SOLVENT ACTION OF NITRIFICATION AND SULFOFICATION

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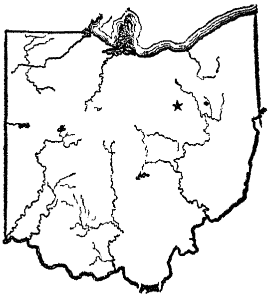

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[1] In cooperation with the College of Agriculture, Ohio State University, Columbus.
[2] In cooperation with the U. S. Department of Agriculture.

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BULLETIN
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SOLVENT ACTION OF NITRIFICATION AND SULFOFICATION

J. W. AMES

Chemical transformations in soils are to a considerable extent due to the activities of micro-organisms. The products of the processes in which various groups of sulphur bacteria and those producing changes in nitrogen compounds have a part, react with and bring about changes in the mineral constituents of soil and added fertilizing materials.

In a previous publication (1) we stated that the beneficial effects following the addition of sulphur to soils may result from an increased solubility of soil constituents due to acidity developed by oxidation of sulphur. More recently investigations (2) (3) (4) have directed attention to sulfofication and nitrification as effective agents for converting phosphorus of rock phosphate into a more available form. Experimental data pertaining to the effects of these processes on rock phosphate and soil minerals are discussed in this bulletin.

The soils used and the additions made have provided widely differing conditions, especially with respect to the supply of basic compounds. Aside from the solvent action of the processes, the influence of sulphur oxidized in soil on nitrification and ammonification has been considered.

METHODS OF PROCEDURE

Several series of mixtures which included the different treatments of soil, peat and sand were used as mediums for determining the effects of sulfofication and nitrification under varying conditions.

G. E. Boltz and T. E Richmond formerly connected with the station assisted in different phases of the work reported in this bulletin.

The soils used, which were a silt loam and a black clay, differ decidedly in their chemical composition and physical characteristics. The acid silt loam, which was used for the larger number of the experimental mixtures, has a requirement for base equivalent to 4,000 parts of calcium carbonate per million of soil and is rather deficient in organic residues. It has a total nitrogen content of 1,000 parts per million.

The black clay soil is naturally basic and contains 4,000 parts of nitrogen per million. The phosphorus content of the black clay is about 1,000 parts per million and the sulphur 500. Both of these elements are present in smaller amounts in the silt loam, the phosphorus content being 450 and the sulphur 200 parts per million of soil.

The soil was air-dried and pulverized so that it all passed through a sieve having circular perforations of 2 mm. in diameter. The quartz sand, 99 percent silica, was thoroughly washed to remove foreign material. The various additions of rock phosphate and sulphur made are stated in the several tables of results.

Casein, dried blood and ammonium sulphate were the nitrogen carriers used. A Tennessee brown rock phosphate analyzing 12 percent phosphorus furnished the supply of insoluble phosphorus. Additions of different amounts of calcium carbonate were made to certain mixtures for the purpose of studying the effect of the processes, with varying degrees of basicity provided.

After the various treatments were thoroughly mixed with the portions of soil or sand, sufficient water was added to satisfy 60 percent of the water-holding capacity and the mixtures transferred to glass containers. In the majority of the mixtures, the quantity of soil used was 500 grams. In a few supplementary mixtures made up with quartz sand, less soil was added to the mixture. Duplicates of all treatments were prepared. After the addition of water at regular intervals to replace that lost by evaporation, the contents of the containers were thoroughly mixed, so that optimum aeration was provided. The soil mixtures were maintained at a temperature of about 30 degrees Centigrade. The interval between the beginning of the experiment and the time when the changes which had occurred were measured was 19 weeks.

For the determinations of the constituents soluble in water, solutions were obtained by extracting 400 gram portions of the mixtures with 2,500 cc. of distilled water. The extraction was continued through a period of 14 to 15 hours. Filtration was made through Berkfeld filters with pressure. Indications of the extent to which sulfofication proceeded are furnished by the amounts of water-soluble sulphur as sulphates. Changes which occurred in the nitrogen compounds added or naturally present are shown by the quantities of nitric and ammoniacal nitrogen at the expiration of the experimental period. Nitric nitrogen was determined by the Devarda reduction method as modified by Allen (5). Ammoniacal nitrogen was determined in the portion of the filtered solution used for determination of nitrates by distillation with magnesium oxide previous to addition of sodium hydroxide, and reduction. Tests for nitrites were made but no appreciable quantities were present, the largest amount found in any of the mixtures was less than one part per million.

Potassium and manganese were determined colorimetrically. Calcium, magnesium and aluminum were determined according to the approved analytical procedures. The phosphorus soluble in neutral ammonium citrate was measured by extracting the soil mixtures with neutral ammonium citrate according to the regular method for available phosphorus in fertilizers. Phosphorus was determined in the filtered citrate solution, after destruction of organic matter by evaporation and ignition with magnesium nitrate solution.

To measure any changes in the solubility of phosphorus in rock phosphate and soil resulting from possible reaction of added materials before biological activities had progressed, portions of the dry mixtures were withdrawn, and citrate-soluble phosphorus determined before addition of water. The relative acidity of the water solutions was determined by titration using methyl red as the indicator.

SULPHUR OXIDATION

In all the mixtures where sulphur was included in the treatment, there was a considerable production of sulphates, the amount of sulphur oxidized depending upon the soil and the treatment. Two different amounts of sulphur were used. In the first series of mixtures where sulphur was included the amount was five-tenths of a gram to 500 grams of soil. The addition of sulphur in the second series was 2 grams to 500 grams of soil. Where the larger amount of sulphur was in contact with soil a greater proportion of the sulphur was oxidized. The sulphur as sulphates in the water extract of the soil mixtures, which included no other treatment than sulphur, was approximately 50 percent of the smaller addition of sulphur, while 70 percent was obtained where the larger addition was made.

TABLE I.—SULPHUR AND NITRIC AND AMMONIACAL NITROGEN IN ACID SILT LOAM

Data are expressed as parts per million of soil

Additions to 500 grams of soil	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen	Acidity*	Alkalinity†
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	20	43	0	0	9
Rock phosphate .5 gm	18	77	0	0	25
Rock phosphate .5 gm., calcium carbonate 2 gm	52	116	0	0	212
Calcium carbonate 2 gm	58	103	0	0	140
Casein 1.75 gm	44	200	132	61	0
Casein 1.75 gm., calcium carbonate 2 gm	56	440	0	0	56
Casein 1.75 gm., rock phosphate .5 gm	32	186	55	24	0
Casein 1.75 gm., rock phosphate .5 gm., calcium carbonate 2 gm	59	400	11	0	87
Sulphur. 5 gm., calcium carbonate 2 gm	671	88	0	0	12
Sulphur .5 gm., calcium carbonate 1 gm	675	22	33	52	0
Sulphur .5 gm., calcium carbonate .5 gm	710	11	46	223	0
Sulphur .5 gm	718	8	33	511	0
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate 2 gm	524	96	10	0	75
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate 1 gm	553	29	38	30	0
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate .5 gm	589	18	43	196	0
Sulphur .5 gm., rock phosphate .5 gm	775	12	48	666	0
Sulphur .5 gm., casein 1.75 gm., calcium carbonate 2 gm	661	295	4	18	0
Sulphur .5 gm., casein 1.75 gm., calcium carbonate 1 gm	808	92	241	76	0
Sulphur .5 gm., casein 1.75 gm., calcium carbonate .5 gm	740	33	208	200	0
Sulphur .5 gm., casein 1.75 gm	725	10	328	144	0
Sulphur .5 gm., rock phosphate .5 gm., casein 1.75 gm., calcium carbonate 2 gm	646	296	88	Neutral	0
Sulphur .5 gm., rock phosphate .5 gm., casein 1.75 gm., calcium carbonate 1 gm	752	98	254	79	0
Sulphur .5 gm., rock phosphate .5 gm., casein 1.75 gm., calcium carbonate .5 gm	683	44	208	128	0
Sulphur .5 gm., rock phosphate .5 gm., casein 1.75 gm	716	44	288	159	0

*Acidity expressed as sulphuric acid.

†Alkalinity expressed as calcium carbonate.

TABLE II.—SULPHUR AND NITRIC AND AMMONIACAL NITROGEN IN BASIC BLACK CLAY

Data are expressed as parts per million of dry soil

Addition to 500 gm. of soil	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen	Alkalinity*
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	38	142	11	90
Rock phosphate .5 gm.	31	141	11	93
Calcium carbonate .5 gm.	38	143	11	106
Rock phosphate .5 gm., calcium carbonate .5 gm.	35	143	0	175
Sulphur .5 gm.	656	107	11	78
Sulphur .5 gm., rock phosphate .5 gm.	790	144	10	78
Sulphur .5 gm., calcium carbonate .5 gm.	811	145	11	43
Sulphur .5 gm., calcium carbonate .25 gm.	707	146	10	93
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate .5 gm.	760	158	11	46
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate .25 gm.	723	145	16	90

*Alkalinity expressed as calcium carbonate.

