EFFECT OF PARTICLE SIZE IN CATION EXCHANGE CAPACITY DETERMINATION

by

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ABSTRACT

The objective of this research was to verify if and how the cation exchange capacity (CEC) of rocks, as measured in the laboratory, varies with the amount of disaggregation of the sample.

Twenty different samples of known composition were ground to 5 different maximum grain sizes: 1.19, 0.42, 0.25, 0.104, and 0.044 mm. Each of the disaggregated samples was cleaned with solvents and boiled in presence of ammonium chloride to remove carbonates. The sample was then shaken for 24 hours in a 1 N ammonium acetate solution for substitution of the exchangeable cations on the clay by ammonium cations. Each sample was then washed with a 70% solution of methanol and distilled water to remove ions not bound to the clays. The ammonium ions were then distilled from the clays in presence of magnesium oxide and forming ammonia that was displaced into a solution of hydrochloric acid. The excess of acid was then titrated with a solution of sodium hydroxide, and the cation exchange capacity calculated, for each one of the pulverized samples. The results were classified by the predominant type of clay in each sample and averaged. After that the CEC was plotted against maximum grain size. The results of this research show that any amount of grinding increases the CEC as measured in the laboratory. The

results show, too, that it is necessary to look for a method of CEC measurement in the laboratory where the sample is not submitted to any disaggregations, to better approximate the CEC of the rock in situ.

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INTRODUCTION

Cation exchange capacity, according to Grim (1), may be explained as:

> "Clay minerals have the property of sorbing certain cations and anions and retaining these in an exchangeable state; i.e., they are exchangeable for other anions or cations by treatment with such ions in a water solution (the exchange reaction also takes place sometimes in a nonaqueous environment). The exchange reaction is stoichiometric. The exchangeable ions are held around the outside of the silica-alumina clay mineral structural units, and the exchange reaction generally does not affect the structure of the silica-alumina packet. A simple and well-known example of the ion-exchange reaction is the softening of water by the use of zeolites, permutites, or carbon exchangers."

Johnson and Linke (2) stated: "Cation exchange capacity is defined as the amount of positive ion substitution that takes place per unit weight of dry rock."

Cation exchange capacity (CEC) is the ability of certain substances to exchange cations with solutions containing other cations. Cation exchange capacity may be defined as the reversible exchange of ions between a liquid phase and a solid phase, which is not accompanied by any radical change in the structure of the solid. The most common exchangeable cations are Ca, Mg, OH, K, Na, and NH_4.

Two major mechanisms contribute to the cation exchange capacity of a clay. They are the broken bond mechanism and the substitutions in the lattice structure of the clay. Broken bonds around the edge of silica-alumina units and exposed hydroxyl units explain part of the cation exchange phenomena (1, 3, 4). For kaolinite and chlorite the broken bond mechanism is the only method by which cations are adsorbed (4). In the case of smectite and illite, the lattice structure cation substitution is the main mechanism for the cation exchange phenomena (3, 4). Johnson (2) calls the kaolinite and the chlorite ineffective clays and the multilayer bentonite, montmorillonite and illite, effective clays. The ineffective clays have a low CEC and do not have a pronounced effect on the resistivity of the rock. They function as electrically inert pore fillers. This group of clays does not have natural radioactivity and the gamma ray log does not respond to them.

The cation exchange capacity is usually expressed in milliequivalents of cations per gram of dry solids. A milliequivalent may be defined as one milligram of hydrogen (H^+) or the mass of any other cation that will displace it. Other cations may be expressed in milliequivalents by changing them over into their hydrogen equivalents (5). Often the cation exchange capacity is given in milliequivalents per 100 grams of dry solids. In this research, the CEC is expressed in milliequivalents per 100 g of solids.

The charge concentration per unit pore volume, Q_V, is related to the CEC by means of Equation 1, derived in

Appendix A.

$$Q_v = \frac{CEC(1-\phi)\rho}{100\phi} \qquad (1)$$

where

Q_v = meq/unit pore volume

CEC = meq/100g

ϕ = fractional porosity

ρ = grain density, in g/cm^3

According to Waxman and Smits (6), a shaly formation behaves like a clean formation with the same porosity, tortuosity, and fluid saturation, except that the water seems to be more conductive than the salinity of the water would suggest. This excess of conductivity is due to additional cations such as K, Na, Ca, etc., that are weakly bonded to the clay lattice. The number of these extra cations is related to the cation exchange capacity of the clay. The effective conductivity of the formation can be calculated as

$$C_{we} = C_w + B\frac{Qv}{S_{wt}} \qquad (2)$$

where

C_{we} = effective conductivity of the water, mho/m

C_w = conductivity of the formation water, mho/m

B = equivalent conductivity of the compensating ions, (mho/m)/meq/cm^3)

Q_v = charge concentration per unit pore volume, meq/cm^3

S_{wt} = water saturation, fraction

In this model, the conductivity of a water-bearing formation (S_{wt} = 100%) is given by:

$$C_o = \frac{1}{F^*} C_{we} = \frac{1}{F^*}(C_w + BQ_v) \qquad (3)$$

where

C_o = conductivity of the water saturated formation, mho/m

F^* = formation factor of the shaly formation, dimensionless, the inverse of the slope of the straight line part of the curve of C_o versus C_w

The equation derived by Archie (7) for the water saturation of a clean formation can be written for the case of a shaly formation as follows:

$$S^n_{wt} = F^* \frac{C_t}{C_{we}} \qquad (4)$$

where

C_t = conductivity of a hydrocarbon-bearing formation, mho/m

n = saturation exponent, dimensionless

Equation 4 can be presented as:

$$C_t = \frac{(S^n_{wt})(C_{we})}{F^*} \qquad (5)$$

Combining equations (2) and (5):

$$C_t = \frac{S^n_{wt}}{F^*}(C_w + B\frac{Q_v}{S_{wt}}) \qquad (6)$$

The apply equation (6), it is necessary to know the parameters Q_v, F*, and B. References 6 and 8 make an analysis of the parameters R* and B. The parameter Q_v is related to the main objective of this research, the cation exchange capacity, using equation (1).

Equation (6) may be presented using resistivities instead of conductivities (2) as:

$$S_{wt} = \frac{-(B)(Q_v)(R_{w2}) + \sqrt{((B)(Q_v)(R_{w2}))^2 + 4(F^*)\cdot(R_{w1})/R_t}}{2} \qquad (7)$$

where

R_{w1} = resistivity of the water at formation temperature, ohm x m

R_{w2} = resistivity of the water at 77°F, ohm x m

R_t = resistivity of the hydrocarbon-bearing formation, ohm x m

The derivation of equation (7) is given in Appendix B.

The main advantage of this model is its simplicity. This model has two major difficulties for its application: Q_v and shale behavior. The charge concentration per unit pore volume, Q_v, is difficult to measure and its value varies with the method used for the measurement. This model assumes that the water in the shales is as salty as the water in the surrounding sands. There is much evidence to indicate this assumption is not true.

