

### LXIII.—*The Interaction of Ammonium Salts and the Constituents of the Soil.*

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It has been observed that the application of neutral ammonium salts, such as the sulphate and the chloride, to soils has resulted in the production of an acid reaction. In the field this was first noticed on the experimental plots of the Royal Agricultural Society at Woburn, where the soil is sandy and deficient in calcium carbonate; the application of 200 lb. per acre of ammonium sulphate and chloride in mixture every year for about twenty-five years brought the soil into such an acid condition that it reddens blue litmus paper and will no longer allow of the growth of barley (see Voelcker, *J. Roy. Agric. Soc.*, 1899, 60, 515, and 1901, 62, 286). A similar acid reaction is found upon some of the permanent grass plots at Rothamsted, where still larger amounts of ammonium salts have been used for a longer period, but the arable plots at Rothamsted show no such acidity, because of the considerable proportion of calcium carbonate contained in their soil. From time to time various observers have noted an acid reaction produced in the laboratory when soil is treated with a neutral solution of an ammonium salt, but this is only true of a few soils, and is due to the formation and subsequent hydrolysis of ferric and aluminium salts (Veitch, *J. Amer. Chem. Soc.*, 1904, 26, 637).

In the course of an investigation into some of the effects brought about by this acidity the action of dilute solutions of ammonium salts on the various constituents of a normal soil was examined in some detail and the present paper deals with that part of the work. The first examination of the action of ammonium salts on the soil is due to Way (*J. Roy. Agric. Soc.*, [i], 11, 323; 13, 123), who showed that a double decomposition takes place, ammonium being withdrawn from solution and an equivalent amount of calcium, magnesium, potassium, or sodium passing into solution. Other investigators (see A. Voelcker, *J. Roy. Agric. Soc.*, [i], 1860, 21, 105; Warington, *Trans.*, 1868, 21; Van Bemmelen, *Zeitsch. physikal. Chem.*, 1895, 18, 331; Armsby, *Amer. J. Sci.*, 1877, [iii], 14, 75) have extended Way's observations and determined quantitative relations between the amounts of soil and the ammonium absorbed. In the general process by which the soil absorbs ammonium salts, none of which washes through the soil into the drainage water under normal conditions, there is also some reaction with the calcium carbonate in the soil with the production of ammonium carbonate and calcium salts, but the comparative magnitude

of the two reactions with the clay and the calcium carbonate has remained doubtful.

The authors have not used soil in their investigations, but have taken its proximate constituents separately, namely, sand, clay, humus, and calcium carbonate. The trials with sand and with silica of various origin may be dismissed at once since no action could be detected. For the experiments with clay a fine modelling clay of a light grey colour was used, showing in the dry state the following composition :

$\text{Al}_2\text{O}_3$ , 20.46 ;  $\text{Fe}_2\text{O}_3$ , 1.04 ;  $\text{CaO}$ , 0.20 ;  $\text{MgO}$ , 0.17 ;  $\text{K}_2\text{O}$ , 1.67 ;  $\text{Na}_2\text{O}$ , 1.03 ;  $\text{SiO}_2$ , 68.70 ; constitutional water, 5.57 ; moisture lost at  $100^\circ$ , 0.82 ; total 99.66.

It is clear that the clay contains a considerable proportion of finely-divided silica ; the alumina present would only be equivalent to about 51 per cent. of kaolinite in the whole. It was dried and powdered, so that from the bulk an equal sample could be taken for each experiment. As a rule 100 grams of dry clay were placed in an Erlenmeyer flask with 300 c.c. of the solution of ammonium salt and the mixture shaken for twenty hours in an end-over-end revolving shaker. It was found that in this period of twenty hours the action was completed, indeed it probably takes place with considerable rapidity. After shaking, the mixture was filtered and an aliquot portion of the clear liquid taken for estimation of the ammonia by distillation with soda and titration.

The following facts were observed :

(1) No production of free acid could be detected ; the reaction of the salt solution was determined, using  $N/100$  acid or alkali and methyl-orange or phenolphthalein as indicators, both before and after shaking with the clay, but no change was found. As it seemed possible that free acid might arise through hydrolysis of the ammonium salt followed by evaporation of the ammonia, other experiments were tried in which the salt solution was allowed to evaporate spontaneously in contact with the clay, or was placed with the clay in a gas washing bottle through which a rapid stream of ammonia-free air was passed for three days, but in neither case was there a measurable development of free acid or any loss of ammonia.

