An Appraisal of the Hydrogeological Processes Involved in Shallow Subsurface Radioactive Waste Management in Canadian Terrain

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Preface

The objectives of this study were twofold:

(1) To provide scientists and engineers in government and industry with a detailed account of the hydrogeological processes that control the movement of radionuclides in the shallow subsurface.

(2) To prepare a set of guidelines based on (1) and the hydrogeological and operational experience of existing Canadian sites, defining the properties of sites that are suitable for the shallow disposal and/or storage of radioactive wastes in Canadian terrain, and to describe the methods of investigation of such sites.

We have attempted to attain these objectives by a literature review, on-site visits and discussions with knowledgeable Canadian and American scientists and engineers. The report is a fairly rigorous state-of-the-art survey of the movement of radioactive contaminants through the shallow subsurface, and consequently it may be of use to scientists and engineers studying the subsurface movement of other contaminants. The basic premise of this report is that the protection of subsurface public water supplies from radioactive or nonradioactive contaminants requires an understanding of the principles of flow through porous media, the hydrogeological properties of surficial deposits, and the physical chemistry of the colloids and aqueous solutions with which the contaminants come into contact.

The original version of this report was prepared in 1974 and was funded at that time through the Office of Research Subventions of the Inland Waters Directorate, Department of the Environment.

Finally, we should like to advise the reader that a complementary report on the design and execution of a hydrogeological site survey for a radioactive waste management site is being prepared by J.A. Cherry and his colleagues at the University of Waterloo.

G.E.G.
R.E.J.
Ottawa, 1977

Abstract

The hydrogeological aspects of the problem of low-level radioactive waste management are introduced with a discussion of the Canadian nuclear power program; the nature of radioactive wastes and their rates of production; and the half-lives and health effects of "waste" radionuclides. As well, a general account is given of the present Canadian policy and procedures for licensing radioactive waste management sites.

Following this introductory material, a detailed account is presented of the geohydrologic processes controlling the transport of radionuclides in groundwater flow systems and the attendant geochemical processes causing the retardation of the radionuclides. These geohydrologic and geochemical processes (i.e., hydrogeological processes) can be evaluated by the measurement of certain variables such as aquifer dispersivity, groundwater velocity, hydraulic conductivity, cation-exchange capacity, and total competing cations. To assess the possible importance of each variable in Canadian terrain, a comprehensive discussion of presently available (Canadian) data that have been compiled pertaining to each variable is presented.

A description is then given of the hydrogeology of and the waste management experiences at radioactive waste management sites at Chalk River, Ontario; Bruce, Ontario; Whiteshell, Manitoba; and Suffield, Alberta. Along with this description there is a brief evaluation of those geohydrologic and geochemical processes that may be of importance at these sites. As a consequence of the above, site criteria outlining the nature of desirable hydrogeological environments for radioactive waste management areas are presented for those situations where the groundwater flow system acts as (a) a barrier to the migration of escaped radioactivity and (b) a joint dispersion-retardation system for liquid wastes.

Résumé

Le présent rapport traite des divers problèmes que pose, du point de vue de l'hydrogéologie, la gestion des déchets radioactifs de faible activité; du programme canadien de développement de l'énergie nucléaire; de la nature et du volume des déchets radioactifs produits; ainsi que de la période et de la nocivité des radionuclides résiduels. En outre, il fournit un aperçu de la politique et des méthodes qu'adoptent actuellement les Canadiens pour autoriser l'utilisation des sites de rejet des déchets radioactifs.

Après cette brève introduction, une description détaillée est donnée des processus géohydrologiques qui régissent la migration des radionuclides dans les réseaux d'écoulement souterrain, en même temps que des processus géochimiques qui ralentissent la migration des radionuclides. Il est possible d'évaluer ces deux types de phénomènes (donc les processus hydrogéologiques) en mesurant certaines variables comme la capacité de dispersion de l'aquifère, la vitesse de circulation des eaux souterraines, la conductivité hydraulique, la capacité d'échange cationique ou la quantité totale de cations en présence. Pour estimer l'incidence possible de chaque variable sur le sol au Canada, il s'est agi de rassembler et d'examiner dans leur ensemble les données actuellement disponibles (au Canada) sur chacune d'entre elles.

D'autre part, le rapport renferme une description sur l'hydrogéologie des sites de gestion des déchets radioactifs à Chalk River (Ontario), Bruce (Ontario), Whiteshell (Manitoba) et Suffield (Alberta), et sur les expériences de gestion des déchets radioactifs qui y ont été effectuées. Il comporte également un bref exposé des processus géohydrologiques et géochimiques qui pourraient y jouer un rôle important. C'est à partir de ce fait que des critères ont pu être établis pour définir les milieux hydrogéologiques favorables pour les zones de gestion des déchets radioactifs, où le réseau d'écoulement souterrain (a) empêche la migration des particules radioactives, et (b) favorise la dispersion des déchets liquides tout en empêchant la migration des particules radioactives.

List of Symbols

A or A^+	Cationic or solute species		F	Faraday constant
A'	Cross-sectional area		F^1	Force of electrostatic attraction
$\overset{o}{A}$	Angstrom		F_x, F_y, F_z	Solute flux in x, y, z directions
Al	Aluminum			
a_1, a_2...	Angle		f	Fanning friction factor
a_L, a_T	Dispersivities, longitudinal and transverse		f^1	Slope of the exchange isotherm
B or B^+	Cationic or solute species		G	Force of gravity
B*	Average medium conductance		H	Hydrogen
b	Half-aperture width of a fracture		^3H	Tritium
			HCO_3^-	Bicarbonate ion
C or C^+	Cationic or solute species		IAP	Ion activity product
C_A	Concentration of solute A		K	Hydraulic conductivity as in K_ℓ, K_1, K_{xx}, etc.
C_0	Initial concentration (i.e., at time 0)		K_A	Fracture distribution coefficient
C_u	Hazen's effective grain-size coefficient		K^+	Potassium ion
c_0	Initial concentration		K_B^A	Selectivity quotient
c_∞, c_∞'	Ionic concentrations in the mobile layer		K_d^A or K_d	Distribution coefficient
			K_{eq}	Equilibrium constant
Ca^{2+}	Calcium ion		k	Instrinsic permeability
Ce	Cerium		L	Length
Cl^-	Chloride ion		$\bar{L}$	Average length of a channel of idealized porous medium
Co	Cobalt			
Cs	Cesium		L_e	Length of a tortuous flow path
D	Coefficient of mechanical dispersion		ℓ	A direction
D_d	Coefficient of molecular diffusion		M	Molar concentration
			Mg	Magnesium
D_d^*	Apparent coefficient of molecular diffusion		Mn	Manganese
D^1	Coefficient of hydrodynamic dispersion (as in D_L^1, D_T^1)		MPC	Maximum permissible concentration
D_c	Computed distribution constant		mol/l	Molal concentration
D_{obs}	Observed distribution constant		mV	Millivolts
d	Grain size diameter (as in d_{10}, d_{50}, d_{60}, etc.)		N	Total number of fractures in a unit cross-sectional area
E^0	Standard half-cell potential		Na	Sodium
Eh	Redox potential		n	Porosity
e^-	Electron		n_f	Fracture porosity
erf	Error function		Pe	Dynamic Peclet number
erfc	Complementary error function		Pu	Plutonium
			p	Gauge pressure

Symbol	Definition
pH	Negative logarithm of the hydrogen ion activity
pK	Negative logarithm of any constant K
P_0	Atmospheric pressure
ppt	Precipitate
Q	Fluid volume discharged per unit time per unit cross-sectional area
Q^+, Q^-	Electropositive and electronegative charges, respectively
q	Charge density
$\vec{q}$	Seepage flux
q_A, q_B	Amount of solute A, B adsorbed or precipitated per unit mass
q_ℓ	Specific discharge
R	Gas constant
R^-	Cation exchanger
Ra	Radium
Re	Reynolds number
R_f	Ratio of fracture surface area/pore volume
Ru	Ruthenium
r	Radius
S	Sulphur as in SO^{2-}, S^{2-}
SI	Saturation index
Si	Silicon
Sr	Strontium
T	Temperature
T^*	Tortuosity
Th	Thorium
t	Time
tan	Tangent
U	Uranium
V	Fluid velocity
V_ℓ	Velocity in the ℓ direction
$V(r)$	Radial velocity distribution
V_x	Velocity in the x direction
W	Number of fractures in a discharging unit width
x	Direction or distance in the x direction
Y_A	Reduced or fractional concentration of A^+ adsorbed on R^-

Symbol	Definition
y	Direction
Zn	Zinc
ZPC	Zero point of charge
z	Direction
z_i	Valence of the ith ion
α	Dimensionless empirical constant characteristic of the porous medium for a given λ, which is the exponent of the Peclet number
γ	Activity coefficient
$\gamma_{A(s)}$	Activity coefficient of A(s)
$\gamma_{B(s)}$	Activity coefficient of B(s)
γ_s	Specific gravity
Δ	Individual fracture spacing
ε	Number of moles of electrons
θ	Volumetric, fractional moisture content
λ	Dimensionless, empirical exponent characterizing the mixing regime
μ	Dynamic viscosity
ν	Kinematic viscosity
ξ	Fracture surface coefficient
ρ	Fluid density
ρ_b	Bulk density
σ, σ^1	Total surface charge
σ_I	Inclusive standard deviation of grain sizes
σ_N	Scalar pore-water velocity conversion
σ_+	Cation-exchange capacity
σ_-	Anion-exchange capacity
τ	Total competing cation concentration
Φ	Hydraulic potential
ϕ	Hydraulic head
Ψ	Pressure head
Σ	Sum of
∇	Vector operator
∇^2	Scalar operator
Δ	Finite increment

Introduction

Nuclear fission breeds responsibilities,
some with long half-lives.

--Lennemann, Parker and West

The energy crisis of the 1970s has crystallized the opinion within the energy production industry of Canada that the Canadian nuclear reactor program will be the key to the efficient and economic creation of electrical energy in Canada to at least the year 2000. It has been noted that owing to the depletion of its fossil fuel resources, North America must become self-sufficient in terms of energy, and in the opinion of Folinsbee and Leech (1974), "a complete conversion from a fossil fuel (where costs can only skyrocket) to a nuclear energy system (fission, fusion, or solar where costs may be stable) will be required within this century."

If this complete conversion occurs certain environmental problems will become more acute. Foremost among these will be the problem of the management of radioactive wastes. This report is an attempt to appraise the hydrogeological factors of managing low- and medium-level radioactive wastes which are and which might be stored in the Canadian shallow subsurface. This last sentence requires a few clarifying definitions. Hydrogeology is the science concerned with the movement of water in the subsurface and the relationships between the quantity and quality of that water and the porous media through which it flows. Low- and medium-level wastes are all wastes produced in the operation of reactors of the Atomic Energy of Canada Ltd.'s (AECL) CANDU design except for the spent fuel elements and those by-products produced by the industrial, scientific and medical uses of radioactivity. For the purposes of this report, the shallow subsurface may be considered to be that depth through which groundwaters of local and intermediate flow systems move, i.e., in the range of 0-500 ft (0-150 m) depth.

The topics covered in this report are wide-ranging. The rest of this Chapter is devoted to such introductory matter as the projected growth of the Canadian nuclear power system, the nature of radioactive wastes and their rate of production, the half-lives and health effects of waste radionuclides, and a general account of present Canadian procedures for the licensing of radioactive waste management sites. Chapter 2 is a statement of the hydrologic principles governing the transport of waste radionuclides by groundwater in the shallow subsurface, and in Chapter 3, a discussion of

the retardation of these radionuclides by geochemical processes is given. Chapter 4
is a survey of the hydrologic and geochemical processes affecting radioactive waste
management in Canadian terrain. In Chapter 5, a hydrogeological description of
currently operating radioactive waste management sites in Canada is presented. Finally,
Chapter 6 considers possible guidelines for the selection and investigation of radio-
active waste management sites in Canadian terrain.

THE CANADIAN NUCLEAR POWER INDUSTRY

The Canadian nuclear power industry is based on a nuclear reactor designed by
AECL known as the CANDU, or Canadian-Deuterium-Uranium, reactor. The singular features
of this reactor are (1) it is fuelled with unenriched uranium oxide and (2) the nuclear
reaction is moderated by heavy water (deuterium oxide).

The total electrical generating capacity of Canadian nuclear power stations
is still quite small compared with the total capacity provided by fossil fuels and
hydroelectric power. At present, only 4600 million watts [megawatts (MW)] of Ontario
Hydro's electrical generating capacity of approximately 20,000 MW is from nuclear

Table 1. CANDU Nuclear Power Reactors (after McIntyre, 1975)

CANDU power reactors	Starting date	Generating capacity (MW)
Rolphton, Ontario		
Nuclear power demonstration plant (NPD)	1962	22
Douglas Point, Ontario		
Operating	1967	200
Gentilly, Quebec		
Boiling light water (BLW) (experimental)	1971	250
Under construction (conventional CANDU)	1979	600
Pickering, Ontario		
Operating	1971	4 x 540
Under construction	1980	4 x 540
Bruce, Ontario		
Under construction	1976	4 x 745
Planned	1982	4 x 750
Point Lepreau, New Brunswick		
Under construction	1980	600
Darlington, Ontario		
Planned	1983	4 x 800

reactors, and Ontario Hydro is by far the largest generator of nuclear power in Canada. Table 1 shows the electrical generating capacity of those CANDU reactors presently used for generating purposes or under construction, or those that have been ordered by utilities. The exponential growth in nuclear power production that is evident in the data summarized in Table 1 may lead to the equivalent of 300 500-MW reactors in Canada by the year 2000 (Campbell, 1973). Many of these will be clustered in nuclear power generating centres such as Pickering and Bruce, Ontario, and Gentilly, Quebec. Dr. J.S. Foster (1972) of AECL has predicted that by the year 2000 one half of the nation's electrical power will be generated by nuclear reactors.

RADIOACTIVE WASTES

There are two sources of radioactivity in nuclear power generation producing radioactive wastes. The first source is the splitting, or "fissioning," of uranium atoms in the fuel elements by neutrons creating fission products such as strontium-90 (^{90}Sr), cesium-137 (^{137}Cs) and ruthenium-106 (^{106}Ru). Campbell (1973) has noted that over 99% of all radioactivity produced in nuclear power generation is through fissioning of the fuel. The spent fuel elements are presently stored under water at the reactor sites, and will remain there until decisions concerning spent fuel reprocessing and ultimate storage have been made. The second and minor source is activation products, such as cobalt-60 (^{60}Co) and tritium (^{3}H), which are produced by neutron capture in the moderator and coolant systems.

By far the largest amount of the radioactivity that is currently stored in the shallow subsurface of Canada has at one time been in liquid or gaseous form within the reactor building, and has been fixed in a solid form by decontamination systems. At Ontario Hydro's Pickering A Generating Station, there are several ion-exchange decontamination systems. Ion-exchange resins are used to decontaminate the moderator and coolant (both heavy water) of activation products causing significant radiation fields and fission products that have escaped from defective fuel elements. Any activity escaping into the spent fuel bay storage water from stored fuel elements is decontaminated by another ion-exchange resin which will therefore contain fission products. Minor amounts of radioactivity are also retained on noncombustible objects such as piping and on combustible substances such as paper during the day-to-day operation of the reactor. Table 2 shows the volumes and activities of the various nonfuel radioactive wastes produced by a 500-MW Pickering-type reactor during the course of operation of one reactor during one year.

Apart from those wastes arising from nuclear power generation, it is also necessary to consider wastes due to the use of radioisotopes in industry, medicine and scientific research. These radioisotopes are produced by AECL reactors, and if not

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Table 2. Annual Production of Solid Wastes from a 500-MW CANDU Reactor

Type of waste	Volume (m^3)	Total activity (Ci)	Retrievable storage technique
Combustible	228	1.1	Concrete trenches
Noncombustible	1	0.015	Concrete trenches
Ion-exchange resins			
(a) Disposable can	0.9	75	In-ground tile holes
(b) Bulk	11	475	In-station storage
Filters (cartridge)	0.3	410	In-ground tile holes

Source: G.A. Vivian, Ontario Hydro (personal communication).

retained for use by AECL laboratories they are sold by the Commercial Products Division of AECL to industries, universities and hospitals. Federal legislation requires that the waste by-products from these uses be returned to the AECL Commercial Products Division, Ottawa, from where they are sent for burial to AECL's Chalk River Nuclear Laboratories (CRNL), 120 mi (200 km) from Ottawa. Also various liquid and solid radioactive wastes, which are stored or disposed of in the shallow subsurface, are produced at AECL's Chalk River Nuclear Laboratories and Whiteshell Nuclear Research Establishment (WNRE) laboratories due to the operation of laboratories and reactors at these centres. This topic is discussed in detail in Chapter 5.

The by-products of nuclear fuel production are an additional source of radioactive waste not produced by nuclear power generation. In refining Canadian uranium-bearing ores, various amounts of radium, thorium and uranium wastes are produced and are disposed of in the ground at several sites close to the Eldorado Nuclear Ltd. uranium refinery at Port Hope, Ontario.

There are several problems in trying to estimate the production rate of radioactive wastes intended for subsurface storage. Estimates of future nuclear power production, and consequently waste production, are continuously being revised because the present energy situation tends to favour nuclear power production. Advances in waste treatment techniques will certainly be made and will affect the quantities of wastes produced and their radioactivity. Finally, changes in the regulations governing what can be stored in the subsurface are quite possible. It is desirable, however, to make some rough estimates of waste production over the next ten years so that the quantities of low- and medium-level wastes intended for shallow, subsurface storage may be estimated. This becomes possible if certain assumptions are made.

First, it will be assumed that wastes produced at CRNL and WNRE will continue to be stored there and can be omitted from these calculations. These amount to approximately 600 m^3/yr and 740 m^3/yr, respectively, of low- and medium-level solids [R.F. Scarth,

Atomic Energy Control Board (AECB), personal communication]. Secondly, it will be assumed that the amount of wastes produced by industrial, medical and university groups--presently 500 m³/yr (R.F. Scarth, AECB, personal communication) of low-level laboratory wastes--will be small compared with the wastes produced by nuclear power generation and can be omitted from these calculations. Thirdly, we shall disregard the uranium refinery wastes. Finally, it is assumed that to be operating in ten years' time, a nuclear power reactor must already have been ordered or will be ordered in the next two years. This suggests that by 1988 Canada will have the 25 reactors listed in Table 1 in operation plus several more elsewhere in Canada.

Table 3. Projected Volumes and Activities of Low- and Medium-Level Solid Wastes to Be Stored in the Shallow Subsurface from the Operation of 30 500-MW CANDU Reactors during 1988

Type of waste	Volume (m³)	Total activity (Ci)	Retrievable storage technique
Combustible	6840	33	Concrete trenches (?)
Noncombustible	30	0.45	Concrete trenches (?)
Ion-exchange resins			
(a) Disposable can	27	2,250	In-ground tile holes (?)
(b) Bulk	330	14,250	In-station storage (?)
Filters (cartridge)	9	12,300	In-ground tile holes (?)
Total in-ground storage (tile holes and trenches)	6906	14,583.45	

Consequently, the solid wastes produced from nuclear power generation in 1988 will be approximately 25 to 30 times those shown in Table 2. Table 3 presents the data from Table 2 multiplied by 30. The significant feature of Table 3 is the annual increment of activity retained on ion-exchange resins and filters that will have to be stored in engineered structures such as tile holes and concrete trenches. These structures possibly, although not necessarily, will be in-ground structures. Since at least two thirds of the reactors will be in southern Ontario, there will be an annual increment of radioactive waste stored in the shallow subsurface at the Ontario Hydro waste management area(s) of about 10,000 Ci by 1988. The vast majority of this radioactivity will be due to ^{137}Cs, ^{134}Cs and ^{60}Co (K. Wong, Ontario Hydro, personal communication).

THE "WASTE" RADIONUCLIDES

In the previous section, several radionuclides were associated with CANDU reactor wastes. They were the fission products ^{90}Sr, ^{137}Cs and ^{106}Ru and the activation products ^{60}Co and ^{3}H. When their radioactivity in solution exceeds a threshold level, which will be defined later, it is necessary that they remain isolated from the biosphere until sufficient radioactive decay and dilution have occurred such that they

no longer exceed this level and consequently do not constitute a health or ecological hazard. One of the reasons why waste storage or disposal areas are located in the subsurface is because any dissolved radioactivity that leaves these areas, either by design or accident, cannot move faster than the groundwater which is transporting it. Often it moves much slower than the groundwater owing to its retention on the solid phase of the porous media through which the groundwater is flowing. Generally, groundwater flow velocities are in the range of centimetres per day as opposed to streamflow velocities which are of the order of centimetres per minute. Consequently, subsurface waste storage provides the advantages of retention time and/or dilution capacity for the reduction of radioactivity levels during subsurface transport.

Those radionuclides commonly stored or disposed of in low-level waste management areas in Canada will be referred to as the "waste" radionuclides. These "waste" radionuclides are listed in Table 4 together with some of their properties and other information concerning their effect on human physiology and the level at which they are considered environmentally hazardous.

Table 4. The "Waste" Radionuclides

Radionuclide	Critical organ	Half-life* (yr)	Radiation emitted[+]	MPC[‡] (μCi/ml)[¶]
^{3}H	Body tissue	12.3	β^-	3×10^{-3}
^{54}Mn	GI**	0.86	γ, k	10^{-4}
^{55}Fe	Spleen	2.7	k	8×10^{-4}
^{60}Co	GI**	5.27	β^-, γ	5×10^{-5}
^{65}Zn	Total body	0.67	β^+, k, γ	10^{-4}
^{90}Sr	Bone	28	β^-	4×10^{-7}
^{106}Ru	GI**	1.0	β^-, γ	10^{-5}
^{134}Cs	Total Body	2.0	β^-, γ	9×10^{-6}
^{137}Cs	Total Body	30	β^-, γ	2×10^{-5}
^{144}Ce	GI**	0.78	β^-, γ	10^{-5}
^{226}Ra	Bone	1,620	α, γ	10^{-8}
^{228}Ra	Bone	5.8	α, β^-, γ	3×10^{-8}
^{232}Th	Bone	1.4×10^{10}	α, γ	2×10^{-5}
^{238}U	Kidney	4.5×10^9	α, γ	6×10^{-7}
^{239}Pu	Bone	24,300	α, γ	5×10^{-6}

*Source: Table of Radioactive Isotopes, Sargent-Welch Scientific Co.
[+]α: alpha particle; β^-: beta particle, an electron; γ: gamma ray; k: k - electron capture; β^+: position. (These symbols apply only to this table and not to the text as a whole.)
[‡]Maximum permissible concentration (MPC) in public zone water. Ten percent of ICRP MPC for 168-hr week. Source: Report of Committee II on Permissible Dose for Internal Radiation, the International Commission on Radiological Protection, or ICRP (ICRP, 1959).
[¶]Microcuries per millilitre.
**Gastrointestinal tract.

That part of the body receiving the highest dose of radioactivity from a radionuclide is called the critical organ for that radionuclide. Those radionuclides for which the critical organ is bone (e.g., ^{90}Sr, ^{226}Ra, ^{228}Ra, ^{232}Th, ^{239}Pu) are

characterized by being similar to calcium in terms of their ionic radii. Owing to this chemical similarity these radionuclides substitute for calcium in bone material. Upon ingestion other radionuclides may pass through and out of the body largely by the gastrointestinal tract. For the case of the isotopes of cesium, which are particularly significant in the Canadian situation, their transport by the bloodstream makes the whole body the critical organ.

The choice of radionuclides comprising Table 4 is based mainly on the principle enunciated by Schulz (1965) that only those radionuclides that would remain in relatively large amounts after a three-month period of decay of mixed fission and activation products are to be considered. The implication of this principle is that only those radionuclides with half-lives greater than about three months are likely to be present in significant quantities at the waste management area at some unspecified time of accidental escape. It should be noted that the "waste" radionuclides would have been at the reactor site for some time following their creation and likely for a much longer time at the waste management site prior to this hypothetical accidental escape.

The column on the right-hand side of Table 4 lists the maximum permissible concentration (MPC) of each radionuclide in public waters, the threshold level referred to above. The MPC is the maximum concentration of each radionuclide which it is assumed can be ingested by the general public without readily apparent ill effects.

LICENSING POLICY AND PROCEDURES

The regulation of radioactive wastes in Canada is vested in the Atomic Energy Control Board (AECB) by the Atomic Energy Control Act. The waste management policy of AECB is (AECB, 1974):

> ...the indefinite retrievable storage of...
> wastes in solid forms in a limited number of
> government-supervised and preferably government-
> operated storage facilities.

Since AECB's health and safety criteria and guidelines for radioactive waste management were under review at the time of writing (1976), it is not possible to be more specific concerning the details of the Board's waste management policy. It is recommended that those interested in the nature of such a policy contact the Atomic Energy Control Board (P.O. Box 1046, Ottawa, Ontario. K1P 5S9) for further details.

This policy of retrievable storage, however, is quite certain to remain at the core of any Canadian radioactive waste management policy in the foreseeable future. Consequently, when an applicant proposes a waste management site to AECB for approval,

he first presents a safety report describing the method of retrievable storage intended for use and a description of the waste management site. Should the proposal satisfy the AECB's Radioactive Waste Safety Advisory Committee's (RWSAC) requirement that the occupational safety of the workers and the public health of neighbouring communities are not endangered by the site and its operation, then RWSAC would recommend to the AECB that the applicant be granted a construction license. Generally, AECB adopts the recommendations of its advisory committees. After completion of construction the applicant then requests an operating license. The request is again vetted by RWSAC. Should AECB and RWSAC be satisfied with the site, the operating license would be granted for a period of a few years during which time the licensee would file regular progress reports. At the end of the period of licensing, the site would again be studied by RWSAC prior to any decision on its relicensing.

Geohydrologic Transport Processes

The purpose of this Chapter is to review the state of knowledge of those transport processes in porous media that are relevant to the present study. In the first section, the fundamental principles of geohydrology or physical hydrogeology are reviewed. The second section contains a theoretical development of transport processes in homogeneous, uniform and isotropic porous media. The final section is a review of recent work on transport processes in heterogeneous, nonuniform and anisotropic porous media, i.e., the natural environments with which the hydrogeologist must work.

PRINCIPLES OF GEOHYDROLOGY

Hydrologic Properties of Porous Media

Any description of porous media must begin with the twin concepts of porosity and permeability. *Porosity* is "the ratio of pore volume to the total volume of a given sample of material," whereas *permeability* "is a measure of the ease with which fluids pass through a porous material" (Davis, 1969).

The porosity of sediments depends on their packing arrangement, size distribution, shape and, in the case of consolidated sediments, cementation. Representative values of porosities for various sediments are given in Table 5.

Table 5. Representative Porosity Ranges for Sedimentary Materials

Material	Percentage porosity (%)
Soils	50-60
Clay	45-55
Silt	40-50
Medium to coarse mixed sand	35-40
Uniform sand	30-40
Fine to medium mixed sand	30-35
Gravel	30-40
Gravel and sand	20-35
Sandstone	10-20
Shale	1-10
Limestone	1-10

Source: Todd (1959).

The intrinsic or specific permeability of a porous medium to a fluid is given by

$$k = \frac{Q\mu}{A'\rho G} \left(\frac{d\phi}{d\ell}\right)^{-1} \qquad (1)$$

where Q is the fluid volume discharged per unit time through a porous medium of cross-sectional area A', μ is the dynamic viscosity of the fluid, ρ is the fluid density, G is the acceleration due to gravity, and $d\phi/d\ell$ is the hydraulic gradient in the direction of flow (Davis, 1969). The intrinsic permeability, k, has dimensions of L^2 and is a function of the geometric properties of the medium. It is usually expressed in darcys (1 darcy = 0.987 x 10^{-8} cm^2). Because of grain orientation in sedimentary deposits, permeability is often dependent on the direction of fluid flow. This feature, called *anisotropy*, necessitates the treatment of permeability as a vector, whereas porosity is a scalar. Typical values of horizontal and vertical permeability for various sediments are summarized in Table 6. Since hydrogeologists are mainly involved with water as the fluid, a more commonly used hydrogeological variable is the *hydraulic conductivity*, K. If the terms in Equation 1 are rearranged the hydraulic conductivity may be defined as

$$K = k \, \rho G/\mu \qquad (2)$$

which is often loosely referred to by hydrogeologists as the "permeability," i.e., the coefficient of permeability, and which has dimensions of L/t.

Table 6. Representative Values of Horizontal and Vertical Permeabilities

Material	Porosity	Permeability Horizontal	Vertical	Median diameter (mm)
Clay	42.3	10^{-4} (9.6 x 10^{-8})	10^{-5} (9.6 x 10^{-9})	0.0028
Silt	36.8	–	10^{-2} (9.6 x 10^{-6})	0.05
Sand	44.8	10^1 (9.6 x 10^{-3})	10^1 (9.6 x 10^{-3})	0.27

Note: Darcy units; equivalent hydraulic conductivities in centimetres per second at 20°C are in parentheses.

Source: Data averaged from Davis (1969, Table 5).

The potential function governing the flow of groundwater in porous media is, in units of energy per unit fluid mass,

$$\Phi = Gz + \int_{P_0}^{P} dp/\rho + \tfrac{1}{2}V^2 \qquad (3)$$

where Φ is the hydraulic potential at a given point, z is the elevation of the given point

above datum, p is the gauge pressure (i.e., absolute pressure minus local atmospheric pressure) at the point, p_0 is the atmospheric pressure, V is the fluid velocity, and ρ and g are as defined. The expression (3) was derived by Hubbert (1940) and is the Bernoulli energy theorem. The kinetic energy term $\frac{1}{2}V^2$ is usually negligible for the case of fluid flow through porous media. By defining $\phi = \Phi/G$ and setting $p_0 = 0$ (i.e., local atmospheric pressure = zero gauge pressure) and letting $p = \rho G \psi$, Equation 3 may be rewritten as

$$\phi = z + \psi \tag{4}$$

where ϕ is the hydraulic or piezometric head, z is the elevational head and ψ is the pressure head. Therefore the water level, ϕ, measured in a manometer placed at a point of elevation, z, is the sum of the heads due to the elevation of that point and the hydraulic pressure at that point.

So far nothing has been said of the state of saturation of the porous medium. Because radioactive waste management areas are generally situated in unsaturated soils some complexities are introduced into these considerations.

The volumetric, fractional moisture content, θ, of a partially saturated porous medium may be defined by

$$\theta = ns \tag{5}$$

where n is the porosity and s, the degree of saturation (0.0 if totally unsaturated, 1.0 if saturated). The relative conductivity of a soil for a liquid or gas is then defined as the ratio of the fluid conductivity for the partially saturated condition to the fluid conductivity at full saturation. It can then be shown that the relative conductivity of liquids increases rapidly as θ increases, and the relative conductivity of gases decreases rapidly as θ increases. The processes are shown conceptually in Figure 1. The inclusion of gases in this discussion is necessary because in unsaturated porous media groundwater can flow by liquid and vapour transfer. Figure 1 can be readily explained by noting that as the fraction of the pore volume filled with liquid decreases, the effect of surface tension on the remaining liquid increases such that the relative conductivity of the porous medium for the liquid must decrease. At the same time, fewer pore necks are blocked with liquid and consequently the relative conductivity for the gas phase may increase. It can therefore be appreciated that a porous medium in an unsaturated state might in some measure retard any radioisotope in solution moving through it.

Figure 1 would suggest that hydraulic conductivity and volumetric moisture content are dependent and independent variables, respectively; they are in fact related, however, by virtue of their sharing a true independent variable--the pressure head,
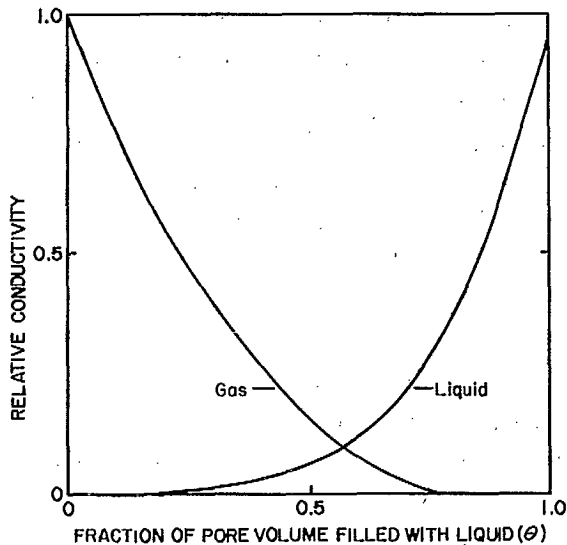
Figure 1. Relative conductivities for liquids and gases in a hypothetical porous medium (after Stallman, 1964).

ψ. Figure 2 shows the functional relationships between pressure head, on the one hand, and hydraulic conductivity and volumetric moisture content, on the other. Hysteresis in these relationships during the wetting and drying of an unsaturated porous medium occurs because of the entrapment of air in some of the larger pores when the porous medium is rewet after drying (Childs, 1969). It has been observed in field studies that flow through the unsaturated zone is not always solely intergranular; flow sometimes occurs through the channels left by decayed roots (Williams and Allman, 1969) or through fractures owing to crustal rebound (Grisak and Cherry, 1975). This topic is considered in more detail later.
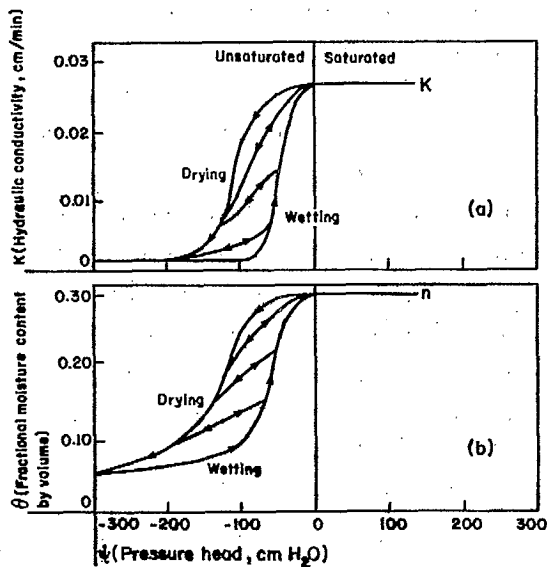
Figure 2. The relationships between pressure head and (a) hydraulic conductivity and (b) moisture content for a hypothetical unsaturated soil (after Freeze 1972a).

Most analyses of groundwater flow in some way involve a principle known as *Darcy's law*, which has already been stated in one form in the definition of intrinsic permeability in Equation 1. It can be rewritten as

$$q_\ell = -K_\ell \left(\frac{d\phi}{d\ell}\right) \tag{6}$$

where q_ℓ = Q/A in Equation 1 and is known as the Darcy or filter velocity, or the specific discharge, and K_ℓ is the hydraulic conductivity in the ℓ direction. The term q_ℓ is not the average pore water velocity but a seepage flux and has the units $L^3/L^2 t$. Equation 6 only holds for a particular set of fluid velocities in porous media which can be defined with the aid of two dimensionless parameters. The first is the Reynolds number, which is the ratio of the inertial forces of fluid flow to the viscous forces:

$$Re = qd/\nu \tag{7}$$

where q is the Darcy velocity, d is a representative grain-size diameter and ν is the kinematic viscosity. The second is the Fanning friction factor:

$$f = 1/2 \; d(d\phi/d\ell)(G/V^2) \tag{8}$$

where V is the fluid velocity (Bear, 1972, p. 126). Figure 3 shows the region of fluid flow in which Darcy's law holds is that environment in which $f > 10^2$ and $Re < 1\text{-}10$. It is in this region that laminar flow occurs and in which the viscous forces predominate over the inertial forces.
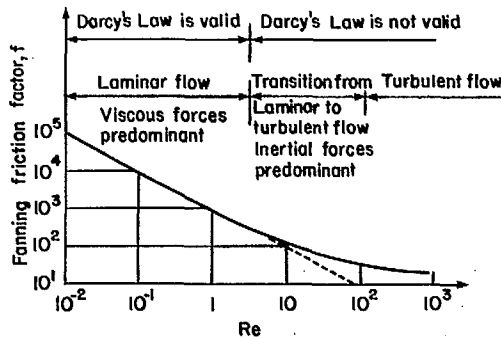
Figure 3. Laminar and turbulent flow regimes in porous media (after Bear, 1972).

The estimation of the average pore water velocity is one of the most important tasks for hydrogeologists interested in the migration of radioactive wastes. The theoretical basis for estimating this velocity can be derived by one of two approaches. Eagleson (1970) has considered, as a starting point, the equations of motion for the laminar flow of a fluid through a porous medium where the pores are

represented by a bundle of parallel, capillary tubes of equal diameter (Fig. 4). For such a conceptual model Eagleson showed that the average pore water velocity, V_ℓ, in similar pores (Fig. 8) is given by the Dupuit-Forcheimer equation (Bear, 1972, p. 23)

$$V_\ell = q_\ell/n = \frac{-K_\ell \left(\frac{d\phi}{d\ell}\right)}{n}$$

(9)

Furthermore, it has been shown that this equation is valid for any "straight, capillaric" porous medium model provided that the cross-sectional area of all the pores is equal (Guin, Kessler and Greenkorn, 1971). The second approach, that of Bear (1972, pp. 22-24), is not quite so restrictive, since in obtaining Equation 9 it is assumed that the porosity across a representative elemental volume of the porous medium may vary "appreciably."
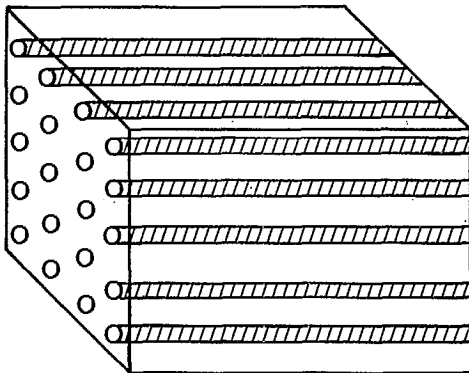
Figure 4. Straight, capillaric model (after Scheidegger, 1960).
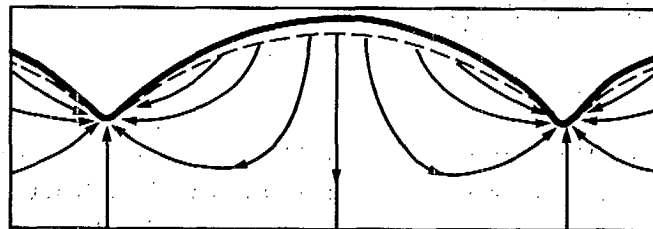
Figure 5. Groundwater flow system in homogeneous isotropic materials showing recharge and discharge areas (after Hubbert, 1940).

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Following the definition of Freeze (1969a), a *groundwater flow system* is a
"three-dimensional, closed system which contains the entire flow paths followed by all
the water recharging the basin." Figure 5 shows such a system for a homogeneous and
isotropic porous medium. Recharge areas are considered to be those parts of the flow
system in which groundwater flow is away from the water table, whereas discharge
areas are those parts in which groundwater flow is toward the water table. Areas
between recharge and discharge zones are called transition zones. The water table is
the upper boundary of the saturated zone along which the gauge pressure equals the
local atmospheric pressure, so that $p = 0$ in Equation 3 and $\psi = 0$ in Equation 4. The
unsaturated zone above the water table is that region in which $\psi < 0$, whereas beneath
the water table, $\psi > 0$.
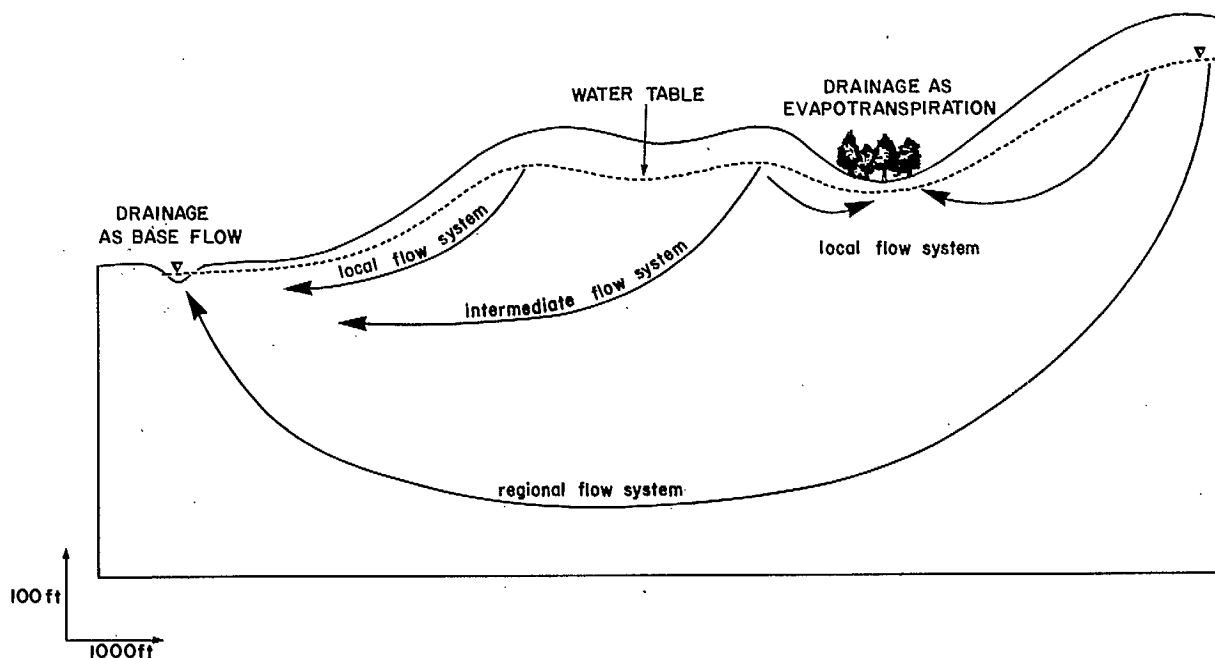
Figure 6. Regional, intermediate and local flow systems.

Hubbert's (1940) model of the flow system (Fig. 5) is a very simplified
case. More complex cases have been analyzed by Toth (1962, 1963) and Freeze (1969a,
1971). Toth (1963) defined three types of flow systems, which are shown in Figure 6.
Local groundwater flow systems are those in which the topographic highs that form the
recharge areas are adjacent to the topographic lows that form the discharge areas.
Intermediate systems have recharge and discharge areas that are not necessarily ad-
jacent to one another. The regional flow system has its recharge area in the topo-
graphically highest point in the basin and its discharge area in the lowest point,
the stream draining the basin.

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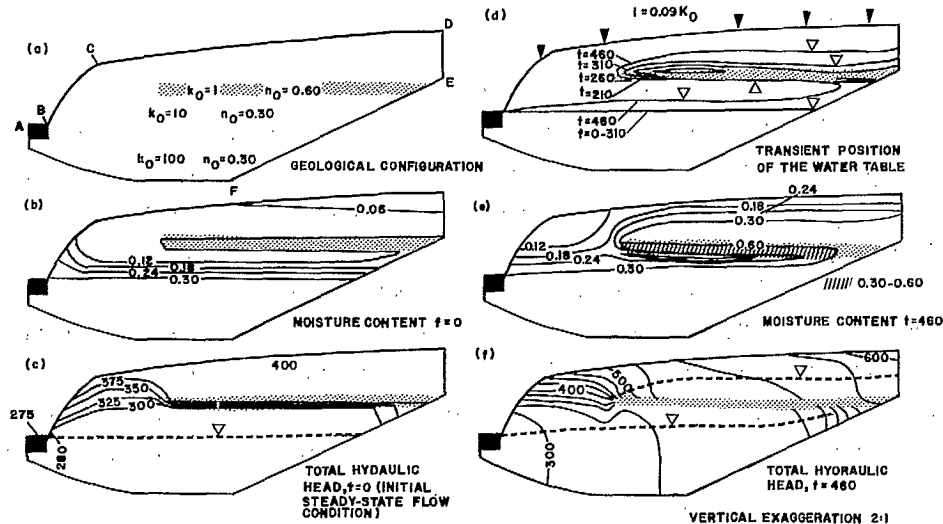
Figure 7. The formation of a perched water table (after Freeze, 1971).

Most radioactive waste management sites and sanitary landfills are located above the water table partly because of the relative ease of construction and operation and partly because any contaminants that might escape would only move at a fraction of the velocity with which they would move if the soil was saturated, as is made evident from consideration of Figure 1. Potential problems might occur if because of the hydrogeology of the waste management site, a temporary water table was created by transient hydrological conditions above the permanent water table. The build-up of these so-called *perched water tables* has been studied by mathematical simulation by Freeze (1971). Figure 7(a) shows a hypothetical cross section with three stratigraphic units, the most significant of which is a clay lens with a hydraulic conductivity a tenth of the surrounding sand and a porosity which is twice as large as the sand. Figure 7(b) shows the moisture content, θ, of the cross section at time $t = 0$; the line $\theta = 0.30$ represents the water table. Figure 7(c) indicates the distribution of the total hydraulic head, ϕ, at time $t = 0$. Figure 7(d) shows the transient position of the water table under the influence of an infiltration rate of 9% of the hydraulic conductivity. After 210 h the perched water table is a small lens above the clay, and by 460 h it has become continuous with the permanent water table. Sections (e) and (f) of Figure 7 show the distribution of θ and ϕ at this point in time. Therefore, the essential condition for the creation of a perched water table in Freeze's model is the occurrence of a low-permeability unit separating two high-permeability units. An important side effect of the creation of the perched water table in Figure 7 is that
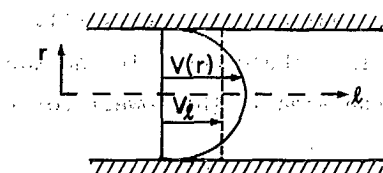
Figure 8. Lumped and distributed pore velocities.

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the groundwater flow pattern is altered, so that increased groundwater flow occurs around the clay lens rather than through it [cf. sections (c) and (f) of Fig. 7].

Fracture Flow

An additional complication that hydrogeologists face at prospective shallow waste management sites in Canada is the probability of fracture systems in both the glacial till cover and the underlying bedrock. Fractures in fine-grained glacial till are ubiquitous in the Interior Plains Region (Grisak *et al.*, 1976) and are likely present in tills in most other parts of Canada as well. Bedrock fracture systems are generally accepted as inherent features of near-surface consolidated or semiconsolidated bedrock. The classical concepts described in the previous section for groundwater flow through porous media are generally inadequate to describe the case of flow through fractured or jointed material. Snow (1968, 1969) has presented general equations for determining the fracture porosity and intrinsic directional permeability of fractured media which require detailed field measurement of fracture data. The data analysis incorporates several simplifying assumptions concerning the geometry and spacing of the fracture sets; nevertheless, it does provide one of several possible frameworks on which to base further investigation of contaminant transport in fractured media.

The intrinsic directional fracture permeability, k (see Equation 1), which has units of L^2, can be calculated for a fractured medium from the equation

$$k = \frac{2}{3} \frac{1}{\Delta} \frac{\Sigma b^3}{N} \tag{10}$$

where Δ is the average fracture spacing, b is the half-aperture width and N is the total number of fractures in the unit measured area. Equation 10 permits apertures to differ from conduit to conduit, but requires that each conduit be uniform in size and direction. If the fracture spacing, Δ, is not known but the fracture half-aperture and the number of fractures in a discharging unit width, W, can be estimated, Equation 11 can be used to calculate intrinsic directional permeability (Snow, 1969)

$$k = \frac{2}{3} \frac{1}{W} \Sigma b^3 \tag{11}$$

Equations 10 and 11 have been used recently (Grisak *et al.*, 1976) to calculate the permeability of fractured tills at several sites in the Interior Plains where detailed fracture measurements have been obtained. The results, although variable, generally agreed with bulk conductivity estimates from other methods. The main significance of these and other conductivity estimates (Freeze, 1969*b*; Sloan, 1972; Clister, 1973) is that they are generally much larger (about two orders of magnitude) than intergranular conductivities obtained from laboratory test data on small samples.

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For discontinuous fractures that are not uniform with variable and relatively rough surfaces equations for calculating intrinsic directional permeability are given by Louis (1974). The permeability tensor of an equivalent porous medium (with a relatively large representative elementary volume, REV) can be calculated from equations given by Bray in Maini and Hocking (1977).

The *effective porosity*, defined as the amount of interconnected pore space available for fluid transmission, is obviously very important when consideration is given to the transport of contaminants through fractured media. The fractures represent the effective zones of groundwater flow, and the transport characteristics of fractured media depend on the physical and chemical properties of the fracture apertures and walls. The fracture or effective porosity of a regular, cubic system of similar fractures can be calculated (Snow, 1968) by

$$n_f = 5.45 \left(\frac{k}{\Delta^2}\right)^{1/3} \tag{12}$$

where n_f is the fracture porosity and k and Δ are the intrinsic permeability and individual fracture spacing, respectively. The effective porosity of a fractured till in southeastern Manitoba has been obtained from Equation 12 and has been shown to compare favourably with a porosity estimate obtained by applying the Dupuit-Forcheimer equation (Equation 9) to the results of a tritium tracer experiment on the same till (Grisak, 1975). The proportionality constant (see Equation 29) has been assumed as unity in this case.

The most reliable estimates of groundwater flow velocities are, of course, from direct field tracer tests rather than from porosity estimates and the Dupuit-Forcheimer relation. The uncertainties involved in instrumentation and tracer monitoring in fractured media, however, introduce an additional complication. If fractured tills or other fractured media are to be considered for prospective radioactive waste management sites, the characteristics of groundwater flow and contaminant transport in fractured or jointed material must be thoroughly evaluated. At the present time these are areas of relative uncertainty. The design and implementation of investigation and monitoring techniques will likely have to be undertaken in a manner much different from that for sands or gravels or other deposits through which intergranular flow occurs.

SOLUTE TRANSPORT IN HOMOGENEOUS, UNIFORM, ISOTROPIC POROUS MEDIA

Basic Concepts

The solute transport processes considered in this section are those that are based on a representation of fluid flow in porous media in which all fluid particles move

at identical velocities through the porous medium, as is shown by V_ℓ in Figure 8. This conceptual model permits the expression of mass transport in porous media by exact mathematical methods, i.e., by a partial differential equation based on Fick's laws of diffusion. This theory is then applied to soil columns of uniform grain size and isotropic permeability.

The driving force of this solute transport is the force due to hydraulic gradients existing within the porous medium and to molecular diffusion. Therefore the flow through the porous medium can be approximated by Darcy's law in a macroscopic sense. This Darcy or convective flow makes no allowance for variations in the fluid velocity within the pore, which exist because of the drag effects of the pore wall on the fluid. Figure 8 shows the average pore velocity, V_ℓ, as predicted by the Dupuit-Forcheimer relation and the true velocity distribution, $V(r)$, which exists because of the drag effects. It is because of this difference that a fictitious process, the *dispersion* process, must be included in the theory developed in the next section so that the results from the theory are in accord with the results observed in experiments (Ogata, 1970). Flow through porous media as described by convective flow, which makes no compensation for the distribution of fluid velocities within the pore, is referred to as *piston*-type flow, or plug flow.

At this point it is necessary to state precisely what is meant by the terms dispersion; diffusion; and a homogeneous, uniform, isotropic porous medium. The following definitions by Simpson (1962) will be used for *diffusion* and *dispersion*:

> *Diffusion*: The spreading of particles, molecules, atoms or ions into a vacuum, a fluid, or a fluid-filled [or a fluid- and gas-filled] porous medium, in a direction tending to equalize concentrations in all parts of the system; it is understood to occur as a result of the thermal kinetic energy of the particles, including that of the particles of the host fluid, but in the absence of fluid convection.
> *Dispersion*: The same as above, but in the presence of fluid convection.

For the purposes of this report, a homogeneous, uniform, isotropic porous medium may be considered to be any soil, geologic stratum or porous medium created in the laboratory in which the mean grain size is everywhere the same, and thus standard deviation in grain size is zero. The medium is therefore *uniform*. This also implies that we are considering only one *homogeneous* soil or geologic unit, and that the permeability of this unit is independent of direction, i.e., the medium is *isotropic*.

A final concept that is useful in explaining transport processes in porous media is that of a *mixing cell*, which is a region of constant volume through which a fluid may flow and within which there is always instantaneous and complete mixing. In flow through porous media the achievement of complete mixing is dependent upon the fluid moving slowly enough through the pores so that there is sufficient time for

molecular diffusion to equalize the concentrations within the pores before the fluid exits from the cell, which can be composed of one or many pores. The application of mixing-cell models to the understanding of the transport of environmental tracers has been discussed by Simpson, Kisiel and Duckstein (1975) and Bear (1972).

Theory

The theoretical development of the *dispersion-convection equation* in this section follows that of Ogata (1970) and makes the founding assumption that Fick's laws of diffusion apply to the problems of solute transport in porous media.

