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I.—*On the part taken by Oxide of Iron and Alumina in the Absorptive Action of Soils.*

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SOME time ago I laid before the Society the results of some experiments upon the solubility of phosphate of calcium under various conditions.* Two of these experiments were upon the behaviour of hydrated ferric oxide and hydrated alumina when placed in contact with a solution of tricalcic phosphate in carbonic water; the result obtained was of a very decided character. In both cases the phosphoric acid was almost entirely abstracted from the solution, while the calcium remained dissolved in the form of carbonate.† This reaction suggested the idea that the power possessed by soils of removing phosphoric acid from its solutions was probably owing to the presence in soils of ferric oxide and alumina; that indeed the absorptive action of soil towards phosphoric acid was nothing more than an ordinary case of chemical affinity, the oxide of iron and alumina of the soil uniting with the phosphoric acid to form insoluble phosphates of iron and aluminium. To ascertain the correctness of this conclusion was the object of the first experiments; it was sought to discover whether the oxide of iron and alumina that occur in soil had the same action towards phosphoric acid as the precipitated ferric oxide and alumina previously employed.

* Jour. Chem. Soc. [2], iv, 296.

† The ferric oxide absorbed 95·7 per cent. of the phosphoric acid present, the whole of the calcium remained in solution. The alumina absorbed 96·8 per cent. of the phosphoric acid, and 95·6 per cent. of the calcium remained dissolved.

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I. *Absorption of Phosphoric Acid by Soil*.—The plan of the experiment was to take a soil and place it in contact with a solution of phosphate of calcium in carbonic water—to treat it in fact precisely as the precipitated ferric hydrate had been treated—to observe if absorption of phosphoric acid took place, and if so, whether this absorption were accompanied by a *decomposition* of the phosphate of calcium.

The conditions of the experiment required that the soils used should be as nearly as possible free from lime; since if lime were present it would dissolve in the carbonic water, and render valueless any determination of the proportion of calcium to phosphoric acid in the liquid after the action of the soil. Two soils were made use of. In the state in which they were employed they had the following composition. :—

	Soil A.	Soil B.
Moisture	1·54	6·57
Organic and volatile matter.....	3·69	17·03
Silica and insoluble silicates.....	87·31	55·29
Oxide of iron and alumina	6·82	19·31
Phosphoric acid	·05	·34
Lime.....	·11	·28
Magnesia.....	·14	·63
Potash.....	·16	·55
Carbonic acid, traces of other substances, and loss	·18	
	<hr/> 100·00	<hr/> 100·00

It will be remarked that soil B contained much more oxide of iron and alumina than soil A.

In the first experiments the attempt was made to free the soils entirely from soluble calcium salts before subjecting them to the action of the phosphate. To this end the soils were treated with water, and a stream of carbonic acid made to pass through the mixture, the water being removed by decantation every two or three days and fresh water substituted. As however after a long treatment of this nature fresh carbonic water still continued to remove traces of lime, the soils were further treated with dilute acetic acid, and then thoroughly washed with water.

Experiment 1.—600 grs. of soil A were freed from lime as above described, and then treated with 8000 grs. of a solution of tricalcic phosphate in carbonic water: carbonic acid was passed through the mixture from time to time. After 18 days the liquid was filtered from the soil, and the latter washed two or three times with carbonic water. The liquid yielded to analysis 1.09 grs. CaCO_3 , and .63 gr. $\text{Mg}_2\text{P}_2\text{O}_7$.

Experiment 2.—600 grs. of soil B treated exactly as soil A. After 17 days the liquid was removed: it yielded .74 gr. CaCO_3 , and .05 gr. $\text{Mg}_2\text{P}_2\text{O}_7$.

Experiment 3.—8000 grs. of the solution of tricalcic phosphate in carbonic water used in experiments 1 and 2, gave 1.92 grs. CaCO_3 , and 1.28 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.*

From these data we find that soil A had absorbed 50.8 per cent. of the phosphoric acid originally present, and 43.2 per cent. of the lime. Soil B had under the same circumstances absorbed 96.1 per cent. of the phosphoric acid, and 61.5 per cent. of the lime.

It is to be remarked in the first place, that soil B (the one containing the large amount of iron) had absorbed a much greater quantity of phosphoric acid than soil A. Next, that in neither case had the absorption of phosphoric acid and lime been equal, as it would have been had the tricalcic phosphate been absorbed without chemical change, but that each soil had removed more of phosphoric acid than lime from the solution, this being especially the case with soil B. Notwithstanding, the soils have not comported themselves entirely as the pure ferric oxide and alumina of the former experiments, for these while absorbing phosphoric acid, left, practically speaking, the whole of the lime in the solution, whereas the soils have each removed lime to a considerable extent. This removal of lime as well as phosphoric acid from the solution might of course be urged as evidence that the absorption of phosphoric acid by the soils could be only partially attributed to chemical affinity; that, in fact, phosphate of calcium had been withdrawn as such from the solution by mere physical attraction.