Clavier, Coates, and Dumanoir (8) made a study of the Waxman-Smits model and they presented a variation called "The Dual Water Model." According to this model, a water-bearing formation behaves as if there were two different waters in the pores.

The first, called "clay water," occupies the pore space very close the clay surface. The fraction of the total pore volume occupied by clay water is:

$$(f_\phi)cw = (v_Q)(\alpha)(Q_v) \qquad (8)$$

where

$(f_\phi)cw$ = fraction occupied by clay water

α = expansion factor for diffuse layer, dimensionless

v_Q = product of the specific clay-area coefficient (ν) by the distance of "outer Helmholtz plane" from clay surface, cm^3/meq

The conductivity of the "clay water" is given by

$$C_{cw} = \frac{(\beta)(Qv)}{(f_\phi)cw} = \frac{\beta}{(\alpha)(v_Q)} \qquad (9)$$

β is the equivalent conductivity of sodium ions, in (mho/m)/(meq/ml).

The second type of water is called "far water," which occupies the space far from the clay surface in the porous space. The fraction of the pore volume occupied by it is given by:

$$(f_\phi)_{fw} = 1 - (f_\phi)_{cw} = 1-(\alpha)(v_Q)(Q_v) \qquad (10)$$

The conductivity, C_{fw}, of this "far water" is equal to the conductivity, C_w, of the bulk water, that is

$$C_{fw} = C_w \qquad (11)$$

The effective conductivity of the formation water is the addition of those two conductivities:

$$C_{we} = ((f_\phi)_{cw})(C_{cw}) + ((f_\phi)_{fw})(C_{fw}) \qquad (12)$$

The conductivity, C_o, of a water-saturated formation is

$$C_o = \frac{C_{we}}{F_o} = \frac{(1 - (\alpha)(v_Q)(Q_V))(C_W) + (\beta)(Q_V)}{F_o} \qquad (13)$$

Reference 8 shows how to determine all the parameters involved in this model. It also gives the equations used for the calculation of water saturation.

F_o is the inverse of the slope of the straight line part of the curve of C_o versus C_w, multiplied by $(1-v_Q \cdot Q_V)$. "The determination of CEC is at best a more or less arbitrary matter and no high degree of accuracy can be claimed"(1).

There are many methods for the measurement of cation exchange capacity. They are described in references 5, 9, 10, 11, 12 and 13.

All methods can be separated into three stages:

1) preparation of the sample;

2) conversion of all exchangeable ions to one species; and;

3) determination of CEC.

In the first stage the same is cleaned, dried, deoiled, and disaggregated. It is the objective of this research to determine the variation of CEC with the amount of grinding of the sample. The CEC should be a function of the amount of new surface area created.

In the second stage, all exchangeable ions are converted to one type and the excess is washed out. It is necessary to be very careful not to overwash nor underwash the sample. An excess of washing can cause loss of finer components and/or hydrolyzing of some of the exchangeable ions. This is the stage that involves the most difficulties and where there are more possibilities of mistakes.

In the last stage, the CEC value is usually determined based on a titration.

In this research, the procedure described in reference 5 (reproduced in Appendix C) was used, with some modifications to compensate for hydrocarbon-impregnated formations and for formation with calcite in the matrix.

LABORATORY PROCEDURE

The laboratory work was begun using the method described by Davidson and Sheeler (5), but the results were inconsistent. This procedure was for surface or very shallow sample, used for agricultural purposes. This method was modified as shown in the flow chart in Figure 1 and described as follows:

1. Approximately 60 grams of dry sample was pulverized mechanically in a steel mortar. It was ground to a size necessary to pass through a number 16 sieve (1.19 mm). The sample was then divided equally and uniformly in 6 portions of approximately 10 grams each. This division was made using a sample splitter. The CEC of one of these samples was determined as described in the following procedure.

   A second portion was again pulverized to pass through a number 40 sieve (0.42 mm) and its CEC was determined. A third portion was ground as many times as necessary so that all the sample passed through a number 60 sieve (0.25 mm); the CEC of this sample was then determined.

   A fourth part was ground to pass all the portion through a number 140 sieve (0.104 mm). The CEC

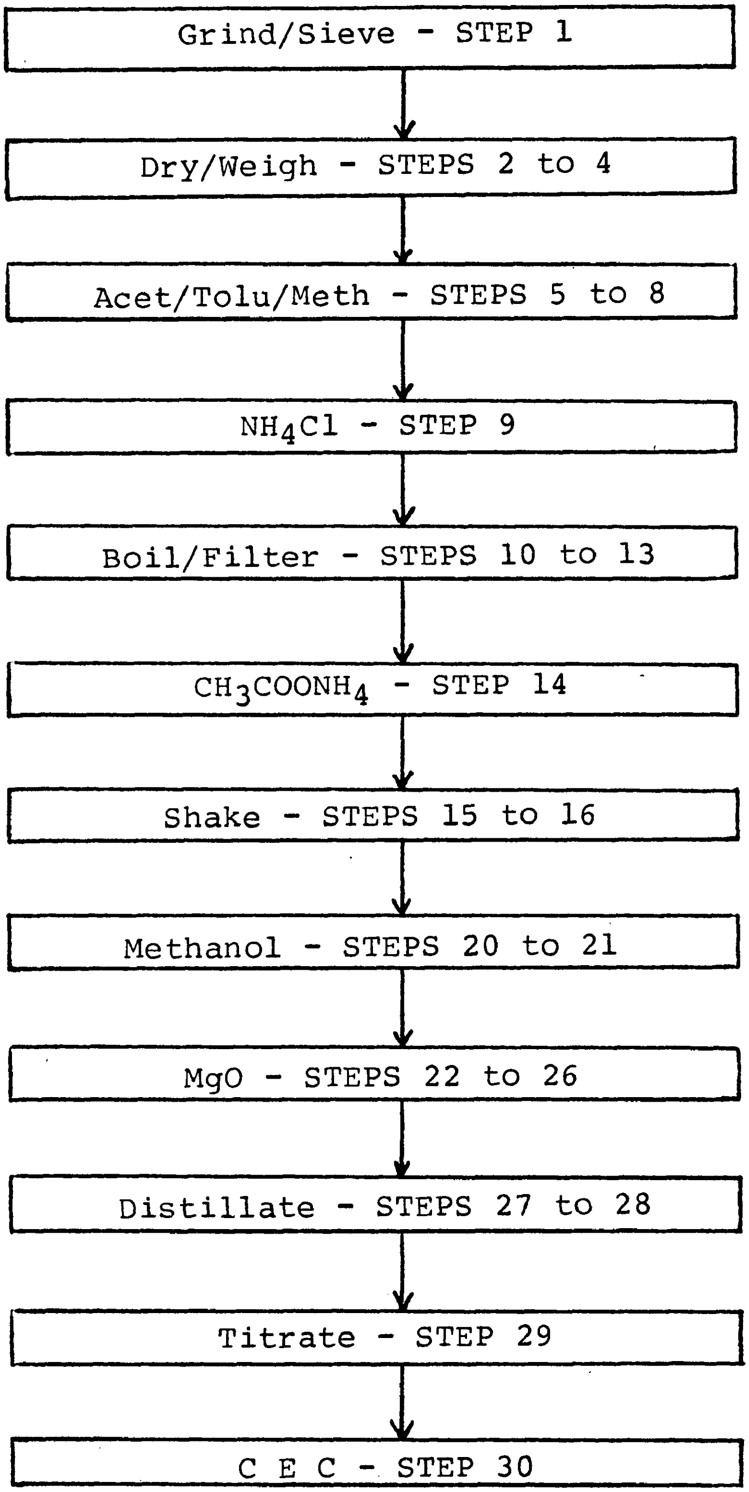


FIGURE 1. Flow Chart of Lab Procedure

of this portion was then determined.