TABLE III.—SULPHUR AND NITRIC AND AMMONIACAL NITROGEN IN ACID PEAT

Data are expressed as parts per million of soil

Addition to 500 grams of soil	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen	Acidity*
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	118	255	259	353
Rock phosphate .5 gm.	108	210	252	412
Calcium carbonate 5 gm.	108	556	122	137
Rock phosphate .5 gm., calcium carbonate 5 gm.	87	560	115	39
Sulphur .5 gm.	937	105	357	294
Sulphur .5 gm., rock phosphate .5 gm.	952	100	392	353
Sulphur .5 gm., calcium carbonate 5 gm.	818	112	399	274
Sulphur .5 gm., calcium carbonate 2.5 gm.	942	80	406	294
Sulphur .5 gm., calcium carbonate 1 gm.	981	58	398	372
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate 5 gm.	1,025	108	318	235
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate 2.5 gm.	935	98	420	118
Sulphur .5 gm., rock phosphate .5 gm., calcium carbonate 1 gm.	881	105	403	235

*Acidity expressed as sulphuric acid.

TABLE IV.—ACID SILT LOAM

Data expressed as parts per million of dry soil mixtures

No.	Additions to 500 grams dry soil	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen	Acidity*	Alkalinity*
		p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
1	None	37	84	13	0	3
2	Calcium carbonate 2 gm.	50	128	0	0	15
3	Dried blood 4 gm.	58	294	67	0	3
4	Dried blood 4 gm., calcium carbonate 2 gm.	95	462	0	0	14
5	Dried blood 4 gm., calcium silicate 2 gm.	122	434	6	0	8
6	Dried blood 4 gm., blast furnace slag 2 gm.	106	478	17	0	4
7	Ammonium sulphate 4 gm.	1,852	54	1,239	0	1
8	Ammonium sulphate, 4 gm., calcium carbonate 4 gm.	1,689	569	178	0	3
9	Ammonium sulphate, 4 gm., calcium carbonate 2 gm.	2,070	100	1,014	0	6
10	Sulphur 2 gm.	2,143	6	50	338	0
11	Sulphur 2 gm., calcium carbonate 4 gm.	1,294	35	27	4	0
12	Sulphur 2 gm., calcium carbonate 2 gm.	1,923	21	46	196	0
13	Sulphur 2 gm., dried blood 4 gm.	1,365	6	246	116	0
14	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 4 gm.	1,559	228	132	10	0
15	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 2 gm.	1,689	29	302	54	0
16	Sulphur 2 gm., dried blaod 4 gm., calcium carbonate 1 gm.	1,551	6	279	84	0
17	Sulphur 2 gm., dried blood 4 gm., feldspar 8 gm.	2,053	21	455	166	0
18	Sulphur 2 gm., dried blood 4 gm., feldspar 8 gm., calcium carbonate 4 gm.	1,256	373	172	0	0

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

TABLE V.—BASIC BLACK CLAY

Data expressed as parts per million of dry soil mixtures

No.	Additions to 500 grams dry soil	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen	Acidity*	Alkalinity*
		p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
1	None	87	153	3	0	8
2	Dried blood 4 gm.	90	491	25	0	3
3	Ammonium sulphate 4 gm.	1,696	280	737	0	1
4	Sulphur 2 gm.	2,156	16	67	42	0
5	Sulphur 2 gm., dried blood 4 gm.	2,225	12	279	17	0
6	Sulphur 2 gm., ammonium sulphate 4 gm.	3,480	42	1,071	30	0

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

The amounts of soluble sulphate as sulphates extracted by water from the differently-treated soils are included in the accompanying tabulations. The soluble sulphur figures for the first series are in Tables I, II and III, those for the second series, in Tables IV and V. Aside from the larger amount of sulphur added in the second series, the chief differences in the two series are the larger additions of calcium carbonate and the use of dried blood and ammonium sulphate as nitrogen carriers in the second. Casein supplied nitrogen in the silt loam soil mixtures of the first series. Calcium carbonate was added to certain mixtures of the first series of the basic clay but not to the second.

Aside from a plentiful supply of oxygen, there are other factors which appear to be necessary for the activities of the organisms which have a part in the sulphur oxidizing process.

Sulfofication is supposed to be analogous to nitrification, in that it is an oxidation process and that somewhat similar environmental conditions are required. One of the requisites for maximum nitrification is an adequate supply of basic calcium and magnesium compounds, especially the carbonates.

The amounts of oxidized sulphur found in some of these experimental mixtures indicate that the process of sulfofication is not retarded by the absence of basic calcium compounds. In some instances the addition of calcium carbonate has tended to depress sulfofication.

The quantities of sulphates found in the water extract of the acid silt loam mixtures are of interest as an index of the effect of different degrees of basicity on sulphur oxidation. The maximum oxidation of sulphur in the silt loam mixtures, where no nitrogen carrier was a part of the treatment, occurred where calcium carbonate was not present. It will be noted that sulphur as sulphates has tended to decrease gradually with the larger additions of calcium carbonate.

This relation between reduced amounts of sulphates and increased basicity of the soil by addition of calcium carbonate is quite consistent throughout all the acid soil mixtures and for the two amounts of sulphur used. The acid soil has a requirement for base equivalent to 4,000 parts of calcium carbonate per million of soil. In the series of mixtures where the addition of sulphur was five-tenths of a gram, calcium carbonate was added at the rate of 4,000, 2,000 and 1,000 parts per million parts of soil. Where 2 grams of sulphur were used these quantities of calcium carbonate were doubled. Oxidation of sulphur in the basic clay soil has been increased where calcium carbonate was supplied at the rate of 1,000 and 500 parts per million.

Conflicting indications were obtained with respect to the effect of calcium carbonate on sulfofication in sand, and in the soil containing no calcium carbonate. From the results in the sand mixtures in Tables VI and VII, it will be observed that in a sand medium the presence of calcium carbonate has promoted the oxidation of sulphur, since in the sand mixture where it was present the quantity of soluble sulphates increased from 42 to 503 parts per million, which indicates that a neutralizing agent, calcium carbonate in this case, is essential for the continued activities of the sulfofying organisms. The soluble sulphates from the mixtures which contained smaller amounts of sulphur were similarly increased.

TABLE VI.—EFFECT OF SULPHUR OXIDATION ON ROCK PHOSPHATE IN SAND AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry sand mixtures

Additions to 500 grams sand	Citrate-soluble phosphorus	Water-soluble	
		Calcium	Sulphur
	p. p. m.	*p. p. m.*	*p. p. m.*
None	7	7	30
Sulphur 2 gm.	8	33	42
Sulphur 2 gm., calcium carbonate 2 gm.	8	656	503
Rock phosphate 8 gm.	214	46	31
Rock phosphate 8 gm., sulphur 2 gm.	242	150	166

TABLE VII.—SULPHUR OXIDATION AND AVAILABILITY OF PHOSPHORUS IN SAND MIXTURES, AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry sand mixtures

Additions to 500 grams sand	Citrate-soluble phosphorus	Water-soluble	
		Calcium	Sulphur
	p. p. m.	*p. p. m.*	*p. p. m.*
Rock phosphate 0.5 gm.	30	25	0
Rock phosphate 0.5 gm., sulphur 0.5 gm.	60	98	70
Rock phosphate 0.5 gm , sulphur 0.5 gm., calcium carbonate 2 gm.	25	722	591

No provision was made for inoculation of the sand mixtures, but regardless of this, the oxidation of sulphur proceeded actively where calcium carbonate was included.

If the results for the sand cultures are considered to furnish the correct explanation concerning the influence of calcium carbonate on sulfofication, a basic compound is essential. The indications obtained from the sulphur oxidized in the acid soil are that bases other than calcium readily combine with the acidity produced, because this soil contains no calcium carbonate and a very small amount of calcium in other combinations. Aluminum and manganese were freely attacked by the acidity produced, and the titration of the solution showed the presence of considerable amounts of acidity.

The small increases of oxidized sulphur that occurred in sand cultures where rock phosphate was added with sulphur in the absence of calcium carbonate indicate that as a source of base necessary for activities of the sulfofying organisms, rock phosphate is much less effective than calcium carbonate. This is also apparent from the results for nitrification of blood and ammonium sulphate in acid soil mixtures which included rock phosphate with these nitrogen carriers.

The nitrogen carriers, casein and dried blood, included in some of the mixtures have also had an influence on the amount of sulphur oxidized. Where casein was a part of the treatment, the optimum basicity for sulfofication was one-half the total lime requirement, the most soluble sulphur being found where 2,000 pounds of calcium carbonate were added, rather than where none was supplied as was the case in the sulphur, and the sulphur and floats groups of mixtures. Dried blood present with rock phosphate has tended to increase the soluble sulphate resulting from oxidized sulphur, while in certain other mixtures a decrease was found.

