THE EFFECT OF TEMPERATURE UPON THE BASE-EXCHANGE CAPACITY OF CLAYS

By ANGEL ALBERTO COLÓN
University of Puerto Rico

INTRODUCTION

Soils, when brought into contact with certain solutions, undergo certain reactions in which the removal of cations from the soil and their replacement by cations from the solution are involved. The most important cations found in soils are usually calcium, sodium, potassium, magnesium, and acid hydrogen. When any one of these cations is replaced by another particular cation, an exchange of cations has taken place; since these cations are mainly basic, the name base-exchange is applied to this process. Next to photosynthesis base-exchange is the most important chemical reaction in the whole domain of agriculture. Naturally, when one cation is replaced by another in the soil, marked changes in the physical and chemical properties of the soil take place as shown by the relative crop producing power of the soil. Therefore, the availability of these "bases" has a direct relation to the fertility; and any condition that affects the base-exchange capacity of the soil is of great importance.

It has been known for a long time that the removal of water from the soil such as occurs commonly in Puerto Rico, Louisiana, and other places of the earth having high summer temperatures, brings about far reaching changes in the availability of some of the essential soil constituents; hence producing a marked effect upon the fertility of the soil. It has generally been believed that the high temperature to which the land is subjected in the torrid zones have the priceless effect of making the land more productive by setting free some of the reserve plant food.

Although there has been an enormous amount of work done recently dealing with the different aspects of the subject, much of it is vague, and a great part is contradictory. It was thus the purpose of this work to attempt to obtain further data on the effect of temperature upon the base-exchange capacity of soils.

The base-exchange capacity of a soil can be determined by adding an excess of a solution of a replacing salt, like ammonium acetate, to the soil; and, by taking advantage of the exchange reaction which occurs between the ammonium acetate and the soil, the total content of the replaceable bases present in the soil can be readily determined. In order for this exchange of bases to proceed to completion it is necessary to use a sufficiently concentrated solution of replacing salt. For ammonium acetate this concentration is approximately one normal. "Since the exchange takes place stoichiometrically, the amount of ammonium absorbed by the soil is chemically equivalent to the sum of all the bases replaced." (6)

But the base-exchange capacity of soil is not constant, it varies in accordance with several factors. Thus Magistad (9) found it to vary with "reaction of soil, moisture, and other factors" which he explained as being due to a building-up and tearing-down of the particles. Wiegner(19) observed that "the hydration of the ions is the cause of their exchange capacity." Perkins and King (12) found that "the base held by a soil had a considerable effect on its capacity to hold water."

Heat is another important factor influencing base-exchange capacity of soils. It may be looked upon in two different ways: intensity of heat, or temperature, and time of heating. Concerning the effect of heat upon the base-exchange capacity there seems to be some contradiction. Steenkamp (17) found that the total exchangeable bases and the degree of saturation of the soils were increased on drying, and that such soils showed a corresponding decrease in acidity. Coles and Morrison (3) repeated Steenkamp's work and found that the effect of heat and dehydration upon the acidity of suspensions of soils showed an increase in acidity accompanied by a decrease in the content of exchangeable bases, and an increase in the amount of those bases present in contact with the soil; and that the total exchangeable bases in the soil were less after heating the soil in the steam oven than in the original soil.

This exchange of bases takes place mainly on the surfaces or interfaces of small soil particles which are of nearly colloidal dimensions. These particles have a maximum diameter of about 0.002 mm. (colloidal size being generally accepted to be about 0.0001 mm. or 0.1μ and are called the clay fraction of the soil. It so happens that this dynamic clay fraction forms only a very small part of the soil, and hence it would seem desirable to work with the clay fraction alone in order to obtain more pronounced effects.

MATERIALS AND METHODS

In order to obtain this so-called colloidal fraction, the soil was dispersed with 0.8 molar ammonium hydroxide in a rotary shaker for 24 hours; the so dispersed soil was allowed to settle for at least another 24 hours and the upper layer of the suspension, to a depth of 9 cm., was siphoned off. According to Stoke's law for particles falling through a column of fluid, particles of diameters of about 0.002 mm. will settle 8.6 cm. in 24 hours; therefore any particle that has not settled this depth in 24 hours is considered to be a clay and in agricultural dialect, "colloidal." The clay fraction was coagulated by addition of calcium chloride, and the coagulated colloids then concentrated by supercentrifuging. The colloids were then divided into groups and each group saturated with one of the chlorides of K, Na, Ca, Mg, and with hydrochloric acid, followed by centrifuging to separate the colloid from the rest of the saturating solution. The colloids were then washed with equal volumes of water until practically free of chlorides (this was to remove excess salt).

