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EXPERIMENTAL METHODS FOR OBTAINING
PERCOL MODEL INPUT AND VERIFICATION
DATA

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1973

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EXPERIMENTAL METHODS FOR OBTAINING PERCOL
MODEL INPUT AND VERIFICATION DATA

by

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WATER AND LAND RESOURCES DEPARTMENT

1973

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SUMMARY

A soil-waste chemical equilibrium model, PERCOL, has been developed to numerically simulate the complex chemical reactions that occur while a solution is percolating through porous media. Experimental procedures for measuring PERCOL model input verification parameters are described, including procedures for preparing both saturated and unsaturated experimental soil columns.

Two methods of determining the soil-cation-exchange, capacity and soil exchange selectivity constants are presented.

Methods for determining the initial soil conditions, a procedure for measuring the apparent porosity of a soil column and an empirical determination of trace ion sorption are also described.

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EXPERIMENTAL METHODS FOR OBTAINING PERCOL MODEL INPUT AND VERIFICATION DATA

INTRODUCTION

A soil-waste chemical equilibrium model, PERCOL, has been developed to numerically simulate the complex chemical reactions that occur while a solution is percolating through porous media. The chemical theory upon which PERCOL is based and the model's incorporation into a transport model are documented elsewhere^{1,2} and a computer user's manual for the PERCOL Fortran V program is also available.³ Procedures for measuring the many parameters and necessary input data are described in this report.

To validate the PERCOL model small experimental columns were packed with soil and simulated waste solutions were pumped through the columns to approximate percolation. The effluent solution was serially collected and its chemical composition determined and compared with PERCOL's predictions. The column verification methods are also described in this report.

Parameters measured include soil cation-exchange capacity, soil cation selectivity constants, soil apparent porosity, soil moisture content, soil bulk density, trace constituent sorption constants, sparingly soluble salt content, soluble salt content, and influent and effluent solute chemical composition.

EXPERIMENTAL COLUMN TECHNIQUES

To verify the PERCOL model experimental soil columns were packed with representative soils from the Hanford Reservation. Simulated waste solutions were pumped through the columns to approximate percolation; then the effluent solutions were collected and their chemical compositions measured. The PERCOL model uses information about the soil type, initial soil conditions, column dimensions and influent composition to predict the one dimensional transport, neglecting diffusion and dispersion, of the solute species. These predictions can be compared with the actual results determined from the effluent of the experimental soil columns.

SATURATED COLUMNS

A standard wall pyrex tubing with an O.D. of 45 mm was chosen for the saturated soil columns. Lengths of the experimental columns were to be 25 cm, 50 cm, and 100 cm, so tubing was cut in lengths of about 35 cm, 60 cm, and 110 cm to allow room for end plugs. Measurement of the inside column diameter with calipers showed the diameter to be 3.7 cm. Single hole rubber stoppers were used for end plugs and short pieces of glass tubing protruding from the stoppers were used to connect influent and effluent lines. The bottom stopper was inserted and cemented into place with RTV rubber cement. A layer of glass wool or glass beads was added to the bottom of the column to prevent soil from plugging the influent line and to facilitate uniform flow away from the source (upflow was utilized for the saturated columns to minimize air pockets). At this point tare weight of the column was obtained.

A homogeneous air dry soil sample was then carefully packed into the column, which was mounted on a vibrating shaker. The soil was added through a long-stemmed funnel which was slowly raised as the column filled. This technique was found to best minimize variations in soil bulk density. By varying the intensity of shaking and rate of soil addition individual columns could be packed to the desired bulk densities.

The length and weight of the full column was then measured and the volume and weight of soil calculated. The bulk density of the soil was calculated as

$$Bd = \frac{\text{weight of soil}}{\text{volume of soil}}$$

Glass wool or a layer of glass beads was then laid on top of the soil and the top stopper cemented in place. The column was covered with black electrician's tape to limit biological activity and weighed to get a total dry weight. Tygon tubing was connected to the column inlet and the influent was pumped using infusion-withdrawal pumps (Harvard Apparatus Series 954). The top of the column or effluent line was run to a carefully sealed fraction collector (Buchler Fractomat Model 3-4200) which was equipped with a plastic lid to minimize evaporation losses. The effluent was collected as small aliquots automatically by the fraction collector, to be analyzed and compared against the influent solute.

The influent solution was stored in a graduated cylinder (covered to minimize evaporation) so that the volume pumped could be continuously monitored.

A comparison between the volume of effluent collected and volume of influent dispensed allowed measurement of evaporation loss. If the loss exceeded 2-5%, a check was made for system leaks, especially from the syringes on the pump. A saturated sponge was maintained in the fraction collector enclosure to minimize evaporation. The chemical comparison between the effluent and influent was the data utilized to validate the chemical model. Standard wet chemical analyses such as atomic absorption and titration were used to determine the concentrations of the solute species of interest. Radioactive trace constituents were measured using appropriate counting techniques. Figure 1 shows the essential components used to perform the saturated column verification work.

FIGURE 1. Schematic of Saturated Column Apparatus

Figures 2 and 3 show the laboratory set-up for saturated columns.

FIGURE 2. Saturated Column Apparatus

FIGURE 3. Saturated Soil Column

UNSATURATED COLUMNS

The specially designed unsaturated column utilized a porous ceramic frit and an outer glass jacket, as shown in Figures 4 and 5. The porous frit, when wetted, allows water to pass through but does not pass air; thus when the frit is saturated a pressure differential can be maintained across it. The positive pressure on the soil column creates the unsaturation. The inner column has the ceramic frit on the bottom and several pin holes along the sides which allow air flow. The soil was packed into the inner column using the method previously described for packing the saturated columns. After the volume and bulk density of the soil were determined, the inner column was placed inside the outer glass jacket. The bottom of the inner column is a glass joint which fits into the outer jacket to prevent air leaks.

