ACID SOIL STUDIES: I. A STUDY OF THE BASIC EXCHANGE BETWEEN SOIL SEPARATES AND SALT SOLUTIONS

R. H. ROBINSON

Oregon Agricultural Experiment Station

Received for publication January 18, 1921

INTRODUCTION

Most soils of Western Oregon, comprising chiefly the Willamette Valley and coast-lands are acid according to the usual methods now employed for the estimation of soil acidity. Field experiments show that while most of these acid soils respond to lime treatment, apparently some of them do not, as is indicated by the failure to get an increase in crop yields from the application of lime. Furthermore, some soils that may be judged neutral or only slightly acid respond well to lime treatment. A study of these different acid soils was undertaken with the hope that some differential factors might be disclosed that would explain the reason why some acid soils respond to lime treatment and others do not.

A phase of the work reported herein considers the reactions of several salt solutions on the soil separates that were segregated by a mechanical analysis of the samples. A review of the literature does not reveal any investigational work that has been done on the soil separates that would give light on the nature of the acidity, whether the sand fraction would show a greater or less acidity than the clay fraction or other points that might bear on the subject at hand.

PROCEDURE

Four characteristic acid soils were selected for the study and given the laboratory numbers 11076 to 11080, inclusive. The lime requirements determined by two methods and the classification according to the nomenclature of the Bureau of Soils, U. S. Department of Agriculture, are given in table 1.

Observations of field tests subsequently confirmed by pot experiments showed that applications of lime in different amounts to soil 11077 did not increase either legumes or grain crops.

The soil separates were obtained by a mechanical analysis of the different samples and each subdivision was isolated for study. In all samples there was only a very small amount of fine gravel which was subsequently discarded. The coarse and medium sand were combined and listed as coarse sand. The fine sand and the very fine sand were likewise combined and listed as fine sand. The silt or particles having a diameter between 0.005 to

0.05 mm. were separated from the clay particles in the usual manner and dried at room temperature. The clay or particles less than 0.005 mm. in diameter were obtained by transferring the soil solutions containing the clay in suspension to large shallow dishes and evaporating to dryness in the sunlight. Soil 11076 contained a very small amount of coarse sand which was added to the fine sand separate. The percentages obtained by this classification are given in table 2.

TABLE 1
Lime requirements of soils by two methods
Pounds of CaCO_3 per 2,000,000 pounds of soil

NUMBER	SOIL TYPE	VEITCH METHOD	JONES METHOD
		pounds	pounds
11076	Willamette silt loam.....	3,200	2,620
11077	Salem gravelly loam.....	1,500	2,160
11079	Clay loam.....	10,000	6,200
11080	Medium sandy loam.....	20,800	12,600

TABLE 2
The percentages of different separates in soils

NUMBER	COARSE SAND	FINE SAND	SILT	CLAY
	per cent	per cent	per cent	per cent
11076		28.0	52.1	19.9
11077	25.6	42.0	22.5	9.9
11079	28.5	26.5	29.2	15.8
11080	38.3	29.4	23.7	8.6

Five different salts, namely potassium nitrate, potassium chloride, potassium acetate, calcium acetate and sodium chloride, were used in the study. Approximately 0.1 *N* solutions of each of these salts were prepared. The exact amount of salt in 50 cc. of the 0.1 *N* solutions was determined by evaporating to dryness on the steam bath and finally to constant weight in the electric oven at 105°C. The amounts found were as follows:

KNO_3	0.4854
KCl	0.3745
$\text{K}(\text{C}_2\text{H}_3\text{O}_2)$	0.5024
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	0.3900
NaCl	0.2900

Of the salt solutions prepared above 150-cc. portions were transferred to 250-cc. bottles and 15 gm. of the various soil separates were added to each respectively. The bottles were then agitated in a mechanical soil shaker for 3 hours and centrifuged at a high speed until all soil particles had settled and the supernatant liquid was clear. Aliquots of 50 cc. were then taken for

titration and for the determination of the salt content. The acidity liberated by the various salt solutions was determined by titration with 0.04 *N* sodium hydroxide with phenolphthalein indicator. Table 3 gives the number of cubic centimeters of 0.04 *N* sodium hydroxide that was required to neutralize the acidity of the soil separates liberated by the different salt solutions.