A fifth part was used to determine the CEC of a sample with grain size equal or less than 0.044 mm; this was accomplished grinding all the sample until it passed through a number 325 sieve.

The sixth portion was kept in case it was needed for other purposes.

2. Take about 5 grams of sample.

   It is recommended to use no more than 5 g of sample because the air bubbles that will be formed during the boiling might be so big that they may force some solution and sample out of the flask.

3. Dry the sample in the air or in an oven.

   This research used air-dried samples. The error in using air-dried samples is very small (12).

   In this research, the air-dried samples were found to create an average error of 0.08% in 44 samples.

   It should be noted that an oven dried sample is a hygroscopic material which quickly resorbs water from the air and returns to about the same state as before drying.

4. Weigh the sample to the closest milligram.

5. Rinse the sample with acetone.

   This step removes most of the oil contained in the sample.

6. Extract the sample with warm toluene.
   The objective to this step is to remove any residual oil still present in the sample.
7. Filter the sample, being careful not to lose any amount of it.
   All filtrations should be made using a vacuum pump for a better operation and to keep the time required for filtration to a reasonable length.
8. Rinse the sample with acetone and then with methanol until the solvents come out clear.
   The objective of this step is to eliminate any oil and/or extraction solvent in the sample.
9. Put the sample and the filter paper in a 500 ml Erlenmeyer flask. Add 150 ml of 2 normal ammonium chloride solution ($2N\text{-}NH_4Cl$) plus 200 ml of distilled water.
10. Boil the mixture for 4 hours, keeping the volume in the flask up to at least 150 ml. When necessary, add hot distilled water to maintain the volume.
    In this step, the carbonates are removed and the sample is refluxed. The refluxing removes residual hydrocarbon and/or solvents. If the sample contains some hydrocarbon or carbonates, the determined CEC will be much lower than the actual value (5).
    The chemical reaction that occurs in this step is:

$$CaCO_3 + 2NH_4Cl \xrightarrow{\Delta} CaCl_2 + CO_2 + 2NH_3 + H_2O$$

11. Filter the sample.
12. Rinse the sample with 150 ml of distilled water. In this step, the excess of ammonium chloride remaining in the sample is washed out.
13. Filter the sample being careful not to lose any portion of the sample.
14. Put the sample and the filter paper in the Erlenmeyer flask. Add 250 ml of ammonium acetate solution with a normality equal to 1 (1N-CH_3COONH_4). In this step the ammonium ions displace all the exchangeable ions of the sample. This chemical reaction is

$$(\text{Cation})(\text{Clay})+CH_3COONH_4 \rightarrow CH_3COO(\text{Cation})+ NH_4(\text{Clay})$$

15. Shake the mixture for 12 hours. The objective of this step is to improve the contact between the sample and the salt solution to better accomplish step 14. In this research, an Eberbach two speed shaker (#6010) was used to shake the mixture. A speed of 180 excursions per minute was used.
16. Filter the mixture being careful not to lose any portion of the sample.

17. Repeat step 14.

    The objective of this repetition is to assure that all the exchangeable ions are substituted by the ammonium ions.

18. Shake the mixture for 4 hours.

    The remarks made for step 15 are applicable for this step.

19. Repeat step 16.

20. Wash the sample with 50 ml of a mixture of methanol and distilled water (70% methanol, by volume).

21. Repeat step 20 until the slurry (sample, methanol, water) has a conductivity of 20 micromho/cm, or less.

    In steps 20 and 21, the cations not bound to the clays are removed.

    In this research, a Conductivity Bridge, model PM-70CB (Sybrom Barnstead) with a Cell Model E3416 (1.0 constant) was used to measure the conductivity of the slurry.

22. Put the sample and the filter paper in a 500 ml Kjeldahl flask.

23. Add 150 ml of distilled water.

24. Add 1 tablespoon of magnesium oxide (MgO). In this step the magnesium ions will displace the ammonium ions sorbed in step 14. This chemical reaction is

$$2NH_4(Clay) + MgO \rightarrow Mg(Clay) + 2NH_3 + H_2O$$

25. Put 25 to 50 ml of a solution of hydrochloric acid with normality equal to 0.1 (0.1N - HCl) in a 500 ml Erlenmeyer flask.

    This acid will react with the ammonia produced in step 24 as shown by the chemical equation

    $$2NH_3 + H_2O + 2HCl \rightarrow 2NH_4CL + H_2O$$

26. Drop a small portion of 0.2% Methyl Red into the acid.

    The objective of this pH indicator is to show the end point of the titration (step 29).

27. Distill the contents of the Kjeldahl flask to dryness.

    Be sure that there are no leaks in the system. The distillation hook-up is shown in Figure 2. Be sure that the receiving tube of the condenser is well extended into the acid.

    In this step all the ammonia produced in step 24 is displaced from the Kjeldahl flask and reacts with the hydrochloric acid contained in the Erlenmeyer flask. The chemical equation of this reaction is

    $$2NH_3 + H_2O + 2HCl \rightarrow 2NH_4Cl + H_2O$$

28. Wash the acid off the receiving tube into the Erlenmeyer flask with distilled water.

29. Titrate the mixture contained in the Erlenmeyer using

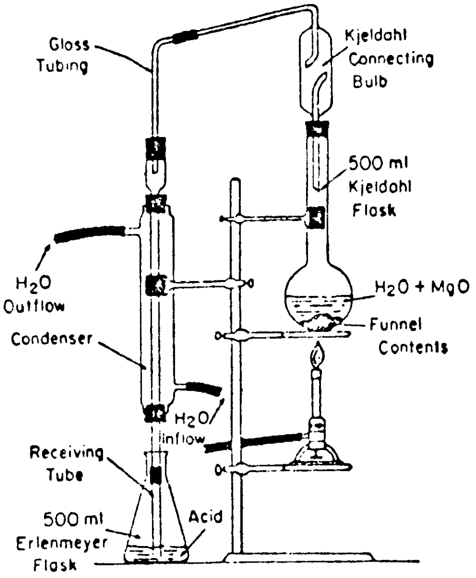


FIGURE 2. Distillation Apparatus
(After Reference 5)

a 0.1 normal solution of sodium hydroxide (0.1N - NaOH). The end point of this titration occurs at a pH of 6.2. Read the burette to the nearest 0.1 ml.

