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A COLUMN CATION-EXCHANGE-
CAPACITY PROCEDURE FOR LOW
EXCHANGE CAPACITY SANDS

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A COLUMN CATION-EXCHANGE-CAPACITY
PROCEDURE FOR LOW EXCHANGE CAPACITY SANDS

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ABSTRACT

A rapid and sensitive cation-exchange-capacity (CEC) column procedure is described in this report. This procedure is particularly useful for measuring the CEC of calcareous low-exchange capacity sands and sandy soils. Entrained salt is removed by washing with an aqueous polyelectrolyte solution, but hydrolysis errors are minimized by limiting the amount of washing solution. A simple technique is described for estimating the extent of washing required. The procedure eliminates the replacement of the index cation, is amenable to the rapid measurement of CEC on large numbers of samples and is sufficiently precise for the measurement of the CEC of low-exchange capacity sands.

FOREWORD

This work was performed in the Water and Land Resources Department of Battelle-Northwest for Application to the Radionuclides in Soils Program sponsored by the Atlantic Richfield Hanford Company (ARHCO).

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INTRODUCTION

The objective of the study discussed in this report was to develop a sensitive column cation-exchange-capacity (CEC) procedure for calcareous, low-exchange, capacity sands. It was necessary that the procedure be adaptable to the measurement of a number of CEC analyses in minimal time.

"Conventional" methods for measurement of the cation-exchange-capacity (CEC) of soils generally employ the following steps: 1) replacement of the native exchangeable cations with an index cation; 2) removal of excess-entrained indexing salts; 3) displacement of the index cation from the soil; and 4) measurement of the quantity of index cation replaced.⁽¹⁻⁴⁾ Step 2 of such a procedure can result in significant error if an inappropriate amount of washing is employed.⁽⁵⁻⁸⁾ If insufficient washing is employed, retained saturating salt will not be removed prior to the replacement step, which will result in a positive error in the CEC measurement. Conversely, if excessive washing is employed, a negative CEC error may result from hydrolysis. Furthermore, ion exchangers differ significantly in their tendency to retain salt and hydrolyze, and these tendencies can be assessed only by extensive laboratory experiments.^(1,5,6,8)

Several CEC procedures, which omit the washing step and therefore eliminate its associated error, have been published.^(5,9,10) However, these procedures are generally lengthy which tends to limit their utility to specialized problems requiring extreme accuracy.

The soils and sediments of the unsaturated zone of the U. S. Atomic Energy Commission's Hanford Atomic Works in Richland, Washington, (maintained in part for the storage of radioactive wastes) are principally calcareous, low-exchange capacity sands and sandy loams with CEC values in the range of 1-5 meq/100 g (Table 1). Modeling of radionuclide transport in these soils and

TABLE 1. Properties of Soil Samples

<u>Soil</u>	<u>CaCO₃, mg/g</u>	<u>Silt, %</u>	<u>Clay, %</u>	<u>CEC (pH 7.0), me/100g</u>	<u>pH in 0.01M, CaCl₂</u>
B1	0.8	10.1	0.5	4.9	7.0
W2	6.0	6.0	1.1	1.9	7.7
E3	8.7	5.4	2.5	4.8	7.6
TF4	26.0	29.5	4.9	4.0	8.0

sediments requires a sensitive CEC procedure which can be adapted to the rapid analysis of a large number of samples. Conventional procedures, in addition to involving possible washing errors, were found to be insufficiently sensitive. Nonwashing procedures mentioned above were too time-consuming to be practical. Thus, the objective of the following study was to develop a sensitive CEC procedure which required less time.

METHODOLOGICAL DEVELOPMENT

In the development of a simple, reliable CEC procedure for this purpose, several criteria were given consideration. First, batch procedures are not easily adaptable to large numbers of CEC measurements due to the necessity of repeated solid-liquid phase separations during saturation, washing, and replacement of index cations. Therefore, a column CEC procedure was investigated. Second, a reliable CEC procedure must either avoid the washing step or reduce the associated errors to an acceptable minimum. Since a column procedure normally requires removal of entrained saturating salt, consideration was given to minimizing possible resulting errors. Third, a suitable index cation should be selectively sorbed to minimize the quantity of solution required for saturation and have a radioactive isotope appropriate for use as a tracer to increase procedural sensitivity and allow elimination of the index cation replacement step. If the radioactive tracer has a γ -ray emission of sufficiently high energy, the entrained solution and the soil can be counted directly and the index ion replacement step is avoided. The index cation should be extrinsic so that any possible interference of mineral dissolution can be avoided. Mixed salt solutions, as suggested by Bauer, Reitemeier, and Fireman,⁽¹⁾ may be employed to buffer the system at a reference pH. With the above requirements taken into consideration, a new procedure was developed.