FIGURE 4. Unsaturated Soil Column

FIGURE 5. Unsaturated Soil Column

Rubber stoppers acted as top plugs for both the inner column and inner to outer column connection (see Figure 5) and RTV rubber cement fortified the end plugs. An inlet connected the outer jacket to a regulated air supply, creating a positive pressure gradient. The air supply bubbled through a water trap to increase the humidity and reduce evaporation in the soil column. Pressure was monitored with a U tube manometer.

The infusion-withdrawal pump utilized for solution input to the column was fitted with special leak resistant high pressure stainless steel (Harvard Apparatus Catalog 761) syringes. Regular syringes develop significant leaks in this system and should not be used.

Collection of effluent and chemical comparison of the effluent and influent were accomplished by the methods described in the previous section on saturated columns. Figure 6 is a schematic of the salient parts of the unsaturated system. Figures 7 and 8 show the laboratory apparatus used for the unsaturated column verification studies.

FIGURE 6. Schematic of Unsaturated Column Apparatus

FIGURE 7. Unsaturated Column Apparatus

FIGURE 8. Unsaturated Column Apparatus

The percent saturation of the soil column is determined at the end of the percolation. Immediately after the influent is removed, the pressure is released and the column dismantled. Subsections of soil versus depth are carefully removed and placed in tared moisture cans. The wet soil is weighed, dried at 105°C for 24 hours and reweighed. The moisture content as percent on a dry basis is calculated and compared with the saturated moisture content. The theoretical saturation moisture content is calculated from the pore volume determined from the bulk density (Bd) and the particle density. The particle density (Pd) is assumed to be constant at 2.65 g/cm³. The pore volume is

$$1 - \text{Bd}/\text{Pd}$$

The percent moisture at saturation on a weight basis is

$$\frac{1 - \text{Bd}/\text{Pd}}{\text{Bd}} = \frac{\text{Pd} - \text{Bd}}{\text{Pd} \text{Bd}}$$

assuming the density of water is 1.0 g/cm³.

$$\% \text{ Moisture Content} = \frac{\text{Soil Wet Wt} - \text{Soil Dry Wt}}{\text{Soil Dry Wt}} \times 100$$

$$\% \text{ Sat} = \text{Moisture Content} / \text{Saturated Moisture Content} \times 100$$

CATION EXCHANGE CAPACITY

Cation exchange between the soil and solution accounts for a significant fraction of the chemical changes which occur as solutes percolate through porous media.

The active constituents of soils with cation-exchange properties consist for the most part of clay minerals and organic matter. One exchange parameter of interest is the cation-exchange capacity, which is defined as the total amount of exchangeable cations that a soil can retain. The cation-exchange capacity is among the input data needed by the PERCOL model.

A small column procedure was developed to measure the cation-exchange capacity of the calcareous low exchange capacity sands and sandy soils present in the Hanford region.⁴ The procedure is outlined below and described in detail in the referenced document:

2.0 g of soil of known moisture content are transferred to a fritted disk sealing tube (Corning 39570). 250 ml of pH 5.0 $\text{Sr}(\text{OAc})_2$ (0.8N - SrCl_2 (0.2N) solution is percolated through the soil at 25 ml increments. 250 ml at pH 7.0 of the same solution is then percolated through the soil. Finally, 250 ml of pH 7.0 $\text{Sr}(\text{OAc})_2$ (0.04N) - SrCl_2 (0.01N) solution traced with approximately 5000 cpm/ml of ^{85}Sr in 25 ml increments is percolated through the soil. Entrained solution is removed by vacuum suction, two 1 ml washes of 1 ppm Magnifloc 905 nonionic polyelectrolyte and two 1 ml washes of methanol-polyelectrolyte (1:1). The concentration of Sr in the 0.05 N solution is accurately determined by atomic absorption. The soil column and a 2 ml aliquot of the trace equilibration solution are then γ counted for ^{85}Sr activity. The specific activity (cpm/me) of the traced equilibration solution is calculated. The cation-exchange-capacity me/g is then calculated by dividing the unit soil activity (cpm/g) by the specific activity of the traced equilibrating solution.

A second method was used to determine the cation-exchange-capacity by the replacement of an index ion⁵ but the ^{85}Sr tracer small column method is recommended for low exchange capacity sands. The tracer method is more accurate and convenient than the batch type replacement method.

SOIL CATION SELECTIVITY RELATIONSHIPS

In natural systems the solute usually contains several cations which compete with each other for the exchange sites on the soil. Different preferences for each cation are found in each soil type. Experiments were designed to determine a soil's selectivity constant K_{A-B} for a binary ion exchange reaction $mB^{+n} + A_nX \rightarrow B_mX + nA^{+m}$ where

x = soil exchange matrix

A,B = competing cations

The selectivity coefficient K_{A-B} is defined as

$$K_{A-B} = \frac{[B_mX][A^{+m}]^n}{[A_nX][B^{+n}]^m}$$

An approximation has been made that the combination of several binary ion exchange reactions models the multicomponent complex exchange reactions occurring in natural systems.

Two methods have been developed to determine the selectivity constant. The first method is a batch type exchange.

