

ELECTRODIALYSIS OF THE COLLOIDAL SOIL MATERIAL AND THE EXCHANGEABLE BASES¹

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INTRODUCTION

Recent investigations in the Bureau of Soils have shown that the colloidal material present in any soil contains 10 or more elements in widely varying proportions (19).² Various attempts to fractionate the material into substances of more definite composition have not met with much success. However, dialysis of the material indicated that one colloid held about 1 per cent of its constituents less firmly than the remainder. Long-continued treatment apparently removed all the lime, soda, and sulphur but only a small part of the magnesia, potash, and other elements.

It was thought that further evidence concerning the firmness with which the different constituents are held in the colloid might be obtained by electro-dialyzing the material. Electro-dialysis is similar to ordinary dialysis, but is much more rapid and effects a separation of the diffusible ions of opposite charge.

The mass of data that has been accumulated on base exchange in soils indicates that the colloidal soil material must contain a fairly definite part of its bases in a reactive condition. It was therefore important to compare the bases that can be removed by electro-dialysis with the quantity removable by base exchange with a salt solution.

PREVIOUS WORK

While electro-dialysis has been used in other fields of investigation, only a few attempts appear to have been made to apply it to the study of soils. Cameron and Bell (4) studied the results of continuously removing the products of hydrolysis from powdered hornblende, apatite, etc., by the use of the electric current. Gradually decreasing, small amounts of monovalent and divalent bases were thus removed. It is therefore evident that the minerals of a soil would be attacked to a slight extent by this treatment.

König, Hasenbäumer, and Hassler (15) and later König, Hasenbäumer, and Kuppe (16) studied the amount of material removable from different soils by the electric current and found that there was some correspondence between the material removed by electro-dialysis and that removed by steam and hydrogen peroxide.

The study of base exchange in soils, which dates back to Way (20), has lately received new impetus through the work of Gedroiz (8) in

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² Reference is made by number (italic) to "Literature cited," p. 566.

Russia, Kappen (17) in Germany, Hissink (13) in Holland, and Kelley and Brown (14) in this country. The following facts established in numerous investigations bear on the subject dealt with in this paper. It has repeatedly been shown that in place of the bases removed from a soil by treating it with a neutral salt solution an approximately equivalent quantity of the cation of the salt is adsorbed. As to the quantity of exchange, it has been shown that while this varies in any single treatment with the concentration and volume of the solution and with the kind of cation, approximately the same end point is reached when different salts and concentrations are used, provided the soil is treated a sufficient number of times. This indicates that a given soil contains a fairly definite quantity of bases present in a particularly reactive condition.

These facts were established for the whole soil, but it was generally believed that the reactive bases were present in the colloidal material and this is now known to be so. A recent study (1) shows that the adsorbing power of a soil for various substances is practically all due to the colloidal fraction, and recent work of Kelley and Brown (14) indicates that this is also true in the case of exchange adsorption with inorganic salts.

Since practically all the investigations of base exchange were conducted on whole soils in which neither the quantity nor composition of the colloid was known, no data are available to show what part of the total bases in the colloid are exchangeable.

METHODS

For the following work colloidal fractions of the Sharkey clay soil and the Norfolk fine sandy loam,³ prepared by the supercentrifuge method as explained in a previous publication (10, p. 16), were selected. These two colloids in chemical composition and colloidal properties are representative of the wide differences that have been encountered in the examination of a large number of soil colloids

(19). The Sharkey colloid is gray in color, has a high $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$

ratio, a high content of monovalent and divalent bases, a high adsorptive capacity for ammonia gas and basic dyes, and is strongly electronegative as measured by the amount of methylene blue required to render a given quantity of the clay isoelectric. The Norfolk colloid is yellow, has a low $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$ ratio, a low content of monovalent and divalent bases, a low adsorptive capacity, and is weakly electronegative.

Table 1 gives the composition of these two soil colloids essentially as determined by the fusion method of the Association of Official Agricultural Chemists (3). Carbonates were absent in both samples, and easily soluble salts, which were low in the original soils, were further reduced by the large quantities of distilled water used in the separation of the colloidal material.

³ The sample of Sharkey clay soil was taken to a depth of 4 inches, near Valley Park, Issaquena County, Miss. The sample of Norfolk fine sandy loam was taken from 12 to 36 inches, one-fourth mile south of Scottsville, Wayne County, N. C.

