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CHEMICAL INVESTIGATION OF BEST CONDITIONS FOR MAKING THE LIME-SULPHUR WASH.

L. L. VAN SLYKE, A. W. BOSWORTH AND C. C. HEDGES.

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BULLETIN No. 329.

CHEMICAL INVESTIGATION OF BEST CONDITIONS FOR MAKING THE LIME SULPHUR WASH.

L. L. VAN SLYKE, A. W. BOSWORTH AND C. C. HEDGES.

SUMMARY.

1. Object.—The work described in this bulletin is a continuation of work published in Bulletin No. 319 and has had for its general object a study of conditions that enable one to utilize the lime and sulphur most completely and with largest formation of the compound containing most sulphur, calcium pentasulphide (CaS_5).

2. Effect of varying proportions of lime and sulphur.— In several experiments, we used 35.7 pounds of lime and 50 gallons of water, while the amount of sulphur varied from 35.7 to 107 pounds, or in the ratio of one to three times the amount of lime used. The ratio of lime and sulphur to water varied from 1:2.9 to 1:5.8.

(a) Sediment.—The amount of sediment varied from 2 to 35 pounds or from 1.8 to 35 per ct. of the lime and sulphur used. The largest amount occurs when the excess of sulphur is greatest in proportion to lime (3:1). The sediment is least when the ratio of lime to sulphur is about 1:2 and this increases when the ratio of lime to sulphur increases.

(b) Sulphur in solution.—The proportion of sulphur used that goes into solution is least when the proportion of sulphur is greatest (3 of sulphur to 1 of lime) and increases as the proportion of sulphur to lime decreases, until practically all of the sulphur is changed into soluble compounds when the amount of sulphur used is not more than 2.25 times the amount of lime used.

(c) Sulphides.—The largest amount of sulphur appears as sulphides of calcium (CaS_4 and CaS_5) when the ratio of sulphur to lime is between 2.25:1 and 2:1. When more lime is used than 1:2 of sulphur, the amount of sulphide sulphur decreases.

(d) Thiosulphate.— Largest amounts of thiosulphate sulphur are formed when lime is used in largest amounts in proportion to sulphur.

(e) Lime.—The proportion of lime used that goes into solution is greatest (96 to 100 per ct.) when the proportion of sulphur is 2 or more times that of lime. When sulphur and lime are used in equal amounts, only 50 per ct. of the lime goes into solution.

(f) Ratio of lime and sulphur in solution.— However large an amount of sulphur is used in relation to lime, the amount appearing in solution is limited and is usually about 2 to 2.2 parts for 1 part of lime. When sulphur is used in excess of these amounts, it goes unchanged into sediment.

(g) Formation of different sulphides.—When sulphur is used in largest proportions to lime, larger amounts of pentasulphide (CaS_5) are formed. When less sulphur is used than 2.25 parts for 1 part of lime, less pentasulphide and more tetrasulphide (CaS_4) are formed.

3. Effect of varying proportions of water.— In another set of experiments, we used 50 pounds of lime and 100 pounds of sulphur but varied the water from 70 down to 30 gallons, so that the ratio of lime and sulphur to water varied from 1:3.9 to 1:1.7.

(a) Sediment.—The amount of sediment is least when we use most water in proportion to lime and sulphur.

(b) Sulphur in solution.—The percentage of sulphur used, going into solution, varies from 85 to 99.7, the largest percentages occurring when the largest proportion of water is used and decreasing as the proportion of water decreases.

(c) Sulphide sulphur.— The proportion of sulphur appearing in solution as sulphides does not vary widely whether we use more or less water.

(d) Thiosulphate.—The proportion of thiosulphate found decreases with the proportion of water used, owing to conversion of thiosulphate into insoluble sulphite.

(e) Lime.—The proportion of lime going into solution is greatest (99.7 per ct.) when the proportion of water is greatest, and least (68.8 per ct.) when least water is used.

(f) Formation of different sulphides.— Under the conditions of the experiments, larger amounts of pentasulphide (CaS_5) are formed when the ratio of water to lime and sulphur is less than 3:1.

4. Additional experiments.—A set of experiments was made in which we used 2.25 parts of sulphur for 1 part of lime and varying proportions of water. When we use 35.7 pounds of lime, 80.3 pounds of sulphur and 50 gallons of water, we obtain, all things considered, the most satisfactory results. The proportion of sediment is small; the percentages of sulphur and lime going into solution are large; the percentage of sulphur used that appears as sulphides is large; and the sulphide sulphur is practically all in the concentrated form of pentasulphide.

5. Effect of concentration of lime-sulphur solutions by boiling. — In concentrating a solution from 50 down to 20 gallons, the chief chemical change occurring is the conversion of thiosulphate into sulphite and free sulphur, in one case 81 per ct. of the thiosulphate being thus changed. Concentrated commercial lime-sulphur solutions contain small amounts of thiosulphate, probably as a result of concentration by boiling.

6. Some of the chemical changes in making lime-sulphur solutions.— Ordinarily, about 17 to 20 per ct. of the sulphur used goes to form thiosulphate, and this is changed, to a greater or less extent, into sulphite, the extent of the latter change depending upon length of boiling and concentration of solution. One part of calcium combines with about 2.25 pounds of sulphur to form soluble compounds. When sulphur is used in excess of these proportions, the surplus goes unchanged into the sediment as free sulphur. When sulphur is used in smaller propor-

tions than 2 to 1 of lime, not enough sulphur is present to combine with the lime and the unused lime appears in the sediment.

7. Conditions favorable to formation of sediment are (a) conditions favoring formation of sulphite; (b) impurities in lime or sulphur; (c) lime used in excess; (d) sulphur used in excess.

8. Efficiency of lime-sulphur solutions in relation to chemical composition.—The effectiveness as a spraying solution stands in a close and direct relation to the amount of sulphide compounds contained in solution, whether these compounds act directly or simply decompose into other compounds that produce the desired results.

9. Keeping-power of solution—A lime-sulphur solution which had been kept in a stoppered bottle was examined when one month old and found to have undergone no appreciable change.

10. Analysis of crystals.— In a barrel of concentrated lime-sulphur solution, large crystals were formed, which, on analysis, were found to consist of a mixture of about equal parts of tetra-sulphide and pentasulphide.