10 g samples of the soil are weighed into 250 ml centrifuge bottles. Carbonates are removed with three 100 ml pH 5 washes with a salt solution consisting of the nitrate of the salt to be used to saturate the exchange media. Three 100 ml washes of this salt solution at pH 7 are then used to saturate the exchange. Excess saturating solution is removed with one 1 ppm Magnifloc wash followed by three methanol-Magnifloc washes (1:1) and the soil is dried in a vacuum oven at 75°C under vacuum. The dry soil is reweighed. Salt solutions of the competing cation are made to cover a concentration range of about 10^{-3} to 10^{-1} N. To the dry soil samples, 100 ml of the competing salt solution at a designated concentration is added after which the system is agitated for 24 hours and centrifuged. The supernatant is analyzed for the equilibrium concentrations in solution of the saturating and competing ions.

Binary exchange reactions analyzed for the PERCOL model were sodium-potassium, sodium-calcium and magnesium-calcium. These three reactions include most of the exchangeable cations in natural porous media. A detailed description of the sodium-calcium binary exchange and subsequent calculations is presented below.

Samples of well-mixed soil weighing 10.0 g are put into 250 ml centrifuge bottles. Carbonates are removed with three 100 ml washes of 1M pH 5.0 $\text{Ca}(\text{NO}_3)_2$. The system is agitated for 10-30 minutes, centrifuged and decanted. The soil is then calcium saturated with three 100 ml washes of 1M pH 7.0 $\text{Ca}(\text{NO}_3)_2$ and again agitated for 10-30 minutes.

Next, the soil is washed with about 50 ml of 1 ppm Magnifloc 905 nonionic polyelectrolyte followed by three washes with a methanol 1 ppm polyelectrolyte solution (1:1). All washes are centrifuged, decanted and discarded. The soil is dried in a vacuum oven at

75°C and reweighed to provide data on loss of fine materials caused by the frequent decants. Loss of material should be kept to a minimum because the fine clay particles are most important in determining the exchange quantities.

Five NaNO_3 solutions were made in the following concentrations: a) .001N, b) .0025N, c) .005N, d) .01N, and e) .1N. The pH of all solutions was 7.0. These sodium solutions were pipetted into triplicate calcium saturated soil samples in quantities of 100.0 mls. The soil-solutions were then agitated for 24 hours, centrifuged and partially decanted; the supernatant solutions were saved.

Sodium concentrations in the influent and equilibrated effluent solutions were measured by atomic absorption (Perkin Elmer Model 303 Na spectral line 5890-5896Å) as was the calcium concentration in the equilibrated solution (Ca spectral line 4227Å).

The initial concentration of calcium on the exchange in the calcium saturated soil was calculated using the cation-exchange-capacity for the specific soil type.

The cation-exchange-capacity (C.E.C.) determination has already been described. The initial calcium on the exchange,

$$\text{CaX}(\text{moles/g}) = \text{C.E.C.}/Z_{\text{Ca}}$$

where

$$Z_{\text{Ca}} = \text{charge on calcium ion} = 2$$

The amount of sodium on the exchange after equilibration, NaX, is calculated from the difference in the initial and final sodium concentrations.

$$\text{NaX} = (\text{Na}_i - \text{Na}_f) V/W$$

where

NaX = sodium on exchange m/g

Na_i = sodium in influent solution m/l

Na_f = sodium in equilibrated (final solution) (m/l)

V = volume of influent solution (l) = .1 l for this case

W = weight of calcium saturated soil (g) ~10g for this case

The equilibrium concentration of CaX is then calculated by difference

$$\text{CaX} = \text{CaX}_{\text{sat}} - \text{NaX}$$

The selectivity constant $K_{\text{Na-Ca}}$ can be determined from the experimental data and a Gapon equation.^{1,6} The Gapon equation

yields the equilibrium relationship

$$K_{\text{Na-Ca}} = \left\{ \frac{\text{Ca}^{+2}}{(\text{Na}^+)^2} \right\} \left[\frac{(\text{Na}_2\text{X}_2)}{(\text{CaX}_2)} \right]^p$$

where

$K_{\text{Na-Ca}}$ = selectivity constant

$\{\text{Ca}\}$ = activity of calcium ion in solution

$\{\text{Na}\}$ = activity of sodium ion in solution

Na_2X_2 = concentration of sodium on soil exchange

CaX_2 = concentration of calcium on soil exchange

p = solid phase soil activity correction constant

Rearranging the equation and substituting concentrations and activity coefficients yields:

$$({K}_{\text{Na-Ca}}) \left[\frac{(\text{CaX}_2)}{(\text{Na}_2\text{X}_2)} \right]^p = \frac{\gamma_{\text{Ca}^{+2}} (\text{Ca}^{+2})}{(\gamma_{\text{Na}^+})^2 (\text{Na}^+)^2}$$

The activity coefficients are calculated by Davies' extension^{1,7} of the Debye-Huckel equation if the ionic strength is below .3 m.

$$-\log \gamma_i = \frac{.509 z_i^2 \sqrt{I}}{1 + \sqrt{I}} - .2 I$$

where

z_i = charge on ion

I = ionic strength

At ionic strengths above .3 m, Bronsted's specific ion interaction theory⁸ is used. The equation for a cation is

$$-\log \gamma_{Mi} = \frac{.509 z_i^2 \sqrt{I}}{1 + \sqrt{I}} + \sum_x B_{Mx} m_x$$

where

M = cations

X = anions

B_{Mx} = adjustable constant for each salt

m_x = molality of specie X

A log-log plot of the ratio of the solution activities (y axis) versus the ratio of the solid phase concentrations (x axis) approximates a straight line with slope = p and an intercept = $\log K_{Na-Ca}$. The logarithms of the experimental ratios are input to a linear regression computer program to determine the best fit values.

Thus, the experimental values of concentrations in solution and on the solid phase can be utilized to determine the selectivity constant and solid phase activity correction. The K_{Na-K} , K_{Ca-Mg} and respective p values are determined in an analogous manner using sodium and calcium respectively for the saturating ion.