The 50-cc. portions taken for the determination of the salt content were evaporated to dryness in a flat-bottom dish and dried to constant weight in

TABLE 3

The amount of NaOH required to neutralize the acidity in 50 cc., employing the 0.1 N salt solution designated

SOIL NUMBER	SEPARATE	K (C ₂ H ₃ O ₂)	KCl	KNO ₃	Ca(C ₂ H ₃ O ₂) ₂	NaCl
		cc.	cc.	cc.	cc.	cc.
11076	Sand	2.50	0.03	0.03	3.00	0.03
11076	Silt	2.50	0.03	0.03	2.70	0.03
11076	Clay	4.50	0.20	0.24	5.30	0.10
11077	Coarse sand	2.00	0.06	0.06	2.44	0.03
11077	Fine sand	1.30	0.03	0.03	1.80	0.03
11077	Silt	2.44	0.14	0.06	3.10	0.03
11077	Clay	1.82	0.40	0.40	2.30	0.20
11079	Coarse sand	4.80	0.20	0.22	5.00	0.11
11079	Fine sand	4.50	0.20	0.20	4.60	0.11
11079	Silt	5.50	0.22	0.22	5.60	0.12
11079	Clay	5.20	0.38	0.40	5.00	0.22
11080	Coarse sand	11.42	1.80	1.40	12.00	0.42
11080	Fine sand	11.30	1.42	1.82	11.40	0.40
11080	Silt	9.80	1.36	1.50	9.40	0.42
11080	Clay	10.40	1.10	1.00	10.60	0.68

the electric oven at 105°C. Table 4 reports the actual amount of salt contained in 50 cc. of the salt solution used, the amount found after contact with the soil separates and the differences, that is, whether there was a greater or less amount of salt after contact with the soil separates than before. The plus (+) sign indicates that the quantity of salt in 50 cc. after contact with the separates was greater by the amount designated, than the amount contained in 50 cc. of the prepared solution; the minus (−) sign indicates the opposite to the plus sign, that is, a decrease in the amount found after contact with the soil particles.

TABLE 4

The amount of salts found in 50 cc. of solution before and after contact with soil separates

