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AN INVESTIGATION OF
URANIUM MILL TAILINGS

by

Douglas Michael Charles Stewart

A report submitted to the Department
of Chemistry in partial fulfilment
of the requirements for the degree of
Master of Science

Carleton University
Department of Chemistry

Ottawa, Ontario

August, 1987

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ABSTRACT

A fresh Key Lake uranium mill tailings sample was studied by a variety of techniques. Radioactivity is widely distributed, and much is contained in precipitates. Two dense minerals (which were radioactive throughout) were studied in detail: the first was a complex intergrowth of hematite and chlorite, with an altered, inactive surface; the second was gersdorffite. Their radioactivity pre-dates ore mining, and indicates that some portion is not released by leaching. It is shown that these radionuclides are held below the surface of large grains, and are screened from detection by overlying material. Adsorption experiments show that arsenate greatly enhances ^{133}Ba adsorption on freshly precipitated ferric hydrous oxide, and is more effective than sulphate. Increasing anion concentration changes the adsorption reaction from ion exchange to (apparently) surface precipitate formation. This suggests that hematite-chlorite will also be successful in sequestering radionuclides released as the tailings age.

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TABLE OF CONTENTS

PAGE

ABSTRACT

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

1.

Introduction to the Problem
Relevant Geology and Geochemistry
Tailings Chemistry and Properties
Alpha Spectroscopy
Adsorption Chemistry

II. METHODS AND METHODOLOGY

37.

Tailings Handling
Density Separation
Gamma Spectrometry
Autoradiography
Microprobe Analysis
Alpha Spectrometry and Spectroscopy
Adsorption Studies

TABLE OF CONTENTS (cont'd)

	<u>PAGE</u>
III. RESULTS AND DISCUSSION	55.
Opening Statement	
Tailings Properties	
Microprobe Analysis	
Autoradiography	
Alpha Spectroscopy	
Adsorption Studies	
Interpretations and Implications	
IV. CONCLUSIONS	125.
V. REFERENCES	128.

LIST OF TABLES

<u>Number</u>	<u>Table</u>	<u>Page</u>
I.	Relative stopping power of various elements, with respect to Al.	15.
II.	Alpha particle ranges for various compounds	17.
III.	Scattering energies for various elements	24.
IV.	Summary of observations from autoradiography of Midwest Lake tailings.	68.
V.	Summary of observations from autoradiography of Key Lake tailings.	68.
VI.	Values of pH_{50} , slope, and linear correlation coefficient for experimental data.	107.

LIST OF FIGURES

<u>Number</u>	<u>Table</u>	<u>Page</u>
1.	Degradation of alpha spectra with increasing amount of carrier	20.
2.	Gamma spectra of Key Lake tailings	58.
3.	Alpha spectra of Key Lake tailings	60.
4.	Scanning electron micrographs of hematite-chlorite	62.
5.	Electron microprobe spectra for hematite-chlorite before and after removal of surface material	65.
6.	Autoradiographs of hematite-chlorite grains before and after removal of surface material	72.
7.	Autoradiographs from hematite-chlorite grinding experiments	76.
8.	Alpha spectra of ^{230}Th with varying amounts of ferric hydrous oxide carrier	81.

LIST OF FIGURES (cont'd)

<u>Number</u>	<u>Table</u>	<u>Page</u>
9.	Alpha spectra of ^{230}Th with varying amounts of $\text{La}(\text{OH})_3$ carrier	84.
10.	Adsorption profile for ^{133}Ba on ferric hydrous oxide in the absence of added anions	90.
11.	Adsorption profiles for ^{133}Ba on ferric hydrous oxide with added sulphate	91.
12.	Adsorption profiles for ^{133}Ba on ferric hydrous oxide with added arsenate	92.
13.	Plot of $\log D$ vs. pH for ^{133}Ba on ferric hydrous oxide in the absence of added anions	99.
14.	Plots of $\log D$ vs. pH for ^{133}Ba on ferric hydrous oxide with added sulphate	100.
15.	Plots of $\log D$ vs. pH for ^{133}Ba on ferric hydrous oxide with added arsenate	102.
16.	Best-fit lines for all anion concentrations with respect to the no-anion case	105.

Introduction

Introduction to the Problem

The residues from mining and milling operations (known as tailings) are very complex chemically and mineralogically. Besides the assemblage of minerals already existing in the orebody, new phases are formed during ore processing and any subsequent mill tailings treatment prior to discharge. The species formed (typically as chemical precipitates) depend on the minerals originally present and on the reagents used, but often include metal hydroxides (also known as hydrous metal oxides), jarosites, and sparingly soluble metal salts such as sulphates, arsenates, etc. [1]. Owing to the high reagent concentrations and extreme conditions often employed, non-stoichiometric compounds and occluded or mixed coprecipitates can also be formed. This complexity and variability in mineral and chemical species makes the modelling and prediction of tailings behaviour difficult. This is especially important in the uranium mining industry, where wastes create not only aesthetic and economic problems, but also public health concerns regarding the release of radio- and chemo-toxic species to the environment. The tailings of the Key Lake uranium operations provide an example of such problems and concerns.

In this section, the relevant theory necessary to examine the chief areas of interest in this study will be presented, with particular emphasis on the unique chemical properties of the Key Lake orebodies and tailings, the use of adsorption studies to model the behaviour of radionuclides, and the application of alpha spectroscopy to tailings

systems. There are still many areas of uncertainty regarding the distribution of radionuclides in uranium mill tailings physically and chemically, their subsequent retention and/or release with weathering of the tailings pile, etc. Since uranium has been mined for only a relatively short time, true long-term data on the migration of the radioactive daughter products of uranium (denoted as U_{rd}) from real tailings piles is not available. Clear-cut, unambiguous solutions to the problems associated with the long-term isolation of hazardous radioactive isotopes are thus difficult to achieve. Little is known about the actual behaviour of U_{rd} on the microscopic scale in tailings, and much of the work in the literature has dealt with bulk characteristics, to control the more immediate problem of short-term release of harmful species to the environment. There remain, however, several areas of particular importance and interest with respect to the situation at Key Lake, where short-term radionuclide release has not (to date) been a problem.

Perhaps the most important questions regarding the behaviour and properties of radioactive mill tailings in general deal with the actual radionuclide distribution, that is, with which minerals and/or compounds the U_{rd} are (at least, initially) associated. Related to this are: the number of host phases involved, that is, whether U_{rd} are widely or specifically distributed; their relative importance as hosts; the location of U_{rd} , at the surface or throughout the particles; and to which phases radionuclides are redistributed as the tailings age.

Studies to date include: simulated leaching with inorganic salts and acids, organic complexing agents, and distilled water [eg. 1-5]; selective extractions, based on the differing solubilities of various

compounds within the tailings [eg. 6]; and high-resolution autoradiography [7]. One of the primary difficulties with this type of work, however, is the lability of the system being investigated, which is highly susceptible to the removal or redistribution of radionuclides with minor changes in the conditions at surfaces and in solution.

Perhaps the greatest difficulty is in dealing with the large amount of very fine material present, consisting of precipitates and coprecipitates, along with crushed (and often partially solubilized) mineral fragments, and clays. The nature of the tailings fines also complicates the interpretation of experimental data; for example, desorption and dissolution may be indistinguishable in some cases - the presence of certain elements along with radionuclides may be the result of the dissolution of some soluble compound with no primary association to radionuclides desorbed from some other phase. Such an occurrence would obviously affect the interpretation of data from leaching or selective extraction studies. The complex chemical and physical nature of the fines also poses severe restrictions on the types of manipulations that can be made without disturbing the microenvironment at particle surfaces.

It has been suggested [8,9] that the presence of arsenic in the ore and tailings may serve to reduce U_{rd} mobilization chemically, by virtue of the extreme insolubility of most arsenates [10]. It has also been demonstrated [eg. 11-13] that anions such as phosphate and arsenate are strongly and specifically adsorbed, and with a sufficiently high concentration may form surface precipitates. It was also shown [12,14,15] that in certain cases the adsorption of cations was increased in the presence of anions, with the possible formation of ternary complexes as

well as surface precipitates. The U_{rd} , then, could be immobilized by arsenic in one (or a combination) of three ways: (1) by coprecipitation with, or occlusion within, insoluble arsenates in solution; (2) by the adsorption of arsenate on particle surfaces, increasing their affinity for U_{rd} ; and (3) by the formation of surface precipitates either incorporating dissolved U_{rd} , or covering underlying U_{rd} trapped by some other mechanism. These three pathways for immobilization are not mutually exclusive; for example, mixed arsenate- U_{rd} adsorption on a substrate surface could result in surface precipitate formation, or alternatively, make the substrate a favourable site for the agglomeration of suspended particulates, particularly those containing arsenate.

The chief aim of the present work is to determine, if possible, the chemical factor(s) controlling the behaviour of uranium daughter products within the Key Lake tailings; specifically, whether the high arsenic content of the ores at Key Lake affects the mobility of such radioactive species. It is possible that such an effect could then be applied to other tailings containment systems. The objectives of this work can be summarized as follows: to determine whether, and how, arsenic affects the adsorption of U_{rd} (specifically radium, which will be modelled by a barium radiotracer); to attempt to determine the mineralogical distribution of radionuclides in the tailings, by a variety of methods; and to then determine the location of radioactive atoms within their host phase(s), that is, whether they are at or beneath particle surfaces, also by a variety of methods. A secondary objective is to attempt to develop or refine techniques to examine fine-grained, radioactive materials. The following pages, then, will

give the background information needed to discuss the results obtained in the present study.

Relevant Geology and Geochemistry

There are four major types of uranium ore, based on their origin: sedimentary-type; quartz-pebble conglomerates; vein-type; and "other" [16,17]. The quartz-pebble conglomerate and vein-type deposits are represented in Canada by the Elliot Lake and Key Lake regions, respectively, and will be discussed in more detail than the others, with particular emphasis on the Key Lake deposits.

In sedimentary-type deposits, the uranium minerals are usually associated with sedimentary traps and reducing environments at redox boundaries, commonly associated with sandstones, or with pyrite. Uranium may be present as detrital grains or reduced from solution by the sulphides.

In quartz-pebble conglomerate ores, the uranium mineralization is found in a host consisting mainly of silica; pyrite is always present. Again, the uranium may occur as detrital grains or as precipitates formed by reaction with sulphides.

In vein-type deposits, the mineralization commonly occurs as filling in cracks, fissures, etc. Uranium may be mobilized from other areas or formed from hydrothermal solutions, and is often associated with geological unconformities, fault and fracture zones, and other structural traps.

"Other" uranium deposits are often in the form of more refractory minerals.

The Elliot Lake uranium deposits are a good example of a quartz-

pebble conglomerate-type uranium ore. The average ore grade is roughly 0.1-0.3% U_3O_8 [18]. The major uranium minerals are uraninite (composition between UO_2 and U_3O_8), brannerite $((U,Ca,Ce)(Ti,Fe)_2O_6)$, and monazite $(Ce,La,Y,Th)PO_4$, held in a fine-grained matrix of quartz (SiO_2), sericite $(KAl_2(AlSi_3O_{10})(OH)_2)$, and feldspar. The deposits are also characterized by a high sulphides content, roughly 5-10%, mostly as pyrite (FeS_2).

The Key Lake ores fall into the category of vein-type uranium deposits and display typical features of this deposit type: association with geological unconformities, which may affect the mobility of dissolved species through impermeable clays deposited over eroded permeable rock; fault and fracture zones in the host rock; restricted ore mineralogy (primarily pitchblende); and typically, a hydrothermal origin for the deposit. It has been proposed [19] that the original uranium deposition at Key Lake was sedimentary; following this, some remobilization and reprecipitation of uranium and nickel in favourable geochemical and structural traps occurred.

The ore grade is extremely variable, with pockets up to 35% U_3O_8 , and the average ore grade is roughly 2.5% U_3O_8 . The main uranium ore minerals at Key Lake [20-22] are pitchblende I (U_3O_7), "sooty" pitchblende, or pitchblende II (U_3O_9) (which was apparently formed by the oxidation of pitchblende I), and coffinite ($USiO_4$), associated with the nickel minerals gersdorffite ($NiAsS$), millerite (NiS), niccolite ($NiAs$), and bravoite $((Fe,Ni)S_2)$. In addition, there is a high arsenic content, roughly 5%, mainly as various arsenides.

It is appropriate to include at this point some relevant infor-

mation on the chemical properties of uranium, thorium, and radium, the radionuclides of most interest in the context of tailings disposal and management. The most important properties of each of these elements, as they relate to their retention and mobilization, will be presented here; more detailed reviews are given elsewhere [eg. 4,23-26].

Uranium is most commonly found in the U^{4+} (uranous) and U^{6+} (uranyl) oxidation states, with the latter being much more soluble; U is dissolved under oxidizing conditions, forming the highly mobile uranyl ion, UO_2^{2+} , or one of many cationic, neutral, and anionic complexes, depending on the pH. Uranium is reversibly adsorbed on a wide variety of substrates, including hydrous metal oxides, soil material, humic acid, etc., and can accumulate on such surfaces by reduction to the U^{4+} state. Since natural uranium contains 99.3% ^{238}U by weight [27], and since the ^{232}Th content of ores is usually low [4], ^{238}U decay series members should dominate in the ore and tailings. Uranium is usually of the least interest with respect to mill tailings, since it is the most efficiently removed by ore leaching.

Thorium is present in solution only as Th^{4+} ; hydrolysis occurs above pH 2-3, with precipitation of the highly insoluble hydroxide ($K_{sp} = 10^{-39}$) above pH 5-6. It may coprecipitate with other metals, in particular ferric hydrous oxide (denoted as FHO), and adsorbs strongly on ion-exchangeable clays, colloidal precipitates, and soil materials. The high charge density of the Th^{4+} ion causes it to form complexes with a variety of inorganic anions. In near-neutral solution thorium is mobilized as colloidal particles or as a soluble complex; mobilization is also favoured by low pH - while normal geologic conditions are seldom highly acidic, such conditions have been found in some tailings

piles. Studies on thorium dissolution during ore leaching indicate that up to 90% of the thorium present in uranium ores (with typical values for Key Lake of about 50% [22]) is released; most of this is carried down during tailings neutralization. Despite its long half-life, ^{230}Th is a major concern in tailings management, since it is the precursor to ^{226}Ra , which presents more immediate hazards.

Radium, as a member of the alkaline earths, is present in solution only as a divalent cation. It has the smallest hydrated radius [28], and thus the lowest tendency to hydrolyze or form complexes within this family; the small hydrated radius also indicates that it competes favourably with other alkaline earth cations in surface adsorption reactions. No known radium minerals have been found; instead, it forms coprecipitates with other metals (especially the alkaline earths), and anions such as carbonate, phosphate, and sulphate - the formation of $(\text{Ba,Ra})\text{SO}_4$ by the addition of barium chloride is used to carry down dissolved radium in tailings treatment for H_2SO_4 circuits (although radium is generally considered not to be present in leach liquors, owing to the insolubility of the sulphate [1]). Radium in tailings can be released by acids such as HCl and HNO_3 , by organic complexing agents such as EDTA, and by water. The latter acts mainly to lower the sulphate content by dissolving gypsum (CaSO_4), thereby favouring $(\text{Ba,Ra})\text{SO}_4$ dissolution; it can be seen that the liquid-solid ratio is critical for radium release by water. Radium can also be found with other phases [eg. 1,5,6,25,29,30], such as metal hydroxides, clays, and jarosites, through surface adsorption and/or coprecipitation. While redox conditions do not have a major effect on radium itself, they may influence the solubility and mobility of the elements and compounds

with which it is associated. Radium, when ingested, concentrates in bones and teeth, and poses a serious health hazard.

Evidence exists that uranium and its radioactive daughter products may be present in discrete mineral phases in the Midwest and Key Lake ore and tailings. Changes in Eh, pH, solution fronts, water table variations, etc., may allow migration of uranium and/or U_{rd} away from their original locations, to be dispersed or reconcentrated in different mineral phases. Based on the above-mentioned chemical properties, uranium is the most likely to be mobilized by relatively subtle changes in solution conditions. Ludwig [31] found evidence of such U_{rd} migration; all pitchblende samples examined "have experienced both lead and long-term $^{238}U_{rd}$ loss". Landa [6] concluded that uranium, radium, and thorium were in different sites in the ore and tailings studied: the uranium was found in the readily acid-soluble portion, radium was concluded to be associated with iron and manganese hydrous oxides, and thorium with alkaline earth sulphates and/or organic matter.

The above findings point to the possibility of radionuclide migration in a geologically "open" orebody (that is, one which is permeable to groundwater), leading to the reconcentration of U_{rd} in new mineral phases. If radium and thorium are no longer contained in readily leachable sites, then these radionuclides may not be leached to as great an extent as assumed by calculations based on a closed system (in which the U_{rd} remain with uranium). It is often concluded or assumed that, since very little dissolved radium is present in subsequent processing stages [32], it must have precipitated during leaching, when actually it may never have been released from its (leach-

resistant) host mineral.

