2 IMMOBILIZATION

Many methods have been proposed to prevent transport of $^{226}Ra$ and other radionuclides from uranium mill waste disposal facilities. The method presently used for $^{226}Ra^{2+}$ is to coprecipitate the $^{226}Ra^{2+}$ as $Ba(Ra)SO_4$ by addition of $BaCl_2$. This process yields a very fine precipitate that tends to remain suspended. To induce settling, a number of coagulation and flocculation processes have been developed [17,18,107], with flocculation of $Ba(Ra)SO_4$ being achieved by addition of $FeCl_3$. Pilot plant studies have produced effluent-water levels of total and dissolved $^{226}Ra^{2+}$ within the standards set (10 pCi/$dm^3$ and 3 pCi/$dm^3$, respectively, see Section 2).

Several other methods of preventing $^{226}Ra^{2+}$ transport have also been investigated. These include surrounding the tailings area by clay liners or synthetic polymeric membranes [108-110]. The sealing ability of clays is attributed to the retention of water by their adsorbed cations, which causes swelling. The expanded clay particles fill the voids in the soil and yield very low permeabilities ($10^{-7}$ cm/s). Generally, montmorillonite, the main constituent of bentonite, is responsible for the swelling. Contaminant transport from unlined and clay-lined pits has been modelled by Nelson et al. [111] for a site in Wyoming. They concluded that it was more important to line the bottom of the disposal area than the sides.

A number of methods of fixing uranium tailings has been discussed by Haw et al. [112]. Four commercial fixation processes were studied:

(1) The Krofchak process: sulphuric acid or calcium hydroxide is mixed with siliceous material to form an inert solid.

(2) The AECL bituminization process: dry tailings are mixed with molten asphalt at 125°C and discharged at 165°C.

(3) The Chemfix process: a solid matrix is produced by the reaction of soluble silicates with silicate setting agents, after mixing with tailings.

(4) The IU conversion process: fly ash and lime-bearing materials are mixed with silica-bearing waste minerals to form a disposable final product similar to Portland cement.

The bituminization process gave the best results but is expensive.

Nathwani and Phillips [113] studied the reduction in the $^{226}Ra^{2+}$ leach rate from uranium mine-tailings after solidifying (consolidating) them with cement or cement plus peat and clay. They found that the leaching process could be described by a simultaneous first-order reaction and diffusion model, and that the effectiveness of the consolidation process could be gauged by comparing the magnitude of the effective diffusion coefficients. A reduction of one to two orders of magnitude in the fraction of $^{226}Ra^{2+}$ leached could be achieved. The most effective consolidation mixture was 70% tailings and 30% cement, peat and clay in the ratio 50:30:20.

The leaching of $^{226}Ra^{2+}$ from Beaverlodge, Saskatchewan, tailings was reduced by a factor of > 2000 by a simple sintering process at 1075°C [74]. Dressen et al. [71] have studied the mineralogical changes when tailings were treated at temperatures in the range 500° to 1200°C:

(1) Gypsum disappeared at temperatures below 500°C, anhydrite ($CaSO_4$) being present above 500°C. Anhydrite starts to disappear at temperatures above 1000°C.

(2) Quartz does not change substantially until 1200°C, where about 60% appears to transform to cristobalite (synthetic $SiO_2$) or to calcium silicates.

(3) Clay minerals including illite disappear at 900°C.

(4) Kaolinite seems to disappear at 500°C.

(5) New minerals, possibly plagioclase-type, form at ≈ 900°C, where the clay minerals and albite are disappearing.

(6) The amorphous content increases substantially at 1100°C.

A reduction in radon emanation appeared to coincide with the destruction of the clay materials at temperatures between 700°C and 1000°C. It is possible that $^{226}Ra^{2+}$ becomes incorporated into the calcium silicate and/or calcium aluminosilicates that form around 900°C, which makes its subsequent leaching difficult.

Brown et al. [64] and Fyfe [75] have shown that gypsum and calcite can be converted to apatite at 25°C simply by mixing with substantial amounts of phosphate, and suggested that the apatite crystals ($Ca_5(PO_4)_3(OH)_3$) should immobilize $^{226}Ra^{2+}$ by incorporation into the apatite lattice. They demonstrated that $Ba^{2+}$ was immobilized in apatite and, once incorporated, was very slow to leach.

Ceramics of the general structural types [NZP] and [NTP], typified by the compositions $NaZr_2(PO_4)_3$ and $NaTi_2(PO_4)_3$, may also have some value as waste forms for $^{226}Ra^{2+}$. Thus Roy et al. [114] have studied the incorporation of alkaline earth cations into such materials. They showed that a whole series of divalent cations, including $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$, could be incorporated into compositions such as $M^{II}Zr_4(PO_4)_6$ and $M^{II}Ti_4(PO_4)_6$. Preliminary leaching studies indicated these structures to be very stable. Given the similarities between $^{226}Ra^{2+}$ and $Ba^{2+}$, it is reasonable to assume that $^{226}Ra^{2+}$ can be incorporated into a similar stable ceramic.

## 7.3 REMOVAL OF RADIUM FROM WASTEWATER

Several methods are available for reducing the $^{226}Ra^{2+}$ levels in water to comply with the regulatory standards (see Section 2). Some of these methods have recently been reviewed by Kosarek [16] and will be discussed briefly here.

(a) Selective membrane mineral extraction methods use membranes (usually proprietary) and a chemical process to remove $^{226}Ra^{2+}$. This method can produce an aqueous stream containing $< 5$ pCi/dm$^3$ providing the input water contains $< 1500$ pCi/dm$^3$. The radionuclides are contained in a discharged slurry.

(b) Reverse osmosis is a membrane separation technique in which a pressure greater than the solution's inherent osmotic pressure is applied across a semi-permeable membrane. The radionuclides are discharged in a brine solution, and an aqueous stream containing $< 5$ pCi/dm$^3$ can be obtained from input water containing up to 750 pCi/dm$^3$. Subramanian and Sastri [115] have studied the separation of $^{226}Ra^{2+}$ from dilute aqueous solutions using porous cellulose acetate membranes (Osmonics Inc.). They found that $> 99\%$ of the $^{226}Ra^{2+}$ could be removed from a feed solution containing 750 pCi/dm$^3$. However, the chloride, nitrate and sulphate salts gave different results: sulphate separation was higher than chloride which was higher than nitrate. This was attributed to the presence of $RaSO_4$ ion-pairs (see Table 5), in the solution. The impact of ion-pairs on separation by reverse osmosis had been demonstrated previously by the same authors.

(c) Inorganic ion-exchange materials, such as Decalso (synthetic zeolite), clinoptilolite (natural zeolite) and barite ($BaSO_4$), and also organic cation-exchange resins, can achieve 95% $^{226}Ra^{2+}$ removal efficiency in lime-neutralized water, i.e. an effluent water with 5 $pCi/dm^3$ can be achieved from feed water containing 100 $pCi/dm^3$. However, $^{226}Ra^{2+}$ adsorption from acid waste waters was inefficient, i.e. $< 15\%$ for clinoptilolite [116].

(d) Adsorption using waste microbial biomass is a relatively new technique for sequestering $^{226}Ra^{2+}$ [117]. Tsezos and Keller [118] have shown that such adsorbents can tolerate higher $^{226}Ra$ loadings than most conventional organic or inorganic ion exchangers. For the biomass of Penicillium chrysogenum, loadings up to an order of magnitude greater than that attainable with natural zeolite can be achieved. Adsorption capacity is a function of solution concentration and pH, optimum $^{226}Ra^{2+}$ adsorption being achieved in the pH range 7-10. Adsorption at low pH (pH = 2) is very limited.

## 8. SUMMARY

The radiological and chemical properties of $^{226}Ra^{2+}$ have been reviewed. The known chemical properties of $^{226}Ra^{2+}$ fit nicely into the trends of the alkaline earth series. Thus unknown properties and behaviour of $^{226}Ra^{2+}$ can often be inferred, and to a first approximation it behaves similarly to barium.

The processes that influence $^{226}Ra^{2+}$ mobility in soils have been discussed. Thus $^{226}Ra^{2+}$ adsorbs on quartz and amorphous ferric oxyhydroxide in the manner expected for cation adsorption on metal oxide surfaces. It adsorbs on clay minerals such as kaolinite and appears to be exchangeable with other cations. The radium-226 cation, which has the smallest hydrated radius of the alkaline earths, appears to be the most strongly adsorbed, the order being

$$Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} .$$

A major influence in determining $^{226}Ra^{2+}$ mobility in soils appears to be the organic content; several studies have shown that the amount of $^{226}Ra^{2+}$ retained by soils is directly related to their organic content. Coprecipitation of $^{226}Ra^{2+}$ appears to be frequent, e.g. with $BaSO_4$, $CaSO_4 \cdot 2H_2O$, $(K,Na)Fe_3(SO_4)_2(OH)_6$, and $KMn^{2+}Mn^{4+}_{7.25}O_{16} \cdot H_2O$. Due to the lack of experimental data, it is not possible to state which of adsorption, ion exchange, or coprecipitation has the biggest influence on $^{226}Ra^{2+}$ retention by soils. A similar lack of information exists for $^{226}Ra^{2+}$ leaching from soils. Radium-226 appears to be leachable via ion-exchange processes, but not in the presence of $Ca^{2+}$ and $Mg^{2+}$.

