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THE BASE EXCHANGE PROPERTY OF
ORGANIC MATTER IN SOILS

By
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THE BASE EXCHANGE PROPERTY OF ORGANIC MATTER IN SOILS

BY
W. T. McGEORGE

INTRODUCTION

The base exchange property of soils was first pointed out by Way as early as 1852. For many years following this time his discovery was applied largely to investigations relating to fixation of plant foods. True, there was some controversy over the two hypotheses, one chemical and one physical, presented to account for the fixation and exchange reactions involved. The true value of Way's discovery was not fully appreciated until recent years, largely because of the dominance of these plant food studies. Reference is made to the nature of the soil constituents which impart to the soil its property of base fixation and exchange and their influence upon most soil properties, which has received such widespread attention of late.

Owing to lack of agreement regarding the exact nature of the base exchange compounds, they are still referred to as the "exchange complex" or "humate-zeolite complex." In other words, this property is assigned to both organic and inorganic soil compounds of indefinite composition. While some rather definite information has been obtained regarding the nature and properties of the inorganic compounds which function as a part of the exchange complex, the role of organic compounds, humates or whatever we choose to call them, has received far less attention and their exchange property has been largely based on assumption.

In reviewing the early literature, Gedroiz (7) cites Schumacher as having prepared artificial humus by treating sugar with sulphuric acid, which material when placed in contact with salt solutions, showed a reduction in concentration of the latter. But he did not show whether the absorption was one of equivalent exchange or of ions or molecules. He referred to the absorption as one of salts—phosphates most and chlorides least. Gedroiz (7) also mentions the work of Eichorn who found an exchange of bases with peat and calcium humates. However, commenting upon the above, and on investigations in general, Gedroiz (7) wrote in 1924, "Summarizing what we know from the literature on absorption by organic substances of the soil, we may say that we know definitely that peat and artificially prepared organic substances are capable of absorbing the base from solutions of salts; but the quantitative side of this phenomenon is so far insufficiently studied."

While Gedroiz (7) was apparently convinced of the base exchange property of humates, from his own experiments, as shown by the reaction between the sodium salts (sodium carbonate) and the calcium of a calcareous organic soil, he says, "It is probably inconsiderable in comparison with that of the mineral part of the soil." Hissink (10, 11, 12) believes that the humate portion of the soil has a far greater absorptive power than the clay portion. He has assigned to clay a K value of 1.1 and to humus a K value of 5 and has employed these in estimating the lime requirement of soils. In other words the clay and humus portions of the soil will absorb approximately 1.1 grams and 5 grams CaO per 100 grams of soil respectively. He apparently did not work with clay-free humus nor with humus-free clay. Alben (1) states that humus has an absorption capacity seven times that of bentonite. Demolon and Barbier (6) have obtained experimental data which lead them to suggest the presence in soils of an argillo-humic complex; in other words, a double complex of the clay and humate soil fractions which functions as such and not individually as single complexes. The formation of this argillo-humic complex is influenced by the cations absorbed by the clay fraction.

Definite proof of the exchange properties of the inorganic compounds has been obtained in studies of the natural clays, notably the bentonites. Such minerals as montmorillonite, leverrierite, natrolite, and even orthoclase as well as synthetic aluminosilicates (4, 5) which may be built up in soils have shown equivalent exchange properties in greater or less degree.

An investigation of the exchange property of organic matter involves methods quite different from a study of the same property in inorganic soil compounds. Among the methods which are available or have already been suggested are: (1) destruction of organic matter by gentle ignition, (2) destruction of organic matter by the well known reaction of hydrogen peroxide with organic compounds, and (3) separation of the organic from the inorganic portion of the soil by solution and reprecipitation. The first two methods assume a destruction of the organic fraction of the soil without injury to the replacement property of the inorganic portion. By determining the replacement capacity of the soil before and after such treatments, any loss in replacement capacity is assumed to be due to the organic matter which has been destroyed. Ignition methods have found little favor because of the impossibility of effecting a combustion of the organic matter without injury to the inorganic fraction. Soil zeolites, possibly through dehydration, very easily lose a large part of their replacement capacity when heated at comparatively low temperatures. On the other hand, use of hydrogen peroxide, as a means of

removing the organic matter from the sphere of action, lends greater promise.

The reaction between hydrogen peroxide and soil organic matter has recently been studied by Robinson (22) who states, "A treatment with hydrogen peroxide, unlike treatment by combustion methods, would not be expected to affect the combined water content or appreciably change weight of the inorganic material." With the exception of several forms of carbon, such as graphite, coal, and charcoal, Robinson found an almost complete destruction of the organic carbon compounds present in soils. This reagent, therefore, should be admirably suited to a "difference method" of demonstrating the exchange capacity of soil organic matter provided there is no destruction of the inorganic zeolites. According to Sokolovskii (23) the removal of humus by oxidation with acid free hydrogen peroxide showed that in a chernozem, humus, even in the layers rich in it, did not appear to be an exclusive factor of absorption. In podzol soil the decrease in ammonium absorption due to this treatment amounted to 65 percent of the original. Kerr (16) digested a peaty soil with hydrogen peroxide and observed a notable reduction in replacement capacity. It is also of interest that he found the same mass action equation held for base exchange in both the organic matter and inorganic zeolite. Using a 10-percent solution of hydrogen peroxide with a 100-gram sample of soil, Gedroiz (7) reduced the exchange calcium from 0.810 gram to 0.056 gram by heating the whole to 40° C. But, and this is a very significant point, the hydrogen peroxide filtrate contained a considerable amount of iron and aluminum. Robinson, (22) too, while he was not primarily interested in the base exchange property, found a notable solution of iron, aluminum, silica, calcium, and magnesium from the reaction between the hydrogen peroxide and the soil compounds. In view of the fact that all of these elements may be present in the zeolite exchange complex, their presence in solution after treating the soil with hydrogen peroxide suggests a partial destruction of the inorganic exchange compounds.

All things considered, a solution and reprecipitation method of demonstrating a replacement property of soil organic matter appears the most feasible. So-called humus, which represents the more active form of organic matter in soils, is readily soluble in dilute aqueous alkaline solutions, from which it may be largely precipitated, practically free from colloidal clay, by acidifying the alkaline extract. It is reasonably certain that the organic matter thus extracted undergoes little or no alteration in chemical composition.

During the several years of rather intensive base-exchange studies in this laboratory, it was early observed that our arid soils appeared to suf-

fer no reduction in replacement capacity when treated with aqueous alkaline solutions. As a matter of fact, an increase in replacement capacity was usually noted. It is true that these soils contain only very small amounts of organic matter. But in view of the utter lack of definite quantitative data on the exchange property of organic matter (this had already attracted the attention of Gedroiz) our observations led us to doubt that such an exchange property existed. We believed that the fixation of a base by organic matter was a purely physical adsorption, entirely unlike that which is recognized as a true exchangeable fixation. These observations received preliminary publication in our Technical Bulletin No. 15 and were intended primarily to call the attention of other investigators to this lack of quantitative data, as well as to stimulate work in this field. Since that time we have assembled a very extensive collection of soil types containing widely varying amounts of organic matter. These include peat and muck types, forest types, several intermediate types, and a number of arid soils which contain only very small amounts of organic matter. A study of these soils has yielded data of a rather definite nature regarding the property of base exchange in the organic fraction of soils, and forms the subject matter of this bulletin.

EXPERIMENTAL

SOILS

A description of the soils used in this investigation follows:*

0. A heavy clay soil from Hawaii high in replaceable magnesium.
1. A black peat bog soil from the Cranberry Station, Pemberton, N. J.
2. A black peat bog soil from the same source as No. 1.
3. A Delmar woody brown, acid peat soil formed in part from hardwood or resinous wood, including spruce, and some sphagnum moss and sedges. Taken near Astoria, Oregon.
4. A finely divided sedge and willow peat from Wapato Lake near Gaston, Oregon.
5. A highly organic soil from a Douglas Fir forest in northern Arizona.
6. A highly organic soil from an English Spruce forest in northern Arizona.
7. A highly organic soil from an Aspen forest, northern Arizona.
8. A highly organic soil from a Yellow Pine forest, northern Arizona.

*The author takes this opportunity of thanking the following for collecting and sending peat and soil samples used in this investigation: C. S. Beckwith, New Jersey Cranberry Station; G. A. Pearson, Southwestern Forest Exper. Sta. at Flagstaff, Ariz.; S. A. Waksman, New Jersey Exper. Sta.; F. J. Alway, Minn. Exper. Sta.; S. D. Conner, Ind. Exper. Sta.; F. E. Hance, Exper. Sta. Hawaii Sugar Planters' Ass'n, Honolulu; H. J. Franklin, Cranberry Exper. Sta., Wareham, Mass.; W. L. Powers, Oregon Exper. Sta.

