Technical Bulletin No. 59 December 15, 1935

University of Arizona
College of Agriculture
Agricultural Experiment Station

OXIDATION OF SULPHUR IN ARIZONA SOILS AND ITS EFFECT ON SOIL PROPERTIES

By
W. T. McGeorge and R. A. Greene

PUBLISHED BY
University of Arizona
TUCSON, ARIZONA

ORGANIZATION

HOMER LeROY SHANTZ, Ph.D., Sc.D.........President of the University

EXPERIMENT STATION STAFF

PAUL S. BURGESS, Ph.D.........Director and Dean

AGRICULTURAL CHEMISTRY AND SOILS DEPARTMENT

WILLIAM T. McGEORGE, M.S.........Agricultural Chemist
JAMES F. BREAZEALE, B.S.........Biochemist
THEOPHIL F. BUEHRER, Ph.D.........Physical Chemist
HOWARD V. SMITH, M.S.........Assistant Agricultural Chemist
ROBERT A. GREENE, Ph.D.........Assistant Agricultural Chemist
RAYMOND H. KELLNER, B.S.........Assistant Chemist
E. OSBORN FOSTER, M.S.........Assistant Agricultural Chemist (Phoenix)

AGRICULTURAL ECONOMICS AND RURAL SOCIOLOGY DEPARTMENT

GEORGE W. BARR, Ed.D.........Agricultural Economist
ELZER D. TETREAU, Ph.D.........Rural Sociologist

AGRICULTURAL ENGINEERING DEPARTMENT (Irrigation)

GEORGE E. P. SMITH, C.E., D.Eng.........Agricultural Engineer
HAROLD C. SCHWALEN, B.S. in M.E., M.S. in C.E.........Associate Agricultural Engineer
*WILLIAM A. STEENBERGEN, B.S. in C.E.........Assistant Agricultural Engineer
LLOYD KELLER, B.S. in M.E.........Assistant Agricultural Engineer

AGRONOMY DEPARTMENT

RALPH S. HAWKINS, Ph.D.........Agronomist
IAN A. BRIGGS, M.S.........Associate Agronomist
ROBERT A. MATLOCK, Ph.D.........Assistant Agronomist
†ARTHUR T. BARTEL, M.S.........Assistant Agronomist

ANIMAL HUSBANDRY DEPARTMENT

ERNEST B. STANLEY, M.S.........Animal Husbandman
EVERETT L. SCOTT, Ph.D.........Associate Animal Husbandman
WILLIAM J. PISTOR, B.S., D.V.M.........Associate Veterinarian

BOTANY DEPARTMENT

JOHN J. THORNBER, M.A.........Botanist

DAIRY HUSBANDRY DEPARTMENT

WALTER S. CUNNINGHAM, M.S.........Dairy Husbandman
RICHARD N. DAVIS, M.S.........Associate Dairy Husbandman

ENTOMOLOGY AND ECONOMIC ZOOLOGY DEPARTMENT

CHARLES T. VORHIES, Ph.D.........Entomologist
ELMER D. BALL, Ph.D.........Economic Zoologist
LAWRENCE P. WEHRLE, Ph.D.........Assistant Entomologist

HORTICULTURE DEPARTMENT

ALLEN F. KINNISON, M.S.........Horticulturist
DAVID W. ALBERT, M.S.........Associate Horticulturist (Tempe)
MALCOLM F. WHARTON, M.S.........Associate Horticulturist (Phoenix)
ALTON H. FINCH, Ph.D.........Associate Horticulturist
JUSTIN G. SMITH, B.S.........Assistant Horticulturist (Tempe)
§KARL HARRIS, M.S.........Assistant Irrigation Engineer (Tucson)

HUMAN NUTRITION DEPARTMENT

MARGARET CAMMACK SMITH, Ph.D.........Nutrition Chemist
LOUISE OTIS, Ph.D.........Assistant Nutrition Chemist

PLANT BREEDING DEPARTMENT

WALKER E. BRYAN, M.S.........Plant Breeder
ELIAS H. PRESSLEY, M.S.........Associate Plant Breeder

PLANT PATHOLOGY DEPARTMENT

JAMES G. BROWN, Ph.D.........Plant Pathologist
RUBERT B. STREETS, Ph.D.........Associate Plant Pathologist
KARL D. BUTLER, M.S.........Research Assistant in Plant Pathology

POULTRY HUSBANDRY DEPARTMENT

HARRY EMBLETON, B.S.........Poultry Husbandman
HUBERT B. HINDS, M.S.........Associate Poultry Husbandman

RANGE ECOLOGY DEPARTMENT

‖WILLIAM G. McGINNIES, Ph.D.........Range Ecologist
ANDREW A. NICHOL, B.S.........Assistant Range Ecologist
JOSEPH F. ARNOLD, B.S.........Research Assistant in Range Ecology

---

*On leave—with Resettlement Administration.

†In co-operation with United States Department of Agriculture, Bureau of Plant Industry.

§In co-operation with United States Department of Agriculture, Bureau of Agricultural Engineering.

‖On leave—with Soil Conservation Service.

TABLE OF CONTENTS

ILLUSTRATIONS

OXIDATION OF SULPHUR IN ARIZONA SOILS AND ITS EFFECT ON SOIL PROPERTIES

By W. T. McGeorge and R. A. Greene

INTRODUCTION

The study of soil conditions which contribute to certain nutritional disturbances encountered in the cropping of alkaline calcareous soils has been a major project in this laboratory for several years. The term "alkaline calcareous" as used here signifies soils containing 2 to 10 per cent or more of calcium carbonate and some replaceable sodium, and which usually have pH values within the range of 8 to 10. These soils contain very little organic matter, possess widely varying physical characteristics, and comprise the major percentage of the soils in the irrigated valleys of this state.

Briefly stated, the work thus far has shown that most of the so-called black alkali soils which are at present being cropped do not contain toxic concentrations of NaOH or Na_2CO_3 (2). Therefore, if these alkali compounds are in any way associated with the low productivity of these soils we must consider their influence as an indirect one.

Since the development of highly accurate methods of measuring the hydrogen- and hydroxyl-ion concentration of soils or soil solutions and plant cultures, chemists and plant physiologists have turned their attention to the effect of the presence of these ions on the absorption of many of the essential nutrient ions by plants. It has been rather definitely shown (2, 3) that in the presence of hydroxyl ions the plant has some difficulty in absorbing negatively charged ions, such as nitrate or phosphate, and therefore will absorb an excess of positively charged ions. In the presence of an excess of hydrogen ions the opposite condition exists, namely, negatively charged ions are absorbed with greater ease. Most of this work has been confined to water cultures, and its significance and application to field conditions have been largely overlooked.

On calculating the hydroxyl-ion concentration of soils from the pH values, it is evident that the concentration present at pH values between 8 and 10 is too low to be considered as directly toxic. This is rather convincing evidence that alkaline soils in which sufficient alkali is present to exercise a direct toxic effect upon the crop are the exception rather than the rule, and that fertility problems connected with the cropping of arable alkali soils are in some way related to the effect of hydroxyl ions on the absorption of essential ions in properly balanced proportions. Results obtained in experiments support the truth of the above statement. That is, when acids or acid-forming compounds are added to these soils, plant growth is benefited, and a better-balanced ion absorption takes place (11).

It is the standard practice to utilize animal manures and green manure cover crops in ameliorating many of the undesirable properties of alkali soils. These organic materials are considered residually acid materials because of the products formed during their decomposition, but high taxes and scarcity of animal manures limit the feasibility of continued, extensive use of organic fertilizers. One of the principal functions of organic matter in alkaline soils is to supply carbon dioxide to the soil environs as carbon dioxide is intimately related to the reaction of the soil through its influence upon the carbonate-bicarbonate ratio. In fact, we have been led to state that carbon dioxide is one of the greatest growth-limiting factors in the productivity of alkaline soils. It reduces the pH value, functions in the availability of phosphate, potassium, and nitrate, in the flocculation of clay, in water penetration, and in fact in most of the desirable characters or properties of these soil types.

As a mild soil amendment for the reduction of hydroxyl-ion concentration of soils and the production of carbon dioxide within the soil confines, organic matter stands at the head of the list of available materials. On the other hand, the same results may be accomplished with sulphur and acids, and their use is entirely feasible. Both have been used effectively in the reclamation of alkali soils, but have not been used like manure for improving the fertility of alkali soils already under cultivation and producing fair crops, in other words, for correcting the adverse influence of small concentrations of hydroxyl ions on ion absorption by plants. In the cropping of alkali soils, a distinction must be drawn between the use of potentially acid materials for reclamation and for continued productivity. Sulphur, after oxidation to sulphuric acid in the soil, should produce gypsum and calcium bicarbonate together with the highly desirable hydrogen, calcium, and bicarbonate ions.

There has been an existing impression that Arizona soils are low in sulphofying power, and so in connection with our soil productivity studies, in which the effect of hydroxyl ions upon plant growth is a major part, it became necessary to give some time to the study of sulphur and sulphofication in Arizona soils.

LITERATURE

The oxidation of sulphur or its conversion to sulphuric acid in the soil may be brought about either by chemical or biological agencies, but the latter process is of far greater importance than the purely chemical transformation. Kappen and Quensell (5) have shown that milk of sulphur will undergo oxidation to sulphuric acid in sterile soils while flour of sulphur is not appreciably changed. They offered the suggestion from their work that sulphur transformations were chiefly chemical rather than biological. MacIntire, Gray, and Shaw (6) also studied the chemical oxidation of sulphur but found that this played a rather insignificant part in the transformation which sulphur undergoes in soils.

