THESIS

on

Some Chemical and Physical Properties of Dry Lime-Sulfur.

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11

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Some Chemical and Physical Properties of Dry Lime-Sulfur.

Within the last ten or fifteen years there has been placed on the market a powdered substitute for liquid lime-sulfur termed dry lime-sulfur or calcium-sulfur. The meaning of the term dry lime-sulfur is self explanatory. A number of patents have been issued covering methods of preparation of dry lime-sulfur, the method most used being the evaporation of liquid lime-sulfur to dryness under reduced pressure after adding a stabilizing material to the solution to lessen decomposition during evaporation. This stabilizer is generally sugar.

Dry lime-sulfur is claimed to be as effective in the control of insect pests and fungous diseases as is liquid lime-sulfur, and, in addition, to be more convenient to handle and more economical to transport since about 70 percent of the weight has been removed as water in the drying process. The claims of the manufacturers in regard to convenience of handling and economy of transportation have never been questioned, but there is considerable diversity of opinion as to the value of dry lime-sulfur as an insecticide whensubstituted for liquid lime-sulfur. Abbott and others (1) have disagreed as to effectiveness especially when used for control of San Jose scale.

Very little information of a chemical nature concerning dry lime-sulfur is available but such analyses as have been reported indicate some definite differences between dry and liquid lime-sulfur. To some of these variations in chemical composition is attributed the difference in control obtained in the use of the two materials.

The present work was undertaken to obtain more data on the chemical and physical properties of dry lime-sulfur with the idea of making practical application of the information obtained.

As a matter of convenience, the work has been divided into three parts: (1) a study of accepted analytical methods and means of preserving samples; (2) a study of factors influencing the composition of solutions of dry lime-sulfur; and (3) a study of oxidation rates of liquid lime-sulfur and solutions of dry lime-sulfur.

Material Used.

For the majority of the work reported here, two samples of dry lime-sulfur were used; one was Sherwin-Williams dry lime-sulfur and the other was Hemingway's dry lime-sulfur. Both samples were obtained in the original sealed tin containers. For a comparison of methods of solution, a sample of unknown brand obtained from the Insecticide Division of the Bureau of Chemistry and Soils was used.

I. Analytical Methods and Methods of Preserving the Solution.

Analytical Methods.

The compounds present in liquid lime-sulfur are calcium polysulfides, calcium thiosulfate, calcium sulfate and traces

of hydrolysis or oxidation products. Dry lime-sulfur contains the same compounds and, in addition, considerable insoluble matter consisting principally of free sulfur.

Two methods of analysis (2) for lime-sulfur solutions are in general use. These are the zinc chloride method and the iodine method.

There has been considerable discussion as to the relative merits of these methods (3) (4). In general the conclusions are that, although requiring more time, the zinc chloride method is less subject to error; on the other hand, the iodine method is rapid and the results are generally within experimental error of those obtained by the zinc chloride method. The determination of sulfide sulfur by the iodine method is difficult.

Both methods are applicable to solutions of dry limesulfur; in this work the zinc chloride method as modified by Gray and associates (5) has been used except where otherwise noted. Distilled water, recently boiled and cooled, was used for all solutions.

Where the term sulfide sulfur is used, it refers to all sulfur combined as sulfides or polysulfides. Where the term monosulfide: sulfide ratio is used it means the ratio of sulfur as calculated from the monosulfide equivalent to the total sulfur combined as sulfide or polysulfide. It can also indicate the molecular ratio of calcium to sulfur in the calcium polysulfides.

Preservation of Lime-Sulfur Solutions.

Because of the instability of lime-sulfur solutions, directions for preserving samples call for filling the container so full that insertion of the stopper displaces all air above the liquid. This necessitates the use of a large number of flasks if samples of a solution are to be used over a considerable period since after one sample is removed, the air admitted to the flask will result in partial oxidation of the remaining solution which must then be discarded.

In an effort to simplify the work involved in the preservation of samples, the following experiments were carried out: three 500 c.c. flasks were half filled with a solution of the dry lime-sulfur obtained by occasionally shaking 10 grams of dry lime-sulfur in a liter of distilled water for a day. Flask No. 1 was stoppered, flask No. 2 was stoppered after adding 50 c.c. of paraffin oil, and flask No. 3 was stoppered after adding 50 c.c. of petroleum ether. Samples were taken immediately, at irregular intervals for a week, and again after forty days for sulfide sulfur determinations. Flask No. 4 was partially filled with a solution obtained by shaking 72 grams of dry lime-sulfur with a liter of distilled water. After sampling, the air over the solution was displaced by hydrogen from a cylinder, then stoppered and paraffined. This solution was analyzed for sulfide sulfur after twelve days, but in the interim the flask had been opened

three times for sampling in connection with other work and each time the air was displaced by hydrogen and the stopper immediately reparaffined.