TABLE 1.—Analysis of the Sharkey clay and Norfolk fine sandy loam soil colloids

Kind of colloid	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Sharkey.....	52.05	0.51	22.52	8.12	0.035	1.36	2.52	1.89
Norfolk.....	39.25	.82	33.61	11.24	.005	.30	.44	.49

Kind of colloid	Na ₂ O	P ₂ O ₅	SO ₃	Ignition	Total	Organic	Mols. SiO ₂	
							Mols. Al ₂ O ₃ & Fe ₂ O ₃	
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>		
Sharkey.....	0.21	0.64	0.20	9.99	100.05	3.92	3.18	
Norfolk.....	.25	.23	.05	14.04	100.73	1.90	1.63	

The exchangeable bases in the colloid were determined by leaching with normal NH₄Cl, essentially as proposed by Hissink (13) for soils, and also by treating with 0.05 normal HCl, as recently proposed by Gedroiz (9). Briefly, the procedure for extraction with NH₄Cl was as follows: A 10 gm. sample of the colloid was shaken up with an ammonia chloride solution and then leached with 1 liter of hot normal NH₄Cl. The bases were determined in the filtrate. The procedure for extraction with 0.05 normal HCl was similar, except that 5 gm. of colloid were used and 300 c. c. of acid.

The apparatus used for electro-dialysis was a three-chambered cell. The central chamber containing the soil material was separated from the outer electrode chambers by means of parchment paper. The cell was constructed by bolting together three U-shaped pieces of soft plate rubber (B₁, C, B₂) and two sheets of parchment paper between two hard rubber plates (A₁ A₂) as shown in Figure 1. The electrodes (E₁ E₂) were of platinum wire gauze and were large enough to extend to the sides and bottom of the chambers. A lattice of glass rods, not shown in the figure, was placed in each of the electrode chambers to support the parchment and prevent bulging when the central compartment was filled with the soil material. The electrode chambers were provided with outlets (O₁ O₂)⁴ to facilitate the withdrawal of the electro-dialysates.

This form of cell was found to be very satisfactory for the electro-dialysis of soils. The large area of the electrodes and the thinness of the central soil chamber reduced the resistance so that when a

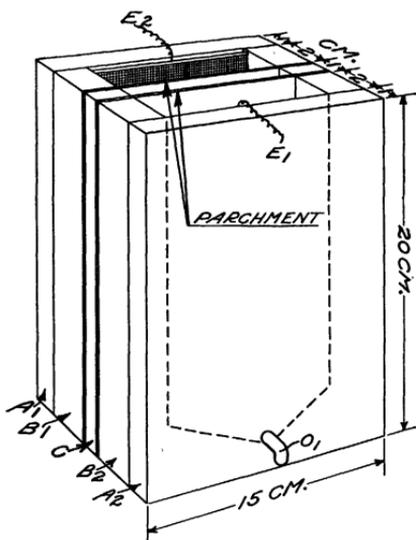


FIG. 1.—Apparatus used for the electro-dialysis of soils and soil colloids

⁴ Outlet O₂ is on the side opposite to O₁ but is not shown in the figure.

220-volt direct current was applied to the cell with a 50 to 25 watt lamp in series the temperature did not rise above 50° C. With a central chamber of the dimensions given in Figure 1, approximately 100 gm. of soil or 60 gm. of the colloid could be electrodialed at one time.

The parchment paper always contains impurities, especially sulphates. These were removed by filling all the chambers with water and allowing the current to flow for some time with a few changes of water.

The removal of anions is somewhat retarded by the electronegative charge of the soil and parchment membrane. The water at the interfaces being correspondingly electropositive, there is an osmotic movement of the liquid toward the cathode which impedes the migration of the anions. The use of an electropositive chrome-gelatin membrane on the anode side has been recommended by Freundlich (?) to nullify this one-sided electromose. There does not seem to be any necessity for using such a membrane when soil materials, which contain a considerable excess of diffusible cations over anions, are subjected to prolonged treatment. It was found that the same proportions of bases and acids were removed from a soil whether the anode membrane was positive or negative. Furthermore, on electrodialed a dilute solution of K_2SO_4 it was found that the retardation of the anions is only temporary and does not prevent a quantitative separation. The alkalinity of the cathode solution was considerably higher than the acidity of the anode solution at the end of the first half hour; but after another half hour, when the electrodialed was completed, a quantitative relationship obtained.

PRELIMINARY EXPERIMENTS ON ELECTRODIALYSIS

Before making quantitative determinations on the colloidal soil material, preliminary tests were conducted with two untreated soils in order to gain an idea of the approximate time required for the electrodialed to reach an end point. The two soils tested were the Sharkey clay, which is high in monovalent and divalent bases, and the Manor loam, which is comparatively poor in these bases.

The rate at which material was removed was determined by withdrawing the electrodialeds from the cathode and anode chambers hourly and titrating the bases and acids with phenolphthalein as an indicator. A 78.35 gm. sample of the Sharkey soil and a 98.85 gm. sample of the Manor soil were electrodialed. The specific conductivity in reciprocal ohms of the Sharkey soil in the pasty condition at 25° C. was 1287×10^{-6} before and 286×10^{-6} after electrodialed, while the conductivity of the Manor soil under the same conditions was only 152×10^{-6} before and 24×10^{-6} after the treatment.