It is well known that lime, in common with other bases, comes within the influence of soil absorption; it seemed therefore not

* The solutions of phosphate of calcium used throughout these experiments were never saturated with the salt, lest any should be deposited in the soil by mere change of temperature or pressure.

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unlikely that the soils in these experiments, impoverished in lime as they actually were, had absorbed it by virtue simply of their affinity for itself: that in fact, the decomposition of the phosphate of calcium might have been *complete* so far as the absorption of phosphoric acid was concerned, and a portion of the carbonate of calcium produced have been subsequently removed from the solution by a distinct action of the soil. If therefore it could be shown that the soils used in the experiments absorbed carbonate of calcium from a carbonic solution, the force of the objection would cease, and the results obtained would become consistent with the idea, that the oxide of iron and alumina were the *only* agents in the absorption of the phosphoric acid.

The next experiment was planned with a view to determine the question. The trial was made with soil B, the soil which had given the greatest absorption both of lime and phosphoric acid.

Experiment 4.—400 grs. of soil B were treated with 5816 grs. of a solution of carbonate of calcium in carbonic water, gas being passed through the mixture from time to time. After three days, 5255 grs. of the solution were removed; they yielded 3.15 grs. CaSO_4 .

Experiment 5.—2371 grs. of the solution of carbonate of calcium used above gave 1.96 grs. CaSO_4 .

From these figures it appears that the solution in contact with the soil had contained 3.53 grs. of carbonate of calcium, of which .97 gr. was removed by the 400 grs. of soil.* This experiment leaves no doubt that the soil really possessed the property of removing lime from its solution in carbonic acid.

It was thought that by employing a soil less exhausted of lime than in the previous experiments, the quantity of lime absorbed by it from the solution might be reduced, and the decomposition of the phosphate of calcium made more evident; in the next experiment the treatment of the soil with acetic acid was therefore omitted.

Experiment 6.—400 grs. of soil B, well washed with carbonic water, were treated with 8000 grs. of a solution of tricalcic phosphate; gas passed each day. After six days the liquid was removed; it yielded 1.32 grs. CaCO_3 , and .12 gr. $\text{Mg}_2\text{P}_2\text{O}_7$.

* That the same soil should give up lime to a solution of carbonic acid, and yet absorb lime from a carbonic solution when offered to it in larger quantity, is quite agreeable to the laws of soil absorption.

Experiment 7.—8000 grs. of the solution of tricalcic phosphate used above yielded 2.59 grs. CaCO_3 , and 1.94 gr. $\text{Mg}_2\text{P}_2\text{O}_7$.

It appears that the soil had here absorbed 93.8 per cent. of the phosphoric acid contained in the tricalcic phosphate, and only 49.0 per cent. of the lime. The decomposition of the phosphate during the absorption is more evident than in the former experiments, owing to the smaller appetite of the soil for lime.

I think it will now be allowed that the two soils operated on have shown a power of decomposing phosphate of calcium, a power quite similar to that possessed by hydrated ferric oxide and alumina: that, in addition to this, the soils had the property of absorbing carbonate of calcium from its solution in carbonic acid. These points have been established, not indeed so fully as they might have been by a more extended research, but yet sufficiently to show that the ferric oxide and alumina of a natural soil, have the same power of removing phosphoric acid from solution and combining with it which is possessed by the precipitated hydrates. Such being the case it follows that in all soils containing a sufficient amount of oxide of iron or alumina, the phosphoric acid will be found in combination with these bases, and not as an alkaline or alkaline-earthly phosphate. It is evident also that in such soils phosphate of iron or aluminium must be the ultimate state of all phosphoric acid applied in manure. When we recollect the small amount of phosphoric acid that occurs in soil, and the universal and generally abundant presence of ferric oxide, it appears that the exceptions to this rule must be very rare.

It is too much however to say that a soil in every case removes phosphoric acid from solution solely by virtue of the oxide of iron and alumina which it contains. Dr. Voelcker has shown that when a solution of superphosphate of lime is brought in contact with various soils, it is the soil which contains most calcium that generally removes the greatest quantity of phosphoric acid. Way has also told us that soils have the property of removing carbonic acid from its solution in water, so that a saturated solution of phosphate of calcium in carbonic water would deposit on contact with soil.

There are thus several ways in which phosphate of calcium may be thrown out of solution on contact with soil; but though the oxide of iron takes no part in these comparatively sudden

actions, it must in every case *finally* convert the phosphate of calcium into phosphate of iron.

