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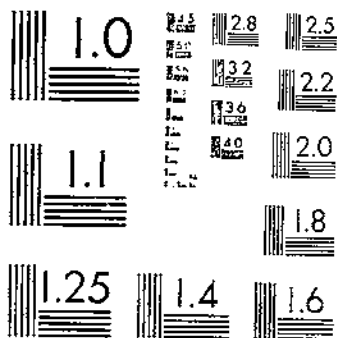
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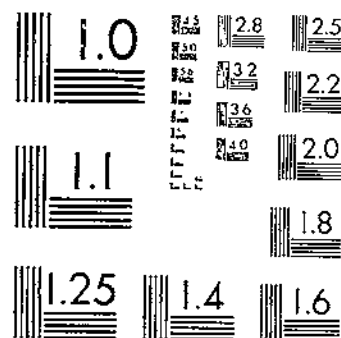
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UNITED STATES DEPARTMENT OF AGRICULTURE

WASHINGTON, D. C.

BASE EXCHANGE AND RELATED PROPERTIES
OF THE COLLOIDS OF SOILS FROM THE
EROSION EXPERIMENT STATIONS¹

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INTRODUCTION

Supplementary to the field work being done at the erosion experiment stations of the Department of Agriculture, an intensive study of the physical and chemical properties of the soil profiles has been carried on in the laboratory of soil chemistry and physics. The previous studies (10, 11)² have included the mechanical and chemical analyses of the whole soil and chemical analyses of the colloids derived from each horizon. These publications also include studies of a very considerable number of other properties of these same soils and their colloids. Since these soils include two or more representatives of four of the great soil groups, their study is of considerable interest as an aid in the development of a systematization of soil properties in relation to field characteristics. This bulletin is the result of a study of the action of twentieth-normal hydrochloric acid on the colloids extracted from these soils.

The importance of base absorption as a property of soils was recognized by Way (17) as early as the middle of the last century. Numerous investigations³ since that time have established the major

¹ This is the third report relevant to the properties and characteristics of the erosion-station soils.

² Italic numbers in parentheses refer to Literature Cited, p. 18.

³ A résumé of such investigations is given by Prescott (12). Various methods of making base-exchange determinations are summarized in the following publication: ROHAMSTED EXPERIMENTAL STATION, HARPENDEN. DETERMINATION OF EXCHANGEABLE BASES AND LIME REQUIREMENT. Tech. Commun. 12. 1930. [Mimeographed.]

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facts of base exchange and have resulted in a variety of methods for the determination of the exchangeable bases at the base-exchange capacity of soils.

No one method has yet been produced, however, which is satisfactory for the determination of exchangeable bases for all classes of soils, or for all purposes. This is due in part to the diverse nature of soils. It is also due to the indefiniteness as to what constitutes exchangeable bases. In general discussion, these are assumed to be calcium, magnesium, potassium, and sodium. The exchangeability of aluminum, iron, and manganese is not established (7) but appears to be definitely associated with the acidity of the soil (6, 7, 15). Moreover, the amount of any base that can be removed from the soil as "exchangeable" is governed to some degree by the conditions of removal, such as the length of time of leaching, the pH of the system, and the concentration of the replacing ion. These limitations to more than approximate values, which result from the chemical-physical characteristics of the soil colloid complex, apply also to determinations of base-exchange capacity, exchangeable hydrogen, and degree of saturation.

The methods to be used, therefore, in any study of these properties depend to a great extent on the particular condition to be satisfied throughout the investigation. In the present study, made on the colloids of the erosion station soils (10, 11), the conditions to be met led to the use of 0.05-normal hydrochloric acid as an extraction agent. Gedroiz (4) appears to have been the first to recommend this reagent in extraction studies, but it has been widely used since by other workers. Working with soil colloids, Mattson (9) found that 0.05-normal hydrochloric acid, normal ammonium chloride, and electro dialysis yielded almost identical amounts of exchangeable bases.

When a complete analysis of the extracted material is to be attempted, as was the case in the present investigation, 0.05-normal hydrochloric acid has a decided advantage over ammonium chloride, or any other salt solution, as an extraction agent, because of the ease with which the acid solution lends itself to an analysis of its constituents. It also offers advantages over electro dialysis with regard to the removal of magnesium. Results for this base when electro dialysis is used are apt to be too low, due to the precipitation of the magnesium as the hydroxide while the element passes through the membrane to the cathode chamber (3). Iron and aluminum are similarly precipitated by electro dialysis and appear, moreover, in both cathode and anode chambers. Considerable manipulative difficulty is encountered in any complete analysis of material removed by electro dialysis.

The most serious criticism of the use of hydrochloric acid appears to be its decomposing action on the colloid complex. It must be admitted that acid extractions remove larger amounts of silica and the sesquioxides than do the salt extractions, but the assumption that this is wholly disadvantageous is open to question. From the standpoint of pure science, the relative solubility of the base-exchange complex is as important as base exchange, and certain conclusions may be drawn from the varying amounts of silica and alumina brought into solution by 0.05-normal hydrochloric acid.

As to the applicability of hydrochloric acid to calcareous soils, the work of Williams (18) seems to indicate that with proper technic, hydrochloric, phosphoric, or acetic acids should be equally effective agents for the extraction of exchangeable bases. One-twentieth-normal hydrochloric acid was found to be entirely satisfactory by workers in this laboratory, easily removing the carbonates and the exchangeable calcium. The correction which is then necessary for calcium carbonate leads to unavoidable errors in the relative amounts of exchangeable calcium and magnesium in the case of dolomitic soils but does not affect the total of exchangeable bases when expressed in milliequivalents.

