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AS SOIL CONDITIONERS

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During the past thirty years or more the question has frequently arisen as to whether pyrite might have some value as a soil conditioner. Thousands of tons of this material, in the form of waste and in varying degrees of purity, exist near smelters in the State. Renewed interest has arisen lately by a proposal to use pyrrhotite as a soil conditioner. A source of this material exists in northern Arizona.

The primary functions of a soil conditioner for alkaline-calcareous soils are (a) replacement of adsorbed sodium from the exchange complex, (b) neutralization or reduction of alkalinity, and (c) structural improvement of the soil mass. Gypsum accomplishes this by supplying soluble calcium for sodium replacement. Sulfur and sulfuric acid function by supplying calcium and hydrogen ions. Gypsum does not neutralize soluble hydroxides and carbonates but does inactivate sodium carbonate. Sulfur, by oxidation, neutralizes and removes sodium carbonate. Iron sulfate, being an acid salt, also neutralizes sodium carbonate and hydroxides.

The value of pyrite or any other sulfide for soil conditioning depends on its ability to oxidize to iron sulfate under soil conditions. For example ferrous sulfide (FeS) oxidizes to iron sulfate quite rapidly when moist and exposed to the air and iron sulfate is a soil conditioner of proven value. Pyrite (FeS_2) which is sometimes referred to as a double sulfide, is a very stable mineral but will oxidize slowly to iron sulfate. Pyrrhotite is a relatively unstable iron sulfide and has been given the formula Fe_nS_{n+1} in which iron and sulfur may vary between Fe_6S_7 and $Fe_{11}S_{12}$. The pyrrhotite used in this study is sold under the trade name "FERRO-SOIL-TIL". It is being recommended by its producer as a fertilizer for chlorotic plants and as an ingredient in composts because of the iron content. Only the soil conditioning value is reported here.

Smith (4) studied the rate of oxidation of pyrite from several sources and found considerable variation. During an incubation period of six weeks the sulfate formed varied between a trace to 10 percent of the sulfide sulfur added to the soil.

MATERIALS USED IN THIS STUDY

The materials used in this study were selected for a comparison of pyrite, pyrrhotite, and sulfur. Representative samples of waste pyrite were examined and from these several were selected on the basis of the percentage of combined sulfur which they contained. The analyses of these are given in Table 1. This table shows the percentage total sulfur in each and also the percentage sulfate sulfur present.

In most cases the waste pyrite in the smelter dumps has been subjected to many years of weathering and during this period a part of the sulfide has been oxidized to sulfate--all the samples examined showed a positive test for water-soluble sulfate. In Table 1, the total sulfur content represents all forms of sulfur present in the material and does not represent an equivalency in conditioner value. The total sulfur, for all the sulfides, was determined as sulfate after oxidation with aqua-regia.

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Confusion exists among farmers as to the conditioner value of sulfur and its compounds. This is due to the fact that some sulfur compounds have conditioner value and a number of sulfate salts are ingredients in commercial fertilizer. Except for the calcium sulfate in single superphosphate none have direct conditioner value. The value of sulfate salts, as soil conditioners, or sulfide, or sulfur, is not specifically the value of sulfur, sulfide, or sulfate but rather of the calcium and hydrogen ions with which the sulfur is linked as sulfate during and after oxidation in the soil. In other words the conditioner value depends upon the cation with which the sulfur is linked.

EXPERIMENTAL PROCEDURE

Sulfur compounds are somewhat like nitrogen compounds in that they are subject to many transformations in the soil depending on the presence of aerobic or anaerobic environment. In most part, biological agencies are responsible for these transformations but there is some evidence, particularly in the case of sulfur and sulfide compounds that chemical agencies may be responsible for some of the changes. In view of this, incubation tests were used to study the soil conditioning value of pyrite and pyrrhotite.

Table 1. Analyses of sulfur, pyrite, and
pyrrhotite materials used in this investigation

Material	Sulfur (S) %	Sulfate (SO_4) %	pH
Sulfur	99.5	0.1	4.7
Pyrite, Joplin, Mo.	46.4	9.6	2.2
No. 2 pyrite, Col. of Mines	21.2	0.8	5.2
Pyrite, Clarkdale smelter dump	13.6	1.4	5.7
Pyrrhotite, Yucca, Arizona	18.1	2.3	3.0

The experimental procedure involved several methods of incubation and all incubations were conducted at room temperature. For the determination of oxidation to sulfate this was conducted by weighing 100 grams of air dry soil into a six-ounce glass tumbler, with cover, the sulfides mixed with the soil, and water added to bring the soil to a selected moisture content. In addition to the incubations which were conducted primarily to determine the rate of oxidation, others were conducted with larger amounts of soil for physical tests and to study the effect on replaceable sodium in the soil. These incubations were conducted in 1-liter glazed clay pots by mixing the materials thoroughly with the soil and incubating at selected moisture percentages.

EXPERIMENT 1

Two soils were selected for the first incubation experiment on the basis of textural difference. One soil was from the Safford Experiment Farm, Safford, Arizona, where a structural problem has arisen because of sodium adsorption from an irrigation water with a high sodium percentage. It represents the silty clay blanket over a sandy substrate which is typical of this area. The other soil is from an experimental area south of Gilbert - a sandy loam soil which is a very troublesome type in that the silt and clay fractions are highly dispersed; dry to a hard surface crust, and work up into a floury dry dust. This soil is marginal with respect to replaceable sodium; has a high replaceable potassium percentage; and is low in organic matter. (Table 2).

Table 2. Partial analysis of soils used in Experiment 1.

	Safford Soil	Gilbert Soil
Cation exchg. cap. m.e. per 100 gms.	29.5	14.9
Exchangeable Na, m.e. per 100 gms.	5.7	2.6
Exchangeable K, m.e. per 100 gms.	2.3	5.6
Exchangeable Mg, m.e. per 100 gms.	6.4	3.3
Moisture equivalent, percent	38.0	22.0
Gypsum requirement, tons per acre foot	10.0	3.0
Organic matter, percent	1.05	0.2

In this first incubation test, 2 grams of sulfur were thoroughly mixed with 100 grams of soil and the pyrite and pyrrhotite mixed with 100 grams of soil in amounts equivalent to 2 grams of sulfur - based on the analyses given in Table 1. In order to determine the effect of organic matter on oxidation, each test was replicated with 2 grams of well rotted manure per 100 grams of soil. The moisture content of the soils for the incubation period was adjusted by adding 21 mls. per 100 grams to the Gilbert soil and 48 mls. per 100 grams to the Safford soil. These were incubated for three weeks. At the end of this period the soils were dried in the air and examined for soluble sulfate by leaching 25 grams soil with 200 ml. of 0.5 percent ammonium chloride solution and determining the sulfate in the leachate by the turbidimetric method using a Cenco Photelometer. When this analysis was completed, the remaining 75 grams of soil was returned to the glass tumblers, moistened, and re-incubated for another three weeks. At the end of this period the soils were again analysed for soluble sulfate and for replaceable sodium. (Table 3).

The data show a wide difference in the rate and total oxidation of sulfur and sulfides in these two soils. The principal difference between the soils is in texture, salinity, and organic matter content--but any influence of organic matter on oxidation should have been corrected by the addition of manure to one series of cultures.

In general, the oxidation of all the sulfur compounds was more active in the Safford soil than in the Gilbert soil at the moisture percentages used in this incubation. In order of activity they were: pyrrhotite, sulfur, Number 2 pyrite, Clarkdale pyrite, and Joplin pyrite. The Clarkdale pyrite represents a dump that has been exposed to weathering for many years. The Joplin and Number 2 pyrite were obtained from the College of Mines, University of Arizona, and details regarding their previous history were not available. The oxidation of sulfur and pyrrhotite was more active during the first three weeks of incubation which showed a rapid rate of oxidation for these two materials. The reverse is true for the pyrite samples: Oxidation was greater during the second three weeks which showed a slow but progressive and continuous oxidation. For the incubations to which manure was added, the additional amount of organic matter did not change the order of activity of the five sulfur-bearing materials but did tend to reduce the oxidation during the first three weeks of incubation.