NITRIFICATION

Casein supplied the added nitrogen in the first series of mixtures. Dried blood and ammonium sulphate were used in the other series. While no attempt has been made to study the phenomena of nitrification and ammonification, the results have contributed some interesting information pertaining to the influence of various treatments on these processes.

Considering first the nitrate nitrogen in the soils to which no nitrogen was added, it will be observed that the largest accumulation was in the acid peat; a smaller amount was found in the basic clay, and the minimum production occurred in the acid silt loam. The nitrates therefore parallel the total nitrogen content of the three soils regardless of wide variations in basicity or acidity. In this connection mention is made of the fact that samples of acid peats, taken during the summer months when conditions were favorable for nitrification, had a nitric nitrogen content of 200 parts per million. The nitrogen data show that the transformation of proteid to nitrate nitrogen in three widely differing types of soil was influenced by several factors.

Nitrification as an indicator of variation in basicity is strikingly illustrated by the production of nitrates in the naturally basic black clay, as compared with that of the silt loam, which has a total requirement of 4,000 pounds of calcium carbonate.

Addition of calcium carbonate did not cause increased nitrification in the basic clay, the amounts of nitric nitrogen were practically the same whatever the treatment. But there is a quantitative relationship between nitrates found and the calcium carbonate additions to silt loam soil when the indications were obtained from the natural nitrogen supply and when proteid nitrogen was supplied by casein.

When sufficient calcium carbonate was present to satisfy the soil's requirement, excluding that necessary for the neutralization of acidity developed by sulfofication, the maximum quantities of nitrates were produced, the quantity found gradually decreasing with the smaller additions of carbonate and the ammoniacal nitrogen increasing. Calcium carbonate in amount considered to be sufficient to satisfy the soil's demand for base, exclusive of the additional requirement resulting from the oxidation of sulphur, increased the production of nitrate where sulphur and casein were included together. This quantity of calcium carbonate, however, was not adequate to satisfy the requirement of the soil for base, and at the same time neutralize the acidity produced by the oxidation of sulphur. Evidence of this is furnished by the amounts of nitrates recovered from the mixtures which included casein with and without sulphur, and additions of calcium carbonate made at the rate of 4,000 pounds per million. Where no sulphur was added, the quantity of nitrates recovered was 440 parts per million and where sulphur was oxidized there was a decrease to 295 parts per million.

The nitrogen results when sulphur has been oxidized in the silt loam mixtures receiving the smallest addition of calcium carbonate, 1,000 parts per million, which is one-fourth the amount required to satisfy the lime requirement, show that this amount of base had very little effect on nitrification, since the amount of nitric nitrogen was practically the same as that recovered from the soil with its requirement entirely unsatisfied. This is so where casein was present, as well as where the indications were obtained from the natural nitrogen supply of the soil.

The effect of increasing basicity is quite pronounced in the peat soil where no oxidation of added sulphur occurred. While the addition of calcium carbonate sufficient to satisfy the lime requirement of the peat soil has caused the largest production of nitrate nitrogen, this increase is only about double that in the peat receiving no calcium carbonate or other treatment.

The nitrogen results show that a measure of either the nitric or ammoniacal nitrogen independently, would not have furnished correct indications of changes from proteid to other forms of nitrogen when oxidation of added sulphur has occurred, for the reason that with certain conditions of treatment no appreciable amounts of nitrates were produced, the transition being to ammonia only, while under other conditions the change has proceeded more completely and practically all of the nitrogen was present as nitrates.

When sulphur was oxidized, the transformation from ammonia to nitrates was depressed unless the acidity produced was neutralized by calcium carbonate. The natural basicity of the clay soil was not sufficient for the nitrification of more than a small part of the nitrogen of dried blood and ammonium sulphate in the presence of sulphur.

Dried blood and ammonium sulphate supplied nitrogen in certain mixtures of the silt loam and basic clay. When calcium carbonate was not present, dried blood was nitrified to a greater extent than ammonium sulphate, the accumulation of nitric nitrogen from ammonium sulphate being less than was present in the untreated soil. The amount of nitrate nitrogen in the untreated soil was 84 parts, and that produced from dried blood was 294 parts per million. The increased base requirement for the nitrification of ammonium sulphate, as compared with dried blood, is shown by the nitric nitrogen produced from these two forms of nitrogen. When the same amount of calcium carbonate was present, that for dried blood was 462 parts per million, in contrast to only 100 parts from ammonium sulphate. Calcium carbonate was added to these mixtures at the rate of 4,000 parts per million. In soil mixtures treated with calcium carbonate at the rate of 8,000 parts per million, which is double the lime requirement of the soil independent of that required for neutralizing acidity resulting from the oxidation of either nitrogen or sulphur, the formation of nitrate nitrogen from ammonium sulphate exceeded the amount produced from dried blood.

Rock phosphate in the absence of calcium carbonate has slightly favored the nitrification of dried blood, but not of ammonium sulphate in the case of the acid soil. It has increased the nitrification of both these carriers in the basic soil.

Calcium silicate and blast furnace slag included in certain mixtures were as satisfactory as the same amount of calcium carbonate for supplying calcium necessary to combine with nitrous acid. The quantities of nitrates formed where these materials were used are stated in Table IV.

A comparison of the ammoniacal nitrogen and acidity found in solution from the soils treated with sulphur furnishes evidence that, in the absence of calcium carbonate, the ammonia produced neutralizing the sulphuric acid was combined as ammonium sulphate, because the acidity of the solution was decidedly less than that of similar mixtures where ammonifying organisms did not have a supply of proteid nitrogen to change to ammonia.

In those cases where conditions resulting from sulfofication and the presence of insufficient base were such that the transformation from ammoniacal to nitric nitrogen was largely prevented, there would be undoubtedly a fixation of a part of the ammonia, since it is an established fact that soils have the capacity for fixing considerable amounts from added ammonium salts. It would seem that following the fixation of ammonia from ammonium sulphate formed, whether this phenomenon of absorption or fixation is the result of chemical interchange or due to physical or other causes, there would be a consumption of calcium, magnesium and other base by the sulphate radical. Since ammonium sulphate is regarded as a physiologically acid salt, in field soils the possible utilization of ammoniacal nitrogen by growing plants would be a cause contributing further to the depletion of soil bases.

Whether the ammonia is changed from its combination as sulphate directly to nitrous acid and nitrate, or whether there is an intermediate reaction with the soil, a base will be required, as is evidenced by the results for ammoniacal and nitrate nitrogen in the soils where sulphur was oxidized and variations in basicity existed.

In this connection, two questions are suggested. To what extent will tricalcium phosphate serve as a source of basic calcium in soil which, while not supplied with calcium carbonate, contains minerals which may be attacked by acidity developed through nitrogen transformations, or by the sulphate radical of ammonium sulphate? The acid radical will be a factor regardless of whether ammonia is oxidized by nitrite bacteria, fixed by soil or utilized in part directly by plants.

And further, if the soil is supplied with calcium carbonate, will the nitrous acid exercise any selective action and unite with the calcium of tricalcium phosphate in preference to calcium carbonate?

When no change was brought about in basicity by calcium carbonate or in acidity by the oxidation of added sulphur, a part of the proteid nitrogen furnished has been completely changed to the nitrate form and a part to ammonia only. The ammoniacal nitrogen found was considerably less than was present in mixtures which were similar except that added sulphur was oxidized, and the nitrates were half the amount produced when the base requirement of the soil was satisfied.

ACIDITY OF SOLUTIONS

A measure of the relative acidity of the solutions was obtained by titration using methyl red as the indicator. The data in Tables I and IV show that the solutions were acid to methyl red when sulphur was added, and in these cases it was decidedly decreased where calcium carbonate was present.

The amounts of water soluble ammoniacal nitrogen found where dried blood was present also furnish evidence that the ammonia formed has neutralized a part of the acidity developed by oxidation of sulphur.

With two exceptions all of the solutions of mixtures from which sulphur was omitted had an alkaline reaction, the alkalinity being somewhat increased by addition of calcium carbonate, and by calcium silicate and blast furnace slag, these three materials supplying approximately equal amounts of calcium. Although the silt loam soil had a lime requirement equivalent to 4,000 parts per million of calcium carbonate, the titration of the water extract gave no indication of a deficiency in bases necessary for the maintenance of an alkaline reaction in this soil. Ammonium sulphate has slightly decreased the alkalinity of the water solutions of both the silt loam soil and the basic clay. The reduction by ammonium sulphate of alkalinity imparted to the solution of the silt loam by calcium carbonate was more pronounced.