Table 2 shows the milliequivalents of titrable bases and acid removed hourly from the two soils.

TABLE 2.—*Bases and acids removed hourly by electrodialysis of two soils*

Time of electro- dialysis	Sharkey clay soil			Manor loam soil		
	Base	Acid	Appearance of cathode dialysate	Base	Acid	Appearance of cathode dialysate
<i>Hours</i>	<i>Milli- equivalents</i>	<i>Milli- equivalents</i>		<i>Milli- equivalents</i>	<i>Milli- equivalents</i>	
1.....	2. 655	0. 860	Clear.....	1. 810	0. 152	Clear.
2.....	2. 340	. 255	do.....	1. 180	. 062	Light-colored sedi- ment.
3.....			do.....			
4.....	2. 282	. 205	do.....	. 410	. 050	
5.....	2. 260	. 175	do.....	. 110	. 042	Do.
6.....	• 2. 710	• . 320	do.....	. 043	. 040	Reddish sediment.
7.....	2. 060	. 090	do.....			
8.....	2. 015	. 090	do.....			
9.....	1. 995	. 090	do.....			
10.....	1. 900	. 085	do.....			
11.....	1. 810	. 085	do.....			
12.....	• 1. 615	• . 085	do.....			
13.....	• 1. 830	• . 250	Light-colored sedi- ment.			
14.....	. 815	. 075	do.....			
15.....	. 550	. 070	do.....			
16.....	. 420	. 065	do.....			
17.....	. 360	. 070	do.....			
18.....	. 300	. 065	Reddish sediment.			
19.....	• . 260	• . 070	do.....			
20.....	• 1. 410	• . 190	do.....			
21.....	. 140	. 060	do.....			
22.....	. 120	. 060	do.....			
Total.....	. 090	. 060	do.....			
	28. 937	3. 375		3. 553	. 346	

• These relatively high values are the result of standing overnight with no current passing.

It will be noticed that the quantity of titrable, or soluble, base removed hourly from the Sharkey clay soil remains high during the first 12 hours and then falls sharply, but is still determinable at the twenty-second hour. In the case of the Manor loam, a sharp decrease is evident at the end of the second hour. Coincident with the rapid falling off in the quantity of soluble bases, the cathode solution becomes turbid. This turbidity is at first light colored and consists chiefly of $Mg(OH)_2$ and $Al(OH)_3$. Later it becomes brownish due to $Fe(OH)_3$. The appearance of the insoluble bases is evidently governed by the hydrogen-ion concentration in the central chamber containing the soil. The electrodialysis of the Sharkey clay was in one case interrupted at the point where a sediment began to appear, and the P_H , as far as could be determined colorimetrically in the rather turbid soil extract, was found to be 5.4. Owing to the alkaline reaction in the cathode chamber, the cations of insoluble bases must be precipitated as soon as they reach this chamber.

In this experiment no definite end point was apparent in the yield of electrodialyzable material. Subsequent tests showed, however, that when the electrodialysis of the Sharkey soil was prolonged to 42 hours, titrable bases in the hourly extract were less than 0.01 milliequivalent and the yield of insoluble bases had practically vanished. This is a fairly definite end point, although it is approached asymptotically. The soil colloids in the following experiments were therefore electrodialyzed until the hourly cathode extract required less than one drop of N/10 acid for neutralization and contained little or no sediment.

It will be noted that the yield of acids in this experiment was only one-eighth to one-ninth that of the soluble bases. The titrable acid consisted chiefly of H_2SO_4 and H_3PO_4 .

While Table 2 shows the rate at which the combined soluble bases are removed from the whole soil, it does not show the rates at which the individual bases are removed from the colloidal material alone. In order to gain information on this point, a sample of the Sharkey colloidal material was electro dialyzed and three successive fractions of the cathode dialysate were analyzed separately.

The Sharkey colloidal material electro dialyzed was not part of the sample, the analysis of which is given in Table 1, but was isolated from the same lot of soil and was very similar in composition. A sample of 54.6 gm. was electro dialyzed for 42 hours, the cathode solution being removed hourly. The last cathode solution required only 1 drop of N/10 acid for neutralization and was about free from sediment. The cathode solutions removed each hour were combined to form three separate fractions that corresponded to the changes observed in the preliminary experiment. The first fraction, A, amounting to 1,850 c. c., contained the first 12 hourly solutions, all of which were clear. Fraction B, of 930 c. c., included the solutions obtained during the 6 succeeding hours and represented the solutions which contained the light-colored sediment. Fraction C, of 3,060 c. c., collected in the last 24 hours, contained all solutions showing an appreciable quantity of brownish sediment.