The use of the ammonium ion for the determination of base-exchange capacities has wide acceptance. Chapman and Kelley (2) have determined the ammonia retained by soils when leached with ammonium acetate and subsequently leached with methyl alcohol.

Puri (19) has saturated H soils with ammonia in the vapor phase and removed the excess by standing his samples for several days over concentrated sulphuric acid. Anderson and Byers (1) have made a series of ammonia-absorption determinations by evaporation of the sample to dryness from 0.05-normal ammonium hydroxide, followed by 4 hours of oven drying. This latter method of ammonification was used in the present investigation to saturate the colloid acids that resulted from the 0.05-normal hydrochloric acid extraction. The experimental procedure is given in more detail in the following pages.

OUTLINE OF PROCEDURE

A sample of 15 to 20 g of noncalcareous colloid is placed in a tall beaker and treated with successive portions of 0.05-normal hydrochloric acid, until a total of 1,000 cc of filtrate has been obtained. On the addition of each 100-cc portion of acid to the beaker, the colloid is thoroughly agitated to break up aggregates of colloid. A mechanical stirrer is helpful. The stirrer used has a vertical metal shaft covered by a long rubber policeman. Filtration is accomplished by means of short Pasteur-Chamberland filters inserted in the beakers. The process is hastened by reversing the pressure from time to time on the filter tubes, causing the layer of colloidal material to slip off. An apparatus found to be very convenient for this filtering process has been described by Shaw (16). The combined filtrate is evaporated to dryness with nitric acid to destroy the organic matter present, taken up with 15 cc of water and 15 cc of concentrated hydrochloric acid, and again evaporated to dryness. Analysis is then made by conventional methods.

If the sample contains carbonates it is treated with successive 200-cc portions of 0.05-normal hydrochloric acid until a sufficient quantity of acid has been used to remove the carbonates as chlorides. The extraction is then continued as in the case of the noncalcareous colloids. The total filtrate in this case is 1,000 cc plus the amount obtained in the removal of the carbonates.

After the removal of exchangeable bases by 0.05-normal hydrochloric acid the samples of colloid are washed several times with water and the filtrate is discarded. The colloid is then transferred

retained the maximum amount of 6 milliequivalents per 100 g. A Cecil colloid retained 4.5 milliequivalents per 100 g. The retained chloride may be regarded as "exchangeable" chloride.

Alcohol was accordingly eliminated as a washing material, following the extraction with 0.05-normal hydrochloric acid. Although water appeared to remove retained chlorides more effectively than alcohol, any attempt to use water for washing the acid colloid resulted in such a highly plastic condition as to render filtration very nearly impossible. It was therefore decided that electro dialysis should be used for removal of chloride, as indicated in the outline of the procedure.

Duplicate determinations of the ammonia absorbed indicated that the method of base-exchange determinations as outlined gave duplicate results. These results are reported in table 2. The pH value of the soils, after treatment with ammonium hydroxide, approximated neutrality. Since the base-exchange capacities of these soils is greater than the amount of their exchangeable bases, unsaturation is indicated. Unsaturation is also indicated by the pH value of these soils (table 5).

TABLE 2.—Exchangeable bases and base-exchange capacities of 2 erosion station surface soils, in milliequivalents per 100 g. of soil

Laboratory no.	Soil type	Mn	Ca	Mg	K	Na	Total exchangeable bases ¹	Base-exchange capacities		
								Soil	Organic matter	Organic free soil
6797	Shelby silt loam.....	0.0	8.4	4.7	0.5	0.3	14.1	19.9	351	12.2
6797	do.....	.0	8.5	4.6	.4	.3	13.8	19.5		
6797	do.....	.0	8.6	4.7	.5	.4	14.2	19.6		
6977	Cecil sandy clay loam.....	1.2	1.9	.4	.3	.1	2.7	6.8	342	2.0
6977	do.....	1.1	1.9	.4	.3	.1	2.7	7.0		
6977	do.....	1.8	2.0	.4	.4	.1	2.9	6.9		

¹ Manganese excluded.

SILICA AND SESQUIOXIDES

The results of the experimental work done on the erosion-station colloids are reported in a series of tables to facilitate a discussion of the data. The analyses for the determination of silica, iron, and alumina, and other pertinent data, are reported in table 3. For comparison, there are included in this table the silica-alumina ratios of these colloids, which have been published previously (10, 11). The several profiles are listed in the table in the order of increasing silica-sesquioxide ratio of the surface soil colloids.

TABLE 3.—Silica, iron, and alumina removed by 0.05-normal hydrochloric acid from the colloids, and other related data

NACOGDOCHES FINE SANDY LOAM

Laboratory no.	Depth	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Total	Mols SiO ₂ /Al _{1.7} O ₃		Portion of total silica removed	Portion of total alumina removed
						Extracted material	Whole colloid		
	<i>Inches</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>			<i>Percent</i>	<i>Percent</i>
9475	0-8	0.35	0.02	0.97	1.34	0.01	1.98	1.3	4.0
9470	8-18	.20	.03	.36	.59	.94	1.97	.6	1.3
9477	18-40	.22	.02	.53	.77	.70	1.83	.7	1.9
9478	40-66	.20	.02	.47	.75	.94	2.06	.7	1.5
9479	66-72	.25	.02	.57	.84	.75	1.94	.8	2.2

CECIL SANDY CLAY LOAM

6677	0-6	0.17	0.04	0.79	1.00	0.37	1.65	0.5	2.3
6678	6-32	.19	.03	.40	.62	.81	1.60	.6	1.1
6679	32-60	.18	.04	.34	.56	.90	1.88	.5	1.1