The largest potential source of $^{226}Ra^{2+}$ in the environment is the leaching of uranium mine-tailings. An attempt has been made to specify how $^{226}Ra^{2+}$ is fixed in the mine-tailings, and how its release is affected by various leaching solutions. The leaching results have been tabulated and the success or failure of the various processes interpreted in terms of the standards discussed in Section 2 for $^{226}Ra^{2+}$ levels. The lowest residual $^{226}Ra^{2+}$ levels (30-50 pCi/g) were generally achieved with a hot, strong-acid leach followed by a further leach with a chelating agent such as EDTA [5]. For salt leaching a reasonable aim for residual $^{226}Ra^{2+}$ is between 100 and 200 pCi/g, depending on the initial level. In general the higher the initial level the higher the residual level.

Several published methods for scrubbing or immobilizing $^{226}Ra^{2+}$ have been reviewed. The soil-scrubbing techniques used to remove Pu and Am from the soils at Rocky Flats have been fairly successful but have not been investigated for other radionuclides. Of the efforts made to chemically "fix" $^{226}Ra^{2+}$ the method of thermal stabilization has been the most successful. Incorporation into a growing apatite crystal is a proposed method with potential, although it has not so far been tried with $^{226}Ra^{2+}$.

Several methods of removing $^{226}Ra^{2+}$ from wastewater streams have been discussed. These include selective membrane extraction, reverse osmosis, use of ion exchangers and adsorption onto waste microbial biomass. The last method appears to be the most successful in removing large amounts of $^{226}Ra^{2+}$.

## 9. RECOMMENDATIONS

Since only a few studies have been made of $^{226}Ra^{2+}$ mobility in soils, or of the leaching of $^{226}Ra^{2+}$ from soils, it is difficult to recommend a leaching strategy. However, if the results of tailings leaching studies can be taken as applicable to soil leaching then the following points can be made.

(i) For material that is originally highly contaminated (> 500 pCi/g), leaching with strong acid followed by EDTA will produce the lowest residual $^{226}Ra^{2+}$ level, though this level is not likely to be lower than 30-50 pCi/g.

(ii) For material containing lower levels of initial contamination a similar leaching treatment will probably produce a residual $^{226}Ra^{2+}$ level < 30 pCi/g.

(iii) It is recommended that on-site leaching be considered for soils of relative low activity, but that highly active soils be removed for treatment elsewhere or for burial at a more acceptable site.

(iv) The scrubbing methods developed at Rocky Flats for the decontamination of Pu- and Am-containing soils may be adaptable to the scrubbing of $^{226}Ra$-containing soils, and should be investigated further. The process is designed to separate contaminated and non-contaminated soil fractions and does not appear dependent on the properties of the radionuclide. Consequently it may be a generally useful method.

(v) If a soil-scrubbing method is to be developed, a series of systematic studies of $^{226}Ra^{2+}$ retention by, and mobility in, soils should be undertaken. The effect of additives on $^{226}Ra^{2+}$ mobility should be tested.

(vi) These studies should be accompanied by more fundamental studies designed to investigate the mechanism of $^{226}Ra^{2+}$ adsorption on well-characterized minerals and clays. In particular, $^{226}Ra^{2+}$ adsorption by expandable clays such as montmorillonite should be undertaken.

(vii) A common mode of $^{226}Ra^{2+}$ fixation is coprecipitation with insoluble sulphates such as $BaSO_4$ and $CaSO_4 \cdot 2H_2O$. These sulphates appear susceptible to bacterially catalyzed decomposition. Such processes should be studied since they offer a possible means of removing $^{226}Ra^{2+}$ from precipitates that are often difficult to redissolve. Also it is possible that bacterial processes in general may offer a slow but effective leaching method.

(viii) If the movement of $^{226}Ra^{2+}$ in geochemical environments is to be understood and modeled, it is necessary to study its mobility relative to that of better studied radionuclides, e.g. $^{137}Cs^{+}$, $^{90}Sr^{2+}$, and other radionuclides in the uranium decay series.

(ix) The claim that apatite minerals can be grown on calcite, and other precipitates likely to have incorporated $^{226}Ra^{2+}$ should be studied, since this may offer a cheap but effective method of immobilizing $^{226}Ra^{2+}$.

(x) The product of any leaching process will be a $^{226}$Ra-contaminated solution. Treatment of this solution for ultimate disposal poses a problem. Two processes appear to have the potential for providing storage media: adsorption onto waste microbial biomass, and incorporation into stable ceramics such as $M^{II}Zr_4(PO_4)_6$ or $M^{II}Ti_4(PO_4)_6$. The incorporation of $^{226}Ra^{2+}$ into such waste forms should be studied.

(xi) Thermal stabilization of material that is difficult to leach should be considered.

# REFERENCES

1. Hickling Partners Inc., "Managing Low Level Radioactive Wastes: Proposed Responsibilities and Management Structure", Report to Energy, Mines and Resources Canada (1981).

2. D.H. Charlesworth, "Low- and Intermediate-Level Waste Management Practices in Canada", Atomic Energy of Canada Limited Report, AECL-7629 (1982).

3. James F. MacLaren Limited, "Production and Accumulation of Low-Level Radioactive Waste in Canada", Report to Energy Mines and Resources Canada, Atomic Energy Control Board, Canada, and Environment Canada (1982).

4. James F. MacLaren Limited, "Radiation Surveys of the McClure Crescent Area of Scarborough, Ontario", Interim Report to the Atomic Energy Control Board, Canada (1981).

5. A.D. Ryon, F.J. Hurst and F.G. Seeley, "Nitric Acid Leaching of Radium and Other Significant Radionuclides from Uranium Ores and Tailings", Oak Ridge National Laboratory Report, ORNL-TM-5944 (1977).

6. L.L. Ames and D. Rai, "Radionuclide Interactions with Soil and Rock Media", U.S. Environmental Protection Agency Report No. 520/6-78-007, Vol. 1 (1978).

7. M.I. Sheppard, "The Environmental Behaviour of Radium", Atomic Energy of Canada Limited Report, AECL-6796 (1980).

8. W.S. Osburn, "Primordial Radionuclides: Their Distribution, Movement and Possible Effect Within Terrestial Ecosystems", Health Phys. 11, 1275 (1965).

9. J.A.S. Adams and W.M. Lowder, The Natural Radiation Environment, W. Chicago Press, Chicago, 1964, p. 949.

10. F.F. Koczy, "The Natural Radioactive Series in Organic Material", in Radioecology, Proceedings of 1st National Symposium, Colorado, 1961 September. V. Schultz and A.W. Klement, Jr. (eds.), Reinhold, New York, 1963, pp. 611-613.

11. International Commission on Radiological Protection (ICRP), Report of Committee II on Permissible Dose for Internal Radiation, ICRP, 1959.

12. D. Moffett and A.J. Vivyurka, "Control of Radium-226 Releases in Liquid Effluents. Management, Stabilization, and Environmental Impact of Uranium Mill Tailings", in Proceedings of the Nuclear Energy Agency Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico, 1978 July 24-28. OECD Nuclear Energy Agency, Paris, ISBN 92-64-01849-2, 1978, p. 259-260.

13. C.R. Phillips and Y.C. Poon, "Status and Future Possibilities for the Recovery of Uranium, Thorium, and Rare Earths from Canadian Ores, with Emphasis on the Problem of Radium", Miner. Sci. Eng. 12, 53 (1980).

14. D.W. Averill, P.M. Huck, G.H. Kassakhian, D. Moffett and R.T. Webber, "Data Base Development for the Design of a Radium-226 Removal Process", J. Water Poll. Contr. Fed. 53(7), 1233 (1981).

15. Ministry of the Environment, "Guidelines and Criteria for Water Quality Management in Ontario", Toronto, Ontario, 1967, p. 22.

16. L.J. Kosarek, "Radionuclide Removal from Water", Environ. Sci. Tech. 13(5), 522 (1979).

17. D. Moffett, L. Whittle, D. Averill, G.H. Kassakhian and R. Webber, "Radium-226 Removal from a Uranium Mill Effluent-Physical/Chemical Treatment Process Development Studies", *Can. Mining Met.* Bull. 73, 148 (1980).

18. J.W. Schmidt and D.W. Averill, "Development of a Physical/Chemical Process for the Removal of Radium-226 from Uranium Mining Effluents", in Proceedings of Seminar on Comparative Ecotoxicity of Uranium Mining and Milling Emissions, Saskatchewan Research Council, Saskatoon, 1981, p. 155.

19. S.R. Borrowman and P.T. Brooks, "Radium Removal from Uranium Ores and Mill Tailings", Bureau of Mines Report of Investigations 8099, Salt Lake City Metallurgy Research Centre, 1975.

20. M.C. Riordan, M.J. Duggan, W.B. Rose and G.F. Bradford, "The Radiological Implications of Using By-Product Gypsum as a Building Material", National Radiological Protection Board, United Kingdom, 1972.

21. M.K. Afanasev and E.M. Krisyuk, Standards for Natural Radioactive Substances in Building Materials, Leningrad Res. Inst. Radiat. Hyg. 1973, p. 387.

22. U.S. Congress, "Use of Uranium Mill Tailings for Construction Purposes", Hearings before Subcommittee on Raw Materials, of Joint Committee on Atomic Energy, 92nd Congress, 1st Session, 1971, p. 226.

23. I.J. Itzkovich and G.M. Ritcey, "Removal of Radionuclides from Process Streams - A Review", Canada Centre for Mineral and Energy Technology, CANMET Report 79-21 (1979).