The derivation of the dispersion-convection equation describing hydrodynamic dispersion of a solute in a solvent of similar density and viscosity is based on a mass balance analysis of transport by convection and dispersion through a cubic element in space (Fig. 9). For the flow parallel to the x-axis only, the two terms can be written

$$\text{Convective transport} = nV_x C_A dydz$$

$$\text{Dispersive transport} = -nD'_x \frac{\partial C_A}{\partial x} dydz$$

where V_x is the average pore water velocity in the x direction, C_A is the concentration of the solute A, dydz is the elemental cross-sectional area of the cubic element, and
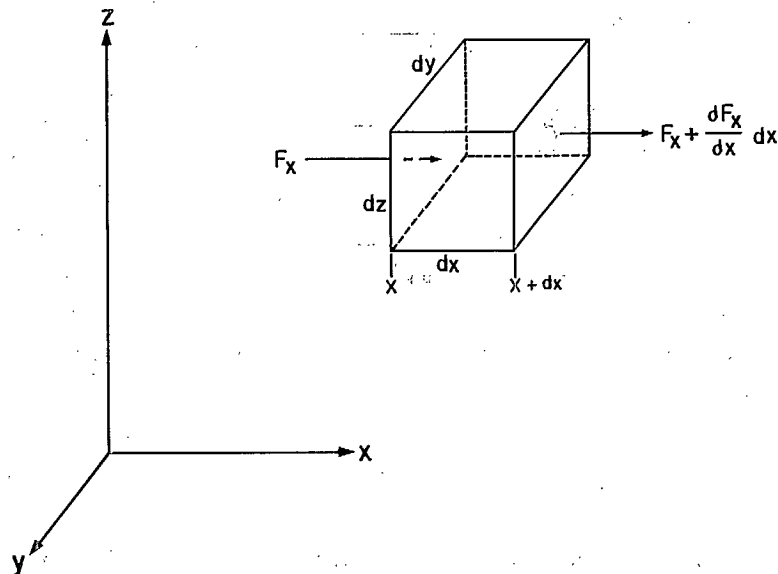
Figure 9. Mass balance in a cubic element in space.

D'_x, *the coefficient of hydrodynamic dispersion* in the x direction, is the measure of the rate at which the concentration gradient $\frac{\partial C_A}{\partial x}$ is dissipated. The negative sign is used to indicate that the direction of flux is positive in the direction of decreasing concentration. The units of the two transport terms are in solute mass per unit time.

If it is assumed that these two components are linearly additive, and if F_x represents the mass flux per unit cross-sectional area transported in the x direction in unit time, then

$$F_x = nV_x C_A - nD'_x \frac{\partial C}{\partial x} A \tag{13}$$

If the flux of solute A is affected not only by convection and dispersion but also by geochemical reaction (i.e., adsorption or precipitation) within the unit cube, then the mass balance equation sought must express the following condition:

| Net change of solute flux between inflow and outflow | = | Rate of change of solute concentration inside of cubic elements | + | Rate of change of solute due to geochemical reactions | (14) |

The two rate terms on the right-hand side of Equation 14 are given by $\partial C_A/\partial t$ and $\partial q_A/\partial t$, where q_A is the amount of solute A *adsorbed or precipitated* per unit mass of the porous medium. Equation 14 can now be written

$$(dy\ dz)\ \{(-n\ D'_x\ \frac{\partial C_A}{\partial x} + n\ V_x\ C_A)_x - (-n\ D'_x\ \frac{\partial C_A}{\partial x} + n\ V_x\ C_A)_{x+dx}\}$$

$$= (dx\ dy\ dz\ n)\ \frac{\partial C_A}{\partial t} + (dx\ dy\ dz\ \rho_b)\ \frac{\partial q_A}{\partial t} \tag{15}$$

where n is the porosity and ρ_b is the bulk density (mass/volume). The subscripts x and x+dx refer to the flux into the cubic element at plane x and out of the element at plane x+dx. By dividing both sides by (dxdydzn) we obtain

$$\frac{(D'_x\ \frac{\partial C_A}{\partial x} - V_x\ C_A)_{x+dx} - (D'_x\ \frac{\partial C_A}{\partial x} - V_x\ C_A)_x}{dx} = \frac{\partial C_A}{\partial t} + \frac{\rho_b}{n}\ \frac{\partial q_A}{\partial t} \tag{16}$$

which is the partial differential equation

$$\frac{\partial}{\partial x}\ (D'_x\ \frac{\partial C_A}{\partial x} - V_x\ C_A) = \frac{\partial C_A}{\partial t} + \frac{\rho_b}{n}\ \frac{\partial q_A}{\partial t} \tag{17}$$

If we assume that D_x' is independent of position in the x direction, and that the average pore water velocity, V_x, is constant, we can write

$$D_x' \frac{\partial^2 C_A}{\partial x^2} - V_x \frac{\partial C_A}{\partial x} = \frac{\partial C_A}{\partial t} + \frac{\rho_b}{n} \frac{\partial q_A}{\partial t} \tag{18}$$

Rearranging terms,

$$\frac{\partial C_A}{\partial t} = D_x' \frac{\partial^2 C_A}{\partial x^2} - V_x \frac{\partial C_A}{\partial x} - \frac{\rho_b}{n} \frac{\partial q_A}{\partial t} \tag{19}$$

In the rest of this Chapter we are concerned only with describing the time rate of change of solute A which will be assumed to be a conservative, i.e., a nonadsorbable and nonprecipitable tracer. The cases for which solute A undergoes adsorption or precipitation are considered in Chapter 3. Therefore dropping, for the time being, subscript A, Equation 19 can be rewritten

$$\frac{\partial C}{\partial t} = D_x' \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} \tag{20}$$

For the initial conditions $x < 0$, $C = C_0$ and $x \geq 0$, $C = 0$, the solution of Equation 20 is (Bear, 1972, p. 585)

$$C/C_0 = \frac{1}{2} \left(1 \pm \text{erf} \left(\frac{x - V_x t}{2\sqrt{D_x' t}} \right) \right) \tag{21}$$

where the sign is positive for $(x - V_x t < 0)$ and negative for $(x + V_x t > 0)$. For the case of interest considered here, i.e., the concentration downstream from the tracer reservoir where $C = C_0$, the sign is negative. Bear has noted that the point $C/C_0 = 0.5$ moves with the average pore water velocity of the fluid.

It can be shown (Bear, *op. cit.*) that for flow through a capillary tube, the length of the *transition zone* along which C varies from $0.9C_0$ to $0.1C_0$ is given by

$$L = 0.52 r V_x (t/D_d)^{\frac{1}{2}} \tag{22}$$

where r is the radius of the straight capillary tube and D_d is the *coefficient of molecular diffusion*. Therefore the transition zone increases with the radius of the pore and the average pore water velocity and decreases with increasing molecular diffusivity. This latter dependency can be explained by considering the functions of the mixing cell in which molecular diffusion works to cause the mixing of the fluid and the dissipation

of concentration gradients built up by the variation of fluid velocity within the pores (Fig. 8). For flow through natural porous media the term 0.52r would necessarily be replaced by a proportionality constant reflecting the properties of the porous medium being considered.

An interpretation of the relative concentration of a tracer in a soil column, as defined by Equation 21, and of the length of the transition zone, as defined by Equation 22, may be obtained by the use of *breakthrough curves*. Figure 10 is a plot of the relative concentration of a tracer (C/C_0) against the number of pore volumes of the porous medium that have been displaced by passing the tracer through it. If the tracer is moved by piston flow its breakthrough curve would be that shown by the broken, vertical line at the abscissa value of unity. If dispersion owing to molecular diffusion is negligible and if the velocities in all pores are approximately equal, the breakthrough curve for the tracer would be similar to that for the glass beads in Figure 10. In this ideal case, $C/C_0 = 0.5$ when the number of pore volumes displaced in the sample is unity. The breakthrough curves for the Yolo loam and Oakley sand are displaced to the left of the breakthrough curve for the glass beads. This is due to a phenomenon called *holdback* by Danckwerts (1953), which is defined as the amount of the original host fluid remaining in the column after one pore volume of displacing fluid has entered. It is a useful measure of dispersive mixing. In Figure 10, the area between the breakthrough curve and the vertical line at which one pore volume has been displaced is a relative measure of the holdback (Biggar and Nielsen, 1960). Consequently, it can be seen that the relatively fine-grained loam has the greatest holdback and that the glass beads have the least.
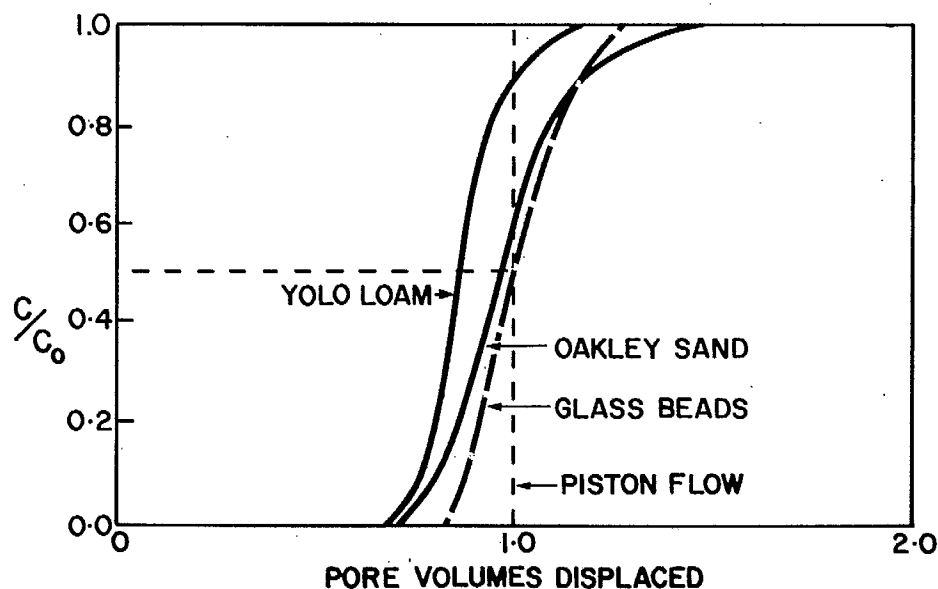
Figure 10. Breakthrough curves for Yolo loam, Oakley sand and glass beads under saturated conditions. Average flow velocities were 1.89 cm/h, 0.30 cm/h and 1.77 cm/h, respectively (after Biggar and Nielsen, 1960).

Figure 11 shows three breakthrough curves for Oakley sand under varying moisture contents (Biggar and Nielsen, 1960). As desaturation occurs the larger, more permeable flow channels are eliminated and there is an increase in the volume of water within the sample that does not readily move. These processes have two significant results. First, a greater number of pore volumes are needed under unsaturated conditions to reach the maximum relative concentration of $C/C_0 = 1.0$. Secondly, the stagnant water zones act as sinks for molecular diffusion which results in a greater holdback. Quite obviously a radioisotope moving through an unsaturated porous medium would undergo much greater dispersion than if the porous medium was saturated. For the Oakley sand under consideration in Figure 11, twice as many pore volumes of water are required to make $C/C_0 = 1.0$ for the unsaturated condition in which $\theta = 0.27$ than for the saturated condition in which $\theta = 0.36$.
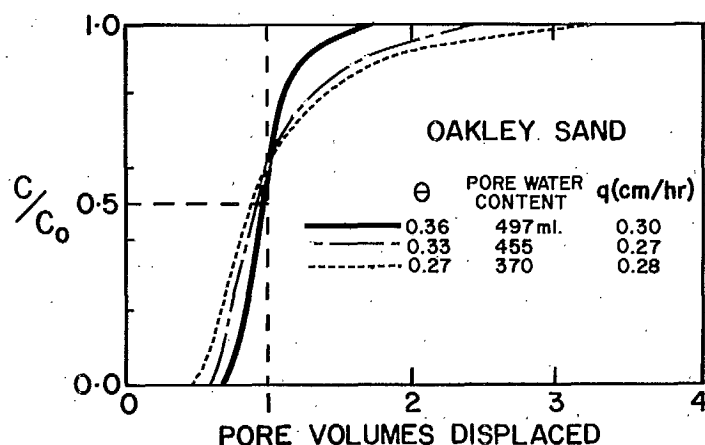
Figure 11. Breakthrough curves for Oakley sand expressed as pore volumes displaced (after Biggar and Nielsen, 1960).

The Nature of the Dispersion Coefficient

It is generally acknowledged that the form of the coefficient of hydrodynamic dispersion, D', used in the last section is (Bear, 1972)

$$D' = D + D_d^* \tag{23}$$

where D is the *coefficient of mechanical dispersion* due to convective mixing processes and D_d^* is an *apparent coefficient of molecular diffusion* in a porous medium. Because free molecular diffusion is hindered in a porous medium by the length and *tortuosity* of the flow paths, $D_d^* \neq D_d$ the coefficient of molecular diffusion. Therefore, the coefficient of hydrodynamic dispersion is a function of the average pore water velocity, the actual molecular diffusion and the tortuosity of the porous medium, which can

be defined as $T^* = (L/L_e)^2$ where L is the length of a straight line connecting the two ends of a tortuous flow path of length L_e.

A more useful representation of the coefficient of hydrodynamic dispersion is that given by Fried and Combarnous (1971) for longitudinal dispersion along the axis of a soil column

$$D_L'/D_d = D_d^*/D_d + \alpha(Pe)^\lambda \tag{24}$$

where D_L' is the coefficient of *longitudinal* hydrodynamic dispersion, D_d^*/D_d is called the tortuosity factor, and α is a dimensionless, empirical constant characteristic of the porous medium for a given λ, which is a dimensionless, empirical exponent characterizing the mixing regime. The dynamic Peclet number, Pe, is defined by:

$$Pe = dV_L/D_d \tag{25}$$

where d is the mean grain size and V_L is the average pore velocity along the column. The Peclet number defines the ratio of the convective to diffusive transport terms (Bear, 1972, p. 600).

A plot of the variables involved in Equation 24 is shown in Figure 12 taken from Pfannkuch (1972). The two curves shown relate the dispersive and the convective terms involved in the migration of a tracer through sandstone cores and through unconsolidated porous materials. It is evident that dispersion in the consolidated or indurated rocks is considerably greater than in the unconsolidated materials, and also that as a first approximation, the dispersion is proportional to the first power of the fluid velocity.

Bear (1972) has outlined the effects of the various dispersive forces operating in the range of $10^{-2} < Pe < 10^3$. For Pe < 0.4, molecular diffusion is the predominant dispersive force with $\lambda = 0.0$. Between 0.4 and 5, molecular diffusion and mechanical dispersion are of the same magnitude. For Pe > 5, mechanical dispersion is predominant, but its effects are reduced by transversal molecular diffusion which reduces longitudinal dispersion by dissipating the concentration gradients within mixing cells. For this range of Peclet numbers the values for the coefficients in Equation 24 are $\alpha = 0.5$, $\lambda = 1.0-1.2$ and $D_d^*/D_d = 0.67$. Pfannkuch (1972) has pointed out that dispersion in both the unconsolidated and the consolidated porous media shown in Figure 12 is controlled by the same process, namely mechanical dispersion with some influence from molecular diffusion.
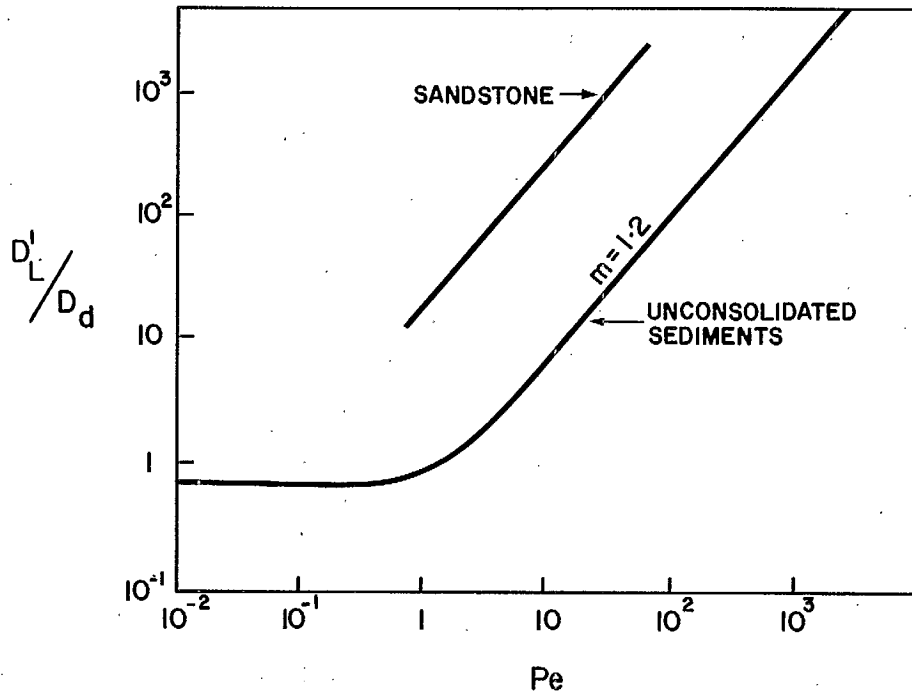
Figure 12.   Dimensionless dispersion in sandstone cores and unconsolidated
porous material as a function of the dynamic Peclet number
(after Pfannkuch, 1972).

A second approach to the representation of the coefficient of hydrodynamic
dispersion disregards the role of molecular diffusion, which is assumed to have a
negligible effect in most field situations. This second approach has found favour
among mathematical modellers who use the following identity which is strictly true only
for an isotropic porous medium (Bear, 1972, pp. 606 and 615)

$$D' = aV \qquad\qquad\qquad (26)$$

where $a = (n^2 \bar{L}/k^2) \, VarB*T*$

In Equation 26, the parameter a is called the dispersivity (dimension: L), V is the
average pore water velocity, n is the porosity, $\bar{L}$ is the average length of a channel
of an idealized porous medium, and k is the intrinsic permeability. The term $VarB*T*$
is the variance of the average directional conductance of the idealized porous medium,
in which B* is the average medium conductance (dimension: L^2) and T* is the tortuosity
(mean $B*T* = k/n$). For dispersion in the direction parallel to the fluid flow,
Equation 23 is often written $D'_L = a_L V$, where a_L is called the longitudinal dispersivity.
Similarly, the coefficient of transverse hydrodynamic dispersion is written as $D'_T = a_T V$.
By this method of representing D' the dispersivity, a, may be considered as a charac-
teristic length of the porous medium with special reference to the dispersion process.

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The Effect of Anisotropy

In the first section of this Chapter, it was stated that permeability is a vector. This is not strictly true. Permeability, hydraulic conductivity and dispersion coefficients are actually all tensors, which are mathematical functions capable (when acting on a vector) of changing its magnitude and direction (Skibitzke, 1964). Tensors describe the directionally dependent physical properties of a system and allow the conversion of these properties from one coordinate system to another.

The most important effects of anisotropy for the hydrogeologist interested in the movement of contaminants in the subsurface are that (1) it complicates the already difficult field estimation of horizontal hydraulic conductivity and (2) it causes groundwater to move in a direction different from that of the hydraulic gradient. The first factor is of indirect concern here, but the second is central to the problem of the prediction of radioisotope movement in the subsurface.
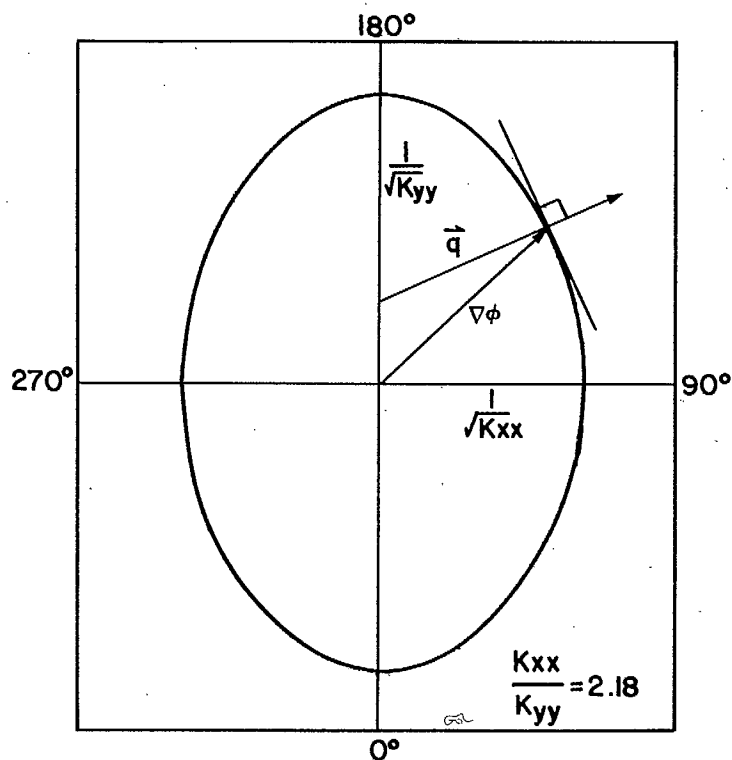
Figure 13. Graphical determination of the direction of the Darcy velocity or flux vector (q) for a given hydraulic gradient ($\nabla\phi$) (after Liakopoulos, 1965).

The methods by which the direction of fluid flow in a two-dimensional flow field are estimated have been outlined by Liakopoulos (1965) for the case in which the hydraulic conductivity is a symmetric tensor, i.e., when the average hydraulic conductivity of a series connection of pores is the same in both directions. Figure 13 shows the graphical determination of the direction of the seepage flux, $\vec{q}$, for a given hydraulic gradient ($\nabla\phi$) in a sandstone core having a symmetric hydraulic conductivity tensor in which $K_{xx}/K_{yy} = 2.18$.

The Effect of Nonuniformity

The effect of *nonuniformity*, or variation in particle sizes, on the hydraulic conductivity of sands has recently been investigated by Lovas (1963), Masch and Denny (1966), Denson, Shindala and Fenn (1968), and by Raimondi, Gardner and Petrick in some unpublished work that is frequently quoted in the literature, e.g., Perkins and Johnston (1963).

Perkins and Johnston (1963) pointed out that the size of the average pore space of a nonuniform sand is dictated by a grain size diameter smaller than the median grain size diameter. Figure 14 shows the grain size distributions for three mixtures of glass beads of varying nonuniformity but with essentially equal permeabilities. For all three packs, the value of the grain size parameter d_{10} is identical, this parameter being defined for any pack by stating that 10% of the pack material is equal to or smaller than d_{10} in diameter. Therefore, since the three glass bead mixtures only have equal permeabilities and this particular grain size parameter in common, the d_{10} value is known as the effective grain size diameter with respect to the permeability of the pack.
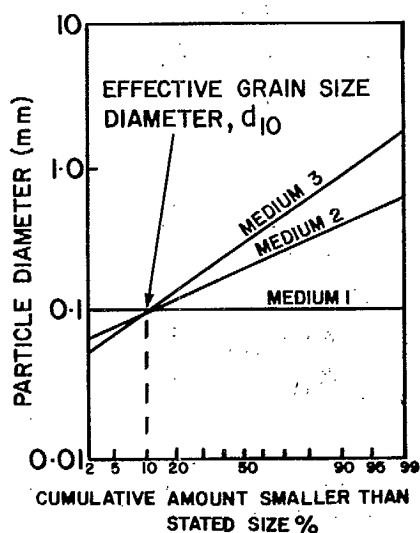
Figure 14. Grain size distribution for three mixtures of glass beads, all having approximately the same permeability (after the unpublished work of Raimondi, Gardner and Petrick; graph from Perkins and Johnston, 1963).

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Masch and Denny (1966) have developed a procedure by which the hydraulic conductivity of a sand may be estimated from its grain size distribution. They expressed the grain size using Krumbein's phi units where phi = $\log_2 d$ where d is the grain size diameter. As a measure of the distribution of the grain sizes, i.e., their statistical dispersion, they used the inclusive standard deviation

$$\sigma_1 = \frac{phi(84) - phi(16)}{4} + \frac{phi(95) - phi(5)}{6.6} \tag{27}$$

where phi(84) is the 84% grain size diameter expressed in phi units. Knowing d_{50} and σ_1 from grain size analyses, the saturated hydraulic conductivity can be calculated from Figure 15. The significance of these diagrams is that at standard deviations approaching 2, the hydraulic conductivity becomes almost independent of the median grain size diameter.
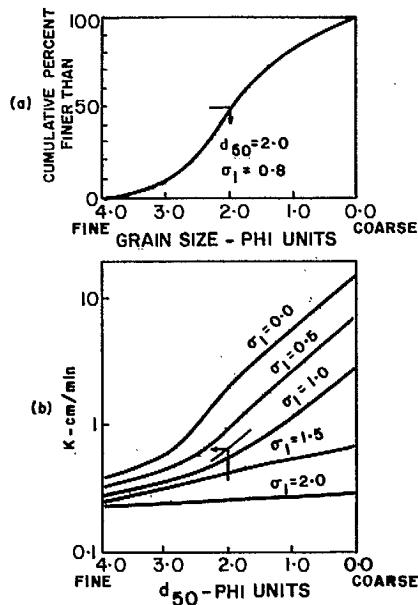
Figure 15. Determination of saturated hydraulic conductivity from grain size distribution curves for unconsolidated sands (after Masch and Denny, 1966; Freeze, 1972*b*).

The work of Denson, Shindala and Fenn (1968) was directed toward examining the effect of dispersed clay particles on the hydraulic conductivity in otherwise clean sands. The sand they used had d_{50} = 0.25 mm and an exclusive standard deviation of 0.18 mm. They showed that if 1% by weight of kaolinite (nonswelling clay) or of montmorillonite (swelling clay) was dispersed throughout the sand there would be a 24% loss in hydraulic conductivity for the sample with kaolinite and an 82% loss for the sample with montmorillonite. Similarly, Lovas (1963) has shown that the hydraulic conductivity of an otherwise clean and well-sorted sand may be reduced by two orders of magnitude when 2% by weight of illite is dispersed throughout the sand and by four orders of magnitude when 2% by weight of montmorillonite is dispersed.

The effect of nonuniformity on dispersion processes has been examined in the works of Orlob and Radhakrishna (1958), Harleman, Mehlhorn and Rumer (1963) and Greenkorn (1970).

Figure 16, from Orlob and Radhakrishna (1958), shows the effect that varying nonuniformity has on dispersion. The nonuniformity is measured by use of Hazen's effective grain size coefficient (Bear, 1972)

$$C_u = d_{60}/d_{10} \tag{28}$$

where the definition of d_{60} is analogous to that of d_{10}.
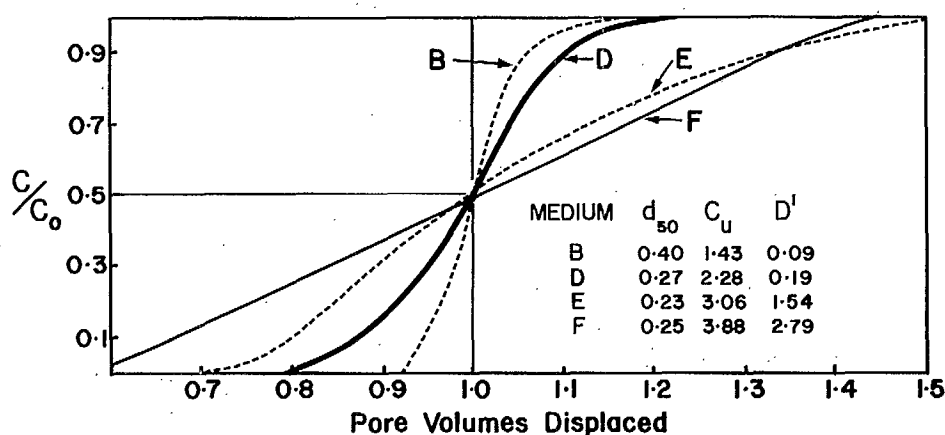
Figure 16. The effect of nonuniformity on dispersion in porous media (after Orlob and Radhakrishna, 1958).

A uniform porous medium has the limiting value of $C_u = 1.0$. The table in Figure 16 shows the direct relationship between C_u and D', i.e., between the nonuniformity and the magnitude of the dispersion.

The studies of Harleman, Mehlhorn and Rumer (1963) and Greenkorn (1970) have been directed toward determining the parameters D_L' and λ in Equation 24. Harleman and his colleagues (1963) showed that λ approaches unity for highly nonuniform porous media. Greenkorn (1970) used the concept of the effective grain size diameter, d_{10}, as shown in Figure 14, to study the relationship between D_L' and V_L, the average pore water velocity in a column, for three mixtures of glass beads with varying nonuniformity but equal permeability. His results are similar to those of Orlob and Radhakrishna (1958) in that he showed that D_L' increased with nonuniformity. Furthermore, Greenkorn's (1970) experimental data indicated that the exponent λ varied between 0.99 and 1.48.

In summary, the difference between the flow of contaminants in uniform and nonuniform porous media of similar median grain size diameter is that in the

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nonuniform porous media the contaminant undergoes greater dispersion as a result of the nonuniformity.

The Effect of Heterogeneity

For the purposes of this report, it is understood that "if a porous medium is *heterogeneous* with respect to some property (e.g., permeability), then that property is functionally dependent on the spatial location" (Nelson, 1966). The main concern of this section, however, is the presence of a discrete set of soil or geologic units which make up a particular flow system. Consequently, the flow system shown in Figure 5, as it is defined, would not constitute a heterogeneous porous medium, whereas that shown in Figure 7 would.

In an analysis of flow in partially saturated heterogeneous porous media, Nelson (1966) developed the following expression for the Darcy velocity or seepage flux vector:

$$\vec{q} = \vec{V}\sigma_N ns \tag{29}$$

where σ_N is a scalar pore water velocity conversion term and the other variables are as previously defined. Nelson (1966) explained that the term σ_N as defined by Equation 29

> is introduced to avoid making the unsubstantiated assumption
> that the traditionally defined seepage velocity is the appro-
> priate reference velocity for hydrodynamic dispersion. If
> the traditional seepage velocity is found to be the valid basis
> for subsequent dispersion analysis, then $[\sigma_N]$ simply reduces
> to unity.

Nelson, himself, did not give any experimentally determined values for σ_N; the data of Ellis, Kevi and Wiebenga (1968), however, can be used to estimate values of $0.98 \leq \sigma_N \leq 1.18$ for the almost uniform, homogeneous sands they used. To our knowledge there have been no attempts to determine σ_N for heterogeneous and nonuniform porous media.

The analysis of dispersion processes in heterogeneous porous media has been undertaken in the laboratory qualitatively by Skibitzke and Robinson (1963) and quantitatively by Greenkorn (1970), and has recently been reviewed by Cherry, Gillham and Pickens (1975) and Gillham, Cherry and Pickens (1975).

Skibitzke and Robinson (1963) were concerned with the divergence of stream lines at facies boundaries (i.e., interfaces between strata). They constructed small

sandstone models by cementing sand grains together with epoxy resin. Sinuous high-permeability units were placed within these models (Fig. 17). They concluded that heterogeneity is the dominant dispersive factor, all others being insignificant.

Figure 17. Dispersion of dyes in an artificial sandstone model with heterogeneity (after Skibitzke and Robinson, 1963).

The process witnessed by Skibitzke and Robinson is due to flow-line refraction described by Domenico (1972) as "merely the bending of flow lines in such a way that fluid mass is conserved when water flows across a boundary between strata of different permeability." In the flow system shown in Figure 18, the hydraulic conductivity ratio

Figure 18. Flow-line refraction in an unconfined system of layered permeability contrasts (after Hubbert, 1940; Domenico, 1972).

Table 7. Porosities, Permeabilities and Hydraulic Conductivities of Porous Media Models Used by Greenkorn (1970)

Model	Bead size range (μm)	Porosity (%)	Permeability (darcy)	Hydraulic conductivity (cm/s x 10⁻⁵, 20°C)
1	590-840	34.0	120	118
2	250-350	34.0	36	35
3	105-149	34.3	5	4.9
4	44-62	36.5	0.5	0.49
1234	-	-	1.8	1.76
4321	-	-	1.8	1.76
2143	-	-	1.8	1.76
3412	-	-	-	-

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32

of the two units forming a facies change is equal to the ratio of the tangents of the angles that the flow lines make with the normal to the interface

$$\frac{K_1}{K_2} = \frac{\tan a_1}{\tan a_2} \text{ and } \frac{K_2}{K_3} = \frac{\tan a_2}{\tan a_3} \tag{30}$$

Greenkorn (1970) investigated the effects of heterogeneity on dispersion using glass bead models of porous media, the properties of which are outlined in Table 7. After the individual models were run separately, they were joined in series. Figure 19 shows the results of the individual and composite runs. Quite obviously dispersion is controlled by the highest permeability unit--model 1--since all the composite models cluster around it.

Recent studies of the migration of contaminant plumes using mathematical models have uncovered some rather anomalous results, the explanation of which perhaps lies in the heterogeneity of the flow system being simulated. In these models the dispersion process is represented by Equation 26 in which the coefficient a is some characteristic length associated with the mixing process. The value of a, the dispersivity for any given porous medium, is a matter of considerable uncertainty. If one considers that the values of a obtained by laboratory experiment should be approximately correct, then the values obtained by field experiment and mathematical simulation would be distinctly anomalous.

Typical laboratory values of a for sand columns [6 in. by 1.125 in. (152 mm by 29 mm) in Lucite cylinders] such as those of Greenkorn (1970), are of the order of 10^{-3} cm to 1 cm. According to Theis (1963), however, dispersivities obtained by field experiments may be two orders of magnitude greater than those determined in the laboratory. For example, Grove and Beetem (1971) analyzed the tritium breakthrough curve for a recharge-discharge well pair in a fractured, carbonate aquifer and obtained a value of a = 3800 cm!

This same difference of several orders of magnitude is also found to exist between the laboratory and computer simulation dispersivities. Examples of this include Bredehoeft and Pinder's (1973) analysis of the salt-water contamination of a coastal limestone aquifer for which a value of a = 6000 cm was obtained, and Robertson and Barraclough's (1973) analysis of chloride transport in basalt flows and inter-bedded sediments for which a value of a = 9000 cm was obtained. Yet in these computer simulation studies the dispersivity is merely a fitting parameter which is adjusted by a trial and error process in calibrating the model with the migration history of the contaminant plume. In this situation it is quite possible that the large dispersivity values are a reflection of the uncertainty in the value of the convective term, V, within the flow system rather than true dispersion (Gillham, Cherry and Pickens, 1975).

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Consequently, much of the mixing due to the convective term would be ascribed to the dispersive term.

To account for these anomalies we must consider the importance of the presence of discrete, heterogeneous units of relatively high hydraulic conductivity existing within a matrix of lower conductivity (Fig. 17). Skibitzke and Robinson (1963) showed
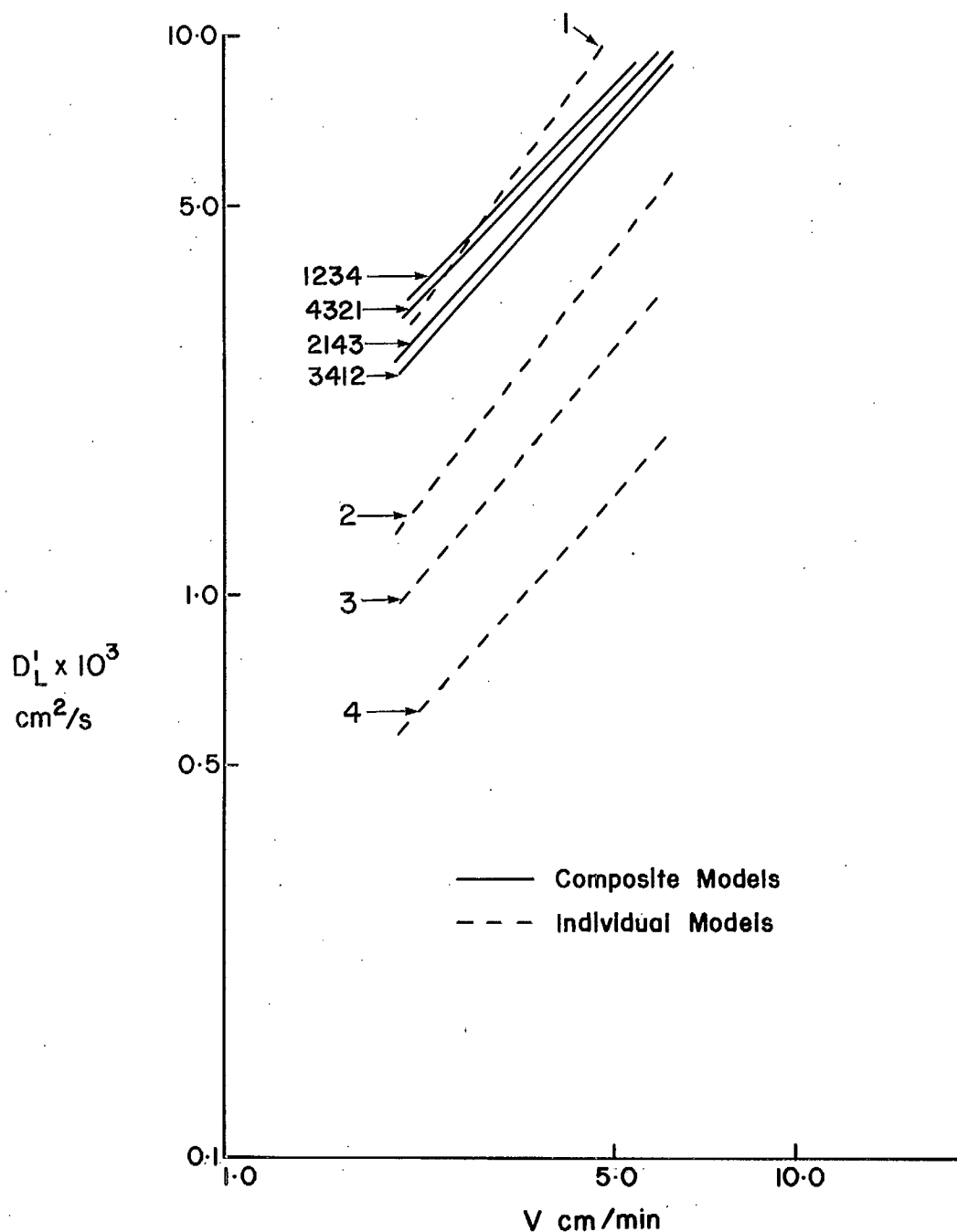
Figure 19.   Dispersion coefficient versus velocity for heterogeneous porous media (after Greenkorn, 1970).

that in such an environment the dispersion of tracer particles was produced by streamline divergence occurring where the high-conductivity heterogeneities pinch out and the fluid must necessarily spread out into the lower conductivity matrix. The effect of such streamline divergence is to increase the variability in the lengths of the possible flow paths available to tracer particles in their progress through the flow system. For example, a tracer particle moving along the top edge of the artificial sandstone model shown in Figure 17 would have a relatively direct flow path to the other end; on the other hand, a tracer particle moving through the centre of the model would be subject to a more circuitous flow path involving passage through both the low-conductivity matrix and the high-conductivity lenses. Therefore the inclusion of high-conductivity lenses in a matrix of relatively lower conductivity results in the increased variability of the flow path lengths of the particles moving through the flow system.

Mathematically this increase in the variability of the flow path lengths is equivalent to an increase in the variance of the tortuosity of the path lengths of the flow system. Since the dispersivity of a porous medium is a function of the variance of the tortuosity of the path lengths of that porous medium (see Equation 26), the observed dispersivity of the total flow system is very much larger than what would be determined by conducting a laboratory dispersivity test on any small part of it. Quite obviously it must be concluded that dispersivities must be measured by field tests if they are to have any validity.

An alternative explanation of the difference between laboratory and computer-simulated values of dispersivity is that since dispersion causes dilution, any dilution owing to improper sampling of the contaminant plume will imply a proportionately higher dispersivity than is the case (Pickens, Merritt and Cherry, 1977).

In summary, the situation faced by the hydrogeologist trying to estimate the rate and direction of movement of radioisotopes in the porous subsurface should they escape from waste management facilities is extremely complex. In general, the hydrogeologist is concerned with heterogeneous, nonuniform, anisotropic porous media. This means that the mean line of dispersion of the radioisotopes will not follow the hydraulic gradient, but will depart from it by an angle dependent on the anisotropic nature of the hydraulic conductivity. Also the dispersion of the radioisotope "slug" as it moves through the groundwater flow system will be primarily due to heterogeneous layers of relatively high hydraulic conductivity within the system. Since these heterogeneous layers may be only a few inches in thickness, it is necessary to conduct geological investigations of corresponding detail.

Geochemical Retardation Processes

INTRODUCTION

There is a pronounced difference between the observed velocities of ground-water and those of some of the ionic species which it transports. This difference is due to the retardation of these ions by either the solid phase of the porous medium through which the groundwater is travelling or the chemical reactions within the groundwater. Lieberman and Simpson (1960) have suggested that the term *relative ionic velocity* be defined as the ratio of the average velocity of the ionic species to the average velocity of the convecting groundwater. Consequently, ions that are considered to be conservative, i.e., nonretardable, tracers will have a relative ionic velocity of unity. Ionic species that are irreversibly removed from solution will have a relative ionic velocity of zero.

Two geochemical processes cause the retardation of ionic species in a porous medium. The process by which ions in solution are attracted to the surface of colloidal particles by chemical and electric forces is called *adsorption*. The second process effective in retarding a radionuclide in porous media is its *precipitation* as a part of an amorphous or crystalline solid. These two processes are the subject of the next two sections of this Chapter. Solute transport in the presence of retardation is then considered, and finally, the retardation mechanisms affecting the various "waste" readionuclides discussed in Chapter 1 (Table 4) are outlined.

ADSORPTION PROCESSES

Colloids

There is no general agreement on what particle-size range defines the colloidal state. Krauskopf (1967) states that the range from 10^{-3} mm to 10^{-6} mm is widely used. Since the upper limit of clay-sized particles is 2×10^{-3} mm (United States Department of Agriculture classification), most clay-sized particles fall within this range. A colloid may be defined as a particle that is large compared with a small molecule, but sufficiently small for interfacial forces as well as inertial forces to be significant in controlling the behaviour of the particle (Sennett and Olivier, 1965).

Because ions at the surfaces and edges of crystals cannot necessarily be electrostatically balanced by ions of opposite charge within the crystal or because of other factors to be considered in the next section, the surfaces and edges of crystals may attract ions of opposite charge in solution. Since the number of ions attracted in this manner is proportional to the number of exposed crystal sites that are electrostatically unbalanced, the propensity for this kind of adsorption increases with the surface area exposed. Figure 20 shows the exponential increase in surface area as the particle diameter is decreased from the silt-sized range to that of colloidal particles. It is because of this enormous chemically reactive surface area that colloidal particles are of such importance in geochemical processes such as adsorption. This does not, however, imply that silt-sized particles are unimportant in adsorption; Figure 20 simply suggests their relative unimportance in comparison with colloids.
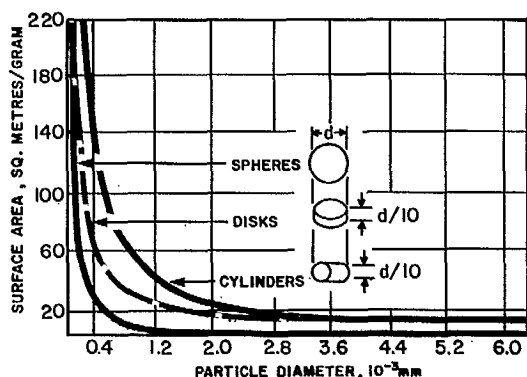
Figure 20. Dependency of surface area on particle size (after Sennett and Olivier, 1965).

During the geochemical weathering of rocks large concentrations of inorganic colloids are formed as weathering products. Fyfe (1974) has suggested that colloids are metastable products of weathering reactions which have a high negative free energy. Consider the example of a ferrous silicate of an igneous rock being weathered in an oxidizing environment:

$$Fe_2SiO_4 + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + Si(OH)_4 \qquad\qquad (31)$$
$$\text{solid} \quad\quad \text{solution}$$
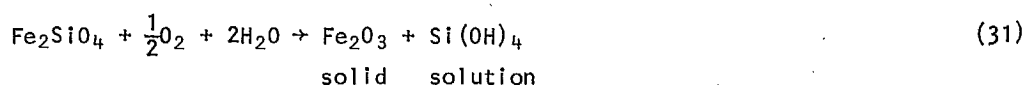
Fyfe pointed out that the high free energy involved in this reaction (-184×10^3 J/mol) is such that intermediate weathering products such as colloidal Fe_2O_3 are likely to be found in metastable equilibrium with a solution supersaturated with respect to crystalline Fe_2O_3. He concluded that the separation of colloids from this weathering environment (and therefore the transport of colloids in watersheds and groundwater flow systems) is made possible by the slow rates of crystal growth.

Electrical Double Layers

Van Olphen (1963) has suggested that the charges on the surface of a colloid and the subsequent creation of an *electrical double layer* originate in two ways:

Type 1.   Imperfections or substitutions within the crystal lattice of the particle can give it a net negative or positive lattice charge, which is compensated for by an accumulation of ions of opposite charge, *counterions*, in the solution immediately surrounding the particle, thereby maintaining electrical neutrality (Fig. 21). The charged surface is called the *fixed layer* and the counterions comprise a *mobile layer*. Together the two layers constitute an electrical double layer.

Type 2.   The surface charge may also be due to the preferential adsorption of specific ions onto the particle surface (Fig. 21). These specific ions, called *potential-determining ions*, are sorbed to the particle surface and comprise the fixed layer. The mobile layer is composed of counterions as in Type 1.
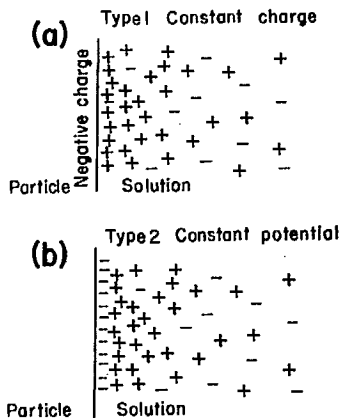
Figure 21.   Electrical double layers. Positive and negative ions are denoted by (+) and (-), respectively (after Berner, 1971; van Olphen, 1963).

Electrical double layers of Type 1 exist in such clay minerals as montmorillonite and vermiculite and are due to the isomorphous substitution of lower-valence for higher-valence cations (e.g., Al^{3+} for Si^{4+}) within the lattice framework. Double layers of this kind create the condition of a *surface of constant charge* that is independent of the chemistry of the surrounding solution (e.g., groundwater).

Electrical double layers of Type 2 are observed on clays, organic colloids, hydrous metal oxides and other inorganic colloids such as silica. The example of the unbalanced forces on the surfaces and edges of the crystal referred to in the previous section results in a Type 2 double layer, and the surfaces are known as "broken-bond" surfaces. Van Olphen (1963) has distinguished several types of adsorption

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mechanisms resulting in Type 2 double layers of which two are of importance in radionuclide adsorption studies:

Type 2a. *Chemisorption*. The potential-determining ions are adsorbed to the surface by chemical bonds (ionic and/or covalent), i.e., strong binding forces.

Type 2b. *Physical adsorption*. The potential-determining ions are adsorbed onto the surface by hydrogen bonds and van der Waals attraction forces, forces that are undirected and relatively nonspecific.

Stumm and Morgan (1970) have used the ionization of a silica surface as an example of charges occurring because of chemical reactions at a surface resulting in chemisorption

$$- Si - OH_2^+ \; \rightleftarrows \; - Si - OH \; \rightleftarrows \; - Si - O^- \qquad (32)$$
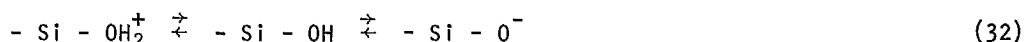
By progressively raising the pH (the negative logarithm of the H^+ activity) of the solution with which the surface is in contact, hydrogen ions are transferred into solution, since an increasing pH means a decreasing H^+ concentration in solution and the reaction proceeds from left to right. If the pH is lowered by the addition of an acid (i.e., H^+ ions), then the reaction proceeds from right to left, since there is a "surplus" of H^+ in solution. It is important to note that the charge on the surface here is controlled by the potential-determining ions in the solution, H^+ and OH^- (Type 2), and not by the structure of the lattice of which the surface is a part (Type 1). This type of reaction involves a free energy of interaction in the order of 125 to 210 x 10^3 J/mol (Hamaker and Thompson, 1972).

Physical adsorption involves much weaker energies of interaction in the order of 4000 J/mol to 40,000 J/mol. An example of ion adsorption in this manner is the adsorption of organic ions onto a clay surface. In general, chemisorption processes are considered more important in radionuclide adsorption in the subsurface.

Since in aqueous solutions the potential-determining ions are usually H^+ and OH^-, electrical double layers of Type 2 and the associated surface charges are strongly dependent on the pH of the solution. Therefore, adsorption processes involving Type 2 electrical double layers are also strongly pH dependent. In the case of the silica surface examined above, the surface charge is dependent on the bulk concentration of potential-determining ions in solution and is independent of all other electrolytes. If the concentration of these potential-determining ions is kept constant the resulting surface is called a *constant potential surface* (Stumm and Morgan, 1970). As the concentration of a potential-determining ion is increased in solution, the charge on the surface of the colloid changes from positive to negative or vice versa.

The point at which the solid surface charge from all sources is zero is called the *zero point of charge*, and the value of pH at this point is denoted by pH_{ZPC}. Berner (1971) has noted that "in general the zero point of charge does not occur at equal concentrations in solution of potential-determining cations and anions since adsorption is due to specific chemical effects (e.g. bonding energies and dipole reactions) which vary from ion to ion." Table 8 lists values of pH_{ZPC} for various minerals and precipitates.

Table 8. Zero Point of Charge for Various Minerals and Precipitates

Mineral	pH_{ZPC}	Source
SiO_2	2.0	Parks (1967)
K-feldspar	2.4	Parks (1967)
Na-feldspar	2.0	Parks (1967)
Kaolinite	4.6	Parks (1967)
Montmorillonite	2.5	Parks (1967)
Calcite	10.8	Fuerstenau, Gutierrez and Elgillani (1968)
Apatite	6.4	Fuerstenau, Gutierrez and Elgillani (1968)
MnO_2	2.0-4.5	Stumm and Morgan (1970, p. 478)
$Fe(OH)_3$ (ppt)	7.1	Marshall (1964, p. 331)
$Fe(OH)_3$ (amorphous)	8.5	Marshall (1964, p. 331)
$FeO \cdot OH$ (lepidocrocite)	5.4	Marshall (1964, p. 331)
$FeO \cdot OH$ (goethite)	3.2	Marshall (1964, p. 331)
$Al(OH)_3$ (ppt)	7.1-8.1	Marshall (1964, p. 331)
$Al(OH)_3$ (amorphous)	8.3	Marshall (1964, p. 331)

Figure 22 shows the distribution of charge density and ionic concentration in an electrical double layer, as described by the theory of Gouy and Chapman (Stumm and Morgan, 1970, pp. 458-466) for both constant potential and constant charge surfaces. In the upper graphs, the total negative charge density of the solid phase is exactly balanced by the total positive charge density of the solution phase, i.e., the two shaded areas are equal. The lower graphs show the concentration of cations and anions within the electrical double layer. Van Olphen (1963) has made an interesting analogy between the atmosphere of the earth and that of the electrical double layer. In the latter, counterions are attracted to the oppositely charged surface, but simultaneously undergo diffusion in the opposite direction, i.e., toward the solution where their bulk concentration is less. In the atmosphere of the earth, gas molecules are subject to a similar competition between gravitation and diffusion. The ionic strength of the solution has no effect on the total surface charge, σ, of a surface of constant charge since the charge is invariant; therefore $\sigma = \sigma'$ in Figure 22. Due to the increase in ionic strength, however, the ionic concentration of the double layer is increased $(c_{\infty} > c'_{\infty})$ in Figure 22. An increase in the ionic strength in an electrical double layer with a constant-potential surface by definition does not change the surface potential. Yet the ionic concentration in the mobile layer

increases $(c_\infty > c'_\infty)$ as does the total surface charge $(|\sigma| > |\sigma'|)$. (For identification of the symbols, refer to Figure 22.)
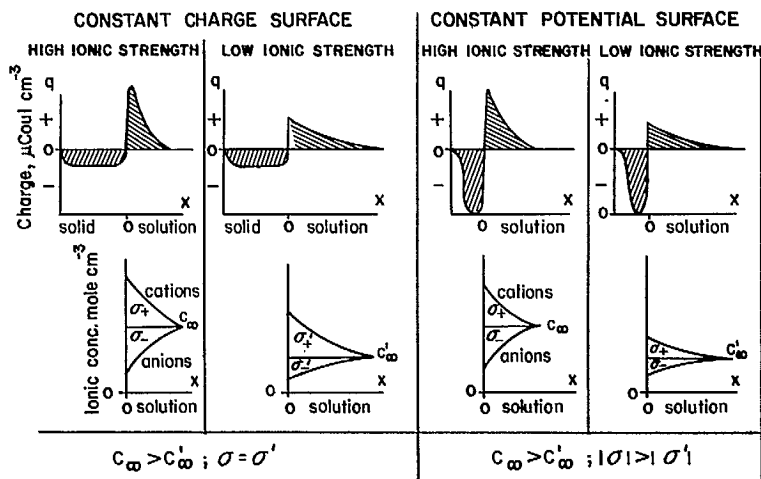
Figure 22. Distribution of charge and ionic
            concentration at an interface (after
            Stumm and Morgan, 1970; van Olphen, 1963).

It is now possible to define a quantity of singular importance in sorption studies:

> The *cation-exchange capacity* of a negative double layer may
> be defined as the excess of counterions in the double layer
> which can be exchanged for other cations (van Olphen, 1963,
> p. 270).