A more convenient and accurate technique for measuring the selectivity constant involves the use of small column experiments and a radioactive tracer. With the batch method there is more chance of sample loss, and the determination of the concentration of competing ion sorbed onto the soil from the difference in influent and effluent concentrations may create large numerical uncertainties.

The isotope ^{22}Na was used to determine the selectivity constants for sodium-potassium and sodium-calcium. The sodium-calcium procedure is similar to the batch method.

Fritted sealing tubes (Corning 39570) are packed with 2.0 g of well mixed soil. 250 ml of .8M $\text{Ca}(\text{NO}_3)_2$ -.2M $\text{Ca}(\text{OAc})_2$ pH 5.0 are percolated through the soil to remove carbonates. 250 ml of 1M $\text{Ca}(\text{NO}_3)_2$ pH 7.0 solution is percolated through the soil to saturate the exchange sites. Entrain solution is removed with several 5 ml washes of .005M $\text{Ca}(\text{NO}_3)_2$ -1 ppm Magnifloc polyelectrolyte at pH 7.0.

Several NaNO_3 - $\text{Ca}(\text{NO}_3)_2$ mixtures in proportions similar to the equilibrium concentrations in the batch procedure were made and spiked with ^{22}Na . Actual mixtures used were a) $5.4 \times 10^{-4}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $7.9 \times 10^{-4}\text{M}$ NaNO_3 ; b) $5.7 \times 10^{-4}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $1.83 \times 10^{-3}\text{M}$ NaNO_3 ; c) $7.2 \times 10^{-4}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $3.8 \times 10^{-3}\text{M}$ NaNO_3 ; d) $8.6 \times 10^{-4}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $7.7 \times 10^{-3}\text{M}$ NaNO_3 ; e) $1.6 \times 10^{-3}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $4.1 \times 10^{-2}\text{M}$ NaNO_3 ; and f) $2.3 \times 10^{-3}\text{M}$ $\text{Ca}(\text{NO}_3)_2$ - $8.0 \times 10^{-2}\text{M}$ NaNO_3 .

250 ml of the spiked solution was then percolated through the soil tubes in 25 ml increments. Effluent samples were collected and ^{22}Na counted. The system was assumed to be at equilibrium when the ^{22}Na activity (cpm/ml) in the effluent equaled the influent. In this experiment no further change in ^{22}Na activity on the soil was found after 50-100 ml; therefore the use of 250 ml should insure saturation for most soils. The entrained equilibrating solution is removed by suction, a 2 ml - 1 ppm Magnifloc wash, and two 2 ml methanol-1 ppm Magnifloc (1:1) washes.

The sodium ion concentration (me/ml) in the equilibrating solution was measured by atomic absorption (Perkin Elmer Model 303 spectral line (5890-5896Å)). ^{22}Na activity in

the spiked equilibrating solution (cpm/ml) and in the soil column were γ counted on a 400 channel analyzer [RIDL model (34-12B)] utilizing a 3" NaI well crystal.

The ^{22}Na specific activity (cpm/me) of the equilibrating solution was calculated from the ^{22}Na influent activity and the influent sodium concentration.

The amount of sodium on the soil exchange, NaX (me/g) was calculated from ^{22}Na solid phase activity (cpm/g) divided by the specific activity of ^{22}Na .

The equilibrium concentration of calcium on the exchange was calculated by difference

$$\text{CaX} = \text{CaX}_{\text{sat}} - \text{NaX}$$

The equilibrium sodium and calcium concentrations in solution were equal to the influent values. Calculation of activity coefficients, the selectivity constant K and the solid phase activity correction p was identical to the batch technique described previously.

A comparison between the batch and ^{22}Na -small column exchange parameter experiments showed no significant differences in results for the Na-Ca or the Na-K systems. The ^{22}Na data did show less experimental scatter and the experiment is more convenient to perform; for these reasons, the small column technique is favored when applicable. Figure 9 shows the ^{22}Na small column data and batch data for the Na-Ca system.

MEASUREMENT OF INITIAL SOIL CONDITIONS

To determine the movement of solute species through a soil profile the initial soil conditions must be determined. The measurement of cation-exchange-capacity and soil selectivity constants have already been described. These quantities along with the initial concentrations of sorbed cations, concentrations of soluble salts and insoluble salt contents define the soil which will be reacting with the solution phase.

The determination of ion concentrations absorbed on the soil exchange for soils from arid regions involves inherent errors.

There are no accurate methods available for determining exchangeable calcium and magnesium in soils containing gypsum and alkaline-earth carbonates.⁹ The U. S. Salinity Lab has had some success with an empirical approach utilizing the relative and total concentrations of soluble cations in the saturation extract to determine the exchangeable ions.¹⁰ This is done with Gapon equations. This technique is also used at BNW for determining the saturation soil extract concentrations of coarse textured slightly calcareous soils. An algorithm in the PERCOL program calculates the initial concentrations of ions sorbed on the soil through use of the Gapon equations and the saturation extract data.

For soil types for which Gapon equations are not applicable or for which exchangeable concentrations are easily determined, the PERCOL model will accept direct input of the exchangeable concentrations. One method for determining exchangeable cations from soils is described by the U. S. Salinity Lab.¹¹ Briefly, the exchangeable-cation contents are determined by the difference between the cations removed per 100 g of soil by a 1N neutral ammonium acetate solution and the cations removed per 100 g of a saturated soil extract utilizing distilled water.