24. K.W. Bagnall, Radium, Chemistry of the Rare Radioelements, Academic Press, New York, 1957, Chapter 11, pp. 131-149.

25. S.B. Schwind and F.E. Croxton, "Radium. A Bibliography of Unclassified Literature", U.S. Atomic Energy Commission Report, TID-363 (1950).

26. J. Sedlet, "Radon and Radium", in Part II of Treatise on Analytical Chemistry, I.M. Kolthoff and P.J. Elving (eds.), Interscience, New York.

27. H.W. Kirby and M.L. Salutsky, "The Radiochemistry of Radium", U.S. Atomic Energy Commission Report, NAS-NS 3057 (1964).

28. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, A Comprehensive Text, 1st Edition, Interscience, New York, 1962, Chapter 7, p. 206.

29. G. Pass, Ions in Solution (3). Inorganic Properties, Oxford Chemistry Series, Clarendon Press, Oxford, 1973, pp. 40-44.

30. L.G. Sillen and A.E. Martell, "Stability Constants of Metal-Ion Complexes", Special Publication No. 17, The Chemical Society, London, 1964.

31. E.R. Nightingale Jr., "Phenomenological Theory of Ion Solvation. Effective Radii of Hydrated Ions", J. Phys. Chem. 63, 1381 (1959).

32. P. Benes, M. Obdrzalek and M. Cejcharova, "The Physicochemical Forms of Traces of Radium in Aqueous Solutions Containing Chlorides, Sulphates and Carbonates", Radiochem. Radioanal. Lett. 50(4), 227 (1982).

33. V.W. Kumok, "Use of the System of Ligand Parameters for Predicting the Stability of Complexes of Europium (II), Radium, Actinium and Promethium", Soviet Radiochem. 20(5), 590 (1978).

34. J.S. Nathwani, "Disposal of Uranium Mill Tailings: A Study of Leaching of Radium-226 and Its Fate in the Environment", Ph.D. Thesis, Univ. of Toronto (1978).

35. V.B. Parker, D.D. Wagman and W.H. Evans, "Selected Values of Chemical Thermodynamic Properties", U.S. Dept. of Commerce, National Bureau of Standards Interim Report 75-968 (1971).

36. F. Weigel, Radium, Gmelin Hanbuch der Anorganischen Chemie, Springer-Verlag, Berlin, 1977, p. 435.

37. A.C. Riese, "Adsorption of Radium and Thorium onto Quartz and Kaolinite: A Comparison of Solution/Surface Equilibria Models", Ph.D. Thesis, Colorado School of Mines (1983).

38. S. Toshima, "Calcium, Strontium, Barium and Radium", in Encyclopedia of Electrochemistry of the Elements, A.J. Bard (ed.), Marcel Dekker, New York, 1973, Vol. 1, p. 405.

39. G. Eisenmann, "Cation Selective Glass Electrodes and Their Mode of Operation", J. Biophys. 2, 259 (1962).

40. G.A. Parks, "Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals. Isoelectric Point and Zero Point of Charge", in Adv. Chem. Ser. 67, Equilibrium Concepts in Natural Water Systems, W. Stumm (ed.), Amer. Chem. Soc., Washington, D.C., 1967, p. 121.

41. D.G. Kinniburgh and M.L. Jackson, "Cation Adsorption by Hydrous Metal Oxides and Clays", in Adsorption of Inorganics at Solid-Liquid Interfaces, M.A. Anderson and A.J. Rubin (eds.), Ann Arbor Science, 1981, Chapter 3, pp. 98-99.

42. G.R. Wiese, R.O. James and T.W. Healy, "Discreteness of Charge and Solution Effects in Cation Adsorption at the Oxide/Water Interface", Disc. Faraday Soc. 52, 302 (1971).

43. J.A. Davis, R.O. James and J.O. Leckie, "Surface Ionization and Complexation at the Oxide-Water Interface", J. Colloid Interface Sci. 63, 480 (1978).

44. J.A. Davis and J.O. Leckie, "Surface Ionization and Complexation at the Oxide-Water Interface. III. Adsorption of Anions", J. Colloid Interface Sci. 74, 32 (1980).

45. J.W. Murray, "The Interaction of Metal Ions at the Manganese Dioxide Solution Interface", Geochim. Cosmochim. Acta 39, 505 (1975).

46. A. Breeuwsma and J. Lyklema, "Interfacial Electrochemistry of Hematite ($\alpha$-$Fe_2O_3$)", Disc. Faraday Soc. 52, 324 (1971).

47. L.L. Ames, J.E. McGarrah, B.A. Walker and P.F. Salter, "Uranium and Radium Sorption on Amorphous Ferric Oxyhydroxide", Chem. Geol. 40, 135 (1983).

48. R.O. James and T.W. Healy, "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. III. A Thermodynamic Model of Adsorption", J. Colloid Interface Sci. 40, 65 (1972).

49. A.W. Fordham, "The Location of $^{55}Fe$, $^{85}Sr$, $^{125}I$ Sorbed by Kaolinite and Dickite Particles", Clays Clay Miner. 21, 175 (1973).

50. A.W. Pommer, "Relation Between Dual Acidity and Structure of H-Montmorillonite", U.S. Geological Survey Professional Paper 386-C (1963).

51. D. Carroll, "Ion-Exchange in Clays and Other Minerals", Geol. Soc. Amer. Bull. 70, 749 (1960).

52. D. Carroll, Rock Weathering, Plenum Press, New York, 1970.

53. M. Schnitzer and S.V. Khan, Humic Substances in the Environment, Marcel Dekker, New York, 1972.

54. W. Stumm and J.J. Morgan, Aquatic Chemistry, John Wiley and Sons, New York, 2nd edition, 1981.

55. J.H. Reuter and E.M. Perdue, "Importance of Heavy Metal-Organic Matter Interactions in Natural Waters", Geochim. Cosmochim. Acta 41, 325 (1977).

56. C.E. Marshall, The Physical Chemistry and Mineralogy of Soils, John Wiley and Sons, New York, 1964.

57. N.A. Titayeva, "Association of Radium and Uranium with Peat", Geochimiya 12, 1493 (1977).

58. G.V. Rusanova, "On the Problem of Studying the Leaching Processes and Migration of Radium in Soils", Sov. Soil Sci. 9, 85 (1962).

59. J.S. Nathwani and C.R. Phillips, "Rates of Leaching of Radium from Contaminated Soils: An Experimental Investigation of Radium-Bearing Soils from Port Hope, Ontario", Water, Air, and Soil Pollut. 9, 453 (1978).

60. V. Prokhorov (1966), see Nathwani reference 34.

61. I.L. Ophel, C.D. Fraser and J.M. Judd, "Strontium Concentration Factors in Biota and Bottom Sediments of a Freshwater Lake", in Proceedings of International Symposium on Radioecology Applied to the Protection of Man and His Environment, Rome, 1971, p. 509.

62. G.E. Grisak and R.E. Jackson, "An Appraisal of the Hydrogeological Processes Involved in Shallow Subsurface Radioactive Waste Management in Canadian Terrain", Fisheries and Environment Canada, Scientific Series No. 84, Ottawa (1978).

63. R.C. Routson, "Review of Studies on Soil-Waste Relationships on the Hanford Reservation from 1944-1967", Battelle Pacific Northwest Laboratories Report, BNWL-1464 (1973).

64. J.R. Brown, W.S. Fyfe, F. Murray and B.I. Kronenberg, "Immobilization of U-Th-Ra in Mine Wastes", Can. Mining J. 102(3), 71 (1981).

65. D. Moffett, D. Zahary, M.C. Campbell and J.C. Ingles, "CANMET's Environmental and Process Research on Uranium", Canada Centre for Mineral and Energy Technology, CANMET Report TI-53 (1977).

66. H.C. Granger, "Radium Migration and Its Effect on the Apparent Age of Uranium Deposits at Ambrosia Lake, New Mexico", U.S. Geological Survey Professional Paper 475-B, B60 (1963).

67. H.C. Granger, E.S. Santos, B.G. Dean and F.B. Moore, "Sandstone-Type Uranium Deposits at Ambrosia Lake, New Mexico", Econ. Geol. 56(7), 1179 (1961).

68. E.B. Fowler, E.H. Essington and W.L. Polzer, "Interactions of Radioactive Wastes with Soils - A Review", Los Alamos Scientific Laboratory Report, LA-UR-79-2910 (1979).

69. I.N. Verkovskaja, P.P. Vavilov and V.I. Maslov, "The Migration of Natural Radioactive Elements Under Natural Conditions and Their Distribution According to Biotic and Abiotic Environmental Components", in Radioecological Concentration Processes, Proceedings of International Symposium, Stockholm, 1966 April, B. Aberg and F.P. Hungate (eds.). Pergamon, Oxford, 1967, pp. 313-328.

70. J.M. Skeaff, "Distribution of Radium-226 in Uranium Tailings", Canada Centre for Mineral and Energy Technology Report, MRP/MSL 76-137(J) (1976).

71. D.R. Dressen, J.M. Williams and E.J. Cokal, "Thermal Stabilization of Uranium Mill Tailings", Los Alamos Scientific Laboratory Report, LA-UR-81-2734 (1981).

72. S. Kaiman, "Mineralogical Examination of Old Tailings From the Nordic Lake Mine, Elliott Lake, Ontario", Canada Centre for Mineral and Energy Technology, CANMET Report, ERP/MSL 77-190(IR) (1977).