In Figure 22 this corresponds to the area marked σ_+.

It can be derived from the Gouy-Chapman theory of the electrical double layer that (1) multivalent ions are adsorbed preferentially over univalent ions and (2) this selectivity decreases with increasing ionic strength (van Olphen, 1963).

Ion-Exchange Equilibria

Ion exchange may be represented by simple chemical equilibria:

$$A^+ + B^+R^- \rightleftharpoons A^+R^- + B^+ \tag{33}$$

where A^+ and B^+ are the counterions and R^- is the cation exchanger (e.g., a clay or

ion-exchange resin). For Equation 33 we may define the selectivity quotient:

$$K_B^A = \frac{(A^+R^-)\ (B^+)}{(A^+)\ (B^+R^-)} = \frac{(A^+R^-)/(A^+)}{(B^+R^-)/(B^+)} \qquad (34)$$

where the parentheses represent molar (i.e., analytical) concentrations. A discussion of the conditions under which the selectivity quotient is equivalent to an equilibrium constant is given by Jenne and Wahlberg (1968) and Truesdell (1972).

A second important parameter in ion-exchange reactions is the *distribution coefficient*, K_d, which is defined as "the number of milliequivalents of an ion adsorbed per gram of exchanger divided by the number of milliequivalents of that ion per millilitre remaining in solution at equilibrium" (Amphlett, 1964). It is, therefore, a direct measure of adsorption from solution.

It is possible to develop an expression relating the selectivity quotient and the distribution coefficient of the system shown in Equation 33 if the cation-exchange capacity, σ_+, of the exchanger, R^-, and the total competing cation concentration in solution, τ, are known (Amphlett, 1964). By definition it is known that

$$(A^+) + (B^+) = \tau$$

and
$$(A^+R^-) + (B^+R^-) = \sigma_+ \qquad (35)$$

Therefore we shall assume that the exchanger represented by R^- in Equation 33 is saturated with B^+ cations and has an exchange capacity of σ_+ milliequivalents (meq) of cations per 100 g of exchanger, and that the concentration of a solution of A^+ and B^+ cations in which the exchanger is placed is equal to τ meq/ml. If we assume equilibrium concentrations of (A^+) and (B^+) in solution and of (A^+R^-) and (B^+R^-) on the exchanger, then by definition

$$K_d^A = (A^+R^-) \ / \ (A^+) \qquad (36)$$

and the selectivity quotient may be rewritten from Equation 35 as

$$K_B^A = \frac{(A^+R^-)\ (B^+)}{(B^+R^-)\ (A^+)} = \frac{(A^+R^-)\ \{\tau - (A^+)\}}{\{\sigma_+ - (A^+R^-)\}\ (A^+)}$$

$$= K_d^A \ \frac{\{\tau - (A^+)\}}{\{\sigma_+ - (A^+R^-)\}} \qquad (37)$$

Since the migration of radiocations through porous media is usually such that they are in trace amounts relative to the other major ions (e.g., Ca^{2+}, Na^+), $(A^+) \ll \tau$ and $(A^+R^-) \ll \sigma_+$. Therefore Equation 37 may be rewritten so that for the case of trace amounts of radiocations

$$K_B^A = K_d^A \, \tau \, / \, \sigma_+ \qquad (38)$$

and

$$K_d^A = K_B^A \, \sigma_+ \, / \, \tau \qquad (39)$$

Thus the distribution coefficient is directly proportional to the cation-exchange capacity and inversely proportional to the total competing cation concentration.

For the case above in which (A^+) and (A^+R^-) are assumed to be very small, $(B^+) \simeq \tau$ and therefore K_d^A is proportional to $(B^+)^{-1}$ from Equation 39. Using similar reasoning for the counterion pair A^{n+} and B^+, it can be shown that K_d^A is proportional to $(B^+)^{-n}$. Therefore assuming that the law of mass action equilibria holds, a plot of $\log K_d^A$ versus $\log (B^+)$ would yield a straight line of slope $-n$ (Amphlett, 1964). Again for the counterion pair A^{n+} and B^{n+}, K_d^A would be proportional to $(B^{n+})^{-1}$. For further information, refer to the works of Tamura (1972) and Baetslé (1969).

Adsorption by Clay Minerals

The clay minerals are a group of hydrous aluminosilicate minerals with sheet-like layer structures of octahedral and tetrahedral atomic lattices. The octahedral (eight-sided) lattice, as shown in Figure 23(a), is an aluminum cation (Al^{3+}) in sixfold coordination with hydroxyl anions, whose relative numbers are adjusted so that the whole sheet structure is electrically neutral. The tetrahedral unit (four-sided), as shown in Figure 23(b), is composed of a central silicate cation (Si^{4+}) in fourfold coordination with oxygen anions. Krauskopf (1967) has pointed out that although the geometric arrangement of the ions in Figure 23 is correct, the relative sizes of the ions are incorrect. The largest ions are the O^{2-} and OH^- anions, with ionic radii of about 1.40 angstroms ($\overset{\circ}{A}$) of which only four can fit around the Si^{4+} cation (0.42 $\overset{\circ}{A}$) and only six around the rather larger Al^{3+} cation (0.51 $\overset{\circ}{A}$).

The clay minerals are formed by a sequential stacking of octahedral and tetrahedral sheets (Fig. 24). The simplest mineral structure is that of *kaolinite* in which the octahedral sheet is linked to the tetrahedral sheet by sharing oxygen ions. This two-layer structure extends indefinitely in the vertical plane, by stacking additional two-layer sheets on top of the one shown, and also in the horizontal plane. These sheets are held together by hydrogen bonding of the OH^- ions at the surface of

◯ and ⬤ = Hydroxyls   ⬤ Aluminums, magnesiums, etc.

◯ and ⬤ = Oxygens   ◯ and ● = Silicons
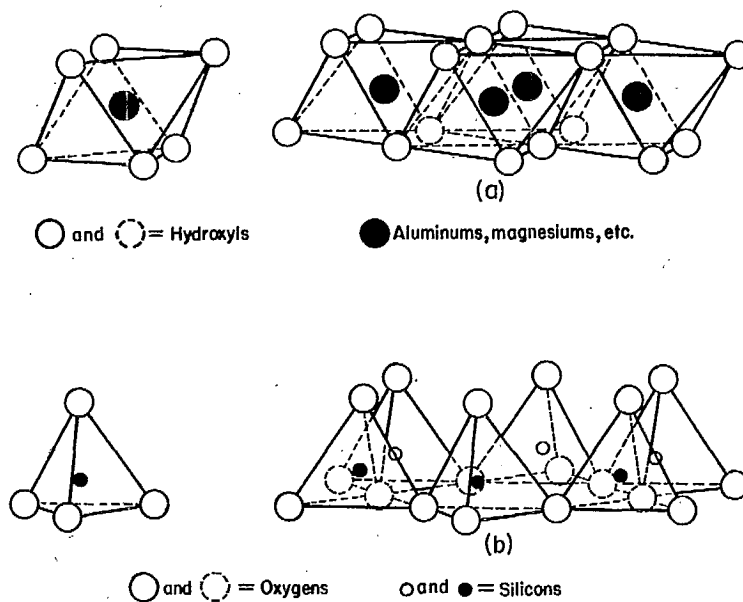
Figure 23. (a) The octahedral sheet and (b) the tetrahedral sheet (after Grim, 1968).

MINERAL	STRUCTURE	COMPOSITION (Idealized)
Kaolinite		$Al_2Si_2O_5(OH)_4$
Montmorillonite	H_2O Ex H_2O	$Ex_x[Al_{2-x}Mg_x]\langle Si_4\rangle O_{10}(OH)_2$
Illite	K^+	$K_{1-x}[Al_2]\langle Al_{1-x}Si_{3+x}\rangle O_{10}(OH)_2$
Chlorite		$[Mg,Al]_3(OH)_6[Mg,Al]_3\langle Si,Al\rangle_4 O_{10}(OH)_2$
Vermiculite	H_2O Ex H_2O	$Ex_x[Mg_3]\langle Al_x Si_{4-x}\rangle O_{10}(OH)_2$

Tetrahedral layer $\langle\ \rangle$
Octahedral layer [ ]

Figure 24. Simplified structure and composition of the principal clay minerals (after Berner, 1971).

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one sheet with the O^{2-} ions at the surface of the adjacent sheet, as is shown in Figure 24. Carroll (1959) has claimed that the surface charge on kaolinite arises from and only from the negative charges of the terminal O^{2-} ions exposed along the edges of the structural sheet. Tamura (1972) implied that isomorphic substitution was significant in kaolinites [probably Fe^{2+} for Al^{3+} (Grim, 1968)] by stating that only 50% of the exchange capacity of kaolinite was due to the ionizable H^+ ions (i.e., chemisorption). Fordham (1973), using an electron microscope, determined that the majority of the positive and also the most reactive negative ion-exchange sites were located along the edges of the kaolinite crystal. Generally, therefore, in kaolinites it is assumed that the unit cell is electrically balanced and the charge deficiency is due to broken bonds along the crystal edges.

The micaceous clay minerals, such as muscovite, biotite and *illite*, are three-layer clays formed by the combination of one octahedral layer between two silica tetrahedral sheets. There is considerable isomorphic replacement of Al^{3+} for Si^{4+}, resulting in a negative charge of 2 per unit cell in muscovite to 1.3 per unit cell in illite. This negative charge is mainly balanced by K^+ ions situated between unit layers. Yet not all the charge deficiency is satisfied in this way in illites, which are a common mineral constituent of Canadian glacial deposits. Other cations such as H^+, Ca^{2+} and Mg^{2+} are also present between the unit layers (Grim, 1968). There is considerable evidence of and research on the irreversible fixation of K^+, Cs^+ and NH_4^+ in micas (Marshall, 1964; Sawhney, 1972).

Vermiculite is quite similar to the micas in that the unit cell is composed of two silica tetrahedral sheets sandwiching an alumina octahedral sheet; the unit cells, however, are separated by a layer of water which has the thickness of two water molecules (4.98 Å). The structure is electrically unbalanced due to the replacement of Al^{3+} for Si^{4+}, which results in a net-charge deficiency of 1.0-1.4 per unit cell. The balancing cation is usually Mg^{2+}, but sometimes Ca^{2+} is found between the unit cells and is generally exchangeable (Grim, 1968).

Montmorillonites are also similar to the micas in that they are composed of two silica tetrahedral sheets with a central alumina octahedral sheet (Fig. 25). The distinguishing feature of the montmorillonites is that polar molecules (i.e., those in which the centres of the positive and negative charges are at opposite sides of the molecule) such as water and certain organics can enter the space between unit cells and cause expansion of the unit cells, so that montmorillonites do not have a fixed dimension along the c-axis. Hydrated cations also occur between unit cells and should the interlayer polar molecules be absent, it is possible to identify the cation species by X-ray crystallography. The net-negative charge is due to isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral units and of bivalent cations such as Mg^{2+} for

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Al^{3+} in the octahedral units, as well as to unsatisfied valences along the edges of the unit cell.
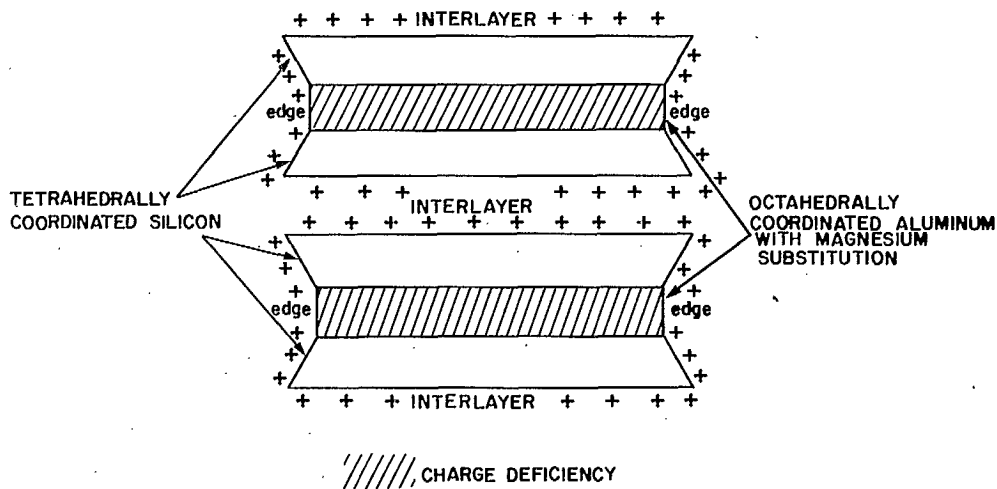
Figure 25. Simplified representation of montmorillonite showing edge and interlayer cations (after Pommer, 1963).

Pommer (1963) treated montmorillonite as a mixture of two acids resulting from the presence of two types of exchange sites--interlayer and edge--both occupied by hydrogen ions. This reasoning is based on the electrostatic attraction between electropositive and electronegative objects as dictated by Coulomb's law:

$$F' \propto Q^+ Q^- / x^2 \qquad (40)$$

where F' is the force of attraction, Q^+ and Q^- are the respective charges on the electropositive and the electronegative objects in coulombs, and x is the distance between them. Pommer (1963) assumed that the silica tetrahedral sheets were electrically neutral and that the net-negative charge resulted from Mg^{2+} substituting for Al^{3+} in the octahedral sheets. The electrostatic attraction between the negatively charged octahedral sheet and the surrounding solution would be greater at the edge sites (Fig. 25) than at the interlayer sites because of the distance factor in Coulomb's inverse square law (Equation 40). The H$^+$ in the edge positions are held by relatively strong electrostatic forces and are not easily ionized or exchanged. That part of the clay acid represented by these H$^+$ will therefore be weaker than that part represented by the interlayer H$^+$ for which the electrostatic field is weaker due to its attenuation across the silica tetrahedral sheet.

The general structure of *chlorite* consists of alternate mica-like (silica-alumina-silica) and brucite-like octahedral layers. The mica sheets have a net-negative

charge owing to isomorphous substitution of Al^{3+} for Si^{4+}. The brucite layers, which are composed of Mg^{2+} and Al^{3+} in octahedral coordination with hydroxyl groups, have a net-positive charge which partially balances the net-negative charge. The result is a net-negative charge of between 1.5 and 0.5 per unit cell (Grim, 1968).

The cation-exchange capacities of the clay minerals are summarized in Table 9. In general, the larger exchange capacities are exhibited by the three-layer clay minerals, such as vermiculite and montmorillonite, which are capable of swelling in solutions of polar molecules, such as water.

Table 9. Cation-Exchange Capacity of Clay Minerals

Mineral	Structural control	Exchange capacity (meq/100 g at pH 7)
Kaolinite	Unsatisfied valences on edges of structural units	3-15
Halloysite ($2H_2O$)	Unsatisfied valences on edges of structural units	5-10
Halloysite ($4H_2O$)	Unsatisfied valences on edges of structural units and on internal surface between the layers	40-50
Montmorillonite group	Substitutions in the octahedral and tetrahedral units giving excess negative charge; unsatisfied valences on edges of units	70-100*
"Illites" (hydrous micas)	As in montmorillonite, plus deficiency of K^+ between the layers	10-40
Vermiculite	Replacement of interlayer cations, substitution within the units, and unsatisfied valences on edge of units	100-150
Chlorite	No data. Possible deficiency of charge owing to substitution in the brucite layer	10-40?
Glauconite	As in "illites"	11-20+
Palygorskite group	Substitution of Al^{3+} for Si^{4+} in structural units, unsatisfied exchange sites within channels in the structure	20-30
Allophane	Porous amorphous structure with unsatisfied valences	~70

*Certain members of the montmorillonite group have a much lower exchange capacity because there is no substitution in the tetrahedral or octahedral units, e.g., stevenite with 36 meq/100 g.

Source: Dorothy Carroll (1959, p. 754).

Because of this variable c-axis spacing, the interlayer cations of these minerals may be of varying hydrated radii. Furthermore, as has been shown by Pommer (1963), the interlayer cations are less strongly held than the edge cations because of the attenuation of the charge across the tetrahedral sheets. Consequently, they are more easily replaced by other cations in solution than cations attracted to edge sites caused by broken bonds, such as those found in all inorganic colloids. The interlayer cation-exchange sites create Type 1 electrical double layers and are therefore constant-charge surfaces, whereas "broken bond" exchange sites create Type 2a electrical double layers and adsorption is by the process of chemisorption. (The processes "ion exchange" and "chemisorption" differ in that the former implies reversibility, whereas the latter may be regarded as leading to the formation of a form of surface compound and is seldom reversible.)

Clay minerals also have capacity for anion exchange. The *anion-exchange capacity*, the area shown as σ_- in Figure 22, can be due to both Type 1 and Type 2 electrical double layers. Yet because of the general practice of lower valence cations replacing higher valence cations (e.g., Al^{3+} for Si^{4+}) in clay minerals, there is generally very little anion-exchange capacity in Type 1 electrical double layers. Type 2 double layers, in contrast, result in significant anion-exchange capacities by pH-dependent chemisorption on edge sites owing to broken bonds. Marshall (1964) states that cation- and anion-exchange sites should exist in a 1:1 ratio on kaolinite edges and in a 2:1 ratio on micas and montmorillonites. Grim (1968) has given the following anion-exchange capacities: kaolinite, 6-20 meq/100 g; montmorillonite, 23-31 meq/100 g; and vermiculite, 4 meq/100 g.

So far it has been assumed that all ions of equal valence have an equal probability of being adsorbed by a colloid; yet this is not the case. There is a well-defined selectivity or *affinity series* that has been derived theoretically by Eisenmann (1962) and which is discussed in terms of clay minerals by Stumm and Morgan (1970) and Marshall (1964). If cation-exchange equilibria are dominated by electrical dipole interactions between the counterions and water molecules and are unaffected by specific ion affinities of certain types of ion-exchange sites (e.g., interlayer illite sites for cesium), then the affinity series for the alkali and alkaline earth metals can be written

$$Cs^+ > K^+ > Na^+ > Li^+$$

and $\quad Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$
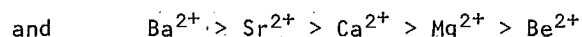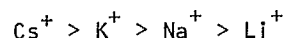
i.e., Cs has a greater affinity for being sorbed than K^+ which, in turn, has a greater affinity than either Na^+ or Li^+. An inspection of the periodic table of elements

shows that affinity for adsorption increases with ionic radius in both Group I and
Group II elements. Yet it is probable that the ions are hydrated and their affinity for
adsorption decreases with the increased size of the hydrated ionic radii (Table 10).

Table 10. Ionic Radii

| Ion | Ionic Radii (Å) | |
	Crystal	Hydrated
H^+	-	2.82
Li^+	0.60	3.82
Na^+	0.95	3.58
K^+	1.33	3.31
Rb^+	1.48	3.29
Cs^+	1.69	3.29
NH_4^+	1.48	3.31
Be^{2+}	0.31	4.59
Mg^{2+}	0.65	4.28
Ca^{2+}	0.99	4.12
Sr^{2+}	1.13	4.12
Ba^{2+}	1.35	4.04
Ra^{2+}	1.52	3.98
Mn^{2+}	0.80	4.38
Fe^{2+}	0.75	4.28
Co^{2+}	0.72	4.23
Zn^{2+}	0.74	4.30
Al^{3+}	0.50	4.75
Fe^{3+}	0.60	4.57
Ce^{3+}	1.1	4.52
OH^-	1.76	3.00
F^-	1.36	3.52
Cl^-	1.81	3.32
CO_3^{2-}	2.66	3.94
SO_4^{2-}	2.90	3.79
NO_3^{2-}	2.64	3.35

Source: Nightingale (1959).

Marshall (1964, pp. 280-281) has summarized the experimental determinations of affin-
ity series by Schachtshabel for montmorillonite, kaolinite, muscovite, biotite and
K-feldspar. From the perspective of this study, the important result was that the
relative position of the important radioelements Sr and Cs in the affinity series
above was generally maintained.

Adsorption by Hydrous Metal Oxides

        In the past several years there has been much interest in the role of the
hydrous oxides of iron, manganese, aluminum and titanium in controlling the con-
centrations of various contaminants and trace elements in aqueous solution. Quite
often these substances are referred to as hydroxides, oxyhydroxides or sesquioxides,

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since their structure and composition are generally poorly understood. Nevertheless, provided that their zero points of charge (pH_{ZPC}) are less than the pH of the groundwater, these hydrous metal oxides are capable of playing a significant role in radiocation adsorption from groundwater.

Of the various hydrous oxides that may be important in radiocation sorption, those of iron and manganese have received the greatest attention. Because iron and manganese may exist in varying oxidation states, i.e., they can have different valences, their nature as either dissolved or solid species is dependent on the pH and reduction-oxidation (redox) potential of the groundwater. The equilibrium *redox potential*, Eh, is defined by the Nernst equation (Garrels and Christ, 1965, p. 134):

$$Eh = E^0 + (RT/\varepsilon F) \, \ln \frac{[\text{oxidized species}]}{[\text{reduced species}]} \tag{41}$$

where   Eh = redox potential in volts;

             E^0 = standard half-cell potential in volts, i.e., the voltage for a particular redox reaction when both oxidized and reduced species are at unit activity;

             R   = gas constant;

             T   = temperature in °K;

             ε = number of electrons transferred in the reaction under consideration;

             F   = Faraday constant;

$\ln \dfrac{[\text{oxidized species}]}{[\text{reduced species}]}$ = natural log of the activities of the species in the reaction in mass-law form. (The activity is an effective thermodynamic concentration which will be more fully defined later.)

For the half reaction

$$aA + bB = cC + dD + \varepsilon e^- \tag{42}$$
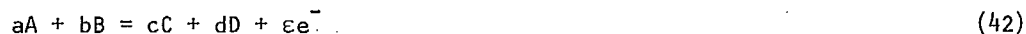
where A and B are the reduced species with stoichiometric coefficients a and b; C and D are the oxidized species with coefficients c and d; and ε denotes the number of

electrons involved in the half reaction, Equation 41 becomes, at 25°C,

$$Eh = E^0 + \frac{0.0592}{\varepsilon} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$ (43)

Should the reactants A and B and the products C and D have unit activities, which is the case for all pure solids and liquids, then the redox potential would be equal to the standard half-cell potential.

An example of a redox reaction is the oxidation of elemental iron (valence zero) to ferric iron (valence three) (Cloke, 1966):

$$Fe + 3H_2O = Fe(OH)_3 + 3H^+ + 3e^- \;\; ; \;\; E^0 = + 0.059 \text{ v}$$ (44)
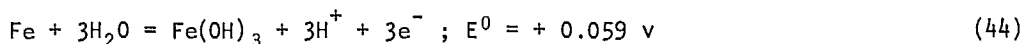
for which we can write

$$Eh = + 0.059 - 0.059 \text{ pH}$$ (45)

[For further information see Champ, Gulens and Jackson (in press).]

Positive Eh values signify a geochemical environment relatively rich in oxidized species and perhaps including some dissolved oxygen, whereas negative Eh values are indicative of reducing conditions. Back and Barnes (1965) measured Eh values varying from -40 mV to +700 mV in well waters from the Atlantic Coastal Plain. The low values are due to the oxygen demand of organic matter in the sediments leading to reducing conditions. Back and Barnes observed that the higher Eh values were found in recharge areas and shallow wells, and that the Eh values decreased along the flow path of the groundwater flow system.

Figure 26 shows an Eh-pH stability diagram for the geochemical system of iron, water and dissolved carbon dioxide. The shaded area shows that region in which most groundwater samples fall, indicating that iron is present either as a solid-phase ferrous carbonate, a ferric hydrous oxide, or as dissolved ferrous iron. Langmuir and Whittemore (1971) have stated that hydrous iron oxide precipitates are generally present as goethite or amorphous particles (1-2 μm). More stable species form in the case of high dissolved Fe^{2+} concentrations (10 mg/l = 10 ppm) as the initial precip-itates recrystallize. Kurbatov, Kulp and Malk, Jr. (1945) showed that identical amounts of ^{89}Sr were taken up by ferric hydrous oxides irrespective of whether the hydrous oxide was precipitated in the absence of the cation, which was later introduced and therefore sorbed, or whether the cation was present in solution when the hydrous oxide was precipitated and was therefore coprecipitated with it.

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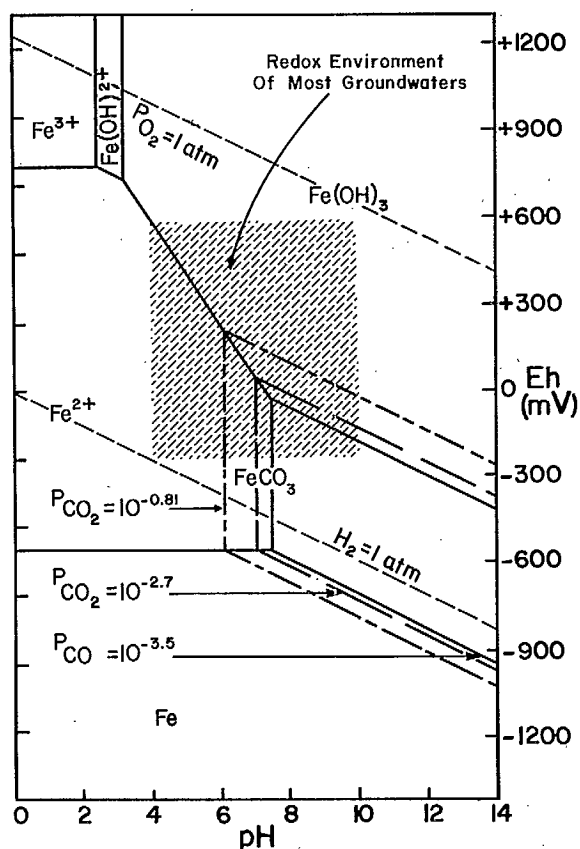
Figure 26. Diagram of Eh-pH stability field for iron. The conditions shown represent the predominant stable geochemical species of iron in an aqueous system of 5.6 mg/l iron; partial pressure of carbon dioxide $= 10^{-0.81}$ atm, $10^{-2.7}$ atm and $10^{-3.5}$ atm; total pressure $= 1$ atm; temperature $= 25°C$ (after Jenne, 1968).

Manganese is considerably more soluble than iron in freshwater environments. In Hem (1972a), Eh-pH diagrams indicate that the boundary between the precipitate, manganese dioxide (MnO_2), and dissolved Mn^{2+} is about 600 mV at pH 7. Consequently manganese dioxide is present in appreciable amounts in only oxidized groundwaters. Murray, Healy and Fuerstenau (1968) have shown that the Group I (alkali metals) and Group II (alkaline-earth metals) cations, such as Cs^+ and Sr^{2+}, are adsorbed into the mobile layer of the electrical double layer of manganese oxide, whereas Co^{2+} is adsorbed into the fixed layer. Egorov and Lyubimov (1969) showed that MnO_2 sorbed Sr^{2+} and in exchange released H^+, K^+ and Mn^{2+} to solution. Amphlett (1964) stated that the cation-exchange affinity series for the Group I cations on $MnO(OH)_2$ with an exchange capacity of 73 meq/100 g was identical with that already defined for the clay minerals.

Adsorption by Organic Colloids

According to Schnitzer and Khan (1972), the organic matter found in soils and sediments is of two types--humic and nonhumic. The humic fraction is resistant to

microbial attack, unlike the nonhumic variety, and consequently is the only type considered here. The humic fraction can be separated into three parts:

(1) *humic acid*, which is soluble in dilute alkaline solution;

(2) *fulvic acid*, which is soluble in acidic and basic solutions;

(3) *humin*, which is insoluble in both acidic and basic solutions due probably to the strength of its attachment to inorganic colloids and water constituents.

Schnitzer and Khan (1972) have pointed out that apart from their resistance to microbial attack, all humic fractions have the ability to form water-soluble and water-insoluble salts and complexes with metal ions and hydrous oxides. For instance, it is known that humic acid readily sorbs nuclear fission products such as ^{90}Sr; the results of Ophel and his colleagues (1971) at Chalk River have shown that the exchangeable ^{90}Sr sorbed on sandy sediments increases exponentially with the organic matter content of the sediments. Furthermore, humic substances play an important role in determining the cation-exchange capacity of clays by blocking exchange sites or adjusting affinity series or causing swelling (Kown and Ewing, 1969).

Geochemically, organic matter is the primary cause of reducing environments. Its presence produces methane and hydrogen sulphide gases and dissolved ferrous iron, all of which are indicative of these environments. Krauskopf (1967) stated that in these environments redox potentials (Eh) may vary between -100 mV and -500 mV and the pH is observed to be less than 7 with a minimum of 4 where decay takes place under aerobic conditions.

Table 11 shows the elementary composition of humic acids from three soils and their exchange capacities. The latter can be compared with those given for the clay minerals in Table 9. It is worth noting that the data in Table 11 demonstrate that the cation-exchange capacities of these soils increase proportionally with carbon content and pH.

Table 11. Elementary Composition of Humic Acid from Various Soils and their Exchange Capacities at Different pH Levels

Soil	Elementary composition (%)			Exchange capacity (meq/100 g)		
	C	H	N	pH 4.5	pH 6.4	pH 8.1
Chernozem	58.29	3.23	3.72	292	433	590
Podzol	56.19	4.23	3.74	243	410	549
Peat marsh	54.29	4.53	3.84	170	286	400

Source: Marshall (1964, p. 163).

Marshall (1964) also summarized several investigations on the affinity series
of cations with respect to humic substances. For the entry of monovalent cations into
potassium- and calcium-saturated peats, the affinity series was

$$H^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$
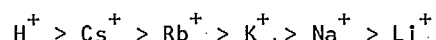
Another experiment, in which crude humic acid was used as the exchanger and the added
cation concentrations were equal to the exchangeable cation concentrations on the
humic acid, gave an affinity series of

$$Ba^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > K^+ > Na^+ > Li^+$$
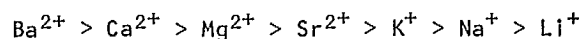
The data presented in Table 11 only apply to surficial soils and not to
tills and other Pleistocene deposits for which there are few data available. Studies
of the fluvial deposits in the vicinity of the Chalk River Nuclear Laboratories by Ophel,
Fraser and Judd (1971) and Jackson *et al*. (1977) have demonstrated the presence of organic
matter in these sediments. Although the amount and type of the humic substances have not
been accurately determined, concentrations of dissolved organic carbon are in the range of
1-2 mg/l (ppm).

PRECIPITATION PROCESSES

In addition to their adsorption from solution, radionuclides may be removed
from solution either by direct precipitation or by isomorphous substitution with an
ion of similar size in a crystal that is forming (coprecipitation) or that has formed
(replacement).

Mechanisms of Direct Precipitation

If we consider a reaction of the type

$$A_x B_y \text{ (solid)} \rightleftarrows xA^{+y} \text{ (aqueous)} + yB^{+x} \text{ (aqueous)} \qquad (46)$$
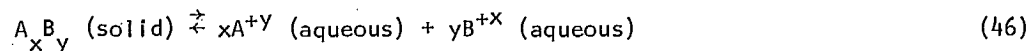
we can write an equilibrium constant

$$K_{eq} = \frac{[A]^x [B]^y}{[A_x B_y]} \qquad (47)$$

where $[A]^x$ is the activity of ion A with mass action coefficient x. The activity of

an ion in aqueous solution is defined by Krauskopf (1967, p. 73) as its "effective concentration, the part of its analytical concentration that determines its behavior toward other ions with which it may react." It is a dimensionless quantity and is defined by the expression

$$[A] = \gamma_A \, m_A \tag{48}$$

where γ_A is the activity coefficient of A and has the dimensions of the reciprocal of concentration and m_A is the molal concentration expressed in milligrams of solute per kilogram of water. In dilute solutions, such as potable groundwaters, the differences between molality and molarity, in which analytical concentrations are expressed in milligrams per litre, are generally negligible. Consequently in this report we shall refer to molar concentrations.

The term $[A_x B_y]$ in Equation 47 is the activity of the solid phase which is undergoing dissolution into its constituent ions A^{+y} and B^{+x}. It is usually assumed to be equal to one, in which case Equation 47 becomes

$$K_{eq} = [A]^x [B]^y \tag{49}$$

The term K_{eq} in Equation 49 is an ion-activity solubility product and is derived by experimental measurements. The actual ion-activity product (IAP) of a groundwater solution is not necessarily the same as K_{eq}. The state of saturation of the solid in Equation 46 relative to K_{eq} is determined by comparing the IAP and K_{eq}, such that

if IAP > K_{eq}, the solution is supersaturated;
if IAP = K_{eq}, the solution is saturated; and
if IAP < K_{eq}, the solution is undersaturated.

Whenever the IAP $\geq K_{eq}$, it is assumed that precipitation of the solid phase is taking place. Similarly, when IAP < K_{eq}, it is assumed that dissolution of the solid is occurring. A commonly used expression showing the relation of the IAP to K_{eq} is the saturation index, SI, where

$$SI = \log (IAP/K_{eq}) \tag{50}$$

For supersaturated solutions SI will be greater than zero and for undersaturated solutions SI will be less than zero.

In calculating the saturation index it is often necessary to take into account the possibility that the aqueous products of mineral dissolution might not all be charged ionic species as is shown in Equation 46, but may be uncharged due to the occurrence of ion pairs or complexes. For instance, a solution of magnesium sulphate will contain not only dissociated Mg^{2+} and SO_4^{2-} ions but also the undissociated and uncharged ion pair $MgSO_4^0$. More examples of ion complexing include the association of OH^- groups at neutral pH with metal ions of valences +3, +4 and higher, such as $Pu(OH)_4$, and the neutral organic complexes that combine with the transition metal ions, such as cobalt. Berner (1971) has stated that inorganic major-ion complexes become important when the ionic strength of the solution reaches 0.005. Ionic strength, I, is defined by:

$$I = 1/2 \ \Sigma \ m_i z_i^2 \tag{51}$$

where m_i is the molality of ion i and z_i, its valence.

Table 12 shows some equilibrium constants for some sulphides, carbonates, sulphates and hydroxides which are relevant to this study. The very low solubility product values for such species as $Pu(OH)_4$ ($K_{eq} = 10^{-55.2}$) and $Fe(OH)_3$ ($K_{eq} = 10^{-40}$) reflect the insolubility of many hydroxides, whereas the relatively large values for the sulphates reflect their relative solubility. Obviously, therefore, such elements as Fe and Pu would be relatively immobile if they existed only as dissociated ions, since only very small concentrations of them would cause their precipitation as hydroxides. Yet this disregards that both might be transported as ionic complexes or in different valence states.

Generally, solubility controls affecting radionuclide attenuation in groundwater flow systems are a function of the pH and Eh of the groundwater. Consequently, Eh-pH diagrams are useful in predicting which geochemical reactions might affect a particular radionuclide. For example, the mechanisms of attenuation of [55]Fe may be suggested by consideration of Figure 26, in which the shaded area represents the redox environment where most groundwaters fall. In this shaded area three species of iron occur: Fe^{2+}, $FeCO_3$ (siderite) and ferric hydroxide. Therefore, by careful field measurements of pH and Eh, clues to the hydrogeochemical controls of radionuclide mobility may be gathered. It should be added that the insolubility of most metal sulphides (Table 12) provides an additional mechanism of radiocontaminant attenuation, in this case at low redox potentials. Therefore, for [55]Fe in the dissolved ferrous iron state, retardation would depend on adsorption from solution. In other geochemical environments there would probably be precipitation from solution as the hydroxide, carbonate or sulphide.

The step-by-step treatment of hydrogeochemical data to calculate SI and thus to determine whether a mineral phase is being dissolved or precipitated is covered

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Table 12. Equilibrium Constants for Some Sulphates, Carbonates, Sulphides and Hydroxides

	Mineral	pK_{eq}*	T°C	Source
Sulphates				
$BaSO_4$	Barite	10.0	25	Sillen (1964)
$CaSO_4 \cdot 2H_2O$	Gypsum	4.6	25	Sillen (1964)
$CaSO_4$	Anhydrite	4.5	25	Sillen (1964)
$SrSO_4$	Celestite	6.5	25	Sillen (1964)
Carbonates				
$CaCO_3$	Calcite	8.36	10	Langmuir (1971)
$CaMg(CO_3)_4$	Dolomite	16.71	10	Langmuir (1971)
$CoCO_3$		12.8	25	Sillen (1964)
$SrCO_3$	Strontianite	9.6	25	Sillen (1964)
$FeCO_3$	Siderite	10.5	25	Sillen (1964)
Sulphides				
CoS	Alpha	20.4	25	Sillen (1964)
	Beta	24.7	25	Sillen (1964)
FeS	Pyrrhotite	17.2	25	Sillen (1964)
MnS	Pink	9.6	25	Sillen (1964)
	Green	12.6	25	Sillen (1964)
ZnS	Wartzite	21.6	25	Sillen (1964)
	Sphalerite	23.8	25	Sillen (1964)
Hydroxides				
$Al(OH)_3$	Amorphous	32.3	25	Sillen (1964)
	Gibbsite	36.3	25	Sillen (1964)
$Co(OH)_2$	Blue	14.2	25	Sillen (1964)
	Pink-aged	15.7	25	Sillen (1964)
$Fe(OH)_3$	Amorphous	37.1	25	Langmuir and
	Crystalline goethite	44	25	Whittemore (1971)
$Mn(OH)_2$	Crystalline	12.7	25	Sillen (1964)
$Pu(OH)_4$		55.2	25	Andelman and Rozzell (1970)
$Zn(OH)_2$	Amorphous	15.5	25	Sillen (1964)

*The numbers are negative logarithms of the activity products; therefore the solubility product for barite is $BaSO_4 = [Ba^{2+}][SO_4^{2-}] = 10^{-10.0}$.

by Berner (1971, Chapters 3 and 4) and Domenico (1972, pp. 197-199). Examples of such calculations are given in Chapter 4 of this report.

Replacement and Coprecipitation

The replacement of one element in a crystal lattice by another element is a common phenomenon in the creation of distinct mineral species. The ground rules that dictate which elements may replace one another are relatively few (Krauskopf, 1967, Chapter 5). First, although there are several important exceptions to this size restriction, the elements should in general have ionic radii (Table 10) which do not differ

by more than 15% so that the replacing ion will fit the space provided by the host lattice. Secondly, only those ions with similar covalent character may substitute for one another. The simplest method of estimating the similarity of covalent bonds is by the use of Pauling's electronegativity differences. Finally, although it is not necessary that the replacing ion be of the same valence as the ion it replaces, there is seldom replacement if the two ions differ by more than one valence unit.

Two ions that satisfy all of these rules are Sr^{2+} and Ca^{2+}. They are of similar ionic radius--1.13 Å for Sr^{2+} and 0.99 Å for Ca^{2+}--and their electronegativity differences vis-à-vis a carbon atom, as in $CaCO_3$ or $SrCO_3$, are identical. Consequently, it is not surprising to find that the replacement of ^{90}Sr for Ca in $CaCO_3$ is an effective method of radiostrontium retardation. Halevy and Tzur (1964) noticed that considerably more radiostrontium was being absorbed by a soil column than the cation-exchange capacity of the calcareous soil would predict. They concluded that the Sr solution passing through the column was dissolving the calcite and precipitating $SrCO_3$. Jenne and Wahlberg (1968) concluded that ^{90}Sr in a Tennessee stream was being retarded by the isomorphous substitution of ^{90}Sr for Ca in *in situ* precipitated $CaCO_3$ (i.e., that which was formed in the stream). Routson (1973) reported that phosphate-rich wastes disposed of in the calcareous glaciofluvial sediments at Hanford, Washington, caused the replacement of calcite with apatite in the alkaline pH range. In the apatite ^{90}Sr then replaced Ca by isomorphous substitution. It is this same reaction, the entry of ^{90}Sr into apatite, by which radiostrontium is incorporated into human bone.

The significant feature of replacement and coprecipitation processes is that the new solid phase (e.g., $SrCO_3$) is more stable in the replacing solution than the original solid phase (Routson, 1973). This implies that the new solid phase is more insoluble than the original solid phase, and that the propensity of a radio-contaminant ion to be absorbed into a mineral lattice can be expressed by solubility arguments. The theory of such reactions has been put forward by Stumm and Morgan (1970, pp. 205-212) and Kinsman and Holland (1969). For the solid solution of B in A, i.e.,

$$A (s) + B (aq) = B (s) + A (aq) \tag{52}$$

where (s) denotes the solid phase and (aq) the aqueous one, we can write the observed distribution constant, i.e., one derived experimentally:

$$D_{obs} = \frac{(A \ (aq))}{(B \ (aq))} \cdot \frac{(B \ (s))}{(A \ (s))} \tag{53}$$

in which the parentheses represent concentrations.

As a first approximation of D_{obs}, we may compute D_c, which is merely the quotient of the solubility products of the two mineral phases

$$D_c = K_{eq} \ (A) \ / \ K_{eq} \ (B) \tag{54}$$

Equation 54 involves the assumption (Stumm and Morgan, 1970, p. 206) that the ratio of the activity coefficients of the two mineral phases is unity. The relative weakness of this assumption is seen in the differences between D_{obs} and D_c in Table 13. The relationship between these two distribution constants may be written

$$D_c = D_{obs} \frac{\gamma_{B(s)}}{\gamma_{A(s)}} \tag{55}$$

where $\gamma_{B(s)}$ and $\gamma_{A(s)}$ are the activity coefficients of $B(s)$ and $A(s)$, respectively. As was noted, however, Equation 54 is a first approximation and can yield information on whether a particular coprecipitation or replacement scheme is feasible. For instance, Table 13 shows that the coprecipitation of ^{90}Sr by gypsum may be significant, whereas barite would not appear to be a receptive host lattice.

Table 13. Replacement and Coprecipitation Schemes

Solid solution	D_{obs}	D_c (25°C)	Source
$RaSO_4$ in $BaSO_4$	1.8 (20°C)	5.9	Stumm and Morgan (1970, p. 207)
$SrSO_4$ in $BaSO_4$	–	0.0003	–
$SrSO_4$ in $CaSO_4 \cdot 2H_2O$	–	79.4	–
$SrCO_3$ in $CaCO_3$	1.15 (30°C)	17.8	Kinsman and Holland (1969)
$CoCO_3$ in $CaCO_3$	–	28183.0	–

Nucleation

The precipitation process in groundwater is not only controlled by the solution chemistry but also by the presence of nuclei about which the crystal forms. In his review of the physical chemistry of precipitation, Berner (1971) has suggested that nucleation in natural waters is most likely to occur on preexisting colloids, such as clay minerals. At high degrees of supersaturation the nucleation rate for insoluble substances such as sulphides and hydroxides is so fast that the precipitate

consists of very small crystallites not much larger than the nuclei, which are often found as X-ray amorphous coatings on clays. This is typically the case for hydrous metal oxides. At lower degrees of supersaturation the crystals tend to be much larger than the nuclei.

SOLUTE TRANSPORT WITH GEOCHEMICAL RETARDATION

The Retardation Equations

In Chapter 2, an expression was derived (Equation 19) describing the change in concentration of an ionic species with time owing to dispersion, convection and geochemical reaction in one-dimensional flow. When the ionic species in question is a radionuclide there is the added effect of radioactive decay to consider, and Equation 19 then becomes

$$\frac{\partial c_A}{\partial t} = D'_x \frac{\partial^2 c_A}{\partial x^2} - V_x \frac{\partial c_A}{\partial x} - \frac{\rho_b}{n} \frac{\partial q_A}{\partial t} - \lambda c_A \tag{56}$$

where c_A is the concentration of ionic species A in solution, q_A is the amount of A per unit mass of porous medium which is removed from solution by geochemical reaction, ρ_b is the bulk density and n is the porosity as previously defined, and λ is the first-order rate constant or disintegration constant for the radionuclide in question. Therefore the rate of change in concentration of ionic species A in solution is equal to the sum of its rates of change because of dispersion minus its rates of change owing to convection, geochemical reaction and decay.

Equation 56 is a satisfactory description of a mass transport process with geochemical retardation, such as ion exchange or precipitation, provided that the geochemical reactions that occur do not affect the ratio ρ_b/n. Should large amounts of a mineral species be precipitating out of solution in a groundwater flow system, it is conceivable that the bulk density and the porosity of the porous medium could be materially affected. In such an extreme case, Equation 56 would be unsuitable as a description of the mass transport process. The case with which we shall be concerned here, however, is traditional in radioactive waste management, i.e., when a radionuclide has accidentally escaped from a waste management area and is in solution in trace amounts relative to the major groundwater cations. For such a case the ion exchange or precipitation of the radionuclide will not affect the ratio ρ_b/n.

For the special case of geochemical retardation owing to ion-exchange

processes such as

$$A^+ + B^+R^- \rightleftharpoons A^+R^- + B^+ \tag{33}$$

it is desirable to change Equation 56 into a form such that the dependent variables, C_A and q_A, are reduced to dimensionless values between 0.0 and 1.0. In so doing we may establish relationships between the independent variables in Equation 56 (Lai and Jurinak, 1972).

For the ion-exchange reaction being considered,

$$\tau = C_A + C_B = \text{total competing cation concentration in solution (meq/mass)}$$

$$\sigma_+ = q_A + q_B = \text{total cation-exchange capacity (meq/mass)},$$

let $\quad C_A = \tau X_A \text{ and } q_A = \sigma_+ Y_A \tag{57}$

where X_A is the reduced concentration of A^+ in solution varying from 0 to 1, and where Y_A is the reduced concentration of A^+ adsorbed on R^-.

For a cation-exchange reaction of constant total competing cation concentration in solution and a constant exchange capacity, τ and σ_+ are constant. Therefore, it is possible to obtain the following expressions in terms of the reduced variables, X_A and Y_A, for the terms in Equation 56

$$\frac{\partial C_A}{\partial t} = \tau \frac{\partial X_A}{\partial t} \tag{58}$$

$$\frac{\partial C_A}{\partial x} = \tau \frac{\partial X_A}{\partial x}$$

$$\frac{\partial^2 C_A}{\partial x^2} = \tau \frac{\partial^2 X_A}{\partial x^2}$$

$$\frac{\partial q_A}{\partial t} = \sigma_+ \frac{\partial Y_A}{\partial t}$$

$$\lambda C_A = \lambda \tau X_A$$

By substituting Equation 58 into Equation 56 and rearranging terms we obtain the

following form for the material balance equation:

$$D'_x \frac{\partial^2 X_A}{\partial x^2} - V_x \frac{\partial X_A}{\partial x} - \lambda \tau X_A = \frac{\partial X_A}{\partial t} + \frac{\rho_b \sigma_+}{n\tau} \frac{\partial Y_A}{\partial t} \tag{59}$$

If we assume that the ion-exchange reaction between A^+ and B^+ is instantaneous, then there is a unique function relating X_A and Y_A which is called the exchange isotherm

$$Y_A = f (X_A) \tag{60}$$

By using the chain rule of differentiation we can write

$$\frac{\partial Y_A}{\partial t} = f' \frac{\partial X_A}{\partial t} \tag{61}$$

where f' is the slope of the exchange isotherm (Fig. 27).

Substituting Equation 60 into Equation 58 we can write

$$D'_x \frac{\partial^2 X_A}{\partial x^2} - V_x \frac{\partial X_A}{\partial x} - \lambda \tau X_A = \frac{\partial X_A}{\partial t} + \frac{\rho_b \sigma_+}{n\tau} f' \frac{\partial X_A}{\partial t} \tag{62}$$

or
$$D_A \frac{\partial^2 X_A}{\partial x^2} - V_A \frac{\partial X_A}{\partial x} - \frac{\lambda \tau X_A}{1 + \frac{\rho_b}{n} \frac{\sigma_+}{\tau} f'} = \frac{\partial X_A}{\partial t}$$

where
$$D_A = \frac{D'_x}{1 + \left(\frac{\rho_b}{n} \frac{\sigma_+}{\tau}\right) f'} \tag{63}$$

and
$$V_A = \frac{V_x}{1 + \left(\frac{\rho_b}{n} \frac{\sigma_+}{\tau}\right) f'} \tag{64}$$

Equations 63 and 64 will be referred to as the retardation equations, since they predict the reduction in the dispersion coefficient and average velocity of cation A^+ relative to the dispersion coefficient, D'_x, and velocity, V_x, of a nonretardable ion. The term V_A/V_x is the relative ionic velocity of Lieberman and Simpson (1960) that was introduced at the beginning of this Chapter. The term $\rho_b \sigma_+$ expresses the total

cation-exchange capacity per unit volume of porous medium, whereas the term n_T expresses the amount of all competing cations (in this case A^+ and B^+) in solution per unit volume of the porous medium. The term f' is called the separation factor (Helferrich, 1962), or the selectivity quotient (Amphlett, 1964) for the case in which A^+ is present only in trace quantities. In this latter case, f' is therefore equivalent to K_B^A in Equation 37. Various exchange isotherms are shown in Figure 27, including an example of a linear isotherm for which $f' = 1$. For linear ion-exchange isotherms in which A^+ is a trace ion the term $\sigma_+ f'/\tau = K_d^A$, the distribution coefficient of A^+ in Equation 36.
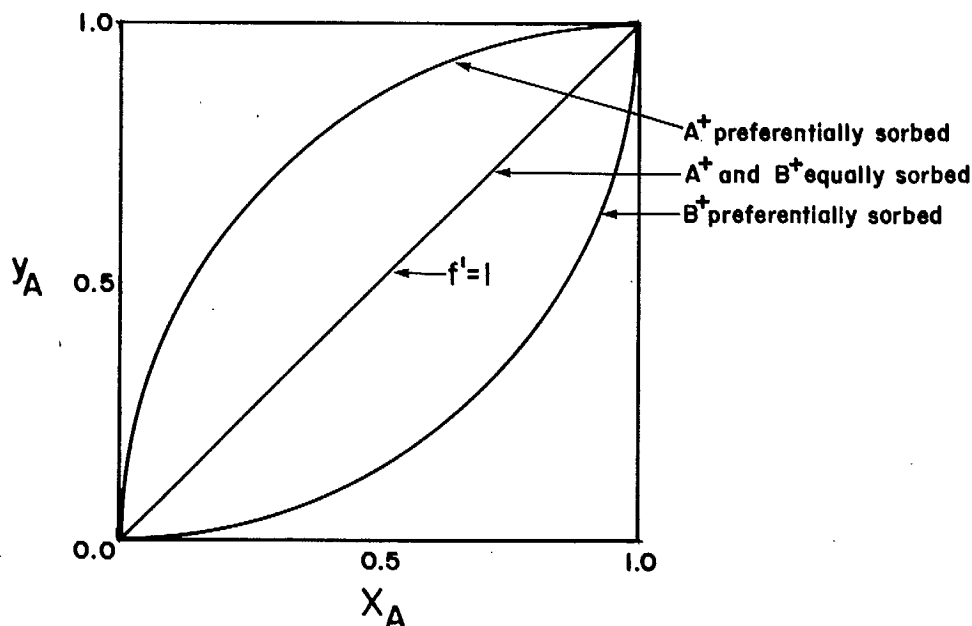
Figure 27. Exchange isotherms.

Ion exchange is an example of a process whereby chemical equilibrium is achieved between the solution and adsorbed phases. Thus, because of changing conditions in solution (groundwater) chemistry, there is a continual migration of A^+ cations between these two phases. Since an adsorbed ion is available for neither convective nor dispersive transport, the observed dispersion and velocity of a group of such ions (non-conservative contaminants) are reduced relative to the dispersion and velocity experienced by ions which do not undergo sorption (conservative contaminants). The extent to which these adsorbable ions are retarded is governed by the magnitude of the independent variables in the denominators of Equations 63 and 64. In Chapter 4 these are discussed in detail with reference to Canadian conditions.

RETARDATION OF THE "WASTE" RADIONUCLIDES

In Chapter 1, 15 radionuclides were introduced as the "waste" radionuclides (Table 4) on the basis of their likelihood of being sources of radioactivity in wastes

intended for storage in the shallow subsurface. The retardation of these radionuclides is now briefly considered in terms of the geochemical processes discussed in this Chapter. They are introduced on the basis of their position in the periodic table in Figure 28, which also lists their atomic numbers and weights.

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
1 H 1·008																	2 He 4·003
3 Li 6·941	4 Be 9·012											5 B 10·81	6 C 12·01	7 N 14·01	8 O 16·00	9 F 19·00	10 Ne 20·18
11 Na 22·99	12 Mg 24·31											13 Al 26·98	14 Si 28·09	15 P 30·97	16 S 32·06	17 Cl 35·45	18 A 39·95
19 K 39·10	20 Ca 40·08	21 Sc 44·96	22 Ti 47·90	23 V 50·94	24 Cr 52·00	25 Mn 54·94	26 Fe 55·85	27 Co 58·93	28 Ni 58·71	29 Cu 63·55	30 Zn 65·37	31 Ga 69·72	32 Ge 72·59	33 As 74·92	34 Se 78·96	35 Br 79·90	36 Kr 83·80
37 Rb 85·47	38 Sr 87·62	39 Y 88·91	40 Zr 91·22	41 Nb 92·91	42 Mo 95·94	43 Tc 98·91	44 Ru 101·1	45 Rh 102·9	46 Pd 106·4	47 Ag 107·9	48 Cd 112·4	49 In 114·8	50 Sn 118·7	51 Sb 121·8	52 Te 127·6	53 I 126·9	54 Xe 131·3
55 Cs 132·9	56 Ba 137·3	57 La 138·9	72 Hf 178·5	73 Ta 180·9	74 W 183·9	75 Re 186·2	76 Os 190·2	77 Ir 192·2	78 Pt 195·1	79 Au 197·0	80 Hg 200·6	81 Tl 204·4	82 Pb 207·2	83 Bi 209·0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226·0	89 Ac (227)															

LANTHANIDES	57 La 138·9	58 Ce 140·1	59 Pr 140·9	60 Nd 144·2	61 Pm (147)	62 Sm 150·4	63 Eu 152·0	64 Gd 157·3	65 Tb 158·9	66 Dy 162·5	67 Ho 164·9	68 Er 167·3	69 Tm 168·9	70 Yb 173·0	71 Lu 175·0
ACTINIDES	89 Ac (227)	90 Th 232·0	91 Pa 231·0	92 U 238·0	93 Np 237·0	94 Pu (242)	95 Am (243)	96 Cm (248)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

Figure 28. Periodic table of the elements.