If some portion of the U_{rd} no longer occur solely within their original host minerals, their actual host(s) become critical, since the extent of release during milling and subsequent treatment is dependent on dissolution and/or ion exchange from these sites. For example, while surface adsorption of large cations such as radium and thorium is possible and expected, desorption may also be fairly simple. Lattice penetration into clays such as kaolinite and illite is not expected to be significant for large cations [33] unless present at the time of clay formation (in which case they could be occluded in the lattice); since large cations would be found only fairly close to the surface, this would allow them to be exchanged more effectively. Similarly, desorption from fine silica is accomplished by relatively minor changes in pH or electrolyte concentration [1,29].

Thus, if radium and thorium are adsorbed and/or coprecipitated with highly leach-resistant phases, they may not be released to a large extent during milling. This leads to the possibility of two types of radium and thorium occurring in the ore and tailings: that associated with the uranium-bearing minerals, that is, which has not migrated from the original minerals since the last geologic period of movement; and that which has migrated from the original phase(s), and has been reconcentrated elsewhere. In the former case, U_{rd} should be released from the host minerals to a large extent, as is the uranium contained in them. In the latter case, there are two possibilities: if the U_{rd} are contained in easily leached or soluble phases, they will be released into the circuit; if they are contained in leach-resistant or insoluble phases, they will not be released to a large extent by milling and

leaching of the ore. This would be expected, obviously, to have an impact on the susceptibility of U_{rd} to release from the tailings, as radionuclides held within highly resistant phases are less likely to be released, reducing the potential for the release of harmful species, at least over short-term periods.

The physical and chemical properties of uranium mill tailings present potentially serious hazards to the environment. Besides the usual problems associated with mining operations, and the presence of toxic metals, there is the additional problem of radioactivity. While uranium extraction is highly efficient (with recoveries often >99% [20]), the radioactive daughters are generally not recovered, and report to the mill tailings; of these, ^{230}Th and ^{226}Ra are of the most concern, for the reasons previously stated.

In general, the total amount of radioactivity in uranium tailings is large; for most ores about 85% of the total radioactivity in the orebody is found with the U_{rd} [4,34]. This activity is typically dispersed throughout a large tailings volume, giving a waste with a low level (concentration) of radioactivity, as opposed to high-level nuclear fuel wastes. In addition to the radioactive species present, there are also non-radiological hazards from heavy metals - the Key Lake ores contain high levels of elements such as nickel and arsenic. The large volumes of material involved are also quite reactive chemically, due to greatly increased surface area and severe chemical attack.

Essentially, then, uranium mining and milling produces a new, low-grade ore deposit. However, instead of this "deposit" being located

underground, removed from weathering processes, it is at the surface, largely unprotected from wind and water erosion, oxidation of the tailings, and leaching by meteoric waters. After close-out of the operation, no more effluents would be added, thus tailings seepage should decrease somewhat. However, precipitation generally exceeds evaporation in Canada's wet temperate climate. There are two means of release of toxic species, physical and chemical. Physical release involves the breakdown with time of impoundment dams and embankments, followed by erosion of the uncovered tailings. This allows contaminated material to wash into soil and river systems. Chemical release involves either leaching of tailings by percolating water, or dissolution of precipitates; in both cases, contaminants are released into groundwater and river systems.

Chemical precipitation is especially important as a means of immobilizing radionuclides; for example, the addition of barium chloride to coprecipitate radium as the insoluble sulphate. The precipitates generated during the leaching and neutralization steps may form an important fraction of the tailings; at Key Lake, roughly 600,000 tonnes of ore were processed in the first three years of operation, yielding roughly 700,000 tonnes of tailings - most of this extra mass is due to the precipitation of gypsum during lime neutralization [8]. Also, due to bulking of the ore, the material volume increases by up to 50% [4,18].

Alpha Spectroscopy

The presence of alpha-emitting radionuclides in the ore and tailings studied necessitates some discussion of the interaction of alpha

particles with matter, since experimental methods based on recording such interactions (such as alpha spectroscopy and autoradiography) often provide useful information.

Since for alpha particles with initial energies of roughly 5-7 MeV nuclear transformation reactions should not be significant [27], an alpha particle travelling through a medium loses its energy in two ways: by electronic interactions (at high velocities, ionizing the material); and nuclear interactions, also known as Rutherford scattering (at lower velocities, causing elastic ion-atom collisions). The amount of particle energy lost per collision decreases with increasing target nuclear mass, since momentum must be conserved; the kinetic energy gained by the target nucleus is known as the recoil energy. It is then obvious that lighter target nuclei will gain more kinetic energy from such collisions, and that their recoil ranges will be larger than for heavy nuclei.

A critical factor determining the range of a particle through a given medium is the stopping power of the medium. This term refers to the rate of energy loss dE/dx of the particle in that medium. It is generally assumed that electronic interactions account for the energy loss over most of the alpha particle range; since the fractional energy lost with each such interaction is very small (owing to the very small electron mass), the deflection from the original direction is also very small. The number of interactions required to stop an alpha particle is thus very large, so the range for all alpha particles with the same E_0 is roughly the same for a given medium [27]. Range and stopping power data have been compiled by Northcliffe and Schilling [35]. The stopping power is a function of ion velocity, mass, and atomic number,

and of target composition; "it is convenient to use the hybrid term E/m (MeV/amu)", as opposed to ion energy or velocity, to describe the energy of the ion, "since ions of different mass have the same velocity" with the same E/m value [35]. It is assumed that the stopping power varies smoothly with E/m and Z . Experimental data have been compiled for a variety of absorbing elements, and the stopping power and range in different media can be determined by interpolation. It is common to compare the stopping power of a material to that of aluminum, which has been studied extensively. Relative stopping powers (with respect to aluminum) for various elements found in the tailings are given in Table I. In determining alpha particle ranges through real materials (as opposed to pure element absorbers), it is also assumed that the matrix is a compact solid with homogeneous composition and consistency. To determine the range of an alpha particle in a compound C, with integer molecular weight M , the stopping power or F_c value of the compound relative to aluminum is given by:

$$F_c = 1/M \sum N_i A_i (X_i/X_{Al}) \quad [1],$$

where X is dE/dx , and N is the number of atoms of mass number A in the compound. It should be noted that this equation does not strictly hold for grossly heterogeneous materials, such as coprecipitates or mixed-phase systems, which may contain void spaces, or phase boundary regions of varying composition.

The range of an alpha particle with a given value of E/m in a compound C can thus be estimated; [27,35] by:

Table I. Relative stopping power of various elements with respect to aluminum ($X = dE/dx$).

Element	X_1/X_{Al}	Element	X_1/X_{Al}	Element	X_1/X_{Al}
^{16}O	1.3	^{32}S	0.90	^{75}As	0.6
^{24}Mg	1.1	^{40}Ca	0.85	^{137}Ba	0.48
^{27}Al	1.0	^{56}Fe	0.75	^{207}Pb	0.36
^{28}Si	0.97	^{59}Ni	0.72		

$$R_{\alpha,c} = R_{\alpha,Al} F_c B \quad [2],$$

where $R_{\alpha,Al}$ is the alpha particle range in aluminum (interpolated from tabulated data), and B is a conversion factor to give the range in mm ($B_{Al} = 0.003705 \text{ mm cm}^2 \text{ mg}^{-1}$). Alpha particle ranges for a variety of compounds found in the Key Lake tailings, for several different E_0 , are presented in Table II. The formula for Fe-chlorite was chosen arbitrarily; this mineral forms a solid solution, and has the general formula $(\text{Fe,Mg})(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2(\text{Fe,Mg})(\text{OH})_6$. Since chlorites in the Key Lake ores are known to be iron-rich [19,36], the formula chosen was $(\text{Fe}_2\text{Mg})(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2(\text{Fe}_2\text{Mg})(\text{OH})_6$. An E/m value of 1.20 (corresponding to an alpha particle emitted from ^{226}Ra , which is also similar in energy to ^{230}Th and ^{234}U) was used to calculate the alpha ranges for all the radionuclides listed; the calculated ranges should be valid for ^{226}Ra and ^{230}Th . The value of E/m is larger for the remaining U_{rd} , but the difference in range is small - for example, the range for 7.7 MeV ^{214}Po alpha particles in calcium sulphate differs by only 2 μm , and by only 1 μm for calcium arsenate; thus, there is little error introduced in basing all range estimations on a single alpha energy. The disparity between the calculated and actual alpha ranges is caused by material heterogeneity, the presence of void spaces in imperfectly-formed precipitates, etc.

The recoil range of the target nucleus can be similarly calculated, and will have a shorter range than that of the scattered alpha particle, for target nuclei heavier than ^4He . Conservation of momentum requires that the recoiling nucleus and alpha particle have the same momentum; the recoil energy E_r of the target nucleus, in centre-of-mass

Table II. Alpha particle ranges for various compounds. F_c is the stopping power relative to aluminum. Range values are given in μm for various E_0 : ^{226}Ra ; R_2 for ^{222}Rn ; R_3 for ^{218}Po ; and R_4 for ^{214}Po .

Compound	F_c	R_1	R_2	R_3	R_4
PbSO_4	0.616	13	15	18	26
NiAsS	0.728	15	18	21	31
FeAsS	0.738	15	18	21	31
BaSO_4	0.763	16	19	22	32
NiS_2	0.814	17	20	24	34
FeS_2	0.830	17	21	24	35
FeAsO_4	0.896	19	22	26	38
Fe_2O_3	0.915	19	23	27	38
$\text{Ca}_3(\text{AsO}_4)_2$	0.923	19	23	27	39
* Fe-chlorite	1.038	22	26	30	44
CaSO_4	1.074	23	27	31	45
SiO_2	1.132	24	28	33	48
Kaolinite	1.145	24	29	33	48

coordinates, is then given by:

$$E_r = m_r / (M_t + m_r) E_0 \quad [3].$$

For ^{226}Ra , the calculated E_r value is 0.082 MeV, and the value of E/m would then be 0.0004; the stopping power with respect to aluminum can only be roughly estimated for such a low value of E/m . For example, a recoiling ^{226}Ra nucleus in Fe_2O_3 would have a range of roughly 0.6 μm . Even allowing for matrix irregularities, etc., the recoil range should be $\leq 1 \mu\text{m}$. The other decay products of ^{238}U should have similar recoil ranges. Radon produced by radium decay is gaseous, and may diffuse through the host medium; the distance travelled in this manner then depends on the diffusion characteristics of the medium. However, in the absence of such effects the recoil range is small compared to the alpha range, and U_{rd} are not expected to travel large distances by alpha recoil. Hence, if they are present more than a few μm below particle surfaces, they should not be released by recoil, and in the absence of rapid outward diffusion, should remain with their current host phases, at least for short-term periods.

Alpha spectroscopy has already been mentioned as a useful analytical tool; for most analytical measurements, the isotope of interest is coprecipitated with a suitable carrier - for example, BaSO_4 and $\text{La}(\text{OH})_3$ are commonly used to carry down radium and thorium, respectively. Interpretation of alpha spectra can yield information regarding not only the amount of a radioactive species present, but may also give clues as to its location within the sample, and perhaps with which particular phase, if any, it is associated.

Data from an alpha detection apparatus can be treated in several ways. The most common is to plot the data as signal intensity (counts per channel) vs. energy (channel number). With the appropriate calibration, the level of alpha activity within a sample can be determined for a particular isotope. Interference can arise when two (or more) species with similar E_0 are present within the sample; for example, in the determination of ^{230}Th and ^{226}Ra , the two must be separated by chemical means before counting since their alpha decay energies are nearly equal (4.77 and 4.78 MeV, respectively [37]).

In alpha spectroscopy, control of the sample thickness is crucial, and to obtain spectra with sharp, narrow peaks, the thinnest possible sample must be used, since the energy of the emitted alpha particle is rapidly degraded by the host matrix. This energy degradation causes broadening of the peaks, and may result in low-energy "tailing". The peak definition has been shown [38] to suffer severe deterioration with increased matrix thickness (mass of carrier), as shown in Figure 1. This occurs because with increasing depth below the surface, the residual energy of an emerging alpha particle will decrease, until the maximum range in that medium has been exceeded; beyond this depth, the alpha particles will not be detected. For radionuclides distributed relatively homogeneously in a thick sample, then, there should be a more or less continuous tail of decreasing intensity with decreasing energy, with maximum intensity at the peak energy corresponding to alpha emission from, or very near to, the sample surface.

Alpha spectra obtained from samples of various thickness, such as tailings grains and fine precipitate particles, could then be interpreted with respect to radionuclide distribution: sharp spectra with

Figure 1 (a-c). Alpha spectra showing the effects of increasing carrier on spectrum definition:

(a) spectrum of ^{226}Ra using 0.5 mg barium carrier [after 38].

(b) spectrum of ^{226}Ra using 2.5 mg barium carrier [after 38].

(c) schematic representation of signal degradation with increasing amount of carrier, with $A < B < C$.

narrow peaks and no low-energy tails would indicate that the majority of the radioactive atoms were at or just below particle surfaces (there may be some discrepancy, based on the degree of mineralization of the various phases present - with increasing mineralization, the actual alpha range should approach the calculated range); broad, "smeared" peaks would indicate radionuclide distribution throughout the particles. This may not hold strictly for extremely fine ($\leq 5 \mu\text{m}$) particles and precipitates, since: (a) if the particles are poorly formed, the amount of energy loss may not be large, limiting the extent of peak-broadening; (b) for very small (and hydrated) particles alpha recoil and outward diffusion may be significant; and (c) for very small particles, a large fraction of the alpha-active nuclei will be close to the particle surfaces.

The above discussion has dealt with the alpha spectra obtained from the counting of thin samples, mainly to determine the content of a particular isotope within a sample. While this is a proven, reliable analytical technique, limitations do exist. One of the most important is that for most cases involving material such as mill tailings, in order to obtain accurate activity determinations, it is necessary for the radionuclides to be present in a thin sample - this often requires leaching or digestion of the sample, followed by chemical separations, precipitations, etc. Although useful information can be gathered in this way (such as bulk radioactivity levels and the extent of release by leaching), the above requirement often makes it impossible to determine whether the radionuclides are associated with a particular compound or compounds. In mill tailings, fines typically comprise a large portion of the total mass and volume, and a large fraction of the total

radioactivity is normally found with the fines [eg. 1,2,5,25]. However, they form complex and intimate intermixtures, solid solutions, and coprecipitates; adsorption on particle surfaces likely also occurs. The use of chemical separation methods may displace adsorbed species, leading to incorrect conclusions regarding their associations within the tailings. In essence, then, it is very difficult to obtain thin samples of such materials for counting without disturbing the surface environment, and hence altering the system.

Non-destructive approaches can be employed, however. One in particular that has found application to a wide variety of problems is the use of nuclear backscattering spectrometry, which makes use of Rutherford scattering. For sufficiently thick targets, impinging atomic particles will be reflected, or scattered, from the surface. Typically, a collimated beam of monoenergetic atomic particles (helium nuclei, protons, neutrons, or electrons) is used to bombard the surface to be tested; the scattering energy profiles obtained are then compared to standard compounds or materials, and interpreted to reveal the composition of the surface.

A particularly elegant application of nuclear backscattering was devised by Turkevich [39], who developed an apparatus for the remote analysis of lunar material. Samples (in vacuo) were bombarded with a collimated beam of 6.11 MeV alpha particles from a ^{242}Cm source; detectors were placed at a fixed angle from the incident beam (160°), and scattering spectra measured. By comparing the profiles to those of standards made of various elements and compounds, a determination of the gross chemical composition was made.

The backscattering method assumes limited penetration of the beam

(alpha) particles into the sample, that is, that the source-sample and sample-detector distances are much greater (cm range) than the depth of alpha penetration (μm range). For fairly low E_0 (a few MeV), alpha interactions should consist primarily of Rutherford scattering, which should occur within the first few μm of the sample surface; thus, the above condition should be satisfied.

It can be shown [39-41] that the energy of a scattered particle, E , for a given scattering angle θ , is given by:

$$E = E_0 [X \cos \theta + (1 - X^2 \sin^2 \theta)^{1/2}]^2 / (1 + X)^2 \quad [4],$$

where E_0 is the initial particle energy, and $X = a/A$; a is the beam particle mass number (4 for alpha particles), and A is the mass number of the scattering nucleus. For the simplest case of 180° scattering, Equation 4 reduces to:

$$E = E_0 [(A - a)/(A + a)]^2 \quad [5].$$

The theoretical values of E for a given E_0 (that is, for a given source) can be calculated for various elements, and can be compared with experimental spectra; scattering energies for various elements found within the tailings are given in Table III. Alternatively, Equation 5 can be rearranged to give:

$$A = a[(1 + Y)/(1 - Y)] \quad [6],$$

where $Y = (E/E_0)^{1/2}$; scattering peak energies can then be used to cal-

culate the corresponding mass number and hence identity of the scattering nucleus.