The biological oxidation of sulphur in soils is carried out chiefly by the genus Thiobacillus which is described by Bergey (1) as: "small rod-shaped organisms deriving their energy from the oxidation of sulphides, thiosulphates or elementary sulphur, forming sulphur, persulphates and sulphates under acid or alkaline conditions and deriving their carbon from carbon dioxide or from bicarbonates and carbonates in solution; some are obligate and some facultative autotrophic, one species is anaerobic." This group is especially interesting because of their ability to secure energy for growth from the oxidation of these inorganic compounds of sulphur and to use this energy in the synthesis of carbohydrates from carbon dioxide or bicarbonates and carbonates in solution.

The biological oxidation of sulphur, its effect upon soil fertility, the physiology of the sulphur-oxidizing bacteria, and other phases of the problem have been studied and reviewed so extensively that no attempt will be made to review the literature. Excellent discussions and bibliographies have been given by Waksman (9), Joffe (4), and Starkey (8). It should be mentioned, however, that investigations show quite definitely that biological transformations are of far greater importance than purely chemical transformations.

The value of sulphur as a soil amendment is manifested by several characteristic properties.

Plant-food value: All plants contain some sulphur, both as organic and inorganic compounds, and many plants require more sulphur than phosphorus. On the other hand, because of the presence of sulphur in rain water, irrigation water, and as an incidental constituent of commercial fertilizers, sulphur rarely appears in agriculture as a plant-food deficiency. The one extensive area in which sulphur fertilization is practiced to supply a plant-food deficiency is in northwestern United States.

Biological value: Many soil workers look upon lowered productive capacity of soil as largely due to neglect of the microbiological machinery of the soil. They lay great stress upon the value of microorganisms in the elaboration of available plant food and the production of a healthy medium for root development. For this reason some of the beneficial effects of sulphur oxidation have been attributed to a stimulation of biological activities.

Indirect effect: As a result of the biological activities connected with the conversion of sulphur into sulphuric acid and finally into alkali or alkaline-earth sulphates, there is a solvent action toward several important plant-food elements which are present in the soil in insoluble or unavailable forms. This is especially true of soils deficient in available phosphorus, potassium, iron, manganese, and calcium.

Physical effects: On incubating a clay soil with sulphur, that is, on mixing a soil with sulphur, bringing to optimum moisture content and allowing to stand for a week or more, a flocculation of the clay particles into larger aggregates will result, accompanied by a notable improvement in the mechanical condition of the soil. This flocculation is due to the formation of calcium sulphate and bicarbonate, both of which are active flocculating agents, and to the temporary presence of sulphuric acid during the sulphofication of the sulphur.

Reducing soil alkalinity: As an acid-soil amendment, sulphur has been shown to be an effective agent for the reclamation of alkali soils. The alkalinity is neutralized by the acid formed during the oxidation of the sulphur, while accompanying chemical reactions improve the physical character of the soil in such a manner as to contribute to a ready removal of alkali by drainage.

EXPERIMENTAL

PRELIMINARY SULPHOFICATION EXPERIMENT

There is no evidence of a deficiency of sulphur as plant food in Arizona soils. Most of the irrigation waters are well supplied with sulphates, and there are extensive deposits of gypsum, sulphide ores, and other sources of sulphur in the state. Therefore, we were not interested in the plant-food value of sulphur. Our interest in this investigation was in its oxidation, and after this the effect of this oxidation upon the activities of the microbiological life of the soil, upon the physical condition of the soil, upon soil reaction, and upon the availability of plant food, particularly phosphate. We were not especially interested at this time in its value for the reclamation of alkali soils but only for the correction of slight concentrations of hydroxyl ions which may often promote an unbalanced ion absorption by crops.

The first experiment was conducted to determine whether Arizona soils contain sulphofying bacteria. One-hundred-gram portions of soil were weighed into glass tumblers, 1 gram of sulphur was added to each after which the whole was thoroughly mixed. Sufficient distilled water was added to bring the soils to optimum moisture content; they were then incubated at 30 degrees C. Distilled water was added at weekly intervals to maintain the moisture content at optimum. A series of the same soils containing no sulphur was treated in a similar manner for controls. At the end of one- and two-week periods, treated and control soils were analyzed in the following manner: The contents of the tumblers (100 grams of soil) were transferred to wide-mouth bottles with 500 cc. of CO_2-free distilled water. They were then placed in an end-over-end shaking machine and shaken for one hour. The bottles were then allowed to stand for a few minutes so that the heavier soil particles could settle. Total soluble salts were determined on this supernatant liquor by means of a portable conductivity bridge. The pH values were determined colorimetrically. Following this, 1 gram of aluminum chloride was added to each bottle to aid flocculation of the colloidal clay; the bottles were then shaken and the contents filtered. Sulphates were determined turbidimetrically in this filtrate. The results obtained are given in Table 1.

An examination of the data in Table 1 shows that there was an increase in total soluble solids, notably sulphates, and a decrease in pH in each case where sulphur was applied. There was also an improvement in the physical condition of the soil as evidenced by a more rapid rate of sedimentation of the soils treated with sulphur. Where sulphur had been added to the soils, they settled rapidly, leaving a clear supernatant liquor, while the unsulphured soils settled more slowly and left a turbid supernatant liquor.

EFFECT OF SIZE OF SULPHUR PARTICLES ON OXIDATION

There is some evidence that the chemical activity of elemental sulphur increases with decrease in size of the particle of sulphur, and this is indicated by the work of Kappen and Quensell (5). Their investigations showed that colloidal sulphur was oxidized chemically in sterile soils while ordinary flour sulphur was not measurably changed. Colloidal sulphur as a soil amendment is too costly to permit its use. On the other hand, there are many grades of sulphur available which vary principally in their degree of fineness. In view of this the next series of experiments was conducted to study the relation of degree of fineness to rate of oxidation.

The soil used for this experiment was a Gila loam which was obtained from the new University farm near Tucson. In order to approximate field conditions, the amount of sulphur used was reduced to 0.2 gram per 100 grams of soil, which corresponds to 2 tons per acre 8 inches of soil, assuming 2,000,000 pounds as the weight of an acre 8 inches. The experimental procedure was the same as described for the previous experiment, and incubations were made at 30 degrees C. At the end of the incubation periods given in Table 2, the soils were transferred to wide-mouth bottles with 500 cc. of CO_2-free water and shaken as in the previous experiment. Total soluble salts were determined by conductivity, and pH measurements were made potentiometrically with the hydrogen electrode. After these determinations had been made, the soil suspensions were treated with carbon dioxide by passing a stream of gas through the suspension for

TABLE 1.—SHOWING REDUCTION IN pH AND INCREASE IN TOTAL SOLIDS AND SULPHATES DURING INCUBATION OF SOIL WITH SULPHUR.

Soil		pH value		Total solids, p.p.m.		Sulphate (SO_4), p.p.m.	
		1 week	2 weeks	1 week	2 weeks	1 week	2 weeks
Gila fine sandy loam,	Chk.	8.6	8.6	500	500	none	none
Gila fine sandy loam,	S	7.8	7.0	5430	5530	3750	5440
Palo Verde sandy gravelly loam,	Chk.	8.4	7.6	327	600	none	none
Palo Verde sandy gravelly loam,	S	8.2	7.2	1160	1900	575	775
Gila loam,	Chk.	8.2	8.0	1260	2520	225	450
Gila loam,	S	7.7	7.4	2050	5200	390	1100
Mohave clay loam,	Chk.	8.6	8.0	458	1342	100	60
Mohave clay loam,	S	8.4	7.6	850	2860	400	1550
Mohave sandy loam,	Chk.	8.5	8.5	190	390	trace	trace
Mohave sandy loam,	S	8.5	7.3	4885	5550	2500	5000

15 minutes with occasional shaking. These were then filtered through filter paper and the clear filtrates analyzed turbidimetrically for sulphates and for phosphate by a modification of the Deniges method.

The soils were treated with carbon dioxide, partly in order that a clear extract could be obtained, and partly because previous investigations in this laboratory (7) have shown that the phosphorus extracted by this treatment is an excellent indication of its availability. The reason for this is that solid-phase calcium carbonate depresses the solubility of phosphates in Arizona soils in the absence of carbon dioxide, and the introduction of carbon dioxide into the soil offsets this undesirable property.

The grades of sulphur used in these incubations were all commercial grades, and the outline of the experiment was as follows:

A. Checks, soils incubated without sulphur additions
B. Commercial flour sulphur (Mule brand)
C. Sulphur flour passing a 200-mesh sieve
D. Sulphur flour passing a 300-mesh sieve
E. Sulphur flour passing a 400-mesh sieve
F. Mist brand wettable sulphur
G. Sunland agricultural sulphur

The following data are presented as a partial analysis of the soil used in this experiment.

Total solute solids	850	p.p.m.
pH (1:5 soil-water ratio)	8.90	
Sulphate	trace	
Phosphate (PO_4) (CO_2-soluble)	0.70	p.p.m.

The data obtained from the analyses of the soils from this series of incubations are given in Table 2.

These data do not show any consistent relationship between the degree of fineness of sulphur and reduction in pH value, sulphates produced, or amount of phosphate rendered soluble. The experiment shows quite conclusively that it makes little difference what grade of sulphur is used as a soil amendment for Arizona soils.

On the other hand, there are many data of interest in this table. They show that there was a progressive increase in soluble salts, sulphates, and available phosphate and a decrease in pH in the sulphur-treated soils. Attention is called to similar changes, though of much less magnitude, in the control incubations. In this case the decrease in pH is probably due to absorption of carbon dioxide from the air and the increased microbiological activity after bringing the soils to optimum moisture content at a favorable temperature. These factors also explain the increase in soluble salts and sulphates in the control incubations.