The amounts of sulfide sulfur remaining in solution at the various times of sampling are shown in Table 1, 100 being taken as the value at the time of the first sampling.

Table 1. Effectiveness of Preservative.

| time | check | paraffin oil | petroleum ether | hydrogen | |
|-------------|-------------------|-------------------|--------------------|----------|--|
| immediately | 100 | 100 | 100 | 100 | |
| 1 day | (95.75) 90.25* | (98.20) 96.50* | (94.00) 87.20* | - | |
| 2 days | 91.75 | 96.40 | 89.15 | | |
| 4 days | 85.20 | 93.80 | 81.45 | - | |
| 7 days | 75.95 | 90.80 | 70.35 | - | |
| 12 days | | • | - | 100 | |
| 40 days | 0.00 | 50.25 | 5.15 | ••• | |

* Imperfect oxidation of sulfide sulfur caused low results. The values in parenthesis are interpolated from a curve plotted from the other values.

It is interesting to note that the sample preserved under petroleum ether decomposed more rapidly than the check solution. Evaporation of a portion of the petroleum ether covering the solution yielded a considerable amount of petroleum ether soluble sulfur. Tartar and Bradley (6) have indicated that a portion of the polysulfide sulfur is in a very weak combination. The solvent action of the petroleum ether no doubt accounts, in part, for the figures indicative of breakdown of polysulfide sulfur under petroleum ether. A covering of paraf-

fin oil was fairly effective in preventing breakdown of polysulfide sulfur for a few days. From the final analysis, however, one would conclude that it is far from a perfect protective agent. Hydrogen gas gave 100 percent protection over the time indicated. Where samples were kept for any length of time for subsequent work, this method of preservation was employed with perfect satisfaction.

II. Factors Which Affect the Composition of Solutions of Dry Lime-Sulfur.

Methods of Solution.

The influence of the manner of dissolving the dry limesulfur on the composition of the resulting solution was next considered. Gray (5)- Method 1- dissolves dry lime-sulfur by placing 2.5 grams in a 250 c.c. volumetric flask, making to the mark with water and shaking intermittently for three hours. This method of solution allows the dissolved polysulfide to react for some time with the free sulfur present in the sludge to produce a higher polysulfide (7). The method used by W.J.Morgan- Method 2- of the Insecticide and Fungicide Laboratory of the Bureau of Chemistry and Soils involves placing the sample in a beaker, addition of 30-40 c.c. of water, stirring and decantation of the supernatent liquid on a filter, with repetition of the operation until the proper volume is obtained. This method of solution prevents any prolonged action of the polysulfides on the free sulfur of the sludge and should yield a solution of less polysulfide content and one having a lower monosulfide: sulfide ratio.

These two methods were compared at 25°C. and 30°C. using the sample obtained from the Insecticide and Fungicide Laboratory. By Method 1, duplicate samples of 2.5 grams of dry lime-sulfur were made to 250 c.c. with distilled water of the proper temperature and immersed in a constant temperature bath which maintained the desired temperature within ± .2°C. The flasks were agitated occasionally over a 20 hour period; their contents were then filtered and aliquots taken immediately for analysis. By Method 2, duplicate solutions were prepared according to the outline above using 2.5 gram samples and distilled water of the proper temperature. The filtrates were each made to 250 c.c. volume and aliquots taken at once for analysis. Table II presents the data from these analyses.

Table II

Effect of Method of Solution on Composition of Solution of Dry Lime-Sulfur

| method | temp. | % sludge | | % mono- sulfide sulfur | % sulfide sulfur | monosulfide: sulfide ratio |
|--------|-------|----------|------|------------------------------|------------------|----------------------------------|
| I | 25°C. | 8.98 | 4.74 | 12.06 | 51.12 | 1: 4.23 |
| II | 25°C. | 13.46 | 4.10 | 12.00 | 47.44 | 1: 3.95 |
| I | 30°C. | 7.35 | 5.38 | 12.07 | 52.44 | 1: 4.35 |
| II | 30°C. | 12.23 | 4.73 | 11.90 | 47.84 | 1: 4.02 |

As was anticipated, solution by Method 1 gave a higher content of polysulfide sulfur, a lower residue of sludge,

and a higher ratio of sulfide to monosulfide sulfur. Although Method 2 probably gives a solution more nearly representative of the actual composition of the dry lime-sulfur, it is thought that the solution obtained by Method 1 approximates more closely that produced in the spray tank and hence is of greater practical significance. Method 1 was used in preparing all solutions required in the remainder of this study.