SOIL NUM- BER	DESCRIPTION	POTASSIUM CHLORIDE			SODIUM CHLORIDE					
		Amount used	Amount found	Difference	Amount used	Amount found	Difference			
		gm.	gm.	gm.	gm.	gm.	gm.			
11076	Sand	0.3745	0.4170	0.0425+	0.2933	0.3456	0.0523+			
11076	Silt	0.3745	0.4118	0.0373+	0.2933	0.3320	0.0387+			
11076	Clay	0.3745	0.4160	0.0415+	0.2933	0.3344	0.0411+			
11077	Coarse sand	0.3745	0.4070	0.0325+	0.2933	0.3176	0.0243+			
11077	Fine sand	0.3745	0.4036	0.0291+	0.2933	0.2972	0.0039+			
11077	Silt	0.3745	0.3794	0.0049+	0.2933	0.2990	0.0057+			
11077	Clay	0.3745	0.3988	0.0243+	0.2933	0.3300	0.0367+			
11079	Coarse sand	0.3745	0.3868	0.0123+	0.2933	0.3398	0.0435+			
11079	Fine sand	0.3745	0.3984	0.0239+	0.2933	0.3200	0.0267+			
11079	Silt	0.3745	0.3998	0.0253+	0.2933	0.3250	0.0317+			
11079	Clay	0.3745	0.4140	0.0395+	0.2933	0.3310	0.0377+			
11080	Coarse sand	0.3745	0.3942	0.0207+	0.2933	0.3256	0.0323+			
11080	Fine sand	0.3745	0.3878	0.0133+	0.2933	0.3134	0.0201+			
11080	Silt	0.3745	0.4000	0.0245+	0.2933	0.3184	0.0251+			
11080	Clay	0.3745	0.4270	0.0475+	0.2933	0.3482	0.0549+			
		POTASSIUM ACETATE			CALCIUM ACETATE			POTASSIUM NITRATE		
		Amount used	Amount found	Difference	Amount used	Amount found	Difference	Amount used	Amount found	Difference
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
11076	Sand	0.4854	0.5066	0.0112+	0.3900	0.3926	0.0026+	0.5024	0.5100	0.0076+
11076	Silt	0.4854	0.4824	0.0016-	0.3900	0.3960	0.0060+	0.5024	0.5240	0.0216+
11076	Clay	0.4854	0.4806	0.0048-	0.3900	0.3832	0.0068-	0.5024	0.5150	0.0126+
11077	Coarse sand	0.4854	0.5046	0.0192+	0.3900	0.3814	0.0086-	0.5024	0.5160	0.0136+
11077	Fine sand	0.4854	0.5038	0.0184+	0.3900	0.3866	0.0034-	0.5024	0.5146	0.0122+
11077	Silt	0.4854	0.4828	0.0026-	0.3900	0.3856	0.0044-	0.5024	0.5040	0.0016+
11077	Clay	0.4854	0.4830	0.0024-	0.3900	0.3878	0.0022-	0.5024	0.5232	0.0232+
11079	Coarse sand	0.4854	0.4678	0.0176-	0.3900	0.3774	0.0126-	0.5024	0.5110	0.0086+
11079	Fine sand	0.4854	0.4814	0.0040-	0.3900	0.3802	0.0098-	0.5024	0.5116	0.0092+
11079	Silt	0.4854	0.4772	0.0082-	0.3900	0.3788	0.0112-	0.5024	0.5160	0.0136+
11079	Clay	0.4854	0.5106	0.0252+	0.3900	0.3836	0.0064-	0.5024	0.5230	0.0206+
11080	Coarse sand	0.4854	0.4646	0.0208-	0.3900	0.3628	0.0272-	0.5024	0.5038	0.0014+
11080	Fine sand	0.4854	0.4652	0.0202-	0.3900	0.3592	0.0318-	0.5024	0.4932	0.0092-
11080	Silt	0.4854	0.4762	0.0092-	0.3900	0.3636	0.0364-	0.5024	0.4944	0.0080-
11080	Clay	0.4854	0.4756	0.0098-	0.3900	0.3891	0.0009-	0.5024	0.5264	0.0240+

DISCUSSION

According to the results given in table 3, the acidity of the various separates of a certain soil was slightly different but the different salt solutions showed a wide range in the amount of acidity liberated. The greatest amount of acidity was set free by the salts of an organic acid, namely, potassium acetate and calcium acetate, while the salts of the inorganic acids, potassium nitrate, potassium chloride, and sodium chloride, gave much lower results. Similar observations have been made by other workers when salt solutions and the soil as a whole were used. It is interesting to note that the smaller particles or the clay separates which may be assumed to contain most of the soil colloids and organic matter, did not show a much higher acidity and in several cases less acidity than the coarse sand separates.

