THESIS

SOME EFFECTS OF SULFUR ON CROPS AND SOILS

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INTRODUCTION.

Considerable attention has been given recently to the use of sulfur as a fertilizer and its effect on the soil. In view of this fact, we conducted some experiments to find the effect, if any, produced on the germination and early growth of alfalfa and clover, by the addition of varying amounts of elemental sulfur to two Michigan soils, and to make a study of the attendant factors which might influence those results. Before entering into a discussion of these experiments, it seems advisable to review certain literature which may have some bearing on the work.

REVIEW OF LITERATURE.

The effect on crops of fertilization with sulfur has been reported by several investigators, many of whom obtained increased yields, especially of legumes and the Cruciferae. Boulanger (9) got increased growth of vegetables, mainly Cruciferae, by the use of light applications of sulfur. Hart and Tottingham (21) found sulfur to give the lowest yields in a series of fertilizer tests on Miami silt loam, under greenhouse conditions. Later (57) they found that 100 lbs. of sulfur increased the yield of clover, Cruciferae and barley on a silt loam soil. Sherbakoff (54) reported injury to clover the following year after making heavy application of sulfur. Duly (18) found the yield of clover was increased and the sulfur was slightly beneficial to the growth of corn and rape. Pitz

(45) and Ames and Boltz (2) found that small applications increased the yield of clover. Brown and Johnson (12 & 13) found that in soils high in sulfur, sulfofication and yield were not always parallel. Shedd (52) obtained increased yields on some soils and decreases on others. Tobacco especially responded to this treatment. He also found (51) that in sand cultures, alfalfa responded to sulfur. Fellars (19) obtained a greater yield of soybeans with applications up to 200 lbs. Reimer and Tartar (46) reported a large increase of alfalfa on various types of Oregon soils. Mc-Taggart (37) obtained increased growth of alfalfa but no effect on soybeans and field peas. Lipman, Prince and Blair (31) obtained uniform germination with barley but later the heavier applications injured the stand. Soybeans following the barley had normal germination on the plots with light applications, but it was depressed by the heavier ones, with practically no germination where the sulfur was applied the heaviest. Olson and St. John (42) obtained increased yields of field crops with elemental sulfur. Rudolphs (47) found soybeans to be stimulated by small amounts of sulfur. Neidig, McDole and Magnuson (40) obtained increased yields of alfalfa on humid soils but no effect on arid soils. McCool (33) reported that field experiments in Michigan showed practically no effect from the addition of sulfur. Bacon and Lint (17) quoted data from the Coastal Plain Experimental Station at Tifton, Ga., showing increased yields of peanuts, tomatoes and peppers from the use of small applications of inoculated sulfur.

Duley (18), Reimer and Tartar (46), and Neidig, McDole and Magnuson (40) obtained their beneficial results on soils naturally low in sulfur. Brown and Kellogg (14) suggested that the use of sulfur not only adds sulfur to the soil, but makes available that already present. Shedd (50) quoted several authorities and concluded that sulfur should be added to the soil as a plant food. Tottingham and Hart (57) concluded that the effect of sulfur on plant growth is (a) by providing the nutrient SO_3, and (b) by rendering P_2O_5 more available. Tottingham (56) said that a deficiency of sulfur supply restricted plant growth of red clover by limiting the synthesis of protein and restricting the elaboration of plant growth. The injurious results obtained by Hart and Tottingham (21) were attributed not to acidity, but to incomplete oxidation of the sulfur to sulfites which exert a toxic effect. Boulanger (9) concluded that the beneficial results were due to the influence on the micro-organisms, as the results were low on sterilized soil.

