STUDIES OF CESIUM AND STRONTIUM
MIGRATION IN UNCONSOLIDATED
CANADIAN GEOLOGICAL MATERIALS

A research report prepared for the
Atomic Energy Control Board by
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RESEARCH REPORT

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

The opinions expressed in this report are those of the authors and do not necessarily reflect those of the Atomic Energy Control Board.
STUDIES OF CESIUM AND STRONTIUM MIGRATION IN UNCONSOLIDATED CANADIAN GEOLOGICAL MATERIALS

ABSTRACT

Distribution coefficients \((K_d)\) were measured for cesium and strontium in 16 samples of Canadian unconsolidated geological materials. The samples were collected to cover a wide range of grain size, clay-mineral composition, cation exchange capacity and carbonate mineral content. Distribution coefficients ranged between \(10^2\) and \(2.0 \times 10^4\) ml/g for cesium and between \(2.5\) and \(10^2\) ml/g for strontium, indicating that most unconsolidated geological materials have a substantial ability to retard the migration of cesium, while strontium could generally be expected to be somewhat more mobile. The measured \(K_d\) values were not significantly correlated with the measured soil properties, but appeared to be significantly affected by the background concentration of stable isotopes of the respective radionuclides.

ETUDES DE LA MIGRATION DU CESIUM ET DU STRONTIUM DANS DES DEPOTS MEUBLLES CANADIENS

RESUME

On a mesuré les coefficients de distribution \((K_d)\) du césium et du strontium dans 16 échantillons de dépôts meubles canadiens. La granulométrie, la composition en minéraux argileux, la capacité d'échanger des cations et le contenu en minéraux carbonatés des échantillons étaient très variés. Pour le césium, le coefficient de distribution varie de \(10^2\) à \(2.0 \times 10^4\) ml/g tandis que pour le strontium, il varie de \(2.5\) à \(10^2\) ml/g. Ces résultats indiquent que la plupart des dépôts meubles peuvent retarder de beaucoup la migration du césium, tandis que le strontium serait plus mobile. Les valeurs \(K_d\) mesurées ne semblent pas correspondre aux propriétés mesurées des sols, mais seraient influencées par la concentration naturelle d'isotopes stables des radionucléides respectifs.
SUMMARY

In Canada, a common practice in the management of solid low-level radioactive waste produced in nuclear power and research facilities involves burial of the waste at shallow depths in containers that are designed to be water tight. In the analysis of the safety of these sites, however, it is necessary to make predictions of the rates of radionuclide migration that would occur in the event that the wastes become wet as a result of groundwater seepage. To make these predictions, information on the geochemical interactions between the radionuclides and the solid matrix of the subsurface geological materials is necessary. These interactions are commonly represented by a parameter known as the distribution coefficient ($K_d$), which is a measure of the partitioning of a particular radionuclide species between the solid and liquid phases of the porous medium. The distribution coefficient is defined as the concentration of the radionuclide in the solid phase divided by the concentration in the solution. It is generally expressed in units of ml/g.

The distribution coefficient has gained widespread acceptance as a parameter of primary importance in the prediction of the velocity of radionuclide migration relative to the velocity of the groundwater that causes the migration. The ratio of the velocity of the groundwater $V_w$ to the velocity of the radionuclide $V_s$ is denoted as the retardation factor. $K_d$ has a dominant influence on this factor, as is evident from the well-known relation: $V_w/V_s = 1 + (\rho/n) K_d$ where $\rho$ and $n$ are the dry weight density and porosity of the material. Providing that fractures are not significant, for most deposits of glacial origin, values of $\rho/n$ are in the narrow range of 4 to 7 g/cm$^3$. Values for $K_d$, however, vary
over many orders of magnitude. Acquisition of reliable $K_d$ values is, therefore, essential for predicting radionuclide migration rates.

The main objective of this study was to determine $K_d$ values for cesium and strontium in a variety of Canadian deposits of glacial origin. It was intended that this information would serve as a basis for at least a qualitative classification of overburden materials with respect to their capability to retard the migration of radiocesium and radiostrontium.

Another objective of the study was to seek correlations between $K_d$ values and commonly-measured physical and chemical soil properties, so that these in turn could be used to obtain indirect estimates of $K_d$ values for other deposits.

Additional experiments were conducted to examine the effect of exposure of samples to atmospheric oxygen on the measured $K_d$ values for cesium. The effect of varying the ratio of the solution volume to the solid weight of material used in the $K_d$ tests was also examined.

Sixteen samples of overburden of glacial origin were collected and characterized with respect to a range of physical and chemical properties including grain-size characteristics, cation exchange capacity, soluble and exchangeable cations, carbonate-mineral content, organic matter content, and soil paste pH.

Nearly all of the $K_d$ determinations were made using the conventional batch (equilibrium) method. In general, a known mass of soil is brought in contact with solution at a known concentration of the ionic species of interest. At equilibrium, the amount remaining in solution is determined and by subtraction from the amount added, the amount adsorbed by
the soil can be calculated. This enables one to calculate the $K_d$ of the system. In dealing with radiocations, the normal procedure is to use a stable isotope of the cation to arrive at the desired equilibrating solution concentration. The solution would also contain a spike of the active isotope; however, its presence normally would not have a significant effect on the concentration of the cation in solution. This presents a convenient method for determining $K_d$ values since the concentration in solution at equilibrium can be determined by comparing the activity of the solution at equilibrium with that of the initial equilibrating solution. The amount adsorbed and thus the $K_d$ can then be calculated. It should be noted however, that this procedure determines the amount remaining in solution of what was added. If the soil contains natural background concentrations of stable isotopes of the same cation, then the concentration in solution could be quite different from that which was measured by the radiometric procedure. This in turn could affect the calculated $K_d$ value. Since cesium and strontium occur naturally in most soils, background effects were found to be significant with respect to the results of this study.

The results showed large variation in the measured $K_d$ values, with values ranging from approximately $10^2$ to $2.0 \times 10^4$ ml/g for cesium and $2.5$ to $10^2$ ml/g for strontium. If these $K_d$ values govern the migration of radiocesium and radiostrontium in groundwater flow regimes, cesium will be essentially immobile over the time scales that are normally of interest. The $K_d$ values for strontium, however, indicate that in some or possibly many circumstances this nuclide would migrate at velocities smaller than the groundwater velocity but at velocities which nevertheless could be significant. There is no significant correlation between $K_d$ values and any of the measured soil properties or combination of soil properties. There is also no correlation of $K_d$ values
with pH of the test solution. From this, it was concluded that the development of predictive regression equations is an impractical if not impossible pursuit.

The concentrations of natural cesium and strontium in waters extracted from soil-water paste mixtures were found to generally correspond with the break points in the graphical plots of measured $K_d$ versus the concentration of cesium in solution at equilibrium. At low equilibrium concentrations of cesium or strontium in the test solutions, measured $K_d$ values showed no change over a large range in concentration. At high solution concentration values the $K_d$ values decrease markedly, as would be expected from ion exchange theories based on the law of mass action. These results suggest that at low concentrations the measured $K_d$ values are simply a measure of the partitioning of the natural background cesium or strontium concentrations between the liquid and solid phases of the porous media.

This interpretation is supported further by the results of the cesium $K_d$ tests using different ratios of the volume of test solution to the weight of soil. In these tests, larger cesium $K_d$ values were obtained at large solution volume to soil mass ratios.

In the initial design of this study, the background concentration of cesium and strontium were not included as primary parameters for evaluation. We became aware of the dominant role of this parameter only in the late stages of the investigation and therefore all of the data that would be desirable for a detailed examination of its influence were not obtained.

A consequence of our interpretation of the role played by the background concentrations on $K_d$ values is the conclusion that if cesium and strontium are leached from solid low-level wastes in burial facilities, the effective $K_d$ values governing the migration rates will be the $K_d$...
values for the natural cesium and strontium in the groundwater. With this in mind, improved methods for determining $K_d$ values for cesium and strontium are being developed.

The results of cesium $K_d$ measurements on samples using the conventional batch method and using a glove-box method designed to prevent aeration of the soil sample and groundwater during $K_d$ tests indicate that in nearly all cases the effects of sample drying and solution aeration on measured $K_d$ values are not significant.
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1. GENERAL INTRODUCTION

1.1 Background

Radioactive wastes are generated from a variety of sources including scientific research, military activities and industrial applications of radioactive materials. In Canada, the principal source of radioactive wastes is thermo-nuclear electric generation. From a modest beginning of 202 MW in 1968, Ontario hydro currently has a nuclear generating capacity of 5200 MW and it is projected that this will increase to in excess of 13,000 MW by 1985 or almost 50% of the province's total generating capacity at that time. Quebec and New Brunswick have also initiated nuclear power programmes and it appears that other provinces are considering a similar course.

The spectacular growth in the nuclear power industry will be accompanied by a corresponding growth in the rate of nuclear waste generation. Thus, although the management of radioactive wastes is currently a problem of modest scale, it may assume substantial proportions within the next decade or two.

Wastes generated as a consequence of the power industry include both high and low-level reactor wastes as well as waste materials from the uranium mining and refining processes. Low-level wastes generally include materials with a low specific activity and have activation products such as cesium-137, strontium-90, cobalt-60 and carbon-14 as the primary sources of activity. High-level wastes are associated with the spent reactor fuel and have uranium decay products as the principal source of radioactivity. The radionuclide of greatest concern with respect to mining and refining wastes is radium-226. This report is directed specifically towards the management of low-level
reactor wastes; however, the principles discussed should be applicable to a much wider range of waste materials.

As a consequence of the rapid expansion in the nuclear power industry, it appears that a substantial gap exists between our technical capability and the current demands for waste management. This is evidenced in the fact that the most recent management facilities are considered to be storage rather than disposal facilities. The proliferation of storage facilities is undesirable in that it only delays the problem of disposal, and puts the current generation in the ethically difficult position of burdening future generations with our wastes.

The industry is currently in the position of having to respond from a position of limited technical support to a concerned public, to vigilant environmental groups and to various government agencies. There is, therefore, an increased necessity for very detailed safety analyses of sites used for storage of wastes and for the evaluation of sites that may be suitable for permanent disposal of low-level wastes.

Although there are several waste management options available, those generally in use for low-level wastes involve some aspect of the shallow geologic and hydrogeologic environment in their design. The concept of geologic waste isolation has been discussed by several authors including Cherry et al. (1977), Mawson and Russell (1970), Carter et al. (1976) and Grisak and Jackson (1977). In order to assess the suitability of such sites generally it is necessary to be able to predict, with some degree of confidence, the potential rates of radionuclide migration in the subsurface system. The purpose of the study described in this report was to provide information that will assist in the development of reliable methods for predictions of subsurface radionuclide migration.
The report contains four main chapters. In the remainder of this chapter, the theoretical framework within which the study was designed is presented followed by a listing of the specific objectives of the study. In Chapter 2 of the literature on adsorption mechanisms for cesium and strontium in geological materials is reviewed. Chapter 3 describes the equilibrium batch experiments used to characterize the partitioning of cesium and strontium in 16 samples of unconsolidated geologic deposits collected in Ontario, Manitoba and Alberta. In Chapter 4 consideration is given to the effects of exposure of samples and test solutions to the atmosphere on the partitioning of cesium. The effects of other experimental conditions such as the volume of solution to mass of soil are also considered.

1.2 Theoretical Framework

Once radioactive waste is deposited in the geologic environment, the pertinent question is how long (if ever) will it take for the radioactive constituents of the waste to reach the biosphere, and at what rate will they be released to the biosphere. The time of release could be delayed by the time required for engineered barriers to be
broken down, or for the barriers to be penetrated by the wastes. This study is concerned only with the rate of migration of the waste through the geologic materials once all artificial or engineered barriers have been breached. The problem is thus reduced to one of predicting the rate of movement of a solute through a porous medium.

The theoretical framework for this process is well established, and full developments of the theory are available in several textbooks on flow through porous media including Bear (1972), Collins (1961) and Scheidegger (1960). Also, the theory has been applied to a variety of problems in such disciplines as petroleum engineering, hydrogeology, soils, sanitary engineering and chemical engineering. The brief mathematical development which follows is intended primarily as a means of identifying and showing the relevance of the various parameters embodied in the theory.

The principle of conservation of mass, when applied to a solute in the solution phase of a porous medium can be expressed as:

\[ \frac{\partial C}{\partial t} - \nabla \cdot J_s + G = 0 \]

where \( C \) is the solute concentration (mass/unit volume of solution), \( J_s \) is the solute flux (mass/unit area of porous medium/unit time) \( \nabla \cdot \) is the vector operator divergence, \( \theta \) is the volumetric solution content (volume of solution/unit volume of porous medium) and is equal to the porosity \( n \) under saturated flow conditions and \( G \) is a source term accounting for the addition or removal of solutes from the solution phase (mass of solute added to or removed from the solution phase/unit volume of porous medium/unit time). The remainder of this discussion
will be limited to saturated flow conditions. The solute flux \( J_s \) includes two terms, flux resulting from the average bulk movement of the solution phase which is referred to as advection, and can be represented by:

\[
\overline{J_A} = n\bar{V} C
\]

1.2

where \( \bar{V} \) is the average linear pore-water velocity; and flux resulting from dispersive effects, which can be represented by:

\[
\overline{J_D} = -n D \text{grad} C
\]

1.3

where \( D \) is the dispersion coefficient and grad is the vector operator gradient. Thus,

\[
\overline{J_s} = \overline{J_A} + \overline{J_D} = n\bar{V} C - n D \text{grad} C
\]

1.4

Substitution of 1.4 into 1.1 and rearranging yields:

\[
\frac{\partial C}{\partial t} = -\text{div}(\bar{V} C - D \text{grad} C) + \frac{1}{n} G
\]

1.5

For simplicity, and since the work of this report involves only one dimensional transport, equation 1.5 will be expressed in its one-dimensional form:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - \bar{V} \frac{\partial C}{\partial x} + \frac{1}{n} G
\]

1.6

If the reaction term is neglected, then equation 1.6 describes the one-dimensional transport of a non-reactive solute. If a line source of the solute is continuously injected at a concentration of \( C = C_0 \) at \( x = 0 \), and if the dispersive term is neglected, then the equation will predict the movement of a vertical concentration profile in the \( x \) direction at a velocity of \( \bar{V} \). This is shown schematically in Figure 1.1 and is frequently referred to as plug flow or piston
FIG 1.1

ADVECTIVE - DISPERSIVE SOLUTE TRANSPORT

PLUG FLOW COMPONENT (ADVECTION)

SPREADING COMPONENT (DISPERSION)

\[ \frac{C}{C_0} \]

\( C_0 = \text{CONCENTRATION OF TRACER SOLUTE IN TRACER SOLUTION (M/L}^3) \)

\( C = \text{CONCENTRATION OF TRACER SOLUTE IN SOLUTION AT SAMPLING POINT (M/L}^3) \)

\( \bar{V} = \text{AVERAGE LINEAR PORE VELOCITY OF SOLUTE (L/T)} \)

\( t = \text{TIME (T)} \)

\( x = \text{DISTANCE IN DIRECTION OF FLOW (L)} \)
flow. The addition of the dispersion term results in a symmetrical spreading of the tracer about the plug flow concentration profile (Fig. 1.1). The amount of spreading increases with the distance traveled, with increasing \( \overline{V} \), and also depends upon the dispersive properties of the medium.

The dispersion coefficient \( D \) is generally considered to be the sum of two components i.e.

\[
D = D_a + D_m \tag{1.7}
\]

\( D_a \) determines the rate of solute spreading as a result of mechanical mixing while \( D_m \) determines the rate of spreading as a result of molecular diffusion. Mechanical mixing is the result of the complex velocity distribution within the porous medium while the spread of the tracer by diffusion is in response to concentration gradients.

It has been found empirically that:

\[
D_a = \alpha \overline{V} \tag{1.8}
\]

where \( \alpha \), the dispersivity, has dimensions of length and is considered to be a characteristic property of the medium. For a particular medium, at high velocities \( D_a \) is much greater than \( D_m \) and thus

\[
D = D_a = \alpha \overline{V} \tag{1.9}
\]

At low velocities diffusion can be the predominant transport mechanism such that

\[
D = D_m \tag{1.10}
\]

\( D_m \) is an effective diffusion coefficient and is less than the diffusion coefficient of the solute in free solution. Bear (1972) has indicated that the dispersion coefficient changes from predominantly diffusion control to predominantly mechanical mixing control at P clet numbers.
between 0.4 and 5, where the Peclet number is defined as:

$$P_e = \frac{\overline{V}d}{D_m} \quad (1.11)$$

and \(d\) equals the average grain diameter of the porous medium. From this, and assuming normal hydraulic gradients, one could expect the transport and mixing of a contaminant in aquifer materials to be controlled by advection and mechanical mixing processes, while in fine grained geologic materials, diffusion should be the controlling mechanism.

In general, by specifying the boundary conditions and initial conditions, and various parameters of the flow system, solutions to equation 1.6, or more generally, equation 1.5, will give the concentration of the solute at any time and at any point within the flow domain. The parameters which must be specified include the dispersion coefficient (\(D\)), the average linear pore water velocity (\(\overline{V}\)) and other parameters associated with the reaction term. \(\overline{V}\) could be measured directly, or more commonly, is determined from solutions of the flow equation; in which case, the hydraulic conductivity (\(K\)) and porosity (\(\phi\)) would also have to be specified. The parameters required in describing the reaction term depend upon the type of reaction and the method used to represent the reaction.

There are many types of reactions which can remove solutes from solution. These may include solute-solute reactions, solute-solid reactions and biological reactions. Common solute-solid interactions include exchange (cation or anion), precipitation and co-precipitation. A convenient method of representing solute-solid interaction is through the use of adsorption isotherms. An adsorption isotherm is a graph of the concentration of solute in solution (mass of solute/unit
volume of solution) vs. the concentration of solute in the solid phase (mass of solute adsorbed/unit mass of porous medium). The isotherm is measured by equilibrating soil samples with solutions containing different concentrations of the solute. At equilibrium, the concentrations in the liquid and solid phases are determined and the isotherm constructed.

Various researchers have found the sorption isotherm for a particular solute to be dependent upon a number of factors, including the mineralogy of the medium, the particle size of the medium, the pH of the solution, the competing constituents present, the concentration of the competing constituents, the concentration of the particular constituent under study, and the temperature (Golubev and Garibyants, 1971). A sorption isotherm may be linear or non-linear. A non-linear isotherm indicates that the distribution between the solution and sorbed phases varies with concentration. Most systems contain a variety of solutes requiring that the solution and sorbed phase concentrations of a particular species are functions of all other species present in both the solution and sorbed phases and thus the isotherm is multi-dimensional. This degree of sophistication in studies concerned with sorption isotherms is generally not considered because of the inherent complexities. Instead, isotherms are obtained for specific solution chemistries and temperatures that are of interest to the researcher. Also, equilibrium sorption and desorption isotherms are not necessarily identical.

The distribution function is a measure of the distribution of a particular species between the sorbed and solution phases. Thus it is the slope of the sorption isotherm defined as the ratio of the
where $K_f$ is the distribution function and is the slope of the adsorption isotherm. As discussed above, in the special case of a linear isotherm, $K_f$ is constant and is called the distribution coefficient $K_d$. Assuming a linear isotherm and substituting 1.13 into 1.6 yields:

$$
(1 + \frac{\rho}{n} K_d) \frac{\partial C}{\partial t} = \frac{3}{3x} D \frac{\partial C}{\partial x} - \nabla \frac{\partial C}{\partial x}
$$

1.14
The retardation factor $R$ is defined by:

$$ R = 1 + \frac{\rho}{n} K_d \quad 1.15$$

Further, defining $D'$, an effective dispersion coefficient as:

$$ D' = D/R \quad 1.16$$

and $\overline{V}'$, an effective velocity as:

$$ \overline{V}' = \overline{V}/R \quad 1.17$$

equation 1.14 becomes:

$$ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D' \frac{\partial C}{\partial x} - \overline{V}' \frac{\partial C}{\partial x} \quad 1.18$$

Equation 1.18 is convenient since it includes the effects of a reactive solute but can be solved by the same methods as the transport equation without a reaction term. In particular, the analytical solutions of Ogata and Banks (1961) are appropriate for equation 1.18. It should be noted however, that equation 1.18 can be solved analytically only if $K_d$ rather than $K_r$ is used. In other situations the reaction term would remain as a separate term in the equation and numerical solutions would be required.

In equation 1.17, $\overline{V}'$ is the advection rate of the retarded solute species. From this relation it can be shown that:

$$ \frac{\overline{V}'}{\overline{V}} = \frac{1}{R} = \frac{1}{1 + (\rho/n)K_d} \quad 1.19$$

or that the velocity of the retarded species is $1/R$ times the average linear pore water velocity. This equation neglects dispersion and predicts a sharp front moving through the medium at a velocity less than that of the average linear pore water velocity. Equation 1.18
gives a similar result but shows a symmetrical spreading of the solute about the front predicted by equation 1.19. The transport process, as described by equations 1.18 and 1.19 are shown schematically in Figure 1.2.

The theoretical model proposed in this section (Equation 1.5 or variations of 1.5) are developed from basic physical and chemical principles and therefore should provide a reasonable base upon which to make predictions of nuclide migration. In addition, the model has been applied in a sufficient number of situations to provide a high degree of confidence in its mathematical formulation.

It should be emphasized that the situations in which the theory has been successfully tested have generally been highly controlled laboratory experiments where the parameters of the system could be determined with a high degree of accuracy. Experiments where the measured concentration distributions for a non-reactive solute have been predicted with a reasonable degree of accuracy by this model have been conducted by Nielsen and Biggar (1962), Biggar and Nielsen (1964), Cassel et al. (1974), Rose and Passioura (1971), and several others. Although fewer studies have been performed using reactive constituents, reasonably good agreement between measured and predicted concentration profiles have been obtained by Kay and Elrick (1967), Lai and Jurinak (1971) and (1972) Mansell et al. (1977) and others.

Although there have been several field applications of the theory, these have generally taken the form of trial and error fitting of numerical solutions of the transport equation to existing contaminant plumes. In effect, the parameters are adjusted until the solution fits the data. There is no assurance that the solution is unique, and
FIG 1.2

REACTIVE AND NON-REACTIVE SOLUTE TRANSPORT

\[ \frac{X}{t} = \bar{V} \]
\[ \frac{X}{t} = \bar{V}' = \frac{\bar{V}}{R} \]

ALL VARIABLES AS DEFINED IN FIG 1.1

--- PREDICTION OF EQUATION 1.19
--- PREDICTION OF EQUATION 1.18
the parameters are not determined independently and thus there is no assurance that the resulting model would predict future trends. Examples of this approach to applications of the theory include Konikow and Bredehoeft (1974), Robson (1974), Pinder (1973), Robertson and Baraclough (1973) and Bredehoeft and Pinder (1973). Although these applications have been useful in understanding and solving the respective problems, and also in developing a further understanding of the transport equation, they cannot be considered as tests of the theory since the parameters were generally not determined independently of the solution.

Use of the theoretical models as a basis for making predictions of radionuclide migration rates clearly depends upon our ability to evaluate the parameters of the model under field conditions. The physical parameters include the dispersivity ($\alpha$) or dispersion coefficient ($D$), the average linear pore water velocity $\bar{V}$, the bulk density ($\rho$) and porosity ($n$). The bulk density and porosity can be determined with a reasonably high degree of certainty in most hydrogeologic environments, however solutions of the transport equation are relatively insensitive to variations in these parameters. As a result, dispersivity and velocity are the physical parameters of greatest interest. Discussions of the problems in determining these parameters under field conditions and methods for their determination are given by Cherry et al. (1975), Fried (1972), and Pickens et al. (1976).