11. Relation of density of solution to percentage of sulphur as a basis for dilution.—An examination of many lime-sulphur solutions, varying widely in density, shows a generally lower percentage of sulphur in relation to density, measured in degress, Beaumé, when the density is lower. The data are used in preparing a table of values varying with density, from which dilutions can be made for different uses of lime-sulphur solution, so that one gallon of diluted solution shall contain a certain number of ounces of sulphur. These dilutions applied to solutions of known composition indicate a greater degree of uniformity and accuracy than shown by other methods of dilution in practice.

12. Efficiency of different formulas used for lime-sulphur wash.—As a result of the investigation embodied in this bulletin, the following proportions are recommended for making lime-sulphur solutions: 36 pounds of lime (based on pure lime, CaO), 80 pounds of high-grade, finely-divided sulphur, and

50 gallons of water. When lime containing 95 per ct. or less than 95 per ct. of calcium oxide is used, more than 36 pounds must be taken, according to amount of impurities (38 pounds for 95 per ct. lime and 40 pounds for 90 per ct. lime), but no lime should be used containing less than 90 per ct. of calcium oxide or more than 5 per ct. of magnesium oxide. In boiling the solution, the liquid must not be allowed to drop more than slightly below the 50-gallon level.

13. Method for approximate determination of impurities in lime.—This test is based upon the fact that when one part of pure lime and two parts of sulphur are boiled with plenty of water for one hour, only slight amounts of sediment appear. If the lime contains impurities, these appear as sediment, the amount of sediment being an approximate measure of the amount of impurities.

INTRODUCTION.

In Bulletin No. 319 of this Station, we published the results of work done in 1909 relating to some of the conditions affecting the chemical composition of the so-called lime-sulphur wash. The work suggested several additional questions for investigation, which have been studied since and the results of our recent work are given in the following pages.

Among the points studied, the following are of chief interest and importance:

(1) Conditions under which it is possible to get the largest amount of lime and sulphur most completely into soluble combination.

(2) Conditions under which it is possible to produce a lime-sulphur solution containing the largest amount of calcium penta-sulphide (CaS_5).

(3) Effect of concentration of lime-sulphur solution by evaporation at boiling temperature.

(4) Some of the chemical changes occurring in the making of lime-sulphur solutions.

(5) Conditions favorable to the formation of sediment in lime-sulphur solutions.

(6) Efficiency of lime-sulphur solutions in relation to chemical composition.

(7) Keeping-power of lime-sulphur solutions on standing.

(8) Analysis of crystals formed in concentrated lime-sulphur solutions.

(9) Relation of density of solutions to percentage of sulphur as a basis for dilution.

(10) Efficiency of different formulas.

(11) Method for the approximate determination of impurities in commercial lime.

These subjects are discussed in a way to connect certain phases of practical application with the underlying chemical facts. Those who are interested in understanding the reasons for certain conclusions may find the entire bulletin useful. Those who care solely for the practical applications without an understanding of underlying principles will be interested chiefly in the last two or three topics.

COMPOUNDS OF CALCIUM AND SULPHUR.

Before taking up the details of our investigation, we will review briefly some fundamental facts relating to the chemistry of the lime-sulphur solution. When we heat a mixture of water, sulphur and lime (calcium oxide, CaO) or of slaked lime (calcium hydroxide, CaH_2O_2), the sulphur combines with the calcium (Ca) contained in the lime compound. As a matter of fact, when lime (calcium oxide) is used, it is converted into slaked lime (hydroxide) before chemical reaction occurs between the lime and sulphur. A definite amount of calcium can combine with varying amounts of sulphur so as to form, at least, five different compounds. Only two of these compounds are present in the freshly-prepared solution, the 4-sulphur compound or *calcium tetrasulphide* (CaS_4) and the 5-sulphur compound or *calcium pentasulphide* (CaS_5). Calcium pentasulphide contains 20 per ct. of calcium and 80 per ct. of sulphur, which is at the rate of 4 parts of sulphur by weight for 1 part of calcium. Calcium tetrasulphide contains 24 per ct. of calcium and 76 per ct. of sulphur, which is at the rate of 3.2 parts of sulphur by weight for 1 part of calcium.[1]

Calcium tetrasulphide and calcium pentasulphide are easily soluble in water, producing an orange-red liquid, which in concentrated condition is strongly caustic, injuring the skin and burning foliage.

In the chemical changes that take place between lime and sulphur when they are heated in water, another compound is unavoidably formed, but in smaller amounts; this is *calcium thiosulphate* (CaS_2O_3), which is easily soluble in water and is therefore contained in the solution along with the sulphides of calcium. Calcium thiosulphate on exposure to air is changed into *calcium sulphite* ($CaSO_3$) and sulphur. Calcium sulphite is insoluble in water and therefore appears in the sediment or the undissolved portion of lime-sulphur preparations, usually forming the chief part of the sediment. The free sulphur formed by decomposition of thiosulphate recombines with calcium and goes into solution in the operation of making lime-sulphur solutions when enough lime is present.

On exposure to air, even at ordinary temperatures, calcium pentasulphide and calcium tetrasulphide absorb oxygen and slowly change into calcium thiosulphate, with free sulphur which separate out as a fine deposit.

EXPERIMENTAL WORK.

In carrying out the necessary experiments, the proportions of lime, sulphur and water have been varied within limits suggested by our previous work. The lime used in the laboratory experiments was pure lime (CaO); the sulphur was high-grade flowers of sulphur in finely divided condition. The general method of conducting the individual experiments has been as follows: The

[1] Bulletin No. 319, pp. 387–389.

desired amounts of lime and sulphur and water were accurately weighed. The laboratory experiments were carried out on the basis of the use of one-half gallon of water. These were supplemented later by making the solution in 50-gallon quantities.

During the operation of boiling, hot water was added from time to time in amounts sufficient to keep the liquid at its original level, as indicated conveniently by the use of a marked stick. After actual boiling had continued one hour, the mixture was allowed to cool and then water was added in just the amount necessary to bring the weight up to that of the original mixture; it was found that the addition of water to a given weight is more accurate for experimental work than adding to a given level. The whole mixture was filtered after boiling and dilution, and the sediment was weighed. The filtered solution was used for analysis, the following determinations being made: (1) Specific gravity, (2) total sulphur, (3) sulphur as sulphides (CaS_4 and CaS_5), (4) sulphur as thiosulphate (CaS_2O_3) and (5) calcium (Ca) or lime (CaO).

EFFECT OF VARYING PROPORTIONS OF LIME AND SULPHUR.