9. A black *Carex* peat, low moor, from Newton, N. J.
10. A brown highmoor peat, a decomposed sphagnum peat in its natural condition, from Maine.
11. A brown peat, Golden Valley peat experiment field, Minnesota.
12. A Milaca peat from Page peat experiment field, Minnesota.
13. A highly organic laterite soil type from Hawaii.
14. A laterite soil of medium organic content from Hawaii.
15. A brownish muck soil from Fulton County, Indiana.
16. A black muck soil from DeKalb County, Indiana.
17. A brown peat from the Cranberry Station, Wareham, Mass.
18. A black peat from the Cranberry Station, Wareham, Mass.
19. A black peat from the Cranberry Station, Wareham, Mass.
20. A sandy black alkali soil from the old University of Arizona Farm.

The determinations made upon these soils and the methods of analysis employed are briefly as follows:

METHODS

Moisture—Loss in weight of air-dried soil at 105° C. for 12 hours.

Ash—By ignition of one gram air-dried soil to constant weight at red heat.

Carbon—By wet oxidation. Methods of analyses A. O. A. C. 1924 p. 25.

Nitrogen—By Gunning-Hibbard method.

Reaction—By hydrogen electrode using a suspension of 5 grams soil in 25 cc. of distilled water.

Replaceable bases—By leaching 5 grams of soil with 500 cc. of normal ammonium acetate solution.

Replaceable hydrogen—By leaching 5 grams of soil with carefully neutralized, normal-barium-acetate solution and titrating the leachate to neutrality using the quinhydrone electrode.

COMPOSITION OF SOILS

In Table I are given the absorbed bases and hydrogen as milli-equivalents together with the percentage of nitrogen, carbon, ash, and the carbon-nitrogen ratio of the soils studied. As will be noted, they represent a wide range of organic as well as inorganic types. The carbon varies from 0.5 to 56.05 percent, the nitrogen from .073 to 2.23 percent, and the carbon-nitrogen ratio from 6.6 to 96.3. They contain small amounts of absorbed sodium and potassium, in some cases considerable amounts of absorbed calcium and magnesium, and show a wide variation in absorbed hydrogen.

TABLE I.—THE PARTIAL ANALYSES OF SOILS: DISPLACED BASES AS M. E. PER 100 GMS. DRY SOIL: OTHER DATA AS PERCENTAGE OF DRY SOIL.

Soil No.	Percent moisture	Percent ash	Percent carbon	Percent nitrogen	Reaction pH	M.E. Abs. Ca.	M.E. Abs. Mg.	M.E. Abs. Na.	M.E. Abs. K.	M.E. Abs. H.	M.E. Abs. Cap. (Sum of bases and hydrogen)	C:N Ratio
0	7.99	85.4	3.32	.272	5.4	15.3	37.4	3.5	1.4	17.3	74.9	13.2
1	2.89	74.3	10.03	.118	3.6	4.8	2.2	1.8	.5	37.8	47.2	85.0
2	11.11	8.4	56.05	.582	3.3	1.6	1.7	3.1	.6	179.7	185.8	96.3
3	6.41	14.07	46.50	1.905	3.6	22.5	1.5	3.4	.8	130.3	156.5	46.5
4	8.66	56.58	22.79	1.560	4.5	33.7	6.8	1.2	.6	50.8	93.0	14.6
5	3.28	79.98	10.84	.443	6.8	43.7	5.8	.9	1.9	8.6	60.8	24.5
6	2.70	90.05	4.38	.249	5.7	12.7	2.9	.2	1.4	16.7	33.9	17.6
7	7.23	49.04	24.23	1.005	6.1	73.4	9.5	2.3	2.1	18.5	106.0	24.1
8	3.49	77.05	8.77	.339	5.6	18.9	6.5	.8	2.0	16.6	44.6	25.9
9	11.21	15.95	44.92	3.180	4.9	108.2	10.3	4	2.2	53.1	174.3	14.2
10	8.72	3.01	47.12	.761	3.7	17.0	7.5	1.3	1.2	118.9	145.9	61.9
11	9.71	14.66	45.14	2.835	5.1	69.0	35.4	2.2	1.2	27.5	135.3	15.9
12	8.87	13.42	46.87	1.761	3.7	14.9	4.9	1.1	1.3	121.1	143.3	26.6
13	11.35	68.55	12.99	.896	5.7	9.0	6.8	.9	2.2	34.8	53.8	14.5
14	14.77	67.89	11.41	.927	5.5	11.6	5.4	.8	2.0	49.4	69.2	12.3
15	12.04	25.90	38.67	3.138	5.5	112.0	14.8	.8	1.7	53.5	182.8	12.3
16	8.35	19.20	46.11	2.346	3.7	13.3	4.7	1.8	2.6	149.5	172.0	19.6
17	9.27	8.70	49.04	1.956	3.6	14.2	8.3	1.8	1.2	133.0	158.7	25.1
18	9.48	19.30	43.87	1.299	3.7	7.8	8.9	1.2	.7	135.2	153.9	33.8
19	7.25	32.90	37.47	3.234	3.6	1.6	1.6	2.4	.4	120.9	126.9	11.6
20	0.86	94.77	0.48	.073	8.6	12.4*	6.6

*By replacement capacity for NH_4 from ammonium acetate.

Attention is called to the unusually high absorbing power of the organic soil types employed. This is considerably greater than the capacity of normal mineral soils which rarely exceeds 50 milli-equivalents per 100 grams. The large amount of replaceable hydrogen is significant. The inorganic exchange complex, the zeolites, will in an acid environment undergo a partial breakdown. Acid clays are therefore very low in replacement capacity. Since the opposite relation apparently applies to organic soils, we would expect organic matter to prevent loss in the absorbing capacity of clay soils. In fact the data in Table I suggest that the fixing power of the organic complex is of greater stability in an acid environment than that of the inorganic complex, and not only no less in fixing power but rather an increase may occur.

In the preceding paragraphs it has been assumed that the displaced bases were absorbed by the organic matter. The next step was to prove this assumption. As an initial attempt, the relation between the absorbing power of the soils and the organic matter content was examined graphically by plotting the percentage of carbon present in the soils against their absorption capacity in milli-equivalents per 100 grams. The result is of no small interest in that the absorption capacity approaches a linear function of the carbon content of the soil as shown in figure 1.* On the other hand, between the nitrogen content of the soils and their absorbing power no such relation exists, as shown in figure 2. Likewise, the carbon-nitrogen ratios, as illustrated in figure 3, show no such relationship. This indicates that the carbon compounds, largely lignins and carbohydrates, function as the principal absorbing agents in organic soils, and that the complex nitrogen compounds, which are largely proteins or protein derivatives, do not take part in the absorbing property of soil organic matter, at least to any appreciable degree, if the ratio of absorption capacity to nitrogen or carbon-nitrogen ratio can be taken as a criterion.

EQUIVALENCY OF BASE EXCHANGE IN ORGANIC MATTER.

Most peat and bog soils in their natural state are highly acid in reaction. It is not surprising, therefore, to note that the absorbed cations are in

*After the completion of this work there appeared in "Chemical Abstracts" an abstract of an article by Tyulin(24) recording similar observations on Russian soils, namely, a constant relation between the ratio of carbon in the absorbing complex and saturation capacity for calcium. It is of additional interest that his observations with regard to the reaction of aluminum with the organic complex are in agreement with ours in that, if the sodium-saturated organic complex is coagulated with the solution of an aluminum salt, no further exchange reaction in the complex can occur, a condition which he designates as passive because hydroxides again render the complex active.

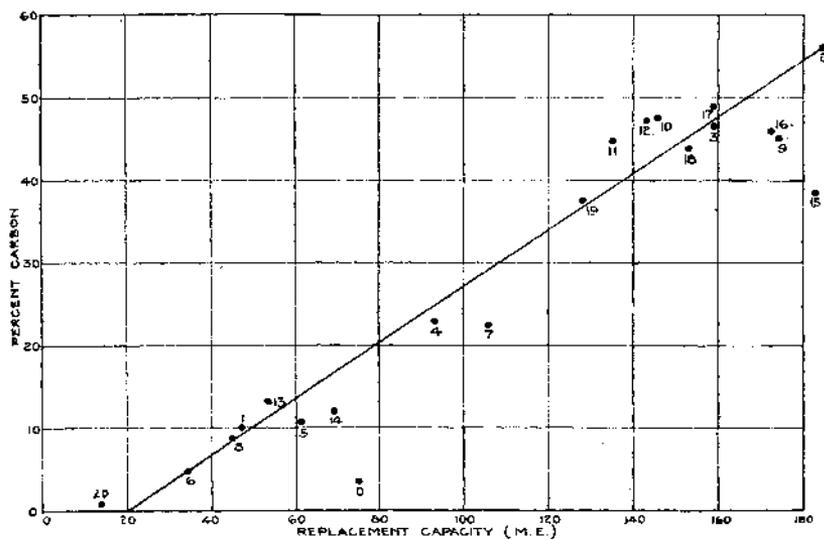


Fig. 1.—The relation between total replacement capacity and percentage carbon.