Table 3 shows the bases present in each fraction, expressed as percentage of the weight of oven-dry colloid.

TABLE 3.—Successive fractions of bases removed by electro dialysis of the Sharkey soil colloid

Fraction	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	MnO	CaO	MgO	K ₂ O	Na ₂ O
A.....	Per cent Trace.	Per cent Trace.	Per cent None.	Per cent Trace.	Per cent 1.075	Per cent 0.007	Per cent 0.091	Per cent 0.030
B.....	0.008	0.054	None.	0.003	.137	.136	.017	.009
C.....	.091	.109	None.	.016	.058	.245	.022	.007
Total.....	.099	.163	None.	.019	1.270	.388	.130	.046

The first or clear fraction contained most of the lime, potash, and soda removed during the whole period of electro dialysis; only a small quantity of magnesia and traces of the other bases were present. In the second fraction magnesia increased markedly, and alumina, iron, and manganese began to appear in determinable quantities. The last fraction differed from the second in a further increase in the magnesia, iron, alumina, and manganese. The order in which the different bases appear in the cathode chamber is about as follows: Ca, K, and Na; Mg; Al, Mn, and Fe.

This order may not represent the order in which the cations are actually released from the soil colloid particles. The maintenance of Fe, Al, Mn, and Mg in solution and consequently their transport by the current is dependent on the P_H . Under the conditions of the experiment, the P_H in the central chamber is modified by the transport of H and OH ions resulting from the electrolysis of acids and bases in the anode and cathode chambers, respectively. At the beginning

of the experiment the layer in the central chamber adjacent to the cathode parchment is alkaline and the layer adjacent to the anode parchment is acid. Later, as the bases are removed, the reaction becomes acid, throughout the chamber.

PART OF THE BASES IN THE COLLOID REMOVED BY ELECTRODIALYSIS

In order to determine what part of the bases in the soil colloid are removable by the action of the current, samples of the Sharkey and Norfolk soil colloids which had previously been analyzed (Table 1) were electrodedialyzed until the hourly cathode dialysate was nearly clear and neutral.

Table 4 shows the quantity of each base removed by electrodedialysis, as percentage of the sample; the quantity of each base present, as percentage of the sample; and the proportion of each base removed, as percentage of the quantity present.

TABLE 4.—Proportion of each base removed by electrodedialysis ^a

Kind of colloid	Determinations	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O	Na ₂ O	NH ₂
Sharkey	Base removed (as percentage of sample).	Per cent 0.29	Per cent 0.14	Per cent 0.017	Per cent 1.33	Per cent 0.37	Per cent 0.16	Per cent 0.04	Per cent 0.12
	Total base present (as percentage of sample).	22.52	8.12	.035	1.36	2.52	1.89	.21	-----
	Proportion of base removed (as percentage of total base present).	1.29	1.72	48.571	97.79	14.68	8.47	19.05	-----
	Base removed (as percentage of sample).	.20	.03	.002	.16	.05	.06	.01	.18
Norfolk	Total base present (as percentage of sample).	33.51	11.24	.005	.30	.44	.49	.25	-----
	Proportion of base removed (as percentage of total base present).	.60	.27	40.000	53.33	11.36	12.24	4.00	-----

^a Most of the ammonia present was adsorbed by the colloid in the course of its separation from the soil.

It is apparent that the total quantity of bases removable by electrodedialysis may vary greatly with different colloids. In the case of the Sharkey colloid the sum of the bases removed amounts to 2.47 per cent of the sample, while in the case of the Norfolk colloid the yield of bases is only 0.69 per cent, or less than one-third as much.

The percentage of each base present which is removed varies less widely for the two colloids than the total quantity removed. With the possible exception of potash, the proportion of base removed to quantity present is greater in the case of the Sharkey colloid than in the case of the Norfolk. This is true even for iron and aluminum, although the Norfolk contains considerably more of these bases. In general, however, the proportion of calcium, magnesium, or manganese removed by electrodedialysis is not very different for the two colloids, considering the widely different quantities of these constituents in the two materials.

While the proportion of each base removed is not exactly the same for the two colloids, it is evident that the various bases are characterized by different degrees of removability. The proportion of the lime or manganese and the proportion of alumina and iron

removable is still less. These differences in the comparative removability of the bases probably hold for the colloids of most humid soils, since the Sharkey and Norfolk colloids are representative of widely different groups. Colloids from alkali or salt soils, may, however, show a greater proportion of the sodium replaceable.