During the first two weeks there was a fair agreement between the total soluble salts and the sulphates. In the last two weeks the soluble sulphates had increased so greatly that they

TABLE 2.—THE EFFECTS OF PARTICLE SIZE ON THE RATE OF OXIDATION OF SULPHUR.

Series	pH values				Sulphate (SO_4); p.p.m.				Phosphate (PO_4), p.p.m.			
	Weeks				*Weeks*				*Weeks*			
	1	2	3	4	1	2	3	4	1	2	3	4
A	8.67	8.68	8.82	8.30	tr	tr	tr	tr	0.72	0.76	0.84	0.84
B	8.23	8.21	8.00	8.06	975	1525	3225	4250	0.73	0.95	1.37	1.70
C	8.28	8.10	8.02	8.03	1290	1875	3300	5100	0.76	0.96	1.28	2.02
D	8.52	8.47	8.00	8.02	1050	1200	3750	5000	0.70	1.21	1.30	2.70
E	8.42	8.25	7.99	8.06	1500	1785	3550	4130	0.86	1.07	1.35	2.30
F	8.45	7.93	7.95	8.07	600	3420	3475	3875	0.88	1.16	1.49	2.35
G	8.68	8.09	8.14	8.07	475	1500	1750	3497	0.76	1.18	1.50	2.52

reduced the accuracy of the conductivity method for determining total solids. The limitations of the conductivity method for determining total solids when composed in large part of sulphates is well known. With a few exceptions, notably series F and G at one and two weeks and Series G at three weeks, the quantities of sulphates were of the same general magnitude.

THE EFFECTS OF RATE OF APPLICATION OF SULPHUR

Table 2 shows that in general the pH values were at a minimum at the end of three weeks, and at four weeks there was a slight increase in pH. The data also indicate that the rate of oxidation had reached a maximum at four weeks. The amount of sulphur added, if completely oxidized should have yielded

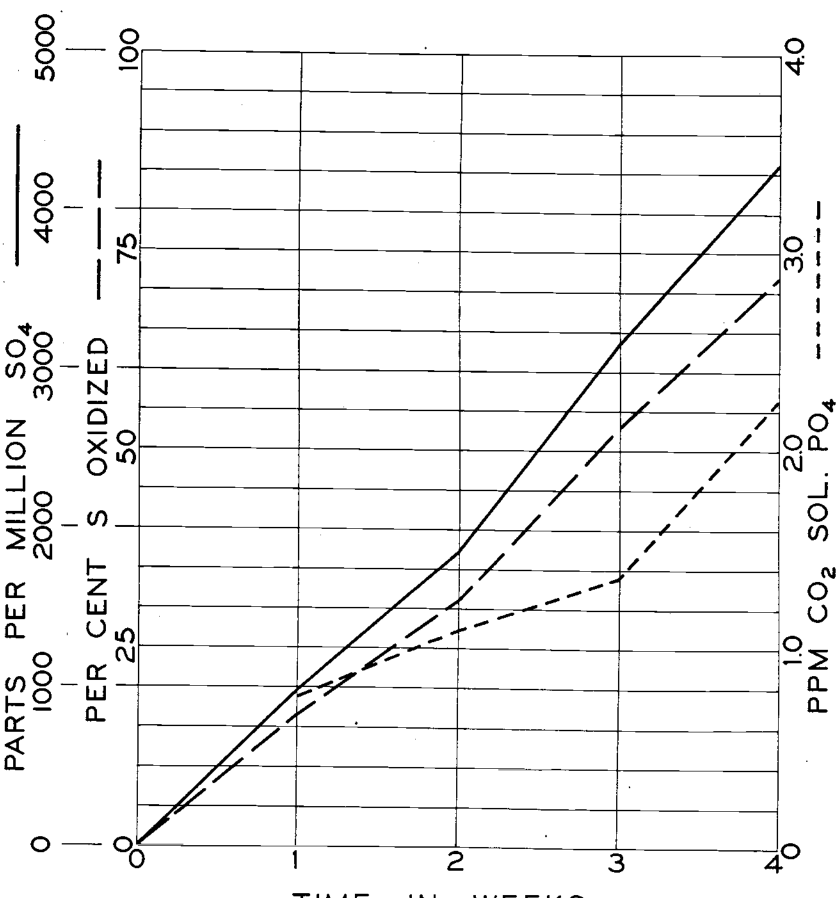

Figure 1.—The relation between percentage of sulphur oxidized, sulphates produced, and the solubility of phosphate during a period of four weeks.

TABLE 4.—EFFECT OF RATE OF APPLICATION ON RATE OF SULPHUR OXIDATION.

Grams sulphur added	0	.1	.5	1.0	0	.1	.5	1.0	0	.1	.5	1.0	0	.1	.5	1.0	0	.1	.5	1.0
Time (weeks)	pH value				Sulphate (SO_4) p.p.m.				Phosphate (PO_4) p.p.m.				Nitrate (NO_3) p.p.m.				Sulphur oxidized per cent			
GILA FINE SAND																				
0	8.54	8.54	8.52	8.53	0	0	0	0	7.5	7.5	7.5	7.5	10	10	10	10	0	0	0	0
1	8.54	8.18	7.77	7.69	0	750	2,250	2,825	11	11	10	10	40	42	5	tr	0	25	15	9.4
2	8.34	6.93	7.08	6.83	0	2,700	4,125	7,900	13	12.7	12.7	12	50	10	tr	tr	0	90	26.1	26.3
3	8.63	7.84	7.69	7.47	tr	3,200	6,500	8,750	10.5	10	10.2	12	60	10	tr	tr	0	106	43.3	29
5	8.69	8.10	7.75	7.64	0	1,800	5,500	7,750	10	10.5	11	10.5	80	40	tr	tr	0	60	36.6	25.6
9	8.82	7.88	7.65	7.50	tr	3,200	8,000	8,200	11	12.5	12	11.5	80	15	tr	tr	0	106	53.3	27.3
18	8.71	8.00	7.73	7.48	tr	3,200	8,500	9,400	11	11	11	13	80	100	10	tr	0	106	56.6	31.3
GILA FINE SANDY LOAM																				
0	8.67	8.67	8.69	8.60	0	0	0	0	19	19	19	19	10	10	10	10	0	0	0	0
1	8.77	8.03	7.60	7.52	0	1,875	6,100	7,500	15	17.5	17.5	18.5	70	47	7	2	0	62.5	40.6	21.4
2	8.71	7.56	6.97	6.93	0	3,350	9,000	11,250	17.5	19.5	22	23.8	70	40	tr	5	0	111	60	37.2
3	8.52	7.89	7.60	7.35	0	3,000	10,000	12,225	14	23	26.5	28	75	45	tr	tr	0	100	66.6	40.7
5	8.77	8.01	7.60	7.61	0	3,000	10,000	9,000	15	17.5	20.5	29.5	100	50	tr	tr	0	100	66.6	30
9	8.75	7.94	7.46	6.65	tr	3,200	10,000	9,000	17	21	25	46	180	100	5	tr	0	106	66.6	30
18	8.77	7.93	7.66	4.85	tr	3,400	10,000	11,500	19	21	31	110	200	120	25	tr	0	113	66.6	38.3
GILA LOAM																				
0	8.41	8.41	8.45	8.44	350	350	350	350	17.9	17.9	17.9	17.9	50	50	50	50	0	30.3	0	0
1	8.66	8.19	7.65	7.46	370	1,150	5,850	150	15	18.2	18.7	18.8	60	55	3	0	0	38.3	39	25
2	8.60	8.13	7.46	7.44	350	1,875	9,000	12,000	16.5	19.7	22	27	45	35	tr	tr	0	62.5	60	40
3	8.62	8.05	7.66	7.40	400	3,125	8,123	13,000	14	19.5	20	29	50	15	tr	tr	0	104	54.2	43.3
5	8.71	8.18	7.75	7.29	400	2,450	8,750	10,000	15	16.7	17.7	37.5	70	40	tr	tr	0	81.6	58.3	33.3
9	8.64	7.89	7.63	6.72	400	3,000	9,000	11,000	16	19	24	50	100	40	tr	tr	0	100	60	36.6
18	8.68	7.90	7.60	5.61	450	3,000	9,000	12,500	17.5	21	26	100	60	40	tr	0	0	100	60	41.7

6,000 parts per million of sulphate (SO_4). The calculations given in Table 3 show the average amounts of sulphates produced and the percentage of sulphur oxidized.

TABLE 3.—SHOWING AMOUNT OF SULPHUR OXIDIZED AND THE INCREASE IN SOLUBILITY OF PHOSPHATE.

Time	SO_4	% sulphur oxidized	CO_2 sol. phosphate (PO_4)
1 week	982 p.p.m.	16.47	0.75 p.p.m.
2 weeks	1866 p.p.m.	31.10	1.09 p.p.m.
3 weeks	3175 p.p.m.	52.92	1.36 p.p.m.
4 weeks	4312 p.p.m.	71.87	2.26 p.p.m.

These data show that there is a general but not an absolute relation between sulphate production and percentage of sulphur oxidized as well as increase in availability of phospate. These data are shown graphically in Figure 1, and it is quite clear from this figure that the greatest increase occurred between the third and fourth week.