We will first consider some illustrative cases in which different proportions of sulphur were used for a fixed amount of lime, the amount of water being the same. The results are presented and discussed below under the following headings: (1) Proportions of lime, sulphur and water used; amounts of solution and sediment. (2) Amounts of sulphur and lime in solution. (3) Percentage composition of solution.

Proportions of lime, sulphur and water; amounts of solution and sediment.— In each of the experiments presented in the three tables following, we used 35.7 pounds of lime and 50 gallons of water, while the amount of sulphur varied from 35.7 to 107 pounds, or in the ratio of one to three times the amount of lime used. Stated on the basis of 50 pounds of lime, the water used would be 70 gallons and the sulphur would vary from 50 to 150 pounds.

Since we used the same amount of water (50 gallons) in each experiment and the sum of the sulphur and lime varied, the ratio of the amount of water to the lime and sulphur used varied also; for each pound of lime and sulphur used, we had from 2.9 to 5.8 pounds of water. The detailed data covering these and other points are presented in Table I following. Experiments 3 and 4 are duplicates and serve to show variations possible in experiments made under approximately uniform conditions.

TABLE I.— AMOUNTS OF MATERIALS USED AND OF SEDIMENT FORMED.

No. of experiment	Pounds of materials used	Pounds of sulphur for one pound of lime	Water used	Total weight of lime, sulphur and water used	Pounds of water used for one pound of lime and sulphur	Weight of sediment	Percentage of lime and sulphur used, in sediment	Weight of solution
	Lime: Sulphur	*Lime: Sulphur*	*Gals.*	*Lbs.*	*Lime and sulphur: Water*	*Lbs.*	*Per ct.*	*Lbs.*
3	35.7—107.0	1 : 3.00	50	560	1 : 2.9	35.5	25.0	524.5
4	35.7—107.0	1 : 3.00	"	560	1 : 2.9	33.0	23.1	527.0
5	35.7— 80.3	1 : 2.25	"	533	1 : 3.6	7.0	6.0	526.0
6	35.7— 71.4	1 : 2.00	"	524	1 : 3.9	2.0	1.8	522.2
7	35.7— 53.6	1 : 1.50	"	506.3	1 : 4.7	9.7	10.9	496.6
8	35.7— 35.7	1 : 1.00	"	488.4	1 : 5.8	17.0	23.8	481.4

The point of special interest to be studied in connection with the data embodied in this table is the weight and percentage of sediment, since this factor represents the chief source of loss in the manufacture of the lime-sulphur solution. The sediment in these experiments varies from 2 to 35 pounds for the amount of solution made. A somewhat better basis of comparison is the percentage that the sediment forms of the total lime and sulphur used; on this basis, the variation is from 1.8 to 25 per ct. The largest amount and proportion of sediment occurs when the sulphur used is largest in proportion to lime. Thus, when we use three pounds of sulphur for one pound of lime, one-fourth of the material does not go into solution, as shown in experiment No. 3. The sediment is least when the amount of sulphur is twice the amount of lime, as shown in experiment No. 6. It is noticeable that the amount of sediment decreases as the amount of sulphur decreases, until the ratio of sulphur to lime drops below 2:1;

when the ratio drops to 1.5:1 (experiment No. 7) and to 1:1 (experiment No. 8), the sediment increases. The reason why the sediment varies in relation to the proportions of sulphur and lime used is discussed in connection with Table II. It may be stated that the sediment obtained was mostly in a state of fine division.

Amounts of sulphur and lime in solution made with 50 gallons of water.— In the table following, the amounts of sulphur in different compounds and of lime in solution are given. The sulphur is given in three forms: (1) Total sulphur in solution; (2) sulphur present in combination as sulphides (calcium tetrasulphide, CaS_4, and calcium pentasulphide, CaS_5); and (3) sulphur in the form of calcium thiosulphate (CaS_2O_3). The sum of the sulphide sulphur and of the thiosulphate sulphur equals the total amount of sulphur in solution.

The value of each constituent is given in two ways: (1) The number of pounds in the solution made with 50 gallons of water, and (2) the percentage of each constituent used that goes into solution. For example, in experiment No. 3, when we used 35.7 pounds of lime and 107 pounds of sulphur, we find 72 pounds of sulphur in solution, which is equal to 67.3 per ct. of the sulphur used; in sulphide form we have 54.7 pounds, which is 51.1 per ct. of the sulphur used; of lime in solution we have 34.3 pounds, which is 96.1 per ct. of the lime used.

Table II.— Amounts of Sulphur and Lime in Solution Made with Fifty Gallons of Water.

No of experiment	Ratio of lime and sulphur	Weight of total sulphur	Percentage of used sulphur in solution	Weight of sulphur as sulphides	Percentage of used sulphur in solution as sulphides	Weight of sulphur as thiosulphate	Percentage of used sulphur in solution as thiosulphate	Weight of lime	Percentage of used lime in solution	Pounds of sulphur for one pound of lime in solution
	Lime : Sulphur	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct.*	*Lime : Sulphur*
3.....	1 : 3.00	72.0	67.3	54.7	51.1	17.3	16.2	34.3	96.1	1 : 2.10
4.....	1 : 3.00	71.4	69.7	56.3	52.6	15.1	14.1	35.7	100.0	1 : 2.00
5...	1 : 2.25	77.1	96.0	63.2	78.7	13.9	17.3	34.8	97.5	1 : 2.22
6.....	1 : 2.00	71.2	99.7	57.6	80.7	13.6	19.0	35.6	99.7	1 : 2.00
7.....	1 : 1.50	53.6	100.0	41.1	76.6	12.5	23.4	27.0	75.7	1 : 2.00
8.....	1 : 1.00	33.8	94.6	24.1	67.5	9.7	27.1	17.8	50.0	1 : 1.90

In studying the data embodied in Table II, attention is called to the following facts of interest:

(1) Total sulphur in solution. The amount of total sulphur in the solution made with 50 gallons of water varies from 33.8 to 77.1 pounds. These figures do not give us any clear idea as to whether the results are satisfactory or not, except in connection with the amounts of sulphur used. We need to know the percentage of the sulphur used that goes into solution, in order to know whether or not the process is reasonably complete. In general, *the proportion of sulphur that goes into solution is least when the proportion of sulphur used is greatest (3 of sulphur to 1 of lime) and increases as the proportion of sulphur to lime decreases, until practically all of the sulphur is changed into soluble compounds, which occurs when the amount of sulphur used is not more than 2.25 times the amount of lime used.* When we use 3 pounds of sulphur for one pound of lime, as in experiments No. 3 and No. 4, not quite 70 per ct. of the sulphur goes into solution; on the other hand, nearly all (96 to nearly 100 per ct.) goes into solution when the amount of sulphur drops to 2.25 pounds or less for each pound of lime used, as shown in experiments 5, 6, 7 and 8.