The property belonging to ferric oxide, alumina, and soil, of readily decomposing phosphate of calcium, had not I think been previously ascertained; several writers have however ascribed to the ferric oxide and alumina of soil the power of combining with phosphoric acid. The only research on the subject I have met with is a recent one of Dr. Peters.* He tried to discover the condition in which phosphoric acid exists in soil by acting upon soils with a variety of solvents. The conclusion he draws from an extended research is, that by far the greater part of the phosphoric acid contained in soils is combined with iron and aluminium. The view thus confirmed is strikingly opposed to that idea of the absorptive power of soils advocated by Liebig, who tells us that the power of absorption depends on a surface attraction enjoyed by all the component parts of a fertile soil, in which the attracted particles enter into no chemical combination; and that the arable soil will withdraw phosphoric acid without any chemical interchange with the constituents of the earth taking place.*

We pass now to another part of the subject. What is the action of the oxide of iron and alumina of a soil towards potash, ammonia, and other bases, which soils are known readily to remove from solution? In the hope of affording some answer to this question, the behaviour of pure hydrated ferric oxide and alumina towards solutions of potassium and ammonium salts was made the subject of the next experiments. The series will be found in many points incomplete, but being at present unable to pursue it further, I must be content to speak with doubt on points where further research might clear the subject.

II. *Absorption of Carbonate of Potassium by Ferric Oxide.*—The ferric oxide was prepared by precipitating a dilute solution of ferric chloride by ammonia; the precipitate was washed by decantation till no trace of chlorine was found in the washings. The ferric oxide was next transferred to a large filter, and the excess of water removed by pressure between blotting paper. The amount of water present was determined in a portion of

* Ueber das Verhalten der Phosphorsäure in Erdboden. (*Annalen der Landwirtschaft*, January 1867, p. 31.)

† Liebig's *Natural Laws of Husbandry*, pp. 67–9.

the mass by ignition, and the remainder taken for the absorption experiment.

Of course all hygroscopic water would diffuse into the salt-solution, while the water of hydration would remain with the ferric oxide. As the absorption of salt was ascertained only by the weakening of the solution, it was essential to know exactly the amount of water diffused into it from the moist hydrate; the state of hydration of the ferric oxide had thus to be determined. This was done in two instances, and being found constant, the result was adopted for all the experiments.

Hydrated ferric oxide prepared as above, and dried over oil of vitriol, gave in one case 15.66 per cent.; in another, 15.45 per cent. of water. According to Wittstein, the hydrate when freshly precipitated contains 25.71 per cent. of water ($\text{Fe}_2\text{H}_6\text{O}_6$), but after keeping for some time under water contains but 14.75 per cent. ($\text{Fe}_4\text{H}_6\text{O}_9$). It is seen that the hydrate prepared as above had not quite reached this last stage.

Two solutions of carbonate of potassium were employed; solution A contained .9905 per cent.; solution B .9993 per cent. K_2CO_3 . In all the experiments with carbonate of potassium, the salt was determined in the form of nitrate.

Experiment 1.—234 grs. of hydrate containing 80 per cent. of water, and 4420 grs. of solution A; the mixture shaken from time to time. After two days the liquid was filtered. 510 grs. of the solution gave 6.62 grs. KNO_3 , or .8872 per cent. K_2CO_3 . The oxide of iron had here removed 2.99 grs. K_2CO_3 , or 6.38 for 100 of the anhydrous oxide present.

Experiment 2.—188 grs. of moist hydrate containing 80 per cent. water, and 4420 grs. of solution A, saturated with carbonic acid before addition of the iron. After five days, 510 grs. of solution gave 6.59 grs. KNO_3 , or .883 per cent. K_2CO_3 . The ferric oxide had here absorbed 3.48 grs. K_2CO_3 , or 8.72 per cent. of the anhydrous oxide present.

Experiment 3.—409 grs. of hydrate containing 84.4 per cent. water, with 2090 grs. solution B. After two days, 652.7 grs. of solution gave 5.55 grs. KNO_3 , or .5812 per cent. K_2CO_3 . The hydrate had here absorbed 6.80 grs. K_2CO_3 , or 10.67 per cent. of the anhydrous oxide present.

Experiment 4.—880 grs. of hydrate kept under water five months, containing 88 per cent. of water, with 3383 grs. solution B. After three days, 561.6 grs. of solution gave 5.46 grs.

KNO_3 , or '6644 per cent. K_2CO_3 . The ferric oxide had here removed 6'31 grs. K_2CO_3 , or 6'00 per cent. of the anhydrous oxide present.

In all these experiments we have a considerable absorption of potassium. Experiments 3 and 4 were the first two made; in these, and especially in 3, the mixture of the pasty hydrate with the potassium solution was less perfect than was afterwards obtained; the absorption is possibly therefore below the normal amount. The smallest absorption is in experiment 6, where the ferric hydrate had been kept several months before use. Leaving out this result, we have a mean absorption of 8'39 K_2CO_3 , or 5'72 K_2O , for 100 anhydrous ferric oxide.