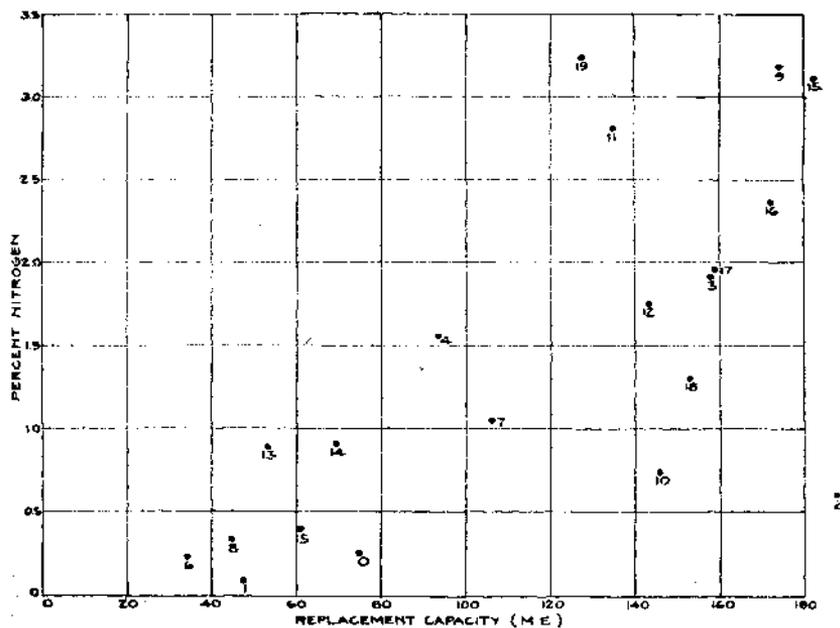


Fig. 2.—The relation between the total replacement capacity and percentage nitrogen.

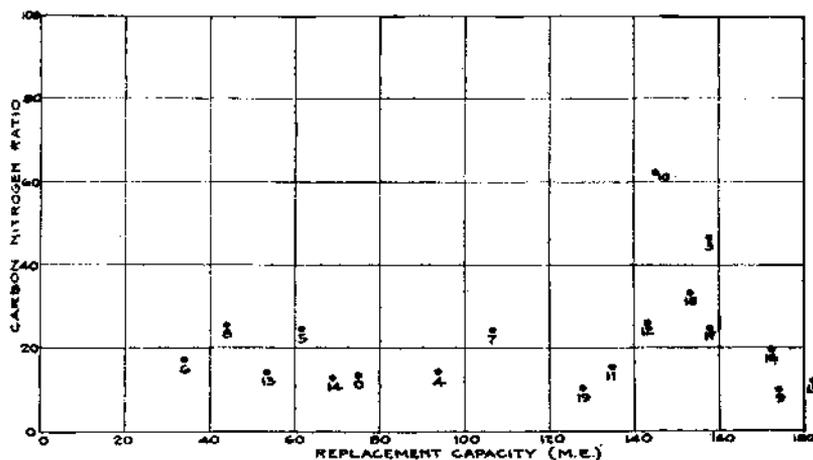


Fig. 3.—The relation between the total replacement capacity and carbon-nitrogen ratio.

very large part composed of hydrogen.* In a number of these soils, however, calcium is the dominant cation. The data given in Table I show a definite fixation of bases, and that these bases and hydrogen are displaced by leaching the soils with ammonium acetate or barium acetate solutions. We next sought to determine whether these cations possessed properties similar to the fixed ions of mineral soil types in which the cations are largely fixed as zeolitic bases, and whether or not the displacement was an exchange of chemical equivalents. It is not the amount of base or hydrogen present in soils which governs the properties that are of greatest agricultural importance, but rather, it is the cations that are fixed in a form which can be readily exchanged for the base of a neutral salt solution. Such cations are available to the plant and exercise a controlling influence on soil properties. In other words, interest centers primarily upon the cations which are subject to stoichiometric exchange.

As an initial step in the study of the equivalency of the exchange, the saturation capacity of the soils for ammonium ion was determined. One-gram samples of soil were weighed into 200 cc. Erlenmeyer flasks, 50 cc. of tenth-normal barium hydrate was added and the whole allowed to stand, with occasional shaking, for 18 hours. The contents of the flasks were then washed into asbestos-padded Gooch crucibles and leached with 400 cc. of neutral-normal ammonium acetate to replace the barium, then with water and alcohol to remove the excess of ammonium acetate. The

*In determining displaced hydrogen the soils were leached with barium acetate until the pH had been raised to pH 7.0 both in the soils and leachate.

fixed ammonium was then determined in these soils by distillation with magnesium oxide. These data are given in Table II and show a very close correlation between the absorbing capacity, as determined by the sum of the bases and hydrogen, and that shown by the capacity of the soil to absorb ammonium after the hydrogen had been neutralized. It is therefore evident that highly organic soils possess the property of fixing ammonium in amounts chemically equivalent to the sum of the absorbed cations.

As a further step in demonstrating this property of organic soils, the following experiment was conducted, using soil number 2 which contained the highest carbon content and is one of the highest in absorbing capacity. One-gram samples were weighed in quadruplicate, treated with barium hydrate solution, according to the method already described, filtered and leached with normal ammonium acetate and finally washed free of this salt. They were then leached with neutral barium acetate, and ammonium determined in the leachate with the following results expressed as milli-equivalents ammonium per 100 grams soil,

(NH ₄)	157	158	165	156
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They were then leached with ammonium acetate and barium determined in the leachate with the following results:

(Ba)	190	214	195	196
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Next they were leached with barium acetate and ammonium again determined with the following results:

(NH ₄)	162	162	162	165
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Then they were leached with ammonium acetate and barium determined in the leachate:

(Ba)	181	179	178	169
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Two of the samples were then leached with a normal solution of calcium chloride and two with a normal solution of potassium chloride and ammonium determined in the leachates with the following results:

(NH ₄)	157	166	162	164
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They were then leached with ammonium acetate and calcium and potassium determined in the leachates:

Ca		K	
167	166	161	160

On treating a soil with barium hydroxide there is some precipitation of barium as carbonate which, during subsequent leachings with neutral salt solutions, is removed very slowly. Also, various substances common to soils, such as colloidal silica or iron and aluminum oxides, have the power of absorbing barium from barium hydroxide. For this reason, as well as for the fact that the barium acetate solution used had a reaction

of pH 7.2, the results obtained in the barium determinations are slightly high in all cases. However, the three separate determinations of ammonium show a very close agreement in absorbing capacity. This is further confirmed by the absorbing capacity for both calcium and potassium. This soil contains 91.6 percent volatile matter (moisture-free basis) and therefore only 8.4 percent inorganic material yet has an absorbing capacity of 185 milli-equivalents per 100 grams (moisture-free basis). Organic materials thus must necessarily function largely as *exchange* compounds. Then, too, on the basis of the data obtained in the above experiment, the chemical equivalency of the exchange reaction is clearly demonstrated.

As a further step in demonstrating an exchange reaction of equivalent proportions, 13 of the soils, after neutralizing with barium hydroxide solution, were leached with normal ammonium acetate solution, then with normal calcium acetate solution and, after washing free of excess calcium acetate, the fixed calcium was determined. These data are given in Table II and demonstrate beyond question that the organic soil complex has a definite exchange capacity, and that cations fixed by the organic complex are, like those fixed by inorganic soil zeolites, present in a form exchangeable on a chemically equivalent basis.

TABLE II.—COMPARING EXCHANGE CAPACITY FOR Ca, NH₄ AND AS DETERMINED BY THE SUM OF THE FIXED BASES AND HYDROGEN.

Soil No.	Rep. Cap. (M.E.) Sum of bases and H	Rep. Cap. (M.E.) Abs. of NH ₄ from NH ₄ C ₂ H ₃ O ₂	Rep. Cap. (M.E.) Abs. of Ca from Ca (C ₂ H ₃ O ₂) ₂
0	68.9	71.0
1	45.8	47.0
2	165.2	163.0	165.6
3	143.6	144.0	140.0
4	85.0	88.0
5	58.8	47.0	52.0
6	33.0	29.0	33.0
7	98.3	85.0	87.0
8	43.1	44.0	41.0
9	156.3	156.0	179.0
10	133.2	140.0	142.0
11	122.2	115.0	119.0
12	130.7	139.0	122.0
13	47.7	51.0
14	59.0	62.0
15	160.8	158.0	168.0
16	157.6	155.0	142.0
17	144.1	146.0
18	139.3	143.0
19	117.7	114.0	115.0

HYDROGEN PEROXIDE AS A MEANS OF DESTROYING THE EXCHANGE PROPERTY OF THE ORGANIC MATTER

As already stated, some attempts have been made to evaluate the role of organic matter in the base exchange property of soils by destroying it with hydrogen peroxide, the assumption being that any loss in replacement capacity is due to the organic fraction. This assumption has been made regardless of the fact that both Gedroiz and Robinson have shown an appreciable solvent effect upon silica and the bases which go to make up the inorganic exchange complex. Considerable time has therefore here been devoted to a study of the reaction between hydrogen peroxide and the exchange complex both organic and inorganic. In treating the soils with hydrogen peroxide, we have in all cases used the method described by Robinson.(22) The hydrogen peroxide solution was of 15-percent strength and prepared by mixing equal parts of distilled water and 30 percent hydrogen peroxide.