The majority of investigators found however that the sulfur was oxidized to sulfate, largely by biological agencies, which might explain the result noted by Boulanger. Duley (18) found that sulfur was oxidized to sulfate both in sand and soil cultures. Ames and Boltz (2) found increased sulfate content in treated soil. Hibbard (20) found that sulfur oxidized to sulfuric acid and neutralized alkali soils. Brown and Kellogg (14) concluded that the oxidation is mostly biological, tho some is due to chemical action. MacIntyre, Gray and Shaw (37) obtained some non-biological oxidation when the sulfur was in contact with iron or iron compounds. Demolon (17) attributed the oxidation to the action of ammonifying organisms. Lipman, McLean and Lint (30) proved that the biological factor was essential, and later Lipman, Waksman and Joffe (33) isolated an organism which produced the action. Brown and Warner (15) found that all manures and the one soil used, contained sulfofying organisms. Shedd (53) obtained sulfofication in all the soils he tested. Lipman, McLean and Lint (29) obtained complete oxidation of sulfur in a compost in 15 weeks. Their result shows that the oxidation is dependent on soil conditions, as there was a difference in effect in three soils. The action is controlled by the number and activity of the bacteria, and these are controlled by physical and chemical soil conditions. Demolon (17) obtained the most results in a light soil high in organic matter. Shedd (51) found that oxidation was more rapid in a fertile soil than in a poor one. Brown and Kellogg (14) found that organic matter aided the action, and these authors as well as Lipman, McLean and Lint (35) found that the moisture content was influential. Joffe (24) found in pot tests of composts that the amount of oxidation depended on the method of maintaining the moisture content, as the oxidation itself and the crystallization of the $CaSO_4$ produced, would use water, even tho there was no loss of weight in the pot.

$$2S + 3O_2 + 2H_2O = 2H_2SO_4$$

$$H_2SO_4 + Ca_3(PO_4)_2 = CaSO_4 \cdot 2H_2O + 2CaHPO_4$$

McLean (35) and Rudolphs (48) found aeration to be beneficial, and Rudolphs further found that light was slightly detrimental and 30°C is the optimum temperature. Lipman and Joffe (27) observed that the initial reaction of the soil had little effect on the amount of oxidation or acidity produced. Ames and Richmond (5) found that lime was necessary for the reaction in sand, but that in acid soil, lime depressed sulfofication. Lipman, McLean and Lint (30) found that in a sulfur, floats, soil compost, the floats neutralized the acid produced so it did not become toxic. Lipman, Waksman and Joffe (32) concluded that the vitality of the organism was decreased if too much acid was present, and also in an alkaline medium. Brown and Johnson (12)(13) found that lime or phosphates on acid soil increased sulfofication and (12) that the presence of sulfates had the same effect. They state also that the sulfofying power of soils can be determined by ten days incubation in the laboratory. Sherbakoff (54) found that injury to clover was less on limed soils and greater on soils low in organic matter.

This oxidation produces an acid condition in the soil. Duley (18) found that sulfur was oxidized to SO_4 in sand and soil cultures, and that it slightly increased the acidity. Ames and Boltz (2) found that sulfur increased soil acidity and the amount of sulfates present. Rudolphs (46) found that on soil fertilized for 30 years, small amounts of sulfur did not affect the soil reaction but on poorer (unfertilized) soil there was a change in reaction.

The H ion concentration increased nearly proportionally to the sulfur application. Lipman, McLean and Lint (29) found that in sea sand the acidity increased up to the 10th week, then was constant. It was greater when floats were present. In heavier soil sulfur alone produced the greater acidity. Tottingham and Hart (57) working with composts, obtained the greatest acidity in 12 weeks. Lint (25) found all the sulfur oxidized in 8 weeks and Martin (38) assumed that total oxidation had occurred in explaining why his results showed maximum acidity in 10 weeks. Shedd (51) found about 60% of the sulfur oxidized after 4 months, regardless of the amount applied. Later (53) he reported that the same per cent of sulfur was oxidized with different applications, tho the weight of sulfur oxidized was greater with the larger applications. Ames and Richmond (5) found 50% of sulfur oxidized in an acid soil. In another case (4) they reported that from 50 to 80% was oxidized in silt loam, clay loam and muck. And recently Ames (1) reported that 50% was oxidized with a ton application and 70% when the application was heavier. Lipman and Joffe (27) concluded from their investigations that the original pH of the soil had little or no effect on the resulting pH value produced by sulfofication, tho below pH 2.4 they seemed to get some variation. They attained a pH of 2.0 in 8 weeks and in other cases lowered the pH of the soil to 1.6 in 3½ years. Joffe in another set of experiments (22) produced a pH of 2.8 and Lipman, Prince and Blair (31) under field conditions got a

pH of 3.5 - 3.6 after 3 months with 4000 lbs. of sulfur. They found that acidity did not increase materially with heavy applications for 6-8 weeks, and attained its maximum in the 16th week. They also ran the lime requirement on these soils by the Veitch method but found no exact correlation, tho one set of results may forecast the other. Duley (18) found that the lime requirement was directly correlated with the amount of soluble sulfate. Contradictory results have been obtained concerning the correlation of pH to lime requirement in natural, untreated soils. Blair and Prince (7) using only one soil, found rather close correlation, while Joffe (22) with a series of different soils, and Johnson (25) found very little correlation between these two methods of measuring soil acidity.