Table 3. Replaceable Na and soluble SO_4 in soils after three
and six weeks incubation with sulfur bearing materials

Treatment	Sulfate, mgms. SO_4 per 100 gms. soil*			Replaceable Na m.e. per 100 gms.
	3 weeks	3-6 weeks	total	after 6 weeks
	mgms.	mgms.	mgms.	
Safford Soil				
Sulfur	329	242	571	1.1
Joplin pyrite	none	none	none	1.3
No. 2 pyrite	32	104	136	1.9
Clarkdale pyrite	29	51	80	1.4
Pyrrhotite	371	234	605	1.1
Safford Soil plus Manure				
Sulfur	249	243	492	0.9
Joplin pyrite	none	none	none	1.4
No. 2 pyrite	24	100	124	1.7
Clarkdale pyrite	none	34	34	1.2
Pyrrhotite	293	342	645	1.0
Gilbert Soil				
Sulfur	none	53	53	1.6
Joplin pyrite	none	40	40	1.2
No. 2 pyrite	46	50	96	1.4
Clarkdale pyrite	none	none	none	1.8
Pyrrhotite	29	68	97	1.4
Gilbert Soil plus Manure				
Sulfur	53	14	87	1.2
Joplin pyrite	none	none	none	1.3
No. 2 pyrite	21	48	69	1.1
Clarkdale pyrite	none	none	none	1.3
Pyrrhotite	30	99	129	1.2

*All SO_4 values are corrected for SO_4 in the control soil culture and for water
soluble SO_4 present in the sulfur bearing materials that were mixed with
the soil.

For the Gilbert soil the rate and total oxidation were very slow for all the sulfur-bearing materials in comparison with the Safford soil. The order of activity of oxidation was somewhat similar and in the order pyrrhotite, sulfur, Number 2 pyrite. The difference between the oxidation of the Joplin pyrite and the Clarkdale pyrite in the two soils appears to be due to inherent differences in the soils. It is possible that the moisture percentage selected for this incubation test may have been closer to the optimum in the Safford soil. The Gilbert soil runs together when wetted which makes the selection of optimum wetness for incubation rather difficult.

This experiment showed that, at the moisture percentages used in this experiment, the unstable form of iron sulfide, represented by pyrrhotite, will oxidize rapidly to sulfate. The more stable pyrite is quite variable both in rate and total oxidation, depending on its source, and while the rate is slow it is progressive.

Sodium replacement. For the Safford soil, sulfur and pyrrhotite produced the most effective sodium replacement. This correlates with their high rate of oxidation. For the Gilbert soil the data on replacement of sodium are not conclusive. Apparently the oxidation of sulfur had not progressed sufficiently to have any great influence on adsorbed sodium.

EXPERIMENT 2

The second experiment was also conducted with 100 grams of soil in glass tumblers. The objectives in this experiment were to reduce the quantity of sulfur bearing materials, to desalinize the soils before incubation, to determine the effect of incubation at lower moisture percentages than used in Experiment 1, and to determine the effect of nitrate nitrogen on oxidation. In a previous study of sulfur oxidation in Arizona soils (3) the disappearance of nitrate in the soil during incubation indicated that an ample supply of nitrate is essential for the oxidation of sulfur by the soil microorganisms.

The Safford and Gilbert soils were used in this experiment and the incubation period was 4 weeks. 100 grams of Safford soil was moistened with 35 ml. of water and the Gilbert soil with 15 ml. of water. In order to further examine the effect of soil moisture percentage on oxidation, one set of cultures for each soil was incubated after wetting with 50 and 25 ml. for the Safford and Gilbert soils respectively.

Following is an outline of the experiment: treatment 1, control untreated soil; treatments 2, 3, 4, and 5, one gram sulfur and the equivalent of 1 gram sulfur from Joplin pyrite, Clarkdale pyrite, and pyrrhotite, in the order given, mixed with 100 grams of dry soil; treatments 6, 7, 8, and 9 same as 2, 3, 4, and 5 except that 30 mgms. ammonium nitrate were mixed with the soil in each; treatments 10, 11, 12, and 13 same as 2, 3, 4, and 5 except that 30 mgms. ammonium nitrate and 2 grams manure were added to each; treatments 14, 15, 16, and 17 same as 2, 3, 4, and 5 except that 2 grams of manure were added to each Gilbert soil only; treatments 18, 19, 20, and 21 same as 6, 7, 8, and 9 except that the soils were incubated after moistening with 50 ml. of water for the Safford soil and 25 ml. for the Gilbert soil.

After 4 weeks incubation the soils were dried in the air and examined for water soluble sulfate, replaceable sodium, and capillary rise of water. These data are given in Table 4 and the capillary rise in Figure 1.

Oxidation to sulfate. At the moisture percentages used in this experiment the order of rate of oxidation, from most to least, was sulfur, pyrrhotite, Clarkdale pyrite, and Joplin pyrite. It is of particular interest that the oxidation of sulfur, pyrrhotite, and Clarkdale pyrite was significantly higher at the lower moisture percentages used in this experiment as compared with Experiment 1. For the very wet cultures in this experiment, neither pyrrhotite nor pyrite showed any measureable oxidation to sulfate. The oxidation of sulfur and pyrrhotite was increased by ammonium nitrate and manure. The oxidation of the Clarkdale pyrite was more active at the lower moisture percentages in Experiment 2, but there was little measureable oxidation of the Joplin pyrite at either soil moisture percentage. This experiment emphasizes the importance of the moisture content of the soil as a function of sulfur and sulfide oxidation. At the soil moisture percentages used here the oxidation of both sulfur and sulfide was stimulated by ammonium nitrate and manure to a much greater extent than the pyrrhotite.

Replaceable sodium. The effect of the incubation of these soils with the several sulfur-bearing materials on replaceable sodium was determined. (Table 4). There was a reduction in adsorbed sodium for all materials. The least reduction was for the soil incubated with Joplin pyrite and this correlates with a slow rate of oxidation.

Capillary rise. The results obtained from the capillary rise test (Fig. 1) are represented as cm. per hour for 24 hours. The incubations with sulfur, pyrrhotite, and Clarkdale pyrite showed a significant improvement in capillary conductance of water. For the Joplin pyrite there was little improvement beyond what might be expected from the soluble sulfate in this material and the low pH. The importance of the moisture content of the soil during incubation is effectively shown in the reduced capillary rise for the soils from the wet cultures. There is a definite trend toward lower rate of oxidation at the higher moisture percentages and its influence was shown to be greater for pyrrhotite and pyrite than for sulfur. The addition of ammonium nitrate and manure had no significant influence on capillary rise.

EXPERIMENT 3

The third experiment was conducted in glazed clay pots using 600 gms. of soil. The several sulfur bearing materials were mixed with the soil in quantities equivalent to 2 gms. of sulfur per 600 gms. of soil - that is one sixth the quantity, per 100 gms. of soil, used in Experiment 1. There were two series of treatments in this experiment. One series consisted of soil mixed with sulfur-bearing materials and the other series had 12 gms. of manure mixed with the soil and materials. Following is an outline of the soil treatments.

1.	Control, soil only	7.	Same as 1 plus 12 gms. manure
2.	Sulfur	8.	Same as 2 plus 12 gms. manure
3.	Joplin pyrite	9.	Same as 3 plus 12 gms. manure
4.	No. 2 pyrite	10.	Same as 4 plus 12 gms. manure
5.	Clarkdale pyrite	11.	Same as 5 plus 12 gms. manure
6.	Pyrrhotite	12.	Same as 6 plus 12 gms. manure

For the incubation, 288 mls. of water was added to the 600 gms. of air dry soil for the Safford soil and 126 mls. for the Gilbert soil. They were incubated for 3 weeks, the covers removed, the soil allowed to dry slowly in the pots. When dry the soil was ground to break up the lumps and then returned to the pots for 4 weeks additional incubation. For the second incubation period, 225 mls. of water was added to the Safford soil and 110 mls. to the Gilbert soil. By using

Table 4. Soluble SO_4 formed by oxidation of sulfur, pyrite, and pyrrhotite in two soils, and effect on capillary rise and replacable Na.