FURTHER EXPERIMENTS ON RATE OF APPLICATION

In view of the results obtained in the preceding experiment another series was started in order to obtain further information

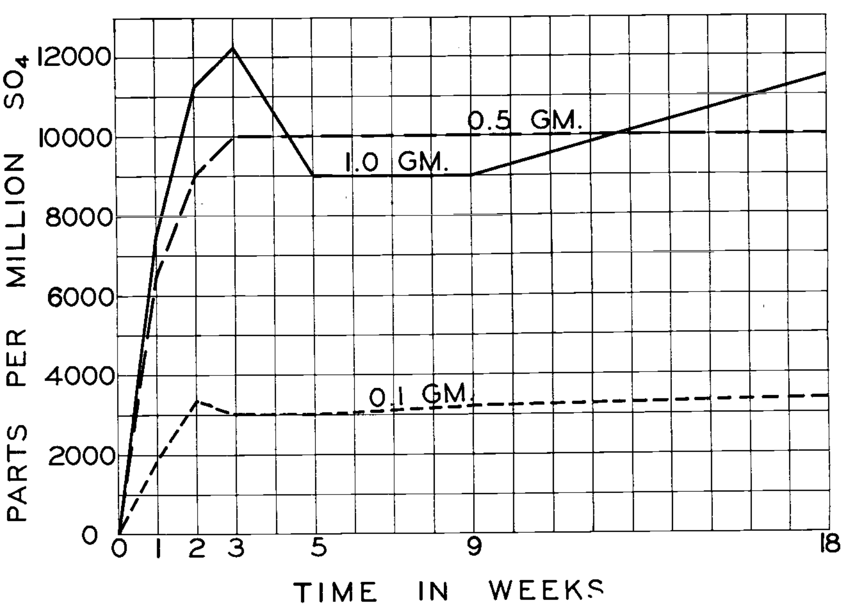

Figure 2.—The effects of rate of application of sulphur on the quantities of sulphates produced in Gila fine sandy loam.

on the effects of rate of application over a longer incubation period. The experimental technique and procedure already described were used. The rates of application were 0.1, 0.5, and 1.0 gram of sulphur per 100 grams of soil. The sulphur used in this experiment as well as those to follow was the commercial grade of agricultural sulphur. The data obtained in this experiment are given in Table 4.

The data in Table 4 show that a larger percentage of sulphur is oxidized in a shorter time when small applications are made to the soil. In general the sulphur was completely oxidized in the 0.1 gram application at the end of three weeks. The heavier applications of sulphur produced larger amounts of sulphate and a greater reduction in pH as well as a greater availability of phosphate. It appears that heavy applications of sulphur will have a more pronounced and possibly a more lasting and permanent effect upon Arizona soils.

The biological oxidation of sulphur is generally believed to favor nitrification. In this experiment there was an increase in

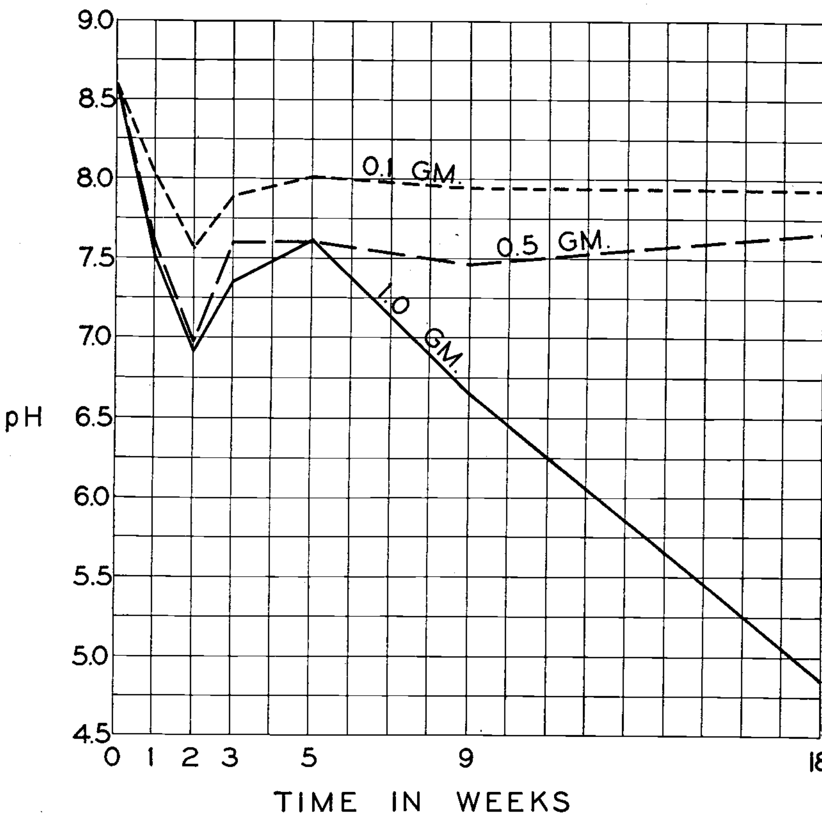

Figure 3.—The effect of rate of application of sulphur on the pH of Gila fine sandy loam, using a 1:5 soil-water ratio for the determination.

nitrates in the controls, but in all those to which sulphur had been added there was a decrease in nitrates. The greater the amount of sulphur oxidized the smaller the amount of nitrate found in the soil extract. It is evident that the sulphur oxidizing bacteria were withdrawing nitrate for their own nitrogen metabolism. It is also interesting to note that the finer the soil texture, regardless of rate of application, the greater the amount of sulphur oxidized. This same relation exists between texture and increase in phosphate availability. The reduction in pH is of especial interest on account of the large amounts of calcium carbonate which these soils contain. Selecting the data for the Gila fine sandy loam as typical, the results are shown graphically in figures 2, 3, and 4.

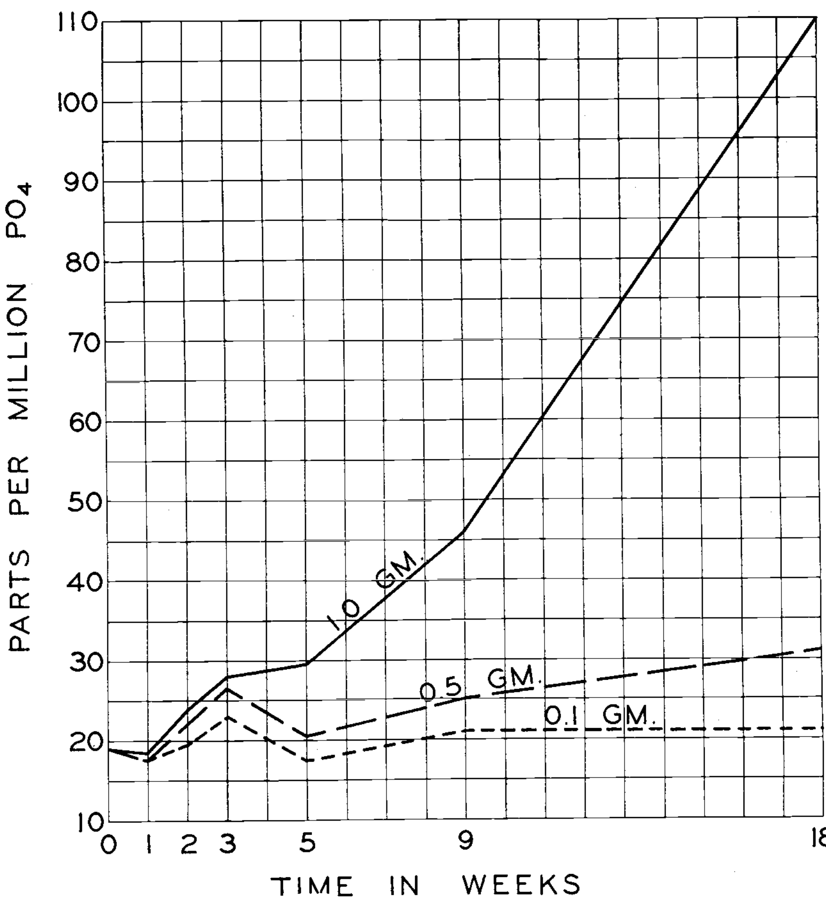

Figure 4.—The effect of rate of application of sulphur on the solubility of phosphate in carbonic acid, Gila fine sandy loam.

SULPHOFICATION EXPERIMENTS WITH ADDITIONAL ARIZONA SOIL SERIES

In the preceding experiments only soils of the Gila series were used, and so the experiment was repeated with two soils from the Mohave series and one each from the Cajon and Pima series. The experimental procedure followed was the same as in the previous experiment. Only one rate of application, namely 0.2 gram per 100 grams of soil was used. In the analyses of these soil extracts, potassium determinations were included. The potassium determinations showed a rather wide variation and for that reason are omitted from the table. In general, there was a slight increase in both water-soluble potassium and the potassium solubility in carbonic acid. The data obtained from these four soils are given in Table 5.

The results obtained with these four soils are similar to those already given for the Gila series, namely a rapid oxidation of sulphur accompanied by an increase in total soluble salts, sulphates and available phosphate, and a decrease in pH. In general, a decrease in nitrates accompanied the increase in sulphates.

PERCOLATION EXPERIMENTS

The preceding experiments have definitely shown that sulphur will undergo rapid oxidation in Arizona soils and that the application of sulphur will be accompanied by an increase in total soluble salts, sulphates and available phosphate, and a decrease in pH. In order to approximate more closely field conditions where the soils are irrigated, another series of incubations was conducted in large glass percolators and the soils leached at specified periods. The experimental procedure was as follows:

Two 1500-gram portions of each of four soils were weighed out in duplicate and to one portion 3 grams (2 tons per acre) of sulphur were added and the whole thoroughly mixed. The soils, sulphured and unsulphured, were then gently packed in Oldberg percolators, having a small plug of nonabsorbent cotton at the outlet. Each percolator was then leached with 1 litre of distilled water and the percolate collected and analyzed. The leachings, which may be compared to displacement by irrigation, were repeated at intervals, using 1 litre of water for each. Between leachings the soils were allowed to remain in the percolators at approximately 27 degrees C., and protected from drying. The results obtained from the analyses of these percolates as well as the time intervals are given in Table 6.