The term of the transport equation which makes it specific for a particular solute (radionuclides in this case) is the reaction term ($G$ of equation 1.5, $K_f$ of 1.13 or $K_d$ of 1.14 or 1.19). The research described in this report concerns the reaction term and methods of formulating the reaction term. More specifically, this study examines
the interactions between cesium and strontium and several Canadian soil materials. Cesium and strontium and their environmental interactions have been the subject of a great deal of research. Much of this research was in response to weapons programmes and was concerned with these isotopes in the food chain or their interactions with surface soil. In addition, much of the work was done prior to the development of the transport equation and therefore was not performed such that the results would be compatible with the transport equation. Another body of literature, which will be reviewed in the following chapter, considers the chemistry of the cation-soil interactions. Much of this work has used purified clay materials, and although it may be extremely valuable in explaining observed interactions, it is of little value in predicting transport rates in natural geologic materials. To our knowledge, only two studies have been conducted in which the interactions between cesium and strontium and natural Canadian geologic materials have been investigated. These include laboratory studies by Mills and Zwarich (1970) who used geologic materials from the Whiteshell Nuclear Research Establishment of AECL and the continuing investigation of the cesium and strontium plumes in shallow groundwater near the Chalk River Nuclear Laboratories of AECL (Jackson et al. 1977).

1.3 Scope and Objectives

The objectives of this study are to:

1) determine the $K_d$ for cesium and strontium in Canadian geologic materials having a range in physical and chemical properties. The information obtained could form the basis for a generic data base
which could be of value, in a qualitative sense at least, in the preliminary stages of a site selection and evaluation programme.

2) determine the effect of various chemical and physical factors on $K_d$. This should increase our ability to predict the $K_d$ of a particular environment and improve our understanding of the geo-chemical retardation process.

3) provide data ($K_d$ values) which could be used in solutions of the transport equation. In the short term these would probably be used in a sensitivity mode; however, if the $K_d$ values prove to have predictable trends, then the data could conceivably be used in the evaluation of actual field sites.

4) evaluate various methods for determining $K_d$ and more specifically, to evaluate possible effects of soil sample disturbance on measured $K_d$ values.

5) evaluate the applicability of a $K_d$ value determined under equilibrium conditions to dynamic flow conditions.

Objectives 1 to 3 were served through a series of batch equilibrium determinations between cesium and strontium, and 16 geologic materials. The geologic materials were selected to represent a range in grain size distribution, cation exchange capacity, carbonate content
and mineralogy. In addition to the range in physical and chemical properties obtained through the soil selection procedure, the effect of pH and the concentration of the radiocation on the measured $K_d$ value was also examined.

The equilibrium studies referred to above were performed on samples which had been air-dried and passed through a 2.0 mm sieve. This procedure exposes the sample to oxygen which could cause geochemical changes in the sample, and could also affect the degree of hydration of the clay minerals. This leads to the possibility that the $K_d$ value determined on the exposed samples could be different from the insitu value. In order to gain some preliminary insight into this problem, distribution coefficients for cesium were determined on samples of the same material, one set of samples having been exposed to the atmosphere and air-dried, while the other set was maintained in an oxygen-free environment. In this part of the investigation four different soil materials were used.

Distribution coefficients determined using equilibrium methods can be useful in comparing the relative abilities of different soils to retard the migration of radiocations. In order for the values to be applicable for use in the transport equation it must be shown that the batch result is appropriate for describing the cation migration in a dynamic system. For this purpose, column experiments were conducted in which the concentration in the column effluent was predicted on the basis of the batch $K_d$ and this result was compared with the measured column effluent concentration.
The column experiments were continued beyond the term of this study. To avoid unnecessary repetition, all aspects of the column studies are included in a separate report (Reynolds et al., 1981). This report includes comparisons of measured and computed breakthrough curves for cesium and strontium, and also compares different solution procedures for the advection-dispersion equation.
2. ADSORPTION OF RADIOCATIONS ON COMMON MINERAL MATERIALS

2.1 Cesium

Investigations into the behaviour of cesium with minerals and natural soils have continued to shed light on the rather unusual behaviour of this element. Cesium is distinct from the divalent alkali earth metals (Ba, Sr, Ca, Mg) and holds a special position among the alkali metals (Rb, K, Na, Li) by having the largest atomic radius but the smallest hydrated radius. Cesium does not form any common, slightly soluble compounds and thus in a natural groundwater regime, its migration is controlled by ion exchange.

An indication of the ability of any mineral to adsorb cations is given by its exchange capacity. The clay mineral groups of kaolinite, illite, and montmorillonite are characterized by a range of capacities; 3-15, 10-40, 100-150 me /100 g respectively and due to their common occurrence are very significant natural adsorbers. Organic matter may have considerable capacity depending on its degree of degradation. In comparison to the clay minerals, most other minerals have very low exchange capacities. Zeolites are a notable exception. Although small, these capacities may be very important in the retardation of trace elements moving in groundwater regimes.

The difference in exchange capacities and strength of cation retention between the clay minerals is due to many factors. Kaolinite consists of units of silica tetrahedrons and octahedral sheets in a 1:1 layering. Substitution of structural cations is minimal and the major source of the exchange capacity is the presence of broken
bonds around the edges of the silica-alumina units.

Illites and montmorillonites are sheet structures composed of two layers of silica tetrahedrons and one central octahedral layer. In illites, some of the silicon is always replaced by aluminum and the resultant charge deficiency is balanced by interlayer potassium ions. The presence of these ions in interlayer positions tends to maintain a closed structure where cation exchange is discouraged.

In montmorillonites, substitution per unit is 1.5 times greater than in illite and occurs primarily in the octahedral layers. The capacity for adsorption is increased by greater surface charge but because cations cannot approach as closely to the seat of charge, cations are held less strongly. This mineral is said to have an "expandible lattice" because variable amounts of water may be associated with interlayer cations causing a change in the interlaying separation.

A third source of exchange capacity is common to all these minerals. This source is hydroxyl groups whose activity is dependent on the solution pH. Reported zero point of charges of pH 4.6 for kaolinite and pH 2.5 for montmorillonite suggest that in most groundwater regimes, cation replacement of hydrogen in these groups would be favoured.

Kaolinites have been reported to have 50-60% of their exchange capacity due to the hydroxyl groups (Russel, 1950). Specific studies of bentonite (Na-montmorillonite) and illite samples by Synder et al. (1969) showed those samples to have 10% and 33% pH dependent exchange capacities respectively. Results of calcium-rubidium exchange experiments on these samples at pH 6 suggested that retention of either cation was markedly less on a pH dependent exchange site than on a permanent charge site.
The strength of cesium adsorption on clay minerals is thus very dependent on the type of exchange site. The total amount of cesium that may be adsorbed is controlled by the exchange capacity of the mineral and the ability of other cations to compete with cesium at each type of exchange site.

Early investigators of cesium exchange were Wahlberg and Fishman (1962). Figures 2.1, 2.2 and 2.3 illustrate some of the results of their batch tests; portions of their data were chosen that might be generally representative of natural competition in groundwaters. Their samples were presaturated with different cations and the exchange of cesium followed in systems of 0.1 g clay and 10 ml of solution.

With a montmorillonite sample at competing cation concentrations of $10^{-2}$ and $10^{-4}$ m, adsorption of cesium was sensitive to the type of competition. Monovalent competition allowed higher cesium adsorption. The relative ability of cations to compete with cesium followed the lyotropic series (Ca $>$ Mg $>$ K $>$ Na). A similar trend occurred with the kaolinite sample, while for illite, potassium was a much more effective competitor than sodium.

Except on sodium treated illite, $K_d$ values remained constant over a wide range of cesium concentrations. The sodium treated illite showed that cesium adsorption on illite is apparently more dependent on the cesium concentration than the concentration of competing cations. In general, for a given competition, $K_d$'s on montmorillonite were about ten times higher than those on kaolinite and illite.

Sawhney (1964) conducted a similar series of experiments using calcium and potassium competition. The conclusions of his study were important because they emphasized that cations such as potassium, which
CESIUM ADSORPTION ON A MONTMORILLONITE
(COMPETITION AS SHOWN WITH PRESATURATED MINERAL)
AFTER WAHLBERG & FISHMAN (1962)
FIG 2.1
FIG. 2.2 CESIUM ADSORPTION ON A KAOLINITE

COMPETITION AS SHOWN; PRESATURATED MINERAL
AFTER WAHLBERG & FISHMAN (1962)
FIG. 2.3 CESIUM ADSORPTION ON AN ILLITE

COMPETITION AS SHOWN; PRESATURATED MINERAL
AFTER WAHLBERG & FISHMAN (1962)
are similar in size and hydration to cesium, could compete more strongly with cesium on some minerals than dissimilar cations such as calcium. The atomic radii of the common cations are listed in Table 2.1. The hydrated radii of potassium, cesium and rubidium are notably smaller than those of other cations although potassium is slightly larger than cesium. However, during the course of cation adsorption at least one water molecule must be released from the hydrated shell about a cation. When this occurs, the higher surface charge of potassium draws the remaining water closer and causes the hydrated radius of potassium to become slightly smaller than that of cesium.

In batch tests, Sawhney used presaturated minerals and soil to water ratios of 0.1 g:10 ml. Solutions contained $10^{-5}$ M Cs and $10^{-1}$ N KCl or CaCl$_2$. The results are presented in Table 2.2. For the kaolinite and montmorillonite samples, cesium adsorption was greater on potassium saturated colloids than Ca saturated colloids. However, the opposite was true of the illite, vermiculite, biotite, and muscovite samples. These minerals also fixed large portions of the adsorbed cesium against extraction. Sawhney explained the unexpected fixation in the potassium micas as cesium exchange with potassium at crystal edges and incorporation into the stable structure.

Tamura and Jacobs (1960) had observed the same phenomena in illite and vermiculite, noting at the same time that high cesium adsorption seemed to be out of proportion with the exchange capacities. They attributed this behaviour to selective sorption of cesium in the interlayer space near particle edges. Here fixation occurred from entrapment by structural collapse around the cesium.
TABLE 2.1

ATOMIC RADII OF SOME COMMON CATIONS

<table>
<thead>
<tr>
<th>Cation</th>
<th>Non-hydrated Radius (Å)</th>
<th>Hydrated Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>1.12</td>
<td>9.6</td>
</tr>
<tr>
<td>Ca</td>
<td>.99</td>
<td>9.6</td>
</tr>
<tr>
<td>Mg</td>
<td>.66</td>
<td>10.8</td>
</tr>
<tr>
<td>Cs</td>
<td>1.67</td>
<td>3.6</td>
</tr>
<tr>
<td>Rb</td>
<td>1.47</td>
<td>3.6</td>
</tr>
<tr>
<td>K</td>
<td>1.33</td>
<td>3.8</td>
</tr>
<tr>
<td>Na</td>
<td>.97</td>
<td>5.6</td>
</tr>
</tbody>
</table>

1 Berry and Mason (1959), p. 167
2 Grim (1968), p. 215

TABLE 2.2

CESIUM ADSORPTION ON CLAY MINERALS

Sawhney, 1964

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Cesium Adsorbed (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolinite</td>
<td>35</td>
</tr>
<tr>
<td>montmorillon</td>
<td>50</td>
</tr>
<tr>
<td>illite</td>
<td>116</td>
</tr>
<tr>
<td>vermicul.</td>
<td>103</td>
</tr>
<tr>
<td>biotite</td>
<td>x</td>
</tr>
<tr>
<td>musc.</td>
<td>x</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clay Type</th>
<th>Cesium Adsorbed (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca saturation</td>
<td>45</td>
</tr>
<tr>
<td>K saturation</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

x individual values not reported but similar to those of illite.
It is now known that illites commonly exist as particles of 5-10 platelets. The surfaces of the tetrahedral layers of these platelets possess "hexagonal" holes between oxygen atoms. Cesium (and potassium, rubidium and $\text{NH}_4^+$) have suitable size to enter these holes and "fix" themselves between adjacent platelets. These cations also have hydration energies that are slightly less than that of adsorption and so are doubly favoured for this type of fixation (Bolt and Bruggerwert, 1976). Sodium, lithium and divalent cations apparently have large enough hydrated radii to prevent their entrance into these holes.

Vermiculites, unlike montmorillonites, exhibit the ability to collapse in a manner similar to that of illite and thus is selective for cesium. The difference in the behaviour of montmorillonite and vermiculite is due to the difference in their octahedral layers. In these layers, hydroxyl groups are centred between three octahedral positions. In montmorillonite, each of these positions is filled by a divalent cation and the electrical forces about the hydroxyl groups remain balanced. In vermiculite, two positions are filled by trivalent cations and the third remains vacant. As a result, the hydroxyl group becomes inclined to the surface. This causes cations held in the hexagonal holes between hydroxyl groups, such as cesium, to be held more strongly. This principle has been demonstrated by Rausell-Colom et al. (1965) using muscovites and trioctahedral micas.

Similarly, Barshad and Kishk (1968) have shown that the oxidation of octahedral ferrous iron in biotites promotes potassium selectivity. Juo and White (1969) confirmed the change in the hydroxyl orientation upon oxidation of Fe$^{++}$ to Fe$^{+++}$. 
In some situations competition can actually increase cesium adsorption. For a vermiculite sample, Jacobs (1963) found that cesium adsorption could be maximized by adjusting the addition of potassium to a $10^{-5}$ M Cs solution before equilibration. Small additions caused an increased selectivity of cesium adsorption but a reduction in the exchange capacity by promoting collapse of the vermiculite structure. An excess of potassium eventually caused direct competition with cesium.

Jacobs also reported on the kinetics of exchange on this material. Several columns were packed with either sodium saturated vermiculite or potassium saturated vermiculite and solutions of $10^{-5}$ M Cs, 0.5 M NaNO$_3$ were passed through them. Cesium loading was determined in the columns after desired time intervals. The results of these experiments are shown in Figure 2.4.

The amount of cesium adsorbed on the sodium treated material increased slowly throughout the period of one week. Cesium adsorption on the potassium treated material peaked after one day and slowly decreased with time thereafter. The increase in cesium adsorption was attributed to slow diffusion of cesium into the mineral lattices. In the latter case, expansion of the vermiculite may have begun after a day as potassium was removed by leaching. Because cesium adsorption could not maintain the close separation of the lattices, cesium selectivity began to decrease with time.

In 1966, Sawhmey demonstrated further peculiarities of cesium diffusion in clay minerals. In his batch tests, 1 g samples of potassium or calcium saturated clays were equilibrated with 50 ml aliquots of a solution of $10^{-4}$ M Cs, pH 2.3. The results are shown in Figure 2.5.
INFLUENCE OF TIME ON THE SORPTION OF CESIUM BY VERMICULITE

FIG 2.4
FIG 2.5 ADSORPTION OF CESIUM WITH TIME ON THREE CLAY MINERALS
    (AFTER SAWHNEY, 1966)
Adsorption in montmorillonite quickly reached equilibrium because the montmorillonite always maintained a partially expanded basal spacing and exchange sites were always accessible. This was not the case with the vermiculites. Cesium adsorption increased with time on calcium vermiculite but decreased with time on the potassium vermiculite. In the first instance, it was suggested that the cesium collapsed the calcium vermiculite along interlayer edges and that these edges afforded channels through which cesium could diffuse into the interlayers. However, the potassium treated vermiculite already had a partially collapsed structure. Here the adsorption of cesium at edge sites closed the edges enough for the coulombic attraction of the potassium to collapse the layers to a 10 Å spacing and cesium was slowly excluded because it had a larger hydrated radius than potassium. A fully cesium saturated sample of this mineral had a 10.0 Å spacing. The theory was defended with X-ray diffraction documentation of the collapse of a potassium vermiculite with cesium loading.

The intermediate behaviour of the illites with cesium showed that illite exists naturally as a collapsed structure with few edge sites.

With regard to the diffusion process, grain size of mineral particles may play an important role. Studies of potassium extraction from weathered micas have shown that the amount of potassium retained per unit weight is larger in smaller sized particles. Also, the area of a collapsed central core relative to the area of the frayed edges is larger in the smaller particles and allows easier closing of the edges (Hill and Sawhney, 1969). As a result, one might expect that smaller particles would show greater selectivity for cesium although
the total capacity for fixation may be greater in larger particles.

Not a great deal of attention has been paid to the adsorption of cesium on minerals other than the clay minerals. However, Schroeder and Jennings (1963) prepared a rather extensive report on this subject. They performed a large number of batch tests by equilibrating 2 g samples with 5 ml of solution over a period of 24 hours. Mineral samples were presaturated with different cations and varying concentrations of competing cations were added to the equilibrating solutions. A presentation of some of their findings is shown in Table 2.3.

Quartz adsorbed very little cesium from $10^{-8}$ M Cs solutions as evidenced by the $K_d$'s of less than 2. Adsorption against calcium cations was slightly higher than against potassium. Microcline was more receptive to cesium adsorption. For calcium competition, adsorption on the 50-60 mesh material was greater than that of the 20-30 mesh material and illustrates that increasing the surface area per unit mass of a low exchange capacity material can increase adsorption significantly. This trend was not apparent with potassium competition. The difference between $K_d$'s at $10^{-6}$ M Cs and $10^{-8}$ M Cs seemed more related to cation competition than cesium concentration. On mineral surfaces such as these, where charge deficiencies arise from broken bonds only, adsorption is mainly controlled by cation exchange of hydrogen associated with structural oxygen. Microcline, with its three dimensional arrangement of silica and alumina tetrahedrons, may show some potassium and cesium selectivity if close approach of these cations between surface tetrahedrons is possible.
TABLE 2.3
SUMMARY OF CESIUM BATCH TEST K\textsubscript{d} VALUES
(Schroeder and Jennings, 1963)
 Approximate K\textsubscript{d} for molarity of saturating ion

<table>
<thead>
<tr>
<th>Material</th>
<th>Grain Size (mesh)</th>
<th>Cesium Conc.</th>
<th>Saturating Cation</th>
<th>pH</th>
<th>10\textsuperscript{-1}</th>
<th>10\textsuperscript{-2}</th>
<th>10\textsuperscript{-3}</th>
<th>10\textsuperscript{-4}</th>
<th>10\textsuperscript{-5}</th>
<th>10\textsuperscript{-6}</th>
<th>10\textsuperscript{-7}</th>
<th>10\textsuperscript{-8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>20-30\textsuperscript{1}</td>
<td>10\textsuperscript{-8} m</td>
<td>K\textsuperscript{+}</td>
<td>7.0</td>
<td>-</td>
<td>0.0</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>quartz</td>
<td>20-30</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>6.6</td>
<td>-</td>
<td>0.6</td>
<td>1.2</td>
<td>1.5</td>
<td>1.7</td>
<td>1.9</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>microcline</td>
<td>20-30</td>
<td>10\textsuperscript{-6} m</td>
<td>K\textsuperscript{+}</td>
<td>7.0</td>
<td>0.2</td>
<td>1.0</td>
<td>4.0</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>microcline</td>
<td>50-60\textsuperscript{2}</td>
<td>10\textsuperscript{-6} m</td>
<td>K\textsuperscript{+}</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>5.0</td>
<td>10.0</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>microcline</td>
<td>20-30</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>6.6</td>
<td>-</td>
<td>17.0</td>
<td>23.0</td>
<td>15.0</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>microcline</td>
<td>50-60</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>6.6</td>
<td>-</td>
<td>28.0</td>
<td>58.0</td>
<td>24.0</td>
<td>32.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>calcite</td>
<td>20-30</td>
<td>10\textsuperscript{-6} m</td>
<td>Ca\textsuperscript{++}</td>
<td>7.6-9.3</td>
<td>-</td>
<td>.7</td>
<td>2.0</td>
<td>3.0</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>calcite</td>
<td>20-30</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>7.3-8.5</td>
<td>11.0</td>
<td>15.0</td>
<td>20.0</td>
<td>15.0</td>
<td>20.0</td>
<td>28.0</td>
<td>34.0</td>
<td>42.0</td>
</tr>
<tr>
<td>limestone</td>
<td>20-30</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>9.3</td>
<td>100</td>
<td>140</td>
<td>180</td>
<td>240</td>
<td>320</td>
<td>430</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>dolomite</td>
<td>20-30</td>
<td>10\textsuperscript{-8} m</td>
<td>Ca\textsuperscript{++}</td>
<td>8.8-9.7</td>
<td>35</td>
<td>100</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{1} 840\mu - 550\mu (coarse sand)
\textsuperscript{2} 300\mu - 250\mu (medium sand)
From solutions of $10^{-6}$ M Cs, adsorption on calcite increased with decreasing calcium concentration to a maximum $K_d$ of 3. This is in agreement with a batch $K_d$ of 1.4 reported by Pirs (1974) for calcite sand in 0.7 M Cs solution. Stumm and Morgan (1970) suggested that the zero point of charge of calcite under atmospheric conditions should be $= \text{pH 8.4}$. Accordingly, cesium adsorption on calcite should not be significant below this pH. However, limestone and dolomite samples in solutions of $10^{-8}$ M Cs, pH 8.8 - 9.7, had $K_d$'s up to 100 times greater. These values seem anomalously high.

Results of studies on iron and manganese oxides, discussed elsewhere in this report (Section 4.2) suggest that the latter might be a significant adsorber of cesium. Tamura (1964) suggested that iron oxides had little direct influence on cesium adsorption. Evans and Dekker (1966) however, concluded that they act as site blocking agents thus tending to reduce adsorption.

In predicting the behaviour of cesium in an actual field situation, one might expect that its adsorption would eventually achieve a thermodynamic equilibrium with each mineral present in the soil. The $K_d$ of a soil sample would then represent a weighted summation of each of the individual $K_d$'s depending on the quantities of each mineral present.

With trace quantities of cesium under the appropriate conditions of potassium competition, cesium adsorption would be selective with weathered micas, vermiculites and illites and would be time dependent. Once the amount of cesium in solution exceeded the sorptive capacity of the frayed edge sites, further cesium adsorption would be less favoured and subject to competition according to the lyotropic series. Only at this stage would true mass action behaviour be expected.
Although many of the common rock forming minerals show an ability to adsorb cesium from solution (Table 2.3), it appears that the clay minerals will generally be the most effective adsorbers of cesium. In view of its high exchange capacity, soils rich in montmorillonite would likely have the highest $K_d$ over the widest range of cesium solution concentrations. At trace cesium concentrations of perhaps $10^{-8}$ M and lower, the $K_d$ of illite may approach that of montmorillonite.

2.2 Strontium

Strontium is a divalent alkali earth metal having a non-hydrated ionic radius of 1.12 Å and a hydrated radius of 9.6 Å (Table 2.1). Since its charge and hydrated radius are similar to those of calcium, one might expect strontium and calcium to have similar exchange properties. In addition to exchange reactions, strontium forms slightly soluble compounds with various anionic constituents of groundwater such as carbonate and sulphate. As a consequence of taking part in both exchange and precipitation reactions, the prediction of strontium migration rates in natural groundwater systems could be considerably more difficult than the prediction of cesium migration rates.