The procedure developed consists mainly of saturating the soil with $\text{Sr}(\text{OAc})_2$ - SrCl_2 (1 N with respect to Sr) in a column prepared from a fritted disk sealing tube. Calcareous soils are

first leached with this concentrated solution at pH 5 to dissolve carbonates, and subsequently, with the same solution adjusted to a selected pH. Following saturation, the soil is equilibrated with a dilute Sr-solution (0.05 N), and traced with ^{85}Sr . A portion of the entrained equilibration solution is removed under vacuum or expelled with a syringe. The remainder of the entrained equilibration solution is washed from the exchanger first with a limited amount of 1 ppm polyelectrolyte solution and finally with a mixed polyelectrolyte-methanol wash. The CEC is calculated from the specific activity of the equilibration solution (cpm/ml) and the equilibrium activity of the soil (cpm/g). The required apparatus, illustrated in Figure 1, is readily adaptable to multiple samples. Additional details of the procedure are given under the Recommended Procedure section of this paper.

Properties of soils used in procedural development are given in Table 1. These soils span the range of properties expected for the sands and sandy loams of the unsaturated zone of the Hanford Project. Factors investigated during the methodological development were: 1) suitability of ^{85}Sr as a tracer; 2) equilibration solution volume required to obtain equilibrium; 3) quantity of washing solution required to remove entrained salt; and, 4) comparison of the measured CEC by the proposed procedure with a nonwashing correlative procedure.⁽⁵⁾

FIGURE 1. Apparatus for Column CEC Procedure

To avoid the necessity for replacement of the index cation in a column CEC procedure, it is necessary that measurement of index cation activity in the equilibrating solution and in the soil column are comparable. For this purpose, counting geometry must be equivalent. To test this requirement, equivalent quantities of an ^{85}Sr solution (1.0 λ) were pipetted into 0.05N $\text{Sr}(\text{OAc})_2\text{-SrCl}_2$ solution (2 ml) and into columns containing sand (3g) and counted. Results are given in Table 2. The average measured activity in

TABLE 2. Comparison of the Measured γ -Activity of Equivalent Quantities of ^{85}Sr (1.0 λ) Added to a Sand in a Column (Bl,3g) and 0.05N Sr Solution (2 ml)

<u>Replicate No.</u>	<u>Detected Activity cpm/sample</u>
Sand 1	21,575
Sand 2	20,860
Sand 3	<u>20,817</u>
Average	21,084 $\pm$ 676
Solution 1	19,900
Solution 2	20.126
Solution 3	<u>21,585</u>
Average	20,537 $\pm$ 915

the sand columns was within one standard deviation of the average measured in the Sr solution. Furthermore, the total deviation is less than might be expected from pipetting with a 0.1 λ pipette. Thus, the self-sorption correction of the ^{85}Sr - γ between the sand and solution is negligible, allowing the direct counting of sand columns provided that the entrained equilibrating solution can be reduced to innocuous levels.

The equilibration of several exchangers including sands, clays, and humates with $\text{Sr}(\text{OAc})_2$ (0.04 N) - SrCl_2 (0.01 N) at pH 7.0 traced with ^{85}Sr is illustrated in Figure 2. These materials had previously been saturated by passing 250 ml of $\text{Sr}(\text{OAc})_2$ (0.8 N) - SrCl_2 (0.2 N) at pH 7.0 through the column.

FIGURE 2. Equilibration and Sr-saturation of several ion exchangers as a function of the volume of $\text{Sr}(\text{OAc})_2$ (0.04 N) - SrCl_2 (0.01 N) solution. C/C_0 (%) is the ratio of the measure column γ -activity at a given throughput volume of equilibrating solution to its equilibrium γ -activity times 100.

Figure 2 shows that 80 ml of the equilibrating solution was sufficient to attain complete Sr equilibration for all of the exchangers investigated. For the sands, 25 ml of equilibrating solution was sufficient to attain complete Sr equilibration. In the case of clays and humates exhibiting high CEC values relative to the sands, complete Sr equilibration is attained with 80 ml of equilibration solution.

A column CEC procedure requires a wash step to remove excess entrained saturating solution. To determine the maximum amount of washing which would be required for sands, an experiment

was designed to determine the influence of washing on the measured CEC of a sandy loam (TF 4). This soil was finer in texture than most of the calcareous soils for which the procedure was developed and was expected to require maximum washing. The average measured CEC Values for the TF 4 soil as a function of the volumes of aqueous wash solution are illustrated in Figure 3.

FIGURE 3. Measured CEC as a function of the volume of wash solution. Numerals are the wash number. Data are the means of 3 analyses. Vertical lines represent the standard deviation of individual measurements.