(2) Sulphide sulphur. The proportion of sulphur used that goes to form calcium terta- and pentasulphide is least when the ratio of sulphur to lime is 3:1 (experiments No. 3 and No. 4) and greatest when the ratio is 2.25 or 2:1 (experiments No. 5 and No. 6); when sulphur and lime are used in a ratio of less than 2:1, the sulphide sulphur decreases (experiments No. 7 and No. 8).

(3) Thiosulphate sulphur. The proportion of sulphur used that forms thiosulphate increases as the proportion of sulphur to lime decreases. When most sulphur is used (3:1, experiments No. 3 and No. 4), about 15 per ct. of the sulphur forms thiosulphate; when equal parts of sulphur and lime are used (1:1, experiment No. 8), the proportion of sulphur that is converted into thiosulphate increases to 27 per ct.

(4) Lime. The proportion of lime that goes into solution is greatest (96 to 100 per ct.), when the proportion of sulphur is 2

or more times that of lime (experiments No. 3 to No. 6). When sulphur and lime are used in equal amounts, only 50 per ct. of the lime goes into solution.

(5) Ratio of lime and sulphur in solution. In the last column of Table II, we show the ratio of calcium, in the form of lime (CaO), and sulphur found in solution. The results indicate that *however large an amount of sulphur we use in relation to lime, the amount that appears in solution, under the conditions employed in this set of experiments, is limited and is approximately 2 to 2.2 parts of sulphur for 1 part of lime.* This point will be considered more fully later.

(6) Indications of preceding facts. The facts stated in the foregoing paragraphs point to the follow conclusions:

(a) Under the conditions of our experiments, the calcium of one part of lime combines with about two parts of sulphur to form soluble compounds, in large part calcium sulphides.

(b) When sulphur is used in excess of these proportions, the extra amount of sulphur is not acted upon but goes unchanged into the sediment as free sulphur (experiments No. 3 and No. 4, Table I).

(c) When sulphur is used in smaller proportions than 2 to 1 of lime, not enough sulphur is present to utilize for combination all the lime, and then the unused lime appears in the sediment (experiments No. 7 and No. 8, Table I).

(d) Generally speaking, if conditions favorable to the chemical reaction are observed, we get the largest proportions of sulphur and lime in solution, and therefore have the least sediment, when the proportion of sulphur used is 2 to 2.25 parts for 1 part of lime. The chemical reaction when most complete appears to call for these approximate proportions (pp. 427–8). Consequently, when we use an excess of sulphur or of lime, the excess remains unused and does not appear in the solution but is found as unchanged material in the sediment.

Percentage composition of solution. In the table following, the percentages are given of sulphur as sulphide and thiosulphate, and of calcium in combination with sulphur as sulphide; we also state the estimated proportions of calcium tetrasulphide (CaS_4) and calcium pentasulphide (CaS_5), which make up the sulphide sulphur.

TABLE III.— PERCENTAGE COMPOSITION OF SOLUTION.

No of experiment	Ratio of	Total sulphur	Sulphur in form of sulphides	Sulphur in form of thiosulphate	Calcium in combination with sulphide sulphur	Ratio of calcium in sulphide to sulphide sulphur	Percentage of sulphide sulphur in form of tetrasulphide (CaS_4)	Percentage of sulphide sulphur in form of pentasulphide (CaS_5)	Sulphur as tetrasulphide (CaS_4) in solution	Sulphur as penta sulphide (CaS_5) in solution
	Lime : Sulphur	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Calcium : Sulphur*	*Per ct.*	*Per ct.*	*Lbs.*	*Lbs.*
3.....	1 : 3.00	13.74	10.45	3.29	2.62	1 : 4.00	0.	100	0	54.7
4.....	1 : 3.00	14.18	11.29	2.89	3.03	1 : 3.73	29	71	16.3	40.0
5.....	1 : 2.25	14.66	12.02	2.64	3.07	1 : 3.92	8	92	5.1	58.1
6.....	1 : 2.00	13.64	11.03	2.61	3.25	1 : 3.40	73	27	42.0	15.6
7.....	1 : 1.50	11.47	8.94	2.53	2.83	1 : 3.20	100	0	41.1	0.
8.....	1 : 1.00	7.18	5.12	2.06	1.40	1 : 3.65	40	60	9.6	14.5

The mere difference in percentages of constituents due to difference in the proportions of water used for a given amount of lime and sulphur is not of special interest; but it is desirable to know something of the proportions of the constituents in relation to one another. The point of chief interest in connection with this table is the form of sulphide produced. In experiments 3, 4 and 5, when sulphur was used in largest proportions in comparison with lime, the largest amount of pentasulphide (CaS_5) was formed, varying from 71 to 100 per ct. of the total sulphide present. When less than 2.25 parts of sulphur for 1 of lime was used, the proportion of tetrasulphide (CaS_4) was usually greater but not uniformly so. Some condition or conditions other than the ratio of sulphur anl lime used apparently influences the proportions of tetrasulphide and pentasulphide formed.

EFFECT OF VARYING PROPORTIONS OF WATER.

We will next take up the results that follow from varying the amount of water when the proportion of lime to sulphur is kept uniform. In carrying out the experiments, we used lime and sulphur in the proportions of 50 and 100 pounds, respectively, and varied the amount of water from the extreme of 70 to 30 gallons. In order that our results may all be comparable, we have calculated them on the basis of 50 gallons of water, making the amounts of lime and sulphur correspond. The results will be discussed in the order already used in considering the preceding experiments.

Proportions of lime, sulphur and water; amounts of solution and sediment.— In each of the experiments presented in Tables IV, V and VI, we kept the proportion of lime and sulphur uniform, 2 parts of sulphur by weight for 1 part of lime, or 50 pounds of lime and 100 pounds of sulphur; in different experiments we used 70, 60, 55, 50, 40 and 30 gallons of water. The results are given for amounts corresponding to the use of 50 gallons of water. The ratio of lime and sulphur to water vary, of course, on account of the variable amount of water used. Experiments No. 21 and No. 22 represent duplicate experiments, carried on under conditions as nearly alike as possible.