The difference in the basicity of the two soils is clearly shown by a comparison of the figures for the acidities of the solutions from the sulphur-treated silt loam, and basic clay soil mixtures. The acidity of the silt loam soil and sulphur mixture is 338. Sulphur added to the basic clay has changed the alkalinity of the water solution to methyl red from 8 parts per million to an acidity of 42 parts per million. Practically the same amount of sulphates, 2,143 and 2,156 parts per million were found in the solutions from both the silt loam and the basic soil treated with sulphur. This quantity of sulphur is equivalent to 6,560 parts per million sulphuric acid, which would require 6,690 parts per million of calcium for neutralization. This requirement was largely provided for by calcium and magnesium in the basic clay. A total of 2,055 parts per million calcium and magnesium was water soluble in the basic clay as compared with 473 for the silt loam soil. Calcium and magnesium being deficient in the silt loam, the acidity resulting from oxidation of sulphur has combined with considerable amounts of aluminum and manganese, the sulphates of these elements exceeding the water-soluble calcium and magnesium. Nitrification of dried blood has not caused the water solution of mixtures where nitrates were present to have an acid reaction to methyl red.

The figures obtained for the relative acidity of the solutions do not give an indication of the total acidity produced during the period that sulphur, dried blood and ammonium sulphate were in contact with the soil in the several mixtures. In considering the effects of acidity due to sulfofication or nitrification, it is obvious that the water-soluble sulphates and nitrates will furnish a more correct basis for any deductions made, for the reason that the products of these processes have combined with the soil constituents. The acidity has been neutralized chiefly by calcium carbonate where it was included as a part of the treatment in the silt loam mixtures, and by the naturally basic calcium compounds of the black clay.

Some of the reactions which occurred between oxidation products of sulphur and soil constituents in these experimental mixtures will no doubt proceed in field soils, although less actively and are not dependent on the presence of added sulphur, as sulphur compounds naturally present in the soil can be a source of acidity under certain conditions.

Iron sulphide, which is a mineral common to many soils, is gradually oxidized to the form of sulphate, and then dissolved and hydrolized, with the precipitation of ferric hydrate and the formation of free sulphuric acid.

Sulphur existing in organic combinations may also be changed into a form which can react with soil bases, if the conclusions of Kappen and Quensell (6) concerning the sulphur cycle in soil are correct. They state that hydrogen sulphide produced by action of bacteria combines with iron, forming iron sulphide, which in turn is decomposed, the iron being oxidized and sulphur liberated in a finely-divided condition which is oxidized, forming sulphates.

EFFECT OF SULPHUR OXIDATION ON ROCK PHOSPHATE

Rock phosphate and sulphur were used in a preliminary experiment at the rate of 1,000 pounds per million of soil. While the sulphur was readily oxidized, and no difficulty was experienced in measuring the sulphates, a satisfactory determination of changes in the availability of phosphorus was not obtained. This was attributed to the absorption capacity of the soil for phosphorus. It was therefore deemed advisable to use larger amounts of phosphate and sulphur than would be practical in the field, in order to obtain indications of interactions which had occurred under different conditions of treatment, and this was done in the experimental work begun in November, 1917.

The quantities of citrate-soluble phosphorus found at the beginning of the experiment, in the soil mixtures receiving additions of rock phosphate and sulphur, and in the soils to which no phosphate was added, do not differ materially. The soil mixtures were dry and samples were withdrawn for measuring action of added materials on phosphate within a few hours after they were incorporated with the soil.

At the end of the 19-week incubation period, there was a small increase of citrate-soluble phosphorus in all the mixtures, the most pronounced increases aside from those observed when rock phosphate and sulphur were in contact, were found in the soils receiving additions of rock phosphate and sulphur separately.

The effects of sulphur oxidation on phosphorus availability in acid soil are shown in Table VIII.

The largest increase was that resulting from oxidation of sulphur incorporated with rock phosphate where no other additions were made. The proportion of rock phosphate to soil was such that phosphorus was added at the rate of 1,900 parts per million. The effect of sulphur when incorporated with rock phosphate in the absence of calcium or nitrogen carriers, was responsible for the accumulation of 630 parts per million parts of available phosphorus on the basis of the dry soil.

While the presence of calcium carbonate has depressed the oxidation of sulphur, the quantity of sulphates found indicates that there was sufficient acidity to have attacked the rock phosphate, providing no calcium carbonate was present. The results for available phosphorus in the acid soil mixtures, to which additions of calcium carbonate were made, show that the action of oxidized sulphur on rock phosphate will be decreased considerably in soil containing calcium carbonate. Further evidence of this is furnished by the results for the black clay soil which is decidedly basic, although its natural calcium carbonate content is only 300 parts per million parts.

TABLE VIII.—EFFECT OF SULPHUR OXIDATION IN ACID SILT LOAM SOIL, AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry soil mixtures

Additions to 500 grams dry soil	Citrate-soluble phosphorus		Water-soluble			Acidity*	Alkalinity*
	At beginning	At end 19 weeks	Calcium	Sulphur	Nitrate nitrogen		
	p.p.m.	*p.p.m.*	*p.p.m*	*p.p.m.*	*p.p.m.*	*p.p.m*	*p.p.m.*
None	45	60	111	37	84	0	3
Calcium carbonate 2 gm.	48	54	270	50	128	0	14
Sulphur 2 gm.	44	99	370	2,143	6	338	0
Sulphur 2 gm., calcium carbonate 4 gm.	53	72	858	1,294	35	4	0
Sulphur 2 gm., calcium carbonate 2 gm.	45	74	785	1,923	21	194	0
Rock phosphate 8 gm.	53	98	114	42	105	0	2
Rock phosphate 8 gm., calcium carbonate 2 gm	67	96	280	64	128	0	14
Rock phosphate 8 gm., sulphur 2 gm.	50	630	728	1,900	6	192	0
Rock phosphate 8 gm., sulphur 2 gm., calcium carbonate 4 gm.	59	120	1,361	1,401	50	6	0
Rock phosphate 8 gm., sulphur 2 gm., calcium carbonate 2 gm.	59	132	981	1,592	12	75	0

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

The basic clay used as a medium contains phosphorus in a form readily acted on by the acidity produced by sulfofication, according to the indications given by the results where no rock phosphate was added either alone or in combination with a nitrogen carrier. It will be observed from the results for the basic clay soil, which are given in Table IX, that while the oxidation of sulphur has proceeded actively, the quantity of sulphates extracted with water being similar to that from the acid soil, rock phosphate has not been attacked to the same extent. Where rock phosphate and sulphur were the additions made, the citrate-soluble phosphorus increased from 129 parts per million at the beginning of the experiment to 479 parts. In all instances where sulphur was in contact with rock phosphate, its oxidation product attacked the phosphate, but the amount of citrate-soluble phosphorus was in no case as large as that obtained when sulphur was used alone with rock phosphate in the acid soil. The natural basicity of the black clay furnishes the explanation of this difference. The concentration of calcium in the water extract of the basic soil shows that it is well supplied with soluble calcium. From the fact that when a nitrogen carrier was included as a part of the treatment with sulphur, its nitrification was depressed considerably as compared with that taking place when either dried blood or ammonium sulphate was included in the soil mixture without sulphur, shows that the natural basicity was only slightly in excess of the sulphur acidity requirement. The calcium in solution where rock phosphate and sulphur were included together is nearly equivalent to the increased phosphorus soluble in neutral ammonium citrate.

TABLE IX.—EFFECTS OF SULPHUR OXIDATION AND NITRIFICATION IN BASIC BLACK CLAY, AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry soil mixtures

Additions to 500 grams soil	Citrate-soluble phosphorus		Water-soluble			Acidity*	Alkalinity*
	At beginning	At end 19 weeks	Calcium	Sulphur	Nitrate nitrogen		
	p. p. m.	*p.p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	130	141	245	87	153	4	0
Sulphur 2 gm	119	270	1,173	2,156	16	42	0
Dried blood 4 gm	130	134	668	90	491	0	3
Dried blood 4 gm., sulphur 2 gm	129	244	1,763	2,225	12	17	0
Ammonium sulphate 4 gm	125	156	1,297	1,696	280	0	7
Ammonium sulphate 4 gm., sulphur 2 gm.	124	259	2,080	3,480	42	30	0
Rock phosphate 8 gm	140	160	249	71	153	0	8
Rock phosphate 8 gm., sulphur 2 gm	129	479	1,746	2,184	0	52	0
Rock phosphate 8 gm., dried blood 4 gm	142	145	702	114	516	0	3
Rock phosphate 8 gm., dried blood 4 gm., sulphur 2 gm	145	323	1,849	2,398	12	23	0
Rock phosphate 8 gm., ammonium sulphate 4 gm	153	180	1,668	2,267	326	0	2
Rock phosphate 8 gm., ammonium sulphate 4 gm., sulphur 2 gm	139	240	2,395	3,649	40	27	0

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

The additions of phosphorus and sulphur made to the peat soils were less than for the other soil series, five-tenths of a gram of these materials being supplied. This soil is considered to be acid, and the considerably higher nitrogen figures when calcium carbonate was added support this opinion. The results for peat soil mixtures are given in Table X. It will be noted that the oxidation of sulphur in the peat soil to which no calcium carbonate was added has increased the soluble calcium concentration. This is interpreted as resulting from the action of sulphur acidity on calcium, present in other forms than basic calcium compounds. The oxidation of sulphur in contact with rock phosphate in these peat mixtures has not increased the soluble calcium over that taken into solution from the peat mixtures which included no other treatment than sulphur. Neither do the results for phosphorus furnish indication of any action of oxidized sulphur on rock phosphate in the peat soil.