Wahlberg et al. (1965) studied the exchange properties of strontium using pure clay adsorbers which had been presaturated with a single competing cation (calcium, magnesium, sodium or potassium). In the equilibrating solutions, the concentration of the competing cation was varied from $10^{-1}$ to $10^{-5}$ N while the strontium concentration was varied from $10^{-1}$ to $10^{-10}$ N. It was concluded that under the
conditions of their experiments, the exchange of strontium could be described adequately by the mass-action equation. The mass action equilibrium constant for calcium or magnesium and strontium exchange was nearly unity and did not vary with exchange capacity. For sodium or potassium exchange with strontium, the equilibrium constant increased as the cation exchange capacity decreased. The adsorption of strontium was greatest for sodium-saturated clay and least for calcium-saturated clay.

Although the site selectivity exhibited by illitic minerals for cesium does not exist for strontium, various authors have indicated the presence of at least two types of exchange sites for strontium in a variety of mineral materials. Heald (1960) reported that kaolinite, illite, bentonite and vermiculite show two sites for strontium exchange. These were referred to as "tight" sites and "loose" sites according to the relative bonding energies. Only about 0.1% of the exchange capacity was due to the "tight" sites. Fordham (1973) demonstrated that the amount of strontium taken up by kaolinite and dickite was small relative to the total exchange capacity and concluded that the most reactive sites were located at the edges of the clay minerals. Murdock and Rich (1972) examined the adsorption and release of Rb and Sr by the 2-0.2µ fraction from vermiculitic soils. The lowest Rb/Sr ratio for adsorption of these two ions occurred in a clay containing montmorillonite while the Rb/Sr ratio tended to increase as the degree of mica to vermiculite alteration increased. Since rubidium has the same hydrated radius as cesium, the increase in the Rb/Sr ratio may reflect an increase in the selectivity for rubidium similar to that discussed for cesium in section 2.1. As a result from this data,
no conclusions can be drawn regarding sight specificity for strontium adsorption.

As a consequence of concern for the migration of strontium-90 through the food chain, various researchers have examined the reactions of strontium in surface soils. Khasawneh et al. (1968) found that the soil mineral fraction preferentially adsorbs strontium over Ca, while the reverse is true of the organic fraction. They obtained selectivity coefficients for 63 Indiana soils which varied from 0.61 (Ca preferring) to 1.51 (Sr preferring). Taylor (1968), working with acid soils from the coastal plain of North Carolina found that significant amounts of radiostrontium could not be recovered by rapid extraction. The mechanism of occlusion of the slowly recoverable strontium was a permanent fixation, and was believed to be the result of a slow exchange reaction in which the rate limiting step is a diffusion process acting within the exchanger matrix of the soil. The amount of strontium occluded could not be correlated with acidity, exchange capacity or clay mineral content, and was believed to reflect variations in the physical or chemical character of the organic matter in the soils examined.

Rhodes (1957) presented evidence to indicate that the $K_d$ of strontium is significantly pH dependent. Working with a calcareous and montmorillonitic Hanford soil, it was found that increasing the pH from 8.5 to 10 with NaOH or to 9.2 with Ca(OH)$_2$ increased the $K_d$ from about 30 to over 100 ml/g. Savannah River soil, which is non-calcareous, showed a similar increase in $K_d$ when NaOH was added but a lower $K_d$ if Ca(OH)$_2$ was used. A pH dependence of the adsorption of cesium was discussed in section 2.1. Generally, the effect of pH was small and
was attributed to the presence of pH dependent exchange sites. In view of the large change in $K_d$ with increasing pH and the fact that montmorillonite has a very small proportion of pH dependent exchange sites, it does not appear that the results obtained by Rhodes can be explained on the basis of exchange properties. The results do appear to be consistent however, with a decrease in the solubility of strontium carbonate or strontium sulphate as the pH increases.

Mokady and Gal (1964) reported that, when 0.01 N strontium chloride solutions were introduced into soils containing CaCO$_3$, radiostrontium was retained by the formation of SrCO$_3$. This was confirmed by x-ray diffraction analysis and the disappearance of CaCO$_3$. Tamura (1965) suggested that as the pH increases the strontium $K_d$ would be expected to show an increase by the reduction in calcium concentration caused by the higher proportion of carbonate ions to bicarbonate ions which limits the solubility of CaCO$_3$. In addition to direct precipitation, it is likely that during the equilibrium reaction forming CaCO$_3$ strontium ions present in the solution can take part in the reaction and be taken up by the CaCO$_3$ (coprecipitation). Menzel (1963) demonstrated that calcareous Huntley soil might fix strontium through such a reaction. Mills and Zwarich (1970) in an investigation of radiostrontium adsorption by the carbonates of glacial till found that a large component of the adsorption was independent of the concentration of Ca and Mg in solution. They concluded that adsorption of radiostrontium by the carbonates is not an important contribution to the total adsorption in a calcareous soil. If "total adsorption" is used to include both ion exchange and precipitation, then this statement is probably true only if the strontium concentration and pH are such that the solution is undersaturated with respect to strontium carbonate.
The formation of strontium-fixing low solubility compounds in soils by the addition of ions to waste solutions or by the addition of various materials to the soil has also been discussed in the literature. The presence of phosphate ions in the active waste greatly improved the ability of the Hanford soil to remove strontium from the waste (Rhodes, 1957). Ames et al. (1958) reported that the presence of mineral calcite and phosphate in the waste resulted in formation of apatite, with radiostrontium substituting for calcium in the reaction. Ames (1960) also studied the calcite-fluoride, gypsum-carbonate and gypsum-phosphate reactions for the purpose of incorporating strontium into the final product. Menzel (1960) suggested that strontium sulphate could be formed by the application of gypsum to the soil. He demonstrated that the fixation of strontium may be induced in soils with a high strontium-to-calcium ratio. Although the preceeding studies were conducted primarily with a view to stabilizing liquid wastes, similar reactions could occur in many hydrogeologic environments.

Various researchers have investigated the mobility of strontium under field conditions. From investigations at the Chalk River Nuclear Laboratories, Parsons (1961) found the rate of movement of cesium to be 7 to 7.5 m/year). The distribution coefficient (Kd) was found to be about 100 for radiocesium and 13 to 35 for radiostrontium. (The characteristics of soils taken from the area in which Parsons conducted his studies are given in Chapter 3). Spitsyn et al. (1958) found that in calcareous sand radiostrontium moved farther from an injection well than radiocesium. Laguna et al. (1958), working with weathered Conasauga shale and alkaline waste containing approximately 0.5 M sodium ions, also found higher adsorption of cesium than strontium.
Radiochemical data from soil samples taken at the USAEC Hanford reservation, in which active wastes were disposed, indicated that radiostrontium had migrated somewhat farther than radiocesium (Linderoth and Pearce, 1961).

From the above, and similar data, Tamura (1965) concluded that most soils will adsorb strontium the least of all the hazardous cationic fission-product radionuclides. The lower adsorption of strontium compared with that of radiocesium, suggests that strontium would migrate greater distances and thus present a greater potential for contamination of groundwater and surface waters.
3. EQUILIBRIUM $K_d$ DETERMINATIONS

3.1 Introduction

As discussed in section 1.2, the distribution coefficient ($K_d$) appears to be a convenient method for representing, in a quantitative manner, the chemical interactions between a solute and the solid matrix. Furthermore, it can be used in mathematical models to predict the rate of migration of reactive solutes.

From Chapter 2 it is apparent that $K_d$ depends upon the properties of both the radiocation and the adsorbing material, and also upon the water chemistry of the equilibrating solution. It is equally apparent that $K_d$ is an empirical number which, in many situations, may represent the combined effects of several chemical processes.

Although it is convenient to be able to represent the geochemical interactions by a single number, the fact that $K_d$ represents the combined effect of several processes makes it virtually impossible to determine on a purely theoretical basis. A second approach to evaluating $K_d$ would be through direct measurement at each site at which solute-solid interactions are of interest. Since these measurements would yield no information on the factors affecting $K_d$, they would need to be made under the same conditions of water and adsorber chemistry as would be encountered by the contaminants. This approach suffers from two disadvantages. There are no laboratory or field methods for determining $K_d$ in which a given set of geochemical conditions can be reproduced exactly. In addition, the geochemical conditions could be altered somewhat at the time of waste disposal from the conditions existing at the time of site evaluation. The direct measurement approach would not
provide a means of evaluating the effect of minor changes in the geochemistry of the system on the measured $K_d$ values.

An approach which could be considered intermediate between the theoretical and direct measurement approaches would be to develop empirical correlations between $K_d$ and measurable system parameters such as pH, cation exchange capacity, concentration of competing cations, mineralogy and others. Information of this type could provide basic information concerning the nature of $K_d$, could permit estimates of uncertainty concerning measured $K_d$ values at particular sites and could also allow for estimates of $K_d$ during preliminary site evaluation programmes. A requirement of the empirical correlation approach is that all the pertinent parameters be identified.

In the present study, batch methods were used to determine $K_d$ values for cesium and strontium in equilibrium with sixteen different soil materials. The soils were selected to represent ranges in common soil chemical and physical properties. It was believed that the resulting data could represent a generic data base from which it would be possible to estimate, at least in a qualitative manner, the $K_d$ for cesium or strontium in most Canadian soil materials. The accuracy with which these estimates could be made would depend to a large extent upon the degree of correlation found between the measured $K_d$ values and the measured geochemical properties. Implicit in the use of the data as a generic data base is the requirement that the physical and chemical properties of the medium and the equilibrating solutions be known. Considerable effort was expended towards this end.
3.2 Sample Collection

Soil samples were selected primarily on the basis of three properties:

1) cation exchange capacity
2) principal clay minerals
3) carbonate-mineral content

Since cation exchange is believed to be a major adsorption mechanism for cesium and strontium, it is apparent that the soil samples should represent a considerable range in exchange capacity. Although the clay mineralogy will affect the cation exchange capacity of a sample, it can exert an independent effect on adsorption by controlling the type of adsorption sites available. As discussed in Section 2.1, this could be particularly significant with respect to cesium adsorption. Although carbonates may provide adsorption sites (Chapter 2) and thus affect the measured $K_d$, their presence or absence may be of greater indirect importance. In particular, the chemistry of groundwater in geologic materials containing carbonates is profoundly different from that of water in areas which do not contain carbonates. Non-carbonate groundwaters generally have a lower pH than carbonate groundwaters, sodium and potassium generally represent a greater proportion of the total cations present and sulfate generally represents a greater proportion of the anions present.

Soil materials of southern Ontario generally contain carbonates and generally have illite as the major clay mineral while soils in the Canadian prairies also contain carbonates, but generally have montmorillonite as the major clay mineral. Soils in central to northern Ontario (located within the Canadian Shield) generally have illite as the major
clay mineral and frequently do not contain carbonates. There are no extensive regions in Canada in which the soils are free of carbonates and have montmorillonite as the principal clay mineral.

An attempt was made to obtain samples covering a range in texture from each of the regions referred to above. In addition, an attempt was made to obtain samples at sites where other groundwater investigations were being conducted by the University of Waterloo or other research groups. This approach provided the advantage of having additional background geochemical and hydrologic information for the area from which the samples came. In addition, it provided a better opportunity for resampling at the same location, and substantially reduced the cost of the sample collection programme.

Of particular note, samples were collected from both the Whiteshell Nuclear Research Establishment and the Chalk River Nuclear Laboratories of Atomic Energy Canada Limited. In addition to meeting the site selection criteria discussed above, samples from these locations offered the additional advantage of having $K_d$ data against which the data of this project could be compared. The data obtained for samples from WNRE could be compared with that of Mills and Zwarich (1970), while the laboratory values of this study could be compared with the laboratory and field values being determined by investigators at CRNL (Jackson et al., 1977).

Additional soil samples were obtained from near Lethbridge, Alberta, at the Bruce Nuclear Power Development site of Ontario Hydro, from the Canadian Forces Base at Borden, Ontario, from two sites near North Bay, Ontario, and from two sites near Leamington, Ontario. A total of sixteen samples were collected, and were numbered in the order in which they were obtained. Throughout much of the discussion of this chapter, the
soils will be identified only by number. Table 3.1 lists the soil number, the location at which it was collected and a qualitative description of the sample. A map showing each sampling location is given in Appendix A.

3.3 Characterization of Soil Samples

Upon receipt in the laboratory, samples were air-dried, passed through a 2 mm sieve and stored in plastic bags. Each soil sample was characterized with respect to a wide range of both physical and chemical properties. Physical properties included bulk density, particle density, porosity and texture. The chemical properties included cation exchange capacity, exchangeable cations, soluble cations, pH, carbonate content, organic matter content and clay mineralogy.

Standard engineering or soil science analytical methods (or slight modifications of those methods) were used for all determinations, and all analyses were performed in triplicate. A brief description of each method and appropriate references are given in Appendix B.

The use of standard methods is obviously convenient in that the procedures are well documented in the literature. Of greater importance however is the fact that since soils are not pure chemical systems, in many instances, the value of a particular parameter depends upon the method used in its determination. Therefore, soils can be compared most reliably if they have been characterized using similar methods. If for example, it is found that the $K_d$ values are highly correlated with the cation exchange capacity, then the $K_d$ of many soil materials could be estimated based on known cation exchange capacity values. In addition, there are many laboratories in Canada which are capable of measuring C.E.C. on a routine basis but only a limited number which are equipped
Table 3.1
Collection location and description of soil samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Location</th>
<th>Depth (m) Sampled</th>
<th>Predominant Clay</th>
<th>Carbonates</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WNRE</td>
<td>5.0</td>
<td>Illite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>2</td>
<td>WNRE</td>
<td>5.0</td>
<td>Illite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>3</td>
<td>WNRE</td>
<td>5.0</td>
<td>Illite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>4</td>
<td>WNRE</td>
<td>2.0</td>
<td>none present</td>
<td>present</td>
<td>coarse sand</td>
</tr>
<tr>
<td>5</td>
<td>Leamington</td>
<td>4.5</td>
<td>Illite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>6</td>
<td>Leamington</td>
<td>3.0</td>
<td>trace present</td>
<td>present</td>
<td>medium sand</td>
</tr>
<tr>
<td>7</td>
<td>CRNL</td>
<td>3.8-4.3</td>
<td>trace present</td>
<td>not present</td>
<td>fine sand</td>
</tr>
<tr>
<td>8</td>
<td>North Bay</td>
<td>6.0</td>
<td>Illite</td>
<td>not present</td>
<td>sandy loam</td>
</tr>
<tr>
<td>9</td>
<td>North Bay</td>
<td>0.9</td>
<td>Illite</td>
<td>not present</td>
<td>silty clay loam</td>
</tr>
<tr>
<td>10</td>
<td>WNRE</td>
<td>0.6-0.8</td>
<td>Illite</td>
<td>not present</td>
<td>sandy loam</td>
</tr>
<tr>
<td>11</td>
<td>WNRE</td>
<td>1.2</td>
<td>Vermiculite</td>
<td>present</td>
<td>sandy loam</td>
</tr>
<tr>
<td>12</td>
<td>BNPD</td>
<td>8.0</td>
<td>Illite</td>
<td>present</td>
<td>loam</td>
</tr>
<tr>
<td>13</td>
<td>C.F.B. Borden</td>
<td>1.5-3.0</td>
<td>trace present</td>
<td>present</td>
<td>sand</td>
</tr>
<tr>
<td>14</td>
<td>Alberta</td>
<td>0.5-1.0</td>
<td>montmorillonite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>15</td>
<td>Alberta</td>
<td>3.0-5.0</td>
<td>montmorillonite</td>
<td>present</td>
<td>clay loam</td>
</tr>
<tr>
<td>16</td>
<td>Alberta</td>
<td>10.0-11.0</td>
<td>montmorillonite</td>
<td>present</td>
<td>sandy loam</td>
</tr>
</tbody>
</table>
or have had experience in determining $K_d$ values.

The results of the physical property analyses are given in Table 3.2. The parameter of greatest significance with respect to $K_d$ values is undoubtedly the particle-size distribution since this factor can influence the cation exchange capacity. The textures vary from sand to clay loam with the percent clay varying from 0.0% to as much as 35% by weight. Although it is not evident from Table 3.2, there was a reasonable range of textures for each of the major mineralogic groups.

With the exception of the x-ray diffraction analyses, the results of the chemical characterization studies are given in Table 3.3. The cation exchange capacity values vary between 0.37 and 32.71 me/100 g of soil and generally increase with increasing clay content. Samples 1, 5 and 14 all have clay contents of approximately 30% but have cation exchange capacities of 8.43, 5.90 and 32.71 me/100 g respectively. This trend in C.E.C. is undoubtedly the result of the mineralogy, with the highest value being associated with the sample having montmorillonite as the predominant clay mineral (Lethbridge, Alberta, sample). The lowest C.E.C. was associated with the sample from Leamington, which had illite as the predominant clay mineral while the intermediate C.E.C. value was associated with the WNRE sample which had illite as the principle clay mineral but also had a significant proportion of mixed layer minerals. Although values are reported as low as 0.37 me/100 g, at values less than 1.0 me/100 g, there is a substantial degree of uncertainty in the absolute value of the determination.

The major cations in groundwater, and those which control most exchange reactions in hydrogeologic systems are $Na^+$, $K^+$, $Ca^{++}$ and $Mg^{++}$. The quantities of these cations occurring on the exchange sites (exchangeable
Table 3.2

Physical Properties of Soil Samples

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Bulk Density</th>
<th>Particle Density</th>
<th>Porosity (%)</th>
<th>% Sand</th>
<th>% Silt</th>
<th>% Clay</th>
<th>Class (U.S.D.A.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.99</td>
<td>2.63</td>
<td>24.0</td>
<td>36</td>
<td>35</td>
<td>29</td>
<td>clay loam</td>
</tr>
<tr>
<td>2</td>
<td>2.04</td>
<td>2.54</td>
<td>20.4</td>
<td>35</td>
<td>36</td>
<td>29</td>
<td>clay loam</td>
</tr>
<tr>
<td>3</td>
<td>1.93</td>
<td>2.62</td>
<td>26.9</td>
<td>34</td>
<td>35</td>
<td>31</td>
<td>clay loam</td>
</tr>
<tr>
<td>4</td>
<td>1.78</td>
<td>2.63</td>
<td>32.1</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>sand</td>
</tr>
<tr>
<td>5</td>
<td>1.83</td>
<td>2.63</td>
<td>30.9</td>
<td>28</td>
<td>41</td>
<td>31</td>
<td>clay loam</td>
</tr>
<tr>
<td>6</td>
<td>1.66</td>
<td>2.62</td>
<td>36.7</td>
<td>93</td>
<td>5</td>
<td>2</td>
<td>sand</td>
</tr>
<tr>
<td>7</td>
<td>1.59</td>
<td>2.67</td>
<td>39.7</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>sand</td>
</tr>
<tr>
<td>8</td>
<td>1.48</td>
<td>2.67</td>
<td>44.6</td>
<td>52</td>
<td>45</td>
<td>3</td>
<td>sandy loam</td>
</tr>
<tr>
<td>9</td>
<td>1.33</td>
<td>2.76</td>
<td>51.8</td>
<td>12</td>
<td>55</td>
<td>33</td>
<td>silty clay loam</td>
</tr>
<tr>
<td>10</td>
<td>1.55</td>
<td>2.67</td>
<td>41.9</td>
<td>59</td>
<td>24</td>
<td>17</td>
<td>sandy loam</td>
</tr>
<tr>
<td>11</td>
<td>1.49</td>
<td>2.68</td>
<td>44.4</td>
<td>62</td>
<td>31</td>
<td>7</td>
<td>sandy loam</td>
</tr>
<tr>
<td>12</td>
<td>1.82</td>
<td>2.78</td>
<td>34.5</td>
<td>52</td>
<td>39</td>
<td>9</td>
<td>sandy loam/loam</td>
</tr>
<tr>
<td>13</td>
<td>1.76</td>
<td>2.69</td>
<td>34.6</td>
<td>96</td>
<td>2</td>
<td>2</td>
<td>sand</td>
</tr>
<tr>
<td>14</td>
<td>1.46</td>
<td>2.75</td>
<td>46.9</td>
<td>34</td>
<td>34</td>
<td>32</td>
<td>clay loam</td>
</tr>
<tr>
<td>15</td>
<td>1.49</td>
<td>2.66</td>
<td>44.0</td>
<td>31</td>
<td>34</td>
<td>35</td>
<td>clay loam</td>
</tr>
<tr>
<td>16</td>
<td>1.45</td>
<td>2.62</td>
<td>44.7</td>
<td>60</td>
<td>22</td>
<td>18</td>
<td>sandy loam</td>
</tr>
</tbody>
</table>
Table 3.3
Chemical Properties of Soil Samples

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>C.E.C.*</th>
<th>Exchangeable Cations *</th>
<th>Soluble Cations (mg/l)</th>
<th>Carbonate (% by wt.)</th>
<th>% Organic Matter</th>
<th>pH (CaCl₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na⁺</td>
<td>K⁺</td>
<td>Ca⁺⁺</td>
<td>Mg⁺⁺</td>
</tr>
<tr>
<td>1</td>
<td>8.43</td>
<td>1.65</td>
<td>6.23</td>
<td>4.72</td>
<td>37.3</td>
<td>7.95</td>
</tr>
<tr>
<td>2</td>
<td>8.32</td>
<td>1.52</td>
<td>6.38</td>
<td>4.64</td>
<td>39.5</td>
<td>5.71</td>
</tr>
<tr>
<td>3</td>
<td>8.62</td>
<td>1.56</td>
<td>6.34</td>
<td>4.84</td>
<td>37.2</td>
<td>7.93</td>
</tr>
<tr>
<td>4</td>
<td>1.40</td>
<td>0.86</td>
<td>5.20</td>
<td>0.22</td>
<td>2.31</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>5.90</td>
<td>1.36</td>
<td>5.97</td>
<td>0.80</td>
<td>5.78</td>
<td>18.7</td>
</tr>
<tr>
<td>6</td>
<td>1.19</td>
<td>0.69</td>
<td>5.14</td>
<td>0.16</td>
<td>5.86</td>
<td>2.61</td>
</tr>
<tr>
<td>7</td>
<td>1.06</td>
<td>1.06</td>
<td>4.37</td>
<td>0.24</td>
<td>1.80</td>
<td>4.74</td>
</tr>
<tr>
<td>8</td>
<td>1.59</td>
<td>0.25</td>
<td>7.64</td>
<td>1.15</td>
<td>3.52</td>
<td>1.40</td>
</tr>
<tr>
<td>9</td>
<td>10.25</td>
<td>0.45</td>
<td>24.16</td>
<td>6.74</td>
<td>9.85</td>
<td>1.07</td>
</tr>
<tr>
<td>10</td>
<td>1.87</td>
<td>0.29</td>
<td>6.47</td>
<td>0.55</td>
<td>0.81</td>
<td>4.54</td>
</tr>
<tr>
<td>11</td>
<td>2.20</td>
<td>0.20</td>
<td>38.60</td>
<td>1.54</td>
<td>2.52</td>
<td>1.20</td>
</tr>
<tr>
<td>12</td>
<td>0.72</td>
<td>0.27</td>
<td>35.08</td>
<td>1.55</td>
<td>10.3</td>
<td>7.97</td>
</tr>
<tr>
<td>13</td>
<td>0.37</td>
<td>0.21</td>
<td>6.56</td>
<td>0.44</td>
<td>1.70</td>
<td>0.53</td>
</tr>
<tr>
<td>14</td>
<td>32.71</td>
<td>0.47</td>
<td>44.74</td>
<td>4.64</td>
<td>11.2</td>
<td>15.1</td>
</tr>
<tr>
<td>15</td>
<td>31.48</td>
<td>0.46</td>
<td>46.08</td>
<td>4.67</td>
<td>14.0</td>
<td>15.4</td>
</tr>
<tr>
<td>16</td>
<td>21.17</td>
<td>0.58</td>
<td>35.79</td>
<td>6.34</td>
<td>14.2</td>
<td>8.14</td>
</tr>
</tbody>
</table>

* me/100 g soil
cations) for each soil are listed in Table 3.3. Since sodium acetate was used to displace the cations from the exchange sites, exchangeable sodium could not be determined. The most striking feature of the exchangeable cation data is the high calcium values which, with the exception of the fine textured samples from WNRE (#1, 2, 3) exceed the exchange capacity of the soil. In an extreme case (Bruce NPD - soil #12) the exchangeable calcium value was 35.08 me/100 g while the C.E.C. was only 0.72 me/100 g. This suggests a source of calcium in the extracting solution other than that which was held in the soil by ion exchange. This is a common observation, particularly in calcareous soils and is believed to be the result of leaching of amorphous or mineral calcium compounds. Common sources of calcium ions include calcite, gypsum and apatite. It does not appear that the exchangeable cation data can be used as a measure of the proportions of the various cations adsorbed onto the soil materials.