73. S. Kaiman, "Mineralogical Examination of Current Elliott Lake Uranium Mill Tailings", Canada Centre for Mineral and Energy Technology Report, MRP/MSL 78-85(IR) (1978).

74. D.R. Wiles, "The Leaching of Radium from Beaverlodge Tailings", in Proceedings of the Nuclear Energy Agency Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico, 1978 July 24-28. OECD Nuclear Energy Agency, Paris, ISBN 92-64-01849-2, 1978, p. 245.

75. W.S. Fyfe, "Immobilization of U-Th-Ra in Mine Wastes by Mineralization", Geoscience Research Grant Program, Summary of Research 1978-79, E.G. Pye (ed.), (1979), pp. 79-83.

76. F.G. Seeley, "Problems in the Separation of Radium from Uranium Ore Tailings", Hydromet. 2, 249 (1977).

77. D.M. Levins, R.K. Ryan and K.P. Strong, "Leaching of Radium from Uranium Tailings", in Proceedings of the Nuclear Energy Agency Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico, 1978 July 24-28. OECD Nuclear Energy Agency, Paris, ISBN 92-64-01849-2, 1978, p. 271.

78. S.D. Shearer and G.F. Lee, "Leachability of Radium-226 from Uranium Mill Solids and River Sediments", Health Phys. 10, 217 (1964).

79. J.S. Nathwani and C.R. Phillips, "Rate-Controlling Processes in the Release of Radium-226 from Uranium Mill Tailings. I - Leaching Study", Water, Air and Soil Pollut. 11, 301 (1979).

80. M. Silver and G.M. Ritcey, "A Simulation of the Effects of Bacteria, Organics and Salt Solutions on Uranium Mine Mill Tailings from Elliott Lake, Ontario", Waste Treatment and Utilization. Theory and Practice of Waste Management, Vol. 2, Pergamon Press, Oxford, 1982, p. 489.

81. M. Silver and J.E. Anderson, "Removal of Radium from Elliot Lake Uranium Tailings by Salt Washing", Water Pollut. Res. J. Can. 15, 217 (1981).

82. B. Havlik, J. Grafova and B. Nycova, "Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams, I The Effect of Different pH of Surface Waters", Health Phys. 14, 417 (1968).

83. B. Havlik, J. Grafova and B. Nycova, "Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams, II The Effect of Different Chemical Composition of Surface Waters", Health Phys. 14, 423 (1968).

84. R.K. Ryan and D.M. Levins, "Extraction of Radium from Uranium Tailings", Can. Inst. Mining Met. Bull. 73, 126 (1980).

85. J.E. Hawley, "Use of Phosphate Compounds to Extract Thorium-230 and Radium-226 from Uranium Ore and Tailings", Hazen Research Inc. Report, PB81219503 (1980).

86. S.G. Yagnik, M.H.I. Baird and S. Banerjee, "An Investigation of Radium Extraction from Uranium Mill Tailings", Hydromet. 7, 61 (1981).

87. J.S. Nathwani and C.R. Phillips, "Rate Controlling Processes in the Release of Radium-226 from Uranium Mill Tailings. II Kinetic Study", Water, Air, and Soil Pollut. 11, 309 (1979).

88. P. Benes, J. Sedlacek, F. Sebesta, R. Sandrik and J. John, "Method of Selective Dissolution for Characterization of Particulate Forms of Radium and Barium in Natural and Waste Waters", Water Res. 15(12), 1299 (1981).

89. R.G.L. McCready, C.J. Bland and D.E. Gonzales, "Preliminary Studies on the Chemical, Physical and Biological Stability of Ba(Ra)$SO_4$ Precipitates", Hydromet. 5, 109 (1980).

90. N. Valverde and C. Wagner, "Investigations on the Rate of Dissolution of Metal Oxides in Acidic Solutions with Additions of Redox Couples and Complexing Agents", Ber. Bunsenges. Phys. Chem. 80, 330 (1976).

91. J.W. Diggle, "Dissolution of Oxide Phases", in Oxides and Oxide Films, Vol. 2, J.W. Diggle (ed ), Marcel Dekker, New York, 1973, p. 281.

92. S. Feigenbaum and I. Shainberg, "Dissolution of Illite - A Possible Mechanism of Potassium Release", Soil Sci. Soc. Amer. Proc. 39, 985 (1975).

93. M. Mehmel, "Ab-und Umbau am Biotit", Chemie der Erde 11, 307 (1937).

94. C.B. Roth, M.L. Jackson, J.M. de Villiers and V.V. Volk, "Surface Colloids on Micaceous Vermiculite", Trans. Int. Soc. Soil Sci. (Aberdeen) Comm II/IV, 217 (1966).

95. J. Rubio and E. Matijevic, "Interactions of Metal Hydrous Oxides with Chelating Agents. I Ferric Hydroxide, β-FeOOH-EDTA", J. Coll. Interface Sci. 68, 408 (1979).

96. H-C. Chang and E. Matijevic, "Interactions of Metal Hydrous Oxides with Chelating Agents. IV Dissolution of Hematite", J. Coll. Interface Sci. 92, 479 (1983).

97. D.G. Lundgren and M. Silver, "Ore Leaching by Bacteria", Ann. Rev. Microbiol. 34, 263 (1980).

98. R.D. Blair, J.A. Cherry, T.P. Lim and A.J. Vivyurka, "Groundwater Monitoring and Contaminant Occurrence at an Abandoned Tailings Area, Elliott Lake, Ontario", 1st International Conference on Uranium Mining Waste Disposal, Vancouver, 1980.

99. J.A. Cherry, R.J. Blackport, R.D. Blair, N. Dubrovsky, R.W. Gillham, T.P. Lim, D. Murray and D. Smythe, "Subsurface Hydrology and Geochemical Evolution of Abandoned Pyrite Tailings in the Elliott Lake Uranium District", in Proceedings 3rd Symposium on Uranium Mill Tailings Management, Colorado State University, Fort Collins, 1980 Nov., p. 353.

100. S. Feenstra, R.D. Blair, J.A. Cherry, J.L. Chalcravatti and E. LaRocque, "Hydrogeochemical Investigation of Two Inactive Tailings Areas in the Elliott Lake Uranium District, Ontario, Canada", ibid p. 367.

101. J.A. Cherry, T.A. Shepherd and K.A. Morin, "Chemical Composition and Geochemical Behaviour of Contaminated Groundwater at Uranium Tailings Impoundments", presented at the American Society of Mechanical Engineers-American Institute of Mining, Metallurgical and Petroleum Engineers Annual Meeting, Dallas, 1982 Feb.

102. R.L. Olsen, J.A. Hayden, C.E. Alford, R.L. Kochen and J.R. Stevens, "Soil Decontamination at Rocky Flats", Rockwell International Corporation Report, RFP-2901 (1979).

103. J.E. Garnett, D.L. Mitchell and P.T. Faccini, "Initial Testing of Pilot Scale Equipment for Soil Decontamination", Rockwell International Corporation Report, RFP-3022 (1980).

104. D.W. Rutherford and J.R. Stevens, "Sampling Design for Use by the Soil Decontamination Project", Rockwell International Corporation Report, RFP-3163 (1981).

105. J.D. Navratil and R.L. Kochen, "Decontamination of Soil Containing Plutonium and Americium", Rockwell International Corporation Report, RFP-3139 (1982).

106. J.H. Horton and E.L. Albenesius, "Volume Reduction of Plutonium-Contaminated Soil", Nucl. Technol. 30, 86 (1976).

107. N.W. Schmidtke, D. Averill, D.N. Bryant, P. Wilkinson and J.W. Schmidt, "Removal of $^{226}$Ra from Tailings Pond Effluents and Stabilization of Uranium Mine Tailings - Bench and Pilot Scale Studies", in Proceedings of Nuclear Energy Agency Seminar on Management, Stabilization and Environmental Impact of Uranium Mill Tailings, Albuquerque, New Mexico, 1978 July 24-28. OECD Nuclear Energy Agency, Paris, ISBN 92-64-01849-2, 1978, p. 299.

108. R.E. Williams, "Control and Prevention of Seepage from Uranium Mill Waste Disposal Facilities", ibid, p. 287.

109. R.V. Osborne, "Optimizing Radiation Protection in the Management of Uranium Mill Tailings", presented at the International Symposium on Management of Wastes from Uranium Mining and Milling, Albuquerque, New Mexico, 1982 May.

110. R.B. Dodds, "Control of Seepage of Radium-226 Using an Alluvial Grout Curtain", in Proceedings of Symposium on Uranium Mill Tailings Management, Fort Collins, U.S.A., p. 245 (1979).

111. R.W. Nelson, A.E. Reisenauer and G.W. Gee, "Model Assessment of Contaminant Seepage from Buried Uranium Mill Tailings", in Proceedings of 1st International Conference on Uranium Mine Wastes. American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA, 1980, p. 245.

112. V.A. Haw, G.M. Ritcey, J.M. Skeaff, N. Dave and M. Silver, "Uranium Tailings Research at the Canada Centre for Mineral and Energy Technology (CANMET)", Atomic Energy of Canada Limited Report, AECL-7764 (1982).

113. J.S. Nathwani and C.R. Phillips, "Leachability of $^{226}$Ra from Uranium Mill Tailings Consolidated with Naturally Occurring Materials and/or Cement. I Empirical Analysis. II Analysis Based on Mass Transport Equations", Water, Air, and Soil Pollut. 14, 379,389 (1980).