TABLE X.—SULPHUR OXIDATION AND AVAILABILITY OF PHOSPHORUS IN ACID PEAT SOIL MIXTURES, AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry mixtures

Additions to 500 grams peat	Citrate-soluble phosphorus	Water-soluble Calcium	Water-soluble Sulphur	Water-soluble Nitric nitrogen
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	356	264	118	255
Calcium carbonate 5 gm.	358	737	108	556
Sulphur 0.5 gm.	365	657	937	105
Sulphur 0.5 gm., calcium carbonate 5 gm.	365	697	818	112
Sulphur 0.5 gm., calcium carbonate 2.5 gm.	335	697	942	80
Sulphur 0.5 gm., calcium carbonate 1 gm.	335	641	981	58
Rock phosphate 0.5 gm.	339	258	108	210
Rock phosphate 0.5 gm., calcium carbonate 5 gm.	365	737	87	560
Rock phosphate 0.5 gm., sulphur 0.5 gm.	368	673	952	100
Rock phosphate 0.5 gm., sulphur 0.5 gm., calcium carbonate 5 gm.	339	818	1,025	108
Rock phosphate 0.5 gm., sulphur 0.5 gm., calcium carbonate 2.5 gm	366	705	935	98
Rock phosphate 0.5 gm., sulphur 0.5 gm., calcium carbonate 1 gm.	389	601	881	105

Phosphorus of rock phosphate, although converted into a more available form, may be fixed by soil to such an extent that a correct measure of changes due to sulfofication or other biochemical processes, cannot be obtained from the phosphorus results alone.

If there is any appreciable reaction between insoluble calcium phosphate and sulphur acidity with the formation of calcium sulphate, the water-soluble calcium will furnish a more reliable indication than the phosphorus soluble in neutral ammonium citrate solution.

TABLE XI.—EFFECT OF SULPHUR OXIDATION AND NITRIFICATION ON ROCK PHOSPHATE IN SAND MIXTURE AFTER 7 MONTHS

Data expressed as parts per million of dry mixtures

Additions to 500 gm. sand and 10 gm. soil	Citrate-soluble phosphorus
Rock phosphate 8 gm.	288
Rock phosphate 8 gm., sulphur 4 gm.	432
Rock phosphate 8 gm., sulphur 4 gm., calcium carbonate 4 gm.	260
Rock phosphate 8 gm., calcium carbonate 4 gm.	76
Rock phosphate 8 gm., dried blood 2 gm.	260
Rock phosphate 8 gm., dried blood 2 gm., calcium carbonate 4 gm.	76
Rock phosphate 8 gm., ammonium sulphate 1 gm.	320
Rock phosphate 8 gm., ammonium sulphate 1 gm., calcium carbonate 4 gm.	84

Where rock phosphate and sulphur were in contact in sand mixtures the fixation of phosphorus was no doubt practically eliminated, and the citrate-soluble phosphorus as well as the calcium should furnish evidence of solvent action of sulphur acidity.

Sulphur in sand cultures, however, was not oxidized appreciably unless calcium carbonate was present. Sulphuric acid formed was neutralized and consequently the quantity of citrate-soluble phosphorus was less than where sulphur and phosphate were mixed with soil.

The data for sand mixture where no soil was added which are given in Tables VI and VII show that the action has been slight. In sand mixtures where more sulphur was used, and soil was added at the rate of 10 grams to 500 grams of sand, a larger amount of citrate-soluble phosphorus was obtained at the end of 7 months; these results are in Table XI.

EFFECT OF OXIDATION OF SULPHUR USED WITH NITROGEN CARRIERS

A series of soil mixtures in which either dried blood or ammonium sulphate was included with sulphur and rock phosphate as a part of the treatment were incubated to study the combined action of sulfofication and nitrification on rock phosphate in the presence of calcium carbonate, as well as in soil which contains no carbonate, and possesses the characteristics of soils which are regarded as acidic on account of their deficiency in bases. The basic soil without addition of calcium carbonate was also used as a medium for the same treatments without the addition of calcium carbonate.

The results showing effect of the oxidation of sulphur, when used with nitrogen carriers, on rock phosphate in an acid soil are presented in Table XII. The effect of similar treatment in the basic clay is shown by the data included in Table IX.

When sulphur and blood were in contact in the acid soil, the oxidation of sulphur proceeded actively. Nitrification, however, in the absence of calcium carbonate was practically inhibited by the acidity resulting from oxidation of sulphur and the transition from proteid to other forms of nitrogen proceeded to a slight extent only beyond ammonia, as the conditions were not favorable for the further change to nitric nitrogen.

The ammonia formed has partially neutralized the acidity produced by the activities of the sulfofying organisms, for the results obtained for phosphorus, when dried blood was added to rock phosphate and sulphur in the soil mixtures, show that considerably less phosphorus was changed into a form soluble in neutral ammonium citrate, than where sulphur and rock phosphate were in contact without the addition of dried blood.

TABLE XII.—RESULTS SHOWING INFLUENCE OF THE OXIDATION OF SULPHUR DURING 19 WEEKS INCUBATION, WHEN USED IN COMBINATION WITH NITROGEN CARRIERS, ON ROCK PHOSPHATE IN ACID SILT LOAM SOIL

Data expressed as parts per million of dry soil mixtures

Additions to 500 grams soil	Citrate-soluble phosphorus		Water-soluble				Acidity*	Alkalinity*
	At beginning	At end 19 weeks	Calcium	Sulphur	Nitrate nitrogen	Ammoniacal nitrogen		
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
Rock phosphate 8 gm., sulphur 2 gm.	50	630	728	1,900	6	65	192	0
Rock phosphate 8 gm., dried blood 4 gm.	90	91	366	64	338	27	0	2
Rock phosphate 8 gm., sulphur 2 gm., dried blood 4 gm.	80	279	798	2,666	6	361	254	0
Rock phosphate 8 gm., sulphur 2 gm., dried blood 4 gm., calcium carbonate 4 gm.	62	62	1,295	1,628	161	225	27	0
Rock phosphate 8 gm., sulphur 2 gm., dried blood 4 gm., calcium carbonate 2 gm.	57	57	917	1,977	18	313	69	0
Rock phosphate 8 gm., sulphur 2 gm., dried blood 4 gm., calcium carbonate 1 gm.	59	323	694	1,926	8	340	112	0
Rock phosphate 8 gm., ammonium sulphate 4 gm.	58	110	429	1,904	56	1,211	0	
Rock phosphate 8 gm., sulphur 2 gm., ammonium sulphate 4 gm.	69	179	645	2,666	8	1,486	13	3
Rock phosphate 8 gm., sulphur 2 gm., ammonium sulphate, 4 gm., calcium carbonate 8 gm.	55	94	4,107	2,596	823	36	0	0
Rock phosphate 8 gm., sulphur 2 gm., ammonium sulphate 4 gm., calcium carbonate 4 gm.	64	61	2,855	2,711	365	468	4	4

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

Where ammonium sulphate was included with rock phosphate and sulphur, there was a further decrease in the amount of citrate-soluble phosphorus. This effect on the solubility of rock phosphate when ammonium sulphate was used could not be due to a neutralization of acidity.

In the basic clay the effect of dried blood when used with sulphur has not been as marked as in the acid soil.

NITRIFICATION AND AVAILABILITY OF ROCK PHOSPHATE

Nitrification in the acid soil proceeded much more actively when the basicity of the soil was increased by the addition of calcium carbonate.

Rock phosphate in the absence of calcium carbonate has slightly favored the nitrification of dried blood but not that of ammonium sulphate, for the amount of nitric nitrogen in the ammonium sulphate mixture was the same as that produced from ammonium sulphate where rock phosphate was not a part of the treatment.

While nitrification of dried blood was stimulated somewhat by the presence of rock phosphate, and an increased amount of calcium was found in the water solution, the figures for phosphorus do not give any indication of the solvent action of nitrous acid on tri-calcium phosphate. Granting that any change with respect to the phosphorus may have been masked by the absorption capacity of the soil, and considering that the increased calcium more correctly reflects any interaction which occurred, the quantity of phosphorus as dicalcium phosphate equivalent to the increased calcium is only 86 parts per million parts of soil.

Ammonium sulphate, from the indications furnished by the calcium as well as phosphorus, has slightly influenced the availability of tri-calcium phosphate, but whatever action ammonium sulphate had, is attributed to the sulphate ion rather than to bio-chemical action, since active nitrification of ammonia did not occur in the acid soil unless calcium carbonate was added.