TABLE IV.— AMOUNTS OF MATERIALS USED AND OF SEDIMENT FORMED.

No. of experiment	Pounds of material used	Gallons of water used	Pounds of water used for one pound of lime and sulphur	On basis of 50 gallons of water				
				Pounds of lime and sulphur used	Total weight of lime, sulphur and water	Weight of sediment	Percentage of lime and sulphur used in sediment	Weight of solution
	Lime: Sulphur		*Lime and sulphur: Water*	*Lime: Sulphur*	*Lbs.*	*Lbs.*	*Per ct.*	*Lbs.*
6	50 — 100	70	1 : 3.9	35.7— 71.4	524.0	2.0	1.8	522.2
11	" "	60	1 : 3.3	41.7— 83.4	542.0	3.5	2.8	538.5
12	" "	55	1 : 3.1	45.5— 91.0	553.4	8.2	6.0	545.2
16	" "	50	1 : 2.8	50.0—100.0	567.0	20.2	13.5	546.8
21	" "	40	1 : 2.2	62.5—125.0	604.5	31.7	17.0	572.8
22	" "	40	1 : 2.2	62.5—125.0	604.5	33.8	18.0	570.7
24	" "	30	1 : 1.7	83.3—166.6	667.0	60.8	24.3	606.2

In using lime and sulphur in the ratio of 1:2, we have amounts which are shown by the data in Table I to yield the least sediment when we use 35.7 pounds of lime with 71.4 pounds of sulphur and 50 gallons of water. In Table IV the data show the effect of maintaining the lime-sulphur ratio at 1:2 but varying the amounts used in proportion to water in the manner shown in the fourth column. The results, as shown in the seventh and eighth columns of Table IV, indicate clearly that sediment increases rapidly when we decrease beyond a certain proportion the amount of water for a given amount of lime and sulphur, or, stated another way, when we increase beyond a certain point the amount of lime and sulphur for a given amount of water. The amount of sediment increases from 2 up to 60.8 pounds as the ratio of water to lime and sulphur decreases from 1 :3.9 to 1 :1.7. Expressed in percentages of lime and sulphur used, the sediment increases from 1.8 up to 24.3 per ct. as the result of increasing the concentration of the lime and sulphur in relation to water. In respect to loss of material, the best results shown by these experiments are given when we use 35.7 pounds of lime (pure CaO) with 71.4 pounds of sulphur and 50 gallons of water, in which case we have 3.9 pounds of water for each pound of lime and sulphur used.

Amounts of sulphur and lime in solution made with 50 gallons of water.— The explanation in regard to the data in Table II applies to Table V following.

TABLE V.— AMOUNTS OF LIME AND SULPHUR IN SOLUTION.

No of experiment	Ratio of lime and sulphur to water	Weight of total sulphur	Percentage of used sulphur in solution	Weight of sulphur as sulphides	Percentage of used sulphur in solution as sulphides	Weight of sulphur as thiosulphate	Percentage of used sulphur in solution as thiosulphate	Weight of lime	Percentage of used lime in solution	Pounds of sulphur for one pound of lime in solution
	L. and S. : Water	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct.*	*Lbs.*	*Per ct*	*Lime : Sulphur.*
6....	1 : 3 9	71.2	99 7	57.6	80.7	13.6	19.0	35.6	99.7	1 : 2.00
11....	1 : 3.3	81.0	97.2	65.3	78.4	15.7	18.8	41.0	98.1	1 : 2.00
12....	1 : 3.1	89.8	98.8	74.8	82.3	15.0	16.5	43.7	96.0	1 : 2.00
16....	1 : 2.8	95.4	95 4	84.4	84.4	11 0	11.0	41.0	82.0	1 : 2.32
21....	1 : 2.2	113.3	90.6	102.0	81 6	11.3	9.0	47.9	76.7	1 : 2.40
22....	1 : 2.2	113.5	90.8	103.2	82.6	10.3	8.2	47.4	76.0	1 : 2.40
24....	1 : 1.7	141.6	85.0	132.4	80.0	9.2	5.0	57.3	68.8	1 : 2.40

The data in Table V suggest several interesting points, among which we call attention to the following:

(1) Total sulphur in solution. The amount of total sulphur in solution varies from 71.2 to 141.6 pounds, on the basis of use of 50 gallons of water. The percentage of total sulphur used that goes into solution varies from 85 to 99.7 per ct. It is seen that as we decrease the amount of water in proportion to lime and sulphur used, a smaller proportion or percentage of the sulphur goes into solution. To illustrate, in experiment No. 6, we used 71.4 pounds of sulphur and found in solution 71.2 pounds or 99.7 per ct. of the amount used; in experiment No. 24, we used 166.6 pounds of sulphur and found in solution 141.6 pounds, about twice as much as in experiment No. 6, but this was only 85 per ct. of the amount used (166.6 pounds), 25 pounds going unused into the sediment. These two experiments are alike in every respect except in relation to the ratio of sulphur and lime to water; in No. 6, the ratio is 1 :3.9, and in No. 24, it is 1 :1.7. The results of the intermediate experiments show a marked decrease in the proportion of sulphur utilized when the proportion of water to lime and sulphur decreases.

(2) Sulphide sulphur. When we consider the proportion of sulphur that goes into solution as sulphides (CaS_4 and CaS_5), it is noticeable that the decrease of water does not appear to affect the results greatly, as shown in the sixth column of Table V. So long as we have the proportions of lime and sulphur uniform, the proportion of water used within the limits shown in Table V does not increase or decrease greatly the percentage of sulphur going into solution as sulphides.

(3) Thiosulphate sulphur. In the seventh and eighth columns, the results show that, when the proportion of water to lime and sulphur decreases, the proportion of sulphur found in solution as thiosulphate decreases also; the decrease is quite regular and marked. The decrease of thiosulphate is due to its being changed into insoluble calcium sulphite ($CaSO_3$) and free sulphur (p. 411).

(4) Lime. The proportion of lime used that goes into solution is greatest (99.7 per ct.) when the proportion of water is greatest (experiment No. 6) and least (68.8 per ct.) when the proportion of water is least (experiment No. 24), under the conditions of the work.