Tottingham and Hart (57) concluded that the acidity produced by sulfofication was due to acid salts and not to the presence of free acids, and Ames (1) found some evidence to the same effect. Mirasol (39) quoted Veitch as having found one or two cases where water soluble sulfuric acid was present (in untreated soils).

Hart and Tottingham (21) did not attribute the injruious effect of sulfur on crop yield to the resulting acidity. Shedd (51) reported that this acidity will prevent growth unless lime is used, and Fellers (19) explained the crop injury in his experiments as being due to produced acidity. Reimer and Tartar (46) in recommending sulfur as a fertilizer, advised the use of lime on acid soils. Sherbakoff (54) found that the injury to clover on sulfur-treated soil was less on limed soils, and greater on soils low in organic matter.

Other investigations have shown that acidity does affect the germination and growth of alfalfa. Joffe (23) in a Penn loam soil obtained alfalfa germination in soils with a pH value of 3.6 - 3.8, but found that it was greatly reduced below pH 4.5. No germination occurred below pH 3.6 and no growth below pH 3.8. He recognized that these results were limited due to the use of only one soil. Salter and McIlvaine (49) found that clover germinated at Ph 2.16 but would not grow at pH 2.96. Alfalfa did not sprout at pH 2.16 or grow below pH 4.11 with the best growth at pH 5.94. Apparently the process of germination is not so susceptible to injury as is the growth of plants. These authors found that the pH values which limit germination varied with the different plants, but a slightly acid medium was best for germination, and bases exerted an injurious effect. Bryan (16) found in quartz sand cultures that alfalfa and clover will germinate at a reaction which is too acid for the growth of seedlings. Young seedlings are more sensitive to acidity than old plants. Red clover germinated and grew to a small extent at pH 4.0 but alfalfa and alsike would not grow at that reaction. Alsike did better at pH 5.0 - pH 6.0 than alfalfa or red clover.

Mirasol (39) found that aluminum salts had the same effect on sweet clover as acidity, and concluded that aluminum was the chief factor of acidity in the soils studied. This was disproven by Blair and Prince (8) and Olsen (43). Olsen also found evidence to contradict the theories that only plants which can use ammonia can grow on acid soils, and that acid soils are low in nutrients while alkaline soils are rich in them. He concluded that it is the H ion concentration of the soil, as such, which exerts considerable influence on the type of vegetation which will grow on a soil. Truog (58) advanced four reasons why acidity affects plant growth:

a. by decreasing favorable physical conditions
b. by decreasing favorable biological conditions
c. by favoring the accumulation of toxic substances
d. by decreasing available lime and other food elements.

In addition to the increase of sulfate content, sulfofication increases the amount of other soluble material in the soil. Brown and Warner (6); Tottingham and Hart (57); Shedd (53); Lipman, McLean and Lint (29) (30); and Lipman and McLean under field conditions (28) found that more phosphorus was made soluble. Ames and Richmond (5) found that in alkaline soils no P_2O_5 was made available from floats as the soil bases reacted to neutralize the acids formed, but in acid soils P_2O_5 was made available. Rudolphs (47) found that phosphorus was not made available until a pH of 3.1 - 3.8 was attained. Tottingham and Hart (57) stated that the addition of sulfur depleted the soil of CaO and P_2O_5. Ames (1) and Ames and Boltz (3) found that potassium, calcium, aluminum and manganese were made soluble in acid soils by the action, direct or indirect, of sulfofication. Ammonium sulfate was formed in some cases. Magnesium was not as soluble as calcium. The potassium was liberated by the acid salts formed rather than by the direct action of the acid. Pitz (45) found in agar plates that sulfur increased ammonification and decreased nitrification. Duley (18) found that the nitrate content varied inversely with the amount of sulfate in the soil. Shedd (53) obtained some evidence that nitrification was aided. Lipman, Prince and Blair (31) found that nitrate content depended on the crop demand and was not necessarily affected by the H ion concentration. McCool and Millar (34) found that the presence of calcium sulfate increased the solubility of soils. Lipman, Wakeman and Joffe (32) offered an explanation of the lag of increase of soluble salts, in that insoluble sulfates were first formed, followed by the production of soluble sulfates.