Group IA Elements--^{3}H, ^{134}Cs and ^{137}Cs

Only two radioelements are of consequence here: the radioisotope of hydrogen, i.e., tritium, and the radioisotopes of cesium. In both cases the only possible mechanism of retardation is adsorption from solution.

Tritium, which is usually in the form of HTO in natural waters, is generally considered not to be significantly adsorbed in any large amount and therefore has an ionic velocity of unity (e.g., Baetslé, 1969). This is not to suggest that the exchange of tritium for hydrogen does not or cannot occur; in fact, the field experiments of Jordan, Stewart and Kline (1974) indicate that tritium exchange may be considerably more important than previously believed.

The fixation (i.e., irreversible adsorption) of radiocesium in dilute solutions by micaceous minerals such as illite, muscovite and biotite has received considerable attention from research workers in the United States. An early interpretation of this fixation reaction was that microconcentrations of radiocesium were fixed to the micas by their precipitation on the mica surface (Schulz, Overstreet and Barshad, 1960). This conceptual model is now in disfavour, since it is unlikely that the saturation of cesium salts occurs in most shallow groundwater flow systems and because a better conceptual model is now available.

This improved paradigm was developed by Tamura and Jacobs at the Oak Ridge National Laboratory, Tennessee (Tamura, 1972). They showed that the highly selective response of illite for ^{137}Cs was due to the 10 Å c-axis spacing of the illite unit cell. To demonstrate the importance of this spacing Tamura and Jacobs saturated a hydrobiotite with potassium, therefore reducing its c-axis spacing from 12.5 Å to 10 Å, and then observed increased radiocesium adsorption despite having reduced the cation-exchange capacity from 70 meq/100 g to 10 meq/100 g (Tamura, 1964). They concluded that the selectivity for ^{137}Cs was due to the limited access of other ions into the interlayer positions near the edges of the illite crystallites.

In Table 14, values of K_d are listed for vermiculite, illite and kaolinite in distilled water and in 0.1 N NaCl. The competition between Na^+ and Cs^+ for ion-exchange sites is particularly obvious for vermiculite and kaolinite. The K_d of illite, however, was actually 10% greater in the case of 0.1 N NaCl. This was probably due to ion-dipole reactions between Cs^+ and Na^+ by which the ion with the larger hydrated radius (Table 10) tends to become displaced by the ion of smaller hydrated radius (Stumm and Morgan, 1970, pp. 492-493). Wahlberg and Fishman (1962) obtained distribution coefficients of the same order of magnitude for kaolinite and illite. Jenne and Wahlberg (1968) reported selectivity quotients for the reaction:

$$2\ Cs^+ + Ca^{2+}\ R_2 - \overset{\rightarrow}{\leftarrow}\ 2\ Cs^+\ R^- + Ca^{2+} \qquad (65)$$
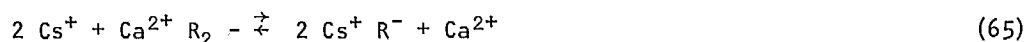
varying from 2.8×10^3 for kaolinite to 4×10^7 for illite. These results were for the case of tracer-level cesium (approximately 10^{-10} N) in the presence of 0.003 N $CaCl_2$. The selectivity quotient which they measured in a stream rich in illitic sediments, however, was of the order of 10^4 rather than 10^7. They speculated that coatings of organic matter and/or iron and manganese oxides on the sediment formed a diffusion barrier which to some extent prevented the adsorption of radiocesium by the sediments. A similar suggestion has been made by Evans and Dekker (1966) concerning Podzolic soils. For this to be the case it would imply that the zero point of charge of the oxide coatings was greater than the pH of the stream- or soil-water containing the cesium.

Table 14. Distribution Coefficients for ^{137}Cs and Selected Clay Minerals

Clay mineral (<2-μm fraction)	Cation-exchange capacity (meq/100 g)	K_d Distilled water	K_d 0.1 N NaCl
Vermiculite	127	52,000	2,700
Illite	20.0	26,000	28,600
Kaolinite	11.2	2,500	94

Source: Tamura (1972).

Group IIA Elements--^{90}Sr, [226]Ra and [228]Ra

The retardation of the Group IIA radioelements may occur because of either sorption or precipitation processes. Although relatively little is known of the environmental mobility of the radium isotopes, much can be inferred from the behaviour of their sister element ^{90}Sr, which has been exhaustively studied. As witness to this there have been several field tests of ^{90}Sr migration which have permitted a privileged view of radiostrontium mobility. Table 15 summarizes the mobility of this isotope in terms of relative ionic velocity--a parameter introduced at the beginning of this Chapter.

Table 15. Relative Ionic Velocities of ^{90}Sr in Porous Media

Relative ionic velocity	Porous medium	Cation-exchange capacity (meq/100 g)	Source
0.011	Sand and gravel	7.69	Ewing (1959)
0.03	Glaciofluvial sands	1	Parsons (1963) and Jackson *et al.* (1977)
0.004	Sandstone	2.5	Tamura (1972)
0.35	Sands and gravels	(K_d = 0.6)	Baetslé (1969)

Wahlberg and his colleagues (Wahlberg and Dewar, 1965; Wahlberg *et al.*, 1965) studied the exchange adsorption of Sr in pure clay-mineral aqueous systems and concluded that mass-action equilibria reactions adequately described the uptake of Sr onto the clays. Values of the mass-action equilibrium constants are shown in Table 16. They further concluded that only when the concentration of stable plus radioactive Sr is greater than 4.4 mg/l will the stable ion effectively compete for exchange sites with the radioactive ion. Few natural waters have stable Sr values greater than 4.4 mg/l. Those at Chalk River contain 0.12 mg/l (Jackson *et al.*, 1977). Exceptions include the waters draining tills rich in $SrSO_4$ in Ohio, which have concentrations of up to 8.0 mg/l Sr^{2+} (Steuber *et al.*, 1975), and the interstitial waters of the Chalk of southern England (Edmunds, Lovelock and Gray, 1973).

Table 16. Selectivity Quotients for the Reactions
$MR_2 + Sr^{2+} \rightleftharpoons Sr\ R_2 + M^{2+}$
or $2MR + Sr^{2+} \rightleftharpoons Sr\ R_2 + 2M^+$ [using
tracer-level strontium in the presence
of a single competing cation (M^+ or
M^{2+})]

Cation-saturated clay	K_M^{Sr}
Na^+-montmorillonite	1.1
Ca^{2+}-montmorillonite	1.1
Na^+-illite	3.0
Ca^{2+}-illite	1.1
Na^+-kaolinite	9.0
Ca^{2+}-kaolinite	1.2

Source: Wahlberg *et al.* (1965).

Tamura (1972), however, takes a pessimistic view of predicting the migration of radioisotopes in groundwater flow systems solely from the results of laboratory studies of pure clay systems:

> However, because most natural formations contain hydrous iron
> and aluminum oxides, whose properties are not well characterized,
> it is not yet possible to predict reliably the K_d of strontium
> even for formations whose clay mineralogy is known.

Tamura (1964) showed that deviations between the observed K_d and that calculated from mass-action equilibria expressions for Sr adsorption on an illitic shale were due to increased Sr adsorption by hydrous iron oxide particles on the shale. Nevertheless, it is possible for amorphous hydrous oxides to decrease the exchange capacity by blocking exchange sites, as was noted in the previous section on cesium.

Laboratory studies of Sr sorption by hydrous metal oxides have been reported by Egorov and Lyubimov (1969) and Kurbatov, Kulp and Malk, Jr. (1945). Table 17 shows the distribution coefficients given by Tamura (1972) for various minerals relative to radio-strontium in natural waters at pH = 7.5 and pH = 10.0. The increase in K_d with pH is due to the increased number of negatively charged potential-determining ions (i.e., OH^-) that are adsorbed to the fixed layer of the colloids at the increased pH level. This necessitates the sorption of an increased number of positive counterions (e.g., Sr^{2+}) into the mobile layer to maintain the electrical neutrality of the double layer. It can be seen from Table 17 that the selectivity quotient, f' or K_B^A, is strongly pH dependent.

Recently, Kinniburgh, Syers and Jackson (1975) showed that ^{90}Sr could be adsorbed to amorphous, hydrous, iron and aluminum oxides even when the solution pH was less than the pH_{ZPC}. They attributed this phenomenon to the chemisorption of the

strontium within the fixed layer of the oxide surfaces. Their conceptual models provide an interesting theoretical basis for discussing the several observations of radiostrontium fixation by silicate materials (e.g., Ophel, Fraser and Judd, 1971; Frere and Champion, 1967).

Table 17. Distribution Coefficients of Selected Materials for ^{90}Sr in Natural Waters

| Material | Size or area* | K_d | |
		pH = 7.5	pH = 10
Montmorillonite	<2 μm	506	–
Illite	<2 μm	117	760
Kaolinite	<2 μm	55	257
Alumina	230 m^2/g	2100	34,000
Muscovite	<50 μm	82	–
Biotite	<50 μm	48	–
Quartz	<50 μm	0	–

*Size in micron diameter; area in square metres per gram.

Source: Tamura (1972).

Studies involving radiostrontium retardation by precipitation processes involving calcium carbonate have already been discussed (Jenne and Wahlberg, 1968; Halevy and Tzur, 1964). As the data in Table 13 imply, however, gypsum (i.e., $CaSO_4 \cdot 2H_2O$) may also be a significantly receptive host lattice for radiostrontium. The generally low level of strontium in the waste plumes referred to in Table 15 makes the direct precipitation of strontium salts unlikely.

Because of its relatively small hydrated radius we might expect that radium is the most strongly adsorbed of all Group IIA elements. Furthermore, we should expect that its chemical similarity with barium should permit it to be coprecipitated with $BaSO_4$ (Table 13). The upper limit of its concentration in groundwaters should be controlled by the insolubility of $RaSO_4$ (pK_{eq} = 10.37; Sillen, 1964). For a sulphate concentration of 10^{-3} M (96 mg/l), the radium concentration would be 4.27 x 10^{-5} mg/l. For ^{226}Ra this is equivalent to 4.2 x 10^{-5} μCi/ml, which is three orders of magnitude greater than its MPC (Table 4). For ^{228}Ra this is equivalent to 1.2 x 10^{-2} μCi/ml, which is six orders of magnitude larger than its MPC. It would not be inappropriate for Canada to invest some of its scientific resources in studying this element, as it would seem to present some kind of environmental hazard.

The Transition Metals--^{54}Mn, ^{55}Fe, ^{60}Co, ^{65}Zn and ^{106}Ru

Two important features characterize the aqueous chemistry of these metals and hence determine their mobility in hydrogeological environments. First, all with

the exception of zinc have variable oxidation states or valences (e.g., Fe^{2+} and Fe^{3+}), and secondly, they possess a great propensity to form inorganic and organic complex ions in solution (e.g., $FeHPO_4^+$). These two features complicate the adsorption or precipitation of these metals. By referring to Figure 26, however, we can attain some perspective on the possible mechanisms of retardation of these radionuclides.

If first only redox reactions are considered, which cause the partitioning of an element into two or more valence states, then in the lower Eh range retardation may be due either to adsorption alone in the low pH range or to adsorption together with precipitation as the carbonate, phosphate or sulphide at higher pH levels and at the appropriate concentrations of the anions in question. In the higher Eh range the hydrous metal oxide may be the stable mineral phase. Similar Eh-pH diagrams are available for manganese (Hem, 1970, p. 128), cobalt (Garrels and Christ, 1965, pp. 248-249) and zinc (Hem, 1972b). Other useful Eh-pH diagrams for iron can be found in Hem (1970, pp. 118-119) and Whittemore and Langmuir (1975).

The hydrogeological implications of the complexing of radiocontaminants by inorganic or organic ligands are largely unknown. What is known is that these ligands may complex the transition metal ions and therefore alter their availability for adsorption or precipitation from solution. Duursma (1970) has shown that the adsorption of radioactive cobalt and zinc is significantly decreased in the presence of dissolved organic carbon (DOC) compounds, which are found in all natural groundwaters (Leenheer et al., 1974). This decrease is due to the formation of organo-cobalt and organo-zinc complexes in which the positive cationic charge is neutralized by anionic groups in the DOC molecule rather than by anionic groups on colloidal surfaces. Figure 29 shows the effect of increasing the DOC concentration on the adsorption of ^{60}Co and [65]Zn by clayey, alluvial sediments. It should also be noted that organic complexing of cobalt and zinc increases their solubility in solution, therefore reducing the effectiveness of precipitation as a retarding mechanism. The complexing of iron and manganese by organic ligands has been studied by Hem (1960 and 1965).

Therefore the mobility and retardation of transition-metal radiocontaminants is very much dependent on the solution chemistry, in particular the pH, Eh, ionic strength and ligand concentration. Being at least divalent, these ions would tend to be readily adsorbed. Furthermore, they have relatively insoluble phosphate, sulphide, carbonate and hydroxide mineral phases (Table 12). To determine the extent of the retardation of these transition metals in any particular hydrogeological environment, however, it would be necessary to conduct a detailed hydrogeochemical analysis of that groundwater flow system. Unfortunately, there are relatively few data to use as guidelines on the distribution coefficients for these radionuclides. Nevertheless, since ^{60}Co is an important waste product of the CANDU reactor, it seems that a brief review of its sorption chemistry is warranted, since sorption

rather than precipitation would seem to be the controlling hydrogeochemical retardation mechanism in this case.

Sediment: Fine clay

Water: $Ca^{2+} = 1.3 \times 10^{-3}M$
$Mg^{2+} = 4.45 \times 10^{-3}M$
$Co^{2+} = 1.6 \times 10^{-8}M$
$Zn^{2+} = 1.7 \times 10^{-6}M$
pH = 8.18

K_d

^{65}Zn

^{60}Co

Millimoles Organic ligand/litre
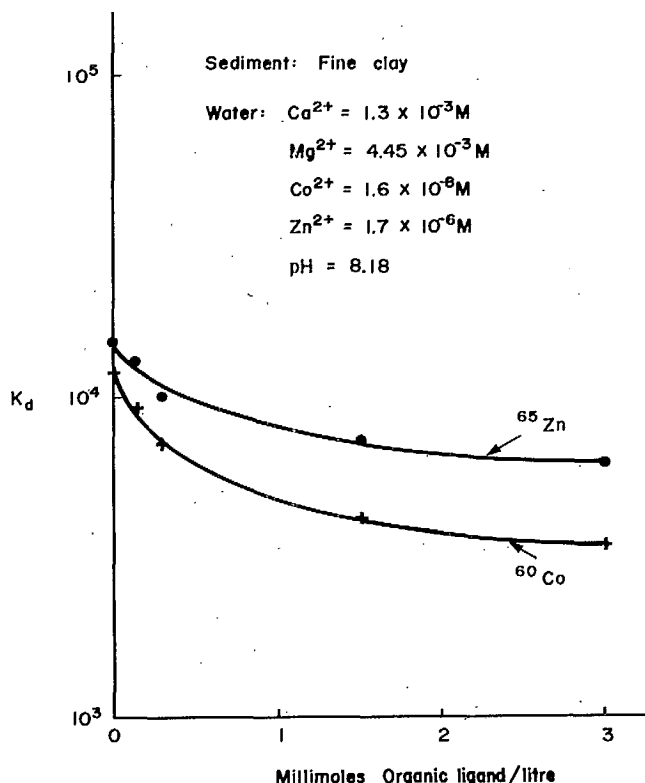
Figure 29. Variation in the distribution coefficient, K_d, with dissolved organic ligand concentration (after Duursma, 1970).

Recent work has shown that the adsorption of cobalt by colloids is a very complex combination of chemisorption and hydrolytic processes. Early work by Tiller and Hodgson (1962) pointed to the pH dependence of cobalt sorption by clays and the importance of the nature of the octahedral layer of the clay mineral. Tiller and Hodgson (1962) and Reynolds (Tamura, 1972) noted that muscovite readily adsorbed ^{60}Co, giving a $K_d = 25,000$ for freshly ground material in the 20-μm to 2-μm size fraction (Tamura, 1972). Reynolds concluded that hydrous aluminum oxides were the cause of this high adsorption. The pH dependence is a direct result of the Type 2a electrical double layer of such a hydrous metal oxide. Further evidence of a hydrous metal oxide control on cobalt adsorption can be found in the study of radionuclide sorption by Jenne and Wahlberg (1968) in White Oak Creek near the Oak Ridge National Laboratory, Tennessee. They concluded that the irreversible adsorption of ^{60}Co by the stream sediments was due to the uptake of the radionuclide by hydrous manganese and iron oxides.

The mechanisms of Co adsorption have been investigated by Murray, Healy and Fuerstenau (1968), who suggested that Co was adsorbed by hydrous manganese oxide by surface oxidation of Co^{2+} to Co^{3+}, and by Healy, James and Cooper (1968), who showed that the

adsorption of Co^{2+} at a silica-water interface was dependent on both the pH and the Co concentration of the solution. Healy and coworkers separated the process into three parts. At low pH (<6.0) and at low cobalt concentrations (<10^{-5} M), Co^{2+} is adsorbed into the mobile layer and can therefore be desorbed. At a pH > 6.5 and at a concentration lower than that which would cause the precipitation of $Co(OH)_2$, Co^{2+} is sorbed by the fixed layer. Finally, when the pH is in the range of 8.5-9.0, $Co(OH)_2$ is formed on the silica surface.

Routson (1973) has noted that ^{60}Co was poorly sorbed by the glaciofluvial sediments at Hanford because it forms soluble anionic and uncharged complexes. The significance of this factor vis-à-vis Canadian sediments is unknown, but since radio-cobalt is such an important by-product of CANDU-generated power it deserves considerable attention.

Lanthanides and Actinides--^{144}Ce, ^{232}Th, ^{238}U and ^{239}Pu

Lanthanides and actinides are also transition metals (of the third and fourth series); what has been stated for the first and second transition metal series concerning redox and complex-ion formation processes is also applicable to them. For instance, Routson (1973) has stated that the lanthanides disposed of in the glaciofluvial sediments at Hanford are generally precipitated as insoluble hydroxides, although they can be made mobile by organic ligands. Hem (1970, p. 213) has suggested that thorium tends to be readily sorbed by clays and not to be carried "extensively" in solution. Uranium, whose redox reactions in sandstone aquifers have been reviewed by Adler (1974), is mobile as the oxidized hexavalent form UO_2^{2+} but not as the reduced tetravalent ion.

Distribution coefficients for these radionuclides are rare or nonexistent, although there are some data on ^{144}Ce (e.g., Jenne and Wahlberg, 1968). There is now, however, a rapidly increasing interest in plutonium and americium due to the fission-able value of the former which can be extracted from the spent fuel by complex fuel-reprocessing operations. It is these operations that create what are generally con-sidered to be the true high-level radioactive wastes.

Unfortunately, the mobility of plutonium in typical, Canadian hydrologic systems is presently unknown (Francis, 1973). Our present understanding of the aqueous chemistry and geochemistry of the element may be summarized as follows.

Early studies by Rhodes at Hanford pointed out that (1) the adsorption of ^{239}Pu by soil is pH dependent, (2) plutonium in aqueous systems is in the form of

a "polymer," or radiocolloid, and (3) plutonium is generally very insoluble and therefore has a very low environmental mobility except that it is readily desorbed from soil by complexing with the acetate anion, $C_2H_3O_2^-$ (Rhodes, 1957a, 1957b). Poor plutonium adsorption by soil in the presence of organic complexing agents has also been mentioned by Routson (1973). Further work at Hanford reported by Hajek (1966) gives a distribution coefficient for total alpha activity (plutonium plus americium) greater than 10^4 ml/g.

Recent work by Tamura (1972) also attests to the importance of pH in the uptake of ^{239}Pu. Table 18 shows that with the exception of apatite, the distribution coefficient of ^{239}Pu increased with the pH of the suspension in which the uptake was measured. The very high value of K_d for apatite may be due to the similarity in the ionic radius of Pu^{4+} (0.93 $\overset{o}{A}$) and Ca^{2+} (0.99 $\overset{o}{A}$), which suggests that the uptake of ^{239}Pu by apatite might be due to isomorphous replacement.

Table 18.   Removal of Plutonium from Water with pH 7 by Selected Sorbents (0.1 g sorbent/25 ml)

Mineral	Percentage removal	Distribution coefficient	Suspension pH
Montmorillonite	71.6	630	9.20
Activated Al_2O_3	75.1	755	8.35
Kaolinite	58.5	352	6.25
Illite	34.0	129	5.90
Quartz	0.0	--	6.35
Apatite	99.7	83,000	6.70

Source: Tamura (1972).

Among the first studies of the aqueous chemistry of plutonium are those of Andelman and Rozzell. In their first paper, they showed that in the pH range of natural waters the dominant form of plutonium is the radiocolloid $Pu(OH)_4$; the size of this particle increases with the age of the colloid (Andelman and Rozzell, 1970). In their second paper, they considered the adsorption of plutonium onto silica surfaces and showed that the uptake of ^{239}Pu was dependent on pH, the ionic strength of ^{239}Pu and the age of the radiocolloid. Furthermore, they pointed out that plutonium adsorption decreased with increasing bicarbonate (HCO_3^-) concentration (Rozzell and Andelman, 1971).

More recently, Cleveland and Rees (1976) reported that the solubilization of plutonium and americium (a radioactive daughter product of plutonium) in contaminated soil by fulvic acid is "slight." They noted that in no instance did the concentration of either radionuclide approach the drinking water limits.

Oklo

Approximately two billion years ago, a very rich deposit of uranium ore in what is now the republic of Gabon in West Africa achieved criticality and began operating as a nuclear reactor (Cowan, 1976). This natural fission reactor continued to operate for approximately 0.5 million years during which time it produced approximately six tons of fission products by the fissioning of ^{235}U. Scientists in France and at the Los Alamos Scientific Laboratories in New Mexico set out to determine the fate of these fission products so that their long-term mobility while in natural geological storage might be deduced. Results announced so far (e.g., IAEA, 1975) indicate that most of the significant "waste" radionuclides were immobilized over geologically long periods of time.

The sedimentary deposits at Oklo, Gabon, in which the uranium ore underwent nuclear fission were laid down during the Precambrian Era as marine deltaic deposits rich in decaying marine algae. Uranium from nearby continental volcanic formations was transported into this deltaic environment by rivers and was subsequently chemically reduced, due to the reducing environment produced by the decaying algae, to uraninite (UO_2). Due to later tectonic activity these sedimentary deposits, by now lithified as shale, were tilted and faulted, providing structural traps in which massive secondary metallogenesis by groundwater occurred. Several parts of the ore body contained 80% uranium. In some of these very rich ore zones criticality was achieved. It is of great significance that these reactor zones were probably saturated or nearly saturated with groundwater which acted as a neutron moderator--in very much the same way that heavy water acts in a CANDU reactor.

Table 19. Mobility of Some "Waste" Radionuclides in the "Zone 2" Reactor at Oklo

Element	Mobility
^{90}Sr (now ^{90}Zr)	Small migration, most decayed in place
Ru	Large fraction retained, redistributed
Cs	Measurable traces (as Ba), mostly missing
Ce	Very little migration
^{232}Th (now ^{236}U, ^{240}Pu)	Mostly retained
^{235}U (now ^{239}Pu)	No ^{239}Pu separation from ^{238}U

Source: Apt, Bryant and Brookins (1976).

The mobility of what we have identified as the "waste" radionuclides is summarized in Table 19. Only cesium showed significant mobility in the Oklo shale; the other radionuclides were largely retained at the reactor site. Brookins (1976) recently completed a preliminary study of the plutonium behaviour at Oklo by the

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Eh-pH stability field approach and concluded that the reasons for the immobility of plutonium at Oklo were fivefold:

(1)   A nearly ideal solid solution is formed by UO_2 and PuO_2;

(2)   The commonest solid species of plutonium, PuO_2, is stable over most of the Eh-pH conditions encountered in nature;

(3)   Over geologically short time periods $Pu(OH)_4$ apparently ages to PuO_2;

(4)   Carbonate complexes with Pu (VI), analogous to those of uranium, probably do not fall in the water stability field and, if so, only under very high Eh-pH conditions; and

(5)   If present at all, Pu-organic complexes did not affect the formation and retention of plutonium.

Transport Variables and Retardation Processes in Surficial Deposits

In Chapters 2 and 3, the general equations of groundwater flow and subsurface transport and retardation were introduced and it was suggested that the variables in these expressions could be measured and the results applied to hydrogeological site evaluations. It is relevant to note that the subsurface mobility of many radionuclides is the subject of considerable current research and that the somewhat over-simplified manner in which transport and retardation must be approached within the scope of this report should not detract from the complexity and the interaction of the processes which ultimately determine the mobility of many contaminants in the groundwater environment.

The general retardation Equations 63 and 64 contain some of the relevant variables related to subsurface contaminant movement. These variables, as well as the hydraulic conductivity (which is included in the V_x term in Equation 64) and the dispersion coefficient, $D_x^!$, are considered in this Chapter because they represent some of the important parameters with respect to the operating or potential transport and retardation characteristics of many hydrogeological environments. The variables are discussed from a practical point of view and a compilation of some of the available data pertaining to each of them is presented. A discussion of the role of precipitation in subsurface radionuclide transport is given, followed by a review of the possible contaminant transport and retardation characteristics of fractured till.

THE TRANSPORT VARIABLES

The variables relevant to transport and sorption-related retardation in groundwater flow systems that are considered in this Chapter are

K -- Hydraulic conductivity of the transmitting medium;

σ_+ -- Cation-exchange capacity of the transmitting medium;

τ -- Total (competing) cation concentration of the transporting solution;

ρ_b -- Bulk density of the transmitting medium;

n -- Porosity of the transmitting medium;

$D_x^!$ -- Coefficient of hydrodynamic dispersion; and

$f^!$ -- Selectivity quotient.

The hydraulic conductivity, K, of the transmitting medium is one of the most important as well as one of the most variable of the parameters under discussion in this Chapter. The bulk effective hydraulic conductivity is the main factor in determining the net mass flux through any particular unit and, as such, is an extremely important variable in any evaluation of contaminant release to the biosphere or potential dose rates as the consequence of subsurface radionuclide transport. Further importance of the hydraulic conductivity is evident from Darcy's law and the Dupuit-Forcheimer relation (see Equation 9), which describes the average linear pore-water velocity, V_x, in Equation 56. The expression for the average linear pore-water velocity can be written in the form

$$V_x = \frac{K}{n\sigma_N} \text{ grad } h \tag{66}$$

where n is the porosity, σ_N is an empirical constant and grad h is the gradient of hydraulic head. The pore-water velocity is clearly directly proportional to the hydraulic conductivity of the transmitting medium. Little is known about σ_N values for deposits with nonuniform grain size distributions; limited experimental data on relatively uniform sands, however, indicate that σ_N is close to unity for these materials. The usual approach is to assume σ_N as unity and proceed with the simple Dupuit-Forcheimer relation, but this assumption requires verification in heterogeneous and nonuniform porous media. The relative importance of the porosity term with respect to groundwater velocities is discussed later.

In considering the hydraulic conductivity of surficial deposits in this Chapter, emphasis is placed on the conductivity of glacial tills and lacustrine clays, which constitute a major percentage of the surficial cover of Canada. The hydraulic conductivity of deposits such as outwash sands and gravels is relatively easily estimated, since these types of deposits are the focus of many water supply studies. On the other hand, there is a relative paucity of data concerning the conductivity of tills and clays, particularly the conductivity that applies to the actual field situation. This section contains a summary of the data available in the literature on the hydraulic conductivity of glacial till and lacustrine clays.

Table 20 lists hydraulic conductivities for glacial tills in Canada and the northern United States. The conductivity of material that is genetically termed "till" ranges from about 10^{-10} cm/s for intergranular values obtained from laboratory consolidation tests on clay-loam tills, to about 10^{-3} cm/s obtained in field studies on sandy tills. Intergranular conductivity values obtained by permeameter tests do not usually apply to the actual field situation, since laboratory samples are normally disturbed and repacked before testing. If undisturbed samples are used

for laboratory permeameter or consolidation testing considerable care must be taken to ensure that a representative sample has been obtained. If the undisturbed samples are tills or lacustrine clays which exhibit fracture systems it may be impossible to obtain a sample which contains a significant number of fractures. In the case of fractured tills, it is necessary to determine the bulk effective conductivity which applies to the deposit as a hydraulically continuous unit. Bulk hydraulic conductivity values (which include the effect of fractures) have been obtained for tills and clays from the Interior Plains in the range from 10^{-6} cm/s to 10^{-7} cm/s (Meneley, 1970; Grisak and Cherry, 1975; Grisak *et al.*, 1976).

The intergranular hydraulic conductivity reported for glaciolacustrine clays is only slightly less variable than that for tills, ranging from about 10^{-5} cm/s to 10^{-10} cm/s (Table 21). These clays, however, may also be fractured (Gilliland, 1965; Render, 1970; Beswick, 1971; Grisak and Cherry, 1975) and the fractures will again influence the bulk hydraulic conductivity of the deposit, although their effect on the net flux through the unit will likely not be as significant with respect to radionuclide transport as their effect on the convective velocity in the fractures.

The hydraulic conductivity of surficial deposits can be determined in several different ways, with the choice of methods strongly influenced by the type of deposit. For a coarse-grained deposit where intergranular flow is dominant, the appropriate methods include aquifer pumping tests, single-well response tests, tracer injection tests or *in situ* tracer analyses (i.e., stable isotopes or fluorocarbons) as well as laboratory permeameter tests on relatively undisturbed samples. For unfractured fine-grained deposits such as tills and clays, the methods used for determining hydraulic conductivity include permeameter and consolidation tests on relatively undisturbed samples, single-well response tests and aquifer pumping tests with piezometer response measurements in the fine-grained deposits that confine the aquifers. The field and laboratory methods available for determining the hydraulic conductivity of fractured media such as tills or clays have been summarized by Grisak *et al.* (1976).

A common method used to estimate the intergranular hydraulic conductivity of unconsolidated material is based on the empirical equation presented by Hazen (1893). Although the relation has been refined in recent years, the Hazen formula

$$K(cm/s) = C_u \, d_{10}^2 \tag{67}$$

essentially relates the hydraulic conductivity, K, to the effective grain-size diameter, d_{10}, by means of the coefficient, C_u (which varies from about 50 $cm^{-1} \, s^{-1}$ to 150 $cm^{-1} \, s^{-1}$).

Table 20. Hydraulic Conductivity of Glacial Till

Hydraulic conductivity (K) (cm/s)	Method	Area	Source	Type of hydraulic conductivity
10^{-6} to 10^{-7}	Estimated groundwater recharge owing to infiltration	Saskatoon, Saskatchewan	Meneley (1970)	Field value for vertical K
10^{-6} to 10^{-7}	Calculated groundwater recharge	Illinois	Walton (1965)	Field value for vertical K
10^{-7}	Calculated from consolidation tests on soils developed on till	Waterloo County, Ontario	Lee (1970)	Laboratory intergranular K
3.6×10^{-4} to 1.2×10^{-5}	Leaky artesian analysis*	Regina, Saskatchewan	Lissey (1962)	Field value for vertical K
1.2×10^{-4}	Tritium determinations on groundwater in upper 30 ft	The Missouri Coteau, Saskatchewan	Mawson (1964)	Tracer velocity yielding K in the direction of the hydraulic gradient
3.6×10^{-4} to 1.5×10^{-4}	Estimates of hydrogeological characteristics of tills	Interior Plains	Meyboom (1967)	Represents field K below zone of active weathering
1.7×10^{-4} to 4.5×10^{-7}	Hvorslev tests on piezometers[†]	Good Spirit Lake, Saskatchewan	Freeze (1969c)	Field value for K immediately around piezometer-screened interval
7.2×10^{-5}	Leaky artesian analysis*	Gravelbourg, Saskatchewan	Freeze (1969b)	Field value for vertical K
1.2×10^{-4}	Leaky artesian analysis*	Moncton, New Brunswick	Data from Carr (1968)	Field value for vertical K
3×10^{-5} to 3×10^{-9}	Hvorslev tests on piezometers[†]	Southeastern Manitoba	Clister (1973)	Field value for K immediately around piezometer-screened interval
1.4×10^{-10}	Calculations from consolidation tests on undisturbed samples	Average of 87 samples from Interior Plains	Grisak and Cherry (1975)	Laboratory intergranular K
2.6×10^{-8} to 5.1×10^{-10}	Calculations from consolidation tests on disturbed samples	Southeastern Manitoba	Shawinigan Engineering Co. Ltd. (1960)	Laboratory intergranular K for disturbed and remolded samples
2×10^{-7}	Digital modeling and multiple layer theory[‡]	Southeastern Manitoba	Grisak and Cherry (1975)	Field and model value for bulk K
2.9×10^{-4} to 2.3×10^{-6}	Leaky artesian analysis*	Lake Ontario basin	Haefeli (1972)	Field value for vertical K

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K	Method	Location	Reference	Remarks
1.7×10^{-3}	Hvorslev tests on piezometers[†]	Guelph, Ontario	Gillham and Webber (1969)	Field value for K immediately around piezometer-screened interval
2.6×10^{-5} to 1.5×10^{-8}	Permeameter tests on diamond core samples	South Dakota	Norris (1963)	Laboratory value for vertical K
4.8×10^{-5} to 4.2×10^{-8}	Permeameter tests on driven core samples, 2 in. by 2 in.	Northeastern Ohio	Norris (1963)	Laboratory value for vertical K
7.8×10^{-6} to 1.1×10^{-6}	Leaky artesian analysis[*]	Rohrers Island, Montgomery County, Ohio	Norris (1959)	Field value for vertical K
2.6×10^{-4} to 5.1×10^{-7}	Permeameter tests on driven cores, 6 in. by 6 in.	Montgomery County, Ohio	Norris (1963)	Laboratory value for vertical K
4.8×10^{-4}	Hvorslev tests on piezometers[†]	Cochrane, Ontario	Parsons (1970)	Field value for K immediately around piezometer-screened interval
10^{-5} to 10^{-6}	Hvorslev tests on piezometers[†]	North Dakota	Sloan (1972)	Field value for K immediately around piezometer-screened interval
2.1×10^{-7}	Permeameter tests on 1-in. long samples, 4-in. diameter	North Dakota	Sloan (1972)	Laboratory value for vertical K
1.4×10^{-3} to 1.3×10^{-6}	Hvorslev tests on piezometers[†]	Southeastern Alberta	Schwartz (1975a)	Field value for K immediately around piezometer-screened interval
6.8×10^{-6}	Leaky artesian analysis	Edson, Alberta	D.H. Lennox (Personal communication)	Field value for vertical K
1.8×10^{-5}	Leaky artesian analysis	Winterburn, Alberta	D.H. Lennox (Personal communication)	Field value for vertical K
4.2×10^{-7} to 1.5×10^{-8}	Permeameter tests on relatively undisturbed samples	Kincardine, Ontario	Gorman (1972)	Laboratory value for vertical K
1.2×10^{-6} to 1.6×10^{-9}	Hvorslev tests on piezometers	Oak River basin, Manitoba	Lissey (1968)	Field value for K immediately around piezometer-screened interval

[*]Hantush and Jacob (1955).
[†]Hvorslev (1951).
[‡]Neuman and Witherspoon (1972).

Table 21. Hydraulic Conductivity of Glaciolacustrine and Marine Clays

Hydraulic conductivity (K) (cm/s)	Method	Area	Source	Type of hydraulic conductivity
10^{-8} to 2.6 x 10^{-10}	Calculated from consolidation tests on undisturbed samples	Glacial clay deposits from the prairies	PFRA*	Laboratory intergranular K
3.6 x 10^{-9}	Calculated from consolidation tests on undisturbed samples	Lake Agassiz, clays, Manitoba	Grisak and Cherry (1975)	Laboratory intergranular K
10^{-5} to 10^{-7}	Calculated from consolidation tests on core samples	Glaciolacustrine clays from bottom of Lake Ontario	Haefeli (1972)	Laboratory intergranular K
5 x 10^{-8} to 1 x 10^{-10}	Calculated from consolidation tests on undisturbed and disturbed samples	Lake Agassiz, Manitoba	Martin (1961)	Laboratory intergranular K
1.2 x 10^{-7}	Hazen formula (1893)	Big Otter Creek	Novakovic and Farvolden (1974)	Theoretical intergranular K

*PFRA--Prairie Farm Rehabilitation Administration written communication.

The hydraulic conductivity is then proportional to the effective grain size of the deposit and, as shown in Chapter 2, is also a function of the degree of uniformity of the particle sizes.

The grain size distribution of the particles comprising typical Canadian tills and clays has been published elsewhere; the compilation of such data in this report, however, is useful for comparative purposes.[1] Figures 30(a) to 30(d) illustrate the grain size and sorting of various tills across Canada. The tills of the Atlantic provinces have a relatively high percentage of sand [Fig. 30(a)], whereas those of southern Quebec and southern Ontario are much more clayey [Fig. 30(b)]. Tills of the Interior Plains Region [Fig. 30(c)] are less variable, and generally classify in or near the clay-loam textural category. The smaller variability of the texture of tills in the Interior Plains Region reflects the relative homogeneity of the bedrock materials within the Western Canada Sedimentary Basin, from which they are derived, as compared with more variable bedrock types of other parts of Canada. Limited data on the grain size and texture of tills in British Columbia [Fig. 30(d)] suggest that they are in the same general textural range as the tills of the Interior Plains. The bedrock of the source areas of British Columbia tills is so varied that these analyses are probably only representative of a portion of British Columbia tills. Glaciolacustrine and marine clays (Fig. 31) are much better sorted than tills and are characterized by a high percentage of silt and clay with only minor amounts of sand-sized particles.

As surficial glacial deposits in Canada are so highly variable in grain size and sorting, it is impossible to assign a "representative" hydraulic conductivity to those deposits genetically termed "glacial till." Table 20 summarizes the hydraulic conductivities of tills obtained from the literature and Table 21, those of glacio-lacustrine and marine clays.

Other coarser-grained deposits that may be found at sites under consideration for use as radioactive waste management sites are those of glaciofluvial origin. The fluvial sands of the Chalk River radioactive waste management site have a hydraulic conductivity in the order of 10^{-3} cm/s (Cherry *et al.*, 1975), whereas outwash sands and gravels, containing a higher percentage of coarse material, may have conductivities in the order 10^{0} cm/s or higher. In porous media such as the sands and gravels mentioned above, the hydraulic conductivity is predominantly controlled by the grain size distribution and the clay minerals present (even in trace amounts). Lovas (1963) indicates the conductivity of an otherwise clean and well-sorted sand can be reduced by two orders of magnitude in the presence of only 2% illite, and by four orders of magnitude in the presence of 2% montmorillonite. Montmorillonite is much more effective in reducing the hydraulic conductivity because of its expansion characteristics

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[1]Coincident with the preparation of the final draft of this report, an excellent review of the geology and texture of Canadian tills was presented by J.S. Scott at "Glacial Till--An Interdisciplinary Conference" in Ottawa, February 17-18, 1975.

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(a)

SAND AND GRAVEL
100%

100%
SILT

100%
CLAY

SURFICIAL TILLS ATLANTIC PROVINCES AND QUEBEC

O   RUSTICO MAP AREA, P.E.I.- General range, very variable
⊕   LA PATRIE - SHERBROOKE AREA, QUEBEC
●   SOUTHEASTERN P.E.I.- sandy till phase
□   SOUTHEASTERN P.E.I.- clayey till phase
⊠   SOUTHEASTERN QUEBEC (McDonald and Shilts,1971)
▧   CAPE BRETON ISLAND (McKeague et al.,1971)
△   ATLANTIC PROVINCES — reddish brown soil parent material
                                          (McKeague and Cann, 1969)
▲   NOVA SCOTIA- till (McKeague et al.,1971)

(c)

SAND AND GRAVEL
100%

100%
SILT

100%
CLAY

SURFICIAL TILLS INTERIOR PLAINS

MANITOBA
O   WINNIPEG AREA
⊕   SOUTHEASTERN AND CENTRAL MANITOBA
●   VIRDEN AREA, CENTRAL MANITOBA
□   SOUTHEASTERN MANITOBA
SASKATCHEWAN
⊠   SASKATOON AREA - Battleford till
                                 (Christiansen,1970).
■   SASKATOON AREA - Floral till (Christiansen,1970)
△   QU'APPELLE AREA
▲   WYNARD AREA
▽   ROSETOWN AREA
▼   REGINA AREA

ALBERTA
◇   EDMONTON AREA
◆   GRANDE PRAIRIE AREA
◇   AVERAGE FOR EAST CENTRAL
                              ALBERTA
◈   SOUTHERN ALBERTA (Pawluk
                              and Bayrock, 1969)
X   SUFFIELD (Schwartz,1975g)

(b)

SAND AND GRAVEL
100%

100%
SILT

100%
CLAY

SURFICIAL TILLS ONTARIO

O   WELLAND - PORT COLBORNE (Owen,1972)
⊕   LONDON - LAKE ERIE — Port Stanley till (Westgate and Dreimanis,1967)
●   ZORRA - WOODSTOCK — Port Stanley till (Westgate and Dreimanis,1967)
□   GALT - Wentworth till (Dreimanis and Vagners, 1971)
⊠   WATERLOO COUNTY - loam till (Lee,1970)
■   WATERLOO COUNTY - silty clay till (Lee,1970)
△   SCARBOROUGH - leaside till, silty and sand till (Karrow,1967)
                                          average of 46 samples
▲   SCARBOROUGH - leaside till (Karrow,1967)
▽   CASTOR, COLWOOD (McKeague et al.,1971)
▼   PEEL, LINCOLN AND HALDIMAND COUNTIES (Matthews et al.,1955)
◇   TYPICAL ILLINOIS - Illinoian (Willman et al.,1963)
                                          average of 140 samples
+   BRUCE NUCLEAR POWER DEVELOPMENT (BNPD) average of 23 samples

(d)

SAND AND GRAVEL
100%

100%
SILT

100%
CLAY

SURFICIAL TILLS BRITISH COLUMBIA

O   TASEKO LAKES MAP AREA
⊕   FRASER LOWLANDS — Surrey till
◐   FRASER LOWLANDS — Semiamu till (Armstrong,1956)
□   FRASER LOWLANDS — Seymour till
⊠   KEEWATIN - clay loam till (Clark et al.,1962)
■   CORDILLERAN - clay loam till
△   VANCOUVER ISLAND (Clark et al.,1967)

Figure 30. Textural composition of surficial tills.

SAND AND GRAVEL
100 %

100 %
SILT

100%
CLAY

GLACIOLACUSTRINE CLAYS

O   LAKE AGASSIZ, MANITOBA
⊕   LAKE REGINA CLAY, SASKATCHEWAN
●   ROSETOWN AREA, SASKATCHEWAN
□   EDMONTON AREA, ALBERTA
⊠   GRAND PRAIRIE, ALBERTA
△   B.C. INTERIOR (Clark et al.,1962)
▲   B.C. LOWLAND CLAYS (Clark et al.,1962)
▽   NORTH CENTRAL B.C. (Floate, 1966)

MARINE CLAY

■   OTTAWA, RIDEAU CLAY

Figure 31.   Textural composition of glaciolacustrine and
marine clays.

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when hydrated. The clay mineral content of coarser glaciofluvial sediments varies over a wide range, and the type of clay mineral is a function of the source of the sediment in the outwash or subglacial water.

The amount of radionuclide retardation in relatively coarse glaciofluvial deposits depends not only on the percentage of clay minerals in the deposit but on their microstratigraphic distribution as well. If the clays present are distributed in fine bands or layers rather than admixed throughout the deposit, radionuclides in solution may not be affected, since groundwater flow will be preferentially through the coarse layers. There is, however, the possibility of clay minerals being present as weathering-product coatings on the aluminosilicate minerals making up the coarse-grained layers or deposits. These weathering-product coatings could play a significant role in radionuclide retardation. They are generally not recognized in X-ray diffraction analyses, either because they are not present in the fine fraction of the sieve analyses (which is the portion usually used for X-ray diffraction) or because they are present in quantities below the detection limit.

Cation-Exchange Capacity--σ_+

In Chapter 3, the principles of ion exchange were discussed and the *cation-exchange capacity*, σ_+, was defined as the excess of counterions in the electrical double layer (on the surface of clay minerals) which can be exchanged for other cations. The ability of a hydrogeological environment to retard the movement of radiocations is largely dependent on the cation-exchange capacity of the transmitting medium. The cation-exchange capacity of a natural geologic medium (below the organic-rich soil zone) is in turn strongly dependent on the amount and type of clay minerals present. The clay minerals and their typical cation-exchange capacities were discussed in Chapter 3; this section covers the variability of clay minerals and cation-exchange capacities of Canadian surficial deposits, as revealed by available published and unpublished data.

The mineralogy or, more specifically, the clay mineralogy of glacial deposits is primarily determined by two factors: (1) the bedrock type in the source area from which the glaciers obtained the ice-transported sediment and (2) the present hydrochemical conditions in the surficial deposit. If material has been transported by continental glaciers from the igneous and metamorphic rocks of the Canadian Shield, the resulting glacial deposits will reflect the mineralogy of these source areas. Since there are few source areas for montmorillonite-type clay minerals in central and eastern Canada, the predominant clay minerals in these areas are illite-chlorite, derived from the rocks of the Canadian Shield. The clay minerals in glacial tills of the Interior Plains Region are predominantly the montmorillonite type, reflecting

the mineralogy of the bentonitic Cretaceous sediments of the Western Canada Sedimentary Basin, the primary source area of the glacial sediments in the Interior Plains.

The second factor influencing the mineralogy of surficial deposits is the present-day groundwater hydrochemical environment. Mineral stability diagrams (Garrels and Christ, 1965; Stumm and Morgan, 1970) have been used to illustrate stable diagenetic minerals under particular groundwater chemical conditions. These diagrams usually plot the concentration of H_4SiO_4 against a particular cation/H^+ concentration ratio and delineate the boundaries of stable mineral fields.

Zeolites, which are particularly good ion exchangers, have not generally been reported to occur in tills or lacustrine clays. Zeolite source areas in Canada are very limited; they typically occur in bedrock in amygdules and fissures and veins or other late-stage hydrothermal deposits (Deer, Howie and Zussman, 1969). They may also occur as aluminosilicate alteration products. Considering basic volcanics as the chief zeolite source, small parts of the glacial cover of southern and central Ontario and eastern Quebec could contain zeolites, as there are relatively extensive possible source areas in the Bancroft and Noranda-Chibougamau districts. The Interior Plateau Region of British Columbia, a basic-to-intermediate volcanic district, could also contain a relatively high percentage of zeolites; as in Quebec and Ontario, however, zeolite-rich tills (if they exist) would probably only occur on a very restricted local basis.

The glacial transport and depositional history of surficial deposits determine the texture and amount of clay-sized particles present in any particular deposit, and hence the cation-exchange capacity of that deposit. Clean, well-sorted sands and gravels in any part of Canada will likely have low cation-exchange capacities, since the necessary fine-grained clay minerals are not present. As discussed in Chapter 3, however, metal oxides and hydroxides and organic matter can also play a significant exchange role. Iron and manganese oxides are commonly present in surficial deposits in the zone of active weathering above the water table as well as throughout the zone of water table fluctuation. The oxides in these upper zones may strongly influence the cation-exchange capacity. Oxides have also been reported on fracture surfaces of tills at depths well below the water table (Grisak *et al.*, 1976) and will obviously affect the cation-exchange capacity of the fracture walls.

Organic colloids can also significantly affect the cation-exchange capacity of soil-water systems, as discussed in Chapter 3. The cation-exchange capacity of three soils in Table 11 is shown to increase proportionally with the organic carbon content. Organic matter in the form of humic substances plays an important role in determining the cation-exchange capacity of clays by blocking exchange sites, causing

their swelling or adjusting the affinity series.

The interrelationship between dissolved organic compounds and relative radio-nuclide mobilities is largely unknown. The variable oxidation states of many contaminants as well as their propensity to form organic complexes in solution sorely complicate any simplified inorganic exchange or precipitation. Organic complexing of metals in many instances not only neutralizes the positive cationic charge but also may increase their solubility in solution and reduce the effectiveness of precipitation as a retarding mechanism. Bottomley (1974) indicates that at least several milligrams per litre of dissolved organic carbon is present in the main groundwater body of a watershed in northwestern Ontario, and Jackson et al. (1977) have determined that the concentrations of dissolved organic carbon in the fluvial sand environment of the Chalk River radioactive waste management site are in a range from 1 mg/l to 4 mg/l.

The cation-exchange capacities, σ_+, below the upper soil horizons of various Canadian surficial deposits are listed in Table 22. The montmorillonites and vermiculites have a much higher σ_+ than other types of clay minerals (Table 9), and accordingly, the surficial deposits of the Interior Plains have higher cation-exchange capacities than deposits of similar grain size in central and eastern Canada. Pawluk and Bayrock (1969) found the σ_+ of tills in Alberta to range from 23 meq/100 g in the north to 68.5 meq/100 g in the southern part of the Province. Intergranular flow in deposits with such high σ_+'s might suggest that these are worthy of consideration as potential waste management sites. The fractures present in the tills and clays of the Interior Plains (Grisak et al., 1976), however, render intergranular flow a secondary process to flow through fractures. The effective surface area and consequently exchange sites available are drastically reduced in fractured tills and clays as compared with intergranular tills and clays. A discussion of a possible approach to analysis of transport in fractured till is presented at the end of this Chapter.

Cation-exchange capacities of the surficial tills and glaciolacustrine clays in Ontario, Quebec and the Atlantic provinces are generally in the order of 5 meq/100 g to 15 meq/100 g. Notable exceptions are the marine Rideau clays in the Ottawa Valley, the exchange capacities of which are about 25% to 50% higher than the rest of the clays and tills in central and eastern Canada.

The tills and clays of British Columbia have a highly variable clay mineralogy, which is reflected in a variation of the σ_+'s of the surficial deposits. Limited data available on the cation-exchange capacity of British Columbia tills and clays indicate a range from about 15 meq/100 g to 45 meq/100 g (Table 22).

In very general terms, the type of clay minerals present in surficial deposits in most parts of Canada (with the notable exception of British Columbia) can be roughly estimated from their regional location. Actual values of cation-exchange capacities below the upper soil horizon are only infrequently reported in the literature. The primary determinant of the cation-exchange capacity, the clay mineralogy, is also relatively unknown from a quantitative point of view, other than on the basis of regional variations. A review of available quantitative and qualitative data on the clay mineralogy of Canadian surficial deposits is presented below.

Atlantic Provinces

Brydon (1958) found that illite is the predominant clay mineral in the soils of the Atlantic provinces [Fig. 32(a)] and that chlorite, kaolinite and vermiculite are often present in significant amounts. According to Allen and Johns (1960), illite and chlorite dominated the clay fraction of 13 clays and shales from the Atlantic provinces. Brydon and Heystek (1958) determined that illite was the predominant clay mineral in six soil samples from Nova Scotia. McKeague, Bourbeau and Cann (1967) found that the soil parent material (till) of two samples from Cape Breton Island was chlorite-dominated with a small percentage of mica, vermiculite and montmorillonite, whereas McKeague and Brydon (1970) indicate that the predominant clay mineral in the parent material of ten reddish-brown soils in the Atlantic provinces was illite, accompanied mainly by chlorite with trace amounts of kaolinite and montmorillonite. This agrees with the later findings of McKeague *et al.* (1971) on three tills and clay-loam tills in Nova Scotia. Stanley *et al.* (1972) found that the Pleistocene muds on the Nova Scotia banks consist primarily of illite and chlorite, with less than 5% montmorillonite.

The clay mineralogy of the marine-overlap clay deposits of the Maritimes and Quebec, which might possibly be considered as potential radioactive waste management sites, has not appeared in the literature. Since the source areas of these marine clays are principally the acidic rocks of the Canadian Shield and the Triassic beds of the Appalachian basin, the marine overlap deposits are probably also illitic.

