THE UNIVERSITY OF MANITOBA

THE BEHAVIOUR OF RADIOSTRONTIUM AND RADIOCESIUM

IN SOIL SYSTEMS

by

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ABSTRACT

Sorption of radionuclides by soil materials is an important factor in the transport of radionuclides by ground water. This factor was investigated theoretically and experimentally; transport was investigated only theoretically. Carrier-free Sr-89, Sr-85, and Cs-137 were used in conjunction with soil samples from the waste management area of the Whiteshell Nuclear Research Establishment, bottom sediment samples from the Winnipeg River, and a Morden bentonite. Characteristics of the samples which affected their sorption properties were studied in detail.

Radiostrontium sorption was studied by batch and column methods using calcareous and non-calcareous soils and solutions of calcium and magnesium salts. Sorption was found to be due to a reversible ion exchange reaction and conventional ion exchange equations were found to be applicable. Methods to predict radiostrontium sorption from easily measurable soil characteristics were developed. Transport theories believed to be applicable to transport in the sediments of the WNRE waste management area were presented and prediction methods developed.

Radiocesium sorption was studied by a column method using simulated ground water solutions. Radiocesium appeared to be fixed in the soil by an irreversible sorption reaction and it was concluded that no appreciable transport of radiocesium would occur in the soils under study.

In a concurrent study, negative sorption of anions, or positive sorption of water, in flocculated soils was studied and the concept of "non-solvent water" presented. A tactoid model of the flocculated soil was found to fit the experimental data.

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CHAPTER I

INTRODUCTION

I. INITIATION OF THE STUDY

Atomic Energy of Canada Limited, through Dr. J.E. Guthrie, Head,

Environmental Control Section, Whiteshell Nuclear Research Establishment,

approached the Department of Soil Science, University of Manitoba to

investigate the sorption properties of the soils within the Whiteshell

Nuclear Research Establishment Waste Management Area and the sediments of

the nearby Winnipeg River. On February 1, 1967, under the provisions of

a research contract between Atomic Energy of Canada Limited and the

University of Manitoba, it was agreed that an investigation would be

conducted by the Department of Soil Science, under the direction of Dr.

M.A. Zwarich.

II. THE SIGNIFICANCE OF RADIOISOTOPE SORPTION

An important consideration in the disposal of radioactive waste by

burial in terrestrial sites is the behaviour and fate of the radionuclides

which are introduced into the soil. The fraction of these radionuclides

consisting of soluble ionic species that escape from their confinement

will, in the absence of interaction with the soil, move with the direction

and velocity of infiltrating surface water or the natural ground water.

Fortunately, cationic species are sorbed by the soil colloids and this

interaction retards the migration of the radioisotopes with respect to the

velocity of the water. In order to utilize this phenomenon to control the

movement of radionuclides in the environment, the pattern of ground water

flow and the radioisotope sorption properties of the soils must be known.

Numerous transport theories are available which relate the migration of

the radioisotope to the sorption properties of the soil and the velocity of the ground water.

III. SCOPE OF THE STUDY

This study is a laboratory investigation of the soil characteristics which affect the transport of radionuclides by ground water with a view to indicate easily measurable soil characteristics which may be used in connection with an appropriate transport theory to predict radioisotope migration. No attempt was made to evaluate transport theories experimentally except to a very limited extent in the case of radiocesium. The isotopes used in the study were those of strontium and cesium because of their importance in the problem of radioactive waste disposal. The soil materials studied are the soils of the WNRE waste management area, sediments from the nearby Winnipeg River, and a Morden bentonite. The available sorption and transport theories were appraised and cast into forms most applicable to the waste disposal situation and the WNRE soils. An extensive investigation of radiostrontium sorption was carried out covering all aspects of the sorption which might affect radiostrontium transport in the WNRE soils. Radiocesium sorption was studied by a method which was designed to simulate the field situation.

IV. ORGANIZATION OF THE REPORT

Chapter II is devoted to a theoretical discussion of the problems of ion exchange, fixation, and transport of radionuclides with an attempt to transform the theory into forms most applicable to the problem of the migration of radionuclides from terrestrial sites. Theory is discussed first in order to present the concepts and models required to evaluate the experimental data.

The experimental methods used in the course of the study are
presented in Chapter III. Original methods are described in detail; a
literature reference and an outline of the principle are given for the
others.

Chapter IV is an account of the three principal experimental topics
of the study. A detailed morphological examination and chemical and
physical analysis of the samples from the waste management area was
carried out in order to characterize the site and the samples and to
provide data for radioisotope studies. Similar analyses were conducted
upon the Winnipeg River sediment samples and the Morden bentonite with a
similar rationale. The second section of Chapter IV concerns radio-
strontium sorption and the third, radiocesium sorption. A review of the
available experimental literature is presented first, followed by a
presentation of the experimental data, and a discussion of results.

Chapter V contains a summary of the study, the conclusions from the
experimental data and a compendium of the models developed in the course
of the study which may be used to predict radioisotope transport. A step
by step procedure for the prediction of radiostrontium migration is
included.

CHAPTER II

THEORETICAL DISCUSSION

The behaviour of ions in a soil-solution system has been the subject of many investigations and a number of theories and models have been proposed to explain sorption and transport phenomena. The aim of this chapter is: to select theories and models which are valid in the situation of the migration of radioactive ions from terrestrial disposal sites and which, in particular, are applicable to the conditions that exist at the WNRE waste management area; to develop concepts, and to present them in forms which are suitable for practical calculations.

1. Ion Exchange and Fixation

Models of Ion Exchange

Ion exchange is a general property of colloids which permits them to release ions in exchange for others. The sorbed ions are held near the surface of the colloidal particle by the electrostatic attraction of the charged surface. The surface charge of a colloid may arise from a strongly sorbed layer of ions at the surface, from discontinuities in the crystal lattice at the surface, or, in the case of the clay minerals, from a permanent charge in the lattice due to isomorphous substitution of lattice ions. Although ion exchange is associated with any mineral species having a large surface area, the minerals in soils exhibiting a useful amount of ion exchange are the clay minerals.

The ion-exchange properties of the clay minerals are due to the presence of a negatively charged lattice and due to the fact that the interlayer surface is accessible to cations as in the expanding layer silicates montmorillonite and vermiculite. The non-expanding layer silicates

kaolinite, chlorite, and mica, which exhibit ion exchange only on the external surfaces of the crystallites, contribute only slightly to the cation-exchange characteristics of most soil materials. A schematic of a crystallite of an expanding layer silicate immersed in a salt solution (24, 2) is given below:

(+) : cation   (-) : anion

In this model, the crystallite is a stack of parallel plates, each of which is an aluminosilicate lattice having a fixed negative charge due to isomorphous substitution. The exchangeable cations reside between the plates and adjacent to the external surfaces. Water near the external surfaces and between the plates is more or less ordered due to hydrogen bonding with the lattice and due to the presence of the charges as is the water near the ions in the external solution. The exchangeable cations are in a kinetic equilibrium with the cations in the external solution,

and due to electroneutrality requirements the charge of the exchangeable cations is equal to the negative lattice charge. This cation exchange capacity is best expressed as milliequivalents per gram of oven-dry clay. To complete this model, a thermodynamic definition of the phase boundary between the sorbed phase and the external solution is required. This definition involves the concepts of negative absorption of anions or non-solvent water and is discussed in Appendix A.

Another model which appears at first glance to be contradictory to the previously mentioned plate model is the diffuse double layer model of Gouy and Chapman (45). This model envisions an atmospheric distribution of ions in the vicinity of a charged surface. Due to a combination of electrostatic interaction and diffusion as given by the Poisson-Boltzman equation, cations are attracted to and anions repelled from the vicinity of a negatively charged surface. This model has been improved by Bolt (46) with the introduction of a distance of closest approach of the counter ions to the charged surface and with corrections to the Boltzman distribution. The impression given by these models of a diffuse cloud of ions in the vicinity of a charged surface is, however, only valid in the case of an isolated surface of low charge density in a solution of very low concent-ration. If charge densities encountered in clay minerals and reasonable solution concentrations are considered, the thickness of the diffuse layer is much reduced and most of the counter ions are found immediately adjacent to the surface. This effect is further enhanced if the interaction due to finite distances between the charged surfaces is considered. The two seemingly contradictory models may be unified with the plate model being most applicable to the internal surfaces of a crystallite and the diffuse

layer model most applicable to the external surfaces. This tactoid model is further discussed in Appendix A in connection with negative absorption and non-solvent water theory.

The mass-action law of thermodynamics (32) may be applied to the ion exchange reaction if appropriate definitions of systems and phases are formulated with regard to the previously mentioned models. A system is defined as a hypothetical region containing a fixed weight of soil in contact with a fixed volume of solution. A system may constitute, for example, a given volume of a field soil within which the soil and solution are an intimate mixture, or a mixture of a dry soil and a solution in a bottle in the laboratory. Within a system, the two phases which participate in the ion exchange reaction must be defined. In thermodynamics, a phase is defined as a homogeneous region (31). The exchanger phase is defined as a surface phase, having no volume, which includes all cations sorbed by the soil particles. The solution phase is defined as the homogeneous solution surrounding the soil particles. The volume of the solution phase is dependent on the definition of the phase boundary between the solid and solution phases; this is treated in detail in Appendix A.

Ion Exchange of Calcium and Radiostrontium

The ion exchange reaction may now be treated as a chemical reaction between ions in the two phases. Considering first a strontium-calcium exchange, the equation is:

$$\text{Ca-clay} + \text{Sr}^{++} \rightleftharpoons \text{Sr-clay} + \text{Ca}^{++}$$
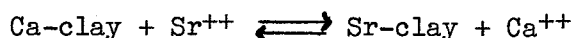
The symbol "-clay" represents the exchanger phase. The resulting equilibrium expression is:

$$K = \frac{(\text{Ca})_s\,(\text{Sr})_x}{(\text{Ca})_x\,(\text{Sr})_s} \qquad [1]$$

K : thermodynamic equilibrium constant

$(Ca)s$: activity of calcium in the solution phase

$(Ca)x$:   "   "   "   " " exchanger phase

$(Sr)s$: activity of strontium in the solution phase

$(Sr)x$ "   "   "   " " exchanger phase

From kinetics (26) the constant K may be shown to be equal to the ratio

of the rate constants of the forward and reverse reactions:

$$K = k_1/k_{-1} \tag{2}$$

k_1 : rate constant of the forward reaction

k_{-1} :   "   "   " " reverse   "

Under normal circumstances equilibrium with an ion exchanger is reached

rapidly and rate constants do not need to be considered. K is constant

at a given temperature if activities are used in the equilibrium expression.

Ionic activities in solution are defined as the product of the

concentration and the activity coefficient:

$$a_+ = \gamma_+ \, m_+ \tag{3}$$

a_+ : cation activity

γ_+ : cation activity coefficient

m_+ : cation molarity

From homovalent exchanges such as the one under consideration, the activity

coefficients of the two ions are nearly equal due to the principle of ionic

strength. This is especially so for similar ions such as calcium and

strontium. Thus concentrations in the solution phase may be used in place

of activities in equation [1] without affecting the value of K. Similarly

total amounts of the ions in the solution phase (moles, equivalents, or

counts per second) may be used instead of activities in solution since the

solution volume is the same for both species.

Activities of cations in the exchanger phase are also defined in the manner of equation [3] and if concentrations or total amounts of ions are used to replace these activities in equation [1], variations of the activity coefficients in the exchanger phase appear as a variation of the constant K with the composition of that phase. K is then called a select-ivity number. If, as in the case of tracer studies, strontium ions are present in the system only in trace quantities, the composition of the exchanger phase is effectively constant, that is, calcium saturated, and K becomes again a constant. In this case K is a property of the exchanger and is constant even for a mixture of exchangers. For the system of a calcium saturated soil in equilibrium with a solution of a calcium salt to which a trace amount of radiostrontium has been added, equation [1] may be rearranged to read:

$$\frac{(Sr)x}{(Sr)s} = K\frac{(Ca)x}{(Ca)s} \qquad [4]$$

(Sr)x : total amount of strontium in the exchanger phase

(Sr)s :   "   "   "   "   " " solution   "

(Ca)x : total amount of calcium in the exchanger phase

(Ca)s :   "   "   "   "   " " solution   "

   K : equilibrium constant

The two ion ratios may be defined as:

$$SrDR = \frac{(Sr)x}{(Sr)s} \qquad [5]$$

$$CaDR = \frac{(Ca)x}{(Ca)s} \qquad [6]$$

SrDR : strontium distribution ratio

CaDR : calcium distribution ratio

and finally:

$$SrDR = K \cdot CaDR \qquad [7]$$

The SrDR is commonly designated as D in the literature. Equation [7] implies that for the simple system, the distribution of radiostrontium between phases may be predicted from a knowledge of the calcium distribution ratio and the equilibrium constant K. The equation also implies that a constant fraction of any radiostrontium added to the system will be sorbed to the exchanger phase. This fraction is:

$$SrAR = \frac{(Sr)x}{(Sr)s + (Sr)x} = \frac{1}{1 + 1/SrDR} \qquad [8]$$

SrAR : strontium absorption ratio

The following results for four hypothetical soils at water contents near saturation illustrates the variation in CaDR that can be expected:

Soil	m	(Ca)x	V	N	(Ca)s	CaDR
Saline clay	100 g.	100 meq	80	.06	4.8 meq	21
Non saline clay	100	100	80	.001	0.08	1200
Saline sand	100	5	40	.06	2.4	2.1
Non saline sand	100	5	40	.001	0.04	120

    m : weight of soil

    V : volume of solution

    N : normality of calcium solution

Since K may be expected to be near unity due to the chemical similarity of calcium and strontium, the table also illustrates expected variations of SrDR.

Radiostrontium Exchange with Calcium and Magnesium in Calcareous Soils

The foregoing discussion has been applied to a simple system of a calcium saturated soil and a calcium salt solution. Naturally occurring

soils represent more complex systems. The major additional components which may affect radiostrontium sorption are the carbonate minerals calcite and dolomite and the diverse ionic species in solution. In Manitoba the principal ionic species present in groundwater are calcium, magnesium, and sulphate. Minor amounts of sodium, potassium, chloride, and bicarbonate are also usually present. If radiostrontium is added to such a system, the solubility product of insoluble strontium compounds will not be exceeded, due to the minute concentration of strontium present, and these compounds will not precipitate. Thus the radiostrontium will be free to participate in ion exchange reactions. The surface of the insoluble calcium and magnesium minerals may add additional ion exchange sites but their contribution to the ion exchange capacity of the entire soil is believed to be small. Under most conditions the only reaction of the radiostrontium is a reversible ion exchange; however, if conditions are such that calcium and magnesium carbonates or sulphates are being precipit- ated from solution, radiostrontium will probably precipitate as well in a mixed crystal.

Equation [4] remains valid in this more complex system as is a similar equation involving magnesium:

$$\frac{(Sr)x}{(Sr)s} = K' \frac{(Mg)x}{(Mg)s} \qquad [9]$$

Either of these equations are usable to predict the SrDR of a field soil. However predictions may be facilitated if the sum of calcium and magnesium in each phase can be used since the sum of calcium plus magnesium in the exchanger phase is approximately equal to the cation exchange capacity, a fundamental characteristic of the soil. Further the sum of calcium and magnesium in the solution phase may be estimated from the electrical

conductivity of the solution (34). The following equation is proposed:

$$SrDR = K \frac{(Ca + Mg)x}{(Ca + Mg)s} \qquad [10]$$

In this equation K is not strictly a constant but from a study of the various ion exchange relationships may be shown to have the following functional relationship to the equivalent fraction of magnesium in the solution phase:

$$\frac{1}{K} = \frac{1}{K_C} - \frac{(1 - K_1)}{K_C} \frac{(Mg)s}{(Ca + Mg)s} \qquad [11]$$

   K_C : equilibrium constant for the Ca-Sr exchange

   K_1 : equilibrium constant for the Ca-Mg exchange

In general K should be relatively constant and characteristic of the soil. Equation [10] may be further modified by combining the characteristic constants:

$$SrDR = KC \frac{m}{(Ca + Mg)s} \qquad [12]$$

   C : cation exchange capacity in meq/g

   m : weight of soil in grams

KC is now characteristic of the soil and m/(Ca + Mg)s characteristic of the solution. For a field soil this solution characteristic may be evaluated as follows:

$$\frac{m}{(Ca + Mg)s} = \frac{100}{N(Vm - Vn)} \qquad [13]$$

   N : normality of calcium plus magnesium in solution (ground water)

   Vm : moisture percentage of the soil

   Vn : non-solvent water percentage of the soil

Vn may be estimated from the cation exchange capacity of the soil as discussed in Appendix A.

The SrDR is the quantity which enters directly into theories of the transport of radiostrontium through soils by ground water. To evaluate this quantity, values are required for the absorption characteristic KC, the normality of calcium plus magnesium in the ground water, and the moisture percentage of the soil.

Radiostrontium Sorption by River and Lake Sediments

For the related problem of the distribution of radiostrontium between a bottom sediment and a body of water there is a more useful measure than the SrDR. This is the strontium concentration ratio or SrCR, commonly symbolized as Kd in the literature, which is defined as the ratio of the amount of radiostrontium in the exchanger phase per gram of sediment to the amount of radiostrontium per cubic centimeter of solution. The relationship is:

$$SrCR = \frac{V}{M} \times SrDR \qquad [14]$$

V : volume of solution

M : weight of soil

By combining equations [12], [13], and [14] the SrCR may be predicted from:

$$SrCR = \frac{KC}{N} \qquad [15]$$

Since the derivation of this equation is based on the assumption of homogeneous phases at equilibrium, this equation may only apply at the immediate interface between the water and the sediment. If there is no movement of water into the sediment, the penetration of strontium into the sediment is by diffusion only and may be very slow. Conversely, the movement of strontium from below the surface to the surface of the sediment is also by diffusion and consequently the above mentioned equation predicts

the SrCR only for those portions of the sediment which are in rapid
equilibrium with the water body.

Ion Exchange Involving Radiocesium

The mass action law may also be applied to the ion exchange reaction
between calcium and cesium:

$$Ca\text{-}Clay + 2Cs^+ \rightleftharpoons 2Cs\text{-}Clay + Ca^{++}$$
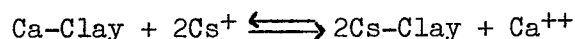
The equilibrium expression is:

$$K = \frac{[Cs]x^2\,[Ca^{++}]}{[Cs^+]2\,[Ca]x} \qquad [16]$$

Square brackets represent activities. Activities in the solution phase
may be evaluated from concentrations and activity coefficients. For
activities in the exchanger phase, an approximation which has been found
suitable (25) is to assume that the activities are equal to the mole
fraction of the ion in the exchanger phase. With the further assumption
that cesium is present in the system only in trace quantities, equation
[16] becomes:

$$K = \frac{(Cs)x^2\,[Ca^{++}]}{(Ca)x^2\,[Cs^+]2} \qquad [17]$$

or

$$K^{\frac{1}{2}} = \frac{(Cs)x\,[Ca^{++}]^{\frac{1}{2}}}{(Ca)x\,[Cs^+]} \qquad [18]$$

Curved brackets represent millimoles. Equation [18] is identical to
Gapon's equation [25]. Converting all units to total milliequivalents in
the system and introducing the activity coefficients, equation [18]
becomes:

$$CsDR = \frac{(Cs)x}{(Cs)s} = \sqrt{\frac{K}{2V}}\ \frac{(Ca)x\ \gamma + Cs}{(Ca)\frac{1}{2}s\ \gamma\frac{1}{2}+\ Ca} \qquad [19]$$

CsDR : cesium distribution ratio

V : volume of solution phase in milliters

K : equilibrium constant

γ_{+Cs} : activity coefficient of cesium

γ_{+Ca} : activity coefficient of calcium

Note that the volume of the solution phase enters directly into the equation for CsDR; this implies that dilution of a system with water will alter the CsDR. This volume effect is characteristic of exchanges involving ions of different valences.

Radiocesium Fixation

Many workers have noted sorption of radiocesium by soils or minerals greatly in excess of that predictable from ion exchange equations which are valid for macroscopic amounts of cesium. This effect has been attributed to fixation or sorption at cesium-specific sites. A useful model is a reversible first order reaction between ions in the exchanger phase and the solution phase (26). The rate of reaction is given by:

$$\frac{dX}{dt} = k_1(Cs)_s - k_{-1}(Cs)_x \qquad [20]$$

X : amount of radiocesium lost from solution

k_1 : forward rate constant (sorption)

k_{-1} : reverse rate constant (desorption)

The rate constants are related by:

$$k_1/k_{-1} = D \qquad [21]$$

D : equilibrium distribution ratio

The observed fixation phenomena correspond to a case in which D is large and the forward reaction is much more rapid than the reverse reaction. Equation [20] may be integrated and expressed in terms of the absorption ratio which is the fraction of the total radiocesium in the system which

is sorbed by the exchanger phase:

$$A_t = A + (A_o - A)/\text{EXP}\ \frac{k_1 t}{A} \qquad\qquad [22]$$

A_t : absorption ratio at time t

A : equilibrium absorption ratio

A_o : absorption ratio at time $t = o$

The two ratios are, of course, related by:

$$D + A/(1 - A) \text{ or } A = D/(1 + D) \qquad\qquad [23]$$

In many cases the approximation may be made that the reaction is irreversible, which implies that the equilibrium absorption ratio is unity. Equation [22] then becomes:

$$A_t = 1 - \frac{1}{\text{EXP}(k_1 t)} \qquad\qquad [24]$$

This equation indicates an exponential time-dependent increase of sorption from the solution phase.

2. Transport Theories

Introduction

Most transport theories are formulated with reference to the situation in which a solution enters one end of a cylindrical column of an ion-exchanger, passes axially along the column, and exits from the other end. This model is seen to be analogous to the situation of the parallel flow of ground water through a field soil since if the axis of a hypothetical column is chosen to be parallel to the ground water flow lines, there is no water movement in a radial direction in the chosen column.

In column theories involving radioisotopes, conditions are generally arranged so that the addition of the tracer does not disturb the chemical composition of the solution in the column. This assumption is valid in

the case of transport of tracers buried in the soil unless large amounts

of water or water-soluble salts accompany the disposal of the isotope.

Two types of inputs of activity to a column are generally considered.

A step function input occurs when the solution entering the column is

suddenly changed from a non-radioactive solution to a similar solution

containing a constant radioactive concentration. The step function input

is defined by:

$$C = 0 \quad \text{for } t < 0$$
$$C = Co \quad \text{for } t \geq 0$$

[25]

C : concentration of radioactivity in solution

Co : concentration of radioactivity in active feed solution

t : time

This input is a good approximation to disposal situations in which

activity is supplied to the ground water at a relatively constant rate as

by slow release from a solid, by leaching of a surface site by infiltrating

rainwater, or by continued additions of soluble activity to a site.

A delta function input to a column occurs when all of the active ions

are introduced into the column in a very short time, following which the

original non-radioactive feed is resumed. This input may also be approx-

imated if activity is added to a narrow band of the soil at the entrance

to the column and non-active solution is fed in. This input corresponds

to a disposal situation in which radioisotopes in a water soluble form are

added to the ground water over a short period of time.

Ion Exchange Equilibrium Theories

If the ion-exchange reaction is reversible and is rapid with respect

to the velocity of the radioisotope, equilibrium transport theories may be

applied (14). This assumption is valid at low to moderate flow rates in the column if specific absorption of the tracer is absent. To describe the concentration in a column at any time after initiation of flow, equilibrium theories require two soil parameters in addition to the linear rate of flow of the solution.

A retardation parameter determines the mean velocity of a front of activity in case of a step function input or the velocity of a band of activity in the case of a delta function input. For all equilibrium theories this velocity is:

$$W = U/(1 + D) \qquad\qquad [26]$$

W : mean velocity of front or band

U : linear velocity of solution flow

D : equilibrium distribution ratio of tracer

This equation follows from the mass balance required to satisfy the ion-exchange equilibrium conditions.

A dispersion parameter determines the rate of spreading of a front or the rate of broadening of a band of activity. This parameter may be calculated from a physical model of the dispersion process or may be determined empirically. Most equilibrium theories predict similarly shaped fronts or bands of activity with the result that the dispersion parameter of one theory may be related to that of another theory. The theory of Lapidus and Amundson (14) attributes the dispersion primarily to longitudinal diffusion. This model is very attractive to explain tracer movement in soil columns at low to moderate flow rates. The concentration-distance equation for a step function input to a column of unit cross sectional area is:

$$\frac{C}{Co} = \frac{1}{2} + \frac{1}{2} \text{ erf } (r_1 - Z_2) + \frac{1}{2} \exp\left(\frac{UZ}{D^1}\right) \text{erfc } (r_1 + Z_2) \qquad [27]$$

where:

$$r_1^2 = \frac{x(1+D)\ U}{4\ D\ D^1} \qquad\qquad r_2^2 = \frac{UD}{4x(1+D)D^1}$$

C : concentration of tracer in solution in column

Co : concentration of tracer in feed solution

Z : distance from input end of column

U : linear velocity of water flow

D' : modified liquid diffusion coefficient

x : average position of the front

D : equilibrium distribution ratio of tracer

The error function erf and the error function compliment erfc are defined as follows:

$$\text{erf } x' = \frac{2}{\sqrt{\pi}} \int_0^{x^1} e^{-x^2}\, dx \qquad\qquad [28]$$

$$\text{erf } x^1 = 1 - \text{erf } x^1 \qquad\qquad [29]$$

The average position of the front, x, is of course calculated from:

$$x = \frac{U\ t}{1+D} \qquad\qquad [30]$$

Under most conditions the second term of equation [27] is negligible and the equation becomes:

$$\frac{C}{Co} = \frac{1}{2} + \frac{1}{2} \text{ erf } (r_1 - Z_2) \qquad\qquad [31]$$

The width of the front of activity, which may be defined as the region over which the relative concentration in solution changes from 0.90 to 0.10, is given by:

$$L = 1.81 \sqrt[4]{\frac{D^1 x}{U}} \qquad\qquad [32]$$

This equation implies that the width of the front is a function of the square root of the elapsed time whereas the position of the front is a direct function of time. The modified liquid diffusion coefficient D' on the basis of a physical model has been expressed as (14):

$$D' = \gamma Do + \lambda dU \qquad [33]$$

γ : labyrinth factor

Do : diffusion coefficient of the tracer in solution

λ : packing factor

d : effective grain size

At flow rates commonly encountered in soils, only the first term of equation [33] is significant. Values found for γ range from 0.50 to 1.0.

The concentration-distance curves predicted by ion-exchange equilibrium theories are illustrated in Figure 1 and Figure 2 for a step function input and a delta function input respectively. In these illustrations the dispersion is caused not by longitudinal diffusion but by the discontinuous nature of the computer model used to produce the curves. The soil column is divided into hypothetical sections or plates and the ion-exchange reaction allowed to come to equilibrium in each plate. The thickness of a plate can be related to the modified diffusion coefficient in a continuous model by:

$$\Delta = 2D'/U \qquad [34]$$

Δ : thickness of a plate in consistent units

For a step function input the width of a front of activity is then given by:

$$L = 1.81 \sqrt{2\Delta x} \qquad [35]$$

In a waste disposal area the movement of the average position of the
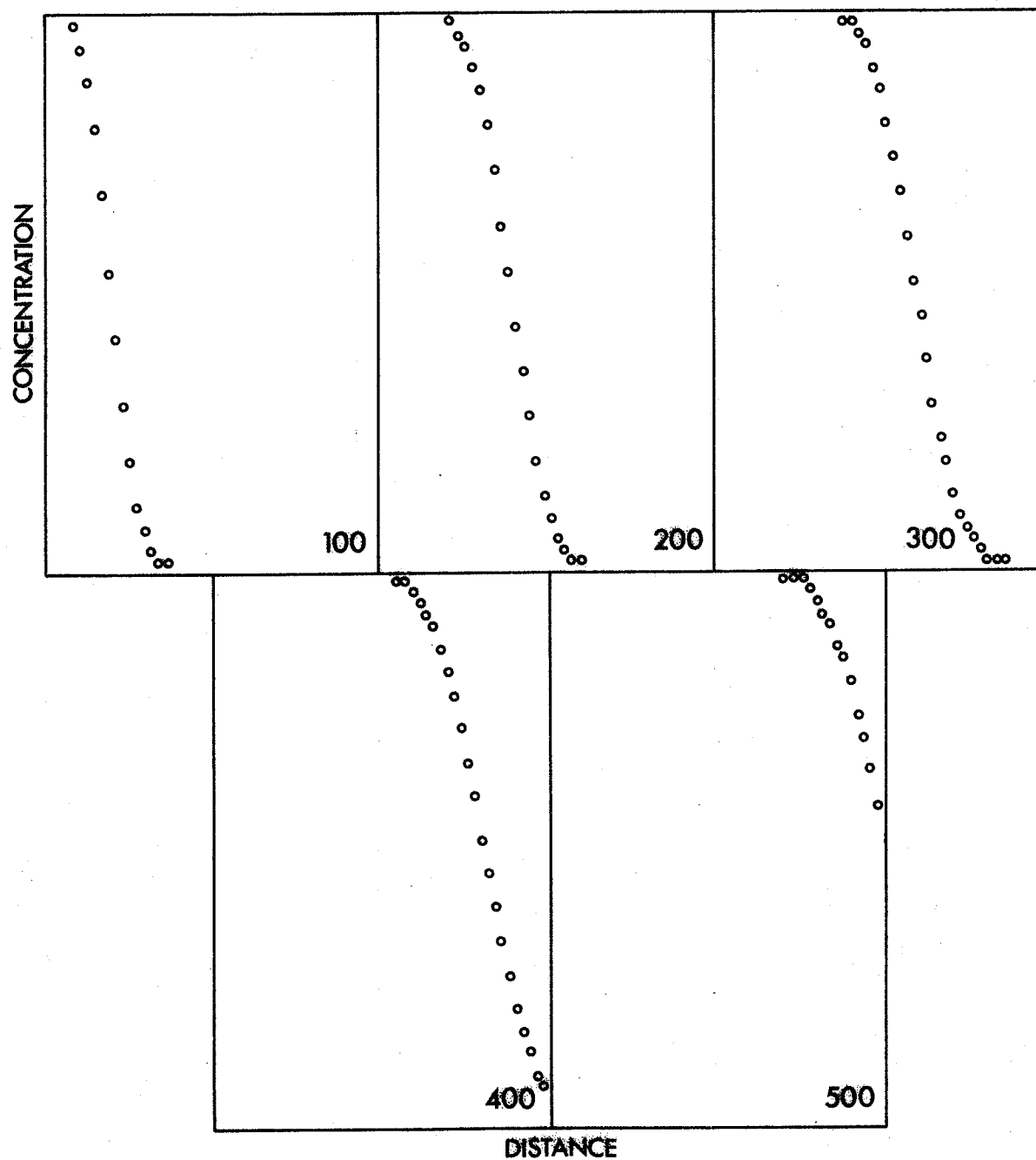
Figure 1. The ion-exchange equilibrium theory: Relative concentration in solution along a column for a step function input of active ions. (D = 9, the column length is 50 plates, and the five graphs represent inputs of 100, 200, 300, 400, and 500 plate pore volumes respectively.)
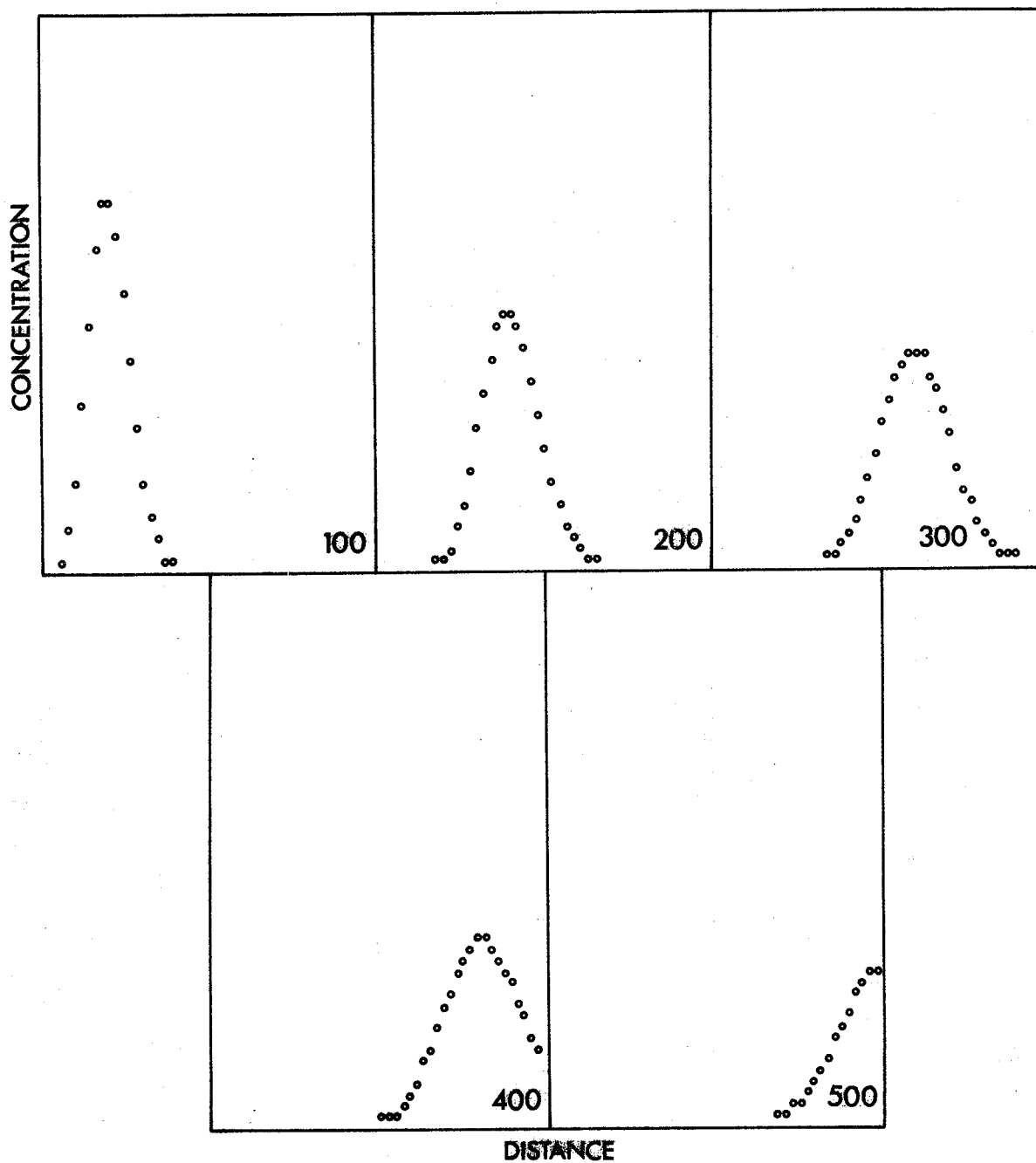
Figure 2. The ion-exchange equilibrium theory: Concentration in
solution along a column for a delta function input of active ions.
(D = 9, the column length is 50 plates, and the five graphs represent
inputs of 100, 200, 300, 400, and 500 plate pore volumes respectively.)

front of activity is the prime consideration; if the equilibrium assumption is valid, this may be estimated from equation [26]. The spreading of the front may be estimated from equations [32] and [33].