(5) Ratio of lime and sulphur in solution. In the last column of Table V, we give the ratio of calcium, in the form of lime (CaO), and of sulphur found in solution. The results indicate that, when we have 3 or more parts of water for one part of lime and sulphur (lime and sulphur being 1:2), we have two parts of sulphur in solution for one part of lime (experiments 6, 11, 12); when the proportion of water is less than 3 parts to 1 part of lime and sulphur, an increased amount of sulphur goes into solution in proportion to lime, 2.3 to 2.4 parts of sulphur being found for one part of lime (experiments 16, 21, 22, 24). This point will be further considered later (pp. 424, 425).

(6) Indication of preceding facts. From the statement of results preceding, we are justified in stating the following conclusions:

(a) Under the conditions of the experiments, less lime and sulphur go into solution when the amount of water decreases or, stated another way, larger amounts of sediment are formed when the proportion of water to lime and sulphur decreases. The sediment under the conditions used in these experiments is largely calcium sulphite ($CaSO_3$).

(b) The proportion of sulphur that goes into solution as sulphide is not greatly different when the proportion of water to lime and sulphur varies considerably (1:3.9 to 1:1.7), other conditions being uniform.

(c) The percentages of calcium and sulphur that remain in solution as calcium thiosulphate (CaS_2O_3) grow less as the proportion of water to lime and sulphur decreases, while the amount of calcium sulphite ($CaSO_3$) increases in the sediment.

Percentage composition of solution.— In Table VI below, we give the percentages of sulphur as sulphides and as thiosulphate, and of calcium in solution in combination with sulphur as sulphide; we also give the calculated proportions and number of pounds of sulphur as calcium tetrasulphide (CaS_4) and calcium pentasulphide (CaS_5).

TABLE VI.— PERCENTAGE COMPOSITION OF SOLUTION.

No of experiment	Ratio of lime and sulphur to water	Total sulphur	Sulphur in form of sulphides	Sulphur in form of thiosulphate	Calcium in combination with sulphide sulphur	Ratio of calcium in sulphide to sulphide sulphur	Percentage of sulphide sulphur in form of tetrasulphide (CaS_4)	Percentage of sulphide sulphur in form of pentasulphide (CaS_5)	Sulphur as tetrasulphide (CaS_4) in solution	Sulphur as pentasulphide (CaS_6) in solution
	L. and S. : Water	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Calcium : Sulphur*	*Per ct.*	*Per ct.*	*Lbs.*	*Lbs.*
6...	1 : 3.9	13.64	11.03	2.61	3.25	1 : 3.39	73	27	42	15.6
11....	1 : 3.3	15.06	12.14	2.92	3.61	1 : 3.36	76	24	50	15.3
12....	1 : 3.1	16.48	13.72	2.76	3.99	1 : 3.44	65	35	48.6	26.2
16....	1 : 2.8	17.45	15.43	2.02	4.09	1 : 3.77	24	76	20.3	64.1
21....	1 : 2.2	19.79	17.81	1.98	4.73	1 : 3.77	24	76	24.5	77.5
22....	1 : 2.2	19.91	18.11	1.80	4.80	1 : 3.77	24	76	24.8	78.4
24....	1 : 1.7	23.36	21.84	1.52	5.80	1 : 3.77	24	76	31.8	100.6

The main point of interest in this table is the form of sulphide produced. In experiments 6, 11 and 12, when dilution with water was greatest, the largest amount of tetrasulphide (CaS_4) was formed, varying from 65 to 76 per ct. of the total sulphide present. When water was used in proportions less than 2.8 parts for one part of lime and sulphur, a larger amount of pentasulphide (CaS_5) was formed, 76 per ct. in experiments 16, 21, 22, 24. Apparently, under the conditions of these experiments, there is a dividing line (3.1 parts of water to 1 part of lime and sulphur), above which dilution up to the limits used gives a larger proportion of tetrasulphide, and below which concentration or use of less water gives larger proportions of pentasulphide. As pointed out later this result does not hold good when we use sulphur in larger proportions than 2 of sulphur to 1 of lime.

ADDITIONAL EXPERIMENTS IN STUDYING EFFECTS OF VARYING PROPORTIONS OF WATER, LIME AND SULPHUR.

Thus far we have discussed two sets of experiments, in each of which variation of only one factor at a time was studied.

(1) In the first set (experiments 3–8, Tables I–III), the amount of lime (35.7 pounds) and of water (50 gallons) was kept the same, but the amount of sulphur used was made to vary from 35.7 to 107 pounds, the ratio of lime and sulphur varying from 1:1 to 1:3. (2) In the second set of experiments, the amounts of lime and sulphur used were kept uniform (50 pounds of lime and 100 pounds of sulphur), while the amount of water varied from 30 to 70 gallons, so that the ratio of lime and sulphur to water varied from 1:1.7 to 1:3.9; or, stated in another way, the amount of water was kept the same (50 gallons) while the amount of lime used was made to vary from 35.7 to 83.3 pounds and the sulphur, from 71.4 to 166.6 pounds, the ratio of lime to sulphur in every case being 1:2. In order to avoid confusion, the discussion of additional experiments involving other variations in proportions of constituents has been postponed but will be now taken up.

Several experiments were tried in which we used 50 pounds of lime and 150 pounds of sulphur with amounts of water varying from 70 to 40 gallons. We do not give the detailed results of these experiments, because we have already shown that when lime and sulphur are used in the ratio of 1:3, more sulphur is used than can possibly combine with the lime, and the unused sulphur simply goes to increase the amount of sediment. The sediment increases when the amount of water used decreases, so that we found in our experiments that from 25 to 38.5 per ct. of the lime and sulphur used goes into the sediment, the largest percentages occurring when we used the lowest amounts (40 and 50 gallons) of water. In other details, the results of these experiments agree with those discussed in Tables IV–VI in respect to the effect of using less water in proportion to lime and sulphur. Any mixture of lime and sulphur in which the ratio of lime and sulphur is 1:3 is not economical to use, whether with large or small amounts of water and we can dismiss this part of our experimental work without need of further discussion.

It is desirable, however, that we consider the experiments in which we used lime and sulphur in the ratio of 1:2.25 with varying amounts of water. Experiments 5, 10 and 15 are laboratory experiments with pure lime; experiment 25 is on a commercial scale and the lime used was not pure. The essential facts can be brought out in the two tables following:

TABLE VII.— AMOUNTS OF MATERIAL USED AND SEDIMENT FORMED.