The analytical determinations included the following: (1) Organic matter by treating 0.2 gram of soil with 10 cc. of water and 10 cc. of 30-percent hydrogen peroxide, on the steam bath until no more bubbles were evolved. (2) The carbon content of the residual soil from this treatment was determined by the wet oxidation method. (3) Silica, iron, and aluminum were determined in the filtrate obtained from filtering off the undecomposed soil in (1). (4) The replacement capacity of the hydrogen-peroxide-treated soil was determined on a separate sample, one gram being treated with 30 cc. of 15-percent hydrogen peroxide until there was no further evolution of bubbles. The whole was then evaporated to dryness, 5 cc. of tenth-normal barium hydrate added and the whole washed into a Gooch crucible. It was then leached with normal ammonium acetate, washed free of this salt, and the absorbed ammonium determined by distillation with magnesium oxide. The data obtained are given in Table III.

These data show a notable solution of silica, iron, and aluminum which is in agreement with the observations of Gedroiz (7) and of Robinson.(22). Whether these came from the inorganic exchange complex remains to be proved. The destruction of carbon was not complete in all soils, which may be explained by certain observations of Robinson (22) namely, that for complete destruction of organic matter it is necessary to have present sufficient inorganic soil material to catalyze the reaction. In view of the fact that we were not interested in a complete destruction of organic matter and could not use additional soil material as a catalyst, no attempt was made to obtain complete destruction. The purpose of our experiment was to determine the solution of silica, iron, and aluminum, and to determine the relation of the amount of organic matter destroyed to loss in replacement capacity.

TABLE III.—THE EFFECT OF H₂O₂ ON CARBON CONTENT AND UPON THE REPLACEMENT CAPACITY OF THE SOIL

Soil No.	Percent carbon	Percent organic by H ₂ O ₂	Percent carbon in residue from H ₂ O ₂ treatment	Percent carbon lost in H ₂ O ₂ treatment	Percent SiO ₂ dissolved by H ₂ O ₂	Percent Fe ₂ O ₃ -Al ₂ O ₃ dissolved by H ₂ O ₂	Rep. cap. (M.E.) of H ₂ O ₂ residue	Rep. cap. (M.E.) destroyed by H ₂ O ₂
0	3.32	0.43	0.0	3.32	1.95	1.60	68.0	6.9
1	10.03	20.39	0.62	9.4339	6.8	40.4
2	56.05	60.10	18.00	38.05	1.07	31.8	154.0
3	46.50	69.92	6.46	40.04	.10	2.28	19.0	139.6
4	22.79	29.6895	2.20	46.6	46.4
5	10.84	13.9198	2.05	15.4	45.4
6	4.38	2.0577	1.88	15.9	18.0
7	24.23	37.40	1.05	1.90	19.1	86.9
8	8.77	8.81	0.0	8.77	1.20	2.00	17.2	27.4
9	44.92	72.91	0.67	44.25	1.05	3.15	17.3	157.0
10	47.12	61.20	13.43	33.70	.50	.50	9.1	136.8
11	45.14	64.46	8.14	37.00	1.45	1.30	14.7	120.6
12	46.87	59.44	12.12	34.75	1.40	1.60	10.9	132.5
13	12.99	14.94	0.0	12.9795	30.6	23.2
14	11.41	11.21	0.0	11.41	.25	1.40	49.4	19.8
15	38.67	58.62	3.69	34.98	.70	1.15	19.6	163.2
16	46.11	55.44	14.18	31.93	.70	1.40	20.0	152.0
17	49.04	60.20	14.33	34.70	.60	1.65	25.7	133.0
18	43.87	61.71	8.56	35.31	.55	2.30	14.2	139.7
19	37.47	42.43	12.78	24.69	.85	2.00	17.9	109.0
20	0.39	0.39	11.3

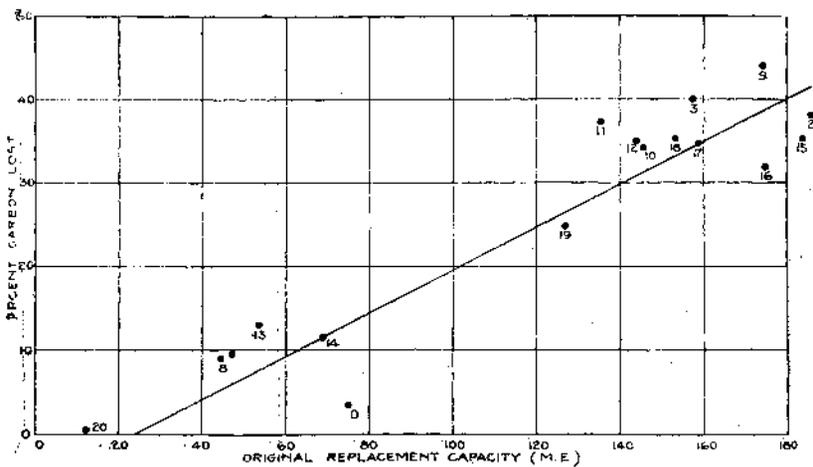


Fig. 4.—The relation between the original replacement capacity and percentage carbon lost by treating with H₂O₂.

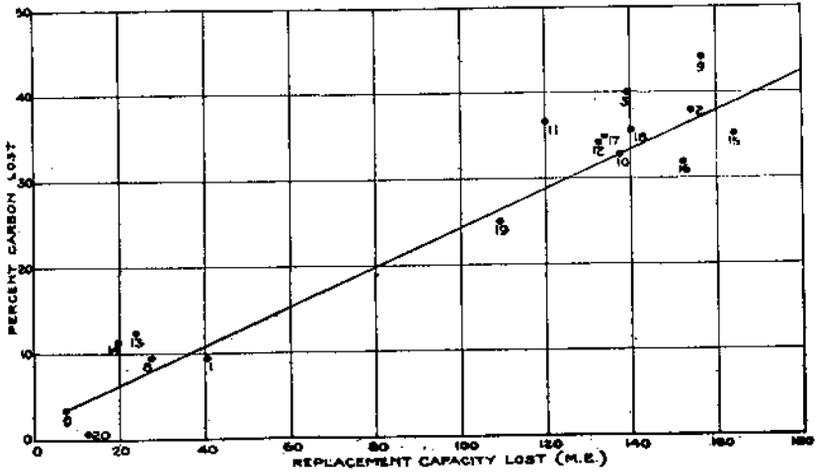


Fig. 5.—The relation between the loss in replacement capacity and percentage carbon lost by reaction with H_2O_2 .

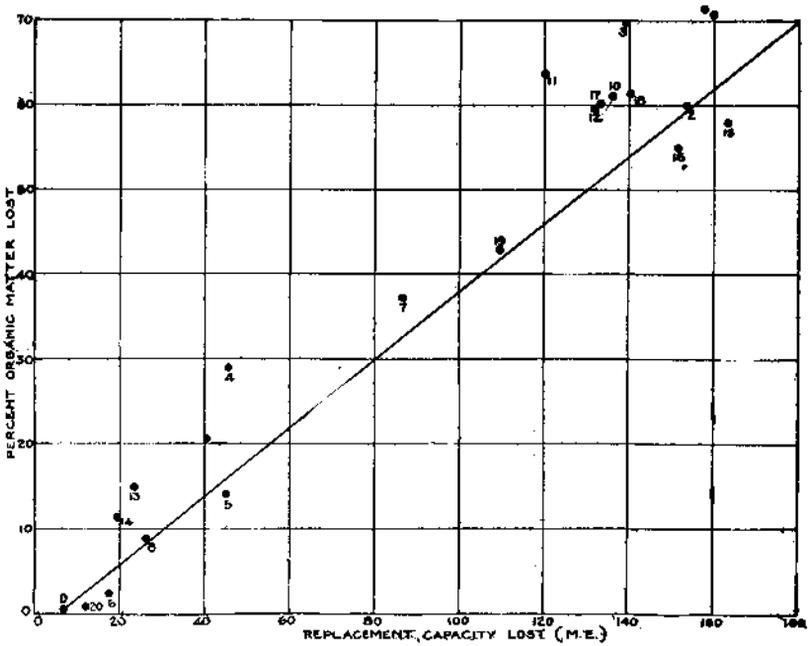


Fig. 6.—The relation between loss in replacement capacity and calculated loss in organic matter by reaction with H_2O_2 .

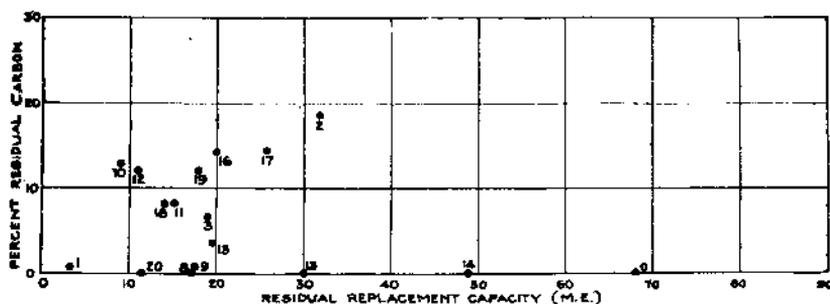


Fig. 7.—The relation between the carbon content and replacement capacity of soil residue from H_2O_2 treatment.