		Safford Soil			Gilbert Soil		
	Treatment	Cap. rise cm. per hr.	SO_4 mgms./100 gms. soil	Rep. Na m.e./100 gms	Cap. rise cm. per hr.	SO_4 mgms./100 gms.	Rep. Na m.e./100 gms.
1.	Control	.46	20	6.6	.77	30	2.6
2.	Sulfur[1]	1.42	288	5.1	1.62	511	2.3
3.	Joplin pyrite	.58	none	5.9	1.25	3	2.6
4.	Clarkdale pyrite	1.46	48	4.1	1.54	117	2.0
5.	Pyrrhotite	1.38	250	4.0	1.67	345	2.3
6.	Sulfur[2]	1.42	318	4.4	1.83	631	1.3
7.	Joplin pyrite	.58	none	5.0	1.67	none	1.9
8.	Clarkdale pyrite	1.46	27	3.7	1.58	38	1.7
9.	Pyrrhotite	1.58	355	3.4	1.88	366	1.7
10.	Sulfur[3]	1.21	655	3.7	1.27	822	2.0
11.	Joplin pyrite	.58	none	5.1	1.08	none	2.7
12.	Clarkdale pyrite	1.38	97	3.5	1.37	31	2.0
13.	Pyrrhotite	1.58	450	3.2	1.37	375	1.6
14.	Sulfur[4]				1.21	584	1.5
15.	Joplin pyrite				1.00	none	2.6
16.	Clarkdale pyrite				1.42	20	2.2
17.	Pyrrhotite				1.29	354	1.7
18.	Sulfur[5]	1.38	137		1.54	55	
19.	Joplin pyrite	.67	none		.92	none	
20.	Clarkdale pyrite	.71	none		.88	none	
21.	Pyrrhotite	.75	none		.96	none	

[1] 2 to 5 all added to soil on basis of 1 gram sulfur or its equivalent
[2] 6 to 9 30 mgms. ammonium nitrate added to each
[3] 10 to 13 2 gms. manure and 30 mgms. ammonium nitrate added to each
[4] 14 to 17 2 gms. manure added to each
[5] 18 to 21 30 mgms. ammonium nitrate added to each and incubated at high wetness

two different moisture percentages during incubation and allowing the soils
to dry slowly in the pots at the end of the incubation periods it was possible
to cover a wide range of soil moisture percentage and to simulate, somewhat,
the type of incubation that would occur under field conditions. At the end of
the second period of incubation the soils were ground to pass a 2 mm. sieve.

The data obtained from the examination of these soils are given in Table 5
and Figure 2. Table 5 shows mgms. SO_4 per 100 gms. soil at the end of the two
incubation periods, rate of capillary rise of water in a column of soil,
infiltration rate, and modulus of rupture for the Safford soil.

Oxidation. The quantity of sulfate formed during incubation was in the
order, most to least: sulfur, pyrrhotite, Clarkdale pyrite, and the other two
pyrites, for the Safford soil, with a trend toward more sulfate in the soils to
which manure was added. For the Gilbert soil the sulfur and pyrrhotite showed
good rate of oxidation but the difference between these two sulfur-bearing
materials is less than for the Safford soil where the total oxidation was
greater. The more active oxidation of the Joplin pyrite in the Gilbert soil,
as compared with the Safford soil, confirms similar observations in other tests
and indicates that we cannot expect the same rate of oxidation of pyrite, from
different sources, for all soils.

Infiltration rate. The infiltration rate, permeability, was determined by
using a column of soil 5.5 cm. high and 5.3 cm. diameter uniformly packed in
plastic tubes having a wire mesh bottom. This column of soil was maintained
under a constant water head of 7.5 cm. above the surface of the soil by means of
a Mariotte bottle. The data given in Table 5 represent mls. per hour drainage
over a 24 hour period.

There is a very significant improvement in infiltration rate for the Safford
soil for both sulfur and pyrrhotite with a further slight increase where manure
was also mixed with the soil. For the Gilbert soil the infiltration rate was
extremely slow for all the treated soils and this is typical of the stubborn
behavior of this soil in the field. This soil showed a greater infiltration rate
and capillary rise than the Safford soil, for the untreated controls, but showed
less improvement from incubation with sulfur and sulfides. All the soils that
were incubated with sulfur showed greater improvement in infiltration rate than
those incubated with sulfides.

Capillary rise. The effect of these several sulfur-bearing materials on
capillary rise of water is somewhat similar to the effect on infiltration rate--
namely, more improvement for the Safford soil than the Gilbert soil. This may be
due to a greater initial capillary rise in the latter. For the Safford soil the
sulfur and pyrrhotite were most effective in improving capillary rise but there
was an appreciable improvement in this experiment for the soils treated with the
Clarkdale pyrite. It is probable that the increased capillary rise and
infiltration rate from the pyrrhotite and the Clarkdale pyrite was due to the
low pH of the materials and the presence of gypsum, as an impurity, in both these
materials.

Modulus of rupture. Modulus of rupture tests were made on the Safford soil
(Table 5). The data show a significant reduction in modulus of rupture for the
soil briquettes made from soils incubated with sulfur, pyrrhotite, and Clarkdale
pyrite. As mentioned above in the discussion of the effect of the two latter on
capillary rise and infiltration rate the low pH and gypsum present in these two
materials is believed to have been effective in reducing the modulus of rupture.
Each test was replicated 6 times using the procedure recommended by Richards (5).

Table 5. Analysis of soils from Experiment 3.

Treatment	mgms. SO_4**	Infilt. rate	Cap. rise	Cap. rise*	Modulus of rupture
	100 gms. soil	ml. per hr.	cm. per hr.	cm. per hr.	m. bars
Safford Soil					
1. Control		7.7	.52	.63	2095
2. Sulfur	184	288.0	1.58	1.87	574
3. Joplin pyrite	12	12.9	.77	.63	1780
4. No. 2 pyrite	12	14.8	.79	.54	1608
5. Clarkdale pyrite	80	30.2	1.29	1.16	856
6. Pyrrhotite	152	143.0	1.71	1.71	635
Safford Soil plus manure					
7. Control		4.7	.42	.42	2238
8. Sulfur	216	329.0	1.37	1.75	1172
9. Joplin pyrite	52	9.5	.58	.50	2030
10. No. 2 pyrite	16	50.6	.83	1.08	1653
11. Clarkdale pyrite	120	35.4	1.13	1.37	666
12. Pyrrhotite	152	316.0	1.42	1.75	756
Gilbert Soil					
1. Control		6.1	.58	.79	
2. Sulfur	50	15.3	.96	1.17	
3. Joplin pyrite	60	14.8	.96	.54	
4. No. 2 pyrite	15	14.9	.96	.67	
5. Clarkdale pyrite	40	10.9	.96	1.08	
6. Pyrrhotite	80	12.4	1.00	1.21	
Gilbert Soil plus manure					
7. Control		11.4	.87	1.17	
8. Sulfur	110	21.7	.96	1.17	
9. Joplin pyrite	70	19.1	.87	1.00	
10. No. 2 pyrite	20	7.4	.96	1.08	
11. Clarkdale pyrite	55	10.2	.96	1.13	

* The capillary rise data in this column were taken on the soils after they had been leached with water and should be compared with the preceding column.

** The SO_4 values have been corrected for soluble SO_4 in soils and sulfur bearing materials.

Table 6. Partial analyses of three soils used in Experiment 4.

	Safford	Gilbert	Greene
Saturation percentage	114	74	76
Cond. Sat. Ext. m.mhos./cm./	4.0	24.5	3.8
Exchange capacity, m.e./100 gms.	37.0	15.0	16.0
Replaceable Na, m.e./100 gms.	10.7	2.6	8.1
Replaceable K, m.e./100 gms.	2.5	5.5	1.7

EXPERIMENT 4

The soil in the Safford and Gilbert areas varies somewhat within the area as a whole, particularly with respect to texture, structure, salinity, and cations adsorbed on the exchange complex. The soils used in this experiment were taken from new locations in these two areas. They were similar in texture but different in salinity and sodium percentage. For additional information a black alkali soil obtained from land of the Greene Cattle Co., in Santa Cruz County, was included in this experiment. A partial analysis of these soils is given in Table 6.