Quebec

Karrow (1957) found that the tills, varved clays and marine clays of the Trois-Rivières area are "rock flour," consisting of illite, chlorite, quartz, feldspar and amphibole [Fig. 32(a)]. Surface soil samples from the eastern townships of Quebec, in which the surficial deposits are believed to be derived from Ordovician

Table 22. Cation-Exchange Capacity (σ_+) and Clay Mineralogy of Canadian Surficial Deposits (below the upper soil horizons)

Location	Surficial material	(σ_+) (meq/100 g)	Dominant clay mineral[*]	Source
Atlantic provinces	Till	13.4	Chlorite	McKeague, Bourbeau and Cann (1967)
	Reddish brown parent material	6	Illite (mica)[†]	McKeague and Cann (1969)
	Reddish brown parent material	4	Kaolinite	McKeague and Cann (1969)
	Reddish brown parent material	7	Kaolinite	McKeague and Cann (1969)
	Reddish brown parent material	8	Illite (mica)	McKeague and Cann (1969)
	Reddish brown parent material	9	Kaolinite	McKeague and Cann (1969)
	Very clay rich parent material	18	Illite (mica)	McKeague and Cann (1969)
	Reddish brown parent material	12	Illite (mica)	McKeague and Cann (1969)
	Reddish brown parent material	12	Illite (mica)	McKeague and Cann (1969)
	Reddish brown parent material	12	Illite (mica)	McKeague and Cann (1969)
	Reddish brown parent material	12	Illite (mica)	McKeague and Cann (1969)
Nova Scotia	Till	3.8	Illite (mica)	McKeague *et al.* (1971)
	Loam till	9.1	Illite (mica)	McKeague *et al.* (1971)
	Clay-loam till	15.0	Illite (mica)	McKeague *et al.* (1971)

Ontario				
Chalk River (CRNL)	Fluvial sand	0.9-2.4	Mica	Jackson *et al.* (1977)
Oneida soil series parent	Clay till	10.92		Matthews, Reid and Olding (1955)
Haldimand soil series parent	Till (?)	12.98		Matthews, Reid and Olding (1955)
Ottawa	Rideau clay	24.5	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay	20.8	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay	23.8	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay	26.6	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay	24.7	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay (sandy)	23.2	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
	Rideau clay (sandy)	19.2	Illite	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
Castor	Fine sand over clay	~4	Illite (mica)	Bourget and MacLean (1963) (σ_+); Allen and Johns (1960) (miner.)
Interior Plains				
Manitoba (WNRE)	Clay-loam till		Montmorillonite	Mills and Zwarich (1970)
Manitoba (WNRE)	Lacustrine clay		Montmorillonite	Mills and Zwarich (1970)
North Dakota	Silty clay	23		Sandoval and Reichman (1971)
North Dakota	Clay	24		Sandoval and Reichman (1971)
North Dakota	Silty clay	25		Sandoval and Reichman (1971)
North Dakota	Clay	26		Sandoval and Reichman (1971)

*If determined.

†10-Å X-ray diffraction reflection.

σ_+--cation-exchange determination.

miner.-- clay mineralogy.

Table 22. Continued

Location	Surficial material	(σ_+) (meq/100 g)	Dominant clay mineral*	Source
North Dakota	Silt	17		Sandoval and Reichman (1971)
North Dakota	Clayey silt	21		Sandoval and Reichman (1971)
Saskatchewan	Average of soils in southern and central Saskatchewan	57		St. Arnaud and Sephton (1972)
Alberta	Colluvium	43	Montmorillonite	Pawluk, Peters and Carson (1968)
	Sandstone colluvium	42	Montmorillonite	Pawluk, Peters and Carson (1968)
Northern Alberta	Lacustrine clay	25.5		Reeder and Odynsky (1965)
	Till	25.1		Reeder and Odynsky (1965)
	Lacustrine clay	26.4		Reeder and Odynsky (1965)
	Lacustrine clay	27.2		Reeder and Odynsky (1965)
	Till	15.4	Montmorillonite	Pawluk and Bayrock (1969)
	Till	35.9	Illite	Pawluk and Bayrock (1969)
	Till	28.5	Illite	Pawluk and Bayrock (1969)
	Till	23.7	Illite	Pawluk and Bayrock (1969)
	Till	36.7	Illite	Pawluk and Bayrock (1969)
East central Alberta	Till	25.7	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Till	20.4	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Till	21.5	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Till	21.1	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)

	Till	30.1	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Till	26	Montmorillonite	Pawluk and Bentley (1956) (σ_+); Pawluk and Bayrock (1969) (miner.)
Wabamun Lake	Till	25.7	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Till	29.2	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Lacustrine silt	29.3	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Pitted delta	20.4	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Pitted delta	9.1	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
	Residual Paskapoo Fm	6.9	Montmorillonite	Lindsay *et al.* (1968) (σ_+); Pawluk and Bayrock (1969) (miner.)
Southern Alberta	Till	68.5	Montmorillonite	Pawluk and Bayrock (1969)
	Till	65.8	Montmorillonite	Pawluk and Bayrock (1969)
	Till	66.9	Montmorillonite	Pawluk and Bayrock (1969)
	Upper till (DRES)	53.6	Illite	Schwartz (1975*a*)
	Middle sand (DRES)	50.4	Illite	Schwartz (1975*a*)
	Lower till (DRES)	52.0	Illite	Schwartz (1975*a*)
	Brown silt (DRES)	93.4	Illite	Schwartz (1975*a*)
West central Alberta	Till	44.9	Montmorillonite	Pawluk and Bayrock (1969)
	Till	59.9	Montmorillonite	Pawluk and Bayrock (1969)
	Till	34.5	Illite	Pawluk and Bayrock (1969)

Table 22. Continued

Location	Surficial material	(σ_+) (meq/100 g)	Dominant clay mineral*	Source
	Till	60.1	Montmorillonite	Pawluk and Bayrock (1969)
British Columbia North central British Columbia	Glaciolacustrine	23	Vermiculite	Floate (1966)
	Glaciolacustrine	42.4	Vermiculite	Floate (1966)
	Glaciolacustrine	15.5	Montmorillonite	Floate (1966)
	Glaciolacustrine	27.6	Montmorillonite	Floate (1966)
	Glaciolacustrine	22.5	Montmorillonite	Floate (1966)
	Glaciolacustrine	31	Montmorillonite	Floate (1966)
Vancouver Island (soil parents)	Gravel over till	8.1		Clark, Green and Nichol (1967)
	Till (?)	14.8		Clark, Green and Nichol (1967)

(a)
MONTMORILLONITE
100%

100% ILLITE — KAOLINITE AND CHLORITE — 100%

CLAY MINERAL COMPOSITION ATLANTIC PROVINCES AND QUEBEC

● ATLANTIC PROVINCES – reddish brown soil parent material (McKeague and Brydon,1970)
□ CAPE BRETON ISLAND – Bisequa soil parent material (McKeague et al., 1967)
▲ NOVA SCOTIA – Pleistocene muds (Stanley et al., 1972)
||||| ATLANTIC PROVINCES AND QUEBEC – general range of soils, clays and tills
(Forman and Brydon , 1961)
▽ NOVA SCOTIA – tills and clay-loam tills derived from Carboniferous shales and sandstones
(McKeague et al , 1971)

(c)
MONTMORILLONITE
100%

carbonate content
X[1] low
X[2] medium
X[3] high
100% ILLITE — KAOLINITE AND CHLORITE — 100%

CLAY MINERAL COMPOSITION INTERIOR PLAINS

X' MANITOBA – Mankato till (Ehrlich et al , 1955)
O INTERIOR PLAINS – characteristic till (Meyboom,1967)
● NORTH DAKOTA – Lake Agassiz clay (Moran, 1972)
□ ALBERTA – Porcupine Hills Regosol (Pawluk, 1961)
■ NORTHERN ALBERTA (Pawluk and Bayrock, 1969)
△ CENTRAL AND SOUTHERN ALBERTA (Pawluk and Bayrock, 1969)
⊗ SUFFIELD, ALBERTA (Schwartz , 1975g)

(b)
MONTMORILLONITE
(+ Vermiculite in □)
100%

100% ILLITE — KAOLINITE AND CHLORITE — 100%

CLAY MINERAL COMPOSITION ILLINOIS AND ONTARIO

O ILLINOIS – Woodfordian till (Willman et al, 1963)
● ILLINOIS – Winnebago till (Willman et al , 1963)
□ CASTOR AND COLWOOD, ONTARIO – soil parent material
(McKeague et al , 1971)

(d)
MONTMORILLONITE
(+ Vermiculite in ●)
100%

100% ILLITE — KAOLINITE AND CHLORITE — 100%

CLAY MINERAL COMPOSITION BRITISH COLUMBIA

● GLACIAL LAKE CLAYS – general range (Clark et al ,1962)
□ FRASER RIVER ALLUVIAL SEDIMENTS – general range
(MacKintosh and Gardner, 1966)
▲ NORTH CENTRAL B.C. – glaciolacustrine general range
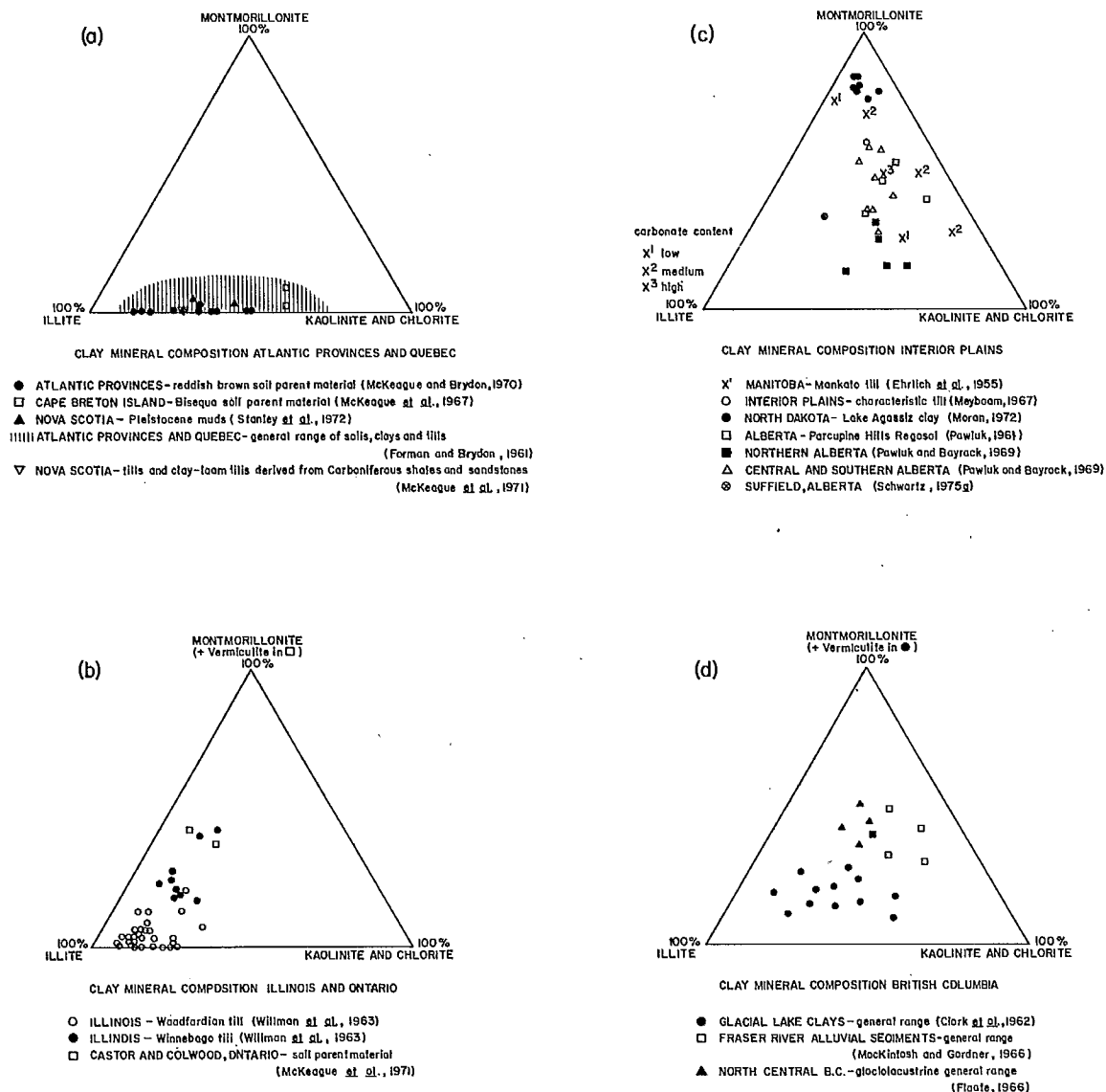(Flaate, 1966)

Figure 32. Clay mineral composition of surficial tills.

limestones and shales, indicate that the predominant clay mineral is illite (Brydon, 1958; Brydon and Sowden, 1959). Allen and Johns (1960) found that eight of a total of 13 samples of shales and clays in southern Quebec were predominantly illite; three samples were principally kaolinite and two were vermiculite with significant amounts of illite. As in the case of Ontario, there is very little published information on the clay mineralogy of surficial tills and soils in Quebec.

Ontario

Published information on the clay mineralogy of Ontario surficial deposits is very scarce [Fig. 32(b)]. Since the source area of both Ontario and Illinois tills is the Canadian Shield and the Paleozoic rocks of southern Ontario, the clay mineralogy of tills in Illinois will likely resemble that of Ontario tills. To summarize the clay mineralogy of Ontario surficial material we will use examples of middle-late Wisconsinan tills in Illinois, which have been mineralogically investigated by Willman, Glass and Frye (1963), as well as data from the limited studies on clay mineralogy of Ontario tills.

Figure 32(b) illustrates the clay mineralogy of the late Wisconsinan tills in Illinois (Willman, Glass and Frye, 1963) and also a few quantitative mineralogical analyses of tills in southern Ontario. The small amount of montmorillonite in the Illinois tills, usually less than 5%, is attributed to weathering of chlorite (Willman, Glass and Frye, 1966). The montmorillonite present in Ontario tills may also be due to chlorite weathering, since chlorite is normally present and the typical Ontario till is probably an illite-chlorite mixture. Webber and Shivas (1953) concluded that the predominant clay mineral of Ontario soils is illite, accompanied by minor amounts of montmorillonite and chlorite. Guillet (1967) indicates that illite is the dominant clay mineral, but that montmorillonite is more common than previously thought. McKeague *et al.* (1971) support Guillet's observations on the presence of montmorillonite, although they also include vermiculite in their analyses. Bottomley (1974) indicates that the clay minerals in the surficial deposits near Kenora, Ontario, are predominantly illite, chlorite and vermiculite and that there are only minor amounts of kaolinite. Glacial tills in the Ottawa Valley area consist of illite with small amounts of vermiculite and chlorite (Allen and Johns, 1960). Jackson *et al.* (1977) found that mica is the dominant clay-sized mineral in the fluvial sands of the Chalk River Nuclear Laboratories radioactive waste management area. Allen and Johns (1960) determined that the marine clays of the Ottawa Valley contain illite and chlorite as well as some mixed-layer clays. Brydon and Patry (1961) also indicate some montmorillonite in the Ottawa Valley marine clays.

Interior Plains

Since the principal source rocks of the surficial deposits in the Interior
Plains Region are the bentonitic sediments of the Western Canada Sedimentary Basin,
the clay mineralogy of the surficial deposits in this region is generally dominated
by montmorillonite [Fig. 32(c)]. Ehrlich, Rice and Ellis (1955) found that montmoril-
lonite was the dominant clay mineral in a surficial till in Manitoba, and Mills and
Zwarich (1970) indicate that montmorillonite is the dominant clay mineral in the
clay-loam tills and lacustrine clays of the Whiteshell Nuclear Research Establishment
in Manitoba. Montmorillonite and lesser amounts of illite and kaolinite have been
found by all investigators to be the dominant clay minerals of the tills and glacio-
lacustrine clays in Saskatchewan and North Dakota (Christiansen, 1959, 1970; Rice,
Forman and Patry, 1959; Warder and Dion, 1952; St. Arnaud and Mortland, 1963; Moran,
1972). In Alberta, montmorillonite is usually dominant and associated with illite
and kaolinite (Rice, Forman and Patry, 1959; Pawluk, 1961). Pawluk and Bayrock (1969)
found that montmorillonite is the dominant clay mineral in central and southern
Alberta and that illite appears to predominate in the northern part of the Province.
Schwartz (1975a), however, found that illite is slightly more prevalent than mont-
morillonite in the glacial drift near Suffield in southern Alberta. Figure 32(c)
summarizes the available published data on the clay mineral composition of the sur-
ficial deposits of the Interior Plains Region. It is clear from Figure 32(c) that the
surficial deposits of the Interior Plains are characterized by a much higher montmorillonite
content than the tills and clays of central and eastern Canada.

British Columbia

The physiography and bedrock geology of British Columbia are highly variable,
and accordingly, the surficial glacial deposits show a large variation in clay mineral
composition [Fig. 32(d)]. Unpublished records of the Ottawa Soil Research Institute
(Forman and Brydon, 1961) show that two soil profiles from the Fraser River valley
had illite as the predominant clay mineral. Armstrong *et al.* (1969) reported that
illite was the dominant clay mineral in three tills in the Fraser Lowlands; yet the
marine clays of the southwestern portion of British Columbia were found to consist
largely of montmorillonite and interstratified montmorillonite, and chlorite or chlori-
tized vermiculite (Clark, Brydon and Hortie, 1962). Mackintosh and Gardner (1966)
determined that the clay fraction of the alluvial sediments of the lower Fraser River
consists principally of montmorillonite and chlorite, with lesser amounts of micas
(illite) and mixed-layer clays. Estimated percentages of the clay minerals in the
lower Fraser River valley are shown in Figure 32(d).

Clark, Brydon and Hortie (1962) found that montmorillonite is predominant in the alluvial deposits of the southern interior of British Columbia and that illite and kaolinite predominate in the central and northern tills and lacustrine clays. Floate (1966) indicates an absence of montmorillonoid minerals in the lacustrine clays of the Fort St. James basin in north-central British Columbia; montmorillonite, however, predominates in the Vanderhoof and Quesnel glacial lake basins. The variation in the geology of the source areas of these glacial-lake deposits is obviously reflected in the resultant clay mineral composition of the lake clays.

The clay mineral composition of surficial deposits on Vancouver Island has received little attention in the published literature.

Total Competing Cation Concentration--τ

In the simplified model of mass transport with geochemical retardation, the total cation concentration in solution, τ, was introduced in the context of a single competing cation-exchange equilibrium reaction $(A^+ + B^+R^- \rightleftarrows A^+R^- + B^+)$ in which $\tau = A^+ + B^+$. Quite obviously there are more than just two cations existing in significant quantities in most groundwaters, and consequently the model would seem to be a gross oversimplification. Nevertheless, because of the size and valence of certain competing cations and the electrical dipole reactions in solution, this oversimplification tends to be warranted when the radiocation and its stable analog are present only at trace levels (Wahlberg and Fishman, 1962). For example, the principal competitor of radiostrontium for exchange sites is usually calcium (Wahlberg *et al.*, 1965). Similarly, only potassium among the major cations can compete effectively with trace concentrations of radiocesium for illitic ion-exchange sites (Wahlberg and Fishman, 1962).[2] In further support of this simplifying assumption, Wahlberg and Dewar (1965) have shown that the adsorption of tracer-level radiostrontium by kaolinite and montmorillonite from solutions containing two competing cations can be successfully predicted from the results that they had previously obtained (Wahlberg *et al.*, 1965) for the adsorption of strontium from solutions containing only one competing cation.

A distinction must be made, therefore, between the total cation concentration in solution, which is the sum of all cations, and the total *competing* cation concentration in solution, which is what τ represents. For a particular groundwater the τ value will be different for radiocesium-potassium competition than for radiostrontium-calcium competition, assuming the radiocation is present only in trace concentrations. In the first case, τ is equivalent to the potassium concentration, whereas in the second, it is equivalent to the calcium concentration.

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[2] Recent (1978) work by R.W. Gillham at the University of Waterloo, however, suggests that the stable ion is the competing ion.

Table 23 shows the wide variation in average values of major ions in some selected surficial Canadian groundwaters. Calcium varies by over one order of magnitude between the Manitoba groundwaters and those of eastern Canada, and the important complexing anion, sulphate, varies by over two orders of magnitude. The very much higher total cation sum for the Manitoba and other prairie groundwaters has been explained by Cherry (1972) as due to the migration of deep brines to the surface during glacial loading of the prairies in Pleistocene time. By the time the glaciers had retreated, the brines had been in contact with the surficial sediments long enough to allow considerable cation and anion exchange to have occurred. Since groundwater flow occurs mainly through fractures in these deposits rather than through the unfractured matrix, the flushing of these invading brines would be a relatively slow process controlled by their rate of desorption and subsequent migration through the matrix to the fracture.

Another difference between the eastern and western groundwaters shown in Table 23 is that the former are a calcium-bicarbonate type, whereas the latter tend to be a magnesium-sulphate type.

Bulk Density--ρ_b

The bulk density of the transmitting medium is the only independent variable in the retardation equation that is fixed within a relatively narrow range. The dry bulk density, or unit weight, of an aggregate of particles can be determined (Terzaghi and Peck, 1948) by

$$\rho_b = (1-n) \ \gamma_s \tag{68}$$

where n and γ_s are the porosity of the medium and specific gravity of the individual particles, respectively. The possible range in ρ_b of a deposit is therefore limited by the possible ranges in particle specific gravities and intergranular porosity. Intergranular porosity values may range between 1% and 60% (Table 5). The specific gravity of the minerals comprising Canadian surficial deposits is variable, with a value of 2.3 for gypsum, 3.2 for hornblende and up to 5.2 for magnetite (Terzaghi and Peck, 1948); the average value, however, is usually taken as approximately 2.65. The dry bulk density of several different types of surficial deposits is given in Table 24. It is readily apparent that the ρ_b of surficial deposits varies over a relatively narrow range, with extremes of approximately 1.0 g/cm^3 and 2.6 g/cm^3. The smaller the range of particle size (and thus the more nearly uniform the soil) or the smaller and more angular the particles, the less the density in the natural state. The greater

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Table 23. Average Values of Major Ion Concentrations (in meq/l) for Selected
Surficial Canadian Groundwaters

Ion	Sample set							
	1	2	3	4	5	6	7	8
Ca^{2+}	26.6	9.1	4.8	3.1	4.4	0.9	2.5	0.9
Mg^{2+}	39.6	22.5	7.0	1.2	1.5	0.7	0.7	0.3
Na^+	20.8	6.9	3.3	0.2	1.2	0.5	0.3	0.5
K^+	-	-	-	-	0.1	0.1	0.0	-
HCO_3^-	6.7	6.7	5.5	3.6	5.1	1.0	3.1	0.8
SO_4^{2-}	63.4	31.8	9.9	0.8	0.6	0.3	0.3	0.2
Cl^-	9.9	3.3	0.3	0.2	1.1	1.1	0.1	0.5
pH	8.0	7.4	7.6	7.8	-	6.5	8	6.8
n*	33	101	24	2	21	2	1	?

*n = sample size.

Sample set description:
(1) Pleistocene silts and clays, Delta, Manitoba (Cherry, 1972).
(2) Lacustrine silts and clays, Pinawa, Manitoba (Cherry, 1972).
(3) Basal sandy drift, Pinawa, Manitoba (Cherry, 1972).
(4) Till overlying lacustrine clays and silts, Big Creek drainage basin, Ontario (Yakutchik and Lammers, 1970).
(5) Sandy, silty till together with sandy kame and sandy glaciolacustrine deposits, upper Nottawasaga drainage basin, Ontario (Sibul and Choo-Ying, 1971).
(6) Fluvial sands, Chalk River Nuclear Laboratories, Ontario (Jackson et al., 1977).
(7) Sandy till, Moncton, New Brunswick (Carr, 1968).
(8) Various till units, Annapolis-Cornwallis Valley, Nova Scotia (Trescott, 1968).

Table 24. Dry Bulk Densities of Unconsolidated Materials

Description	Porosity (%)	Dry bulk density (g/cm^3)
Standard Ottawa sand	44	1.48
Clean uniform sand, loose	46	1.43
Clean uniform sand, dense	34	1.75
Mixed grained sand, loose	40	1.59
Mixed grained sand, dense	30	1.86
Uniform inorganic silt, loose	52	1.28
Uniform inorganic silt, dense	29	1.89
Silty sand, loose	47	1.40
Silty sand, dense	23	2.04
Silty sand and gravel, loose	46	1.43
Silty sand and gravel, dense	12	2.34
Micaceous sand, loose	55	1.22
Micaceous sand, dense	29	1.93
Fine to coarse sand, loose	49	1.36
Fine to coarse sand, dense	17	2.22
Glacial till, very mixed grained	20	2.12
Soft glacial clay	55	1.77

Sources: Terzaghi and Peck, 1948; Lambe and Whitman, 1969.

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the range of particle size present, the greater the density, since the voids among
the larger particles can be filled with smaller ones.

Porosity--n

Representative porosities of some sedimentary and surficial materials were
presented in Chapter 2; Table 5 contains intergranular porosity values of these mate-
rials. Care must be observed, however, to distinguish between the terms *porosity* and
effective porosity. Porosity is defined in Chapter 2 as "the ratio of pore volume
to the total volume of a given sample of material," whereas effective porosity is
defined as "the amount of interconnected pore space available for fluid transmission."
It is the effective porosity which is generally more important in the consideration of
transport in groundwater flow systems. In relatively uniform deposits exhibiting inter-
granular flow, the effective porosity is likely very similar to the actual porosity, with
the difference being in the order of a few percent. In fine-grained fractured deposits
such as till and clays, however, the fractures serve as the effective zones of groundwater
flow and the fracture porosity must be evaluated to determine the effective porosity.
Grisak (1975) found that the fracture or effective porosity of a till in southeastern
Manitoba was about 0.02%, or approximately three orders of magnitude lower than the
intergranular porosity. This value for fracture porosity is similar to the fracture
porosities determined by Snow (1968) for several types of fractured rocks at dam sites
in the United States. The fracture porosities at these dam sites varied between about
0.3% and 0.001%. The significance of these fracture porosity values is that they are
much lower than intergranular values, and since the fractures are the effective zones
of groundwater flow, the groundwater velocity through the fractures is comparatively
high (see Equations 9 and 29). Further discussion of the significance of fracture
porosity in contaminant movement is presented later in a section on fractured till.

Although the fracture velocity will be large, it is also important to evaluate
the net convective flux through the fractures and the net diffusive flux from the
fractures into the intergranular matrix. These will be the significant terms with
respect to potential contaminant emergence into the biosphere, and understanding the
interrelationship between convective and diffusive transport in fine-grained materials,
whether they are fractured or not, is critical to the hydrogeological evaluation at
any potential waste management site.

Selectivity Quotient--f'

Only two sources of information exist for this particular parameter with
respect to Canadian soils and sediments. The first is a laboratory-based study of

the soils at the Whiteshell Nuclear Research Establishment at Pinawa, Manitoba, by Mills and Zwarich (1970). The second is a continuing series of studies of actual ex- perimental waste disposals to the subsurface at the Chalk River Nuclear Laboratories. These latter studies were originally completed by Parsons (1961) and are now being updated by Jackson *et al.* (1977).

Mills and Zwarich chose to experiment with two soils from the waste manage- ment area at WNRE. The distinctive features of these two soils are summarized in Table 25. Both soils have similar clay mineralogies, being dominated by an interstrat- ified illite-montmorillonite. Not surprisingly, they also have similar radiostrontium selectivity quotients--1.2 for WDA2 and 1.3 for WDA3 for the case of Sr versus Ca competition. There is a slight preference for radiostrontium over calcium. It is interesting to note that these values are close to what would have been obtained if Mills and Zwarich had only determined the clay mineralogy and then referred to the data of Wahlberg and Dewar (1965) shown in Table 14 to estimate the selectivity quo- tient for Ca^{2+}-montmorillonite or Ca^{2+}-illite.

The field experiments at Chalk River have permitted the calculation of the selectivity quotient and the distribution coefficient ($K_d = \sigma_+ f'/\tau$) through the use of Equation 64, the retardation equation. The retardation value of K_d shown in Table 26 for radiostrontium is, in fact, a mean of three values with the range 5.6 ml/g to 7.3 ml/g obtained by field mapping of the waste front migration over three dif- ferent time periods. Knowing the cation-exchange capacity, σ_+, and the total (competing) cation concentration, τ, it is then possible to compute f' from the K_d. These field values can be complemented by the radiochemical analysis of the contaminated sediments and the surrounding pore waters.

The selectivity quotients as calculated by the retardation equation tend to be much lower than those given by radiochemical analysis. This is partly because the radionuclide velocity in the retardation equation is calculated from the migration rate of the fastest radionuclide particles (i.e., the plume front), whereas the ground- water velocity is a mean value. In this sense they are conservative estimates.

As time progresses, the fastest radionuclide particles will become even more separated from the position of the radionuclide particles of mean velocity. Thus even lower K_d and f' values will be observed when front-to-front calculations are used. This is illustrated in Table 27, which shows the decrease in distribution coefficient and selectivity quotient for the ^{90}Sr plume for three successive mappings of the front.

The values K_d and f' are significantly higher for ^{137}Cs than for ^{90}Sr pri- marily because of the presence of mica in the clay fraction of the CRNL sands. The

Table 25. Analytical Data on WNRE Soils

Analysis	WDA2	WDA3
Cation-exchange capacity (meq/100 g)	26.0	11.8
Carbonate content (percentage by weight)		
Calcite	8.4	13.2
Dolomite	16.5	12.0
Total	24.9	25.2
Particle size distribution after removal of carbonates (percentage by weight)		
Sand	8.5	40.0
Silt	17.8	27.3
Clay	73.7	32.8
Clay mineralogy (percentage by weight)		
Illite	25	34
Montmorillonite	66	55
Other	9	11
Selectivity quotient (^{89}Sr)	1.2	1.3

Source: Mills and Zwarich (1970).

Table 26. Values of K_d and f' for CRNL Sediments

Radionuclide	Retardation Equation		Radiochemical Analysis	
	K_d (ml/g)	f'	K_d (ml/g)	f'
^{90}Sr	6.6	0.60	16.7	1.5
^{137}Cs	110	1.1	510	5.1

Source: Jackson et al. (1977).

Table 27. Variation in K_d and f' for ^{90}Sr when Calculated by the Retardation Equation and Employing Front-to-Front Plume Mapping

Survey date	K_d (ml/g)	f'
September 1965	7.3	0.66
January 1971	7.0	0.63
June 1974	5.6	0.50

Source: Jackson et al. (1977).

data for ^{137}Cs are based on the migration of the radiocesium front over the 15-year period 1960 to 1975. The values of τ used in Tables 26 and 27 are based on the concept of radiostrontium-calcium competition (see the previous section on τ for explanation).

COEFFICIENT OF HYDRODYNAMIC DISPERSION--D'

The importance of the coefficient of hydrodynamic dispersion, D', and the component processes of which dispersion is the result have been discussed in detail in Chapter 2. A relatively comprehensive review of the subject has been presented by Cherry, Gillham and Pickens (1975). Dispersion is the process by which a trans- ported solute in a groundwater flow system gradually spreads and occupies an ever- increasing portion of the flow domain. From laboratory experiments on intergranular media it has been established that

$$D' = aV^{\lambda} \tag{26}$$

where a is a characteristic property of the medium (with units of length) called the dispersivity, V is the average groundwater flow velocity and λ is an exponent commonly close to unity (Bear, 1972). In laboratory investigations on homogeneous granular materials, the values obtained for a are in the order of 10^{-2} cm to 1 cm, which essen- tially means that dispersion in uniform granular materials (or simple layered granular systems) is a relatively minor process. The relatively small laboratory dispersivities are in marked contrast to the dispersivities that appear to apply to some field situa- tions. Actual field-measured values of dispersivity for geologic media are rare in the literature. Digital two-dimensional dispersion models have been used to simulate field contamination patterns in several areas of intergranular groundwater flow (Konikow and Bredehoeft, 1974; Robson, 1974; Bredehoeft and Pinder, 1973). Disper- sivities obtained from these simulation studies were in the range of 10 m to 100 m, again much larger than typical laboratory values. Harpaz (1965), however, obtained field dispersivities for granular material in the order of 0.1 m to 1 m during sub- surface water storage studies in Israel. Recent field tests at the Chalk River waste management site (Pickens, Merritt and Cherry, 1977) and in a heterogeneous gravel aquifer near Fort Macleod, Alberta (Grisak, Merritt and Williams, 1977) indicated similarly small dispersivities with the use of multiple-level point sampling devices.

The heterogeneity of natural geologic materials is likely responsible for the apparently large field dispersivities obtained in earlier studies. The concen- trations recorded during the tests at which large dispersivities were obtained repre- sent, in intergranular aquifers, a composite of the total flow into the wells which are generally screened over relatively large depth intervals.

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The problem of dispersion in fractured or jointed media where groundwater flow is primarily through the fractures is presently in a state of relative uncertainty. Grove and Beetem (1971), using a two-well tracer method in the field, obtained a dispersivity value for a fractured carbonate aquifer of 38 m. Krizek, Kardi and Socias (1972) demonstrated with a simulation model that very irregular dispersion patterns can be predicted by relatively simple fracture systems. Fracture patterns in natural materials are usually much more complex than the simple patterns of the simulation model above (e.g., Babcock, 1973; Grisak et al., 1976) and in many situations would likely produce contamination patterns that would be impossible to monitor effectively. The orientation of the fracture systems with respect to the direction of groundwater flow appears to be critical. In many instances, it will likely be impossible to treat flow in fracture systems on the basis of homogeneity or, particularly, isotropy.

THE ROLE OF PRECIPITATION

As shown in Chapter 3, the geochemical retardation of radionuclides can occur not only by ion exchange but also by direct precipitation of the radionuclide or by its coprecipitation with another mineral species. Among the possible reactions that can be considered are the precipitation of strontium and cobalt as carbonates, and the coprecipitation of strontium with gypsum ($CaSO_4$), calcite ($CaCO_3$), dolomite ($CaMg (CO_3)_2$) and barite ($BaSO_4$). In this section, we shall consider the state of saturation of three groundwaters from Table 23 with respect to several of the mineral species above by use of the saturation index (SI) concept introduced in Chapter 3.

As an example of the use of the SI concept we shall consider a particular analysis of a sample of groundwater from Chalk River (one of the two analyses which were averaged and then tabulated as sample No. 6, Table 23). In this case we shall compute the saturation index for $SrCO_3$ by

$$SI = \log (IAP/K_{eq}) \tag{50}$$

in which K_{eq} is the ion-activity solubility product for a particular mineral species as defined in Equation 49 and IAP is the actual ion-activity product of the groundwater solution in question.

The method of computation of SI is as follows:

(1) Compute the ionic strength of the groundwater solution by Equation 51;
(2) Compute the activity coefficients γ_{Sr} and γ_{CO_3} by the Debye-Hückel equation

(see Garrels and Christ, 1965, pp. 61-62) or by graphs (see Hem, 1970, p. 21). (For this particular case of $SrCO_3$, we shall compute the activity of the carbonate ion, $[CO_3]$, from γ_{HCO_3} and $[HCO_3]$ by using the second dissociation constant for carbonic acid.);

(3) Compute the activities $[Sr]$ and $[HCO_3]$ from Equation 48;

(4) Compute $IAP = [Sr] [CO_3]$ after solving for $[CO_3]$ through $[HCO_3]$;

(5) Either obtain K_{eq} from Table 12 or compute it at the groundwater temperature by the Van't Hoff equation (Krauskopf, 1967, pp. 208-213);

(6) Compute $SI = \log IAP - \log K_{eq}$, noting that negative values indicate subsaturation, whereas positive values indicate supersaturation.

A worked example is given by Domenico (1972, pp. 197-199).

The relevant concentrations for the groundwater sample in question are

$$(Sr) = 0.14 \text{ mg/l} = 1.6 \times 10^{-6} \text{ M}$$

$$(HCO_3) = 56.1 \text{ mg/l} = 0.92 \times 10^{-3} \text{ M}$$

(69)

and pH = 6.5. The ionic strength, I, was calculated by Equation 51, using the molar concentrations for the following ions: calcium, magnesium, strontium, sodium, potassium, bicarbonate, chlorite and sulphate. Factors for converting milligrams per litre to millimoles per litre (i.e., 10^{-3} M) are given by Hem (1970, p. 83). For $I = 0.003$ we can calculate the activity coefficients from Hem's (1970, p. 21) graph as

$$\gamma_{Sr} = 0.79 \text{ and } \gamma_{HCO_3} = 0.94 \tag{70}$$

Therefore the following activities were computed using Equation 48:

$$[Sr] = (0.79) (1.6 \times 10^{-6}) = 10^{-5.90}$$

$$[HCO_3] = (0.94) (0.92 \times 10^{-3}) = 10^{-3.06}$$

(71)

The activity of the carbonate ion may be computed by the use of the second dissociation constant, K_2, for carbonic acid, H_2CO_3;

$$[CO_3] = \frac{K_2 [HCO_3]}{[H]} \tag{72}$$

where $K_2 = 10^{-10.56}$ at 5°C, which is approximately the groundwater temperature. There-

fore we can write, remembering $pH = -\log[H]$,

$$[IAP] = \frac{[Sr]\, K_2\, [HCO_3]}{[H]} \tag{73}$$

or $\log IAP = \log [Sr] + \log K_2 + \log[HCO_3] + pH$

$$= -5.90 - 10.56 - 3.06 + 6.5$$

$$= -13.0$$

At $5°C$ the equilibrium constant for $SrCO_3$ was computed by the Van't Hoff equation to be the same as at $25°C$, therefore from Equation 47

$$K_{eq} = \frac{[Sr]\, [CO_3]}{[Sr\, CO_3]} = 10^{-9.6} \tag{74}$$

Therefore $SI = \log IAP - \log K_{eq} = 13.0 + 9.6 = -3.4$. Since the saturation index is less than zero, it may be concluded that the groundwater is undersaturated with respect to $SrCO_3$ and therefore that precipitation of radiostrontium as $SrCO_3$ in the Chalk River groundwaters is not a plausible explanation of its retardation.

By similar reasoning the state of saturation of the groundwaters may be calculated from Table 23 (numbers 2, 4 and 6) with respect to calcite and gypsum. Figure 33 shows the regions of supersaturation and undersaturation for the two mineral species and the state of saturation of each of the groundwaters. The axes were computed as follows:

$$\log IAP_{calcite} = \log [Ca] + \log [HCO_3] + pH + \log K_2 \tag{75}$$

At saturation we may write using Equation 50

$$SI = \log IAP - \log K_{eq} = 0 \tag{76}$$

At $10°C$

$$\log K_{eq} = -8.36 \tag{77}$$

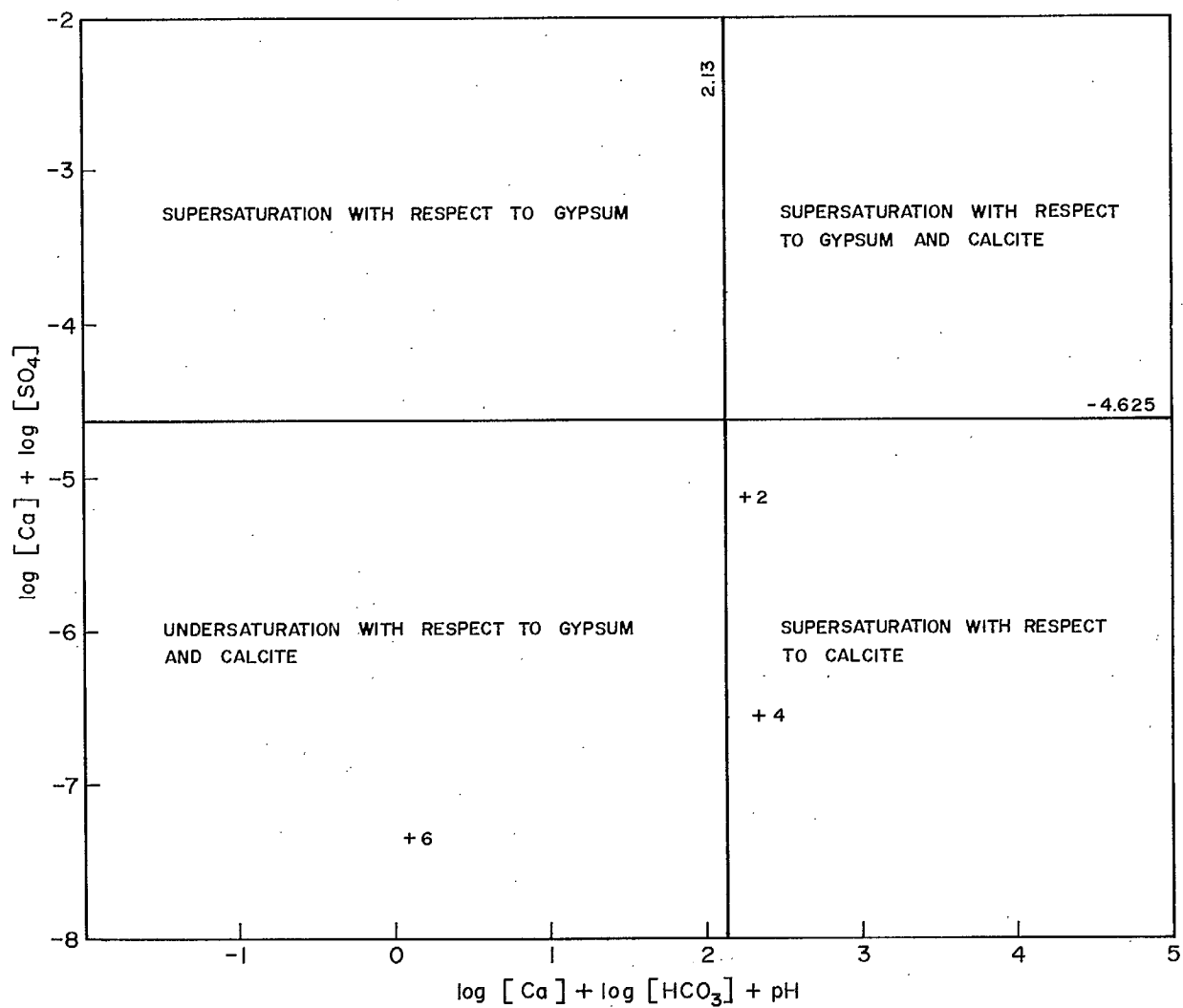Therefore, at saturation at $10°C$

$$\log IAP = -8.36 \tag{78}$$

Figure 33. Calcite and gypsum equilibrium solubility limits, 10°C and 1 atm pressure (after Hem, 1970).

At 10°C

$$\log K_2 = -10.49 \tag{79}$$

and in Equation 75

$$\log IAP - \log K_2 = \log [Ca] + \log[HCO_3] + pH \text{ or } -8.36 + 10.49 = 2.13 \tag{80}$$

Therefore, for a groundwater at 10°C to be saturated with respect to calcite, the sum of the logarithms of the calcium and bicarbonate activities plus the pH must be at least 2.13. Similar reasoning is used to compute the gypsum saturation axis of -4.625.

When significant quantities of complexing ions are present in groundwaters, it is necessary to consider their effect on the activities of the other ions in solution. In the case of sulphate concentrations in excess of approximately 100 mg/l, a significant proportion of the calcium and sulphate ions will be in the form of an uncharged complex ion, $CaSO_4^0$, which is known as the calcium-sulphate ion pair. For groundwater sample number 2 (from Pleistocene silts and clays, Pinawa, Manitoba) the calcium and sulphate concentrations were 182 mg/l ($10^{-2.34}$ M) and 1526 mg/l ($10^{-1.80}$ M), respectively, and the ionic strength was 0.069. Calcium and sulphate activity coefficients of 0.45 and 0.40, respectively, were estimated, and an activity coefficient of 1.00 for the calcium-sulphate ion pair was assumed. The activities of the three species--Ca^{2+}, SO_4^{2-} and $CaSO_4^0$--were computed by solution of the following equations:

$$m_{TOTAL\ Ca} = \frac{[Ca]}{\gamma_{Ca}} + \frac{[CaSO_4^0]}{\gamma_{CaSO_4^0}} \tag{81}$$

$$m_{TOTAL\ SO_4} = \frac{[SO_4]}{\gamma_{SO_4}} + \frac{[Ca\ SO_4^0]}{\gamma_{CaSO_4^0}} \tag{82}$$

$$\frac{[CaSO_4^0]}{[Ca]\ [SO_4]} = 10^{2.31} \tag{83}$$

where the m_{TOTAL} stands for total molar concentration (i.e., analytical concentration). The results show that only one third of the calcium and sulphate ions were in solution as free ions, the rest being in the form of the ion pair.

The activities are:

$$[Ca] = 10^{-2.86}$$
$$[SO_4] = 10^{-2.28} \tag{84}$$

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In Figure 33, the three groundwaters were chosen on the basis that they represented three different hydrogeochemical environments. Number 2 is a brackish water (I = 0.069) from Pleistocene silts and clays, No. 4 is a more potable water from a till-lacustrine environment in southern Ontario (I = 0.0068) and No. 6 is a ground-water of low ionic strength (I = 0.003) from a sandy Shield environment. Both No. 2 and No. 4 are supersaturated with respect to calcite; none, however, is saturated with respect to gypsum. Furthermore, Cherry (1972) has noted that groundwaters No. 1 and No. 2 from Table 23 are supersaturated with respect to dolomite.

The estimation of the state of saturation of groundwaters by the means above or by computer programs (e.g., Truesdell and Jones, 1974) should be an established method of analyzing the retardation potential of a radioactive waste management area with respect to precipitation.

TRANSPORT AND RETARDATION IN FRACTURED TILL

From the discussions in the previous section of this Chapter, it is obvious that in the authors' opinion, the groundwater flow and transport and retardation characteristics of fractured till are a major concern. The concern is founded primarily on the likelihood that many tills in Canadian terrain may display a fracture network to some degree, and it is consequently the responsibility of investigators to evaluate the effect fractures may exert on the transport potential of a till unit. The hydraulic conductivity, porosity and dispersive characteristics of fractured tills have been briefly discussed under previous headings; a more comprehensive review of possible transport and retardation phenomena in fractured till is presented below.

A discussion of some of the factors pertinent to contaminant movement in fractured till has been presented by Grisak et al. (1976). Considering the very low effective porosity of fractured till and the Dupuit-Forcheimer relation (see Equations 29 and 66), it is reasonable to expect that contaminants will be transported by groundwater more quickly through fractured till than through unfractured till. Field studies of a tritium tracer injection experiment in fractured till at the Whiteshell Nuclear Research Establishment support this expectation (Grisak, 1975). Under normal hydraulic gradients in surficial deposits (usually in the range of 0.1 to 0.001) the average velocity of groundwater through the fractures in these tills would be in the range of 4000 cm/yr to 4 cm/yr. This velocity is in marked contrast to the intergranular velocity of material of the same textural classification, which under the same hydraulic gradients would range from 5 cm in 100 yr to 5 cm in

10,000 yr. The rate of intergranular groundwater movement in tills is almost insignificant compared with the relatively active flow system in the fracture networks.

Although the fractures control the velocity of contaminant movement, the bulk effective hydraulic conductivity of a fractured till unit, as determined by the interaction of the total hydrodynamic system, controls the net contaminant flux through the unit and consequently the potential rate of contaminant release to the biosphere or the public domain. Therefore, for the purpose of predicting release rates, a fractured unit such as till must be treated as a hydraulic continuum and the net flux be calculated on the basis of this approach.

Although the total fractured unit should be handled as a continuum for the purpose of net flux prediction, the treatment of contaminant transport and retardation does not readily lend itself to this approach. It is of course possible to solve the intergranular transport equation on different scales, i.e., a larger scale is required to treat flow through fractures in the same Darcian manner as intergranular flow through the matrix, and to couple the net result. The interrelationships between the fractures and the matrix, particularly from the retardation viewpoint, however, appear to require more direct treatment on a discrete basis. One example of a discrete approach (Grisak, Williams and Cherry, 1977) treats the transport of a conservative contaminant through fractured till on the basis of individual fracture-matrix units with a periodic interfracture boundary situation which provides an extension of the results to the scale of a continuum, and consequently the appropriate scale for net flux calculations.

It has become apparent from laboratory investigations and theoretical consideration of transport in fractured till that diffusion from a fracture opening into the unfractured matrix plays an important role in a contaminants transport history through fractured materials. The diffusive flux of a contaminant from a fracture into the matrix results in a form of retardation caused by diffusion phenomena dissimilar to the sorption or precipitation reactions to which retardation is usually attributed. A similar line of reasoning is employed by Young, Oakes and Wilkinson (1976) to account for the observed retardation of nitrate and tritium profiles in unsaturated portions of fractured chalk and sandstone aquifers in the United Kingdom. Although the discrete approach to transport in fractured till requires some knowledge of the fracture spacing and has inherent assumptions required to extend its concepts to the continuum scale, the necessary field data required are not inordinately large nor do the assumptions contradict geologic evidence.

Radionuclide retardation in the subsurface by sorption processes is also severely affected if a till is fractured. Contaminants that are transported by groundwater through fractures are afforded an opportunity to react with the mineral constituents

only in a thin veneer on the exterior of the till blocks called the *penetration distance* (Grisak *et al.*, 1976). This distance is obviously not a well-defined unit of length, but depends on such factors as the type of minerals of which the till is composed, the weathering surface (if any) on the block, the roughness of the fracture surface, the hydraulic conductivity of the block, the velocity of a contaminant and the length of time it is in contact with any particular portion of a fracture surface, and numerous other site-specific factors. Of critical importance is the possibility that the groundwater velocity through the fractures may not allow the solute-medium interaction to be considered an equilibrium reaction and that it may not only be a nonlinear sorption term but also be transient. If this is the case, and it is future research which must investigate and broaden our presently primitive knowledge of fracture transport phenomena, then it would seem appropriate to approach fracture transport in the intervening period as conservatively as possible. An example of one possible approach, the parameters of which are currently the subject of ongoing research, is presented below.

It would be convenient to be able to treat transport in fractured till in the same simplified conceptual manner as that of the intergranular approach in Equations 63 and 64. In the fractured case a K_d equivalent on the basis of effective available surface area, such as the K_a proposed by Burkholder (1976), seems appropriate, and a surface area to fracture pore-volume ratio, R_f, may replace the ρ_b/n term in the retardation equation. The transport equation derivation described in Chapter 3 can be seen to be valid in the fractured case (providing the terms of reference are of large scale and the fracture pore space is considered the effective porosity) if the porosity term is thought of in terms of dimensioned volume and the bulk density (ρ_b) is redefined in terms of equivalent surface area. There is a considerable body of literature concerning surface areas of various mineralogical and textural soil groups (Grim, 1968; Heilman, Carter and Gonzaliz, 1965). The determined surface areas generally refer to the laboratory dispersed state and unfortunately not to the actual "effective available surface area" field state of a semiconsolidated material such as glacial till. Yet if a surface area equivalent which represents the actual bulk density field situation can be defined, then the derivation in Chapter 3 can be equally valid for a surface area K_a approach.

It is proposed at this point that the variables on which the penetration distance is dependent as well as the fracture surface roughness be incorporated in a surface coefficient, ξ, which in the case of a perfectly planar and impenetrable fracture surface has a maximum value of 1.0. The value of ξ for any fracture surface with roughness or penetration potential is less than 1.0. The fractured case equivalent of the simplified retardation equation, recalling that the conceptual scale is that of a continuum with the fractures representing the effective paths of groundwater

flow, is

$$V_A = \frac{V}{1 + K_a R_f / \xi} \qquad (85)$$

where $\quad K_a$ = fracture distribution coefficient (L)

R_f = ratio of fracture surface area/pore volume (1/L)

ξ = fracture surface coefficient.

Paces (1973) has shown with a simple cubic model that on the basis of surface area alone, the coefficient ξ would likely range between 0.8 and 0.1. Therefore considering the remaining variables on which ξ is dependent, it is proposed here that the effective value of ξ in fractured tills is unlikely to be larger than 0.5 simply on the basis of observed macro roughness and probable micro roughness and that the remaining variables serve to reduce it even more. Definition of the lower limit of ξ presents a considerable task and at present the relative influence of the various factors on which ξ is dependent is uncertain.

The relationship between K_d and K_a is a conceptually simple matter of expressing the equilibrium K_d determined in standard batch or column intergranular experiments in terms of millilitres per square centimetre rather than millilitres per gram, although the actual measurement of surface area is much more difficult than simply weighing a sample, and the application of K_a to a field transport situation remains to be seen. Areas in urgent need of research are the measurement of effective surface area, which reflects fractured semiconsolidated field conditions (in the case of fractured till), and the establishment of the reliability of transferring the equilibrium K_d, expressed as K_a, measurement to the fractured field situation. A laboratory experiment employing the K_a concept (Grisak, Williams and Cherry, 1977) has outlined some of the uncertainty regarding the concerns above. Added to these difficulties are the previously mentioned problems involving the relatively high velocities through fractures which may not allow medium-solute equilibrium to be attained even on the exposed surface. Laboratory K_d investigations generally require a period of four to eight hours to attain equilibrium, and although intergranularly the flow velocities in a clayey material may be negligible and equilibrium is almost assured, this may not be the case in fractured materials. Furthermore, there is no obvious laboratory or mathematical treatment of the undetermined relationships between velocity, penetration distance, contaminant species and matrix diffusion. This formidable list of difficulties is reiterated to emphasize the inherent difficulties in fracture transport and the simplification resulting from the accumulation of unknowns into a term such as ξ, or for that matter, K_a or K_d.