On samples of each type of clay, base-exchange capacity and total exchangeable bases were determined before any heating.

In each of four ovens at 25°, 50°, 75°, and 100° C, respectively, samples of the different clays were placed and heated for 5, 12, and 46 days; and on each sample base-exchange and total exchangeable bases were determined.

Potassium clay. Potassium was determined by precipitation and weighing as potassium-sodium-cobalti-nitrite according to the method of Addie and Wood (1) as used by Van Rysselberge. (18)

Sodium clay. Sodium was determined by precipitation and weighing as the triple salt sodium-uranyl-magnesium-acetate as recommended by Piper. (13)

Calcium clay. Calcium was determined by precipitation as calcium oxalate in an alkaline solution, washing the precipitate free of any excess ammonium oxalate; dissolving the precipitate in hot concentrated sulfuric acid, and titrating the oxalic acid formed with standard potassium permanganate.

Magnesium clay. Magnesium was determined by precipitation as magnesium ammonium phosphate, ignited, and weighed as magnesium pyrophosphate. (2, 8)

Hydrogen clay. Acid hydrogen was determined by direct titration with standard sodium hydroxide using methyl red as an indicator.

The base exchange capacity was determined by adding fifty milliliters of a neutral solution of ammonium acetate, as recommended by Schollenberger and Dreibelbis (16), to the sample; the contents were well stirred, and the replacing reaction allowed to proceed overnight (it is generally accepted that the exchange reaction takes place quantitatively within the first five minutes). In the case of the hydrogen clay the solution used for replacing the absorbed ions was normal-neutral barium acetate. (20)

In every case the total exchangeable bases were determined by boiling with concentrated sodium hydroxide in a Kjeldahl apparatus, absorbing the evolved ammonia in boric acid solution, and titrating directly with standard sulfuric acid using methyl red as indicator.

RESULTS

In the potassium clay the amount of replaceable potassium was found to decrease from 40.8 milliequivalents (me.) at 0 days to 31.93 me. after 46 days heating at 25° C. For any one temperature there was a decrease in the amount of replaceable potassium upon prolongation of the time of heating.

The temperature also showed a marked effect, decreasing the amount of replaceable potassium. For clays heated during the same length of time, the one heated at the highest temperature (100° C.) showed the smallest amount of replaceable potassium, that is, the largest decrease. For instance, with the clays treated for 46 days, the amount of replaceable K was 31.93 me. for the clay heated at 25° C., and only 26.9 me. for the 100° C. clay. (See table 1.)

TABLE 1. MILLIEQUIVALENTS OF K/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	40.80	34.51	32.76	31.93
50°C	40.80	32.81	31.95	31.10
75°C	40.80	32.29	30.54	29.48
100°C	40.80	30.67	29.16	26.90

The total replaceable bases on the other hand, showed a marked increase upon prolonged heating. Thus the samples heated at 25° C. increased from 96.53 me. at 25°C. to 88.23 me. at 100° C. (See table 2.)

TABLE 2. MILLIEQUIVALENTS OF BASES/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	78.37	87.45	94.98	96.53
50°C	78.37	85.17	88.33	95.60
75°C	78.37	80.45	87.45	90.83
100°C	78.37	78.42	86.78	88.23

Note: The samples of the K clays were all of the same weight—1.8939 g. when dry.

In the sodium clay there was an increase in the amount of exchangeable sodium present both upon prolonged and intense heating. For example, the samples heated at 25° C. showed an increase from 30.86 me. at 0 days to 40.04 me. after 46 days of heating. For the samples heated at the same temperature but for different lengths of time: the samples heated for 46 days gave 40.04 me. at 25° C. and 41.37 at 100° C. (See table 3.)

TABLE 3. MILLIEQUIVALENTS OF Na/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	30.86	34.53	36.08	40.04
50°C	30.86	36.22	39.31	41.40
75°C	30.86	33.90	38.46	41.13
100°C	30.86	34.87	40.31	41.37

The total exchangeable bases in the case of the sodium saturated clay showed a regular decrease in the amount of replaceable bases both upon prolonged heating and upon increasing the temperature; thus for the clays heated at 25° C., the one at 0 days gave a value of 92.63 me. while that heated for 46 days only gave 59.20 me. of replaceable bases. For the samples treated for the same length of time, those heated at 25° C. gave 59.20 me. and those at 100° C. gave 47.84 me. when both had been heated for 46 days. (See table 4.)