EXPERIMENTAL.

Experiments were carried on in the laboratory, testing the influence of sulfur on germination and early growth of clover and alfalfa, and the effect on the acidity and the solubility of the soils used, to determine if there was any correlation between these different effects. Other experiments were made investigating the effect of leaching on the acidity produced by the sulfur treatment. Some lime requirement determinations were also made and compared with the pH values of the same soils. A small number of field experiments were conducted to find the influence of different amounts of sulfur on the stand of clover and on soil acidity.

POT EXPERIMENTS. The first series of pot experiments was run on a Coloma medium sand. It had not been limed recently, but building material had been stored on it, so it became charged with lime. Alfalfa grew well on it in the field, and when tested in the laboratory it showed the presence of free carbonate. The sulfur used was first washed with distilled water until the mixture with water showed no depression of the freezing point.

The sulfur was mixed with the soil at the rates of 0 lbs. 500, 1000, 1500, 2000 and 3000 lbs. per acre respectively. The soil was then made up to what was considered to be the optimum moisture content, or 10%, and stored in the dark, the moisture content being kept as uniform as possible by frequent weighing and the addition of water. Duplicate pots were made from each treatment at the following intervals: immediately, 10 days, 20 days, 30 days and 60 days after mixing. The entire samples were thoroughly mixed and aerated each time the pots were filled. In each pot were planted 50 red clover and 50 alfalfa seeds of high germination, and the seedlings were counted and removed each second day. The number of seedlings appearing above the surface was considered as representing the germination in every case except in the pots of 3000 lbs. sulfur after 60 days incubation. In this case, germination occurred but no growth took place, so the seeds were found and taken out of the soil, and the per cent of germination determined. At the end of ten days, germination was considered to be complete and the soils were air-dried and stored for further determinations. Hence the results obtained in these later determinations were really those for 10, 20, 30, 40 and 70 days after treatment.

The freezing point depression was used as a measure of the total soluble salts present in the soil samples. This is based on the fact that the magnitude of the difference between the freezing point of a solution and of pure water is dependent on and is a measure of the quantity of substance dissolved. The freezing point depression was found by the method developed by Bouyoucos and McCool (10)(11). The solution to be tested is put into a freezing tube, the Beckman thermometer inserted so the bulb is covered, and the tube is put into a freezing bath, a mixture of ice, water and salt with a temperature of about -3°C. When the thermometer shows that the solution is supercooled about 1°C. the solution is shaken or stirred to cause it to freeze, and when this occurs the mercury in the thermometer starts to rise. The tube is then removed from the freezing bath and placed in an air-bath immersed in the freezing bath. When the mercury column stops rising and the thermometer reading becomes constant, it is taken to be the freezing point of the mixture. In this case 30% water was added to the air-dry sand and the mixture was frozen. This was above the saturation point of the soil, but Parker (44) has shown that the presence of finely divided solids in a concentrated solution will affect the freezing point depression, and this amount of water will eliminate that cause of error. The data given is the actual freezing point depression in degrees Centigrade rather than parts per million of solute, as there is no proof that the factor obtained by Bouyoucos would be correct with the treatment given, and the depressions vary directly as the amount of solute present.

The acidity was found in terms of pH, that is, the logarithm of the reciprocal of the H ion concentration. This was determined electrometrically on the Wendt's Electro-Titration apparatus, following the method described by Spurway (55). This is a process of measuring the difference in potential between a calomel half cell of known potential and a half cell produced by dipping a hydrogen electrode into a solution containing hydrogen ions. From this potential difference as shown by a voltmeter may be calculated the strength of the solution of H ions, or from a table, the voltmeter reading may be interpolated into pH reading.