30. Calculate the CEC using the equation

$$\text{CEC} = \frac{0.1\ (X-Y)}{w}\ 100 \qquad (14)$$

where

CEC = cation exchange capacity in meq/100g

X = amount of HCl in ml, used in step 25

Y = amount of sodium hydroxide in ml, used in step 29

w = weight of dry sample determined in step 4, in grams

In Appendix E, an example of this calculation is shown.

RESULTS

The results obtained in this research are shown in Tables I through VI, and in Figures 3, 4, and 5.

Table I presents the cation exchange capacity for the 20 samples, each one with 5 different grain sizes. The maximum grain size for each one of the 5 portions is shown in the top of the table and given in mm. The CEC is given in meq/100g. The data shown in this table were classified by the predominant type of clay (the one with the highest percentage by weight) and averaged for each type, as shown in Table IV and in Figure 3. The composition, in weight percentage, of all samples is shown in Table VII. The composition of the samples was obtained by X-Ray Diffraction Analysis.

In Table II, the normalized data of Table I are shown. For each sample, the CEC for different grain sizes was divided by the CEC of the largest grain size. This was done for better comparison of the variation of the CEC for different samples. In this table the notation CEC_i means the CEC of a sample ground enough to pass through a number "i" sieve. The data of Table II are shown in Table V and in Figure 4, classified and averaged for the predominant clay in the sample.

In Table III the absolute variation of the CEC for different grain sizes in relation to the CEC of the largest grain size is shown. This was done taking the differences between the CEC of different grain sizes and the CEC of the largest grain size. These data were classified by the predominant clay, averaged, and presented in Table VI and in Figure 5. The repeatability of the CEC values found in this research is ±0.1 meq/100g. The determination of the CEC for sample D, for d≤1.19 m, was repeated two times. It was found the values of 0.7 and 0.8 meq/100 g.

The amount of grinding (the grain size) alters the CEC measured in the laboratory, as shown by data in Tables I and IV and by Figure 3. This result is in agreement with the ones obtained by Patchett (14) and Davidson (5). The cation exchange capacity increases with decreasing grain size. The higher the surface area of the sample the higher is the measured CEC.

The plot in Figure 4 and the data in Tables II and V show that the relative increase of CEC is larger for the sample with small CEC values, like kaolinite. For kaolinite and chlorite the broken bond mechanism is the only method by which cations are adsorbed (4). The more a sample is ground the more the bonds are broken. "Broken bonds around the edge of silica-alumina units would give rise to unsatisfied charges which would be balanced by adsorbed cations" (1). The samples with small CEC are more affected by the amount of grinding than the ones with higher CEC.

For the samples with small CEC, the absolute increase of CEC with increased grinding is smaller than the increase observed in the ones with large CEC. This trend is shown in Figure 5 and in the data in Tables III and VI.

The trend of all the curves in Figure 3 shows that any amount of crushing of a sample alters its CEC value as determined in the laboratory. The CEC calculated in the laboratory by any method where the sample is disaggregated is higher than that determined at actual conditions in the formation.

The anomalies in samples E and I are probably due to sampling operations.

Grain Dia. / Sample	d≤ 1.19mm	d≤ 0.42mm	d≤ 0.25mm	d≤ 0.104mm	d≤ 0.044mm
C	0.5	1.3	1.8	2.4	2.5
D	0.7	0.9	1.1	2.4	2.5
E	1.1	1.1	1.1	0.9	1.1
F	0.8	1.1	1.5	2.8	5.0
G	1.0	1.0	1.0	1.1	1.3
H	0.8	1.2	1.4	1.7	2.0
I	3.2	3.3	3.2	3.3	3.6
J	2.2	2.3	2.6	2.7	3.4
K	5.4	5.8	7.2	9.4	12.0
L	6.7	7.3	8.2	8.3	8.6
M	8.2	9.5	9.5	10.6	13.8
N	8.0	9.1	10.3	10.9	13.3
O	9.1	9.1	9.5	10.5	11.1
P	9.5	9.9	10.0	10.4	12.4
Q	8.2	8.8	9.6	10.3	11.2
R	1.1	2.1	2.9	3.1	3.3
S	1.7	2.1	2.5	2.9	3.4
T	1.6	1.9	2.3	2.6	3.5
U	1.8	2.0	2.0	2.6	3.3
V	2.2	2.3	2.3	3.3	4.0

TABLE I. Cation Exchange Capacity, in meq/100 g

Sample	$\frac{CEC_{16}}{CEC_{16}}$	$\frac{CEC_{40}}{CEC_{16}}$	$\frac{CEC_{60}}{CEC_{16}}$	$\frac{CEC_{140}}{CEC_{16}}$	$\frac{CEC_{325}}{CEC_{16}}$
C	1.00	2.60	3.60	4.80	5.00
D	1.00	1.29	1.57	3.43	3.57
E	1.00	1.00	1.00	0.82	1.00
F	1.00	1.38	1.88	3.50	6.25
G	1.00	1.00	1.00	1.10	1.30
H	1.00	1.50	1.75	2.13	2.50
I	1.00	1.03	1.00	1.03	1.13
J	1.00	1.05	1.18	1.23	1.55
K	1.00	1.07	1.33	1.74	2.22
L	1.00	1.09	1.22	1.24	1.28
M	1.00	1.16	1.16	1.29	1.68
N	1.00	1.14	1.29	1.36	1.66
O	1.00	1.00	1.04	1.15	1.22
P	1.00	1.04	1.05	1.09	1.31
Q	1.00	1.07	1.17	1.26	1.37
R	1.00	1.91	2.64	2.82	3.00
S	1.00	1.24	1.47	1.71	2.00
T	1.00	1.19	1.44	1.63	2.19
U	1.00	1.11	1.11	1.44	1.83
V	1.00	1.05	1.05	1.50	1.82

TABLE II. Relative Variation of CEC (CEC of Different Grain Sizes Divided by the CEC of the Largest Grain Size)

Sample	$CEC_{40}-CEC_{16}$	$CEC_{60}-CEC_{16}$	$CEC_{140}-CEC_{16}$	$CEC_{325}-CEC_{16}$
C	0.8	1.3	1.9	2.0
D	0.2	0.4	1.7	1.8
E	0.0	0.0	-0.2	0.0
F	0.3	0.7	2.0	4.2
G	0.0	0.0	0.1	0.3
H	0.4	0.6	0.9	1.2
I	0.1	0.0	0.1	0.4
J	0.1	0.4	0.5	1.2
K	0.4	1.8	4.0	6.6
L	0.6	1.5	1.6	1.9
M	1.3	1.3	2.4	5.6
N	1.1	2.3	2.9	5.3
O	0.0	0.4	1.4	2.0
P	0.4	0.5	0.9	2.9
Q	0.6	1.4	2.1	3.0
R	1.0	1.8	2.0	2.2
S	0.4	0.8	1.2	1.7
T	0.3	0.7	1.0	1.9
U	0.2	0.2	0.8	1.5
V	0.1	0.1	1.1	1.8

TABLE III. Absolute Variation of CEC (Difference between the CEC of Different Grain Sizes and the CEC of the Largest Grain Size)

Predominant Clay	d≤ 1.19mm	d≤ 0.42mm	d≤ 0.25mm	d≤ 0.104mm	d≤ 0.044mm
Illite	0.8	1.1	1.3	1.9	2.5
Kaolinite	1.8	2.2	2.5	2.8	3.3
Smectite	7.9	8.5	9.2	10.1	11.8

TABLE IV. Cation Exchange Capacity, in meq/100g, averaged for the predominant type of clay.