KIRVIN FINE SANDY LOAM

6678	0-12	0.29	0.06	0.88	0.93	0.85	2.75	0.7	2.2
6679	12-24	.25	.06	.38	.70	.72	2.88	.7	1.3
6680	24-51	.20	.06	.20	.55	1.17	2.42	.5	1.0
6681	51-63	.20	.08	.32	.58	1.06	2.48	.5	1.1
6682	63-75	.23	.05	.42	.70	.93	2.47	.6	1.5

MUSKINGUM SILT LOAM

B407	0-7	0.19	0.12	0.53	0.84	0.61	2.80	0.4	2.0
B408	7-13	.29	.09	.42	.80	1.17	2.68	.7	1.5
B409	14-24	.13	.09	.19	.41	1.16	2.43	.3	.6
B410	25-46	.12	.04	.09	.26	2.26	2.49	.3	.3
B411	47-72	.15	.05	.10	.30	2.55	2.54	.3	.3

PALOUSE SILT LOAM

8069	0-20	0.70	0.08	0.82	1.60	1.45	3.23	1.0	3.5
8070	20-33	.78	.17	.94	1.80	1.43	3.31	1.7	4.0
8071	33-62	.88	.14	1.07	2.09	1.40	3.25	1.9	4.4
8072	62-75	.93	.14	1.06	2.13	1.49	3.45	1.9	4.5
8073	75-84	.91	.12	1.01	2.04	1.53	3.50	1.9	4.4

VERNON FINE SANDY LOAM

6718	0-3	0.42	0.03	0.55	1.00	1.30	3.45	1.0	2.6
6719	3-10	.49	.04	.63	1.16	1.32	3.12	1.1	2.6
6720	10-27	.45	.04	.65	1.14	1.18	2.91	1.0	2.5
6721	27-53	.28	.02	.25	.53	1.77	2.88	.6	.9

SHELBY SILT LOAM

6797	0-7	0.70	0.11	1.30	2.20	1.03	3.31	1.7	5.5
6798	8-12	.68	.08	1.06	1.76	1.15	3.30	1.4	4.1
6799	12-20	.72	.08	.97	1.77	1.20	3.28	1.5	3.9
6800	20-24	.76	.09	.82	1.67	1.57	3.36	1.6	3.4
6801	24-48	.78	.08	.84	1.59	2.07	3.57	1.6	2.8
6802	48-60	.79	.08	.69	1.47	2.24	3.54	1.6	2.6
6802B	60-84	.79	.05	.48	1.30	2.92	4.33	1.6	2.4

TABLE 3.—Silica, iron, and alumina removed by 0.05-normal hydrochloric acid from the colloids, and other related data—Continued

Laboratory no.	Depth	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Total	Mols SiO ₂ /Al ₂ O ₃		Portion of total silica removed	Portion of total alumina removed
						Extracted material	Whole colloid		
CLINTON SILT LOAM									
	Inches	Percent	Percent	Percent	Percent			Percent	Percent
10382	0-8	0.40	0.11	0.99	1.50	0.69	3.10	0.9	4.1
10383	8-20	.51	.17	.82	1.50	1.05	3.17	1.1	3.2
10384	20-32	.60	.16	.80	1.56	1.27	3.44	1.3	3.4
10385	32-44	.57	.16	.71	1.43	1.36	3.03	1.2	.8
10386	44-66	.45	.06	.24	.74	3.18	2.72	.9	
MARSHALL SILT LOAM									
8736	0-13	0.99	0.07	0.72	1.78	2.33	3.69	2.1	3.3
8737	13-24	.49	.07	.73	1.29	1.14	3.06	1.0	3.3
8738	24-45	.68	.10	.73	1.41	1.35	3.72	1.2	3.2
8739	45-71	.57	.12	.74	1.43	1.31	3.57	1.2	3.2
HOUSTON BLACK CLAY									
6096	0-3	1.33	0.04	0.87	2.24	2.50	3.90	2.7	4.1
6097	14-20	.80	.04	.88	1.81	1.72	3.92	1.8	4.1
6098	24-36	.84	.04	.89	1.77	1.80	3.91	1.7	4.1
6099	36-50	.99	.05	.94	1.98	1.79	3.97	1.9	4.3
COLBY SILTY CLAY LOAM									
6842	2-10	1.17	(¹)	0.92	2.09	2.16	4.25	2.3	4.5
6843	10-20	.84	(¹)	.72	1.57	1.96	4.18	1.6	3.5
6844	20-33	.90	(¹)	.57	1.47	2.08	4.20	1.7	2.7
6845	33-47	.84	(¹)	.37	1.21	3.86	4.27	1.6	1.7
6846	47-60	.83	(¹)	.40	1.23	3.52	4.38	1.5	1.9
6847	60-72	.89	(¹)	.37	1.26	4.09	4.37	1.6	1.8

¹ Not determined.

As revealed in table 3, the percentage of iron removed by 0.05-normal hydrochloric acid is small, nowhere exceeding 0.17 percent. This is the figure obtained for the colloids of the second horizons of the Palouse and Clinton soils. Reference to the iron oxide-alumina ratios of these colloids previously published, (10, 11) indicates that the increased percentage of soluble iron in these horizons is due to the extent to which iron has been deposited in them by podzolic processes. In the B horizon of a true podzol larger amounts should be dissolved. The low percentage of iron oxide removed from the Houston colloid is probably due to its low iron content. However, the total amount of iron in a colloid bears no general relation to the amounts of iron removed. The Nacogdoches colloids, highest in iron content of them all, showed the smallest percentage of dissolved iron. The Cecil, Kirvin, and Vernon colloids, all from red soils, similarly gave low percentages of dissolved iron. The condition of the iron of the colloid has an important bearing on the ease with which it enters into solution. Because the percentages of iron oxide extracted were so small, no attempt is made to use them to derive other data.