In making these determinations 10 grams of air-dry soil and 50 cc of freshly boiled, distilled water were placed in an 8 oz. shaker bottle and shaken fro two hours, after which the mixture stood for 24 hours before making the determination. The mixture was put in a funnel shaped dish and the hydrogen electrode dipped into it, always at the same depth. A glass stirrer, running from an electric motor, kept the mixture agitated. Free hydrogen was kept bubbling over the electrode at the rate of two bubbles a second. At five minute intervals the arm of the calomel electrode was introduced into the suspension, always at the same depth, and the resistance was adjusted until the galvanometer showed no deflection. The voltmeter was then read, and the pH obtained from a table. This was continued until there was no change in two readings of the instrument. Before and after each reading the arm of the calomel electrode was rinsed out with N KCl solution, and after removing a sample from the apparatus, the container, stirrer and hydrogen electrode were rinsed with distilled water.

A second series of pots was run on an acid Miami silt loam. In this series, the two smallest applications of sulfur were omitted, so the set as run consisted of the soil plus sulfur at the rate of 0 lbs., 1500, 2000 and 3000 lbs. per acre. The moisture content of the soil was maintained as nearly as possible at 16% by the methods used in the first series. Alfalfa and clover were potted in duplicate at ten day intervals as before, but the 60 day planting was omitted. The freezing point depression and pH of these samples were found as with the sand, except that when freezing this soil, 35% of water was used to supersaturate it.

RESULTS. As these pots were run in duplicate, the results given represent the average of the duplicates in each case. The figures on germination and growth are per cents of the total number of seeds planted in each treated soil. Figures are shown of both clover and alfalfa, except in the case of 500 lbs. sulfur potted immediately, in which case mice destroyed the seedlings.

Table 1. Germination and Growth in Medium Sand.

		0 days		10 days		20 days		30 days		60 days	
		C	A	C	A	C	A	C	A	C	A
0#	S	94	62	84	51	89	59	91	68	88	65
500#	S	-------		89	55	82	56	84	64	91	62
1000#	S	89	62	93	58	86	55	88	65	90	62
1500#	S	90	67	91	51	89	64	89	59	78	42
2000#	S	89	55	97	54	90	59	86	57	48	51
3000#	S	88	57	90	60	94	49	(5	7)	(52	74)
								Growth (61 33) germination		Germination only, one pot	

Table 2. pH of Sand.

		0 days	10 days	20 days	30 days	60 days
0#	S	7.95	8.2	8.15	8.2	8.05
500#	S	7.75	7.5	7.6	7.5	7.5
1000#	S	7.65	7.35	6.75	6.7	6.3
1500#	S	7.7	7.2	5.6	5.0	4.3
2000#	S	7.65	7.2	4.5	4.4	3.9
3000#	S	7.6	6.7	4.4	4.1	3.65

Table 3. Freezing Point Depression of Medium Sand.

		0 days	10 days	20 days	30 days	60 days
0#	S	.007	.016	.017	.015	.017
500#	S	.011	.028	.042	.043	.042
1000#	S	.034	.037	.043	.043	.047
1500#	S	.041	.045	.047	.051	.070
2000#	S	.041	.043	.058	.060	.080
3000#	S	.045	.051	.060	.073	.112

Table 4. Germination and Growth on Miami Silt Loam.

		0 days C	0 days A	10 days C	10 days A	20 days C	20 days A	30 days C	30 days A
0#	S	63	59	86	72	89	64	80	69
1500#	S	89	62	90	64	93	60	73	63
2000#	S	92	68	83	59	91	61	24	10
3000#	S	86	64	74	54	70	52	2	0

Table 5. pH of Miami Silt.

		0 days	10 days	20 days	30 days
0#	S	4.9	5.05	4.97	5.05
1500#	S	4.85	4.35	3.95	3.62
2000#	S	4.75	4.1	3.75	3.4
3000#	S	4.75	3.5	3.4	3.16

Table 6. Freezing Point Depressions of Silt Loam.

		0 days	10 days	20 days	30 days
0#	S	0.011	0.019	0.017	0.021
1500#	S	0.0215	0.042	0.0495	0.054
2000#	S	0.023	0.051	0.076	0.085
3000#	S	0.024	0.059	0.1045	0.1165

Discussion. From the above results it can be seen that in the medium sand cultures, there was little apparent effect of the sulfur on the germination and growth above ground, except with the two heaviest applications after 30 and 60 days, tho to some extent the 10 and 20 day samples showed a slight increase over the checks of those periods. In the cases where heavier applications stood moist for some weeks, however, the growth as indicated by the appearance above ground, was much decreased. There was practically no difference in the effect produced on clover and on alfalfa, except that in the 3000# - 60 day pots, where germination alone was counted, the alfalfa gave higher results than in any other case, while the clover showed a decrease. This bears out the statements already quoted, that alfalfa and clover will germinate at a lower pH than they will grow. The seedlings are evidently more sensitive to acidity than are the seeds.