Transport in Media with a Block and Channel Structure

The preceding discussion has been predicated on the assumption of the uniform flow of ground water through a body of soil. A different situation may occur in the case of an impermeable body of clay or glacial till. The body may be fractured into blocks so that most of the ground water flow takes place in the narrow channels between the blocks. Radiotracers present in the ground water would then be transported along the channels by convection but would be free to diffuse into or out of the soil blocks. The shape of the concentration-distance curve for the radioisotope would be governed by three factors: the size of the channels and blocks, the distribution ratio of the isotope, and the velocity of ground water flow in the channel.

Considering this model of radioisotope movement, it is apparent that if the diffusion is sufficiently rapid, relative to the flow velocity in the channel, the ion-exchange equilibrium assumption remains valid. This means that equation [26] still predicts the correct rate of movement of the tracer if U, the linear velocity of ground water flow, is calculated on the basis of a uniform flow of water through the soil body. Note that this U is not the actual velocity in a channel. Alternatively, the rate of movement of a tracer under these conditions may be predicted from:

$$W = U'(1 + 1/\lambda) \hspace{2cm} [36]$$

W : mean velocity of a front or band

U' : velocity of water in a channel

γ: dimensionless parameter

γ is defined in analogy to the diffusion theory of Crank (8) as:

$$= \frac{a}{\ell(1 + D)\mathcal{E}}$$ [37]

2a : width of a channel

2ℓ : width of a soil block

D : equilibrium distribution ratio of tracer

$\mathcal{E}$: void fraction of soil block

These equations are derived from the equilibrium distribution of the tracer between the soil and solution in a block and the solution in a channel.

If the assumption of ion-exchange equilibrium cannot be made, the situation becomes very complex. In order to investigate the convection-diffusion model a computer simulation was devised. The channel is assumed to be sufficiently small and the flow sufficiently slow that the solution may be considered to be homogeneous over a cross section perpendicular to the flow direction. A hypothetical column is divided into plates and the diffusion reaction within each plate is simulated by the method of finite differences (9). The result of the computer simulation is a plot of the concentration of the tracer in the channel and the average concentration in the block for each plate. The two dimensionless parameters which describe the curves are γ from equation [37] and T which is defined as:

$$T = \frac{D_o t}{(1 + D)\ell^2}$$ [38]

D_o : diffusion coefficient in solution

t : contact time in a plate

The contact time in a hypothetical plate is determined from:

$$t = \Delta/U^1 \qquad\qquad [39]$$

Δ : plate height

The concentration-distance curves for the block and channel model are illustrated in Figures 3, 4, and 5 for various values of the dimensionless parameters. It should be noted that the velocity of a front is governed mainly by the parameter γ but that the front in the channel leads the front in the block by an amount which depends upon the parameter T. If γ is small, however, most of the tracer will be contained in the block, and very little of the tracer will occur in the front of the channel.

Non-Equilibrium Theories

Since only the ions which are in the solution phase of a column at any given time are mobile, non-equilibrium theories attribute the dispersion of a front or band of radioactivity to the lack of equilibrium between the solution and exchanger phases (14). The statistical theory proposed by Newton (27) is also a non-equilibrium theory. This lack of equilibrium can occur if the solution velocity in the column is very high or if the isotope is sorbed at specific sites from which it is only slowly released. This second case is a good approximation to the fixation reaction which has been noted with tracers such as radiocesium.

Non-equilibrium transport theories may be expressed in terms of two parameters. One is the equilibrium distribution ratio of the tracer and the other is a function of the rate constant of the exchange reaction. The fixation reaction is a limiting case in which the distribution ratio D is assumed to be infinite; that is, the reaction goes to completion. The concentration-distance curve in the column for a step function input then reduces to:
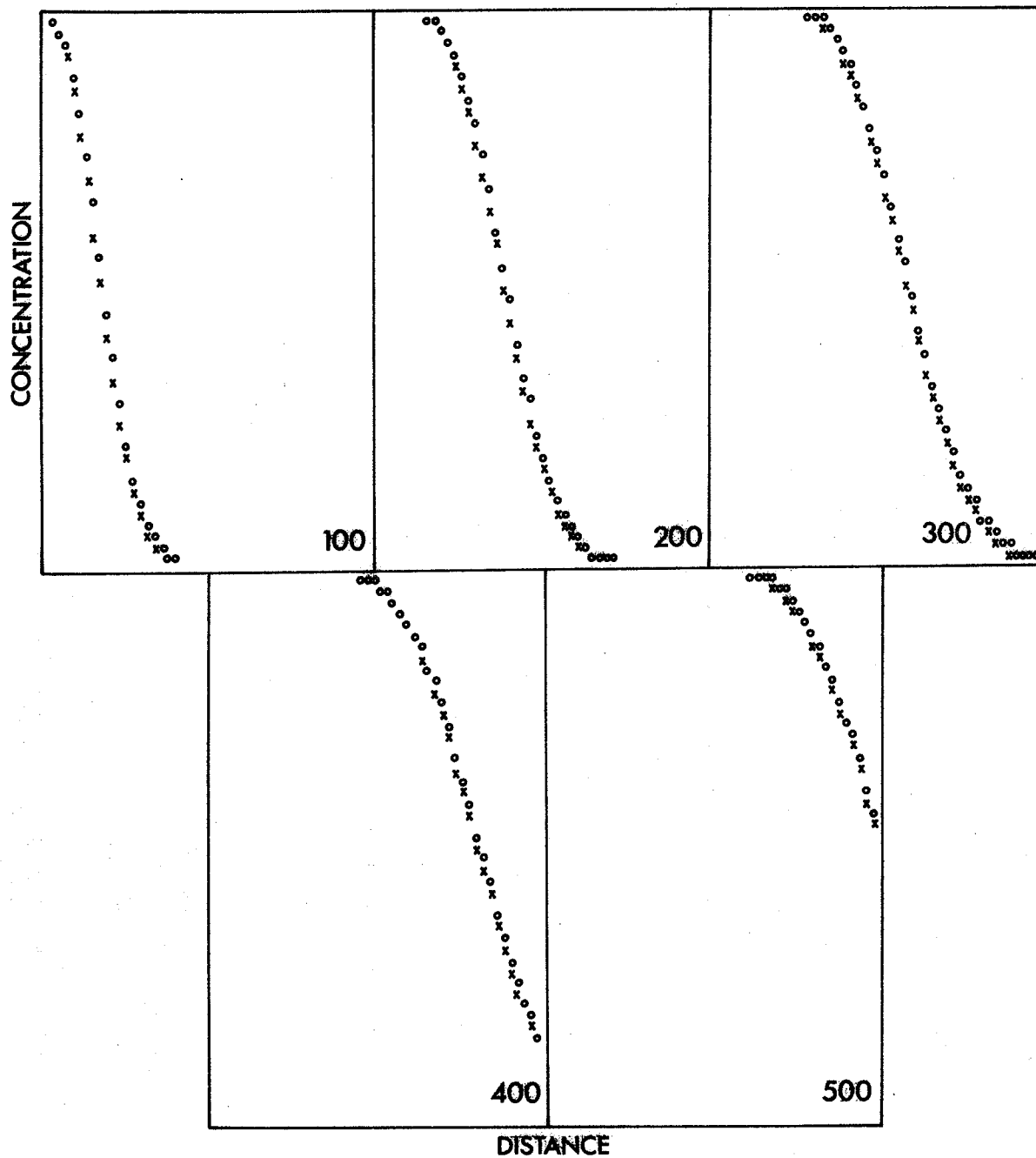
Figure 3. The convection-diffusion model: Relative concentration in solution (o) and concentration in the exchanger phase (x) along a column for a step function input of active ions. (a = 0.10, T = 0.050, the column length is 50 plates, and the five graphs represent inputs of 100, 200, 300, 400, and 500 plate pore volumes respectively.)
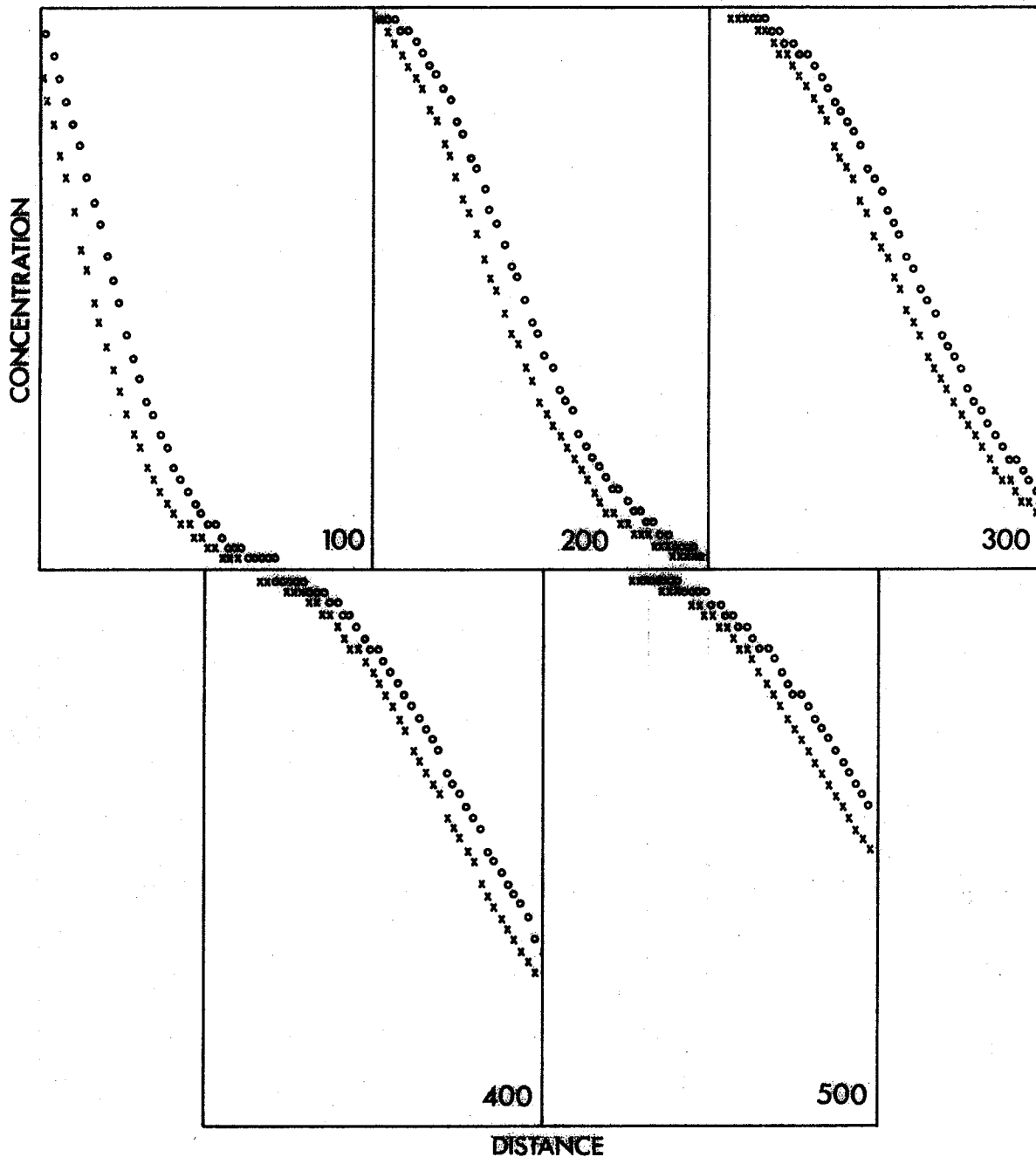
Figure 4. The convection-diffusion model: Relative concentration
in solution (o) and concentration in the exchanger phase (x) along a
column for a step function input of active ions. (a = 0.10, T = 0.010,
the column length is 50 plates, and the five graphs represent inputs of
100, 200, 300, 400, and 500 plate pore volumes respectively.)
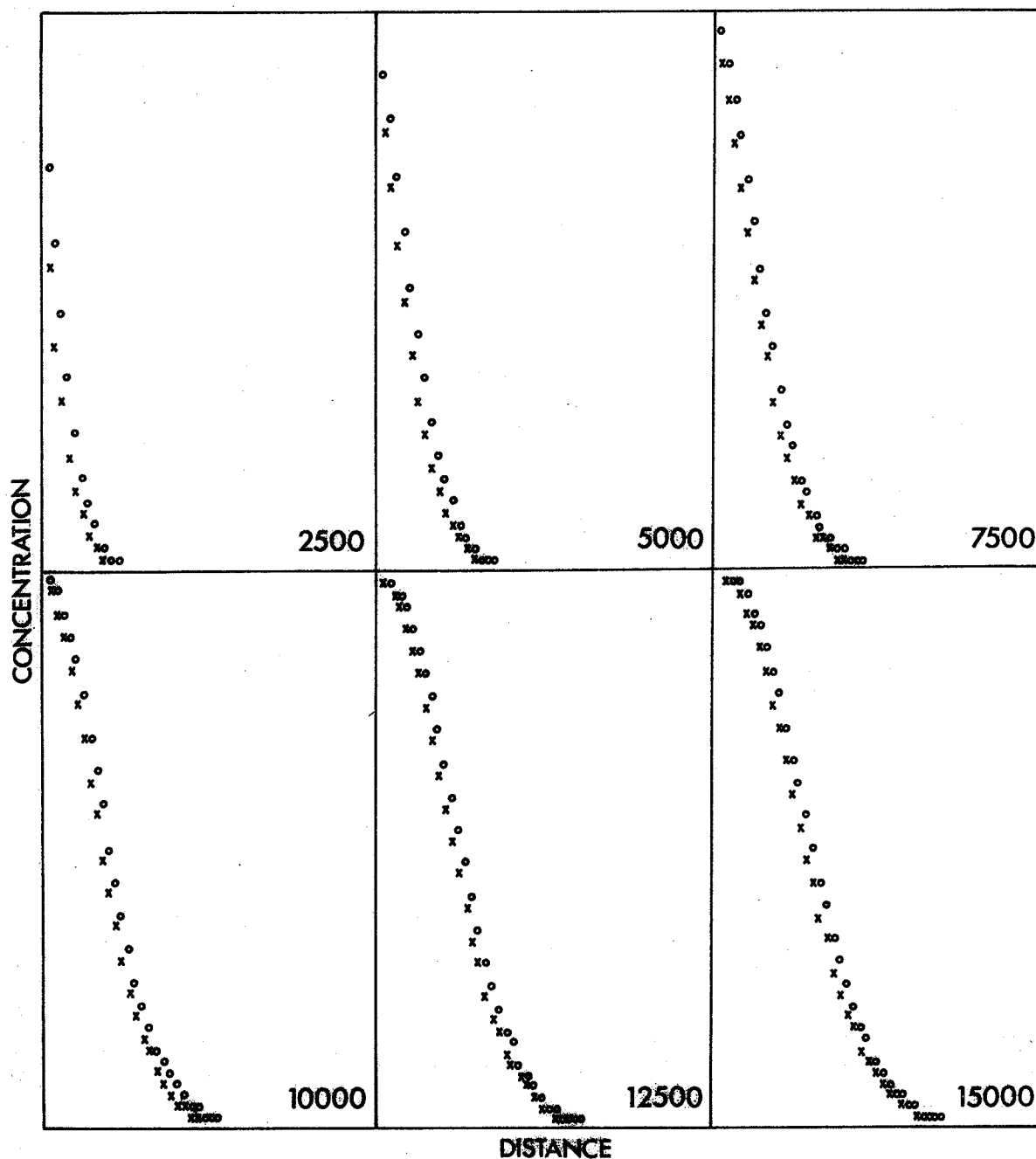
Figure 5. The convection-diffusion model: Relative concentration in solution (o) and concentration in the exchanger phase (x) along a column for a step function input of active ions. (a = 0.0010, T = 0.00020, the column length is 50 plates, and the six graphs represent inputs of 2500, 5000, 7500, 10000, 12500, and 15000 plate pore volumes respectively.)

$$C = Co/EXP \frac{kx}{U} \qquad [40]$$

C : concentration in solution

Co : influent concentration

k : forward rate constant

x : distance along column

U : solution velocity

The sorbed concentration is a similar exponential expression which increases with time. The concentration-distance curves of non-equilibrium theories are illustrated in Figures 6 and 7 for the reversible and fixation cases respectively. The dispersion parameter of the curves is:

$$\eta = kt \qquad [41]$$

η : dispersion parameter

k : forward rate constant

t : contact time in a plate

It should be noted in the illustrations that D is most important in front movement and η most important in dispersion of the front.
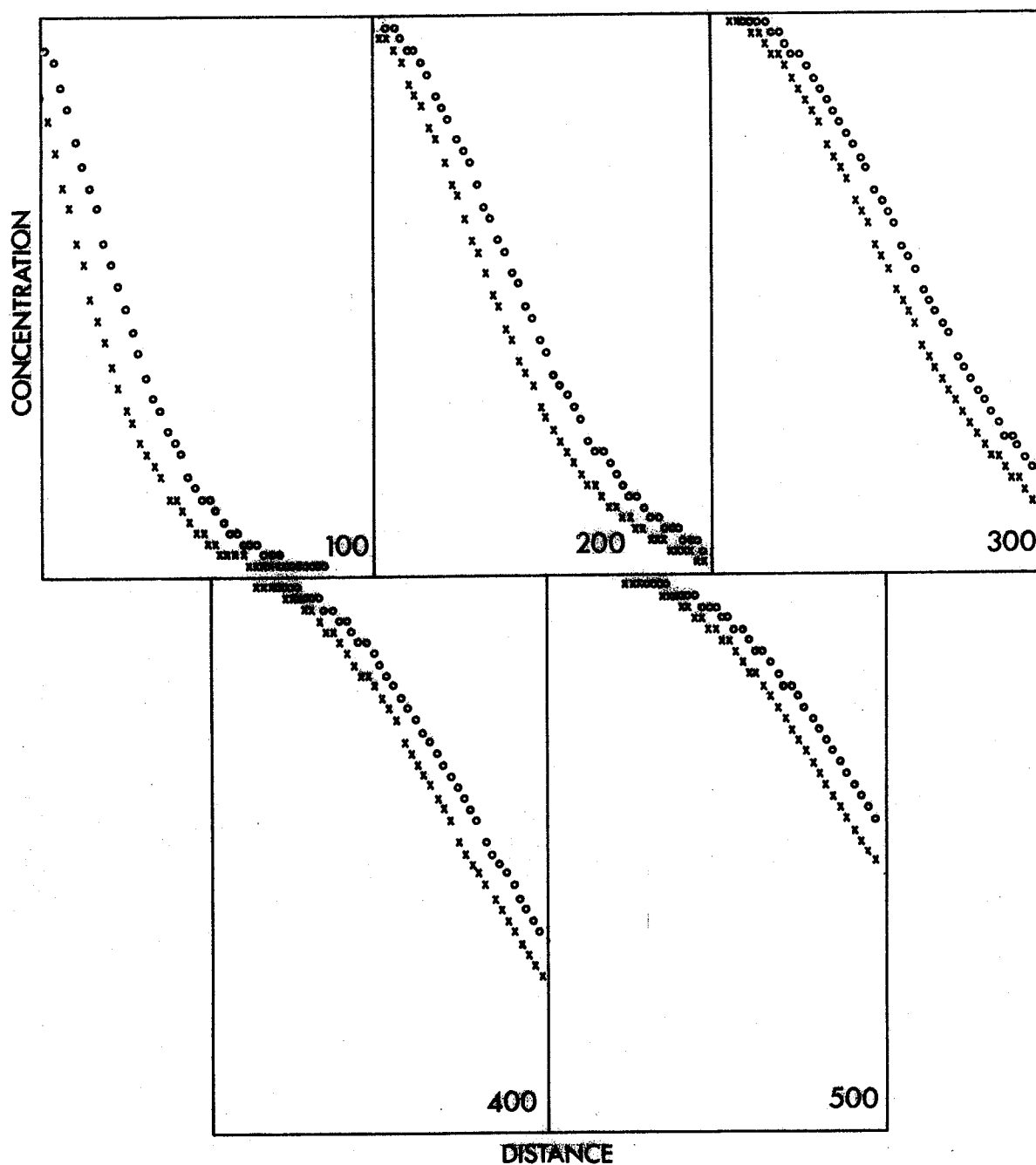
Figure 6. The non-equilibrium theory: Relative concentration in solution (o) and concentration in the exchanger phase (x) along a column for a step function input of active ions. ($D = 9$, $\eta = 0.20$, the column length is 50 plates, and the five graphs represent inputs of 100, 200, 300, 400, and 500 plate pore volumes respectively.)
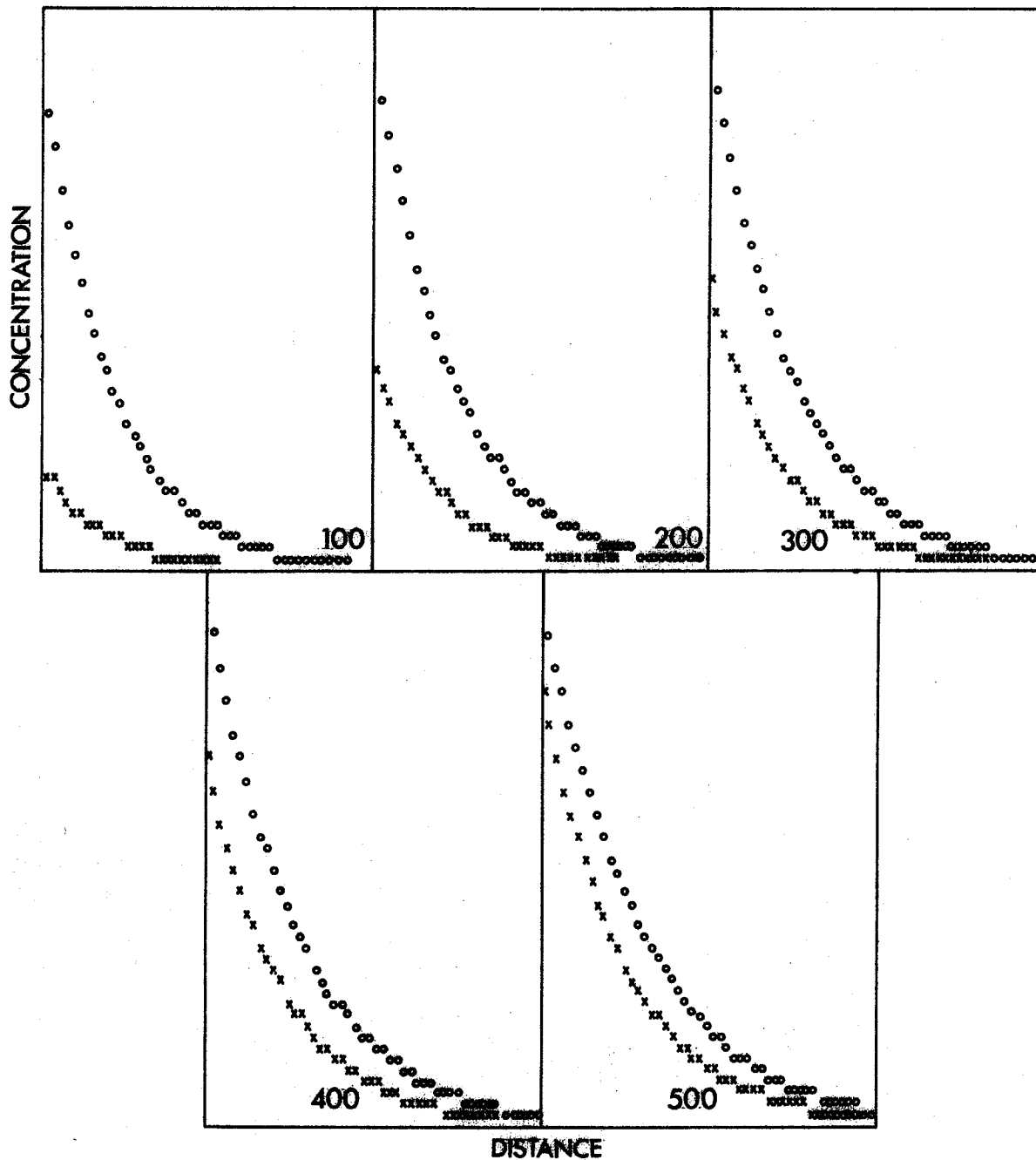
Figure 7. The non-equilibrium theory: Relative concentration in solution (o) and concentration in the exchanger phase (x) along a column for a step function input of active ions. (D = 99, η = 0.104, the column length is 50 plates, and the five graphs represent inputs of 100, 200, 300, 400, and 500 plate pore volumes respectively.)

CHAPTER III

METHODS AND MATERIALS

Soil materials used in this study were soil samples from the WNRE waste management area, sediment samples from the Winnipeg River, and a bentonite from Morden, Manitoba. A large number of methods were employed to characterize the materials as completely as was considered necessary. A few carefully chosen methods were used to investigate the various aspects of sorption of radiostrontium and radiocesium by the various materials.

I. MATERIALS

1. Soil Samples from the WNRE Waste Management Area

Location

The WNRE waste management area, shown in Figure 8, is located to the northeast of the plant site in Section 28 of Township 14, Range 11E. The area lies about one mile from the Winnipeg River and slopes gently in the general direction of the river.

Sampling

Seventy-seven soil samples were collected by WNRE personnel, at 18 to 24 inch intervals, during the installation of five observation wells, in the waste management area in the fall of 1967. The location of these wells is shown in Figure 8. Depth of the holes ranged from 21 to 30 feet. The samples were obtained with a 36 inch diameter auger.

Descriptions

The samples were examined visually, and simple chemical and physical tests were conducted to characterize the samples with regard to carbonate content, presence of concretions, texture, colour, iron mottling and quantity and nature of pebbles. Descriptions of the samples are presented
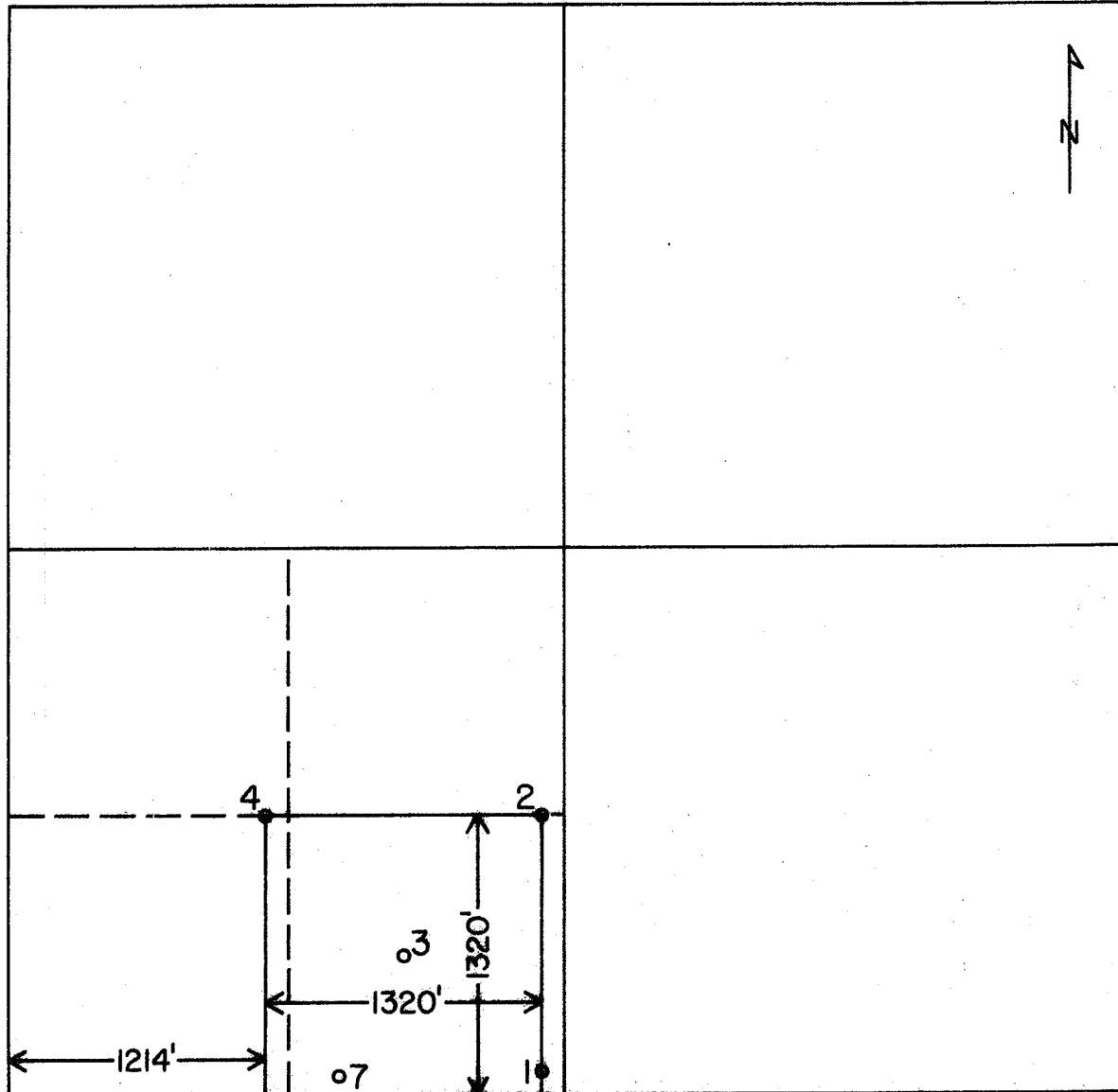
Figure 8. Plan of Section 28, Township 14, Range 11E, showing the location of the WNRE active waste manatement area and the five soil sampling sites.

in Appendix C. In general the surface deposit is a lacustrine clay. As illustrated in Figure 9 the clay is underlain by a clay loam till, which in turn is underlain by a sandy layer. The considerable variation in the character of the sediments in the various test holes is an indication of the complexity of the glacial deposits in the area. Texture* varies from clay at the surface to a medium sand in the deepest layers sampled implying that permeability of the lower layers is much higher than that of the over-lying sediments. Movement of water in the clay textured layers is probably very slow. The iron mottling shown in Figure 9 indicates a region of alternate oxidizing and reducing conditions due to a fluctuating water table. A net upward movement of groundwater in the waste management area is indicated by the finding of gypsum and carbonate concretions near the surface.

2. The Composite Soil Samples

The seventy-seven soil samples from the waste management area were combined on the basis of similar characteristics into five composite samples, each of the five samples being representative of a soil layer. The depth ranges from each test hole included in each composite are given in Table I. The soils were then air-dried, ground, and sieved at 2 mm. Analyses reported were conducted upon the less than 2 mm. soil.