In another experiment the air was replaced by carbon dioxide, but with a similar negative result.

(2) There is no withdrawal of the acid radicle from solution. Determinations were made of the chlorine in the solution before and after shaking with the clay, but no change could be estimated. Similarly, when ammonium sulphate was used determinations of the sulphuric acid in solution before and after shaking showed no withdrawal of sulphuric acid. This agrees with the observations of previous workers.

Since there is no change of reaction and no withdrawal of the acid radicle from solution, it follows that there is no "adsorption" or "laking out" of the salt as a whole, at any rate not in quantities appreciable by ordinary gravimetric methods. In another connexion in the Rothamsted laboratory measurements were made of the conductivity of very dilute solutions of ammonium salts before and after adding a small amount of clay; no change in the conductivity of the solution occurs such as would be found if an appreciable amount of the salt were withdrawn from solution.

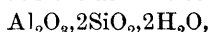
It follows then that the reaction of the ammonium salts on the clay must be purely one of double decomposition, and by qualitative analysis calcium, magnesium, and potassium were found in the final solution.

In a quantitative experiment the following results were obtained on shaking up 300 grams of clay with 900 c.c. of  $N/5$  ammonium chloride:

	Gram.
$\text{NH}_3$ absorbed per 100 grams of clay	= 0.1200
Ca in solution per 300 c.c.	= 0.0283 = 0.0481 gram of $\text{NH}_3$
Mg    "      "	= 0.0506 = 0.0717   "      "
K      "      "	= 0.0076 = 0.0033   "      "
	<hr/>
	0.1231

No aluminium was found in solution. It will be seen that the calcium, magnesium, and potassium in solution were equivalent to the ammonium precipitated, sodium being present only in traces if at all.

Clay is a product of the weathering of various double silicates like the felspars, and although in the main it consists of kaolinite,



as the analysis shows, it still contains other bases which form with the alumina, double hydrated silicates of a zeolitic nature. That the reaction is with zeolitic substances in the clay may be inferred from the following experiments, in which 50 grams of the clay, 50 grams of a washed kaolin, and 50 grams of natrolite (pure picked crystals ground fine) respectively, were shaken with 300 c.c. of  $N/10$  solution of ammonium chloride:

	Gram $\text{NH}_3$ removed from solution.	$\text{NH}_3$ in solution.
Clay .....	0.073	0.437
Kaolin .....	0.051	0.459
Natrolite .....	0.061	0.449

The natrolite gives results intermediate between those of the clay and the kaolin and all three are of the same order. The compound formed by the introduction of ammonium into the clay molecule is a stable one, which does not yield up ammonium on washing with pure water, as has been stated.

It is seen that the absorption of the ammonium from the solution is by no means complete; although as much as 50 grams of clay were in contact with only 1.605 grams of ammonium chloride, in the position of equilibrium attained, there was six times as much ammonia in solution as was combined with the clay.

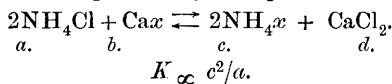
Further experiments were then made to ascertain the character of the reaction: in the first series the amount of clay was kept constant, and it was always present in large excess; the amount of water was also constant, the ammonium salt being the variable. The following results were obtained:

TABLE I.—*Reaction of 100 grams clay with 300 c.c. solution.*

<i>Ammonium chloride.</i>				
Original concentration of $\text{NH}_4\text{Cl}$ .	Gram $\text{NH}_3$ originally present in 300 c.c.	Gram $\text{NH}_3$ left in solution.	Gram $\text{NH}_3$ on solid.	Percentage removed.
<i>N</i> /10	0.51	0.384	0.126	24.7
<i>N</i> /12	0.408	0.293	0.115	28.1
<i>N</i> /15	0.34	0.236	0.104	30.5
<i>N</i> /20	0.255	0.165	0.090	35.3
<i>N</i> /30	0.17	0.102	0.068	40.26
<i>N</i> /50	0.102	0.053	0.049	48.0
<i>N</i> /100	0.051	0.020	0.031	60.0