The acidity of the soils, and the amount of soluble material increased with the amount of sulfur applied and the length of time it was allowed to stand. The pH at which growth was inhibited was about the same both the 30 and the 60 day series, and this is also true of the freezing point depression. Fairly good growth was obtained at pH 4.3, but practically none at pH 4.1. There appears to be a close correlation between the pH and the amount of soluble material present. This is noticeable in the 500 lb. treatment in all periods, in the 1500 and 2000 lb. applications after 0 days and 10 days, and in the 2000 application after 20 and 30 days. The increased soluble material in these soils must be due to some action on the sulfur or on the soil, and not the mere presence of the sulfur, as, before applying, it was washed until it gave no freezing point depression.

The results in the silt loam are very similar, but the correlation between the pH and freezing point depression is not so marked. Also the soils became more acid, and growth was obtained at much greater acidity than in the sand. A pH value of 3.5 appears to have decreased the growth slightly, but no great damage was done until the acidity of the soil was changed to pH 3.4 or less. The growth in the 1500 and 2000 lb. pots after 20 days was as great as in any of the pots in the series, even tho in both cases the pH was below 4.0.

From the fact that growth practically ceased in the sand at pH 4.1 while in the silt loam the plants grew well at pH 3.5, it is apparent that the acidity at which a plant will grow is a property of the soil and not entirely of the plant itself, and will vary with each soil used. And it is evident also that this is due to some effect on the growth of the seedling, and not on germination. In the heavier soil, the plants are able to withstand a much greater acidity than in the lighter one. It can be seen from these results and from those of other experiments quoted that the pH produced in a soil, and its effect on plant growth, are controlled by soil conditions and will vary in different soils, thus explaining the apparently contradictory results of some authorities quoted.

In the sand cultures it will be observed there was less growth with the 3000 lb. application after 30 days than with the 2000 lb. after 60 days, altho in the latter case the pH was less. In the same pots, the one with the greater amount of soluble salts gave the better growth. This is also apparent in similar pots in the silt loam

series, which would seem to indicate that the death point was not due to too great a concentration of the soil solution.

Altho Joffe (18) when composting sulfur, found that the amount of moisture used by the reaction and taken up by the crystallizing $CaSO_4$ was great enough to influence the bacterial action, that would not be a factor in this case, as the oxidation of the maximum amount of sulfur applied would decrease the moisture content less than .5%.

In the untreated pots, the solubility of the soil was increased as it stood with optimum moisture content, but the maximum was soon reached.

The pH values increased slightly when the soils stood moistened after being air-dried. This was found also by Spurway (55) but is contradictory to the results of Noyes and Yoder (40) who found that acid soil, either bare or cropped, increased in acidity when allowed to stand with its water holding capacity half satisfied.

B. Leaching. In the leaching experiments, samples weighing 230 grams were taken of one of the treated sand cultures and of the untreated sand. These samples were placed in glass cylinders, making soil columns 8.5 cm. and 8.0 cm. high respectively. Each column was leached by percolation with 5 liters of water. Samples of the leachings were taken after the first 250 cc. had passed through, and the last 250 cc. of percolate were also collected. These leachings were analysed for Ca and SO_4 and the pH was taken.

The pH of soil samples, taken after 4½ liters had passed through, were also found, for comparison with the unleached soils.

Percolation was faster in the treated soil, although this column was slightly higher.

Table 7. Results of Leaching in Treated and Untreated Soils.

	$BaSO_4$ in 50 cc	CaO in 50 cc	pH
Treated unleached soil			5.5
" leached soil			5.3
First leachings	0.0320	0.0085	5.6
Last leachings	trace	trace	4.4
Untreated unleached soil			7.5
" leached soil			6.9
First leachings	0.0004	0.0010	7.5
Last "	------	trace	5.6

Discussion. These figures show that although the sulfate was practically all removed by leaching, the acidity produced by sulfofication coult not be leached out, but, on the contrary, leaching made the soil slightly more acid. Apparently the sulfuric acid reacted with the soil bases as fast as it was formed, and the increased soil acidity was due to insoluble acids or acid salts. The alkaline soil was made much more acid by leaching, and the last leachings from this soil were strongly acid.