Sample WDA1 is the surface foot and a half of the lacustrine clay and is dark-coloured due to the presence of organic matter. Sample WDA2 represents the remainder of the lacustrine clay, averaging six feet in thickness, and contains carbonate or gypsum concretions. Sample WDA3

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* Texture is the relative amounts of sand, silt, and clay in a soil sample. Further details and textural class nomenclature are found in Appendix D.
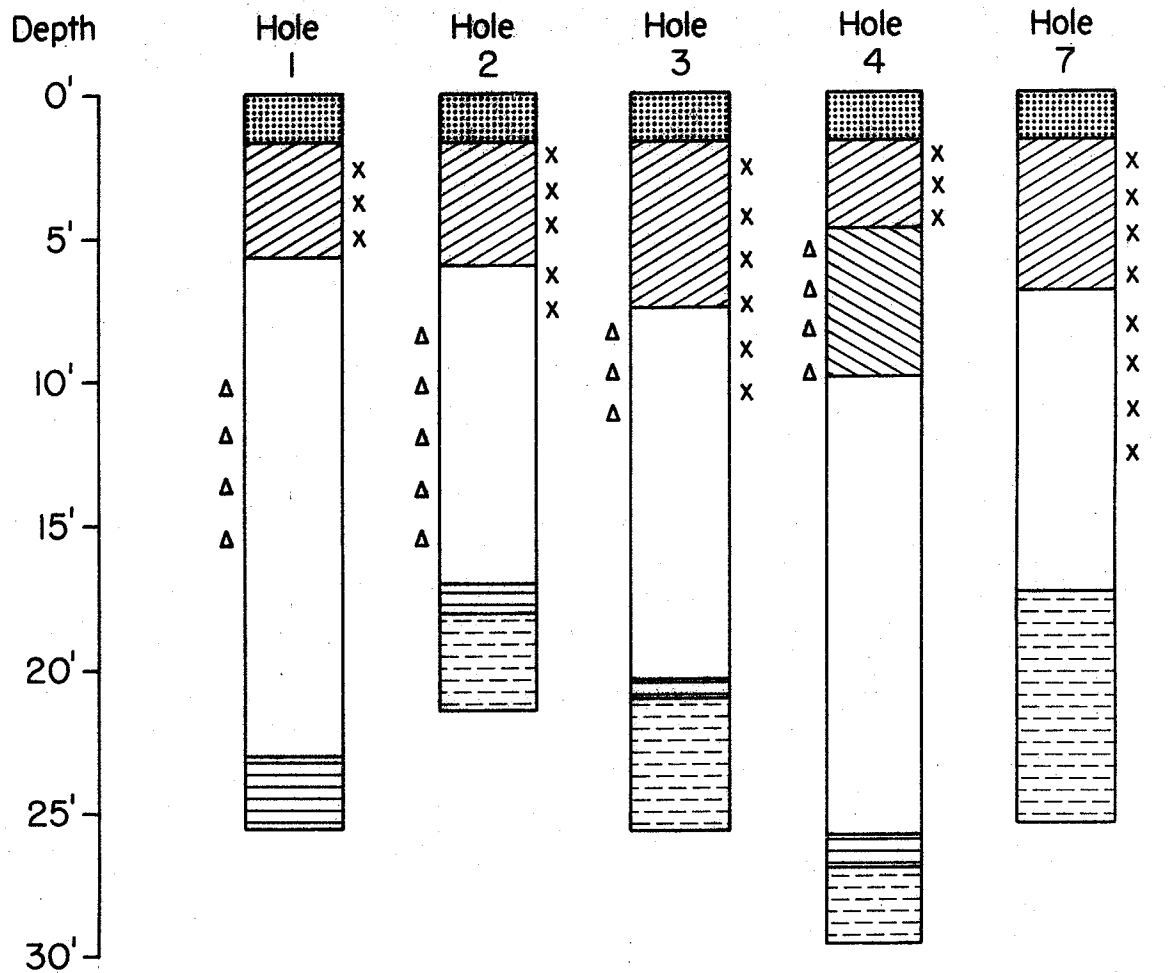
Figure 9. General characteristics of the soil samples from the WNRE waste management area.

represents the clay till which varies in thickness from 10 to 21 feet in
the waste management area. Sample WDA4 is a narrow transition zone between
the till and sand layers and may be an artifact due to the sampling process.
Sample WDA5 is representative of a sandy layer which at one point exceeds
eight feet in thickness and which probably rests on granite bedrock.

TABLE I

DEPTH RANGES OF SAMPLES INCLUDED IN COMPOSITES

Sample	Hole 1	Hole 2	Hole 3	Hole 4	Hole 7
WDA1	0-1'6"	0-1'6"	0-1'6"	0-1'6"	0-1'6"
WDA2	1'6"-5'8"	1'6"-6'0"	1'6"-7'4"	1'6"-4'9"	1'6"-7'0"
WDA3	5'8"-23'0"	6'0"-17'0"	7'4"-20'4"	4'9"-26'0"	7'0"-17'6"
WDA4	23'0"-25'6"	16'0"-18'0"	20'4"-21'0"	26'0"-27'0"	None
WDA5	None	18'0"-21'6"	21'0"-25'8"	27'0"-29'8"	17'6"-25'6"

3. Bottom Sediment Samples from the Winnipeg River

Five bottom sediment samples from the Winnipeg River were collected
from the sites indicated in Figure 10 by WNRE personnel in the summer of
1967. In addition the river water was sampled later that year at a
position opposite the plant site.

The sediment samples were air-dried, ground, and passed through a 2
mm. sieve. The fraction greater than 2 mm. was retained and designated
as pebbles. Further analyses were conducted on the less than 2 mm.
fraction.

4. The Morden Bentonite Sample

The Morden bentonite sample, a commercial bentonite sold under the
name of Filtaclay-75 and mined near Morden, Manitoba, was obtained from
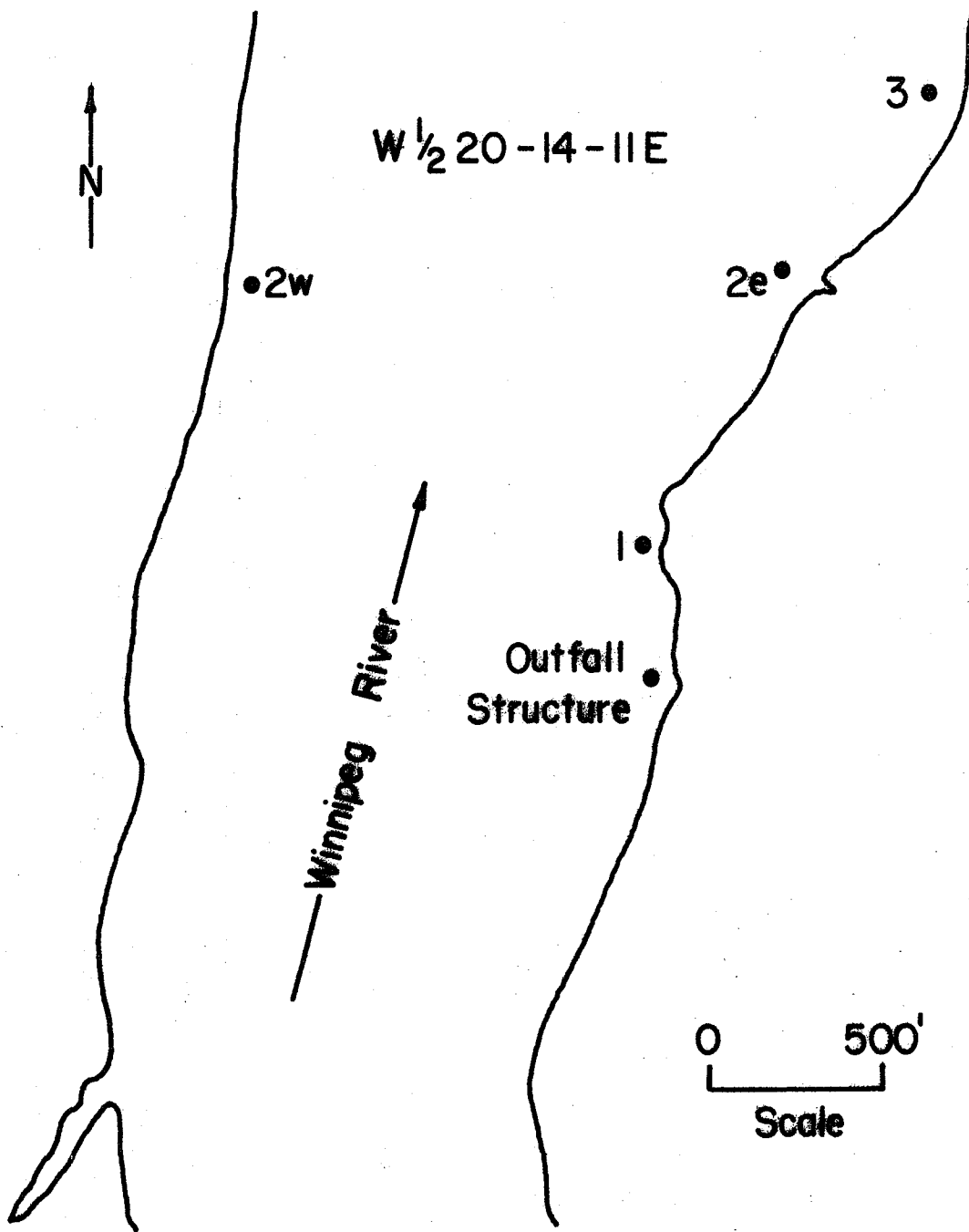
Figure 10. Location of the sediment samples from the Winnipeg River.

Pembina Mountain Clays Ltd., Winnipeg, Manitoba.

5. The Prepared Samples

These samples, which were used in some of the radioisotope sorption studies, were prepared from composite samples of WDA2 and WDA3 and the Morden bentonite sample. Some samples were prepared several times as stocks were exhausted. All the prepared samples were free of soluble salts. A list of the samples is given below:

Sample	Saturating Cation	Carbonates
WDA2	Ca	Removed
WDA3	Ca	Removed
WDA2	Ca	Present
WDA2	Mg	Present
WDA3	Ca	Present
Bentonite	Ca	None

For the preparation of one sample 500 grams of air-dry soil were placed in a 4000 ml. beaker and subjected to a number of treatments. Each treatment consisted of adding a solution, stirring the mixture well, allowing the soil to settle overnight, and siphoning off the clear supernatant. At the conclusion of a series of treatments, the final supernatant was removed and the soil was transferred to six 11 cm. Buchner funnels and vacuum flasks. When air began to pass through the filter cakes, they were transferred to a plastic sheet and air-dried. The samples were then ground and sieved to less than 2 mm. Sequence of treatment for various purposes are given below:

Carbonate Removal and Calcium Saturation for Composite Samples. For samples containing about 30% CaCO3 equivalent, add 3 liters of water and 70 ml glacial acetic acid. Adjust the pH to 4.5 with additional acetic acid and boil the sample gently for one-half hour. This constitutes the first treatment. Add 1 N calcium acetate, adjust the pH to 4.5 with acetic acid, and boil the sample one-half hour. Repeat this treatment two more times. Add water and adjust the pH to 7.0 with calcium hydroxide. Wash the sample five times with 1 N calcium chloride, once with water, three times with 0.01 N calcium chloride, and three times with ethanol.

Calcium or Magnesium Saturation of the Composite Samples. Wash the samples three times with water, five times with 1 N calcium or magnesium chloride, once with water, three times with 0.01 N calcium or magnesium chloride, and twice with ethanol.

Calcium Saturation of the Morden Bentonite. Wash the sample three times with water, and once with 1 N calcium acetate. Add 1 N calcium acetate and adjust the pH to 7.0 with calcium hydroxide. Add 0.5 N calcium chloride and adjust the pH to 7.0. Wash twice with 0.01 N calcium chloride and continue washing with ethanol until a negative chloride test is obtained on the supernatant.

II. METHODS

1. Particle Size Distribution

The distribution of particle diameters among the ranges designated as sand (2.0 to 0.05 mm), silt (50 to 2 microns), and clay (less than 2 microns) was determined by the pipette method (35). The sample was treated with hydrogen peroxide to destroy organic matter and was dispersed by overnight shaking with a Calgon* solution. Sand was removed by wet

* Product of Calgon Corporation, Pittsburgh, Pennsylvania.

sieving. The silt and clay were dispersed in a cylinder and the particles allowed to sediment. From samples of the suspension, obtained with a pipette at appropriate positions in the cylinder and at appropriate times, the silt and clay contents were determined.

2. Carbonate Mineral Content

The amounts of the carbonate minerals, calcite and dolomite, were estimated by the manometric method (43) which is based upon the different rates of decomposition of the two minerals in hydrochloric acid solutions. The sample was contained in a bottle and the progress of the reaction was followed by reading a manometer attached to the bottle which indicated the pressure of the evolved carbon dioxide. Calcite and dolomite were obtained by graphical analysis of the pressure versus time data. A calcium carbonate equivalent figure, which is the total carbonate content expressed as calcium carbonate, was also obtained from the total carbon dioxide evolved.

3. Soluble Salt Analysis

A 1:1 soil:water extract. Equal weights of air-dry soil and distilled water were mixed and allowed to stand in containers with tight fitting covers for sixteen hours. The slurry was then transferred to a dry filter paper in a Buchner funnel attached to a vacuum flask. The extract was collected in a test tube inside the vacuum flask.

A 1:2 soil:water extract. For the Morden bentonite one part of weight of air-dry sample was mixed with two parts of distilled water and the extract was obtained as outlined above.

The Electrical Conductivity and Magnesium Sulphate Equivalent of the Water Extract. The electrical conductivity of the water extract was obtained by means of a conductivity cell and a suitable resistance bridge

(35). If the soluble salts are predominantly calcium and magnesium sulphates, it is useful to calculate the magnesium sulphate equivalent from the conductivity, as this figure is a good approximation to the total concentration of the soluble salts (34). Magnesium sulphate equivalent is defined as the concentration of magnesium sulphate having the same electrical conductivity as the solution under consideration.

Chemical Analysis of the Water Extract. The water extract may be analyzed to determine its ionic constituents by conventional quantitative or qualitative methods. The most common constituents would be calcium, magnesium, sodium, potassium, sulphate, chloride, carbonate and bicarbonate ions. In this study, calcium and magnesium were determined by the EDTA method detailed below and other constituents were noted by qualitative tests.

4. Calcium and Magnesium Determination

All calcium and magnesium data reported in this study were determined by the EDTA method (35). In some instances only the calcium plus magnesium figure was required and calcium was not determined separately. When, as in some of the radiostrontium sorption experiments, the sample was known to contain only calcium, the calcium plus magnesium titration was employed and the result reported as calcium. Details of the EDTA method are given below:

Reagents

    (1) Sodium Diethyldithiocarbamate Solution - 1% in water.

    (2) Buffer Solution, pH 10 - Mix 135 g of NH_4Cl and 1140 ml of concentrated NH_4OH and dilute to 1800 ml. Add 50 ml of the standard magnesium solution and an equivalent amount of the

EDTA solution. Dilute to 2000 ml.

(3) Hydroxylamine Hydrochloride - $NH_2OH \cdot HCl$ - powder.

(4) Potassium Cyanide Solution - 2% in water.

(5) Eriochrome Black T Indicator (EBT) - Grind 0.25 g of the dye with 50 g of KCl powder.

(6) Sodium Hydroxide Solution (6N) - 240 g/l.

(7) Cal-Red Indicator (Dilute).

(8) Standard Calcium Solution (0.0200 N) - Dissolve 1.000 g of dry $CaCO_3$ in a minimum of HCl and dilute to 1000 ml with distilled water.

(9) Standard Magnesium Solution (0.0200 N) - Dissolve 1.2039 g of dry $MgSO_4$ in water and dilute to 1000 ml.

(10) Disodium Dihydrogen Ethylenediamine Tetraacetate Solution (EDTA) (0.01 N) - Dissolve 1.8612 g of $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$ in water and dilute to 1000 ml.

Calcium Plus Magnesium Titration

Place the aliquot of the sample solution, containing up to 0.5 meq of Ca and Mg, in the titration flask and dilute to 50 ml with water. Add 2 drops of carbamate, 5 ml of buffer, a few crystals of NH_2OH, 1 ml of KCN, and a pinch of EBT. Titrate with EDTA to a pure blue end point. Similarly titrate a magnesium standard and a blank.

Calcium Titration

Place the aliquot, containing up to 0.5 meq of Ca, in the titration flask and dilute to 50 ml with water. Add 2 drops of carbamate, sufficient NaOH to bring the pH to 12.5 - 13, a few crystals of NH_2OH, 1 ml of KCN, and a pinch of Cal-Red. Titrate with EDTA to a pure blue end point.

Similarly titrate a blank.

Calculations

Calculate the normality of the EDTA from the titer of the standard and corresponding blank. Calculate the concentration of calcium plus magnesium or calcium in the sample from:

meq/l = (volume of EDTA - blank) x N x 1000/volume of aliquot [42]

N is the normality of the EDTA. The concentration of magnesium is determined by difference.

5. System Analysis of a Calcareous Soil

The following scheme of analysis was used to obtain the total water soluble salts, carbonate mineral content, and cation exchange capacity of calcareous soils.

Total Water Soluble Salts

Wash a 10.0 g sample of air-dry soil four times in a centrifuge tube. Begin the washing with water and change first to 50% ethanol and then to 95% ethanol when the soil begins to disperse. Combine the decantates, boil to expel the ethanol, and dilute to 500 ml. Determine calcium and magnesium on a suitable aliquot of the combined decantates. Other constituents may also be determined.

Carbonate Mineral Content

Transfer the now salt-free soil to a beaker, add 6 N HCl in an amount equivalent to the carbonate content, and adjust to pH 4 with HCl. Boil gently for a few minutes, and centrifuge the liquid portion of the suspension. Retain the clear supernatant and transfer the precipitate back to the beaker. Repeat the pH adjustment, boiling, and centrifugation three more times, combining the clear supernatants. Wash the soil with

water, which has been adjusted to pH 4 with H_2SO_4, until a negative

chloride test is obtained on the washings. Combine the washings with the

previous supernatants and dilute to 1000 ml. Determine calcium and

magnesium upon a suitable aliquot of the solution. (It may be necessary

to remove the R_2O_3 group before determining calcium and magnesium.)

Calculate the calcite and dolomite contents of the soil from the theoret-

ical formulae $CaCO_3$ and $CaMg(CO_3)_2$ respectively.

Cation Exchange Capacity

Wash the carbonate-free sample once with 1 N calcium acetate adjusted

to pH 7, once with 1 N calcium chloride, and once more with the calcium

acetate. Wash twice with 0.01 N $CaCl_2$, wash with ethanol until a negative

chloride test of the supernatant is obtained. Wash four times with 40 ml

portions of 1 N ammonium acetate, combining the decantates and diluting

to 250 ml with ammonium acetate. Determine calcium upon an aliquot of

the ammonium acetate extract and calculate the cation exchange capacity

of the soil.

6. Selective Dissolution and Particle Size Separation

Samples upon which a mineralogical analysis was desired were treated

to remove soluble salts, exchangeable cations, carbonates, organic matter,

and free iron oxides, were boiled in sodium carbonate, and were separated

into particle size fractions by the methods of Jackson (16). Brief

outlines of the various procedures are given below.

Removal of Soluble Salts, Exchangeable Cations, and Carbonates

The sample was treated with an acetic acid - sodium acetate buffer

having a pH of five. Boiling several times in this solution and subsequent

washing selectivity removed soluble salts and carbonates and displaced the

exchangeable cations.

Removal of Organic Matter

Organic matter was removed by several treatments with hydrogen peroxide.

Extraction of Free Iron Oxides

Sodium dithionite was used as a reducing agent and sodium citrate as a complexing agent to dissolve selectively the free or amorphous iron oxides from the sample.

Removal of Colloidal Silica and Alumina

The sample was boiled in a sodium carbonate solution in order to remove cementing materials such as colloidal silica and alumina and complete the dispersion of the soil particles.

Separation into Particle Size Fractions

Separation of the sand fraction was accomplished by wet-sieving. The finer fractions were separated by repeating sedimentation and decant-ation using gravitational or centrifugal acceleration. Soils are normally separated into the following ranges of particle diameters:

Sand	2.0 mm to 0.05 mm (50u)
Coarse Silt	50 u to 20 u
Medium Silt	20 u to 5 u
Fine Silt	5 u to 2 u
Coarse Clay	2 u to 0.2 u
Fine Clay	Less than 0.2 u

Any fraction may be further subdivided if the situation warrants.

7. Clay Mineral Analysis

The clay mineral content of the samples was investigated by means of

X-ray diffraction, chemical analysis, and cation exchange capacity

determinations. In some cases quantitative estimates of mineral species

or components were obtained.

X-Ray Diffraction Analysis

The X-ray diffraction analysis was carried out in accordance with

the methods given by Jackson (17). The equipment used was a Philips X-ray

generator equipped with a cobalt target tube, and a Philips diffractometer

and powder camera. Parallel orientated specimens for the diffractometer

were prepared by drying a slurry of the fine clay, coarse clay, or fine

silt on a glass slide. Two slides were prepared for each fraction of each

sample: a magnesium saturated glycerol solvated specimen and a potassium

saturated specimen. The potassium saturated specimen was X-rayed after

drying at room temperature and after heating at $300^{\circ}C$ and $550^{\circ}C$ so that,

for each fraction, four diffractograms were obtained.

The powder camera technique was used only with the Morden bentonite

sample. The specimen, which was mounted in a capillary, was a calcium or

magnesium saturated glycerol solvated sample of the coarse clay. It was

prepared as a random powder by the benzene-ethanol method of Jackson (17).

In general the interpretation of the diffractograms and films followed

the identification criteria given by Brown (5).

Chemical Analysis of Clay Fractions

Clay fractions were prepared for chemical analysis by saturation with

a particular cation, removal of soluble salts and oven-drying at $105^{\circ}C$.

In general the scheme of analysis followed was similar to that given by

Shapiro and Brannock (41). A sodium hydroxide fusion was used for silica

and alumina which were determined by the molybdenum blue method and the

aluminon method, respectively. A solution prepared by a hydrofluoric-sulphuric acid fusion was used for the determination of the remaining oxides. Titania was determined by the tiron method, total ferric oxide by the orthophenanthroline method, lime and magnesia by the EDTA method, and soda, potash and lithia were determined by flame photometer. The ignition loss, by heating at $900^{\circ}C$ for two hours, was also determined.

Cation Exchange Capacity

The cation exchange capacity of the clay fractions was determined by a method similar to the one used by Jackson (1). Approximately 200 mg of clay was treated three times with the sodium acetate buffer of pH 5 in a 90 ml centrifuge tube. The clay was then washed three times with 2 N sodium chloride, twice with 50% ethanol, and once with 95% ethanol. The clay was washed with acetone to remove the last traces of chloride as indicated by qualitative tests on the supernatant. The sodium saturated clay was then transferred to a 15 ml centrifuge tube and was washed five times with 15 ml portions of 0.5 N magnesium chloride, the decantates being combined and diluted to 100 ml with magnesium chloride. Sodium was determined by flame photometry on a five time dilution of this extract by comparisons with standards of zero to 20 ppm sodium in 0.1 N magnesium chloride solutions. The clay was washed three times with ethanol and was dried in the tubes at $107^{\circ}C$ to obtain the sample weight. The cation exchange capacity was calculated from the flame photometry data and the sample weight.

Quantitative Clay Mineral Analysis

The mica content, including discrete mica and mica layers in inter-stratified species, was estimated on the assumption of a 10% K_2O content

of the pure mineral. Similarly montmorillonite, in the absence of vermiculite, was estimated from the equation given by Jackson (1):

$$\% \text{ mont} = \frac{CEC - 5}{105} \times 100 \qquad [43]$$

CEC : cation exchange capacity in meq/100 g.

8. Hydraulic Conductivity

A constant head method (21) was used for the hydraulic conductivity determinations. Specimens were contained in polystyrene tubes having an inside diameter of about 3 cm. Dilute calcium chloride was used as the feed solution in order to prevent dispersion of the clay. The pressure head ranged from 40 to 60 cm. To minimize evaporation, the effluent was collected in polyethylene bags which were attached to the columns with elastic bands. Specimens were prepared by two quite different techniques: (1) The dry 2 mm soil was loaded into the cylinders and was subsequently wetted, (2) The soil was mixed with water, puddled in a high speed stirrer, and poured into the cylinders.

9. Analysis of Soil Moisture

Two methods were used to obtain a chemical analysis of the soil moisture at specific moisture contents:

Extraction of Moisture with a Pressure Extractor

A volumetric moisture extractor* was used to extract moisture from slurries prepared at moisture contents between field capacity and saturation. The method is given below:

Mix 200 to 1000 grams of air-dry soil with an appropriate amount of distilled water. Cover the slurry tightly and allow it to stand overnight.

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* Supplied from Soilmoisture Equipment Co., Santa Barbara, California.

Rinse the porous plate of the extractor by passing distilled water through it and dry the plate overnight by passing air over both surfaces. Then transfer the slurry to the extractor and press it into contact with the plate. The soil pad must form a good seal at the edges to prevent air leaks through the plate. Remove a subsample of soil for a moisture determination and close the chamber. Apply air pressure of one third atmosphere to the chamber and begin to collect approximately five milliliter portions of the soil solution. When outflow ceases, increase the pressure in steps up to a limit of two atmospheres and continue the collection. Calcium and magnesium are determined upon the collected solutions by the EDTA method.

Extraction of Moisture at the Saturation Point

Approximately 100 g of air-dry soil was mixed with distilled water until the s aturation point was reached as evidenced by the characteristic appearance (35). The paste was covered tightly and allowed to stand for 16 hours at which time it was well mixed with a spatula and a subsample was taken for a moisture determination. A Buchner funnel was assembled to a suction flask and the paste was transferred to a dry filter paper in the funnel, the extracted moisture being collected in a test tube in the flask. Calcium and magnesium were determined on the extract by the EDTA method.

10. Exchangeable Cations and Cation Exchange Capacity

Two methods were used for the determination of the exchangeable cations and cation exchange capacity of soils and prepared samples:

The 2 N Sodium Chloride Method

This method has been developed for the determination of the exchange-

able calcium and magnesium and the exchange capacity of calcareous soils.
In the case of soils containing an appreciable quantity of soluble salts
of calcium and magnesium the analysis of the NaCl leachate will represent
both exchangeable and soluble cations but the analysis of the $MgCl_2$
leachate will still represent the cation exchange capacity unless the
soluble salts are present in such a quantity that they are not fully
removed by the MaCl leaching. Detailed instructions follow:

(1) Weigh 25.0 gm of air-dry soil into 250 ml beakers.

(2) Wet the soils with 25 to 50 ml of 2 N NaCl solution and allow to
stand for one hour.

(3) Using a stream of 2 N NaCl from a wash bottle quantitatively transfer
the soils from the beakers to 11 cm Buchner funnels fitted with
Whatman No. 42 filter papers. Catch the filtrate in 250 ml suction
flasks.

(4) Leach the soils with small portions of 2 N NaCl until the leachate
volume reaches approximately 225 ml.

(5) Dilute the leachates to 250 ml with 2 N NaCl and determine exchange-
able calcium and magnesium by suitable analysis of the leachate.

(6) Leach the soils with 95% ethanol in small portions until the liquid
dripping from the tip of the funnel is free of chloride as revealed
by tests with $AgNO_3$.

(7) Discard the alcohol leachate and rinse the flasks with distilled water.

(8) Leach the soils with 200 ml of 1 N $MgCl_2$ in small portions. Dilute
the $MgCl_2$ leachates to 250 ml with 1 N $MgCl_2$ in volumetric flasks
and store in poly bottles.

(9) The cation exchange capacity is determined by a suitable analysis of

the sodium content of the $MgCl_2$ leachate.

(10) Exchangeable calcium and magnesium and the cation exchange capacity

are expressed in terms of milliequivalents for 100 gm of air-dry

soil.

The Ammonium Acetate - Centrifuge Washing Method

Ten gram samples were washed with 70 ml of 1 N ammonium acetate a

total of six times. The combined decantates were diluted to 500 ml and

an aliquot taken for analysis. Ammonium acetate was removed from the

aliquot by evaporation with nitric acid and calcium and magnesium were

determined by EDTA titration.

11. Analysis of Water Samples

Electrical conductivity was determined with a conductivity cell and

a resistance bridge. Calcium and magnesium were determined by EDTA.

12. Moisture Determinations

The sample, upon which moisture was to be determined, was placed in

a tared tin box with cover. The weight was determined and the sample,

with the cover open, was dried in the oven at $107^{\circ}C$ for 24 to 48 hours.

The box was recovered, cooled in a desiccator for one half hour, and again

weighed. The moisture percentage was equal to the weight loss upon drying

as a percent of the dry soil weight. In some cases the water content was

calculated from the weight loss as a percentage of the wet soil weight.

13. Non-Solvent Water Content

Non-solvent water content was determined by the methods in Appendix

A.

14. Radioactivity Counting Procedures

Three radioactivity counting techniques were used; a Philips PW4251

counter, ratemeter, and single channel pulse height analyzer was used with all of these. The various detectors and procedures are given below.

Beta Counting with an End-Window Geiger Tube

A Philips 18536 end-window Geiger tube was positioned in a lead castle with the window facing downward. A three milliliter aliquot of the solution to be counted was placed in a 5 ml beaker which was positioned directly below the window of the Geiger tube. All counts were corrected for background and, to correct for coincidence, some solutions were diluted so that all samples counted produced approximately 20,000 counts in 1000 seconds.

Beta Counting with a Glass Wall Geiger Tube

By pipette, 10 ml aliquots of the beta emitting solution were introduced into a Baird-Atomic Number 8-725 glass wall pour-in type Geiger tube. All counts were corrected for background and in order to correct for coincidence the amounts of the radioisotope used and the dilutions of some solutions were adjusted to produce approximately 50,000 counts in 1000 seconds.

Gamma Scintillation Counting

Gamma-emitting specimens were inserted into the well of a Conuclear well-type scintillation probe which was situated in a lead castle. The window of the pulse height analyzer was adjusted to accept the 0.514 mev. photopeak of Sr-85 or the 0.662 mev. photopeak due to Cs-137. Liquid specimens were contained in 6 ml flat bottomed vials. Since the counting efficiency is a function of the geometry of the specimen, the same volume of liquid, measured by pipette, was used for specimens which were to be compared to each other. All counts were corrected for background.

15. Radiostrontium Sorption Determinations

Two radioisotopes of strontium were used in the sorption determinations. Sr-89[*] was received as 1 mc of Sr-89 in 0.15 ml of 1 N HCl. This was diluted with distilled water to 1000 ml and aliquots of this stock were used to prepare the solutions for the sorption studies which contained calcium chloride in the range of 5 to 40 meq/l and Sr-89 in the range of 10 to 80 uc/l. Sr-85^{+} was received as 1 mc of Sr-85 in 1 ml of 0.5 N HCl. A stock solution of Sr-85 was prepared by diluting the isotope to 100 ml with distilled water and aliquots of this stock were used to prepare solutions for the sorption studies which contained about 20 uc/l of Sr-85 and 5 to 40 meq/l of calcium chloride. No difficulty was encountered in handling the active solutions with ordinary glassware and in using ordinary chemical laboratory techniques.

Two very similar methods were used in the radiostrontium determinations, one being used with calcium saturated non-calcareous soils and calcium chloride solutions, and the other being used is systems of calcareous soils and solutions containing both calcium and magnesium. These are outlined below.

Calcium-Radiostrontium Equilibria Method

Transfer the required weight of air-dry soil into a 45 ml screw-capped centrifuge tube. Add the required volume of the radioactive solution to the tube with the aid of a pipette. Cap the tube, shake well by hand until the soil is well suspended, and shake the tube overnight on an oscillating shaker. Assemble a 5.5. cm poly Bucher funnel to a suction flask and

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[*] Supplied by Oak Ridge National Laboratory, Oak Ridge, Tennessee.
[+] Supplied by Nuclear Science Division, International Chemical and Nuclear Corp., Pittsurgh, Pa.

insert a test tube to catch the filtrate. Filter the suspensions with a Whatman No. 42 filter paper and retain the clear filtrate. Count the radioactivity of an aliquot of the filtrate and an aliquot of the original solution. Determine the calcium concentration of the filtrate by EDTA titration. The aliquots used for counting may also be used for the titration.

The calculations for an experiment were begun with a determination of the solvent volume of the system:

$$V = V_1 + \frac{(V_m - V_n)\ m}{100} \qquad [44]$$

V : solvent volume

V_1 : volume of solution added

V_m : air-dry moisture percentage

V_n : non-solvent water percentage

m : weight of oven-dry soil

The amount of calcium in the two phases was calculated by:

$$(Ca)x = Cm \qquad [45]$$

$$(Ca)s = (T - b)N\ V/A \qquad [46]$$

$(Ca)x$: total meq of calcium in the exchanger phase

$(Ca)s$: "   "   "   "   " " solution   "

C : cation exchange capacity as meq/g

T : titration volume of EDTA for sample

b :   "   "   "   "   " blank

N : normality of EDTA

A : aliquot of sample for titration

and the calcium distribution ratio by:

$$CaDR = (Ca)x/(Ca)s \qquad [47]$$

The total radiostrontium in the system was calculated by:

$$(Sr)_o = (Sr)_1 \frac{V_1}{V} \qquad [48]$$

$(Sr)_o$: total radiostrontium in the system

$(Sr)_1$: radiostrontium activity in the original solution

The activity in the solution phase was determined by direct counting and

the activity in the exchanger phase by:

$$(Sr)_x = (Sr)_o - (Sr)_s \qquad [49]$$

$(Sr)_x$: activity in the exchanger phase

$(Sr)_s$:   "   " " solution   "

Then the strontium distribution ratio was calculated by:

$$SrDR = (Sr)_x/(Sr)_s \qquad [50]$$

and the equilibrium constant by:

$$K = SrDR/CaDR \qquad [51]$$

Method for Calcium-Magnesium-Radiostrontium Equilibria with Calcareous Soils

The method used was identical to the above method except that both

calcium and magnesium concentrations in the solution phase were determined

by the EDTA method.

With a few changes the calculations also followed the scheme used

with the above method. Calcium and magnesium in the solution phase were

calculated from the EDTA titration data. Calcium and magnesium in the

exchanger phase were determined from a mass balance of calcium and magnesium

originally in the soil and solution and in the final system after mixing.

The quantity $m/(Ca + Mg)s$ of equation [12] was then calculated. Final data

obtained were the equilibrium constants of equations [4] and [9] and KC of

equation [12]. The equivalent fraction of magnesium in solution was also

calculated to be used in connection with equation [11].

16. Reversibility of the Calcium-Radiostrontium Exchange

In order to test the reversibility of the Sr-Ca ion exchange, a technique was devised whereby the final equilibrium was approached both from the direction of high radiostrontium sorption and from the direction of low radiostrontium sorption.

To approach equilibrium from the direction of high sorption, 15.0 grams of air-dry soil were placed in a centrifuge tube and 25.0 ml of a very dilute calcium chloride solution containing Sr-85 was added. The soil was well suspended by hand shaking and was shaken mechanically overnight. Then 10 ml of 1 N calcium chloride solution was added to cause desorption of much of the radiostrontium and the tube was again shaken overnight. The suspension in the tube was then centrifuged and an aliquot of the clear supernatant was taken for scintillation counting. A similar method was used to approach the equilibrium from the direction of low sorption except in this case the calcium chloride was added before the first overnight shaking and the radiostrontium was added before the second shaking.