In table 4 we observe that the various salt solutions have a widely different effect on the soil separates as judged by the amount of the salt in solution after contact with the soil fractions. Here again we see a distinct difference between the action of salts of the organic and inorganic acids. Calcium-acetate and potassium-acetate solutions contained in almost every case a lower salt content after contact than before contact with the soil separates. The salts of the mineral acids, on the other hand, gave an increased amount after treatment with the soil particles. This was contrary to the results reported by Parker (3) in his work on selective adsorption by soils where he found a loss in salt content after contact with the soil. Furthermore, sodium chloride, although liberating the smallest amount of acidity, gave the highest salt content in solution after contact with the soil particles. In order to ascertain if possible the reason for the variation in the acidity of the soil separates, the causes for the difference in salt content of a solution after contact with the soil separates, and the manner in which the salts of organic and inorganic acids react, the experiment was repeated, and close observation of any significant reaction noted. Besides using 0.1 *N* salt solutions, normal solutions of the salts also were prepared and used in a similar manner to the weaker solutions. The salt content of the normal solutions was not determined after contact with the soil particles, since it was thought that the solvent effects and reaction of the stronger solutions on the soil particles would be so great that no reliable inferences could be drawn therefrom. Table 5 gives the number of cubic centimeters of 0.04 *N* NaOH required to neutralize the acidity liberated by normal salt solutions.

The presence of aluminum in a salt extract of an acid soil has long been known and reported by many workers. Likewise, during the titration of the potassium-chloride and potassium-nitrate solutions with sodium hydroxide after contact with the soil particles, it was observed that an appreciable amount of aluminum hydroxide and in most instances small amounts of iron hydroxide were precipitated out. The amounts varied somewhat for the separates of the different soils and may be summed up as follows: no. 11076

gave no visible amount of iron hydroxide; no. 11077, on the other hand, showed larger amounts of iron than aluminum, the quantity of the former varying somewhat in the different separates; the precipitate from no. 11079 and 11080 consisted chiefly of aluminum hydroxide with varying amounts of iron hydroxide in the separates. These observations were substantiated by the qualitative colorimetric method recently suggested by Comber (1) in which the characteristic red color of ferric thiocyanate was developed by treating the soil separates with alcoholic potassium-thiocyanate solution, the potassium of the potassium thiocyanate, displacing the iron which subsequently formed the color reaction. Furthermore, potassium-nitrate and chloride solutions after contact with soil 11080 showed only a slight acidity

TABLE 5

The amount of NaOH required to neutralize the acidity in 50 cc., employing the 1.0 N salt designated

SOIL NUMBER	SEPARATE	K(C ₂ H ₃ O ₂)	KCl	KNO ₃	Ca(C ₂ H ₃ O ₂) ₂
		cc.	cc.	cc.	cc.
11076	Sand	4.40	0.20		5.60
11076	Silt	4.00	0.10		5.00
11076	Clay	10.70	0.16		5.24
11077	Coarse sand	4.30	0.03		7.40
11077	Fine sand	2.40	0.03		4.30
11077	Silt	5.10	0.03		8.00
11079	Coarse sand	11.20	0.90	0.70	10.26
11079	Fine sand	9.90	0.90	0.70	10.40
11079	Silt	12.86	0.90	0.75	13.16
11079	Clay	12.30	0.94	0.72	
11080	Coarse sand	20.80	5.20	4.82	18.50
11080	Fine sand	19.40	4.12	4.80	19.10
11080	Silt	24.50	5.00	4.86	16.10

to methyl orange indicator, while after contact with the other soils the salt solutions were apparently neutral. Since salt solutions of aluminum chloride and aluminum nitrate are neutral to methyl orange and acid to phenolphthalein and appreciable amounts are present in the salt solution after contact with the separates, it is evident that the acidity liberated by salts of inorganic acids of the soil under observation is due to basic exchange in which the stronger basic elements, potassium and sodium, displace iron and aluminum and the latter pass into solution as nitrate or chloride depending upon the salt used for extraction, and may subsequently be titrated with sodium hydroxide, with phenolphthalein as an indicator. This conclusion was further substantiated by means of Truog's (6) zinc-sulfide method for acidity. It was observed in the Truog test for acidity in which calcium chloride and zinc sulfide is used and the degree of acidity present estimated by the intensity

of coloration of lead acetate paper, that the salts aluminum nitrate, aluminum chloride and ferric chloride gave similar indications of acidity depending upon the amount of salt used. Consequently, comparisons were made between the intensity of color produced by an amount of aluminum nitrate, approximately equal to the quantity of aluminum and iron hydroxide liberated from soil 11079 by a normal solution of potassium nitrate, and the intensity of color produced by the acidity of the soil as a whole. The intensity of the color produced by the aluminum nitrate and by the soil was approximately the same.