TABLE 4. MILLIEQUIVALENTS OF BASES/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	92.63	80.79	66.50	59.20
50°C	92.63	89.42	74.00	62.90
75°C	92.63	78.22	57.54	50.86
100°C	92.63	75.85	56.12	47.84

Note: The samples of the Na clays were all of the same weight—1.5887 g. when dry.

The calcium clay showed a decrease in the amount of replaceable calcium upon prolonged heating at the same temperature; thus the samples heated at 25° C. decreased from 41.11 me. at 0 days to 28.12 me. after 46 days heating. (See table 5.)

TABLE 5. MILLIEQUIVALENTS OF Ca/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	41.11	32.08	31.66	28.12
50°C	41.11	41.01	40.28	37.47
75°C	41.11	31.72	26.32	26.32
100°C	41.11	32.21	31.50	30.34

The total exchangeable bases showed a slight decrease upon prolonged heating at the same temperature; thus at 25° C. the samples had 78.95 me. at 0 days and only 55.73 me. after 46 days of heating. (See table 6.)

TABLE 6. MILLIEQUIVALENTS OF BASES/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	78.95	61.59	60.85	55.73
50°C	78.95	71.44	67.44	66.64
75°C	78.95	62.39	57.89	57.77
100°C	78.95	63.00	62.20	61.59

Note: The samples of the calcium clays were all of the same weight—1.5960 g. when dry.

In the case of the magnesium clays it was found that the amount of replaceable magnesium increased upon prolonged heating at any one temperature. Thus the clays heated at 25° C. increased from 34.80 me. of replaceable magnesium at 0 days to 43.58 me. after 46 days of heating.

An increase in temperature had no appreciable effect upon the amount of replaceable magnesium: Thus after 46 days heating the 25° C. clay showed 43.58 me. of replaceable Mg. whereas the 100° C. sample gave a value of 42.04 me. (See table 7.)

TABLE 7. MILLIEQUIVALENTS OF Mg/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	34.80	38.56	40.88	43.58
50°C	34.80	39.58	41.52	44.63
75°C	34.80	39.18	36.22	41.14
100°C	34.80	37.38	41.39	42.04

The total exchangeable bases showed a large increase with prolonged heating. Thus at 25° C. the 0 days sample had 50.96 me. and while the 46 days sample had 63.85 me. An increase in temperature also brought an increase in the amount of replaceable bases; thus after 46 days of heating the sample at 25° C. gave a value of 63.86 me. while the sample at 100° C. showed 89.92 me. of replaceable bases (See table 8.)

TABLE 8. MILLIEQUIVALENTS OF BASES/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	50.98	53.10	63.01	63.86
50°C	50.98	54.87	66.55	68.68
75°C	50.98	72.92	80.71	85.31
100°C	50.98	81.77	84.61	89.92

Note: The samples in the magnesium clays were all of the same weight—1.3886 g. when dry.

In the acid hydrogen clays the amount of replaceable hydrogen decreased upon prolonged heating. Thus the samples treated at 25° C. showed 28.45 me. of replaceable hydrogen at 0 days and only 7.17 me. after 46 days heating. (See table 9.)

TABLE 9. MILLIEQUIVALENTS OF H/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	28.45	20.52	10.93	7.17
50°C	28.45	15.64	9.08	7.01
75°C	28.45	16.41	14.91	8.27
100°C	28.45	15.01	13.49	6.90

The total exchangeable bases showed an increase upon prolonged heating. Thus the samples heated at 25° C. increased from 42.06 me. of replaceable bases at 0 days to 101.44 me. after 46 days of heating. (See table 10.)

TABLE 10. MILLIEQUIVALENTS OF BASES/100 G. OF CLAY

Tempt.	0 Days	5 Days	12 Days	46 Days
25°C	42.06	62.68	76.70	101.44
50°C	42.06	45.44	51.13	84.94
75°C	42.06	48.00	52.78	87.42
100°C	42.06	45.77	52.78	69.44

Note: The samples in the H clays were all of the same weight -1.1917 g. when dry.