114. R. Roy, L.J. Yang, J. Alamo and E.R. Vance, "A Single Phase ([NZP]) Ceramic Radioactive Waste Form", presented at Symposium on Scientific Basis for Nuclear Waste Management, Boston, MA, 1982 Nov.

115. K.S. Subramanian and V.S. Sastri, "Reverse Osmosis Separation of Radium from Dilute Aqueous Solutions", Sep. Sci. Tech. 15(2), 145 (1980).

116. W.D. Arnold and D.J. Crouse, "Radium Removal from Uranium Mill Effluents with Inorganic Ion Exchangers", Ind. and Eng. Chem. Process Des. Devel. 4(3), 333 (1965).

117. H. Prochazka, K. Stamberg, R. Jilek, J. Fuska and J. Katzer, "Decontamination of Uranium-Mine Waste Water from Ra by Means of Biosorbent", in Proceedings of International Conference on Physics in Industry. Pergamon Press, Oxford, 1976, p. 531.

118. M. Tsezos and D.M. Keller, "Adsorption of Radium-226 by Biological Origin Absorbents", Biotech. and Bioeng. 25(1), 201 (1983).

## TABLE 1

## RADIUM-226 LEVELS IN SAMPLES OF PORT HOPE SOIL COMPARED TO LEVELS IN URANIUM MINE-TAILINGS

| Location | $^{226}$Ra pCi/g |
|---|---|
| A. Alexander Street<br>(fine black ash) | 220 |
| B. Strachan Ravine<br>(greyish white ash) | 74 000 |
| C. Brewery Pond<br>(red/brown slag & soil) | 3 500 |
| D. Pine Street Extension<br>(black topsoil) | 180 000 |
| E. Rollins Ravine | |
| (grey sand) | 15 |
| (white chalk/clay) | 1 900 |
| (composite) | 150 |
| F. Northern Ontario<br>Mine-Tailings | 200-800 [22] |
| G. Beaverlodge, Saskatchewan<br>Tailings | 170-1 700 [73] |
| H. Australian Mine-Tailings | 700-5 200 [76] |

## TABLE 2

## SOLUBLE SALTS OF RADIUM [26] AT 20°C

| Salt | Solubility g/100 g $H_2O$ |
|---|---|
| $RaCl_2$ | 24.5 |
| $(BaCl_2)$ | (30.7) |
| $RaBr_2$ | 70.6 |
| $Ra(NO_3)_2$ | 13.9 |

## TABLE 3

## SOLUBILITY PRODUCTS (LOG $K_{SP}$) OF ALKALINE EARTH CATIONS WITH COMMON ANIONS [30]

| | Sulphate | Carbonate | Phosphate ($PO_4^{3-}$) | Phosphate ($HPO_4^{2-}$) |
|---|---|---|---|---|
| $Mg^{2+}$ | - | -7.46 | -23.77 | - |
| $Ca^{2+}$ | -4.625 | -8.03 | -28.70 | -6.66 |
| $Sr^{2+}$ | -6.55 | -8.80 | -27.39 | -7.06 |
| $Ba^{2+}$ | -10.00 | -8.31 | -22.47 | -7.04 |
| $Ra^{2+}$ | -10.37 | - | - | - |

N.B. These values quoted from reference 30 are not necessarily the most accurate, but are representative of the range of published values. Most values are for 20°C or 25°C and zero ionic strength.

## TABLE 4

## IONIC RADII OF ALKALINE EARTH CATIONS [31]

| Ion | Ionic Radii (Å)* | | Ratio of Charge to Crystal Radius |
|---|---|---|---|
| | Crystal | Hydrated | |
| $Be^{2+}$ | 0.31 | 4.59 | 6.45 |
| $Mg^{2+}$ | 0.65 | 4.28 | 3.01 |
| $Ca^{2+}$ | 0.99 | 4.12 | 2.02 |
| $Sr^{2+}$ | 1.13 | 4.12 | 1.77 |
| $Ba^{2+}$ | 1.35 | 4.04 | 1.48 |
| $Ra^{2+}$ | 1.52 | 3.98 | 1.32 |

*1Å = 0.1 nm

## TABLE 5

## STABILITY CONSTANTS (LOG $K_1$)* FOR COMPLEXES OF GROUP IIA CATIONS WITH INORGANIC ANIONS

| | $F^{-}$(a) | $Cl^{-}$(a) | $SO_4^{2-}$ | $CO_3^{2-}$ | $HPO_4^{2-}$ |
|---|---|---|---|---|---|
| $Mg^{2+}$ | 1.8 | 0.6 | 2.27(b) | 3.4(b) | 2.50(b) |
| $Ca^{2+}$ | 1.0 | - | 2.28(b) | 3.2(b) | 2.70(b) |
| $Sr^{2+}$ | - | - | 2.55(c) | - | |
| $Ba^{2+}$ | 0.45 | -0.13 | 2.30(c) | - | |
| $Ra^{2+}$ | - | - | 2.43(c) | 2.48(c) | |

$*K_1 = [MA]/[M^{2+}][A^{n-}]\ mol^{-1}\cdot dm^3$
where [ ] denote concentrations.

(a) Reference 29 (conditions not given)

(b) Reference 30 (T = 25°C; Ionic Strength (I) = 0)

(c) Reference 32 (T = 25°C; I = 0)

## TABLE 6

## STABILITY CONSTANTS (LOG $K_1$)* FOR COMPLEXES OF GROUP IIA CATIONS WITH ORGANIC LIGANDS

| | Oxalate | Tartrate[(a)] | Citrate[(b)] | EDTA[(c)] | DTPA[(c,d)] |
|---|---|---|---|---|---|
| $Mg^{2+}$ | 3.43 | 1.36 | 3.2 | 9.12 | - |
| $Ca^{2+}$ | 3.00 | 1.80<br>(2.80) | 3.15 | 11.0 | 10.63 |
| $Sr^{2+}$ | 2.54 | 1.94 | 2.70 | 8.80 | 9.68 |
| $Ba^{2+}$ | 2.31 | 1.62<br>(2.54) | 2.54 | 7.78 | 8.63 |
| $Ra^{2+}$ | 1.2(e) | 1.24 | 2.36 | 7.07(f) | 8.5(f) |

*See Table 5

(a) - Values recorded in 0.2 $mol \cdot dm^{-3}$ KCl. Values in brackets for I → 0 (reference 30)

(b) - $M^{2+} + HL^{3-} \rightleftharpoons MHL^{-}$ (reference 30)

(c) - Reference 30

(d) - Diethylenetriaminepentaacetate

(e) - Estimated (reference 33)

(f) - Reference 34

## TABLE 7

## PROPERTIES OF ALKALINE EARTH CATIONS

| $Mg^{2+}$ ------------ $Ra^{2+}$ | |
|---|---|
| ← | Solubilities |
| → | Ionic Crystal Radii |
| ← | Hydrated Ionic Radii |
| ← | Complexation with EDTA, Oxalate, etc. |
| ← | Standard Electrode Potentials |

## TABLE 8

## CATION-EXCHANGE CAPACITIES OF CLAYS [51,52]

| | |
|---|---|
| Kaolinite | 3-15 |
| Smectites | 36-100 |
| Illite | 10-40 |
| Vermiculite | 100-150 |
| Montmorillonite | 70-100 |
| Chlorite | 4-47 |

## TABLE 9

## CONSTITUENTS OF ELLIOTT LAKE ORE AND MINE-TAILINGS

| Original Ore | |
|---|---|
| Brannerite | $(U,Ca,Ce)(Ti,Fe)_2O_6$ |
| Uraninite | $UO_2$ |
| Quartz | $SiO_2$ |
| Pyrite | $FeS_2$ |
| Monazite | $(Ce,La,Y,Th)(PO_4)$ |
| Feldspars + Clays + Trace Minerals | |
| **Tailings** | |
| Quartz | $SiO_2$ |
| Calcite | $CaCo_3$ |
| Barite | $BaSO_4$ |
| Gypsum | $CaSO_4 \cdot 2H_2O$ |
| Jarosite | $KFe_3(SO_4)_2(OH)_6$ |
| Chlorapatite | $Ca_5(PO_4)_3Cl$ |
| Iron Oxides | e.g. $\alpha$-$Fe_2O_3$ |
| Feldspars + Clays + Trace Minerals | |

# TABLE 10

## WATER LEACHING OF URANIUM MILL TAILINGS

| | Reagent | Number of Leaching Stages | Nature of Tailings | $pCi \cdot g^{-1}$ | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | Initial | Percent Leached | Residual | |
| A. | | | | | | | |
| (i) | Distilled $H_2O$; $25^{\circ}C$; 1 h; $S/L \approx 0.01$ | 1 | Mine Tailings, Colorado, USA | | | | 78 |
| | | | 300-590 µm | 173 | 6.2 | 162 | |
| | | | < 100 µm | 972 | 1.5 | 957 | |
| (ii) | Dist. $H_2O$; $25^{\circ}C$; 1 h | | | | | | |
| | (a) $S/L = 0.01$ | 1 | < 100 µm | 972 | 0.49 | 9.67 | |
| | (b) 0.002 | 1 | < 100 µm | 972 | 3.80 | 935 | |
| | (c) 0.005 | 1 | < 100 µm | 972 | 13 | 846 | |
| | (d) 0.0001 | 1 | < 100 µm | 972 | 40 | 583 | |
| B. | | | | | | | |
| | Dist. $H_2O$; Room Temp.; 16 h; $S/L \approx 0.033$ | | Ambrosia Lake, N.M. | | | | 76 |
| | | 1 | Slimes solids (i.e. fines) | 3300 | 11 | 2973 | |
| C. | | | | | | | |
| | Dist. $H_2O$: Room Temp.; 68 d | | Weathered Tailings, Elliott Lake, Ont. | | | | 79 |
| | (i) $S/L = 0.05$ | 1 | " | 912 | 0.8 | 905 | |
| | (ii) 0.005 | 1 | " | 912 | 7.6 | 834 | |
| | (iii) 0.0005 | 1 | " | 912 | 7.9 | 831 | |