The fact that more calcium carbonate was taken into solution from soil treated with ammonium sulphate than by the sulphur acidity following oxidation of sulphur, can be explained by the nitric nitrogen figures when the largest addition of calcium carbonate was necessary to furnish sufficient base for active nitrification; and by the sulphate ion where one-half this quantity of calcium carbonate was not adequate for the formation of any considerable amount of nitric nitrogen from ammonium sulphate.

The data for nitrification and availability of phosphorus in acid soil are in Table XIII.

TABLE XIII.—EFFECT OF NITRIFICATION IN ACID SILT LOAM SOIL, AFTER 19 WEEKS INCUBATION

Data expressed as parts per million of dry soil mixtures

Additions to 500 gm. dry soil	Citrate-soluble phosphorus		Water-soluble			Acidity*	Alkalinity*
	At beginning	At end 19 weeks	Calcium	Sulphur	Nitrate nitrogen		
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
None	45	60	111	37	84	0	3
Calcium carbonate 2 gm.	48	54	270	50	128	0	14
Dried blood 4 gm.	53	63	255	58	294	0	2
Dried blood 4 gm., calcium carbonate 2 gm.	51	54	736	95	462	0	14
Ammonium sulphate 4 gm.	42	81	355	1,852	54	0	0
Ammonium sulphate 4 gm., calcium carbonate 4 gm.	42	95	2,198	1,689	569	0	3
Ammonium sulphate 4 gm., calcium carbonate 2 gm.	45	49	1,070	2,070	100	0	6
Rock phosphate 8 gm.	53	98	114	42	105	0	2
Rock phosphate 8 gm., calcium carbonate 2 gm.	67	96	280	64	128	0	14
Rock phosphate 8 gm., dried blood 4 gm.	90	91	366	64	338	0	1
Rock phosphate 8 gm., dried blood 4 gm., calcium carbonate 2 gm.	63	97	667	93	394	0	13
Rock phosphate 8 gm., ammonium sulphate 4 gm.	58	110	429	1,904	54	0	3
Rock phosphate, ammonium sulphate 4 gm., calcium carbonate 4 gm.	59	95	2,058	1,919	424	0	4

*Acidity expressed as sulphuric acid and alkalinity as calcium carbonate.

In the absence of rock phosphate or calcium carbonate, the nitrification of dried blood, as well as the action of ammonium sulphate without oxidation of its nitrogen, has increased the soluble calcium content, which is evidence that the natural calcium of the soil, existing chiefly as silicates, and partly in other combinations is more readily attacked than rock phosphate. In considering the functioning of rock phosphate as a base and promoting nitrification, it should be stated that the rock phosphate used contained a small amount of calcium carbonate, approximately 3 percent.

The data for the basic soil mixtures which are given in Table IX show that there was active nitrification of blood, which was accompanied by a greater concentration of water-soluble calcium than was found for the untreated soil. Although the natural basicity of the clay soil supported a more limited nitrification of ammonium sulphate, the amount of calcium converted into calcium sulphate through its action was almost double the calcium changed into a water-soluble form through the instrumentality of the nitrifying process where dried blood was present.

Rock phosphate as a part of the treatment has slightly increased the production of nitric nitrogen from both dried blood and ammonium sulphate, and it is assumed that the slightly larger amounts of calcium, which accompanied the increased accumulation of nitrates in the basic soil, were obtained from the rock phosphate.

In the group of mixtures where rock phosphate was added to a peat soil, no additions of dried blood or ammonium sulphate were made. The quantities of nitric nitrogen produced in the peat where rock phosphate was added furnish no indication that it has supplied basicity necessary for the nitrifying process. Where calcium carbonate was added without sulphur, there was an increased accumulation of nitrates. The availability of rock phosphate incorporated with the peat does not appear to have been changed.

The indications obtained from sand mixtures which included rock phosphate, dried blood and ammonium sulphate are not different from those for similarly-treated soils; the data are in Table XI.

No increase of citrate-soluble phosphorus was obtained where rock phosphate and dried blood were in contact. The solubility of phosphorus in this mixture was less than that from rock phosphate. When ammonium sulphate was present, there was a small increase.

The results for citrate-soluble phosphorus, water-soluble calcium and nitric nitrogen do not indicate that rock phosphate incorporated with soil has been freely acted upon by the products formed during the transformation of either organic nitrogen or ammonium sulphate to nitrates. By contrasting the phosphorus availability where nitrogen carriers were included in the soil mixtures, with those where sulphur was in contact with rock phosphate, it will at once be apparent how feeble the action of nitrification has been.

So far as the data which have been obtained under the experimental conditions described, furnish any information, the nitrification of dried blood or ammonium sulphate as an agency for rendering the tri-calcium phosphate of floats available in amount sufficient for the requirement of plants must be regarded as a contributing factor rather than being adequate in itself.

More significance should probably be attached to nitrification as an indirect agency, in conjunction with rock phosphate, for increasing crop yields. With a supply of available nitrogen furnished, plant growth is stimulated so that the phosphorus of rock phosphate can be utilized to better advantage.

Field results at the Ohio Station (7) confirm this opinion. Where nitrate of soda was added to soil which had received heavy applications of rock phosphate, the yield of wheat was much larger than that produced by rock phosphate without a supply of available nitrogen.

POTASSIUM SOLUBILITY

The results obtained for water-soluble potassium are of interest because they furnish indications of the effect of salts formed as the result of acidity developed by micro-organisms which produce changes in sulphur and nitrogen carriers. This effect on potassium compounds in the soil appears to have been a more important factor than the direct action of acidity resulting from the processes of either nitrification or sulfofication.

The solubility of potassium in soil and potassium bearing minerals as affected by various salts, is a subject to which much attention has been directed. Sodium salts, including nitrate and chloride, liberate potassium according to some investigators, while the opposite conclusion has been arrived at by others. Many conflicting statements also are presented in the literature pertaining to the effect of lime, calcium carbonate, calcium sulphate and other calcium salts on potassium solubility.

Gardiner and Shorey (8) found that potassium of muscovite and orthoclase were rendered soluble to some extent by treatment with various concentrations of ammonium sulphate solution. The work of Morse and Curry (9) indicates that lime and gypsum increased the solubility of potassium in feldspar. The experimental work of Bradley (10) with Oregon soils shows that with some soils there was an increase of water-soluble potassium brought about by the addition of gypsum. Investigations reported by McMiller (11) show that various mineral soils mixed with 1 percent of gypsum, and the water content brought to a point approximating the moisture equivalent and kept in this condition for 3 months gave marked increases in water-soluble potassium.

Results obtained by Ruprecht and Morse (12) in an investigation of Massachusetts soils which had received additions of ammonium sulphate as a part of the fertilizer treatment show that there has been a slight solvent action on potassium in the absence of lime.

Lipman and Gericke (13) from experiments conducted for the purpose of determining how calcium carbonate and calcium sulphate affect the solubility of soil constituents, conclude that all soils do not behave alike when treated with these materials. Their results showed an increased solubility in some soils but not in others. The conclusions of Briggs and Breazeale (14) based both on the results of the analyses of the solutions, and on the measurement of the potassium content of wheat seedlings grown in the solutions, are that the availability to plants of the potassium in soils derived from orthoclase-bearing rocks is not increased by the addition of lime or gypsum. They found in some instances a marked depression of the solubility in the presence of gypsum.

TABLE XIV.—EFFECT OF NITRIFICATION ON POTASSIUM IN ACID SILT LOAM

Data expressed as parts per million of dry soil mixtures

No.	Additions to 500 gm. dry soil	Water-soluble	
		Potassium	Nitrate nitrogen
		p. p. m.	*p. p. m.*
1	None	18	84
2	Calcium carbonate 2 gm.	7	128
3	Dried blood 4 gm.	30	294
4	Dried blood 4 gm., calcium carbonate 2 gm.	24	462
5	Dried blood 4 gm., calcium silicate 2 gm.	33	434
6	Dried blood 4 gm., blast furnace slag 2 gm.	39	478
7	Ammonium sulphate 4 gm.	30	54
8	Ammonium sulphate 4 gm., calcium carbonate 4 gm.	21	569
9	Ammonium sulphate 4 gm., calcium carbonate 4 gm.	26	100

The results obtained in our experimental work on the effect of nitrification and sulfofication on soil constituents show that with certain conditions of treatment, there has been some effect on the potassium compounds in the soil, although the amounts of potassium obtained in water solutions are generally much less than the quantities of some of the other elements determined. Considered collectively, the data for potassium, calcium and sulphur in solution, as well as the ammoniacal nitrogen produced under certain conditions of treatment, indicate that potassium has been liberated chiefly by calcium sulphate and ammonium sulphate.