DISCUSSION

In order to understand the changes effected by heat upon the clay complex, it is first necessary to know the nature of the colloids. It was the assumption of earlier workers on soils that the clay was amorphous in character, but recent works point to a crystalline structure. Powell (14) questioned the emulsoid nature of clays on the basis of viscosity determinations. Ross (15), using X-rays observed that clays have a crystalline nature; and his work was corroborated by that of Hendricks and Fry (4). Marshall (10) brought forward further evidence supporting the crystalline nature of clays (from a study of their refractive properties) and concluded that exchange cations are present in the interior of the crystal as well as on the surface.

These minerals exhibit a platy crystalline structure analogous to mica, and it may be maintained that this structure, involving large surface development and large contact areas between particles is sufficient to explain the properties of the clay. Besides the presence of cations on the inner and outer surfaces of the crystals, it has been shown by Kelley, Dore and Brown (7) that there are inner, non-exchangeable cations present within the lattice of the crystalline plates, which can be set free under conditions that would cause the rupture of the crystals, such as intensive grinding. Hoffman, Endell, and Wilm (5) have shown that the distance between the crystalline plates of a clay colloid varies with moisture content.

It is natural that as we heat the clay, the crystalline plates move closer together due to a loss of water. It appears that when these plates move closer together they trap some of the exchangeable cations that were present between the plates thus rendering them non-replaceable. This was the case with the calcium and potassium clays (and H clays), which showed a decided decrease in their amounts of replaceable cations present upon prolonged heating.

There may be, however, another effect produced by the heating; the plates may move closer together due to the loss of water, but if the heating were too intense, or if the crystalline structure were somewhat unstable (due perhaps to the very nature of the absorbed cations) then the atomic vibrations within the crystal lattice increase to a point where the whole structure collapses. At this moment the cations that were originally inside the crystalline lattice, and which were non-replaceable, now are set free and become replaceable; and thus the apparent total amount of the particular cations determined is found to increase considerably. This was the case with the sodium and magnesium clays where a marked increase in the amount of the exchangeable cation was found after prolonged thermal treatment.

Ions with small ionic radius (11) (sodium 0.95Å, and magnesium 0.65Å) tend to become more available upon heating. That is, they cause instability and rupture of the crystalline structure. Ions with larger ionic radii (calcium 0.99Å, and potassium 1.33Å) are rendered unavailable by heat. The hydrogen ion does not obey this rule, but then hydrogen never behaves normally considering its small radius.

SUMMARY

The purpose of this work was to obtain data that would throw light upon the nature of the changes brought about by heat on the base exchange capacity of soils.

The clay fraction of a Crowley silt loam soil was obtained, divided into five equal portions, and each of these portions was saturated with the chlorides of potassium, sodium, calcium, magnesium and hydrogen (HCl), respectively. Each of the so saturated portions was subdivided into smaller fractions which were heated at 25°, 50°, 75°, and 100° C. for 0, 5, 12, and 46 days respectively. The amount of the particular replaceable base with which the clay had been saturated and the total exchangeable bases were determined after each thermal treatment.

It was found that the amounts of replaceable potassium, calcium, and acid hydrogen decreased with prolonged treatment, whereas that of sodium and magnesium increased.

The amount of total exchangeable bases showed an increase in the potassium and acid hydrogen clays, and a decrease in the sodium, calcium, and magnesium clays upon prolonged thermal treatment.

The reasons for these markedly different behaviours of clays saturated with different cations are not well understood at present. An interpretation based on ionic radii is proposed.

ACKNOWLEDGMENT

The author wishes to express his deep appreciation to Dr. E. A. Fieger for his wholehearted supervision of this work.