# TABLE 11

## SALT-SOLUTION LEACHING OF URANIUM MILL TAILINGS

| Reagent | Number of Leaching Stages | Nature of Tailings | pCi·g$^{-1}$ | | | Ref. |
|---|---|---|---|---|---|---|
| | | | Initial | Percent Leached | Residual | |
| A. | | Australian Mine Tailings | | | | 84 |
| (i) 5 mol·dm$^{-3}$ NaCl; 25°C; S/L ≃ 0.2; 0.5 h | 4 | Ranger Mine | 775 | 91 | 71 | |
| (ii) 3 mol·dm$^{-3}$ NaCl; 25°C; S/L ≃ 0.2 | 11 | Nabarlek Mine | 5178 | 94 | 311 | |
| (iii) " | 6 | Mary Kathleen | 311 | 80 | 63 | |
| (iv) " | 8 | Koongarra | 1126 | 80 | 226 | |
| (v) " | 5 | Jabiluka | 1429 | 90 | 142 | |
| B. | | Rio Aigom. Elliott Lake, Ont., Tailings | | | | 80 |
| (i) $H_2O$ wash; then | | | | | | |
| (ii) 2 mol·dm$^{-3}$ KCl; then | | | | | | |
| (iii) $H_2O$ wash | | | 205 | 50 | 102 | |
| Each 30 min; 20°C | | | | | | |
| C. | | | | | | |
| Hexametaphosphate | | | | | | 85 |
| (i) 25 g/dm$^3$ | 1 | | 860 | 68.6 | 270 | |
| (ii) 50 g/dm$^3$ | 1 | | 510 | 75 | 130 | |
| (iii) 100 g/dm$^3$ | 1 | | 735 | 81 | 140 | |

continued...

TABLE 11 (continued)

| | Reagent | Number of Leaching Stages | Nature of Tailings | pCi·$g^{-1}$ Initial | Percent Leached | pCi·$g^{-1}$ Residual | Ref. |
|---|---|---|---|---|---|---|---|
| D. | 16 h; Room Temp.; S/L ≈ 0.033 | 1 | Ambrosia Lake, N.M. Tailings (slimes solids) | | | | 76 |
| (i) | $H_2O$ | 1 | " | 3300 | 11 | 2937 | |
| (ii) | 1.0 mol·$dm^{-3}$ HCl | 1 | " | 3300 | 34 | 2178 | |
| (iii) | 1.0 mol·$dm^{-3}$ LiCl | 1 | " | 3300 | 11 | 2937 | |
| (iv) | 1.0 mol·$dm^{-3}$ NaCl | 1 | " | 3300 | 36 | 2112 | |
| (v) | 1.0 mol·$dm^{-3}$ KCl | 1 | " | 3300 | 12 | 2904 | |
| (vi) | 1.0 mol·$dm^{-3}$ $NH_4Cl$ | 1 | " | 3300 | 15 | 2805 | |
| (vii) | 1.0 mol·$dm^{-3}$ $CaCl_2$ | 1 | " | 3300 | 73 | 891 | |
| (viii) | 1.0 mol·$dm^{-3}$ $BaCl_2$ | 1 | " | 3300 | 65 | 1155 | |
| (ix) | 1.0 mol·$dm^{-3}$ $AlCl_3$ | 1 | " | 3300 | 20 | 2640 | |
| (x) | 1.0 mol·$dm^{-3}$ $FeCl_3$ | 1 | " | 3300 | 59 | 1353 | |
| | Batch countercurrent leach 4 stages + 2 with $H_2O$; 1 mol·$dm^{-3}$ NaCl + 0.1 mol·$dm^{-3}$ HCl; 30 min/stage; S/L ≈ 0.033 | 4 + 2 | | | | | |
| E. | 1 h, 30°C; S/L ≈ 0.1 | | Elliott Lake, Ont. Mine Tailings | | | | 81 |
| (i) | 1.0 mol·$dm^{-3}$ KCl | 1 | " | 170 | 32 | 116 | |
| (ii) | 1.0 mol·$dm^{-3}$ $KNO_3$ | 1 | " | 170 | 24 | 129 | |
| (iii) | 1.0 mol·$dm^{-3}$ $KHSO_4$ | 1 | " | 170 | 7 | 159 | |
| (iv) | 1.0 mol·$dm^{-3}$ $KHCO_3$ | 1 | " | 170 | 16 | 143 | |
| (v) | 1.0 mol·$dm^{-3}$ $KH_2PO_4$ | 1 | " | 170 | 2 | 166 | |

TABLE 11 (continued)

| | Reagent | Number of Leaching Stages | Nature of Tailings | $pCi \cdot g^{-1}$ | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | Initial | Percent Leached | Residual | |
| E. (cont'd.) | | | | | | | |
| (vi) | 1.0 $mol \cdot dm^{-3}$ NaCl | 1 | " | 170 | 5 | 161 | |
| (vii) | 1.0 $mol \cdot dm^{-3}$ $NH_4Cl$ | 1 | " | 170 | 7 | 157 | |
| (viii) | 1.0 $mol \cdot dm^{-3}$ $CaCl_2$ | 1 | " | 170 | 5 | 161 | |
| (ix) | 1.0 $mol \cdot dm^{-3}$ LiCl | 1 | " | 170 | 7 | 159 | |
| (x) | prewash with $H_2O$; then 1.0 $mol \cdot dm^{-3}$ KCl | 1 | " | 170 | 52 | 82 | |
| (xi) | prewash with $H_2O$; then 1.0 $mol \cdot dm^{-3}$ NaCl | 1 | " | 170 | 31 | 118 | |
| (xii) | prewash with $H_2O$; then 1.0 $mol \cdot dm^{-3}$ $NH_4Cl$ | 1 | " | 170 | 47 | 91 | |
| F. | 5 $mol \cdot dm^{-3}$ NaCl; 25°C 30 min/stage; S/L = 0.2 | 4 | Australian Mine Tailings | | 92 | | 77 |
| G. | 25°C; S/L = 0.01; 1 h | | River Sediment, Colorado Plateau area, USA | | | | 78 |
| (i) | $H_2O$ | 1 | " | 296 | 0.1 | 296 | |
| (ii) | $10^{-2}$ $mol \cdot dm^{-3}$ HCl | 1 | " | 296 | 0.3 | 295 | |
| (iii) | $10^{-2}$ $mol \cdot dm^{-3}$ NaCl | 1 | " | 296 | 0.1 | 296 | |
| (iv) | $10^{-2}$ $mol \cdot dm^{-3}$ KCl | 1 | " | 296 | 0.1 | 296 | |
| (v) | $10^{-2}$ $mol \cdot dm^{-3}$ $MgCl_2$ | 1 | " | 296 | 0.1 | 296 | |
| (vi) | $10^{-2}$ $mol \cdot dm^{-3}$ $CaCl_2$ | 1 | " | 296 | 0.4 | 295 | |
| (vii) | $10^{-2}$ $mol \cdot dm^{-3}$ $SrCl_2$ | 1 | " | 296 | 2.1 | 290 | |
| (viii) | $10^{-2}$ $mol \cdot dm^{-3}$ $BaCl_2$ | 1 | " | 296 | 10 | 266 | |

continued...

TABLE 11 (continued)

| | Reagent | Number of Leaching Stages | Nature of Tailings | $pCi \cdot g^{-1}$ Initial | Percent Leached | $pCi \cdot g^{-1}$ Residual | Ref. |
|---|---|---|---|---|---|---|---|
| G. (cont'd.) | | | | | | | |
| | $25^oC$; S/L = 0.01; 1 h | | River Sediment, Colorado Plateau area, USA | | | | 78 |
| (i) | $10^{-4}$ $mol \cdot dm^{-3}$ $BaCl_2$ | 1 | " | 296 | 0.1 | 296 | |
| (ii) | $10^{-3}$ $mol \cdot dm^{-3}$ $BaCl_2$ | 1 | " | 296 | 6 | 277 | |
| (iii) | $10^{-2}$ $mol \cdot dm^{-3}$ $BaCl_2$ | 1 | " | 296 | 13 | 258 | |
| (iv) | $1.5 \times 10^{-2}$ $mol \cdot dm^{-3}$ $BaCl_2$ | 1 | " | 296 | 17 | 247 | |
| H. | | | | | | | |
| | Room Temp.; 5-8 h; S/L ≈ 0.1 | | Sediments from tailings pond, Bytiz, Czechoslovakia | | | | 83 |
| (i) | pH = 1 (HCl) | 1 | " | 14 | 22 | 11 | |
| (ii) | pH = 2 (HCl) | 1 | " | 14 | 10 | 13 | |
| (iii) | pH = 3 (HCl) | 1 | " | 14 | 10 | 13 | |
| (iv) | pH = 4 (HCl) | 1 | " | 14 | 8 | 13 | |
| (v) | pH = 6 ($H_3BO_3$) | 1 | " | 14 | 5 | 13 | |
| (vi) | pH = 8 ($NaHCO_3$) | 1 | " | 14 | 4 | 13 | |
| (vii) | pH = 10 ($NaHCO_3$) | 1 | " | 14 | 4 | 13 | |
| (viii) | pH = 13 (NaOH) | 1 | " | 14 | 5 | 13 | |
| | Room Temp.; S/L ≈ 0.1 | | Sediments, Bytiz | | | | |
| (i) | $10^{-2}$ $mol \cdot dm^{-3}$ KCl; 1 h | 1 | " | 14 | 10 | 13 | |
| (ii) | $10^{-1}$ $mol \cdot dm^{-3}$ KCl; 1 h | 1 | " | 14 | 54 | 7 | |
| (iii) | 1.0 $mol \cdot dm^{-3}$ KCl; 1 h | 1 | " | 14 | 100 | 0 | |

continued...