17. Desorption of Sorbed Radiostrontium

Another experiment concerning irreversibility was designed to permit direct counting of the Sr-85 activity sorbed to the soil. One gram samples of soil were placed in screw-capped test tubes of the proper dimensions to fit the well of the scintillation crystal. With this technique, after treatment with a solution, the tube could be centrifuged, the supernatant discarded, and the activity in the sediment determined. The disadvantage of this technique is that the maximum amount of radioactivity that could

be removed in one treatment is limited by the ion-exchange reaction and the volume of solution held up in the sediment.

Five milliliters of a dilute calcium chloride solution containing Sr-85 was added to each tube and the mixtures were shaken overnight. The tubes were centrifuged, supernatants decanted, and radioactivity determined. The samples were then washed five times with 1 N calcium chloride with counting following each washing. Calcium chloride was added and the samples again shaken overnight with the washing continued in the morning. Following this was one additional calcium chloride washing. The samples were then treated twice with a sodium acetate buffer which is normally used for carbonate removal, with counting following each treatment.

18. Kinetics of Radiostrontium Sorption

Five grams of air-dry soil and 100 ml of 0.02 N CaCl$_2$ were placed in 200 ml centrifuge bottles. At zero time, 10 ml of Sr-89 solution was added and the samples were shaken mechanically. At specific intervals of time, the bottles were centrifuged and a 10 ml aliquot of the clear supernatant withdrawn for beta counting. After counting the aliquot was returned to the system and shaking was resumed. Total radiostrontium was determined by counting aliquots of a similar solution to which no soil was added.

19. Radioisotope Sorption in Columns

The construction of the columns is illustrated in Figure 11. When in use, the inlet of the column was connected via a three-way stopcock to a length of PVC tubing which was connected to the feed solution reservoir. A head of about 120 cm was required. The lower end of the column entered
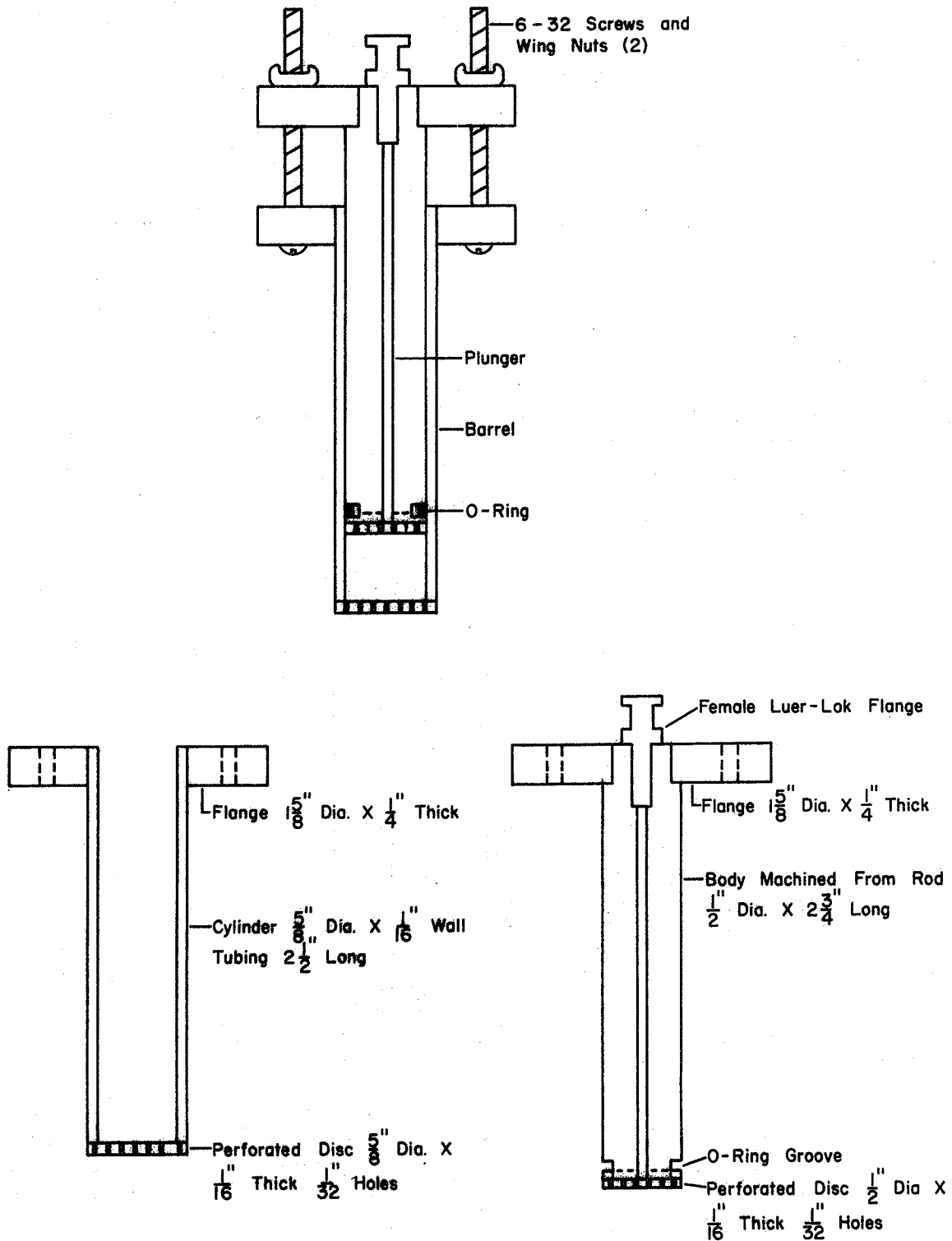
Figure 11. Construction of the columns used in the sorption experiments with Sr-85 and Cs-137.

a flask or vial in which the effluent was collected. Evaporation was prevented by a plug of cotton.

To prepare a column for use, a one-half inch Whatman number 42 filter paper was inserted into the barrel section. Air-dry soil was then transferred into the barrel with the use of a funnel, the weight being determined from the gross and tare weights. A second filter paper was placed on top of the soil and the plunger section, with the O-ring suitably lubricated, was inserted into the barrel. The wing-nuts were then attached and the three-way stopcock connected to the inlet fitting of the column. The lower end of the column was then placed in water and a slight suction applied to wet the soil. After the soil was thoroughly wetted, the column was placed in a beaker of the non-active feed solution and suction was applied to the inlet. In this manner the solution was passed through the column until all air was expelled. The column was then connected to the reservoir of non-active feed solution and the wing-nuts were tightened to establish a suitable flow rate. The column was run over night with this feed solution and was then ready for the radio-isotope sorption experiment.

To begin a sorption experiment, the feed was changed to an identical solution which contained the radioisotope. This feed was continued until the radioactivity in the effluent was equal to that in the feed or until the run was terminated. At various times during a run as well as at the end of a run, the feed tubing was disconnected, a rubber device slipped over the end of the column, and the assembly inserted into the well of the scintillation crystal for counting. Aliquots of the feed solutions and blanks were also counted and during some runs, aliquots of the effluent

were counted. After the column was counted it could be reconnected to the feed tubing and the run continued if desired.

At the end of a run, the length of the soil plug was measured. The column was then disassembled and the plug expelled from the barrel by means of air pressure. The plug was transferred to a tared tin box and a moisture determination made upon it.

Since the counting efficiency of the scintillation crystal is a function of the dimensions of the specimen inserted into the well, a curve was constructed to correct for changes in counting efficiency due to the length of various soil plugs. A curve was also constructed to correct for the radioactivity contained in the dead volume above the soil plug. Both corrections were minor, amounting to a few percent.

The pore volume of the system was calculated from the moisture determination on the soil plug

$$\text{Pore Vol.} = \text{water loss at } 110^{\circ}\text{C} \times \frac{\text{oven-dry soil weight}}{\text{oven-dry plug weight}} \quad [52]$$

From these data and the length of the plug the bulk density and the particle density were also calculated. The solvent volume was calculated from the pore volume and the non-solvent water data. The activity in the solution phase was calculated from:

$$\text{Solution activity} = \text{Feed solution activity} \times \frac{\text{solvent volume}}{\text{feed solution aliquot}} \quad [53]$$

and the activity in the exchanger phase from:

$$\text{Exchange activity} = \text{Total activity} - \text{solution activity} \quad [54]$$

From these data the distribution ratio of the isotope was calculated.

These techniques were used in experiments with Sr-85 and Cs-137 and, in addition, an investigation of the Cs-137 activity in the effluents from the columns was carried out. Details of the methods are given below.

Radiocesium Sorption in Column Experiments

Active and non-active feed solutions were prepared to be identical
in chemical composition except that Cs-137 was added to the active solution
to a level of about 3 μc/l. The composition of the five solutions and the
corresponding soil samples are given in Table II. Sorption from these
solutions was determined as given above.

TABLE II

SOILS AND CORRESPONDING SOLUTIONS USED IN THE RADIOCESIUM SORPTION STUDIES

Number	Soil	Ca	Mg	Na	K	SO_4	Cl
				meq/l			
1	WDA3	18.7	21.3	0.0	0.0	40.0	0.0
2	WDA3	18.7	21.3	4.0	0.2	40.0	4.2
3	WDA2	26.8	37.3	5.0	0.2	64.1	5.2
4	WDA5	5.0	5.0	1.0	0.2	10.0	1.2
5	Bentonite*	20.0	0.0	0.0	0.0	0.0	20.0

* Calcium saturated prepared sample

Radiostrontium Sorption in Column Experiments

Experiments with Sr-85 were carried out similarly to the radiocesium
experiments given above. The solutions were identical to solution 1 in
Table II except that the active solution contained about 2 μc/l of Sr-85.

Radiocesium Activity in the Effluent from Columns

At appropriate times during a sorption experiment with Cs-137, while
the active solution was being fed in, the effluent was collected in a plastic
vial. The volumetric flow rate was determined from the amount collected and
an aliquot of the effluent was transferred to a counting vial. This, and a
similar vial of the feed solution, were counted by gamma scintillation.

CHAPTER IV

EXPERIMENTAL

I. CHARACTERISTICS OF SAMPLES AND SITES

1. Introduction

Chemical and physical analyses were conducted on the soil samples,
river sediment samples, and the Morden bentonite in order to characterize
the samples and to provide data for subsequent radioisotope sorption
studies. In some cases the analyses were also used to characterize the
sampling sites; results were correlated with the findings of previous
and present geological investigations of the WNRE waste management area
and its surroundings.

2. Field Investigations of the WNRE Waste Management Area

A study of the plant site and its surroundings by The Shawinigan
Engineering Company Limited (42) indicated that the regional overburden
consisted of impermeable clays and that the water table was high and in
general slopes toward the river.

A preliminary groundwater study in the vicinity of the present waste
management area was carried out in 1964 by Charron (6). On the basis
of surface observations, a well inventory, and two drill-holes in Section
28, Charron identified two recharge areas of permeable sands and gravels;
one to the northeast and one to the southwest of the waste management area.
He stated that the groundwater from the main recharge area to the north-
east of the waste management area rose to the surface in the vicinity of
the southwest quarter of Section 35 to form bogs and marshes which drained
into the Winnipeg River. Sediments encountered in drilling were clays of
clayey tills which were considered to be impermeable. However, water rose

rapidly in the holes and was presumed to originate in sandy stringers encountered during drilling. The conclusion of the study was that groundwater movement in the clays or clayey till would be very slow due to the low hydraulic gradient and the impermeable character of the sediments.

Brief field examinations of the soils in the waste management area were conducted by the authors with the cooperation of WNRE personnel at various times during 1967. These examinations, in conjunction with water level readings from observation wells in the area, led to the preliminary conclusion that a slow upward movement of groundwater existed in the waste management area.

In 1968, at the request of Dr. J.E. Guthrie, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, a hydrogeological investigation in the vicinity of the present waste management area was begun by the Department of Earth Sciences, University of Manitoba. In a progress report of this study Cherry and Beswick (7) stated that the glacial deposits in Section 28 and vicinity occur as four distinct geological units: a silty upper lacustrine unit, a clayey lower lacustrine unit, a unit of glacial till beneath the lacustrine clay, and a basal sandy unit immediately overlying the Precambrian bedrock. These units become progressively exposed in the uplands portion of the region. The upper lacustrine unit does not extend into the present waste management area. Cherry and Beswick concluded that three areas of groundwater recharge or discharge were located in the vicinity of Section 28. The waste management area was found to be located in a discharge area which extends to the north and south of the area. The recharge areas occur to the east and the west of this central discharge area.

3.   Results and Discussion

Composite Samples from the WNRE Waste Management Area

Preliminary Analysis of the Five Composite Samples. The results of

the preliminary analysis are given in Table III. The wide range of

particle size distribution of the five composite samples is evident.

All samples are calcareous and contain both calcite and dolomite. There

is a noticeable accumulation of water-soluble salts in the lacustrine

clay layers which may be attributed to translocation of salts by discharging

groundwater.

TABLE III

PARTICLE SIZE DISTRIBUTION, CARBONATE CONTENT
AND SOLUBLE SALT CONTENT OF FIVE COMPOSITE SAMPLES

Analysis	WDA1	WDA2	WDA3	WDA4	WDA5	Units
Sand 50u	5.6	9.6	34.6	51.2	61.3	%
Silt 50-2u	12.6	33.7	29.8	26.7	29.2	%
Clay 2u	81.8	56.7	35.6	22.2	9.5	%
Calcite	–	11.8	18.6	13.5	8.5	%
Dolomite	–	16.2	9.8	3.6	5.9	%
$CaCO_3$ equivalent	–	29.4	29.3	17.4	14.9	%
Salts soluble in 1:1 extract expressed as $MgSO_4$ equiv.	49	58	14.6	10.0	4.7	meq/l

Detailed Analysis of WDA2 and WDA3. Composite samples WDA2 and WDA3

were selected for a detailed chemical and physical analysis since they

represent the two major soil deposits in the waste management area.

Results of the detailed analysis are given in Table IV. The soluble

TABLE IV

SOLUBLE SALT AND CARBONATE CONTENTS, CATION EXCHANGE CAPACITY

AND PARTICLE SIZE DISTRIBUTION OF SOIL SAMPLES WDA2 AND WDA3

Analysis	WDA2	WDA3	Units
Salts soluble in a 1:1 extract			
Ca^{++}	2.40	0.605	meq/100 g
Mg^{++}	3.50	0.757	"
$Ca^{++} + Mg^{++}$	5.90	1.362	"
Total water soluble salts			
Ca^{++}	15.6	1.0	meq/100 g
Mg^{++}	9.6	0.8	"
Ca + Mg	25.2	1.8	"
Carbonate content			
Calcite	8.4	13.2	%
Dolomite	16.5	12.0	"
Total carbonates	24.9	25.2	"
Cation exchange capacity	26.0	11.8	meq/100 g
Particle size distribution after removal of carbonates			
Sand (50u)	8.5	40.0	%
Coarse Silt (50-20u)	1.0	8.0	"
Medium Silt (20-5u)	12.0	16.6	"
Fine Silt (5-2u)	4.8	2.6	"
Coarse Clay (2-1u)	24.4	10.9	"
Medium Clay (1.0-0.2u)	6.9	2.6	"
Fine Clay (0.2-0.1u)	10.6	5.8	"
Very Fine Clay (0.1u)	31.8	13.5	"
Total Sand (50u)	8.5	40.0	%
Total Silt (50-2u)	17.8	27.3	"
Total Clay (2u)	73.7	32.8	"

salts of samples WDA2 and WDA3 are principally calcium and magnesium sulphates. Sample WDA2 contains large quantities of gypsum which is not soluble at a 1:1 soil:water extract or at lower moisture contents. In contrast, most of the salts are soluble at a 1:1 extract in sample WDA3. Carbonate minerals are a major component of the soils and their interaction with radioisotopes should be established. The low cation exchange capacities indicate a low montmorillonite mineral content in the soils. Sample WDA2 is very high in clay; much of the clay in both samples is very fine, less than 0.1 micron diameter. Since the sorption of ions is associated mainly with the clay fraction, a detailed study of the clay fraction was conducted.

Clay Mineralogy of WDA2 and WDA3. Complete details of the mineralogical investigation are given in Appendix B; only a summary of the results is given here. The dominant mineral species of the 0.2 micron clay fraction of both soils is interstratified mica-montmorillonite. Minor amounts of kaolinite, interstratified chlorite-montmorillonite, chlorite, and quartz occur. Sample 2 contains 25% mica layers, 66% montmorillonite layers, and 9% other minerals whereas sample 3 contains 34%, 55% and 11%, respectively. The 1.0 and 0.2 micron clay fraction of both soils contains, in order of abundance, interstratified mica-montmorillonite, kaolinite, interstratified chlorite-montmorillonite, chlorite, feldspars and quartz. The 2 to 1 micron clay fraction of both soils contains free or interstratified mica and montmorillonite, kaolinite, feldspars, and quartz. The 5 to 2 micron fractions contain quartz, feldspars, vermiculite, kaolinite, and illite. The cation-exchange properties of the soils may be attributed to the montmorillonite layers of the clay fractions.

Hydraulic Conductivity of the Composite Samples. Results were found
to be highly dependent upon the physical state of the sample. Samples
which were mixed with water before being poured into cylinders had a
lower conductivity than those which were wetted after being poured into
cylinders. These data are presented below:

Sample	Puddled with Water	Loaded Dry
WDA2	0.008 cm/hr	0.017 cm/hr
WDA3	0.007 "	0.027 "
WDA5	-	0.632 "

These conductivities will not apply in the field because the physical
structure has not been preserved and the bulk density was not controlled.
However samples WDA2 and WDA3 may be classified (21) as very slow or
impermeable and sample WDA5 classified as moderately slow. A solid block
of sample WDA2 or WDA3 would be practically impermeable to groundwater.
However groundwater could move in cracks, channels, or pores in the clay
layers or in the sand layers.

Analysis of Extracted Soil Moistures. The concentration of calcium
and magnesium in solutions extracted from a given sample at various suctions
was found to remain constant. Data for samples WDA2 and WDA3 at various
initial moisture contents are presented in Table V.

TABLE V

TOTAL CONCENTRATION AND RATIO OF CALCIUM AND MAGNESIUM IN THE SOLUTION PHASE

Soil WDA2			Soil WDA3		
Moisture (%)	Ca + Mg (meq/l)	Ca:Mg	Moisture (%)	Ca + Mg (meq/l)	Ca:Mg
56.4	67.6	0.709	34.5	40.3	0.88
63.0	64.1	0.72	49.8	28.0	0.911
83.6	60.9	0.727	71.6	21.42	0.916
109	59.2	0.792	102	16.81	1.01

The variation of salt concentration with moisture content is less pronounced for sample WDA2 than for sample WDA3 due to the presence of solid phases such as gypsum. Data for the five composite samples at moisture saturation are given in Table VI.

TABLE VI

CALCIUM AND MAGNESIUM CONCENTRATION IN THE SOLUTION PHASE
AT MOISTURE SATURATION

Sample	Moisture (%)	Ca + Mg (meq/l)
WDA1	89.7	62.4
WDA2	86.0	59.4
WDA3	46.6	27.1
WDA4	32.3	25.4
WDA5	24.2	15.9

These data are not an exact simulation of saturation under field conditions since the bulk density is not controlled but they have the advantage of being easily obtainable.

The Sediments and Water from the Winnipeg River

Particle Size and Carbonate Analysis. Wide variations in texture and pebble content occur in the river bed (Table VII). All samples are calcareous but a considerable variation also occurs in carbonate mineral content.

TABLE VII

PARTICLE SIZE DISTRIBUTION AND CARBONATE CONTENT OF THE RIVER SEDIMENTS
(expressed as percent of the < 2 mm soil)

Sample	Pebbles	Sand	Silt	Clay	Calcite	Dolomite	$CaCO_3$ Equiv.
1	18	54.4	16.9	28.7	4.7	6.5	11.8
2E	10	71.3	11.4	17.3	1.4	3.4	5.1
2W	0	3.1	8.8	88.1	2.3	4.4	7.0
OF	95	45.3	21.4	33.3	11.6	7.0	19.2
3	20	54.2	19.2	26.6	5.2	9.1	15.1

Cation Exchange Analysis. A major portion of the investigations
involving radiostrontium concerns the sorption of radiostrontium by calcar-
eous soils containing both calcium and magnesium as exchangeable cations.
Equation [12] states that KC is characteristic of the soil with K being
the apparent equilibrium constant of the exchange and C the cation exchange
capacity; therefore, it was desired to compare KC data from radiostrontium
studies to cation exchange data.

The usual ammonium acetate method for the determination of exchangeable
cations and cation exchange capacity is not valid for calcareous soils due
to the solubility of the carbonate minerals in the exchange solution.
Consequently a method for calcareous soils was developed using sodium
chloride as the exchange solution.

The exchangeable cations and cation exchange capacity of the river
sediments are presented in Table VIII. For comparison, the data obtained
for sample WDA3 are also included. The exchange capacity of the river
sediment samples is nearly saturated with calcium and magnesium. Sample
WDA3 contains 1.8 meq/100 g of soluble salts which accounts for the total

cations being somewhat higher than the exchange capacity.

TABLE VIII

EXCHANGEABLE CATIONS AND CATION EXCHANGE CAPACITY

OF THE RIVER SEDIMENTS AND SOIL SAMPLE WDA3
(meq/100 g)

Sample	Ca	Mg	Ca + Mg	Cation Exchange Capacity
1	14.7	3.1	17.8	18.1
2E	8.3	2.4	10.7	10.5
2W	24.8	13.7	38.4	40.4
OF	10.4	6.5	16.9	17.5
3	10.8	3.7	14.5	15.4
WDA3	6.5	5.4	11.9	10.5

Analysis of the River Water. A sample of river water obtained on
September 8, 1967 was also subjected to calcium and magnesium analysis by
the EDTA method (Appendix D). The concentrations, expressed as meq/l of
water, are given below:

Ca^{++}	Mg^{++}	Ca + Mg
0.630	0.296	0.926

These concentrations will, of course, vary somewhat from month to month
in accordance with the proportions of surface runoff or groundwater
discharge being added to the river water. For example, the concentrations
of calcium plus magnesium reported by The Shawinigan Engineering Company
(42) in samples obtained from the Winnipeg River, opposite the plant site,
on February 22, 1960 and April 5, 1960 amounted to 1.74 meq/l and 1.13
meq/l, respectively.

The Morden Bentonite Sample

It was originally thought that this material might prove useful as a column packing in treatment of radioactive effluent and therefore charact- erization was begun with this in mind. After its mineralogical properties had been investigated it was also used as a reference material in the radioisotope sorption investigations.

General Characteristics. A preliminary examination revealed that the sample was saline and extremely acid. The electrical conductivity of the soil solution obtained from a 1:2 soil:water extract was 6.20 mmho/cm. The soluble cations were calcium, magnesium, sodium and hydrogen. As is characteristic of bentonites, the cation exchange capacity was very high. The free iron oxide extracted by the citrate-dithionate method was 4.97%. Separation into particle size fractions revealed that the dominant size fraction is coarse clay (2.0 - 0.20u). Hydraulic conductivity was measured by the dry loading method used for the composite soil samples and was found to be 0.036 cm/hr. This is higher than the values found for WDA2 and WDA3 but may still be rated as very slow (21). Such a low conductivity may create a problem if the clay is to be used in columns.

Mineralogical Analysis. Further attention was directed upon the coarse clay fraction in order to identify and characterize the clay mineral. The diffractogram of a magnesium saturated, glycerol solvated coarse clay fraction is shown in Figure 12. Six orders of the 17.8A$^{\circ}$ basal spacing are evident. This spacing is indicative of montmorillonite (4). Diffracto- grams of the potassium saturated clay, which have been heated to 550°C, reveal a 9.69A$^{\circ}$ basal series. This indicates that the mineral is an expanding layer silicate.
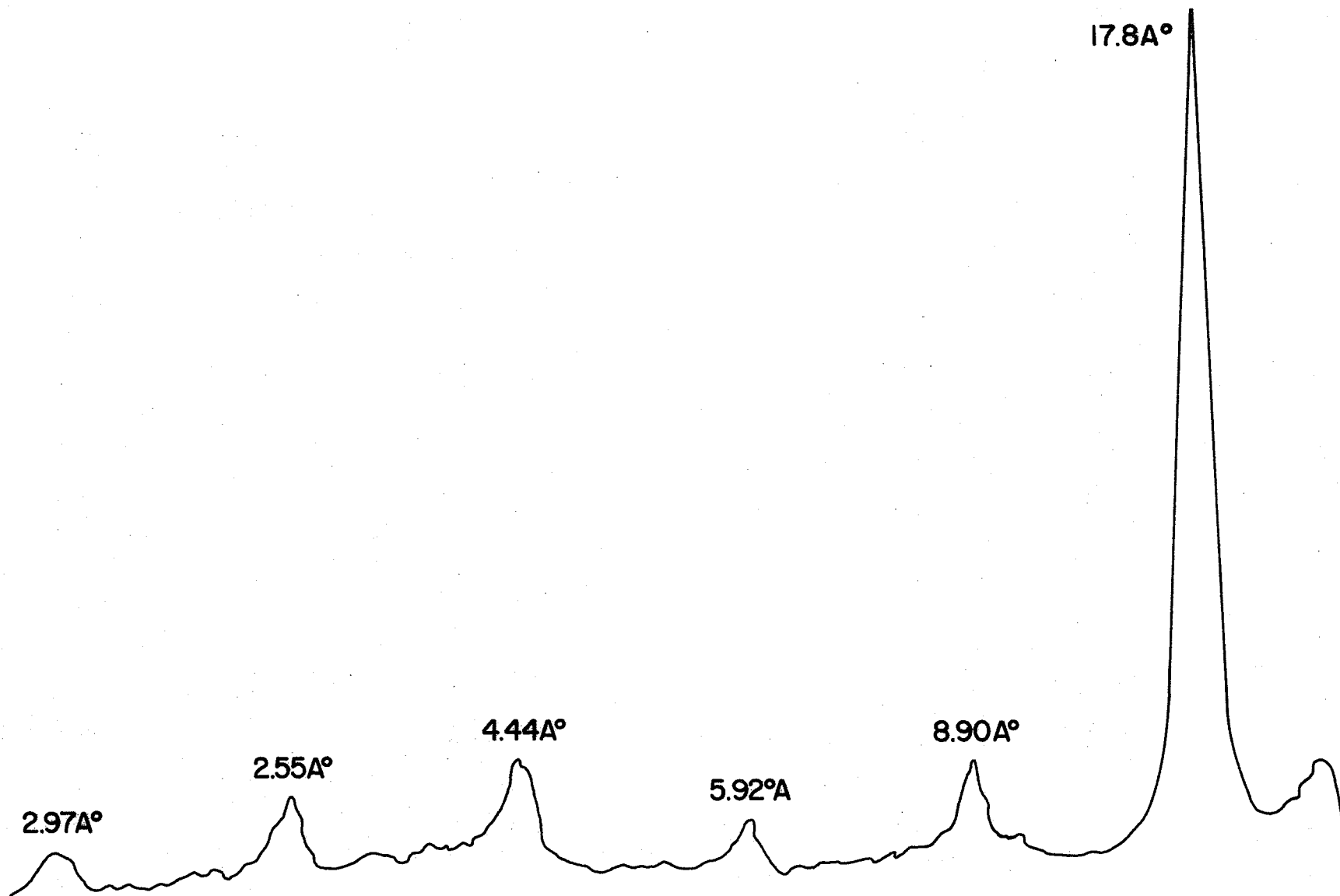
Figure 12. X-ray diffractogram of the magnesium saturated, glycerol solvated coarse clay fraction of the Morden bentonite.

The diffraction patterns, obtained from random powder specimens, were used to investigate the non-basal diffraction peaks which are not recorded by the diffractometer technique. The pattern of a calcium saturated, glycerol solvated sample is given in Table IX. The hk bands are characteristic of a dioctahedral layer silicate with random layer displacements (24). The cation exchange capacity of the coarse clay is 1.255 meq/g which is indicative of a high charge montmorillonite.

TABLE IX

X-RAY DIFFRACTION PATTERN OF A RANDOM POWDER SPECIMEN
OF A CALCIUM SATURATED, GLYCEROL SOLVATED COARSE CLAY FRACTION
OF THE MORDEN BENTONITE

Spacing	Intensity	Indices
17 A^o	10	001
8.85 A^o	6	002
5.90 A^o	4	003
4.48 A^o	10 broad	02, 11
3.52 A^o	5	005
2.94 A^o	1 broad	006
2.57 A^o	1 broad	13, 20
1.696 A^o	$\frac{1}{2}$	31, 15, 24
1.496 A^o	7	33, 06
1.293 A^o	$\frac{1}{2}$ broad	26, 40
1.248 A^o	$\frac{1}{2}$	35, 17, 42

A chemical analysis of a lithium saturated sample of the coarse clay is presented below:

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Li_2O	Loss on Ign.
58.81	19.87	1.15	0.59	0.0	4.02	0.08	0.17	1.51	10.72

From the chemical analysis the following structural formula was calculated
(19) in which X represents exchangeable cations, the first brackets
enclose the tetrahedral layer, and the second brackets enclose the octa-
hedral layer:

$$X_{1.01} (Si_{7.92}Al_{0.08}) (Al_{3.02}Fe^{III}_{0.12}Mg_{0.82}) O_{20} (OH)_4 \cdot nH_2O$$
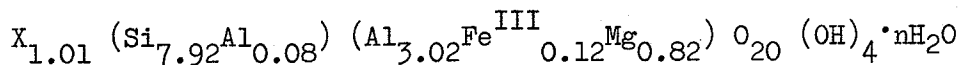
This is the structural formula of a high charge montmorillonite which is
situated very close to the montmorillonite end of the montmorillonite-
beidellite series as evidenced by the isomorphous substitution in the
octahedral sheet (24). The formula is similar to that of Wyoming bentonite
except for the higher lattice charge, higher magnesium content and lower
iron content of the Morden material.

The Prepared Samples

To provide a simple system for preliminary studies with radiostrontium,
the carbonate minerals were removed and the exchange sites saturated with
calcium. Other samples were prepared with the carbonates intact. Soluble
salts were removed to allow complete control of salt concentration and
ionic species in laboratory systems. In one case similar samples were
prepared in calcium and magnesium saturated states so that the exchanger
phase composition of laboratory systems could be varied by the simple
expedient of mixing the calcium saturated with the magnesium saturated
samples in various proportions.

Before the prepared samples could be used in the radioisotope studies,
cation exchange, air-dry moisture, and non-solvent water data were
required. Air-dry moisture of the samples was determined gravimetrically
at regular intervals during the investigations. Non-solvent water
(negative adsorption) data were estimated as detailed in Appendix A.

Several methods were investigated to obtain accurate and precise cation exchange analyses, particularly in the case of the calcareous samples.

Exchangeable Cations and Cation Exchange Capacity of Prepared Samples. The principal difficulty encountered in cation exchange determinations on calcareous soils is due to the solubility of the carbonate minerals in the displacing solution. In this respect, sodium chloride is more desirable than the commonly used ammonium acetate solution. A centrifuge washing technique was devised by which 10 gram samples were washed four times with 50 ml portions of sodium chloride solution and analysis conducted upon the combined decantates. This technique was rejected since the displacement of exchangeable cations was found to be incomplete and release of calcium and magnesium from the carbonate minerals was unacceptably large. It is apparent that a more efficient displacement technique which used a minimum volume of solution was required.

To this end the funnel washing method described in Chapter III was developed. In essence 25 grams of soil is washed in a Buchner funnel with small portions of 2 N sodium chloride until the filtrate volume is nearly 250 ml. Displaced cations are determined by analysis of the NaCl leachate and cation exchange capacity by analysis of a subsequent magnesium chloride leachate. This method was found to be suitable according to two criteria: (1) For the non-calcareous samples, the method yielded results comparable to those of an ammonium acetate method, (2) For the calcareous samples, the exchangeable calcium and magnesium was equal to the cation exchange capacity within experimental error.

The ammonium acetate-centrifuge washing technique was used for the non-calcareous prepared samples. The exchangeable cation data for the

prepared samples which were used in the radioisotope sorption studies
are given in Table X. The small but significant differences in some of
the data for similar samples, prepared at different dates, may be
attributed to imperfect mixing of the bulk samples. The incomplete
saturation of the calcareous samples can be attributed to the slight
solubility of the carbonate minerals in the wash solutions.

TABLE X

EXCHANGEABLE CATIONS OF THE PREPARED SAMPLES
(meq/100 g of oven-dry soil)

Sample	Saturating Cation	Carbonates	Preparation Date	Ca^{++}	Mg^{++}
WDA2	Ca	Removed	May 1967	43.1	
WDA2	Ca	Removed	May 1968	43.0	
WDA2	Ca	Removed	Dec. 1968	41.5	
WDA2	Ca	Present	June 1967	31.0	1.1
WDA2	Mg	Present	June 1967	4.9	26.4
WDA3	Ca	Removed	May 1967	14.0	
WDA3	Ca	Present	Dec. 1968	11.2	0.4
Bentonite	Ca	None	May 1967	108.8	
Bentonite	Ca	None	Nov. 1968	103.2	

II. RADIOSTRONTIUM SORPTION INVESTIGATIONS

1. Introduction

The first set of experiments with radiostrontium was designed to
test the validity of equation [4] in laboratory systems of the carbonate-
free, calcium saturated, prepared samples. This was accomplished by
noting the effect of the variation of the components of the system upon

the equilibrium constant K. In a similar manner, the second set of experiments was designed to validate equation [12] using calcareous soils saturated with calcium and magnesium and to determine the absorption characteristic, KC. The third set of experiments was conducted to relate KC to the cation exchange capacity in order to facilitate prediction of radiostrontium distributions in field soils. In the fourth set of experiments, specific absorption and the reversibility and the kinetics of the exchange reaction were investigated. In the final experiments a few column studies were conducted with radiostrontium in order to develop a technique to be used in subsequent radiocesium studies.