LITERATURE CITED

1. **Addie and Wood.** J. Chem. Soc., **77:** 1076. 1900.
2. **Anonymous.** Association of Official Agricultural Chemists "Official and Tentative Methods of Analysis," Fourth Ed. 1935.
3. **Coles, H. G. and Morrison, C. G.** "Dehydration and Soil Acidity." Soil Sci. **29:** 59-70. 1930.
4. **Hendricks, S. B. and Fry, W. H.** "The Results of X Ray and Mineralogical Examination of Soil Colloids." Soil Sci. **29:** 457-76. 1930.
5. **Hoffman, U. K. Endell and Wilm, D.** Angewandte Chemie, **47:** 539. 1934—from Robinson's "Soils, Their Origin, Constitution and Classification."
6. **Kelley, W. P. and Brown, S. M.** "Replaceable Bases in Soils." Univ. of Cal.—Agric. Exp. Sta. of College of Agric. Tech. Bull 15. 1924.
7. **Kelley, W. P., Dore, W. H. and Brown, S.M.** "The Nature of the Base-Exchange Material of Bentonite Soils and Zeolites as Revealed by Chemical Investigation and X Ray Analysis." Soil Sci. **31:** 25-26. 1931.
8. **Kolthoff, I. M. and Sandell, E. B.** "Quantitative Inorganic Analysis." Macmillan, New York. 1936.
9. **Magistad, O. C.** "The Use of Artificial Zeolites in Studying Base-Exchange Phenomenon." J. Am. Soc. Agron. **21:** 1045-56. 1929.
10. **Marshall, C. E.** "The Orientation of Anisotropic Particles in an Electric Field." Part I—General. Part II—Application to the Determination of the Double Refraction of Clays. Trans. Faraday Soc. **26:** 173-89. 1930.
11. **Pauling, L.** "The Nature of the Chemical Bond." Cornell University Press. Ithaca, N. Y. 1940.
12. **Perkins, A. T. and King, H. H.** "Relation of pH Drift to Moisture Content and Base Held in Soil." Soil Sci. **32:** 409-16. 1931.
13. **Piper, C. S.** "The Determination of Sodium by Precipitation as the Triple Salt Sodium Uranyl Magnesium-Acetate." J. Agri. Sci. **22:** 676-87. 1932.
14. **Powell, E. B.** "Soil Colloids as Simple Suspensions." Soil Sci. **19:** 407-9. 1925.
15. **Ross, C. S.** "The Mineralogy of Clays." Proc. 1st Int. Congr. Soil Sci. **4:** 555-61. 1928.
16. **Schollenberger, C. J. and Dreibelbis, F. R.** "Analytical Methods in Base-Exchange Investigations on Soils." Soil Sci. **30:** 161-73. 1930.
17. **Steenkamp, J. L.** "Soil Dehydration and Colloid Content." Soil. Sci. **25:** 163-239-327. 1928.
18. **Van Rysselberge, P. J.** "Quantitative Determination of Potassium by Sodium Cobaltinitrite Method." Ind. Engin. Chem. (Annual Ed.) **3:** 3-4. 1931.
19. **Wiegner, G.** "Some Physico-Chemical Properties of Clays. I Base-Exchange Capacity, or Ionic Exchange." J. Soc. Chem. Ind. Feb. **1931:** 65-71, J. 1931.
20. **Wright, C. H.** ."Soil Analysis." Thomas Murby and Co., London. 1934.

SUMARIO

El efecto del factor temperatura y del factor calor sobre la capacidad de los suelos para sufrir intercambio de iones (base-exchange) fué estudiado con muestras de coloides arcillosos (clay colloids) que estaban saturados con una de cada una de las siguientes bases: sodio, potasio, calcio, magnesio, e hidrógeno (ácido).

Cada una de las muestras así saturadas fué sometida a un tratamiento termal que variaba, para las distintas muestras, tanto en longitud de tiempo como en intensidad de calor (temperatura). Antes y después del tratamiento termal se determinó en cada muestra su capacidad para intercambiar el catión característico con el cual el coloide estaba saturado, así como también la capacidad total del coloide para intercambiar bases (total base-exchange capacity).

Los resultados fueron, brevemente, los siguientes:

Sodio—aumentó la cantidad intercambiable de sodio.
Calcio—aumentó la cantidad intercambiable de calcio.
Potasio—disminuyó la cantidad intercambiable de potasio.
Magnesio—disminuyó la cantidad intercambiable de magnesio.
Hidrógeno—aumentó la cantidad intercambiable de hidrógeno.

Este modo de comportarse no ha sido explicado claramente hasta la fecha. El autor hace notar, sin embargo, la relación que parece existir entre el radio iónico de las bases y su modo de comportarse hacia el calor:

Coloides saturados con metales de radio iónico relativamente grande (Na, Ca) demuestran un aumento en la cantidad de base intercambiable despúes de ser calentados. Aquellos coloides saturados con metales de radio iónico relativamente pequeño (K, Mg) sufren una disminución en la cantidad de base intercambiable al ser calentados.