Predominant Clay	d≤ 1.19mm	d≤ 0.42mm	d≤ 0.25mm	d≤ 0.104mm	d≤ 0.044mm
Illite	1.00	1.45	1.81	2.73	3.42
Kaolinite	1.00	1.28	1.50	1.72	2.03
Smectite	1.00	1.08	1.18	1.30	1.53

TABLE V. Relative Variation of CEC, averaged for the predominant type of clay.

Predominant Clay	d≤ 0.42mm	d≤ 0.25 mm	d≤ 0.104mm	d≤ 0.044mm
Illite	0.3	0.5	1.1	1.7
Kaolinite	0.3	0.6	1.0	1.5
Smectite	0.6	1.3	2.2	3.9

TABLE VI. Absolute Variation of CEC, averaged for the predominant type of clay.

SAMPLE	Quartz	Siderite	Dickite	Illite	K-Spar	Plagio.	Calcite	Kaolinite	Smectite	Mica	Dolomite	Chlorite	Pyrite	Barite
C	85.7	5.6	3.8	5.0										
D	90.4	2.4	2.8	4.4										
E	80.3	10.5	4.4	4.8										
F	79.1	15.0	4.2	1.6										
G	80.8	1.7	6.5	11.0										
H	84.0				11.9	0.9	0.3	2.9						
I	65.1				8.4	1.1	23.9	1.6						
J	61.2				7.0	6.2	24.2	1.3						
K	76.7			1.9	8.2	8.9			4.3					
L	46.0			0.6	21.9	26.9		0.4	2.4	1.7				
M	24.7				9.6	14.5	12.8		7.7	1.9	6.7	4.8		
N	33.8				14.4	16.5	7.5		5.1	1.4	9.7	1.7		
O	34.9				11.4	16.3	9.0		5.5	2.2	8.6	2.5		
P	40.9				10.1	16.6	6.8		5.5	1.8	7.1	1.9		
Q	22.9				7.3	11.3	10.8		10.6	1.4	8.3	4.3		
R	46.4			2.8	22.0	11.8		2.9		12.0		2.0	0.1	
S	39.1			0.4	37.7	17.5		1.1		3.3		0.8		
T	52.7			1.5	20.8	14.4		5.2		3.5		0.7	1.0	0.1
U	22.2			2.6	33.0	8.6		3.6		24.6		4.5	0.3	0.6
V	18.9			5.1	34.0	17.6		7.5		14.0		2.7	0.2	

TABLE VII. Composition of Samples, in weight percentages, obtained by X-Ray diffraction analysis.

SAMPLE	X-RAY DIFFRACTION	CORE ANALYSIS
C	2.732	2.700
D	2.689	2.680
E	2.797	2.770
F	2.850	2.870
G	2.693	2.670
H	2.640	2.679
I	2.660	2.676
J	2.659	2.684
K	2.638	2.667
L	2.626	2.632
M	2.695	2.637
N	2.678	2.678
O	2.681	2.693
P	2.676	2.683
Q	2.707	2.649
R	2.667	2.674
S	2.626	2.669
T	2.667	2.662
U	2.709	2.664
V	2.670	2.680

TABLE VIII. Grain Density (Determined by X-Ray Diffraction and by Core Analysis, in g/cm^3)

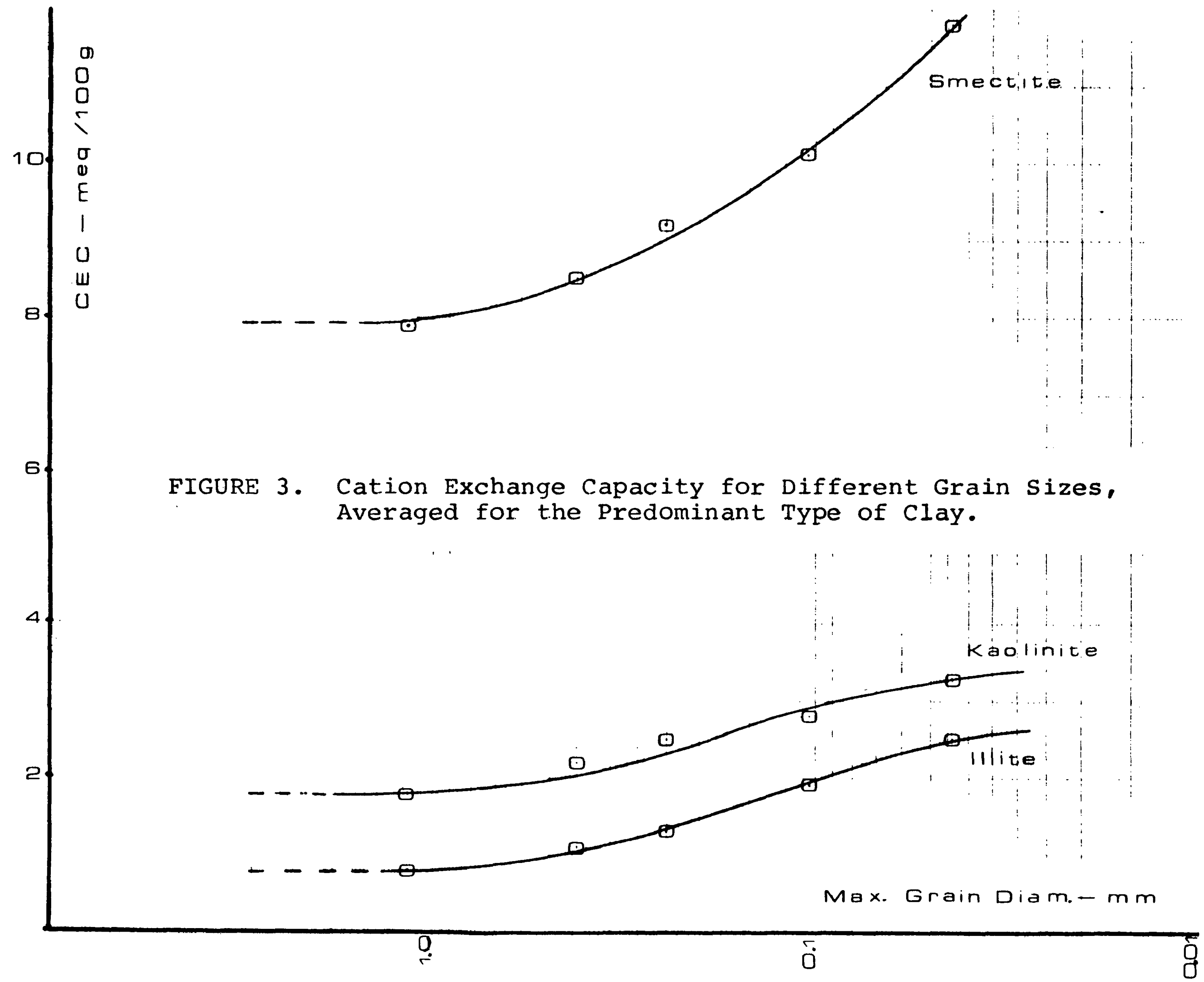


FIGURE 3. Cation Exchange Capacity for Different Grain Sizes, Averaged for the Predominant Type of Clay.