The data obtained in this percolation experiment show the same general effects of sulphur on the soil as the incubation experiments and that the products of sulphofication will be leached into the lower soil horizons if sufficient irrigation water is applied. In each case there was a rapid oxidation of sulphur accompanied by a decrease in pH and nitrate and an increase

TABLE 5.—SHOWING SULPHOFYING POWER OF CAJON, MOHAVE, AND PIMA SOIL SERIES.

Weeks	pH value		Sulphate (SO_4) p.p.m.		Phosphate (PO_4) p.p.m.		Nitrate (NO_3) p.p.m.		Sulphur oxidized per cent	
	Control	Sulphur	Control	Sulphur	Control	Sulphur	Control	Sulphur	Control	Sulphur
Cajon Loamy Sand										
0	8.81	8.76	0	0	13	13	5	5	0	0
1	8.88	7.87	0	1750	13	14	25	tr	0	29
2	8.93	7.91	0	2900	14	16	15	tr	0	48
3	8.81	7.71	0	5000	15	17	25	0	0	83
5	8.82	7.63	0	6200	15	19	35	0	0	103
13	9.01	7.77	0	6300	15	21	40	5	0	105
Mohave Sandy Loam										
0	8.72	8.74	tr	tr	9	9	5	5	0	0
1	8.81	7.94	tr	2375	9	10	25	tr	0	39
2	8.86	7.95	tr	2900	10	12	25	tr	0	48
3	8.68	7.72	tr	5000	11	15	30	tr	0	83
5	8.81	7.71	tr	5850	11	15	40	tr	0	98
13	8.76	8.02	tr	6000	12	15	40	tr	0	100
Mohave Clay Loam										
0	8.66	8.66	tr	tr	12	12	15	15	0	0
1	8.73	7.93	tr	1450	12	14	47	17	0	24
2	8.73	7.78	tr	4000	13	17	50	10	0	67
3	8.62	7.84	tr	4900	14	18	60	9	0	82
5	8.71	7.77	tr	5750	14	19	60	25	0	96
13	8.80	7.87	tr	6000	13	19	100	40	0	100
Pima Silty Clay Loam										
0	8.58	8.49	250	250	15	15	100	100	0	0
1	8.66	7.98	287	2125	15	16	180	110	0	31
2	8.72	7.86	310	3950	17	19	180	100	0	61
3	8.30	7.71	400	5000	17	19	200	100	0	77
5	8.35	7.74	400	6000	17	20	200	70	0	93
13	8.26	7.85	450	6100	17	20	150	70	0	96

TABLE 6.—SHOWING EFFECT OF SULPHUR OXIDATION ON COMPOSITION OF SOIL PERCOLATES (p.p.m.).

Treatment	Period (weeks)	Time for percolation to start (min.)	Time for 250 cc. to percolate (min.)	Total volume percolate (cc.)	Total solids	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Chlorine (Cl)	Sulphate (SO_4)	Carbonate (CO_3)	Bicarbonate (HCO_3)	Nitrate (NO_3)	Phosphate (PO_4)	pH
Gila Fine Sand																
check	0	51	154	468	997	187	0	91	32	96	110	0	439	40	2.2	8.10
sulphur	0	56	141	458	1,006	187	0	92	30	96	120	0	439	40	2.2	8.06
check	4	25	240	650	403	75	15	tr	22	10	35	0	165	80	1.1	7.72
sulphur	4	50	240	700	4,100	900	75	tr	36	10	2,750	0	146	tr	1.1	7.41
check	7	44	375	700	246	52	7	tr	22	8	30	0	146	30	.6	8.45
sulphur	7	35	298	720	4,739	915	30	451	30	6	3,200	0	105	2	.7	8.05
check	11	74	434	600	309	45	15	tr	24	24	40	0	120	40	.9	8.60
sulphur	11	59	284	610	2,893	854	15	tr	26	12	1,880	0	85	20	1.1	7.95
Gila Fine Sandy Loam																
check	0	59	100	480	1,123	150	15	95	81	52	150	0	537	40	3.0	8.05
sulphur	0	55	100	490	1,126	150	15	95	84	52	150	0	537	40	3.0	8.10
check	4	....	135	700	394	30	11	17	60	10	30	0	185	50	1.3	7.75
sulphur	4	....	100	740	4,518	900	75	236	150	10	3,000	0	141	5	1.7	7.20
check	7	....	120	730	309	22	7	14	58	8	25	0	139	35	.6	8.48
sulphur	7	....	180	730	5,928	108	52	547	135	8	4,000	0	105	1	.9	7.80
check	11	11	183	630	346	45	11	tr	48	12	50	0	139	40	1.0	8.48
sulphur	11	34	142	640	4,384	955	22	300	93	12	3,000	0	97	3	1.9	7.71
Gila Loam																
check	0	235	275	248	5,589	1,050	244	197	240	1,520	1,300	0	537	500	1.5	7.93
sulphur	0	295	215	270	5,202	1,050	244	40	270	1,360	1,300	0	537	400	1.5	7.75
check	4	....	....	650	793	30	11	114	105	16	140	0	376	30	1.0	8.18
sulphur	4	....	....	710	5,336	1,050	112	182	300	16	3,500	0	175	tr	1.5	7.80
check	7	155	1,400	620	580	15	7	60	111	12	50	tr	310	15	.8	8.68
sulphur	7	75	1,300	670	5,043	735	30	550	300	8	3,250	0	171	tr	1.0	8.10
check	11	281	2,510	450	583	22	7	85	72	12	80	14	254	36	1.4	8.83
sulphur	11	136	1,440	490	5,691	930	37	624	228	8	3,750	tr	112	tr	1.6	8.23
Pima Silty Clay Loam																
check	0	18	72	250	10,590	1,500	112	1,780	240	3,920	1,500	0	537	1,000	1.4	8.00
sulphur	0	18	48	280	10,652	1,500	112	1,912	170	3,920	1,500	0	537	1,000	1.4	7.87
check	4	....	....	340	1,548	22	4	408	37	20	140	67	828	20	2.0	8.62
sulphur	4	....	....	540	5,874	750	75	877	99	20	3,750	24	278	tr	5.6	8.10
check	7	170	....	....	....	....	....	....	....	....	....	....	....	....	.4	9.04
sulphur	7	129	1,185	550	5,734	1,004	30	630	90	8	3,750	17	204	tr	1.1	8.40
check	11	1,420	....	15*	....	....	....	....	....	....	....	....	....	....	....	....
sulphur	11	280	5,760	305	4,532	975	52	235	93	16	3,000	7	154	tr	.9	8.15

*This soil "froze up" from hydrolysis of NaZ. At the end of three weeks only 15 cc. percolate had been obtained so analysis of last two checks was omitted.

in sulphates, total salts, and water-soluble phosphate. The increase in phosphorus is small but definite and increases with the amount of sulphur oxidized. There was a definite increase in solubility of potassium due in most part to replacement by the large amount of calcium dissolved during the oxidation of sulphur. This indicates that there may be a loss of potassium from sulphur fertilization on such soils as these. The data show that the increase in soluble salts accompanying sulphofication is largely calcium sulphate.

The sulphur treatments markedly improved the physical condition of all four soils. In general the rate of percolation and volume of percolate were increased. It was also very noticeable that the percolates from the sulphured soils were clear while those from the unsulphured soils were quite turbid.

There was a general increase in the pH of successive leachings. However, in each case the pH value of the percolates from the sulphured soils was lower than in the checks. The fact that the leachate from the sulphured soil contained more sodium and potassium is further evidence of replacement by calcium.

PRODUCTION OF CARBON DIOXIDE

As already mentioned, the evolution of carbon dioxide formed during the decomposition of organic matter in alkali soils represents one of the most important properties of this material. Likewise such a property is desired in sulphur or any other material used as a substitute for organic matter in alkaline calcareous soils. Alkalinity is due largely to the absence of sufficient carbon dioxide to convert soluble normal carbonates to bicarbonates. Likewise, phosphate unavailability is due to solid-phase calcium carbonate and the absence of appreciable amounts of carbon dioxide and probably calcium bicarbonate. The preceding tables have shown that sulphur will materially reduce the pH of alkaline calcareous soils. The pH of Gila fine sandy loam was reduced in eighteen weeks from 8.60 to 4.85 by sulphur treatments at the rate of 10 tons per acre. In Table 6, the increase in soluble salts is due largely to the increase in soluble calcium and in sulphates. The calcium obviously comes from the calcium carbonate in the soil.

Assuming that the following reactions represent the oxidation of sulphur

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$
$$2CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + Ca(HCO_3)_2$$
$$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O + 2CO_2$$

there is evidence in these reactions that carbon dioxide should be a product of sulphur oxidation in calcareous soils.

In order to determine whether carbon dioxide is produced by the oxidation of sulphur in calcareous soils five 1,500-gram portions of Gila fine sandy loam were prepared as follows. Two portions were left untreated for checks and to each of the remaining three 15 grams of sulphur were added. These were well mixed in order to get the sulphur evenly and thoroughly distributed throughout the soil, and the soils were transferred to five Fernback flasks of 2,800-cc. capacity. Sufficient distilled water was then added to bring the soils to optimum. Following this, the flasks were connected in an aeration unit of the type described by Fred and Waksman (10). The air drawn through the flasks was washed with 40 per cent sodium hydroxide to remove carbon dioxide and then with water in order to keep the air well humified and prevent desiccation of the soils. All incubations were conducted at room temperature and the carbon dioxide produced was absorbed in standardized barium hydroxide solution. Aeration was not conducted continuously but for seven-hour periods each day. Carbon dioxide was measured by

TABLE 7.—CARBON DIOXIDE PRODUCTION BY GILA FINE SANDY LOAM (MG. OF CO_2 PRESENT AT STATED TIMES).