TABLE 11 (concluded)

| | | | $pCi \cdot g^{-1}$ | | | |
|---|---|---|---|---|---|---|
| Reagent | Number of Leaching Stages | Nature of Tailings | Initial | Percent Leached | Residual | Ref. |
| H. (cont'd.) | | | | | | |
| 25$^{\circ}$C; S/L ≈ 0.1 | | Sediments, Bytiz | | | | |
| (i) 1 mol·dm$^{-3}$ KCl; 1 h | 1 | " | 14 | 100 | 0 | |
| (ii) 1 mol·dm$^{-3}$ NaCl; 6 h | 1 | " | 14 | 95 | 1 | |
| (iii) 1 mol·dm$^{-3}$ $MgCl_2$; 5 h | 1 | " | 14 | 9 | 13 | |
| (iv)* 1 mol·dm$^{-3}$ $SrCl_2$; 1 h | 1 | " | 14 | 10 | 13 | |
| (v)* 1 mol·dm$^{-3}$ $BaCl_2$; 1 h | 1 | " | 14 | 1 | 14 | |
| (vi)* 1 mol·dm$^{-3}$ $CaCl_2$; 3 h | 1 | " | 14 | 48 | 7 | |
| (vii)* 1 mol·dm$^{-3}$ $K_3PO_4$; 6 h | 1 | " | 14 | 2 | 14 | |
| (viii)* 1 mol·dm$^{-3}$ $Na_3PO_4$; 6 h | 1 | " | 14 | 7 | 13 | |
| (ix)* 1 mol·dm$^{-3}$ $MgCO_3$; 5 h | 1 | " | 14 | 2 | 14 | |
| (x)* 1 mol·dm$^{-3}$ $(NH_4)_2SO_4$; 8 h | 1 | " | 14 | 28 | 10 | |
| (* pH = 2.0) | | | | | | |

## TABLE 12

## ACID LEACHING OF URANIUM MILL TAILINGS

| | | | $pCi \cdot g^{-1}$ | | | |
|---|---|---|---|---|---|---|
| Reagent | Number of Leaching Stages | Nature of Tailings | Initial | Percent Leached | Residual | Ref. |
| A. | | Ambrosia Lake, N.M.<br>Mill Tailings | | | | |
| 3 $mol \cdot dm^{-3}$ $HNO_3$; 1 h/stage<br>85°C; S/L ≃ 0.25;<br>2 or 3 Cascade stages | 2<br>or<br>3 | (i) Slimes solids<br>(ii) Sand Tailings | 3300<br>150 | 98<br>97 | 73<br>4 | 76 |
| B.<br>1.5 $mol \cdot dm^{-3}$ HCl; 30 min/stage;<br>60°C; S/L ≃ 0.25 | 3 | Acid Process Tailings<br>Salt Lake City | 500 | 92 | 40 | 19 |
| C.<br>1.0 $mol \cdot dm^{-3}$ HCl; 16 h<br>Room Temp.; S/L ≃ 0.033 | 1 | Ambrosia Lake, N.M. | 3300 | 34 | 2178 | 76 |
| D.<br>40.5% $HNO_3$; 25°C; S/L = 0.1 | | Rio Algom Ltd.,<br>Elliott Lake, Ont. | | | | 86 |
| (i) 15 min | 1 | " | 768 | 66 | 261 | |
| (ii) 1 h | 1 | " | 768 | 71 | 223 | |
| (iii) 2 h | 1 | " | 768 | 76 | 184 | |
| (iv) 2.5 h | 1 | " | 768 | 73 | 207 | |
| (v) 10 h | 1 | " | 768 | 67 | 253 | |

continued...

TABLE 12 (concluded)

| Reagent | Number of Leaching Stages | Nature of Tailings | pCi·$g^{-1}$ | | | Ref. |
|---|---|---|---|---|---|---|
| | | | Initial | Percent Leached | Residual | |
| E. 3 mol·$dm^{-3}$ $HNO_3$; 70°C; 5 h | | N. Mexico, Utah, Wyoming Tailings | | | | 5 |
| (i) S/L = 0.25 | 1 | " | 910 | 22 | 712 | |
| (ii) S/L = 0.33 | 2 | " | 910 | 94 | 51 | |
| (iii) S/L = 0.17 | 3 | " | 910 | 96 | 34 | |
| 0.1 mol·$dm^{-3}$ + 1 mol·$dm^{-3}$ $Ca(NO_3)$; 70°C; 3 h | | | | | | |
| (i) S/L = 0.1 | 1 | " | 910 | 19 | 740 | |
| (ii) S/L = 0.05 | 1 | " | 910 | 38 | 560 | |
| (iii) S/L = 0.01 | 1 | " | 910 | 83 | 156 | |
| (i) 3 mol·$dm^{-3}$ $HNO_3$; 85°C; 5 h; S/L = 0.03 | 1 | " | 910 | 96 | 39 | |
| (a) 6 mol·$dm^{-3}$ $H_3PO_4$; 70°C; 5 h; S/L = 0.33 | 1 | " | 910 | 78 | 198 | |
| (b) 0.5 mol·$dm^{-3}$ $Ba(NO_3)_2$; 25°C; 168 h; S/L = 0.33 | 1 | " | 910 | 73 | 250 | |
| (c) Dist. $H_2O$; 168 h; 25°C; S/L = 0.33 | 1 | " | 910 | 80 | 184 | |
| (d) HF; 25°C; < 1 h; S/L = 0.33 | 1 | " | 910 | 54 | 417 | |

## TABLE 13

## CHELATE LEACHING OF URANIUM MILL TAILINGS

| | Reagent | Number of Leaching Stages | Nature of Tailings | $pCi \cdot g^{-1}$ Initial | Percent Leached | Residual | Ref. |
|---|---|---|---|---|---|---|---|
| A. | | | | | | | |
| (i) | 6.65% DTPA; 25°C; $\geq$ 30 min; S/L = 0.12 | 1 | Rio Algom Ltd. Elliott Lake, Ont. Mine Tailings | 768 | 72 | 215 | 86 |
| (ii) | 0.3 $mol \cdot dm^{-3}$ EDTA; 25°C; 30 min; S/L = 0.24 | 1 | " | 394 | 60 | 236 | |
| B. | | | | | | | |
| (i) | 0.15 $mol \cdot dm^{-3}$ EDTA; 5 h 60°C; S/L = 0.15 | 1 | Acid Process Tailings Salt Lake City | 500 | 80 | 100 | 19 |
| (ii) | 0.15 $mol \cdot dm^{-3}$ EDTA; 5 h 60°C; S/L = 0.15 | 3 | " | 500 | 92 | 40 | |
| (iii) | 0.3 $mol \cdot dm^{-3}$ EDTA | 1 | " | 500 | 80 | 100 | |
| (iv) | 0.15 $mol \cdot dm^{-3}$; 2 h 60°C; S/L = 0.15 | | Alkaline Process Tailings, Tuba City Arizona | | 56 | | |
| C. | | | | | | | |
| (i) | 1.0 $mol \cdot dm^{-3}$ $Na_4$ EDTA; 16 h; Room Temp.; S/L ≃ 0.033 | 1 | Ambrosia Lake, N.M., Tailings Slimes | 3300 | 93 | 231 | 76 |
| (ii) | 1.0 $mol \cdot dm^{-3}$ $Na_5$ DTPA; 16 h; Room Temp.; S/L ≃ 0.033 | 1 | " | 3300 | 94 | 198 | |

continued...