The chemical composition of the soil separates and the distribution of organic matter and soil colloids in the different separates may be factors that would influence the results reported in the tables above and thus account for any variation that appears abnormal. In a consideration of these points it may be assumed that most of the soil colloids are present in the finest particles or clay separates. The chemical composition of soil separates prepared

TABLE 6
The average amount of several constituents in soil separates

CONSTITUENT	SAND	SILT	CLAY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
SiO ₂	88.50	83.05	45.52
Fe ₂ O ₃	1.66	1.96	8.73
Al ₂ O ₃	5.48	8.44	22.57
CaO.....	0.59	0.48	0.64

TABLE 7
Percentage of organic matter in the separates of a soil

SOIL NUMBER	COARSE SAND	FINE SAND	SILT	CLAY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
11079	4.60	3.67	5.95	6.06

from ten different samples has been investigated by Steinkoenig (5). The average amounts of silicon oxide, iron oxide, aluminum oxide and calcium oxide found in the various soil separates are given in table 6.

The results indicate that the large particles or sand separates contain the highest amount of silicon oxide while the finer or silt separates contain higher amounts of calcium, iron and aluminum oxides. Failyer *et al* (2) report greater amounts of lime, magnesia, potash and phosphoric acid in the finer particles or clay separates, which was confirmed also by Steinkoenig (5). In regard to the distribution of organic matter it is probable that larger amounts will be found in the finer particles or clay separate. In order to confirm this assumption a determination of organic matter in the separates of soil 11079 was made. The Rather (4) hydrogen fluoride method was followed. The results are given in table 7.

The very fine particles or the clay and silt separates contain approximately the same amount of organic matter. The coarse sand, apparently, contains a higher amount of organic matter than the fine sand but this is probably due to the fact that small roots and other debris that were too large to be classified with the very fine sand were present in visible quantities in the coarse sand. When we consider, therefore, the differences in the composition of the various soil separates, the unequal distribution of colloids and organic matter, the molecular weight of the elements that take part in the basic exchange, and the solvent effect of the salt solutions, it is obvious that the slight variation in the acidity of the soil separates and the variation in the amount of salt found after contact with the separates, may be explained.

From the results obtained with the salts of the organic acid, namely, calcium acetate and potassium acetate, it is apparent that a different reaction has taken place from that indicated by the salts of mineral acids. A far greater amount of acidity was liberated while there was a decrease in the salt content of 50 cc. after contact with the soil separates. If the reaction had been similar, but more intense as indicated by higher acidity, to the reaction of the salts of mineral acids, a large increase in the salt content of the 50 cc. would be expected after contact with the soil separates. On account of the dissimilarity of the reactions another explanation was sought.

Examinations of the organic salt solutions after contact with the soil separates did not show the presence of iron and aluminum hydroxide when neutralized with sodium hydroxide, as was evident with the salts of inorganic acids. A determination of the calcium content of the calcium-acetate solution before and after contact showed that appreciable quantities of calcium had been taken up by the soil but no metallic elements had been displaced in the reactions. Furthermore, since there was a decrease in the salt content after reaction with the soil, it was thought that the calcium may have been selectively adsorbed or by basic exchange had replaced the hydrogen of hydrous silicates. In either case free acetic acid would be formed and by distillation could be quantitatively determined. Accordingly, 20 gm. of soil 11079 was introduced into a bottle containing 200 cc. of calcium-acetate solution, the calcium content of which had been accurately determined. The bottle was then shaken in a mechanical shaker for 3 hours, centrifuged to clarify the solution and filtered. Fifty-cubic-centimeter portions of the clear solution were then taken for the determination of the acidity liberated as indicated by titration immediately with sodium hydroxide, with phenolphthalein as an indicator, and 50 cc. for distillation which would give the acetic acid present. The distillation was allowed to proceed nearly to dryness and the distillate titrated with sodium hydroxide, with phenolphthalein as an indicator. Also 25-cc. aliquots were taken and the calcium content determined and calculated to calcium acetate. The results are given in table 8.