FIGURE 4. Relative Variation of the CEC for Different Grain Sizes Averaged for the Predominant Type of Clay.

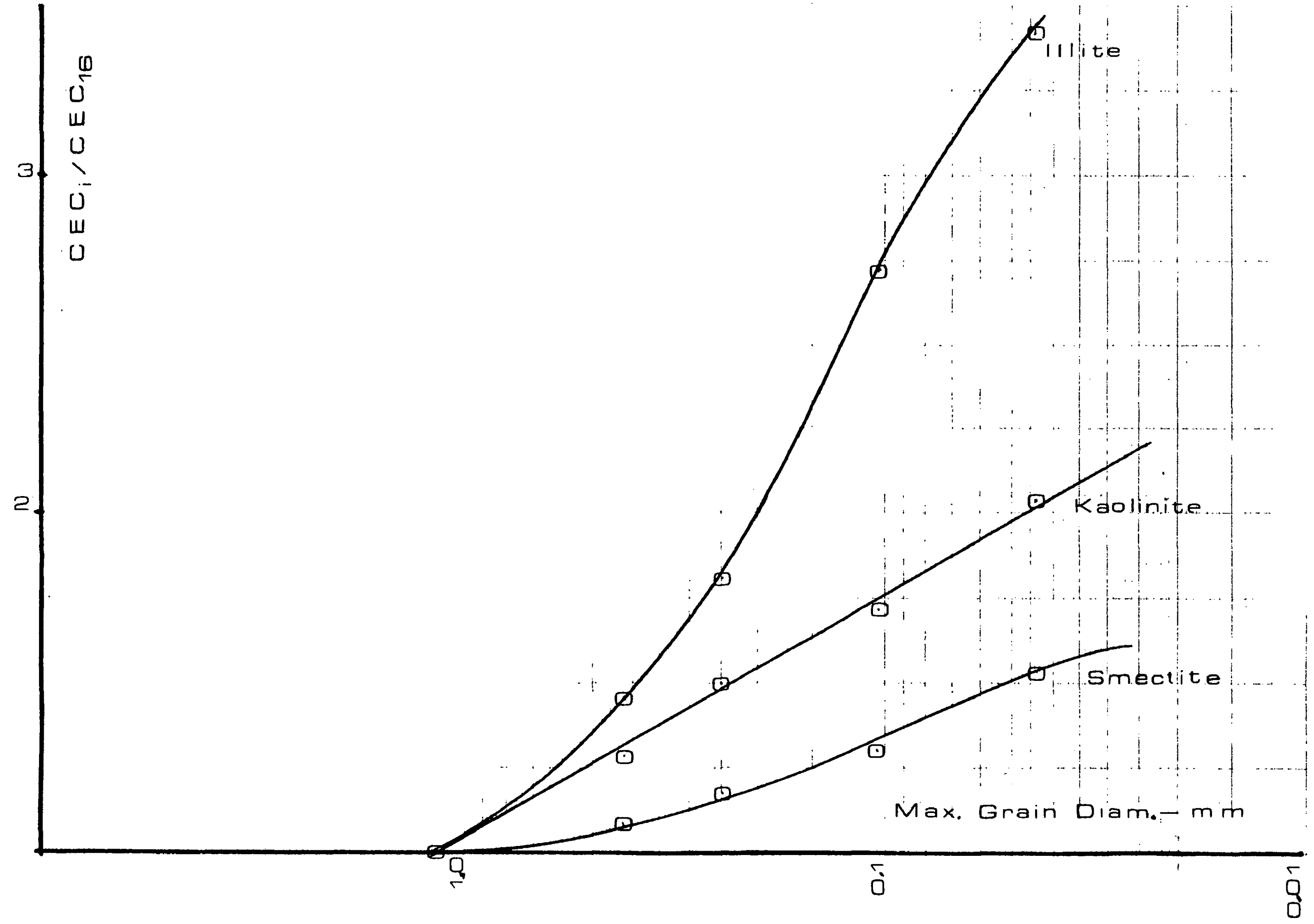
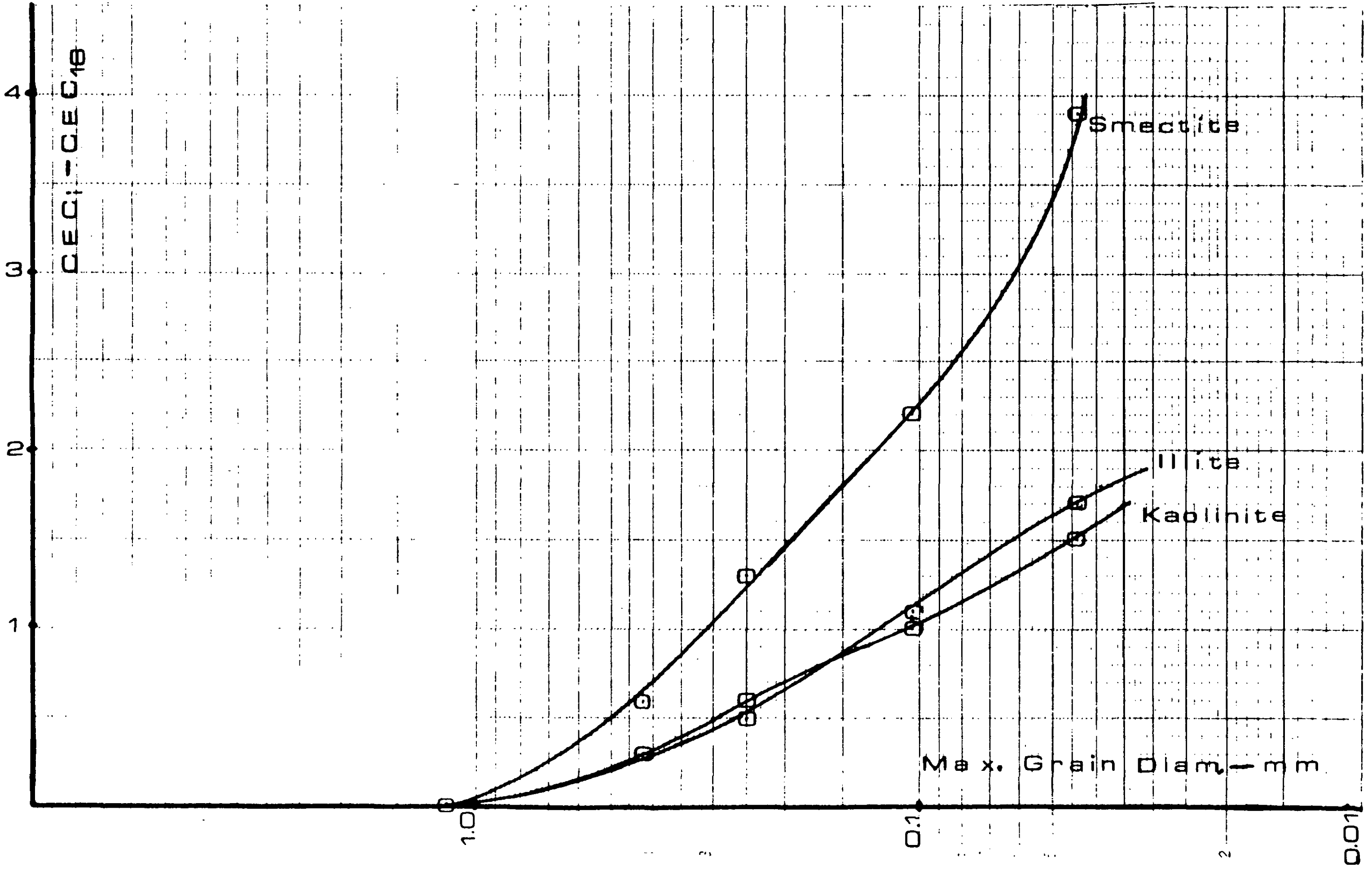