Soluble ion concentrations of calcium, magnesium, strontium, sodium and potassium in the initially dry soil are determined from the saturated soil extract by atomic absorption on a Perkin Elmer Model 303 double beam spectrophotometer. The spectral lines utilized are:

Calcium	4227 Å [°]
Magnesium	2852 Å [°]
Strontium	4607 Å [°]
Sodium	5890-5896 Å [°]
Potassium	7665 Å [°]

The soluble anions determined are chloride, fluoride, sulfate, carbonate, bicarbonate and nitrate. Chloride is determined amperometrically with a Buchler-Cotlove Model B5950 chloridometer. Fluoride is measured colorimetrically by the SPADNS method¹² on a distilled extract sample. Distillation is

performed with an automatic batch fluoride still, Hach Model 592. Sulfate is measured by the barium sulfate turbidimetric method¹³ utilizing Hach reagents.¹⁴ Nitrate is measured colorimetrically by the cadmium reduction method utilizing Hach reagents.^{15,16} Carbonate and bicarbonate are determined by titration with sulfuric acid utilizing the phenolphthalein and methyl orange end points, respectively.¹⁷

Because the slightly soluble salts in the soil can appreciably effect the movement of chemical species with the solute, this must be incorporated in the PERCOL model. The initial concentrations of slightly soluble calcium carbonate, calcium sulfate and calcium fluoride are measured in the dry soil.

The solid phase limestone, calcium carbonate, content of the soil is determined by the Volumetric Calcimeter Method¹⁸ utilizing 4N HCl and a reducing agent, SnCl_2 , to react with the calcium carbonate and release CO_2 . The CO_2 released is a quantitative measure of the calcium carbonate present. Sodium carbonate is the primary standard.

The solid phase gypsum (calcium sulfate dihydrate) content of the soil is determined by precipitation with acetone¹⁷ from a filtered soil extract. The solubility of gypsum in a water-acetone solution is very low. The precipitate formed from the water-acetone solution is redissolved in water and the calcium concentration is determined. From the total calcium concentration in the sample, the soil to solution ratio of the extract, and the volume of extract utilized the gypsum content may be calculated.

The solid phase calcium fluoride content of the soil is determined as total fluoride. A sodium fusion as described by Ingamells¹⁹ is performed, then the leachate is distilled in the Hach automatic batch fluoride still. Fluoride in the distillate is measured colorimetrically using the SPADNS method.¹²

The solubility products of the limestone, gypsum and fluorite are not experimentally determined. As a first approximation the literature values²⁰ for the crystalline forms are used.

INFLUENT AND EFFLUENT SOLUTE MEASUREMENTS

The reactions of soluble chemical constituents within the soil profile are determined by the differences between concentrations of the constituents in the influent and effluent solutions.

The PERCOL model predictions of the effluent compositions for a given influent and initial soil conditions are compared with the experimental column effluents. A good comparison suggests that PERCOL has successfully modeled the soil-solution chemical reactions and transport in one dimension.

Sodium, potassium, calcium, magnesium, strontium, nitrate, chloride, sulfate, fluoride, and bicarbonate-carbonate ions in the synthetic waste influent solution and column effluent solutions are measured in the same manner as ions from soil extracts; i.e., the cations by atomic absorption and the anions by the various colorimetric, turbidimetric and titration methods discussed in the previous section. Radioactive trace ions which are introduced into the synthetic wastes are measured with appropriate counting instruments. Isotopes that have been utilized in these column studies include ^{85}Sr , ^{60}Co , ^{134}Cs , ^{137}Cs , ^{22}Na , ^{133}Ba , $^{152-154}\text{Eu}$, and ^3H . All the isotopes except tritium have been successfully determined by gamma ray counting, using a 400 channel analyzer (RDL Model 34-12B) with a 3" NaI well crystal. ^3H is measured with a Packard Liquid Scintillator using refrigerated samples. Non-radioactive trace ions present in synthetic wastes are measured by appropriate wet chemical analyses.

APPARENT POROSITY MEASUREMENTS FOR EXPERIMENTAL COLUMNS

Analyses of soil column verification data showed that the columns contained dead end and/or restricted channels which were not transmitting solute. This discrepancy was taken into account in the PERCOL model by modifying the theoretical porosity. The modified porosity was designated as the apparent soil porosity, which was found to be dependent on the soil type and solute velocity.

According to dispersion theory^{21,22} the one dimensional movement of a plug of unsorbed solute can be mathematically described. A breakthrough plot of the normalized effluent

(C_{eff}/C_{inf}) versus pore volumes should show a value of 0.5 breakthrough at 1.0 pore volumes.

Soil column experiments were devised to measure the movement of unsorted tracers. Both saturated and unsaturated soil columns, as described previously, were packed with selected soils. Two tracers, chloride and tritium, were utilized in preliminary work to determine whether the clay double layer might cause anion exclusion, but the absence of significant differences between the chloride and tritium movements indicated that anion exclusion does not preclude the use of chloride as an unsorted tracer in the soils tested. Chloride is more convenient and much less expensive to measure than tritium and was therefore used in the remaining studies.

The solutes utilized were mixed chloride salts similar to the mixed nitrate solutions employed as simulated waste and the same relative ratios of Na: Ca: K were used as in the simulated wastes. The densities of the chloride solutions were made identical to those of the simulated waste solutions by dilution with distilled water. The density was measured with a hydrometer and kept constant to prevent gradients from interfering with the plug flows.

The dry soil columns were first leached with the simulated nitrate waste solution to remove all the naturally occurring chloride; this was usually completely accomplished by two column volumes of leaching.