<i>Ammonium sulphate.</i>				
Concentration of $(\text{NH}_4)_2\text{SO}_4$ .				
<i>N</i> /10	0.5082	0.3888	0.1194	23.5
<i>N</i> /12	0.4278	0.3234	0.1044	24.4
<i>N</i> /15	0.3474	0.2562	0.0912	26.25
<i>N</i> /20	0.2616	0.1812	0.0804	30.7
<i>N</i> /30	0.1686	0.1059	0.0627	37.2
<i>N</i> /50	0.1074	0.0603	0.0471	43.8
<i>N</i> /100	0.0521	0.0234	0.0287	55.1

These results can be expressed by an equation of the type,



Thus for strengths of ammonium chloride between *N*/10 and *N*/100 the mean value of *K* is 0.046, whilst for ammonium sulphate it becomes 0.0354.

The accompanying curves show a comparison between the experimental result and the calculated curve, using the mean values for *K* already given; the discrepancy between the result with *N*/10 ammonium chloride and the calculated position is due to the fact that about this point the clay ceases to combine with any further ammonium.

Other salts of ammonium were also tried, the carbonate and the phosphate, and as the results show when expressed in the curves,

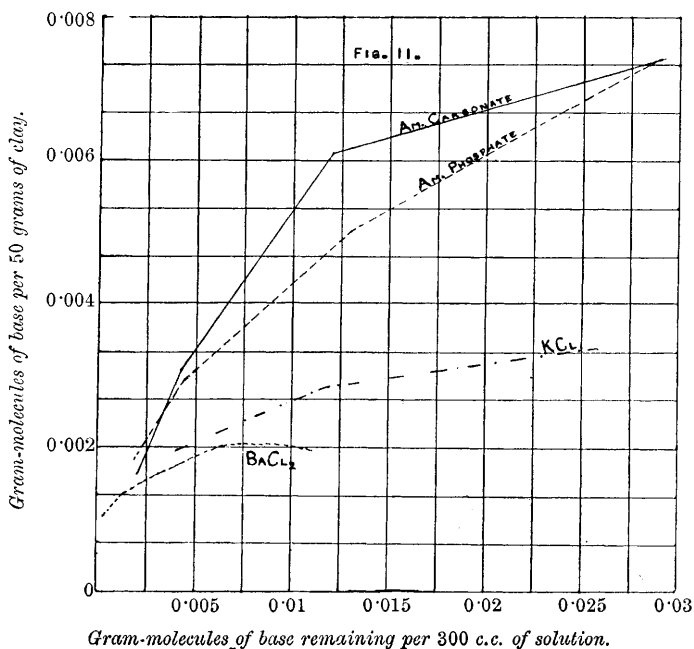
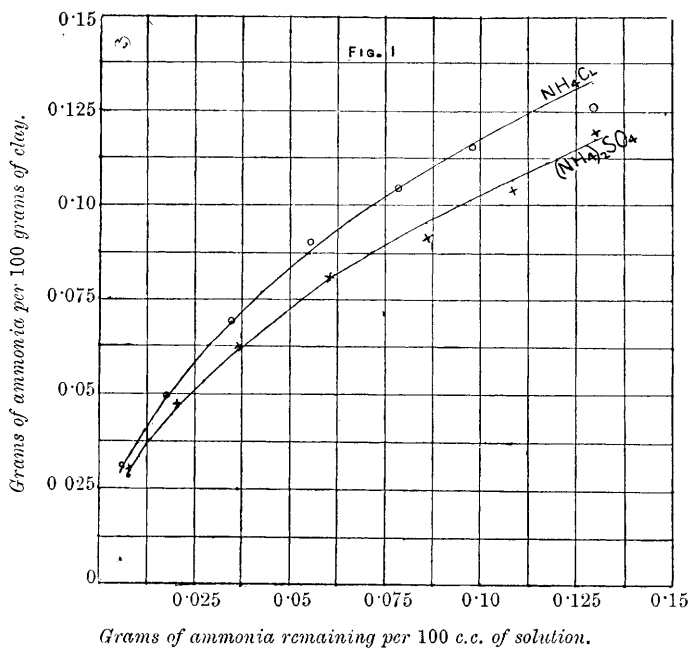