No. of experiment	Pounds of material used	Water used	Pounds of water used for one pound of lime and sulphur	On basis of 50 gallons of water: Pounds of lime and sulphur used	Weight of sediment	Percentage of lime and sulphur used in sediment	Weight of solution
	Lime: Sulphur	*Gals.*	*Lime and sulphur: Water*	*Lime: Sulphur*	*Lbs.*	*Per ct.*	*Lbs.*
5	50—112.5	70	1 : 3.6	35.7— 80.3	7.0	6	526
10	" "	60	1 : 3.1	41.7— 93.8	8.1	6	544
15	" "	50	1 : 2.6	50.0—112.5	17.9	11	562
25	36*—81	50	1 : 3.6	36.0— 81.0	4.2†	3.6	530

* This represents 40 pounds of commercial quicklime containing 90 per ct. pure lime (CaO).
† This is loss due to calcium sulphite and does not include the 4 pounds of useless material in the commercial lime. The total sediment is 8.2 pounds.

TABLE VIII.— LIME AND SULPHUR IN SOLUTION.

No. of experiment	Ratio of lime and sulphur to water	Percentage of sulphur used in solution	Percentage of sulphur used in solution as sulphide	Percentage of sulphur used in solution as thiosulphate	Percentage of lime used in solution	Ratio of calcium in sulphide to sulphide sulphur
	Lime and sulphur: Water	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Calcium: Sulphur*
5	1 : 3.6	96	78.7	17.8	97.5	1 : 3.92
10	1 : 3.1	95.9	77.7	18.2	97.6	1 : 3.96
15	1 : 2.6	88.6	71.4	17.2	94.5	1 : 3.72
25	1 : 3.6	98.0	......	......	......	1 : 3.93

In studying Tables VII and VIII, we observe the following facts:

(1) Sediment. When we use, as in experiment No. 5, 35.7 pounds of lime and 80.3 pounds of sulphur (ratio of lime to sulphur, 1:2.25) with 50 gallons of water (ratio of lime and sulphur to water, 1:3.6), the total sediment amounts to 7 pounds, or 6 per ct. of the lime and sulphur used. The same proportion

of loss occurs in experiment No. 10 when we use 41.7 pounds of lime and 93.8 pounds of sulphur (ratio, 1:2.25) with 50 gallons of water (ratio of lime and sulphur to water, 1:3.1) When, however, we increase the lime to 50 pounds and the sulphur to 112.5 pounds with 50 gallons of water, the proportion of sediment is about double, as shown in experiment No. 15. In experiment No. 25, carried out with commercial lime and on a larger scale (50 gallons of water) than the other experiments, the actual weight of sediment found was 8.2 pounds, of which amount 4 pounds was due to impurities in the commercial lime used and 4.2 pounds to the result of regular chemical change, or the amount that would have been found if pure lime had been used. In this and several other experiments carried out on a commercial scale, the sediment has been found to be inappreciable when we use 36 pounds of lime (equal to 40 pounds of 90 per ct. lime) and 80 pounds of sulphur with 50 gallons of water. In our experience, the sediment is not only slight in amount but is very fine.

(2) Sulphur and lime recovered in solution. In Table VIII, we see that nearly all of the sulphur used (96 to 98 per ct.) is found in solution, as shown in experiments 5, 10 and 25. In experiment No. 15, when we used more lime and sulphur in proportion to water (1:2.6), less than 90 per ct. of the sulphur used was found in the solution. It is seen also that the lime goes into solution more completely when the water is used in larger proportion to lime and sulphur. The percentage of sulphur appearing as thiosulphate does not vary greatly in the different experiments.

(3) Pentasulphide and tetrasulphide. In experiments 5, 10 and 25, we have for 1 part of calcium in combination with sulphur nearly 4 parts of sulphur, which means that the sulphide is practically all in the form of calcium pentasulphide (CaS_5). In experiment No. 15, where the amounts of lime and sulphur used were greater in proportion to the water used, we have a mixture of about one-third tetrasulphide (CaS_4) and two-thirds pentasulphide.

EFFECT OF CONCENTRATION OF LIME-SULPHUR SOLUTIONS BY EVAPORATION AT BOILING TEMPERATURE.

Two experiments were made in which two different lime-sulphur solutions were concentrated by evaporation at boiling temperature. In one case the concentration was equal to the reduction of 50 gallons to 30 gallons and in the other, of 50 gallons to 20 gallons. The data of special interest are contained in the following table:

TABLE IX.— EFFECT OF CONCENTRATING LIME-SULPHUR SOLUTIONS BY BOILING

No. of experiment	Volume of solution		Density of solution		Percentage of sulphur in solution		Thiosulphate sulphur		Ratio of calcium to sulphur in sulphides		Percentage of thiosulphate sulphur changed to sulphite on boiling
	Before concentration	After concentration	Before concentration	After concentration	Before concentration	After concentration	Before concentration	After concentration	Before concentration	After concentration	
	Gals.	*Gals.*	*Deg. B*	*Deg. B*	*Per ct.*	*Per ct.*	*Lbs.*	*Lbs.*	*Lime : Sulphur*	*Lime : Sulphur*	*Per ct.*
1	50	30	21	32.8	13.74	21.43	13.45	12.30	1 : 3.72	1 : 3.70	8.5
2	50	20	24.5	33.8	16.14	25.91	15.40	2.90	1 : 3.71	1 : 3.66	81.0

The principal point of importance in connection with this table is the fact that more or less of the thiosulphate (CaS_2O_3) is changed into insoluble calcium sulphite ($CaSO_3$) and free sulphur when the lime-sulphur solution is concentrated by boiling. In the first experiment, 8.5 per ct. of the thiosulphate sulphur was changed into sulphite and free sulphur, appearing as sediment; this was equal to a loss of 1.15 pounds of thiosulphate sulphur present in the original 50 gallons of solution. In the second experiment, where the boiling was continued longer and the concentration was considerably greater, the change of thiosulphate into sulphite and free sulphur was much greater, amounting to about 81 per ct. of the thiosulphate in the original solution; this loss was equivalent to 12.5 pounds of thiosulphate sulphur for 50 gallons of original solution.