By the same token, it may be possible to interpret alpha scattering spectra obtained in systems where the radioactivity originates from within the sample, rather than from an external source. If, for example, radioactive atoms are located within some material, at or near the surface, and the emitted alpha particles collide with atoms in that material, scattering peaks should be observed. Radionuclide atoms located at the surface, after all, represent a limiting case analogous to the backscattering technique. Interference could arise in two forms for radionuclides distributed homogeneously throughout a sample: first, through energy dissipation with depth; and second, through scattering over large ranges in θ - while radionuclide atoms at the surface would be expected to show scattering predominantly at angles near 180° , giving fairly sharp peaks, the scattering angle at depth will be increasingly random, giving broad peaks of lower intensity, which may then be difficult to distinguish from the background noise. Thus, while this approach would likely apply only to radionuclides held near the surface and not at great depth, such a method could prove useful in the analysis of materials such as mill tailings, where the identities of the host phases are not yet known with certainty, and where the host-radionuclide associations may be altered by chemical analysis. Such differences are a corollary to the previously cited effect of sample thickness on the overall alpha spectrum shape; scattering peaks are not likely to be observed where the majority of the radioactive atoms occur at significant depths below the surface, owing to the higher background intensity, as well as wider variations in θ - the two

effects will then combine to obliterate any scattering peaks which may exist. Conversely, for "thin" samples, that is, where the majority of radioactive atoms are at the surface, scattering peaks will be sharp; the background will also be low, allowing the peaks to be observed, and θ will be close to 180° .

Adsorption Chemistry

It is generally accepted [eg. 1,4,6,25] that adsorption plays a major role in the removal of U_{rd} from leach liquors, and effluent and pore waters in tailings; adsorption of ionic species, therefore, is an important consideration. Several aspects of adsorption theory relevant to the tailings situation will be discussed below. Particular reference will be made to the description of adsorption data, and to the effects of increasing adsorbate concentration on the nature and properties of the adsorbent.

Ions and molecules adsorb in two ways, physically or chemically. Physical adsorption is primarily electrostatic, involving weak, long-range (Van der Waals) interactions. There is no activation energy, and enthalpies of about 20 kJ mol^{-1} are typical [42]. Since the binding energy is low, ions or molecules that are physically adsorbed are often easily desorbed, and the adsorption reaction is often readily reversible. Chemical adsorption involves the formation of (usually) covalent bonds between the surface and the adsorbing species. An activation energy may be required for bond formation, and enthalpies are much higher - roughly 200 kJ mol^{-1} ; the adsorption reaction is often irreversible.

Ions may be specifically or non-specifically adsorbed at the adsor-

bent surface. The extent of adsorption in non-specific adsorption is the same for all ions of the same valency; for specific adsorption, the extent of adsorption is different for ions of a given valency [43].

The surfaces of hydrous oxides normally possess a charge, which results from the presence of unequal numbers of hydrogen and hydroxyl groups at the surface, and is believed to arise from the dissociation of adsorbed water molecules. A general amphoteric surface group can be denoted as SOH^0 (where S represents the adsorbent surface), which can undergo protonation to give SOH_2^+ or deprotonation to give SO^- [44].

The relative proportions of these surface species is dependent on the solution pH, and determines the surface charge. As the pH increases, the surface charge changes from positive to negative; this can be considered in terms of proton release, or hydroxyl adsorption, to restore the equilibrium at the surface. The pH at which the surface charge is zero (considering all species present) is known as the point of zero charge, denoted as pH_{pzc} or PZC. At pH values below the PZC, the surface is positive (favouring anion adsorption), and at pH values above the PZC, negative (favouring cation adsorption). The isoelectric point, or IEP, refers to the pH at which a zero surface charge arises only from H^+ , OH^- , and "species capable of interacting with H^+ , OH^- , or H_2O to form species present in the solid lattice" [45]; that is, where no specific adsorption occurs. In the absence of specific adsorption, the PZC and IEP are equal; likewise, the two are equal if symmetrical specific adsorption occurs [46]. Generally, however, specific adsorption is asymmetric, thus the PZC and IEP are usually different. The IEP can be considered a limiting case when dealing with natural (environmental) systems, which typically have a complex composition of

ionic species. For such systems the PZC is more commonly employed.

The definition of the IEP refers to interacting ionic species which form species found in the adsorbent lattice. Such ions, along with H^+ and OH^- , are known as potential-determining ions, or PDI. Strongly and specifically adsorbed cations and anions could also be included as PDI, since they are often only poorly desorbed, and do affect the surface charge of the adsorbent [43]. The specific adsorption of anions and cations causes a shift in the value of the PZC and IEP; anion adsorption produces a positive shift in PZC (and a negative shift in IEP), and the reverse occurs with cation adsorption, again to restore surface equilibrium. The occurrence of these shifts is also a criterion for distinguishing specific from non-specific adsorption. A shift occurs because the specifically adsorbed anions or cations are present at higher levels than would occur by purely electrostatic interactions; that is, the magnitude of the surface charge (either positive or negative) is greater in the presence of specifically adsorbed ions.

Description of data

Data from adsorption experiments may be described in any of several ways, depending on the information desired and the experimental conditions employed. Three common methods involve the use of: adsorption isotherms, which plot the quantity adsorbed at a fixed pH as a function of adsorbate concentration; adsorption profiles, which plot the fraction of adsorbate removed from solution as a function of some solution parameter - usually pH; and distribution coefficients, which plot the ratio of the adsorbate concentration on the adsorbent to the concentration of the adsorbate remaining in solution, as a function of some

solution parameter - again, usually pH.

The best-known isotherms are the Langmuir, Freundlich, and BET, derived from gas adsorption studies. The Langmuir isotherm is the simplest, and yields a linear plot; it assumes that maximum adsorption is restricted to monolayer coverage of the surface - that is, for low adsorbate concentrations. At higher adsorbate concentrations, data are often better described by a Freundlich-type isotherm [47], which gives a non-linear expression; data are linearized by log-log plots. An advantage of this model is that adsorption is not limited to monolayer coverage. The BET isotherm also considers multilayer adsorption, which often yields sigmoidal isotherms. This method is used primarily for gas-solid systems, but has been applied to certain aqueous systems involving surface precipitation [48]; this will be discussed later.

The second common means of representing adsorption data is by the use of adsorption profiles. The adsorption profile will be useful in the present study, in that it provides a sensitive measure of selectivity in adsorption. This approach is particularly useful when considering adsorption over a wide pH range. Adsorption of ionic species depends strongly on the surface charge, which is itself primarily controlled by pH. Adsorption is low in unfavourable pH ranges, increasing with increasing pH from almost no adsorption to high adsorption over a range of 1-2 pH units. This abrupt change is referred to as the "pH-adsorption edge". Selectivity in adsorption is related to the position of the profile with respect to pH; for example, a cation is considered to be more selectively adsorbed if, under similar experimental conditions, it is adsorbed at a lower pH [49]; the reverse is true for anion adsorption. The location of the adsorption edge with respect to

pH is not an intrinsic characteristic [50], but rather a function of the adsorbate and adsorbent concentrations, equilibration time, and liquid-solid ratio. Of these factors, it has been shown [50,51] that the most important is the adsorbent concentration. The adsorption selectivity of alkaline earth cations on FHO was found [52] to decrease in the order:

and to correlate with the ionic radius: barium, with the largest crystal ionic radius (and smallest hydrated radius [28]), also has the lowest dehydration energy; this facilitates partial dehydration of the hydrated cation which in turn facilitates adsorption. For more easily dehydrated cations the formation of inner-sphere complexes (that is, where the cation is bound directly to a surface hydroxyl group and not through an intervening water molecule, as for outer-sphere complexes) is made more favourable, which should be more strongly and selectively adsorbed. The greater selectivity observed for transition metals, with respect to, say, alkaline earth cations, shows that between groups of elements the hydrolysis characteristics are one of the chief factors in adsorption; within a group, especially for the alkaline earth cations, with their low tendencies to hydrolyze, hydration and dehydration properties become important.

The third common method of data treatment is by the use of distribution coefficients, to interpret adsorption data (in this case, in terms of the law of mass action). The chief advantage in the use of distribution coefficients is that adsorption profiles, which are often

sigmoidal in shape (and may require five or more parameters to fit the data), can be simplified to a two-parameter linear plot. This plot enables one to compare the relative selectivities for different adsorbates, and to calculate the number of protons released per cation adsorbed. Since specific adsorption of cations usually results in the release of protons from the surface, it is convenient to describe proton release in terms of a $H^+ - M^{n+}$ exchange. The number of protons released per cation adsorbed, α , can be determined for both cations and anions (which consume H^+ or release OH^-), but is more often used with cation adsorption.

It is generally recognized [eg. 46,47,53,54] in adsorption studies of (for the most part) cations on various adsorbents that at low concentrations the data can be described by a Langmuir isotherm, and at moderate concentrations, by a Freundlich isotherm. However, problems arise in trying to fit data for higher adsorbate concentrations and at high pH, where precipitation may occur, since the surface complexation approach predicts monolayer saturation for adsorption. Also required is the introduction of modifications such as sites of varying binding strength, adsorption of different species, and coulombic interactions [48] to fit data at higher adsorbate concentrations; such modelling contains multiple fitting factors, complicating matters considerably, while still predicting monolayer saturation. Furthermore, where precipitation at the surface occurs, the surface complexation model predicts a sudden change from adsorption to precipitation reactions, related to K_{sp} , which is contrary to observation. There is also the inherent assumption in complexation models that soluble (and thus re-

versible) complexes are formed by adsorption.

An extension of adsorption to higher concentrations may involve the formation of precipitates on the adsorbent surface; this, obviously, may drastically alter the nature of the adsorbent surface. Several authors have concluded from adsorption studies [eg. 12,55-57] that surface precipitates have formed, and that they may be very important in industrial systems such as tailings piles, where concentrations are generally much higher than used in laboratory studies. This importance arises in part from the observation that the formation of precipitates at the adsorbent surface can radically change the characteristics of the adsorbent. James and Healy [55] found that the adsorption of Co(II) on SiO_2 led to the formation and condensation of cobalt hydroxide at the surface; this coating seemed to "reproduce the properties of bulk Co(OH)_2 solid after from 5 to 10 layers of condensed cobalt hydroxide". Tewari and Lee [56] concluded that surface precipitation of Co(OH)_2 on TiO_2 and Al_2O_3 occurred before hydroxide precipitation in the bulk solution. Weise and Healy [57] observed a shift in the isoelectric point (IEP) of TiO_2 with Al^{3+} adsorption; they found this shift to be "consistent with progressive nucleation of a coating of aluminum hydroxide". The shift in IEP continued with increased aluminum concentration until a limiting value "typical of the IEP of solid aluminum oxides and hydroxides" was reached. In their work on the removal of arsenate and phosphate from solutions by natural sediments, Holm et al. [58] concluded that "since the loss from solution occurred only when the sediments were present, either sorption or surface precipitation must be controlling the (solution) concentration". Most relevant to the present work was a study of ferric ion

reduction in soils, in which Willett and Cunningham [59] found that saturating FHO with phosphate "results in a strengite-like surface"; strengite is a naturally occurring iron-phosphate species with the formula $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and is analogous to the iron-arsenate mineral scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$).

It was shown by Benjamin and Bloom [12] that drastic changes in cation adsorption on FHO could be produced by the co-adsorption of certain anions. Their conclusion was that above a certain solution concentration of the anion, surface precipitation occurred, creating a new adsorbing surface; this new surface could increase, or have little effect on trace cation adsorption, depending on the relative affinities of the adsorbing cation for the new anion surface and the original substrate (a correlation with compound insolubility was also inferred). They also concluded that "the secondary phase appears to be an iron-anion solid rather than a trace metal-anion solid", even though cation and anion were added almost simultaneously to the suspension. Conversely, Benjamin [51] later demonstrated the reverse phenomenon, that is, a large increase in the removal of anions from solution by the adsorption of sufficient cation to produce a secondary surface phase, probably $\text{M}(\text{OH})_2$. It was also concluded that electrostatic interactions were not of primary importance, that is, the increased surface potential owing to metal adsorption was not the main factor in the increased anion removal.

In a review comparing adsorption with precipitation at solid-liquid interfaces, Corey [13] reached a similar conclusion, namely that heterogeneous nucleation of a secondary solid phase at the adsorbent surface occurred once a critical solution concentration had been ex-

ceeded; adsorption reactions would be the controlling factor below this critical concentration. Once the nucleation of a second solid phase had occurred, the solubility (or desorption) of the adsorbate would be controlled by the solubility of the new solid phase and not by adsorption reactions. Adsorption and precipitation are treated as analogous processes, with adsorption possibly leading to precipitate formation, depending on system conditions. However, it was concluded that, while analogous, the two processes operate in different ranges of conditions and shift from one to the other, depending on whether the critical adsorbate concentration has been exceeded.

Surface precipitates of iron on various adsorbents have also been reported. Gherardi and Matijevic [60], in a recent study of the interaction of precipitated iron with TiO_2 , found that depending on experimental conditions (iron concentration and pH), three types of interaction were observed: independent particles of hematite were produced; there was a mixture of independent hematite particles, along with TiO_2 coated to varying degrees with hematite; and the formation of a surface phase only. Generally, independent hematite and TiO_2 particles were observed with increasing pH and iron concentration; pure surface precipitation was observed in a narrow pH range (2.0-2.3) for $2 \times 10^{-4} \text{ M Fe}^{3+}$. Anderson et al. [61] determined three adsorption processes to describe Fe^{3+} adsorption on porous silica: adsorption of monomeric species, at low Fe^{3+} concentration; adsorption of oxyhydroxide polymers, mainly on the external silica surface, under similar conditions; and the formation of oxyhydroxide polymers from low-molecular-weight species (for fresh iron solutions where larger polymers had not yet formed). X-ray photoelectron spectroscopy data showed that the

iron was generally spread evenly over the whole surface.

It has already been noted that the surface complexation approach requires complicating modifications to explain moderate surface coverages, competition from other ions, and surface precipitation. In a recent paper, Farley et al. [48] have proposed a surface precipitation model, which is basically an extension of the surface complexation approach, and is mathematically analogous to the BET isotherm for gas adsorption. The model considers multilayer adsorption as surface coverage increases: as cations are adsorbed, a hydroxide (assuming no strongly binding anions such as sulphate or arsenate are present) surface is formed, allowing further metal adsorption. In effect, the interface is extended into the solution, as each succeeding surface layer is covered by new material from solution and the "old surface" is buried under the "new surface". The "secondary surface phase" previously described [12] is defined by Farley et al. as a "surface phase whose composition varies continuously between that of the original solid and a pure precipitate of the sorbing cation", which also agrees with the previously cited work of James and Healy. This model allows for a smooth transition between surface complexation reactions dominating at low adsorbate concentrations, to precipitation reactions at high concentrations, and treats the forming surface precipitate as essentially a solid solution. The concept of solid solution formation in the model accounts for the observed phenomenon of surface precipitation occurring before precipitation in the bulk solution.

The H^+/M^{n+} stoichiometry of cation adsorption can be dramatically affected by the formation of surface precipitates. As the new surface phase forms, and surface properties approach those of the new phase,

adsorption may also approach that expected for the new phase. It was shown [12] that Cd^{2+} adsorption onto FeAsO_4 was "very similar" to that on FHC with arsenate adsorbed.

The surface precipitation model can also predict shifts in the pH-adsorption edge for varying sorbate/sorbent ratios without modification of model constants, that is, without the inclusion of multiple fitting parameters; it can also be extended to competitive systems and anion adsorption. In addition, it was more recently shown [62] that the surface precipitation approach could be included in a multiple site-type surface complexation treatment of adsorption data without adding further parameters. While useful mainly for amorphous oxides, the model may be applicable to crystalline oxides (despite their lower surface areas and reactivity), if it is considered that more time will be required for the establishment of solid solution equilibria; it has already been noted [5,33] that surface coatings of hematite on sediment grains are ubiquitous in natural systems.

II. Methods and Methodology

To answer the questions raised in this study, several experimental approaches were taken. To determine the identities of the U_{rd} host phase(s), an actual sample of "fresh", unweathered Key Lake tailings was examined by a variety of non-destructive means, including density separation, alpha and gamma counting, and autoradiography; specific grains were also sent for X-ray diffraction and microprobe analysis. To determine the effect of arsenate on the removal of radium from solution, a series of adsorption experiments was carried out, using radioactive ^{133}Ba tracer to model radium, with ferric hydroxide (FHO) as the adsorbent. This adsorbent was chosen for several reasons: it has been extensively studied in the literature [eg. 12,14,46,50,53, 54,63]; its PZC is such that the surface charge can be made positive or negative at near-neutral pH values; it can be prepared simply and reproducibly; and its occurrence in natural systems as coatings on mineral and soil material surfaces is ubiquitous [33]. The results from experiments with added arsenate and sulphate, at various solution concentrations, were compared to each other and to experiments carried out in the absence of specifically adsorbing anions. In the case of mineral identification, previous results [7] were used as a guide in the choice of grains for testing.

Tailings Handling

A sample of freshly deposited Key Lake mill tailings (Gaertner ore-body) was obtained in March, 1986 (sample was taken November, 1985)

through the National Uranium Tailings Program. The sample was typical of the material produced by ore leaching and subsequent treatments [8]. The first step in handling was drying a portion of the tailings to be examined. Several grams of tailings were placed in a beaker, and left on a hot plate at low heat for several hours; a nickel disk was suspended above the beaker to trap any polonium released. The dried material was broken up with a glass rod, and some set aside for bulk gamma counting. The remainder was sieved to -80/+230 mesh (63-180 μm), for further work.