## TABLE 13 (concluded)

| Reagent | Number of Leaching Stages | Nature of Tailings | $pCi \cdot g^{-1}$ Initial | Percent Leached | $pCi \cdot g^{-1}$ Residual | Ref. |
|---|---|---|---|---|---|---|
| D. | | | | | | |
| 3 $mol \cdot dm^{-3}$ $HNO_3$<br>S/L = 0.33; 70°C; 5 h | 1 | New Mexico, Utah Wyoming Tailings | 910 | 96 | 39 | |
| followed by | | | | | | |
| 0.5 $mol \cdot dm^{-3}$ EDTA; S/L = 0.23; 80°C; 5 h | 1 | " | 39 | 26<br>(97)* | 29 | |
| 3 $mol \cdot dm^{-3}$ $HNO_3$; S/L = 0.1; 70°C; 5 h | 1 | " | 910 | 67 | 396 | |
| followed by | | | | | | |
| (i) 0.5 $mol \cdot dm^{-3}$ EDTA;<br>S/L = 0.23; 80°C; 5 h | 1 | " | 296 | 83<br>(94)* | 49 | |
| (ii) 3.0 $mol \cdot dm^{-3}$ EDTA;<br>S/L = 0.1; 25°C; 168 h | 1 | " | 296 | 88<br>(96)* | 36 | |
| (iii) 7.5 $mol \cdot dm^{-3}$ EDTA;<br>S/L = 0.33; 110°C; 24 h | 1 | " | 296 | 89<br>(97)* | 31 | |

* Overall % extracted by combined acid/EDTA leaching

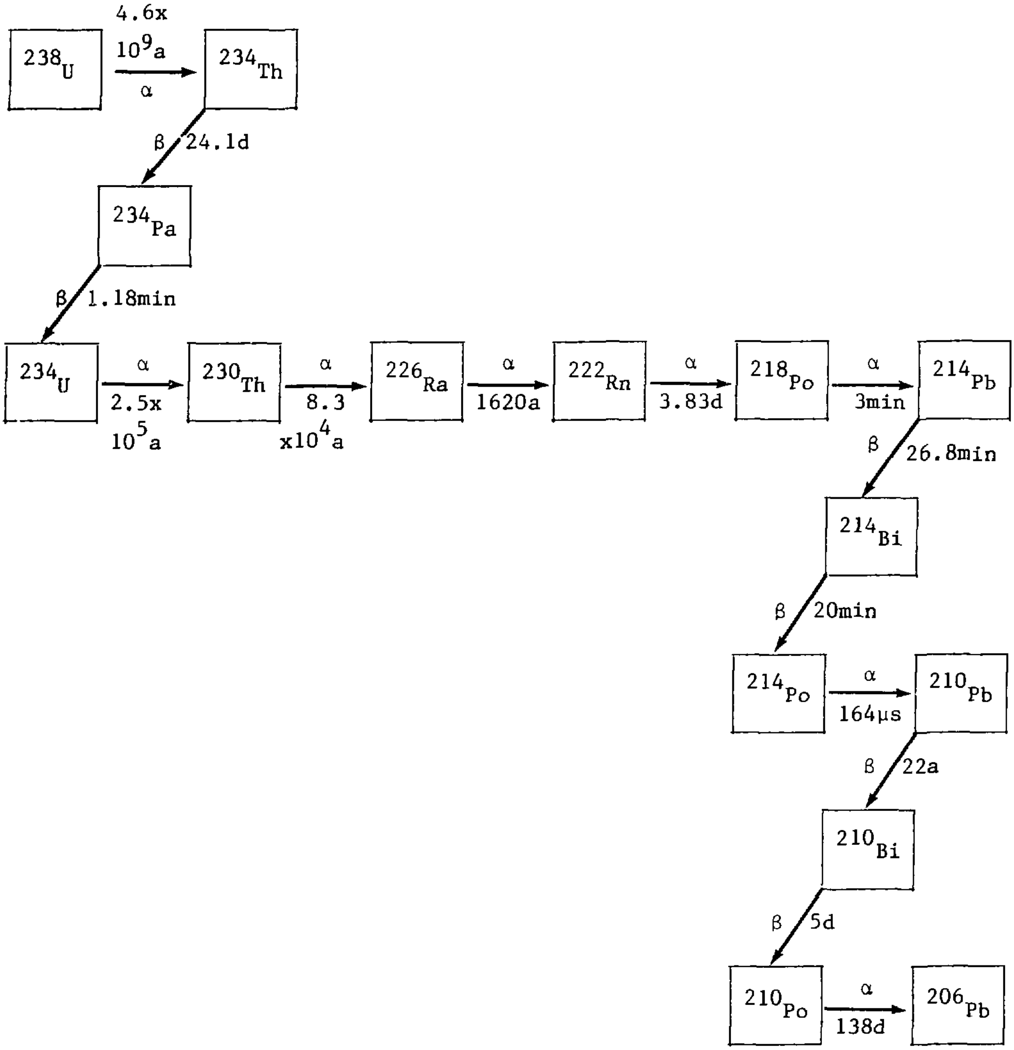
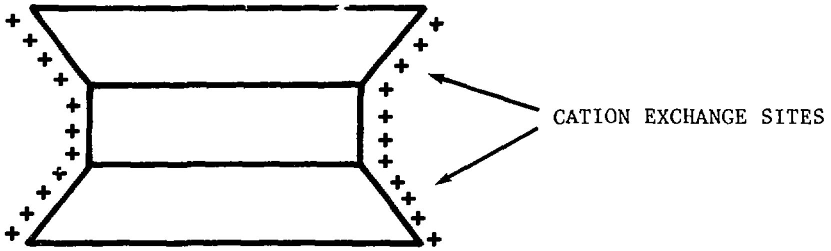


FIGURE 1: Uranium Series Decay Scheme

A. <u>TWO-LAYER CLAY</u> (e.g. kaolinite)



B. <u>THREE-LAYER CLAY</u> (e.g. montmorillonite)

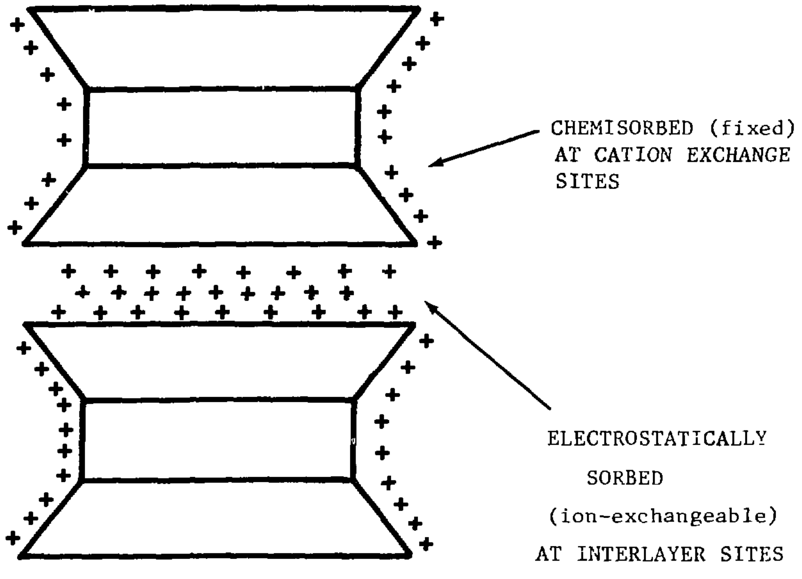


FIGURE 2: Simplified Schematic of Clay Structures Indicating Ion-Exchange Sites

(1) Neutralization

$$ {}^{226}\mathrm{Ra}^{2+} + 2\mathrm{CO}_3^{2-} + 2\mathrm{H}^+ \xrightarrow{\mathrm{Ca(OH_2)}} ({}^{226}\mathrm{RaCO}_3)(\mathrm{CaCO}_3) + 2\mathrm{H}_2\mathrm{O} $$

(2) Precipitation

$$ \mathrm{Ca}^{2+} + {}^{226}\mathrm{Ra}^{2+} + 2\mathrm{SO}_4^{2-} + 2\mathrm{H}_2\mathrm{O} \longrightarrow ({}^{226}\mathrm{RaSO}_4)(\mathrm{CaSO}_4)2\mathrm{H}_2\mathrm{O} $$

$$ \mathrm{Ba}^{2+} + {}^{226}\mathrm{Ra}^{2+} + 2\mathrm{SO}_4^{2-} \longrightarrow ({}^{226}\mathrm{RaSO}_4)(\mathrm{BaSO}_4) $$

$$ \mathrm{SiO}_2 + {}^{226}\mathrm{Ra}^{2+} + \mathrm{SO}_4^{2-} \longrightarrow ({}^{226}\mathrm{RaSO}_4)_{\mathrm{ads}}\mathrm{SiO}_2 $$

(3) Adsorption

$$ \left.\begin{array}{l} \text{Clays} \\ \text{Feldspars} \\ \text{Quartz} \\ \text{Minerals} \end{array}\right\} + {}^{226}\mathrm{Ra}^{2+} \longrightarrow \left.\begin{array}{l} \text{Clays} \\ \text{Feldspars} \\ \text{Quartz} \\ \text{Minerals} \end{array}\right\} {}^{226}\mathrm{Ra}_{\mathrm{ads}} $$

(4) Weathering

$$ \left.\begin{array}{l} ({}^{226}\mathrm{RaSO}_4)(\mathrm{CaSO}_4)2\mathrm{H}_2\mathrm{O} \\ \\ \alpha - \mathrm{Fe}_2\mathrm{O}_3 \end{array}\right\} \xrightarrow{\mathrm{K}^+} (\mathrm{K}, {}^{226}\mathrm{Ra})\mathrm{Fe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6 $$

$$ ({}^{226}\mathrm{RaCO}_3)(\mathrm{CaCO}_3) \xrightarrow[\mathrm{Cl}^-]{\mathrm{PO}_4^{3-}} \mathrm{Ca}_{5-x}{}^{226}\mathrm{Ra}_x(\mathrm{PO}_4)_3\mathrm{Cl} $$

FIGURE 3: Possible Reactions Leading to Radium Incorporation or Adsorption

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