Time (days)	Check (mg.)	S (mg.)
1	31.46	53.13
2	56.98	95.15
3	88.22	154.85
5	144.98	257.15
6	201.18	357.35
7	245.95	462.29
8	278.90	567.89
9	321.70	761.03
10	356.68	997.33
12	402.99	1387.78
13	441.80	1627.07
14	481.04	1832.57
15	514.41	2014.27
16	538.92	2172.04
17	567.94	2294.58
19	602.34	2492.12
20	663.90	2611.45
21	693.35	2734.93
22	729.75	2860.46
23	761.30	2990.21
24	791.07	3119.37
26	837.27	3367.39
28	903.50	3613.03
30	962.50	3874.94
33	1023.00	4124.23
37	1095.82	4433.38
41	1173.37	4786.19
45	1247.30	5079.49
50	1329.47	5406.69
55	1435.51	5712.72
57	1501.18	5936.17
61	1589.18	6196.32
71	1753.48	6629.28
75	1842.74	6864.83

titrating the excess of barium hydroxide used as absorbent and calculating therefrom the carbon dioxide absorbed.

These data are given in Table 7, in which the amounts of carbon dioxide produced in the respective time intervals are given. The results reported are the average of two checks and three sulphured soils.

These data not only reveal that large quantities of carbon dioxide are produced by sulphuring Arizona soils but also that appreciable amounts will be formed by unsulphured soils if maintained at optimum moisture and temperature conditions. The relation between the sulphured and unsulphured soils as well as the amounts of carbon dioxide evolved are shown graphically in Figure 5.

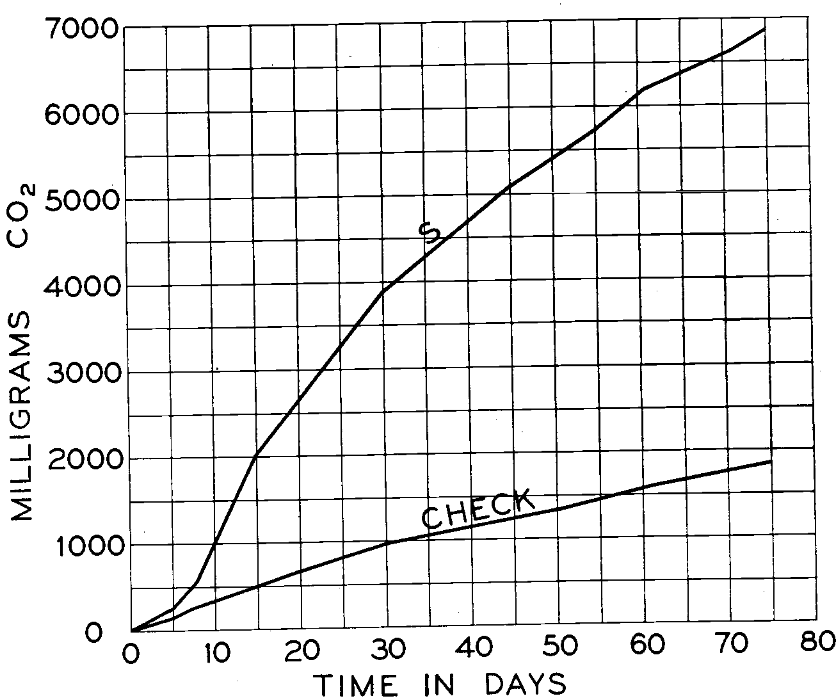

Figure 5.—The production of carbon dioxide from sulphured and unsulphured Gila fine sandy loam.

This experiment shows that in so far as offering a potential supply of carbon dioxide is concerned sulphur can be considered as an excellent substitute for organic matter on these soils. As a matter of comparison some data obtained by incubating organic matter with the same apparatus are submitted in Table 8. These data show the amount of carbon dioxide produced from 1,000 grams of Mohave sandy loam to which 10 grams of glucose, starch, cellulose, or lignin were added.

TABLE 8.—CARBON DIOXIDE (IN MG.) FORMED FROM ORGANIC MATTER (1000 GRAMS OF MOHAVE SANDY LOAM AND 10 GRAMS ORGANIC MATTER).

Time (days)	Check	Glucose	Starch	Cellulose	Lignin
1	16.94	99.5	6.6	14.26	44.46
2	27.72	240.8	35.6	16.26	102.76
3	37.34	374.9	76.6	23.85	144.45
4	45.04	516.8	112.9	33.75	176.35
5	54.12	653.7	134.0	58.17	207.37
6	61.38	705.4	155.1	94.89	239.49
8	75.90	997.3	170.5	124.32	299.11
9	86.46	1110.2	194.3	155.56	346.85
10	98.78	1203.6	210.6	171.94	358.51
11	107.58	1286.8	226.2	187.34	371.05
13	115.38	1416.8	246.2	252.66	402.07
16	130.78	1496.8	266.2	292.66	442.07

The data given in tables 7 and 8 show that the sulphuric acid, produced during sulphofication, generated larger amounts of carbon dioxide than did the incorporation of organic matter. It should be mentioned, however, in this connection that the two sets of data are not entirely comparable as different soils were used and the data given in Table 8 were obtained during the winter months when the room temperature was slightly lower than during the time the sulphur experiments were conducted. In spite of this, it is believed that the results show sulphur to be an excellent potential source of carbon dioxide for our alkaline calcareous soils.

PLANT CULTURE STUDIES

The value of sulphur in the cropping of alkaline calcareous soils especially from the standpoint of ion absorption by plants and the availability of some essential plant-food elements has also been studied by means of the Neubauer method, by pot experiments in which corn was grown and to a limited extent with citrus trees in field studies.

EFFECT OF SULPHUR AS MEASURED BY THE NEUBAUER METHOD

The Neubauer method has been used quite extensively in studying the availability of phosphate and potassium in Arizona soils. With few exceptions, this method has shown a great deficiency of phosphate and an ample supply of available potassium. Briefly, the Neubauer method consists in growing one hundred rye plants in 100 grams of soil for a period of fourteen to eighteen days and determining, by chemical analysis, the amount of phosphate and potassium which the one hundred plants contain or have absorbed from the soil during this period. The difference between this analysis and the analysis of the same number of plants grown in silica sand gives the amount of phosphate or potassium removed from the soil by the plant. The value obtained, which is known as the Neubauer value, has been standardized by several workers, notably Neubauer himself, and Thornton, by the designation of a minimum limit value below which the soil is considered deficient in one or both of these elements.

In applying the Neubauer method to a study of the effect of sulphur on plant-food availability in these soils a comparison was made, in the first experiment, of sulphur, animal manure, and ground alfalfa. The series of soil treatments was divided so that one test of each treatment was incubated and the other was not. The incubation period was from October 3 to November 13 and was conducted by bringing 100 grams of soil to optimum moisture content after adding the sulphur, manure, or alfalfa. The whole was maintained at optimum moisture content throughout the period of incubation. The Neubauer values obtained in this experiment are given in Table 9 together with the description of the treatments.

TABLE 9.—EFFECT OF SULPHUR, STABLE MANURE, AND ALFALFA ON NEUBAUER VALUES OF AN ALKALINE CALCAREOUS SOIL.

Number	Treatment	Neubauer values	
		K	PO_4
1	100 gms. soil 1 gm. manure incubated	....	2.3
2	100 gms. soil 5 gms. manure incubated	45.4	12.1
3	100 gms. soil 10 gms. manure incubated	52.9	21.1
4	100 gms. soil 1 gm. manure not incubated	27.4	1.5
5	100 gms. soil 5 gms. manure not incubated	28.2	17.5
6	100 gms. soil 10 gms. manure not incubated	39.4	19.5
7	100 gms. soil 1 gm. alfalfa incubated	27.4	7.8
8	100 gms. soil 5 gms. alfalfa incubated	56.3	11.3
9	100 gms. soil 10 gms. alfalfa incubated	57.4	13.4
10	100 gms. soil 1 gm. alfalfa not incubated	24.4	3.7
11	100 gms. soil 5 gms. alfalfa not incubated	34.9	.....
12	100 gms. soil 10 gms. alfalfa not incubated	33.8	.....
13	100 gms. soil .5 gm. sulphur incubated	24.4	2.6
14	100 gms. soil 1.0 gm. sulphur incubated	35.7	3.1
15	100 gms. soil .5 gm. sulphur not incubated	30.0	4.1
16	100 gms. soil 1.0 gm. sulphur not incubated	24.4	4.7
17	100 gms. soil control	23.3	.8

Phosphate: The limit value, that is, the value below which soils are considered deficient in phosphate, has been placed at 10.7 mg. PO_4 for European soils by Neubauer, and 5.3 mg. PO_4 for American soils by Thornton. The data in Table 9 show a Neubauer value of 0.8 for this soil which indicates a great deficiency of phosphate. Manure increased the value but it required excessive amounts to raise the soil above the limit value of deficiency. There was not a great deal of difference between the incubated and unincubated manure. Like the manure, the alfalfa greatly increased the value when the material was allowed to decompose before planting the rye. Toxicity was shown where the alfalfa was allowed to decompose during the growth of the plants and the Neubauer values were less than for the controls. The sulphur showed a fair increase in Neubauer value with little difference from previous incubation. The values are still less than the limit recognized as an indication of phosphate deficiency.