It is obvious that some of the most useful information regarding fracture transport will be obtained from field investigations under field conditions, and although our conceptual breadth may be influenced by well-planned laboratory investigations, the importance of radioactive waste management suggests that the principal task at hand is understanding the problem in its field context. If sites are evaluated and planned to the point that we are totally confident in our predictions of potential transport rates and directions, this implies that we have complete knowledge of the characteristics of a particular site, which further implies that we have been involved in its conception, i.e., it is an *engineered* geologic and hydrogeological situation. The concept of engineered sites is discussed in detail in Chapter 6, but it is relevant to suggest that if particular hydrogeological situations or physico-chemical properties or engineering methods are in a state of considerable uncertainty, then it is hoped that these uncertainties will not be incorporated into sites selected on the basis of current expertise and that we will not export to the future the necessity of unravelling the uncertainties.

Operational Experiences

The purposes of this Chapter are (1) to outline, on the basis of available data, the hydrogeology and waste management experiences at operating waste management sites in Canada and (2) to offer a brief evaluation of the possible geohydrological transport and hydrogeochemical retardation characteristics of these sites. Since several factors identified in previous chapters will require considerable research efforts to evaluate their influence on subsurface radionuclide transport and retardation (e.g., groundwater flow in fractured tills and clays, the effect of microstratigraphy and heterogeneity on dispersion and effective groundwater flow paths, the transport or retardation role of dissolved and colloidal organic material and secondary clay-mineral coatings on weathered aluminosilicates), this Chapter will of necessity be somewhat general. Each site is discussed in as much detail as available data permit, including, where appropriate, a brief discussion of radionuclide migration experiences. Throughout this Chapter as many examples as practical are given of the methods and calculations currently used to predict contaminant migration rates and directions.

A general discussion of the types and amounts of radioactive wastes that are currently or projected to be stored in the shallow subsurface in Canada has been presented in Chapter 1 (Table 3). Most of the radioactivity in the waste management facilities has at one time been in liquid or gaseous form within a reactor building and is now fixed in a solid form by decontamination systems. Minor amounts of radioactivity are retained on combustible substances such as paper and on noncombustible objects such as piping during the normal operation of a reactor; these constitute a large portion of the material received at waste management sites. As discussed in Chapter 1, spent fuel is not technically regarded as waste in the Canadian nuclear industry; the spent fuel elements are currently stored in water-filled bays in buildings at the reactor sites.

Radioactive wastes can be classified in several ways. The solid waste classification system used by Ontario Hydro is presented below as an example of a classification incorporating the necessary limitations of practical field measurement.

> Solid Waste, Type 1 - Beta-Gamma activity after primary collection (before any volume reduction process) less than 200 mRad/h at contact (with nominal 0.05 m^3 waste contained within plastic garbage bag).
>
> Solid Waste, Type 2 - Beta-Gamma activity after primary collection (before any volume reduction process) less than 20 Rad/h but more than 200 mRad/h at contact.

Solid Waste, Type 3 - Beta-Gamma activity after primary collection
     (before any volume reduction process) greater than 20 Rad/h at
     contact.
Radioactive solid wastes are further categorized by their physical
state as follows
a) *Combustibles* - wood, paper, plastic, fabric, wool, rubber.
b) *Concreted wastes in drums* - from liquid waste systems, incinera-
   tor ash-disposal systems or resin slurry systems.
c) *Filters and expendable ion exchange columns.*
d) *Miscellaneous Noncombustible Wastes* - metallic equipment and
   components; dry filters, etc.

An additional category could include low-level liquid wastes such as slightly
tritiated cooling water. Low- and medium-level liquid wastes assigned to ground dis-
posal sites are produced in appreciable quantities at only one site in Canada, the
Chalk River Nuclear Laboratories (Mawson, 1967). These particular types of wastes
are not a routine product from the CANDU nuclear system.

For convenience in this Chapter, the solid waste classification system above
is used if descriptive classes are noted. Low- and medium-level liquid wastes are
defined in context where applicable.

Presently there are five areas in Canada at which subsurface radioactive
waste management facilities are located. Two of the sites are operated by Atomic
Energy of Canada Ltd.: one is at the Chalk River Nuclear Laboratories about 200 km
northwest of Ottawa and the other is at the Whiteshell Nuclear Research Establishment
in southeastern Manitoba. The CRNL and WNRE sites receive a variety of low- and
medium-level wastes and very small amounts of high-level wastes, almost all solid.
Facilities for low- and medium-level wastes are located at the Bruce Nuclear Power
Development (BNPD) operated by Ontario Hydro, and at the Gentilly Nuclear Power
Development (GNPD) operated by Quebec Hydro.[3] A small amount of miscellaneous low-
level solid waste (for example, luminous aircraft dials) is stored in shallow trenches
at the Defense Research Establishment, Suffield (DRES) in southeastern Alberta.

A general discussion and comparison of the five Canadian sites have been
presented by Cherry, Grisak and Jackson (1974), and since individual site analyses
are presented later in this Chapter, this brief comparison is sufficient.

     All the radioactive waste-management sites are situated in
     sandy, silty, or clay materials deposited by or near Pleistocene
     glaciers. Except for the Suffield site, the bedrock at each of
     the sites is at depths less than 20 m below ground surface, and
     in some cases it is very close to the bottom of the burial zone.

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[3]Detailed information on the Gentilly site had not been received at the time of preparation
of this report.

The wastes are buried in the Pleistocene deposits at depths less than 7 m below ground surface. The burial zone at the WNRE site is below the water table [Cherry, Grisak and Clister, 1973]; at the other sites it is above the water table, although except at the Suffield site the separation between the water table and the burial zone is generally only a few metres or less.

At the CRNL and WNRE sites, which handle most of Canada's solid radioactive wastes, the low-level solid wastes are generally put directly into unlined trenches excavated to depths of 3 to 6 m below ground surface. Although much of the waste is in plastic bags, the bags are generally not watertight. The trenches are filled to within 1 m of the original ground surface and then covered with the excavated soil. Medium-level solid wastes and some low-level wastes are placed in concrete bunkers, in concrete standpipes lined with steel, or in tile holes. These installations extend to depths of 3 to 5 m below ground surface. Recently, at CRNL, used-fuel elements have been put into storage in standpipes lined with steel and concrete which are buried within 5 m of ground surface. The fuel elements are above the present water table table and will not directly encounter infiltrating water, unless corrosion seriously affects the containers.

At the Bruce, Gentilly, and Suffield sites the wastes are normally put in concrete bunkers, concrete trenches, or standpipes. Although these containers are generally lined with asphalt, plastic sheeting, or steel, their integrity [as a waterproof membrane] cannot be assured for more than a few decades because of the corrosive action of soil water and groundwater which contains various ionic constituents. Much of the radioactive waste contains ^{90}Sr and ^{137}Cs, with decay half-lives of 28 and 30 years respectively. Depending on the initial concentrations of these radionuclides in the waste, several hundred years of decay-time may be required to reduce the radioactivity to harmless levels. In some cases, therefore, the containers [tile holes, bunkers, etc.] should be regarded only as an interim means of preventing radionuclides from entering the subsurface hydrologic environment. The wastes are usually packaged so that they can be retrieved if problems arise.

CHALK RIVER NUCLEAR LABORATORIES (CRNL)

The Chalk River Nuclear Laboratories waste management area is located in the lower Perch Lake basin (Fig. 34) about 200 km northwest of Ottawa. The site has received radioactive wastes from the CRNL research laboratories since 1946 and more recently from the Ontario Hydro nuclear power facilities and the AECL Commercial Products Division in Ottawa.

The major physiographic areas of interest to this report are the sandy uplands, south swamp, Perch Lake swamp and the shore zone. The latter is now the location of the dike road. Waste management activities occur in the Quaternary deposits, which range in thickness from a maximum of about 30 m below Perch Lake swamp to about 4 m in the sandy uplands. These surficial deposits are mainly fluvial sands, with clays being more common at depth. On the uplands west and northeast
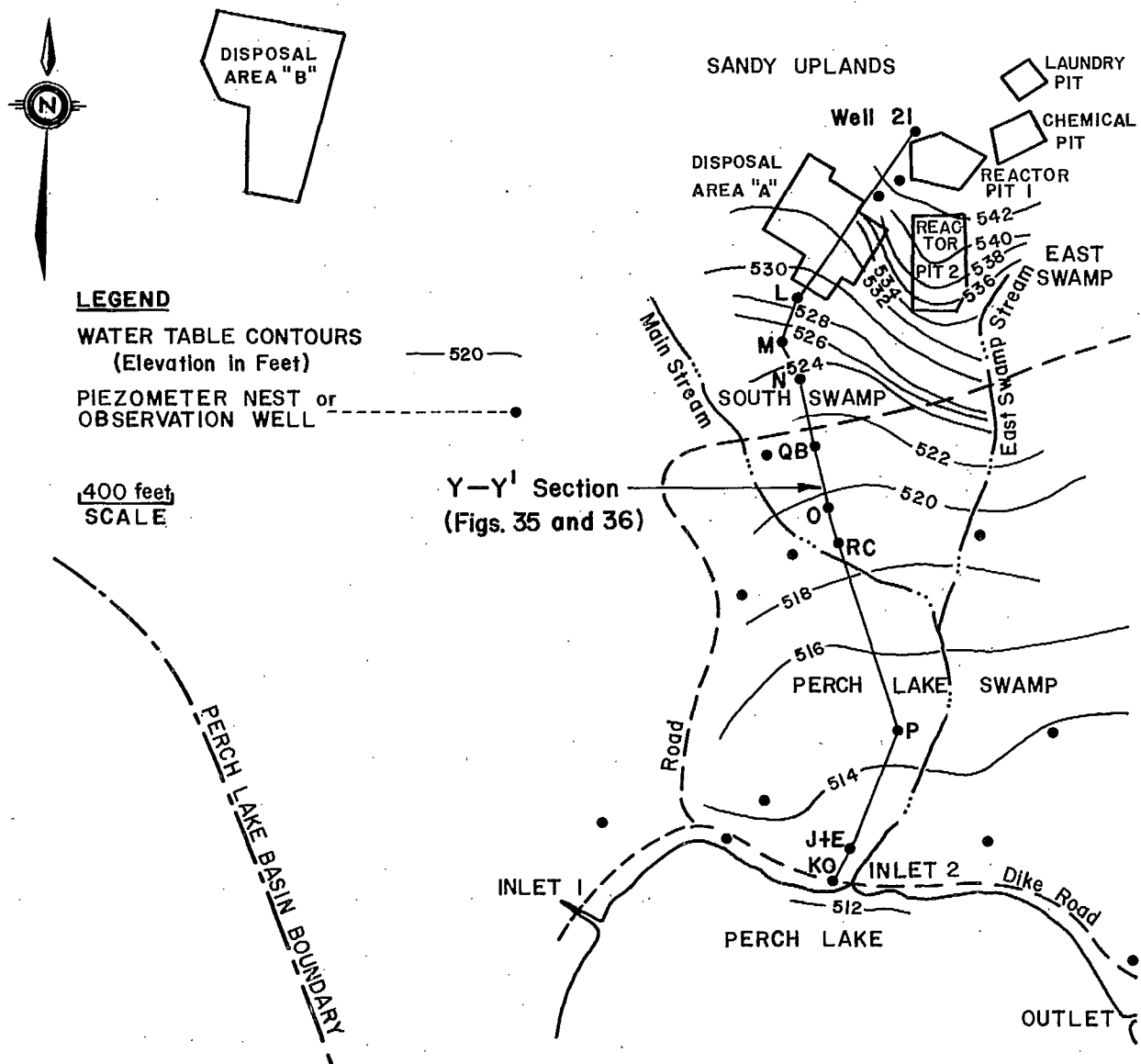
Figure 34. Map of lower Perch Lake basin and disposal areas "A" and "B".

of the swamps, outcrops of fractured granitic bedrock are common. The subsurface topography of the bedrock is typical of weathered Precambrian Shield topography, with local relief of 15 m to 40 m. Perch Lake is situated above a trough in the bedrock. Beneath the lake are deposits of soft organic muck (gyttja) overlying sandy Quaternary deposits on top of the bedrock. Surface relief in the CRNL waste management area is typically about 15 m, with local topographic high areas consisting of bedrock outcrops at the swamp boundaries or stabilized sand dunes to the north.

Hydrogeology

The CRNL waste management area has been the subject of virtually continuous study, including that by Ophel and Fraser (1957), Evans (1958), Gadd (1958, 1959), Parsons (1960, 1961, 1962a, 1962b, 1963), Merritt and Parsons (1960), Merritt (1964), Mawson (1965), Merritt and Mawson (1967), Mawson and Russell (1970), Cherry et al. (1975) and Jackson et al. (1977). The hydrogeological investigation, in particular that of the lower Perch Lake basin, is continuing as a cooperative effort with the involvement of CRNL, Fisheries and Environment Canada, and the University of Waterloo. The present and historical waste management operations have not been confined to the lower Perch Lake basin, although most of the detailed hydrogeological information to date is from this area.

Studies of the surficial geology of the basin by Gadd (1958, 1959) culminated in a map of the surficial deposits of the area. Gadd has said that the bedrock in the lower Perch Lake basin is "much faulted and fractured." The occurrence of fractures in at least the upper portion (3 m) of the subsurface bedrock has since been corroborated in diamond drill cores obtained in 1973 by the authors of this report.

The subsurface geology of the area north of Perch Lake is summarized in cross section Y-Y' in Figure 35. The stratigraphy shown in Figure 35 is an interpretation by Cherry et al. (1975) based on the results of Parsons (1960) and continuing investigations. In the upland area to the north, the surficial deposits are clean, fine- and medium-grained sand of aeolian origin. Beneath the sand is a bouldery, sandy, silty glacial till overlying the bedrock. The position of the bedrock surface in this area is problematic at present due to the lack of deep test holes; bedrock outcrops to the immediate north of the cross section, however, suggest a thin Quaternary cover. At the southern edge of the sandy upland, the aeolian sand grades into water-deposited (probably deltaic) sands, silts and clays.

Beneath the swamps between the sandy upland and the dike road north of Perch Lake there are three relatively clean sand units designated as the upper, middle
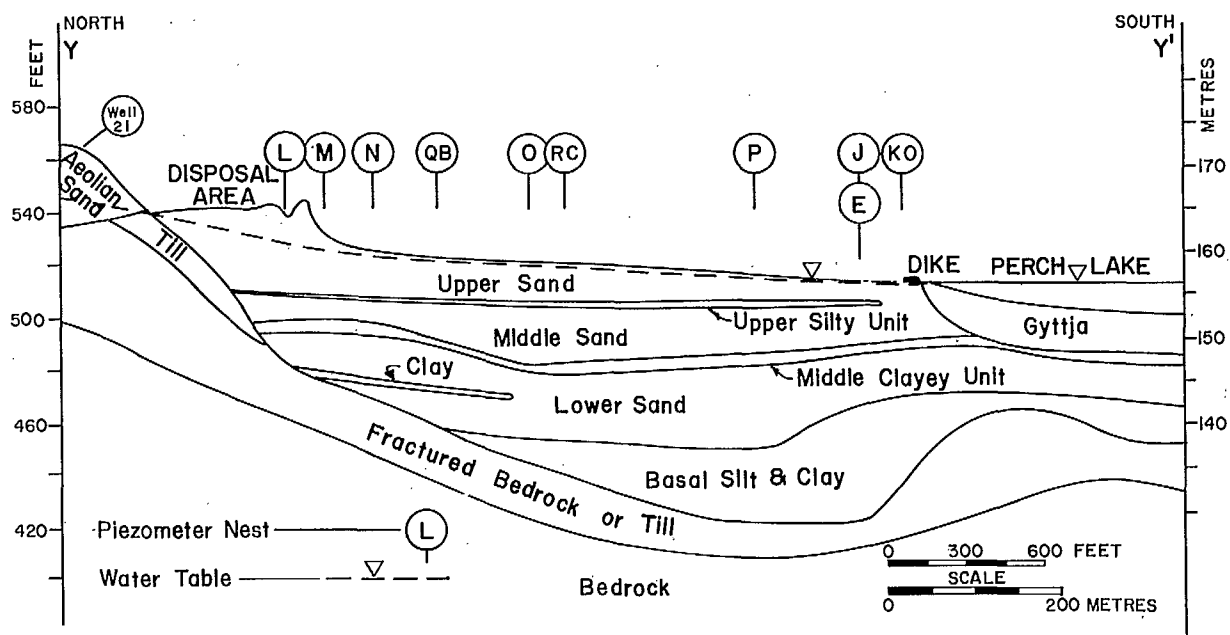
Figure 35. Hydrostratigraphy of the lower Perch Lake basin along the Y-Y' cross section (after Cherry *et al.*, 1975).
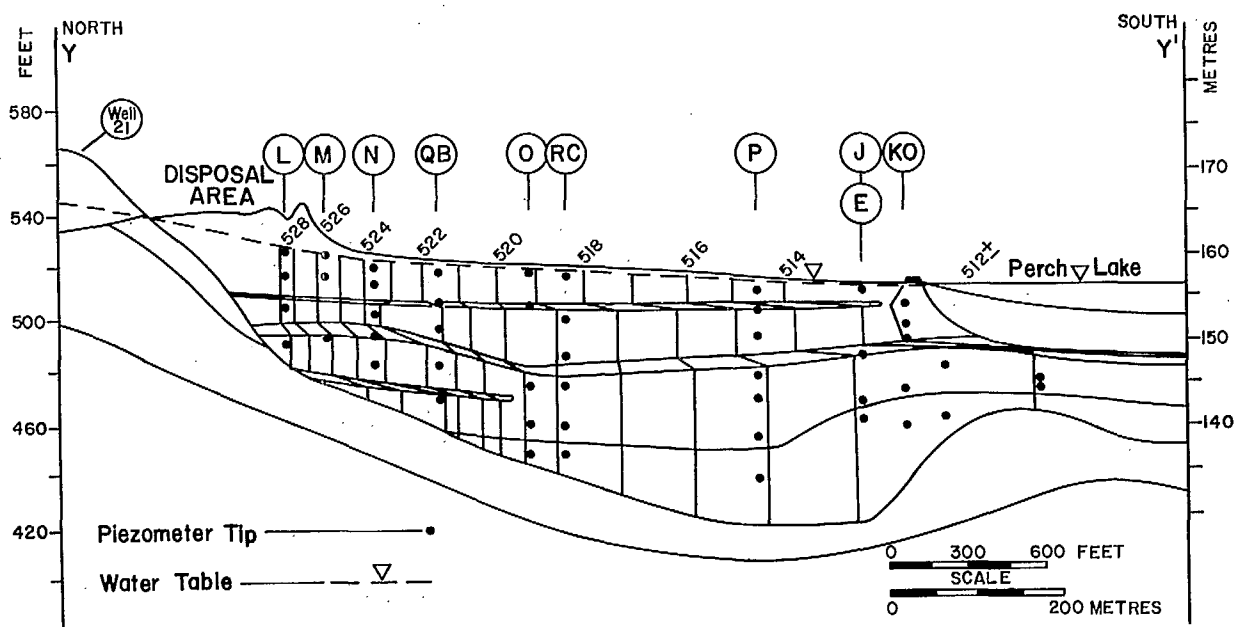

Figure 36. Hydraulic head pattern from field data for the Y-Y' cross section (after Cherry *et al.*, 1975).

and lower sand (Cherry *et al.*, 1975). Between the upper and middle sands is a thin, relatively continuous silty unit which appears to have considerable influence on the groundwater flow system. The middle and lower sands are separated by an additional silty-clayey zone, referred to as the middle clayey unit, composed of numerous thin beds of clay, silt and very fine sand. The middle clayey unit appears to be continuous beneath the swamp area and possibly extends beneath Perch Lake as well.

Between the lower sand and the bedrock there is a unit designated as the basal silt and clay. Although very little is known about this unit because of lack of core data, it appears that it lies either directly on the fractured bedrock or on a layer of till resting on bedrock, as suggested by Parsons (1960).

Analyses of the Perch Lake basin surficial sediments using X-ray diffraction (Jackson *et al.*, 1977) indicate the <5-μm fraction is dominated by a highly crystalline mica, along with amphibole, plagioclase, K-feldspar and chlorite. Studies of the mineralogy of the sediments in the Perch Lake basin and the Chalk River area, conducted by Traill (1957), Evans (1958) and Dell (1963), found the coarser fraction of the sands and silts primarily composed of plagioclase and quartz, with lesser amounts of K-feldspar and hornblende. Garnet, biotite, pyroxene and iron oxide occurred in minor amounts.

An interpretation of the cross-sectional groundwater flow system in the lower Perch Lake basin is shown in Figure 36. The sand dunes to the north, where the waste management area is located, serve as the major recharge area to the groundwater zone. Water entering the groundwater zone in this area moves downward and then laterally into the central part of the basin. Groundwater flow is primarily horizontal through the upper, middle and lower sand units into the zones beneath Perch Lake. Although the continuity of the low-conductivity silt and clay units is somewhat speculative, there is a definite tendency for upward seepage across these layers, based on the assumption that vertical head differences between piezometers in the upper, middle and lower sands are controlled by the low-conductivity silt and clayey units. The continuity of these low conductivity layers has been substantiated to some degree by pumping tests in the various sandy units (Cherry *et al.*, 1975). The tendency for upward seepage reflects that the groundwater recharge in the uplands becomes confined beneath the lower conductivity silt and clay layers as it moves southward along the hydraulic gradient.

At site P the hydraulic head in the deepest piezometer is commonly below the head in the overlying piezometers in the lower sand. This has been interpreted by Cherry *et al.* (1975) as an indication of deep groundwater flow out of the cross-sectional plane. The outflow may be due to a high-conductivity layer of sand or gravel near the

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bedrock surface that permits flow out of the cross-sectional plane to the east or west, or may be caused by flow into the fractured bedrock. If the downward flow is into the fractured bedrock it may possibly leave the basin by way of bedrock flow to the Ottawa River. More boreholes and piezometers in the bedrock are required to clarify the details of this situation. The downward gradient condition does not extend to the edge of Perch Lake nor is it temporally continuous. This lack of continuity is probably due to water table variations in the recharge area and the swamps caused by rainfall and evapotranspiration. Piezometers installed beneath the bottom of Perch Lake indicate that at least a portion of the lake bottom receives upward groundwater seepage.

The groundwater flow system interpretation outlined above has been assisted by digital flow simulation studies throughout the investigation. A transient flow model to simulate an upper water table boundary fluctuating in response to recharge is currently under development (Cherry *et al.*, 1975).

Waste Management Methods

The waste management facilities at CRNL have been discussed in considerable detail by several authors, notably Mawson and Russell (1959, 1970) and Merritt and Mawson (1967). The facilities include disposal area "A", with associated liquid disposal facilities, and disposal area "B", the present medium-level solid waste management area, both of which are located in the lower Perch Lake basin (Fig. 34). Area "C", outside the Perch Lake basin, is used exclusively for low-level solid wastes. Solid waste disposal in area "A" was discontinued in 1959 after a portion of the area had been used for that purpose from 1946.

The bulk of the liquid which has entered the ground in the "A" area is from the spent-fuel storage bays in the reactor buildings. Until 1956 Reactor Pit 1 received 50,000 gal/day to 100,000 gal/day of low-level active water from the fuel storage bays and laboratory facilities. In 1956, Reactor Pit 2 was built, and flow was transferred from Reactor Pit 1, which was partially filled in and its use discontinued. By 1961 Reactor Pit 2 was receiving approximately three times the volume per day that Reactor Pit 1 had received. In April 1961, the flow to Reactor Pit 2 was drastically reduced (Parsons, 1963), following the introduction of a recirculating water treatment plant for the rod-bay water. Morrison (1974) has stated that 75 m^3 of liquid waste is discharged daily into the recently expanded Reactor Pit 2.

A chemical pit that has received various types of laboratory wastes since 1956 is located about 100 m east of Reactor Pit 2. A similar pit, about 30 m northeast

of the chemical pit, occasionally receives contaminated water from the laundry facilities at CRNL.

According to Parsons (1961), three batches of radioactive liquids were disposed of in the ground in disposal area "A": (1) about 1×10^6 gal of contaminated water from an accident in the NRX Reactor in 1952; (2) 1500 gal of liquid in 1954 with approximately 170 Ci of mixed fission products, including 60 Ci ^{90}Sr and about 4600 lb of ammonium nitrate; and (3) 11,000 gal of active liquid in a nitric acid solution (900 Ci of mixed fission products including 300 Ci of ^{90}Sr).

The present medium-level solid waste management area, disposal area "B", comprises about 6 ha and receives wastes from the CRNL facilities and the AECL Commercial Products Division, as well as some from the commercial nuclear power stations. A few used fuel rods not stored for reprocessing are cemented into concrete tile holes, 3 m deep, and other wastes are generally placed in concrete-lined asphalt-coated bunkers that are sealed with steel lids and concrete when they are full.

In disposal area "C", low-level solid wastes and garbage are placed in unlined trenches about 3 m deep, 4.5 m wide and 60 m long. The filled trenches are covered with the excavated sandy material.

During 1953-54, radioactive liquids from a small ammonium nitrate decomposition plant were discharged into an excavated pit to the southwest of 233 Lake, which is located just outside the western boundary of the Perch Lake basin. An estimated 1000 Ci to 1500 Ci of mixed fission products, of which 700 Ci to 1000 Ci were probably ^{90}Sr (Parsons, 1962a), were discharged to the pit. After one year of operation the nitrate decomposition process was halted and use of the pit was discontinued.

Waste Migration Experiences

To date there have been no documented subsurface contamination experiences due to solid waste leaching and subsequent migration in the CRNL area. Merritt (1967) has conducted an experimental disposal of two blocks of highly radioactive nitric acid solutions that had been incorporated into a nepheline syenite glass. He placed the two glass blocks in the ground below the water table and in 1967 reported the results of six- and eight-year monitoring periods of the individual blocks. The leaching rate of the glass tended to decrease with time to approximately 10^{-10} g/cm^2/day, within the acceptable limits of release indicated by Watson, Aiken and Bancroft (1960). Merritt indicated that this method would be suitable for permanent disposal, even in

1952 Disposal
1x10^6 Gallons Water
1000 Curies ^{90}Sr (into trench system)

"A" DISPOSAL AREA

1955 Disposal
11,000 Gallons (high acid waste)
900 Curies mixed fission products
300 Curies ^{90}Sr

Path of highest concentration

1954 Disposal
1500 Gallons (high nitrate content)
170 Curies mixed fission products
60 Curies ^{90}Sr

Track separates into upper and lower paths

Upper track

Lower track

"Front" ^{106}Ru – June, 1960

Path of highest concentration

"Front" ^{137}Cs – June, 1960

– February, 1975

—"Front" ^{90}Sr Upper Track November, 1960

SOUTH SWAMP

Mass of ^{90}Sr

"Front" ^{90}Sr lower track – April, 1961

"Front" ^{90}Sr
–February, 1961
– 1965
–January, 1971

–May, 1975

ROAD

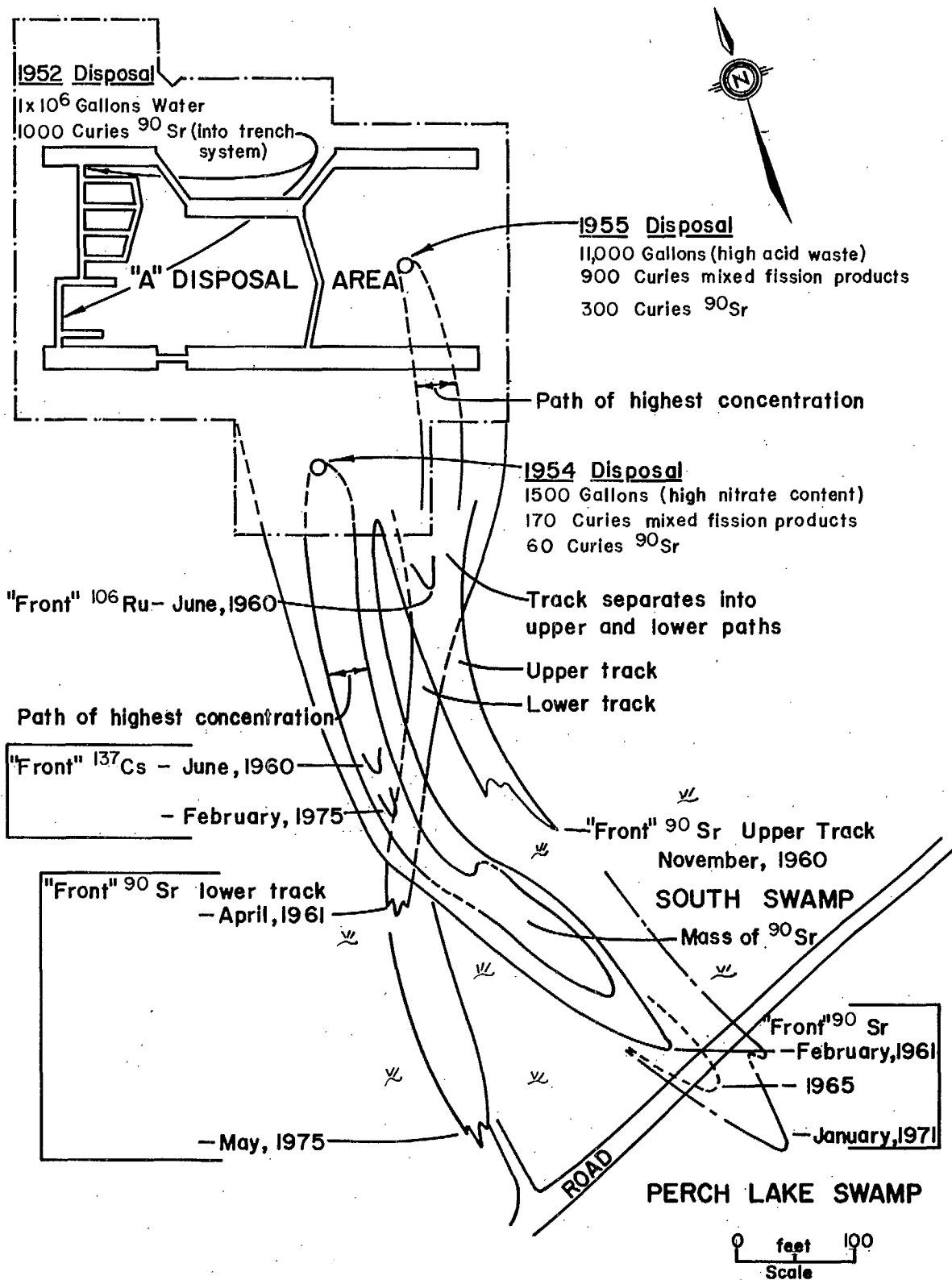PERCH LAKE SWAMP

0   feet   100
Scale

Figure 37. Plan of disposal area "A", lower Perch Lake basin, indicating fronts and migration direction of the 1952, 1954 and 1955 liquid disposals (after Parsons, 1961).

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areas of saturated sand of low exchange capacity, and suggested as well that burial above the saturated zone in an arid region would result in even less release of radioactivity from the glass. Monitoring of the glass blocks is continuing.

The waste migration experiences that have been documented at CRNL are virtually all from liquid disposal activities. Although solid waste was buried in disposal area "A" for nine years, the extensive contamination from the liquid waste disposals affords little possibility for field studies of the extent (if any) of contamination owing to solid waste leaching. Monitoring of disposal area "B" indicates that as yet there is only minor contamination from this solid waste facility.

Figure 37 is a plan view of disposal area "A", indicating the fronts and migration directions of the 1952, 1954 and 1955 liquid disposals. The groundwater velocities in the subsurface system in the lower Perch Lake basin have been determined to be in the range of 0.2 ft to 1.7 ft/day (0.06 m to 0.5 m/day) (Parsons 1960, 1961; Merritt, 1964). The rate of ^{90}Sr and ^{137}Cs movement is approximately 3% and 0.3%, respectively, of the groundwater velocity. From the results of field experiments and radiochemical and laboratory analyses, Jackson *et al.* (1977) have obtained the distribution coefficients and selectivity quotients for ^{90}Sr and ^{137}Cs in the CRNL sediments (Table 26). The distribution coefficients, K_d, were obtained by successive field mapping of the waste front migration at three different times. Knowing the cation-exchange capacity, σ_+, and the total (competing) cation concentration, τ, the selectivity quotient, f', was calculated from the relationship $K_d = \sigma_+ f'/\tau$. The values in Table 26 will be used to illustrate the use of the retardation Equation 64 in the prediction of future waste migration rates. Additional examples later in this Chapter are based strictly on field hydrogeological techniques and laboratory analyses, rather than actual waste migration experiences.

The K_d for ^{90}Sr from Table 26, based on the results of front-to-front mapping, is 6.6 ml/g. The average velocity of the groundwater, V_x, will be taken as about 15 cm/day. The average velocity of ^{90}Sr, $V_{90_{Sr}}$, is then given by the retardation equation[4]

$$V_{90_{Sr}} = \frac{V_x}{1 + (\rho_b \, \sigma_+/n\tau) f'} \tag{64}$$

$$= \frac{15 \text{ cm/day}}{1 + \frac{1.8 \text{ g/cm}^3}{0.35} (6.6 \text{ ml/g})}$$

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[4]In the first line of Equation 64, ρ_b and n are taken from Table 24 and from Parson's data (1960), respectively.

$$V_{90_{Sr}} = 0.43 \text{ cm/day}$$

The calculation above, used simply to illustrate the retardation equation, indicates the average velocity of the ^{90}Sr is about 3% of the groundwater velocity, suggesting considerable retardation by sorption (see Chapters 3 and 4 for discussion of sorption mechanisms). Similar calculations using the K_d for ^{137}Cs can also be completed, with significantly higher sorption apparent owing to the presence of mica in the clay fraction of the CRNL sands.

As noted in Chapter 4, the values of K_d and f' as calculated by the retardation equation tend to be lower than those given by radiochemical analyses. This is partly because radionuclide velocity in the retardation equation is calculated from the plume fronts, whereas the groundwater velocity is a mean value; consequently such estimates are conservative. It is also important to recall that low concentrations, in the case of some radionuclides exceeding permissible limits, will likely occur at much earlier times than would be calculated using the average groundwater velocity.

Reactor Pits 1 and 2 and the chemical and laundry pits (Fig. 34) have contributed to the groundwater contamination evident at CRNL, but to a lesser degree than the disposals in 1952, 1954 and 1955. A cross section through Reactor Pit 1 (Fig. 38) indicates that contaminated groundwater surfaces at the base of the sand hills, travels along the surface for approximately 15 m and then returns by groundwater recharge to the subsurface (Parsons, 1962b). Contamination appears to be limited to the sand deposits above the glacial till. A cross section through Reactor Pit 2 (Fig. 39) indicates contamination of the more permeable sands above the glacial till. A north-south cross section through the chemical pit (Fig. 40) indicates that contaminated groundwater has reached the east swamp through the upper sands unit.

Tritiated water, which is received in Reactor Pit 2, migrates through the subsurface at approximately the same rate as the groundwater, affected only by hydrodynamic dispersion processes. The extent of tritium contamination as of 1963 is shown in Figure 41. Although Figure 41 was drawn in 1963 (Parsons, 1963), the configuration of the high-level front has not changed considerably since then. Following a recent review of the tritium disposal, Barry and Entwistle (1975) have concluded that roughly two thirds of the tritium released to the reactor pit reaches Perch Lake within a few months by seepage and subsequent surface streamflow, and the remaining one third enters relatively long-term storage (mean residence time of approximately ten years) in the groundwater reservoir. More discussion of the tritium disposal operation is presented in Chapter 6 as part of the concept of a subsurface retardation waste management scheme.
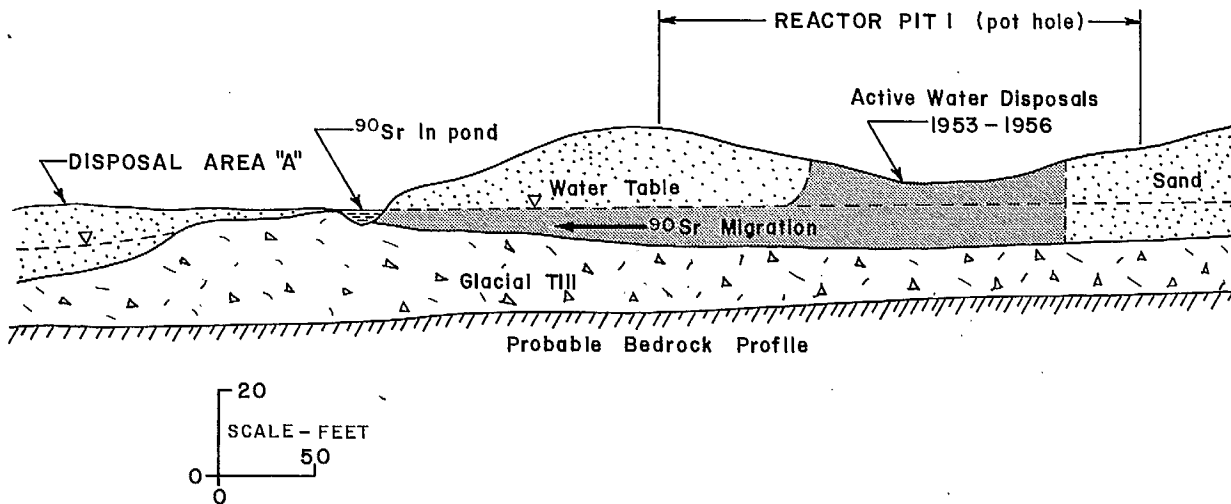
Figure 38. Cross section through Reactor Pit 1, lower Perch Lake basin, indicating contaminated groundwater flow path. Groundwater surfaces at the base of the sand hills, travels along the surface for approximately 50 ft (15 m) and then returns by groundwater recharge to the subsurface (after Parsons, 1962b).
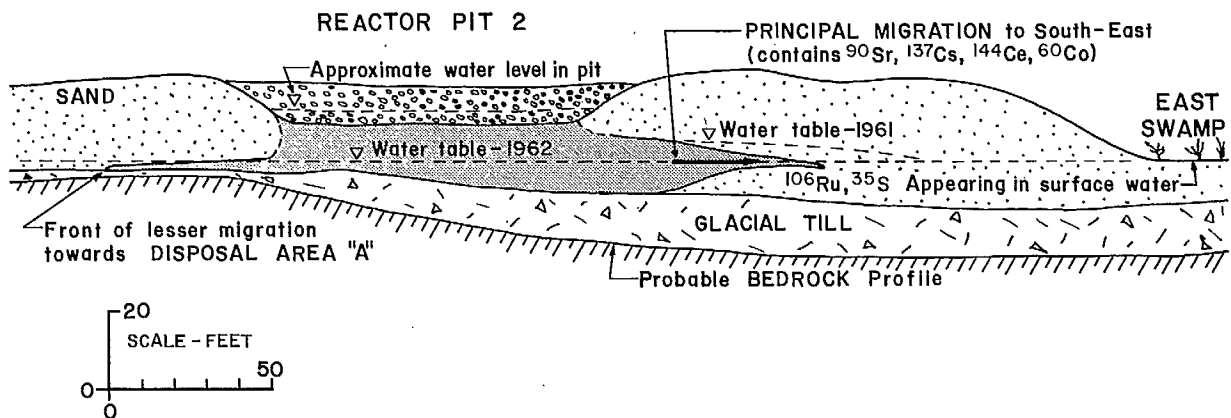

Figure 39. Cross section through Reactor Pit 2, lower Perch Lake basin, indicating contaminated groundwater flow path (after Parsons, 1962b).
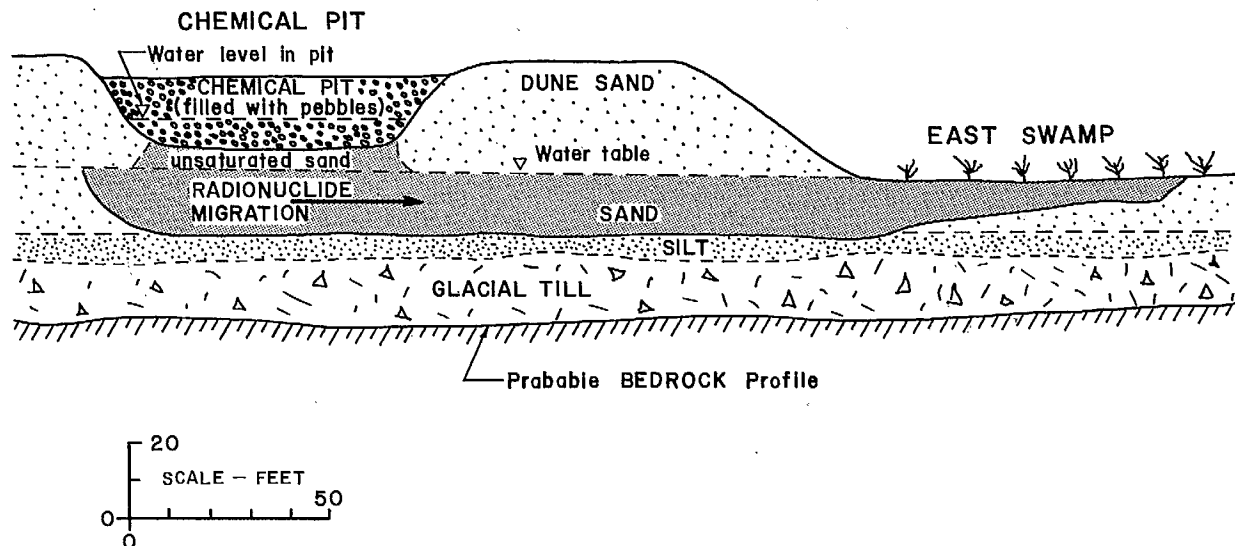

Figure 40. Cross section through the chemical pit and the east swamp, lower Perch Lake basin (after Parsons, 1962b).
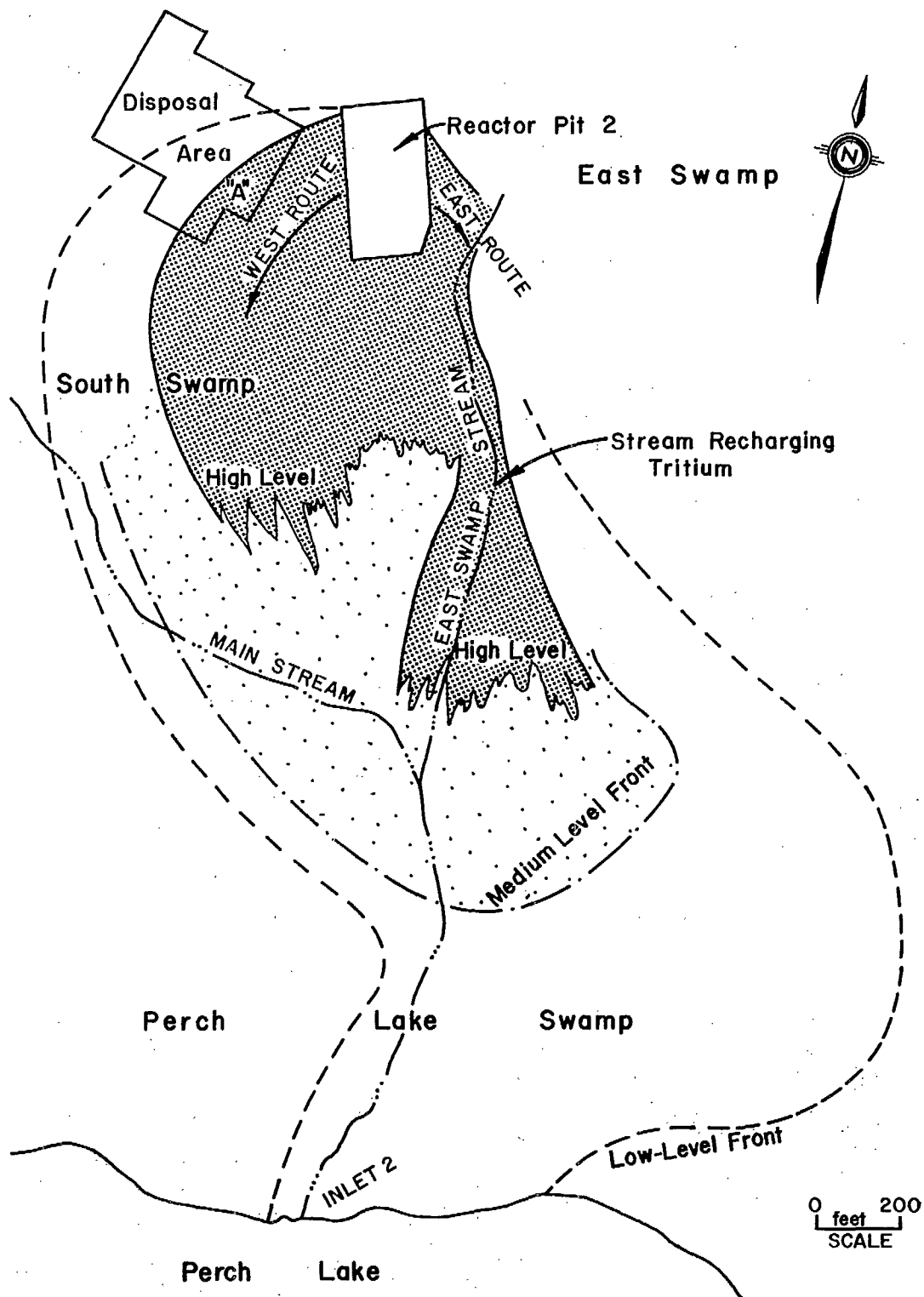
Figure 41.   Plan of lower Perch Lake swamp indicating the extent and
concentration of tritium contamination in 1963 (after Parsons,
1963).

Another waste migration experience has been documented at the 1953-54 nitrate decomposition plant disposal pit (Parsons, 1962*a*). Figure 42 indicates that the ^{90}Sr front in 1962 was about 200 m from the disposal pit and moving in the direction of Perch Swamp (Parsons, 1962*a*). The ^{90}Sr was moving at about 1.5% of the groundwater velocity, and Parsons (1962*a*) predicted that the water would emerge in Perch Swamp about 130 years after the time of disposal. The release to the swamp was predicted to be slow enough that the maximum permissible concentrations (ICRP) would not be exceeded.
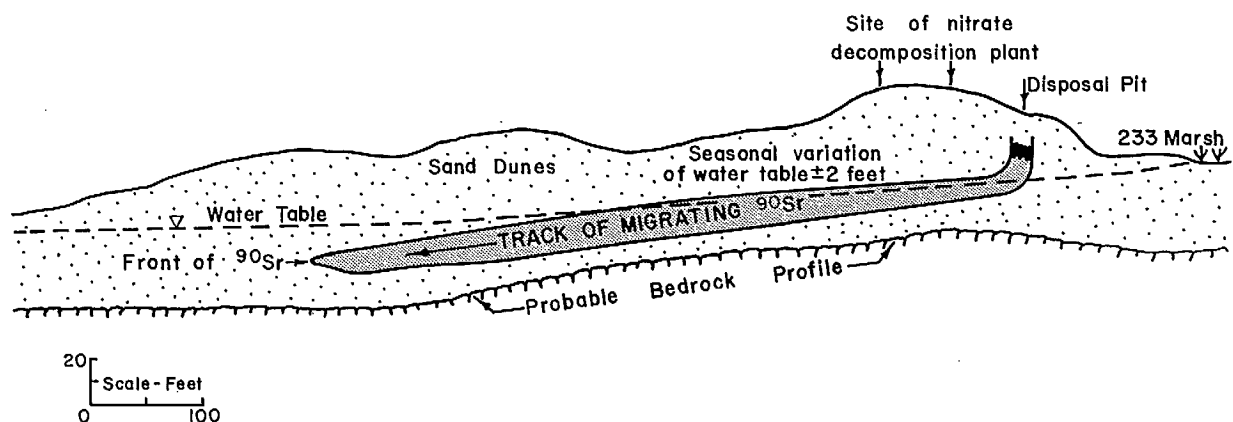

Figure 42. Cross section of the nitrate decomposition plant disposal pit in the upper portion of the Perch Lake basin (after Parsons, 1962*a*).

It is clear from the discussion and summary above that contamination of the CRNL groundwater system owing principally to liquid waste management and experimental activities has been relatively extensive. Previous investigators (Parsons, 1962*b*; Mawson, 1967) have suggested that extensive surface contamination will not result from emergence of contaminated groundwater. The slow subsurface rate of hazardous radionuclide movement, which offers considerable time for decay, and the predicted slow rate of release to the environment have been offered as support for this observation. In further support of this conclusion, Merritt and Mawson (1973) reported that of the 32,000 Ci of mixed fission products disposed of in the Perch Lake basin between 1945 and 1972, only 13 Ci had reached the Ottawa River. Further field investigations, particularly those concerning the extent and hydraulic conductivity of bedrock fractures and the lateral continuity of the subsurface stratigraphy, are currently in progress and are required to substantiate these conclusions.

WHITESHELL NUCLEAR RESEARCH ESTABLISHMENT (WNRE)

The Whiteshell Nuclear Research Establishment is located in southeastern Manitoba on the eastern edge of the Manitoba Plain, about 120 km northeast of

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Winnipeg. The waste management area occupies about 2.5 ha and has been in operation since 1964. WNRE is situated on the western edge of the Canadian Precambrian Shield. The granitic bedrock in the area is overlain by 10 m to 27 m of Pleistocene sediments, mainly lacustrine clay, clayey till and sand. The water table is normally within a few feet (about a metre) of ground surface. Solid low- and medium-level radioactive waste is buried in the upper 5 m.

Hydrogeology

The geology of the WNRE area, as defined by test drilling and coring (Cherry, Grisak and Clister, 1973; Grisak and Cherry, 1975), is summarized by the geologic cross section in Figure 43. The wedge-shaped silt unit blanketing the western half of the cross section includes thin laminated beds of fine-grained sand, sandy silt and clay. The contact between the silt and the underlying clay unit is varved and contains numerous carbonate pebbles and clasts of till. A layer of clay-bound Precambrian cobbles and boulders occurs at the base of the clay-loam till.
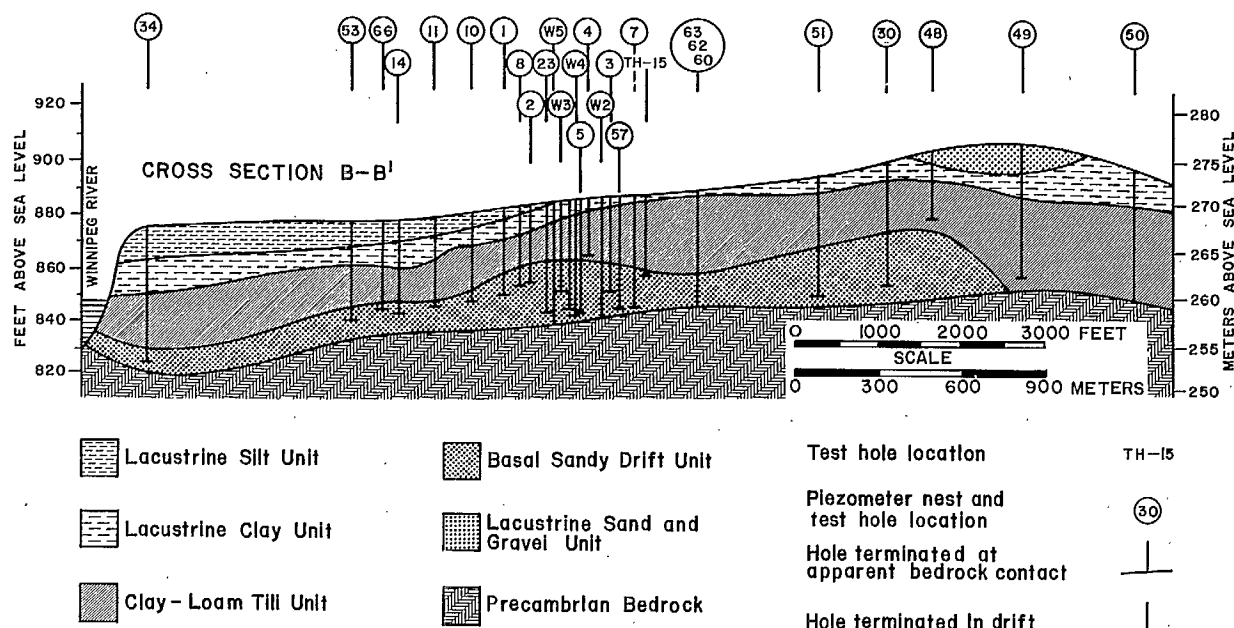

Figure 43. Geologic cross section through WNRE waste management area (after Cherry, Grisak and Clister, 1973).

Between the till and the Precambrian bedrock there is a sandy drift deposit referred to as basal sand. It is the only aquifer in the area and appears at the surface in the eastern portion of the cross section as a medium-grained well-sorted sand. It grades laterally westward into a heterogeneous sandy unit with numerous lenses of sandy silt, silt and clay.

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Mills and Zwarich (1970), on the basis of X-ray diffraction and petrological studies, report that the lacustrine silt, clay and clay-loam till have essentially the same mineralogy. The units consist of fine-grained calcite and montmorillonites, kaolinite, chlorite, vermiculite, feldspars and quartz. The predominant clay minerals are of the montmorillonite group. The pebbles and cobbles in the clay-loam till are predominantly dolomite and the rest are weathered Precambrian material. The basal sandy drift and lacustrine sand are composed of quartz and feldspar with minor amounts of other silicate minerals, calcite and dolomite.