It appears from experiment 4, that the presence of carbonic acid is no hindrance to the absorption.

With a view of throwing some light, if possible, on the precise nature of the absorptive action which took place in the above experiments, the amount of carbonic acid removed by the ferric oxide from the carbonate of potassium solution, was determined in three cases. The determination of carbonic acid was effected by means of an ammoniacal solution of chloride of barium.

It appeared that in every case more potassium had been taken from the solution than carbonic acid. In experiment 1, for 10 equivalents of potassium absorbed, 3'6 equivalents of carbonic acid were absorbed. In experiment 3, for 10 equivalents of potassium, 4'5 equivalents of carbonic acid were absorbed. In experiment 4, the proportion was for 10 of potassium, 7'9 of carbonic acid.

The proportions here are very various, much more so than can be accounted for by ordinary experimental error. The variation is certainly connected with the difference in the *amount* of the absorption; the smaller the extent of the absorption, the larger is the proportion of potassium removed. This is at once evident on comparing the figures already quoted.

	Potassium absorbed for 100 originally present.	Equivalents of car- bonic acid absorbed, for 10 of potassium.
Experiment 1	6'84	3'6
Experiment 3	18'67	4'5
Experiment 4	32'57	7'9

The reason of this behaviour is readily perceived. The

ferric oxide commences by absorbing potash, almost to the exclusion of carbonic acid; by so doing, the proportion of carbonic acid in the liquid is increased, but this accumulation of carbonic acid in the liquid now acts as a check on the further decomposition of the potassium salt, which consequently takes place to a less and less extent as the absorption progresses. The experiments are too few, and differ too much in their conditions to give a precise account of this action, they only point to its existence.

III. *Absorption of Nitrate of Potassium by Ferric Oxide.*—The nitrate of potassium solution used contained 1·049 per cent. KNO_3 .

Three experiments were made with ferric oxide;* in the first no absorption took place, in the second the absorption amounted to ·45 per cent. of the anhydrous oxide, in the third experiment the absorption was ·46 per cent. of the anhydrous oxide present. Rejecting the first trial, which is open to the same objection as experiment 3 in the last section, we have a mean absorption of ·455 KNO_3 , or ·211 K_2O , for 100 of anhydrous ferric oxide.

It is a well known fact that soils absorb but little from many salts of potassium and ammonium, unless carbonate of calcium be at the same time present; and that when absorption has taken place under these circumstances, the acid of the salt is found remaining in the solution in combination with calcium. That is to say, soils can absorb but little potassium and ammonium from certain salts; but if these salts be decomposed by carbonate of calcium, then absorption takes place. With these facts in view experiments were made to see if the presence of carbonate of calcium would increase the amount of potassium removed by the ferric oxide.

The residue from the third experiment was taken: to it were added some more nitrate of potassium solution, and 33 grs. of dried, precipitated, carbonate of calcium. After seven days there had been a further absorption of ·14 gr. KNO_3 ; or ·10 for 100 of anhydrous oxide.

The absorption being so small, the residue from the above was further treated with 50 grs. carbonate of calcium, and carbonic acid gas passed for eight hours through the mixture.

* The details of these and of the subsequent experiments were given in the original paper, they are here omitted for want of space.

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After two days it was found that no additional absorption had taken place.

It appears then that the addition of carbonate of calcium only very slightly increased the absorption of the potassium salt, and that saturation of the liquid with carbonic acid produced no greater effect.

IV. *Absorption of Sulphate of Potassium by Ferric Oxide.*—The sulphate of potassium solution employed contained 1·077 per cent. of sulphate of potassium.

In the experiment with hydrated ferric oxide the absorption amounted to 2·27 K_2SO_4 , or 1·23 K_2O , for 100 of anhydrous oxide. The addition of 50 grs. carbonate of calcium gave no further absorption in three days.

V. *Absorption of Chloride of Potassium by Ferric Oxide.*—The chloride of potassium solution contained 1,053 per cent. of chloride of potassium.

In the absorption experiment the ferric oxide was found to have taken up ·42 KCl, or ·27 K_2O , for 100 of the oxide present.

VI. *Absorption of Carbonate of Potassium by Alumina.*—The experiments with alumina were performed exactly as those with oxide of iron, the same salt-solutions were employed. The alumina was prepared by precipitating a solution of alum with ammonia, and except in the earlier experiments, the precipitate was, after some washing, re-dissolved in hydrochloric acid, and again thrown down by ammonia; washing by decantation being then continued, till no chlorine could be detected in the washings.

The water of hydration was determined in a specimen thus prepared:—Dried over oil of vitriol, it lost on ignition 33·14 per cent.; the formula $Al_2H_6O_6$ requires 34·50 per cent. As the water of hydrated alumina has not been observed to alter in amount with the age of the hydrate, the theoretical percentage was adopted in all the calculations.