Inspection of the figures for dissolved silica (table 3, columns 3 and 9) does not show any definite trend. Not more than an indication is present of any relationship between the amount of silica dissolved

and the silica-sesquioxide ratio of the colloid. The percentage of total silica extracted, however, is lower on the average for the first 4 profiles given in table 3 than it is for the last 4 profiles. No more exacting comparison than this should be attempted, because of the changes in the amounts of silica dissolved with changing time of extraction (table 4). To comparisons within a profile this criticism does not apply, for the colloids of each profile constituted a single laboratory set and were therefore subject to extraction periods of the same length. Nevertheless, a comparison of the percentages of silica, as obtained for each profile, also fails to reveal any well-marked relationships. In six cases the silica percentage and the percentage of total silica removed is higher at the surface than it is in the horizon immediately below. In five cases the reverse is true. A partial correlation is indicated for silica dissolved and type of cover. Four of the five grassland soils (Palouse, Shelby, Marshall, Houston, and Colby) show relatively more easily removable silica at the surface. All the remaining soils were developed under forest cover. Of this group, the Nacogdoches is the only one to show any significant increase of soluble silica in the surface soil. The work of Robinson, Steinkoenig, and Miller (14) indicates the relatively high silica content of the grasses as compared to other vegetation, and this fact may account for the high silica solubility of grassland soil colloids.

As in the case of the silica determinations, the amounts of alumina extracted are notably less for the first 4 soil profiles represented in table 3 than for the last 4. This again indicates the greater solubility in general of those colloids having a high silica-sesquioxide ratio. Total solubility effects are to be observed for this same grouping of the colloids by a summation of the percentages of silica, iron, and alumina. These data are given in table 3, column 5. It is of interest to note that the maximum solubility occasioned by the use of this procedure appears to be about $2\frac{1}{4}$ percent. Also, colloids from soil layers at or near the surface appear to be more soluble than those from lower depths. To include the Clinton and Vernon soils in this generalization the depth considered has to be extended to about 30 inches. The Palouse soil seems to be an outright exception. The only explanation applicable seems to be that the loess deposit on which this soil is formed originally contained relatively large amounts of "soluble" silica and alumina, and the lower amounts now found at the surface are the result of leaching or some other process which has not yet affected the remainder of the profile. The Marshall soil, also formed on a loess deposit but leached somewhat more than the Palouse, shows the usual increased solubility of the surface colloid.

Figures for the percentage of total alumina extracted indicate a tendency toward greater solubility of the alumina of the surface horizon, but the interpretation to be attached is uncertain. The increase in percentage of total alumina removed from the surface horizon may represent an accumulation of hydrated aluminum hydroxide caused by the decomposition of more complex aluminosilicates. On the other hand, and particularly in the acid soils, it may represent the formation of a humate complex precipitated in the surface soil, analagous to the precipitation of sesquioxides

and organic matter in the B horizon as a part of the process of podzolization (1).

The molecular ratios of the silica and alumina removed from these colloids are reported in table 3, column 7. They appear to follow in a somewhat haphazard manner the order established by the silica-alumina ratios of the colloids from which they are extracted. Further examination of these ratios shows that extraction with 0.05-normal hydrochloric acid removes from the colloid proportionately more alumina; that is to say, the silica-alumina ratio of the extracted material is less than the same ratio of the corresponding colloid. This is so in all but two cases. The excess of alumina may be accounted for as exchange alumina, free alumina (probably hydrated), or by the decomposition of aluminosilicates accompanied by a failure to extract the corresponding amount of silicic acid freed by the same process.

Whatever the source of the excess alumina over silica which has just been discussed, the silica-alumina ratio of the extracted material (which is too low) does not generally approach that of the colloid on continued extraction. The results of the 24- and 48-hour extractions of the Shelby and Cecil soils indicate such an approach, but other pertinent data are available. These data are given in table 4. The 0.05-normal hydrochloric acid extract from several colloids was collected in a first and second portion and so analyzed. From the silica-alumina ratios obtained by this procedure, it is to be seen that in most cases the silica-alumina ratios obtained from the analyses of the second portions of the extracts are lower than the corresponding ratios obtained from the analyses of the first portions.

TABLE 4.—Percentage of silica and alumina extracted in varying periods

Soil or colloid	Laboratory no.	Material analyzed	SiO ₂	Al ₂ O ₃	Mols SiO ₂ Al ₂ O ₃
			<i>Percent</i>	<i>Percent</i>	
Shelby soil.....	6797	Filtrate from 24 hours' extraction.....	0.054	0.172	0.53
	6797	Filtrate from 48 hours' extraction.....	.007	.232	.71
Cecil soil.....	6977	Filtrate from 24 hours' extraction.....	.021	.213	.17
	6977	Filtrate from 48 hours' extraction.....	.036	.274	.22
Shelby colloid.....	6797	First portion of filtrate.....	.50	.09	1.02
	6797	Second portion of filtrate.....	.20	.31	1.09
Shelby colloid.....	6798	First portion of filtrate.....	.52	.73	1.21
	6798	Second portion of filtrate.....	.10	.27	1.01
Shelby colloid.....	6799	First portion of filtrate.....	.56	.69	1.38
	6799	Second portion of filtrate.....	.10	.28	.97
Cecil colloid.....	6977	First portion of filtrate.....	.08	.45	.30
	6977	Second portion of filtrate.....	.00	.34	.46
Cecil colloid.....	6978	First portion of filtrate.....	.11	.23	.81
	6978	Second portion of filtrate.....	.06	.17	.80
Cecil colloid.....	6979	First portion of filtrate.....	.11	.19	.96
	6979	Second portion of filtrate.....	.07	.15	.79
Nacogdoches colloid.....	9475	First portion of filtrate.....	.15	.46	.55
	9475	Second portion of filtrate.....	.20	.51	.52
Nacogdoches colloid.....	9476	First portion of filtrate.....	.11	.18	1.04
	9476	Second portion of filtrate.....	.09	.18	.85
Nacogdoches colloid.....	9477	First portion of filtrate.....	.13	.28	.79
	9477	Second portion of filtrate.....	.09	.25	.81
Colby colloid.....	6842	First portion of filtrate.....	.65	.43	2.57
	6842	Second portion of filtrate.....	.52	.49	1.80
Colby colloid.....	6844	First portion of filtrate.....	.30	.14	4.73
	6844	Second portion of filtrate.....	.51	.43	2.01
Colby colloid.....	6845	First portion of filtrate.....	.32	.09	6.04
	6845	Second portion of filtrate.....	.52	.28	3.16