Effect of Time on the Solubility of Dry Lime-Sulfur.

For this work Sherwin-Williams dry lime-sulfur was used. Eight 2.5 gram samples were placed in 250 c.c. volumetric flasks; after making to mark with distilled water they were immersed in a constant temperature bath at 20°C. ± .2°C. and frequently agitated during the day time. At the end of each 24 hour period two flasks were removed, the solution filtered and aliquots taken immediately from each duplicate solution for analysis. The results are presented in Table III.

Table III

Effect of Time on Solubility of Dry Lime-Sulfur

| | | | | - | |
|---------|---------|------------------------------|------------------------------|------------------------|----------------------------------|
| time | %sludge | % thio- sulfate sulfur | % mono- sulfide sulfur | % sulfide sulfur | monosulfide: sulfide ratio |
| 24 hrs. | 14.34 | 2.51 | 11.68 | 44.88 | 1: 3.84 |
| 48 hrs. | 13.61 | 2.60 | 11.40* | 45.36 | 1: 3.98 |
| 72 hrs. | . 12.41 | 2.78 | 11.76 | 45.88 | 1: 3.90 |
| 96 hrs. | 11.56 | 3.01 | 11.76 | 46.40 | 1: 3.95 |

^{*} Aliquots for monosulfide sulfur determination taken after 24 hours under paraffin oil. This low value makes a correspondingly high value for the monosulfide: sulfide ratio.

Increase in time has brought about the solution of more sludge (which in this dilution is practically all sulfur) and combined it to form more calcium thiosulfate and more calcium polysulfides having a higher proportion of sulfur to calcium.

Two explanations may be offered for the increase in thiosulfate. First, if the stoppers of the volumetric flasks were not air-tight a slight oxidation would result. Second, it is well known that thiosulfates in solution gradually decompose to form sulfites according to the reaction

$$CaS_2O_3 = CaSO_3 + S$$

Although calcium sulfite is highly insoluble, enough could be brought into solution at the dilution used, so that if titrated with standard iodine and calculated as calcium thiosulfate an apparent increase in thiosulfate would result. On the other hand such an explanation would disturb the approximate constancy of the sum of sludge (free sulfur), thiosulfate sulfur and sulfide sulfur. Analysis indicated only traces of sulfate sulfur in all solutions.

Effect of Temperature on the Solubility of Dry Lime-Sulfur

For this experiment both Sherwin-Williams and Hemingway dry lime-sulfur were used. Duplicate 2.5 gram samples in 250 c.c. volumetric flasks were made to the mark with distilled water and placed in a constant temperature bath for 48 hours at 20°C. , 25°C. , and $30^{\circ}\text{C.} \pm .2^{\circ}\text{C.}$ The flasks were frequently shaken during the day time. Similar duplicate solutions were

heated on a steam bath at about 95°C. for two hours. Longer heating resulted in partial decomposition with the formation of hydrogen sulfide and the separation of free sulfur and calcium sulfite. After filtration aliquots for analysis were taken at once. Table IV shows the composition of the solutions.

Table IV

Composition of Solutions of Dry Lime-Sulfur Obtained at Different Temperatures as Percent of Dry Material

| | | · . | | | | | | |
|-----------|------------------|---------|---------|---------|--------------|--|--|--|
| | | % thio- | % mono- | % | monosulfide: | | | |
| temp. | % sludge | sulfate | sulfide | sulfide | sulfide | | | |
| | | sulfur | sulfur | sulfur | ratio | | | |
| 1 4 4 | Sherwin-Williams | | | | | | | |
| 20°C. | 13.51 | 2.60 | 11.40* | 45.36 | 1: 3.98 | | | |
| 25°C. | 10.30 | 2.85 | 12.16 | 48.08 | 1: 3.95 | | | |
| 30°C. | 8.81 | 3.26 | 12.12 | 49.32 | 1: 4.03 | | | |
| 95°C. | 0.28 | 6.05 | 11.36 | 54.92 | 1: 4.83 | | | |
| Hemingway | | | | | | | | |
| 20°C. | 11.58 | 2.26 | 12.08* | 49.16 | 1: 4.07 | | | |
| 25°C. | 8.48 | 2.59 | 12.80 | 49.88 | 1: 3.90 | | | |
| 30°C. | 5.88 | 2.98 | 12.76 | 55.12 | 1: 4.32 | | | |
| 95°C. | 0.13 | 5.49 | 12.32 | 58.16 | 1: 4.72 | | | |

^{*}Aliquots for monosulfide sulfur determination taken after 24 hours under paraffin oil. This low value makes a correspondingly high value for the monosulfide: sulfide ratio.