A study of the data showing the relation between loss in replacement capacity and loss of carbon reveals much of interest. In order to show these relationships the data have been plotted graphically in figures 4, 5, 6, and 7. Figure 4 shows the relation between the original replacement capacity of the soils (M.E.) and the percent carbon lost by digestion with 15-percent hydrogen peroxide. Figure 5 shows the relation between the loss in replacement capacity (M.E.) and percent carbon lost by digesting with 15-percent hydrogen peroxide. Figure 6 shows the relation between the loss in replacement capacity (M.E.) and loss in organic matter as determined by the loss in weight of soil by digestion with 15-percent hydrogen peroxide. In all cases the relations are those of linear functions similar to figure 1. On the other hand, as shown by figure 7, there is no relation between the residual carbon, that is, the carbon compounds not destroyed by hydrogen peroxide, and the replacement capacity of the soil after digestion. Thus there is presented further evidence of the important role which soil organic matter plays in the base exchange reaction of soils, and that it is a function of the nitrogen-free carbon compounds rather than of the proteins or related substances.

REACTION OF HYDROGEN PEROXIDE ON THE INORGANIC EXCHANGE COMPLEX

The appearance in solution of silica, iron, aluminum, and other bases, after treating the soil with hydrogen peroxide, suggests a reaction with the inorganic as well as the organic exchange compounds of the soil. To study this phase of the problem a number of natural and synthetic zeolites were obtained:

1. A natural bentonite from South Dakota.
2. A natural bentonite from California.
3. Montmorillonite from California.

4. Commercial zeolite water softener.
5. A synthetic sodium zeolite made in this laboratory.
6. A synthetic potassium zeolite made in this laboratory.
7. A sample of natrolite.
8. A sample of orthoclase.
- *9. A natural bentonite from Belle Fourche, S. D.
10. A natural bentonite from Waldo, N. M.
11. A natural bentonite from Boyer, Texas.

These materials were treated with hydrogen peroxide by the method already described, and their replacement capacity before and after treatment was determined. These data are given in the following table.

TABLE IV.—EFFECT OF H_2O_2 UPON THE EXCHANGE CAPACITY OF INORGANIC EXCHANGE COMPOUNDS.

Sample		Rep. cap. M.E. before treating with H_2O_2	Rep. cap. M.E. after treating with H_2O_2
Bentonite.....	1	103	100
Bentonite.....	2	92	88
Montmorillonite.....	3	17	16
Com. Zeolite.....	4	229	121
Syn. NaZ.....	5	453	406
Syn. KZ.....	6	416	379
Natrolite.....	7	19	8
Orthoclase.....	8	1.5	1.5
Bentonite.....	9	87	89
Bentonite.....	10	108	108
Bentonite.....	11	68	68

It will be noted that montmorillonite, orthoclase, and the natural bentonites are not affected by the hydrogen peroxide treatment. The very slight differences may be attributed to the error in using such a small sample and the difficulties involved in working quantitatively with such highly colloidal materials. On the other hand, the natrolite, the synthetic zeolites, and the zeolite water softener all show considerable loss from the action of the peroxide. Some inorganic zeolites are therefore capable of resisting the action of hydrogen peroxide while others are not.

In order to determine whether or not the fixed base was in any way associated with this loss of replacement capacity, the California bentonite was leached with solutions of the four bases calcium, magnesium, potassium, and sodium. These four prepared zeolites were then treated with hydrogen peroxide and all failed to show any loss of replacement capacity, thus indicating the stability of the bentonite regardless of its basic composition.

*The author takes this opportunity to thank C. S. Ross, U. S. Geological Survey, for supplying the three samples of bentonite numbers 9, 10, 11.

The zeolitic water softener which showed the greatest loss of replacement capacity when treated with hydrogen peroxide was next saturated with calcium, magnesium, and sodium by leaching with normal solutions of the chlorides of these bases. These were then treated with hydrogen peroxide and the following losses in replacement capacities were obtained.

CaZ	35 M.E. per 100 gm.
MgZ	37 M.E. per 100 gm.
NaZ	38 M.E. per 100 gm.

All agree very closely, which suggests that the nature of the absorbed base is without influence upon the reaction with hydrogen peroxide.

We next sought to determine if this loss in replacement capacity was progressive. One-gram samples of three zeolites, namely, California bentonite, synthetic sodium zeolite, and the water softener were treated with 15-percent hydrogen peroxide three successive times, the whole being filtered free of hydrogen peroxide after the first and second treatments. A determination of the replacement capacity under these conditions showed that the reaction with peroxide was not progressive but was completed in one treatment. That is, the loss in replacement capacity of the synthetic zeolite and the water softener was the same after three treatments as after one treatment, while there was no loss in replacement capacity of the bentonite even after three separate digestions with 15-percent hydrogen peroxide.

Since soils always contain organic matter, and often iron and manganese oxides which react actively with hydrogen peroxide, some experiments were conducted in which these materials were added to natural or synthetic zeolites to determine if a catalyser would influence the reaction. But here again these materials failed to exert any influence upon the reaction between hydrogen peroxide and the exchange capacity of the natural bentonites or the synthetic zeolites. The conclusion seems warranted that in treating a soil with hydrogen peroxide, natural bentonites and montmorillonite will show no loss in replacement capacity, but that any "new zeolites" which have been recently synthesized within the soil mass, and such has been shown to be possible especially in alkaline soils,(5) will show some loss in replacement capacity. This also holds true for aluminosilicates of the natrolite type.

It has already been demonstrated in this laboratory (4) that soil zeolites usually suffer a break-down in an acid environment. The hydrogen peroxide reagent (C.P.), is always quite strongly acid, so we next sought to determine if this acidity was in any way associated with the loss in replacement capacity. Eight 1-gram samples of synthetic potassium zeolite (5) were weighed into covered beakers and treated, in duplicate, as

follows: (1) After the hydrogen peroxide reaction was complete the cover was removed from the beaker and evaporation continued to dryness. (2) Ten cc. of tenth-normal barium hydrate was added instead of 10 cc. of water with the 10 cc. hydrogen peroxide. (3) Treatment was the same as in 2 except that the whole was evaporated to dryness after the reaction of the peroxide was complete. (4) The samples were not treated in any way but were conducted as controls. After their respective preliminary treatments all were washed into Gooch crucibles, leached with ammonium acetate, washed free of excess salt, and the fixed ammonium determined by distillation with magnesium oxide. The replacement capacity expressed as milli-equivalents was found to be as follows:

- (1) 392
- (2) 378
- (3) 383
- (4) 409 (original exchange capacity)

These results indicate that the loss in replacement capacity is not a "break-down," as this term usually implies but is rather a complete destruction of a rather definite portion of the exchange complex through a reaction with hydrogen peroxide. If the loss in exchange capacity had been due to "break-down" it would have been rebuilt either from the $\text{Ba}(\text{OH})_2$ or by evaporation to dryness. A similar experiment was conducted with the zeolitic water softener by adding barium acetate to the soil-hydrogen-peroxide mixture, but here again the loss in replacement capacity was not prevented by the barium acetate. We also compared the effect of neutralizing the hydrogen peroxide with barium hydrate before use, but the results obtained with neutralized hydrogen peroxide agreed very closely with those in which unneutralized hydrogen peroxide was used. This led to the conclusion that the loss in replacement capacity was caused by the hydrogen peroxide and not by its attendant acidity.

A similar experiment was conducted with one of the highly organic soils to determine whether or not the loss in replacement capacity resulted in a complete destruction of the exchange compounds, in a temporary "break-down," or in a solubility effect, the products of which were removed in solution. The following is a description of this experiment, each part of which was carried out in duplicate on a 1-gram sample of soil.

1. The sample was digested with 30 cc. of 15-percent hydrogen peroxide, filtered and the exchange capacity of the residue determined.

2. After digestion as in (1), 25 cc. of 0.1 normal barium acetate was added, the whole evaporated to dryness on the steam bath, taken up in distilled water, filtered, and the exchange capacity of the residue determined.

3. After digestion as in (1) 25 cc. of 0.1 normal barium acetate and 10 cc. of 0.1 normal barium hydroxide were added, the whole evaporated to dryness on the steam bath, taken up in distilled water, filtered and the exchange capacity of the residue determined.

4. The sample was treated as in (1), except that the whole was evaporated to dryness and taken up in water again before filtering.

5. The sample was digested with 30 cc. of 15-percent hydrogen peroxide prepared by diluting 15 cc. of 30-percent hydrogen peroxide with 15 cc. of 0.1 normal barium hydroxide, filtered and the exchange capacity of the residue determined. The results obtained in this experiment are given in the following table:

TABLE V.—NATURE AND EFFECT OF EXCHANGE CAPACITY DESTRUCTION BY HYDROGEN PEROXIDE.