The same results are evident if first portions are compared with total extracts (tables 3 and 4). Apparently, 0.05-normal hydrochloric acid consistently removes proportionately more alumina than silica over extended periods of extraction. In less acid extractions the order presumably tends to reverse.

MINOR CONSTITUENTS

The data for titanium, phosphorus, and sulphur, as determined by analysis of the acid extracts, are not presented in tabular form but may be discussed briefly. None of the extracts showed measurable amounts of titanium. More than traces of sulphur were found only in extracts from colloids high in carbonate content. In organic colloids Anderson and Byers (1) have shown that calcium oxide aids in the removal of sulphur, as sulphates. Calcium carbonate appears to have a similar effect. Small quantities of phosphate were extracted from all the colloids except those from lateritic soils. The latter colloids are, however, exceptionally high in phosphate content. The colloid of the Vernon surface soil showed a somewhat higher extractable phosphate content than the lower horizons. This may possibly be attributed to the high content of this horizon in organic matter. It contains 8.5 percent of organic matter (10). The largest yields of extracted phosphate were shown by the high silica-sesquioxide ratio colloids, the Colby and Houston. In general, the amounts, as determined, were too small to furnish an accurate basis of comparison. On the basis of general theory, it would appear that the phosphate content of high silica-sesquioxide colloids should be the more soluble. There are two grounds for this assumption: These colloids are more strongly acid and hence less basic than those of lower ratio; also, the phosphates of ferric iron and alumina are notably insoluble. Gile (5) has found that colloids of low ratios have increased depressive effects on the availability of added superphosphates.

EXCHANGEABLE BASES

The exchangeable bases, including manganese, are calculated on a basis of milliequivalents per 100 g and reported in table 5. The quantities in this table are calculated for the colloids free from carbonates. Carbonates are present in the Colby and Houston profiles and the lower horizons of the Shelby profile (10). In all cases the equivalent of the carbon dioxide found is subtracted from the calcium present. This is probably not exact, since, doubtless, a part of the carbon dioxide is associated with magnesium. However, the total base equivalent values are not affected by this uncertainty of distribution. No carbon dioxide could be found in any colloid after extraction. Table 5 also contains determinations of the base-exchange capacity of the colloid, the ammonia-soluble organic matter, and the "organic-free" colloid. A listing is also made of the pH values for the soils from which these colloids were extracted. Certain general relationships are evident, which are of interest because of the wide range of soil types represented and because of the large amount of other data on these same soils.

TABLE 5.—Exchangeable bases and base-exchange capacities of the colloids of the erosion-station soils expressed as milliequivalents per 100 g of carbonate-free colloid