MATERIAL REMOVED BY ELECTRODIALYSIS COMPARED WITH THAT REMOVED BY BASE EXCHANGE

It is quite apparent from the work of other investigators on base exchange that various salt solutions extract a fairly definite quantity of bases from the colloidal soil material. A comparison of the bases removed by electro dialysis with those removed by methods in use on base exchange was desirable, since both procedures yield a fairly definite quantity of bases.

As the reagents most commonly used at the present time for determining the exchangeable bases in soils are normal NH_4Cl and 0.05 normal HCl , the exchangeable bases in the Sharkey and Norfolk colloid were determined by these solutions, following the standard procedure described on page 554. The colloidal materials used were portions of the lots that were prepared for the work on electro dialysis.

Table 5 shows the quantities of bases and acids removed from the two colloids by the NH_4Cl and HCl solutions compared with the quantities removed by electro dialysis. The quantities are expressed as percentages of the weight of oven-dried colloid.

TABLE 5.—Bases and acids extracted from colloidal soil materials by base exchange reagents and by electro dialysis

Kind of colloid	Treatment of colloid	SiO_2	Fe_2O_3	Al_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3
Sharkey	{Extraction with N/1 NH_4Cl .	Per ct. None.	Per ct. Trace.	Per ct. Trace.	Per ct. 0.016	Per ct. 1.33	Per ct. 0.36	Per ct. 0.13	Per ct. 0.03	Per ct. Trace.	Per ct. (a)
	{Extraction with N/20 HCl .	0.14	0.35	0.80	.019	1.39	.41	.14	.03	0.06	0.04
	{Electro dialysis.....	.05	.14	.29	.017	1.33	.37	.16	.04	.04	.04
Norfolk	{Extraction with N/1 NH_4Cl .	None.	Trace.	Trace.	.002	.15	.04	.07	.02	Trace.	(a)
	{Extraction with N/20 HCl .	0.09	0.05	0.52	.002	.16	.03	.08	.01	0.01	0.04
	{Electro dialysis.....	.02	.03	.20	.002	.16	.05	.06	.01	.01	.04

^a Not determined.

It is apparent that base exchange methods and electro dialysis remove approximately the same quantities of constituents from the soil colloids. The agreement between the methods is very close, except in the case of alumina, iron, and silica. The greater quantities of these constituents removed by HCl and by electro dialysis than by NH_4Cl is probably conditioned by the P_H of the solution in contact with the colloid. The P_H of the total NH_4Cl extract of the Sharkey colloid was 6.2 and that of the Norfolk 6.1; the P_H of the electro dialyzed colloids was about 5.0; while the P_H of the final HCl extract may be assumed to be the same as that of the N/20 HCl solution, about 1.5. Doubtless the NH_4Cl treatment would have removed some Al and Fe from the Norfolk colloid in its natural condition. The Norfolk colloid is naturally acid; but in isolating

this colloid from the soil a small amount of ammonia was used to promote dispersion and this was apparently sufficient to render the colloid nearly neutral.

In view of the practical identity of the material removed by the different procedures, the conclusions regarding the material removed by electro dialysis also apply to the material removed by base exchange. Briefly, the total quantity of bases removed by base exchange from the two colloids varies widely; the part of each base removed is not the same for the two colloids, but it is sufficiently similar to justify the conclusion that in most colloids lime and manganese are removed to a greater extent than magnesia, potash, or soda, and that a still smaller part of the alumina and iron are removable.

The proportion of one base to another in the materials extracted by electro dialysis and by base exchange is also of interest. This is shown in Table 6 for the monovalent and divalent bases. Iron and aluminum were omitted in this calculation, since such different quantities were extracted by the various methods that the inclusion of these bases would have obscured the relationship that obtains between the other bases. Ammonia was determined only in the electro dialysates and is therefore also omitted.

Table 6 gives the total milliequivalents of Ca, Mg, K, Na, and Mn extracted from 1 gm. of colloid by electro dialysis and by base exchange reagents and the proportion of each base in the total. The bases exchanged with methylene blue, which are included in this table, were determined in connection with another investigation and do not represent the maximum quantity that can be displaced by this reagent, since only a small quantity of the dye was used.

TABLE 6.—Proportions between the bases in material removed from the colloids by electro dialysis and by base exchange

Kind of colloid	Treatment	Mn, Ca, Mg, K, and Na extracted per gm. colloid	In 100 milliequivalents were found—				
			Mn	Ca	Mg	K	Na
		<i>M. eq.</i>	<i>M. eq.</i>	<i>M. eq.</i>	<i>M. eq.</i>	<i>M. eq.</i>	<i>M. eq.</i>
Sharkey	Electrodialysis.....	0.712	0.67	66.7	26.0	4.8	1.8
	Displaced by N/1 NH ₄ Cl.....	.698	.66	68.1	25.8	4.1	1.4
	Displaced by n. 0.05 HCl.....	.746	.72	66.5	27.2	4.2	1.3
	Displaced by methylene blue.	^a .486	^b N. D.	65.5	27.6	4.9	2.0
Norfolk	Electrodialysis.....	.099	0.61	57.6	25.2	13.1	3.3
	Displaced by N/1 NH ₄ Cl.....	.096	.62	56.3	20.9	15.6	6.3
	Displaced by n. 0.05 HCl.....	.093	.65	61.2	16.1	18.3	3.3
	Displaced by methylene blue.	^a .061	^b N. D.	58.3	20.5	16.4	4.9

^a Mn not included.