For this experiment 1 kg. of air-dry soil was incubated in glazed clay pots for 60 days after mixing each separate 1 kg. portion with sulfur, Joplin pyrite, Clarkdale pyrite, pyrrhotite, and no. 2 pyrite, and iron sulfate. All were added to the soil on a 1 and 4 ton sulfur and sulfur equivalent basis. For incubation the Safford soil was moistened with 220 mls. of water, the Gilbert soil with 130 mls., and the Greene soil with 150 mls. of water. The pots were kept covered during the incubation period to prevent evaporation loss. At the end of the incubation period the soils were dried and ground to pass a 2 m.m. sieve. They were then analysed for soluble sulfate, capillary rise, infiltration rate, and replaceable Na and K. These data are given in Tables 7 and 8 and the capillary rise and infiltration rate differences are shown in Figure 3.

Oxidation. In all these soils, particularly the black alkali soil, the oxidation of sulfur and pyrrhotite was, as in the previous experiments, most active; followed by the Clarkdale pyrite, with the other pyrite showing little oxidation. For some reason, which is not evident, the oxidation of pyrite was more active in the Gilbert soil than in the other two soils. The soluble sulfate in the soils treated with iron sulfate are not consistant and indicate a fixation or change to a less soluble form.

Capillary rise. As illustrated in Figure 3 the capillary rise data correlate quite well with the oxidation of the sulfur bearing materials. Iron sulfate gave the greatest improvement in capillary rise in this experiment. For the others the sulfur and pyrrhotite gave the only significant improvement.

Infiltration rate. The infiltration rate data correlate quite well with the quantity of sulfate produced in these soils except for the black alkali soil. This soil gave practically no permeability response to any of the conditioners. There was no drainage from this soil at the end of 48 hours under a 7.5 cm. head of water. At the end of 72 hours there was 10. mls. drainage from the soil treated with 4 tons per acre of sulfur and 15 mls. from the soil treated with 4 tons iron sulfate.

Table 7. Analyses of soils from Experiment 4 after incubation, sulfate formed during incubation, capillary rise, infiltration rate sulfate values for treated soils are corrected for SO$_4$ in controls.

Treatment	Mgms. SO$_4$ per 100 gms. soil**			Cap. rise, cm. per hr.			Infilt. rate, mls. per hr.		
	Safford	Gilbert	Greene	Safford	Gilbert	Greene	Safford	Gilbert	Greene
Control				.21	.54	.17	.67	1.71	none
Sulfur, 1 ton per acre	35	53	18	.33	.71	.15	.87	3.58	none
Sulfur, 4 tons per acre	140	123	88	.43	1.04	.21	5.84	8.19	10*
No. 2 pyrite, 1 t.p.a.	5	26	0	.21	.71	.13	.33	2.08	none
No. 2 pyrite, 4 t.p.a.	2	48	5	.25	.71	.12	.41	3.00	none
Iron sulfate, 1 t.p.a.	60	53	33	.33	.80	.17	.83	3.96	none
Iron sulfate, 4 t.p.a.	155	113	183	.40	1.50	.25	7.50	12.33	15*
Joplin pyrite, 1 t.p.a.	7	23	0	.23	.61	.17	.50	1.50	none
Joplin pyrite, 4 t.p.a.	15	38	18	.25	.64	.15	.75	2.54	none
Pyrrhotite, 1 t.p.a.	20	58	28	.29	.73	.15	.37	3.25	none
Pyrrhotite, 4 t.p.a.	77	70	83	.33	1.21	.17	6.45	4.79	none
Clarkdale pyrite, 1 t.p.a.	10	23	8	.23	.63	.13	.50	1.50	none
Clarkdale pyrite, 4 t.p.a.	30	58	58	.27	.87	.15	1.40	5.00	none

* No drainage in any case at end of 48 hours, represents total volume drainage 72 hours. For Safford and Gilbert soils values represent rate per hour for 24 hours.

** The SO$_4$ values have been corrected for soluble SO$_4$ in soils and sulfur bearing materials.

Table 8. Analyses of soils from Experiment 4 after incubation;
replaceable Na and K as millequivalents per 100 gms.

Treatment	Replaceable Na m.e./100 gms.			Replaceable K m.e./100 gms.		
	Safford	Gilbert	Greene	Safford	Gilbert	Greene
Control	10.7	2.6	8.1	2.6	5.5	1.7
Sulfur, 1 ton per acre	9.3	2.4	6.0	2.3	5.5	0.8
Sulfur, 4 tons per acre	6.3	1.0	5.6	2.4	4.7	1.1
No. 2 pyrite, 1 t.p.a.	9.1	2.1	7.2	2.7	5.4	1.4
No. 2 pyrite, 4 t.p.a.	8.8	2.8	7.2	3.1	4.9	1.4
Iron sulfate, 1 t.p.a.	7.6	1.4	6.0	2.7	5.1	1.5
Iron sulfate, 4 t.p.a.	6.4	1.6	4.9	2.5	4.2	1.0
Joplin pyrite, 1 t.p.a.	9.4	1.1	6.1	2.9	5.7	1.2
Joplin pyrite, 4 t.p.a.	8.8	2.5	6.4	3.0	5.8	1.5
Pyrrhotite, 1 t.p.a.	9.1	1.5	6.3	2.8	5.4	1.2
Pyrrhotite, 4 t.p.a.	7.0	2.2	6.2	3.1	5.2	1.3
Clarkdale pyrite, 1 t.p.a.	9.6	2.2	6.4	2.8	5.3	1.8
Clarkdale pyrite, 4 t.p.a.	9.3	2.0	6.2	2.8	5.4	1.2

Replaceable bases. Sulfur and iron sulfate produced the greatest reduction
in replaceable sodium and there was no consistent effect on replaceable potassium.

EXPERIMENT 5

A study of the oxidation products of pyrite and pyrrhotite and their effect
on the soil would be incomplete without the inclusion of a comparative study of
iron sulfate and gypsum because iron sulfate is the principal product of the
oxidation of iron sulfide and gypsum is the soil conditioner which has been in use
over a long period. In the experiment presented here the mineral copiapite was
used as a source of iron sulfate. This mineral has been given the formula
$Fe_2(FeOH)_2 (SO_4)_5 18H_2O$ and the material used in this experiment was obtained
from a deposit near Congress Junction, Arizona. The analysis of this mineral
showed 38.6 percent iron (Fe) and 47.1 percent sulfate (SO_4) as compared to a
theoretical 21.5 percent Fe and 45.3 percent SO_4 based on the formula of the
mineral as given above. It was completely soluble in water except for a trace
of insoluble residue. An analysis of the parent rock adjacent to the copiapite
deposit from which this sample was taken showed the presence of pyrite and this is
evidence that the copiapite had been formed by the oxidation of pyrite. In view
of this it offered an ideal form of iron sulfate for inclusion in a comparative
study of pyrite and pyrrhotite.

The Safford, Greene, and Gilbert soils used in Experiment 4 were selected
for this experiment. 500-gram portions of each soil were weighed into 14 glazed
clay pots and the following rates of gypsum and copiapite were mixed with the
soils; 0 (control), 1, 2.5, 5, 7.5, 10, and 15 tons per acre foot of soil. The

minerals and soil were well mixed and then leached with the equivalent of 2 acre-feet of water.

The drainage from each pot of soil was tested to learn the extent of the reaction between the soils and gypsum. This test was qualitative and was made by mixing equal volumes of drainage water and acetone. Tests on the drainage from the Safford soil were negative for the applications of 1, 2.5, 5, and 7.5 tons gypsum per acre and were positive for the drainage from the applications of 10 and 15 tons per acre. Tests on the drainage from the gypsum treated Gilbert soil were all positive. Tests on the drainage from the Greene soil (50.6 percent adsorbed Na) were all negative, showing that all of the gypsum had reacted with and been absorbed by the soil.

After leaching the soils with the equivalent of 2 acre-feet of water the soils were dried in the air and ground to pass a 2 m.m. sieve for testing. These data are given in Table 9.