The soluble cation concentrations were determined from a 1:1 water extraction, and the data was used to prepare the equilibrating solutions for the K_d determinations. The data of Table 3.3 shows the soluble cation concentrations to follow trends similar to those observed in the exchangeable cation data; for example, soluble potassium concentrations tended to correspond to high exchangeable potassium concentrations. There are several exceptions to this generality, and these can probably be related to the mineralogy of the samples or the concentrations of the competing cations.

The carbonate content of the samples varied from zero to 43.4%. The four samples which were free of carbonate were a sandy sample from Chalk River, the two samples from the North Bay area and a coarse sand
sample collected at a shallow depth below ground surface at WNRE.

The pH of the samples which were free of carbonates was less than 7.0 while the pH values of the samples with carbonate were close to 8.0.

Most of the soils had an organic matter content of less than 0.5%. Exceptions are sample No. 5 (1.27%) and sample No. 16 (2.05%). Sample No. 16 was collected within 1 m of the ground surface and thus the high value is not unexpected. Sample No. 5 was collected from a depth of approximately fifteen feet below ground surface. The sample was from a depressional area which had a thick accumulation of organic matter at the surface as well as several microstratigraphic layers which appeared to be high in organic matter. As a consequence the high organic matter content of the sample is probably a result of the mode of deposition.

For the purpose of interlaboratory comparison, subsamples of soils No. 1 through 7 were sent to the Alberta Department of Agriculture laboratories at Lethbridge, Alberta, for analyses of C.E.C., exchangeable cations and soluble cations. The results of the analyses were generally in good agreement with those obtained at the University of Waterloo. An exception was exchangeable calcium which was even higher in the Alberta Department of Agriculture results. This difference in calcium concentration was believed to be the result of slightly different analytical procedures. A more detailed discussion of the interlaboratory comparisons is given in the 1976 progress report of this project.

Cation exchange is probably one of the major geochemical retardation processes for most cations, and in inorganic soil materials the clay minerals are the primary source of exchange sites. As a consequence, the $K_d$ of a particular solute-soil reaction may be highly dependent upon
the clay mineralogy of the soil material. The principal clay minerals (along with their C.E.C. expressed in me/100 g) are kaolinite (3-15), illite (10-40), montmorillonite (100-150), vermiculite (150) and inter-stratified minerals. The interstratified minerals consist of layers of structural units of different clay minerals. The C.E.C. of such materials can be highly variable, depending upon which structural units are present and in what proportion.

The results of the x-ray diffraction analyses are given in Table 3.4. As discussed in Appendix B, the methods of analysis used in this study give semiquantitative results. As a consequence, actual percentages are not given but rather the clay minerals of a particular soil sample have been separated into major, intermediate and minor constituents.

As anticipated, the soils which have illite as the predominant clay mineral tend to have relatively low cation exchange capacities, and these soils are associated with southern Ontario. For example sample No. 5 (Leamington) has a clay content of 31% but a CEC of only 5.9 me/100 g and the sample from Bruce N.P.D. (No. 12) has a clay content of 9% and a C.E.C. of only 0.72 me/100 g. The clayey samples from northern Ontario and eastern Manitoba tended to have both interstratified and illite as the predominant clay minerals. This resulted in generally higher C.E.C. values (soil No. 1, 8.43 me/100 g) than for the illitic soils of southern Ontario. The predominant clay minerals of the Alberta samples (14 and 15) are interstratified and montmorillonite. The presence of montmorillonite results in the high C.E.C. values (30 me/100 g) of these soils. Sample No. 16 was taken at the same location as No. 14 and 15 but at a shallower depth. The lower C.E.C. value for this sample (21 me/100 g) could be attributed to the higher proportion of
### Table 3.4
Clay Mineral Composition of Soil Samples

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Major Species</th>
<th>Intermediate Species</th>
<th>Minor Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Interstratified, Illite</td>
<td>Montmorillonite</td>
<td>vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>2</td>
<td>Interstratified, Illite</td>
<td>Montmorillonite</td>
<td>vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>3</td>
<td>Interstratified, Illite</td>
<td>Montmorillonite</td>
<td>vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>4</td>
<td>No clay</td>
<td>No clay</td>
<td>No clay</td>
</tr>
<tr>
<td>5</td>
<td>Illite</td>
<td>--</td>
<td>Interstratified chlorite, vermiculite, kaolinite, montmorillonite</td>
</tr>
<tr>
<td>6</td>
<td>No clay</td>
<td>No clay</td>
<td>No clay</td>
</tr>
<tr>
<td>7</td>
<td>Very little clay</td>
<td>Very little clay</td>
<td>Very little clay</td>
</tr>
<tr>
<td>8</td>
<td>Interstratified, Illite</td>
<td>Vermiculite</td>
<td>Montmorillonite, chlorite, kaolinite</td>
</tr>
<tr>
<td>9</td>
<td>Illite, Interstratified</td>
<td>Montmorillonite</td>
<td>Vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>10</td>
<td>Interstratified, Illite</td>
<td>--</td>
<td>chloride, vermiculite, montmorillonite, kaolinite</td>
</tr>
<tr>
<td>11</td>
<td>Interstratified, Vermiculite</td>
<td>--</td>
<td>Montmorillonite, chlorite, kaolinite</td>
</tr>
<tr>
<td>12</td>
<td>Illite</td>
<td>--</td>
<td>Interstratified, vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>13</td>
<td>Very little clay</td>
<td>Very little clay</td>
<td>Very little clay</td>
</tr>
</tbody>
</table>

(con't)
Table 3.4 continued

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Major Species</th>
<th>Intermediate Species</th>
<th>Minor Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Montmorillonite, Inter-stratified</td>
<td>Illite</td>
<td>Vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>15</td>
<td>Montmorillonite, Inter-stratified</td>
<td>Illite</td>
<td>Vermiculite, chlorite, kaolinite</td>
</tr>
<tr>
<td>16</td>
<td>Montmorillonite, Illite</td>
<td>Interstratified</td>
<td>Vermiculite, chlorite, kaolinite</td>
</tr>
</tbody>
</table>
illite present than in the deeper samples; however, it is more probably the result of the lower clay content of this sample (18%).

3.4 Methods Used in $K_d$ Determinations

3.4.1 General

As discussed in an earlier section of this report (1.2), an adsorption isotherm is a graph of the amount of a particular solute adsorbed onto the solid phase (mg solute/g of soil) vs. the concentration of the solute in solution (mg/l). The distribution coefficient is the ratio of the amount adsorbed to the amount in solution (ml/g) and the distribution function is a graph of the distribution coefficient vs. the concentration of the solute in solution. Consequently, a single determination in which solution containing the cation of interest is brought to equilibrium with a known amount of adsorber gives a single point on the adsorption isotherm, one value of the distribution coefficient and one point on the distribution function. By using various concentrations in the equilibrating solution, a corresponding number of points can be determined on the adsorption isotherm and distribution function.

Experimentally, the problem is to establish equilibrium between the solution and solid phases and to determine the solute concentrations in the solution and solid phases at equilibrium. Either static or dynamic equilibrium conditions can be established. In the static methods, the more common of the two, a known solution volume with a known solute concentration is added to a known mass of solids. The solution and solids are contacted, generally by shaking, for some predetermined length of time until equilibrium is established (until
there is no change in the solute concentrations in the solution and solid phases. The solute concentrations in the solution and solid phases are then determined. It is generally most convenient to measure the concentration in the solution phase at equilibrium and to subtract this from the initial concentration and to use the change in concentration to calculate the solute concentration in the solid phase. It is particularly important to be certain that all solids are removed from the solution when determining the equilibrium solution concentrations. This can present difficulties when dealing with fine textured soils but can generally be accomplished by filtering, or more commonly, by centrifuging.

The dynamic equilibrium methods generally involve the continuous passage of the equilibrating solution through a small sample of the soil. When the concentration of the solute species of interest in the effluent becomes constant with respect to time, then the solute in the adsorbed and solution phases should be in equilibrium. The concentration in the solid phase can then be determined and the distribution coefficient calculated. This has been referred to as the "short column" method and has been investigated by Serne et al. (1974) of Battelle Pacific Northwest Laboratories. This method has the advantage of not requiring shaking and centrifuging and therefore could be more rapid than the static methods. In addition, if the concentration in the solid phase could be determined nondestructively (by radiometric methods), then by introducing step changes in the solute concentration of the influent solution, the complete adsorption isotherm could be determined on a single soil sample. This would also be a more convenient method for determining desorption isotherms than the static equilibrium methods.
Serne et al. (1974) showed examples of amount adsorbed vs. time (volume of effluent) curves in which the amount adsorbed rose to a maximum and then declined and became constant at some value less than the maximum. This phenomenon is probably the result of chemical changes in the sample resulting from the continuous leaching process, and gives rise to the problem of not knowing which adsorbed concentration is the most appropriate for the purpose of calculating $K_d$ values. In addition, the passage of a sufficient volume of effluent to be certain that equilibrium had been established could be quite time consuming. For these reasons, the $K_d$ values of this study were determined using static methods.

3.4.2 Cesium $K_d$ Determinations

In the cesium experiments, 1 g of soil and 5 ml of the equilibrating solution were used. The equilibrating solution for a particular soil contained concentrations of the major cations equal to those shown in the soluble cation data of Table 3.3. The solutions were prepared using deionized water which was passed through a second deionizing column in the laboratory. With the exception of sodium, cations were added as the chloride salts. Sodium was added as NaOH in order to overcome the problem of low initial pH values which were observed when only chloride salts were used. All equilibrating solutions for samples No. 1 through 7 contained $^{137}$Cs at a concentration of $8.38 \times 10^{-12}$ N. Equilibrating solutions of higher cesium concentration were obtained by adding stable cesium as CsCl. The cesium concentrations used in determining the adsorption isotherms were:

- $8.38 \times 10^{-12}$ N (carrier free)
- $1.84 \times 10^{-11}$
This range is from $1.1 \times 10^{-6}$ mg/l to $1.33 \times 10^4$ mg/l. In order to obtain improved counting statistics the amount of active cesium was doubled in the equilibrating solutions for samples No. 8 through 16.

The adsorption isotherms for soil No. 1 through 7 were determined at three different pH values of the equilibrating solution; a pH near the natural soil pH as determined from Table 3.3 and at approximately one pH unit above and below the natural pH. The equilibrating solutions, when first prepared had a pH above 9 in most cases. The pH was lowered to the desired value by adding dilute HCl. Since the solutions contained pure ionic species, they were poorly poised and had virtually no buffering capacity. As a result, the adjustment of pH was extremely tedious and time consuming. Based upon the results obtained for soils No. 1 through 7, the $K_d$ values for the remaining soils were determined at the natural pH only.

Prior to determining the distribution coefficients, the shaking time required in order to establish equilibrium was determined. Replicate samples containing 1 g of soil and 5 ml of the equilibrating solution with a cesium concentration of $10^{-4}$ N were prepared and shaken for varying lengths of time. When removed from the shaker, the samples were centrifuged and the activity in the supernatant determined. Figure 3.1 shows the change in count rate with time for soil No. 5 and soil No. 6. The time at which there appeared to be no further decrease in the activity of the supernatant was considered to be the minimum time for equilibrium to be reached; approximately 2 hr for the sand and 8 hr
FIG 3.1: GRAPH SHOWING THE SHAKING TIME REQUIRED FOR CESIUM TO REACH EQUILIBRIUM
for the clay of Figure 3.1. The experiments were generally conducted using a shaking time of at least double the minimum determined by the above procedure and the times varied from about 4 hr to 20 hr with the fine textured soils requiring the longest shaking times.

Thus, for a particular soil, 12 one g samples were placed in centrifuge tubes. The 12 equilibrating solutions were prepared and 5 ml added to the respective soil samples. The centrifuge tubes were then capped and shaken in a wrist-action shaker for the appropriate length of time. The samples were then centrifuged for 10 min and 3 ml of the supernatant transferred to counting tubes. The activity in the 3 ml aliquots was determined by gamma counting. A counting time of 10 min was used. This process was repeated for each of the three pH values of the equilibrating solutions for samples No. 1 through 7 and at the natural pH for soils No. 8 through 16. (Sample No. 2 was omitted since, based on Tables 3.1 through 3.4, it appeared to have physical and chemical properties identical to sample No. 1). All analyses were performed in triplicate.

Initial sample counting was done on a Nuclear Chicago manual counter in the Department of Chemistry. In view of the rather long counting time and the large number of samples, this proved to be quite impractical. Consequently, a Nuclear Chicago model 1085 automatic gamma counter was acquired in late April, 1976. Subsequent difficulties with this machine resulted in much of the counting for soils No. 1 through 7 being done on a Nuclear Chicago model 1085 gamma counter in the Department of Biology. Duplicate data generated by the three different counters indicated that the results were not affected by changing counting equipment. All counting in 1977 (Cs experiments for
soils No. 8 through 16 and all Sr determinations) was performed using the Department of Earth Sciences automatic gamma counting equipment.

3.4.3 Strontium $K_d$ Determinations

The methods used to determine the strontium $K_d$ values were similar to those described for cesium. Tracer strontium ($^{85}$Sr) was added to all equilibrating solutions to a concentration of $1.99 \times 10^{-12}$ N. Carrier strontium was added to give equilibrating solutions with total strontium concentrations of

\[
\begin{align*}
1.99 \times 10^{-12} \text{ N (carrier free)}
\end{align*}
\]

\[
\begin{align*}
1.00 \times 10^{-9}, -8, -7, -6, -5, -4, -3, -2, -1
\end{align*}
\]

This range is from $8.8 \times 10^{-8}$ mg/l to $4.4 \times 10^3$ mg/l. (A tracer concentration of $3.78 \times 10^{-12}$ N was used for the fine textured soils). Strontium -85 was chosen as the tracer since it is a gamma emitter (0.51 Mev), does not have daughter products to interfere with the analyses, and has a convenient half-life (64 days).

Strontium $K_d$ values were determined only at the natural pH of the soil. There was an insufficient supply of soil No. 12 for the strontium experiments; consequently, no results are shown for this soil.
3.4.4 Calculations

The concentration of the cation (either cesium or strontium) in solution at equilibrium was determined from

\[ C_e = f_s C_o \]  \hspace{1cm} (3.1)

where \( C_e \) is the concentration of the cation in solution at equilibrium (mg/l), \( f_s \) is the fraction remaining in solution at equilibrium and \( C_o \) is the initial concentration of the cation in the equilibrating solution (mg/l). \( f_s \) was determined by dividing the number of counts determined for the 3 ml aliquot of soil solution by the number of counts determined for a 3 ml aliquot of the equilibrating solution. In order to compensate for possible effects of radioactive decay and instrument drift, a sample of the equilibrating solution was generally counted for every six equilibrated samples.

The concentration of the adsorbed cation was calculated from:

\[ \bar{C}_e = (C_o - C_e) \cdot \frac{V}{M} \]  \hspace{1cm} (3.2)

\( \bar{C}_e \) is the concentration of the adsorbed cation (mg cation/g soil), \( V \) is the volume of equilibrating solution added to the soil (ml) and \( M \) is the mass of dry soil (g). Plotting \( \bar{C}_e \) vs. \( C_e \) for each concentration of the equilibrating solution gives the adsorption isotherm.

The distribution coefficient \( K_d \) was calculated from

\[ K_d = \frac{\bar{C}_e}{C_e} = \frac{C_o - C_e}{f_s \cdot C_o} \cdot \frac{V}{M} \]  \hspace{1cm} (3.3)

The distribution function can then be obtained by plotting \( K_d \) vs. \( C_e \).

A major source of uncertainty in the calculated results, particularly at low radionuclide concentrations or high \( K_d \) values (low counting rates) is a result of the counting statistics. The only term of
equation 3.3 which includes measured counts is $f_s$, the ratio of the sample counts to the standard (equilibrating solution) counts. Equation 3.3 can be rewritten as

$$K_d = \left( \frac{C_o - C_e}{C_o} \right) \left( \frac{y}{x} \right) \left[ \frac{m - n}{m + n} \sqrt{\frac{(x+b)}{m^2} + \frac{(y+b)}{n^2}} \right]$$

(3.4)

where

$$m = \frac{(x-b) + \sqrt{x+b}}{2}$$

$$n = \frac{(y-b) + \sqrt{y+b}}{2}$$

(3.5)

where $x$ is the recorded number of counts for the equilibrating solution, $y$ is the recorded number of counts for the sample, $b$ is background and thus $m$ and $n$ are the number of counts for the equilibrating solution and sample respectively. It can be seen from equation 3.4 that as the number of sample counts, $m$, becomes small, the uncertainty in the calculated $K_d$ value will become large.

3.5 Results and Discussion - Cesium

3.5.1 Presentation of Results

The results of the distribution coefficient experiments for cesium are tabulated and also presented graphically in Appendix C. The results of the triplicate determinations are given and no spurious data has been removed. The absence of a replicate generally indicates that the sample was lost during the analytical procedure.

The tables on pages C-1 through C-46 are headed by the soil number, the pH at which the determination was made, the background for the counting equipment used for that particular set of measurements and the counting rate (counts/10 minutes) of the equilibrating solutions. The cesium concentration of each equilibrating solution ($N$) is listed and
the corresponding value of:

1) equilibrium sample counting rate (counts/10 minutes)
2) equilibrium concentration in solution (mg/l)
3) amount adsorbed (mg/g of soil)
4) calculated distribution coefficient

The adsorption isotherms are plotted on pages C-47 through C-74 and the distribution coefficients as a function of the equilibrium solution concentration on pages C-75 through C-102.

3.5.2 Assessment of Data Quality and Experimental Variability

The accuracy of the calculated $K_d$ values depends upon the accuracy with which the steps in the analytical procedure can be performed and also, as discussed in Section 3.4.4, the counting statistics. A formal analysis of the variability introduced into the data by the experimental procedures was not performed. Nevertheless, some indication of the experimental precision can be obtained by observing the scatter in the replicates of Appendix C. The best visual impression of this scatter can be obtained from the graphs of distribution coefficient vs. concentration in the equilibrium solution (pages C-75 to C-102).

Generally, the replicate analyses are in very good agreement, with the greatest scatter occurring at low concentrations. Replication was generally the poorest in soils No. 1 and 3. Figure 3.2 shows the data for soil No. 1 and the variability which could be expected from counting statistics alone. The confidence bars represent plus or minus two standard deviations calculated according to equations 3.4 and 3.5. Almost all the data fall within the confidence limits and thus it appears that counting statistics is the greatest single source of
FIG 3.2 EXAMPLES OF UNCERTAINTY INTRODUCED BY COUNTING STATISTICS

DISTRIBUTION FUNCTION

RADIOCATION - CS
SOIL #1
PH = 8.5

± TWO STANDARD DEVIATIONS

DATA POINTS

CONC. IN INITIAL SOLN (mg/l)
scatter in the data.

Other factors which could affect replication include the difficulty of obtaining 1 g samples which are identically representative of the bulk sample, variable times to reach equilibrium (a possible result of sample aggregation), incomplete removal of the suspended material during centrifuging, and the removal of small amounts of sediment when the supernatant was removed from the centrifuge tubes for counting. Occasional samples were observed to contain sediment. The data obtained from these samples is included in Appendix B but was removed from further interpretation. In general, these factors do not appear to have had a major effect on the quality of the data.

Occasional data points show good replication but are inconsistent with the trend of the curves. In soils No. 1 through 7, these data usually appear at all three pH values for a particular soil (e.g. soil No. 4, equilib. solution concentration of approximately 1 mg/l, C81-C84). This trend is consistent with dilution errors since the three pH determinations were generally made by adjusting the pH of the same equilibrating solution. The dilutions were 1:100 which should be quite accurate and thus this explanation is not totally satisfactory. The possibility of the apparent inconsistencies being real cannot be discounted.

In the 1976 progress report, the data for soil No. 7 at pH 8.0 appeared to be inconsistent with the data for that soil determined at the other two pH values. The pH 8.0 determinations were repeated during the past year and gave results which are consistent with the other pH data. The soil No. 7 pH 8.0 data for both 1976 and 1977 are included in Appendix C; however, only the 1977 data will be considered in further
Increasing the concentration of cesium-137 in the equilibrating solutions for soils No. 8 through 16 improved the counting statistics thus reducing the uncertainty in the $K_d$ values. This is reflected in the excellent replication obtained for these soils, as demonstrated in Appendix C.

3.5.3 Discussion of Distribution Functions

*General Characteristics* — For all the soils, the log-log plot of the adsorption isotherm (Appendix C, 49-76) appears linear and to have a slope of unity at low cesium solution concentrations. At higher concentrations, the slope is less than one. This indicates that if plotted with linear axes, the adsorption isotherm would be a straight line at low concentrations and curvilinear at higher concentrations. This would result in constant $K_d$ values or a horizontal linear distribution function at low cesium concentrations, and deviations from the horizontal at higher concentrations. This is generally confirmed by the graphs of distribution coefficient vs. solution concentration (Appendix C, 77-1r3). The distribution functions appear to consist of two straight line segments, the low concentration constant $K_d$ segment, and a high concentration region where, when plotted on the log-log scale, the $K_d$ decreases linearly with increasing equilibrium cesium concentration. It is also interesting that in going from soil to soil, the high concentration lines have similar slopes. The distribution functions of Appendix C are qualitatively similar to those appearing in the literature including the work of Wahlberg and Fishman (1962) and many others.
For the purpose of using $K_d$ numbers in mathematical models for predicting the rate of cation migration, the important features of the distribution function ($K_f$) are the range in solution concentration over which $K_f$ is horizontal ($K_d$ is constant) and the absolute value of $K_d$. Since in all cases, $K_d$ appears to be constant at low solution concentrations, the important parameter with respect to the range in applicability of $K_d$ is the upper limit of the cesium concentration in solution which will yield a constant $K_d$.

For the fifteen soils for which $K_d$ values were determined, $K_d$ varied over almost four orders of magnitude while the limiting solution concentration varied over approximately six orders of magnitude. The remainder of this discussion will be an attempt to relate this variability to the measured properties of the soil samples.