Two absorption experiments were made with the carbonate of potassium solution; in the first the salt absorbed was 2·24 per cent. of the alumina present; in the second it amounted to 2·31 per cent. The mean is 2·275 K_2CO_3 , or 1·55 K_2O , for 100 of alumina. In the first experiment the alumina was several months old; the amount of absorption is, however, very slightly below that shown by freshly prepared alumina.

One experiment was made to determine whether any absorption of carbonic acid had taken place; the result showed that no carbonic acid had been absorbed. I made no further experiments on the decomposition of carbonate of potassium by alumina; but it is evident that alumina, like ferric oxide, possesses the power of decomposing the salt.

VII. *Absorption of Nitrate of Potassium by Alumina.*—One experiment was made; the absorption was $\cdot 42$ KNO_3 , or $\cdot 195$ K_2O , for 100 of alumina.

The residue from the experiment was treated with carbonate of calcium, and the liquid saturated with carbonic acid; a further absorption of $\cdot 04$ per cent. KNO_3 took place: this amount is so small as to be quite within the errors of experiment.

VIII. *Absorption of Sulphate of Potassium by Alumina.*—The absorption in one experiment amounted to $\cdot 84$ per cent. of the alumina present, or to $\cdot 45$ per cent. reckoned as K_2O . The solution at the end of the experiment was observed to be slightly alkaline.

IX. *Absorption of Carbonate of Ammonium by Ferric Oxide.*—The carbonate of ammonium employed was the sesquicarbonate of commerce; the opaque coating of each fragment was, however, removed; the analyses made showed that the salt was nearly two-thirds monocarbonate.

Two solutions of carbonate of ammonium were employed. One contained $\cdot 3222$ per cent. NH_3 ; the other $\cdot 3363$ per cent. NH_3 . The determinations were all made by titration.

Three absorption experiments were made. In the first, 100 of ferric oxide absorbed $2\cdot 08$ NH_3 ; in the second the ferric oxide had been preserved for several months, the absorption was here $1\cdot 58$ per cent.; in the third experiment the absorption was $2\cdot 39$ per cent. Taking the mean of the two trials with freshly-prepared hydrate, we have an absorption of $2\cdot 235$ NH_3 for 100 of ferric oxide, or $6\cdot 31$ per cent. reckoned as $2(\text{NH}_4)\text{CO}_3$. The hydrated oxide which had been kept long under water showed, as in the previous instance, a lower absorptive power.

Carbonic acid determinations were made in the carbonate of ammonium solution, and in the solution after absorption in the second experiment. The result showed that for 10 equivalents of ammonia $10\cdot 12$ equivalents of carbonic acid had been taken up by the ferric oxide in that experiment; the ammonia had thus been absorbed as mono-carbonate. It appears then that ferric hydrate is capable of decomposing the supercarbonates of

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ammonium; more than this can hardly be concluded from a single experiment.

X. *Absorption of Sulphate of Ammonium by Ferric Oxide.*—The solution of sulphate of ammonium employed contained $\cdot 356$ per cent. NH_3 , or $1\cdot 382$ per cent. of sulphate of ammonium. In this and all the other experiments with salts of ammonium, excepting those with the carbonate, the ammonia was determined by distillation with caustic potash and titration.

Two absorption experiments were made. In the first the ferric oxide took up $2\cdot 40$ per cent.; in the second experiment $2\cdot 69$ per cent. of sulphate of ammonium. The mean absorption was therefore, $2\cdot 545$ $2(\text{NH}_4)\text{SO}_4$, or $\cdot 66$ NH_3 , for 100 of ferric oxide. The liquid became very distinctly alkaline during the absorption.

Carbonate of calcium was added to the residue from the second experiment, and the liquid saturated with carbonic acid, but no further absorption was obtained.

XI. *Absorption of Chloride of Ammonium by Ferric Oxide.*—The solution of chloride of ammonium contained $\cdot 958$ per cent. of that salt, or $\cdot 3044$ per cent. NH_3 .

The ferric oxide absorbed in one experiment $\cdot 24$ NH_4Cl , or $\cdot 08$ NH_3 , for 100 of the oxide present. The solution became distinctly alkaline.

On the addition of carbonate of calcium a further absorption took place, amounting to $\cdot 32$ NH_4Cl for 100 of ferric oxide.

XII. *Absorption of Nitrate of Ammonium by Ferric Oxide.*—The salt-solution contained $1\cdot 552$ per cent. nitrate of ammonium, or $\cdot 3298$ per cent. NH_3 .

In one experiment the absorption of nitrate of ammonium amounted to $\cdot 41$ per cent. of the ferric oxide, or to $\cdot 09$ per cent. reckoned as NH_3 . The solution, as in the preceding experiments, became distinctly alkaline.