While the effect of temperature is similar to the effect of time on the solution of dry lime-sulfur, the differences are much more pronounced. With one exception (Hemingway at 25°C.) the value for the sum of sludge, thiosulfate sulfur

and sulfide sulfur is quite constant for each brand regardless of temperature. This indicates that, as the sludge dissolves, a corresponding amount of polysulfide and thiosulfate is formed. It is also important to note that near the boiling temperature practically all sludge is dissolved and the monosulfide: sulfide ratio shows that the resulting solution has about the same proportion of tetrasulfide (CaS₄) and pentasulfide (CaS₅) as a good liquid lime-sulfur, although the content of thiosulfate is considerably higher than contained in the latter. In interpretation of these results, it should be borne in mind that the data were obtained on dilute solutions of a strength ordinarily used for analysis.

Effect of Concentration on Composition of Solutions of Dry Lime-Sulfur.

To determine the relationship between concentration and the composition of solutions of dry lime-sulfur, solutions were prepared containing 2.5 grams, 5 grams, 10 grams, and 15 grams of Sherwin-Williams dry lime-sulfur made to the mark in 250 c.c. volumetric flasks with distilled water and shaken intermittently for three hours at room temperature. A fifth solution was prepared by heating 15 grams in 250 c.c. volume on a steam bath for 45 minutes. Upon filtering, aliquots were immediately taken for analysis. The resulting data are presented in Table V.

In the higher concentrations at ordinary temperatures, it is obvious that a considerable amount of the insoluble

Effect of Concentration on Composition of Solutions of Dry Lime-Sulfur as Percent of Dry Material Dissolved

| temp. | grams per 100 co | % sludge | % sludge sulfur | %thio- sulfate sulfur | | % sulfide sulfur | mono- sulfide: sulfide ratio |
|--------------|------------------------|-------------|-----------------------|-----------------------------|-------|------------------------|---------------------------------------|
| room | 1 | 15.12 | 15.04 | 3.85 | 11.44 | 43.20 | 1: 3.77 |
| room | 2 | 15.90 | 14.30 | 3. 65 | 11.20 | 44.70 | 1: 3.99 |
| room | 4 | 19.71 | 13.75 | 2.40 | 10.37 | 44.10 | 1: 4.25 |
| room | 6 | 23.75 | 14.15 | 2.54 | 9.70 | 42.80 | 1: 4.42 |
| 95 °C | 6 | 0.18 | 0.07 | 5.12 | 12.18 | 53.97 | 1: 4.42 |

material is not free sulfur. In the sludge from the flask containing 6 grams of dry lime-sulfur per 100 c.c. some undissolved polysulfide was present as shown by the color of the residue and from the yellow solution which resulted from treatment of the dried residue with water. After washing the sludge thoroughly to remove this polysulfide, the dried residue was found to contain about 70 percent of free sulfur and the remainder was composed of calcium thiosulfate and calcium sulfite. The sludge from the more dilute solutions was higher in sulfur and probably the balance is mostly calcium sulfite since the thiosulfate is the more soluble of the two compounds. The percentage of calcium polysulfides dissolved is less in the more concentrated solution but the proportion of the tetrasulfide (CaS₄) and pentasulfide (CaS₅) is higher.

The solution of six to seven grams of dry lime-sulfur in

100 c.c. of water gives a solution comparable in concentration to that used as a dormant spray. The above observations and the data from Table V would lead to the inference that considerable polysulfide as well as other active ingredients remain undissolved when mixed in the spray tank since the spray is generally applied as soon as mixed. The application of such a suspension might not be as effective as the solution of a like amount for the control of plant pests.

It is quite evident both from this table and the preceding one that temperature is a very important factor in bringing about complete solution of dry lime-sulfur.