**Relationships Between $K_d$ and Soil Characteristics** - From the discussions of section 2.1, the primary retardation mechanism for cesium is ion exchange. As a result one would anticipate that the $K_d$ would be related to the cation exchange capacity of the soil and other factors which could affect the exchange process such as the concentrations of the competing cations. Since illitic materials have exchange sites which are selective for cesium and potassium, one would further anticipate some relationship between $K_d$ and the amount of illite in the sample and the concentration of potassium in the equilibrating solution.

Table 3.5 shows the cesium distribution coefficient, the cation exchange capacity, total concentration of competing cations in the equilibrating solution and potassium concentration in the equilibrating
<table>
<thead>
<tr>
<th>SOIL NO.</th>
<th>CESIUM K&lt;sub&gt;d&lt;/sub&gt; (ml/g)</th>
<th>CEC (me/100g)</th>
<th>CONC. OF COMPETING CATIONS (me/l)</th>
<th>CONC. OF POTASSIUM (me/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.78 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>8.43</td>
<td>5.47</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>----</td>
<td>8.32</td>
<td>5.85</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>1.84 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>8.62</td>
<td>6.01</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>1.19 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.40</td>
<td>0.96</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>1.81 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>5.90</td>
<td>7.44</td>
<td>0.48</td>
</tr>
<tr>
<td>6</td>
<td>1.37 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.19</td>
<td>2.13</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>7.4 x 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>1.06</td>
<td>4.71</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>1.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.59</td>
<td>0.41</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>2.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>10.25</td>
<td>1.73</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>1.0 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.87</td>
<td>2.54</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
<td>1.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>2.20</td>
<td>2.57</td>
<td>0.03</td>
</tr>
<tr>
<td>12</td>
<td>1.5 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.72</td>
<td>9.96</td>
<td>0.20</td>
</tr>
<tr>
<td>13</td>
<td>5.0 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.37</td>
<td>1.17</td>
<td>0.01</td>
</tr>
<tr>
<td>14</td>
<td>1.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>32.71</td>
<td>29.54</td>
<td>0.39</td>
</tr>
<tr>
<td>15</td>
<td>1.0 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>31.48</td>
<td>36.38</td>
<td>0.39</td>
</tr>
<tr>
<td>16</td>
<td>1.0 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>21.17</td>
<td>5.56</td>
<td>0.21</td>
</tr>
</tbody>
</table>
solution for each soil. The distribution coefficient values in this table were determined by averaging all the distribution coefficient values in the horizontal portion of the distribution functions. Data points which were obviously anomalous were omitted from the averaging process. The \( K_d \) data of Table 3.5 includes only the data determined at the natural pH of the soils. Soil No. 7 was from CRNL and had a \( K_d \) value of 74 ml/g. From a review of previous work and from experimentation, Jackson (1977) reported cesium \( K_d \) values ranging between 80 and 500 ml/g for soils from the same area. Thus, although there is little comparative data, that which is available tends to support the absolute value of the results of this study.

A cursory examination of Table 3.5 gives little reason for optimism regarding the possibility of being able to directly relate \( K_d \) to common soil physical and chemical properties. This is further demonstrated in Figures 3.3 through 3.5.

Figure 3.3 is a graph of the measured \( K_d \) vs. the cation exchange capacity of each soil. Although there is some indication of an increase in \( K_d \) with increasing CEC, there are many exceptions and certainly the trend is not sufficiently distinct to be used as a predictive relationship. Eight of the fifteen tested soils have CEC values of 2 me/100 g or less, but the distribution coefficients for these soils vary from 74 ml/g to 10,000 ml/g. On the other hand, soil No. 16 has a CEC value of 21 me/100 g but a \( K_d \) of only 100 ml/g. Soils 14, 15 and 16 all appear to deviate from the "trend" in that they have relatively low \( K_d \) values considering their high CEC values. The apparently low \( K_d \) values may be the result of these samples having montmorillonite as the principal clay mineral, and the fact that they have relatively high
FIG 3.3 CESIUM $K_d$ vs. CATION EXCHANGE CAPACITY
FIG 3.4 CESIUM $K_d$ vs. TOTAL CONCENTRATION OF COMPETING CATIONS
FIG 3.5 CESIUM $K_d$ vs. POTASSIUM CONCENTRATION IN EQUILIBRATING SOLUTION

CESIUM $K_d$ (ml/g)

POTASSIUM CONCENTRATION (mg/l)
Figure 3.4 is a plot of $K_d$ vs. total concentration of competing cations. On the basis of cation exchange theory, one would anticipate that as the concentration of competing cations increases, the $K_d$ would decrease. There is no evidence of this trend.

Figure 3.5 is a plot of $K_d$ vs. the potassium concentration in the equilibrating solutions. Since potassium is the primary competitor of cesium, particularly for the selective exchange sites of illite, one would anticipate that as the potassium concentration increases, the $K_d$ would decrease. This trend (or any other trend) is not evident in Figure 3.5.

Figures 3.3, 3.4 and 3.5 tend to show similar distributions of the data points. That is, the data point for a particular soil tends to appear in the same region of all three graphs. This may reflect an interdependance of the independant variables (CEC, competing cation concentration and potassium concentration). Soils with high cation exchange capacities tend to have the highest solute concentrations in the soil solution and the highest potassium concentrations. There are of course many other factors which can affect both the total concentration of competing cations and the potassium concentration.

Based upon Figures 3.3, 3.4 and 3.5, the anticipated relationships between $K_d$ and the soil properties do not exist. Further comparisons of the $K_d$ values with the other soil properties of Tables 3.2 and 3.3 such as organic matter content, pH, carbonate content etc. similarly showed no trends. Since the $K_d$ will be the result of the combined effect of several factors, comparisons of $K_d$ with a single factor could be very misleading. In order to avoid possible...
misinterpretations, a multiple regression analysis was performed in which $K_d$ was the dependent variable and CEC, concentration of competing cations, potassium concentration in the equilibrating solution, carbonate content and mineralogy were all treated as independent variables. The results of the analysis lent support to our previous suspicion that there was no significant correlation between $K_d$ and any of the measured soil properties or any interaction of the soil properties.

Considering the wide range of soil materials used in this study, and the inescapable conclusion arrived at in the preceding paragraph, it appears that a generic data base of $K_d$ values for cesium in different soil materials would be of little value. It also appears that the possibility of estimating cesium $K_d$ values on the basis of other commonly measured soil properties is rather remote.

Effect of Natural Cesium - The notable lack of success in relating $K_d$ to what were believed to be the controlling parameters prompted a search for additional factors. From a reasonably thorough review of the literature during this study, as well as the review by Jackson and Grisak (1977) it appears that the effect of natural background cesium in the soil samples has generally been neglected, or has been dismissed as being insignificant. In experiments where the exchanger is saturated with a single cation or some known combination of cations, this is probably a reasonable assumption. In experiments in which natural soils and natural waters are used, the justification for neglecting background concentration effects is not as clear. The cesium occurring naturally in a soil will be partitioned between the solid and solution phases according to the $K_d$ appropriate for the
particular solution concentration. If the amount of cesium added in a $K_d$ determination is significantly less than the amount naturally present, then the total amount present would not be changed significantly and that which is added would be partitioned in the same proportions as that which was initially present. The same would be true of all lower concentrations of added cesium. This would result in constant $K_d$ values over some range of added cesium concentrations with the upper limit of the range being less than that naturally present in the soil.

In order to examine the effects of background cesium on the measured $K_d$ values, soluble cation extracts were taken from each soil according to the method of Appendix B. The extracts were analyzed for cesium by neutron activation methods. The analyses were performed at Chalk River Nuclear Laboratories under the direction of W. F. Merritt. The results of the analyses are given in Table 3.6. With the exception of sample No. 9, which had no detectable cesium, the background cesium concentrations ranged between $5.1 \times 10^{-6}$ and $5.5 \times 10^{-3}$ mg/l.

Additional parameters listed in Table 3.6 which may be relevant to considerations of the background concentration include the total amount of background cesium in a $K_d$ determination (soluble plus adsorbed), equilibrium cesium concentration corresponding to the point at which $K_d$ ceased to be constant, initial cesium concentration corresponding to the point at which $K_d$ ceased to be constant and the amount of cesium added at the point where $K_d$ ceased to be constant.

Direct measurements of the adsorbed background cesium were not made; therefore, this parameter was calculated using the background solution concentrations and the measured $K_d$ values. The cesium concentration in the equilibrium solution at the point where $K_d$ ceased
TABLE 3.6  Cesium distribution and background cesium parameters

<table>
<thead>
<tr>
<th>SOIL NO.</th>
<th>$K_d$</th>
<th>BACKGND Sr CONC.</th>
<th>EQUILIB* Sr CONC.</th>
<th>INITIAL Sr CONC.</th>
<th>TOTAL BACKGND Sr (mg)</th>
<th>Sr ADDED* (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.78 \times 10^4$</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$2.1 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.84 \times 10^4$</td>
<td>$4.6 \times 10^{-5}$</td>
<td>$5 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$8.5 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>$1.19 \times 10^2$</td>
<td>$9.4 \times 10^{-6}$</td>
<td>$1 \times 10^{-2}$</td>
<td>$5 \times 10^{-1}$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>$1.81 \times 10^3$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
<td>$1 \times 10^{-1}$</td>
<td>$1.8 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>$1.37 \times 10^3$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$5 \times 10^{-5}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td>$7.40 \times 10^1$</td>
<td>$5.5 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$4.1 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>7</td>
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<td>$1.3 \times 10^{-5}$</td>
<td>$5 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>8</td>
<td>$2.0 \times 10^4$</td>
<td>N.D.</td>
<td>$5 \times 10^{-3}$</td>
<td>$5 \times 10^{0}$</td>
<td>---</td>
<td>$2.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>9</td>
<td>$1.0 \times 10^3$</td>
<td>$5.9 \times 10^{-6}$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-1}$</td>
<td>$5.9 \times 10^{-6}$</td>
<td>$5.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>10</td>
<td>$1.0 \times 10^4$</td>
<td>$8.5 \times 10^{-6}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$8.5 \times 10^{-5}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>11</td>
<td>$1.2 \times 10^2$</td>
<td>$2.1 \times 10^{-5}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$5 \times 10^{-1}$</td>
<td>$3.1 \times 10^{-6}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>12</td>
<td>$5.0 \times 10^2$</td>
<td>$5.1 \times 10^{-6}$</td>
<td>$5 \times 10^{-5}$</td>
<td>$1 \times 10^{-2}$</td>
<td>$2.6 \times 10^{-6}$</td>
<td>$5.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>13</td>
<td>$1.0 \times 10^4$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>$1 \times 10^{-5}$</td>
<td>$5 \times 10^{-2}$</td>
<td>$1.8 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>14</td>
<td>$1.4 \times 10^5$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-1}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>15</td>
<td>$6.2 \times 10^{-6}$</td>
<td>$5 \times 10^{-3}$</td>
<td>$5 \times 10^{-1}$</td>
<td>$6.2 \times 10^{-7}$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

* Parameters evaluated at the point where $K_d$ became a function of the solution concentration.
to be constant was determined by inspection of the $K_f$ curves of Appendix C. As a result of scatter in the data and the gradual change to the non-constant condition, this parameter generally had an uncertainty of one half order of magnitude associated with it ($\pm (X5)$). The concentration in the initial solution (equilibrating solution prior to addition to the soil) corresponding to the point at which $K_d$ ceased to be constant was determined from graphs of $K_d$ vs. initial concentration. These curves are not included in the report but are similar to the distribution functions of Appendix C. The amount of cesium added at the point of non-constant $K_d$ was determined by multiplying the concentration in the equilibrating solution by the volume added (5 ml).

Comparing columns 3 and 5 of Table 3.6 shows the cesium concentrations in the equilibrating solutions (prior to addition to the soil and corresponding to the point where $K_f$ is no longer horizontal) to be several orders of magnitude greater than the background cesium concentration. This in itself would suggest that the background cesium is not affecting the $K_d$ determination. On the other hand, a comparison of columns 3 and 4 shows that for several soils, the background cesium concentration is approximately one half order of magnitude lower than the equilibrium solution concentration at the point of non-constant $K_f$. This is shown graphically in Appendix C where the arrows on the horizontal axes indicate the background cesium concentration in solution. The exceptions are soils No. 4, 9, 10, 12, 13 and 16. In these soils the background concentrations are approximately two orders of magnitude below the equilibrium concentration. This suggests that for the nine remaining soils, the point at which the distribution function becomes horizontal is controlled by the natural cesium in the soil.
Figure 3.6 is a schematic diagram demonstrating the proposed influence of background cesium on the measured $K_d$ values. Curve I is the distribution function which would be determined for a particular soil in the absence of background cesium. This curve can be explained on the basis of mass action principles. The high concentration portion of the curve shows $K_d$ to be a function of concentration and indicates the region where cesium is significant with respect to the concentration of competing ions. At the low concentration, horizontal portion of curve I, the cesium concentration is insignificant with respect to the competing cations and thus $K_d$ is constant. Curves II and III are measured distribution functions for the same soil but with different amounts of background cesium present. In the high concentration range, the cesium added in the $K_d$ determination is large with respect to the natural cesium. As a result, the three curves are colinear in this region. As the amount of cesium added decreases, that which is present naturally becomes a greater proportion of the total present and causes the actual amount of cesium in solution to be greater than the amount measured experimentally on the basis of the activity in the solution. Since the actual concentrations are higher than the measured values, the $K_d$ values would fall below the values for curve I at the same solution concentration. As the amount of cesium added becomes even less, at some point it will be insignificant with respect to the amount present naturally. Although the experimental procedure will show decreasing solution concentrations, the actual concentration will remain constant and equal to the background concentration. The point at which the measured distribution function departs from the zero background curve will depend upon the concentration of background
NO NATURAL CESIUM PRESENT

NATURAL CESIUM PRESENT ($C_s^{III} > C_s^{II}$)

EQUILIBRIUM SOLUTION CONCENTRATION
(CALCULATED FROM RADIOMETRIC MEASUREMENTS)

FIG 3.6 SCHEMATIC DEMONSTRATING THE EFFECT OF BACKGROUND CESIUM ON MEASURED $K_d$ VALUES
cesium. Thus, for a given soil, the measured $K_d$ (the $K_d$ in the constant $K_f$ range) should also be a function of the background cesium concentration, with the $K_d$ decreasing as the background concentration increases. One might expect the same relationship to hold when comparing different soils provided the high concentration regions of the distribution functions coincided.

Figure 3.7 is a graph of $K_d$ vs. background cesium for the fifteen soils on which cesium $K_d$ values were determined. On initial inspection, and based upon a regression analysis, there is no significant relationship between $K_d$ and the background cesium concentration. As discussed above, if such a relationship does exist we would anticipate that it would apply only to soils in which the background cesium concentration is close to the break in the $K_f$ curve. On this basis, the data for soils No. 4, 9, 10, 12, 13 and 16 should be eliminated from the analysis. The data for soil No. 3 shows considerable variability resulting in uncertainty in the calculated $K_d$ value as well as in the determination of the break in the $K_f$ curve. On this basis it may also be reasonable to eliminate this sample from the analysis. The regression line of Figure 3.7, drawn through the remaining eight data points, has a correlation coefficient of -0.99 indicating a significant correlation between $K_d$ and background cesium concentration. In examining Figure 3.6, the data appears in groups. This would tend to result in a high correlation coefficient even if no relationship existed between the variables. As a result, the apparently high correlation must be treated with a considerable degree of uncertainty. More data would be required in order to test the validity of the regression equation.

The six soils not included in the regression of Figure 3.7
$\log y = -1.17 \log x - 0.154$

$r = -0.99$

**FIG 3.7 CESIUM $K_d$ vs. BACKGROUND CESIUM CONCENTRATION**
have a low natural background cesium concentration as a common characteristic (generally less than $10^{-5}$ mg/l). Based upon Table 3.6 and Figure 3.7, it could be suggested that an alternate method for determining the $K_d$ in a soil or hydrogeologic environment could be the measurement of the background cesium concentration in solution. If this concentration exceeds $10^{-5}$ mg/l, then the $K_d$ could be determined by substituting the concentration into the regression equation of Figure 3.7. Such a procedure would require considerably more testing and documentation before it could be recommended for general use.

The foregoing discussion provides strong evidence that the background cesium concentration has a significant influence on the measured $K_d$ values. The explanation of this phenomenon is probably related to the amount of cesium added in the equilibrating solution relative to the total amount naturally present (adsorbed and in solution), rather than just to the solution concentration as implied in the discussion of Figure 3.6. That is, until the amount of cesium added becomes a significant proportion of the total amount present, the $K_d$ will be constant and will be controlled by the natural cesium in the system. The total background cesium and the amount added at the point where $K_f$ becomes non-linear is given in columns 6 and 7 of Table 3.6. For the soils included in the regression analysis, the amounts of background cesium and added cesium are comparable. Although one would anticipate that the amount added would be less than the total background, the uncertainty in the data is such that this hypothesis cannot be reliably tested. In particular, the uncertainty in determining the point at which $K_f$ becomes non-linear introduces substantial uncertainty. For the six soils not included in the regression, the total background cesium
is substantially less than the amount added at the break in the $K_f$ curve. This provides further evidence that at least for the regressed data, the break in the $K_f$ curve is controlled by the background cesium and that this results in the background cesium having a controlling effect on the $K_d$ of the soil.

It appears that the $K_d$ values of the soils not included in the regression line of Figure 3.7 (No., 3, 4, 9, 10, 12, 13 and 16) are not controlled by the natural cesium concentrations and that this is probably the result of the low cesium concentrations in these soils. As a consequence, we might expect the $K_d$ values for these soils to be controlled by their ion-exchange properties. An examination of Figures 3.3, 3.4 and 3.5 indicated no significant correlation between the $K_d$ values and cation exchange capacity, concentration of competing cations and the soluble potassium concentrations. Thus for soils where the $K_d$ is not controlled by the background cesium, no predictive relationship is apparent.

Effect of pH of the Equilibrating Solution - During the early stages of the study, the effect of pH of the equilibrating solution on the measured $K_d$ values was examined. Three pH values were used, one near the measured pH of the soil and one at one pH unit higher and lower. As a consequence of the buffering capacity of natural soil materials, the pH of the solutions at equilibrium were probably very close to the natural soil pH. Consequently, the effect of this procedure is probably not to change the concentration of hydrogen ions competing for exchange sites, but rather to cause slight changes in the concentrations of the other competing cations.
Figure 3.8 shows the distribution functions for soil No. 1 as determined at three pH values. Changing the pH of the equilibrating solution does not appear to have changed the general shape of the distribution function. On the log-log plot shown here, pH appears to have had only a minor effect on the maximum distribution coefficient. This graph is typical of the results for all soils.

Table 3.7 shows the pH values and corresponding distribution coefficients for each of the first six soils studied. The most striking features of the data are that there is no substantial change in $K_d$ with changes in pH and that there is no consistent trend in the changes in distribution coefficient with changes in pH. A pronounced and consistent pH effect would probably be observed if the pH of the system at equilibrium were altered. In order to achieve this however, would require major alterations in the chemical properties of the soil samples. For example, in the soils containing carbonate, the pH is controlled by carbonate equilibria. In order to significantly change the pH of the soil it would be necessary to remove the carbonate from the soil or to control the partial pressure of CO$_2$ in contact with the soil-solution system. Experimentally, controlling the partial pressure of CO$_2$ would be extremely difficult, while removal of the carbonates would alter the soil to such an extent that the $K_d$ values determined would have little significance with respect to the original soil. In view of the low sensitivity observed, the pH experiments were discontinued after soil No. 7.
Figure 3.8 Graph of the distribution function for soil No. 1 determined at three values of Ph.
Table 3.7 Effect of equilibrating solution pH on cesium distribution coefficients

<table>
<thead>
<tr>
<th>SCIL</th>
<th>pH</th>
<th>KD</th>
<th>LOG(KD)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>6.6</td>
<td>0.671E+05*</td>
<td>4.674</td>
</tr>
<tr>
<td># 1</td>
<td>8.5</td>
<td>0.178E+05</td>
<td>4.223</td>
</tr>
<tr>
<td># 1</td>
<td>9.7</td>
<td>0.678E+05</td>
<td>4.654</td>
</tr>
<tr>
<td># 3</td>
<td>6.8</td>
<td>0.145E+04</td>
<td>3.137</td>
</tr>
<tr>
<td># 3</td>
<td>8.0</td>
<td>0.184E+05</td>
<td>4.242</td>
</tr>
<tr>
<td># 3</td>
<td>9.7</td>
<td>0.131E+05</td>
<td>4.105</td>
</tr>
<tr>
<td># 4</td>
<td>6.5</td>
<td>0.392E+03</td>
<td>2.575</td>
</tr>
<tr>
<td># 4</td>
<td>8.0</td>
<td>0.119E+03</td>
<td>2.064</td>
</tr>
<tr>
<td># 4</td>
<td>9.7</td>
<td>0.911E+02</td>
<td>1.933</td>
</tr>
<tr>
<td># 5</td>
<td>6.3</td>
<td>0.301E+04</td>
<td>3.462</td>
</tr>
<tr>
<td># 5</td>
<td>7.1</td>
<td>0.181E+04</td>
<td>3.239</td>
</tr>
<tr>
<td># 5</td>
<td>7.8</td>
<td>0.264E+04</td>
<td>3.381</td>
</tr>
<tr>
<td># 6</td>
<td>6.8</td>
<td>0.190E+04</td>
<td>3.260</td>
</tr>
<tr>
<td># 6</td>
<td>8.0</td>
<td>0.326E+02</td>
<td>1.488</td>
</tr>
<tr>
<td># 6</td>
<td>9.7</td>
<td>0.137E+04</td>
<td>3.125</td>
</tr>
<tr>
<td># 7</td>
<td>4.8</td>
<td>0.553E+02</td>
<td>1.732</td>
</tr>
<tr>
<td># 7</td>
<td>7.0</td>
<td>0.740E+02</td>
<td>1.863</td>
</tr>
<tr>
<td># 7</td>
<td>10.0</td>
<td>0.622E+02</td>
<td>1.782</td>
</tr>
</tbody>
</table>

* Read as 0.671 x 10^5
3.6 Results and Discussion - Strontium

3.6.1 Presentation of Results

The results of the strontium $K_d$ determinations are given in Appendix D. The tabulated data, pages D-1 through D-15 is presented in the same format as described previously for the cesium data. The adsorption isotherms are presented on pages D-16 through D-30 and the distribution functions on pages D-31 through D-45.

All data points are included in Appendix D. From an examination of the graphs, it can be seen that the replication was extremely good and there are few spurious data points. The fact that the replication for strontium is generally better than for cesium is undoubtedly the result of the lower strontium $K_d$ values resulting in higher counting rates and thus improved counting statistics.