Density Separation

To determine the partitioning of radioactivity with respect to density (most mineral oxides are more dense, while precipitates are generally expected to be less dense, respectively, with respect to heavy liquids), a sample of the sieved tailings was weighed out, and placed in a separatory funnel, to which a heavy liquid was added; bromoform (CHBr_3 , density = 2.87 g cm^{-3}) was used. After allowing sufficient time for separation of the density fractions (overnight), the heavier material was drawn off and collected on Whatman #52 paper by gravity filtration. The filtered material was then rinsed with several portions of methanol to remove the bromoform, then with acetone, and allowed to air-dry. The light fraction was then drawn off and treated as above. A further separation of the heavy fraction was planned using methylene iodide (CH_2I_2 , density = 3.33 g cm^{-3}), but was not performed owing to the very small quantities of heavy material recovered from the bromoform separation. The heavy and light fractions were then weighed and counted for their gamma activity; a 3 x 3 inch Na(Tl)I gamma-ray

detector (Harshaw), with a +1000 V charge maintained by a stabilized high-voltage power supply (Fluke 408B), was coupled to a 512-channel analyzer (Northern NS-900); the output was sent to a printer. The above apparatus was used for all gamma counting measurements; calibration and relative efficiency were determined by comparison with certified reference standards of known specific gamma activity. For tailings samples, the 0.186 MeV decay peak of ^{226}Ra (4% abundance) was used to calculate the ^{226}Ra content of the sample; the amplifier gain was adjusted to separate this peak from others of similar energy. Counting times varied, depending primarily on sample mass, and were generally on the order of 600-4000 s. The total peak signal was corrected for background, to determine the net counting rate, and finally the specific gamma activities of ^{226}Ra for the heavy and light fractions. This was later repeated, using larger samples, at the Radiation Protection Branch of Health and Welfare Canada, by Mr. J. M. Quinn (using a Canberra hyperpure germanium detector and Canberra amplifier, with a resolution of 0.5 keV/channel). Further material was separated as required, following the above procedure.

Autoradiography

Alpha-autoradiography of representative grains from the two density fractions was carried out, to determine whether the observed radioactivity was widespread, or restricted mainly to specific minerals. It should be noted that precipitated material was not examined by autoradiography, owing to its softness and extremely small particle size (which made handling and sample preparation impractical); only solid grains were used. The grains to be tested were removed from the

separated tailings sample by hand picking, and embedded in Parafilm covering a glass slide; most grains were obtained from the heavy fraction. Autoradiographs were then made using Kodak LR115A high-resolution autoradiography film (12 μ m thickness cellulose nitrate emulsion on an acetate base), by placing the film in direct contact with the mineral slide; exposures were 96 hr. Autoradiographic films do not record information in the same manner as conventional silver halide emulsions; the alpha particles emitted from within the sample pass through the cellulose nitrate emulsion, leaving behind disordered "damage tracks", which are revealed by etching (in this case, with 10% KOH_(aq)). The disordered emulsion is removed more rapidly than the unaffected emulsion; the alpha tracks can then be distinguished from the background, as a pattern of dots. Following exposure, the films were etched for 130 min. in a 10% solution of KOH at 55 °C without agitation, washed 30 min. in running water, rinsed briefly in 95% methanol, and allowed to dry. The fixed exposure time allowed direct comparison of results for different samples, and etching conditions were chosen to reveal most of the alpha tracks without allowing too high a background image density.

Grains of the more alpha active classes were identified by single-crystal X-ray diffraction, carried out by Mr. R. Conlon on a Philips system (PW 1080/01 diffractometer, coupled to a PW 1750/10 generator).

Previous work by the author [7] pointed out a relationship between the level of observed alpha activity, shown by a higher track density on autoradiographs, and mineral type. One of the most radioactive minerals was identified by X-ray diffraction as hematite; the presence or absence of a friable surface was believed to influence the observed

level of alpha activity. An experiment to confirm the radioactivity level of the surface material for Key Lake tailings was carried out: eight grains were embedded in Parafilm in a rectangular grid, and an autoradiograph made; the surfaces of the grains were then scraped, and another autoradiograph made; the grain cores were then moved from their original locations, and a third autoradiograph made. The original orientation was maintained for all grains throughout these experiments. Similarly, scraped and unscraped grains were sent for microprobe analysis, in an effort to determine (by comparison) the composition of the friable surface material; analysis was carried out using a Cambridge Microscan 5 electron microprobe, by Mr. P. Jones of Carleton University.

Another autoradiograph slide was prepared, consisting of 33 hematite grains in a rectangular grid, to determine qualitatively the overall level of alpha activity of this phase. It had also been previously determined that the "hematite" grains from Midwest Lake actually consisted of an extremely fine intermixture of hematite with a calcium-rich aluminosilicate phase(s); the resolution of the instrument was insufficient to identify unambiguously the secondary phase(s). Several Key Lake "hematite" grains were sent to CANMET's Mineral Sciences Laboratories, and were examined using several means by Mr. J. Laflamme. X-ray diffraction was used to identify the crystalline phase(s) present; quantitative wavelength dispersive spectrometry (WDS) was carried out on a JEOL-733 system at 20 kV, with a beam current of 15 nanoamperes. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were also used for qualitative analysis.

In order to determine the distribution of radionuclides throughout

the "hematite" grains, several grains were embedded in a disk of polyester resin with epoxy cement. Fine (#1000) Tech-Met silicon carbide powder was used to grind the disk by hand; autoradiographs were made after successive amounts of surface had been removed, to follow the radionuclide distribution with successive cross-sections of the grains. Silicon carbide powder was used rather than cerium oxide, owing to the natural radioactivity (which may be considerable) associated with the latter. This was later repeated for ten grains of various mineral types, for a comparison of radionuclide distributions within other minerals. These grains were identified, if required, by microprobe analysis; photomicrographs were also made (Leitz system); the film used was either Kodak Panatomic-X or Ilford Pan F; films were processed in Microdol-X developer according to the manufacturer's recommendations. The photomicrographs were then combined with autoradiographs printed to the same optical scale; it was anticipated that the superimposition of the two images would allow U_{rd} -mineral associations to be determined for multi-phase grains.

Alpha Spectroscopy

Preliminary alpha spectroscopy results were not encouraging; alpha peaks overlapped, preventing clear distinctions between radium and thorium levels from being made (the difference between alpha energies of the two is less than 0.1 MeV). For this reason, as well as degradation of the spectra (with peaks and noise at lower energies, not seen with thin radium and thorium sources), alpha spectroscopy was not initially thought to be useful in this work. However, it was reasoned that this very signal degradation could be useful; it has been shown

[38] (see Figure 1) that as the sample thickness increases, the alpha spectrum becomes increasingly degraded, with the lower-energy portion of the spectrum tapering fairly smoothly. It was thus surmised that, if radionuclides were present primarily beneath grain surfaces, then the spectra would be less well defined than if the U_{rd} were present primarily at outer grain surfaces; this information could then be used as an indicator of radionuclide location, and thus lead to interpretations regarding the origin and extent of redistribution of radionuclides from their original locations.

Accordingly, alpha spectra were obtained, using samples of heavy and light tailings fractions mounted on masking tape; old thorium and radium leach samples were used as references. Aliquots of ^{230}Th were also precipitated in the presence of varying amounts of FHO and $\text{La}(\text{OH})_3$; the amounts of iron and lanthanum added were calculated to give 1, 2, 3, and 4 mg of the metal. This was done to allow a comparison to be made with the tailings sample spectra. It was anticipated that, since with increasing carrier mass (and thus thickness) the alpha spectrum should be degraded, a comparison of the overall shapes of these spectra with the tailings sample spectra could allow a qualitative interpretation to be made with respect to the average depth of U_{rd} below particle surfaces.

Alpha counting was done in vacuo, with a surface barrier detector mounted in a vacuum chamber (Ortec Br-024-300-100). The charge bias on the detector was maintained at -100 V with a stabilized power supply (Lambda); the detector was connected to a preamplifier (Canberra 2003 BT) and amplifier (Canberra 2012). The alpha detection system was calibrated with ^{241}Am and ^{230}Th alpha standards; energy resolution was

100 keV per channel. Data were then sent to a 128-channel analyzer (custom made by Mr. Paul Isaacs, Denbeigh, Ont.), and the output sent to a printer.

It was discovered near the completion of this project that an apparent electronic interference in the alpha detection system resulted in spurious peak intensities at lower energies. These were not observed with thin samples, since the signal intensity at low energies was not significantly above background levels. To confirm (and, if necessary, correct) interpretations made from such possibly suspect spectra, the samples were sent for alpha counting to the Radiation Protection Branch of Health and Welfare Canada; counting, again, was performed by Mr. J. M. Quinn (using a Canberra detector and amplifier). The resolution of this system was 10 keV/channel.

Alpha spectra obtained from bulk samples were expected to give some indication of the elements (and thus minerals) with which radionuclides were associated, from the scattering peaks produced (interaction with specific elements should produce consistent, discrete peaks). A certain degree of ambiguity, however, was also expected to remain; a scattering peak from oxygen, for example, could indicate a wide variety of phases, such as quartz, clays, and oxyacid salts.

It was decided that a useful approach would be to obtain backscattering spectra from inactive samples of particular minerals and/or compounds. This was accomplished by a method based on that of Turkevich [39,64]. The reasoning behind this experiment was as follows: alpha particles from a monoenergetic source should produce distinctive backscattering peaks for single-mineral targets; it should then be possible to correlate the peak scattering energies of the various

elements within the target with any scattering peaks observed arising from within the tailings samples. The source chosen was ^{230}Th , since it is present in the ore; this allows simpler interpretation of spectra than a source with a significantly different initial energy (which would require scaling of data). Radium was not used, as the ingrowth of daughter products would complicate interpretation; the daughter levels for the ^{230}Th solution used were much lower, yielding "cleaner" spectra.

The apparatus used for the backscattering experiments was adapted from the existing alpha counting equipment; a second sample holder was added below the first. The alpha source was prepared as follows: an aluminum planchet was drilled and punched, to produce a hole approximately 1.5 cm in diameter, with a raised lip to prevent emitted alpha particles from travelling directly to the detector. The underside of the planchet was coated to prevent creeping of the evaporating thorium solution; small drops (with a total volume of about 30 μL) of a fairly radioactive ($1 \times 10^6 \text{ pCi mL}^{-1}$) ^{230}Th stock solution were then placed around the hole to form a thin ring, which was allowed to evaporate slowly. The source planchet was then inverted (so that the alpha particles would be emitted downward), and placed in the upper sample holder, with the sample to be tested in the lower holder; backscattering spectra were then obtained (with counting times of several hours).

Backscattering samples were prepared in one of two ways: the first was to place a suitable quantity of crushed mineral on a planchet covered with masking tape; the second was to filter precipitated material (in the case of FHO) or slurry (in the case of CaSO_4) by suction onto 0.45 μm filter disks (Gelman Sciences DM-450 Metricel).

Background spectra were prepared by using planchets covered with masking tape and filter disks, respectively. Thin slabs of mineral hematite and gypsum were also prepared, by Mr. P. Nagrel (Carleton University). The spectra obtained from such samples were then compared to those made with the tailings samples, to establish which prepared samples correlated best with the tailings spectra, and thus perhaps the association of the radionuclides with the corresponding mineral or precipitate species in the tailings.

It must be noted that the energies of the scattered particles [Equations 4-6] are dependent on the scattering angle, and that the E values will increase as the scattering angle decreases from 180° . The effect of scattering angle increases with decreasing atomic number, and can be expected to result in broadening of the spectrum peaks. This cannot be completely avoided; while the sources were prepared in such a way as to minimize the spread of thorium across the planchet surface, compromises were necessary regarding the size of the hole in the planchet. Ideally, the hole should be small so as to allow only those alpha particles with backscattering angles close to 180° to reach the detector; on the other hand, it must be large enough to permit reasonably short counting times. The backscattering method also assumes limited penetration of the source alpha particles into the sample, for a given value of E_0 . That is, the source-sample and sample-detector distances are much greater (cm range) than the alpha penetration (μm range); this should be valid for the fairly low E_0 employed in these experiments.

Several scattering sources were prepared; the average hole size was roughly 1-1.5 cm. The radioactivity of the source was limited by the

nature of the solvent used for the tracer solution, 2.5 M HClO_4 (which was used to minimize thorium adsorption on glass surfaces). Even after dilution of an aliquot of this stock solution with 1 M HCl , enough HClO_4 remained to react with the coating on the planchet, forming a crumbly surface layer. This reduced the physical stability of the source, and may have caused variations in the energy of emitted alpha particles.

Adsorption Studies

It was expected (based on the low leaching rates of radium and thorium from Midwest Lake tailings [7]) that anions, in particular arsenate, may play a significant role in aiding the removal and/or retention of U_{rd} from leaching solutions and in the tailings. Adsorption experiments were carried out to determine whether the presence of specifically adsorbing anions would affect adsorption of ^{133}Ba (cf. radium) onto FHO, and to what extent this is influenced by the choice of anion. The anions tested were sulphate and arsenate; the former is, naturally, present in very large amount in H_2SO_4 leaching, and the latter is formed in significant amounts through the oxidation of arsenides. Arsenate also forms extremely insoluble compounds with both iron and barium; it was anticipated, then, that arsenate would show more effect than sulphate. Adsorption of the anions themselves was not studied, however; it has been established by many authors that sulphate and arsenate are strongly adsorbed onto FHO. Similarly, desorption of the tracer was not studied, inasmuch as the method of sample collection did not lend itself to desorption studies.

All reagents used were analytical grade or better; prepared

solutions were used without further purification. Experimental vessels were Pyrex or Kimax glass; storage bottles for prepared solutions were polyethylene. A stock solution of $(1.0000 \pm 0.0003) \times 10^{-2}$ M ferric iron was prepared by dissolving and making up the calculated amount of ferric nitrate (Analar, BDH) to 1000 mL in a volumetric flask with 0.1 M HNO_3 (diluted from Anachemia concentrate). Anion solutions were prepared using sodium arsenate (Analar) and sodium sulphate (Fisher Scientific). Stock solutions of (1.000 ± 0.001) M arsenate and $(1.000 \pm 0.003) \times 10^{-1}$ M sulphate were prepared as above; more dilute solutions were prepared by dilution of the stock solutions. The radioactive tracer used to model ^{226}Ra was ^{133}Ba ; working solutions were prepared by Mrs. I. deJong, by dilution from the original sample (received from Amersham Radiochemicals in 1977, 400 mCi as BaCl_2 in 1 M HCl) with a small volume of concentrated HCl and dilution with 0.1 M HNO_3 . Thorium was not used as an adsorbate, since its strong hydrolysis would have severely limited the pH range that could be studied. Reference standards were prepared by evaporating an aliquot of the working tracer solution in an aluminum counting planchet previously coated with spray lacquer (Chesterton); the reference samples were then counted repeatedly to determine their average gamma activity. Over the course of the adsorption experiments, two tracer solutions were employed: for the first, with an average specific activity of $500.95 \text{ c s}^{-1} \text{ mL}^{-1}$, 0.100 mL aliquots were used; for the second, with an average specific activity of $863.34 \text{ c s}^{-1} \text{ mL}^{-1}$, 0.050 mL aliquots were used.

The experimental procedure followed for all adsorption experiments, using a batch preparation of FHO, was similar to that of Davis and

Leckie [14], in which various cations and/or anions were added to a suspension of aged FHO; where both anions and cations were used, the anion was added first, followed by cation addition 1 hr. later. A 1.00 mL aliquot of the stock ferric iron solution was transferred to a clean 50 mL beaker with an Eppendorff pipetter, to which 50.00 mL of distilled water was then added, using a volumetric pipette. Ferric hydrous oxide was precipitated by the dropwise addition of 0.1 M NH_4OH (diluted from Canlab concentrate) from a buret, while stirring with a Teflon rod. The volume of base added was varied to give a wide range of final suspension pH values, and was recorded. It should be noted that this resulted in a (narrow) range of final volumes; 0.1 M NH_4OH was used throughout the experiments (instead of a more concentrated solution for the higher pH range) in order to more reproducibly precipitate the FHO. Also, to obtain a high pH with dilute base would require volumes large enough to greatly change V/m; the maximum pH reached was roughly 9. Each sample was then allowed to stand under atmospheric conditions at laboratory temperature (20-22 °C) for 3 hr., after which time a 0.100 mL aliquot of the desired anion solution was added with a variable pipetter (Gilson P-200), with brief and gentle stirring of the suspension; following an equilibration period of 1 hr., an aliquot of the ^{133}Ba tracer was added (also using a Gilson pipetter) with brief and gentle stirring, and the suspension left to stand for a further 2 hr. Roughly 30 s prior to anion and tracer additions a small volume of 0.1 M NH_4OH (0.1-0.3 mL) was added to maintain the desired pH (by counteracting the acidity of the added solutions), and the volume recorded. It is well established [eg. 47,65] that the initial adsorption of species such as sulphate and arsenate on FHO is very rapid

(>90% within 15 min.); while a true equilibrium is not reached within the experimental time frame (because of the changing nature of the adsorbent), a quasi-equilibrium can be expected to be reached in 1-2 hr. Experiments were also conducted in the absence of added anions, as a control; for these experiments, the suspension was allowed to stand 4 hr. prior to the addition of tracer. The precipitate was then collected by suction on weighed 0.1 or 0.2 μ m membrane filter disks (Gelman Sciences HT-100 and HT-200, respectively), using Teflon filter towers. To minimize sample loss on the filter towers, during collection the suspension was first decanted, and then filtered in small portions. Distilled water adjusted to pH 9 with 0.1 M NH_4OH was used in sample collection and rinsing, to minimize any desorption of tracer due to changes in pH. The filters were then placed on aluminum planchets and left to dry at a temperature of about 35 $^{\circ}\text{C}$ for 20 min. The samples were then counted for their gamma activity, and the sample counts obtained compared to the reference standard, to determine the fraction of the tracer adsorbed by the FHO. For these experiments, the 0.276, 0.302, 0.356, and 0.382 MeV decay peaks of ^{133}Ba were measured. These peaks overlap considerably, and so were taken as one "composite" peak; the same peaks were measured for the reference. The samples were then allowed to air-dry for several days or weeks, and then alternately heated and cooled for 40 min. until a constant weight was obtained.