Treatment	Orig. Rep. Cap. M.E.	Rep. Cap. of residue M.E.	Loss in Rep. Cap. M.E.
1	159	14	145
2	159	23	136
3	159	23	136
4	159	28	131
5	159	33	126

These data show quite conclusively that the reaction between hydrogen peroxide and the exchange compounds of organic soils is a destruction of major proportions, and one from which the exchange capacity cannot be rebuilt from its constituents by alkaline treatments except to a minor degree. In this respect it is very similar to that obtained by digesting the synthetic zeolites with this reagent.

As an additional experiment, a number of arid soils, very low in organic matter were selected and digested quantitatively with 15-percent H_2O_2 using 5 grams soil and 30 cc. of H_2O_2 . The replacement capacity of these soils before and after digestion with H_2O_2 was determined by leaching with neutral normal-ammonium-acetate solution and determining the amount of NH_4 fixed. The non-carbonate carbon content was also determined. The results are given in Table VI.

There is little or no change in the exchange capacity of these soils by digestion with hydrogen peroxide. This group was chosen because they are as low in organic matter as ever found in cultivated soils. All determinations may be considered to be within the range of experimental error.

TABLE VI.—EFFECT OF H₂O₂ ON EXCHANGE CAPACITY OF ARID SOILS CONTAINING LITTLE ORGANIC MATTER.

No.	Source of soils	Rep. cap. as M.E. per 100 grams before digestion	Rep. cap. as M.E. per 100 grams after digestion	Percent carbon	Percent moisture
1	Peoria, Ariz.....	16.8	17.8	0.38	2.18
2	Yuma, Ariz.....	17.3	19.0	0.35	1.97
3	Wellton, Ariz.....	4.2	4.0	0.02	0.54
4	Phoenix, Ariz.....	13.2	13.4	0.18	1.61
5	Phoenix, Ariz.....	22.3	20.7	0.35	2.03
6	Littlefield, Ariz.....	4.6	3.5	0.54	0.54
7	Fresno, Calif.....	5.1	4.6	0.18	0.24
8	Tucson, Ariz.....	11.3	12.0	0.39	0.86

There is thus considerable evidence favoring the employment of hydrogen peroxide as a reagent in a "difference method" for determining the replacement capacity of organic matter. Clay materials of the bentonite type will resist any action of hydrogen peroxide while any new recently-formed zeolites are destroyed only in small part. That fraction of soil organic matter which functions in base exchange is in greatest part destroyed and the degree of destruction is not influenced by the absorbed bases, by the reaction, or by carbonates.

NATURE OF THE ORGANIC EXCHANGE COMPOUNDS.

Although soil organic matter has been the subject of considerable study during the past century and references in the literature are legion,* the very complex nature of the compounds which compose this important group of soil constituents has greatly retarded advancement in our knowledge of its nature and properties. Of necessity soil organic matter must consist of the intermediary products of decomposition between the organic materials of plant and animal origin and the final residual products of the many chemical and biological reactions involved in their destruction. Some of these products, in their intermediary or final state, are assimilated by the plant and thus removed from the soil environs while others, notably the final gaseous products, are lost by volatilization. Still others are retained within the soil in residual forms which strongly resist both biological and chemical reactions. The latter accumulate to produce, to a large extent, the bodies which compose the so-called humus.

*For a thorough review of the literature the reader is referred to an excellent series of papers by Waksman, "The origin and nature of soil organic matter or soil humus" in *Soil Science*, Vol. 32, pp. 123-162; 221-232; 323-333; 395-406, and 421-436.

Recently, due largely to the very systematic studies of Waksman, (25) the subject has been somewhat clarified and has now assumed a more concrete form. Fresh undecomposed plant materials are largely composed of proteins, lignins, celluloses, and hemicelluloses. Of these materials the proteins are the most reactive, both biologically and chemically, under the environment present in soils, and should therefore decompose most rapidly and be removed from the sphere of action. Since nitrogen is in many cases a limiting growth factor and an extremely essential plant food, the plant plays a large part in removing the nitrogenous compounds from the soil environs. Of the three other materials, celluloses and hemicelluloses are decomposed more readily than lignin, which latter must therefore tend to accumulate in variable amounts depending upon the soil type, its biological flora, and upon the factors which govern aeration.

Comparing the composition of the undecomposed plant materials with the organic matter in soils, Waksman (25) has shown that there is a notable disappearance of cellulose. "From one of the most abundant groups of constituents in mature plants they have become reduced to a minor group in the soil." On the other hand, he has shown a notable increase in the proportion of lignins. Proteins, too, compose a larger percentage of the soil organic matter than of mature plant materials, but this he believes to be built up from the cellular substances of the soil organisms active in the decomposition of the plant materials in the soil. From his investigations he reaches the very logical conclusion that, "soil organic matter is made up predominantly of two groups of organic complexes namely the nitrogenous compounds and the ligin-like substances. The latter originate from the lignins in the plant materials due to the greater resistance to decomposition."

Of the carbohydrates which compose the materials that are present as soil organic matter, hemicelluloses (pentosans, hexosans, etc.), usually predominate over the celluloses. The former are more resistant to microbiological action and are to a certain extent synthesized by these organisms.

To complete the above brief discussion on the nature of soil organic matter, it is of interest to add the very comprehensive definition from Waksman. (25) "Soil organic matter or soil humus is a mixture of dark colored amorphous organic compounds formed in the soil as a result of decomposition of organic matter of plant and animal origin by microorganisms, under aerobic or anaerobic conditions; it consists largely of substances which are resistant to further decomposition (largely lignins and modified lignin complexes), of substances in the process of decomposition (hemicelluloses, some cellulose, and proteins), of substances result-

ing from decomposition (organic acids, bases, etc.) and of microbial synthesized substances (largely organic nitrogenous complexes and hemicelluloses)."

Our investigations have already demonstrated a fairly quantitative relation between the carbon content of organic soils and their replacement capacities, and the absence of any such relation between nitrogen content and replacement capacity or the carbon-nitrogen ratio and this property. The base exchange property of soil organic matter must therefore be largely a function of either the lignin complex, the hemicellulose complex or a combination of the two.

A hemicellulose may be broadly defined as a poly-saccharide soluble in dilute alkali and convertible into simple sugars by heating with dilute acids at atmospheric pressure (and insoluble in hot water to distinguish from starch). They are anhydrides of hexose and pentose sugars. As examples, xylan, araban, mannan, and galactan may be cited. They may be distinguished from cellulose in that they are dissolved by dilute alkalis and readily hydrolysed by dilute mineral acids, while cellulose is resistant to these.

According to Schorger* lignin represents the non-carbohydrate portion of lignified tissue after it has been freed from tannins, resins, fats, and similar secondary constituents. Its composition is not considered uniform and it is difficult to isolate it unchanged. The non-uniformity lies largely in the number of methoxyl, hydroxyl, and acetyl groups. While in some cases there has been evidence of ketonic and aldehydic groups their presence has not been satisfactorily proved. For lignin isolated from oat hulls and corn cobs Phillips (21) determined the formula $C_{98}H_{31}O_{12}(OCH_3)_4(OH)_3$. Lignin is believed by some to be synthesized from pentosans and hexosans. Also, the lignin complex has been subdivided into alpha and beta lignins, the sulphonate of the former being precipitated by calcium chloride, while the latter is not. Numerous references are to be found in the literature upon the lignosulphonate salts but few deal with direct combinations of lignin with the base. Beckmann, Liesche, and Lehmann (3) prepared sodium lignate, by evaporation of a lignin-sodium hydroxide solution to dryness, which appeared to contain two molecules of sodium. Paschke (20) precipitated lignin with solutions of barium chloride, calcium chloride, and other metallic salts. Melander (19) found that sodium chloride precipitates, from waste sulphite liquors, a sodium-chloride-containing product which is a mixture of the sodium salts of alpha-lignosulphonate and a product in which the sodium is not bound to the sulphonate. Beckmann and Lie-

*Chemistry of Cellulose and Wood—McGraw-Hill Co., 1926.

sche (2) determined dissociation constants and the electrical conductivity of sodium lignate solutions. Gillespie and Wise (8) have shown by means of the hydrogen electrode that the addition of the chlorides of sodium, potassium, or barium to humus suspensions lowers the potential of the gas chain, showing an increase in the hydrogen ions. At equivalent concentrations they found that barium chloride exerts the greatest effect on the potential. There is therefore evidence in the above references of the existence of basic lignates.

A plentiful supply of organic matter is usually considered a characteristic of a fertile soil, both as regards its influence upon the physical as well as its chemical properties. Such soils tend toward a black color, which from early times has been attributed to the presence of the so-called humus. The principal chemical property of humus is its solubility in alkaline solutions of monovalent bases and its partial precipitation, from this alkaline solution as an insoluble complex, by acids. This property is also one which is characteristic of lignins and hemicelluloses, and has been extensively utilized in preparing these as well as soil humus for study. A number of early observations on the property of soil humus are of interest. Humus being soluble in dilute alkali and being precipitated relatively unchanged by acids led to the assumption that this insoluble acid formed soluble salts with sodium, potassium, or ammonium. But the fact that a greater solubility of humus followed a preliminary treatment of the soil with dilute HCl served as the basis of a further assumption that calcium formed an insoluble salt with humus. In view of the rather definite nature of the property, it is not surprising that humus was for many years looked upon as a definite chemical body. In spite of its non-homogeneous nature the property of forming compounds, chemical or adsorptive, with bases is definite. What then of the chemical equivalent exchange property of these bases in isolated humus material?