The groundwater flow system, as interpreted from extensive field data and two-dimensional digital modelling, is shown in Figure 44. Water enters the groundwater zone in the upland recharge area and moves downward and then laterally toward the Winnipeg River. As the water moves westward upward hydraulic gradients in the overlying till and clay cause some of the water to flow upward into the central discharge area. Most of the water, however, continues to flow westward in the basal sand to a groundwater *sink* located about 0.8 km east of the Winnipeg River. The sink, which is also apparent in the third dimension on plan-view maps, is an area of anomalously low hydraulic head into which water flows from the east and west and from above. By correlation between two cross sections (Cherry, Grisak and Clister, 1973), the anomalously low hydraulic head zone is interpreted as a north-south trending bedrock fracture or fracture zone which has sufficient hydraulic conductivity to channel water out of the basal sand.
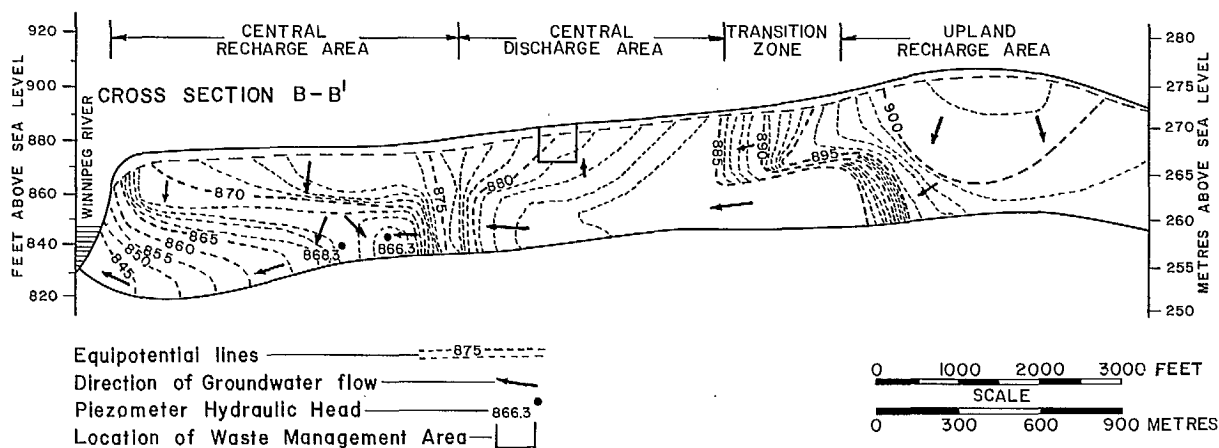

Figure 44. WNRE waste management area groundwater flow pattern from water level data (after Cherry, Grisak and Clister, 1973).

The lacustrine clay and clay-loam till at WNRE are fractured throughout their entire depth, as indicated by observations in Shelby tube samples and fresh excavations as well as by pumping test response analyses (Grisak and Cherry, 1975).

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The fractures are mainly in a vertical direction and are typically coated with iron oxide and calcite. From the hydraulic head distribution it is apparent that groundwater flows through the till and clay and that the fractures determine the effective bulk hydraulic conductivity of these units. These conclusions are supported by (1) the results of tritium tracer experiments (Clister, 1973; Grisak, 1975) which indicate that groundwater moves through the till and clay at rates much higher than intergranular conductivity would allow and (2) the rapid response of piezometers in the till and clay to pumping of the underlying sandy aquifer. A general discussion of fracturing in the tills of the Interior Plains has been presented by Grisak *et al.* (1976).

Waste Management Methods

Most of the radionuclides placed in the WNRE waste management area consist of activation products from structural materials, impurities, corrosion products, fission products from the reactor, and other wastes from research and development laboratories and decontamination facilities. The wastes contain such a multiplicity of radionuclides that complete analyses of all the radionuclides present in the waste have not been practical. The main constituents are radioisotopes of uranium, plutonium, strontium and cesium. It is estimated that approximately 12,000 Ci of ^{90}Sr and ^{137}Cs have been put into the area, almost entirely in the form of solid wastes.

On a volume basis most of the radioactive materials buried at the WNRE site are classified as low-level waste. These wastes are placed in the fractured lacustrine clay and clay-loam tills in unlined trenches, 3.5 m deep, about 15 m long and 6 m wide (Fig. 45). The filled trenches are covered and compacted with the excavated fill, mainly clay and till.

A series of concrete standpipes, 0.6 m in diameter and 3.6 m deep, are located in the southwest section of the waste management area. These standpipes are used for medium-level solid and liquid waste and for occasional small flasks of high-level liquids. The first standpipes were asphalt-coated precast concrete placed in augered holes on wet cement pads and then backfilled. These standpipes were not watertight, and some have subsequently been found to contain up to 2.5 m of water. The latest type of standpipe is poured in place and steel-lined. An asphalt-coated concrete bunker, 3.6 m in depth, receives the larger volumes of medium-level solid waste. A portion of this bunker has been in place for approximately ten years with only slight leakage evident to date.
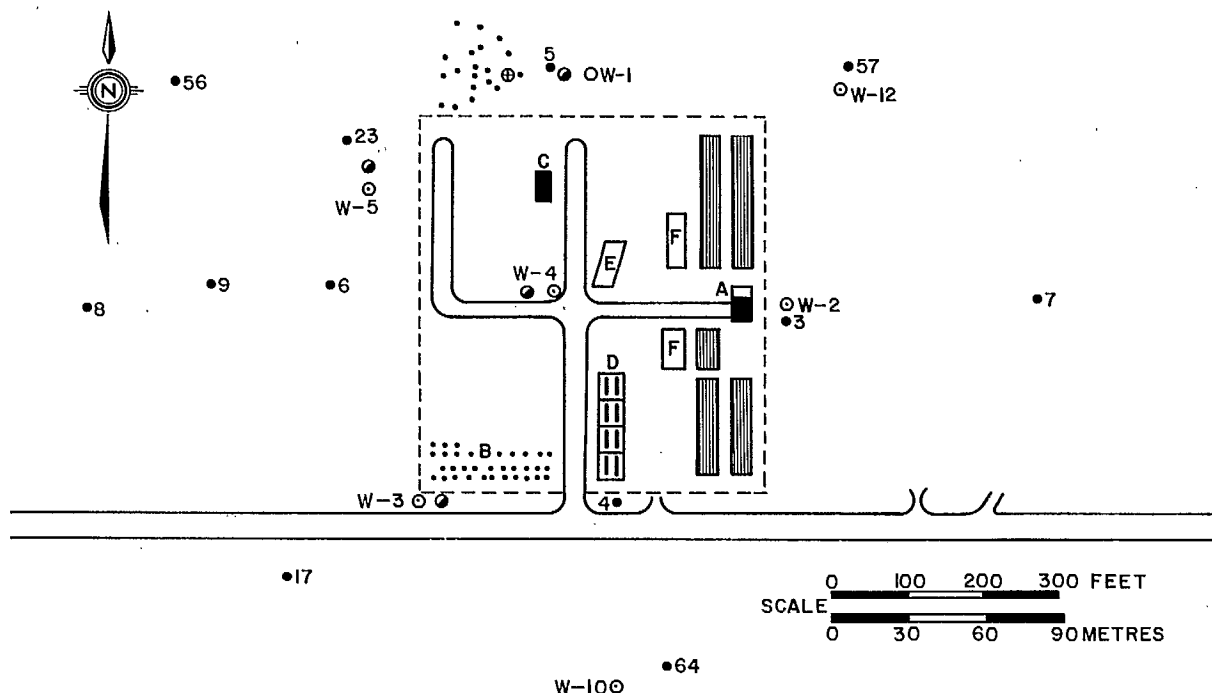
A——INCINERATOR and STACK	RECORDING WATER-TABLE WELL————◕
B——CONCRETE STANDPIPES	RECORDING WELL(in basal sand)————⊙
C——BURIED STAINLESS-STEEL TANKS	PIEZOMETER NEST——————●
D——CONCRETE BUNKERS	TRITIUM INJECTION WELL(in basal sand)—⊕
E——UNLINED TRENCH (medium-level solids)	PIEZOMETER (for tritium monitoring)——∴
F——UNLINED TRENCHES (low-level waste)	
▥—COVERED TRENCH (low-level waste)	

Figure 45. WNRE waste management area facilities (after Cherry, Grisak and Clister, 1973).

Two 450-l double-walled stainless steel tanks are buried in a concrete receptacle in the north-central portion of the waste management area. The tanks are designed to receive high-level liquid waste and are equipped with monitoring facilities at the surface. The original excavation in which the concrete receptacle was poured was about 5.7 m below ground surface, which is approximately 1 m above the top of the basal sand.

Waste Migration Experiences and Predictions

There has been no documented waste migration or groundwater contamination to date at the WNRE waste management area. Since the groundwater flow direction in the waste management area is upward, leaching and decomposition of the solid wastes in the excavated trenches will result in localized shallow groundwater contamination.

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Cherry, Grisak and Clister (1973) concluded that although the water table at WNRE is close to the ground surface, it is not a major detrimental factor to the safety or operation of the site *as long as the site receives continual monitoring and maintenance*. Digital model simulation studies, groundwater geochemistry, and field monitoring of water levels since 1968 indicate that the relationship between the groundwater discharge and recharge areas will likely persist over a long period of time, even if large water table fluctuations occur. This, however, does not detract from the fact that the waste trenches will result in a locally contaminated portion of the shallow groundwater system, which in years of excessive precipitation may make a relatively large amount of contaminated water available to the surface biosphere and perhaps to local surface runoff as a result of groundwater discharge.

In the event of container failure and subsequent leakage of high-level liquid wastes into the groundwater zone, the contaminants would either be localized at shallow depths or could move downward, because of density effects, into the basal sand. If radionuclides entered the sand, under existing conditions, they would be transported westward. Monitoring of their movement could probably be accomplished until they reach the fracture anomaly, at which point their migration would become unpredictable. Radionuclide migration in the basal sand from the waste management area to the fractured bedrock zone would take several decades, which should provide time for implementation of remedial measures, provided these can be accomplished. Cherry, Grisak and Clister (1973) and Grisak (1974) concluded that the subsurface hydrologic regimen at WNRE could be manipulated using techniques such as well pumping, and manipulation schemes could be employed to control or remove contaminants from the basal sand. Nevertheless, it is apparent that these techniques constitute a form of crisis management and are not recommended as an integral part of a hydrogeological waste management scheme. The potential for transport through the fractured till and clay in which the trenches are situated is a subject of continuing research (Grisak and Cherry, 1975; Grisak *et al.*, 1976). The last section of Chapter 4 contains a discussion of the investigative approach to transport in the fractured Quaternary deposits at WNRE.

As an example of the use of the retardation equation in its intergranular form, we can attempt to predict the velocity of a hypothetical ^{90}Sr contamination front in the WNRE basal sand. We will assume the basal sand is homogeneous with respect to hydraulic conductivity between the waste management area and the fractured bedrock zone, where groundwater monitoring becomes much more uncertain. To calculate the average groundwater velocity, V_x, from the Dupuit-Forcheimer relation as expressed in Equation 66, we require the hydraulic conductivity, K, the porosity, n, the empirical coefficient, σ_N, and the gradient of hydraulic head, grad h. The average hydraulic conductivity of the WNRE basal sand unit is approximately 7.5×10^{-4} cm/s, and the

average hydraulic gradient in the basal sand in the flow path under consideration is about 0.01. The sand has an intergranular porosity of about 0.35, and we will assume the empirical coefficient, σ_N, is unity. The average groundwater velocity is then

$$V_x = \frac{K}{n\sigma_N} \text{ grad } h \tag{66}$$

$$= \frac{7.5 \times 10^{-4} \text{ cm/s}}{0.35 \times 1} \times 0.01$$

$$= 1.85 \text{ cm/day}$$

The rest of the variables in the simplified version of the retardation Equation 64 will be estimated from various field and laboratory studies. From Table 24 the bulk density, ρ_b, of the basal sand is about 1.9 g/cm^3 and the cation-exchange capacity, σ_+, is about 1.4 meq/100 g (Gillham, personal communication). For the case of ^{90}Sr versus Ca competition, the total (competing) cation concentration, τ, is about 4.8 meq/l (Table 23). We will assume the selectivity quotient, f', in the basal sand is approximately 1.3, the same as for Sr versus Ca competition in the sandy WNRE soil analyzed by Mills and Zwarich, 1970 (Table 25). With appropriate adjustments for unit conversions, the average velocity of ^{90}Sr in the basal sand is calculated as

$$V_{^{90}Sr} = \frac{V_x}{1 + (\rho_b \sigma_+/n\tau)f'} \tag{64}$$

$$V_{^{90}Sr} = \frac{1.85 \text{ cm/day}}{1 + [(1.9 \text{ g/cm}^3 \times 0.014 \text{ meq/g})/(0.35 \times 0.0048 \text{ meq/ml})]1.3}$$

$$= 0.086 \text{ cm/day}$$

or approximately 5% of the average groundwater flow velocity. As indicated in the CRNL section, this velocity is likely a conservative estimate and does not represent the velocity of the actual migration front but rather the rate for a particle of average velocity. As a further caveat it should be recognized that these calculations can easily be in error by as much as an order of magnitude due to the assumption of a homogeneous hydraulic conductivity between the waste management area and the bedrock fracture zone; they are simply presented as an illustration of the use of the retardation equation.

It would appear appropriate also to evaluate the combined effects of dispersion and retardation (Equations 63 and 64); however the analytical solution of this problem in both two and three dimensions is unwieldy and it is best solved by

numerical methods (Gupta and Greenkorn, 1974; Pickens and Lennox, 1976). The one-dimensional analytical solution for contaminant transport modified only by hydrodynamic dispersion effects can perhaps be used to illustrate, in an extremely simplified manner, the relative effects of various dispersivities in the basal sand. Recalling the solution is valid for the one-dimensional case only, we will oversimplify the field situation and assume absolutely horizontal flow and complete vertical contamination of the basal sand. With these approximations and by considering lateral dispersion as negligible, contaminant movement through the basal sand might be considered analogous to a horizontal laboratory column experiment. In this case, we consider the hypothetical situation of a nonhydrogeochemically retarded contaminant, such as tritium in the form of tritiated water. A more complete discussion and clarification of terms and boundary conditions in the following example was presented in Chapter 2.

If we assume tritium is introduced on a continuous basis to the basal sand beneath the WNRE waste management area (and recalling the assumptions above that are necessary to approximate conditions for the one-dimensional solution), the transport with dispersion can be evaluated by Equation 20, for which an alternative solution (Ogata and Banks, 1961) is

$$C_{(x,t)} = \frac{C_0}{2} \, \mathrm{erfc} \left\{ \frac{x - V_x t}{2\sqrt{D'_x t}} \right\} + \exp\left(\frac{V_x x}{D'_x}\right) . \mathrm{erfc} \left\{ \frac{x + V_x t}{2\sqrt{D'_x t}} \right\} \tag{86}$$

where $C_{(x,t)}$ = concentration of contaminant at distance x, time t,

V_x = groundwater velocity in the x direction,

D'_x = coefficient of hydrodynamic dispersion in the x direction (aV_x),

a = dispersivity (units L), and

C_0 = concentration at the source.

Assuming a dispersivity, a, of 1 m, the concentration at a distance of 50 m from the source after a time of 1000 days is calculated as

$$C_{(50 \, m, \, 1000 \, days)} = \frac{C_0}{2} \, \mathrm{erfc} \left\{ \frac{50 \, m - (0.0185 \, m/day \times 1000 \, days)}{2\sqrt{1 \, m \times 0.0185 \, m/day \times 1000 \, days}} \right\}$$

$$+ \exp\left(\frac{0.0185 \text{ m/day} \times 50 \text{ m}}{1 \text{ m} \times 0.0185 \text{ m/day}}\right) . \text{erfc} \left\{\frac{50 \text{ m} + (0.0185 \text{ m/day} \times 1000 \text{ days})}{2\sqrt{1 \text{ m} \times 0.0185 \text{ m/day} \times 1000 \text{ days}}}\right\}$$

$$\simeq 0.00001$$

Obviously, the contamination is barely detectable at 50 m after 1000 days with a dispersivity of 1 m. A dispersivity of the order of 10 m, however, increases the concentration at 50 m after 1000 days to about $0.09 \, C_0$. For a dispersivity of 100 m the concentration is $0.53 \, C_0$ at 50 m. The larger dispersivity increases the time required for the concentration at 50 m to approach C_0 while also significantly increasing the distance between the source and the front of detectable contamination. The magnitude of the dispersivity required to approximate true field situations is significantly affected by the scale of the flow system under investigation and, in many instances, is selected to reflect the heterogeneity of an aquifer rather than its classically laboratory defined "dispersive" characteristics. The uncertainties involved in the choice of a have been discussed in Chapter 4, and the problem of appropriate field dispersivities for various hydrogeological situations requires more extensive evaluation. The calculation above is, of course, only valid for the one-dimensional case and should simply be regarded as an illustration of the effects of dispersivity on nongeochemically retarded contaminants.

DEFENSE RESEARCH ESTABLISHMENT, SUFFIELD (DRES)

The Defense Research Establishment, Suffield is located in southeastern Alberta, encompassing approximately 500 km^2 of prairie grassland north of Medicine Hat. A small quantity of low-level solid radioactive waste is stored in two shallow trenches excavated in a silty clay-loam till on a local topographically high area of the hummocky moraine typical of the site. The surficial deposits, a complex sequence of till, glaciolacustrine sediments and outwash, are approximately 35 m thick beneath the waste management area and are underlain by Cretaceous bentonitic shales with interbedded sandstones. The thickness of the surficial deposits in the DRES area varies between about 6 m and 90 m. Currie and Waterman (1972) and Schwartz (1975a) have conducted successive hydrogeological investigations of the area.

Hydrogeology

Schwartz (1975a) has identified five stratigraphic units and designated these as the upper till unit, middle sand unit, lower till unit, brown silt unit and

Cretaceous shale unit (Fig. 46). Analysis of the <2-μm fraction of the drift units using X-ray diffraction indicates that illite is the dominant clay mineral and comprises 40% to 50% of the total clay minerals. Montmorillonite and illite are present in approximately equal amounts of 40% in the bedrock samples. Kaolinite and chlorite make up the remaining percentage of the bedrock, and montmorillonite (35%), kaolinite (10%) and chlorite (8%) complete the clay mineral fraction of the drift units.
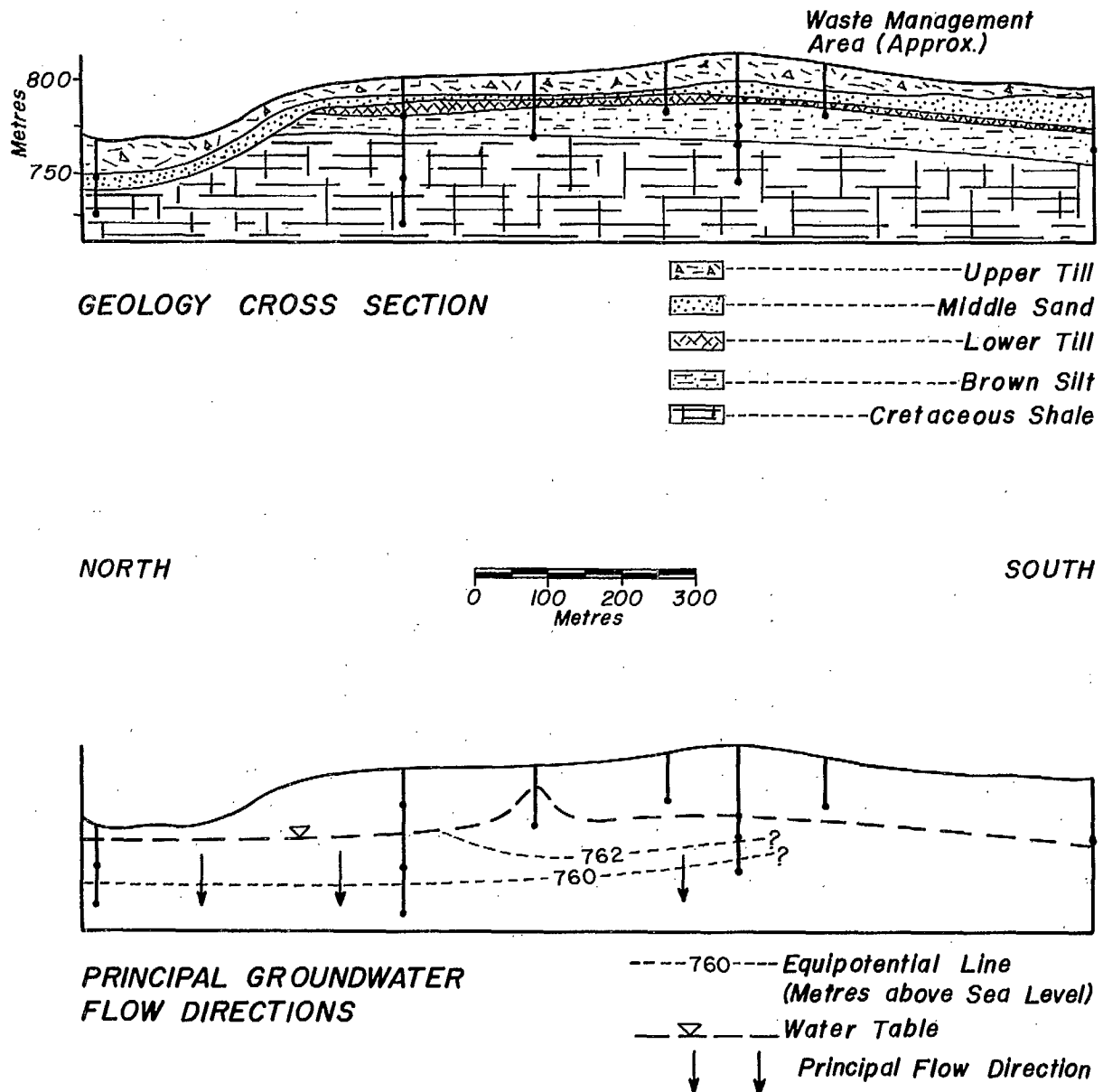

GEOLOGY CROSS SECTION

	Upper Till
	Middle Sand
	Lower Till
	Brown Silt
	Cretaceous Shale

NORTH

0   100   200   300
Metres

SOUTH

PRINCIPAL GROUNDWATER
FLOW DIRECTIONS

----760---- Equipotential Line
(Metres above Sea Level)

Water Table

Principal Flow Direction

Figure 46.   DRES geology cross section and principal groundwater flow directions (after Schwartz, 1975a).

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Currie and Waterman (1972) concluded that the till at the waste management site is fractured and that the fractures provide the means of limited infiltration and subsequent recharge. Although the dimensions and extent of fracturing are relatively unknown, Currie and Waterman presented evidence indicating that the fractures transported a large volume of drilling fluid. Within 10 m of an existing disposal trench a rotary drill lost circulation at 18 m depth and pumped away 272 kg of drilling mud and 13,500 l of water before regaining circulation. They believed that the drilling fluid was being pumped into fractured till at a depth of 18 m to 20 m.

From response tests in piezometers, Schwartz (1975a) reported a median hydraulic conductivity for the upper till unit of 2×10^{-5} cm/s, with a range of 7×10^{-4} cm/s to 1×10^{-6} cm/s based on four tests. For the lower till unit in which seven tests were performed, he reported a median value of 3×10^{-5} cm/s, with a range of 1×10^{-3} cm/s to 4×10^{-7} cm/s. Grain size analyses of 45 samples of the surficial till and nine samples from the deeper till indicate that the clay content is generally between 15% and 20% and the silt content is between 45% and 50%. Schwartz states that "none of the drawdown response tests exhibit a response that is characteristic of fractured media" and that "fracture permeability within the drift...is not significantly developed." Grisak et $al.$ (1976) considered this conclusion to be erroneous. The hydraulic conductivities reported by Schwartz for the till units are three to four orders of magnitude larger than the average intergranular values typical of clay-loam tills (Grisak and Cherry, 1975). On the assumption that the piezometers were adequately sealed, the conductivity data presented by Schwartz are taken as strong evidence that the tills at DRES are highly fractured and that the fractures are the dominant control on the hydraulic conductivity of the tills.

The location of the water table and the direction of groundwater flow beneath the DRES site, as determined from piezometer measurements, are shown in Figure 46. The water table in the area generally coincides with the bedrock surface; yet groundwater mounds have developed beneath topographic depressions which presumably act as precipitation and runoff collection areas.

The only major aquifer in the area, apart from intertill sand units, is the buried preglacial sands and gravels of the Lethbridge Valley (Fig. 47) underlain by the Cretaceous Foremost Formation. The thalweg of the valley is about 10 km south of the radioactive waste management site. Major flow directions indicated by Schwartz (1975a) in Figure 46 are downward; nevertheless, there are indications in Figure 4 of Schwartz (1975a) that a lateral component of southward groundwater flow may possibly exist. He suggests that a deep meltwater channel 1.6 km south of the site is an important groundwater discharge area.
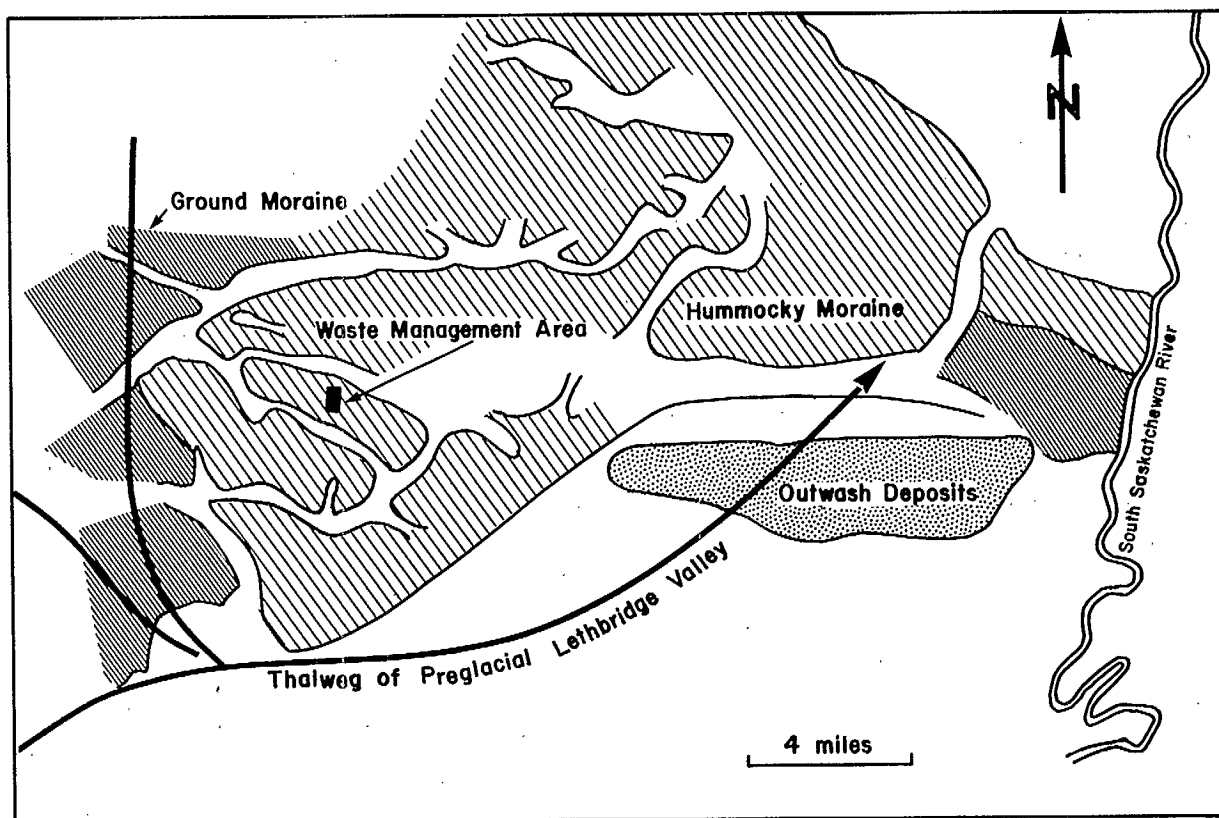
Figure 47.   Map of DRES waste management area showing location of surficial glacial meltwater channels and preglacial Lethbridge Valley sand and gravel aquifer (after Currie and Waterman, 1972).

Drilling at DRES has indicated that some of the intertill sand lenses are saturated beneath topographic depressions, whereas the drift above and below the sand appears unsaturated. Soil moisture blocks have been installed in the drift in an attempt to determine moisture contents and variations at specific depths in the unsaturated zone. Specific conclusions other than those related to recharge from topographic depressions have not yet been formed from the soil moisture data.

Speculatively, water likely moves downward, primarily through fractures in the till, from topographically low areas into the intertill sand units (where present) where a subsequently slower rate of movement out of the sand probably results in locally saturated conditions. The slower rate of movement out of the sands might possibly be due to a decrease of fracture density with depth as is the case in many fractured rock situations. The moisture contents which increase with depth under the topographic depressions (Schwartz, 1975a) may also serve to narrow the fracture apertures, owing to clay mineral expansion, resulting in a decreased net flux in the deeper till units. From water-level graphs (Schwartz 1975a) it appears that the volume of water moving through the unsaturated zone to the water table is very

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small, since there is no apparent seasonal fluctuation or precipitation response over a period of three years. A descriptive discussion of the direction of groundwater movement at DRES, such as presented for the CRNL and WNRE areas, is not possible. It is, however, apparent that any radionuclides that may be leached from the disposal sites must travel downward through a relatively thick unsaturated zone before reaching the water table. The movement would likely take place through fractures; however as very little recharge appears to be reaching the water table, the net flux would likely be quite low.

Waste Management Methods

The waste management facility at DRES is presently comprised of two shallow unlined trenches in which a small quantity of low-level solid radioactive waste was placed during the period 1967 to 1971. Currie and Waterman (1972) suggested that for future disposal a sulphate-resistant concrete structure be engineered to keep the waste dry and that the floor of the structure be maintained above the water-level elevation of the saturated sand lenses. They also suggested that the structures should be covered and contoured to the land surface during and after filling to prevent infiltration of precipitation. It was observed that the present trench acted as an artificial collector of precipitation, particularly snow, and that the portion not evaporated had infiltrated to the subsurface.

Currie and Waterman also conducted a background gamma-ray neutron logging of the holes drilled in the area. Subsequent logging using equivalent calibration techniques could possibly detect any increase in background radioactivity owing to migrating gamma-emitting radionuclides (e.g., ^{137}Cs).

Waste Migration Experiences and Predictions

There is no documented occurrence of any solid waste leaching or radionuclide migration from the DRES site. If the suggestions by Currie and Waterman are implemented, the susceptibility of wastes to leaching and migration would be minimal. If any leaching was to occur, the subsurface migration route would probably be downward through fractures to the water table and subsequently through the saturated bedrock to the major meltwater channel, a distance of about 1.6 km. The groundwater flow in the bedrock would likely be most active through the fractures, which Schwartz (1975a) has indicated are present in at least one drill site.

The uncertainty of groundwater monitoring in fractured media as well as the virtually unknown transport and retardation characteristics of fracture flow systems

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was discussed in considerable detail in Chapter 4. Since the choice of independent variables in the retardation equation would essentially amount to guesses at DRES, no predictions are made concerning any radionuclide transport rates in either the unsaturated or saturated zone.

Schwartz (1975a) has estimated that the *intergranular* seepage velocity in the bedrock at DRES is about 5×10^{-6} cm/s, and suggested that 1100 yr is the appropriate groundwater travel time in the saturated zone between the waste management area and the discharge area in the meltwater channel. This is based on an estimated porosity of 0.05, and measured and average values of hydraulic conductivity and gradient, respectively. If, however, groundwater flow in the bedrock is through fractures rather than intergranular interstices, the velocity estimate above could be revised to reflect fracture rather than intergranular porosity. Revised estimates of groundwater velocities which assume limited fracturing of the bedrock and a minimum effective porosity of 0.001 are presented by Schwartz (1977) as the "worst case" with respect to groundwater velocities in the bedrock at DRES. The revised estimate would then represent a decrease in the travel time above to approximately 22 yr.

Various scenarios representing assumed best and worst cases for transport parameters related to cation exchange are presented by Schwartz (1977) in a comprehensive paper on predictive mathematical modelling at DRES. He concludes that there is reason for optimism with respect to the ability of the subsurface environment at DRES to provide confinement and to attenuate the concentrations of such radioisotopes as ^{137}Cs and ^{90}Sr. This conclusion is based on what are considered the positive features of the site, which include "the arid climate, the thick unsaturated zone, the depression focused character of recharge, the dominant recharge gradient, the low hydraulic conductivity of the bedrock unit, the significant cation exchange reservoir provided by the drift and bedrock units, and discharge by evaporation in a closed depression."

Notwithstanding the positive features of the site, we are in agreement with the final conclusions of the paper (Schwartz, 1977) which state that model development must be matched with a parallel field research and case history documentation in order to reduce the presently large uncertainties in many of the transport parameters.

BRUCE NUCLEAR POWER DEVELOPMENT (BNPD)

The Bruce Nuclear Power Development is located on the shore of Lake Huron near Kincardine, Ontario. The surficial deposits range from 0 to 18 m thick, with the thickening increasing from west to east away from Lake Huron (Gorman, 1972). The Pleistocene deposits consist of a dense, silty till underlain by discontinuous sand

lenses which overlie a weathered, fractured Paleozoic dolomite (Fig. 48). A recent
layer of bedrock-derived sand, gravel and cobbles covers most of the area to a
thickness of up to 1.8 m. Use of the initial waste management area, Site 1, which
comprises about 0.7 ha, has been discontinued in favour of a large area, Site 2,
approximately 6 ha in size. The thickness of the till at Site 2 is approximately 12 m.
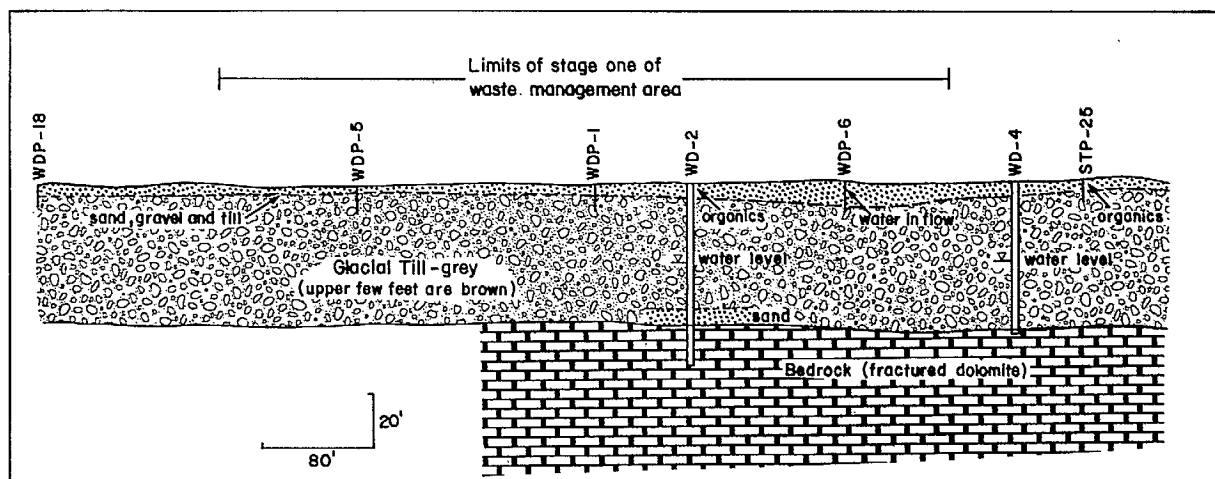

Figure 48. Geologic cross section through the BNPD Site 2 waste management area.

Hydrogeology

The Pleistocene till, which overlies the bedrock and contains at least two
sand lenses immediately above the bedrock contact, is classified by Gorman (1972) as a
"very dense impervious till." Laboratory tests of five relatively undisturbed core
samples gave a mean hydraulic conductivity of 1×10^{-7} cm/s, with a range between
1.5×10^{-8} cm/s and 4.2×10^{-7} cm/s. The till classifies generally as a loam to
silty loam with about 12% to 15% clay-sized particles. Preliminary mineralogical
and X-ray diffraction analysis has tentatively identified illite, dolomite and quartz
in the fine fraction of the till and calcite, dolomite and igneous and metamorphic
rock fragments in the coarser fraction.

In some instances, the sand units above the bedrock contact are referred to
by Gorman (1972) as the "lower aquifer," and "piezometric contours" (Gorman) have been
constructed for this unit (Fig. 49). The sand unit appears only as discontinuous
lenses on the cross sections constructed by Ontario Hydro, and it is difficult to
determine the extent and continuity of the sand from the information available. It
is also difficult to interpret the groundwater flow pattern in the third dimension
from the information available. To this end more piezometers in the interval between
the water table and the bedrock surface would be useful as well as information on

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the type and installation procedure of the piezometers and the depth at which the
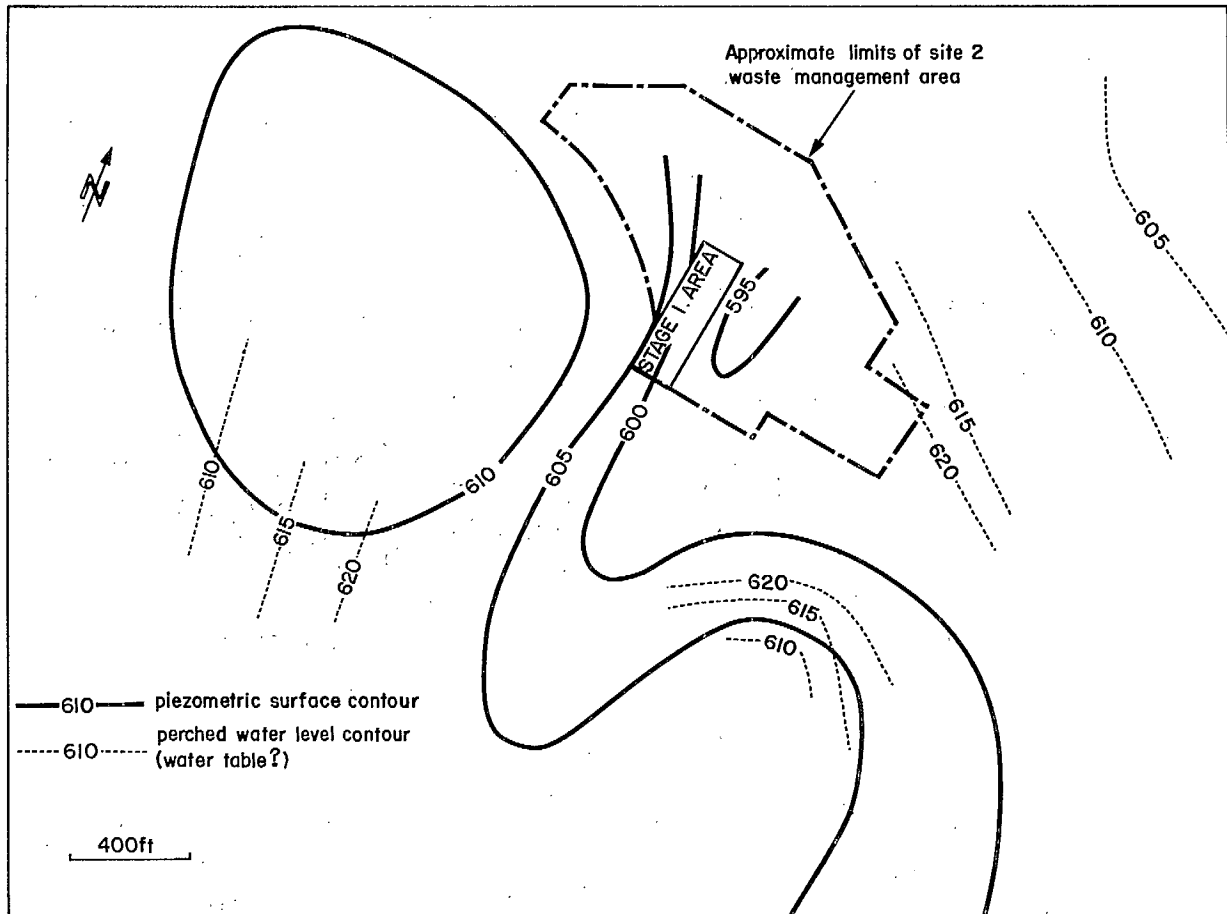piezometer is open to the sediments.

Figure 49.   BNPD waste management area and perched water level (water table?) contours
(after Ontario Hydro BNPD Drawing No. GEOL-B-83, 1971).

From the piezometer and water table information available it is obvious
that in the vicinity of Site 2 a strong downward hydraulic-head gradient exists
from the water table to the "lower aquifer." The water table gradient, which varies
from about 0.06 south of the site to about 0.02 east of the site, is exceeded by the
downward vertical gradient which appears to have a maximum value of about 0.4 in the
vicinity of the Site 2 area. This suggests that the major direction of groundwater
flow near Site 2 is downward.

There have been suggestions that springs occurring at the contact between
the surface gravelly deposits and the till may be indicative of a perched water
table. Considering the density of the till, the low moisture contents reported do
not necessarily indicate an unsaturated state, but again piezometers in the till at

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intermediate depths would clarify the situation.

Waste Management Methods

The radioactive waste management site at BNPD receives low-level waste in the form of combustible objects, e.g., failed equipment, and medium-level waste in the form of ion-exchange columns and filters. The wastes are placed in concrete-lined trenches or tile holes. Some time ago there was some experimental open-pit burning of combustible objects followed by a backfill cover and additional burnings; however, the resulting ash-soil mixture has subsequently been excavated and placed in a concrete trench. There has been no other burial of radioactive materials directly in the soil at the BNPD site. The solid waste classification system cited at the beginning of this Chapter has been developed by Ontario Hydro on the basis of practical and operational limitations.

Waste Migration Experiences and Predictions

To date there has been no documented experience of release or migration of radioactive wastes from the BNPD sites. Possible waste migration directions and rates can be postulated on the basis of available information summarized above and on laboratory investigations conducted by Brown (1972) on the BNPD sediments.

Brown found that the (Mg^{++}) cation-exchange capacity, σ_+, of the subsurface material at BNPD ranged between about 0.24 meq/100 g and 4.0 meq/100 g, with influent concentrations of 100 mg/l and 200 mg/l Mg^{++}, respectively. Exchange capacities at influent concentrations of 100 mg/l ranged between 0.030 meq/100 g and 0.139 meq/100 g and between 0.18 meq/100 g and 0.54 meq/100 g for ^{137}Cs and ^{60}Co, respectively. On the basis of batch-type laboratory analyses, Brown concluded that the soil retains cobalt and cesium ions, provided their concentrations in a transporting groundwater solution are sufficiently higher than such ions as K^+, Na^+, Mg^{++} and Ca^{++}. He also concluded that although the conditions for sorption of cesium and cobalt in trace concentrations are disadvantageous, there would be very little elution (or leaching) once exchange had taken place. Some correlation appeared to exist between concentration of leachable cations and exchange capacity as well as between organic matter and exchange capacity.

The investigations conducted by Ontario Hydro have of course been directed to determining the suitability of the site for radioactive waste management. It should, however, be noted that the Ontario Hydro philosophy for operation of the

BNPD Site 2 solid waste management facility does not depend to a significant degree on the hydrogeological environment to maintain isolation of the waste materials. According to Hydro officials, the concrete trenches, waterproof membranes, surface drains and a continuously drained and monitored interspace between the trench and the soil provide the isolation. In the opinion of the authors, these engineering structures do not eliminate the need to investigate the transport and retardation characteristics of the hydrogeological regimen in the waste management area.

For comparative purposes, the available information is utilized to speculate on the "worst case" event, i.e., the escape of radionuclides from the isolated environment noted above and migration in the groundwater system. We will assume the water table elevations in Figure 49 represent the upper boundary of a fully saturated zone.

The major direction of groundwater flow in the vicinity of Site 2 is downward, under a maximum hydraulic gradient of about 0.4. The vertical groundwater velocity, V_z, can be estimated from Equation 66, using the average laboratory-determined vertical hydraulic conductivity, K_z, and assuming n (porosity) and the empirical constant, σ_N, to be 0.2 and unity, respectively. The average groundwater velocity is then

$$V_z = \frac{K_z}{n\sigma_N} \text{ grad } h \qquad\qquad (66)$$

$$= \frac{1 \times 10^{-7} \text{ cm/s}}{0.2 \times 1} \times 0.4$$

$$= 2 \times 10^{-7} \text{ cm/s}$$

$$= 0.017 \text{ cm/day}$$

This of course assumes that the till is not fractured and that the effective velocity is intergranular. We will illustrate the use of the simplified retardation Equation 64 for the case of ^{137}Cs migration by intergranular flow, considering K^+ as the primary competing cation and cation exchange as the retardation mechanism.

Most of the variables in the retardation equation have either been determined by Ontario Hydro or can be estimated from information presented in previous Chapters. The dry bulk density, ρ_b, can be taken from Table 24 as about 2.2 g/cm^3 (dense silty till). The exchange capacity, σ_+, for ^{137}Cs will be taken as approximately 0.1 meq/100 g. The concentration in the groundwater of K^+, the competing cation, is

about 0.1 meq/l. The selectivity quotient, f', will be estimated at about 1.5 based on the CRNL experience in a sandy aquifer with a small percentage of illite (the value of f' could possibly be higher due to Cs-illite affinity). The estimated downward velocity of the radionuclide ^{137}Cs beneath BNPD Site 2 (assuming escape from the engineered environment and intergranular flow) is according to the retardation equation

$$V_{Cs} = \frac{V_z}{1 + (\rho_b \sigma_+ / n\ \tau)\ f'} \tag{63}$$

$$= \frac{0.017\ \text{cm/day}}{1 + [(2.2\ \text{g/cm}^3 \times 0.001\ \text{meq/g})/(0.2 \times 0.0001\ \text{meq/ml})]\ 1.5}$$

$$= \frac{0.017\ \text{cm/day}}{166}$$

$$\simeq 1 \times 10^{-4}\ \text{cm/day}$$

or about 0.6% of the average groundwater velocity. Should ^{137}Cs escape from the BNPD storage and drainage environment, it appears that on the basis of the assumptions above and considering only cation exchange, the average intergranular nuclide velocity would be less than a metre per thousand years. The leading edge of the contamination front would have a significantly higher velocity, although the concentration would be much lower than the 0.5 C/C_0 concentration of the average velocity. Further studies recommended to refine the hydrogeological interpretation at the site would include (1) piezometer and response tests at intermediate depths within the till; (2) investigations on the possible existence of fractures in the till; (3) determination of the magnitude of the selectivity quotient, f'; and (4) a somewhat more detailed field and laboratory evaluation of the site after the method suggested in Chapter 6.

Suggested Guidelines for Selection and Investigation of Shallow, Subsurface Radioactive Waste Management Sites

The purposes of this Chapter are to consider what may constitute a suitable hydrogeological environment for radioactive waste management sites in the shallow subsurface of typically Canadian terrain and to suggest procedures by which prospective sites might be investigated. A complementary report covering in detail the design and execution of prospective site investigations is being prepared by J.A. Cherry and colleagues at the University of Waterloo.

HYDROGEOLOGICAL SITE CRITERIA

Since the radioactive waste management policy of the Atomic Energy Control Board is presently under review, an appraisal of potential hydrogeological site criteria is in order. A discussion of the hydrogeological factors in Canadian radioactive waste management has been presented by Cherry, Grisak and Jackson (1974) which contains a proposed evaluation scheme that can be applied to potential radioactive waste management sites. Much of the discussion in this Chapter is based on the general evaluation criteria presented in that paper.

The first published statement (of which the authors are aware) that is directly concerned with site criteria in Canadian environments is that of Mawson and Russell (1970). Four of their requirements are

(1) The site should be well drained in the sense that standing surface water would be present infrequently, and would disappear rapidly.
(2) The soil should have as high a cation exchange capacity as practicable. (Note that conditions [1] and [2] are difficult to reconcile. Soils with good adsorptive properties--typically silts and clays-- are often poorly or imperfectly drained.)
(3) There should be a good depth of soil to the water table--about 5 m would be a reasonable minimum.
(4) The ground water should be moving slowly (cms/day).

Another set of criteria has been advanced by Cherry, Grisak and Jackson (1974) for the cases of (1) intermediate-term burial of solid wastes with a commitment to maintenance and monitoring and (2) long-term burial of solid wastes in a site with suitable perpetual characteristics. In both these instances, the prime

consideration is *site predictability*, i.e., the prediction of the contaminant migration characteristics of a particular site within an acceptable degree of accuracy. The criteria presented by these authors are suitable to describe the desirable characteristics of a waste management site and are presented below (in a slightly modified form) as a general guide.

Sites for intermediate-term burial....
1. The land surface should be devoid of surface water, except during snowmelt runoff and exceptional periods of rainfall. In other words, the sites should not be located in swamps, bogs, or other types of very wet terrain.
2. The burial zone should be separated from fractured bedrock by an interval of geologic deposits sufficient to prevent migration of radionuclides into the fractured zone.
   Except in unusual circumstances, the direction and rate of groundwater flow as well as the retardation effects are very difficult or impossible to predict in groundwater regimens in fractured rocks. This lack of predictability necessitates that fractured rock be regarded as a major hazard in terms of subsurface radioactive-waste management. In fact, it is doubtful if contaminated groundwater could be effectively detected and monitored in some types of fractured rock.
3. The predicted rate of radionuclide transport in the shallow Quaternary deposits at the site should be slow enough to provide many years or decades of delay time before radionuclides are able to reach public waterways or any other area in the biosphere that might be considered hazardous. In other words, considerable time should be available for detection of contamination and for application of remedial measures if necessary.
4. The site should have sufficient depth to water table to permit all burial operations to occur above the water table, or as an alternative the site should be suitable for producing an adequate water table depth by flow-system manipulation.
5. The site should be well-suited for effective monitoring and for containment by flow-system manipulation schemes.
   In the recharge segments of subsurface flow systems, the water table can be lowered simply by reducing the amount of infiltration through the unsaturated zone. The amount of water-table reduction will depend on the area over which infiltration barriers are placed, the efficiency of the barriers, and the permeability and hydraulic gradients in the shallow groundwater zone. Further water-table decline can be achieved by reducing the amount of lateral groundwater seepage to the zone of water-table depression.
   In the discharge segments of subsurface flow systems, water-table reduction may be considerably more difficult because water is supplied to the water-table zone from above and from below. In addition to artificial barriers to prevent vertical infiltration, other techniques such as subsurface drains, pumping wells or grout curtains would be necessary to prevent upward-flowing groundwater from entering a zone of intended water-table depression.

Sites for long-term burial....
1. The land should be generally devoid of surface water and be relatively stable geomorphically. In other words, erosion and weathering should not be proceeding at a rate that could significantly affect the position and character of the land surface during the next few hundred years.
2. The subsurface flow pattern in the area must be such that the flow lines from the burial zone do not lead to areas [where

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contamination would be] particularly undesirable, such as frac-
tured bedrock, public waterways used by man, aquifers used for
water supply, and others.

3. The predicted residence time of radionuclides within an acceptable
    part of the subsurface-flow system must be of the order of several
    hundred. years. The hydrogeological conditions must be simple
    enough for reliable residence-time predictions to be made.

4. The natural water table should be below the burial zone by at
    least several metres, and the hydrogeological setting should be
    such that large water-table fluctuations are very unlikely. This
    condition would provide additional assurance that leaching of
    radionuclides would not occur quickly in the event of corrosion
    of the waste containers, or in the event that low-level wastes
    are put directly in the ground.

    If maintenance and monitoring are not assured, most of the
    methods discussed above for producing artificial water-table
    depressions beneath waste management sites cannot be considered
    reliable for long periods of time. Therefore, at sites for long-
    term burial, it is desirable to have sufficient water-table depth
    without controls based on artificial materials such as plastic,
    concrete, or pumps.

The difficulty in locating areas in Canada with sufficient water table depth
may necessitate alternative waste management practices to those discussed in this report.
One possible alternative, presented in Cherry *et al.* (in press), consists of burial in
large-diameter holes in thick sequences of till and clay below the water table. This
alternative relies on the diffusive properties of the till and clay and on the absence
of open fractures.

The criteria above are useful from a general point of view, since they
provide a fairly comprehensive review of desirable hydrogeological characteristics
for radioactive waste management sites. Short-term burial (storage) sites or long-term
sites that manipulate the hydrogeological system by artificial means such as drains or
pumps necessitate a commitment to involved maintenance and monitoring and impose
that commitment onto future management schemes. Nevertheless, even in the long-term
geomorphically and hydrogeologically stable sites, it is apparent that monitoring
and confirmation of the successful operation of a site will be necessary. Therefore
the ability to monitor any prospective site adequately is considered integral to its
use.

As discussed in the preceding Chapters, the movement of radionuclides in
the subsurface is dependent on a large number of variables (Chapter 4 contains a
discussion of some of the independent variables) which are determined by the physical
and hydrogeochemical aspects of the hydrogeological environment in the vicinity of a
waste management site. Various combinations of the variables may afford some degree
of containment and retardation at any particular site, and consequently no attempt
is made to outline specific site criteria in the manner of those listed by Cherry,

Grisak and Jackson (1974). A discussion of some possible purposes that a hydrogeological environment could serve is presented and the important variables involved are outlined, keeping in mind the general criteria presented above.