Data Treatment

Data treatment was mentioned briefly in the introduction; in this study, the latter two approaches (adsorption profiles, and distribution coefficients or ratios) were used to interpret the adsorption data.

Plots of percentage adsorption vs. pH were prepared, to determine qualitatively any change in the adsorption profiles with changing conditions. Distribution ratios were also calculated, to determine the relative selectivity, and the H^+/M^{n+} exchange, of the substrate for ^{133}Ba in the three series of experiments.

Interpretation of adsorption data in terms of the law of mass action was first undertaken by Kurbatov, Wood, and Kurbatov [63], who described the adsorption of dilute ($\leq 10^{-5}$ M) cobalt solutions as an equilibrium exchange of adsorbent protons with Co^{2+} ions in solution. Under the experimental conditions employed, that is, constant amounts of cation, adsorbent, and sample volume, with varying pH, a plot of $\log D$ vs. pH (known as a Kurbatov plot) should be linear, with the slope $\times$ giving the number of protons released per cation adsorbed. Kurbatov et al. considered the quantity of adsorbent to be constant if it remained large with respect to the quantity of cation. The distribution ratio D is given by:

$$D = y/(1-y) \quad [7],$$

where y is the fraction of adsorbate removed from solution. For the present work, D is defined as follows:

$$D = C_s / (C_{\text{ref}} - C_s) \quad [8],$$

where C_s is the sample counting rate (dis s^{-1}), and C_{ref} is the reference counting rate (which varied slightly from day to day). It is more appropriate for adsorbents such as FHO to employ distribution ratios,

rather than coefficients, since true equilibrium is not likely to be reached for adsorption periods of several hours, and indeed may never be reached (owing to the changing nature of the adsorbent with aging). The mass law approach has been cited more recently [66]; the authors noted that, in addition to the H^+/M^{n+} exchange ratio, a selectivity criterion can be obtained from a second parameter of the $\log D$ vs. pH plot. This is the intercept at $\log D = 0$, representing the pH at which 50% of the adsorbate is removed from solution, and is denoted as pH_{50} . Since increased selectivity can be defined as adsorption occurring at a higher and lower pH for anions and cations, respectively, comparing the values of pH_{50} for various adsorbates under similar conditions (or for a single adsorbate at varying concentrations), can give an indication of the adsorption selectivity. The pH_{50} serves as an arbitrary but convenient benchmark for adsorption selectivity; like the position of the pH-adsorption edge, it does not have an intrinsic value for a given adsorbent or adsorbate, and will vary depending on the experimental conditions employed. However, for a series of similar experiments, the effects of differing cation (or in the present work, anion) concentration can be determined by following the changes produced in the pH_{50} and/or χ .

The mass law approach has also been used by others [eg. 29,67]; Benes, Ströjc, and Lukavec [29], recognizing that adsorption is affected by the liquid-solid ratio (which was held constant by Kurbatov et al.), defined their distribution coefficient as:

$$K_d = (m_a/m_b)(V/m) \quad [9],$$

where m_a and m_s represent the equilibrium amounts of adsorbate at the surface and in solution, respectively, V is the total volume in cm^3 , and m is the adsorbent mass in grams; there is an inherent assumption in this equation that the mass contributed by adsorbed ions is negligible.

In the present work, Equation 8 will be used to determine x and the pH_{50} for the experimental adsorption data: the amount of radioactive tracer added is extremely small when compared to the amount of adsorbent, and is virtually constant; the volume of iron stock solution used was constant; finally, the total solution volume should be fairly constant, thus (barring significant mass changes as a result of ion adsorption, sample loss, etc.) V/m should also be fairly constant. An equation similar to Equation 9 should not be needed, then, to describe the adsorption data; Equation 8 should be satisfactory as long as the mass recovered does not vary greatly.

Any tracer remaining in solution was removed from the filtrates by the addition of 2 mL of 7×10^{-3} M BaNO_3 and 1 mL of concentrated H_2SO_4 , to precipitate BaSO_4 ; this step was repeated if counting of the filtrate showed ^{133}Ba activity significantly above background level. Some tracer was adsorbed onto the glass beakers, or trapped in fine particles of precipitate that were not removed during rinsing; tests showed that up to 5% of the tracer could be found with the sample beakers. The following method was found to be effective in reducing any remaining ^{133}Ba to background levels: following filtration of the iron precipitate, roughly 60 mL of 0.5 M HNO_3 was added to each of the beakers, which were then left to stand at low heat on a hot plate for 30 min.; the beakers were then rinsed with distilled water, 60 mL of

1% EDTA was added, and left to stand another 30 min. at low heat, after which they were rinsed copiously with distilled water. The Teflon filter towers and stirring rods were left to stand overnight in 1% EDTA diluted 1:1 with distilled water, and rinsed copiously with distilled water before re-use.

III. Results and Discussion

Opening Statement

As has been noted, the present work was based on results obtained from contract analysis of a bench-scale sample of tailings from Midwest Lake, an orebody similar to the Key Lake orebodies; these results provided a starting point for the present work. One such result was that dense minerals, while comprising only about 2% of the sample mass, accounted for about 98% of the radium shown to be present by digestion analysis. Also, grains identified by X-ray diffraction as hematite were found by electron microprobe analysis to be an intimate intermixture of hematite with a then unidentifiable silicate phase. Autoradiography showed this mixed phase to be quite radioactive, and identified several other minerals which were somewhat radioactive. The similarities observed between the two orebodies suggested similarities in the behaviour (and thus location) of radionuclides, specifically radium and thorium, within the tailings. As will be shown below, this belief was, in general, justified.

The results will be discussed for each type of work performed: examination of bulk tailings, microprobe analysis, autoradiography, alpha spectroscopy, and adsorption trials. Following this, the results will be interpreted with respect to the Key Lake tailings system, with a view to possible implications for uranium mill tailings in general.

Tailings Properties

The sample of Key Lake tailings, as received, consisted of a light brown, very soft putty-like mass of fine-grained material, forming an essentially homogeneous mixture of components, with some local concentrations of light- or dark-coloured minerals. After drying (water content of the sample tested was almost 50% by weight) the material broke up easily under light pressure into a fine powder similar to dried clay or mud, with a light tan colour. This tan-coloured material appeared to be a mixture of crystallites and fine laths (probably gypsum), and amorphous or extremely fine particles of other compounds.

The density separation (using bromoform) was not as efficient as in previous work for the Midwest Lake tailings, owing to the large clay and fines content of the Key Lake sample. The clays and other fine material present (largely precipitated CaSO_4) had a tendency to cement particles together, or to surround small dense particles in a lighter matrix. Conversely, it is possible that very fine particles of dense minerals were mixed with less dense material in the light fraction. Partitioning of the tailings on a mass basis showed that the denser minerals comprised a very small fraction of the total mass - only 2.3% of the material recovered after separation of a weighed sample was more dense than bromoform. The two density fractions will be referred to as "light" and "heavy", for material less dense, and more dense, respectively, than bromoform.

The overall appearance of the light fraction was very similar to the unseparated tailings. Coarse mineral grains made up a very minor proportion of the sample, $\leq 10\%$ from visual estimates. Most of the larger grains were clear and vitreous, and assumed to be quartz (which

was later confirmed by X-ray diffraction); the other common mineral was black and micaceous (probably biotite mica). Grains were often found to be completely surrounded in a tan-coloured matrix. There were also fine mineral fragments, roughly 10-20 μm in size, within the same tan matrix; some of which were reddish in colour.

The heavy fraction was coarser, with a "salt and pepper" appearance; the tan-coloured mixture was also present as a cement and as a covering on some mineral grains. There were also clumps of fine material which had a greenish colour. There was a much wider variety of minerals, several of which could be identified visually as sphalerite, pyrite, pyrrhotite, and hematite; some galena, and a variety of gray to black metallic minerals, was also present.

Gamma counting was carried out on the light and heavy fractions as recovered from a bromoform separation trial, to obtain an estimate of their specific activities. The light fraction was calculated to contain $(9.2 \pm 0.9) \times 10^3 \text{ pCi g}^{-1}$, while the heavy fraction contained about $(1.6 \pm 0.7) \times 10^4 \text{ pCi g}^{-1}$, as ^{226}Ra ; it is immediately evident that the uncertainty on the latter value was very large (owing to the very small sample mass). These measurements were later repeated on larger samples, using equipment with higher resolution, in an attempt to more precisely determine the levels of alpha and gamma activity; determination of the latter in particular was greatly improved. The gamma activities of the light and heavy fractions, respectively, were $(1.3 \pm 0.1) \times 10^4$ and $(1.12 \pm 0.06) \times 10^4 \text{ pCi g}^{-1}$ as ^{226}Ra . Gamma spectra for these samples are given in Figure 2. From these results it is apparent that there is a roughly equal partitioning of radium between the two fractions. This is in sharp contrast to results from

Figure 2 (a) and (b). Gamma spectra for Key Lake tailings, shown as number of counts vs. channel number:

(a) light density fraction

(b) heavy density fraction.

the Midwest Lake tailings, where >90% of the total gamma activity was associated with the heavy fraction - there was, however, very little fine material within the Midwest Lake sample studied.

Estimation of alpha activities was much less precise; as can be seen in Figure 3, there is a fairly high low-energy tail for both samples, particularly for the heavy fraction. Since all alpha-emitting daughter products are present in the samples, and thus contribute to the low-energy background, the relative amounts of radium and thorium were estimated by comparison of peak heights. The Th/Ra ratios, as estimated by peak heights, are 1.31 and 1.13 for the light and heavy fractions, respectively. Thus, there appears to be a slightly higher proportion of thorium in the light fraction. This could be the result of an excess of thorium in the light fraction, or a deficiency in the heavy fraction; it is not possible to distinguish between the two with these data.

Microprobe Analysis

As in previous work, representative grains of the most radioactive minerals in the tailings were subjected to microprobe analysis, with an emphasis on minerals already shown to be radioactive (initially, work was concentrated on grains identified by X-ray diffraction as hematite).

Once again, preliminary examination found that the "hematite" grains were actually intergrown with a second phase; this second phase was tentatively identified at Carleton University as a layer silicate, possibly chlorite. The unknown phase was then analyzed at CANMET by EDS and WDS, in an attempt to define its identity with a higher degree

Figure 3 (a) and (b). Alpha spectra for Key Lake tailings, shown as $\log(\text{counts})$ vs. channel number:

(a) light density fraction

(b) heavy density fraction.

of certainty. The most likely identity for the silicate phase was determined to be chlorite (X-ray diffraction performed at CANMET had already confirmed the presence of hematite) - elements consistent with chlorite were detected, and this mineral is found in the orebodies [19,36]. A high calcium content indicated a possible third, calcium-rich, microcrystalline phase, perhaps CaSO_4 (which is precipitated in large amounts during the lime neutralization stages of ore processing). As with the Midwest Lake sample, scanning electron microscopy (SEM) showed a complex, extremely fine intergrowth of the two primary phases (see Figure 4). This intergrowth proved to be on such a fine scale (with bands as narrow as $1\text{ }\mu\text{m}$ or less) that single-phase zones large enough for reliable spot analysis with the CANMET instruments could not be isolated; indeed, because of the high variability of spot analyses, it was necessary to de-focus the microprobe beam and obtain bulk analyses. The results showed large amounts of iron, with slightly less aluminum and silicon, minor amounts of calcium, and trace quantities of potassium, with the results varying from spot to spot. Radionuclides were not detected; this is not surprising, since the detection limit for an element is roughly 1% by weight in the sample; on a mass basis, radium and thorium can be expected to be at trace levels. It would be impossible, at any rate, to identify conclusively with which phase(s) the radionuclides were associated, given the nature of the material studied.

The primary phase in the reddish Key Lake grains was thus identified (by X-ray diffraction) as hematite; microprobe analysis results indicated that the secondary silicate phase is most likely a chlorite; an unidentified, calcium-rich third phase may also be present in trace

Figure 4(a). Secondary electron micrograph of a hematite-chlorite grain from Key Lake tailings. Bar scale indicates 40 μm .

Figure 4(b) . Backscattered electron image, showing the complex intergrowth of hematite with chlorite. Bar scale indicates 10 μm . Light gray areas are hematite, dark gray areas chlorite.

Figure 4(a)

Figure 4(b)

amounts. In addition to this, a dark metallic mineral was identified by microprobe analysis as gersdorffite (NiAsS). It should be noted that separation of large numbers of grains of this mineral was not considered practical, owing to similarities in its visual characteristics to other minerals present in the sample.

One of the difficulties in examining the hematite-chlorite grains was their very low content in the tailings; another, obviously, was their small size ($\sim 100\text{--}200\ \mu\text{m}$). It was hoped that an analysis of the friable surface material could be made - this would have allowed a determination of the compounds present to be made, and thus indicate the most likely origin of the material, that is, recent agglomeration/surface precipitation vs. chemical attack of a pre-existing iron-rich mineral. However, the two above factors precluded collection of sufficient material for conventional X-ray diffraction or wet chemical analysis. Since a typical electron microprobe beam penetrates to a depth of only $1\text{--}1.5\ \mu\text{m}$ below the sample surface [68], and since the thickness of the friable layer exceeded this (roughly $5\text{--}20\ \mu\text{m}$ thickness, based on visual observation), microprobe analysis can be considered a surface analysis; probes carried out for samples with and without the surface material present could then allow conclusions regarding its composition to be made. Accordingly, scraped and unscraped grains were sent for such analysis. Examples of the spectra obtained are shown in Figure 5. The unscraped grains show (expectedly) strong iron peaks, along with silicon and aluminum; calcium and nickel were also prominent, with some potassium, and significant arsenic. There was some interference from lead; its L_γ line (at $10.549\ \text{keV}$) corresponds very closely to the K_α line of arsenic (at $10.543\ \text{keV}$).

Figure 5 (a) and (b). Representative electron microprobe spectra of Key Lake hematite-chlorite grains:

(a) friable surface intact

(b) friable surface removed.

Arsenic can be distinguished, however, by its L (1.282 keV) and K (11.725 keV) lines. Vanadium was also detected; this should not be surprising, since V^{5+} can substitute for As^{5+} [69]. Some lead was detected as well, although since its peaks coincide with those of silicon (at low energies) and arsenic (at higher energies), the relative amount of this element was difficult to determine. The most notable change in the spectra with surface removal was the decrease in nickel and arsenic content. The absence of the 11.725 keV peak for scraped grains indicates very low to negligible arsenic levels (although vanadium levels did not change greatly) for scraped grains. It can therefore be concluded that arsenic was predominantly associated with the friable surface. The actual composition of this material was not determined, thus it is not possible to conclude, based solely on microprobe analysis, whether it represents primarily new or altered, original material.

Autoradiography

The mineralogical distribution of radioactivity in identifiable minerals was examined by alpha autoradiography of individual grains. The clays/fines mixture was not examined by autoradiography, for several reasons: as already mentioned, the extremely fine nature of this material would make the work impractical; it would not be possible to specify which phase within such a mixture was alpha active; and finally, it has been generally accepted that a large portion of the total radioactivity in tailings is usually associated with the fines. The grains chosen for these tests were similar to those used previously [7]; also, fewer grains were identified by X-ray diffraction, when they

could be matched easily with grains already identified, or could be unambiguously identified by visual and physical characteristics.

As with the previous study (see Table IV), quartz was found to be inactive; brassy grains (probably pyrite or pyrrhotite) were very weakly alpha active; greenish yellow to brown, sub-vitreous grains (probably sphalerite) were also weakly active; reddish grains with a friable surface (hematite-chlorite) were variably active; some hard, black grains (probably gersdorffite) were moderately to strongly active; and several soft, blackish grains (possibly uraninite) were found to be very strongly active. These observations are summarized in Table V. As has already been discussed, the reddish grains were identified by X-ray diffraction as hematite - extra diffraction lines observed may indicate goethite; a secondary phase was identified by microprobe analysis as chlorite. Two hard black grains were similarly identified as gersdorffite. Other soft, blackish grains were identified as pyrite, plus a secondary unidentified phase, possibly CaSO_4 (these grains were cemented agglomerates, and may contain small radioactive particles in a basically inactive matrix).

In general, the radioactivity distribution is less mineral-specific than for the Midwest Lake sample, with the exception of quartz, which was inactive for both samples. The overall level of alpha activity of the Key Lake sample was also higher, as evidenced by a higher density of alpha tracks in the autoradiographs. This can be explained in part by the fact that the Key Lake sample represents fresh, unweathered tailings, with no opportunity for leaching or redistribution of radionuclides. It is interesting that quartz showed essentially no alpha activity, even for this fresh material. This indicates that radio-

Table IV. Summary of observations from autoradiography of Midwest Lake tailings [after 7].