Washes 1 and 2 were made with an aqueous solution of 1 ppm Magnifloc 905 nonionic polyelectrolyte. Washes 3-7 were made from equal volumes of 1 ppm polyelectrolyte and methanol. The effect of the polyelectrolyte on CEC of several sands and clays had been previously checked and was found to be negligible.

From Figure 3 it is evident that 1 ml of an aqueous wash reduces the apparent CEC (Wash 0) to a value within 1 standard deviation of the final measured CEC (Wash 7). Additional washes failed to significantly change the measured CEC. The final value of the measured CEC, which was attained for Washes 3-7, is interpreted as resulting from the removal of nearly all of the entrained equilibrating salt. Furthermore, the minimum rate of change of the measured CEC with additional washes suggests that for the limited amount of washing of this soil the hydrolysis error was negligible.

Less washing is generally required with a column procedure than with a batch procedure because it is essentially a displacement process. In contrast, washing with a batch procedure is a dilution process, requiring several washes to dilute the entrained salt. The quantity of washing solution per unit weight of soil is low in the above procedure amounting to about 1 ml/g compared to batch procedures which may require 100 ml/g.⁽¹¹⁾ Furthermore, the relatively simple technique described above can easily be used to estimate the extent of washing required for any soil. Previous experiments with the displacement of NO_3^- solutions by Cl^- and ^3H solutions in larger columns packed with the TF 4 soil

showed that only 1.2 pore volumes of solution were required to replace at least 93% of the NO_3^- solutions. One ml of wash solution would be about 2 pore volumes in the column CEC procedure, confirming that only a small volume of wash solution would be sufficient to remove the bulk of the entrained equilibrating solution, suggesting that the initial reduction in measured CEC with 1 ml of wash solution was due primarily to removal of entrained equilibrating solution.

Table 3 gives a comparison of the CEC of three low-exchange capacity sands measured with the proposed procedure and a nonwashing batch procedure.⁽⁵⁾ There is good agreement between the two procedures for the investigated samples, indicating that hydrolysis errors due to washing were minimized with the column procedure.

TABLE 3. CEC Determined by the Washing Procedure (Column Procedure) and Nonwashing Procedure(a)

Sample No.	<u>CEC</u> ^(b)	
	Washing	Nonwashing
	me/100g	
B1	4.9	5.1
W2	1.9	1.9
E3	4.8	4.8

(a) See Reference 5

(b) Mean of 3 Analyses

RECOMMENDED PROCEDURE

Transfer 0.1-2.5 g of soil of known moisture content to a sealing tube (e.g., Corning 39570 tube) which has been cut off immediately below the fritted disk. Select a sample size with a total exchange capacity between 0.01-1.0 me. If the sample is calcareous, percolate 250 ml of pH 5.0 $\text{Sr}(\text{OAc})_2$ (0.8 N) - SrCl_2 (0.2 N) in 25 ml increments through the soil and allow the soil to partially drain between increments. Following the dissolution of carbonates, percolate 250 ml of $\text{Sr}(\text{OAc})_2$ (0.8 N) - SrCl_2 (0.2 N) adjusted to the appropriate pH in 25 ml increments. This solution should be open to the atmosphere through an ascarite column to insure that the system remains at a selected pH. Percolate 250 ml of the selected pH $\text{Sr}(\text{OAc})_2$ (0.04 N) - SrCl_2 (0.01 N) solution traced with approximately 5000 cpm/ml of ^{85}Sr in 25 ml increments. Remove as much of the entrained equilibration solution as possible using vacuum suction or expulsion with a syringe fitted with a stopper the size of the column. Wash the sample with two 1-ml increments of 1 ppm Magnifloc 905 nonionic polyelectrolyte and as many additional methanolpolyelectrolyte washes (1:1) as required to reduce the activity to a constant level. Often one or two washes are sufficient. Determine the concentration of Sr in the final equilibration solution. Count 2 ml of the final equilibration solution and the column with a suitable γ -analyzer. Either a single or multichannel analyzer can be used if equivalent geometry is maintained with 2 ml of equilibration solution and the soil column.

In the studies described herein, Sr was determined with a Perkin Elmer model 303 dual-beam atomic absorption spectrophotometer using the $4607 \text{ \AA}$ spectral line. Strontium-85 activity was determined with a RIDL Model 34-12B 400 channel γ -analyzer with a 3-in. NaI well crystal into which the soil column could be inserted directly. Calculate the specific activity (cpm/ml) of the equilibration solution. Calculate the CEC (me/g) by dividing the column activity per unit weight of soil (cpm/g) by the specific activity of the equilibration solution.

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