3.6.2 Discussion of Distribution Functions

*General Characteristics* - The general characteristics of the adsorption isotherms and distribution functions for strontium are similar to those of cesium discussed previously. The adsorption isotherms (D16-D30) are linear with a slope of unity at low solution strontium concentrations and show a gradual decrease in slope at higher strontium concentrations. The distribution functions (D31-D45) showed constant $K_d$ values over the lower range of strontium solution concentrations and a declining $K_d$ at the higher concentrations. The change from constant to decreasing $K_d$ was generally more gradual than was observed for the cesium distribution functions. The strontium $K_d$ values generally remained constant to higher solution concentrations than was found for cesium. The $K_d$ value for a particular soil was determined
by averaging all the measured values in the linear portion of the distribution function. The strontium $K_d$ values covered a much narrower range than the cesium values, generally falling within one order of magnitude, 10 to 100. The variation, from soil to soil, of the solution concentration at which the distribution function became non-linear was also much less than observed for cesium ($10^{-5}$ to $10^2$ mg/l for cesium and $5 \times 10^{-2}$ to $10^2$ mg/l for strontium). The strontium $K_d$ for soil No. 7 was 15 ml/g. Jackson (1977) reported values ranging between 5.0 and 50 ml/g for soils from the same area (CRNL). Soils No. 1 and 2 had $K_d$ values of 20 ml/g. Mills and Zwarich (1970) reported values ranging between 3.8 and 11.2 ml/g for soils of similar characteristics which were collected in the same area. Thus, although there are differences, the comparative data lends support to the results of this study.

**Relationship Between $K_d$ and Soil Characteristics** - Unlike cesium, strontium can form precipitates with ions commonly found in groundwater. The most common of these include strontium carbonate (stronianite) and strontium sulphate (celestite). As a consequence, one could anticipate that the $K_d$ would be the result of the combined effects of ion exchange and precipitation processes. In the literature reviewed in section 2.2, it appeared that strontium retardation was treated primarily as an exchange process and there was little quantitative evidence relating strontium $K_d$ values to precipitation processes. Mills and Zwarich (1970) discounted the presence of carbonate as having had an influence on the strontium $K_d$ values which they measured. Based upon the results of the cesium studies, the presence of carbonates may be of greater
importance in acting as a source of background strontium than providing ions with which the added strontium can precipitate (strontianite is commonly co-precipitated with calcite and dolomite). It is apparent that in attempting to explain the $K_d$ data, exchange processes as well as precipitation and background effects will need to be considered.

The strontium distribution coefficient determined for each of the fifteen soils is listed in Table 3.8, along with the exchange properties (cation exchange capacity and total competing cations) of the respective soils. It is apparent from an examination of this table that there is no significant relationship between the $K_d$ values and either the CEC or the competing cations. An example of the variability which cannot be explained on the basis of CEC are soils No. 14, 15, 16. These samples were taken from the same drill hole near Lethbridge Alberta, with No. 16 being taken at the shallowest depth and 14 at the deepest. Other than having been subjected to a greater degree of weathering, soil No. 16 should be similar to 14 and 15. However, No. 16, which has a CEC of approximately 20 me/100 g, has a $K_d$ of 50 ml/g, while soils 14 and 15, which have higher CEC values (approximately 30 me/100g) have substantially lower $K_d$ values (8 ml/g). Similarly, samples 8 and 9 were both collected near North Bay and both have $K_d$ values of 100 ml/g; however, sample 9 has a CEC of 10 me/100 g while sample 8 has a CEC of only 1.59 me/100 g. The lack of correlation between the $K_d$ values and soil exchange properties was confirmed by a regression analysis of the data. A visual comparison of the $K_d$ values with the other chemical properties of Table 3.3 similarly shows no distinct relationships. Soils 8 and 9 are noteworthy in that they have by far the highest $K_d$ values. The most distinctive characteristic of these soils is that they are
Table 3.8 Strontium distribution coefficients (K$_d$) and selected soil parameters

<table>
<thead>
<tr>
<th>SOIL NO.</th>
<th>STRONTIUM $K_d$ (mL/g)</th>
<th>CEC (me/100g)</th>
<th>CONC. OF COMPETING CATIONS (me/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.0 \times 10^1$</td>
<td>8.43</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>$2.0 \times 10^1$</td>
<td>8.32</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>$2.0 \times 10^1$</td>
<td>8.62</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>$2.0 \times 10^1$</td>
<td>1.40</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>$1.0 \times 10^1$</td>
<td>5.90</td>
<td>0.48</td>
</tr>
<tr>
<td>6</td>
<td>$2.5 \times 10^0$</td>
<td>1.19</td>
<td>0.07</td>
</tr>
<tr>
<td>7</td>
<td>$2.0 \times 10^1$</td>
<td>1.06</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>$1.0 \times 10^2$</td>
<td>1.59</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>$1.0 \times 10^2$</td>
<td>10.25</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>$2.5 \times 10^1$</td>
<td>1.87</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
<td>$5.0 \times 10^1$</td>
<td>2.20</td>
<td>0.03</td>
</tr>
<tr>
<td>12</td>
<td>-----</td>
<td>0.72</td>
<td>0.20</td>
</tr>
<tr>
<td>13</td>
<td>$1.0 \times 10^1$</td>
<td>0.37</td>
<td>0.01</td>
</tr>
<tr>
<td>14</td>
<td>$8.0 \times 10^0$</td>
<td>32.71</td>
<td>0.39</td>
</tr>
<tr>
<td>15</td>
<td>$8.0 \times 10^0$</td>
<td>1.48</td>
<td>0.39</td>
</tr>
<tr>
<td>16</td>
<td>$5.0 \times 10^1$</td>
<td>21.17</td>
<td>0.21</td>
</tr>
</tbody>
</table>
It is quite apparent that the strontium $K_d$ values cannot be explained on the basis of soil exchange properties. Having profited from the experience with cesium, the same soil extracts analyzed for cesium by neutron activation, were also analyzed for strontium. The implications of those results are discussed below.

**Strontium Background and Precipitation Effects** - As in the case of cesium, the effect of natural strontium on $K_d$ determinations appears to have been all but neglected. Wahlberg et al. (1965) working with pure clay systems concluded that background strontium would not affect $K_d$ measurements unless the background plus the added strontium exceeded a concentration of 4.4 mg/l. Jackson and Cherry (1974) reported strontium concentrations in the groundwater at CRNL of 0.12 mg/l. From this, as well as other groundwater strontium data, Grisak and Jackson (1977) concluded that background concentrations would generally not be a factor in strontium $K_d$ determinations. The strontium concentrations as determined in the soluble cation extracts are listed in Table 3.9. These concentrations are also indicated by the arrows on the horizontal axes of the distribution functions of Appendix D. It should be noted that the background values are generally one to two orders of magnitude lower than the 4.4 mg/l criterion of Wahlberg et al. (1965). The equilibrium solution concentration of strontium at which the distribution function appeared to become non-linear is also listed in Table 3.9.

Keeping in mind that it is difficult to estimate the location of the break in the $K_f$ curve closer than about one half an order of
<table>
<thead>
<tr>
<th>SOIL NO.</th>
<th>$K_d$ (ml/g)</th>
<th>BACKGND Sr CONC. (mg/l)</th>
<th>EQUILIB* Sr CONC (mg/l)</th>
<th>INITIAL Sr CONC (mg/l)</th>
<th>TOTAL BACKGND Sr (mg)</th>
<th>Sr ADDED* (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.0 \times 10^1$</td>
<td>$1.46 \times 10^{-1}$</td>
<td>$1 \times 10^0$</td>
<td>$5 \times 10^1$</td>
<td>$2.92 \times 10^{-3}$</td>
<td>$2.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>$2.0 \times 10^1$</td>
<td>$1.31 \times 10^{-1}$</td>
<td>$1 \times 10^0$</td>
<td>$5 \times 10^1$</td>
<td>$2.62 \times 10^{-3}$</td>
<td>$2.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>$2.0 \times 10^1$</td>
<td>$1.50 \times 10^{-1}$</td>
<td>$1 \times 10^0$</td>
<td>$5 \times 10^1$</td>
<td>$3.00 \times 10^{-3}$</td>
<td>$2.5 \times 10^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>$2.0 \times 10^1$</td>
<td>$1.63 \times 10^{-2}$</td>
<td>$1 \times 10^0$</td>
<td>$5 \times 10^1$</td>
<td>$3.26 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>5</td>
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<td>$3.33 \times 10^{-1}$</td>
<td>$2 \times 10^2$</td>
<td>$5 \times 10^2$</td>
<td>$3.33 \times 10^{-3}$</td>
<td>$2.5 \times 10^0$</td>
</tr>
<tr>
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<td>$3.20 \times 10^{-2}$</td>
<td>$1 \times 10^1$</td>
<td>$5 \times 10^1$</td>
<td>$8.00 \times 10^{-5}$</td>
<td>$2.5 \times 10^{-1}$</td>
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<td>$5 \times 10^1$</td>
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<td>$1 \times 10^1$</td>
<td>$2.70 \times 10^{-3}$</td>
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</tr>
<tr>
<td>9</td>
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<td>$1 \times 10^{-1}$</td>
<td>$1 \times 10^1$</td>
<td>$2.90 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>10</td>
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<td>$3.30 \times 10^{-2}$</td>
<td>$2 \times 10^0$</td>
<td>$1 \times 10^1$</td>
<td>$8.25 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-2}$</td>
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<tr>
<td>11</td>
<td>$5.0 \times 10^1$</td>
<td>$1.40 \times 10^{-2}$</td>
<td>$1 \times 10^0$</td>
<td>$1 \times 10^1$</td>
<td>$7.00 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>12</td>
<td>$-----$</td>
<td>$3.50 \times 10^0$</td>
<td>$-----$</td>
<td>$-----$</td>
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<td>$3.10 \times 10^{-2}$</td>
<td>$5 \times 10^{-1}$</td>
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<td>$3.10 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-3}$</td>
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<td>$9.30 \times 10^{-1}$</td>
<td>$5 \times 10^1$</td>
<td>$5 \times 10^2$</td>
<td>$7.40 \times 10^{-3}$</td>
<td>$2.5 \times 10^0$</td>
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<tr>
<td>15</td>
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<td>$1.20 \times 10^0$</td>
<td>$5 \times 10^1$</td>
<td>$5 \times 10^2$</td>
<td>$9.60 \times 10^{-3}$</td>
<td>$2.5 \times 10^0$</td>
</tr>
<tr>
<td>16</td>
<td>$5.0 \times 10^1$</td>
<td>$1.41 \times 10^{-1}$</td>
<td>$5 \times 10^0$</td>
<td>$1 \times 10^2$</td>
<td>$7.05 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

* Parameters evaluated at the point where $K_d$ became a function of the solution concentration
magnitude on the equilibrium strontium concentration axis, it appears from Table 3.9 that the background concentration is generally about one order of magnitude lower than the equilibrium strontium concentration at which $K_f$ becomes non-linear. With the exception of soil No. 6, in which the difference was about three orders of magnitude, the difference is surprisingly consistent from soil to soil. This suggests that in the case of strontium, the natural background concentration has a strong influence on the strontium concentration at which $K_f$ becomes non-linear. As in the case of cesium, one might further speculate that the background strontium controls the measured strontium $K_d$ values. Figure 3.9 is a graph of strontium $K_d$ vs. background strontium concentration. The regression line was calculated using all data except soil No. 6. This soil was omitted since the background concentration was well below (three orders of magnitude) the strontium concentration at which $K_f$ became non-linear. The regression line has a correlation coefficient of -0.65 indicating that $K_d$ and the background strontium concentration are not significantly correlated.

We believe that the consistent difference between the background concentrations and the point on the $K_f$ curves at which $K_d$ is no longer constant, is strong evidence that the break in the curve and thus the shape of $K_f$ is influenced by the background strontium. It does not necessarily follow however, that a positive correlation between background strontium and $K_d$ should exist. A positive correlation would be expected if the background strontium in the same soil could be varied, or in different soils if the high concentration regions of the $K_f$ curves tended to be colinear. In effect, the $K_d$ may be the result of a complex interaction of a set of factors of which the background strontium
FIG 3.9 STRONTIUM $K_d$ vs. BACKGROUND STRONTIUM CONCENTRATION
concentration is only one. The effect of uncertainties in the data should also not be neglected. As discussed previously, any parameter determined on the basis of estimating the point at which $K_d$ becomes a function of concentration will have a substantial degree of uncertainty associated with it.

Since the total background strontium in the soils was not measured, it was calculated on the basis of the measured soluble strontium values and the measured $K_d$ values. The results, along with the amount added in the equilibrating solution at the point where $K_f$ becomes non-linear are included in Table 3.9. Generally the amount added at the point where $K_f$ becomes non-linear exceeds the total background strontium by two to three orders of magnitude. This tends to be inconsistent with our previous explanations of background effects. In particular, one would expect $K_d$ to be constant when the amount added was small with respect to the amount of background strontium present, but to become a function of concentration as the amount added became a significant proportion of the total amount present. In the data of Table 3.9 it appears that $K_d$ did not become a function of concentration until the amount added was considerably greater than the amount naturally present. This may again reflect the interaction of several factors of which background strontium is only one. It may also be the result of inaccurate estimates of the total background present. These values were obtained from the background concentration in solution and the measured $K_d$ values. Since strontium can undergo exchange reactions as well as precipitation with carbonate and coprecipitation with calcium carbonate, the concentrations measured in the soluble cation extracts may not be representative of the background concentrations present in the equilibrated $K_d$ solutions. A better assessment of the
effect of background strontium could probably be obtained by measuring
the total amount of strontium in the equilibrated solutions (that
remaining in solution of what was added plus the background strontium
in solution), or by measuring both the soluble and "exchangeable"
strontium naturally present in the soils.

Considering the wide range in soil materials, as well as the
diverse hydrogeologic environments from which they were collected, the
rather narrow range in background strontium concentration was surprising
(1.4 \times 10^{-2} \text{ to } 3.5 \times 10^{0} \text{ mg/l}). It was hypothesized that the narrow
range could be the result of geochemical controls such as precipitation
or co-precipitation on the solution concentration.

Possible Effects of Precipitation and Co-Precipitation - The
equilibrium expression for strontium precipitation can be obtained from
the law of mass action

\[ K_{\text{SrCO}_3} = (\text{Sr}^{2+})(\text{CO}_3^{2-}) \] 3.6

where \( K_{\text{SrCO}_3} \) is the equilibrium constant for the mineral strontianite
and the quantities in brackets are ion activities in solution. In the
chemical analysis of natural waters the pH and concentration of \( \text{HCO}_3^- \)
are normally measured. The activity of \( \text{CO}_3^{2-} \) is obtained from the
equilibrium reaction

\[ K_{\text{HCO}_3} = \frac{(\text{H}^+)(\text{CO}_3^-)}{\text{HCO}_3^-} \] 3.7

which upon substitution into Eq. 3.6 yields

\[ (\text{Sr}^{2+}) = \frac{K_{\text{SrCO}_3}}{K_{\text{HCO}_3}} \frac{(\text{H}^+)}{(\text{HCO}_3^-)} \] 3.8
At 25°C, values for $K_{\text{SrCO}_3}$ and $K_{\text{HCO}_3}$ are $10^{-9.1}$ and $10^{-10.3}$ respectively. Eq. 3.8 becomes

$$\langle \text{Sr}^{2+} \rangle = 10^{+1.2} \frac{(\text{H}^+) / (\text{HCO}_3^-)}{3.9}$$

To obtain an indication of the possibility of Sr$^{2+}$ precipitation in groundwater, values of pH and $\text{HCO}_3^-$ will be considered. In groundwater environments in which significant amounts of calcite or dolomite occur (even a fraction of a percent by weight can be significant), the pH typically ranges from 7 to 8 and the concentration of $\text{HCO}_3^-$ from about 200 mg/l ($3.3 \times 10^{-3}$ m) to 600 mg/l ($9.9 \times 10^{-3}$ m). Considering groundwaters that are non-saline, the difference between concentrations of $\text{HCO}_3^-$ expressed as molality and activity are small. Using the above ranges of pH and $\text{HCO}_3^-$ values in Eq. 4, yields the following range of equilibrium Sr$^{2+}$ activities.

$$\text{Sr}^{2+} \approx 0.01 \times 10^{-3} \text{ m to } 0.5 \times 10^{-3} \text{ m}$$

or as expressed in milligrams per litre,

$$\text{Sr}^{2+} \approx 0.8 \text{ to } 44$$

These calculated equilibrium concentrations are many orders of magnitude larger than the natural Sr$^{2+}$ concentrations detected in the soil-water extract samples of this investigation (Table 3.9). We conclude that under field conditions Sr$^{2+}$ will not be removed from solution by precipitation as strontianite.

Using a somewhat similar approach the potential for strontianite precipitation to cause removal of Sr$^{2+}$ from solution during the $K_d$ experiments described in this study will be evaluated. Of the 15 samples on which $K_d$ tests were conducted, 11 contained significant
amounts of the carbonate minerals, calcite and dolomite. The water that is equilibrated with the samples during the $K_d$ determinations is aerated and therefore is in equilibrium with the atmosphere. Equilibrium calculations indicate that at 25°C water that is equilibrated with atmospheric $CO_2$ (partial pressure of $CO_2$ in the atmosphere = $10^{-3.5}$) is capable, providing that there are no additional sources of $H^+$, of dissolving calcite or dolomite to an equilibrium pH of approximately 8.4 and a $HCO_3^-$ concentration of about 70 mg/l ($1.15 \times 10^{-3}$ m). Substituting these pH and $HCO_3^-$ values in Eq. 3.9 yields an equilibrium $Sr^{2+}$ concentration of 5.3 mg/l. This is an extremely large value in comparison to the concentrations of natural strontium in the soil-water extracts. The pH values of the waters extracted from soil-water pastes of the soil samples containing carbonate minerals were in the range of 7.6 to 8.3 (Table 3.3). These values are significantly lower than the calculated value for conditions of calcite or dolomite equilibrium at atmospheric $CO_2$ partial pressure. This may be due to sluggish dissolution rates that do not yield equilibrium within the time period of the test. If this is the case, the $HCO_3^-$ concentrations in the water would be somewhat lower than the 70 mg/l equilibrium value indicated above. For the measured pH values, $HCO_3^-$ concentrations in the range of about 30 to 65 mg/l would be expected to occur. Substitution of the pH values in the observed range and these $HCO_3^-$ values into Eq. 3.9 yields equilibrium strontium values that are extremely large in comparison to the observed values. Another possible explanation that would account for the observed pH's of the carbonate-mineral rich samples is that additional carbonate-mineral dissolution may have occurred as a result of a release of a
small amount of H$^+$ due to oxidation of sulfide minerals (pyrite or marcasite for example) in the samples. The additional H$^+$ would cause increased HCO$_3^-$ and equilibrium pH values below the calculated value for the atmospheric CO$_2$ equilibrium case. Equilibrium Sr$^{2+}$ would nevertheless be very large relative to the measured values.

The samples that do not have significant carbonate mineral content have pH values for soil-water extracts in the range of 5.0 to 6.5 (table 3.3). HCO$_3^-$ concentrations in these samples are expected to be on the order of $10^{-4}$ m. From Eq. 3.9 it is evident that equilibrium Sr$^{2+}$ values are much larger than those indicated in any of the previous cases.

From this analysis, we conclude that the natural strontium in the soluble cation extract solutions is not controlled by the precipitation of strontianite and thus the uniformity in the concentrations is not the result of strontium precipitation. From this it can further be concluded that with the possible exception of the highest strontium solution concentrations in the equilibrating solutions, the measured $K_d$ values were not affected by the precipitation of strontianite.

Because of its geochemical similarity to calcium, strontium is a common impurity within crystals of calcite and dolomite. As a result, when carbonates are dissolved, the strontium which was co-precipitated with the calcium also goes into solution. Mason (1966) lists 610 ppm as a representative strontium content of carbonate rocks. At this concentration, dissolution of 0.1 millimoles/litre of calcite would release $7.0 \times 10^{-3}$ mg/l of strontium to solution.
In conducting a batch $K_d$ test, addition of the equilibrating solution to the soil sample would be accompanied by dissolution of a small amount of calcite and/or dolomite. Since the solution-soil mixtures are in contact with carbon dioxide in the atmosphere and since the initial equilibrating solutions would have very low carbonate concentrations, it is not unreasonable to expect that dissolution of a few tenths of a millimole of calcite or dolomite per litre of solution would occur. Based on the strontium content of carbonates referred to above, this could result in solution concentrations of strontium on the order of $10^{-2}$ mg/l.

Inspection of Table 3.9 shows the strontium concentration calculated on the basis of calcite dissolution to be similar to the concentrations measured in the soluble cation extracts. It should be noted that in this estimation no allowance was made for removal of carbonate-mineral derived strontium by adsorption.

If the $K_d$ is indeed dependent upon the concentration of natural strontium in the equilibrating solution, and if the concentration in solution is dependent upon mineral dissolution, then there is reason to suspect that conventional laboratory batch $K_d$ values would differ from field values. As a result of elevated carbon dioxide partial pressures in the unsaturated zone, infiltrating water would tend to dissolve more carbonate than would occur under the conditions of the laboratory experiments. As a result, the solution concentrations of strontium would be higher under natural conditions and this in turn could result in a lower effective strontium $K_d$ value than would be determined in the laboratory. It must be recognized however, that the effects of different amounts of carbonate dissolution on $K_d$ could be masked by cation exchange.
processes, particularly in soils with high cation exchange capacities. Further experimentation is required to determine the importance of these processes.

3.7 Implications of the Batch $K_d$ Experiments

The distribution functions for both cesium and strontium had forms typical of those appearing in the literature. For pure clay systems and simple solution chemistries, the shapes have generally been explained by invoking the laws of mass action (Wahlberg et al., 1965, and Wahlberg and Fishmar, 1962). In this study both the exchanger properties and solution properties were much too complex for an application of mass action principals to be practical or meaningful. Nevertheless, trends which would be qualitatively compatible with mass action were anticipated. The poor correlation between the $K_d$ values and the exchange properties of the soils indicates that mass action is of little value either in predicting $K_d$ values or interpreting measured values in natural soil systems.

Based upon the evidence of the previous sections, it appears that background concentrations are probably the single most important factor in determining $K_d$ values for both cesium and strontium. This observation is particularly significant since it appears that in the past, background effects have generally been neglected in determining $K_d$ values in natural soil materials.

With respect to the objectives of this study, if the background concentration of the particular cation of interest is indeed the controlling parameter on $K_d$, then the development of a generic data base for estimating $K_d$ numbers does not appear to be a practical pursuit. In
addition it does not appear that $K_d$ values can be estimated from correlations with readily available soil parameter data. Although the regression equation given in Figure 3.7 suggests that $K_d$ could be determined from the measured background cesium in solution, the method would require that the cesium concentration in the groundwater be measured, and the result would be subject to a significant element of uncertainty. With little more effort, the $K_d$ for the soil could be measured directly.

The methods used for measuring $K_d$ should consider the possible effects of background concentrations of the cation being studied. In particular, it is important that the measurements be made at the natural background solution concentration. This will be discussed further in Chapter 4. In column methods, where the equilibrating solution is continuously leached through the column, unless the concentration in the influent is equal to the natural concentration, the background will change with time and will result in a measured $K_d$ value which is not representative of the natural condition.