NACOGDOCHES FINE SANDY LOAM											
Laboratory no.	Depth	Mn	Ca	Mg	K	Na	Ex-changeable bases ¹	Base-exchange capacities			Soil acidity
								Colloid	Inor-ganic colloid	Organic matter	
	<i>Inches</i>										<i>pH</i>
9476	0-8	2.0	25.0	4.5	1.3	0.6	31.4	30.3	19.7	-----	5.3
9476	8-18	.1	11.4	4.0	1.1	.3	18.8	19.8	17.3	-----	4.4
9477	18-40	.1	7.1	4.0	1.3	.3	12.7	20.0	17.0	-----	4.0
9478	40-68	.0	5.0	3.0	1.1	.0	9.7	20.0	18.6	-----	5.0
9476	66-72	.6	9.3	3.5	1.1	.0	14.5	19.1	17.3	-----	5.1
GECIL SANDY CLAY LOAM											
6977	0-6	3.0	9.6	1.5	1.1	0.3	12.5	15.5	10.0	342	5.6
6978	6-32	1.6	5.7	2.0	.0	.3	8.6	12.5	10.7	-----	4.0
6979	32-60	.1	2.1	1.0	.8	.3	4.2	11.0	9.7	-----	4.6
KIRVIN FINE SANDY LOAM											
6678	0-12	1.4	21.4	4.0	2.3	1.3	29.0	23.0	18.9	-----	6.2
6679	12-24	.1	12.8	7.0	1.0	1.6	24.2	26.7	23.9	-----	4.5
6680	24-51	.1	10.3	6.9	1.5	1.0	19.7	28.0	25.4	-----	4.2
6681	51-63	.0	7.1	4.5	1.5	1.0	14.1	32.9	31.1	-----	3.8
6682	63-75	.0	4.0	3.5	1.7	1.0	10.8	30.3	26.7	-----	4.0
MUSKINGUM SILT LOAM											
B407	0-7	1.7	13.6	6.5	1.9	1.3	23.3	35.0	30.2	349	4.7
B408	7-13	1.0	15.7	7.9	1.5	1.0	26.1	33.5	31.9	-----	4.8
B409	14-24	.5	7.5	6.0	1.3	1.0	15.8	21.3	26.7	-----	4.8
B410	25-46	.7	9.3	6.5	1.1	1.0	17.9	19.8	18.5	-----	4.8
B411	47-72	.8	12.8	8.4	1.1	1.0	23.3	17.2	17.2	-----	6.4
PALOUSE SILT LOAM											
8060	0-20	1.4	31.0	28.8	2.5	1.0	63.3	56.5	51.0	344	6.7
8070	20-33	.8	32.4	37.2	1.5	1.0	72.1	54.8	55.0	-----	6.0
8071	33-62	1.1	32.8	41.2	1.5	1.3	76.8	54.3	65.2	-----	7.0
8072	62-75	1.1	39.9	38.2	1.6	1.3	80.0	56.8	56.8	-----	7.1
8073	75-84	1.1	40.6	36.7	1.7	1.0	80.0	56.6	55.6	-----	7.3
VERNON FINE SANDY LOAM											
6718	0-3	13.2	37.5	11.9	2.5	1.0	62.9	51.2	32.8	394	7.6
6719	3-10	3.1	26.4	10.4	2.8	1.3	49.9	39.8	34.2	-----	7.0
6720	10-27	1.1	25.3	12.4	2.3	1.3	41.3	41.6	32.6	-----	6.4
6721	27-58	.3	25.0	14.9	1.9	.6	42.4	39.0	36.0	-----	6.7
SHELBY SILT LOAM											
6797	0-7	0.6	38.9	21.9	2.8	1.3	61.9	62.5	49.5	376	5.4
6798	8-12	.4	42.1	23.8	2.1	1.3	60.3	61.4	54.4	-----	5.6
6799	12-20	.5	41.1	25.8	2.5	1.3	70.7	60.6	63.0	-----	7.0
6800	20-24	.6	43.2	30.3	2.5	1.0	77.9	61.0	54.4	-----	8.2
6801	24-48	.8	36.1	44.7	2.6	1.9	85.2	52.0	62.0	-----	8.0
6802	48-60	.8	25.0	47.7	2.3	1.0	76.9	53.3	51.1	-----	8.6
6802B	60-84	.3	23.2	52.1	2.8	1.0	80.0	54.9	53.1	-----	8.7

¹ Manganese excluded.

TABLE 5.—Exchangeable bases and base-exchange capacities of the colloids of the erosion-station soils expressed as milliequivalents per 100 g of carbonate-free colloid—Continued

CLINTON SILT LOAM

Laboratory no.	Depth <i>Inches</i>	Mn	Ca	Mg	K	Na	Ex- change- able bases	Base-exchange capacities			Soil acidity <i>pH</i>
								Colloid	Inor- ganic colloid	Organic matter	
10362	0-8	3.0	30.4	11.4	1.0	2.3	52.0	47.4	42.4	324	5.0
10363	8-20	.9	27.5	13.0	2.1	2.3	45.8	53.5	52.6	-----	5.3
10364	20-32	.8	20.6	17.3	2.1	2.3	51.3	54.5	64.5	-----	5.2
10365	32-44	.8	34.6	20.3	1.0	2.3	59.1	54.5	55.6	-----	5.4
10366	44-56	.1	25.3	12.4	1.7	2.3	41.7	45.0	45.4	-----	5.6

MARSHALL SILT LOAM

8736	0-13	0.8	38.9	17.4	2.5	1.3	60.1	65.1	59.4	333	5.5
8737	13-24	.4	40.0	19.8	2.1	1.0	62.9	65.8	64.7	334	5.0
8738	24-45	.4	38.5	24.8	1.7	1.0	65.0	64.7	65.4	302	5.0
8739	45-71	.4	38.5	24.3	1.7	1.0	65.5	64.4	60.7	-----	5.7

HOUSTON BLACK CLAY

6006	0-3	0.5	103.2	11.4	3.6	2.3	120.5	93.4	86.2	383	8.1
6007	14-20	.5	126.2	8.9	2.3	2.3	142.7	92.3	88.1	386	8.1
6098	24-35	.4	126.8	9.4	2.5	2.0	144.6	84.8	86.4	381	8.2
6009	35-50	.3	123.2	9.4	2.3	1.6	142.5	80.4	81.0	-----	8.2

COLBY SILTY CLAY LOAM

6842	2-10	0.8	73.5	17.4	4.5	3.2	98.6	74.0	58.7	354	8.3
6843	10-20	.7	71.4	14.4	4.3	3.5	93.6	64.0	68.7	362	8.4
6844	20-33	.3	72.1	19.4	4.0	4.2	90.7	64.0	68.0	-----	8.6
6845	33-47	.4	53.1	22.3	4.7	4.5	81.6	64.0	69.4	-----	8.5
6846	47-60	.3	52.1	24.3	4.0	4.2	85.5	61.7	63.0	-----	8.5
6847	60-72	.3	47.5	20.8	5.1	4.5	83.0	64.5	58.0	-----	8.5

Calcium and magnesium constitute the major portion of the exchange bases, to such an extent that the determination of these constituents, only, would result in a very fair estimation of the total exchangeable bases. Tests made on the extracted residues of some of these colloids showed that all the calcium had been removed, but considerable percentages of magnesia and potash remained unextracted. The maximum total of exchangeable potassium and sodium was found in the lowest horizon of the Colby soil and amounted to 9.6 milliequivalents per 100 g. In the second horizon of the Cecil soil they amount to less than 1 milliequivalent per 100 g.