Practically all the soluble calcium and sulfate sulfur were washed from the soil. The untreated soil contained practically no sulfates. Although the untreated soil was alkaline and showed the presence of excess carbonate when treated with acid, the first leachings from the treated soil contained more calcium than those from the untreated. This shows that the treatment makes the calcium more soluble.

From the fact that water percolated faster through the treated soil, it would seem that the treatment flocculated the colloids present.

C. Lime Requirement. Following a method outlined by Spurway (55), the lime requirement produced by the sulfur treatment was found in the following samples:

Sand plus 2000 lbs. sulfur after 60 days
" " 3000 lbs. " " 30 days
Silt loam plus 2000 lbs. sulfur after 30 days
" " " 2000 " " " " "

Ten grams of soil were placed in each of several shaker bottles. Normal tenth equivalents of $Ca(OH)_2$ were added in steps from 1 cc to 10 cc and sufficient neutral water was added to raise the volume to 50 cc. The bottles were then shaken for two hours and allowed to stand for 24 hours, when the pH of the contents was determined electrometrically. By plotting curves of these results it was possible to find the $Ca(OH)_2$ required to neutralize the acidity produced by the sulfur, and bring the soil back to its original reaction. From these results were calculated the amount of $CaCO_3$ required per acre to neutralize the effect of the treatment, also the weight per acre and per cent of sulfur oxidized.

Table 8. Lime Requirement and Amount of Sulfur Oxidized.

	Lime Req.	Lbs.S per A oxidized	% S oxidized
Sand - 2000# S-60 days	4100# $CaCO_3$	1312	65.6%
Sand - 3000# S-30 days	4450#	1424	47.47%
Silt loam - 2000# S-30 days	3570#	1242	62.1%
Silt loam - 3000# S-30 days	4570#	1462	48.7%

Discussion. Since these pots were kept in the laboratory, away from undesired influences, the acidity and change in pH produced was due entirely to the treatment. Thus by titrating this acidity it should be possible to determine the amount of acid produced, and from this, the amount of sulfur oxidized. In the sand however, the soil originally contained carbonates which were broken down and the CO_2 lost when the pH fell below 7. In this case, titrating with $Ca(OH)_2$ would not give the same reaction in the soil after the neutral point was reached, so this probably was not an accurate measure of the amount of acid which changed the soil from its original pH of 8.1 to the pH value at the end of the period. However the results obtained are quoted for comparison. In the silt loam, where the initial reaction was acid, this objection would not hold, and the lime requirement produced by the treatment, and the amount of sulfur oxidized can be measured.

From the curve of the titration, it will be seen that the heavier application of sulfur after 3o days incubation, caused a greater buffering of the soil and required more lime to neutralize it than did the lighter application after 60 days, though the latter gave a slightly lower pH value.

The lime requirement in the sand is low, considering the final acidity of the soil, but this soil is slightly buffered, so a little acid or base will readily change the reaction.

In both cases it appears that a greater percent of sulfur was oxidized with the smaller application, even though the actual amount was less. This is also shown by the tables of pH values and freezing point depressions already given, as there, with the lighter applications, the pH and soluble salt content became constant during the last two or three periods, indicating that all the sulfur had been oxidized. Approximately the same per cent of sulfur was oxidized with the same application, in the two soils.

In one soil, the pH might show a correlation with the lime requirement but in two different soils there is no correlation.

D. Plot Experiments. The field in which the plot work was conducted was largely Plainfield loamy sand with a ridge of Coloma just bordering it. Eight plots, 12 by 30 feet, were laid out in two sections, plots 1-4 being on the Plainfield, while plots 5-8 were along the border of the Coloma. Plots 1 and 8 were untreated and the others were treated on May 21, 1923, with sulfur at the rates of 200, 500, 1000, 1500, 2000 and 3000 lbs. respectively. All were planted with mammoth clover on May 22. Samples of soil were taken from these plots on June 4, June 14, June 25 and Sept. 25, and the growth was noted on these days and on Aug. 31. Unoxidized sulfur was observed in all the treated plots at each time they were sampled. The clover catch was poor and the vegetation produced was mainly quack grass and other weeds. However some data was taken.