2. Review of Experimental Literature

Due to the biological significance of Sr-90, a considerable body of literature has accumulated concerning radiostrontium in soils. Much of this literature is in the form of surveys of fallout-derived radiostrontium in various surface soils. Many sorption studies or leaching studies of an empirical nature have also been reported. The results of such empirical investigations, while useful for the particular soils studied, are difficult to extrapolate to other soils or situations. Only a few studies have been characterized by a theoretical approach. This is understandable if a phenomenon is not well understood or if no suitable theory exists. Consequently, in this study, the applicability of theory was investigated before resorting to empirical methods.

Krishnamoorthy and Overstreet (22), in an evaluation of ion exchange equations, conclude that equations similar to equation [1] yield satisfactory equilibrium constants for homovalent cation pairs and that these constants, for a given pair, are independent of the presence of other ions

in the system. No evidence of irreversibility was found for the colloids studied and equilibrium was achieved rapidly. For the calcium-strontium exchange, equilibrium constants as defined in equation [1] were found to be 1.10 for Utah bentonite and 1.35 for Yolo clay. No experiments were conducted with carrier-free radioisotopes, however, and extrapolation to this situation is open to question. Fixation or absorption of radiostrontium at specific sites may occur which is not observed when macroscopic amounts of strontium are present.

Frissel and Poelstra (15), in the course of transport experiments, concluded that no specific absorption of carrier-free Sr-90 occurred in resin-sand mixtures. Taylor (44) investigated the retention and slow release of radiostrontium by some acid soils and attributed this effect to the incorporation of radiostrontium in soil organic matter. Salam and Zahra (36) reported that Ca-45 exchanged with the surface calcium of calcium carbonate, phosphate, and sulphate minerals. This exchange may also be significant for radiostrontium.

3. Results and Discussion

Ion Exchange Equilibria of Radiostrontium and Calcium

Careful consideration was given to the design of a method to measure the distribution of radiostrontium between the solid and solution phases in laboratory systems. Methods which required washing of the solid phase, prior to counting to remove activity in solution, were rejected since losses of activity from the solid phase could occur during the washing. A more suitable method, if distribution ratios are relatively high, was found to be one in which the radioactivity in solution was determined before and after mixing of the phases and the sorbed activity determined

indirectly. Since carrier-free radioisotopes were being used, possible

losses of activity during handling of the radioactive solutions were

carefully investigated. The soil to solution ratio of the systems was

maintained as high as practicable in order to approach field conditions,

except in a few experiments in which this ratio was a variable. In most

experiments the concentration of salts in solution was varied over a

range which included the expected concentrations in the field.

The end-window beta counting technique was used in the first three

experiments. For these experiments approximately ten times as much radio-

strontium was added to the systems as was added in later experiments due

to the low counting efficiency of the technique. The soils used in this

set of experiments were the calcium-saturated carbonate-free samples

prepared from WDA2, WDA3, and the bentonite.

The composition of the systems and the results of calculations for

the first set of radiostrontium experiments are given in Table XI. One

similar experiment with Sr-85, the use of which will be discussed later,

is also included. The Sr-85 experiment was conducted in order to correlate

data obtained with both isotopes of strontium.

The means and standard deviations of the equilibrium constants are:

$$WDA2 \qquad K = 1.200 \pm 0.038$$

$$WDA3 \qquad K = 1.341 \pm 0.015$$

$$Bent. \qquad K = 1.113 \pm 0.012$$

From these data it may be concluded that the equilibrium constant K, as

defined in equation [4], is independent of variations in the amount of

radiostrontium in the system, variations in the soil to solution ratio,

and variations in the amount of calcium in solution and is characteristic

TABLE XI

CALCIUM-RADIOSTRONTIUM EQUILIBRIA WITH WDA2, WDA3,

AND MORDEN BENTONITE

Soil	m (8.)	V_1 (ml.)	(Ca)x (meq.)	(Ca)s (meq.)	(Sr)x (cps)	(Sr)s (cps)	CaDR	SrDR	K
WDA2*	24.04	35.0	10.36	0.449	246.0	9.356	23.07	26.29	1.14
WDA2*	24.04	35.0	10.36	0.873	241.7	16.883	11.87	14.38	1.21
WDA2*	24.04	35.0	10.36	1.604	225.9	29.071	6.46	7.77	1.20
WDA2	4.81	25.0	2.07	0.180	505.7	36.480	11.49	13.86	1.21
WDA2	9.61	25.0	4.14	0.209	531.2	21.401	19.86	24.82	1.25
WDA2	14.42	25.0	6.22	0.229	546.9	16.481	27.11	33.18	1.22
WDA2	14.42	25.0	6.22	0.236	499.4	15.844	26.33	33.64	1.28
WDA2	14.42	25.0	6.22	0.343	496.7	23.171	18.12	21.44	1.18
WDA2	14.42	25.0	6.22	0.653	480.8	42.246	9.52	11.38	1.20
WDA2+	14.28	25.0	6.14	0.276	667.8	25.751	22.25	25.93	1.17
WDA2+	14.28	25.0	6.14	0.402	655.6	36.517	15.27	17.95	1.18
WDA2+	14.28	25.0	6.14	0.666	429.1	38.984	9.22	11.01	1.20
WDA2+	14.28	25.0	6.14	1.234	275.4	47.304	4.98	5.82	1.17
WDA3*	19.75	20.0	2.77	0.262	209.6	14.984	10.57	13.99	1.32
WDA3*	19.75	20.0	2.77	0.572	199.5	30.298	4.84	6.58	1.36
WDA3*	19.75	20.0	2.77	1.094	182.2	50.522	2.53	3.61	1.43
WDA3	19.75	25.0	2.77	0.204	507.3	28.254	13.60	17.96	1.32
WDA3	19.75	25.0	2.77	0.326	487.5	43.638	8.49	11.17	1.32
WDA3	19.75	25.0	2.77	0.636	464.2	81.976	4.35	5.66	1.30
Bent.*	11.40	25.0	12.40	0.303	218.4	4.862	40.92	44.92	1.10
Bent.*	11.40	25.0	12.40	0.601	216.7	9.308	20.63	23.28	1.13
Bent.*	11.40	25.0	12.40	1.139	207.1	16.964	10.89	12.21	1.12
Bent.	1.823	25.0	1.983	0.290	441.3	58.426	6.84	7.55	1.10
Bent.	4.558	25.0	4.959	0.313	482.4	27.409	15.84	17.60	1.11
Bent.	9.117	25.0	9.919	0.343	511.2	15.823	28.92	32.31	1.12

* counted in beakers with an end-window tube

+ Sr-85 experiment

Bent. - Morden bentonite

of the soil material. The values of K are close to unity indicating that the exchanger phase has only a slight preference for Sr over Ca or that radiostrontium behaves similarly to calcium.

Calcium-Magnesium-Radiostrontium Equilibria with Calcareous Soils

Calcareous soils saturated with calcium or magnesium were used, separately or in mixtures, in this second set of experiments. The objectives of the experiments were to investigate equation [12] with respect to variations in the salt concentration in the solution phase and the relative amounts of calcium and magnesium present in the system. Preliminary indications of the validity of equation [12] were obtained by a graphical technique in which SrDR data were plotted against corresponding m/(Ca + Mg)s data. In accordance with equation [12], the locus was found to be a straight line passing through the origin.

In an attempt to investigate radiostrontium sorption by the carbonate fraction of the soil, similar experiments were conducted with pure carbonate minerals. At this point two unusual effects were noted. Firstly, the line obtained when SrDR versus m/(Ca + Mg)s data were plotted did not pass through the origin. This indicated that a large component of the sorption was independent of the concentration of Ca and Mg in solution, and was considered to be anomalous in view of the chemical similarity of strontium and calcium or magnesium. Secondly, considerable radioactivity was found on the caps and glass walls of the centrifuge bottles used in the experiments. The cause of these unusual effects was finally traced to the presence of yttrium-90 in the solutions. This was confirmed by chemical separation and measurements of beta range and half-life.

The Y-90 isotope, the daughter of Sr-90, was present in the original

stock solution of Sr-89 but became apparent only when Sr-89 had decayed through about four half lives. Calculations indicated that the activity due to Sr-90 and Y-90 was 2% of the total activity in the solution at the beginning of the first set of sorption experiments and had risen to 8% at the end of the sorption experiments with calcareous soils. In the later period when the sorption of radiostrontium by the pure carbonate minerals was being investigated, the activity due to Sr-90 and Y-90 rose from 30 to 60 percent of the total radioactivity. These figures were, of course, accentuated by the higher counting efficiency of the glass wall geiger tube for Y-90 than for Sr-89.

A number of calculations were made which indicated that the first effect of Y-90, assuming complete sorption, would be an increase in the slope of the line obtained from equation [12] followed by a shifting of the line away from the origin. This is in accord with the data and confirms that the Y-90 was strongly sorbed on any available surface due to the high valence of Y-90 or to radio-colloid formation.

The problem encountered with the Sr-89 could have been eliminated by allowing Y-90 to grow to equilibrium or by chemical separation of Y-90 before counting. When the latter method was employed, and some of the experiments of the carbonate sorption series were repeated, it was found that radiostrontium was not sorbed by the caps, and that sorption of radio-strontium by the carbonate minerals was zero or very small.

To avoid the difficulties encountered with Sr-89, it was decided to use Sr-85 in the remaining experiments as this isotope could be obtained carrier-free and free of interfering radioisotopes. Some earlier experiments were repeated using Sr-85 in order to evaluate the data obtained

with Sr-89 and the sorption studies were resumed as originally intended.
The method used to study Sr-85 sorption was similar to that outlined
previously for Sr-89 except that 2, 3, or 5 ml aliquots of the soil
extract and corresponding aliquots of the original solution were placed
in vials for scintillation counting. These aliquots were used for calcium
and magnesium determinations after counting was completed.

As indicated previously, the prime objective of the remaining radio-
strontium sorption studies was to investigate the applicability of equation
[12] to a practical system. This entailed a study of the dependence of KC
upon the composition of the system. The equilibrium constants with respect
to calcium or magnesium as defined in equations [4] and [9] were also to
be investigated. An added objective was a comparison of data obtained
with Sr-89 and Sr-85.

Plots of SrDR versus $m/(Ca + Mg)s$ for sample WDA2 and WDA3 are
presented in Figures 13 and 14, respectively. The slope of the line is
KC. It is apparent from Figure 13 that KC is a function of the calcium
and magnesium composition of the system but when the extremes are neglected,
KC is reasonably constant. A constant KC is also found for WDA3; however,
this data is obtained for a nearly calcium saturated system. In general,
it may be concluded that, if the calcium and magnesium composition of the
system is relatively constant, equation [12] gives a good approximation to
the radiostrontium sorption.

Table XII reveals that both K and K', as defined in equations [4] and
[9] respectively, appear to be constant. The K and K' values expressed to
only two significant figures are unreliable since they were obtained from
the CaDR in a nearly magnesium saturated system or the MgDR in a nearly
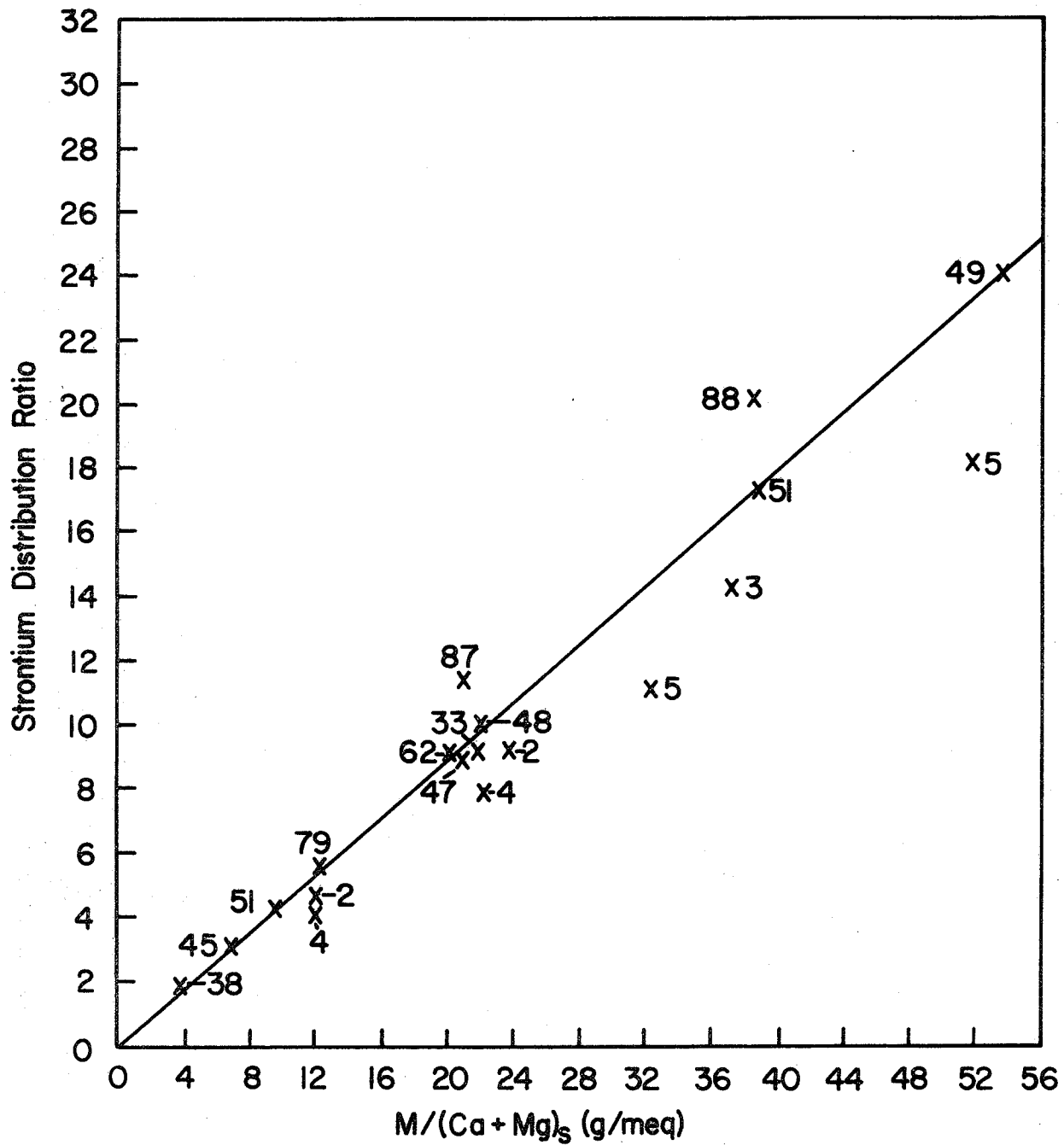
Figure 13. Radiostrontium equilibria on soil sample WDA2. Values of Emg are attached to each data point.
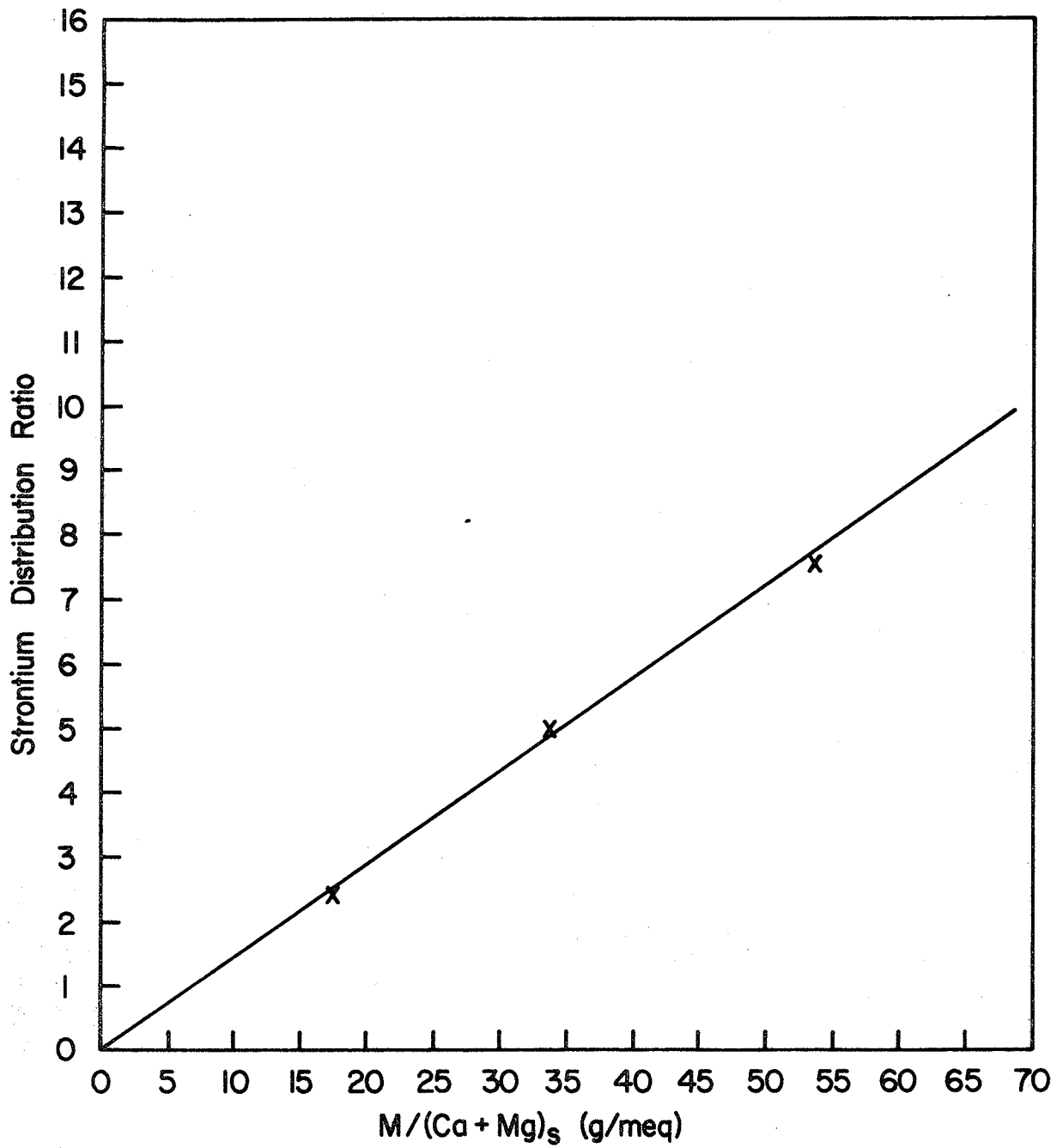
Figure 14. Radiostrontium equilibrium on calcium-saturated soil sample WDA3.

TABLE XII

CALCIUM-MAGNESIUM-RADIOSTRONTIUM EQUILIBRIA WITH CALCAREOUS SOILS

Soil	m (g.)	V_1 (ml)	Emg (%)	CaDR	MgDR	SrDR	K	K'	KC (meq/g)
WDA2	14.57	25.0	61.7	8.16	4.98	9.14	1.12	1.84	0.445
"	14.57	25.0	47.0	7.42	5.09	8.88	1.20	1.74	0.428
"	14.57	25.0	33.4	7.39	5.16	9.23	1.25	1.79	0.426
"	4.78	25.0	37.5			1.854			0.485
"	9.56	25.0	44.9			3.125			0.461
"	14.34	25.0	51.0			4.337			0.458
"	14.57	25.0	49.1	18.71	13.95	24.00	1.28	1.72	0.450
"	14.57	25.0	51.3	14.72	9.40	17.32	1.18	1.84	0.446
"	14.57	25.0	47.7	7.98	5.31	10.02	1.26	1.89	0.458
"	14.57	25.0	2.8	11.52	14	14.19	1.23	1.0	0.382
"	14.57	25.0	1.5	7.22	17	9.20	1.27	0.5	0.391
"	14.57	25.0	1.7	3.68	7	4.70	1.28	0.7	0.387
"	14.58	25.0	88.1	14.0	9.64	20.08	1.4	2.08	0.522
"	14.58	25.0	86.7	12.0	5.36	11.43	1.0	2.13	0.547
"	14.58	25.0	78.8	5.77	3.10	5.71	1.0	1.84	0.467
"	+14.49	25.0	4.9	16.32	11	18.07	1.107	1.6	0.349
"	+14.49	25.0	4.6	10.09	7	11.14	1.104	1.6	0.344
"	+14.49	25.0	4.4	7.02	4	7.92	1.128	2.0	0.356
"	+14.49	25.0	3.8	3.78	3	4.12	1.090	1.4	0.340
WDA3	+19.63	25.0	-	-	-	13.19	-	-	-
"	+19.63	25.0	5.3	6.04	3	7.56	1.25	2.5	0.141
"	+19.63	25.0	4.7	3.88	2	4.99	1.29	2.5	0.148
"	+19.63	25.0	4.6	2.03	0.6	2.42	1.19	4.0	0.137

+ Sr-85 experiment

Emg : equivalent fraction of magnesium in solution

calcium saturated system and the mass-balance calculation used renders

these ratios unreliable. Neglecting these data the means and standard

deviations of the equilibrium constants are :

Soil WDA2 $K = 1.192 \pm 0.074$

Soil WDA2 $K' = 1.87 \pm 0.144$

Soil WDA3 $K = 1.24 \pm 0.05$

These data may be used with equations [4] or [9], however, the equations

are somewhat difficult to apply in practice due to experimental difficulties

in the determination of the calcium or magnesium distribution ratios.

It was previously noted that KC of equation [12] is a function of

the calcium and magnesium composition of the system. This relationship

is theoretically predicted by equation [11]. For soil sample WDA2,

sufficient data is available to test equation [11] and Figure 15 is a

plot of 1/KC versus the equivalent fraction of magnesium in solution in

accordance with the equation. Although considerable scatter is evident,

a straight line plot is indicated. This line may be used to predict KC

for other systems if the equivalent fraction of magnesium in solution is

known.

Some conclusions pertaining to radiostrontium sorption, by the

carbonate fraction of the soil, may be drawn from a comparison of data

obtained from the calcareous and non-calcareous samples of the same soil.

As the non-calcareous systems were calcium saturated, only the data obtained

from calcium saturated calcareous soils can be used. The KC value for the

non-calcareous soils is the product of the equilibrium constant and the

cation exchange capacity. For comparison with the calcareous soils this

figure must be multiplied by the percentage of non-carbonate material in
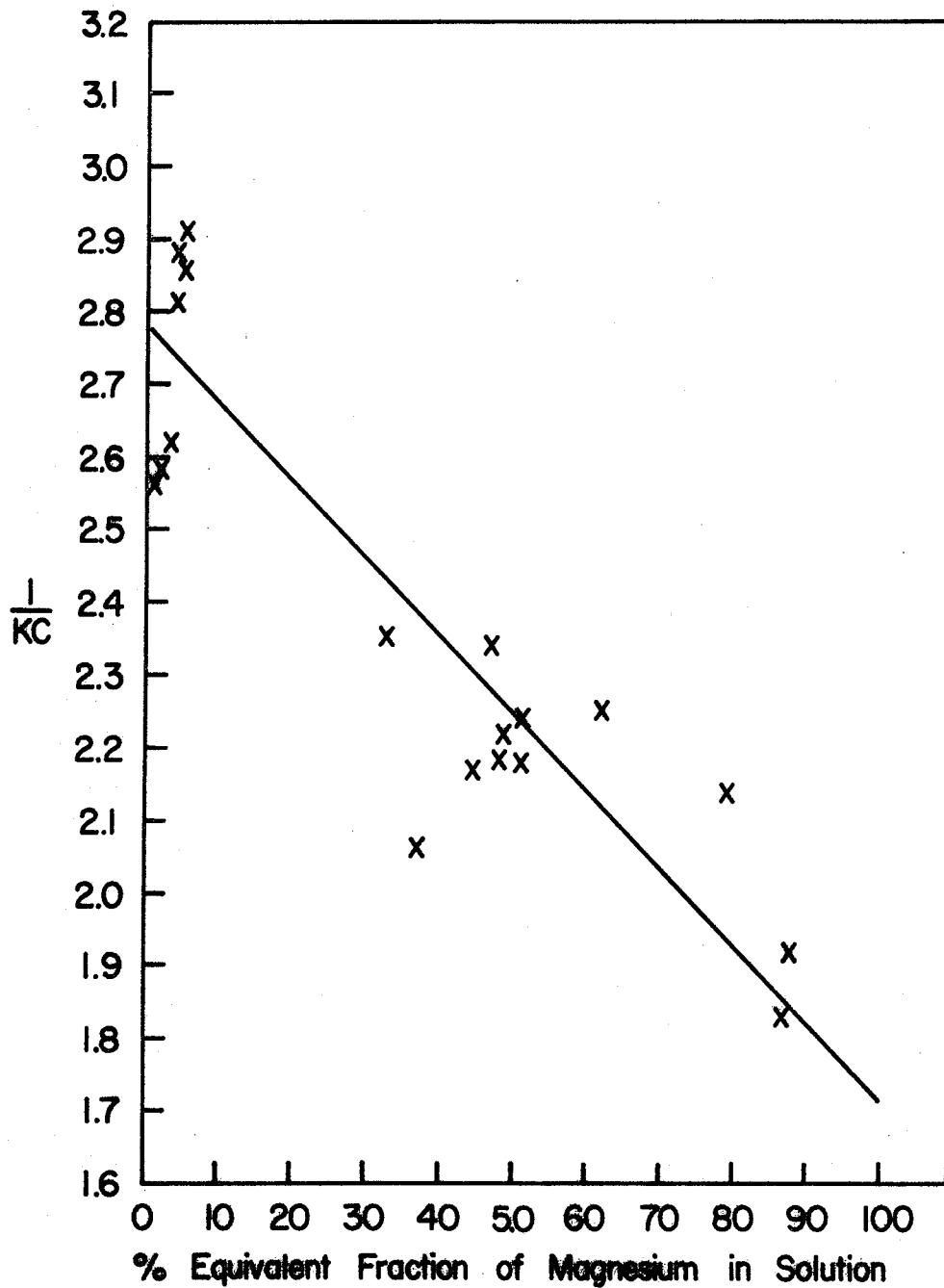
Figure 15. Variation of KC with the equivalent fraction of magnesium in solution for sample WDA2.

the soil. The comparisons are shown below:

	Non-calcareous Soil		Calcareous Soil		
Soil	K	C	Non-Carbonate Soil	Calculated KC	Experimental KC
		(meq/g)	(%)	(meq/g)	(meq/g)
WDA2	1.20	0.431	72.9	0.377	0.364
WDA3	1.34	0.140	73.4	0.138	0.142

These comparisons indicate that most of the radiostrontium sorption is due to the non-carbonate fraction of the soil and that sorption by the carbonates is negligible.

A comparison of values of K and KC from similar experiments using Sr-89 abd Sr-85 (Table XII) reveals that the data obtained with Sr-89 are slightly higher than those obtained with Sr-85 and that the Sr-89 figures appear to increase slightly with time. These indications, if significant, may be attributed to the aforementioned interference of Y-90.

Radiostrontium Sorption by Soil Samples WDA1, WDA4, WDA5 and River Sediments

Since studies had indicated the utility of equation [12] in the exchange of radiostrontium with calcium and magnesium, a series of experiments was conducted to determine KC values for the river sediment samples and the remaining composite soil samples. The KC data shown in Table XIII may be used to predict radiostrontium sorption in a naturally occurring sediment or soil by means of an appropriate equation. However, note that KC is the product of an apparent equilibrium constant and the cation-exchange capacity. Since KC is relatively insensitive to changes in the equivalent fraction of magnesium in solution, the apparent equilibrium constant K should be relatively constant. Using the cation-exchange data

for the river sediment samples the K values calculated are presented in Table XIV.

TABLE XIII

RADIOSTRONTIUM EQUILIBRIA WITH THE RIVER SEDIMENTS AND COMPOSITE SAMPLES

Sample	m (g.)	V_1 (ml)	Emg (%)	SrDR	$m/(Ca + Mg)s$ (g/meq)	KC (meq/g)
1	14.7	25.0	19.3	8.827	35.42	0.249
2E	14.8	25.0	23.0	6.735	45.82	0.147
2W	14.4	25.0	38.1	24.091	47.68	0.505
OF	14.7	25.0	35.7	9.914	41.76	0.225
3	14.8	25.0	25.8	7.200	38.49	0.187
WDA1	14.4	25.0	65.5	9.936	14.20	0.700
WDA4	14.8	25.0	40.1	3.748	37.81	0.099
WDA5	14.9	25.0	25.5	1.784	46.30	0.039

TABLE XIV

CALCULATION OF THE APPARENT EQUILIBRIUM CONSTANT OF THE RIVER SEDIMENTS

Sample	KC (meq/g)	C (meq/g)	K
1	0.249	0.178	1.40
2E	0.147	0.107	1.37
2W	0.505	0.384	1.32
OF	0.225	0.169	1.33
3	0.187	0.145	1.29

Mean K $= 1.34 \pm 0.04$

The constancy of K indicates that this mean value may be used to obtain

a good estimate of KC from cation exchange data.

Radiostrontium Sorption by Carbonate Minerals

A series of experiments was carried out to investigate sorption of radiostrontium by carbonate minerals and to determine if any irreversibility existed in the ion exchange of radiostrontium.

Although previous results, by an indirect method, had indicated that radiostrontium sorption by the carbonate fraction of soils was negligible, no reliable indications had been obtained directly. Three carbonate minerals were therefore selected and radiostrontium sorption was determined by the previously used Sr-85 method. The samples used were reagent grade calcium carbonate, ground Spearhill Devonian calcitic limestone, and ground Stonewall Silurian dolomite. The data obtained are shown in Table XV.

TABLE XV

RADIOSTRONTIUM SORPTION BY CARBONATE MINERALS

Sample	m (g.)	V_1 (ml)	(Ca + Mg)s (meq.)	SrDR	m/(Ca + Mg)s (g/meq.)
$CaCO_3$	15.0	25.0	0.130	0.0567	115.4
$CaCO_3$	15.0	25.0	0.255	0.0532	58.82
Calcite	25.0	25.0	0.180	3.271	138.9
Calcite	25.0	25.0	0.299	1.890	83.61
Colomite	25.0	25.0	0.283	1.054	88.34
Dolomite	25.0	25.0	0.403	0.7138	62.03

From these data the following values of KC were obtained by the previously mentioned graphical technique:

$$CaCO_3 \quad KC = 0.0006 \text{ meq/g}$$
$$Calcite \quad KC = 0.0234 \text{ meq/g}$$
$$Dolomite \quad KC = 0.0117 \text{ meq/g}$$

Good straight lines were obtained except in the case of the reagent grade calcium carbonate in which the very low SrDR could not be determinated accurately. The KC values are all low in comparison to most soils, indicating that radiostrontium sorption by carbonates is not an important contribution to the total sorption in a calcareous soil. It is possible that the higher KC data obtained for the ground limestones, in relation to the calcium carbonates, may be attributed to the presence of small quantities of clay minerals in the limestones.

Reversibility of the Exchange

The reversibility of the ion exchange of calcium and radiostrontium was investigated by attempting to approach the same equilibrium from the directions of high and low initial sorption of Sr-85. The three soils used were a calcium saturated non-calcareous WDA2, a calcium saturated calcareous WDA2, and a calcium saturated calcareous WDA3. The data in Table XVI show that near or complete reversibility of the ion-exchange reaction exists. The difference in sorption for the calcareous WDA3, for example, amounts to approximately 1% of the total radiostrontium in the system.

TABLE XVI

RADIOACTIVITY IN SOLUTION AT THE CONCLUSION OF THE REVERSIBILITY TEST

Sample	Carbonates	Initial Sorption	Sr-85 Radioactivity (cps)
WDA2	None	High	154.18
WDA2	None	Low	152.48
WDA2	Present	High	168.92
WDA2	Present	Low	170.18
WDA3	Present	High	203.59
WDA3	Present	Low	207.01

Desorption of Sorbed Radiostrontium

A series of chemical treatments were employed to investigate the ease or difficulty of removal of sorbed Sr-85. The samples used were the calcium saturated calcareous WDA2 and the calcium saturated non-calcareous WDA2. Figure 16 is a graph of the net radioactivity present in the soil following each treatment. It may be seen that, for the first one or two washings, the activity decreased in a manner predictable from ion exchange and dilution factors. After this, the activity decreased more slowly with washing, probably due to a slow approach to equilibrium. A small amount of activity appears to be trapped in carbonate precipitates which may have been produced during washings by reaction with atmospheric carbon dioxide.

Kinetics of Radiostrontium Sorption

The kinetics of the ion-exchange reaction was investigated using Sr-89 and calcium saturated, calcareous and non-calcareous WDA2 soil samples. Results were expressed as the percent of the total activity sorbed by the soil, the SrAR, and are presented in Figure 17. Ion exchange equilibrium is reached in less than one hour for the non-calcareous sample, but a slower approach to equilibrium is apparent for the calcareous sample. This effect should not create any difficulties in laboratory or field ion exchange reactions if contact time is sufficiently large.