The addition of carbonate of calcium produced a further absorption of $\cdot 28$ per cent. NH_4NO_3 .

XIII. *Absorption of Carbonate of Ammonium by Alumina.*—The same salt-solutions were used in the following experiments with alumina, as in the corresponding trials with oxide of iron:—

Two experiments were made. In the first the absorption of ammonia amounted to $\cdot 76$ per cent. of the alumina present; in the second experiment the absorption was $1\cdot 45$ per cent. of the alumina. The difference between these experiments is very great; it was unfortunately not observed till there was no

longer an opportunity of repeating the experiments. The mean gives an absorption of 1.105 NH_3 for 100 of anhydrous alumina, or 3.12 per cent. reckoned as $2(\text{NH}_4)\text{CO}_2$.

No experiment was made as to the proportion of carbonic acid absorbed.

XIV. Absorption of Sulphate of Ammonium by Alumina.—In one experiment the absorption of sulphate of ammonium amounted to 1.13 per cent. of the alumina present, or to .29 per cent. reckoned as NH_3 .

The solution at the end of the experiment was found to be decidedly alkaline; the same fact has been already mentioned as having been observed in the experiments with ferric oxide; the reaction is apparently due to a decomposition of the salt, and a greater absorption of its acid than of its base. In the experiment above described, the alkaline reaction was perhaps more marked than in any of the preceding experiments; it was thought, therefore, worth while to determine the absorption of acid which had taken place. The result showed that while 3.09 per cent. of the ammonia present had been absorbed, there had been removed 8.71 per cent. of the sulphuric acid; or for 10 equivalents of ammonia, 28.2 equivalents of sulphuric acid had been taken up.

No experiments were made as to the absorption of chloride or nitrate of ammonium by alumina.

To facilitate the discussion of the results arrived at in the before-mentioned experiments, the proportion of each salt absorbed by the ferric oxide and alumina is given in the following table:—

Absorption of Salts of Potassium by Hydrated Ferric Oxide and Hydrated Alumina.

Salt employed.	Strength of Solution.		Amount absorbed by 100 anhydrous ferric oxide.		Amount absorbed by 100 anhydrous alumina.	
	Per cent. of salt.	Per cent. of K_2O .	Amount of salt.	Amount of K_2O .	Amount of salt.	Amount of K_2O .
Carbonate of potassium.....	.995*	.678*	8.39	5.72	2.27	1.55
Sulphate of potassium	1.077	.582	2.27	1.23	.84	.45
Chloride of potassium	1.053	.664	.42	.27	no experiment	
Nitrate of potassium	1.049	.488	.45	.21	.42	.19

* Two solutions of the salt were employed; their strength differed but little.

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Absorption of Salts of Ammonium by Hydrated Ferric Oxide and Hydrated Alumina.

Salts employed.	Strength of solution.		Amount absorbed by 100 anhydrous ferric oxide.		Amount absorbed by 100 anhydrous alumina.	
	Per cent. of salt.	Per cent. of NH_3 .	Amount of salt.	Amount of NH_3 .	Amount of salt.	Amount of NH_3 .
Carbonate of ammonium†	·930*	·329*	6·31	2·23	3·12	1·10
Sulphate of ammonium	1·382	·356	2·54	·66	1·13	·29
Chloride of ammonium	·958	·304	·24	·08	no experiment	
Nitrate of ammonium	1·552	·330	·41	·09	no experiment	

It is probable that if stronger solutions had been employed, the absorption by the oxide of iron and alumina would have been greater, and, on the other hand, that if weaker solutions had been used, the absorption would have been less. This rule has been well ascertained in the case of soil absorption. It follows, of course, that the figures quoted above expressing the amount of absorption can refer only to those particular conditions under which the experiments were made. The potassium solutions all contained about 1 per cent. of salt. With the ammonium solutions a better plan was adopted; each solution contained nearly the same amount of ammonia—about ·33 per cent.

On looking at the results collected in the table, it is at once evident that the absorptive power of alumina is not nearly so great as that possessed by ferric oxide. Of carbonate and sulphate of potassium the ferric oxide absorbs about three times as much as the alumina; with the corresponding ammonium salts it takes up about twice as much as the alumina. This was an unexpected fact, as from the lower equivalent of alumina it was presumed that it would exhibit a greater power of absorption than ferric oxide.

* Two solutions of the salt were employed; their strength differed but little.

† The carbonate of ammonium is here reckoned as $(2\text{NH}_4)\text{CO}_3$; for the actual composition of the carbonate used, see back.

The other prominent fact exhibited by the table is the very different absorption of the different salts. Both with potassium and ammonium salts the carbonate is absorbed to a considerable extent, the sulphate to a small extent, while of the chloride and nitrate only traces are taken up. The order of absorption appears to be the same for alumina as for ferric oxide, as far as the experiments allow us to judge.