^b Not determined.

It is evident that the proportions between the various monovalent and divalent bases are practically identical in the material removed by the four different methods of extraction within the limits of experimental error.

The proportions between the bases in the Sharkey extract are somewhat different from the proportions in the Norfolk extract. It will be noted, however, that the two colloids differ less widely in the proportions between the bases extracted than in the total quantity

removed or than in the proportions between removable and non-removable bases shown in Table 4.

The proportions between the exchangeable bases in the two colloids are about the same as those reported by other investigators. Apparently these proportions hold approximately for such soils. This is perhaps not surprising, since the river waters of humid regions, such as the Atlantic slopes of North America and western and central Europe, contain about the same equivalent proportions of the monovalent and divalent cations (5, p. 75, 97).

DISPLACEMENT OF HYDROGEN FROM ELECTRODIALYZED COLLOIDS

It has repeatedly been shown that when the exchangeable bases in a soil are displaced by the cations of a salt, an equivalent quantity of the displacing ions are retained by the soil. Since the material removed by electro dialysis was identical with that removed by the neutral salt, except for iron and aluminum, it seemed possible that in electro dialysis there might also be an exchange of cations. Furthermore, the fact that in cataphoresis determinations the electro dialyzed colloid behaved in a manner similar to that of the original colloid, showed that it must contain some adsorbed cations. The only cations available to take the place of the cations removed by electro dialysis would be the hydrogen ions of the water.

If hydrogen were adsorbed by the colloid on electro dialysis, it should appear as acid when the material is treated with a neutral salt solution. The Sharkey colloid was therefore leached with 2 liters of a hot four normal KCl solution and the filtrate titrated with tenth normal NaOH, brom thymol blue being used as an indicator. Five grams of the colloid yielded 3.28 milliequivalents of acid to the first liter and only 0.03 milliequivalent to each of the third and fourth half liters. A normal CaCl₂ solution gave almost identical results. It is thus evident that neutral salts displace a fairly definite quantity of acidity from the electro dialyzed colloid. The quantities of acid displaced from the Sharkey and Norfolk colloids by 1 liter of normal CaCl₂ are given in Table 7, calculated as milliequivalent of hydrogen ion per gram of colloid.

After treatment with the CaCl₂ solution, the two colloids were washed free from chlorides and again electro dialyzed to determine how much Ca had been adsorbed in displacing the hydrogen from the electro dialyzed material. The quantities of Ca removed by the second electro dialysis are also given in Table 7.

It will be seen that in the case of the Sharkey colloid the Ca removed by the second electro dialysis was almost exactly equivalent to the acidity produced by the CaCl₂ treatment, while in the case of the Norfolk colloid, the Ca removed was slightly greater than the acidity. Evidently the electro dialyzed colloid gives the same type of exchange reaction with neutral salts as the untreated soil or colloid, the only difference being that the electro dialyzed material exchanges hydrogen for the cation of the salt instead of a mixture of monovalent and divalent bases or a mixture of these bases and hydrogen. In the case of the electro dialyzed Sharkey colloid, the exchange capacity is shown by either the acidity liberated or by the Ca adsorbed; but in the case of the Norfolk colloid the Ca adsorbed is probably a more

accurate measure of the exchange capacity than the acidity developed. Work in progress indicates that the discrepancy of 0.036 milliequivalent between acidity developed by CaCl_2 treatment and Ca adsorbed is probably due to an adsorption of Cl ions by the electrolyzed Norfolk colloid.

In Table 7 the exchange capacity of the electrolyzed colloids is compared with that of the untreated colloid as measured by the monovalent and divalent cations removed in electrolysis and as determined by the Ca adsorbed from neutral CaCl_2 .⁵

TABLE 7.—Exchange capacities of the Sharkey and Norfolk soil colloids before and after electrolysis

Determination	Milliequivalent per gram of colloid	
	Sharkey	Norfolk
Ca adsorbed from neutral CaCl_2 by the original colloids.....	0.796	0.207
Total monovalent and divalent cations removed by electrolysis.....	.785	.208
Hydrogen displaced from electrolyzed colloids by CaCl_2 solution.....	.640	.164
Ca adsorbed by electrolyzed colloids from the CaCl_2 solution, determined by a second electrolysis.....	.647	.201

It will be seen that the exchange capacities of both colloids are almost the same when measured by Ca adsorbed as when measured by monovalent and divalent bases removed by electrolysis. The exchange capacity of the electrolyzed Norfolk colloid is almost identical with that of the untreated material. The exchange capacity of the electrolyzed Sharkey, however, is about 20 per cent less than that of the original colloid. The results on the whole tend to substantiate the idea that in the process of electrolysis there is an exchange of hydrogen for all, or most, of the bases removed and the adsorbed hydrogen can in turn be replaced by other cations.