FIGURE 5. Absolute Variations of the CEC for Different Grain Sizes Averaged for the Predominant Type of Clay.



CONCLUSIONS

The following conclusions can be taken from the foregoing results:

- The cation exchange capacity determined in a laboratory depends on the grain size of the sample.
- Any amount of grinding of a sample alters the CEC determined in the laboratory.
- The CEC determined in the laboratory increases with the amount of mechanical grinding of the sample.
- The relative increase of the CEC, when compared with the CEC of the largest grain size sample, is more accentuated for rock with initial low CEC values.
- The CEC value determined in the laboratory with disaggregated sample appears to be higher than the value at formation conditions.
- The CEC value of an unaltered sample may be approximated by extrapolating the flat part of the curve of CEC versus maximum grain size.

RECOMMENDATIONS

It is recommended for future research the following subjects:

- The CEC variations with the grain size distribution, i.e., to determine the CEC for different ranges of grain sizes and find which range is more responsible for the CEC of the disaggregated sample.
- How the CEC determined in the laboratory correlates with some borehole measurements.
- How the CEC can be determined in the laboratory by a non-destructive method that reflects better the actual condition in the formation. One suggestion is to flow a salt solution (like ammonium acetate) of known ion concentration through a core and measure the ion concentration in the effluent, using mass balance the loss of salt ions (adsorbed ions) can be calculated and from this result, calculate the CEC.
- How the CEC determined in the laboratory varies with temperature.

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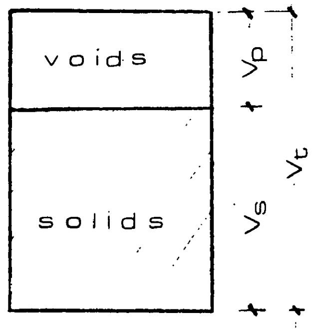
APPENDIX A

Relation between Q_v and CEC.



V_p = porous volume, cm^3

V_s = solid volume, cm^3

V_t = total volume, cm^3

ϕ = porosity (fraction)

ρ = density (g/cm^3)

Q_v = meq/unit pore volume

CEC = meq/100g

W = weight of the sample, gram

$$Q_v = \frac{meq}{V_p}$$

$$Q_v = \frac{meq}{\phi \cdot V_t}$$

$$V_s = \frac{W}{\rho}$$

$$V_t = \frac{V_s}{1-\phi} = \frac{W}{\rho} \cdot \frac{1}{(1-\phi)}$$

$$Q_v = \frac{meq}{\frac{W \cdot \phi}{\rho(1-\phi)}}$$

$$CEC = \frac{meq}{W} \times 100$$

$$Q_v = \frac{(CEC).\rho.(1-\phi)}{100 \times \phi} \qquad (1)$$

APPENDIX B

$$C_t = \frac{S_{wt}^n}{F^*} \left(C_w + B \frac{Q_v}{S_{wt}}\right) \qquad (6)$$

$$S_{wt}^n = \frac{F^* \cdot C_t}{C_w + B . Q_v / S_{wt}} = \frac{F^* \cdot C_t \cdot S_{wt}}{C_w S_{wt} + B . Q_v}$$

$$C_w S_{wt}^{n+1} + BQ_v S_{wt}^n - C_t F^* S_{wt} = 0$$

$$C_w S_{wt}^n + BQ_v S_{wt}^{n-1} - C_t F^* = 0$$

For n = 2, we have

$$C_w S_{wt}^2 + BQ_v S_{wt} - C_t F^* = 0$$

$$S_{wt} = \frac{-BQ_v + \sqrt{(BQ_v)^2 + 4C_w C_t F^*}}{2C_w}$$

$$= \frac{-BQ_v/C_w + \sqrt{(BQ_v/C_w)^2 + 4C_t F^*/C_w}}{2}$$

Using resistivities instead of conductivities, we have,

$$S_{wt} = \frac{-BQ_v R_w + \sqrt{(BQ_v R_w)^2 + 4R_w F^*/R_t}}{2} \qquad (7)$$

APPENDIX C

The method used by Davidson and Sheeler (5) is reproduced below.

Exchange of cations. The exchange of cations is accomplished by shaking a mixture of soil and ammonium acetate solution in a bottle. This method requires the use of a centrifuge. The weighed air-dry sample is placed in a rubber stoppered centrifuge and shaken by hand or electric shaker, with 250 ml of ammonium acetate solution, for 3 minutes. The suspension is then centrifuged until all soil particles are packed in the bottom of the bottle. The clear supernatant liquid above the sample is suction-filtered through a Beuchner funnel fitted with a dense filter paper, and the centrifuge bottle is refilled with 250 ml of fresh ammonium acetate solution. After the shaking and centrifuging operation has been repeated, the supernatant liquid is filtered through the Beuchner funnel and the soil washed into the funnel and filtered. The soil cake is then washed with 150 ml of neutral 70% methyl alcohol solution prior to determine the amount of ammonium ions adsorbed by the soil.