TABLE XV.—EFFECT OF NITRIFICATION AND SULFOFICATION ON POTASSIUM IN BASIC BLACK CLAY

Data expressed as parts per million of dry soil

No.	Additions to 500 gm. dry soil	Water-soluble		
		Potassium	Nitrate nitrogen	Sulphur
		p. p. m.	*p. p. m.*	*p. p. m.*
1	None	31	153	87
2	Dried blood 4 gm.	44	491	90
3	Ammonium sulphate 4 gm.	72	280	1,696
4	Sulphur 2 gm.	48	16	2,156
5	Sulphur 2 gm., dried blood 4 gm.	60	12	2,225
6	Sulphur 2 gm., ammonium sulphate 4 gm.	85	42	3,480

The data for soluble potassium which are given in Tables XIV and XV show that the process of nitrification, considered from the viewpoint of nitrous acid as a solvent, has affected the solubility less than where the transformation of organic nitrogen occurred in the presence of oxidized sulphur.

The effect produced where nitrogen was supplied by dried blood may be due to calcium or to other nitrates formed, rather than to the direct action of acidity. In the acid and basic soils used in this investigation, the addition of dried blood has caused a small increase of water-soluble potassium.

It will be noted from the results in Table XVI showing the effect of sulfofication on potassium in the acid silt loam, that where dried blood and sulphur were the additions made a further increased solvent action has taken place. This is considered to be the result of the action of ammonium sulphate, since in the presence of sulphur, gradually being oxidized, the ammoniacal nitrogen formed has combined with the sulphur acidity. The quantity of ammoniacal nitrogen found at the end of the experimental period was 246 parts per million parts. The amount actually present, however, was in excess of this, for ammonia added to soil cannot all be recovered except by distillation with magnesium oxide. The addition of sulphur and dried blood to the basic soil has affected the solubility of potassium in a similar manner.

TABLE XVI.—EFFECT OF SULFOFICATION ON POTASSIUM IN ACID SILT LOAM

Data expressed as parts per million of dry soil

No.	Additions to 500 gm. dry soil	Water-soluble		
		Potassium	Sulphur	Acidity*
		p.p.m.	*p.p.m.*	*p.p.m.*
1	Sulphur 2 gm.	18	2,143	338
2	Sulphur 2 gm., calcium carbonate 4 gm.	32	1,294	4
3	Sulphur 2 gm., calcium carbonate 2 gm.	53	1,923	196
4	Sulphur 2 gm., dried blood 4 gm.	52	1,365	116
5	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 4 gm.	49	1,559	10
6	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 2 gm.	49	1,689	54
7	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 1 gm.	62	1,551	84

*Acidity expressed as sulphuric acid

The potassium obtained in solution from the acid silt loam mixtures which included dried blood and sulphur is given in Table XVI, and the results for the mixtures to which either dried blood or ammonium sulphate were added are shown in Table XIV.

In the acid silt loam more potassium was changed to a soluble condition by the combined action of sulphur and dried blood than by ammonium sulphate. The potassium solubilities of the basic clay mixtures which are stated in Table XV show that added ammonium sulphate has had an appreciable effect; the increases for this soil being greater than those found in the water solution from the acid soil where ammonium sulphate was added.

Considering the effect of oxidation of sulphur on potassium, the results show that oxidized sulphur has produced less solubility in the acid soil than in the basic clay. The effect of sulphur treatment alone, and when added with blood and calcium carbonate, is shown by the results for the acid soil in Table XVI and for the basic clay in Table XV. It will be noted that in the acid soil there has been no increase of water-soluble potassium where sulphur was the only addition, but when included with calcium carbonate or dried blood the solubility of the potassium was found to be appreciably increased.

Sulfofication proceeded no less actively in the absence of calcium carbonate and dried blood; in fact, the quantity of sulphur from the acid soil mixture treated with sulphur alone was greater than when these materials were added. The acidity of the water extract was also greater when dried blood and calcium carbonate were not added.

The formation of ammonium sulphate has been offered as the explanation of the effect of sulphur when used with dried blood. With calcium carbonate added, the acidity from the oxidation of sulphur has reacted with calcium carbonate and a considerable amount of calcium sulphate has been formed in the mixtures. This is evident from the amounts of water-soluble calcium obtained from the silt loam mixtures receiving additions of calcium carbonate and sulphur, as well as in the basic clay where no calcium carbonate was supplied. The amounts of water-soluble calcium found in the various mixtures, including those treated with sulphur, are presented with the data in Tables XVIII and XIX.

The presence of calcium sulphate in the mixtures which have just been discussed is considered to have been the agency chiefly responsible for the liberation of potassium from the insoluble combinations in which it existed in these soils.

The general conception of the action of calcium sulphate in liberating potassium has been that this phenomenon is brought about through the exchange of calcium with other soil bases. A more recent hypothesis has been advanced by Nolte (15), who considers that calcium sulphate acts on the soil by means of both its constituents, double decomposition occurring with the mineral compounds of the soil.

Where the soils were treated with sulphur, dried blood and calcium carbonate in the case of the acid silt loam, there was no doubt a combined effect of ammonium sulphate and calcium sulphate. Calcium nitrate produced where nitrification of dried blood occurred, especially in the presence of calcium carbonate, calcium silicate and blast furnace slag, may have had an effect on potassium compounds in the soil.

Since soluble potassium salts added to soils are very rapidly fixed to such an extent that only small quantities can be recovered by extraction with water, it is very probable that the amounts of potassium obtained do not represent the total quantities which may have been changed from insoluble compounds in the soil to more soluble forms by the processes taking place in the soil mixtures during the period of incubation.

TABLE XVII.—SOLUBILITY OF POTASSIUM SUPPLIED BY FELDSPAR IN SAND AND SOIL

Data expressed as parts per million of dry mixtures

No.	Additions to 500 gm. sand and soil	Potassium	Nitrate nitrogen	Ammoniacal nitrogen	Sulphur
		p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*
1	Sand	0	0	0	0
2	Sand, sulphur 2 gm	0	0	0	42
3	Sand, sulphur 2 gm., calcium carbonate 2 gm	0	0	0	503
4	Sand, feldspar 8 gm	0	0	0	0
5	Sand, feldspar 8 gm., dried blood 4 gm., sulphur 2 gm	52	27	325	478
6	Sand, feldspar 8 gm , dried blood 4 gm., sulphur 2 gm., calcium carbonate, 2 gm	33	21	58	1,937
7	Soil	18	84	13	37
8	Soil, dried blood 4 gm., sulphur 2 gm	52	6	245	1,365
9	Soil, feldspar 8 gm., dried blood 4 gm., sulphur 2 gm	96	21	465	2,053
10	Soil, feldspar 8 gm., dried blood 4 gm., sulphur 2 gm., calcium carbonate 2 gm	58	373	172	1,256

Further indications of the effect produced by nitrogen and sulphur transformations are furnished by data obtained where feldspar was included with sand and with soil. The treatment and the amounts of water-soluble potassium obtained are stated in Table XVII. Dried blood and sulphur where 8 grams of feldspar was added to 500-gram portions of sand have decidely increased the solubility of potassium in the feldspar. With calcium carbonate included in the treatment, solubility is decreased, and a similar effect has taken place where feldspar was included with dried blood and sulphur in acid silt loam soil mixture.

SOLUBLE CALCIUM AND MAGNESIUM

It is apparent from the results for calcium in Tables XVIII and XIX that considerable amounts, present as other combinations than carbonate, have been changed to more soluble compounds in the differently treated soil mixtures. Where dried blood was nitrified in the silt loam soil, which is deficient in basic calcium, the calcium in solution was 255 parts per million as compared with 111 parts per million from the untreated soil. The addition of calcium carbonate stimulated nitrification, consequently a larger amount of calcium nitrate was formed. Calcium supplied as silicate and by blast furnace slag was made soluble in a similar manner.