Infiltration rate. For each soil the infiltration rate was substantially stepwise and proportional to the increase in quantity of the two materials mixed with the soils. Gypsum was somewhat more effective than copiapite for the Safford and Greene soils and at the lower rates it was also more effective for the Gilbert soil. The infiltration rates show a good correlation between the gypsum absorption capacity and the effectiveness of gypsum over copiapite. The Gilbert soil has a low gypsum requirement and this explains why there was little difference between gypsum and copiapite when the two were applied at rates above the quantity actually required for conditioning the soil. The differences are illustrated in Figure 4.

Capillary rise. The relation between capillary rise of water in the columns of soil and the quantity of the two materials mixed with these three soils, like the infiltration rate, was also stepwise and proportional to the quantity applied. For the Safford soil there was no increase in capillary rise below 7.5 tons gypsum per acre and there was little or no difference in the effectiveness of gypsum and copiapite for this soil. For the Greene soil, the black alkali soil, gypsum was more effective than copiapite and the improvement in capillary rise was obtained with as little as 2.5 tons per acre. For the Gilbert soil, which has the lowest gypsum absorbing capacity, there is a measureable response to 1 ton gypsum per acre. Gypsum was more effective than the copiapite for the 1 and 2.5 tons per acre applications but at 10 and 15 tons per acre the copiapite produced a slightly higher rate of capillary rise. The differences are illustrated in Figure 5.

pH reduction. The pH determinations were made on the 1 to 10 soil water ratio. The pH reduction was less effective for the Greene soil than for the other two soils and there was a more effective reduction in pH from the copiapite, on all soils, than for gypsum. The pH of the copiapite used in this experiment was 2.5. Gypsum does not neutralize hydroxyl ions but does inactivate sodium carbonate. It reduces pH in some soils by replacement of adsorbed sodium. Sulfur during oxidation neutralizes alkalinity and will reduce alkalinity due to sodium carbonate as well as adsorbed sodium. Iron sulfate is an acid salt, as shown by the pH of copiapite given above, and will therefore neutralize and reduce alkalinity.

Replaceable sodium. This was significantly reduced by both gypsum and copiapite but the copiapite gave a more effective reduction in adsorbed sodium than the gypsum for the black alkali soil. The low pH of the copiapite is undoubtedly the reason for this reduction.

Table 9. Analyses of soils after incubation, Experiment 5.

Treatment Tons per acre	Cap. rise cm. per hr.	Infilt. rate mls. per hr.	pH	Repl. Na m.e./100 gms.	Cap. rise cm. per hr.	Infilt. rate mls. per hr.	pH	Repl. Na m.e./100 gms.
	Gypsum				Copiapite			
	Safford Soil							
0-c	.85	4.2	9.0	7.8	.85	4.2	9.0	7.8
1	.68	6.3	8.9	7.8	.64	1.9	8.7	7.3
2.5	.75	5.2	9.3	7.1	.69	2.1	8.6	7.4
5	.74	7.3	9.1	7.4	.75	5.4	8.5	6.8
7.5	1.02	8.8	8.7	6.4	1.08	6.9	8.4	6.5
10	1.06	10.7	8.6	6.2	1.09	7.5	8.4	6.5
15	1.25	11.7	8.4	6.1	1.19	7.7	8.3	6.1
	Gilbert Soil							
0-c	.70	3.5	8.7	2.7	.70	3.5	8.7	3.4
1	.90	3.7	8.5	3.4	.80	2.6	8.8	3.3
2.5	1.10	5.6	8.3	2.7	1.00	4.6	8.7	2.9
5	1.10	6.1	8.5	2.6	1.10	7.5	8.5	2.5
7.5	1.20	9.9	8.3	2.5	1.20	7.5	8.2	2.9
10	1.20	8.7	8.1	2.5	1.30	9.8	8.0	2.7
15	1.10	10.5	8.1	2.3	1.30	10.5	7.8	2.4
	Greene Soil							
0-c	.08	0	10.6	10.6	.08	0	9.8	10.6
1	.06	0	9.7	11.5	.08	0	9.8	10.9
2.5	.12	0	9.9	10.4	.08	0	9.7	10.1
5	.17	.2	9.7	9.6	.12	.24	9.7	9.7
7.5	.23	.6	9.8	8.4	.11	.31	9.6	7.1
10	.50	1.0	9.5	8.9	.15	1.0	9.4	6.4
15	.71	9.2	9.4	7.1	.50	7.6	9.0	6.2

EXPERIMENT 6

Elemental sulfur and a number of the sulfur compounds are somewhat like nitrogen and nitrogen compounds in that they are subject to a variety of transformations in the soil through the agency of soil micro-organisms - both aerobic and anaerobic depending on the degree of aeration in the soil. In addition to biological transformations there is some evidence that both elemental and combined sulfur may be oxidized or reduced by chemical agencies in the soil. Biological oxidation of sulfur in soils is primarily by the <u>Thiobacillus</u> group but there are several other groups of bacteria, which use sulfur as a source of energy, capable of oxidizing elemental and combined sulfur. There are several sources of energy for these organisms in the soil. Carbon dioxide and bicarbonates serve as a source of carbon and nitrate as a source of nitrogen.

In order to gain some information on the carbon dioxide evolution from the soils used in these experiments, during incubation, and the relation between carbon dioxide evolution and oxidation of sulfur and sulfides to sulfate in the soils, incubation experiments were conducted in which carbon dioxide evolution was measured. The technique employed was essentially that recommended by Heck (2) using 100 grams of soil and measuring the carbon dioxide evolution by absorption in standard alkali solution. The incubation period used was three weeks and the moisture content the same as for Experiment 2.

Four 100-gram portions of soil were mixed with 1 gram of sulfur or 1 gram sulfur equivalents of Clarkdale pyrite, Joplin pyrite, and pyrrhotite making a total of 16 cultures. One of each of the four portions of soil was incubated without further treatment, to one of each 30 mgms. ammonium nitrate and 2 grams of manure were added. One set of incubations was made with the original soil to which manure and ammonium nitrate were added. The evolution of carbon dioxide from these is shown in Table 10 as mgms. CO_2 per 100 gms. of soil over a period of three weeks.

This experiment shows that throughout the period of incubation there was an ample supply of carbon dioxide available for the sulfur oxidizing bacteria in these three soils. The supply was least in the Gilbert soil but it was increased by the addition of manure. For the Greene soil, the black alkali soil, carbon dioxide evolution was less for the soil treated with sulfur, pyrrhotite, and pyrite than for the control culture. In all three soils carbon dioxide evolution was increased by both ammonium nitrate and manure but there is no evidence that an additional supply was needed for the oxidation of the sulfur bearing materials used in this experiment. The order of active oxidation of the sulfur-bearing materials as shown in previous experiments, from most to least, was sulfur, pyrrhotite, Clarkdale pyrite, and Joplin pyrite. The data obtained from the determination of CO_2 evolution during the incubation of these materials show that an ample supply of CO_2, as a source of carbon, was available and therefore the difference in rate of sulfur oxidation, for the several materials is not related to a carbon source.

SUMMARY

The minerals gypsum and gypsite are available in large quantities in Arizona and therefore have found extended use as soil conditioners for problem soils in the State. Elemental sulfur, which does not occur in mineral form in the State, is also extensively used. One ton of sulfur is equivalent in conditioner value to 5 or 6 tons of gypsum and this equivalency makes sulfur competitive with gypsum despite the transportation costs.

Table 10. Evolution of carbon dioxide by three soils during incubation with sulfur and sulfides.

Treatment	mgms. CO_2 per 100 grams soil		
	Safford	Gilbert	Greene
Control	232	207	347
Ammonium nitrate	313	215	458
Manure	319	258	278
Ammonium nitrate plus manure	396	249	395
Sulfur	313	252	338
plus ammonium nitrate	323	238	396
plus manure	422	292	368
plus manure and ammonium nitrate	392	283	429
Clarkdale pyrite	294	206	328
plus ammonium nitrate	271	209	266
plus manure	436	227	365
plus manure and ammonium nitrate	415	227	453
Pyrrhotite	406	201	266
plus ammonium nitrate	317	225	389
plus manure	394	242	312
plus manure and ammonium nitrate	423	260	480
Joplin pyrite	271	229	240
plus ammonium nitrate	284	231	354
plus manure	423	249	572
plus manure and ammonium nitrate	481	263	456

During the past 15 years, farmers have shown increasing awareness of soil conditioner materials and new interest in several sulfur-bearing materials has arisen. Prominent among these are pyrrhotite and pyrite both of which are available in the State. Many tons of pyrite occur as waste in dumps near smelters and a supply of pyrrhotite exists near Kingman in northern Arizona.