In the preceding considerations of the exchange capacity of the electrolyzed colloids, the Fe and Al were not regarded as constituting part of the exchangeable cations, although the CaCl_2 treatment yielded quantities of the trivalent cations in addition to those already removed by electrolysis. The electrolyzed Sharkey yielded 0.458 milliequivalent of combined Al and Fe, 0.353 milliequivalent of which was Al, and the Norfolk colloid gave 0.353 milliequivalent of the trivalent cations, 0.124 milliequivalent being Al. If Fe and Al did exchange with the Ca of the CaCl_2 solution, they would of course be hydrolyzed and produce acidity; so both acid and trivalent bases should not be included in calculating the exchange capacity. Inasmuch as the combined Fe and Al in the CaCl_2 filtrate was sufficient to account for only approximately two-thirds of the acidity, the acid was apparently the fairer measure of the exchange capacity, even if part (or all of it) resulted from exchanged Fe and Al.

On the whole, it appears as though electrolysis may be looked upon as a form of base exchange, in which hydrogen ions are substituted for monovalent and divalent bases. While by the usual methods of base exchange in the soil we continually introduce a high

⁵ The Ca adsorbed after prolonged leaching of the colloid with neutral CaCl_2 solution was determined by subsequent displacement with NH_4Cl .

concentration of the displacing cation and continually withdraw the displaced ions, we arrive in electro dialysis at the same result by the mere withdrawal of the cations, in which case the displacing ion must be the ever-present hydrogen ion of the water. Both methods are in principle the same: A displacement or equilibria either by increasing one factor or by decreasing the other; in one case we apply a push, in the other a pull.

CONDITION OF THE BASES REMOVED BY ELECTRODIALYSIS OR BASE EXCHANGE

It was shown (Table 4) that electro dialysis removed about half the manganese present in the two colloids, most of the calcium, and only a small part of the magnesium, potassium, and sodium. A neutral salt removed almost identical proportions of these bases (Table 5). It is thus apparent that part of each of the monovalent and divalent bases is more reactive than the remainder. This would indicate that each of the monovalent and divalent bases in the colloid is present in two conditions. The condition of the nonreactive part of the bases might be described simply by the facts as nonexchangeable, in the absence of definite information regarding the ultimate chemical constitution of the insoluble part of the soil colloid particle.

The exchangeable bases are usually regarded as being present in the adsorbed condition. From the rapidity of base exchange reaction, Hissink (13) concludes that the exchangeable bases are situated on the surface of the soil particles in the adsorbed condition and ascribes the charge of the particles to a partial dissociation resulting in a Helmholtz double layer. Wiegner (21) identifies the exchangeable cations with the cations of the outer Helmholtz layer. In fact he calculates what size the primary particles in a clay having an exchange capacity of 3.5 milliequivalents per gram would have to be in order to accommodate all the exchangeable cations in the outer layer.

Wiegner arrives at a value of 7.29 $\mu\mu$ for the diameter of the primary particles which would afford the required surface. However, an error occurs in his calculations in that he assumes the surface per gram of clay varies inversely as the square of the radius instead of inversely as the radius.⁶ If this error is corrected, the diameter of the hypothetical primary particles becomes 0.106 $\mu\mu$, or about that of a hydrogen ion. This is obviously absurd.

In a previous publication it was shown that there is an intimate relation between the exchangeable bases and the electrokinetic potential of soil colloids (18). Although the exchangeable cations influenced the charge of the particles, it appeared quite improbable that all the exchangeable cations were present in the outer Helmholtz layer. The fact that on neutralizing the charge of the particles with methylene blue the cataphoretic movement was not markedly reduced until most of the exchangeable cations had been replaced indicated that only a part of the cations were dissociated.

From the formula connecting the charge on a particle with the electrokinetic potential, applied by Von Hevesy (12), Freundlich (6, p. 538), and others to colloidal particles in general and by Wiegner

⁶ The surface presented by 1 gm. of colloid is equal to the surface of one particle, $4\pi r^2$, multiplied by the number of particles per gram $\frac{1}{\frac{4}{3}\pi r^3 \times \text{sp. gr.}}$; hence surface = $\frac{3}{r \times \text{sp. gr.}}$.

to clay particles, the number of electronic charges on a particle of the Sharkey colloid has been calculated, using the values for the electrokinetic potential and the radius of the particles reported in previous publications (2) and assuming a thickness of the double layer of $5 \mu\mu$.⁷ The number of charges in terms of univalent ions or electrons on a particle of the Sharkey colloid was thus found to be 857 ions.