The consequences of the measured $K_d$ values with respect to predictions of contaminant migration rate are considered in some detail in Reynolds et al. (1981). At this point however, it may be of value to show quantitatively, the significance of the absolute values and variability in the measured distribution coefficients. This discussion will be based on equation 1.19 of Chapter 1 which was given as

$$\frac{\bar{V}_f}{\bar{V}} = \frac{1}{1 + (\rho/n) K_d} \quad 3.10$$
where \( \bar{V}_i \) is the velocity of the solute species, \( \bar{V} \) is the average linear groundwater velocity, \( \rho \) is the bulk density and \( n \) porosity. In unfractured quaternary materials \( \rho \) and \( n \) generally vary over fairly narrow limits and a typical value for the ratio of \( \rho/n \) would be 5.0. In addition, \( K_d \) values for cesium and strontium, (at least those of this study) are considerably larger than one. As a result 3.1 can be simplified to

\[
\frac{\bar{V}'}{\bar{V}} = \frac{1}{5 K_d}
\]

Cesium \( K_d \) values ranged from approximately \( 10^2 \) to \( 10^4 \) ml/g. As a result, the velocity of cesium in groundwater could vary from approximately \( 2.0 \times 10^{-3} \) to \( 2.0 \times 10^{-5} \) times that of the groundwater. It is particularly noteworthy that large \( K_d \) values are not necessarily associated with fine textured materials and thus some granular geologic materials could provide a high degree of chemical retardation. Typical groundwater velocities for sand and clay could be on the order of \( 1.0 \times 10^2 \) and \( 1.0 \times 10^{-3} \) m/year. Based on these figures, the maximum migration rate in a sandy material would be \( 2.0 \times 10^{-1} \) m/year and \( 2.0 \times 10^{-6} \) m/year in a clayey material. On the other hand, the minimum migration rate in a sand would be \( 2.0 \times 10^{-3} \) m/year and in clay, \( 2.0 \times 10^{-8} \) m/year. As a result of the physical flow parameters, the migration rates in clay were always lower than in sands. Nevertheless, sand with a high \( K_d \) value can exhibit extremely low rates of cation migration (2 mm/year for cesium).
Strontium $K_d$ values are similar to those of cesium in that there can be considerable variability within the same textural class. As a result, the retardation of strontium in clayey materials is not necessarily greater than in sandy materials. However, as in the case of cesium, the strontium migration rate in clays would generally be considerably less than in sandy materials. The most significant difference between cesium and strontium is that the $K_d$ of strontium is about one to two orders of magnitude below that of cesium. As a result, strontium would tend to move through geologic materials at a rate of about ten to one hundred times that of cesium.
4. EFFECTS OF SAMPLING AND HANDLING PROCEDURES ON MEASURED $K_d$ VALUES

4.1 Introduction

In the evaluation of a specific waste management area, one would expect insitu $K_d$ determinations to be the most reliable for estimating potential contaminant migration rates. At the present time there is no established methodology for performing such tests; nevertheless, it seems certain that such tests would be time consuming and expensive. On the other hand, the methods used in Chapter 3 require a minimum of specialized equipment and are relatively fast and inexpensive. However, the geochemical conditions during these tests may be substantially different from the insitu conditions.

Differences could arise because:

1) The concentration of Cs$^+$ added in the test solutions may be significantly different from the natural Cs$^+$ concentrations in the insitu groundwater, thereby causing the measured $K_d$ values to be different from the effective insitu values.

2) The major-ion chemistry of the equilibrating solution is different from the natural groundwater. Although an effort was made to have similar major-cation concentrations, the initial anion concentrations are quite different. This may have significance because of the possible effects of dissolution of carbonate minerals.

3) Exposure of the sample to the atmosphere could result in the oxidation of minerals thus altering the chemical characteristics of the solution and of the solids.
4) Drying the sample may irreversibly alter the degree of hydration of certain clay minerals and other colloidal materials and may cause precipitate coatings to form on clays and other particles. These coatings may not be entirely redissolved when the sample is immersed in the test solutions.

5) The process of sieving and shaking may physically alter the sample, increasing the proportion of fines and thus the area available for adsorption.

6) The solution to solid ratio is much greater than under insitu conditions.

As indicated in Chapter 3, the first two factors listed above have been identified as having potential to exert a significant influence on observed $K_d$ values from batch tests. Of the remaining four factors, exposure of the sample to oxygen appeared to be one that would be particularly difficult to avoid in routine measurement procedures and yet would be a factor that could have a substantial effect on the measured $K_d$ value. In this section of the study, the effect of sample oxidation was examined by conducting batch $K_d$ tests in the conventional manner and in a manner in which exposure to the atmosphere was prevented. These experiments represent only a preliminary evaluation of the effects of sample exposure to the atmosphere. It is reasonable to expect that the importance of sample exposure may vary depending on the nature of the geologic material and its associated groundwater. To provide an outlook on this topic that is more general than the specific experiments that were conducted, the experimental work is preceded by a brief review
of some of the geochemical consequences that could arise as a result of exposure of soil samples and groundwater to atmospheric oxygen. The final section of this chapter concerns the effect of solution to solid ratio on $K_d$ values determined by batch procedures.

4.2 Effect of Sample Oxidation on Measured $K_d$ Values

4.2.1 Potential Consequences of Oxidation Processes

Exposure of samples to oxygen has potential to cause creation of new solid phases in the sample. This may either increase or decrease the ability of the solid material to adsorb radionuclides. Of particular concern in this regard is the potential for precipitation of oxyhydroxides of iron and manganese from the original pore solutions. Precipitation would be enhanced by sample drying.

The presence of oxygen may also cause significant changes as a result of oxidation of sulfide minerals such as FeS$_2$ (pyrite or marcasite). This oxidation would provide iron to solution which could produce additional amounts of oxyhydroxide precipitates. Sulfide mineral oxidation also releases $H^+$ to solution. This would change the chemistry of the pore solution as a result of mineral-water interactions arising because of $H^+$ production. If the samples contain carbonate minerals such as calcite or dolomite $H^+$ production could cause dissolution release of impurities such as Mn, Fe, Cs, and Sr in addition to the major dissolution products, Ca, Mg, and $HCO_3^-$. Small amounts of disseminated sulfide mineral matter is a common component of glacial deposits. The oxidative release of $H^+$ is therefore not an unlikely process to occur upon exposure of samples to atmospheric oxygen.
In this discussion attention will be focused on cesium. Figures 4.1 and 4.2 show the stability fields for Fe\(^{2+}\) and Mn\(^{2+}\) and their main solid phases displayed as a function of Eh and pH. The Eh-pH domain typical of shallow groundwater is also indicated on the diagrams. These figures indicate that over a major part of the Eh-pH domain of shallow groundwater the stable species of iron and manganese are Fe\(^{2+}\) and Mn\(^{2+}\) which, depending on Eh and pH conditions can occur at concentration levels that are considerable. If groundwaters in this Eh-pH domain are exposed to the atmosphere, Fe\(^{3+}\) and Mn\(^{3+}\) become the stable ionic species. Precipitation of Fe(OH)\(_3\) and MnO\(_2\) (known as oxyhydroxides) occurs because of the extremely low solubility of these solid phases. These solid phases created upon exposure to the atmosphere can form colloidal precipitate coatings on the original particles that comprise the soil sample.

Information on the Cs exchange capacity of iron oxyhydroxides which is summarized in Table 4.1, indicates that this substance has only a very weak capability for Cs adsorption. This suggests the possibility that rather than cause an increase in cesium adsorption, iron oxyhydroxide precipitates may cause a decrease. Oxide coatings would in some cases tend to accumulate on the charged surfaces of clay minerals, thereby obliterating much of the selectivity of these surfaces for cesium. As indicated in section 2.1, cesium adsorption on micas and illites occurs selectively at charged sites on weathered edges. Adsorption of iron oxyhydroxide on these edges may significantly reduce cesium selectivity. Greenland (1971) reports that in kaolinites, edge rather than basal surfaces are generally the preferred location for attachment of oxide coatings.
TABLE 4.1
CESIUM EXCHANGE CAPACITY OF IRON OXIDES (me/100g)

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>CESIUM EXCHANGE CAPACITY</th>
<th>EXPERIMENTAL CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kourim and Kritl (1958)</td>
<td>0.4</td>
<td>retention by occlusion adsorption or chemisorption at pH 8-9</td>
</tr>
<tr>
<td>Glazman, Straghesko and Bisikalova (1958)</td>
<td>&lt;0.05</td>
<td>adsorption of Cs⁺ in the coagulation of positive sol of Fe(OH)₃ by CsCl</td>
</tr>
<tr>
<td>Pushkarev (1956)</td>
<td>not detectable</td>
<td>adsorption of ¹³⁷Cs by Fe(OH)₃ studied by addition of isotope (1) before, (2) during and (3) following precipitation of oxide</td>
</tr>
</tbody>
</table>
Eh-pH DIAGRAM OF IRON & OXYGEN COMPOUNDS
(AFTER HEM)

NOTE: SHADED AREA INDICATES COMMON GROUNDWATER CONDITIONS

FIG 4.1
Eh-pH DIAGRAM OF MANGANESE & OXYGEN COMPOUNDS
AFTER CRERAR & BARNES

NOTE: SHADIED AREA INDICATES COMMON GROUNDWATER CONDITIONS

FIG 4.2
In our review of the literature no information was obtained on the Cs adsorption capacity of manganese oxides. By analogy with the alkali earth metals (see table 4.2) there is reason to expect that this oxide has a reasonably large cesium adsorption capacity. As aqueous colloids manganese oxides have large specific surface areas. Values in the range of 100 to 300 m²/g have been reported by Murray (1974) and Loganatham and Burau (1973). The zero point of charge for fresh manganese oxide precipitates is very low, which is further indication that under the pH conditions typical of groundwater or of Kₐ test conditions, the exchange capacity for cations is large.

In summary it can be stated that at least in theory, the processes of oxidation of soil samples has potential (1) to cause changes in the nature of mineral surface as a result of formation of oxide coatings and (2) to cause changes in the chemistry of the pore solution as a result of reactions initiated by release of hydrogen ions by oxidation of sulfide minerals. In order to obtain an indication of whether or not these and possibly other oxidation process do in fact exert a significant effect on batch-type Kₐ measurements, a series of experiments were conducted. These experiments are described below. A brief description of the results is presented in section 4.4. For a more detailed interpretation the reader is referred to Kewen (1978).

4.2.2 Experimental Methods

Field procedures—Field samples were taken from four locations where the hydrogeology and hydrochemistry had already been investigated by others.
### TABLE 4.2

**ADSORPTION CAPACITY OF SOME ALKALI EARTH METALS ON MANGANESE OXIDE**  
(me/100g)

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH 4</th>
<th>pH 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>182¹</td>
<td>260²</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td>200²</td>
</tr>
</tbody>
</table>

¹ Loganatham and Burau (1972)  
sorption from Langmuir isotherm

² Posselt, Anderson, Weber (1968)  
sorption from Langmuir isotherm
The locations include the Perch Lake Basin near Chalk River, Ontario; the Bruce Nuclear Power Development near Port Elgin, Ontario; the Whiteshell Nuclear Research Establishment near Pinawa, Manitoba and the Canadian Forces Base, Borden, Ontario. The samples were collected at the same locations as samples No. 7, 12, 3 and 13 of Chapter 3 of this report. The locations are shown in the maps of Appendix A. The first three areas are of particular interest because radioactive materials are presently being deposited at these sites.

At the Chalk River location, a plume of groundwater contaminated with cesium-137 is moving away from a disposal area where waste was emplaced over 20 years ago. Soil samples were taken adjacent to these disposal areas. The location of sample sites, depth from which the samples were taken, sampling methods, hydrogeology of the sites and other sampling information is summarized in Table 4.3.

At Base Borden and Chalk River, the deposits consisted of medium to fine sands. Cores from below the water table at depths of about 3 m below ground surface and 10 m respectively were taken with Shelby tubes. After sampling, the cores were sealed in the tubes with wax and tape to prevent drainage and the entrance of air. Two cores of stiff stony till were taken at the Bruce site. Core number one, from a depth of 8.2 m (Table 4.3) was a Shelby tube sample; core number two was a split spoon sample taken from a depth of about 10 m (see Appendix A for locations). In the latter case, the core was removed from the sampler and immediately covered with several layers of wax. All the cores were sealed and stored at reduced temperature to allow as little chemical disturbance of the cores as possible. The Whiteshell till sample was dug with a shovel from
## TABLE 4.3

SUMMARY OF INFORMATION REGARDING SAMPLE COLLECTION

<table>
<thead>
<tr>
<th>Site</th>
<th>Exact Core Location</th>
<th>Depth of Core Below Ground</th>
<th>Depth of Core Below Water Table</th>
<th>Type of Deposit</th>
<th>Sampling Method</th>
<th>Method of Sample Preservation</th>
<th>Specific Site Hydrogeologic Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perch Lake Basin, Chalk River, Ont.</td>
<td>100 m south of position of Cs plume front (Feb. 75) as in Fig. 4, Jackson et al. (1977); at intersection of the roads leading to the main meteorological station &amp; &quot;A&quot; disposal area.</td>
<td>9.25-10. m</td>
<td>2.9-3.6 m</td>
<td>coarse grained silicate minerals sands, glacial outwash</td>
<td>Modified Bishop sampler (Parsons sampler) with inner plastic sample tube forced into sand; good recovery</td>
<td>Wooden plug forced into plastic tube to exclude air; ends of tube then sealed with plastic caps and taped</td>
<td>Cher. et al. (1975) Jackson et al. (1977)</td>
</tr>
<tr>
<td>Bruce Nuclear Power Dev, Port Elgin Ont.</td>
<td>core #1: along northeastern edge of the main low level waste disposal area.</td>
<td>8.2-8.3 m</td>
<td></td>
<td>silty clay till with stones</td>
<td>uncoated Shelby tube forced into till; poor recovery</td>
<td>sample left in tube; wax coatings on ends of core</td>
<td>Rehm et al. (1977)</td>
</tr>
<tr>
<td></td>
<td>core #2: at southwestern edge of disposal area at piezometer installation WN-D-34 (Rehm et al, 1977)</td>
<td>8.2-8.3 m</td>
<td></td>
<td>silty clay till with stones</td>
<td>uncoated split spoon sampler forced into till; good recovery</td>
<td>till removed from sampler; till covered with several layers of wax</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Exact Core Location</th>
<th>Depth of Core Below Ground</th>
<th>Depth of Core Below Water Table</th>
<th>Type of Deposit</th>
<th>Sampling Method</th>
<th>Method of Sample Preservation</th>
<th>Specific Site Hydrogeologic Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whiteshell Nuclear Res. Establ. Pinawa, Man.</td>
<td>approx. 25 m northwest of piezometer nest 7 as in Fig. 1, Grisak &amp; Cherry (1973); this site is about 100 m due west of the edge of the waste management area.</td>
<td>4.5 m</td>
<td>clay loam till unit</td>
<td>blocks of till dug with shovel from face of a fresh excavation</td>
<td>blocks packaged in plastic</td>
<td>Cherry et al (1973) Grisak &amp; Cherry (1975)</td>
<td></td>
</tr>
<tr>
<td>Canadian Forces Base, Borden, Ont.</td>
<td>northwestern edge of a good pit immediately southeast of the intersection of Dieppe and Batoche Roads.</td>
<td>3.0-3.3 m 2.0-2.3 m</td>
<td>coarse grained silicate mineral sands of fluvioglacial outwash</td>
<td>exopylined Shelby tube forced into sand; moderately good recovery</td>
<td>sample left in tube; wax coating on ends of core</td>
<td>Gartner Lee Assoc. Ltd. (1977)</td>
<td></td>
</tr>
</tbody>
</table>
a fresh excavation and stored in plastic (see Appendix A for sampling location). No precautions were taken to prevent this sample from drying out or to prevent exposure to the atmosphere.

At each of the first three sites, piezometers were installed in the same holes from which the cores were taken. Samples of ground-water to be used in the batch tests were collected from these piezometers at later dates. The permeability of the sands at the Base Borden and Chalk River sites was high enough to allow samples to be collected by pumping water through a peristaltic pump directly into plastic bottles which had been flushed with nitrogen beforehand. This was not possible at the Bruce site due to the water-level depth in the piezometer. In this case, water could not be brought to the surface by suction. Therefore, as much water as possible was drawn by vacuum into the tubing. The tubing was clamped to prevent drainage and brought to the surface where the water was drained into plastic sample bottles.

Field determinations of pH and alkalinity were carried out at the Borden and Chalk River sites but only pH was determined at the Bruce site. pH measurements were done using a Radiometer pH meter and a combination electrode placed in a sample beaker open to the atmosphere. Alkalinity titrations were done using 50 ml water samples titrated to an end point of pH 4.2 with 0.0223 N-HCl.

Water samples were taken for major cation and total iron and manganese analysis. Samples for iron and manganese were acidified in the field and all samples were cooled during the transportation and storage. Samples for cation analysis were filtered in the lab. Analyses were by atomic absorption spectrophotometry using a Perkin Elmer spectrophotometer, model 305.
Laboratory Procedures—Soil samples were characterized with respect to particle size distribution, soil pH, cation exchange capacity, mineralogy, carbonate content, organic matter content and soluble cation concentrations. Standard methods of soils analysis were used as described in Appendix B.

The method of batch $K_d$ determination used in this study consisted of adding a known amount of cesium to the water sample, bringing 5ml of this solution to equilibrium with 1 g of dry soil and then determining the distribution of cesium between the soil and water. This procedure is described in section 3.4 of this report. For the tests on the samples from the Chalk River, Borden, and Bruce No. 1 sites, water collected from the piezometers was used. For the tests on the Whiteshell and Bruce No. 2 samples and for other tests on the Chalk River sample and on the Bruce No. 1 sample, de-aerated simulated groundwater was used. This water consisted of distilled water to which cations as chloride salt were added to attain concentrations equal to those determined in the soluble cation extractions. The solution was de-oxygenated by bubbling nitrogen through it.

Since it was of interest to determine $K_d$'s over a wide range of initial cesium concentrations, a serial dilution method was used to provide concentrations for $10^{-1}$ M to $10^{-9}$ M.

Batch tests were performed in the inert atmosphere of a glove box using unoxidized field cores of soil and unoxidized groundwater. These same materials were then used in conventional batch tests in the laboratory atmosphere following air drying of the soil samples. Experimental conditions were the same in each case except for the presence of oxygen in the latter. In later experiments, tests were done in both types
of atmosphere using air dried materials and water with the composition of a soil water determined by the soluble cation extraction method.

These tests were performed to investigate the possibility of manganese release from the soil samples due to dissolution during the batch tests.

The batch procedure described in section 3.4 was used in the performance of all tests. When the procedure was used in the glove box, an inert atmosphere was maintained in the sample test tubes by sealing them before their removal from the glove box for shaking.

The glove box was a rectangular box (90 cm wide x 60 cm high x 50 cm deep) made of 1 cm thick plexiglass. An entry door on one end was used to place samples and equipment into the box. Arm length, 0.04 cm thick neoprene gloves fitted around two 19 cm diameter ports on the front face allowed handling of items inside the box.

When a series of batch tests were to be performed, the box was sealed and the atmosphere inside was purged of oxygen before samples were handled. The purification was accomplished by continuous dilution with oxygen free nitrogen. In this regard, three important operational features of the box are of interest: (1) manner of oxygen removal in the incoming nitrogen stream, (2) the direction of gas flow to achieve purging and (3) the determination of oxygen concentrations in the box.

The nitrogen was purified through the use of a self regenerating gas scrubber shown in Figure 4.3. Nitrogen entering the scrubber lifts bubbles of chromous solution through the small diameter tube to the top of the glassware. In so doing, any oxygen present is consumed through oxidation of chromous ions to chromic. After the gas and solution percolate down through a column of zinc pellets, the gas exits while the solution returns to the reservoir. During percolation through
SCHEMATIC OF OXYGEN SCRUBBER

FIG 4.3
the zinc, any chromic ions are reduced through a transfer of electrons to zinc and thus the effectiveness of the scrubbing solution is maintained. The nitrogen flow rate was between 1.5 and 2.0 L/min.

The direction of gas flow in the box is shown in Figure 4.4. Nitrogen entered the box along the upper edge of the back face and was distributed evenly along the length through a series of widely spaced holes in the inlet tube. A similar tube, placed along the bottom edge of the front face, was used to collect gas leaving the box. The advantage of this arrangement was that because nitrogen is lighter than oxygen, the heavier oxygen would be flushed toward the exit.

Before leaving the box, gas was forced to bubble through a water trap. The main purpose of the trap was to eliminate the possibility of oxygen entering the box through the exit. The most serious situation in which this might occur would be a reversal of gas flow caused by suddenly enlarging the volume of the box when the gloves extending into the box are withdrawn. A second purpose was to maintain a higher than atmospheric pressure within the box to prevent oxygen entering the box through undetected leaks.

Using a diffusion coefficient of $4 \times 10^{-10}$ cm$^2$/sec for oxygen diffusion through neoprene, (Shriver 1969, p. 231), it was determined that such diffusion would not increase the oxygen level in the box by more than 1 ppm in a 24 hr. period.

A final step to prevent oxygen contamination was to purge all glassware with 10 volume changes of nitrogen and then re-seal immediately following the beginning of the atmospheric flushing.

If it is assumed that the incoming nitrogen mixes perfectly
GAS FLOW WITHIN GLOVE BOX
FIG 4.4
with the air inside the glove box, then the fraction \( f \) of the original atmosphere present at any time is given by

\[
f = e^{-n}
\]

where \( n \) is the number of times that a volume of nitrogen equal to the volume of the box has entered (Shriver, 1969).

A working atmosphere containing less than 10 ppm oxygen was considered low enough to prevent oxidation of materials. To achieve this, a minimum of 10 volume turnovers was required; in practice, a 24 hour period at a nitrogen flow rate of 1/5 l/min (9.8 volumes).

The pH, Ca and \( \text{HCO}_3 \) levels of the batch test water were measured following equilibration. In all experiments with soils containing carbonate minerals, alkalinities were determined on the portions of water that were used for gamma counting in the \( K_d \) determinations. Bicarbonate concentrations were calculated from titrations to an end point of pH 4.2 with 0.00223 M HCl.

For the experiments using the Borden sample, five 50 ml centrifuge tubes were filled with 40 ml of water in the glove box. In four tubes, the water contained tracer and stable cesium at \( 10^{-5} \) M. In the remaining one, the water contained no tracer. Eight gram portions of soil taken from the unoxidized soil sample were added to each of the five tubes. The tubes were sealed before removal from the box and shaken. At equilibrium, the water was tested for iron levels in two tubes and manganese levels in two tubes. In the fifth tube, the water (without tracer) was analysed for calcium by atomic absorption spectrophotometry. This procedure was also followed in analyzing the
water from five similar batch tests on the Borden sand using air dried soil sample.

The iron and manganese concentrations were determined colorimetrically using bathophenanthroline as the colored iron complex (Golterman, 1969) and formaldehyde oxime as the coloured manganese complex (Morgan and Stumm, 1965). Absorbance readings were taken using a Beckman DU spectrophotometer. One of the attractive features of this type of analysis was the containment of the radioactivity in the samples and the excellent sensitivity. However, the analyses required at least 20 ml of water to achieve adequate precision at the low concentrations.

In later work on Chalk River and Whiteshell samples, iron and manganese concentrations were determined by atomic absorption spectrophotometry on tracerless samples. With these samples, a soil to water ratio of 1 g to 5 ml was used. Analyses were done at cesium concentrations of $10^{-1}$M, $10^{-3}$M, $10^{-5}$M, $10^{-7}$M and $10^{-9}$M. Following equilibrium, 1 ml of water was withdrawn, diluted ten times and analyzed for calcium. The remaining 4 ml of water were used for analyses of iron (Chalk River) and manganese (Whiteshell and Bruce core #2). Analyses by atomic absorption proved to be much less sensitive then by colorimetric methods in the range of concentrations encountered.