The pyrite content of the material in the smelter dumps is variable and their economic value as soil conditioners would be limited to the percentage pyrite present - if pyrite should prove to be useful as a soil conditioner. The examination of samples from several of these dumps showed the presence of iron sulfate which proves that oxidation to iron sulfate is taking place progressively under the influence of weathering agents. There is no evidence to show whether biological or chemical agents are involved. It is, however, evident that pyrite will oxidize to iron sulfate and since the value of pyrite as a soil conditioner depends on its ability to so oxidize the question has arisen as to the value of pyrite.

Some of the material in these smelter dumps contain variable quantities of gypsum and this has probably been formed by the reaction between the acidity of the material and caliche, $CaCO_3$, which is also present in the dump.

The investigation presented in this bulletin gives a comparison of the rate of oxidation of elemental sulfur, pyrrhotite, and pyrite from several sources.

The rate of oxidation was greatly influenced by the moisture percentage of the soil and was most active at low degrees of wetness. Elemental sulfur was less affected by variation in wetness than pyrite and pyrrhotite.

Elemental sulfur and pyrrhotite oxidize to sulfate very rapidly in the soil and, on the whole, at closely equivalent rates. Oxidation of pyrite is very slow and varies for pyrite from different sources. There is evidence that prolonged exposure to weathering agents will increase the rate of oxidation of pyrite from smelter dumps and in the soil.

The oxidation experiments show that sulfur and pyrrhotite will oxidize at a sufficient rate to effectively serve as soil conditioners when applied to the soil at rates somewhat equivalent to the gypsum-absorbing capacity of the soil and that pyrite oxidizes too slowly to have any conditioner value within a reasonable time after application to the soil.

Since nitrate nitrogen and carbon dioxide, as sources of nitrogen and carbon, are essential for biological oxidation of sulfur and sulfides in soil, incubation tests were conducted to examine the evolution of carbon dioxide during the incubation of the sulfur-bearing materials and the effect of ammonium nitrate and manure. These tests showed that an ample supply of carbon dioxide was present during the incubation experiments presented here. Therefore the slow oxidation of pyrites was not due to lack of a source of carbon or nitrogen.

The final measure of a soil conditioner is its effect on soil structure - particularly the rate of water movement in the soil. The examination of the incubated soils for structure improvement was made by determining the capillary conductance of water, the infiltration rate, and in one experiment the modulus of rupture was determined. The tests showed a significant structural improvement from incubation with sulfur and pyrrhotite and copiapite which is a naturally occuring oxidation product of pyrite. There was only a very limited improvement in water movement for the soils incubated with pyrite and this was somewhat related to the presence of soluble sulfate, calcium and iron sulfates, in the material and the amount of weathering to which the pyrite dump had been subjected.

Modulus of rupture tests on the Safford soil, after incubation with the several sulfur-bearing materials showed a structural improvement for the soils treated with sulfur, pyrrhotite, and Clarkdale pyrite.

This investigation was not concerned with agricultural uses of sulfur-bearing materials other than as soil conditioners. However the incubation tests showed that the rate of oxidation of pyrrhotite should make it a useful source of iron when it is applied to the soil or to a compost.

BIBLIOGRAPHY

1. Gardner, R. Some soil properties related to the sodium salt problem in irrigated soils, U. S. D. A. Tech. Bul. 902 (1945)

2. Hech, A. F. A method for the determination of total carbon and also the estimation of carbon dioxide evolved by soil, Soil Sci. 28: 225-255 (1929).

3. McGeorge, W. T. and Greene, R. A. Oxidation of sulfur in Arizona soils and its effect on soil properties, Ariz. Agr. Exper. Sta. Tech. Bul. 59 (1935).

4. Smith, H. V. The effect on plant growth of treating soils with copper-bearing pyrite, Jour. Amer. Soc. Agron. 22; 903-915 (1930)