Except in the surface horizons manganese appears in even smaller quantities throughout. A notable amount of manganese is dissolved from the colloid of the Vernon surface soil, evidently from the decomposition of manganese dioxide. If so, it does not represent exchangeable base. Manganese is known to be effective as an exchange base (8), but, because of the likelihood of dissolved manganese dioxide and also because the amounts of manganese are in most cases negligible, this element was excluded from the summation of the exchangeable bases shown in table 5, column 8.

Examination of the data of table 5 reveals the fact that a general parallelism exists between the total exchangeable bases and the base-exchange capacities of the colloids. These quantities are in general proportional to the silica-sesquioxide value of the colloids (10, 11). That is, when the silica-sesquioxide ratio is high, the base exchange and base-exchange capacity are also high. The base values also bear a rough relation to the pH values of the soils. The data show the wide range of these various values which ought to be expected when widely different soil types are compared. The Houston colloid, for example, has approximately tenfold the base content of the Cecil colloid. The relations shown are, however, by no means quantitative. Indeed, a quantitative relation should not be expected, since the leaching processes ought not to be expected to keep step with the independent process of rock decomposition. Variation also is to be expected as a result of variable organic content.

A very interesting relation exists between the pH values of the soils and the relative quantities of the total bases and the base-exchange capacities. In general, the acid soils tend to have a base-exchange capacity in excess of the total base content; in other words, they are unsaturated, but the soils of high pH values have a total base content in excess of the base-exchange capacity as measured by ammonification and drying. This is to be expected when it is considered that the soil bases are all stronger, as bases, than is ammonia and ought to form "saturated" salts of the soil acids with a greater relative base content. It is understood, of course, that even in "saturated" soils the soil acids are not completely neutralized, even at pH values above 7. A few random observations have also been made, which show that, although colloids of low silica-sesquioxide ratio absorb smaller quantities of ammonia than do higher silica-sesquioxide ratio soils, the pH values of the latter are materially lower. Thus, colloids of the Nacogdoches and Cecil profiles, when debased and saturated with ammonia, show an average pH value of 7.3, and the Colby profile gives a corresponding value of 6.6. This is, of course, an evidence of stronger acidity of the more siliceous colloids. This phase of the investigation will be more fully reported in a subsequent publication.

ORGANIC BASE EXCHANGE

Columns 9 and 10 of table 5 show how organic matter increases base-exchange capacity, particularly in the surface soil. It unquestionably plays a large part in the retention of the exchangeable bases at the surface, preventing their rapid removal by leaching waters. In the Nacogdoches and Kirvin soils, for example, the amount of exchangeable bases held by the surface soil colloid far exceeds the base-exchange capacity of the inorganic portion, yet both these soils are developed under fairly high rainfall. In cases such as these it appears probable that the destruction of the soil organic matter should result in an immediate and severe loss of exchangeable bases to the percolating waters.

The Vernon colloid (organic content 8.5 percent) shows the effect of organic matter at its maximum. Organic matter accounts for 18.4 milliequivalents of the recorded base-exchange capacity, or

nearly 36 percent of the total. Similarly, the organic matter accounts for a large percentage of the total base-exchange capacity of the Nacogdoches and Cecil surface soil colloids. In other cases the effect of the organic matter is less well marked, either because the organic-matter content is low, or because of an increased base-exchange capacity of the inorganic colloid.

Except for their organic content, surface soil colloids in general appear to have a slightly lower base-exchange capacity than those of the next lower portion of the profile. Inclusion of the organic matter does not always give the surface soil colloid a superiority in base-exchange capacity. Determination of the ammonia absorbed by the inorganic colloids results in a series of figures which indicate that base-exchange capacity tends to remain constant throughout the profile in the cases examined, but exceptions are frequent enough to prevent any generalization as far as other soil profiles are concerned. The Muskingum profile, as a notable example, shows a consistent decrease in base-exchange capacity with increasing depth. The Muskingum soil is a shallow podzolic soil grading down rapidly into weathered rock at slight depths. The base-exchange capacities of this soil evidently reflect a degree of weathering not indicated by the silica-alumina ratios.

The organic matter extracted from various colloids has a mean base-exchange capacity of 362 milliequivalents per 100 g on an ash-free basis. The importance that should be attached to this figure is somewhat doubtful, because the samples of material available for the determinations were small and in some cases were undoubtedly contaminated by chloride. Traces of chloride not removed by electro dialysis of the colloid were unavoidably concentrated in these small samples of organic matter. However, a check on this mean figure for organic matter was obtained by electro dialyzing samples of Colby and Cecil soil, avoiding the use of hydrochloric acid as an extraction agent. Larger samples of organic matter, free from chlorides, were obtained by extracting these dialyzed soils with ammonia. Base-exchange capacities were then determined on these samples. The results of these determinations were, respectively, 326 and 337 milliequivalents per 100 g. In magnitude, therefore, the mean figure obtained from determinations on the colloid organic matter is essentially correct. Williams (19), in a series of experiments in which the base-exchange capacities of the inorganic colloid were maintained as a constant by excess calcium carbonate, found the following formulas to be applicable:

$$B = 0.57K + 6.3C_0$$

$$B = 0.57K + 4.55C_T$$

The relationship between total exchangeable bases (B), clay (K), and oxidizable carbon (C_0) indicates a base-exchange capacity for oxidizable soil organic matter of 365 milliequivalents per 100 g. This figure is obtained by dividing the constant for oxidizable carbon by the conversion factor 1.724 and multiplying by 100. If it were allowable to assume accuracy of this conversion factor, the comparison between the base-exchange capacity of oxidizable organic matter and ammonia-extracted organic matter would be particularly fine. Unfortunately, the correlation is better than the method by which it is obtained.