Column Experiments with Radiostrontium

The final set of experiments with radiostrontium was designed to determine if the column method, which was later used in sorption studies with radiocesium, yielded reasonable radiostrontium sorption data. In essence, an untreated WDA3 soil sample was placed in a small cylindrical column and a tagged solution simulating the natural ground water was passed
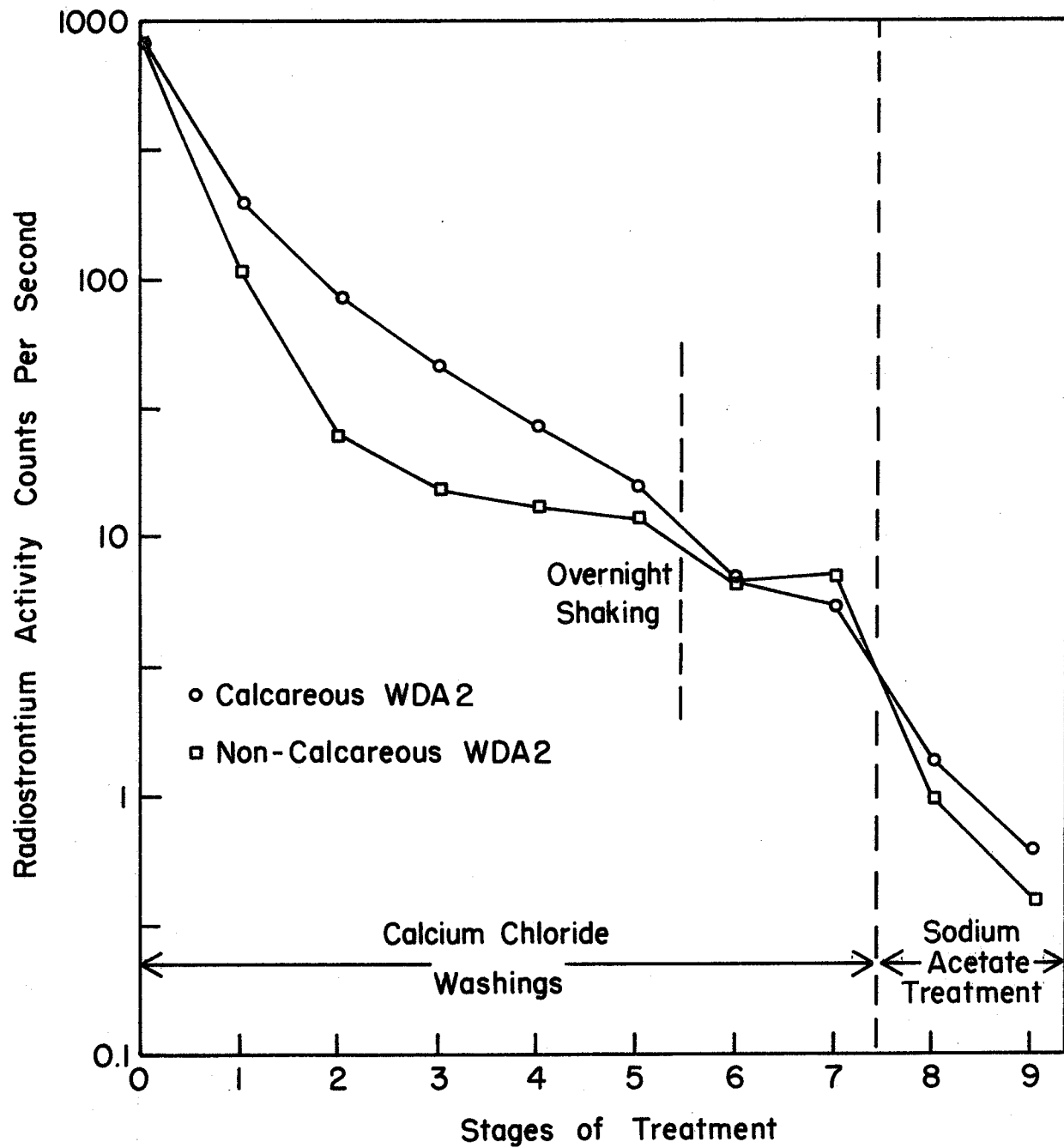
Figure 16. Removal of sorbed radiostrontium by various chemical treatments.
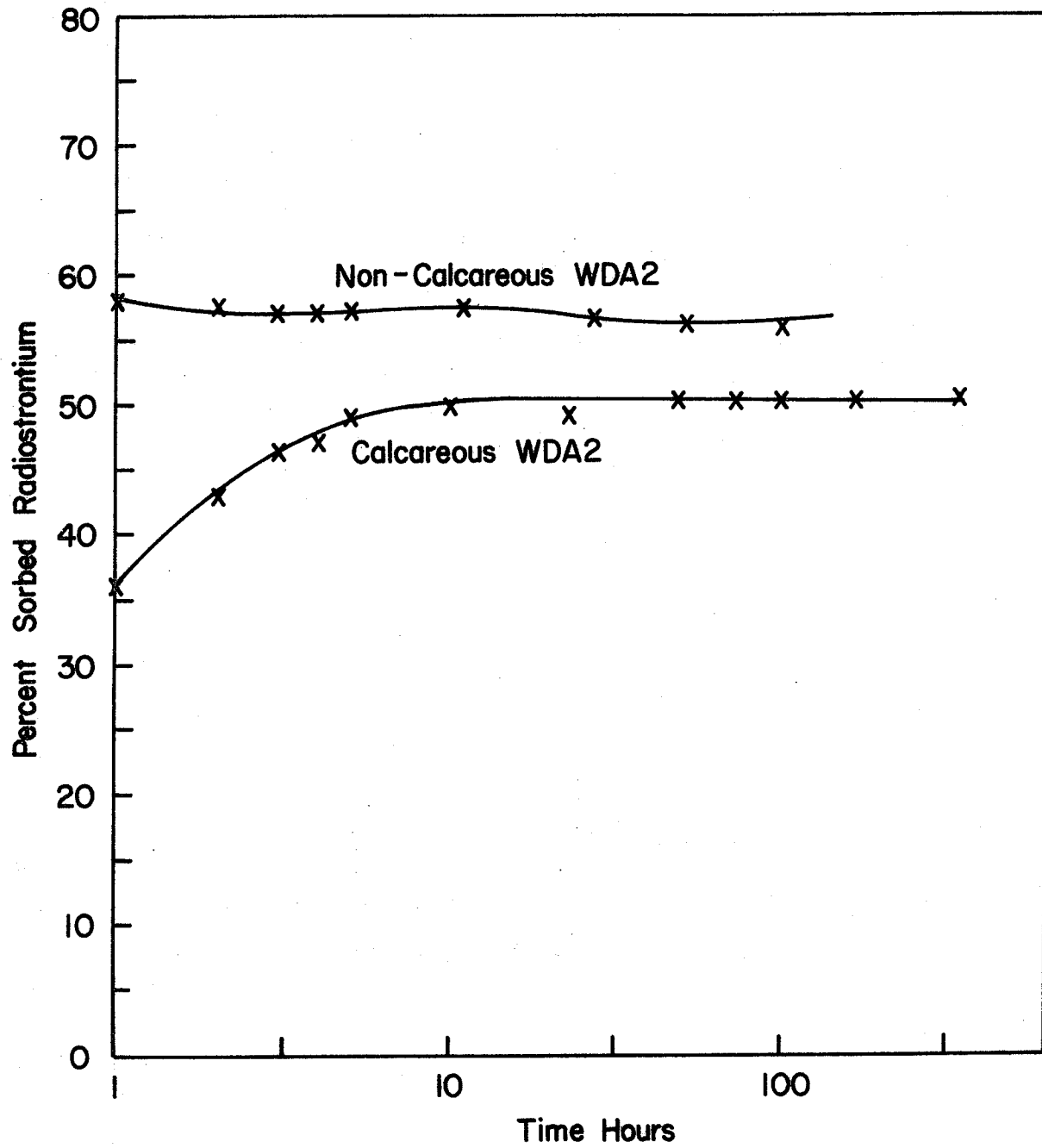
Figure 17. Sorption of radiostrontium by two samples as a function of time.

through the sample at a very slow rate. The method was designed for

equilibrium studies in that the solution was to be passed through until

the radioactivity in the effluent was equal to that in the influent

solution. The total radioactivity in the system was determined by direct

counting of the small column in the well of the scintillation crystal.

The ratioactivity in the solution phase was calculated from the pore

volume of the sample and the activity in the feed solution. From these

data the SrDR was calculated. Corrections were made for the geometry of

the column and the activity in the influent tube above the sample. The

results for sample WDA3 are given in Table XVII. The last column is the

SrDR predicted from Equations [12] and [13]. Reasons for the discrepancy

between the experimental and predicted data are not clear. Some unforeseen

bias may have entered into the experimental determination. If the experi-

mental SrDR data are correct they may be due to some irreversible sorption,

either an artifact or the technique or characteristic of the soil. However,

as will be seen, these data do not invalidate the technique for the planned

purpose of radiocesium sorption studies.

TABLE XVII

EXPERIMENTAL AND ESTIMATED SrDR DATA OBTAINED IN TWO COLUMN EXPERIMENTS

Solution Composition				Bulk			Experimental	Estimated
Ca^{++}	Mg^{++}	$SO_4^{=}$	m	Density	V_m	V_n	SrDR	SrDR
	(meq./l)		(g.)		(%)	(%)		
18.7	21.3	40.0	2.539	1.485	26.43	1.84	18.9	15.8
18.7	21.3	40.0	1.173	1.319	30.61	1.84	18.0	13.5

III. INVESTIGATIONS INVOLVING RADIOCESIUM

1. Introduction

The final set of experiments of this study was an investigation of the

sorption of Cs-137 by the composite samples under simulated field conditions. For comparison, an experiment with the Morden bentonite was also included. The column method, which had been evaluated with radio-strontium in the previous section, was used with the radiocesium.

2. Review of Experimental Literature

The literature concerning sorption and fixation of cesium by soils or minerals is extensive due to the importance of Cs137 as a fission product. The mechanism of the reaction of micro quantities of cesium with soil minerals is, at present, open to question and most of the work involving sorption or fixation is of an empirical nature. For example, sorption is often defined as removal from solution regardless of mechanism, and fixation as retention against removal by ion exchange. Few attempts have been made to formulate a mathematical relationship involving the sorption or fixation of micro quantities of cesium. In contrast, the reactions of macroscopic amounts of cesium are fairly well understood.

Krishnamoorthy and Overstreet (22) tested equation [19] on Utah bentonite and concluded that the equation yielded a satisfactory equilibrium constant over a wide range of cesium and calcium saturation of the exchanger phase. For this soil material, the equilibrium constant was found to be 1284 ± 46. This constant may be expected to vary considerably for other exchangers. No irreversibility was noticed with this exchanger but of course macroscopic amounts of cesium were used. Other workers (38,37,12) have encountered fixation or specific absorption when cesium was present in macroscopic or in carrier-free concentrations. The mechanism of the sorption is probably different at these widely differeing concentrations.

Sawhney (38) investigated the kinetics and mechanism of cesium

sorption from 10^{-4} m cesium solutions by montmorillonite, vermiculite, and illite. He postulated that the three distinct sorption sites for cesium or potassium were: external planar sites readily accessible and non-specific, interlattice edge sites readily accessible but specific for K or Cs, and interlayer sites that may be slowly accessible if the silicate lattice is collapsed as in a mica or may be highly accessible if the lattice is fully expanded as in a montmorillonite. These explanations may not be applicable to the sorption of carrier-free radiocesium.

Sawhney (37) studied sorption of cesium from solutions containing 10^{-5} m cesium and 10^{-2} N concentrations of various cations. He found that fixation was associated primarily with the minerals biotite, illite, muscovite, and vermiculite and he postulated that the cesium was sorbed at interlayer sites at the edge of the mica-like lattice. For all minerals, less cesium was fixed against exchange with potassium than with calcium.

Evans and Dekker (12) investigated radiocesium fixation by soils and soil separates. Fixed cesium was defined as that not extractable by ammonium acetate. Sand, silt, and clay fractions all fixed large amounts of carrier-free Cs-137. Only moderate amounts were fixed when Cs-137 was introduced with carrier cesium. Fixation of Cs-137 by whole soils was found to be proportional to the applied dose over a thousand-fold range of concentrations. It was suggested that sesquioxide coatings in podzolic soils could block Cs-137 fixation sites.

Investigations of the active waste disposal pits at Chalk River, Ontario (28,30, 29) have indicated that, in general, Cs-137 does not migrate with the ground water but is fixed at the disposal site. One exceptional case (28), in which a Cs-137 migration was detected, was

attributed to massive amounts of ionic compounds such as ammonium nitrate which accompanied the disposal.

3. Results and Discussion

During these investigations of radioisotope sorption by soils, methods were devised which allowed the factors known to influence the sorption to be varied over a range which included their values in the field. This was done to ensure the applicability of the laboratory data to the field situation. In the case of radiostrontium sorption, the relevant factors are the amounts of calcium and magnesium in the exchanger and solution phases. However, according to equation [19], an addional factor, the volume of the solution phase, enters into ion-exchange studies with radiocesium. Since a dilution of a soil-solution system would displace the ion-exchange equilibrium, a method was developed which would, as closely as possible, simulate the field situation. The soil-solution system was confined in a small cylinder through which a salt solution, representing the ground water could be passed. If a solution containing a radioisotope is passed through such a column, the system will sorb the tracer until the concentration of the radioisotope in the effluent is equal to that in the feed solution. When this occurs, the distribution of the tracer between phases may be determined by a suitable radioactivity determination of the system and the feed solution in conjunction with some physical measurements.

The non-active feed solutions were made from calcium sulphate and magnesium sulphate to simulate the natural groundwater of the particular soil used. In some cases small amounts of sodium and potassium chloride, similar to that in the groundwater, were added in order to investigate the effect of these cations on the radiocesium sorption. The active solutions

were prepared similarly except that Cs-137 was added to a level of about 3 $\mu c/l$.

During the radiocesium sorption experiments it became evident that carrier-free Cs-137 has a strong affinity for glassware. Two thirds of the activity was lost when an active solution prepared in a volumetric flask was transferred to an erlenmeyer flask. Considerable activity was also retained by pipettes used in taking aliquots of active solutions. These problems were alleviated by the use of polyethylene bottles and polypropylene pipettes. Silicone coated pipettes were tested but were found to be no better than non-coated glass pipettes.

As mentioned previously, the column method was designed for ion-exchange equilibrium measurements. Unfortunately equilibrium was never reached in any experiment with Cs-137. This meant that cesium distribution ratios could not be calculated as planned since the activity in the column effluent never became equal to that of the feed solution. However for comparison purposes the calculations were carried out as outlined previously and the resulting distributions labelled apparent cesium distribution ratios (Table XVIII). In order to gain some information about the non-equilibrium situation in the columns, effluent from the columns were sampled at various times during passage of the active feed solutions through the columns. These samples were counted along with aliquots of the feed solutions and blanks. In the later stages of the sorption study, emphasis was shifted almost entirely to the radioactivity of the effluent in an attempt to obtain some useful data from the experiments.

Column Experiments with Cs-137

In Table XVIII, n is the approximate number of pore volumes of active solution which were passed through the column. The last column of figures

is the equilibrium distribution ratio predicted from equation [19] using
the constant obtained by Krishnamoorthy and Overstreet, which was the
only one available. It may be seen that the apparent distribution ratio
often exceeds this equilibrium distribution ratio and in fact seems to
follow the number of pore volumes fed in. It is apparent that all of the
Cs-137 fed in was retained in the column. When, in the first two experi-
ments, after the active solution had been fed in, the non-active solution
was reconnected and fed for a considerable time, the radioactivity of the
columns did not decrease but actually increased slightly. This indicates
that Cs-137 was not leached from the columns but was relatively immobile.
It may be concluded that the equilibrium constant is much higher than that
found by Krishnamoorthy and Overstreet or that the ion-exchange equilibrium
is invalid due to fixation or specific absorption of Cs-137 by the soil.
The case of the bentonite is open to question since the estimated CsDR was
not greatly exceeded. It is apparent, from the experiments with solutions
1 and 2 in Table XVIII, that the addition of small amounts of the monovalent
cations sodium and potassium had no noticeable effect on the sorption of
the Cs-137.

Cs-137 Activity in the Column Effluent

As noted previously, equilibrium was not achieved in any of the columns
and counting of the effluent was turned to in an attempt to investigate the
non-equilibrium process in the columns. The data obtained for the last
six columns is given in Table XIX. All activities were corrected for back-
ground which was about 0.6 cps[*]. From these data it may be stated that
virtually all of the Cs-137 fed in remained in the column, Indeed, there
is some question that the effluent activities are different from zero.

* cps = counts per second.

TABLE XVIII

APPARENT AND ESTIMATED CsDR DATA OBTAINED IN EIGHT COLUMN EXPERIMENTS

Soil	Solution	m	Bulk Density	Vm	Vn	n	Apparent CsDR	Estimated CsDR
WDA3	1	1.76	1.38	31.0%	1.84%	70	74.5	86.5
WDA3	1	1.26	1.35	31.4	1.84	80	82.3	84.5
WDA3	1	1.16	1.28	32.0	1.84	200	182.2	83.7
WDA3	2	0.86	1.46	27.0	1.84	400	404.6	100.7
WDA2	3	0.80	1.03	50.9	7.1	200	162.0	119.2
WDA2	3	0.72	0.94	58.5	7.1	400	350.0	81.7
WDA5	4	2.62	1.73	18.1	0.0	500	284.5	52.9
Bentonite*	5	0.54	0.35	104.6	27.1	300	383.3	283.0

* Calcium saturated prepared sample

Cs-137 appears to be immobilized in the soil column. There is not sufficient data to establish whether the cesium is sorbed by a reversible equilibrium, with a large constant, or is sorbed by an irreversible fixation reaction. If the former mechanism is chosen, the equilibrium constant must be at least twenty times that found by Krishnamoorthy and Overstreet. If the latter is chosen, equation [40] is applicable. If a maximum possible value of the relative concentration in the effluent is taken as 0.003, the equation yields minimum values in the range of 4 hr^{-1} to 17 hr^{-1} for the first order reaction rate constant. In any case it is obvious that Cs-137 in these soils will not move at all or will move extremely slowly in response to ground water movement.

TABLE XIX

RADIOCESIUM ACTIVITY IN THE EFFLUENT FROM SIX COLUMN EXPERIMENTS

Soil	Solution	Sampling Time (hr)	Flow Rate (ml/hr)	Effluent Activity (CPS)	Feed Activity (CPS)
WDA3	1	21	1	0.029	22.1
"	1	45	0.8	0.033	21.6
"	1	71	0.4	negative	21.3
WDA3	2	21	1.8	0.011	20.8
"	2	46	1.7	0.030	20.7
WDA2	3	24	1.2	negative	22.7
"	3	50	0.53	1.078	22.7
"	3	75	0.31	0.052	22.7
"	3	95	0.25	0.032	22.7
WDA2	3	21	1.7	0.003	22.4
"	3	45	1.3	0.015	22.4
"	3	70	1.2	0.059	22.4
"	3	95	1.1	0.059	22.4
WDA5	4	22	5.4	0.044	22.3
"	4	44	2.1	0.008	22.3
"	4	71	0.068	0.008	22.3
Bentonite	5	25	0.96	negative	20.0
"	5	51	0.45	0.066	20.0
"	5	74	0.29	0.038	20.0
"	5	93	2.0	0.017	20.0
"	5	119	1.4	negative	20.0

CHAPTER V

SUMMARY AND CONCLUSIONS

I. INTRODUCTION

The principal concern of this study is an investigation of the

sorption phenomena of carrier-free radiostrontium and radiocesium in soil-

solution systems. The objectives are to relate the sorption of the two

radioisotopes to the chemical and physical characteristics of the soil-

solution systems and to develop methods to predict the sorption from

easily measurable quantities. It is well known that sorption phenomena

are the cause of the retardation of radioisotope movement relative to

ground water movement which occurs during transport of radioisotopes by

ground water. Transport theories were investigated theoretically, not

experimentally, in order to be able to select the most appropriate theories

which could be used in connection with sorption equations to provide models

of radioisotope transport in soils.

The radioisotopes used were Sr-89, which was detected with a geiger

tube, and Sr-85, and Cs-137 which were detected with a scintillation

crystal. The soil materials were five composite soil samples from the WNRE

waste management area, five sediment samples from the Winnipeg River, and

a bentonite from Morden, Manitoba.

Extensive chemical and physical analyses of the samples were conducted

to characterize the soil samples and to provide data to be used in the

radioisotope sorption studies. The ion-exchange reaction between radio-

strontium and calcium was studied with calcium saturated samples to

investigate the theoretical equation and provide data for the samples. An

extrapolation of the theoretical equation was then investigated in systems

of calcareous soils and calcium and magnesium solutions to provide data
which could be applied to field soils. Sorption experiments with radio-
cesium were carried out in columns in order to simulate field conductions.

II. CHARACTERIZATION OF SAMPLES

The texture of the five composite samples from the WNRE waste manage-
ment area ranges from clay at the surface to sandy loam at the bedrock
contact. All are moderately or strongly calcareous. Water soluble salts
decrease with depth and there is an accumulation of gypsum in the form of
concretions in the two surface-most samples due to translocation of soluble
salts by discharging ground water. Cation exchange capacities are
relatively low (3 to 50 meq/100 g) and decrease with depth. The dominant
clay mineral is an interstratified mica-montmorillonite. In the laboratory
the three samples closest to the surface are classified as impermeable to
water and the deepest sample as moderately slowly permeable. The
relatively high soluble salt levels and low cation exchange capacities of
the five composite samples are somewhat unfavourable for retardation of
radioisotope migration by ion exchange.

The five sediment samples from the Winnipeg River are calcareous and
the textures range from clay to sandy loam. The cation exchange capacities
range from 10 to 40 meq/100 g, depending upon texture. Due to the very low
soluble salt content of the river water, radioisotope sorption by ion
exchange is very favourable in these sediments.

The Morden bentonite sample is a nearly ideal montmorillonite mineral.
In its natural state, the deposit is saline and extremely acid. The cation
exchange capacity is very high (105 meq/100 g). The montmorillonite
mineral exists in a larger crystallite size than many other clays; this

accounts for the higher hydraulic conductivity which is higher than in the clay-textured soil samples (WDA2, WDA3). The hydraulic conductivity is still quite low, however, and may constitute a disadvantage if the clay is to be used in columns for water treatment. The high cation exchange capacity is an advantage for radioisotope sorption by ion-exchange but the salt content of the influent solution must also be taken into account.

III. RADIOSTRONTIUM SORPTION

The most useful measure of radiostrontium sorption in soils is the strontium distribution ratio (SrDR), commonly referred to as D in the literature. For a given soil-solution system, the SrDR is defined as the ratio of the total amount of radiostrontium in the exchanger phase to the total amount in the solution phase. For a calcium saturated soil and a calcium chloride solution system, the following equation was found to relate the radiostrontium sorption to the characteristics of the system:

$$SrDR = K \frac{(Ca)x}{(Ca)s} \qquad [4a]$$

K : mass action constant

(Ca)x : total amount of calcium in the exchanger phase (meq)

(Ca)s : " " " " " " solution " (meq)

For systems of calcareous soils and solutions of calcium and magnesium salts, the following equation is useful:

$$SrDR = KC \frac{m}{(Ca + Mg)s} \qquad [12]$$

KC : absorption characteristic (meq/g)

m : weight of soil (g)

(Ca + Mg)s : amount of calcium plus magnesium in solution (meq)

KC is characteristic of the soil, is reasonably constant, and is equal to

the product of the cation exchange capacity and the apparent equilibrium constant.

For radiostrontium sorption by river or lake sediments the most useful measure of sorption is the strontium concentration ratio (SrCR), commonly referred to as K_d in the literature. SrCR is defined as the ratio of the amount of radiostrontium in the exchanger phase per gram of sediment to the amount of radiostrontium in solution per cubic centimeter of water. The equation for SrCR analogous to Equation [12] is:

$$SrCR = KC/N \qquad\qquad [15]$$

N = normality of calcium plus magnesium in solution

KC is, of course, the same as the previous equation.

The carbonate fraction of soils is relatively inert with respect to radiostrontium sorption. Very little irreversibility was noted in batch methods used in the laboratory for radiostrontium sorption studies. However, column studies with calcareous soils have demonstrated that some fixation of radiostrontium does occur. It is not known if this will occur in the field. If it does it is an advantage and in any case Equation [12] provides a good working figure for the SrDR.

IV. RADIOCESIUM SORPTION

In column experiments, designed to simulate the field situation, virtually all of the Cs-137 fed in was retained in the columns. Although no satisfactory equations were developed to explain the sorption, it appears that the very strong sorption of radiocesium by the soils can probably be attributed to a fixation reaction. This situation is, of course, very favourable to the retardation of radiocesium migration in the soil.

V. RADIOSTRONTIUM SORPTION PREDICTION

The following equation may be used to predict the SrDR of field soils:

$$SrDR = KC \frac{100}{N(Vm - Vn)} \qquad [12a]$$

N : normality of calcium plus magnesium in the solution phase

Vm : moisture percentage of the soil

Vn : non-solvent water percentage

As indicated in Appendix A, Vn may be obtained from the following regression equation:

$$Vn = -1.9 + 30.5 \; C \qquad [A36]$$

C : cation exchange capacity in meq/g

Likewise KC may be estimated from the following equation if radioisotope data are not available:

$$KC = 1.34 \; C \qquad [55]$$

Vm may be determined by a simple gravimetric moisture determination upon a field sample and N by a chemical analysis of a ground water sample obtained, for example, from a piezometer. The only other experimental quantity required in the above equation is the cation exchange capacity which may be obtained by the sodium chloride method of Chapter III.

In Table XX, the prediction method is illustrated using the data obtained from the previously described moisture extraction method with the composite soil samples. The variation of SrDR with field moisture content is not rapid and is most pronounced with sample WDA2 due to the presence of an insoluble gypsum phase. The SrDR is similar in all five samples due to the concurrent decrease in cation exchange capacity and in soluble salt content with sampling depth.

TABLE XX

PREDICTED SrDR OF THE COMPOSITE SAMPLES AT VARIOUS MOISTURE CONTENTS

Sample	Vm (%)	Vn (%)	N (meq/ml)	KC (meq/g)	SrDR
WDA2	56	7.1	0.0676	0.467	14.0
WDA2	63	7.1	0.0641	0.465	13.0
WDA2	84	7.2	0.0609	0.465	10.0
WDA2	109	7.2	0.0592	0.459	7.6
WDA3	35	1.8	0.0403	0.155	11.8
WDA3	50	1.8	0.0280	0.155	11.5
WDA3	72	1.8	0.0214	0.155	10.4
WDA3	102	1.8	0.0168	0.155	9.0
WDA1	89.7	9.7	0.0624	0.700	14.0
WDA2	86.0	7.2	0.0594	0.465	10.0
WDA3	46.6	1.8	0.0271	0.155	12.8
WDA4	32.3	1.7	0.0254	0.099	12.7
WDA5	24.2	0.0	0.0159	0.039	10.1

A similar approach may be used to predict the SrCR of river or lake sediments. The relevant equation is:

$$SrCR = KC/N \qquad [15]$$

KC : absorption characteristic

N : normality of calcium plus magnesium in solution

KC may be obtained from a sorption experiment or estimated from the cation exchange capacity and N may be obtained from chemical analysis of the river or lake water. For the five river sediment samples the predictions

shown in Table XXI are obtained using the value N = 0.000926.

TABLE XXI

PREDICTED SrCR OF THE WINNIPEG RIVER SEDIMENTS

Sample	KC (meq/g)	SrCR
1	0.249	268
2E	0.147	158
2W	0.505	545
OF	0.225	242
3	0.187	201

The SrCR data are quite high due to the very low soluble salt concentration
in the river water. The variation among samples is obviously due to
variations in cation exchange capacity.

VI. RADIOSTRONTIUM TRANSPORT IN A HOMOGENEOUS SOIL

The transport of radionuclides in soils by ground water may be
visualized by means of a model in which a solution of the carrier-free
radioisotope in the ground water flows along a column filled with a
granular ion-exchanger. The flow rate must be sufficiently slow that ion-
exchange equilibrium is established everywhere in the column. Fixation of
the radioisotope must be absent. The mean velocity of a front or a band
of activity is given by:

$$W = U/(1 + D)$$
[26]

W : mean velocity of front or band

U : linear velocity of ground water flow

D : equilibrium distribution ratio of tracer

In Equation [26], D is the SrDR, as previously defined, and may be

predicted as indicated above. The ground water velocity, U, may be obtained by the use of non-exchanging tracers such as tritium or dyes or may be estimated from hydraulic conductivity and gradient depending upon the accuracy required. This equation was verified experimentally by Frissel and Poelstra (15) with columns of resin-sand mixtures and illite clays.

If the velocity of the front is sufficiently low that dispersion can be attributed to longitudinal diffusion and to a finite grain size, the following equation gives the "width" of the front of radioactivity:

$$L = 1.81 \sqrt{\frac{4 \ D'x}{U}} \qquad\qquad [32]$$

   L : distance including 80% of the concentration change

   D' : modified liquid diffusion coefficient

   x : position of front

   U : ground water velocity

D' is related to the model by:

$$D' = \gamma \ Do + \lambda \ dU \qquad\qquad [33]$$

   γ : labyrinth factor

   Do : diffusion coefficient of the radioisotope

   λ : packing factor

   d : effective grain size

At the low flow rates common in soils, the contribution of the second term becomes negligible. This equation was also investigated and found to be acceptable by Frissel and Poelstra (15).

In most situations the velocity of a front is more important than the shape or width of the front especially if the front is sharp. The velocity

may be obtained from Equation [26] and if an estimate of the width is required, Equations [32] and [33] may be used.

VII. RADIOSTRONTIUM TRANSPORT IN SOILS WITH A BLOCK AND CHANNEL STRUCTURE

If the soil in question is an impermeable clay or clay till which is fractured into blocks, and if it is established that ground water flow exists primarily in the channels between the blocks, then a different radioisotope transport model is required. The simplest applicable model is one which considers a rectangular column packed with the soil having a narrow channel adjacent to one wall. The ground water containing the radio-isotope flows along the channel and the radioisotope enters or leaves the soil block by diffusion only, since there is no flow of ground water in the block. This is a non-equilibrium model with the dispersion of the front being dependent upon the rate of diffusion into or out of the block as compared to the velocity in the channel. The velocity of the radio-strontium behind the front is given by:

$$W = U'(1 + 1/\alpha) \qquad\qquad [36]$$

W : velocity of radiostrontium

U' : velocity of water in a channel

α : dimensionless parameter

is characteristic of the model and is defined as:

$$\alpha = \frac{a}{\ell(1 + D)\varepsilon} \qquad\qquad [37]$$

2a : width of a soil channel

2ℓ : width of a soil block

D : equilibrium distribution of radioisotope

ε : void fraction of soil block

D is the SrDR and may be estimated as outlined previously. The other data required are the geometry of the blocks and channels, the velocity in the channels, and the void fraction which may be estimated from the field moisture content. Some of these data may be difficult to obtain or may be variable in the field.

The dispersion is difficult to predict theoretically. However, if the rate of diffusion in the block is comparable to the rate of transport in the channel, ion-exchange equilibrium will prevail, and the front will be relatively sharp.

VIII.   RADIOCESIUM TRANSPORT

No mathematical relationship has been developed to predict radiocesium transport. In the soils studied Cs-137 will either be immobile or move at less than one fortieth the velocity of radiostrontium. In most situations the radioisotope of most concern will be Sr-90 and useful predictions are available for transport of this isotope.

IX.   RADIOSTRONTIUM MIGRATION PREDICTION

Introduction

This section is designed to delineate methods of prediction of radio-strontium migration which may be applicable to the sediments in the vicinity of the WNRE waste management area. The accuracy of the predictions depends upon both the validity of the assumptions upon which the theoretical equations are based and the reliability of the field and laboratory data used. The prediction methods require water movement data for all the sediments through which the radiostrontium will move; these may be obtained from tracer studies or from hydraulic gradient and conductivity measurements.

In addition, chemical analysis of the ground water, field moisture content and cation exchange capacity data for the soils along the expected migration path are required. It is also necessary to ascertain the type of permeability network of the sediments. According to the accuracy required, some data may be estimated from known characteristics of the sediments or may be extrapolated from data for nearby samples assumed to be similar.

Prediction Methods

As radioisotope migrations can be expected to follow the ground water flow lines, it is important to obtain reliable data on hydrogeology of a given area. The controlling permeability network of the field soil must be determined and, if flow is other than intergranular, the dimensions of the network must be determined. According to Cherry and Beswick (7), water movement in the till and lacustrine units in the vicinity of the WNRE waste management area may be due to a block and channel fracture network whereas movement in the basal sandy unit may be assumed to be intergranular.

A path over which the migration is to be predicted is then chosen, following a ground water flow line. The path is divided into regions within which the physical and chemical characteristics of the soil and ground water may be assumed to be uniform, and the calculations given below are followed. The total transit time for water or radiostrontium is obtained by a summation of the individual transit times for each region.

Calculations

The water flux in the region is calculated from Darcy's law:

$$F = -k \, \nabla H \tag{56}$$

F : flux (cm/day)

k : hydraulic conductivity

H : hydraulic gradient

If water flow is intergranular, the linear flow rate of ground water is calculated from:

$$U = F/\mathcal{E} \tag{57}$$

U : linear flow rate (cm/day)

$\mathcal{E}$: pore fraction (volumetric water content of the soil)

If water movement is due to a block and channel fracture network, the linear flow rate in the channels is calculated from:

$$U' = F\ell/a \tag{58}$$

U' : flow rate in a channel (cm/day)

2ℓ : width of a soil block (cm)

2a : width of a channel (cm)

Alternatively U or U' may be obtained directly from studies with tritium or other non-exchanging tracers.

Radiostrontium migration rates in the region are calculated using the transport theories discussed earlier in this chapter:

$$W = U/(1 + D) \tag{26}$$

or:

$$W = U'/(1 + 1/\alpha) \tag{36}$$

W : mean velocity of a radiostrontium front (cm/day)

D : equilibrium SrDR

α : dimensionless parameter

The quantities D and α are calculated from chemical and physical data of the soil and ground water using Equations [12a) and [37] respectively.

X. RECOMMENDATIONS

For any proposed active waste disposal area, it is recommended that detailed information be obtained on the hydrogeology and the soil and water chemistry of the site. Radiostrontium migrations predictions may aid in the evaluation of proposed sites.