5. Diagnosis and Improvement of Saline and Alkali Soils, U. S. D. A. Agriculture Handbook No. 60.
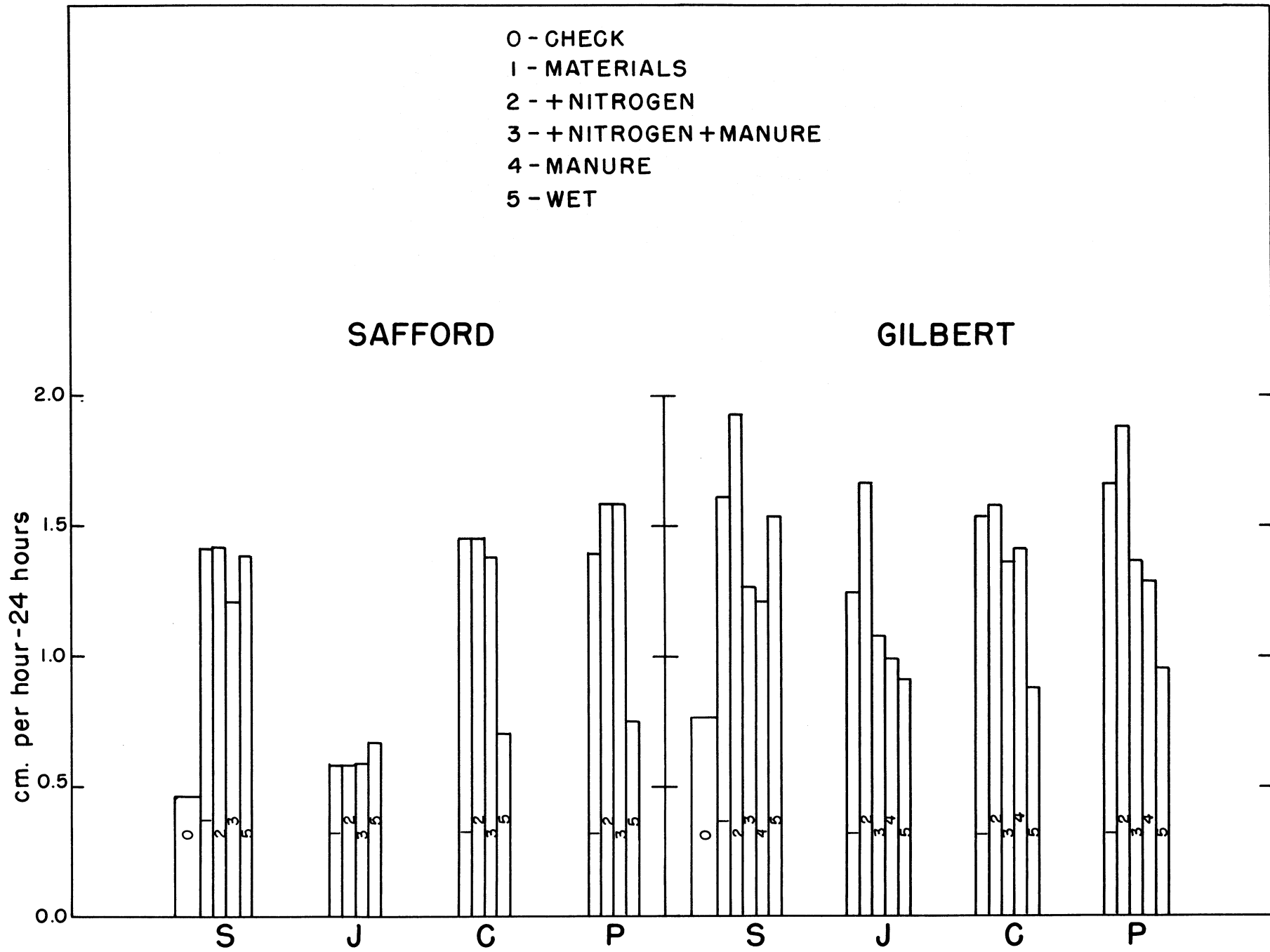
Figure 1. Capillary rise in Safford and Gilbert soils after incubation with sulfur bearing materials, Experiment 2. S, sulfur; J, Joplin pyrite; C, Clarkdale pyrite; P, pyrrhotite.
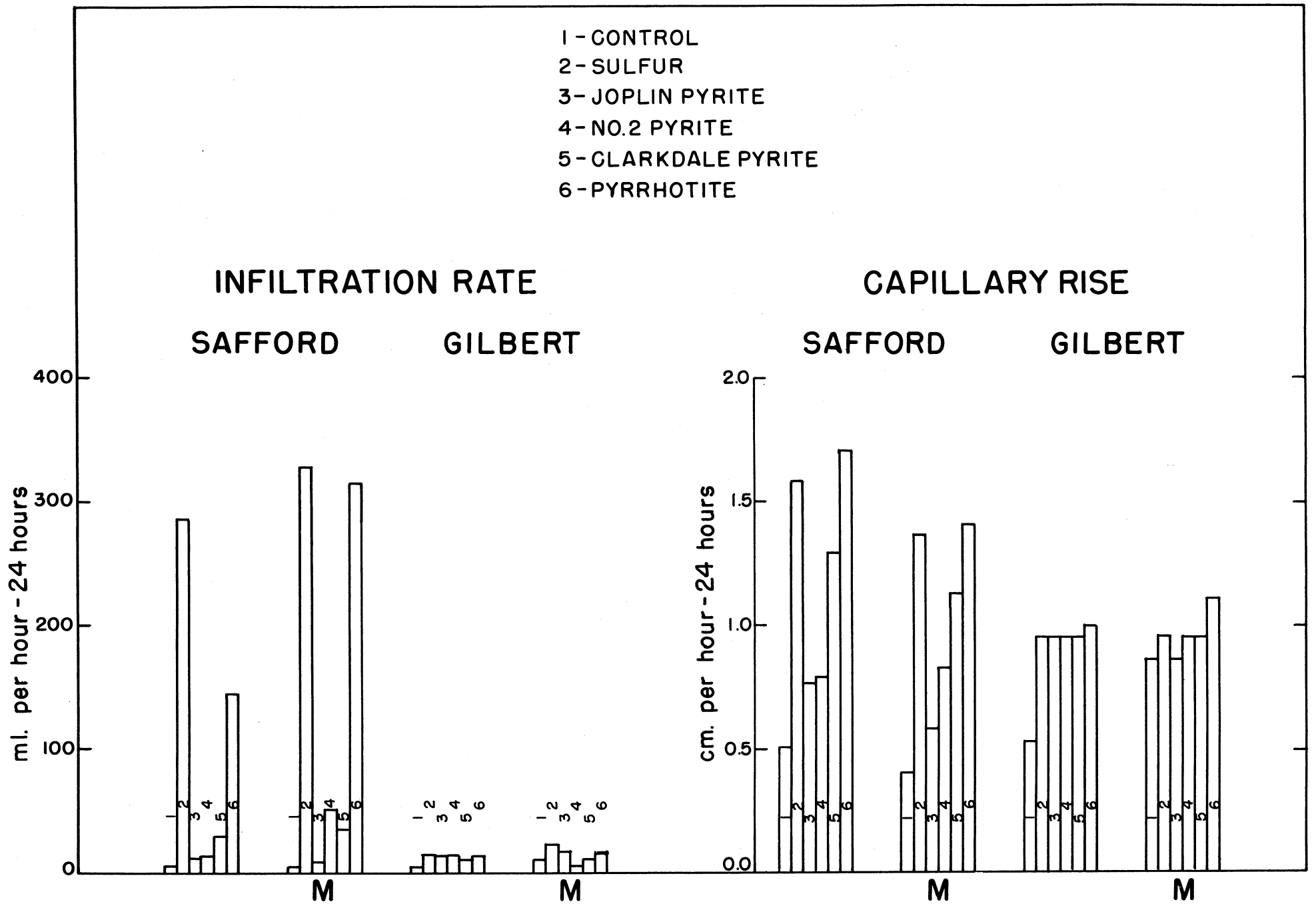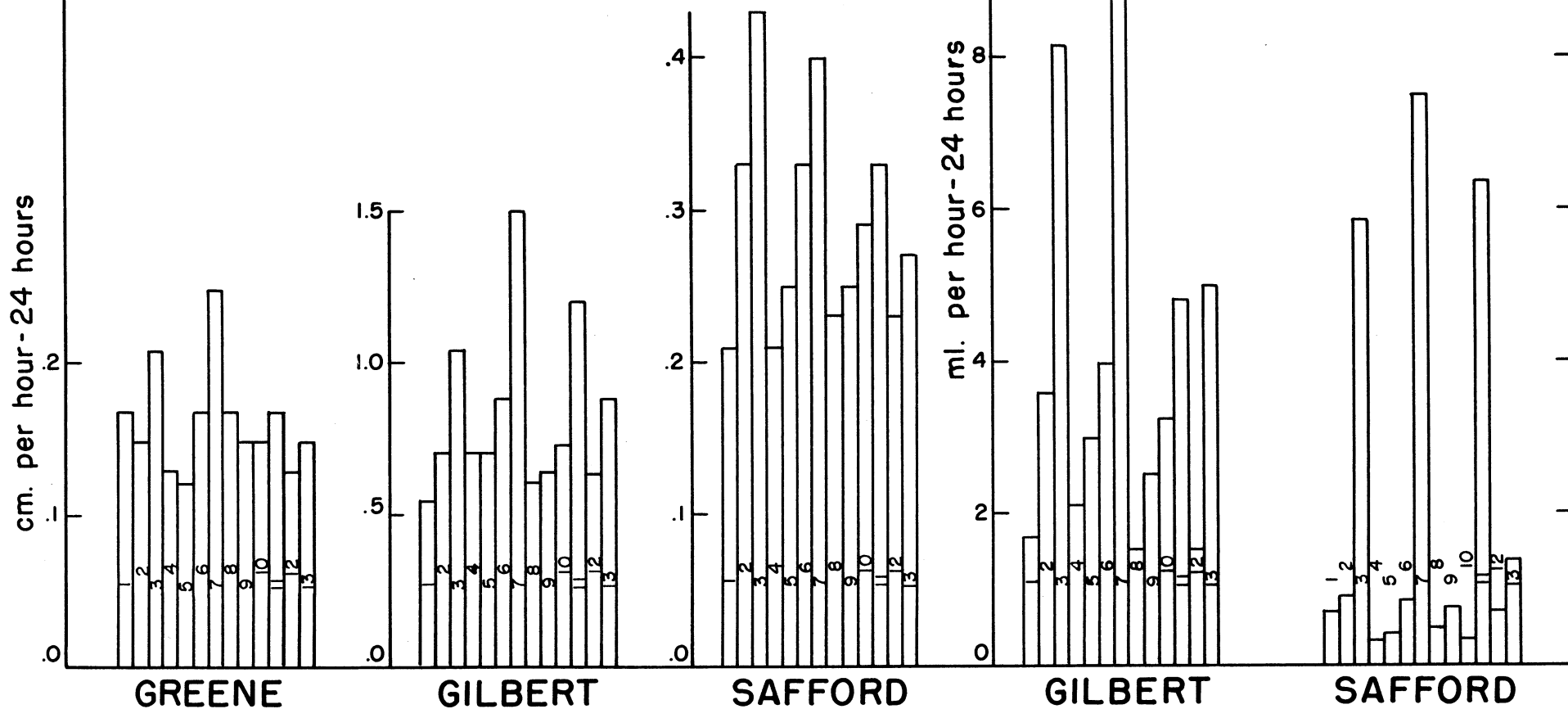
Figure 2.   Capillary rise and infiltration rate for Safford and Gilbert soils after incubation with sulfur bearing materials, Experiment 3. The soils to which manure was added are marked M.