Fig. 2, the reaction was of a similar nature, as also was the reaction with barium and potassium chlorides and hydrochloric acid. In the case of ammonium phosphate and carbonate some of the acid was also removed from solution, as would naturally be the case through the formation of insoluble salts of calcium and magnesium. Determinations are given below for the amount of phosphoric acid going out of solution :

*Fifty grams clay shaken with 300 c.c. solution.*

Strength of solution.	After shaking.	Percentage of $P_2O_5$ withdrawn.
5.22 grams $P_2O_5$ per litre	4.73 grams $P_2O_5$ per litre	9.4
1.044     "     "	0.901     "     "	13.7
0.522     "     "	0.423     "     "	18.96

Attempts were made to determine the absorption of ammonium hydroxide, but failed owing to difficulties of manipulation. The clay became deflocculated and would not settle from the mixture even when left to stand for months, for the same reason it could not be filtered, and attempts to bring about a separation by centrifuging also failed.

TABLE II.—*Reaction of 50 grams clay with 300 c.c. solution.*

Concentration of Am. phosphate.	Gram $NH_3$ originally present in 300 c.c.	Gram $NH_3$ left in solution.	Gram $NH_3$ on solid.
N/10	0.51	0.407	0.103
N/20	0.255	0.1846	0.0704
N/50	0.102	0.061	0.041
N/100	0.051	0.026	0.025
Concentration of Am. carbonate.			
N/10	0.51	0.406	0.104
N/20	0.255	0.169	0.086
N/50	0.102	0.059	0.043
N/100	0.051	0.023	0.023
Concentration of $BaCl_2$ .	Grams Ba originally present in 300 c.c.	Grams Ba left in solution.	Gram Ba on solid.
	1.747	1.483	0.264
	1.164	0.882	0.282
	0.873	0.632	0.241
	0.349	0.165	0.184
	0.175	0.038	0.137
Concentration of KCl.	Grams K originally present in 300 c.c.	Grams K left in solution.	Gram K on solid.
	1.1367	1.0053	0.1314
	0.5688	0.4604	0.1084
	0.2274	0.055	0.0724

TABLE II.—*Reaction of 50 grams clay with 300 c.c. solution (continued).*

Concentration of HCl.	Gram H originally present in 300 c.c.	Gram H left in solution.	Gram H on solid.
<i>N</i> /10	0·03	0·0258	0·0042
<i>N</i> /20	0·015	0·01146	0·00354
<i>N</i> /50	0·006	0·0037	0·0023

In all the above cases the clay was present in large excess; when the ammonium salts are in excess the reaction proceeds until a definite point is reached and then stops, so that a given weight of clay removes the same amount of ammonium from solution whatever the strength of the solution of ammonium salt with which it is in contact.

It is difficult to attain a satisfactory degree of accuracy in the experiments bearing on this point; it is impossible to remove the clay by filtration and wash it free from the adhering liquid, because as soon as the salts in the latter have been reduced below a certain point the clay becomes deflocculated and begins to pass through the filter paper. When, again, the concentration of the solution in ammonium is determined before and after shaking with the clay, as in the previous experiments, and the ammonium withdrawn by the clay determined by difference, we have to deal with large quantities of ammonium and all the errors in their estimation are multiplied and thrown on the small difference which is the quantity sought. This method, however, had to be followed: the solutions were made up by weight and the quantities weighed, and other precautions were taken to ensure accuracy, but still the figures sought, the ammonium withdrawn from solution by 100 grams of clay, are not in very close agreement, although sufficiently so to indicate the nature of the reaction.

The following table shows the results of shaking 900 c.c. of *N*/5, *N*/10, and *N*/20 ammonium chloride solution with 225, 150, 60, and 30 grams of clay respectively:

TABLE III.—*Reaction of clay with ammonium chloride in excess.*

Grams clay.	Grams $\text{NH}_4\text{Cl}$ solution.	Grams $\text{NH}_3$ in original solution.	Grams $\text{NH}_3$ in solu- tion at end.	Gram $\text{NH}_3$ removed by clay.	Gram $\text{NH}_3$ re- moved by 100 grams clay.
<i>N</i> /5 Series.					
125	504·48	1·7067	1·5373	0·1694	0·136
83·33	504·15	1·7057	1·5582	0·1475	0·177
60	907·45	3·0701	2·9925	0·0776	0·129
					} mean 0·147
<i>N</i> /10 Series.					
225	905·35	1·5409	1·2401	0·3008	0·133
150	903·70	1·5376	1·2842	0·2534	0·169
60	905·58	1·5408	1·4560	0·0848	0·141
					} mean 0·148

TABLE III.—*Reaction of clay with ammonium chloride in excess*  
(continued).