After the chloride removal, the chloride monitoring solution was pumped through the column and the normalized chloride effluent concentration determined in relation to volume of solution pumped. The procedure is similar to that described previously for the experimental soil columns used in PERCOL verification. Since only about one pore volume of chloride solution is needed to perform the experiment, extreme control is required on the mass balance. Depending on the column utilized, one pore volume represents only 5-100 mls of solution. The slightest bit of syringe leakage, evaporation, excess solution trapped in hoses or sample loss not accounted for has a large effect on the apparent porosity calculations. Several mass balances should be performed during the experiment to detect problems and signal changes in conditions.

To minimize errors, each sample collecting tube must be weighed. (Weighing has been found to be more convenient and more accurate

than volume measurement for volumes less than 20 mls). The density of the chloride solution is determined and weights converted back to volumes. The influent is contained in an airtight small graduated cylinder (the smaller the cylinder the easier it is to read small differences in volume pumped) which is refilled with a pipet. A compromise must be made between the size of the cylinder and the number of refillings needed.

A sample size of about 0.2 pore volumes is acceptable for the first one half pore volume of effluent collected. After .5 pore volume has been collected, the sample size should be reduced to .05 pore volume because the breakthrough curve becomes quite steep in the region of 0.5-1.2 pore volumes.

To facilitate mass balance all solution losses which occurred before the solution reached the soil are subtracted from the volume of influent pumped. All solution losses after soil entry are added to the volume collected. The corrected effluent collected should agree with the corrected influent pumped.

The chloride concentrations in the influent and effluent samples are determined amperometrically, as previously described. Corrections for evaporation are made on the concentration (all reasonable unexplained loss of volume is attributed to evaporation). Evaporation should be constant for a constant flow rate, so by taking several mass balances throughout the experiment and correcting for other losses evaporation can be estimated.

A plot of the corrected breakthrough (C_{eff}/C_{inf}) versus the corrected effluent is constructed and the theoretical point of .5 breakthrough at 1 pore volume is plotted. The actual volume at which .5 breakthrough is found yields the apparent porosity.

$$\theta_{App} = \frac{\text{Experimental volume at which .5 breakthrough occurs}}{\text{Theoretical volume at which .5 breakthrough occurs}}$$

The theoretical pore volume is calculated from the total volume of the column, soil bulk density of the column, Bd , and particle density, Pd . The fraction of pore space per unit volume is

$$1 - \frac{B_d}{P_d} = \frac{P_d - B_d}{P_d}$$

The particle density is assumed to be constant at 2.65 g/cm³ for all soil particles. The total theoretical pore volume of the soil column in mls is

$$\text{Pore Volume} = \frac{(P_d - B_d)}{(P_d)} (\text{Vol. of Column})$$

EXPERIMENTAL DETERMINATIONS AND STATISTICAL ANALYSES OF TRACE CONSTITUENT SORPTION

The sorption of micro (trace) constituents was modeled as an empirical function of the soil type, equilibrium macro solute concentrations and pH. The empirical approach was found necessary because a theoretical determination of the cation exchange between the soil and trace solute species is masked by the more plentiful macro species and thus is difficult to isolate.

The general empirical variable, K_d, defined as the ratio of the equilibrium concentration of tracer sorbed on the soil divided by the equilibrium concentration of tracer in the solute, is easily measured by experiment

$$(K_d = \frac{A_{\text{soil}}}{C_{\text{solution}}})$$

The K_d is known to be a function of the trace constituent of interest, of the soil type, of cation concentrations in the solute, and of pH. The many variables which affect the K_d can be investigated best by using factorial experiments. Factorial experimentation is efficient because every observation supplies information on all the variables included in the experiment and their interactions.

Both batch and small column sorption experiments were designed using a two level factorial scheme. As an example, the sorption of trace concentrations of the radionuclide ⁸⁵Sr from a mixed salt waste containing sodium, potassium and calcium nitrates will be described in detail.

For each different soil type an experimental design using sodium, calcium, potassium and pH was employed. Two levels, high (H) and low (L), were chosen for each variable. The values should correspond to the range normally encountered in the system; for this particular example the values are listed in Table 1. To determine all the effects for this

TABLE 1. HIGH AND LOW VALUES FOR ^{85}Sr SORPTION EXPERIMENT

	<u>Low</u>	<u>High</u>
Calcium	.002M	.05M
Sodium	.02M	.20M
Potassium	.00M	.05M
pH	6.0	8.2

two-level experiment required 2^4 sorption observations. The experimental design is shown in Table 2.

The sixteen simulated waste solutions were made and each of the sorption experiments carried out. The experimentally determined Kd values were then statistically analyzed to yield regression coefficients for the sixteen treatments.

The experimental techniques utilized in the sorption experiments will be described in the following paragraphs followed by the data analysis.

The small column sorption experiment, which is similar to the small column CEC experiment, is favored over the batch method when applicable because it is faster, easier to perform and less affected by washing errors. This technique is effective for radionuclide tracers which sorb moderately or poorly. This is equivalent to stating that the soil in the small column will reach equilibrium in a reasonable time and with reasonable throughput of waste solutions. Kds in the range of 0-200 are readily determined by the small

TABLE 2. OBSERVATIONS IN ^{85}Sr SORPTION EXPERIMENT

<u>Treatments</u>	<u>pH</u>	<u>Ca⁺⁺</u>	<u>Na⁺</u>	<u>K⁺</u>
1	H	H	H	H
2	H	H	H	L
3	H	H	L	H
4	H	H	L	L
5	H	L	H	H
6	H	L	H	L
7	H	L	L	H
8	H	L	L	L
9	L	H	H	H
10	L	H	H	L
11	L	H	L	H
12	L	H	L	L
13	L	L	H	H
14	L	L	H	L
15	L	L	L	H
16	L	L	L	L

column technique; however, this technique must be used with caution or abandoned for trace constituents in which pH dependent precipitation is important because the small column soil often exhibits a large capacity to buffer acid wastes and can cause pH dependent precipitation which inflates the K_d value.