The exchange capacity of the Sharkey colloid at the point of neutrality is about 0.8 of a milliequivalent. This is equal to $4.8 \times 10^{+20}$ ions. Since 1 gm. of the colloid would contain $9.6 \times 10^{+14}$ particles with a radius of $45.5 \mu\mu$, the number of exchangeable cations per particle is 505,208, or about 590 times the number of cations that should, according to the above calculation, be present in the outer, electropositive layer surrounding the particle. If, therefore, the assumed thickness of the double layer and the size of the particle determined by ultramicroscopic count represent the true values, it is evident that only a very small fraction of the exchangeable bases exist in the dissociated condition.

A thickness of the double layer of $5 \mu\mu$ is probably too low rather than too high, since the cataphoretic movement was measured in distilled water, under which conditions Gouy (11) assumes a much greater thickness. But even if a thickness of the double layer of molecular dimensions were assumed, the charge on the particles would not nearly account for all the exchangeable bases.

It is of course probable that the ultramicroscopic particles of the colloid consist of aggregates of smaller, so-called primary particles. However, the primary particles would have to be $0.077 \mu\mu$ in radius to afford sufficient surface for 0.8 milliequivalent of ions, if the number of ions per unit surface is assumed to be the same as was calculated for the particle with $45 \mu\mu$ radius. This value is absurd. Hence, if the theoretical deductions involved in the formulas connecting electrical migration with electrokinetic potential and charge of the particles are correct, it would appear that only a part of the exchangeable bases are present in the dissociated condition.

SUMMARY

Two soil colloids, which are representative of widely different groups of colloidal soil materials, were electrodialyzed in order to determine what part of the bases can be removed by this process. The quantities of bases removed by electrodialysis were compared with the quantities removed by methods commonly used for determining the exchangeable bases in soils.

Preliminary work showed that the quantity of bases that can be removed by electrodialysis is fairly definite and that the order in which the different bases appear in the cathode chamber is about as follows: Ca, K, and Na; Mg; Al, Mn, and Fe. It is pointed out, however, that this may not represent the order in which the cations

⁷ The charge, e , on a colloidal particle = $\frac{\zeta D r (r + \delta)}{\delta}$, where ζ is the electrokinetic potential, D the dielectric constant of the dispersion medium, r the radius of the particle and δ the thickness of the double layer. In the case of the Sharkey colloid, $\zeta = 33$ millivolts or $\frac{.033}{300} = 1.1 \times 10^{-4}$ electrostatic unit, and $r = 4.55 \times 10^{-6}$ cm. D is taken as = 81 for water and δ is assumed to be $5 \mu\mu$, or 5×10^{-7} cm., the value generally assumed. The charge for the Sharkey particle becomes 4.09×10^{-7} electrostatic unit. Since one ion has 4.77×10^{-10} electrostatic unit, the charge on the Sharkey particle would be that of 857 ions.

are released from the colloid particles, since the appearance of the bases in the cathode chamber is largely affected by the hydrogen-ion concentration in the compartment containing the colloid.

The total quantity of bases that electro dialysis removed from one colloid was about five times that removed from the other. While the percentages of the Ca or Na in the colloid that are removable do not agree closely in the case of the two colloids, it is evident that the various bases are characterized by different degrees of removability. The proportion of the total lime or manganese removable by electro dialysis is much greater than the proportion of magnesium, potassium, or sodium, and the proportion of the total aluminum or iron removable is still less.

Extraction of the two colloids with normal NH_4Cl or $\frac{\text{N}}{20}\text{HCl}$ yields quantities of the monovalent and divalent bases that are almost identical with those obtained by electro dialysis.

Treatment of the electro dialyzed colloids with a CaCl_2 solution develops quantities of acidity that approximate the base exchange capacities of the untreated colloids. It appears that in the process of electro dialysis there is a substitution of hydrogen ions from the water for most of the monovalent and divalent cations removed by the electric current.

It is evident that each of the monovalent and divalent bases in the colloid is present in two conditions which might be defined simply as exchangeable and nonexchangeable.

The quantity of the exchangeable bases that can exist as cations in an outer Helmholtz layer surrounding the particle is considered. It is pointed out that if the deductions involved in formulas connecting electrical migration with electrokinetic potential and charge of the particles are correct, only a part of the exchangeable bases in the colloid are present in the dissociated condition.

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