For the purposes of radioactive waste management, a hydrogeological environment could conceivably be utilized in two ways:

(1) As a second line of defense against contamination of public waters by radionuclides that have escaped from engineered structures (the engineered structures are the first line of defense, i.e., a *barrier* in AECB terminology).

(2) As an integral part of the waste management facility design, chosen to afford a favourable combination of transport and retardation characteristics such that any radionuclide migrating into the public domain enters the domain below the maximum permissible concentration.

These will be referred to as (1) the containment option and (2) the retardation option, respectively.

In both the containment and retardation options it is implied that adequate monitoring facilities can be installed in the hydrogeological system. This suggests that the system is simple enough to predict potential contaminant migration paths. With this relatively simple system, provided that adequate monitoring facilities can be installed, it may in some instances be feasible to design a system which could be amenable to manipulation should the monitoring indicate contamination beyond acceptable levels. This possibility forms the basis of another purpose that the natural or engineered subsurface system should serve at a radioactive waste management site. *The hydrogeological environment should provide a suitable medium for monitoring any escaped radioactivity and the potential for manipulation of the contaminated portion of the subsurface system should the contamination exceed acceptable levels at the monitoring points.* Potential manipulation methods could include pumping wells or pumping-injection well schemes which would attempt to modify the natural flow direction and velocities and to provide collection points for contaminants in the system. Other methods might include the prior installation of subsurface drains as a contingency approach or perhaps even excavation and relocation of contaminated volumes of subsurface material.

Under any operating philosophy, of which the containment and retardation options are only two, a reliable monitoring system must be considered the key factor. If the hydrogeological system at a potential site is too complicated to offer a reliable monitoring capability, the only acceptable options seem to be

relocation or an engineered hydrogeological environment. Provided that the site offers reliable monitoring capability, the containment and retardation options could be considered as possible operating philosophies.

The containment option implies that the hydrogeological environment will be used to contain and concentrate within as limited an area as possible any radioactivity which leaves (escapes) the engineered storage structures. The retardation option implies that the hydrogeological environment will be used as an agent for contaminant retardation and may be suitable for low-level solid or liquid waste disposal operations. A major difference between the two operations is the extent of contaminantion. The containment option suggests a low volume of relatively concentrated nuclides, whereas the retardation option suggests a larger contaminated volume but a lower nuclide concentration. Both options require adequate monitoring facilities to ensure that the subsurface system is operating as predicted, and both require essentially the same manner of investigative methodology.

The retardation option is discussed and presented in this Chapter as an operating philosophy, since the subsurface disposal of tritium at the Chalk River Nuclear Laboratories site might be considered as an example. Yet the retardation option is not necessarily advocated by the authors, since it involves contamination of a subsurface flow system. It may perhaps be considered on the basis of the available options and the "scenario" approach to alternatives at any particular site. For example, the options to subsurface management under a retardation scheme might be discharge to surface waters or complete decontamination, and in these cases the retardation philosophy may offer some environmental or economic advantages.

Containment Option

The containment option implies that any radionuclides migrating beyond the limits of an engineered storage structure (such as a concrete bunker) will be contained and concentrated within as limited a volume as possible. It is worth noting at this point that the most effective means of ensuring the reliability and predictability of the hydrogeological system under a containment option scheme is to construct or engineer this environment artificially from local or imported geologic materials. The engineered hydrogeological system would then offer a predictable environment between such structures as concrete bunkers and the natural hydrogeological system. *This type of intermediate engineered geologic environment is considered by the authors to offer the most reliable form of subsurface waste management available to Canadian authorities.*

The containment option requires first that the contaminated volume of geologic material (assuming escape from an engineered storage structure) be restricted to a minimum. The relative magnitude of contaminated volumes that might be anticipated should contaminants escape from engineered storage facilities can be illustrated using the hypothetical example of a faulty tile hole containing approximately 250 Ci of waste material including ^{3}H, ^{90}Sr and ^{137}Cs. We will assume that the water table exists or has risen above the bottom of the tile hole, intercepting a fracture in the tile, and that the groundwater is transporting radionuclides out through the fracture and into the groundwater water flow domain. Under *extremely simplified* hydrogeological conditions, the escaped radioactivity can be expected to spread gradually and occupy a predictable and ever-increasing portion of the flow domain. If we assume that the shape of the potential contaminated zone is a cone with a basal radius, r, of 10% of the height, h (Fig. 50), then the relative volumes of contaminated material can be calculated providing the distance, h, from the tile to the basal end of the cone is known

$$\text{Contaminated volume}_A = 0.01047h^3 \tag{87}$$

If we further simplify conditions and assume negligible dispersion in the direction of groundwater flow and a completely homogeneous system (which is geologically unlikely), the distance h for each of the contaminants can be approximated by employing Equation 64

$$V_A = \frac{V}{1 + \frac{\rho_b}{n} K_d} \tag{64}$$

where V_A = average velocity of radionuclide,

V = average groundwater flow velocity,

ρ_b = dry bulk density of the hydrogeological medium,

n = porosity, and

K_d = distribution coefficient (see Equation 36).

To complete the relative contaminated volume calculation we will assign values to the following parameters:
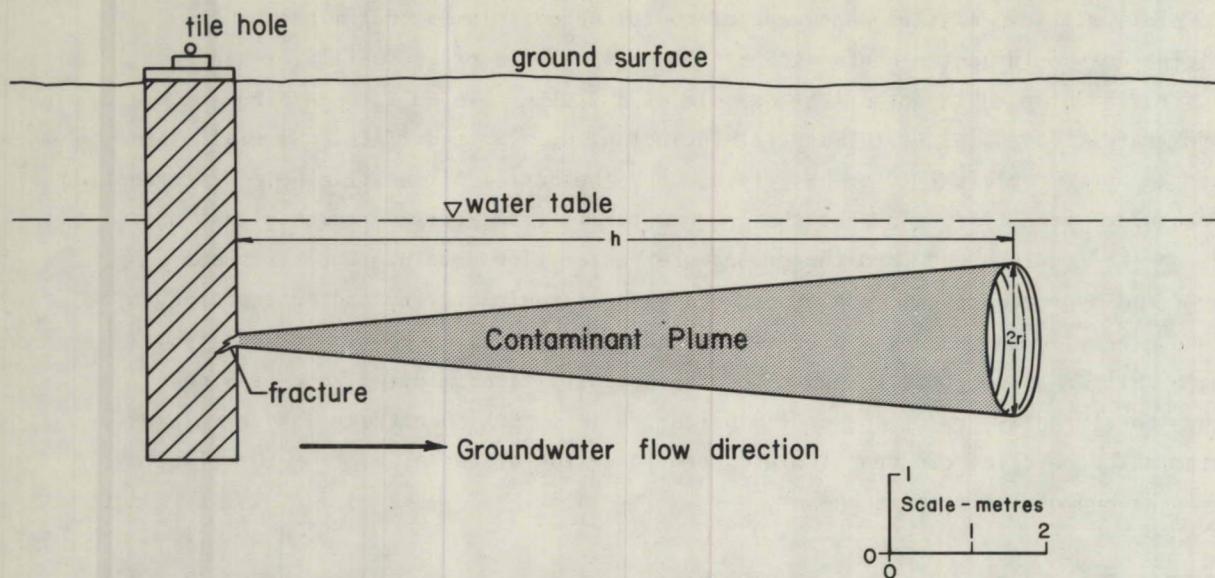
Figure 50. Simplified schematic representation of the potential contaminated zone owing to groundwater transport of radionuclides from a faulty tile hole.
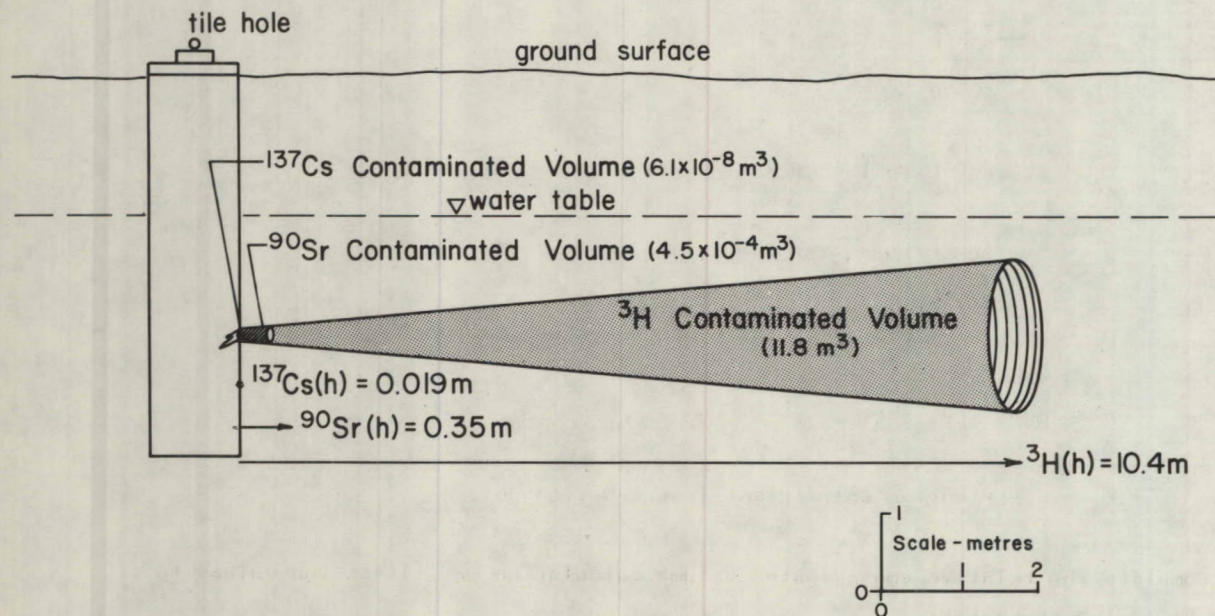

Figure 51. Chromatographic separation of the radionuclides ^{137}Cs, ^{90}Sr and ^{3}H in the potential contaminated zone.

Hydraulic conductivity (K) = 10^{-3} cm/s,

Porosity (n) = 30%,

Hydraulic gradient (grad h) = 0.01,

Dry bulk density (ρ_b) = 1.7 g/cm^3,

^{90}Sr distribution coefficient (^{90}SrK_d) = 5 ml/g,

^{137}Cs distribution coefficient (^{137}CsK_d) = 100 ml/g, and

^{3}H distribution coefficient (^{3}HK_d) = 0.

The average groundwater velocity calculated from Equation 66 is 10.4 m per year. The distances, h, calculated for the radionuclides ^{3}H, ^{90}Sr and ^{137}Cs after one year of transport in the groundwater system are 10.4 m, 0.35 m and 0.018 m, respectively. The respective volumes contaminated by each of the radionuclides after one year of transport (Equation 87) are 11.8 m^3, 4.5 x 10^{-4} m^3 and 6.1 x 10^{-8} m^3. The contaminated zone caused by the tile hole leak would conceptually resemble a chromatographic column with the highly retarded radionuclides (such as ^{137}Cs) near the tile fracture and those with very low or zero distribution coefficients (such as ^{3}H) at the extreme front (Fig. 51). Although the example is extremely simplified, the implications of the contaminated volume increasing with the cube of the distance are clear. Several factors can contribute to restricting this volume, the most important of which are the sorptive capacity of the transmitting medium and the groundwater flow velocity. Sorption and flow velocities have been discussed in considerable detail in previous Chapters and it is simply suggested that the most desirable type of hydrogeological system for the containment option is one offering both a high capacity for sorption and a low groundwater flow velocity. A prime factor that could dramatically increase the contaminated volume as well as decrease the ability to monitor any system is the heterogeneity which is likely in a geologic environment.

The most obvious choice of geologic materials to obtain a high sorptive and low velocity system is clay. In areas where desiccation and other geologic processes such as postglacial rebound have caused cracking or tension fracturing of clayey units (Grisak *et al.*, 1976), however, the predominant flux of groundwater is through the fractures. The reliability of monitoring installations in such environments or even the capability to monitor groundwater and contaminant movement through fractured media is very uncertain. On the basis of current knowledge, a

seemingly favourable hydrogeological medium for long-term containment would likely be an illitic sandy silt with a clay content of approximately 20%. The inclusion of illite in such a medium is necessary to effect the retardation and containment of radiocesium, for which it has a high affinity. A lower, but still significant, clay content would offer the required sorptive capacity and be less likely to fracture should the moisture conditions change. A certain amount of homogeneously distributed organic material may also be desirable. Such a medium could be created by simply ordering and mixing the required material and placing it in the desired locations.

A hydrogeological system in which the hydrogeochemistry is conducive to radionuclide precipitation is also considered advantageous under the containment option. Considerable care must be observed in choosing such a site from a hydrogeochemical point of view, since a minor change in hydrogeochemistry could result in a reversal of the precipitation or sorption processes. The long-term stability of the hydrogeochemistry must be assured in using a system relying only on precipitation as the containment process. Obviously, a system offering high sorptive capabilities, low flow velocities and long-term intergranular flow integrity, with precipitation as an added attaction, would be considered a prime candidate for use under the containment option. As stated above, it is the opinion of the authors that the most reliable way of assuring at least some of these desirable qualities is actually to construct a hydrogeological environment intermediate to the engineered storage structures and the natural subsurface environment.

The concept of engineered hydrogeological systems is not new and, in fact, has been suggested in several instances. For example, a "dry" storage structure in the unsaturated zone at the Whiteshell Nuclear Research Establishment has been suggested as a possible alternative to the present waste management site [Cherry, Grisak and Clister (1973); Cherry, Grisak and Jackson (1974)]. These authors indicate that specifically placed coarse-grained sediments within a much finer-grained porous medium can act as a barrier to infiltration and thereby prevent leaching of solid waste. The design is based on the concept of the "wick effect." Column experiments, dye tracers and digital simulations were used by Corey and Horton (1969) to establish that pore water in a partially saturated fine-grained material overlying an unsaturated clean gravel will not drain into the gravel, provided that the fine-grained clayey material remains less than completely saturated. The infiltrating water will move around the gravel owing to the relatively high capillary tension in the fine-grained medium, and movement into the gravel will only occur after the clay becomes saturated at the gravel-clay contact. It has been suggested that low-level solid waste could be placed in this type of gravel-clay structure, and by appropriate layering above the solid waste (and surface

diversions in higher precipitation areas), infiltration and leaching of the solid waste could be reduced to a minimum [Cherry, Grisak and Clister (1973); Cherry, Grisak and Jackson (1974)].

Retardation Option

If a site is regarded as suitable for use under the retardation option the waste management philosophy implies the use of the hydrogeological environment as an integral part of the waste management system. The retardation option suggests transport of radionuclides in the subsurface, but requires that the hydrogeological environment be capable of retarding the movement and diluting the concentration of these nuclides to the extent that any radionuclide migrating into the public domain enters the domain below the maximum permissible concentration. This method of operation is not necessarily advocated, since the most important factors in ensuring that subsurface radionuclide residence times are adequate for the retardation option are the sorptive and dispersive properties of the hydrogeological media; our appreciation of these processes is the subject of considerable current research.

A very high dispersive capacity, which is likely only available in systems that are extremely heterogeneous and consequently difficult to monitor, would offer dilution characteristics that approach the requirements of the retardation option. Since dispersion is directly proportional to flow velocity (see Equation 26), however, a very high dispersive capacity would imply high flow velocities, which would further imply either clean sands or gravels with very few fine-grained silts or clays, or fractured media. Subsurface systems with very high dispersive capacities would likely result in large, contaminated, heterogeneous volumes. Additionally, permeable near-surface hydrogeological environments are generally suitable as domestic or other water supply sources, and a large contaminated area renders this type of environment unsuitable from that point of view.

An example of a waste management area that could possibly be termed a retardation site is the Chalk River Nuclear Laboratories facility in Ontario. The Chalk River sands are quite clean with only a small percentage of clay-sized particles, and the groundwater flow velocity is in the order of a few centimetres per day. Barry and Entwistle (1975) have recently reviewed and updated a study by Parsons (1963) concerning tritium disposal as tritiated water into the liquid disposal area in the Perch Lake basin (Chapter 5 and Fig. 41). Water containing tritium is discharged into pits in the liquid disposal area from which it percolates into the groundwater system. Parsons (1963) found that some of this tritiated water emerges at the surface as seeps below the sand dunes and travels via surface streams

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to Perch Lake. The rest of the tritium, according to Parsons, travels in the subsurface groundwater system in the general direction of Perch Lake where it eventually discharges. Following a recent tritium-budget analysis of groundwater tritium surveys completed by Merritt (1969), Barry and Entwistle concluded that roughly two thirds of the tritium released to the reactor pits reaches Perch Lake within a few months by surface stream flow, whereas the remaining one third enters relatively long-term storage in the groundwater reservoir. They indicate the mean residence time in the groundwater reservoir to be at least ten years. This is about twice the groundwater residence time suggested by Parsons (1963); yet the volume entering via surface water routes is apparently greater than Parsons anticipated. Considering only the tritium travelling in the groundwater system, the residence and decay time offered by the transport of tritiated water in the groundwater reservoir could be considered to fit within the concept of a retardation option scheme.

Although the percentage of clay-sized particles in the Chalk River sand is small, the sands have sufficient sorptive capacity to reduce the velocity of a ^{90}Sr contamination front (see Chapters 4 and 5) to about 3% of the groundwater flow velocity. In the Perch Lake basin groundwater system, the retardation owing to sorption allows for subsurface ^{90}Sr residence times in the order of 300 yr to 1000 yr. This period of residence time permits considerable decay of ^{90}Sr as well as decay of ^{137}Cs, which travels, as a contamination front, much more slowly than ^{90}Sr. Although this may also be interpreted in terms of the retardation option, it is not necessarily advocated by the authors as a totally acceptable example of a retardation option.

As in the containment option, the most reliable means of assuring a defined, predictable retardation option waste management site is to engineer the hydrogeological environment. The size of the engineered site, however, would be much larger than that of a containment site and therefore could be too large an undertaking to be considered economically feasible. Consequently, there may be no feasible alternative within the retardation option philosophy to finding a suitable natural hydrogeological system having the desired residence-time properties to allow for the dilution and decay of the anticipated waste radionuclides. This scheme would generally require that the entire flow system from recharge to discharge areas be delineated as part of the waste management site and that it be removed from the public domain as well as be continuously monitored.

SITE INVESTIGATION PROCEDURES

From this discussion of the containment and retardation options it is obvious that, in the authors' opinion, construction of an engineered geologic medium between the storage structures and the natural hydrogeological environment represents the most reliable and predictable subsurface waste management procedure. A much higher degree of predictive certainty can be associated with an engineered geologic medium that has not been subjected to the variations and uncertainties of the geologic processes of deposition and subsequent consolidation or diagenetic alteration. In some cases, natural hydrogeological environments may offer the required characteristics for either option as well as for monitoring and manipulation, but the site investigation must be completed in enough detail to assure long-term reliability and predictability.

Under any operational philosophy, the site investigation should lead to a full description of the hydrogeological environment to the depth and the lateral extent of the natural or engineered hydrogeological system that might conceivably be affected by the operation of the waste management site. In general, this investigation should include the geotechnical, geochemical and hydrogeological characteristics, as well as a general description of the hydrogeological environment to the point of discharge from the subsurface and/or entry to the public domain. Specifically, the hydrogeological investigation should include:

(1) The three-dimensional groundwater flow pattern as defined by fluid potential gradients.

(2) The variation of hydraulic conductivity in the vertical and lateral directions, or in other words, the heterogeneity of the porous medium.

(3) The variation of geochemical retardation characteristics, including sorptive properties as well as possible precipitation and dissolution reactions.

(4) The hydrodynamic dispersion characteristics of the critical areas.

(5) The variation of intergranular and/or fracture porosities (where present), bearing in mind that fracture porosity is considered undesirable from the points of view of containment, retardation and reliable monitoring.

(6) An analysis of the flow regime and of the water-quality and water-level variations of any surface water system into which any escaped contaminants may eventually be discharged or released.

(7) An analysis of the predicted extent and degree of possible
    contamination, using information from (1) to (6) above and applying
    these data to suitable hydrogeological and mathematical models.

The general requirements above are established to attain reliability and
predictability at any subsurface radioactive waste management site. In the case of
an engineered hydrogeological environment, particularly under the containment option,
the investigation may be primarily directed toward the geologic material to be used
for containment. *The degree of predictability for an engineered environment will
likely be much greater than that attainable for any natural system.* Additionally,
the effort (e.g., field investigations, modelling, etc.) involved in attaining a
desired degree of predictability for a natural hydrogeological environment is likely
to be much greater than that involved under engineered circumstances.

As there is no published statement known to the authors concerning
hydrogeological methods of investigation for Canadian radioactive waste management
sites, in the following sections a sequence of field, laboratory and model
investigations is suggested as a general guide to the determination of the
hydrogeological retardation and transport characteristics discussed in previous Chapters.
The field investigation procedures are listed in their preferred order of execution.
They are suitable for use under either the containment or the retardation options
and are, of course, subject to modification, particularly in the case of the
containment option in an engineered hydrogeological environment where the areal
extent of the investigation will likely be more limited. Laboratory and model
investigations should be carried out simultaneously and in conjunction with the
field investigation, utilizing acquired data and mathematical analyses to assist
and modify the individual investigation accordingly.

Field Investigation

The field investigation procedures should be conducted in the following order:

(1) A surface geophysical survey, including seismic and resistivity methods
    correlated with borehole data, should be conducted to determine the bedrock
    contact and thickness of the surficial deposits.
(2) Continuous core samples of the surficial deposits should be taken within
    boreholes spaced at intervals small enough to ensure reliable definition of
    stratigraphic units and variations within them. These cores should be
    stratigraphically logged on a meso and micro scale, with particular attention
    being given to the distribution of grain sizes in the samples. It should be

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noted whether the clays present are in bands or admixed throughout the samples. The continuously cored holes should be stratigraphically correlated, with the number of cored holes, if possible, being sufficient to ensure that stratigraphic correlation is certain between the site and the discharge area(s).

Continuous cores of the bedrock to a depth of at least 6 m into the bedrock should be taken at each continuous core site. Bedrock cores should be logged and kept intact, with the degree of fracturing and weathering noted. Piezometers should be installed in the bedrock core holes. A schematic diagram of a bedrock piezometer installation is shown in Figure 52.

Samples of the surficial material and the bedrock should be obtained for laboratory analyses of parameters such as hydraulic conductivity and distribution coefficients. If the natural hydrogeological environment is to be used as a containment or retardation medium undisturbed samples should be used for these tests. Where the same sample cannot be used for different tests (e.g., after mechanical analysis the sample is disturbed and cannot be used for conductivity testing), a sample from the same site at the same depth should be used.
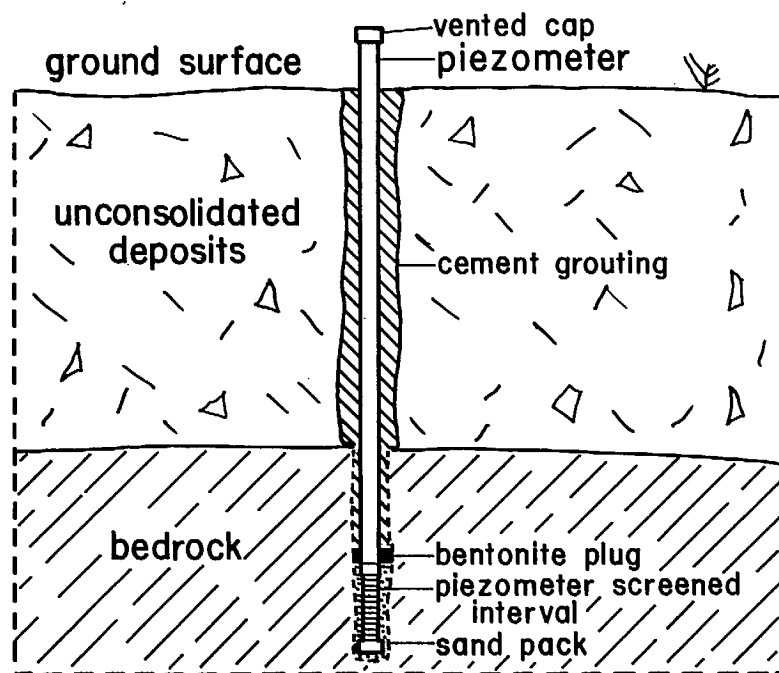

Figure 52.   Piezometer installation in a bedrock
cored hole.

(3)   Borehole geophysical logging may in some cases be useful (Table 28), although in many instances the scale of investigation at potential sites may be too limited for borehole logging to offer useful information.

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Table 28. Summary of Borehole Geophysical Log Applications in Water Resources
          Investigations

Required information on the properties of rocks, fluid, wells or the ground-water system	Widely available logging techniques which might be utilized
Lithology and stratigraphic correlation of aquifers and associated rocks	Electric, sonic or caliper logs made in open holes; nuclear logs made in open or cased holes
Total porosity or bulk density	Calibrated sonic logs in open holes, calibrated neutron or gamma-gamma logs in open or cased holes
Effective porosity or true resistivity	Calibrated long-normal resistivity logs
Clay or shale content	Gamma logs
Permeability	No direct measurement by logging; may be related to porosity, injectivity, sonic amplitude
Secondary permeability--fractures, solution openings	Caliper, sonic or borehole televiewer or television logs
Specific yield of unconfined aquifers	Calibrated neutron logs
Grain size	Possible relation to formation factor derived from electric logs
Location of water level or saturated zones	Electric, temperature or fluid conductivity in open hole or inside casing; neutron or gamma-gamma logs in open hole or outside casing
Moisture content	Calibrated neutron logs
Infiltration	Time-interval neutron logs under special circumstances or radioactive tracers
Direction, velocity and path of groundwater flow	Single-well tracer techniques--point dilution and single-well pulse; multiwell tracer techniques
Dispersion, dilution and movement of waste	Fluid conductivity and temperature logs, gamma logs for some radioactive wastes, fluid sampler
Source and movement of water in a well	Injectivity profile. Flowmeter or tracer logging during pumping or injection; temperature logs
Chemical and physical characteristics of water, including salinity, temperature, density and viscosity.	Calibrated fluid conductivity and temperature in the well; neutron chloride logging outside casing; multielectrode resistivity

Table 28. Continued

Required information on the properties of rocks, fluid, wells or the ground-water system	Widely available logging techniques which might be utilized
Determining construction of existing wells, diameter and position of casing, perforations, screens	Gamma-gamma, caliper, collar and perforation locator; borehole television
Guide to screen setting	All logs providing data on the lithology, water-bearing characteristics, and correlation and thickness of aquifers
Cementing	Caliper, temperature, gamma-gamma; acoustic for cement bond
Casing corrosion	Under some conditions caliper or collar locator
Casing leaks and/or plugged screen	Tracer and flowmeter

(4) Piezometer nests should be installed to determine the three-dimensional groundwater flow pattern as defined by fluid potential gradients between the waste management site and the area(s) of groundwater discharge. A piezometer nest should consist of a series of closely spaced piezometers, with the intake zones situated at the depths in the various hydrostratigraphic units which will define the three-dimensional hydraulic potential field with contour intervals of 0.5 m or less. Figure 53 is an example of this type of piezometer spacing. Areal spacing of piezometer nests (which controls the accuracy with which lateral variation of hydraulic head can be determined) will be strongly dependent on the results and interpretation of the continuous-core sampling program. An area of well-defined and relatively homogeneous hydrostratigraphy will likely require less instrumentation than a heterogeneous area where the hydrostratigraphy is discontinuous and poorly defined.

Once the three-dimensional groundwater flow pattern has been determined, cross sections should be constructed in the plane of groundwater flow (where flow is two-dimensional) from the waste management site to the area(s) of discharge. The cross-sectional flow patterns from CRNL (Fig. 36) and WNRE (Fig. 44) are typical examples of cross sections in the plane of groundwater flow.

(5) Recording observation wells (10-cm diameter minimum) should be used to obtain continuous water level data. Continuous water level data is particularly important in the water table zone where the maximum and minimum yearly levels are necessary to establish depths at which engineered facilities might be installed.
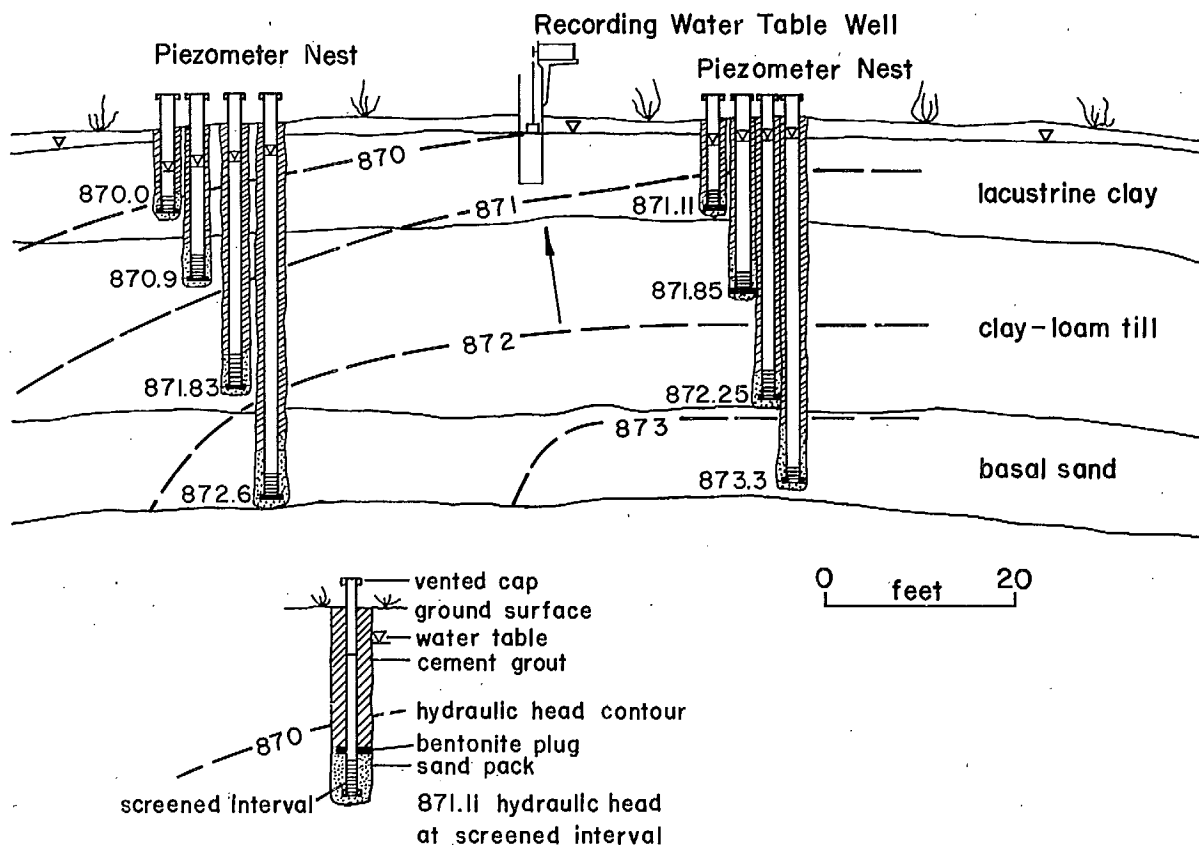
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Figure 53. Typical pair of piezometer nests in the stratigraphic units at WNRE. The spacing of piezometer tips and nests is close enough to permit reliable hydraulic head contouring at 1-ft (0.3-m) intervals.

(6) Each piezometer and observation well should be "slug"-tested for hydraulic conductivity using the analytical methods outlined in Hvorslev (1951) or Cooper, Bredehoeft and Papadopulos (1967). A "slug" test consists of instantaneously adding to or withdrawing from a piezometer a known volume of water and measuring the rate of recovery of the piezometer water level until it returns to its initial value. The Hvorslev analysis method is well known, but the method of Cooper, Bredehoeft and Papadopulos has received only slight attention. Vonhof (1975) has recently shown the usefulness of the latter method in observation well installation and development. An example of this type of slug test analysis is shown in Figure 54 for an observation well at WNRE.

(7) Pumping wells should be installed in the subsurface units of higher conductivity and relatively long-term pumping tests should be conducted. A *long-term* pumping test would last a week or more. Response should be measured in each piezometer and recording well, and the pumping tests should be analyzed using the technique most applicable to the local hydrogeological situation. Walton (1970) discusses some of the common hydrogeological situations and pump-test
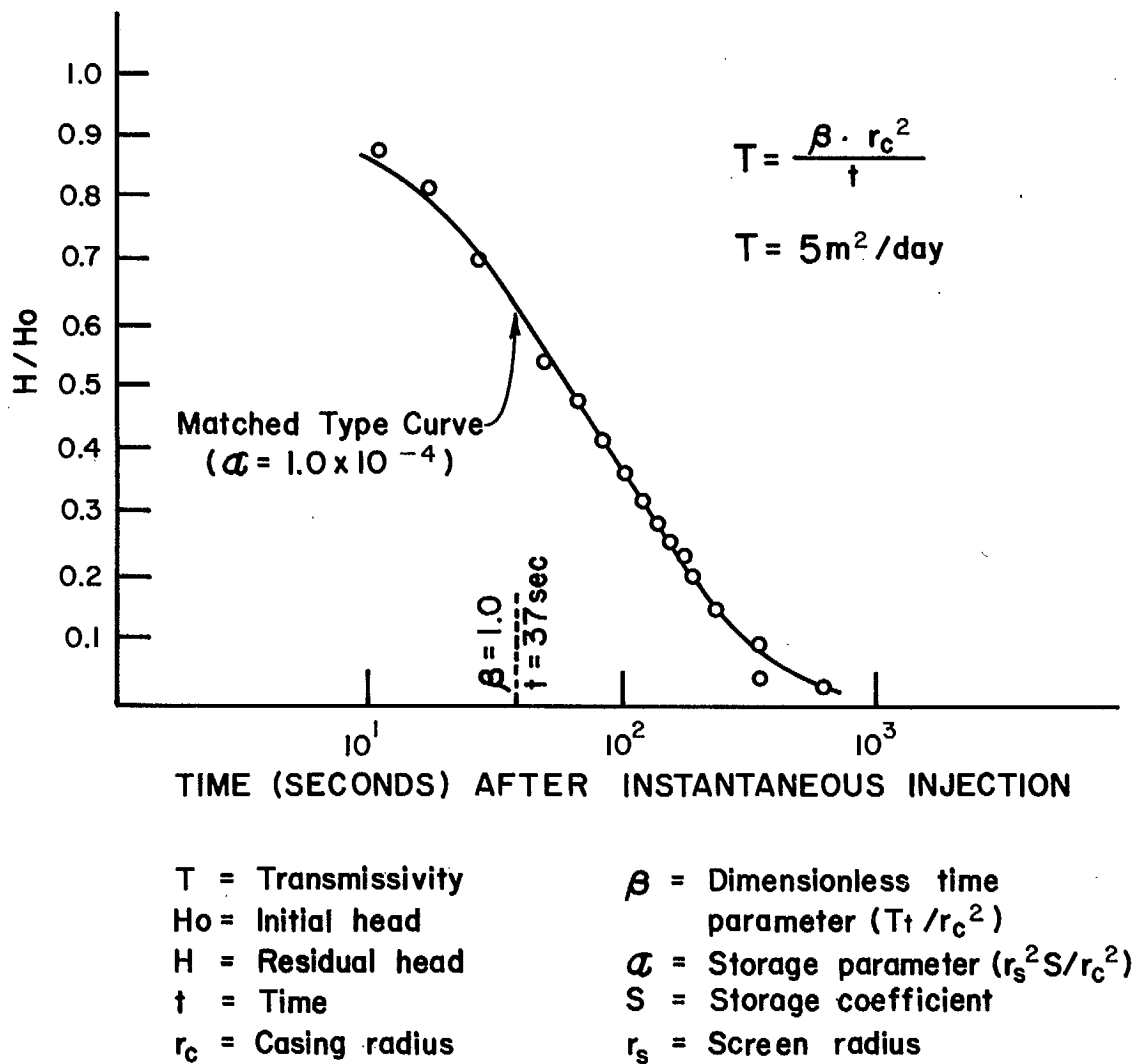
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Figure 54. Example of a recording observation well slug test at WNRE waste management area. The slug test is analyzed using the Cooper, Bredehoeft and Papadopulos (1967) method.

analysis techniques; however variations of these may be required for individual investigations (e.g., Grisak and Cherry, 1975).

The main purpose of pumping tests in the investigation of waste management sites is to determine the hydraulic continuity of the permeable and relatively impermeable beds. Relatively long-term pumping tests are therefore required to obtain data from the confining or less permeable zones. Examples of the usefulness of long-term pumping test data are evident in the WNRE studies (Grisak and Cherry, 1975).

(8) The groundwater velocity along the flow path(s) from the waste management site to the discharge area(s) should be determined by such methods as tracers (e.g., ^{3}H, ^{35}S) or point-dilution techniques.

(9) The heterogeneity and dispersive characteristics of the subsurface environment in the predicted transport direction(s) should be determined, probably by means of small-scale tracer studies.

(10) Distribution coefficients, using very small-scale field tracer studies for the radionuclides of interest, should be investigated if possible. This approach has of course the disadvantage of contaminating the subsurface to some extent, and the effect of these tests on the future monitoring should be kept in mind.

(11) Reliable precipitation gauges should be installed at the site to permit recharge-rate studies.

(12) Water level records of the piezometers and the recording wells should be maintained on a continuous basis. At least a one-year record of biweekly piezometer measurements, continuous recording well charts and precipitation data should be received before site approval is considered. The precipitation and piezometer and well records indicate the magnitude of fluctuations in the groundwater flow system in response to precipitation during the year. It should be determined whether the precipitation during the year is representative and, if not, to what extent it differs from the average.

(13) Copies of charts, graphs and basic data should be included with the report on the waste management site. These include stratigraphic drill logs and microstratigraphic core logs; information on the types of piezometers installed (diameter, depth, screened interval and construction material) and installation procedure; "slug" test procedures; pumping-test response data; borehole geophysical logs (if utilized) and surface geophysical data; condensed copies of recorder charts from all continuous recorders; precipitation data; and breakthrough or decay data from tracer and point dilution tests.

Laboratory Investigation

The laboratory investigations should be carried out simultaneously with the field studies. Chemical analyses of the groundwater should be completed immediately after sampling. Specific conductance, pH, Eh and dissolved oxygen of the groundwater should be determined in the field at field temperatures, and natural groundwater or water of similar chemistry should be used for laboratory determination of hydraulic conductivity.

The nature of the laboratory investigations should be such that a composite evaluation of the transport and retardation characteristics of the sediment-groundwater system is obtained. Some of the laboratory tests that might be conducted on the sediments and groundwater at a radioactive waste management site are listed below.

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(1) Most importantly, a distribution coefficient (K_d) for all radionuclides of interest (see Chapter 1) should be determined for the subsurface zones that the field investigation has shown to be in the potential radionuclide migration path(s). Preferably, K_d's should be determined in the field with tracer tests or on undisturbed samples in laboratory column tests, particularly if the natural hydrogeological system is regarded as an integral part of the waste management system.

(2) Hydraulic conductivity tests should be completed on as many representative borehole samples as possible, particularly those from the most permeable zones. It is desirable to conduct these tests on undisturbed samples; however the most permeable zones, which are the zones of critical flow paths, present the most difficulty in terms of adequate sampling. Sampling tools such as the Bishop sampler (Parsons, 1963) could be used to obtain undisturbed samples of fine sands and silts. In very coarse sands and gravels, field data from pumping tests and point dilution tests are likely the most reliable source of hydraulic conductivity data.

(3) Samples for groundwater chemistry should be taken from each piezometer and observation well. The investigator should be certain that representative groundwater samples are obtained by pumping and cleaning each of the piezometers and wells before sampling.

Specific conductance, pH, Eh and dissolved oxygen measurements should be performed in the field at field temperatures. Alkalinity may be measured by titration either in the field or within 24 h of sampling in the laboratory. Laboratory analyses should include Ca, Mg, Na, K, Fe, Mn, Si, Cl, SO_4, NO_3, stable Sr and dissolved organic carbon.

Chemical equilibria calculations for the principal minerals in the hydrogeological environment should be completed as outlined in Chapter 4.

(4) Analyses of ^{14}C and ^3H (tritium) should be conducted on groundwater samples from the entire flow system to aid the determination of possible subsurface radionuclide residence time. If, for example, there is a relatively high tritium concentration (from thermonuclear atmospheric testing) in the natural groundwater, it has likely been in the subsurface in the order of 20 yr or less. With appropriate adjustments for open and closed dissolution systems, ^{14}C dates may be useful when the age of the groundwater is in the order of thousands or a few tens of thousands of years. Wigley (1975) describes possible ^{14}C age-dating methods with corrections based on stable carbon isotope data, and Payne (1972) and Brown *et al.* (1972) give general descriptions of the use of radioactive and stable isotopes in hydrology.

(5) All basic data, analyses and calculations should be included with the report in a digested form, including descriptions or references to the procedures and analytical methods used in the laboratory analyses.

Modeling

Subsurface flow and, more recently, mass transport computer-simulation models have been available for several years and should play a conjunctive role in the hydrogeological investigation of waste management sites. Flow models can offer considerable insight during all stages of the hydrogeological investigation of an engineered or natural system. Transport models utilizing both field and laboratory-derived values for the various transport and retardation parameters will undoubtedly serve as the final predictive tool in the site analysis. Although the models may serve as the predictive tool in the investigation, they are, of course, only as reliable as the field and laboratory data serving as input. Furthermore, the field and laboratory data are valuable only if the hydrogeological environment has been defined within acceptable limits of certainty.

Pickens and Lennox (1976) have recently developed a two-dimensional finite-element model based on a Galerkin technique which they use to "(1) solve for the hydraulic head distribution and seepage velocities in a cross-section of a groundwater flow system, and (2) solve for the transient concentration distribution of conservative and non-conservative contaminants in this system." The model above does not specifically concern radionuclide movement and consequently does not include the effect of radioactive decay on the contamination levels, although this is being developed (Pickens, personal communication). Schwartz (1975b) has presented a model utilizing the method of characteristics to solve "a mass balance equation that considers physical transport modified by radioactive decay and binary exchange." Combined flow and transport models similar to those mentioned above should be used during the hydrogeological investigation and subsequent predictive analysis of any radioactive waste management site.

SUMMARY

Chapter 6 presents a discussion of the purposes that could conceivably be served by the hydrogeological environment in the vicinity of a radioactive waste management site. Essentially, the hydrogeological environment could be considered as

    (1)   a containment medium, which would retain in a relatively small volume any radionuclides that enter the subsurface flow system by escape from engineered structures such as concrete bunkers or

    (2)   a retardation medium which would serve to retard and disperse contaminants such that any radionuclide migrating into the public domain enters that domain below the maximum permissible concentration.

The ability to monitor and manipulate the subsurface system is considered of prime importance under any operating philosophy, of which the containment and retardation options are only two.

An engineered hydrogeological environment located as an intermediate medium between the first-line storage structure (such as concrete bunkers or tile holes) and the natural subsurface environment is considered by the authors to be the most reliable means of attaining predictability under either the containment or the retardation option. Field investigations, instrumentation and monitoring procedures are similar under both options; yet the areal extent of investigation may be somewhat more limited under the containment option. Site investigation procedures for the investigation of a natural hydrogeological environment and the instrumentation of a natural or engineered environment are briefly outlined in the final sections. It is suggested that laboratory and field investigations be executed simultaneously and in conjunction with the mathematical modeling, utilizing acquired data and mathematical analyses to assist and adjust all phases of the investigation accordingly.

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Glossary of Terms

Acidic rock--a descriptive term applied to those igneous rocks containing more than 66% SiO_2 as contrasted with intermediate and basic rocks.

Amygdules--a small gas bubble in lava or other igneous rock usually filled with a secondary mineral such as zeolite, calcite or quartz.

Aquifer--a formation or group of formations, or part of a formation that contains sufficient saturated permeable material to yield significant quantities of water to wells and springs.

Attenuation--the reduction in the concentration of contaminant ions in the subsurface owing to dispersion and retardation processes.

Average pore water velocity--the Darcy velocity divided by the porosity. It is the average velocity within a pore, i.e., V_ℓ in Figure 8.

Basic rocks--a general description or descriptive term for those igneous rocks that are comparatively low in silica.

Bedrock--any preglacial rock underlying unconsolidated glacial material or recent deposits of gravel, sand, clay, etc.

Bentonite--a clay formed from the decomposition of volcanic ash, largely composed of the clay minerals montmorillonite and beidellite.

Borehole geophysical logging techniques-- these techniques include spontaneous potential, resistivity, gamma, calibrated neutron, gamma-gamma, sonic and calliper logs. For descriptions of individual techniques, refer to Keys and MacCary, 1971.

Bulk density, dry (unit weight) ρ_b--the density of the porous medium, $\rho_b = (1-n) \gamma_s$, where n and γ_s are the porosity and the particle density, respectively.

Cation-exchange capacity--the excess of counterions in a negative electrical double layer that can be exchanged for other cations.

Chemisorption--the adsorption of potential-determining ions to a colloid surface by chemical bonds.

Clast--an individual constituent of till, detrital sediment or sedimentary rock produced by the physical disintegration of a larger mass.

Colloid--a particle that is large when compared with a small molecule, but sufficiently small so that interfacial forces as well as inertial forces are significant in controlling the behaviour of the particle.

Complex--complexes are combinations of cations with molecules or anions which contain unsatisfied pairs of electrons (bases).

Counterions--ions that are attracted to oppositely charged ion-exchange sites and thus satisfy the requirement of the electrical neutrality of the particle-solution system.

Darcy velocity--the seepage flux per unit area of seepage face, q = Q/A in Equation 1.

Deltaic deposits--alluvial deposits usually triangular in areal shape at the mouth of a river or stream.

Diffusion--the spreading of particles, molecules, atoms or ions into a vacuum, a fluid or a fluid-filled (or a fluid-

and gas-filled) porous medium, in a
direction tending to equalize concen-
trations in all parts of the system;
it is understood to occur in the
absence of fluid convection and as a
result of the thermal kinetic energy
of the particles, including that of
the particles of the host fluid.

Digital models--mathematical models
employing numerical solutions to the
equations of groundwater flow and
transport.

Discharge area--an area in which ground-
water moves upward to the water table
where it is removed from the ground-
water flow system by evapotranspiration
and surface runoff. Recharge and
discharge areas are generally
separated by transition zones in which
the flow is mainly lateral.

Dispersion--the same as in diffusion but
occurring in the presence of fluid
convection.

Distribution coefficient (K_d)--the number
of milliequivalents of an ion
adsorbed per gram of exchanger divided
by the number of milliequivalents of
that ion per millilitre remaining in
solution at equilibrium.

Effective bulk conductivity--the field
hydraulic conductivity applying to a
hydrostratigraphic unit. For example,
fractures may impart an effective bulk
conductivity to a till which also has
intergranular hydraulic conductivity,
but the intergranular conductivity
may be much lower than that imparted
to the bulk till unit by the fractures.

Effective porosity--the amount of
interconnected pore space available
for fluid transmission.

Electrical double layer--the environment at
the solid-solution interface where ion-
exchange processes occur.

Evapotranspiration--return of a portion of
precipitation to the atmosphere by a
combination of direct evaporation and
transpiration by vegetation, with no
attempt being made to distinguish
between the two.

Fissure--an extensive crack, break or
fracture in a medium.

Gamma log--record of natural gamma radioactive
intensity in strata penetrated by a well.

Glacial--pertaining to characteristics of,
produced or deposited by, or derived
from a glacier.

Glaciofluviatile--equivalent to glaciofluvial.

Glacial meltwater channel--the channel
produced by runoff water from melting
glacier ice.

Glaciofluvial--pertaining to streams flowing
from glaciers or to the deposits made
by such streams.

Glaciolacustrine--pertaining to either
supraglacial or proglacial lakes and
the deposits derived from them.

Groundwater flow system--a three-dimensional
closed system which contains the entire
set of flow paths followed by all the
water recharging a basin.

Heterogeneity--spatial variation of the
physical properties and isotropic or
anisotropic conditions of a porous
medium. May imply the presence of a
number of discrete units with
homogeneous properties.

Homogeneity--the characteristic of a porous
medium whereby the physical properties
and isotropic or anisotropic conditions
do not vary spatially.

Hydraulic conductivity--if a porous medium

is isotropic and the fluid is homogeneous, the hydraulic conductivity of the medium is the volume of water at the existing kinematic viscosity that will move in unit time under a unit hydraulic gradient through a unit area measured at right angles to the direction of flow. The units of hydraulic conductivity are LT^{-1}.

Hydraulic gradient--the change in hydraulic head per unit of distance in a given direction (dimensionless).

Hydraulic head--a potential function which is the sum of the pressure head and elevation head at any point in a groundwater flow system. The hydraulic head equals the elevation, above a standard datum, of the liquid level in a piezometer inserted in the potential field (flow system).

Hydrodynamic dispersion--the total dispersive effects of mechanical dispersion (i.e., convective mixing) and molecular diffusion.

Hydrothermal--an adjective applying to heated or hot magmatic emanations rich in water, and to the processes in which they are involved.

Hydrostratigraphic unit--a hydrostratigraphic unit is a body of rock or unconsolidated sediment with considerable lateral extent in which distinctive hydro-geologic properties are relatively uniform throughout the unit.

Intergranular porous medium--a medium in which the effective porosity is controlled by the interstices between the grains of the medium.

Ion exchange--the process by which ions in solution are exchanged for ions adsorbed to the surface of colloidal particles.

Isomorphous replacement or substitution-- the replacement of, or substitution for, elements within a crystal lattice by elements in solution.

Lamination--layering or bedding less than 1 cm thick in sedimentary deposits.

Marine overlap deposits--fine-grained clayey deposits derived under shallow marine conditions during periods of landward encroachment by the sea following land depression by a continental ice sheet.

Mechanical dispersion--dispersion owing solely to convective mixing.

Milliequivalents--a measure of the concentration of an ion in solution.

Mixing cell--a hypothetical region of constant volume through which a fluid may flow and within which there is assumed to be instantaneous and complete mixing.

Moisture content--a portion of water expressed as a percentage of the total volume contained in the intergranular or fracture voids in a material.

Molecular diffusion--see diffusion.

Perched water table--the water table above an impermeable bed underlain by unsaturated material of sufficient permeability to permit movement of groundwater. Perched water tables may be created by several types of stratigraphic arrangements.

pH--the negative logarithm of the hydrogen ion activity.

Physical adsorption--adsorption of potential-determining ions by physical rather than chemical bonds.

Piezometer--field instrument which measures the hydraulic head at a point in a subsurface flow system.

Piezometer nest--a group of piezometers

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which either have all been placed
within the same borehole or have been
placed within a number of closely spaced
boreholes at the same geographic site.
Generally, their open or slotted
intervals are distributed over a range
of depths so as to define vertical
hydraulic head gradients within a
specified aquifer or flow system.

Porous medium--a solid containing voids or
pores.

Potential-determining ions--those ions
which are specifically adsorbed to a
particle surface and which determine
the electrical charge of the surface.

Precipitation--the removal from solution
by crystallization of ions which were
once part of the solution.

Proglacial lake--a lake occupying a basin
in front of a glacier and generally
in direct contact with the ice.
Deposits in these lakes are commonly
varved.

Porosity--the porosity of a rock or soil is
its property of containing interstices
or voids and may be expressed quan-
titatively as the ratio of the volume
of its interstices to its total volume.

Pumping test--a pumping test consists of
pumping water from or into a well at
a known rate and measuring the response
(i.e., change in water level) in the
pumped well and, possibly, in a
neighbouring observation well or wells.

Recharge area--an area in which water moves
downward from the water table into the
groundwater flow system (see discharge
area).

Relative ionic velocity--the ratio of the
average velocity of an ion to the
average velocity of the convecting
groundwater.

Selectivity quotient--for a simple ion-
exchange process involving two competing
cations, the selectivity quotient is
the ratio of their concentrations in
the solid phase divided by that of
their concentrations in the equilibrium
solution.

Shelby tube sample--subsurface samples taken
in a driven core barrel.

Slug test--a slug test consists of instan-
taneously adding to, or withdrawing
from, a piezometer a known volume of
water and measuring the recovery of the
water level in the piezometer until it
returns to the initial water level
existing before the test.

Sorting--a term used to indicate the degree
of similarity with respect to grain
size, shape and physical arrangement
in a mass of material.

Stratigraphy--that branch of geology which
treats the formation, composition,
sequence and correlation of stratified
rocks as parts of the earth's crust.
A stratigraphic unit generally consists
of stratified, mainly sedimentary
material grouped for descriptive
mapping and correlation.

Subglacial deposits--sand, gravel, silt or
clay deposited by running water under
glacial ice.

Supraglacial lakes--a lake existing on the
surface of a glacier with glacial ice
as its base.

Uniformity--a uniform porous medium is one
in which all particle sizes are equal.

Vadose zone--unsaturated zone.

Varve--(1) any sedimentary bed or lamination
that is deposited within a period of
one year or (2) a pair of contrasting
laminae representing seasonal sedi-
mentation, e.g., summer (light) and

winter (dark) within a single year.

Winnebago tills--early Wisconsinan tills in
northeastern Illinois.

Woodfordian tills--middle-late Wisconsinan
tills in northeastern Illinois.

Zero point of charge--the point at which
the solid surface charge from all
sources is zero.