Such seem to be the principal facts regarding the amount of absorption; it may be next asked, what is the real nature of the action here observed? There is a considerable amount of evidence that the absorption is due to a weak chemical affinity. First, it is found that a decided preference is shown for the salts of certain acids. It is also observed, that in these cases of ready absorption, the salt is nearly always decomposed to a considerable extent. Ferric oxide and alumina in absorbing carbonate of potassium take up much more potassium than carbonic acid; sesquicarbonate of ammonium is decomposed by ferric oxide in a similar manner. Sulphate of potassium and sulphate of ammonium are decomposed by alumina, and, especially in the case of the latter salt, much more sulphuric acid is taken up than base. Ferric oxide also decomposes sulphate of ammonium, and to a less extent the chloride and nitrate of ammonium. The absorption of sulphate of potassium by ferric oxide is the only instance of a notable absorption, apparently unattended with decomposition. It appears then, that chemical affinity was engaged in the process of absorption. That to the action of such affinity the absorption should be referred in every case is very probable, but hardly permits of being established by evidence.

The compound of the metallic hydrate and the alkaline salt is decomposed by water, but not without some difficulty. The action of water was tried on ferric hydrate saturated with carbonate of potassium. After two washings, with thorough agitation, each washing remaining in contact one day, the iron was found to have lost two-thirds of its potassium. The washing was sufficient to have reduced a perfectly soluble salt to $\frac{1}{4}$ th its original quantity.

The amount of ammonia present in the ferric hydrate prepared for use in the absorption experiments was determined. The ferric hydrate, precipitated by ammonia from ferric chloride, was of course originally saturated with ammonia; to render it free

of chlorides, it received in the instance selected 14 washings. By calculation only $\frac{1}{5000000}$ th of the salt originally present would remain with the hydrate at the end of the operation. On distilling a portion of it with caustic potash it yielded ammonia equal to .042 per cent. of the anhydrous oxide present. A trace of ammonia was thus pertinaciously held by the ferric oxide, notwithstanding the abundant washing it had undergone.

Such is the character, as far as the present investigation goes, of the absorptive action of hydrated oxide of iron and alumina. Do the properties here recognized agree with those actually possessed by soils? may we in short conclude, that the absorptive power exhibited by soil towards potash and ammonia is in any way connected with the presence in soil of the hydrates of ferric oxide and alumina?

It is well known that soils usually contain a considerable proportion of ferric oxide in a more or less hydrated condition; they appear also to contain small quantities of uncombined alumina. Unless there be some preventing cause, the absorptive powers belonging to these bodies must therefore certainly be possessed by ordinary soil.

In entering on this subject, it must not be forgotten, however, that other ingredients of soil, the humus,* and especially the hydrated silicates, have been shown to possess absorbent powers. We do not therefore expect to find that the comparative absorptive power of different soils is exactly in the proportion of the metallic hydrates which they contain; all we can hope to discover is, that some of the peculiarities of the absorption by metallic hydrates are generally met with in cases of soil absorption.

I have no experiments of my own to quote; a collation of the results of others seems to indicate that in one peculiarity, the preference of the various salts in a certain order, the behaviour of soils very generally agrees with what we have seen to be the action of hydrated ferric oxide, namely, that more of the carbonate is absorbed than of the sulphate, and that more of the sulphate is absorbed than of either the chloride or nitrate.†

* Humus appears to be capable of removing free ammonia from a watery solution. (Brustlein, Jahresbericht der Agrikultur-Chemie, 1859-60, p. 1.)

† In order to ascertain the comparative absorption of different salts, it is necessary that the same soil should be treated with equivalent quantities of those salts, the same proportion between the soil and the salt-solution being maintained in

With soil, however, the difference between the amount of the various salts absorbed is much smaller than is the case with the pure hydrated oxides. Only a trace of the chloride and nitrate of potassium or ammonium was removed from solution by ferric hydrate, while by most soils considerable quantities of these salts, or rather of the alkali they contain, are taken up. The reason is well known. The carbonate of calcium, or the calcium silicate of fertile soils, decomposes the chloride, nitrate, or sulphate brought in contact with it: the alkaline carbonate or silicate thus formed is absorbed by the soil, and the action continues till the soil is saturated, or the solution rendered too dilute for further change to take place. If the action of the calcium were *complete*, and in some soil experiments this may possibly happen, every salt of potassium and ammonium would be absorbed to the same extent, provided the salts were applied in equivalent proportions: but it is rarely that the action of the calcium goes as far as this, and consequently some margin is

every experiment. The following are the only experiments I have found which seem to satisfy these conditions: a great majority of the results will be seen to agree with the statement made in the text.