Figure 3.　Capillary rise and infiltration rate for Safford, Gilbert, and Greene soils after incubation with sulfur-bearing materials, Experiment 4.
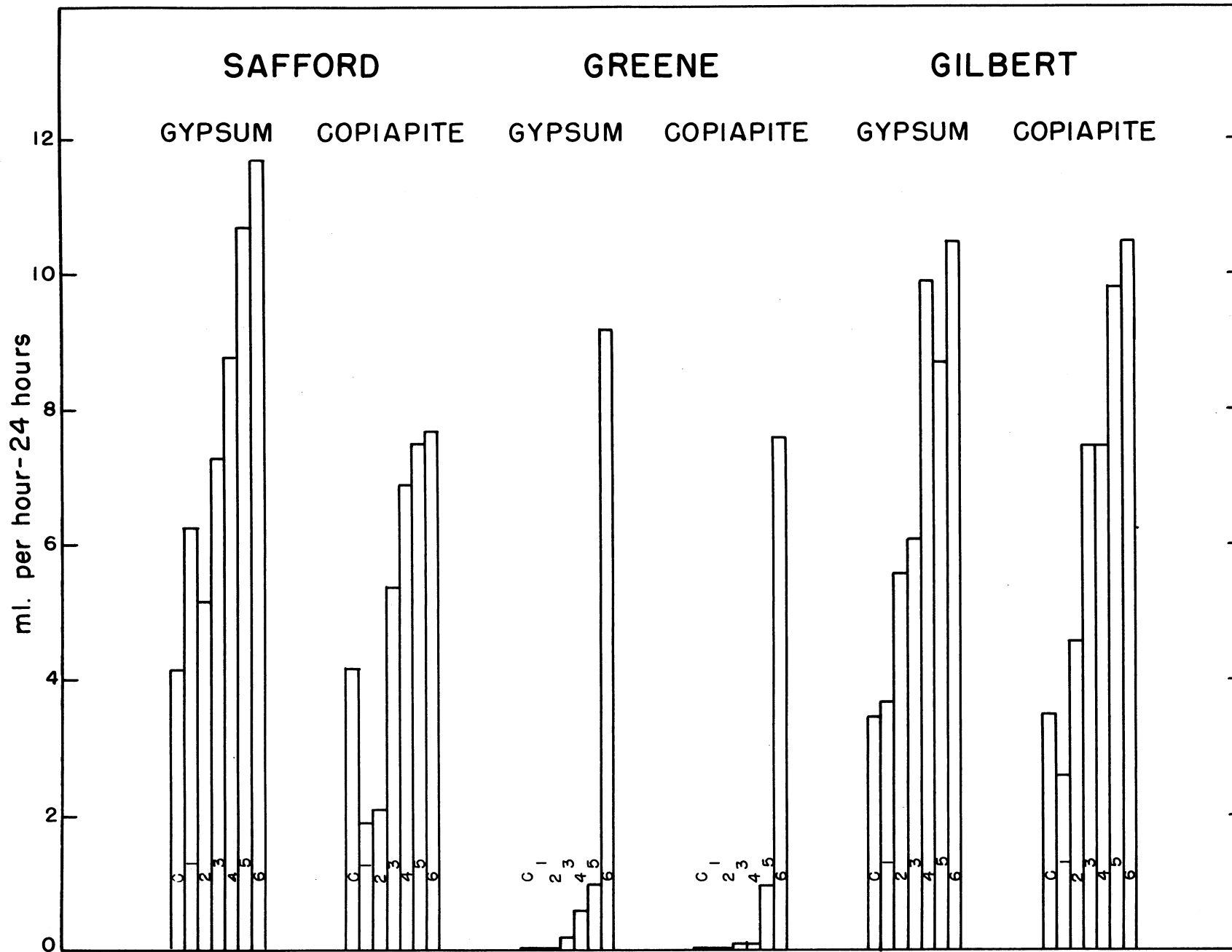
Figure 4.   Infiltration rate for Safford, Gilbert, and Greene soils treated with gypsum and copiapite, Experiment 5. Treatments are designated as C, control; 1, 1 ton; 2, 2.5 tons; 3, 5 tons; 4, 7.5 tons; 5, 10 tons; 6, 15 tons per acre foot of soil.
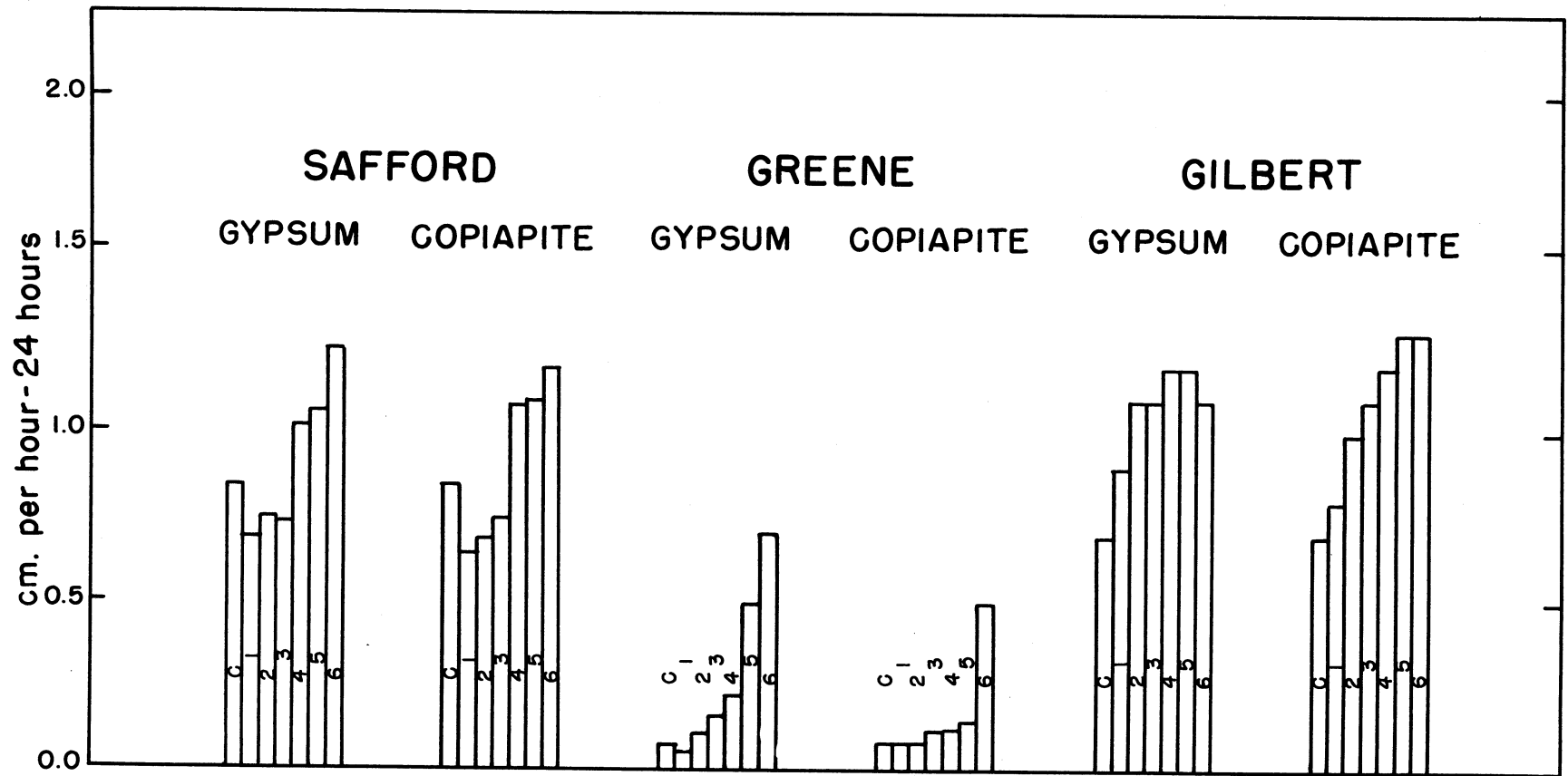
Figure 5.   Capillary rise for Safford, Gilbert, and Greene soils after treatment with gypsum and copiapite, Experiment 5. Treatments are designated as C, control; 1, 1 ton; 2, 2.5 tons; 3, 5 tons; 4, 7.5 tons; 5, 10 tons; 6, 15 tons per acre foot of soil.