Grams clay.	Grams $\text{NH}_4\text{Cl}$ solution.	Gram $\text{NH}_3$ in original solution.	Gram $\text{NH}_3$ in solu- tion at end.	Gram $\text{NH}_3$ removed by clay.	Gram $\text{NH}_3$ re- moved by 100 grams clay.
<i>N/20 Series.</i>					
125	500.7	0.4275	0.3106	0.1169	0.094
83.33	502.32	0.4289	0.3370	0.0919	0.110
60	903.3	0.7713	0.7029	0.0684	0.114
30	904.17	0.7721	0.7311	0.0410	0.137

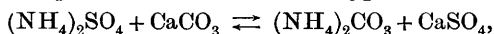
It will be seen that when varying quantities of clay were shaken with  $N/5$  and  $N/10$  solutions of ammonium chloride, 100 grams of clay withdrew approximately 0.147 gram of ammonium from solution, whatever the quantity of solution with which it was in contact. With the  $N/20$  solution, and particularly with the large amounts of clay, the mass of the clay began to exercise a sensible influence on the result, and the amount of ammonium withdrawn per 100 grams of clay fell.

Only when the amount of clay was reduced to 30 grams in contact with 900 c.c. of  $N/20$  ammonium chloride did the amount of ammonium withdrawn per 100 grams of clay approximate to the amount withdrawn when the clay was in contact with the stronger solutions.

The particular limit of saturation for the ammonium on the clay indicated in these experiments, 0.147 gram per 100 grams of clay, was found to vary with each sample of clay employed. Even variations in the drying process, through which portions of the stock material were put, altered the limit, so that it is necessary to prepare at one time a sufficient quantity to carry through the whole series. The clay used in the latter experiments is thus not strictly comparable with the clay used in the previous series, although they were originally two samples from a common stock.

#### *Effect of Calcium Carbonate.*

Since the share taken by calcium carbonate in the absorption of ammonium salts by soil is still doubtful, the authors made some determinations by shaking up 300 c.c. of similar ammonium sulphate solutions with 50 grams of powdered calcium carbonate. The results showed that an equilibrium reaction of the type:



takes place, and that only a small proportion of the ammonium sulphate changes into carbonate, even when the calcium carbonate is present in large excess.



A fuller series of experiments made with 200 c.c. of solutions of ammonium chloride and 20 grams of finely-divided calcium carbonate (a precipitate obtained in a hard-water softening process on a large scale) gave the following results. Preliminary trials showed that the reaction was complete in the twenty-four hours allowed for shaking :

TABLE IV.—20 Grams of calcium carbonate and 200 c.c. of ammonium chloride solution.

NH <sub>3</sub> present (grams per 200 c.c.).	CaO finally in solution (gram per 200 c.c.).	NH <sub>3</sub> equivalent to Ca dissolved (gram per 200 c.c.).
3·398	0·0506	0·0308
2·832	0·0442	0·0268
2·269	0·0428	0·0261
1·700	0·0348	0·0211
0·680	0·0240	0·0145
0·340	0·0162	0·00982
0·17	0·0110	0·0066

These figures conform to an equation of the type :

$$K \propto \frac{(\text{CaCl}_2)^2}{\text{NH}_4\text{Cl}},$$

which is of the same type as the reaction with clay.

These experiments do not agree with the statements of Way (*loc. cit.*) and Knop (*Boniterung der Ackereide*, 1871, 49), who maintain that calcium carbonate is without action on the ammonium salts.

When ammonium chloride solutions were shaken with a mixture of 50 grams of clay and 10 grams of calcium carbonate, the total precipitation of ammonium was somewhat increased, but the type of the reaction remained unchanged, as shown by the results below :

TABLE V.