It will be noted that the values obtained for the sulphur tests not previously incubated are higher than for those which had been incubated before planting, and this indicates that the carbon dioxide generated during the decomposition of the sulphur has materially aided phosphate availability and absorption by the plant.

Potassium: The limit value established for potassium in European soils by Neubauer is 19.9 mg. potassium (K) and for American soils, as established by Thornton, is 8.3 mg. potassium. The data given in Table 9 shows an ample supply of potassium in all the tests made in this experiment. The value was increased by the organic materials in proportion to the amount added. Sulphur also increased the value in every case, but the results are not so consistent as those obtained with organic materials. They do, however, show that the availability of potassium is increased by sulphur and indicate that the differences would probably be more outstanding if a potassium-deficient soil had been available for the experiment.

EFFECT OF SULPHUR UNDER FIELD CONDITIONS

For the next Neubauer test soils were taken from the field. In this particular case the sulphur had been applied to citrus trees at the rate of 50 pounds per tree and 25 pounds per tree; application was made in a trench about 1 foot deep circling the tree at the drip. The trench was filled with soil, after applying the sulphur, in order to cover it. At the end of one year's time, after the sulphur had been applied, soil samples were taken at the tree drip from this field experiment. Both first and second feet of soil were sampled and kept separate. The Neubauer values obtained from these samples together with the pH values of the soil are given in Table 10.

TABLE 10.—SHOWING NEUBAUER VALUES OF SOILS WHICH HAD BEEN SULPHURED IN THE FIELD.

Sulphur applied	Depth of sample	pH of soil	Neubauer value PO_4	Neubauer value K
25 lbs.	1st ft.	7.70	13.0	35
25 lbs.	2nd ft.	9.05	1.1	32
50 lbs.	1st ft.	6.25	25.5	44
50 lbs.	2nd ft.	8.70	0.0	32
25 lbs.	1st ft.	8.95	4.6	38
25 lbs.	2nd ft.	9.05	1.3	32
Check	1st ft.	8.95	1.9	35
Check	2nd ft.	9.25	.0	35

Here again we find a soil greatly deficient in available phosphate and well supplied with available potassium. The soil from the check tree which received no sulphur shows the lowest phosphate value, namely 1.9, for the surface foot and zero for the second foot. In one case where sulphur was added at the rate of 25 pounds per tree the pH of the soil is still quite high, while in the other soil which received 25 pounds of sulphur the pH is materially reduced. The phosphate Neubauer values are directly related to the reduction in pH of the soil. That is, where there was little or no reduction in pH the Neubauer value had only been increased to 4.6 while it was increased to 13.0 where the pH was reduced to pH 7.7. In the case where 50 pounds of sulphur were added the pH of the soil was reduced to 6.25, and accompanying this was a greatly increased Neubauer value, namely 25.5. It is quite evident from this experiment that under field conditions sulphur will exercise a great influence upon the availability and absorption of phosphate, and that this is related to the pH of the soil or the evolution of carbonic acid arising from the reaction between sulphuric acid and calcium carbonate. It is of interest that in every case the effect of the sulphur had failed to appear in the second foot of soil at the end of one year's time, and that there had been little or no influence upon the Neubauer value of the subsoils.

POT EXPERIMENT

In this experiment a comparison was made between the effects of stable manure, alfalfa, and sulphur on the availability and absorption of phosphate by corn plants. The soils were again alkaline-calcareous types. Each pot contained 2 kilos of soil. Manure was added at the rate of 20 grams per pot when used alone and 10 grams per pot where applied in combination with sulphur. Sulphur was added at the rate of 5 grams per 2 kilos of soil and ground alfalfa at the rate of 10 grams. The pots were planted to four corn plants each and the plants were grown for six weeks, harvested, and analyzed for phosphate. This experiment was conducted in two series, using two different soils. The data obtained are given in Table 11 as per cent phosphate (PO_4) in plant dry matter.

TABLE 11.—AVAILABILITY OF PHOSPHATE IN CALCAREOUS SOILS AS INFLUENCED BY SULPHUR AND ORGANIC MATTER.

Treatment	Soil No. 1 per cent phosphate (PO_4)	Soil No. 2 per cent phosphate (PO_4)
Check	0.41	0.141
Manure	0.59	0.241
Sulphur	0.49	0.201
Sulphur and manure	0.63	0.254
Alfalfa	0.43	

This experiment gives further evidence that sulphur will materially increase the availability of phosphate in the soil and absorption of phosphate by plants and indicates that its effectiveness is greatly enhanced by mixing with manure.

DISCUSSION

It is clearly shown in this study that Arizona soils are well supplied with a biological flora capable of oxidizing sulphur to sulphuric acid. Also that during the progress of this oxidation the physical condition of the soil will undergo a material improvement, there will be an appreciable reduction in soil alkalinity, a material increase in availability of phosphate and potassium and associated with these changes a measurable evolution of carbonic acid which is of fundamental value and related to the above changes.

Phosphate exists in Arizona soils largely as calcium carbonato-phosphate, a compound in which tricalcium phosphate and calcium carbonate are chemically combined, and the properties of which are such that its lowest solubility is shown in the presence of the solid-phase calcium carbonate. Its greatest solubility under soil conditions is shown when carbon dioxide or hydrogen ions are present and attack the calcium carbonate of the carbonato-phosphate complex. The data presented in this bulletin definitely show that sulphur as well as organic matter will accomplish these things and consequently will increase phosphate availability.

While an increase in solubility and availability of potassium is also evident from this investigation, this fact is less important. Potassium salts are nothing more nor less than alkali salts, as all soluble salts are considered, and so in semiarid districts where there is a tendency for alkali to accumulate, potassium salts also accumulate and with few exceptions potash is the last plant food which it becomes necessary to use in fertilizing semiarid soils. Even in the absence of organic matter or sulphur, plants grown on Arizona soils will absorb ample supplies of potassium.

As already mentioned, the principal solvent effect of sulphur oxidation is on the calcium carbonate in the soil, and this investigation shows that the principal increase in soluble solids is represented by calcium salts. This property of sulphur, too, is of great importance in the fertility of alkali soils. Many of our semiarid alkaline calcareous soils contain no measurable amounts of water-soluble calcium. This is due to the fact that the solubility of calcium carbonate decreases with increase in pH. As will be shown by a later publication, an apparant calcium deficiency is an outstanding character of citrus trees growing on these soil types. Sulphur will therefore increase the availability of calcium as plant food in alkaline calcareous soils. But in addition, we must consider the part which calcium plays in the physical condition of our soils. Calcium exercises a very strong flocculating effect upon clay, and the presence of calcium salts in the soil solution promotes a better mechanical condition in the soil.

While on the subject of calcium, a discussion of irrigation water will be of interest. The physical condition of a soil is largely governed by the amount or ratio of calcium and sodium combined with the base-exchange complex. A certain excess of calcium in the water usually assures a soil of good mechanical texture, while a certain excess of sodium works for puddling or poor mechanical texture. In irrigated agriculture the quality of the irrigation water is the greatest factor contributing to the ratio of calcium to sodium in the base-exchange complex of the soil. If the waters are high-sodium waters, that is soft waters, the exchange complex will absorb sodium in excess of calcium while the opposite condition will exist if the waters are hard, that is high-calcium waters. Most of the waters of Arizona are predominantly soft or high-sodium waters, and the solubility of calcium brought about by the solvent effect of sulphur in the soil will tend to change soft waters into hard waters just as soon as they come in contact with the soil.

The size of the sulphur particles has no great effect upon the rate of oxidation or the effects produced. Therefore, the cheapest form of agricultural sulphur will be suitable for Arizona soils. Also all the soils used in the experiment contained sulphofying bacteria which indicates that there is no reason for using inoculated sulphur for Arizona soils.

The effect of sulphur upon the ionization of orthophosphate is also of interest. As shown in a previous publication, orthophosphates undergo step ionization as follows:

$$H_3PO_4 : H_2PO_4^-, HPO_4^{--}, \text{and } PO_4^{---}$$

Above pH 6.8, HPO_4 is the dominant ion, while below this pH H_2PO_4 is the dominant ion, and PO_4 ion is present at all pH values in soils in too small amounts to be considered. In view of the fact that evidence indicates that H_2PO_4 is the ion preferred by plants, sulphur should exercise a favorable influence upon the ionization of phosphates in alkaline soils. Our observations that plants do not absorb phosphate ion if the pH of the soil-root contact film is approximately 7.6 or higher (2) is further evidence of the value of sulphur in the cropping of alkali soils. That is, the decrease in pH following the application of sulphur will help the crop to meet its phosphate requirements through enhanced absorption by the roots.

The experiment showing the evolution of carbon dioxide during the incubation of sulphur in alkaline calcareous soils shows that as a potential source of carbon dioxide sulphur is a good substitute for organic matter. The occurrence of sulphuric acid in the presence of calcium carbonate must be transitory. The action occurs in two steps:

1. $2CaCO_3 + H_2SO_4 \rightarrow Ca(HCO_3)_2 + CaSO_4$
2. $Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O + 2CO_2$

The first reaction occurs at pH 8.0 to 8.5 and the second at pH 4.2 to 4.5. Table 7 shows that considerable quantities of carbon dioxide are produced during sulphur oxidation. While we recognize that a pH determination as made on a 1:5 or 1:10 soil-water mixture is not always the same as the true soil solution due to the effect of soil-water ratio on the pH value of soils it is not believed that the soil reached a pH of 4.5 except possibly in localized spots. In Table 6 the increase in concentration of the leachate was chiefly due to calcium sulphate and there is no increase in bicarbonate. Therefore the carbon dioxide produced must have been liberated as gaseous carbon dioxide and the action of sulphuric acid on calcium carbonate may be considered as:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2$$

It is believed that this reaction is extremely localized and probably occurs only within the immediate vicinity of the sulphur particles and does not occur throughout the entire soil. It is clearly evident, however, from the experimental evidence submitted that even though largely localized the carbon dioxide produced is able to markedly influence soil properties especially plant food availability.