The results show that the calcium taken up by the soil from the calcium-acetate solution was equivalent approximately to the acetic acid liberated.

Furthermore, we see that the acidity of the distillate was the same as the acidity of the salt solution that had not been distilled. This indicates that all of the acidity liberated in the reaction was acetic acid. Considered from this standpoint, the reason for an actual decrease in the salt content of the organic salt solutions after reaction with the soil particles, can be understood. The calcium was removed from the salt solution and was replaced by hydro-

TABLE 8

Amount of calcium acetate in solution before and after contact with soil and the calcium acetate equivalent of the acetic acid liberated

SOIL NUMBER	BEFORE CONTACT	AFTER CONTACT	DIFFERENCE	ACID LIBERATED	ACIDITY OF DISTILLATE
	gm.	gm.	gm.	gm.	gm.
11079	0.3520	0.2982	0.0538	0.0484 (12.27 cc. 0.05 N NaOH)	0.0479 (12.12 cc. 0.05 N NaOH)

TABLE 9

H⁺ ion concentration of soil separates

SOIL NUMBER	SEPARATE	$E \frac{N}{10}$	pH
11076	Sand	0.650	5.31
11076	Silt	0.650	5.31
11076	Clay	0.654	5.38
11077	Coarse sand	0.696	6.09
11077	Fine sand	0.686	5.92
11077	Silt	0.683	5.87
11077	Clay	0.683	5.87
11079	Coarse sand	0.658	5.44
11079	Fine sand	0.640	5.14
11079	Silt	0.668	5.61
11079	Clay	0.666	5.58
11080	Coarse sand	0.642	5.17
11080	Fine sand	0.644	5.21
11080	Silt	0.642	5.17
11080	Clay	0.640	5.14

gen. The difference in the atomic weight of calcium and hydrogen would necessarily result in a smaller salt content even though the acetic acid were not removed during the evaporation process.

The actual acidity of the soil separates as indicated by the hydrogen-ion concentration was determined by the gas-chain method. Three-gram portions of the different soil separates were transferred to small bottles that served as the electrode vessel. Two cubic centimeters of conductivity water was added to each separate and allowed to stand 24 hours. Immediately

before the determination was made, more water was added to obtain 3 gm. of soil to 30 cc. of water. The increase in potential due to the H^+ ion, was obtained by taking readings directly from a millivoltmeter. The voltage at 25° , $E \frac{N}{10}$, and the Sorensen pH values are given in table 9.

The results indicate that the hydrogen-ion concentration of different separates of the soils under observation is approximately the same. Apparently, therefore, the size of the soil particles, the presence of colloids or organic matter in the clay separates or the composition of the different separates does not have a great influence on the hydrogen-ion concentration.

SUMMARY

A study of the action of several salt solutions on the soil separates has been made.

The acidity of the different soil separates liberated by action of a certain salt solution is approximately the same.

The manner in which the salts of mineral acids, KNO_3 , KCl and $NaCl$ react with the soils studied, is apparently different from the salts of an organic acid, $K(C_2H_3O_2)$ and $Ca(C_2H_3O_2)_2$.

The so-called acidity liberated by potassium nitrate, potassium chloride, and sodium chloride was due mainly to aluminum and iron rendered soluble by basic exchange.

The acidity produced by calcium acetate and potassium acetate was due to acetic acid liberated either by replacement of the hydrogen of hydrous silicates or by selective adsorption of the basic element in the salt solution.

The hydrogen-ion concentration of different separates of the soil was constant.

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