Gram NH <sub>4</sub> per 300 c.c.	Gram NH <sub>4</sub> taken up by 50 grams clay alone.	Gram NH <sub>4</sub> taken up by 50 grams clay + 10 grams CaCO <sub>3</sub> .
0·51	0·073	0·084
0·255	0·057	0·069
0·102	0·034	0·036

Since few soils would contain as much as 10 grams of calcium carbonate per 50 grams of clay, it may be concluded that the main reaction when ammonium salts are applied to the soil takes place with the clay, although the calcium carbonate will afterwards continue to decompose the zeolitic ammonium compound as ammonium carbonate is removed by nitrification. It has been shown (Hall and Miller, *Proc. Roy. Soc.*, 1905, B, 77, 1) that the ultimate result of applying ammonium salts to the soil is the removal of an approximately equi-

## 686 AMMONIUM SALTS AND THE CONSTITUENTS OF THE SOIL.

valent amount of calcium carbonate, although Ashby (*Jour. Agric. Science*, 1907, 2) found that the zeolitic ammonium compound can be nitrified without further base.

*Experiments with Humus.*

The action of clay on ammonium salts having failed to give rise to any acid reaction, a similar series of trials was made with humus in place of clay.

Three samples of peat were employed :

(1) A sandy peat such as is used for orchid growing, consisting mainly of the debris of bracken not greatly decomposed.

(2) A loose sphagnum peat commonly sold as peat moss litter, still showing considerable vegetable structure.

(3) A solid black Irish peat from some depth, with no visible vegetable structure.

Qualitative tests for the production of acidity were also made with the decayed peaty grass residues which are to be found on the surface of some of the Rothamsted grass plots where the acid reaction of the soil is most in evidence, and with the loose friable humus obtained from the interior of a hollow tree. In all cases the peat was first washed repeatedly with hot distilled water, although its acid reaction could never be entirely removed.

The first tests showed that there was no production of acidity when any of these samples of humus were shaken up with the solutions of ammonium salts. Determinations were made of the acidity of distilled water and of the ammonium salt solutions after shaking with equal weights of the same peat ; the acidity was barely measurable, but was less with the salt solutions than with pure water. Ammonium had, however, been removed from solution, hence some base must have been dissolved from the peat to maintain a neutral reaction. Qualitative tests showed this base to be calcium, and analysis of the peat ash showed the presence in the dry (No. 3) peat of 1.2 per cent. of CaO. It is concluded that the peat contains this calcium combined as humate, and that the reaction with ammonium salts consists in a double decomposition between the calcium humate and the ammonium salt.

The absorption of ammonium was then determined in the same way as with clay, after shaking 300 c.c. of the solution of the salt with 25 grams of peat. The following results show the reaction to be of a similar type to that with clay :

*25 Grams peat moss litter with 300 c.c.  $\text{NH}_4\text{Cl}$  solution.*

Strength of solution taken.	$\text{NH}_3$ in 300 c.c. originally.	$\text{NH}_3$ left in solution.	$\text{NH}_3$ on peat.
<i>N</i> /10	0·51	0·458	0·052
<i>N</i> /20	0·255	0·221	0·034
<i>N</i> /100	0·051	0·0424	0·0086

A further 50 grams of peat were then extracted with hydrochloric acid for forty-eight hours and repeatedly washed with hot distilled water to remove acid as far as possible. The residue was then shaken with *N*/10 ammonium chloride as before. After filtering, the solutions showed an acid reaction and ammonium had been withdrawn from solution, but the acidity was small, and some of the precipitated ammonium had been replaced by calcium, small quantities of which could be detected in solution, despite the digestion with strong acid to which the peat had been previously subjected. It seems, however, certain that free "humic acid" can to some extent decompose ammonium salts with the formation of an insoluble ammonium compound, and this is confirmed by the observation that whereas the humus, after all mineral acid had been washed away, yielded a brown solution on shaking with pure water, when shaken with the ammonium salt a colourless solution resulted.

As free "humic acid" does not appear to be a normal constituent of soils, this experiment does not vitiate the general conclusion reached by the authors that the constituents of the soil do not react with solutions of ammonium salts to produce a free acid. For the acid observed in the field experiments quoted a biological origin has now been found.

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