The manganese content of carbonate in each sample was determined by following the process of slow dissolution and relating manganese and carbonate concentrations with time. A series of 1 g samples were dissolved in 5 ml of 0.15 M HCl with gentle shaking, and at various intervals the solutions were sampled after centrifuging at 3,000 rpm for 2 minutes. Manganese and calcium concentrations were determined
using atomic absorption spectrophotometry.

The use of a reducing agent such as hydroxylamine hydrochloride may have promoted more efficient extraction of manganese but was not used since we wished to confine manganese release to carbonates only. It is assumed that the majority of dissolution was calcite rather than dolomite due to the much greater dissolution rate of calcite in mild acid solution.

The role of sulphide oxidation in promotion of carbonate dissolution was investigated in solutions that were equilibrated with each of the carbonate rich samples. The presence of sulfate produced from sulphide oxidation was tested by using a turbidimetric method (Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 13th Edition, p. 334-335). A Pye Unicam SP6-500 UV spectrophotometer was used in the procedure.

4.2.3 Experimental Results and Discussion

i) Sample Characterization

A summary of the characteristics of the five soils used in this study is presented in Table 4.4. Some of the important features are as follows. The Bruce till is a fine textured, dolomitic, quartz rich material with the dominant clay mineral being illite. The Whiteshell till is also fine grained with a high proportion of mixed layer clay minerals and calcite and dolomite. This till has the highest exchange capacity (8.62 me /100 g ) of the five materials. The Borden and Chalk River sands are coarse silicate mineral mixtures. The Borden sample had a carbonate content of 11.1% while the Chalk River sand had no
<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Texture</th>
<th>Mineralogical Composition</th>
<th>Carbonate Content</th>
<th>Organic Matter Content</th>
<th>Cation Exchange Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bulk Sample</td>
<td>Clay Sized Fraction</td>
<td>% Total</td>
<td>% Calcite</td>
</tr>
<tr>
<td>Perch Lake</td>
<td>96% sand</td>
<td>65% quartz</td>
<td>mica = chlorite(^1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Basin,</td>
<td>4% silt</td>
<td>20% feldspar, garnet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalk River</td>
<td>clay</td>
<td>10% biotite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% hornblende</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whiteshell Nuclear</td>
<td>34% sand</td>
<td>55% quartz</td>
<td>mixed layer(&gt;) illite(\rangle)</td>
<td>34.1</td>
<td>19.3</td>
</tr>
<tr>
<td>Research Establ.</td>
<td>35% silt</td>
<td>35% carbonates</td>
<td>illite(\rangle) kaolinite(^2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31% clay</td>
<td>15% feldspar</td>
<td>trace biotite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>trace hornblende</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bruce Nuclear Power</td>
<td>52% sand</td>
<td>45% carbonates</td>
<td>kaolinite(\rangle) illite(\rangle) montmorillonite</td>
<td>43.4</td>
<td>12.8</td>
</tr>
<tr>
<td>Develop. (No. 1)</td>
<td>39% silt</td>
<td>40% quartz</td>
<td>montmorillonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9% clay</td>
<td>12% feldspar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3% carbonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>rx chips</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>trace hornblende</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canadian Forces Base</td>
<td>96% sand</td>
<td>55% quartz</td>
<td>n.d.</td>
<td>11.1</td>
<td>6.7</td>
</tr>
<tr>
<td>Borden</td>
<td>2% silt</td>
<td>35% feldspar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2% clay</td>
<td>10% carbonates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% hornblende</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)from Jackson et al (1977)
\(^2\)Mills and Zwaich (1970) also found mixed layer minerals predominant in samples from this area. Montmorillonite was considered as a component of this group.
detectable amount as determined by the Chittick method of analysis, and by a distilled water immersion test. Upon immersion in distilled water, the pH of the water did not rise with time but remained constant at pH 5.7. This confirmed that no carbonate-mineral matter was present.

The chemistry of the groundwater samples and the soluble cation extractions are presented in Tables 4.5 and 4.6. The low cation concentrations of dissolved cations of the Chalk River soil extract are almost identical to those of the groundwater sample. The calcium, magnesium and bicarbonate levels of the Whiteshell soil extract are significantly lower than field values likely because the extract was equilibrated with the atmosphere rather than a higher p CO₂ which would be typical of the insitu conditions.

ii) Comparison of Results From Conventional Batch Tests and Glove-Box Tests

The results of K_d tests using the conventional batch and the glove-box tests are displayed in Figures 4.5, 4.6, 4.7, 4.8, and 4.9 which show K_d values versus initial concentration of added cesium. Nearly all of the tests were conducted in duplicate or triplicate. Except for the Chalk River sand, all of the graphical plots show larger K_d's at lower initial Cs concentrations in the test solution. The most pronounced range of values was obtained for the Whiteshell till, with K_d's ranging from less than 1 ml/g at initial cesium values on the order of 0.1 M to values greater than 10,000 ml/g at initial cesium values on the order of 10⁻⁹ M. The least variation is displayed by the
Table 4.5
Chemistry of the Groundwater Samples From Piezometers At or Near the Sample Sites
(all values in mg/l)

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Field pH</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perch Lake Basin, Chalk River</td>
<td>7.7</td>
<td>10.3</td>
<td>3.8</td>
<td>4.5</td>
<td>1.7</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>7.7</td>
<td>.2</td>
</tr>
<tr>
<td>Whiteshell Nuclear Res. Establishment¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-7 11.3 (deep)</td>
<td>-</td>
<td>265</td>
<td>440</td>
<td>165</td>
<td>8</td>
<td>8</td>
<td>401</td>
<td>1960</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P- 18.5 (deep)</td>
<td>-</td>
<td>195</td>
<td>215</td>
<td>155</td>
<td>15</td>
<td>10</td>
<td>-</td>
<td>1260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bruce Nuclear Power Develop. (Sample #1)</td>
<td>9.1</td>
<td>16</td>
<td>12</td>
<td>109</td>
<td>17</td>
<td>8</td>
<td>160</td>
<td>55</td>
<td>.85</td>
<td>.07</td>
</tr>
<tr>
<td>Canadian Forces Base Borden</td>
<td>8.2</td>
<td>29</td>
<td>1.2</td>
<td>.8</td>
<td>.3</td>
<td>2</td>
<td>80</td>
<td>8</td>
<td>.06</td>
<td>.07</td>
</tr>
</tbody>
</table>

¹Values from Beswick (1971) in piezometers adjacent to sample site.
Table 4.6
Chemistry of the Soluble Cation Extractions
(all values in mg/l)

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>pH in. 1M CaCl₂</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perch Lake Basin, Chalk River</td>
<td>6.3</td>
<td>26.3</td>
<td>1.8</td>
<td>11.7</td>
<td>3.3</td>
<td>73</td>
</tr>
<tr>
<td>Whiteshell Nuclear Research Establ.</td>
<td>8.1</td>
<td>80</td>
<td>22</td>
<td>30</td>
<td>6</td>
<td>258</td>
</tr>
<tr>
<td>Bruce Nuclear Power Development</td>
<td>8.1</td>
<td>95</td>
<td>56</td>
<td>10</td>
<td>8</td>
<td>245</td>
</tr>
</tbody>
</table>
Chalk River sand, with nearly all $K_d$ values in the range of 10 to 100 ml/g over the entire range of initial cesium concentrations.

The second major feature that includes both the oxidized and unoxidized data of Figures 4.5 through 4.9 is the general increase in the differences between individual values obtained from the duplicate or triplicate tests at lower initial Cs concentrations. In this regard it is necessary to keep in mind that the coordinates on the graphs are logarithmic scale. At the lowest initial Cs concentrations, triplicate variations are in the range of 10's of ml/g for the Chalk River sand, 100's of ml/g for the Bruce till, and 1000's of ml/g for the Whiteshell till. As discussed in Chapter 3, the decreased precision in the $K_d$ values at low cesium concentrations in solution is most likely the result of poor counting statistics.

The third major feature indicated by the graphs is that four of the five samples tested did not yield significant general differences between the two types of $K_d$ values. This includes the samples from the Whiteshell, Chalk River, Borden, and Bruce sample No. 2. By this we mean that although for a given sample at a particular initial cesium concentration there are minor differences between the means of the triplicate or duplicate analyses, there are no distinctive trends in the differences between the two types of $K_d$ values. At one initial Cs concentration the glove box $K_d$ is slightly higher and at another concentration it is slightly lower. This conclusion applies to the Borden sand in which groundwater from a piezometer was used as the test solution and it applies to the Bruce till (sample no. 2) and the Whiteshell till in which soil extract water was used as the test solution. For the Chalk River sand two types of waters were used. Groundwater was used for conventional and glove box
CESIUM Kd ON BRUCE 21 TILL

FIG 4.5
CONVENTIONAL TEST WITH MOCK GROUNDWATER

GLOVE BOX TEST WITH MOCK GROUNDWATER

INITIAL CONCENTRATION OF Cs (M)

CESIUM Kd OF BRUCE #2 TILL

FIG 4.6
- CONVENTIONAL TEST WITH GROUNDWATER
+ GLOVE BOX TEST WITH GROUNDWATER

**Fig 4.7**

*INITIAL CONCENTRATION OF Cs (M)*

**CESIUM Kd ON BORDEN SAND**

**Fig 4.7**
CECIUM Kd OF WHITESHELL TILL

CONVENTIONAL TEST WITH MOCK GROUNDWATER

GLOVE BOX TEST WITH MOCK GROUNDWATER

FIG 4.8
* CONVENTIONAL TEST WITH GROUNDWATER
+ GLOVE BOX TEST WITH GROUNDWATER
○ CONVENTIONAL TEST WITH MOCK GROUNDWATER
× GLOVE BOX TEST WITH MOCK GROUNDWATER

INITIAL CONCENTRATION OF Cs (M)

CESIUM Kd OF CHALK RIVER SAND

FIG 4.9
tests and then the same tests were conducted using simulated groundwater (cations added as chloride salts). Figure 4.9 shows that the two types of waters yielded different $K_d$ values; however there appeared to be no significant difference between the results of the conventional tests and the glove-box tests. The fact that the tests with groundwater yielded the lowest $K_d$ values at low initial cesium concentrations is in agreement with the hypothesis (Chapter 3) that natural cesium concentrations can have a major influence on the results of $K_d$ measurements. The background natural cesium in the groundwater samples would be greater than the background cesium in the simulated groundwater.

Of the five samples that were subjected to both conventional and glove-box $K_d$ tests, only the Bruce sample No. 1 gave results in which large differences between the two types of $K_d$'s are evident. The large differences only occurred if the initial cesium concentrations were very low (less than $10^{-5}$ M). At larger initial cesium concentrations, however, there appears to be no significant differences. Detailed discussions of the results of these tests on Bruce sample No. 1 and of other investigations on this sample are presented by Kewen (1978). There is a possibility that the large differences encountered at the two concentration levels are a result of experimental error. An investigation using other samples from the Bruce site is currently in progress.

4.3 Dependence of Cesium Batch $K_d$ Values on Solution to Soil Ratio

4.3.1 Potential Effects of Solution to Solid Ratio

Various solution to soil ratios have been used in the determination of batch $K_d$ values. Wahlberg and his associates (1965, 1962) used a ratio of 10 ml solution: 0.1 g clay, while several studies including
Mills and Zwarich (1970) and the work of Chapter 3 in this study used a ratio of 5 ml solution: 1.0 g soil.

In natural groundwater systems, the solution to solid ratio would generally be in the order of 1 ml: 5 g dry soil. To use the same ratio in laboratory $K_d$ determinations would be extremely difficult. Since the mixture would not be a slurry, it would be difficult to insure a uniform distribution of the solution throughout the soil material, and thus shaking (mixing) times could be extremely long in order to achieve equilibrium. In addition, removal of sufficient soil solution for analysis would be difficult. If found to be necessary, however, these difficulties could be overcome.

The current practice of using much higher solution to soil ratios than exist naturally gains support from the law of mass action. A cation exchange reaction between a monovalent cation such as cesium, and a monovalent competing cation can be represented by:

$$\text{Cs}^+ + \text{A}^+ + \text{Cs}^+ + \text{A} \quad (4.2)$$

$$K = \frac{[\text{Cs}^+][\text{A}^+]}{[\text{Cs}^+][\text{A}^+]} \quad (4.3)$$

where $\text{Cs}^+$ and $\text{A}^+$ are cations in solution and $\text{Cs}^+$ and $\text{A}^+$ are cations adsorbed onto the exchanger. $K$ is the thermodynamic equilibrium constant for the reaction and the square brackets denote activities of the species in solution and mole fractions of the adsorbed species. By definition, the $K_d$ for cesium is given by

$$K_d(\text{Cs}) = \frac{[\text{Cs}^+]}{[\text{Cs}^+]} \quad (4.4)$$

Substitution into 4.3 and rearrangement gives:
Thus $K_d$ is not a direct function of the solution to solid ratio. Furthermore, $K_d$ would be constant provided $[S^+]/[\bar{A}^+]$ is constant. In normal batch $K_d$ measurements, this would generally be true provided the quantity of cesium in the system is small with respect to the quantity of the competing cation. Following equation 4.5, changing the solution to solid ratio should not affect $K_d$ unless $[A^+]/[\bar{A}^+]$ changes. Provided equilibrating solutions are used which have the same concentrations of major cations as the natural soil solution, then $[A^+]/[\bar{A}^+]$ should not be a function of the solution to solid ratio. Furthermore, in soils with high cation exchange capacities, the amount of cations in solution is generally very small with respect to the amount adsorbed. In this situation, the volume of pure water added to a given quantity of soil could be varied over a wide range without having a major effect on the $[A^+]/[\bar{A}^+]$ ratio. Thus, from considerations of mass action, it appears that solution to soil ratios would be a factor in $K_d$ determinations only in soils with low cations exchange capacity and only if the equilibrating solutions have cation concentrations substantially different from the concentrations in the natural soil solutions or groundwater.

Considering the apparent lack of applicability of the law of mass action to natural systems (as discussed in Chapter 3), it appeared that some preliminary experiments into solution to solid ratio effects were justified. Two soils having quite different chemical characteristics were selected for these tests, the sand from CRNL (Sample No. 7), and the till sample from WNRE (Sample No. 1).
4.3.2 Chalk River Sand Experiments

Batch $K_d$ tests were conducted on the Chalk River sand using solution volume (ml) to dry soil mass (g) ratios of 10, 5, 4, 3, 2 and 1. Three cesium concentrations were examined at each ratio, $10^{-4}$, $10^{-6}$ and $10^{-8}$ M. The equilibrating solutions all contained competing cations in concentrations equal to the soluble cation data of Table 3.3.

The results of these experiments are shown in Figure 4.10 as $K_d$ vs. volume of water added to 1 g of dry soil. Figure 4.10A indicates that at cesium concentrations of $10^{-4}$ M, the $K_d$ values were relatively constant over the solution to solid ratios examined. The results for the $10^{-6}$ and $10^{-8}$ M cesium solutions are similar to each other and show a marked increase in $K_d$ with increasing solution volumes. At a solution to solid ratio of one, the $K_d$ was approximately 30 ml/g while at a ratio of ten the $K_d$ was approximately 45 ml/g. From these results, it is apparent that it cannot generally be assumed that the measured $K_d$ is independent of the solution to solid ratio.

Two explanations for the data of Figure 4.10 have been considered. The first explanation concerns the effect of natural background cesium in the soil sample. From Table 3.6, each gram of soil No. 7 would contain $4.1 \times 10^{-4}$ mg of natural cesium. At $10^{-4}$ M Cs, one ml of the equilibrating solution would contain $1.37 \times 10^{-2}$ mg of cesium, or almost two orders of magnitude more than the total background cesium. As a result, the amount of cesium in the system was essentially independent of what was present naturally. As a result, the $K_d$ should follow the mass action principles as discussed above. From the tables of Appendix C it can be seen that for soil No. 7, an initial solution concentration of $10^{-2}$ mg/l does not correspond with the constant $K_d$ range of the distribution.
FIG 410 RELATION BETWEEN CESIUM Kd AND SOLUTION TO SOIL RATIO (CHALK RIVER SAND)
function. That is, from mass action principals, the amount of cesium is not insignificant with respect to the competing cations. Within this range, the $K_d$ should decrease with increasing cesium concentrations. At equilibrium, there was an increase in the measured cesium concentrations as the solution volumes increased. This could account for the slight decrease in $K_d$ as the solution volume of Figure 4.10A increased.

One ml of $10^{-6}$ m Cs solution contains $1.37 \times 10^{-4}$ mg or approximately one half the amount present in the soil naturally. Since the natural cesium constitutes a significant proportion of the total cesium present, as the volume of solution added increases, the cesium is effectively diluted resulting in lower solution concentrations and thus higher $K_d$ values at higher solution volumes. A similar explanation would apply to the $K_d$ values measured at a cesium concentration of $10^{-8}$ M (Figure 4.10C). The similarity between Figures 4.10B and C suggests that in both cases the $K_d$ values are being controlled by the background cesium concentrations.

A second explanation of the results is based on the mineralogy of the samples and the selectivity of adsorption sites. Biotite constitutes approximately 10% of the Chalk River sand while quartz and feldspars make up most of the remaining 90%. The weathered edges of biotite particles contain sites for the selective adsorption of cesium while quartz and feldspars are non-selective and generally weak adsorbers of cesium. The mechanism of cesium adsorption in biotite has been discussed in detail by Sawhney (1972).

Since biotite makes up a small proportion of the sand, the selective edge sites probably constitute a very small proportion of the total exchange sites. One could speculate that in solution of $10^{-4}$ M
cesium, even 1 ml of solution would contain cesium considerably in excess of the adsorptive capacity of the edge sites. As a result, at $10^{-6}$ M Cs, the adsorption would be controlled by the non-selective sites. As a result, with no change in the initial dissolved cesium concentration, the addition of increasing solution volumes to 1 g of sand would result in near constant $K_d$ values.

At the low Cs solution concentrations ($10^{-6}$ and $10^{-8}$ M), the amount of cesium present may be small or at least comparable to the adsorptive capacity of the selective sites. As a result, the cesium is adsorbed at these sites, and the more cesium introduced, the more that is adsorbed. This results in an increased $K_d$ with increasing amounts of cesium added (increasing volumes of solution).

4.3.3 WNRE Till Experiments

Experiments similar to those conducted on the Chalk River sand were conducted on the WNRE sample. Solution volume (ml) to soil mass (g) ratios of 1, 2, 3, 4, 5 and 10 were used at two cesium concentrations, $10^{-4}$ and $10^{-8}$ M. The results are shown in Figure 4.11. As in the case of cesium, the $K_d$ value at an initial solution concentration of $10^{-4}$ M was very nearly constant for all solution to soil ratios. At a solution concentration of $10^{-8}$ M however, the $K_d$ increased from approximately 1,000 ml/g to 10,000 ml/g as the solution volume increased from 1 ml to 10 ml. The total background cesium in 1 g of this soil is $2.1 \times 10^{-4}$ mg. As a result, the explanation based on background cesium used for the Chalk River sand applies equally well to the WNRE sample. Furthermore, from Table 3.4, the WNRE sample contains a significant proportion of mixed layer clay minerals. As a result, both selective and
RELATION BETWEEN $K_d$ AND WATER TO SOIL RATIO (WHITESHELL TILL)

**Fig A**
$10^8$ M Cs

**Fig B**
$10^4$ M Cs
non-selective exchange sites will probably be present. Thus an explanation based on selective exchange as applied to the Chalk River sample could also be applied to the WNRE sample.

The explanations of the results based on the selectivity of exchange sites requires a considerable degree of speculation for both the CRNL and WNRE samples. In the absence of more definitive data concerning the nature of the exchange sites in the soils, the explanation based on the background cesium concentration seems to be the most logical and defensible.

4.3.4 Practical Implications

The results of these tests appear to have considerable practical significance. In Chapter 3 it was concluded from the cesium and strontium results that in many soil materials, the measured $K_d$ value was strongly influenced by the background concentration of the cation of interest. The results of this section indicate that the background concentration during a batch $K_d$ test can be influenced quite significantly by the solution to solid ratio used in the test. In order to avoid background effects in $K_d$ determinations, where isotopes of the radionuclide occur naturally in the soil, it appears that the equilibrating solution should have a concentration of the cation identical to that of the natural groundwater. This suggests three approaches to $K_d$ determinations:

1) Tests similar to those of Chapter 3 could be conducted, with the concentration of the cation of interest in the artificial groundwater being made equal to that of the actual groundwater in the area from which the sample was taken.

2) Similar tests could be conducted but with the use of natural
groundwater from the area. This could avoid the need for measuring background concentrations but could introduce other geochemical problems (such as precipitation of iron or other slightly soluble compounds).

3) A third approach would be entirely different from the first two and would make use of the natural cations present. From samples of both the groundwater and soil, the concentration of the cation in solution and adsorbed onto the solids could be determined, and the $K_d$ for the cation calculated directly from these measurements. This approach is very attractive in that it would give results which would be as close to the natural conditions as could probably be achieved. It would be limited however in that it would not show how the $K_d$ would change under changing environmental conditions. A technological limitation could be the need to obtain accurate measurements of the cation at trace concentrations.

In view of the possible significance of the results of this section, the experiments should be repeated using both cesium and strontium, and a wider range of soil materials. In particular, soils in which the background cesium was not believed to be controlling the $K_d$ values should be examined.
5. SUMMARY OF CONCLUSIONS

1. Values of distribution coefficients for cesium measured on fifteen samples of unconsolidated materials obtained from a variety of types of geologic deposits in Ontario, Manitoba, and Alberta varied between 100 ml/g and 20,000 ml/g. Considering that samples represented a wide range of soil properties, the results indicate that most unconsolidated geologic materials in Canada will have a substantial ability to retard the migration of cesium in the groundwater zone.

2. Distribution coefficient values determined for strontium in the same set of samples used for the cesium measurements varied between 2.5 ml/g and 100 ml/g. Thus the ability of most unconsolidated materials to retard the migration of strontium is substantially less than their ability to retard cesium. In some unconsolidated geologic materials strontium retardation may be negligible.

3. There was no significant correlation between the $K_d$ values for cesium or strontium and any of the measured physical or chemical properties of the samples. Reliable indirect estimates of $K_d$ based on parameters such as clay content, cation exchange capacity, or major cation contents are therefore generally not obtainable. From this it follows that the establishment of a generic data base for the classification of different unconsolidated geologic materials with respect to their ability to retard the migration of cesium and strontium is probably not a practical pursuit.

4. Natural cesium and strontium in the soil materials appeared to have the greatest influence on the measured $K_d$ values.
5. Preliminary experiments indicated that cesium $K_d$ values determined in batch tests are sensitive to the solution to solid ratio used in the test, and that this in turn is related to the presence of background cesium.

6. Air drying of the samples and exposure of samples and test solutions to oxidizing conditions during $K_d$ measurements generally has no major effect on the measured $K_d$ values for cesium. Considering the manner in which $K_d$ values are generally applied, the observed differences between oxidized and unoxidized samples was not considered to be significant.

7. Obtaining and maintaining soil samples and water samples in their natural geochemical state is a difficult problem. If this is indeed considered to be a necessary condition for $K_d$ measurements, then developments in sampling and preservation methods would be required in order for reliable $K_d$ measurements to be made.

8. Considering the difficulty in maintaining natural geochemical conditions in stored water and soil samples, it would be appropriate to consider methods for performing insitu $K_d$ measurements.
REFERENCES