The small column sorption procedure follows.

Two gram samples of well mixed soil are accurately weighed into fritted disk sealing tubes (Corning 39570). The soil is leached with 200-500 mls of 2N NaNO_3 at the pH of the waste solution. Then 250-500 mls of the particular waste solution containing the radionuclide trace constituent is percolated through the soil at 25 ml increments. To maintain the desired pH the influent vessel is vented through an ascarite column to remove carbon dioxide and water vapor.

The activity in the effluent is periodically compared with the influent. System equilibrium is attained when the activities in the effluent and influent are the same. Counting the activity of the soil is a second check. When the soil activity reaches a constant value the soil and waste solution are assumed to be in equilibrium for the trace sorption. When equilibrium is attained, the excess solution is removed from the soil column by suction. The small column is then washed and solution removed by suction. The washing sequence is one wash of 2 mls 1 ppm Magnifloc 905 polyelectrolyte and two 2 mls washes of 1 ppm Magnifloc-Methanol (1:1) by volume.

The soil column and influent sample are then counted with appropriate instruments. The counting is straightforward for γ radiation but for β radiation differences in soil and liquid attenuation must be accounted for.

The K_d is calculated from the above activities:

$$K_d = \frac{\text{cpm in soil column/g soil counted}}{\text{cpm in influent/mls influent counted}}$$

Note that K_d is not a unitless constant and therefore a convention must be adopted. It is convenient to report K_d with units of mls/g.

The batch sorption technique is utilized with nonradioactive trace constituents, trace constituents with very high K_d s and those in which pH dependent precipitation of the trace constituent is important.

The batch sorption procedure follows.

Tare weights are determined on 250 ml polycarbonate screw cap centrifuge bottles. From 5-10 g of well mixed soils are weighed into the centrifuge bottles. Fifty mls of the simulated waste solution without the trace constituent are added to the centrifuge bottle. A piece of PARAFILM sealing material is placed over the mouth of the bottle before screwing down the cap to prevent solution leakage through the threads of the cap during the mixing stage. The capped bottle is placed in a variable speed shaker and moderately agitated for 30 minutes. The bottles are then centrifuged for 15-20 minutes at 4000 rpm and the supernatant is carefully decanted. Loss of soil should be avoided. Three prewashes of the matrix solution (solution without the trace constituent) are performed. After the third decanting the centrifuge bottle is reweighed and the amount of residual solution is calculated by difference. This value is needed because of the residual solution's dilution effect. Fifty mls of the simulated waste solution containing the trace constituent are then pipeted into the centrifuge bottle and the capped bottle is agitated for a designated period. For tracer work in which pH is not important shaking times of 18-24 hours are utilized. For pH dependent reactions shaking times vary with the rate of change of solution pH; solutions are centrifuged and extracted when the mixed solution attains the desired pH. The sample is centrifuged as before and an effluent sample is extracted for analysis of the trace constituent.

Samples of the effluent and influent are then analyzed for the trace constituent. The K_d is calculated from equation

$$K_d = \frac{rC_o - C_e}{C_e} \frac{A}{B}$$

where

A = total mls of solution in last treatment
(50 ml + X residual mls)

B = total g of soil present

r = ratio of tracer solution to total solution
(50/50 + X)

C_o = concentration of trace constituent in
influent solution m/l, cpm/ml, etc.

Ce = concentration of trace constituent in
effluent solution.

After the experimental determination of the Kd for all the different combinations of variables is completed a predictor equation (response surface in statistical terminology) is developed according to the following process. First the experimental Kd values are analyzed by factorial statistics, a special form of analysis of variance statistics^{23,24} and the means of the effect totals from the factorial calculations become coefficients²⁴ of the predictor equation.

An example of the Kd data reduction will be presented for clarity. Preliminary studies of ⁸⁵Sr sorption from a mixed salt waste solution by a sandy loam soil showed that pH over its expected range (6.0-8.2) has negligible effect on strontium sorption. Dropping pH from the experimental design leaves the sodium, potassium and calcium concentrations as factors. A 2³ factorial design was followed using the concentration ranges in Table 1 and maintaining pH at 7.0.

The 2³ factorial design treatments reduce to the first eight combinations in Table 2 because pH no longer is variable. Three replications of each treatment were run using the batch Kd methods. Measured Kd values in ml/g are presented in Table 3.

TABLE 3. EXPERIMENTAL RESULTS OF Kd of ⁸⁵Sr

<u>Treatment</u>	<u>Replications</u>	<u>Totals</u>
1	.38, .28, .31	.97
2	.54, .49, .56	1.59
3	.38, .29, .38	1.05
4	1.05, .91, 1.06	3.02
5	2.46, 2.36, 2.38	7.20
6	5.68, 5.28, 4.90	15.86
7	3.73, 3.44, 3.85	11.02
8	15.88, 16.74, 15.61	<u>48.23</u>
GRAND TOTAL		88.94

The sum of squares and degrees of freedom are shown in Table 4.