Recommendations regarding the use of sulphur as an amendment for alkali soils is often problematical. The alkalinity of Arizona soils is due to replaceable sodium and calcium carbonate. The former is developed by the absorption of sodium from the soil solution by clay. The latter is developed by poor aeration of the soil which tends to convert bicarbonates to normal carbonates. As such, calcium carbonate may have a pH value of 9.5 or higher. It is usually considered feasible to remove or reduce replaceable sodium below the point of injury by applications of sulphur at the rate of 1 or 2 tons per acre. Obviously though a complete neutralization of calcium carbonate is out of the question. A soil containing 5 per cent calcium carbonate would contain 100,000 pounds, per acre 8 inches, weighing 2,000,000 pounds. However, it is not necessary to neutralize the calcium carbonate as the presence of a small amount of carbon dioxide in the soil atmosphere or a small percentage of calcium bicarbonate will reduce the alkalinity of calcium carbonate below the point of injury. This is proven by our experiments. It is evident then that so far as calcium carbonate is concerned the better aeration following an application of sulphur and its attendant reactions with certain soil constituents will correct the injurious effects of calcium carbonate alkalinity without the complete elimination of the solid phase.

With regard to the methods of applying sulphur to such soils, another problem arises. That is, when broadcast and distributed throughout the soil the amounts required may be prohibitive. The following example will illustrate. One ton of sulphur per acre was applied, broadcast and plowed under. At the end of one year soil samples were taken from two places in the sulphured areas and from the adjacent unsulphured check soil. These soils were analyzed for pH, total soluble solids, and sulphate (SO_4), and the results are given in Table 12.

TABLE 12.—EFFECT OF BROADCASTING 1 TON PER ACRE SULPHUR ON YUMA-MESA CITRUS GROVE.

	pH	Total solids, p.p.m.	Sulphate (SO_4), p.p.m.
1 sulphur topsoil	8.50	2025	1500
1 sulphur subsoil	9.15	1065	225
2 sulphur topsoil	9.15	1005	375
2 sulphur subsoil	9.25	615	100
3 check topsoil	9.18	735	160
3 check subsoil	9.20	555	......

The data indicated an uneven distribution of sulphur. In the first soil sample there was an appreciable reduction in pH, probably a complete neutralization of the hydroxyl ions from calcium carbonate. The soil was in a well-flocculated condition and so, on the whole, a measurable reaction from sulphur was obtained. In the second sample there was little or no reduction in pH, the soil was not well flocculated, and the sulphate determination shows that little of the sulphur was present in the spot where this sample was obtained.

Its use in basins or trenches for citrus trees appears more hopeful. As already mentioned we are not, at present, interested in the reclamation of soils highly impregnated with black alkali but rather in creating a medium within a certain portion of the root zone where a balanced absorption of inorganic ions by the roots can take place. In order for this to be accomplished only a slight reduction in pH of soils which are not excessively high in pH is required. It is not necessary to broadcast the sulphur in citrus groves for by applying it in the trenches around the trees its effectiveness is increased, and amounts of sulphur required may be reduced.

SUMMARY

1. An examination of several typical Arizona soils revealed that they possess a very active sulphur-oxidizing flora.
2. Within the usual particle size limits of agricultural sulphur the coarse-grained material gave practically as good oxidation as the finer and more expensive grades.
3. Small applications, namely 1 ton per acre, are oxidized very rapidly, and oxidation was usually complete in two or three weeks at optimum moisture content and temperature.
4. Heavy applications of sulphur, 2 to 10 tons per acre, have a more prolonged and more pronounced effect upon the soil.
5. In every case the oxidation of sulphur was accompanied by increases in soluble salts, calcium, sulphates, potassium, and phosphate with a decrease in pH and soluble nitrate.

6. Percolation experiments showed that the physical condition of the soil is improved by sulphur oxidation. The percolates from the sulphured soils were also higher in soluble salts mentioned in 5.
7. There is a very active production of carbon dioxide during sulphofication in Arizona soils. Apparently some of the sulphuric acid formed neutralizes some of the calcium carbonate, liberating gaseous carbon dioxide.
8. Sulphur is a very efficient agent for reducing the alkalinity of Arizona soils, for improving their physical condition, and for increasing the availability of calcium, phosphorus, and potassium. Since there is an increased production of carbon dioxide it can be well recommended as a substitute for organic matter.
9. It is shown by the Neubauer method and by pot experiments that the availability of phosphate and potassium in the soils and their absorption by plants in alkaline calcareous soils is greatly increased by sulphur fertilization.

ACKNOWLEDGMENT

The authors are indebted to Alfred Fenton of the Texas Gulf Sulphur Co. for the samples of sulphur used in this investigation.

APPENDIX

In view of the high cost of sulphur in Arizona which is principally due to excessive freight rates the question of substitution of other acid materials which can be obtained locally arises, and most important among the available substitutes is sulphuric acid which is a by-product of the smelters that smelt sulphide ores. This acid has been used in a number of nutrition experiments which will be reported in a later bulletin. On the other hand it appears rather an opportune time to present some unpublished data obtained by C. N. Catlin and S. P. Clark in 1922, in order that their work may be given proper recognition and priority.

The purpose of their experiments was to test the practicability of sulphuric acid as an agent for the reclamation of alkali soils. The experiments were conducted in the Casa Grande Valley on nine different areas. The acid was applied with a tank wagon equipped with a sprinkler. After application the soil was disced, irrigated, plowed, and planted. While the experiments were conducted under trying conditions, from a quantitative basis, due to lack of sufficient water for irrigation and leaching, destruction of crops by jack rabbits and other hazards, the results are of interest. One of these experiments will be given here to illustrate the results obtained.

The soil, a McClellan loam, was a hard, deflocculated soil containing from .047 to .148 per cent Na_2CO_3 in the top 6 inches of soil and .4 to 1.18 per cent total soluble salts. Acid was applied at the rates of 200, 350, 500, and 700 gallons per acre. After the reaction from the acid had stopped the soil was disced, irrigated, plowed, and planted to wheat. Due to uneven distribution of alkali and inadequate supply of water, the growth of the crop was very "spotty" in many of the borders receiving the smaller amounts of acid. A comparison of a check border with one receiving 700 gallons of acid per acre is given in Plate I which is taken from their unpublished report.

Plate I.—The value of sulphuric acid in the reclamation of alkali soils: left, 700 gallons 60 degrees Baumé acid per acre; right, check border which received no acid.

While it was unfortunate that these experiments of Catlin and Clark were discontinued they nevertheless demonstrated that sulphuric acid can be used for the reclamation of alkali soils. Percolation experiments which they conducted on the soils from the acid-treated plots showed that a considerable increase in percolation rate had been developed which they attributed to the calcium sulphate and calcium bicarbonate formed during the reaction between sulphuric acid and calcium carbonate. A comparison between sulphuric acid and gypsum indicated the superiority of the former, which they attributed to calcium bicarbonate.

However, in order to make its use economically feasible, it would be necessary to accomplish the reclamation with less acid than used in these experiments. Seven hundred gallons of acid, equivalent to about 9,500 pounds, would cost about $35 at the smelter at the rate of $8 per ton in carload lots. It is believed that much smaller amounts of acid will suffice if plenty of water is available for leaching.

It is our opinion that the place of sulphuric acid in the cropping of alkali soils lies in its use in very small amounts in the irrigation water for the purpose of correcting slight concentrations of hydroxyl ions which interfere with normally balanced ion absorption. This phase of the problem is now under study in this laboratory.

BIBLIOGRAPHY

1. Bergey, D. H.
1930.—Manual of determinative bacteriology. The Williams and Wilkins Co., Baltimore.

2. Breazeale, J. F. and McGeorge, W. T.
1932.—Nutritional disorders in alkaline soils as caused by a deficiency of carbon dioxide. Ariz. Agric. Exp. Sta. Tech. Bul. 41.

3. Hoagland, D. R.
1917.—The effect of hydrogen and hydroxyl ion concentration on the growth of barley seedlings. Soil Sci. 3:547.

4. Joffe, J. S.
1922.—Biochemical oxidation of sulphur and its significance in agriculture. N. J. Agric. Exp. Sta. Bul. 374.

5. Kappen, J. and Quensell, E.
1915.—The transformation of sulphur and sulphur compounds in soils. Land. Vers. Stat. 86, p. 1.

6. MacIntyre, W. H., Gray, F. J., and Shaw, W. M.
1921.—The non-biological oxidation of sulphur in quartz media. Jour. Ind. Eng. Chem. 13:310.

7. McGeorge, W. T. and Breazeale, J. F.
1931.—Phosphate solubility studies on some unproductive calcareous soils. Ariz. Agric. Exp. Sta. Tech. Bul. 35.

8. Starkey, R. L.
1935.—Isolation of some bacteria which oxidize thiosulphate. Soil Sci. 39:197.

9. Waksman, S. A.
1932.—Principles of soil microbiology. 2nd Ed. Williams and Wilkins Co., Baltimore.

10. Waksman, S. A. and Fred, E. B.
1928.—Laboratory manual of general microbiology. McGraw-Hill Co., New York.

11. Unpublished work of this laboratory.