Henneberg and Stohmann experimented with a garden soil; the order of greatest absorption was, free ammonia, sulphate of ammonium, chloride and nitrate of ammonium about equal.—*Jahresbericht der Agrikulturchemie*, 1858-9, p. 25.

E. Peters, experimenting on a soil with potassium salts found the following order of greatest absorption; carbonate, nitrate, sulphate, chloride. The nitrate here unexpectedly breaks the order.—*Ibid.* 1860-1, p. 9.

Fraas applied equivalent quantities of carbonate, sulphate, and nitrate of potassium to soils placed above lysimeters in the open air; there passed through into the lysimeters for equal quantities of water, the following amounts of potash, the quantity yielded by unmanured soil being deducted.—From the carbonate 3.80 grm.; from the sulphate, 8.89 grm.; from the nitrate, 10.27 grm. of potash. In another series the potassium salts were mixed with superphosphate of lime: there passed into the lysimeters from the manure, for equal quantities of water, 9.33 grm. of potash from the sulphate, and 12.02 grm. from the nitrate. The absorption by the soil was, of course, inversely as the drainage into the lysimeter.—*Ibid.* 1861-2, p. 11.

Küllenberg made elaborate experiments on one soil with salts of ammonium, potassium, sodium, magnesium, and calcium, each salt being used of five different strengths of solution. With salts of ammonium the order of greatest absorption was, carbonate, sulphate, chloride and nitrate about equal. With potassium salts the same order obtained; and with the salts of calcium and magnesium a like result. With sodium salts the order was to some extent inverted.—*Ibid.* 1865, p. 15.

Voelcker, experimenting with solutions of chloride and sulphate of potassium, obtained with a sandy soil rather more absorption of the chloride, and with a marl rather more absorption of the sulphate.—*Jour. R. Agricultural Soc.* xxv, 333.

left for the display of the particular affinities of the ferric and aluminic hydrates, the result being that some preference is shown for carbonates and sulphates over the chlorides and nitrates.

An account has been already given of the attempt made to imitate the conditions of a soil by adding carbonate of calcium to the ferric hydrate; the experiments, as already narrated, were attended with little success, the further absorption which took place on adding carbonate of calcium to the salt-solution being in every case very small. Can this result be consistently explained?

On testing the solution at the end of each experiment, a small quantity of lime was always found to have been dissolved; some carbonate of the alkali must therefore have been produced, but in so small an amount as to form an excessively dilute solution, from which no practical absorption could be expected. The difference in the case of soil I believe to be this. The particles of ferric hydrate are there already saturated with calcium, and the decomposition of the alkaline salt takes place consequently on their *surface*; the ferric hydrate thus absorbs from a thin film of concentrated salt-solution, and the absorption has thus no difficulty in keeping pace with the decomposition. Whether this theory be correct or not, it is evident that the ferric hydrate would have no difficulty in taking up potassium or ammonium from either the chloride or nitrate if these salts were effectually decomposed by carbonate of calcium, since we have seen that ferric hydrate has a powerful affinity for the carbonates of these bases.

The experiments of Henneberg and Stohmann, E. Peters, and Küllenberg show, that of all the salts of the alkalies experimented with, the phosphate was the salt from which the soil removed the largest quantity of base; the absorption from the phosphate even exceeding that from the carbonate. This fact agrees remarkably well with what we have now seen to be the properties of oxide of iron and alumina. The ferric hydrate and alumina of the soil would require no aid from a calcium-salt to enable them to decompose an alkaline phosphate, their own powerful affinity for phosphoric acid would immediately effect the decomposition of the salt, and liberate its base for absorption.

There appear then to be several facts in the chemical his-

tory of soil, the explanation of which is at once afforded by ascribing to the ferric oxide and alumina of soil those properties I have proved to be possessed by the artificially prepared hydrates of these oxides.

In advocating the claims of ferric oxide and alumina, as constituents of the soil, taking an active part in its absorption of potassium and ammonium, I am advancing no new idea. The belief that such is the case is to be found in several published papers discussing soil absorption; what I have tried to do has been to set the matter on an experimental basis. The present research, though touching only the outline of the subject, has I think shown that the hydrated ferric oxide and hydrated alumina of a soil perform most important functions. Their presence gives the soil its power of taking up phosphoric acid from solutions of basic phosphates, and in conjunction with the hydrated double silicates, it is the source of that property of the soil by which it absorbs alkalies and alkaline earths from the solutions of their salts. In these actions, the ferric oxide, as generally most abundant, and in regard to the alkaline salts more energetic in action than alumina, will usually have the greatest share; indeed for many soils it must be the chief promoter of the absorptive power. I need hardly say how opposed are the facts and arguments here advanced to the theory of physical attraction already referred to.

The experiments detailed in the present paper, were made in the laboratory of the Royal Agricultural College, Cirencester.