III. Comparison of Oxidation Rates of Liquid Lime-Sulfur and Solutions of Dry Lime-Sulfur.

Shafer (8) was one of the first investigators to suggest that the insecticidal value of lime-sulfur is largely due to its power to absorb oxygen. Consequently it was thought that a study of the rates of oxidation of liquid lime-sulfur and solutions of dry lime-sulfur might give some information by which to judge the relative insecticidal worth of the two materials.

Since calcium thiosulfate oxidizes very slowly in comparison with the polysulfides, solutions for this study were made up to contain equivalent amounts of calcium polysulfide by weight regardless of which-trisulfide (CaS₅), tetrasulfide (CaS₄) or pentasulfide (CaS₅) - predominated in the solution. Any difference in behavior of oxidation due to differ-

ences in the type of polysulfide present in liquid limesulfur and solutions of dry lime-sulfur could then be noted.

The oxidation reactions of the various polysulfides are represented by the equations

$$CaS_5 + 3 O = CaS_2O_5 + 3 S$$

 $CaS_4 + 3 O = CaS_2O_5 + 2 S$
 $CaS_5 + 3 O = CaS_2O_5 + S$

From these equations it is calculated that one gram of CaS₅, one gram of CaS₄ and one gram of CaS₅ require .24 gram, .29 gram and .35 gram of oxygen respectively for the primary oxidation reaction. It follows that if equal weights of the various polysulfides are oxidized in the same length of time, then the rate of oxygen absorption is greatest for the compound of lowest sulfur content; conversely, if the rate of oxygen absorption is constant then the time required for equal weights of the polysulfides will be greatest for the compound having the lowest sulfur content.

Three methods of measuring the oxidation of the solutions were tried. Two methods proved unsatisfactory and will only be mentioned here. In the first method Petri dishes of equal area were partly filled with the solution and after a definite interval the solution was filtered and the deposited sulfur weighed. It was found that after a surface film formed the oxidation was very slow and the amounts of sulfur deposited were small and identical for both liquid limesulfur and solutions of dry lime-sulfur for a one hour

observation period. The second method consisted in the aspiration of a definite volume of air in a definite length of time through a definite volume of solution contained in a Nessler tube, with subsequent filtration and weighing of the precipitated sulfur. In no case was a precipitate of sulfur obtained in one hour of aspiration except in three very dilute solutions of liquid lime-sulfur. In concentrations such as are used for dormant spray no deposit resulted and so the method was discarded.

The third method will be described in more detail since the data to be presented were obtained by its use. Two Erlenmeyer flasks having an actual capacity of 1150 c.c. were fitted with a two-hole rubber stopper in each. One hole of the stopper carried a glass manometer tube of about 2.5 millimeters internal diameter and having each leg about 20 centimeters long. The bottom U bend was filled to a height of 8-10 centimeters with mercury. The other hole of the stopper was plugged with a short piece of glass rod of a diameter to fit tightly. A lead collar weighing about two kilograms was placed around the neck of each flask and the whole immersed in a constant temperature bath to a depth such that the water level was about one centimeter from the top of the flask.

A piece of filter paper, 6.25 centimeters wide by 100 centimeters long was folded in a manner best described by the dressmaker's term of accordion pleating. This folded

paper was placed in the flask and arranged in a more or less spiral shape on the bottom of the flask with the aid of a glass rod. A paper of this size has 1250 square centimeters surface area (both sides) and will completely absorb 10 c.c. of liquid. This furnished a lime-sulfur film which might be expected to oxidize in a manner similar to that occuring when lime-sulfur is sprayed on trees. After the atmosphere in the flask had reached the temperature of the bath, the stopper was removed from the flask and the glass plug was removed from the stopper. The sample of lime-sulfur solution was distributed over the paper as evenly as possible by means of a pipette, the stopper inserted firmly in the flask and the plug placed in the stopper. In this way insertion of the stopper did not cause a compression of the atmosphere in the flask. The stopper and the plug were paraffined as it was found that the partial vacuum created in the flask by the oxygen absorption caused leakage otherwise. With this set-up, measurement of the difference in mercury level in the manometer was made at two or three minute intervals in the early stages of oxygen absorption; as the absorption rate decreased the time intervals between measurements were made longer. It is essential that the transfer of the sample and the stoppering of the flask be performed rapidly; it can be done in one minute or less if the apparatus is conveniently arranged. The oxygen in 1150 c.c. of air is sufficient to complete the primary oxidation of about .85 gram of CaS,

1.05 grams of CaS4 or 1.25 grams of CaS5.