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APPENDIX A

NON-SOLVENT WATER IN FLOCCULATED CLAY-SOLUTION SYSTEMS

I.   INTRODUCTION

This study was inspired by a remarkable paper by El Swaify et al. (11) in which the term non-solvent water was introduced in quotation marks. Upon consideration of the experimental results and concepts set forth in this paper, it became evident that the concept of non-solvent water or the equivalent concept of negative absorption of anions should be taken into account in the interpretation of results of a study of ion exchange between calcium and radiostrontium in concentrated clay suspensions, which was then in progress. Accordingly a laboratory investigation was carried out utilizing, with one exception, the soils and soil materials studied in the ion-exchange experiments.

The phenomena of non-solvent water, more properly referred to as positive absorption of water, and of negative absorption of anions arise from the definition of the phase boundary in clay-solution systems. Consider the simple situation of a clay mineral immersed in an electrolyte solution, for example, sodium chloride. The presence of the negative surface charge alters the concentrations of the components of the solution in the vicinity of the clay surface. However, these alterations are not directly measurable, but must be inferred from the total amounts of each component in the system and the concentrations in the solution at a large distance from the clay surface. The variations in concentration with distance from a planar charged surface are illustrated in the following diagram. It must be emphasized that the equations derived below apply to any configuration of the charged surface; the planar case is illustrated

because of its simiplicity.
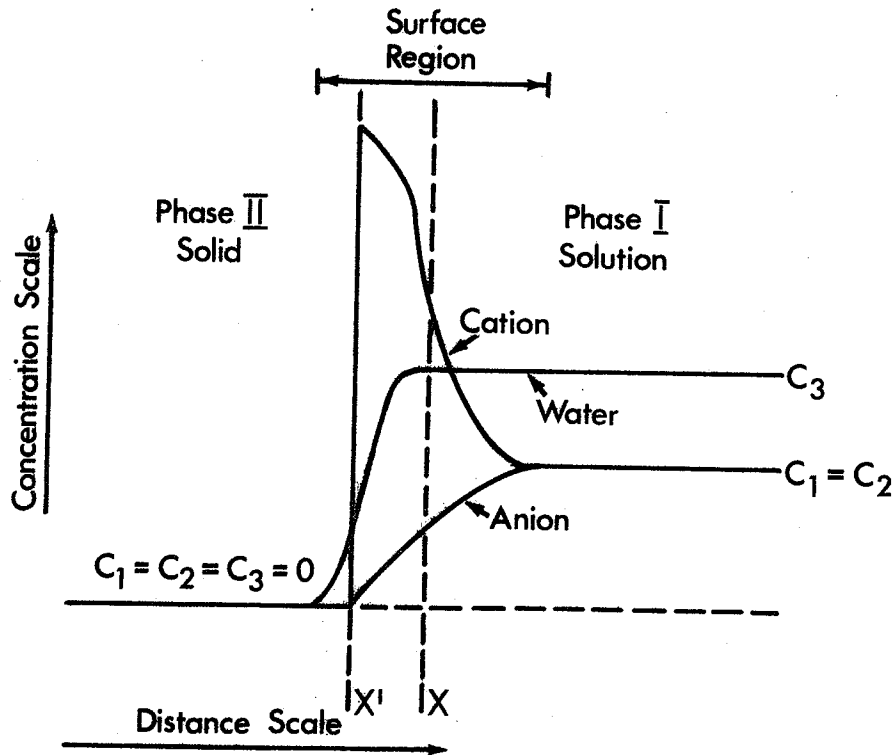
The surface region is a region of small but finite thickness in which the
properties differ appreciably from the properties in the interior of either
phase. As the surface region is approached from the solution side, the
cation concentration increases and the anion concentration decreases due
to the presence of the solid and the concentrations of the components of
the solution must all be zero in the interior of the solid phase. Due to
electroneutrality requirements, the concentrations of the cation and anion
in the solution phase must be equal at distances far from the surface.

In their thermodynamic treatment of surface effects, Lewis and Randall
(33) define a surface concentration of any component as the excess of that

component in the system over that calculated from the volume of each

phase and the concentrations of the component in the interior of each

phase. These surface concentrations are expressed in terms of amount per

unit of surface area and may be positive or negative. In the notation of

Lewis and Randall the three surface concentrations in the clay – solution

system may be defined as follows, if the volumes of the phases are fixed

by the introduction of an arbitrary phase boundary parallel to the surface

region.

$$\Gamma_1 As = n_1 - C_1^I V_I - C_1^{II} V_{II} \qquad [A1]$$

$$\Gamma_2 As = n_2 - C_2^I V_I - C_2^{II} V_{II} \qquad [A2]$$

$$\Gamma_3 As = n_3 - C_3^I V_I - C_3^{II} V_{II} \qquad [A3]$$

Γ : surface concentration

As : surface area

n : total moles or equivalents

C : concentration

V : volume

I : solution phase

II : solid phase

1 : cation

2 : anion

3 : water

The magnitude and sign of these surface concentrations depends upon the

position of the phase boundary and, in general, any one concentration may

be made equal to zero by a proper choice of the boundary. In order to make

the surface concentrations usable quantities, the position of the phase

boundary must be specified; a conventional but arbitrary choice is the plane x^1 in the diagram which makes the surface concentration of water zero. The consequences of this choice are that the volume of the solution phase is defined by the amount of water in the system:

$$V_I = n_3/C_3^I \qquad [A4]$$

and that the inherent negative surface charge of the clay surface is balanced by a positive absorption of cations and a negative absorption of anions which are given by:

$$\Gamma_1 As = n_1 - C_1^I V_I \qquad [A5]$$

$$\Gamma_2 As = n_2 - C_2^I V_I \qquad [A6]$$

A second equally arbitrary choice is the plane x in the diagram; this phase boundary is positioned to make the surface concentration of the anion zero. The volume of the solution phase is then defined by the amount and concentration of the anion in the system:

$$V_I = n_2/C_2^I \qquad [A7]$$

The negative surface charge of the clay mineral is entirely balanced by a positive absorption of cations given by:

$$\Gamma_1 As = n_1 - C_1^I V_I \qquad [A8]$$

There exists a positive absorption of water, the non-solvent water, which is given by:

$$\Gamma_3 As = n_3 - C_3^I V_I \qquad [A9]$$

Although arbitrary, this second convention resulting in the concept of non-solvent water has several advantages over the first convention which results in the concept of negative absorption of anions. To begin with, the concept of a negative absorption is somewhat alien to workers in the soils field.

The cation exchange capacity remains constant and independent of the composition of the solution phase. Finally in some circumstances, as in the study by El Swaify et al. (11), the non-solvent water content is nearly characteristic of a soil or clay mineral.

In any event, there is a simple relationship between the negative absorption of the first convention and the non-solvent water of the second convention which may be derived from equations [A4], [A6], [A7], and [A9]:

$$\frac{\Gamma_3 As}{C_3} = -\frac{\Gamma_2 As}{C_2} \qquad [A10]$$

C_3 may be eliminated by defining it as being equal to unity. In the literature of negative absorption, the quantity $\Gamma_2 As/C_2$ is often referred to as the exclusion volume or the quantity Γ_2/C_2 as the exclusion distance; in effect the non-solvent water concept is being used rather than the negative absorption concept although they are arbitrary and interchangeable.

II. LITERATURE REVIEW AND THEORY

Parallel Plate Model. A model of a clay-solution system to which many theories have been applied consists of negatively charged parallel plates, infinite in extent, between which an electrolyte solution is situated. The distribution of the ions in the vicinity of the plates is governed by the charge of the plates. The volume of water between the plates is equal to one half of the product of the surface area and the distance between the plates. A table of symbols used in connection with this model is presented below.

Γ : surface charge density in meq/cm^2

2X : distance between plates in cm

v : valence of the cation

p : ratio of valence of cation to anion

q : a valence factor

β : constant equal to 1.06 x 10^{15} cm meq^{-1}

n : electrolyte normality

Γ^- : negative absorption in meq/cm^2

A table of the valence factor q is given by Schofield and Talibuddin (40).

The Gouy Theory. The electric double layer theory of Gouy as extended by Schofield (39) results in the following equation for the exclusion distance for the case of infinite plate separation and ideal solution:

$$\frac{\Gamma^-}{n} = \frac{q}{\sqrt{v\beta n}} - \frac{4}{v\beta\Gamma} \qquad [A11]$$

This equation is a good approximation provided that the first term is more than five times the second. Schofield and Talibuddin (40) state that for plate separations given by:

$$v\beta\Gamma \ X > 30 \qquad [A12]$$

the Gouy equation is valid for normalities in the range:

$$\frac{4q^2}{v\beta X^2} < n < \frac{v\beta q^2 \Gamma^2}{(15)^2} \quad \text{if } p = 1 \qquad [A13]$$

At very low normalities the diffuse layers expand to fill the interplate volume. For this situation Schofield and Talibuddin give the following equation:

$$\frac{\Gamma^-}{n} = X - bn^{1/p} \qquad [A14]$$

b is a constant. This equation is valid for normalities in the range of:

$$0 < n < \frac{q^2}{v \, \beta \, X^2} \qquad [A15]$$

when the first term is several times the second.

Substitution of values of Γ commonly found in clays into expression [A12] indicates that Gouy theory is usable if X is greater than 20A^O for a sodium-clay or greater than 10A^O for a calcium-clay. These figures correspond to X-ray d-spacings of 50A^O and 30A^O respectively. Since calcium-clays do not exhibit d-spacings greater than 20A^O (13, 2), the Gouy equations are only applicable to freely expanding sodium (or lithium) saturated clays.

The Donnan Theory. Donnan equilibrium theory may be applied to the case of narrow plate spacing and ideal solution. Schofield and Talibuddin give the following equation:

$$\frac{\Gamma}{nX} = \left(1 - \frac{\Gamma_-}{nX}\right)^{-p} - \left(1 - \frac{\Gamma_-}{nX}\right) \qquad [A16]$$

for spacings given by:

$$v \, \beta \Gamma X < 10 \qquad [A17]$$

For normalities less than one, equation [A16] may be modified to:

$$\frac{\Gamma_-}{n} = X - \frac{X^2 n}{\Gamma} \quad \text{if } p = 1 \qquad [A18]$$

$$\frac{\Gamma_-}{n} = X - \sqrt{\frac{X^3 n}{\Gamma}} \quad \text{if } p = 2 \qquad [A19]$$

From expression [A17] the maximum values of X are 6A^O for a sodium clay and 3A^O for a calcium clay; corresponding X-ray d-spacings are 22A^O and 16A^O respectively. These spacings are compatible with a flocculated sodium-montmorillonite or a flocculated sodium or calcium-vermiculite.

The Theory of de Haan. F.A.M. de Haan (10) has derived expressions for negative absorption in systems with interacting double layers. For

normalities and spacings given by:

$$n < 0.1 \quad \text{and} \quad X < 14 \times 10^{-8} \text{ cm} \qquad [A20]$$

the expression is:

$$\frac{\Gamma}{n} = X - \frac{X^3 \beta}{2\pi^2} n - \frac{4}{v\beta\Gamma} \quad \text{if } p = 1 \qquad [A21]$$

Unfortunately the third term is not valid when:

$$v \beta \Gamma X < 20 \qquad [A22]$$

since this term must be zero when the exclusion distance approaches X.

The Tactoid Model. A number of studies (2, 23) have shown that, in calcium-montmorillonite suspensions, the clay plates are grouped into packets or tactoids having an X-ray d-spacing of approximately 19A°. The fundamental physical units of the suspension then are the tactoids, which may be called crystallites, rather than single clay plates as in the case of a dispersed sodium-clay. The tactoids, which may be viewed as stacks of parallel clay plates with a fixed spacing, possess both internal and external surface areas. The fractions of these surface areas are dependent upon the average number of plates in a tactoid as follows:

$$\frac{Ae}{As} = \frac{1}{k} \qquad \frac{Ai}{As} = \frac{k-1}{k} \qquad [A23]$$

Ae : external surface area

Ai : internal surface area

As : total surface area

 k : average number of plates in a tactoid

The observed exclusion volume of a tactoid suspension is due to the anion exclusion within the tactoids as well as the exclusion associated with the diffuse layer on the external surfaces of the tactoids. The apparent exclusion distance is given by:

$$\frac{Ve}{As} = \frac{k-1}{k} \frac{\Gamma i^-}{n} + \frac{1}{k} \frac{\Gamma e^-}{n} \qquad [A24]$$

Ve : total exclusion volume

Γi^- : internal negative absorption

Γe^- : external negative absorption

A complete theoretical expression for the exclusion volume of a flocculated clay-solution system may be obtained if suitable expressions for the internal and external negative absorption are substituted into equation [A24]. This will be illustrated with data obtained from anion exclusion studies reported in the literature and will be used in the interpretation of data obtained from an experimental investigation of the anion exclusion of a number of soils and soil materials.

Interpretation of the Data of Jacobs. Jacobs (20) studied the exclusion of chloride by a hydrobiotite in sodium chloride solutions. The sample used was an interstratified biotite-vermiculite mineral having a cation exchange capacity of 0.753 meq/g. The exclusion volume in sodium chloride solutions was obtained from measurements of apparent pore volumes for tritium and chloride in solumns packed with the mineral. These data, as read from Jacobs' graph, are given below:

Normality of sodium chloride n (meq/ml)	Exclusion Volume Ve (ml/gm.)
1.0	0.102
0.1	0.123
0.01	0.134
0.001	0.149
0.0004	0.162

The Donnan equation, equation [A18], is applicable to the interlayer region of the vermiculite layers of the crystallites, and the Gouy equation, equation [A11], is applicable to external surfaces of the crystallites of hydrobiotite. The complete expression for the exclusion volume is then:

$$Ve = As \frac{1}{k} \frac{2}{\sqrt{\beta}} n^{-\frac{1}{2}} - As \frac{1}{k} \frac{4}{\beta\Gamma} + As \frac{k-1}{k} X - As \frac{k-1}{k} \frac{X^2}{\Gamma} n \qquad [A25]$$

Since the second and third terms are constant, and the last term is significant only at high normalities, a linear graph should result if Ve is plotted against $N^{-\frac{1}{2}}$. When Jacobs' data is plotted in this manner (Figure A1), a straight line, having a slope of 7.2×10^{-4} and an intercept of 0.127 ml/g., is obtained over most of the graph. The curved portion may be ascribed to the effect of the last term of equation [A25].

From the complete expression, the slope may be seen to be equal to:

$$As \frac{1}{k} \frac{2}{\sqrt{\beta}} = 7.2 \times 10^{-4} \qquad [A26]$$

and the external surface area of the crystallites is:

$$As \frac{1}{k} = 1.17 \ m^2/g \qquad [A27]$$

Also from equation [A25], the intercept of the line may be seen to be equal to:

$$As \frac{k-1}{k} X - As \frac{1}{k} \frac{4}{\beta\Gamma} = 0.127 \qquad [A28]$$

The first term on the left hand side is the Donnan constant and the second, the Gouy constant. From the X-ray d-spacing of wet vermiculites (47), X may be estimated to be 2.77×10^{-8} cm. Γ may be estimated to be 1.8×10^{-7} meq/cm^2 from the cation exchange capacity and theoretical surface area of vermiculites (18). In this case, however, the contribution of the Gouy
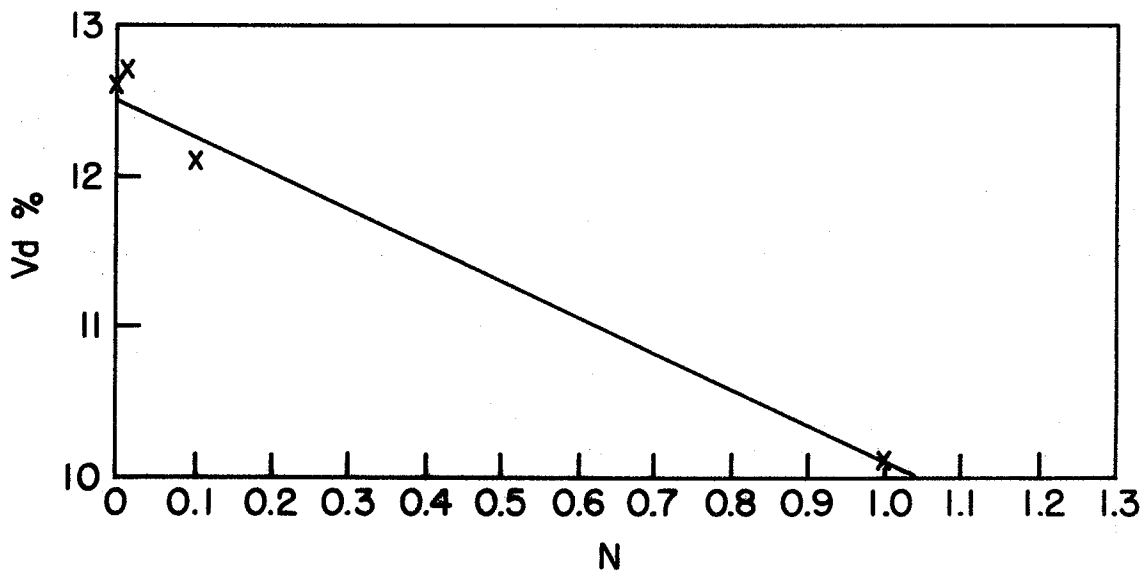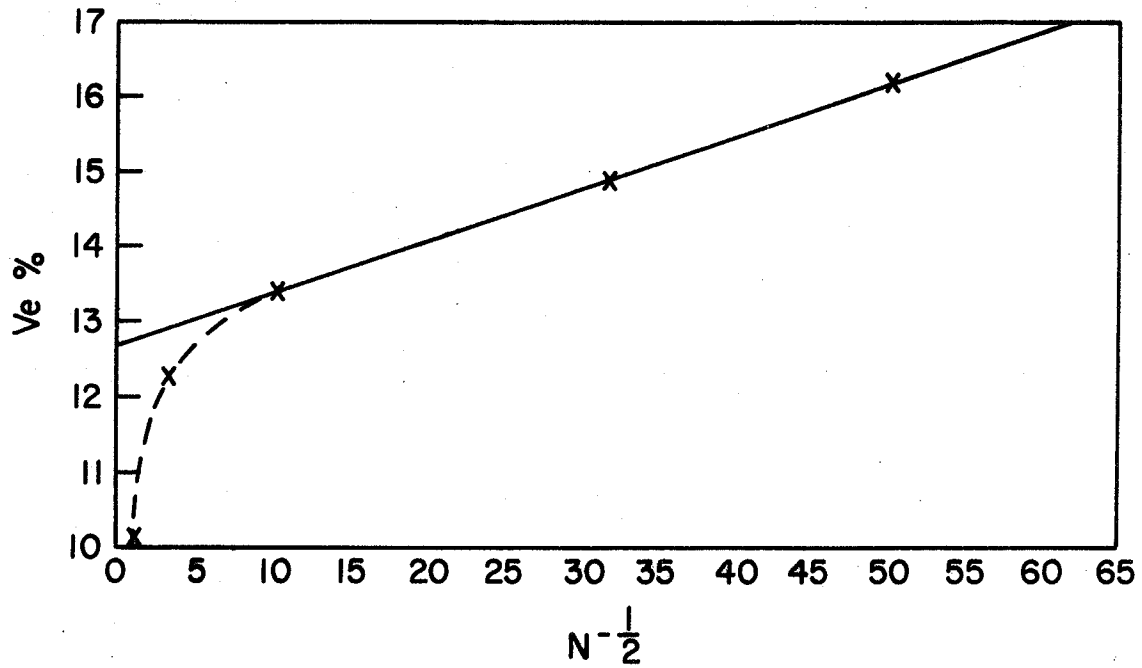
Figure Al. Top: Exclusion volume of hydrobiotite in sodium chloride solutions as a function of the reciprocal square root of normality. Bottom: Interlayer exclusion volume of hydrobiotite as a function of normality. (Recalculated from Jacobs (20).)

constant is insignificant. The internal surface area of the crystallites

may be calculated to be:

$$As \frac{k - 1}{k} = 459 \ m^2/g \qquad [A29]$$

and the average number of vermiculite layers in a crystallite may be

calculated to be:

$$k = 459/1.17 + 1 = 393 \qquad [A30]$$

The average thickness of a crystallite, excluding the biotite layers, may

be calculated as:

$$1 = 393 \ x \ 14.5 \ x \ 10^{-8} = 5.7 \ x \ 10^{-5} \ cm = 0.57\mu \qquad [A31]$$

The total accessible surface area of the crystallite, obtained from the

sum of [A27] and [A29], compares favourably with a figure of 400 m^2/g,

obtained from the theoretical surface area of vermiculite (18) and the

fraction of vermiculite layers in the hydrobiotite as derived from the

cation exchange capacity. The average number of vermiculite layers in a

crystallite, k, is also a reasonable figure.

Previously, the curved portion of the graph of Figure A1 was ascribed

to the variable term of the Donnan equation. If the Gouy contribution

is subtracted from the observed values of Ve, the result is the contrib-

ution to the total exclusion volume due to the Donnan equilibrium within

the crystallites, which should follow the equation:

$$V_d = V_e - V_g = -As \ \frac{k - 1}{k} \frac{X^2}{\Gamma} \ n + As \ \frac{k - 1}{k} \ X \qquad [A32]$$

V_d : Donnan exclusion volume

V_g : Gouy exclusion volume

When Jacobs' data are plotted in accordance with this equation (Figure A1),

the linear graph confirms the validity of the Donnan equation in this

situation. The slope of the line is found to be -0.024; this compares favourably with a value, calculated from data previously obtained, of:

$$-As \frac{k-1}{k} \frac{X^2}{\Gamma} = -0.0214 \qquad [A33]$$

The Donnan equation is therefore applicable to the anion exclusion by the interlayer volume of vermiculite, and the Gouy equation is applicable to the anion exclusion of the external surface area of the crystallites.

Interpretation of the Data of Bower and Goertzen. For the more common situation of a calcium-saturated soil containing montmorillonite or interstratified montmorillonite layers, in equilibrium with a calcium chloride solution, the most suitable equation is:

$$Ve = As \frac{1}{k} \frac{1.464}{\sqrt{2\beta}} n^{-\frac{1}{2}} + As \frac{k-1}{k} X - As \frac{k-1}{k} bn^{\frac{1}{2}} - As \frac{4}{\sqrt{2\Gamma}} \qquad [A34]$$

The last term is somewhat questionable at the small spacings encountered within a tactoid. The third term, derived from equation [A14], becomes negligible at low and moderate normalities and may be eliminated by suitable extrapolation.

Bower and Goertzen (3) report negative absorption data in calcium chloride solutions for three soils formed under arid or semiarid climates. The clay mineral may be assumed to be montmorillonite. The specific surface areas, by glycol absorption, are stated to be:

Traver   36 m^2/g

Sebree   164 m^2/g

Chino   246 m^2/g

In Figure A2, Bower and Goertzen's exclusion volume data for the three soils are plotted as a function of $n^{-\frac{1}{2}}$. Since the data was stated on an oven-dry weight basis, estimates of the ignition loss at $300^{\circ}C$ were made
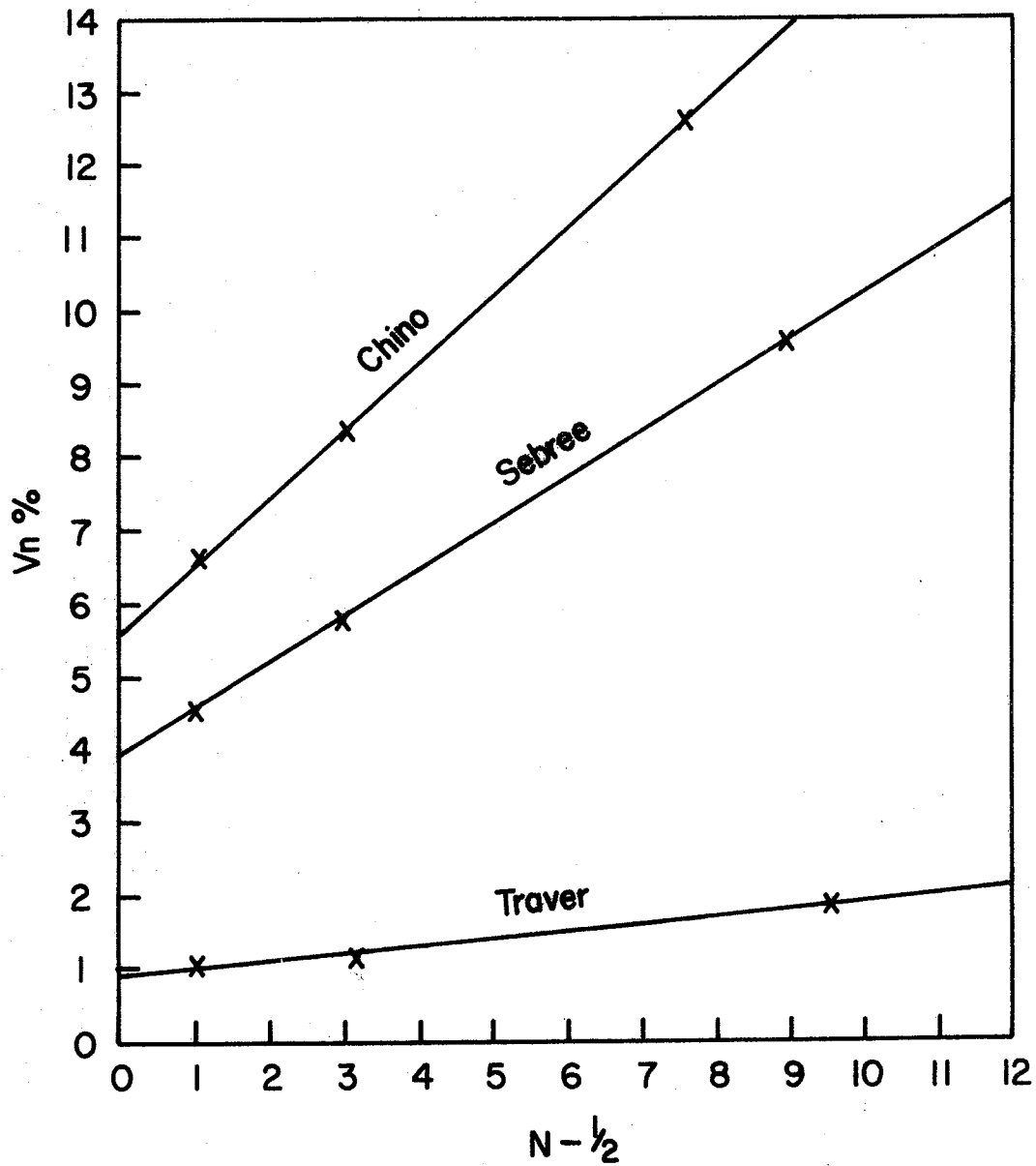
Figure A2. Non-solvent water content of three soils in calcium chloride solutions as a function of the reciprocal square root of normality. (After Bower and Goertzen (3).)

and these were added to Bower and Goertzen's data. The slopes and intercept of the three lines are:

Traver	0.99×10^{-3}	0.0103
Sebree	6.4×10^{-3}	0.0452
Chino	9.0×10^{-3}	0.0662

From the slopes, the external surface areas are:

Traver	$2.78 \ m^2/g$
Sebree	$17.9 \ m^2/g$
Chino	$25.2 \ m^2/g$

Using the experimental total surface areas, the average number of plates in a tactoid, k, may be calculated:

Traver	13
Sebree	9.1
Chino	9.8

The interlayer half-distance, X, was estimated to be 4.8×10^{-8} cm (2), and the surface charge density, Γ , was estimated to be 1.5×10^{-7} meq/cm^2 from data for montmorillonite (18). From these data and the intercepts, the internal and total surface areas may be calculated to be:

Traver	30.8	$33.6 \ m^2/g$
Sebree	137	$155 \ m^2/g$
Chino	202	$227 \ m^2/g$

The calculated total surface areas are in substantial agreement with the experimental values given by Bower and Goertzen.

III. EXPERIMENTAL

Experimental technique is very important in exclusion volume or negative absorption studies because the quantity being determined is the

difference between two larger quantities. In this study, several techniques were investigated, and considerable effort was expended to identify and evaluate all sources of bias in the technique which was eventually used. This technique is similar to that of El Swaify et al. (11) except that centrifuge washing was substituted for the funnel washing of the latter. A calcium-saturated, salt-free soil sample was washed repeatedly with a particular calcium chloride solution to ensure that the composition of the solution phase of the system was identical to the composition of the calcium chloride solution. The sample was then centrifuged, the supernatant decanted, and the total weight, weight of the oven-dry soil, and the chloride content of the soil paste was determined. From these data the non-solvent water content, expressed on an oven-dry weight basis was calculated.

Materials. Most of the experimental investigation involved three soils or soil materials: (1) a calcium-saturated, carbonate-free sample prepared from composite sample WDA2. The predominant clay mineral of the sample is an interstratified mica-montmorillonite. The sample contains 74% clay and half of this clay is less than 0.1μ in diameter. (2) a calcium-saturated sample of Morden bentonite. This sample is a near-ideal montmorillonite; the dominant particle size is coarse clay $(2.0 - 0.2\mu)$. (3) a swelling bentonite of unknown origin. This sample is mineralogically similar to the Morden bentonite except that the dominant particle size is fine clay $(<0.2\mu)$. In addition, a calcium-saturated, carbonate-free sample prepared from composite sample WDA3 and the five sediment samples from the Winnipeg River were used in some determinations. The river sediment samples are calcareous and range in texture from fine sandy loam to clay.

<u>Non-Solvent Water Determination</u>. Solutions of 0.02 N, 0.04 N, and

0.20 N and 1 N calcium chloride were prepared. Four grams of air-dry

sample was placed in a tared 45 ml short conical centrifuge tube and the

sample was washed five times with a particular calcium chloride solution.

At the conclusion of the last washing, the supernatant was decanted, the

neck of the tube was wiped dry, and the tube was quickly weighed. The

sample was then washed five times with 1 N calcium nitrate and the combined

washings were diluted to 200 ml. To determine the sample weight, the

sample was washed twice with 50% ethanol and twice with 95% ethanol and

was dried in the centrifuge tube at 105°C for several days. The sample

was then removed from the oven, soaked in water for an hour, and replaced

in the drying oven. Daily, until the drying test was completed, the sample

was cooled in a desiccator for one half hour, weighed, and returned to the

oven. Weighing was continued until a constant weight loss, approximately

0.03% per day for samples high in clay, was achieved. The base weight used

in calculations was taken at the point at which the weight loss during

drying changed from a rapid loss to a slow constant loss.

Suitable aliquots of the washing solution and the calcium nitrate

extract were diluted to 200 ml with 1 N calcium nitrate for the chloride

determination which was accomplished by automatic titration with 0.01 N

silver nitrate. To detect the end-point, a silver-silver chloride indicating

electrode and a saturated calomel reference electrode, equipped with a 1 N

potassium nitrate salt bridge, were used.

Neglecting tare weights and blanks the calculation is:

$$W_n = W_1 - W_2 - \frac{200 \ d \ A_1 T_2}{A_2 T_1} \qquad [A35]$$

W_n : weight of non-solvent water

W_1 : weight of wet system

W_2 : base weight of oven-dry soil

 d : density of wash solution

A_1 : aliquot of wash solution

T_1 : titration for wash solution

A_2 : aliquot of calcium nitrate extract

T_2 : titration for calcium nitrate extract

<u>Determination of X-Ray d-Spacings</u>. Calcium-saturated samples were shaken overnight with 1.0 N or 0.02 N calcium chloride and were centrifuged and the supernatant decanted. The wet sample was placed in the specimen mount of a Philips PW 1064 specimen rotator, levelled with a spatula, and covered with polyethylene film. The specimen was X-rayed with a Philips X-ray generator and diffractometer using cobalt K_2 radiation. For an accurate determination of the d-spacing, a scanning speed of 1/4 degree per minute was used. The polyethylene film effectively prevented evaporation and contributed only a moderately strong peak near 4.14A^o.

<u>Ignition Loss Determinations</u>. In order to determine the adsorbed water which is not driven off at 105°C, the ignition loss of the samples was determined. Upper temperature limits of 300°C for soil clays and 350°C for well crystallized clays were selected to differentiate between adsorbed water and hydroxyl water. Calcium saturated samples were dried to "constant weight" at 107°C and were heated for eighteen hour periods at 300°C or 350°C until "constant weight" was again achieved. Ignition loss was calculated as a percent of the weight at 105°C.

<u>Cation Exchange Capacity Determinations</u>. A centrifuge washing technique

based upon displacement of exchangeable cations by ammonium acetate was
used to determine the cation exchange capacity of the calcium saturated
non-calcareous samples. An analagous funnel washing technique using 2 N
sodium chloride was employed with the calcareous samples. Calcium and
magnesium were determined by EDTA titration.

IV. RESULTS AND DISCUSSION

Evaluation of the Data. The results of the non-solvent water
determinations are presented in Table AI. Variation between duplicates
is within experimental error in most cases. For the Morden bentonite and
the WDA2 sample, for example, the estimated experimental error ranged from
5% to 12%. For sample WDA3 and the river sediment samples, no duplicates
are available, but the variations between determinations at different
normalities are within estimated experimental errors, which range from
26% to 66%. Consequently, no conclusions regarding the variation of the
non-solvent water content of these samples with normality may be drawn
from these data.