TABLE XVIII.—DATA FOR CALCIUM MAGNESIUM ALUMINUM AND MANGANESE. ACID SILT LOAM

Expressed as parts per million

No.	Additions to 500 gm. dry soil	Calcium	Magnesium	Aluminum	Manganese	Sulphur	Nitrate nitrogen
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	None	111	30	0	0	37	84
2	Calcium carbonate 2 gm.	270	13	0	0	50	128
3	Dried blood 4 gm.	255	54	0	34	58	294
4	Dried blood 4 gm., calcium carbonate 2 gm.	736	34	0	0	95	462
5	Dried blood 4 gm., calcium silicate 2 gm.	549	57	0	0	122	434
6	Dried blood 4 gm., blast furnace slag 2 gm.	596	50	0	0	106	478
7	Ammonium sulphate 4 gm.	355	80	0	38	1,852	54
8	Ammonium sulphate 4 gm., calcium carbonate, 4 gm.	2,199	87	0	69	1,689	569
9	Ammonium sulphate 4 gm., calcium carbonate 2 gm.	1,067	85	0	18	2,070	100
10	Sulphur 2 gm.	370	103	660	468	2,143	6
11	Sulphur 2 gm., calcium carbonate 4 gm.	858	108	68	297	1,294	35
12	Sulphur 2 gm., calcium carbonate 2 gm.	785	64	413	471	1,923	21
13	Sulphur 2 gm., dried blood 4 gm.	317	76	234	330	1,365	6
14	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 4 gm.	1,505	113	11	325	1,559	228
15	Sulphur 2 gm,, dried blood 4 gm., calcium carbonate 2 gm.	1,858	111	103	419	1,689	29
16	Sulphur 2 gm., dried blood 4 gm., calcium carbonate 1 gm.	417	92	185	395	1,551	6

TABLE XIX.—DATA FOR CALCIUM MAGNESIUM ALUMINUM AND MANGANESE. BASIC CLAY SOIL

Expressed as parts per million

No.	Additions to 500 gm. dry soil	Calcium	Magnesium	Aluminum	Manganese	Sulphur	Nitrate nitrogen
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	None	245	41	0	0	87	153
2	Dried blood 4 gm.	668	97	0	16	90	491
3	Ammonium sulphate 4 gm.	1,297	183	0	8	1,696	280
4	Sulphur 2 gm.	1,773	282	40	48	2,156	16
5	Sulphur 2 gm., dried blood 4 gm.	1,763	248	52	44	2,225	12
6	Sulphur 2 gm., ammonium sulphate 4 gm.	2,080	275	79	56	3,480	42

The calcium in solution from the basic clay soil was dissolved from its natural supply, since no calcium carbonate was added to this soil which contains a large amount of readily-salifiable base, most of which is evidently combined as silicate, and a small proportion as carbonate. The total calcium content of this soil is 9,400 parts per million as compared with 2,300 in the other soil. Nitrification of dried blood, and the original nitrogen of the clay soil proceeded to the extent that the soluble calcium was considerably in excess of the amounts extracted from similar mixtures of the silt loam. Lyon and Bizzell (16) have reported data which show that a large removal of nitrates from an unplanted soil, where conditions were favorable for nitrification, was associated with a correspondingly large loss of calcium.

Ammonium sulphate, independently of the ammonia being nitrified, reacted with calcium either originally present or added as carbonate, and the solutions of the soil mixtures in which this treatment was included contained large amounts of calcium. These results for soluble calcium corroborate the information obtained from the analyses of drainage water from soils which have received application of ammonium sulphate, that this material depletes the supply of basic calcium compounds.

Acidity resulting from the oxidation of sulphur has freely attacked the soil constituents, including calcium, the amount in solution varying with the treatment. Where sulphur and dried blood were in contact, calcium was changed to a soluble form by a combination of reactions which resulted in the formation of ammonium sulphate. In these mixtures the basicity was not sufficient to neutralize the acidity produced, so that complete nitrification of ammonia was prevented, and a part of the ammonia combined with sulphuric acid resulting from oxidation of sulphur.

Comparatively small amounts of magnesium were changed to a soluble state, considering the total content of the soils. The silt loam soil contains approximately 2,800 parts per million, slightly more than the total calcium; and the magnesium in the basic clay is 7,000 parts per million. Where sulphur was not added to the silt loam, the soluble magnesium exceeds the aluminum and manganese found, but is decidely less than the calcium brought into solution. In the solutions from mixtures where considerable acidity was produced by the oxidation of sulphur, some small increases are observed but they are not comparable with the much larger amounts of soluble manganese and aluminum.

Larger quantities of soluble magnesium were found in the solutions from the basic clay, which is in accord with the total magnesium in the soil. The concentration of magnesium in solutions for the clay soil was also greater than that of manganese and aluminum, being the reverse of what was found for the silt loam soil.

ALUMINUM, IRON AND MANGANESE

So far as evidence is furnished by the quantities of aluminum in the several solutions, the process of nitrification has had no solvent action on aluminum compounds in the two soils used in this experimental work.

No aluminum was extracted from mixtures which did not include sulphur as part of the treatment. The largest amount of aluminum sulphate was present in solution from soil where sulphur was oxidized in the absence of calcium carbonate.

The addition of calcium carbonate at the rate of 8,000 parts per million of soil, decreased the solubility of aluminum to 68 parts per million as compared with 660 parts per million where basic calcium and magnesium compounds were not sufficient to enter into combination with more than a small part of the acidity developed.

Acidity resulting from the oxidation of sulphur in the basic clay reacted chiefly with calcium and magnesium. Much smaller amounts of manganese and aluminum sulphates were formed in this soil than in the silt loam.

Nitrification of dried blood had a slight effect on manganese in both soils. Ammonium sulphate also had a slight solvent action. Manganese, existing in the soil as oxides and in decomposed silicates was freely attacked by the acidity resulting from oxidation of sulphur. The manganese found in the solution generally exceeds the aluminum. No indication was obtained that iron compounds were appreciably affected by the processes of nitrification and sulfofication.

SUMMARY

The indications obtained from this experimental work are as follows:

Approximately 50 percent of sulphur incorporated with soil at the rate of five-tenths of a gram to 500 grams of soil was changed to form of sulphate. When a larger addition was made, 2 grams of sulphur to 500 grams of soil, 70 percent was oxidized.

While sulfofication was somewhat depressed in an acid soil by the addition of calcium carbonate, in sand mixtures the presence of calcium carbonate was essential.

Oxidation of sulphur in soils devoid of basic calcium compounds depresses activities of nitrifying organisms.

Although basicity in excess of the requirement of the soil was supplied by calcium carbonate, nitrification was decreased by oxidation of added sulphur.

A further decided depression occurred with decreased basicity, so that there was a quantitative relationship between the amounts of nitrates found and the calcium carbonate additions.

The increasing quantities of ammoniacal nitrogen which accompanied the decreased amounts of nitrates when sulphur was oxidized, cannot be considered as indicative of sulfofication having a stimulating effect on ammonification. This inverse relation between ammonia and nitrates is due to the deficiency of base, necessary for neutralizing sulphuric acid, having inhibited the transition from ammoniacal to nitric nitrogen. The ammonia formed neutralized acidity and remained as ammonium sulphate.

In the absence of other bases the calcium of rock phosphate did not serve as a base for the sulfofying process to any appreciable extent.

The proportion of rock phosphate to soil was such that phosphorus was added at the rate of 1,900 parts per million parts. The oxidation of sulphur incorporated with rock phosphate in the absence of calcium carbonate or nitrogen carriers, has changed 630 parts of phosphorus into a form soluble in neutral ammonium citrate solution.

When calcium carbonate was added to the mixture prepared with an acid soil, the oxidation of sulphur had practically no effect on rock phosphate.

In a basic soil, the acidity resulting from sulfofication was partially neutralized by calcium naturally present as carbonate and in other combinations, so that the solvent action on rock phosphate was much less than occurred in the acid soil.

Ammonium sulphate has not changed the availability of rock phosphate to an appreciable extent. Whatever action ammonium sulphate has had, is attributed to the sulphate ion, rather than to biochemical action, since nitrification of ammonia did not occur in a soil deficient in bases unless calcium carbonate was added.

Active nitrification of dried blood and ammonium sulphate occurred in the mixtures when conditions were favorable.

Nitrification has been stimulated by rock phosphate to a very limited extent. This fact, independent of the results for either phosphorus or calcium solubility, is sufficient indication that the process has had no appreciable action on rock phosphate in soil.

Nitrification of dried blood, so far as the citrate soluble figures furnish evidence of availability, is not an active agent for increasing the availability of rock phosphate mixed with soil.

In the absence of rock phosphate or calcium carbonate, the nitrification of dried blood as well as the action of ammonium sulphate, independent of the oxidation of its nitrogen, has increased the concentration of water-soluble calcium. More calcium has been taken into solution from the soil than from added rock phosphate. This is evidence that the calcium of the soil, existing chiefly as silicates and partly in other combinations is more readily attacked than rock phosphate by process of nitrification.

Nitrification of dried blood and oxidation of sulphur in soil mixtures increased the water soluble potassium.

The liberation of potassium was brought about by salts formed rather than by the direct action of acidity on insoluble potassium compounds. Calcium nitrate was present where nitrification was stimulated by calcium carbonate. Ammonium sulphate was formed by the reaction between sulphuric acid and ammonia from dried blood, where a deficiency of basic calcium compounds restricted the nitrification of ammonia. Considerable amounts of calcium, aluminum and manganese sulphate were also present in certain mixtures.

Ammonium sulphate, independent of the ammonia being nitrified, affected the solubility of potassium.

Calcium naturally present in the soil as silicate, and in other combinations has been readily attacked by the acidity resulting from nitrification and sulfofication. Ammonium sulphate was also an active solvent of calcium.

Magnesium compounds were much less resistant to the action of these solvent agencies.

Large quantities of aluminum and manganese were converted into soluble forms where sulphur was oxidized in an acid silt loam soil. Small amounts of these elements were made soluble by this action in a basic clay. Nitrification had no effect on aluminum.

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