Hummelchen and Kappen (13) found that small quantities of free bases are fixed completely and irreversibly by humus acid. With high concentrations of base the fixation was incomplete and partially reversible. Their studies indicated an exchange of ions by the humus. Heilmann and Kappen (9) studied the reaction between humus and neutral salt solutions and found a balanced reaction between the neutral salt and free humic acid which yielded a humus salt and free acid. They also observed a replacement reaction between iron and aluminum humates and neutral salts. Their studies indicated that real exchange acidity can be produced in soils by humus only on treatment with such substances as aluminum chloride and when humus contains sodium, potassium, and calcium bases as humates.

Kotzmann (17) found that humus can be saturated with bases to a variable extent according to the method employed and therefore concluded that humus can combine with bases both chemically and physically. He found an equivalent weight of 308.7 for NH_4 absorbed as ammonium humate and a similar equivalent for Ca. This does not vary greatly from results which we have obtained. He ventured the conclusion that only the so-called Grandeau-Hilgard organic material takes part in the absorption.

In view of the difficulties involved in the separation and purification of humus from soils, it has been extensively prepared synthetically. There are many evidences of similarity between the properties of the synthetic and the natural product. Of especial interest is the insoluble nature of the compound formed with divalent bases and the solubility of the compounds formed with monovalent bases as well as the properties of the acid humates. It is not surprising therefore to note that a number of investigations have been conducted upon the nature of soil humus using the synthetic substance. A number of organic materials have been found to yield compounds not greatly unlike soil humus. The variety of materials which may be used suggests that naturally occurring soil substances are rarely homogeneous products of any one type of reaction or any one group of parent substances, but rather are accumulations of the more resistant end products of a number of reactions both chemical and biological. Carbohydrates represent a group which readily yields dark colored substances under the action of aqueous solutions of strong acids. These, like soil humus, are soluble or highly dispersed in alkaline solutions and precipitated by acids. There is much basis, therefore, for an analogy between the natural humus and such synthetic products from carbohydrates of plant origin, namely, sugar, starch, and cellulose, which compose a major part of the parent material of the organic complex of the soil. The question of the base exchange property of synthetic humus is therefore of additional interest.

An excellent review of the literature on synthetic humus has been prepared by Kawamura, (15) whose own investigations upon the absorption isotherms of the bases and acids of synthetic humus are of interest. His investigation indicated the formation of a definite compound, a humate, when synthetic humic acid was neutralized by an alkali and that the humic acid which he prepared from sucrose was a real acid. On titrating with $\text{Ba}(\text{OH})_2$ it behaved in a manner similar to stearic acid, except that after neutralization there was a further absorption of barium hydroxide by the material. Kawamura, while he obtained the formation of definite salts, was not interested in their exchange property.

EXPERIMENTS WITH THE ORGANIC EXCHANGE COMPLEX

Methods used in the preparation of lignin and hemicellulose-like materials, for a study of their exchange properties, is given briefly below. Soil number 2, being the highest in replacement capacity and organic matter content with very small amounts of inorganic material, was chosen for the extraction of humus bodies. In making these extractions, advantage was taken of the difference in solubility of the several humus bodies in alcoholic and aqueous solutions of alkali. That is, alcoholic sodium hydroxide is a solvent for lignin, but in order to include the solution of hemicelluloses, the pentosans and hexosanas, aqueous sodium hydroxide solutions must be used as these are insoluble in alcohol.

Lignin extraction was conducted according to the method used by Phillips (21) in his investigations on the lignins of corn cobs, oat hulls, etc. Five hundred grams of soil were treated with 2.5 liters of 2-percent alcoholic NaOH (prepared by dissolving 50 grams of NaOH in 1 liter of water and adding sufficient 95-percent alcohol to make a volume of 2.5 liters) and allowed to stand at room temperature for 24 hours. The liquor was then poured off, neutralized with HCl and the alcohol distilled off under reduced pressure. Ten cubic centimeters of Con. HCl was then added to the aqueous residue and the precipitated lignin removed by filtration. This lignin was washed with water until free from chlorides, after which it was dried to constant weight in a dessicator.

For the aqueous alkaline extract, which should contain the hemicelluloses in addition to lignin, a similar experimental procedure was followed, except that the 500 grams of soil was leached with 2,500 cc. of 2-percent aqueous solution of NaOH, the leachate neutralized with HCl, concentrated under reduced pressure, 10 cc. of Con. HCl added, and the whole filtered. The precipitated organic matter was washed free of chlorides and dried to constant weight in a dessicator. This material was of a very deep black color, while a brown colored material was obtained from the alcoholic extraction.

Synthetic humus was prepared by treating 200 grams of pure sucrose, in a large evaporating dish, with 20 cc. of 10-percent HCl. The mixture was warmed on a steam bath for about 5 hours, with occasional stirring. An excess of hot water was then added to the mass, the whole triturated, filtered, and washed free of chlorides. This crude humus was then treated with warm 5-percent aqueous NaOH solution and filtered. The filtrate was then neutralized with HCl, an excess added, and the precipitated humic acid removed by filtration and dried to constant weight in a dessicator. A sample of lignin was also obtained from Dr. Max Phillips* of

*The author takes this opportunity to thank Dr. Phillips for supplying the corn cob lignin used in these investigations.

the Bureau of Chemistry and Soils, United States Department of Agriculture and which he had prepared from corn cobs.

As a preliminary experiment the exchange property of corn cob lignin and that prepared from soil number 2 was studied. One-gram samples were weighed into small beakers, to which was also added 15 cc. portions of neutral normal barium acetate. The whole was stirred until the materials had become completely wetted, after which they were washed into asbestos-padded Gooch crucibles. They were then leached with 200 cc. portions of the barium acetate solution. The excess barium acetate was then removed by leaching with distilled water, after which the materials were leached with 0.1 normal CaCl_2 and barium determined in the leachate with the following results:

Milli-equivalents Ba per 100 gms. fixed by corn cob lignin.....	18.6
Milli-equivalents Ba per 100 gms. fixed by soil lignin.....	160.6

They were then washed with water until free from soluble calcium, again leached with barium acetate, and the replaced calcium determined with the following results:

Milli-equivalents Ca per 100 gms. fixed by corn cob lignin.....	20.6
Milli-equivalents Ca per 100 gms. fixed by soil lignin.....	161.2

The evidence of a chemically equivalent exchange in lignin is therefore quite convincing. On the basis of this work a more complete experiment was planned and conducted.

Duplicate 0.5-gram samples of (1) lignin (alcoholic NaOH soluble material) from soil number 2, (2) synthetic humus prepared from sugar, (3) and (4) lignin-hemicellulose (aqueous NaOH soluble material) from soil number 2 were studied. The two latter represent material prepared from the same soil but by two separate extractions.

(A) These samples were leached with 200 cc. of normal barium acetate, washed free from excess of this salt, with distilled water, leached with 200 cc. of neutral normal CaCl_2 and the replaced barium determined with the following results expressed as milli-equivalents per 100 grams:

	1	2	3	4
M.E. Ba per 100 grams.....	65	162	385	391

(B) They were then leached free of CaCl_2 , with distilled water, leached again with 200 cc. of normal barium acetate, and calcium determined in the leachate with the following results:

	1	2	3	4
M.E. Ca per 100 grams.....	67	156	381	370

They were again leached as in (A), then again as in (B), and the calcium determined in the leachate as follows:

	1	2	3	4
M.E. Ca per 100 grams.....	69	154	374	378

These results show beyond question an equivalent base exchange property of lignin-like materials in soils. It is significant that this property is demonstrated by the synthetic humate, as well as that prepared from the soil. Lignin, as prepared by extraction with alcoholic NaOH solution, shows a lower replacement capacity than the material prepared by an aqueous NaOH extraction. Referring back to the data showing the exchange capacity of lignin prepared from undecomposed material, namely, corn cobs, an even lower replacement capacity will be noted. This indicates that the replacement capacity of lignin will vary with its source treatment or composition. It also indicates that either the hemicelluloses possess base exchange properties or else that the exchange property of the lignin-hemicellulose complex is greater than lignin alone.

The same materials were also leached with 0.2 normal HCl, washed free of excess acid, and the fixed hydrogen determined by leaching with carefully neutralized normal barium acetate. The leachate was then titrated with 0.1 normal barium hydroxide, using the quinhydrone electrode. Here, again, an equivalent exchange was obtained, giving a close agreement, on a milli-equivalent basis between the three cations, barium, calcium, and hydrogen.

The monovalent "lignin" salts are very soluble in alcohol which makes the application of these to base exchange studies very difficult and uncertain. The removal of excess soluble salt from the base exchange complex preparatory to determining the amount of base fixed, by the use of water, allows too great a hydrolysis of monovalent salts and therefore will yield low results. Then again, the monovalent "lignin" salts are soluble under certain conditions in salt solutions, very much so in acetate solutions which hydrolyse and yield OH ions. In view of this little use was made of the salts of monovalent bases in these studies.