Plots 5 and 6 are omitted from the results shown, as they quickly became covered with wind blown sand from adjacent fields.

Table 9. pH of Samples from Treated Plots.

	June 4	June 14	June 25	Sept. 25
1. 0# S	6.2	5.87	6.1	5.2
2. 200# S	6.1	5.7	5.35	4.25
3. 500# S	5.8	4.9	4.1	3.55
4. 1000# S	5.7	4.25	4.17	3.75
7. 3000# S	5.35	3.75	4.9	3.1
8. 0# S	5.8	5.8	5.95	5.45

Notes on Stand.

June 4. Fair on plots 1-2-3-8
Poor on plot 4
None on plots 5-6-7

June 14. Stand fair on all plots.

June 25. Stand fair on plots 1-2-3-8
Poor on plot 4
Practically none on plots 5-6-7

Aug. 31. Growth poor on all plots. In a rough way the stand varied inversely with the amount of sulfur applied. Quack grass and weeds dominant, but the grass was thin on the heavily treated plots.

Sept. 25. Same as above. Soil samples taken contained unoxidized sulfur in plots 3-4-6-7, especially the last two. Plots 1 to 4 showed very plainly the decrease in clover due to the addition of sulfur. Plots 5 and 6 were covered 1 to 3 inches deep with wind-blown sand from an

adjacent field. Plot 7 had a few clover plants. Plot 8 had a fair stand.

Discussion. The soil in these plots before treatment was fairly acid, so the stand, even on the check plots, was poor. Also, the plots received no care from June 25 to Sept. 25, and the weeds started first and crowded out the clover. So the only good results obtained are of the acidity produced.

The figures show that on a light, acid soil, the application of 3000 lbs. of sulfur produced an acidity of pH 3.1 in four months. The acidity produced in the other plots was roughly in the order of the amount of sulfur applied, and varied with the length of time after application that the sample was taken.

There was some growth even on the most acid soil, showing that after once getting a start, the plants will stand a great H ion concentration. At the time of germination, the soil was not so acid, but on June 14 the plants were only one or two inches high, and plot 7 had a pH value of 3.75. This is a greater acidity than the crops on the sand in the pot tests were able to withstand.

After 34 days there was little difference in the pH value of the plots receiving 500 lbs. and 1000 lbs. of sulfur, and after 4 months the 500 lb. application gave a slightly greater acidity.

Summary.

Pot cultures of clover and alfalfa were made on sulfur treated soils after different intervals, and other determinations were then made on these soils.

Sulfur in light applications or in the early stages of incubation had no effect on growth, but heavy applications decreased it.

The acidity and soluble salt content of the soils increased with the amount of sulfur applied and with the length of the incubation period.

There is some correlation between the pH and total soluble salt content of the soils.

In the heavier soils, the plants were able to withstand a much greater acidity than in the lighter ones.

Decrease in growth was not due to too great a concentration of the soil solution.

Germination will occur at a lower pH than growth. Germination occurred in sand at pH 3.65 and some growth at pH 3.9, while in the silt loam some growth occurred at pH 3.4 and a normal stand was found at pH 3.75.

The pH produced by this treatment, and the acidity which a plant can stand appear to be controlled by soil conditions and will vary in different soils.

The pH value of untreated soils increased slightly when they stood moistened after being air-dried.

The acidity produced by sulfofication cannot be leached out. Apparently it is not due to soluble sulfuric acid nor acid sulfates.

The treatment increased the solubility of calcium.

The heavier applications with short incubation periods produced a greater buffering effect in the soil than lighter applications with longer incubation periods.

In one soil there may be some correlation between pH and lime requirement but this is not true with figures obtained from different soils.

In both soils used, the lighter applications showed a greater per cent of sulfur oxidized, and the per cent was about the same with equal applications in the different soils.

In the plot experiments, the stand was poor on all plots, but some growth of mammoth clover was observed on a soil with a pH of 3.1, and a fair growth occurred on soils with pH 3.55 - 3.75.

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Lime Requirement

of

Sulphur Treated Soils

148 Sand - 3000 lb S - 30 days

158 Sand - 2000 lb S - 60 days

230 Silt loam - 2000 lb S - 30 days

232 Silt loam - 3000 lb S - 30 days