Distillation. Immediately following the alcohol washing the soil sample containing ammonium that has been taken by exchange is transferred to a 500 ml Kjeldahl flask and covered with 150 ml of distilled water. The transfer of soil from the Beuchner funnel employed in the shaking method is best accomplished by rolling up the soil sample in the filter paper and transferring paper and sample to the Kjeldahl flask. Wetting the caked soil slightly facilitates this operation. Soil grains clinging to the sides of the funnel may be transferred by wetting a clean sheet of filter paper with distilled water and wiping the inside of the funnel clean; the filter paper is then placed in the flask.

Next, measure exactly 50 ml of 0.1000 N hydrochloric acid and place in the 500 ml Erlenmeyer flask. Place the flask under the condenser with the receiving tube of the condenser extending well into the acid. Add 1 ml of 0.2 percent methyl red solution to the acid and a full teaspoon of magnesium oxide to the contents of the Kjeldahl flask. Check all the connections of the distillation apparatus to make sure they are tight enough to prevent any escape of ammonia. Then light the burner under the Kjeldahl flask and distill the contents nearly to dryness.

Care should be taken throughout the distillation to prevent acid from being sucked up into the Kjeldahl flask. Should the acid start to be sucked up into the condenser, the connecting tube at the top of the condenser should be momentarily opened. Make sure that the flame is on throughout the distillation, as a loss of heat source will create a vacuum in the distillation system, and suck acid into the condenser. At the end of the distillation, disconnect the Kjeldahl connecting bulb before removing the flame.

Titration. Remove the Erlenmeyer flask and wash the acid off the receiving tube into the flask with distilled water. Titrate the excess acid with 0.1000 N sodium hydroxide, reading the burette to the nearest 0.1 m. The end-point of the titration occurs exactly at a pH of exactly 6.20. The end-point can be determined most accurately by the use of a pH meter, but if no pH meter is available, the end-point is evidenced by a yellow-orange color. At a pH of about 5.7, the color turns from red, to red-orange and then fades to yellow-orange as the titration proceeds to pH 6.20; there is a difference of 0.5 to 0.7 ml between 5.7 and 6.2.

Calculations. The cation exchange capacity of the sample may now be calculated in milliequivalents per 100g of oven-dry soil.

The oven-dry weight of the sample used is determined by correcting the air-dried weight for hygroscopic moisture as follows:

$$d = a\frac{100}{100+p} \qquad \text{(C-1)}$$

where

d = weight of oven-dry sample in grams

a = weight of air-dry sample in grams, and

p = percent hygroscopic moisture.

The cation exchange capacity is calculated from the following equation:

$$c = \frac{A-B}{d} 100 \qquad (C-2)$$

where

c = cation exchange capacity in m.e. per 100g

A = (ml of HCl used)(Normality of HCl)

B = (ml of NaOH used)(Normality of NaOH), and

d = weight of oven-dry sample in grams

APPENDIX D

Composition of the solutions used to measure the cation exchange capacity of clay in this research:

A) 2N - Ammonium Chloride

NH_4Cl

N: 1 x 14 = 14

H: 4 x 1 = 4

Cl: 1 x 35.5 = 35.5

M W = 53.5g

1 N ———————— 53.5g/1

2 N ———————— Y Y = 107g/1

In 1 liter of a solution of ammonium chloride with normality 2, there are 107 grams of NH_4CL

B) 1N - Ammonium Acetate

$CH_3COO\text{-}NH_4$

C: 2 x 12 = 24

H: 7 x 1 = 7

O: 2 x 16 = 32

N: 1 x 14 = 14

M W = 77g

1 N ——————— 77 g/1

There are 77 grams of ammonium acetate in 1 liter of 1N solution of this salt.

C) 0.1N - Sodium Hydroxide

$NaOH$

Na: 1 x 23 = 23

O: 1 x 16 = 16

H: 1 x 1 = 1

M W = 40g

1 N ———————— 40 g/l

.1 N ———————— Y Y = 4g/l

There are 4 grams of NaOH in one liter of .1N solution of this base.

D) 0.1N - Hydrochloric Acid

HCl

H: 1 x 1 = 1

Cl: 1 x 35.5 = 35.5

M W = 36.5g

1 N ———————— 36.5 g/l

.1 N ———————— Y Y = 3.65g/l

There are 3.65 grams of HCl in one liter of .1N solution of this acid.

APPENDIX E

An example of CEC determination:

Weight of dry sample: $W = 4.395$ g

Normality of solutions: $N = 0.1N$

HCl used: $X = 21$ ml

NaOH used: $Y = 20.65$ ml

From Equation (14):

$$\text{CEC} = \frac{21 \times 0.1 - 20.65 \times 0.1}{4.395} 100 = 0.8 \text{ meq/100g}$$

APPENDIX F

A wet sieving was made in all samples after the first grinding; i.e., the sample was ground to pass through a number 16 sieve.

Each fraction was oven-dried (110°C) before weighing.

The results are tabulated in cumulative weight percent, as shown on the next page.

Sieve Sample	16	35	50	60	80	100	120	200	325	30μ
C	0.0	7.2	36.5	48.7	60.6	67.6	70.1	75.1	77.6	83.9
D	0.0	13.4	35.2	43.4	63.4	71.7	76.2	82.8	84.6	84.9
E	0.0	18.2	34.5	43.7	60.1	67.2	70.8	76.2	79.9	86.8
F	0.0	34.1	50.7	57.9	72.2	75.0	79.5	82.1	86.8	87.1
G	0.0	19.5	33.5	38.8	49.8	53.2	57.3	67.2	73.7	79.7
H	0.0	0.05	8.6	17.3	51.3	77.3	85.9	88.8	90.2	93.9
I	0.0	1.2	8.9	15.3	44.6	61.1	72.4	77.5	82.6	83.5
J	0.0	0.1	6.9	17.9	26.2	44.0	50.8	59.0	64.5	90.5
K	0.0	3.1	6.3	7.8	26.6	54.7	61.2	68.8	71.8	75.6
L	0.0	7.1	14.3	18.6	49.7	69.7	75.3	80.9	83.6	90.9
M	0.0	0.04	0.06	0.09	0.2	1.3	2.5	5.3	7.2	29.6
N	0.0	0.0	0.03	0.06	0.2	1.6	2.9	13.9	22.9	84.6
O	0.0	0.0	0.02	0.02	0.04	1.0	2.1	4.5	10.4	54.6
P	0.0	0.0	0.0	0.0	0.1	0.1	1.3	21.2	26.5	60.5
Q	0.0	0.0	0.0	0.0	0.0	1.0	2.1	3.3	3.4	8.7
R	0.0	0.1	1.2	1.3	1.3	2.3	4.4	68.2	78.2	90.9
S	0.0	0.2	10.5	44.0	73.2	81.2	85.4	31.6	92.7	97.0
T	0.0	2.1	18.3	37.1	73.8	79.7	81.8	85.7	87.8	88.8
U	0.0	0.1	0.2	0.2	3.3	7.9	30.2	67.0	68.8	83.2
V	0.0	2.1	25.3	43.7	68.8	75.5	80.3	84.6	86.9	90.9