Description	Mineral	Radioactivity
black, resinous, soft	uraninite	very strong
greenish, black inclusions	pyrite + uraninite	strong
reddish, some with crumbly exterior	hematite + unknown	variable
light green, translucent	sphalerite	medium
light brown, translucent	sphalerite	medium
light pink, translucent	zircon	weak
clear, colourless, vitreous	quartz	inactive
clear, dark red, adamantine	rutile	inactive
black, metallic	magnetite	inactive
whitish to greenish, soft	annabergite	inactive

Table V. Summary of observations from autoradiography of Key Lake tailings.

Description	Mineral	Radioactivity
blackish, soft	uraninite	very strong
black, hard, sub-metallic	gersdorffite	moderate to strong
reddish, some with crumbly exterior	hematite + chlorite	variable
yellow to brown, sub-vitreous	sphalerite	weak
brassy, metallic	pyrite, pyrrhotite	weak
clear, colourless, vitreous	quartz	inactive

nuclides may never have been present on quartz (at least, crystalline quartz) in spite of references in the literature [1,29] to its favourable adsorption qualities, especially at low pH. It is also possible that any radionuclides present at some time during ore processing were released during further stages before release to the tailings. This result allows the following conclusion to be made: since the light fraction shows an overall level of radioactivity similar to that of the heavy fraction, and since the most common crystalline phase within the light fraction is essentially inactive, thus the fines must contain most of the radioactivity within the light fraction. Further, since fines are also present in the heavy fraction, they may account for some of the radioactivity within this fraction as well. Finally, since the precipitate is expected to contain gypsum, various metal hydroxides, and arsenates in proportions of roughly 71/22/7 [22], and since these precipitates are formed fairly rapidly, it is probably reasonable to expect a similar partitioning of radionuclides among these phases.

A very weak trend of increasing radioactivity for hematite-chlorite grains with a darker red colour was observed, but this was neither conclusive nor strictly consistent - some light red grains were strongly radioactive, and some dark red grains were only moderately radioactive. As has already been noted, gersdorffite grains were not separated in quantity, owing to difficulties in identification - there are several other minerals present with similar appearance. However, of the grains identified as gersdorffite (see below), one was very radioactive, and another was much less so. It is expected, then, that the variation in radioactivity would be similar to that observed for the hematite-chlorite grains.

It was anticipated that high-resolution autoradiography could be used to determine which of the two primary phases within the hematite-chlorite grains was more radioactive. To this end, alpha active grains were photographed, and then superimposed (at the same optical scale) with autoradiographs. Superimposition of greatly enlarged (240X) images was expected to reduce placement errors, providing a great improvement over attempts made by matching original (1:1) negatives through a microscope. However, it was found in all cases that the diameter of the autoradiograph image was greater than the photomicrograph image of the grain. This is caused by the random trajectories of alpha particles emitted from the grains, resulting in alpha tracks at all angles of incidence from 0-90°; maximum resolution will be achieved when the majority of alpha tracks have incident angles close to 90°. The etching time and temperature were established as the optimum conditions for which a majority of alpha tracks would be revealed, without removing so much emulsion that they would be lost in a high background image density. Therefore, processing of the autoradiographs to manufacturer's recommendations does not allow discrimination to be made with respect to the incident angle of alpha particles; thus the effective resolution (when dealing with adjacent alpha active and inactive zones) is limited. The effective resolution could be improved, however, in two ways: by the screening of alpha particles with incident angles less than some arbitrarily chosen angle θ ; or by a change in the etching time and/or temperature, to reveal only those alpha tracks with θ close to 90°. In the first case, varying thicknesses of a material with well-known particle stopping properties, such as Mylar, would be interposed between sample and film; alpha particles with

incident angles less than θ would expend their energy within the screen, and thus not register on the film. Normal film processing would then reveal only those tracks registered, that is, those with near-normal incidence. In the second case, the rate of alpha track etching (as a function of θ), with respect to general emulsion removal, would have to be determined; once this relationship had been established, etching conditions could be chosen such that alpha tracks with incident angles less than θ , while registering on the film, would not be revealed by etching. While one or both of these techniques could be used to improve the effective resolution, however, it is unlikely that it could be improved to the point where phase boundaries as narrow as those encountered with the hematite-chlorite grains could be distinguished.

Experiments carried out to determine if the outer surface material of the hematite-chlorite phase was radioactive (see Figure 6) showed results similar to those obtained in previous work. When the outer surface is removed, the observed alpha activity (track density) increases. The material removed showed no alpha activity; if it had, alpha tracks would have been observed over a wide-spread area around the grains. The increase in alpha activity with surface removal was observed for all grains tested; some small areas of alpha activity not associated with the central grain cores were observed, but these were found to be associated with small grain fragments (which had broken up under pressure during scraping). Some of this increase in radioactivity may be due to an improvement in the film-grain contact as the grains were "planed down". This, however, is not likely to be a major factor; a change in the surface-to-film distance of a few micrometres

Figure 6 (a-c). Autoradiographs of hematite-chlorite grains:

(a) before removal of surface material

(b) after removal of surface material

(c) after moving grain cores.

Figure 6(a)

Figure 6(b)

Figure 6(c)

should not have significantly altered the number of alpha particles registered on the film. Also, autoradiographs made after the grains were scraped show a rough grayish outline of the underlying grain. This would appear to be caused by "fogging" of the film by alpha tracks which were not fully revealed by etching; this indicates that the alpha particles responsible for these tracks are partially blocked, that is, seem to originate from beneath the grain surface - which would explain why this fogging is not observed prior to scraping, if the surface material is sufficient to block the underlying alpha particles from reaching the film (it is possible that the radioactivity is associated with sub-surface material which could not be removed using the soft Parafilm mount). Autoradiographs made after the cores of the grains were moved (Figure 6(c)) confirm that essentially all of the observed alpha activity is associated with the grains and not with the friable surface; some small patches of alpha activity near the original grain locations were again due to fracturing of the grains, and do not appear to be associated with material removed by scraping. The conclusions to be reached from this experiment are: that there was no significant radioactivity associated with the surface material removed by the scraping of hematite-chlorite grains, and that this material apparently acts to screen alpha particles within the grain from detection.

Further experiments, similar to those above (using polyester resin disks as a support, and epoxy cement to hold the grains in place), were carried out to determine with more certainty the distribution of radionuclides throughout the hematite-chlorite grains; that is, whether radionuclides are restricted to the near-surface portions of the grains or spread homogeneously throughout the grain interior. This could lead

to conclusions on the most probable origin of the radionuclides and thus the most likely time of their deposition. Careful grinding with very fine grit permitted several cross-sections of the soft grains to be made without gouging or plucking. Since the exposed grain surfaces were flat, the film-grain contact was not significantly changed as the experiment progressed. The results are shown in Figure 7.

After the first grind of the disk (Figure 7(a)), the autoradiograph shows track densities typical for other work involving the hematite-chlorite; some fogging is observed, outlining the grains, as was expected from the above results. As more surface is removed, track densities increase for all grains; after the third grind (Figure 7(c)), they are high enough for two of the grains to obliterate detail, that is, the area of the grains is completely exposed. This is a very strong indication that: the alpha activity is dispersed throughout the grains; the "fogging" observed in this and other work is caused by partially blocked alpha particles originating beneath the surface; and that there is a higher concentration of alpha activity toward the center of these grains than at the rims - which may indicate partial leaching at the outer grain surfaces. These results have several possible implications regarding the origin of the radioactivity associated with this phase.

The above procedure was later repeated using a variety of minerals, to determine whether other phases show a homogeneous radionuclide distribution. It was found that, of the grains tested, one other mineral was radioactive throughout, and was identified as the nickel mineral gersdorffite. Two grains were so identified; one was strongly radioactive throughout, and the other only weakly so at the grain rims;

Figure 7 (a-c). Autoradiographs of cemented hematite-chlorite grains:

(a) after first grind of surface

(b) after second grind

(c) after third grind.

Figure 7(a)

Figure 7(b)

Figure 7(c)

these grains were harder (more compact and crystalline) than the hematite-chlorite, and can be expected to have a lower surface area for ion adsorption. This provides further evidence that at least some of the radionuclides present in the tailings were not leached from their original hosts, which is supported by work on the release of radium from tailings. It was concluded [5] that most of the radium and uranium in the tailings was not "adsorbed on particle surfaces, but rather are associated with minerals of uranium ores, or partly trapped inside the colloidal hydroxides of iron and manganese coated on the sediment". If it can be assumed, then, that these phases (and perhaps others) are leach-resistant, there could be important implications regarding the mobilization and retention of radionuclides in tailings piles.

Alpha Spectroscopy

As described in the introduction, it was anticipated that secondary or Rutherford scattering could be observed from tailings samples, and that secondary peak energies could then be used to identify the associated elements and thus, perhaps, minerals or compounds acting as radionuclide hosts; such an observation would be persuasive evidence of the participation of a limited number of mineral hosts. The prominence or "sharpness" of such peaks was also expected to be an indication of the average depth of radionuclides beneath particle surfaces.

As can be seen from Figure 3, no statistically valid low-energy peaks were observed; repeated sample counting showed that apparent, marginal peaks were not persistent, as had been indicated by previous (and, as was later found, spurious) results. Scattering peaks may in

fact be present, but could have been obscured by high background noise, caused by wide variations in scattering angle, or near-homogeneous and/or widespread radionuclide distribution within the tailings. The absence of scattering peaks, however, may still serve as an indicator of the radionuclide distribution and location within the tailings, by providing evidence that the radionuclides appear to be widespread mineralogically; within single grains, the radioactivity would be distributed homogeneously rather than concentrated at the surface.

Results from the backscattering experiments were inconclusive; this was most likely due to technical difficulties. As was mentioned previously, it seems that the perchloric acid used to reduce thorium adsorption on the glass container reacted with the lacquer used to protect the aluminum planchet from chemical attack. The crumbly, brittle material formed was physically unstable, and flaked away from the planchet; some creeping of the thorium also occurred. Both of these factors would tend to degrade the energy of the emitted thorium alpha particles (which would then no longer be monoenergetic), and decrease the amount of scattered signal; they would also limit the maximum amount of thorium (and thus beam intensity) that could be employed. The other major source of error was in the method of detection itself. The apparatus was modified from an existing alpha detector; this equipment allowed only a collinear alignment of the alpha source, sample, and detector. As was also described previously, this forced several compromises to be made. The alpha source was ring-shaped, and thus could not be considered a point source; the alpha particle beam could not be collimated, as this would have made counting times excessively long; similarly, a slit could not be used to restrict the scattering

angle detected - with a collinear alignment, the slit would have to be so narrow as to greatly lengthen the counting time. Finally, if the hole in the source planchet was large enough to permit reasonable counting times, a wide variation in the detected scattering angles would occur. All of the above would act to obscure any scattering peaks which might otherwise have been observed.

The results from ^{230}Th -loaded iron and lanthanum hydroxides were also inconclusive, at least with respect to Rutherford scattering; the alpha spectra are shown in Figures 8 and 9, respectively. While not useful as evidence of scattering, comparison of these spectra with those of the tailings samples provides some insight into radionuclide distribution, both with respect to depth beneath sample surfaces and possible radionuclide partitioning between the density fractions.

The effects of increasing the amount of carrier are similar to those observed [38] for ^{226}Ra carried down by BaSO_4 ; that is, increasing the amount of carrier causes a progressive signal degradation, reducing the intensity of the main peak while increasing the background levels at lower energies. There were two major sources of uncertainty in the present work: the thickness of precipitate collected, which appeared to vary across the filter; and that, upon drying, the samples showed a reticulated appearance caused by shrinkage cracks (for FHO only). These factors combined to produce a non-uniform surface for alpha counting, increasing the uncertainty of estimates regarding the depth of radionuclides beneath particle surfaces. However, while not ideal, the average sample thickness did increase with increasing amount of carrier. It can then be concluded that the signal degradation observed is due to the increase in average sample thickness; the change

Figure 8 (a-d). Alpha spectra for ^{230}Th coprecipitated with
varying amounts of ferric hydrous oxide:

- (a) 1 mg Fe^{3+}
- (b) 2 mg Fe^{3+}
- (c) 3 mg Fe^{3+}
- (d) 4 mg Fe^{3+} .

Figure 8(a)

Figure 8(b)

Figure 8(c)

Figure 8(d)

Figure 9 (a-c). Alpha spectra for ^{230}Th coprecipitated with varying amounts of lanthanum hydroxide:

- (a) 1 mg La^{3+}
- (b) 2 mg La^{3+}
- (c) 3 mg La^{3+} .

Figure 9(a)

Figure 9(b)

Figure 9(c)

2 of/de 2

Micro-D

in spectrum shape can then be attributed to the screening of alpha particles emitted from within the precipitate. The result of this is that with a sufficient thickness of overlying material, a portion of the alpha activity can be blocked from detection.

In comparing the tailings sample spectra with the spectra in Figures 8 and 9, it appears that the shape of the light fraction spectrum is matched by an FHO spectrum containing less carrier than for the heavy fraction (the lanthanum spectra are less useful in this regard, and do not match well with either of the tailings spectra). From visual inspection it can be seen that for the light fraction the general spectrum shape is best approximated between the 1 and 2 mg FHO spectra; similarly, for the heavy fraction, the closest approximation is the 3 mg spectrum. The comparisons are hampered, however, by the obvious compositional differences between the FHO used for the comparative spectra and the heterogeneous material making up the tailings samples. A further complication is the occurrence of all U_{rd} (or more specifically, Th_{rd}) in the tailings sample, which also contribute to the low-energy signal. If the FHO spectra can be considered to serve as at least rough approximations, it appears that radionuclides within the heavy fraction are associated with larger grains and/or with more well-formed precipitates; that is, the radium and thorium are, on average, further beneath grain surfaces than in the light fraction.

One further comparison of interest to be made between the light and heavy fractions concerns the 5.31 MeV ^{210}Po peak for both samples (see Figure 3); that is, the height of this peak relative to that of ^{226}Ra , its "sharpness", and the relative amounts of this radionuclide in the two fractions. By comparing polonium peak heights, it can be shown

that the light fraction contains a slightly higher relative amount of polonium. However, when $^{226}\text{Ra}/^{210}\text{Po}$ peak height ratios were calculated, it was found that there is apparently more polonium than radium in the heavy fraction. For this fraction the ^{210}Po peak is also sharper than for the light fraction, in contrast to the other peaks observed for the heavy fraction, which show considerable signal degradation. This is evidence that the ^{210}Po is located nearer to grain surfaces than other radionuclides. If this is the case, it would suggest that the polonium is preferentially adsorbed, coprecipitated with certain phases within the heavy fraction, or otherwise concentrated in the near-surface region; alternatively, given the possibility that some radionuclides at depth are not detected by alpha spectrometry, the actual ratio of Ra/Po may be closer to unity, but with polonium again occurring mainly near particle surfaces.

While alpha spectroscopy has provided some useful information in this study, a significant limitation was present, in that it was necessary from a practical standpoint to work with material separated by density only - this meant that many minerals and compounds were present in the sample when the spectra were obtained. Better approximations could probably be made for tailings material which was further segregated mineralogically; this may be difficult to achieve without disturbing the original radionuclide locations, however, especially for the light material, much of which occurs as an intermixture of precipitates. Alternatively, comparative spectra could be prepared for each compound considered to be a potentially important host - matching of spectra could then perhaps be used to identify the major host phases for a given tailings sample. This would be most useful in cases where

only a small number of potential host phases exist.

The above results suggest a possible relation between the average grain size and the level of detected alpha radioactivity. While this observation is not new in itself (it has generally been concluded or assumed in the literature [eg. 1,2,5,25] that tailings fines are more radioactive than coarser material), it is possible that for the coarse material not all of the radioactivity present is detected.

Adsorption Studies

As stated previously, it was expected that addition of both sulphate and arsenate would result in a greater selectivity of the adsorbent for Ba^{2+} than in their absence, which would be manifested by a downward shift in the pH_{50} . Arsenate was also expected to show more effect than sulphate, since it is the more strongly adsorbed of the two [70], and since barium arsenate is much less soluble than the sulphate. The pH_{50} for the arsenate experiments should then occur at a lower pH than for sulphate. Most of these predictions were satisfied.

The adsorption profiles (percentage tracer removed from solution vs. pH) are presented in Figures 10-12. The shapes of the profiles obtained from the sulphate and arsenate trials are generally similar to that from the control case; that is, roughly sigmoidal, with the extent of adsorption increasing with increasing pH. The instrumental uncertainty on all data was less than about 2%. It must be noted, however, that the maximum tracer recovery was less than 100%, owing to tracer adsorption on glass surfaces, etc. (the actual maximum value is probably closer to 95%). There was also some scatter caused by variable experimental errors such as sample loss and changes in the

Figure 10. Adsorption profile (percentage ^{133}Ba tracer adsorbed vs. pH) for ferric hydrous oxide in the absence of added anion solutions.

Figure 11 (a) and (b). Adsorption profiles for ferric hydrous oxide with added sulphate. The anion concentration is given above the corresponding profile.