Variation of Non-Solvent Water with Normality. In Figure A3 the non-
solvent water contents of sample WDA2, the Morden bentonite, and the
swelling bentonite are plotted against the reciprocal square root of the
normality. In accordance with theory, a linear relationship is evident
in the low normality range. The intercepts and slopes of the tangents are
given below:

Soil WDA2	0.0712	7.02×10^{-3}
Morden bentonite	0.260	1.6×10^{-3}
Swelling bentonite	0.201	17.7×10^{-3}

TABLE AI

NON-SOLVENT WATER CONTENT OF THE SAMPLES

IN EQUILIBRIUM WITH VARIOUS CALCIUM CHLORIDE SOLUTIONS

Sample	Normality	% Non-Solvent Water	
WDA2	0.02177	12.0	
(Calcium-saturated	0.04315	*11.2	*8.7
Carbonate-free)	0.2188	8.7	8.5
	1.100	7.6	7.4
Morden bentonite	0.02170	*23.7	*34.6
(Calcium-saturated)	0.02121	27.4	25.2
	0.04321	27.0	28.5
	0.04087	26.0	25.7
	0.2176	26.3	26.2
	1.1050	26.3	26.1
Swelling bentonite	0.0206	*31.8	*21.4
	0.0402	28.7	29.8
	0.203	23.4	24.8
	1.03	21.6	19.8
WDA3	0.04383	2.4	
(Calcium-saturated)	0.2217	2.5	
	1.1252	2.7	
River Sediments			
1	0.04390	3.1	
	1.1262	3.7	
2E	0.04390	0.7	
	1.1262	2.0	
2W	0.04390	9.8	
	1.1262	11.2	
3	0.04390	1.7	
	1.1262	3.4	
OF	0.04390	2.4	
	1.1262	3.7	

* Variation between replicates exceeds estimated experimental error.
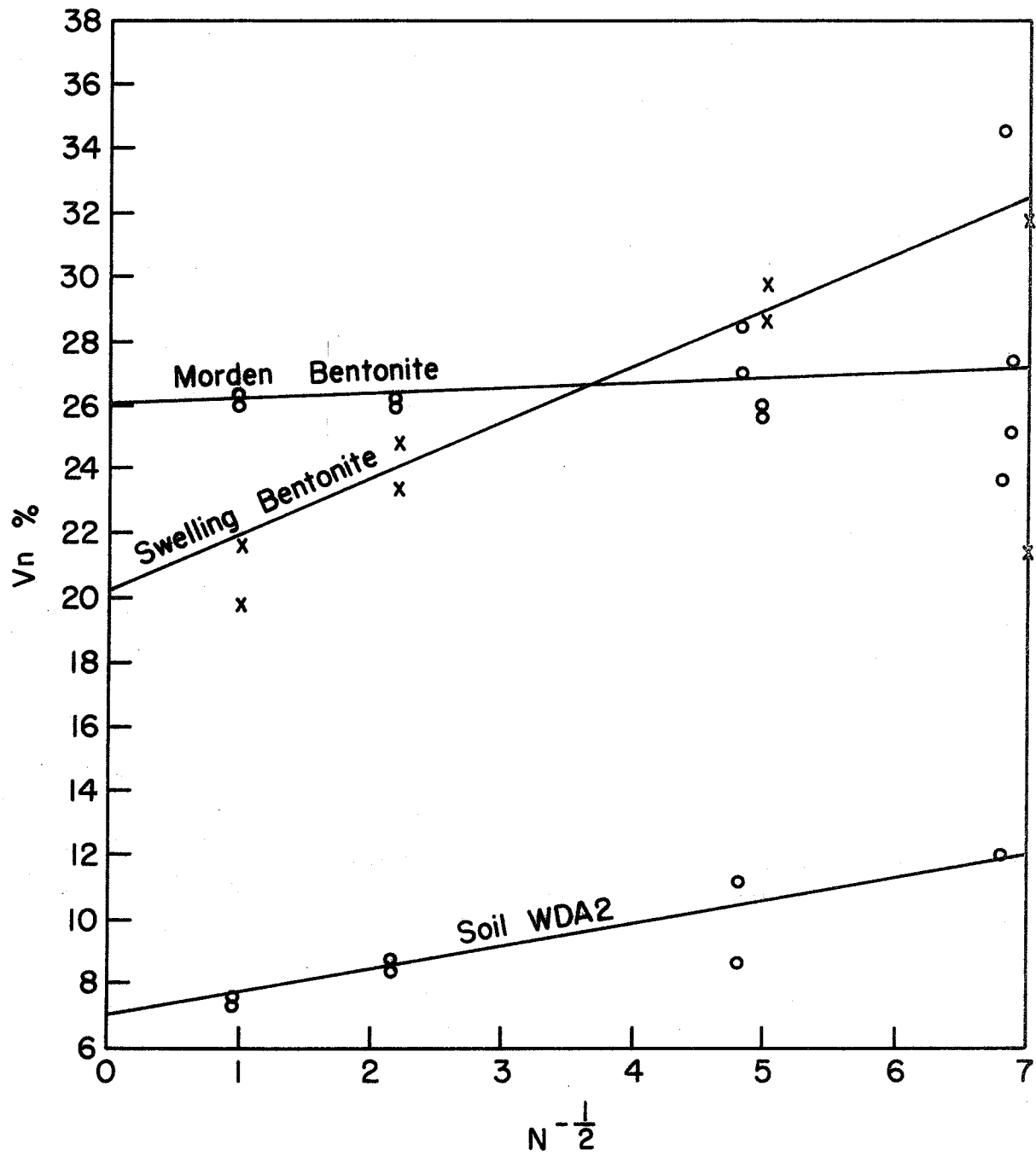
Figure A3. Non-solvent water percentage as a function of the reciprocal square root of the normality.

Interpretation of the Non-Solvent Water Data by the Tactoid Theory.
The ignition loss between 107°C and 300°C must be added to the non-solvent water data and to the above intercepts to obtain exclusion volume figures. For soil WDA2 and the Morden bentonite respectively, the ignition loss was found to be 1.4% and 2.0%. An estimated value of 3.0% was used for the swelling bentonite.

Equation [A34] is the most applicable equation to the situation of montmorillonitic tactoids in a calcium chloride solution. Using this equation and the slopes of the lines in Figure A3, the external surface area, $As \frac{1}{k}$, may be calculated:

Soil WDA2	22.1×10^4 cm^2/g
Morden bentonite	5.0×10^4 cm^2/g
Swelling bentonite	55.7×10^4 cm^2/g

If the total surface area, As, is estimated using the charge density of montmorillonite, the number of layers in a crystallite, k, and the thickness of a crystallite, l, may be calculated:

	As	k	l
Soil WDA2	280 m^2/g	13	0.025μ
Morden bentonite	740 m^2/g	150	0.28μ
Swelling bentonite	640 m^2/g	12	0.023μ

The interlayer half-distance, X, is derived from the X-ray diffraction data and the internal surface area, $As \frac{k-1}{k}$, is obtained from the intercepts of the lines in Figure A3. The last term of equation [A34) is estimated using the above total surface area data. A calculated value of the total surface area, As, is obtained from the sum of the external and internal surface areas. These data are tabulated below.

	X	As $\frac{k-1}{k}$	As
Soil WDA2	4.9A$^{\circ}$	248 m^2/g	270 m^2/g
Morden bentonite	4.65A$^{\circ}$	808 m^2/g	813 m^2/g
Swelling bentonite	4.8A$^{\circ}$	654 m^2/g	710 m^2/g

The calculated surface areas are in good agreement with the estimated values. In addition the crystallite thickness data compare favourably with the particle size data of the three materials.

Relation of Non-Solvent Water Content to Cation Exchange Capacity.
Non-solvent water content would be expected to be strongly dependent upon the cation exchange capacity of a soil material since both quantities are related to the surface area. According to the tactoid theory, the non-solvent water content should also be a function of the normality of the equilibrium solution and the average dimensions of the tactoids. To investigate the dependance upon cation exchange capacity the two non-solvent water figures, at 0.04 N and 1.0 N, for each of the river sediment samples and sample WDA3 were averaged and were compared to the respective cation exchange capacity figures. These data are presented in Table AII and are plotted in Figure A4. Data for sample WDA2, the Morden bentonite and the swelling bentonite in 0.04 N calcium chloride solutions are also included.

If the Morden bentonite point is neglected, the remaining data points indicate a linear relationship between non-solvent water content and cation exchange capacity. The Morden bentonite sample is considered abnormal in this group of samples because of its large crystallite size. The straight line of Figure A4 has the regression equation:

$$V_n = -1.9 + 30.5 \ c \qquad\qquad [A36]$$

V_n : non-solvent water percentage

c : cation exchange capacity (meq/g)
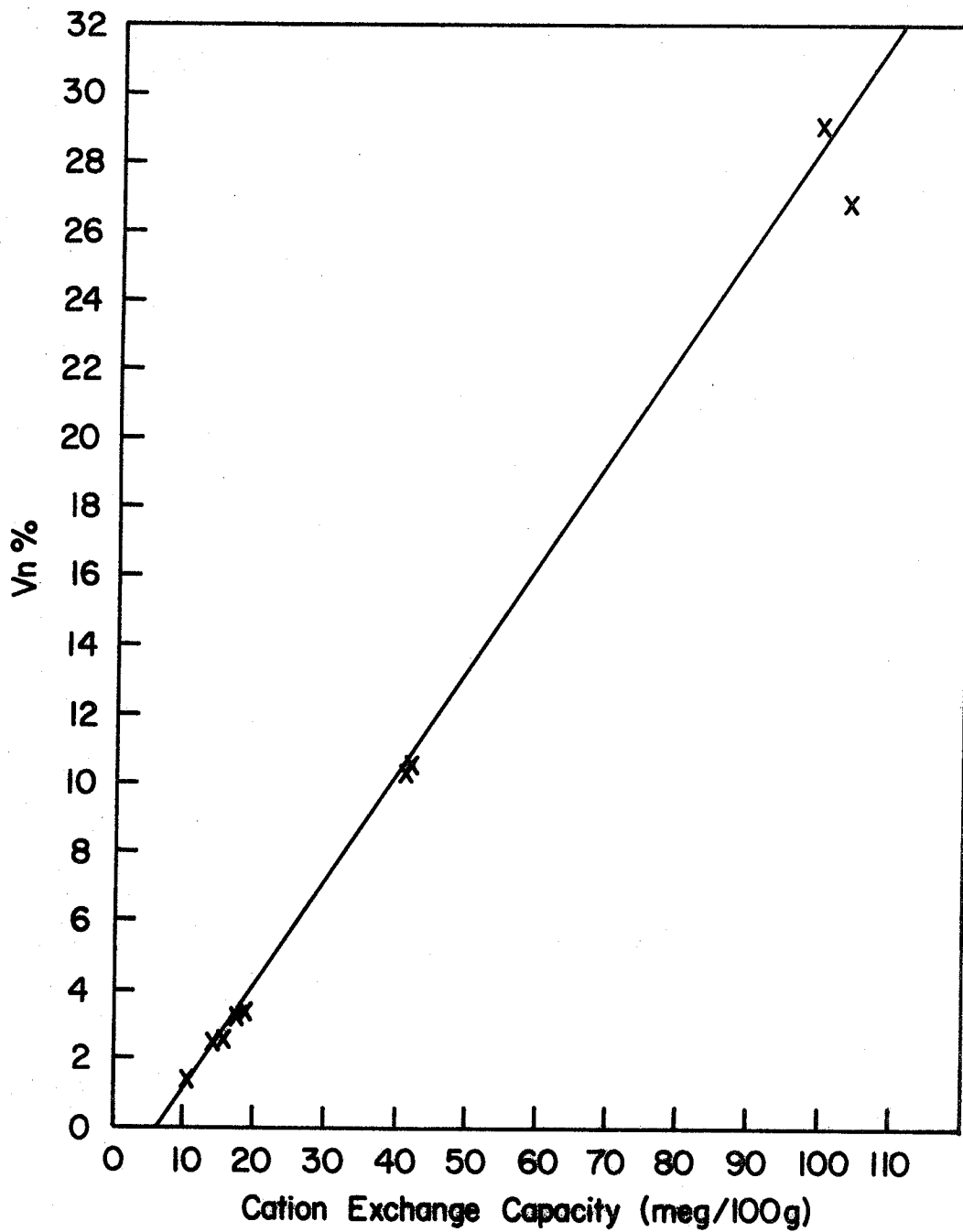
Figure A4. Non-solvent water content of five samples as a function of cation exchange capacity.

TABLE AII

AVERAGE NON-SOLVENT WATER CONTENT AND CATION EXCHANGE CAPACITY

OF THE SAMPLES

Sample	Non-Solvent Water (%)	Cation Exchange Capacity (meq/100 g)
WDA3	2.5	14.0
1	3.4	18.1
2E	1.4	10.5
2W	10.5	40.4
3	2.6	15.4
0F	3.2	17.5
WDA2	10.5	41.5
Morden bentonite	26.8	103.2
Swelling bentonite	29.0	99

Theory predicts a similar line which passes through the origin: the experimental line passes through the point: $V_n = 0$, $C = 0.06$. This discrepancy may be attributed to a small component of the cation exchange capacity which is not associated with a surface.

V. CONCLUSIONS

Suitability of the Tactoid Theory. The tactoid theory, in which ion exclusion by the external surface of the tactoids is given by the Gouy equation and ion exclusion by the internal surface by the Donnan or Gouy extrapolation equation, predicts that non-solvent water content or exclusion volume is a linear function of the reciprocal square root of the solution normality. Data obtained from soil sample WDA2, the Morden bentonite, and the swelling bentonite in calcium chloride solutions are in substantial

agreement with this prediction over a wide range of normalities. Further-more, the intercepts and slopes of the lines, when treated according to the theory, yield reasonable values of the surface area and number of plates in a tactoid.

Non-solvent Water Data to be Used in Ion-Exchange Studies. For soil sample WDA2, the Morden bentonite, and the swelling bentonite, non-solvent water data may be read from the graphs of Figure A3. Data for soil sample WDA3 and the river sediment samples may be obtained from Table AII. If necessary data for soil samples WDA2 and WDA3 should be adjusted to account for the carbonate content of the original composite samples.

Relation of Non-Solvent Water Content to Cation Exchange Capacity. The regression, equation [A36], may be used to obtain a reasonable estimate of non-solvent water content of soils in calcium chloride solutions. This may be useful since cation exchange data are often available and determinations are relatively simple.

APPENDIX B

CLAY MINERALOGY OF COMPOSITE SAMPLES WDA2 AND WDA3

The samples chosen for the investigation were composite samples WDA2 and WDA3 obtained from the WNRE waste management area which are representative of the lacustrine and till layers, respectively. The particle size fractions used were fine silt (5 - 2μ), coarse clay (2 - 1μ), medium clay (1.0 - 0.2μ) and fine clay ($<$0.2μ), with most attention being devoted to the fine clay fraction. To facilitate the X-ray interpretations, the fine clay fraction was further subdivided into (0.2 - 0.1μ) and $<$0.1μ fractions. X-ray diffraction was used for identification and semi-quantitative determination of mineral species. To estimate the chemical composition of the dominant species, chemical analysis and cation exchange capacity determinations were employed. These determinations also allowed quantitative determinations of some mineral components to be made. The various methods employed are outlined in Chapter III.

1. X-Ray Diffraction Analysis

Typical X-ray diffractograms are presented in Figure B1 and the interpretations of all diffractograms are presented in Table BI. Non-clay minerals such as quartz and feldspars predominate in the coarser fractions. Clay minerals such as montmorillonite and interstratified mica-montmorillonite begin to appear in the medium sized fractions and predominate in the finer fractions. Kaolinite is most evident in the medium sized fractions. In general the clay mineralogy of samples WDA2 and WDA3 is similar, both in distribution and species present.

Only in two fractions was montmorillonite found as a discrete species; most of the montmorillonite is present as a component of interstratified
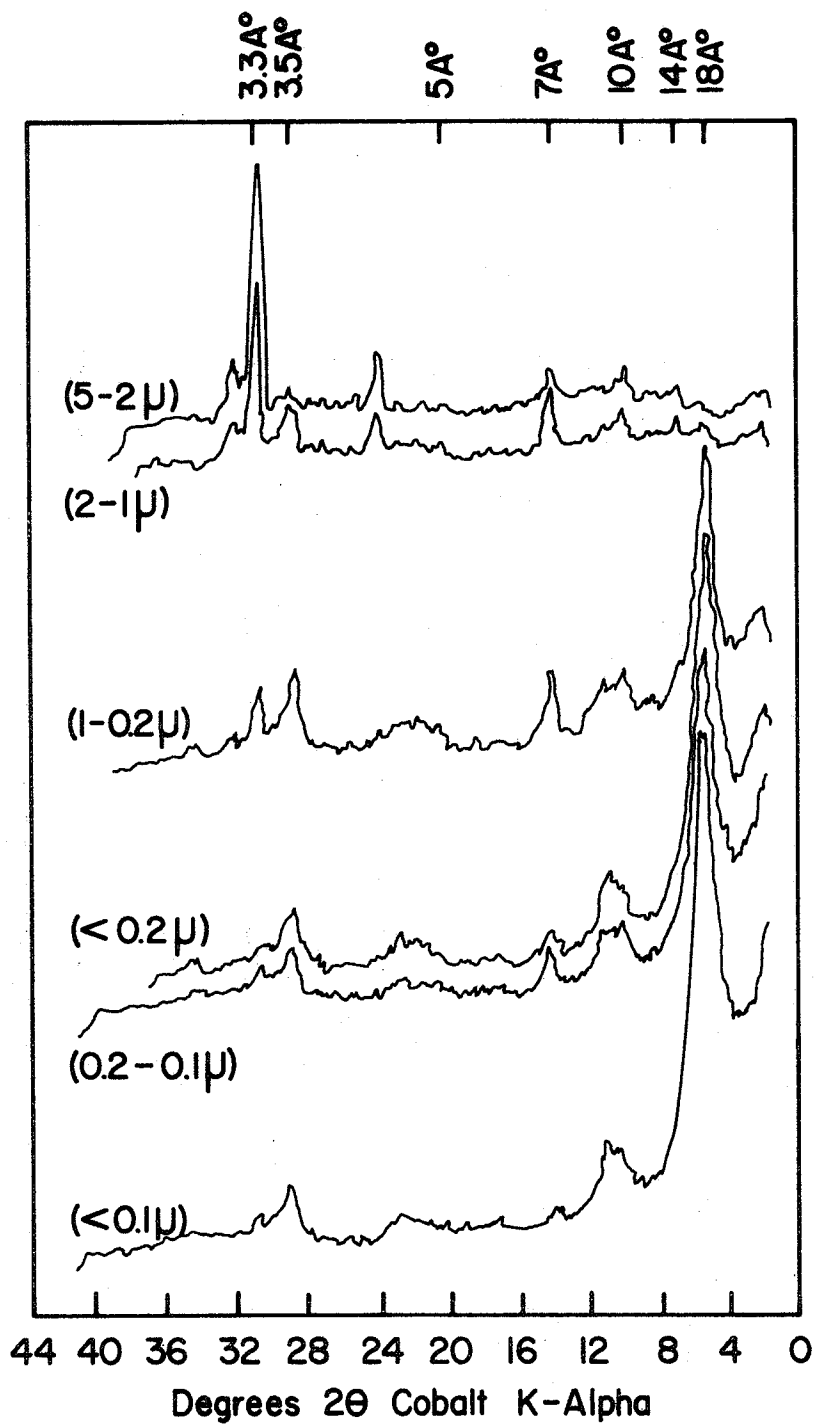
Figure B1. X-ray diffractograms of magnesium saturated, glycerol solvated, parallel orientated specimens of various particle size fractions of composite sample WDA2.

minerals. These minerals, which are the dominant minerals of the clay fractions finer than 1 micron, are composed of collapsed layers, which are presumed to be mica, and expandable layers, which are presumed to be montmorillonite. The fraction of mica layers in the mineral is given by the probability coefficient Pa. A second probability coefficient, Paa, describes the stacking sequence of the layers. In Table BI, Paa is always greater than Pa, indicating a tendency to segregation of layer types.

2. Chemical Analysis and Cation Exchange Capacity

The results of the chemical analysis of lithium-saturated fine clay fractions of WDA2 and WDA3 and of the cation exchange capacity determinations for the same fractions are given below:

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	C_2O	MgO
WDA2	52.91	20.82	0.53	8.27	0.00	2.76
WDA3	51.13	20.09	0.60	7.97	0.00	3.17

Sample	Na_2O	K_2O	Li_2O	Ign. Loss	C.E.C.
WDA2	0.22	2.33	0.99	8.68	0.749 meq/g
WDA3	0.48	3.07	0.84	9.42	0.629 meq/g

From these data the following layer silicate structural formulae were calculated:

WDA2 Fine Clay

$$Na_{0.21}K_{0.44}X_{0.63}(Si_{7.24}Al_{0.76})(Al_{2.53}Fe^{III}_{0.90}Mg_{0.60})O_{20}(OH)_4$$

WDA3 Fine Clay

$$Na_{0.13}K_{0.55}X_{0.53}(Si_{7.22}Al_{0.78})(Al_{2.56}Fe^{III}_{0.85}Mg_{0.67})O_{20}(OH)_4$$
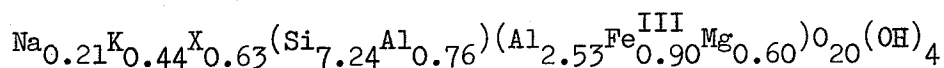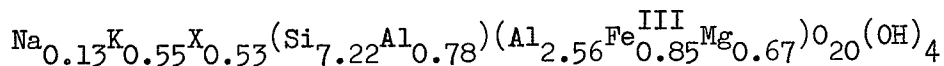
TABLE BI

MINERAL SPECIES OF SOME PARTICLE SIZE FRACTIONS OF COMPOSITE SAMPLES WDA2 AND WDA3

Fraction	Sample WDA2		Sample WDA3	
	Major Species	Minor Species	Major Species	Minor Species
Fine Silt (5-2μ)	Quartz Plagioclase	Kaolinite Mica Vermiculite Chlorite K-Feldspar Cristobalite	Quartz Plagioclase	Kaolinite Vermiculite Mica Chlorite K-Feldspar Cristobalite
Coarse Clay (2-1μ)	Quartz Kaolinite	Illite Int. Mica-Mont. (.7/.95) Plagioclase K-Feldspar Chlorite Vermiculite Cristobalite	Quartz Kaolinte	Plagioclase Vermiculite Int. Mica-Mont. (.5/.8) K-Feldspar
Medium Clay (1.0-0.2μ)	Int. Mica-Mont. (.25/.7) Kaolinite	Quartz Feldspars Chlorite Int. Chlorite	Int. Mica-Mont. (.5/.85) Kaolinite	Plagioclase Quartz Vermiculite Int. Mica-Vermiculite
Fine Clay (0.2u)	Int. Mica-Mont. (.55/.7) Mont.	Kaolinite Int. Chlorite-Mont. (.8/.8) Int. Mica-Chlorite	Int. Mica-Mont. (.6/.85)	Kaolinite Int. Chlorite
(0.2-0.1μ)	Int. Mica-Mont. (.6/.9) Illite	Kaolinite	Int. Mica-Mont. (.6/.7) Illite	Kaolinite Chlorite Int. Mica-Chlorite
(<0.1μ)	Int. Mica-Mont. (.5/.8) Mont.	Kaolinite	Int. Mica-Mont. (.5/.7)	Kaolinite

Int. = Interstratified   Mont. = montmorillonite

Numbers in brackets following the name of an interstratified mineral are values of the probability coefficients Pa and Paa.

The first set of brackets represent the tetrahedral layer and the second, the octahedral layer. The interlayer ions are sodium, potassium, and the exchangeable cations. The sum of the octahedral ions is very close to four indicating that the silicate is dioctahedral as is typical of montmorillonite and illite. The formulae must be considered as averages since the X-ray data indicate that the dominant mineral is an interstratified mica-montmorillonite with two distinct layer types.

3. Quantitative Determination of Mineral Components

Assuming that the mica layers of the interstratified mineral have the potassium content of an ideal muscovite, the percent mica component of the fine clay fraction may be calculated. Similarly the montmorillonite component may be calculated, assuming that the montmorillonite layers have the cation exchange capacity of an ideal montmorillonite. The quantitative estimates are given below:

Sample	% Mica	% Mont.
WDA2 Fine Clay	23	66
WDA3 Fine Clay	31	55

These data are not in accord with the Pa values from the X-ray diffraction analysis, suggesting that the mica layers contain less potassium than ideal muscovite.

APPENDIX C

DETAILED DEXCRIPTIONS OF THE SOIL SAMPLES

FROM THE WNRE WASTE MANAGEMENT AREA

The complete descriptions of the seventy-seven soil samples obtained from five sites in the WNRE waste management area are given in Tables CI to CV. Depths given refer to the bottom of the hole at the time the auger was raised to secure the sample. Texture was determined by hand texturing. When concretions or mottles were evident, the approximate fraction of an exposed surface occupied by these features was estimated. Carbonate content was estimated from effervescence upon application of dilute hydrochloric acid and moist and dry colors were determined with a Munsell color chart. In the case of samples containing concretions, carbonate content and colors were determined on both the concretions and the matrix portion of the sample. Quantity and type of pebbles and other significant characteristics were also noted.

The following abbreviations and classifications are used:

Texture (see Appendix D)

C	Clay	L	Loam
SiC	Silty clay	SL	Sandy loam
SiCL	Silty clay loam	LS	Loamy sand
CL	Clay loam	MS	Medium sand

Concretions (Conc.)

(M)   Matrix

(C)   Concretions

<u>Carbonate Content</u> (Carb.)

0 Non-calcareous	3 Strongly calcareous
1 Weakly calcareous	4 Very strongly calcareous
2 Moderately calcareous	5 Extremely calcareous

<u>Mottles</u> (Mott.)	<u>Pebbles</u> (Pebb.)
f Few (2%)	L Limestone
c Common (2 - 20%)	G Granite

TABLE CI

LOG OF SITE NUMBER 1

Depth ft, in	Text.	Concr. %	Carb.	Moist Color	Dry Color	Mott.	Pebb.	Remarks
1, 6	C		0	10YR2/1	10YR2/1			No pebbles
3, 4	C	15	2(M)	10YR4/2(M)	10YR5/1(M)		L	Few pebbles
			4(C)	10YR7/2(C)	10YR8/1(C)			
5, 8	C	5	1(M)	10YR4/1(M)			L, G	Few pebbles
			4(C)	10YR7/2(C)	10YR7/2(C)			
7, 6	SiC		4	10YR5/3	10YR7/2		L, G	
9, 4	SiC		4	10YR4/2	10YR6/2		L, G	
11, 0	SiC		3	10YR4/2	10YR6/2	f	L, G	
13, 6	SiCL		3	5Y 4/2	10YR6/2	f	L, G	
16, 0	SiCL		2	10YR4/2	10YR6/2	f	L, G	
18, 0	SiCL		3	10YR4/2	10YR6/2		L, G	
20, 6	SiCL		3	10YR4/2	10YR6/2		L, G	
23, 0	SiCL		2	10YR4/3	10YR6/1		L, G	
24, 4	CL		2	10YR4/2	10YR6/2		L, G	
25, 6	CL		2	10YR4/2	10YR6/1		L, G	Pockets of organic matter

(M) = Matrix   (C) = Concretions

TABLE CII

LOG OF SITE NUMBER 2

Depth ft, in	Text.	Concr. %	Carb.	Moist Color	Dry Color	Mott.	Pebb.	Remarks
1, 6	C		2	10YR3/1			L	
4, 0	C	10	2(M)	10YR3/1(M)	10YR4/1(M)		L	
			4(C)	10YR7/2(C)	10YR8/1(C)			
6, 0	C	5	3(M)	10YR4/1(M)	10YR5/1(M)		L	
			4(C)	10YR6/2(C)	10YR7/1(C)			
8, 0	SiC	5	2(M)	10YR4/1(M)	10YR5/1(M)	f	L	
			4(C)	10YR6/2(C)	10YR7/1(C)			
9, 6	SiC		4	5Y 4/2	5Y 6/2	f	L, G	
11, 0	SiC		3	5Y 5/3	5Y 6/2	f	L, G	Varved
12, 6	SiCL		4	5Y 4/2	5Y 6/2	c	L, G	
14, 0	SiCL		3	5Y 5/2	5Y 6/2	c	V	
15, 6	SiCL		3	5Y 5/2	5Y 6/2	f	V	
17, 0	SiCL		3	5Y 5/2	5Y 6/1		V	Few pebbles
18, 0	CL		3	10YR4/2	10YR6/2		G	Few large pebbles
20, 6	L		2	10YR4/2	10YR6/2		V	" " "
21, 6	LS		2	10YR4/2	10YR6/2		V	" " "

(M) = Matrix   (C) = Concretions

TABLE CIII

LOG OF SITE NUMBER 3

Depth ft, in	Text.	Concr. %	Carb.	Moist Color	Dry Color	Mott.	Pebb.	Remarks
1, 6	SiC		3	10YR2/1	10YR4/2			No pebbles
3, 0	SiC	25	2(M)	10YR3/1(M)	10YR4/1(M)			No pebbles
			4(C)	10YR7/2(C)	10YR8/1(C)			
5, 0	SiC	10	2(M)	10YR3/2(M)	10YR4/1(M)		L	Few small pebbles
			2(C)	10YR6/2(C)	10YR7/1(C)			
7, 4	SiC	10	1(M)	10YR3/1(M)	10YR4/1(M)		L	
			2(C)	10YR7/1(C)	10YR8/1(C)			
9, 0	SiC	15	2(M)	10YR3/1(M)	10YR4/2(M)	f	L, G	
			3(C)	10YR6/3(C)	10YR7/2(C)			
10, 10	SiCL	50	3(M)	10YR3/2(M)	10YR4/2(M)	c	L	Few pebbles
			3(C)	10YR6/2(C)	10YR7/1(C)			
13, 6	SiC		3	10YR4/2	10YR7/1		L	Few pebbles
15, 8	SiC		3	10YR5/3	10YR7/2		L, G	
17, 0	SiC		3	5Y 5/3	5Y 6/1		L, G	
18, 6	SiC		4	5Y 4/3	5Y 6/3		L, G	
20, 4	SiC		4	5Y 5/3	5Y 6/2		L, G	
21, 0	CL		3	5Y 5/2	5Y 6/1			Very few pebbles
22, 6	LS		2	5Y 5/3	5Y 7/1		L, G	Larger pebbles
24, 0	MS		2	5Y 5/3	5Y 7/1		L, G	" "
25, 8	MS		2	5Y 5/3	5Y 7/2		L, G	" "

(M) = Matrix   (C) = Concretions

TABLE C IV

LOG OF SITE NUMBER 4

Depth ft, in	Text.	Concr. %	Carb.	Moist Color	Dry Color	Mott.	Pebb.	Remarks
1, 6	C		2	10YR2/1	10YR4/2			No pebbles
3, 0	C	.10	2(M)	10YR3/1(M)			L	Small pebbles
			4(C)	10YR6/3(C)	10YR7/1(C)			
4, 9	C	10	1(M)	10YR4/2(M)				No pebbles
			3(C)	10YR5/2(C)	10YR7/1(C)			
6, 6	C		1	10YR4/2	10YR7/2	c		" "
7, 9	C		1	10YR4/3	10YR6/2	c		" "
10, 0	C		1	10YR4/2	10YR7/2	c		" "
11, 6	C		3	10YR4/2	10YR6/1		L	
12, 6	C		4	5Y 5/2	5Y 6/2		L	
15, 2	C		3	5Y 4/3	5Y 7/3		L, G	
16, 0	SiC		4	5Y 4/3	5Y 6/1		L, G	
18, 3	SiC		4	5Y 5/3	5Y 7/2		L	
20, 9	SiC		3	5Y 4/1	5Y 6/1		L, G	
21, 9	SiC		3	5Y 4/1	5Y 6/1		L, G	
24, 6	SiCL		3	5Y 4/1	5Y 6/1		L, G	
26, 0	SiCL		3	5Y 4/1	5Y 6/1		L, G	
27, 0	CL		3	5Y 4/1	5Y 6/1			
27, 9	SL		2	5Y 5/2	5Y 6/1		L	
29, 6	LS		2	5Y 5/2	5Y 6/1		L, G	
29, 8	LS		2	5Y 5/2	5Y 6/1		L, G	

(M) = Matrix   (C) = Concretions

TABLE C V

LOG OF SITE NUMBER 7

Depth ft, in	Text.	Concr. %	Carb.	Moist Color	Dry Color	Mott.	Pebb.	Remarks
1, 6	C		0	10YR2/1				No pebbles
3, 6	C	5	2(M)	10YR4/3(M)				" "
			2(C)		10YR7/1(C)			
5, 0	C	5	1(M)	5Y 3/1(M)				" "
			0(C)		5Y 7/2(C)			
7, 0	C	5	1(M)	10YR3/2(M)				" "
			4(C)		10YR8/1(C)			
8, 0	SiC	10	1(M)	10YR4/2(M)			L	
			4(C)		10YR8/1(C)			
9, 6	SiC	5	1(M)	10YR4/1(M)			L	
			4(C)		10YR8/1(C)			
11, 8	C	5	1(M)	10YR3/1(M)			L, G	Few pebbles
			3(C)		10YR8/1(C)			
13, 0	C	10	1(M)	10YR4/2(M)			L	Varved
			3(C)		10YR8/1(C)			
14, 6	C		2	5Y 5/3	5Y 7/2		L	
16, 6	C		3	5Y 5/3	5Y 7/3		L	
17, 6	C		3	5Y 4/2	5Y 7/1		L, G	
18, 0	SL		2	5Y 5/2	5Y 7/2		L, G	
20, 4	SL		3	5Y 5/3	5Y 7/2		L, G	
21, 6	SCL		3	5Y 4/2	5Y 6/1		L, G	
24, 0	SL		2	5Y 5/2	5Y 7/1		L, G	
24, 6	SL		2	5Y 6/2	5Y 7/1		L, G	Large pebbles
25, 6	MS		2	5Y 6/2	5Y 7/1		L, G	" "

(M) = Matrix   (C) = Concretions

APPENDIX D

THE CLASSIFICATION OF SOIL TEXTURE

The texture of a soil refers to the relative amounts of sand, silt, and clay. Sand is defined as particles having diameters between 20 mm and 0.05 mm (50μ). Similarly silt and clay are defined as particles having diameters between 50μ and 2μ and less than 2μ respectively. Soil texture is classified in accordance with the textural triangle given below. In addition the word sand may be preceded by the dominant sand size (very fine, fine, medium, coarse, very coarse).