The question of fixation of trivalent bases by the exchange complex of soils is one which has been widely studied. An excellent review of the literature has been given by Magistad (18) who also has demonstrated quite conclusively that trivalent bases cannot take the place of divalent or monovalent exchangeable bases in the zeolite portion of soils. It is true that exchangeable bases are released by leaching a zeolite with solutions of trivalent bases, but the trivalent cation does not apparently take the place of the replaced bases in the complex for the zeolite loses all base exchange capacity when leached with solutions of the trivalent salts.

The property of base exchange can, however, be completely restored by treating the inactivated zeolite with alkaline solutions.

The reaction of trivalent salts with the organic exchange complex was studied by using the same materials employed in the preceding study of the equivalency of the exchange. After leaching with HCl they were leached with 200 cc. of 0.2 normal $Al_2(SO_4)_3$, then washed free of soluble $Al_2(SO_4)_3$ with distilled water and finally leached with normal calcium acetate. The leachings all gave a negative test for aluminum showing that none had entered the exchange complex in an exchangeable form. They were then leached with 0.1 normal barium acetate and calcium determined in the leachate with the following results:

	1	2	3	4
M.E. Ca	26	43	85	88

These data show a notable loss in replacement capacity as compared with the original replacement capacity of the samples. They were then leached with four 10-cc. portions of 0.1 normal $Ba(OH)_2$, with 200 cc. of normal calcium acetate, then with .1 normal barium acetate and calcium determined in the leachate with the following results:

	1	2	3	4
M.E. Ca	203	170	374	374

The soil ligno-hemicelluloses have been completely restored to their original replacement capacity while the lignin and synthetic humus have been greatly increased.

After the above treatments the same samples were again leached with 0.1 normal aluminum chloride, washed free of excess salt and then leached with exactly neutral normal barium acetate solution. These leachings were tested qualitatively for aluminum and all were negative. They were also titrated with 0.1 normal barium hydroxide using the quinhydrone electrode with the following results:

	1	2	3	4
Replaceable H as M.E.....	140	120	250	256

These experiments indicate that organic matter possesses exchange properties somewhat similar to those of the inorganic exchange complex except that in the case of the inorganic compound there was no fixation of hydrogen from the aluminum salt solution and the exchange capacity was completely lost. The organic complex loses a part of its replacement capacity which is completely restored by subsequently treating the material with an alkaline solution, but fixes some hydrogen in replaceable form. Additional experiments were conducted to confirm these observations. Half-gram samples of (1) corn cob lignin, (2) soil lignin (resi-

due from alcoholic NaOH extract of soil No. 2) and (3) lignohemicellulose from soil No. 2 (aqueous NaOH soluble material) were weighed into 100-cc. beakers. Twenty-five cc. of normal sodium acetate (pH 7.5) were added, well mixed and allowed to stand for 18 hours. An excess of normal AlCl_3 was added, sufficient to make the whole distinctly acid. After several hours they were filtered and the residue leached with 100 cc. of 0.1 normal AlCl_3 , then with normal calcium acetate, carefully leached with distilled water and then leached with 200 cc. of 0.1 normal barium acetate. Calcium was determined in the leachate with the following results:

	1	2	3
Orig. rep. cap. as M.E.....	60*	160	350
Final rep. cap. as M.E.....	62	60	195

These were then leached with 0.2 normal HCl to remove the fixed barium, then leached slowly with four 10-cc. portions of saturated $\text{Ba}(\text{OH})_2$ solution, then with 250 cc. of normal CaCl_2 and the fixed calcium determined by subsequent leaching with dilute HCl. The results are given in the following table:

	1	2	3
Orig. rep. cap. as M.E.....	60	160	350
Final rep. cap. as M.E.....	99	168	345

Thus by means of a different experimental procedure the exchange capacity of the soil organic matter has been greatly reduced, by treating the sodium salt with AlCl_3 in the presence of an excess of the sodium ion after which the replacement capacity was completely restored by treatment with a solution of $\text{Ba}(\text{OH})_2$.

A similar experiment using a divalent salt of the organic complex was also conducted employing the same materials designated above by the numbers 1, 2, and 3. These were treated in duplicate with 25 cc. of saturated $\text{Ba}(\text{OH})_2$ solution for 18 hours. They were then filtered and leached with 200 cc. of normal calcium acetate, then with 200 cc. of 0.1 normal barium acetate and calcium determined in the leachate with the following results:

	1	2	3
Rep. cap. as M.E.....	120	210	355

*These figures for corn cob lignin do not show a loss in replacement capacity. It is believed that there was actually a loss of a portion built up during the sodium acetate treatment. This is indicated by the final replacement capacity of 99 M.E. given in the next table and the fact that the replacement capacity of lignin is markedly increased by contact with alkaline salt solutions.

They were then leached with 200 cc. of 0.1 normal AlCl_3 and barium determined in the leachate with the following results:

	1	2	3
Rep. cap. as M.E.....	126	200	354

They were then leached with distilled water and one each of the duplicates leached with normal ammonium acetate and the others with 0.1 normal barium acetate. Neither of these leachings gave a test for aluminum showing that none had been fixed in replaceable form. The replacement capacities, or rather the amounts of ammonium and barium fixed in the above, are given in the following table:

	1	2	3
Rep. cap in M.E. NH_4	49	82	241
Rep. cap. in M.E. Ba.....	79	145	334

It is thus shown that the humus materials are not capable of fixing aluminum in a form which is replaceable by bases of neutral salt solutions. A slightly alkaline salt solution, better an acetate, will gradually restore the lost capacity of base exchange to the partially "killed" lignin complex. Restoration is more rapidly effected with a divalent acetate than with the acetate of a monovalent base, but the solution of a divalent hydroxide is best suited for a rapid and effective restoration. These observations are similar to those of Tyulin (24) which have already been cited namely that the exchange property of sodium humate is "killed" or, as he expresses it, is rendered passive by the solution of an aluminum salt. Hydroxides again render the complex active. On the other hand, the observations of Kappen (14) are somewhat at variance. He speaks of the aluminum and iron ions of raw humus being exchangeable for the bases of neutral salt solutions. This property was present in many of the plants making up raw humus and was not developed by humification.

In the preceding experiments it will be noted that there is a wide variation in the exchange capacity of lignin depending upon the preliminary treatment to which the material is subjected. On the other hand, this does not hold true for the organic complex extracted by aqueous NaOH which is remarkably constant in all cases.

Using an exactly neutral solution of barium acetate (pH 6.8—7.0) a replacement capacity of only 18 M.E. per 100 grams was obtained for corn cob lignin which could be gradually and steadily increased by continuously leaching with this same solution. A higher replacement capacity was obtained by using a more alkaline solution of barium acetate such as pH 7.4. Finally the highest replacement capacity was obtained by treating the lignin with barium hydroxide solution by which it was increased from 18 M.E. to 126 M.E.

This indicates that the lignin complex during the long time when it is subjected to chemical and biological soil reactions, undergoes certain changes in properties, possibly a rearrangement of the elements or a change in the nature of the groups themselves, which increases the exchange capacity of this material. In other words, our investigations indicate a lower replacement capacity in lignin from original plant material than that from soil, but a greater capacity for "build-up" in the former.

SUMMARY

1. A study of the base exchange property of highly organic soils has been made.
2. The exchange capacity of highly organic soils is approximately a linear function of the percentage carbon in the soil.
3. There is no relation between the nitrogen or nitrogen-carbon ratio and the exchange capacity of highly organic soils.
4. Base exchange in highly organic soils takes place in chemically equivalent proportions.
5. Using hydrogen peroxide as a reagent for destroying organic matter in soils, the loss in exchange capacity is approximately a linear function of the amount of organic matter destroyed.
6. This loss in exchange capacity is due to a destruction of the organic fraction which functions in base exchange reactions. That is, the active organic fraction is not simply rendered passive as happens when it is treated with solutions of aluminum salts.
7. Digestion with hydrogen peroxide does not affect the replacement capacity of natural bentonites but destroys a rather definite part of the exchange capacity of synthetic zeolites.
8. Hydrogen peroxide is of value for the approximate determination of the exchange capacity of the organic matter of soils by a "difference method."
9. Lignin, ligno-hemicellulose, and ligno-cellulose or related bodies function largely as the exchange compounds of soil organic matter.
10. Lignin from corn cobs, lignin from soil (prepared by extraction with alcoholic NaOH), synthetic humus, and ligno-hemicellulose (prepared by extracting the soil with aqueous NaOH) all showed a definite chemically equivalent exchange capacity.
11. Our experiments indicate that the trivalent aluminum ions of $Al_2(SO_4)_3$ or $AlCl_3$ cannot enter the organic exchange complex and replace the divalent or monovalent ions absorbed by the lignin or lignin-like bodies.

12. There is a partial loss in replacement capacity of lignin-like bodies when they are leached with a solution of aluminum chloride which loss is however restored by treating the soil with a basic hydroxide or the solution of a salt, such as an acetate, which will yield hydroxyl ions by hydrolysis.

13. Further work on the nature of the exchange reaction of organic matter is being continued in this laboratory.

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