For dormant application, liquid lime-sulfur is diluted sufficiently to contain about 4 percent of calcium polysulfides. The first solution used in the oxidation work contained 3.90 percent of calcium polysulfides and all other solutions, after analysis, were diluted to contain the same concentration, except that used for the data presented in Figure 1.

All oxidations were run in duplicate and to insure against inclusion of any oxidized material a clean pipette was used for each duplicate. Duplicates were found to agree very closely in practically all cases; the few which showed disagreement were repeated. Both liquid lime-sulfur and solutions of dry lime-sulfur were investigated. Oxidations were run before and after the addition of some of the dried sludge previously mentioned. All curves were plotted with time in minutes as abscissa and length of mercury column in millimeters as ordinate.

The curves of Figure 1 represent the oxidation data of a liquid lime-sulfur in concentrations of 2 percent, 4 percent and 6 percent of calcium polysulfide.

The curves show, as one might predict they would, that the amount of oxygen required is approximately proportional to the polysulfide content of the solutions. They also show that the time required for complete oxidation is approximately proportional to the concentration of the calcium

polysulfides. Near the end of the oxidation, decrease in oxygen concentration is responsible for the slight deviation from the proportion just mentioned. In the presence of a constant oxygen concentration, as on a sprayed tree, the break in the curve would be sharp and more of the shape of that representing the two percent solution of polysulfide.

Figure 2 is a comparison of the oxidation rates of a liquid lime-sulfur with and without the addition of .15 gram of sludge to 10 c.c. of solution. The sludge was added to the solution and well shaken in an atmosphere of hydrogen before withdrawing the samples. Apparently sludge did not materially affect the rate of oxidation although the total oxygen absorbed was slightly higher in the samples to which sludge was added. Possibly that was due to the presence of so much thiosulfate and sulfite in the sludge.

The data for Figure 3 were obtained from a solution prepared by shaking at intervals for three hours 18 grams of Sherwin-Williams dry lime-sulfur in 250 c.c. volume at room temperature. The solution used for the data in Figure 4 was prepared by heating 15 grams of Sherwin-Williams dry lime-sulfur in 250 c.c. volume on a water bath for 45 minutes. The difference in the monosulfide: sulfide ratio of the two solutions indicates a difference in the type of polysulfides present, but the curves are practically identical with the exception of the slight rise near the end of the oxidation in those samples to which sludge was added.

A careful consideration of Figures 2, 3 and 4 fails to provide any basis for the assumption that there is any difference in the oxidation rates of liquid lime-sulfur and solutions of dry lime-sulfur of the same calcium polysulfide concentration. The presence of sludge has a very slight if any effect on the oxidation rate of such solutions.

Summary

- 1. Lime-sulfur solutions can be preserved without change in composition in tightly stoppered flasks if the space above the liquid is filled with hydrogen.
- 2. A layer of paraffin oil on the surface of the solution delays decomposition materially but is far from satis-factory as a preventive of oxidation reactions.
- 3. Solutions of dry lime-sulfur prepared by shaking the powder in water contain more polysulfides than do those prepared by leaching the dry material with water.
- 4. For a given temperature, the longer the contact of dry lime-sulfur with water the greater is the polysulfide content of the resulting solution and the less is the residue of sludge. The thiosulfate content and the ratio sulfur to calcium in polysulfides are slightly increased with time.
- 5. Increase in temperature increases the solubility of dry lime-sulfur. It increases also the polysulfide and thiosulfate content of the resulting solution. The high-

est temperature employed (95°C) produced a solution the monosulfide: sulfide ratio of which approached that of a good liquid lime-sulfur.