The base-exchange capacity of the total organic matter calculated in a similar manner from the constant 4.55, for total carbon (C_T), gives a value of 264 milliequivalents per 100 g. Since it has been shown by Anderson and Byers (1) that the base-exchange capacities of mixtures of organic and inorganic colloids are not simple additive functions and also because of the known inherent inaccuracy of the factor 1.724, it ought not to be expected that the value so reached should represent the true base-exchange capacity of organic matter.

If we calculate the base-exchange capacity of the organic matter of a colloid from the capacities of the organic-bearing and organic-free colloid, the results so obtained are subject to the same criticisms as those mentioned. Nevertheless, these calculations were made for each of the surface soil colloids. The results, not tabulated, show a maximum value for the Nacogdoches organic colloid of 426 milliequivalents per 100 g and a minimum of 145 milliequivalents for the organic matter of the Clinton colloid. The mean value for the 11 surface soil colloids is 245 milliequivalents per 100 g. This mean is a reasonable approach to the value 264 calculated from the Rice Williams formula. It is difficult to account for this double correlation as a matter of coincidence. It is even more difficult to claim general validity for the formulas, especially in view of the varying base-exchange capacities shown for the organic colloids, as a means of calculation of the base-holding capacities of organic matter.

Attempts to calculate base-exchange capacities of colloids from data on the corresponding soils, and vice versa, have never been very satisfactory. Unquestionably, the arguments advanced by Anderson and Byers (1) in discussing the properties of organic colloids in mixtures have a direct bearing on this problem, and need not be repeated here. What seems to be a far more potent disturbing influence, as far as soils and colloids are concerned, is the fact that inorganic and organic colloids are not removed in their normal ratio when an extraction of the colloidal material is made. For illustration, the data reported in this bulletin on the Shelby and Cecil soils may be compared to the corresponding colloid data. The percentages of colloid by water-vapor absorption and the percentages of organic matter involved, are obtained from a former publication (10). The Shelby soil containing organic matter has a base-exchange capacity of 19.7 milliequivalents per 100 g. Its colloid content is 23.1 percent. Assuming the base-exchange capacity of the soil to be wholly due to this percentage of colloid, then by calculation the base-exchange capacity of the colloid should be 85.3 milliequivalents per 100 g. But by actual determination it is only 62.5 milliequivalents per 100 g. On the other hand, the colloid contains 5.96 percent organic matter, which should make the organic matter of the soil equal to 1.37 percent, on the assumption that the organic matter is extracted in the same proportion as is the inorganic colloid. Actual determination shows the organic matter of the soil to be 3.23 percent. Because the soil contains proportionately more organic matter than the colloid, base-exchange capacities on the colloid, figured from the soil data, must be too high, as is shown to be the case.

Confirmation of the reasonableness of this point of view is found in an examination of the data for the "organic-free" materials. On

this basis the Shelby soil has a base-exchange capacity of 12.2 milliequivalents per 100 g. The base-exchange capacity of the inorganic colloid should therefore be 52.8 milliequivalents per 100 g. By actual determination, 49.5 is the correct value. The agreement is sufficiently close to show that when the effect of disproportionate percentages of organic matter is eliminated, base-exchange data on soils can be transposed to base-exchange data on colloids. Similar data and the same conclusions are obtained from an examination of the Cecil colloid-soil data.

SUMMARY AND CONCLUSIONS

The work here reported is a part of a wide investigation of the various horizons of the soils and colloids of the erosion experiment stations. The immediate subject is concerned with the soluble materials produced by treatment of the colloids of the various horizons with twentieth-normal hydrochloric acid and with the base-exchange properties of the residual material and of the soil organic matter.

Analyses of the extracted material show not only the exchangeable ions but all the constituents normally reported for soils and colloids. The quantities of silica, alumina, and iron oxide dissolved by the acid are reported, and their significance is discussed. The quantities of titanium, sulphur, and phosphorus are not reported, but their relationships are discussed.

It is shown that silica, alumina, and iron oxide are extracted from the colloids in ratios markedly different from their relative amounts in the original material and particularly that lateritic soils, though high in iron content, yield essentially no soluble iron. The inference is drawn that in grassland soils, particularly, free soluble silica is present in the surface horizons.

The quantities of the exchangeable bases, including manganese, vary widely with the character of the soils from which the colloids were extracted. The proportions of the different bases vary with the character of the soil and often vary within a particular profile.

The base-exchange capacities of the colloids are determined after acid extraction and subsequent electro dialysis by treating with half-normal ammonium hydroxide, drying, and determination of the ammonia after distillation with magnesium oxide. There is, in most cases, a fairly definite relation between the total exchangeable bases and the base-exchange capacity and the silica-sesquioxide ratio.

A large part of the organic material of the colloids is extracted by ammonia, and the base-exchange capacity is determined on the material extracted as well as on the organic-free colloids. The organic colloids have very high base-exchange capacities as compared with the organic-free colloid. The fact is pointed out that organic matter in colloids is present in altered ratio as compared with the corresponding soils.

The total exchange base content of the colloids of the 11 soil profiles examined ranges from a minimum of 4.2 milliequivalents per 100 g in the C horizon of Cecil sandy clay loam to 144.6 milliequivalents in the subsoil of Houston clay. The base-exchange capacities of the colloids are, as a rule, greatest for the A horizons in all profiles when the organic matter is present, but when the organic

matter is removed the base-exchange capacities show uniformity to a striking degree in each profile. This uniformity is not shown by the slightly weathered profile of Muskingum silt loam. The values range from 9.7 milliequivalents for the Cecil C horizon to a maximum of 88.1 for the subsoil of Houston clay.

By contrast, the values obtained for the base-exchange capacity of the ammonia-soluble organic matter show a range of but 324 for Clinton silt loam to 394 for Vernon fine sandy loam.

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