TABLE 4. ANALYSIS OF VARIANCE OF ⁸⁵Sr SORPTION EXPERIMENT

<u>Treatments</u>	<u>D.F.</u>	<u>Sum Squares</u>	<u>Mean Square</u>
$\frac{\sum (\sum X)^2}{3} - \frac{\sum \sum X^2}{24}$	7	591.95	
$\frac{\sum (.97)^2}{3} + \frac{(1.59)^2}{3} + \dots + \frac{(48.23)^2}{3}$ $- \frac{(88.94)^2}{24}$			
ERROR (Total-Treatments)	16	1.12	.07
TOTAL	17	593.07	

$$\frac{\sum \sum X^2}{24} - \frac{\sum \sum X^2}{24}$$

$$\sum \sum (.38)^2 + (.28)^2 + \dots + (15.61)^2$$

$$- \frac{(88.94)^2}{24}$$

The treatments can be further subdivided into seven single degrees of freedom representing three main effects (Na, K, Ca), three two-factor interactions (NaCa, NaK, CaK), and one three-factor interaction (NaCaK).

A simple way to subdivide the treatment sum of the squares was developed by Yates.²³ The eight treatments are arranged in the order shown in Table 5. The statistical meaning and reasons for creating this table are explained in Yates²³ and

TABLE 5. FACTORIAL ANALYSIS FOR ^{85}Sr SORPTION EXPERIMENT

<u>Treatment</u>	<u>Total</u>	<u>(A)</u>	<u>(B)</u>	<u>(C)</u>	<u>(D)</u>	<u>(E)</u>
8 (I)	48.23	64.09	82.31	88.94	---	3.71
6 (Na)	15.86	18.22	6.63	-37.70	59.22	-1.57
7 (K)	11.02	4.61	-36.19	-48.46	97.85	-2.02
5 (NaK)	7.20	2.02	-1.51	29.90	37.25	1.25
4 (Ca)	3.02	-32.37	-45.87	-75.68	238.64	-3.15
2 (CaNa)	1.59	-3.82	-2.59	34.68	50.11	1.44
3 (CaK)	1.05	-1.43	28.55	43.28	78.05	1.80
1 (CaNaK)	.97	- .08	1.35	-27.20	<u>30.83</u>	-1.13
					591.95	

Snedecor.²⁴ The numbers beside the treatment symbols correspond to the treatment numbers in Table 2. The column designated totals are the sums of the three replications for each treatment. The first four numbers in Column A are the sums of the four pairs of totals, (I+Na, K+NaK, etc.) and the last four numbers are the differences of the pairs of totals, the upper number being subtracted from the lower in each case (Na-I, NaK-Na, etc.). Column B is formed from Column A in a similar fashion. Column C is formed from Column B by the same manipulations and these numbers are called the effect totals. Column D represents the partitioning of the sum of the squares for treatments and is generated by taking the effect totals (Column C), squaring, and dividing by 24 (number of treatments X replications). In this example there are eight treatments and three replications. The sum of Column D, neglecting the (I) treatment, gives the total sum of the squares due to treatments (see Table 4). Numbers in Column E represent the effect means and are generated by calculating the average of each effect total (Column C/24). These effect means are the coefficients to the response surface which becomes the predictor equation for K_d .

The effects of each treatment are tested for significance

by running an F test on each individual partitioned sum of squares versus the mean square for errors, which is an estimate of the standard deviation for the experiment and has been calculated in Table 4 as .07. The F test for 1,16 degrees of freedom at the 95% confidence level is 6.12.

The smallest partitioned sum of squares, 30.83 (Column D Table 5), is for the three factor interaction (CaNaK). The F test,

$$F = \frac{30.83}{.07} = 440,$$

shows that this treatment and thus all the others are highly significant. Since all the treatments are significant no further simplification is warranted. The predictor equation will have to include terms for all the main effects and interactions.

To derive the predictor equation, the treatment variables are coded to give values between ± 1 over the range studied. For example, the coded variable for the calcium treatment variable becomes:

$$X_{Ca} = \frac{Ca - \frac{H_{Ca} + L_{Ca}}{2}}{\frac{H_{Ca} - L_{Ca}}{2}}$$

where

H_{Ca} = high calcium concentration used in the factorial design

L_{Ca} = low calcium concentration used in the factorial design

Ca = value of calcium for which Kd is being predicted

For the Kd experiment being investigated, Table 1 gives the concentration ranges for the three factors (Ca,Na,K).

The three coded variables become

$$x_{Ca} = \frac{Ca - .026}{.024}$$

$$x_{Na} = \frac{Na - .11}{.09}$$

$$x_K = \frac{K - .025}{.025}$$

The Kd predictor equation is the sum of contributions of each treatment effect in terms of the coded variables and is weighted by the effect means (Column E, Table 5).

The Kd predictor equation is

$$\begin{aligned} Kd = & 3.71 - 1.57x_{Na} - 2.02x_K + 1.25x_{Na}x_K - 3.15x_{Ca} \\ & + 1.44x_{Ca}x_{Na} + 1.80x_{Ca}x_K - 1.13x_{Ca}x_{Na}x_K \end{aligned}$$

which becomes

$$\begin{aligned} Kd = & 3.71 - 1.57 \frac{(Na-.11)}{.09} - 2.02 \frac{(K-.025)}{.025} \\ & + 1.25 \frac{(Na-.11)}{.09} \frac{(K-.025)}{.025} - 3.15 \frac{(Ca-.026)}{.025} \\ & + 1.44 \frac{(Ca-.026)}{.025} \frac{(Na-.11)}{.09} + 1.80 \frac{(Ca-.026)}{.025} \frac{(K-.025)}{.025} \\ & - 1.13 \frac{(Ca-.026)}{.025} \frac{(Na-.11)}{.09} \frac{(K-.025)}{.025} \end{aligned}$$

The calculations are done utilizing computer programs which determine the analysis of variance, Yates' Factorial calculations and calculation of the final form of the Kd equation. Experimental Kd values and ranges utilized for each variable are the only necessary input to the computer programs.

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