Figure 12 (a-d). Adsorption profiles for ferric hydrous oxide with added arsenate. The anion concentration is given above the corresponding profile.

1.8×10^{-3} M ARSENATE

Figure 12(a)

1.8×10^{-4} M ARSENATE

Figure 12(b)

2

1.8×10^{-5} M ARSENATE

Figure 12(c)

1.8×10^{-6} M ARSENATE

Figure 12(d)

liquid-solid ratio; the latter were caused almost entirely by changes in the mass of sample recovered, as the solution volume was very nearly constant (with a standard deviation of less than 3% from the average for all cases).

Several studies [eg. 12,14,15,50,51] have been performed to determine the effects, if any, of anions on the adsorption and retention of cations. Within the surface complexation model, the adsorbent surface is treated as a complexing ligand; anions added to the system will therefore compete with the surface for cations, with adsorption of a metal-ligand complex being comparable to mixed-ligand complex formation [50].

Cations and anions can interact either in the bulk solution, or at the adsorbent surface; if the interaction is in solution, the complex formed may or may not adsorb, depending on the relative bond strengths between the surface and the metal-ligand complex, compared to those of the surface and the uncomplexed cation. Non-specifically adsorbed anions may therefore compete with the surface for cations, especially at pH values above the PZC. It has already been stated that specific anion adsorption can change the microenvironment at the adsorbent surface (by shifting the PZC and possibly changing the surface potential). If the adsorbed anion strongly complexes with the cation, then cation adsorption may be enhanced. On the other hand, strong adsorption of large, non-interacting anions may reduce cation adsorption due to steric hindrance. The presence of anions can thus enhance, inhibit, or have no significant effect on cation adsorption.

These ternary complexes, as they are known, may occur with the anion or cation closer to the surface, and are denoted as S-L-M and

S-M-L complexes, respectively. Thermodynamically and mechanistically, the adsorption of a complex formed in solution and the formation of a complex at the surface after adsorption are indistinguishable using adsorption data [14,15,50]. Benjamin and Leckie [50] characterized the adsorption of complexes (equivalent to adsorption followed by complexation) as metal-like or ligand-like, depending on the trend of adsorption with pH. Increasing adsorption with increasing pH is termed metal-like, as the adsorption roughly parallels adsorption of cations alone; similarly, ligand-like complex adsorption follows that of anions alone. They found that sulphate and chloride complexes of cadmium adsorbed in metal-like fashion, with adsorption profiles roughly parallel to that of uncomplexed Cd^{2+} ; they also found that both of these ligands decreased Cd^{2+} adsorption, leading to the conclusion that "chloro and sulphato complexes of Cd^{2+} adsorb less strongly than uncomplexed Cd^{2+} ions in these systems". It was also suggested that Cd^{2+} surface complexation was hindered by anions such as sulphate, with which it forms a soluble sulphate complex. There would not, then, be the same driving force towards bond formation as exists for insoluble sulphates or arsenates.

The stereochemistry of the adsorbed complex can be expected to be strongly influenced by the relative bond strengths of the component ions, with the stronger bond being favoured. This may not always hold; for example, steric restrictions may destabilize what would otherwise be the stronger bond. It is usually expected that the component with the greater specific adsorption energy will form a bond with the surface, unless "complexation decreases the driving force for forming a metal-surface bond much more than that for forming a ligand-surface

bond" [50]. Another possible factor is the order in which the component ions are added to the system. The above discussion generally assumes that the cation and anion are added simultaneously; thus, steric effects and/or relative binding energies are the main factors in determining the orientation of the adsorbed complex. If, on the other hand, one of the components was allowed to equilibrate with the surface before the other (as is the case in this study), the orientation could be affected; the amount of influence this would have would depend on the similarities in bond strengths (relative affinities) of the separate components to the surface. For example, if both components were specifically and/or strongly adsorbed, the order of addition would be expected to have more influence on the stereochemistry than if one was non-specifically and/or weakly adsorbed. Where the component ions have similar affinities for the adsorbent, solubility may become a relevant factor, especially for 1:1 compounds, which would form insoluble surface species more readily than those containing more than two component ions.

As mentioned above, the adsorption profiles for sulphate and arsenate are roughly sigmoidal. The trend of increased Ba^{2+} adsorption with increasing pH would seem to indicate metal-like adsorption; from this trend alone it could be inferred that the metal bonded directly to the surface, as in the literature studies cited above. However, in this work the anion and cation were not added simultaneously (which would have allowed complexation in the bulk solution prior to adsorption); indeed, for the present work, the anion was given time to equilibrate with the adsorbent (60 min. should have been sufficient in light of the rapid adsorption of sulphate and arsenate on FHO [65])

prior to addition of the ^{133}Ba tracer. Since the anion was adsorbed first, one might expect ligand-like adsorption, since sulphate and arsenate are, to a large extent, irreversibly held by adsorbents such as FeO ; this was not observed, however. Possible pathways to account for this apparent contradiction will be discussed later.

Interpretation of the adsorption profiles is limited, in that the data are not readily analyzed; certain generalizations can be made, however. An examination of the profiles reveals that, while their shapes are similar for all cases studied, the positions of the pH-adsorption edge vary with concentration and, more importantly, with the choice of added anion. By comparing the results obtained with added sulphate and arsenate to those in their absence, it can be seen that the addition of arsenate increases tracer adsorption; sulphate, on the other hand, appears to actually inhibit tracer adsorption. While increased anion concentration resulted, in the case of arsenate, in a progressive shift in the position of the adsorption edge to lower pH, increased sulphate concentration did not greatly change its position (at least, for the concentrations tested).

The effectiveness of added arsenate as a means of improving barium adsorption can be more clearly seen from the Kurbatov plots, presented in Figures 13-16. For Figures 13-15, the data for each anion concentration are shown with the no-anion case serving as a reference; for clarity, Figure 16 shows the best-fit lines for all concentrations with respect to the no-anion case. Linear regression was used to determine the best line for all the data in each set. Data which were grossly outlying were then rejected; data were also rejected when the linear correlation coefficient C ($C = \pm 1.0$ for perfect linearity) could be

Figure 13. Plot of $\log D$ vs. pH for ferric hydroxide in the absence of added anion solutions. Rejected data are included as solid points.

Figure 14 (a) and (b). Plots of $\log D$ vs. pH for ferric hydrous oxide with added sulphate. The anion concentration is given above the corresponding plot. Rejected data are included as solid points.

1.8×10^{-4} M SULPHATE

Figure 14(a)

 1.8×10^{-6} M SULPHATE

Figure 14(b)

Figure 15 (a-d). Plots of $\log D$ vs. pH for ferric hydrous oxide with added arsenate. The anion concentration is given above the corresponding plot. Rejected data are included as solid points.

Figure 15(a)

Figure 15(b)

1.8×10^{-5} M ARSENATE

Figure 15(c)

1.8×10^{-6} M ARSENATE

Figure 15(d)

(a)

(b)

Figure 16 (a) and (b). Best-fit lines from Figures 13-15 for experimental data, shown with respect to the no-anion case.

significantly improved. Rejected data are shown in Figures 13-15 as solid points. Regression was then repeated for the remaining data, and used to derive the pH_{50} and slope values; these are given, along with values for the linear correlation coefficient, in Table VI.

Two observations can be made immediately regarding the pH_{50} and slope values obtained. The first is that arsenate does indeed improve the adsorptive properties of FHO for Ba^{2+} . The second is that at low concentration, the slopes are roughly parallel to that for the no-anion case; at some intermediate concentration (which differed for the two anions) the slope is drastically reduced, and the pH_{50} actually increases; and at higher concentrations (seen for arsenate only), the slope does not change greatly, but the pH_{50} steadily decreases. The abrupt change in slope with increasing concentration suggests a change in the reaction pathway; this will be discussed in more detail, following a discussion of error sources and possible reaction pathways.

An examination of the Kurbatov plots shows that while in some cases the $\log D$ vs. pH plots were highly linear, in other cases (eg. for 1.8×10^{-3} M arsenate) there was considerable scatter. There were several potential sources of error which could have caused such variations in the value of $\log D$, such as: instrumental variations in the pH meter or gamma counting equipment; desorption of tracer during filtration; and changes in tracer concentration, the extent of FHO precipitation, or the liquid-solid ratio. Instrumental variations should have had minimal effect on the results; the pH meter was checked against a standard buffer prior to each reading, and all gamma measurements were compared to the barium reference. It was initially thought that the slower filtration observed for the arsenate samples would

Table VI. Values of pH_{50} , slope, and linear correlation coefficient C for experimental data. Uncertainty given on the slope is the standard deviation σ .

Concentration (M)	pH_{50}	Slope	C
No Anion	8.18	0.88 ± 0.03	0.993
Arsenate			
1.8×10^{-3}	5.61	0.4 ± 0.2	0.665
1.8×10^{-4}	6.32	0.44 ± 0.05	0.933
1.8×10^{-5}	8.68	0.42 ± 0.06	0.935
1.8×10^{-6}	8.12	1.31 ± 0.05	0.995
Sulphate			
1.8×10^{-4}	8.80	0.58 ± 0.05	0.909
1.8×10^{-6}	8.44	0.93 ± 0.07	0.964

result in partial desorption of the tracer. This is not believed to have been a serious problem, since tracer adsorption was more complete for FHO in the presence of arsenate than sulphate. The tracer concentration can be considered essentially constant for all experiments, owing to the fairly small range in total volumes. The amount of FHO produced should also have been fairly constant, since iron hydrolysis occurs above pH 2-3; the pH range employed should thus have been sufficiently high for essentially complete iron hydrolysis by the time anion and tracer solutions were added.

Changes in the liquid-solid ratio would be expected to have an impact on the value of $\log D$ - obviously, with large changes from one run to the next, samples with the same final suspension pH could show differing amounts of tracer adsorption and therefore different $\log D$ values. As well, although V/m is not a component of the Kurbatov equation, it is assumed that it will be constant; changing sample mass could then affect the validity of this equation and thus the interpretations based thereupon. However, the adsorbent mass is so much greater than the mass of barium ions present that the equation should remain valid for this study. Since the total volume was nearly constant, changes in sample mass (which varied considerably) likely accounted for almost all the variation in V/m , and most likely comprised the largest single source of error for the adsorption data. Several possible causes for such variations are: increases in mass by adsorption of ions; incomplete drying of the sample; and loss of sample during collection and filtration.

Barium ions from the tracer solution would add negligible mass to the sample - even if completely adsorbed, the mass increase would only

be about 3×10^{-19} g. Complete adsorption of the added anion could significantly change the mass, however. For example, complete adsorption of the arsenate contained in an aliquot of the 0.1 M stock solution would add roughly 1 mg. The effect of anions is difficult to estimate, since their adsorption (which is a function of pH, concentration, etc.) was not followed. Also, the calculated mass of adsorbent for the iron stock solution used, assuming formation of $\text{Fe}(\text{OH})_3$, is 1.1 mg, which is roughly the same as the average sample mass.

Incomplete drying is more likely to increase the apparent sample mass. Samples were allowed to air-dry for several days or weeks before weighing, but water trapped within the precipitate could have remained. At any rate, it would be very difficult to maintain a fully dehydrated sample, since FHO readily picks up water vapour [71].

The above effects would tend to cause an increase in sample mass; as stated above, since the amount of adsorbent greatly exceeds the amount of adsorbate, the Kurbatov plots should remain valid. Sample loss, however, would reduce the apparent tracer adsorption and thus the value of $\log D$. It was observed that the adsorbent coagulated to a much greater extent in the sulphate rather than arsenate experiments. It appears that arsenate inhibits FHO coagulation; this may have allowed some material to pass through the filter. A more definite factor was loss of some material on the filter towers; the uncertainty contributed in this manner is very difficult to quantify, since the mass adhering to the towers could not be practically determined. The final calculated uncertainty on values of D varied considerably, from about 5% to 30% in some cases (for very high or low adsorption); the average uncertainty was roughly 5-10%. This is more than sufficient to

demonstrate the trends in adsorption with changing concentration and added anion - while the absolute values for the pH_{50} and slope may vary, the relative values will still be useful, that is, the slope and pH_{50} did decrease with increasing anion concentration, and adsorption was more selective in the presence of arsenate than sulphate.

There are two factors which simplify the determination of the most plausible reaction pathway(s) to account for the observed trends in tracer adsorption. The first is that there should not be major competition for barium from other cationic species in solution; added cations were predominantly Na^+ and NH_4^+ , from anion solutions and base, respectively. Both of these cations are monovalent, and are non-specifically adsorbed. Thus, they should not have seriously impaired barium adsorption. The second factor arises as a consequence of the chemistry of the alkaline earths in general, and barium in particular. These elements generally show poor hydrolysis characteristics; unless the pH is high enough for hydrolysis to occur, the solution concentration of hydrolyzed species will be much less than that of the non-hydrolyzed cation. Morgan and Stumm [67] concluded in a study of Mn^{2+} adsorption on MnO_2 that "since over most of the pH range considered in this study, the equilibrium concentration of $Mn(OH)^+$ is many orders of magnitude smaller than that of Mn^{2+} , appreciable sorption of $Mn(OH)^+$ would be possible only if its affinity for MnO_2 were many orders of magnitude greater than that of Mn^{2+} ". While consideration of hydrolyzed species has been shown to be successful for elements such as cadmium and zinc [54], it would not be so for poorly hydrolyzing elements such as the alkaline earths, and especially barium and radium, which do not hydrolyze significantly below pH 9 [52]. In fact, based on equilibrium con-

siderations, a pH of about 13 would be required for only 1% of the tracer to be present as $\text{Ba}(\text{OH})^+$.

There are three main reaction pathways to account for the observed adsorption phenomena: the first two basically involve ion exchange; the third involves interactions between surface-bound species and ions in solution.

The first possibility is that the Ba^{2+} ions adsorb primarily or exclusively at uncovered adsorbent sites, with the adsorbed anions acting merely to stabilize cation adsorption. This could explain in part why the arsenate-covered surface was more favourable than for sulphate, since the latter has a lower negative charge; with adsorption, some of this negative charge would be "neutralized" by bond formation with the positive substrate. Changes in the Kurbatov slopes could be explained by the anions reacting with protons released by tracer adsorption; this would reduce the net proton release. A sudden downward shift in the value of pH_{50} could not be explained, however, since protonation of the adsorbed anions would tend to produce a positive shift in the pH_{50} , by reducing the amount of stabilization provided by the adjacent adsorbed anion for Ba^{2+} .

A second possibility is that barium adsorbs by displacing the adsorbed anions. For this to occur, the adsorptive bond between the surface and the adsorbed anion would first have to be broken; the Ba^{2+} ion would then either adsorb directly to the surface, or undergo complexation with the displaced anion before adsorption of the complex. The effect on proton release is uncertain; H^+ may or may not protonate released anions, depending on their speciation and the pH. This is probably not a likely pathway - more steps are involved, and the acti-

vation energy for displacement of adsorbed anions may be high enough to make the reaction kinetically unfavourable; this would be particularly so for arsenate, which forms an insoluble compound with iron (while for sulphate displacement may be possible). This type of pathway would be expected to increase the value of pH_{50} , more so for arsenate than sulphate, owing to differences in the iron-anion bond strengths. Also, since it forms a soluble complex with iron, sulphate would be expected to show more favourable adsorption with this scenario than arsenate. This, however, is contrary to observation.

A third possibility is that a surface precipitate is formed; the added barium ions would then adsorb onto a $Fe-SO_4$ or $Fe-AsO_4$ surface instead of a $Fe-OH$ surface. With such a scheme, the concept of metal- or ligand-like adsorption becomes irrelevant since the substrate has undergone significant changes, and its surface properties are no longer those of the original adsorbent. The number of protons released would then depend predominantly on the reactions occurring between the Ba^{2+} ions and the adsorbed anions; if multilayer anion adsorption were to occur, protons released upon cation adsorption could possibly become associated with the underlying anions. As well, cation adsorption on a FHO -anion surface could promote further anion adsorption, providing new sites for cation adsorption.

Anion speciation is another factor in determining tracer adsorption; as the pH increases, the ionization of polyprotic acid anions increases. For the sulphate experiments, this is not an important consideration, since sulphate will be completely ionized above pH 2-3. For arsenate, however, pK_a values [10] are higher ($pK_1 = 2.25$, $pK_2 = 6.77$, $pK_3 = 11.14$); in the pH range employed, then, AsO_4^{3-} and

H_3AsO_4 are not expected (on the basis of equilibrium calculations for ideal solutions) to contribute greatly to the system composition; H_2AsO_4^- and HAsO_4^{2-} should make up the bulk of the anion composition.