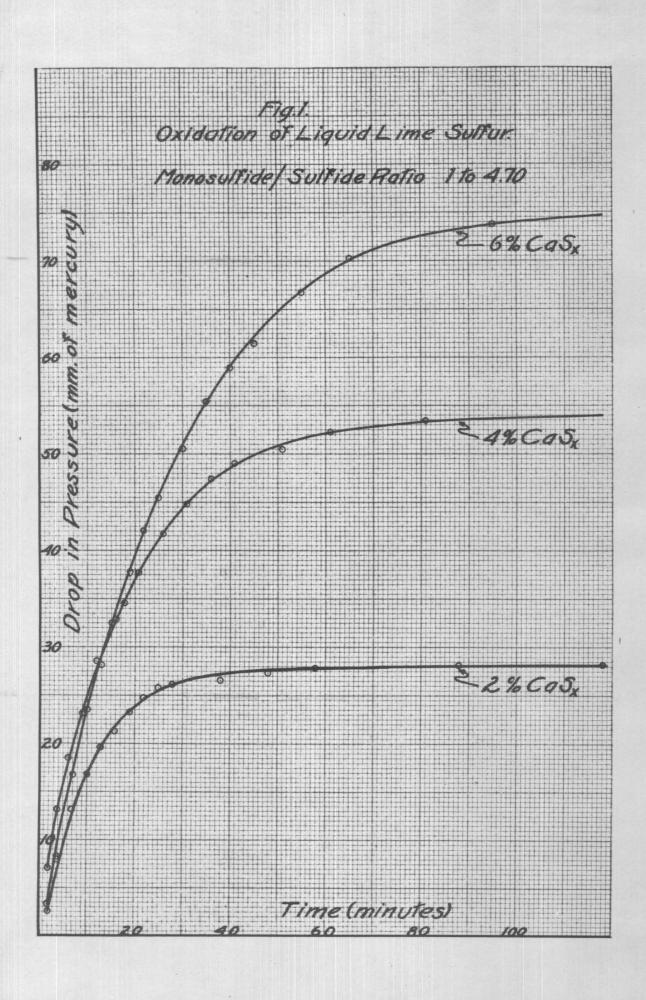
6. At room temperature, the greater the amount of dry lime-sulfur added to a volume of water the greater is the residue of sludge.

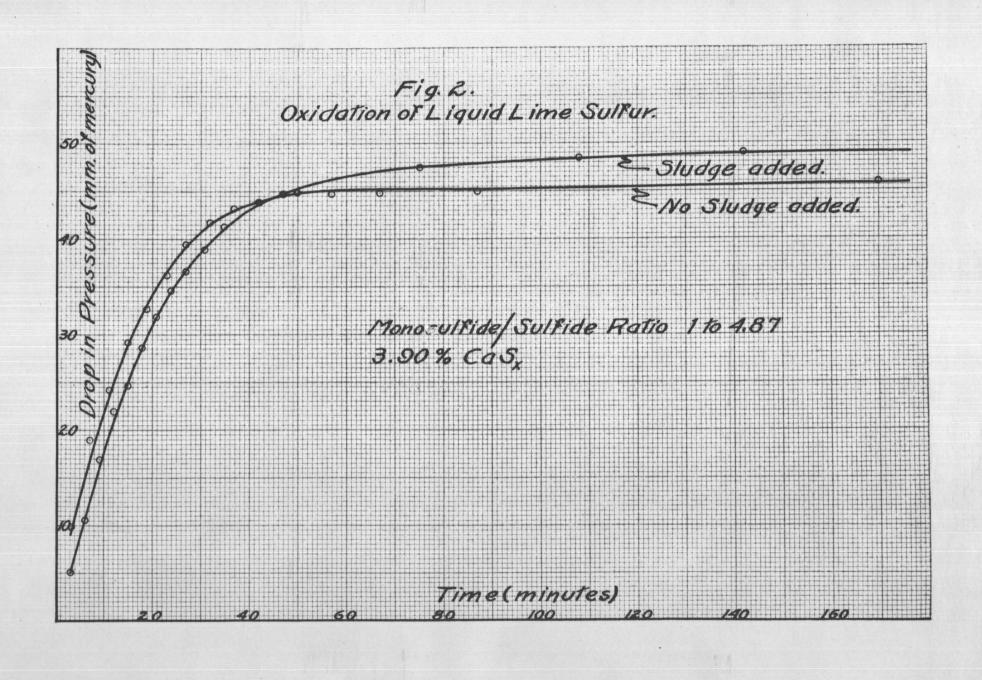
With increase in sludge comes a greater retention by it of calcium thiosulfate and calcium sulfite, as well as some calcium polysulfide.