A further consideration deals with the possible differences between the charge at the adsorbent surface and that at the actual solid-liquid interface; with sufficient anion adsorption, the two may in fact be different (recall that in the surface precipitation model the interface is considered to be extended into solution as multilayer adsorption proceeds). Below the PZC, the FHO surface is positively charged; with sufficient anion adsorption, the outer surface exposed to the bulk solution may become negatively charged (more so for arsenate than sulphate). The magnitude of this negative charge would be reduced, however, by the positively charged substrate, thereby inhibiting cation adsorption. As the pH increases, anion adsorption is expected to decrease as a result of changes in the surface charge of the adsorbent; it should remain significant, however, for anions such as arsenate, which has been shown [72,73] to adsorb at pH values above the PZC, probably by hydrogen bonding to negative surface sites. If the pH was increased after anion adsorption, desorption may not be extensive, especially for arsenate (sulphate may or may not desorb); anions adsorbed at lower pH values can then be expected to remain at the surface at superequivalent adsorption densities. The surface charge of FHO becomes less positive as the PZC is approached, until above the PZC it becomes increasingly negative; there is thus less reduction of the negative charge at the outer surface, resulting in a stronger overall attraction of Ba^{2+} ions to the anion-covered adsorbent. In such a case, the extent of adsorption would be expected to increase at any

given pH, that is, the anion-covered adsorbent would become more selective for cation adsorption. The pH_{50} would also be expected to drop; the effect on γ would depend on the type and proportion of the various possible reactions mentioned above.

It is proposed that the observed results cannot be accounted for by a single reaction pathway, and that they are consistent with surface precipitate formation; that is, a fairly smooth transition between two different pathways, each dominating in different concentration ranges. It is also proposed that ion exchange-type reactions dominate at low anion concentrations, while surface interactions dominate at higher concentrations.

The chief evidence for such a phenomenon is the effect of increased anion concentration on the slope and pH_{50} ; since the tracer concentration was essentially constant in all experiments, any changes at the solid-liquid interface must have been caused by the changing amounts of anion present in solution. Assuming the data of Davis and Leckie [46,54] regarding the surface site density for FHO is reasonable, an aliquot of even the most dilute anion stock solution used would be sufficient to approach monolayer saturation, since the adsorption of each anion would block 3-4 surface sites [53]. There is little doubt, then, that the substrate can be saturated with anions in the concentration range employed in this study.

It is interesting that sulphate and arsenate showed similar trends as their concentration was increased; this suggests that similar reactions occurred in both cases, although, as noted previously, the concentration at which the slope was drastically reduced differed for the two anions. This was probably the result of differences in ionic

charge and the solubilities of the respective barium compounds. It seems likely that this sudden change represents the anion concentration at which the two pathways overlap. This would also explain the decreased selectivity for barium, seen as a positive shift in pH_{50} . At low anion concentrations (and thus surface densities), ion exchange of Ba^{2+} with surface-bound protons would dominate; adsorbed anions would block some sites, but might serve to stabilize adsorbed barium ions, and adsorption would be similar to that in the absence of sulphate and arsenate. At the "crossover concentration", the surface density of anions would be high enough to block access to most surface (and internal) sites, inhibiting ion exchange, but not yet sufficient for complete surface precipitation, resulting in decreased adsorption; the dominant reaction, however, would be changed, as seen by a decrease in Kurbatov plot slope. Above this concentration, the surface would have adsorption properties more like $\text{Fe}_2(\text{SO}_4)_3$ or FeAsO_4 than FeOH ; this change would become more apparent as anion concentration was increased, and the surface composition approached that of the new phase. It was recently shown [74] that ferric arsenate was an excellent adsorbent for radium; it has also been demonstrated [12] that Cd^{2+} adsorption on pre-formed FeAsO_4 was very similar to that on FeOH in the presence of arsenate. The formation of an iron-arsenate surface in the present study is thus a reasonable expectation, and appears to be justified by the observed increase in the amount of tracer adsorbed (as shown by a progressive decrease in pH_{50}) with increasing anion concentration.

In examining the experimental results, based on the above discussion, a decrease in slope can be justified based on a change in the dominant reaction(s) responsible for Ba^{2+} removal from solution. In

systems measuring only cation adsorption, the Kurbatov plot slope gives the stoichiometry of the H^+/M^{n+} exchange, with values for the alkaline earths typically between 0.8 and 1.2 [66], indicating roughly equimolar exchange. While changes in the apparent H^+/Ba^{2+} stoichiometry indicated in the present study appear to be valid, the reliability of the actual slope values is questionable since, if surface precipitation reactions are dominant for higher anion concentrations, protons are no longer necessarily exchanged for Ba^{2+} ions. This may also be true at lower concentrations; each aliquot of tracer contained roughly 10^8 Ba^{2+} ions, with roughly 10^{18} adsorbent sites available. Assuming near-monolayer coverage, there would then be a much larger number of adsorbed anions, in various ionization states, than Ba^{2+} ions; it should then be possible for any H^+ released by exchange to protonate the adsorbed anions - indeed, it was concluded [53] that anions protonate more easily at the adsorbent surface than in solution.

Most of the above discussion has focused on arsenate; it was noted earlier that the sulphate experiments appeared to follow trends similar to those of arsenate, but required higher anion concentrations to achieve a similar effect. One important difference between the two anions was their effect on FHO, which coagulated to a much higher degree in the presence of sulphate. This would tend to decrease barium adsorption, by reducing the number of available surface sites. As well, the ionic charge of sulphate is lower than arsenate, and the corresponding barium salt is much more soluble. From the results obtained for added arsenate, and from the similarities in adsorption trends between the two anions, it seems reasonable to predict that at higher anion concentrations, surface precipitation would also occur in the

presence of sulphate, and that the adsorption selectivity would increase, although probably not to the same extent as observed with arsenate.

In conclusion, then, the adsorption experiments carried out indicate that: the removal of barium (and thus radium) from solution by FHO can be increased by certain strongly adsorbing anions; arsenate was more effective in this regard than sulphate, which required a roughly ten-fold increase in concentration to achieve similar results; there appeared to be two main pathways for barium adsorption, with ion exchange dominating at low anion concentrations, and surface interactions (consistent with the surface precipitation model) dominating at higher concentrations; and finally, in such cases where surface precipitation occurs, the Kurbatov plot loses relevance as an indicator of H^+/M^{n+} exchange, although there appears to be no reason to doubt the validity of the pH_{50} values obtained. This may have important implications for the study of the Key Lake tailings, since the adsorption data provide a possible mechanism for the adsorption of radionuclides, specifically radium, on hematite or hematite-chlorite. The extremely low solubility of $FeAsO_4$ also provides a means for long-term protection of underlying radionuclides from leaching.

Interpretations and Implications

In this section, the results obtained from the various experiments performed in this work will be assembled and discussed in terms of their relevance to the Key Lake tailings. That is, they will be used to answer some of the questions raised at the outset of this thesis, as well as questions arising from the results themselves. One such

question was raised by the observation of alpha activity throughout two mineral phases found within the tailings; this seems to contradict the assumption [1] that most, if not all, of the radionuclides are released during the leaching stage of sulphuric acid-type ore processing (which is a non-selective process [64,75], attacking all acid-soluble phases), and are then subsequently reprecipitated. This section will focus on three main topics in this regard: 1) the origin of the friable surface material associated with hematite-chlorite grains; 2) the observed radionuclide distribution within this mixed phase and the mineral goethite, leading to conclusions regarding the most likely origin of the radionuclides; and, 3) from a consideration of the above, conclusions regarding the potential usefulness of one or both of these materials as a means of improving radionuclide retention in the tailings.

As mentioned in the discussion, there are two likely mechanisms to account for the presence of the friable surface on hematite-chlorite grains: precipitation and/or agglomeration of fines along with iron hydroxides on the surface; and alteration of the original surface by chemical attack during ore leaching. It must be emphasized that there is no evidence of a primary association of elements such as nickel and arsenic with hematite-chlorite, and it is assumed that they are secondary in origin.

The physical state of the surface material agrees well with that expected for rapid deposition on a substrate; another possible reason for its low cohesion would be coprecipitation and occlusion of different phases within the predominant iron hydroxide. The almost complete elimination of nickel and arsenic with removal of the friable

surface, as shown by microprobe analysis, gives a strong indication that these elements are associated with the surface material only; this, presumably, would be the result of the coprecipitation and agglomeration of nickel- and arsenic-containing compounds on the hematite-chlorite grains, although they could also have been adsorbed after iron precipitation. However, the observed absence of significant alpha activity in the surface material, as shown by autoradiography, is strong evidence against this mechanism; precipitation and/or agglomeration during ore processing and leach residue treatment would be expected to carry down some portion of the radionuclides, unless they were completely reprecipitated before iron. This is not plausible - considerable amounts of radioactive species (notably thorium) remain dissolved after completion of the leaching stage, and iron hydrolyzes at a lower pH than thorium (iron hydrolysis is extensive even at pH 2-3 [76]). Finally, this friable material was observed only with hematite-chlorite grains; to satisfy a secondary origin, it would have to be deposited either very specifically, or very slowly, neither of which is to be expected.

The evidence for a pre-existing origin is strong. In such a case, its friable nature would be the result of severe chemical attack during leaching; chlorite is susceptible to acid dissolution, as is hematite, although to a lesser extent. The lack of alpha activity at the grain surface, compared to that shown to be present within, could be explained by partial leaching of the outer grain rim. The presence of nickel and arsenic could be largely accounted for by their adsorption onto active surface sites created by leaching; some agglomeration and/or surface precipitation could also have occurred, and indeed

should be expected - the surface area of a leached grain should be higher than that of the unaffected mineral, and most large grains in the tailings sample were at least partly coated with precipitated material. While there is no evidence that radionuclides were carried down with FHO (which was found only on the hematite-chlorite grains), it is possible that non-radioactive elements such as nickel and arsenic were adsorbed, precipitated, or agglomerated at the grain surface. The arsenic may not be associated entirely with nickel; it may have precipitated with iron during lime neutralization.

It is concluded, then, that: there is sufficient evidence to reject precipitation/agglomeration as the primary mechanism to account for the friable surface observed on hematite-chlorite grains; and that there is evidence supporting alteration of original material. Subsequent adsorption, precipitation, or agglomeration of other species cannot be excluded, given the complexity of the system.

The second topic to be discussed concerns the intraparticle radionuclide distribution. It is expected, naturally, that radionuclides would be present on the surfaces of tailings fines, and dispersed more or less homogeneously through precipitates. The alpha activity observed throughout fairly large grains of hematite-chlorite and gersdorffite (which was not extensively studied) was not expected, however. There are two possibilities which could account for such observations: that the observed radioactivity represents original (and thus unleached) radionuclides; or that radionuclides became associated with these phases only after mining, that is, during ore processing, tailings treatment, or after tailings deposition (which can be dismissed in this case).

A secondary "emplacement" of uranium and/or U_{rd} would involve fairly rapid inward diffusion; this possibility does not seem plausible, and is contradicted by evidence found both in the present work as well as in the literature. The first contradiction is that both phases, although very different in chemical composition, lattice structure, and (most likely) diffusion characteristics, showed similar trends in radioactivity distribution. Indeed, the observed distribution was the opposite of that expected to be the result of inward radionuclide diffusion - the hematite-chlorite grains were, without exception, more radioactive toward the grain centers. Also, since the surface material on these grains contained significant arsenic, yet was not radioactive, and since the adsorption experiments demonstrated an increase in barium (and thus radium) adsorption on FHO (a primary component in the friable surface material) in the presence of arsenate ions, at least some radioactivity should have been detected. Similarly, gersdorffite shows an increase in radioactivity with surface removal - this mineral has been shown [36] to form around pitchblende and coffinite at Key Lake (which are the primary uranium minerals), providing a means of radionuclide incorporation.

The above evidence clearly favours the incorporation of radionuclides prior to mining, and suggests that the radionuclides observed represent the decay of long-held radioactive species, which probably accumulated in the two phases in quite different ways. The cited growth of gersdorffite around cores of uranium minerals mentioned above, combined with autoradiography results from this work, indicates a "closed" system with regard to radionuclide mobility. For the hematite-chlorite, it is likely that adsorption on, or incorporation

within, the chlorite phase was followed by, or concurrent with, the conversion of chlorite to hematite; this mixed phase may constitute a more "open" system, owing to the reversible adsorption and limited lattice penetration [33] of large ions for layer silicates. Given the differences in mobility of uranium, thorium, and radium, and the observation [6,31] that in certain cases uranium and U_{rd} may be held within discrete phases, it is possible that uranium (and perhaps radium) migrated away from the original chlorite phase, leaving thorium behind; conversely, mobilized uranium could have been adsorbed by chlorite and subsequently trapped. The conversion of chlorite to hematite (plus a clay mineral) is not an uncommon geochemical reaction [77], and appears to have occurred in the Key Lake orebodies. An absence of uranium from the hematite-chlorite, combined with the (geologically) short half-life of ^{230}Th , would indicate a fairly recent event. An obvious possibility for such an event would be fluctuations in the redox potential and pH caused by glacial activity; during periods of glacial retreat, the water table is lowered, favouring oxidizing conditions, which would solubilize uranium. Later periods of glacial advance would raise the water table (favouring reducing conditions), causing precipitation of uranium compounds; given the small quantity of hematite-chlorite that could practically be separated, it was not possible to determine how much (if any) uranium was present. It might be tempting to conclude, based on the high reported uranium recoveries by leaching, that there is little or no uranium within the hematite-chlorite; however, since this mixed phase comprises a very small portion of the total tailings content, uranium could easily be present without greatly reducing the extent of recovery. This does not allow firm conclusions to be made

regarding the origin of radionuclides within this material, although the above suggests that uranium was mobilized and migrated away from chlorite, leaving thorium behind.

From the above discussion, it can be seen that the hematite-chlorite and gersdorffite phases, while different in many ways, have one factor in common, namely that they both appear to have retained their original radioactivity despite rigorous leaching conditions. It is thus clear that, in this case at least, they are both highly leach-resistant, and are excellent hosts for radionuclides.

Gersdorffite has been described [19] as "ubiquitous" within the orebodies, and has been shown in the present work to contain relatively high levels of alpha activity. While the number of such grains studied was too small to allow broad generalizations, there are nonetheless indications that a substantial portion of the radioactivity within the heavy fraction could be held within this mineral. If so, it would be a more significant host overall than the hematite-chlorite, owing to its higher content in the tailings. However, this mineral is expected to be a host primarily for original radionuclides only. The grains examined showed no signs of surface alteration, or formation of a friable surface layer, as seen with hematite-chlorite. Thus, barring the formation of a similar layer, the effectiveness of gersdorffite is limited to the retention of its original radioactivity. The hematite-chlorite phase, on the other hand, shows potential as a host phase for radionuclides released as the tailings age, in addition to high retention of original radioactivity. The adsorption experiments demonstrated that FHO in the presence of arsenate provides a highly effective adsorbent for radium (and, perhaps, thorium). The outer

grain surface, as a result of chemical attack, would be expected to have a large number of surface sites for adsorption, and the arsenic present at the surface should improve its adsorptive properties. This material could then provide prime sites for redistributed radio-nuclides.

IV. Conclusions

In summary, the experimental results of this work allow several statements to be made regarding the state and distribution of radionuclides in the tailings. The mineralogy of the Key Lake sample was similar to that at Midwest Lake, but with a more widespread radionuclide distribution; the light and heavy density fractions contained roughly the same amounts of radium, in sharp contrast to previous results - this was in large part due to the presence of tailings fines in the Key Lake sample, which were concluded to contain most of the radioactivity within the light fraction. While a larger number of minerals showed some radioactivity in the present case, two in particular were found to be strongly alpha active throughout, and may account for much of the total radioactivity within the heavy fraction; these were identified as gersdorffite (which had been shown elsewhere to contain inclusions of uranium minerals) and an intergrowth of hematite with chlorite and a possible third phase. The surface of the latter was friable, and contained a variety of elements along with iron, notably nickel and arsenic, which appeared to be associated with the surface only; this surface was concluded to have formed primarily as the result of chemical attack of the original hematite-chlorite followed by adsorption and/or agglomeration of ions and precipitated material. The intraparticle radionuclide distribution, as revealed by autoradiography, indicated that the radioactivity found with the above minerals was most likely of a pre-mine origin.

An examination of the tailings alpha spectra did not provide evi-

dence of element-specific Rutherford scattering. This was primarily due to technical difficulties and to the complexity of the system being investigated; alternatively, this could be further evidence of the widespread radionuclide occurrence in the tailings. While not successful in the present study, the use of Rutherford scattering in tailings analysis should be possible for less complex systems, or where a sufficient quantity of single minerals can be obtained from the tailings. Comparisons of tailings spectra, both with each other and with samples of ^{230}Th contained in varying amounts of FHO matrix, indicated that radionuclides were held closer to particle surfaces for the light fraction than the heavy fraction. This is further evidence not only that radionuclides are contained within fines in the light fraction, but also that they are held below particle surfaces in the heavy fraction; the latter is supported by the screening of underlying radionuclides for hematite-chlorite, as shown by autoradiography. The one exception to this among the U_{rd} was ^{210}Po , which appeared to be closer to, or at, particle surfaces in the heavy fraction, possibly due to preferential adsorption.

Adsorption experiments demonstrated clearly that the presence of arsenate increased barium adsorption on FHO; sulphate was also shown to require a roughly ten-fold increase in concentration to achieve similar results. Abrupt and large changes in the slopes of Kurbatov plots with increasing anion concentration strongly indicated a change in reaction from simple ion-exchange to a more complex pathway; the recently developed surface precipitation model would seem to provide a logical and reasonable explanation of this phenomenon for the above experiments, and suggests that the surface region of the hematite-chlorite

grains, while not presently radioactive, may provide an excellent site for the sequestering of radionuclides released from their original hosts in the tailings (unlike gersdorffite, which also seemed to be highly leach-resistant but not favourable for surface adsorption of ionic species).

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