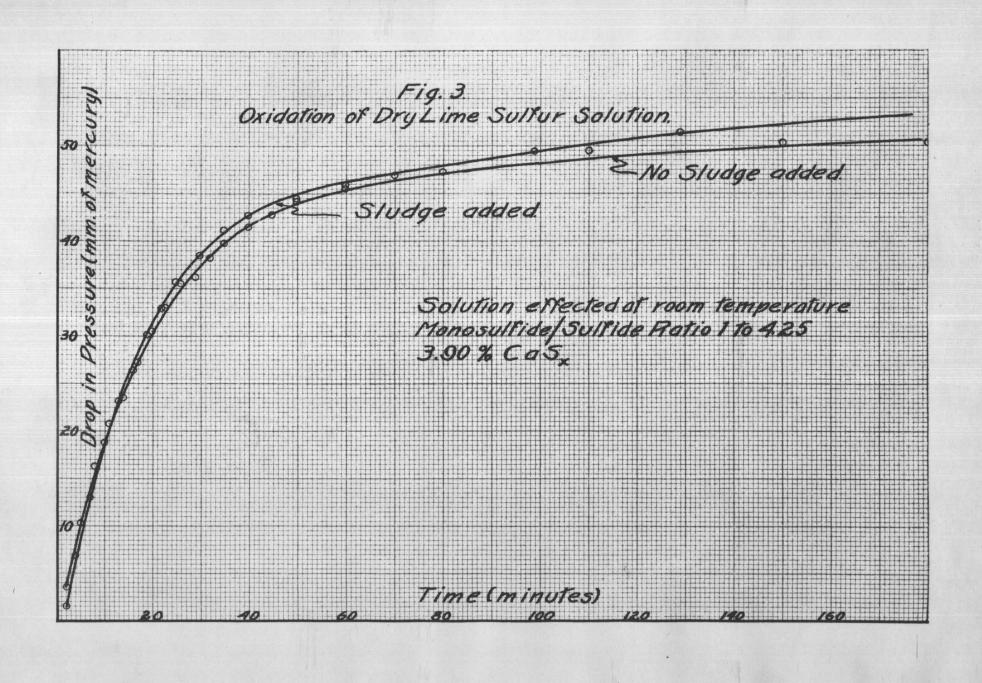
The greater the amount of dry lime-sulfur added to a definite volume of water the smaller is the proportion of thiosulfate and polysulfides that can be recovered in the resulting solution.

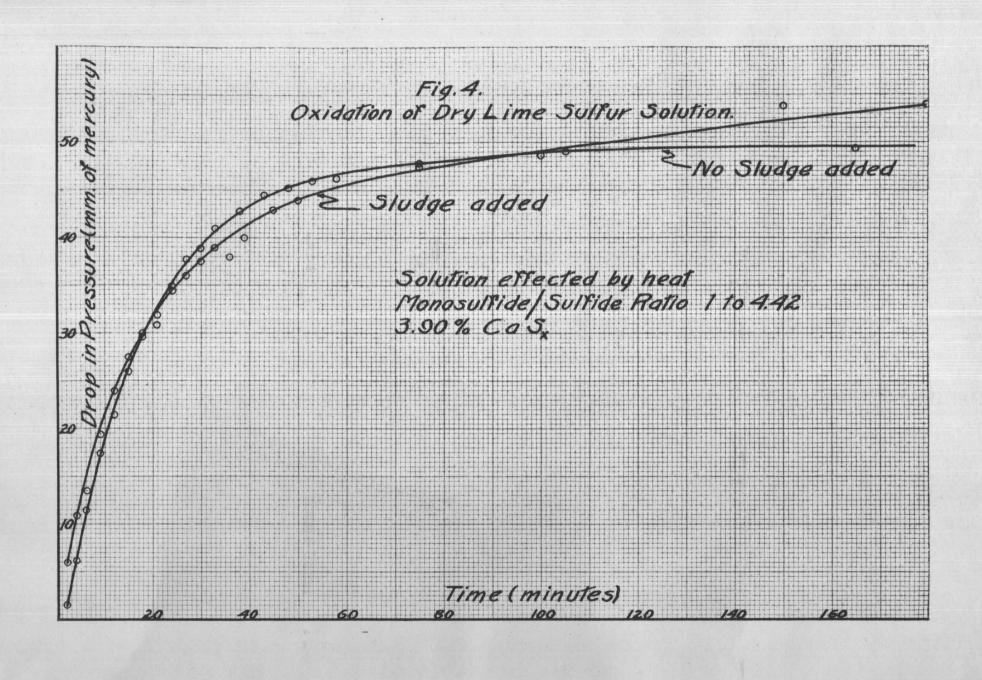
The ratio of sulfur to calcium combined as polysulfide increases with increased concentration of dry lime-sulfur in water.

- 7. Dry lime-sulfur in the concentrations studied, is practically completely soluble in water if heat is applied.
- 8. The rate of oxidation of liquid lime-sulfur and dry lime-sulfur solutions is the same at equal concentrations of calcium polysulfide. Sludge does not materially affect the rate of oxidation.









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