These facts serve to illustrate the effects of evaporation by long-continued boiling of lime-sulphur solutions for the purpose of producing concentrated solutions with high percentage of soluble sulphur. Low percentage of thiosulphate sulphur is characteristic of commercial, concentrated lime-sulphur solutions. Fresh solutions containing less than 17 per ct. of total soluble sulphur usually contain 2.5 to 3.5 per ct. of thiosulphate sulphur. Concentrated solutions of commerce containing 25 per ct. or more of total sulphur usually contain only 0.6 to 0.9 per ct. of thiosulphate sulphur, rarely going above 1 per ct. This condition is suggestive that these concentrated solutions have been prepared by evaporation at boiling temperature.

The question has arisen among fruit-growers as to why home-made preparations are not as high in soluble sulphur as are commercial preparations. The reason of the difference is simply a matter of evaporation of water, and any properly home-made preparation can, if desired, be made as concentrated as any commercial mixture. While this treatment may be desirable in commercial preparations in order to reduce the cost of barreling and of transportation, it is extremely doubtful if it will ever be found economical, or for any sufficient reason desirable, for those who prepare home-made solutions. The only gain lies in reducing somewhat the number of barrels required for storage in those cases where the preparation is made some weeks or months before it is needed for use. Against the small gain in the matter of reducing the number of barrels needed for storage must be placed, (1) the cost of fuel required to concentrate the solution, (2) the amount of time used in the process and (3) the loss of thiosulphate sulphur with corresponding increase of sediment. While thiosulphate sulphur is not at present regarded as of equal value with the penta-sulphide and tetrasulphide sulphur, at least for destruction of scale insects, it is of sufficient value to save from needless loss.

SOME OF THE CHEMICAL CHANGES OCCURRING IN THE MAKING OF LIME-SULPHUR SOLUTION.

The exact chemical changes taking place when lime and sulphur are boiled in water are not known in full. In the simplest kind of change, there is formed a large amount of pentasulphide (CaS_5) or tetrasulphide (CaS_4) and a relatively small amount of thiosulphate (CaS_2O_3). If only pentasulphide with thiosulphate is formed, there is required for one pound of lime 2.28 pounds of sulphur; if only tetrasulphide and thiosulphate are formed, then the reaction calls for 1.90 pounds of sulphur for one pound of lime; if both pentasulphide and tetrasulphide along with thiosulphate are formed, the amount of sulphur required for one part of lime varies between 1.90 and 2.28 pounds. Some additional or secondary changes may take place which require more sulphur, but these are details about which we are lacking in full knowledge for the most part; though the chief and best known of these secondary changes is the formation of calcium sulphite ($CaSO_3$) and free sulphur by decomposition of calcium thiosulphate (CaS_2O_3). We will call attention to three points in connection with the ratio of sulphur and lime called for, as shown by the results of our experimental work: (1) The proportions of sulphides and thiosulphate formed; (2) the change of thiosulphate into sulphite; and (3) the proportions of lime and sulphur found in solution.

Proportions of sulphides and thiosulphate formed.— In the simplest kind of chemical change, when we have only sulphide and thiosulphate formed, about 17 to 20 per ct., or one-sixth to one-fifth, of the sulphur used goes to form thiosulphate sulphur, provided water, lime and sulphur are used in proportions such that they go into solution most completely (1 of lime: 2—2.25 sulphur. See Table II, exp's 5 and 6). Ordinarily we have in the freshly made lime-sulphur solution 4 to 4.5 parts of sulphide sulphur for 1 part of thiosulphate sulphur. When lime is used in greater proportions than 1 to 2 of sulphur, large amounts of thiosulphate appear (Table II, exp's 7-8). When a lime-sulphur solution is made with an amount of water such that the ratio of water to lime and sulphur is much below 3:1, the thiosulphate is changed to sulphite and therefore appears in much smaller percentage in solution (Table V, exp's 16-24); under such conditions, there may be left in solution so small an amount of thiosulphate as to form only about one-tenth of the sulphide sulphur.

Change of thiosulphate into sulphite. Small amounts of thiosulphate in solution in proportion to sulphides indicate that the thiosulphate was originally formed in the usual amounts (17-20 per ct. of solution) but has been subsequently changed into the insoluble compound, calcium sulphite, together with some free sulphur. This conversion of thiosulphate into sulphite and sulphur is favored by use of too small an amount of water in proportion to the lime and sulphur used (Table V, exp's 16-24) or by boiling too long (Table IX) or by combination of both conditions.

Proportions of lime and sulphur in solution. Taking the amounts of total sulphur and lime, equivalent to calcium, in solution in our different experiments, we find that, for one pound of lime, the sulphur varies from 1.9 to 2.40. These figures agree with the amounts called for by the reaction commonly given, as already referred to. The effect of using an amount of sulphur in excess of the proportion of 2.25 to 1 is shown by the following results:

TABLE XI.—PROPORTIONS OF LIME TO SULPHUR IN SOLUTION.

No. of experiment	Pounds used	Pounds of sulphur used for one of lime	Pounds of water used for one of lime and sulphur	Pounds of sulphur found in solution for one of lime
	Lime: Sulphur	*Lime: Sulphur*	*Lime and sulphur: Water*	*Lime: Sulphur*
3	35.7—107	1 : 3.00	1 : 2.9	1 : 2.10
4	35.7—107	1 : 3.00	1 : 2.9	1 : 2.00
13	50 —150	1 : 3.00	1 : 2.1	1 : 2.23
1	25 — 70.5	1 : 2.80	1 : 4.4	1 : 1.94
9	42 —111	1 : 2.70	1 : 2.7	1 : 2.12
2	31 — 75	1 : 2.40	1 : 3.9	1 : 2.26
5	35.7— 80.3	1 : 2.25	1 : 3.6	1 : 2.22
10	42 — 94	1 : 2.25	1 : 3.1	1 : 2.21
15	50 —112.5	1 : 2.25	1 : 2.6	1 : 2.10
6	36 — 72	1 : 2.00	1 : 3.9	1 : 2.00
11	42 — 84	1 : 2.00	1 : 3.3	1 : 1.98
12	45.5— 91	1 : 2.00	1 : 3.1	1 : 2.05

The fact is shown quite strikingly by the data in this table that when we use more sulphur than 2.25 parts for 1 part of lime, we do not get any more sulphur into solution in proportion to lime. When we use 3 parts of sulphur for 1 of lime, we have in solution 2 to 2.23 parts of sulphur for 1 of lime. This indicates that the chemical reaction is a fairly definite one and when we use more sulphur than can combine with the lime, the surplus sulphur remains unchanged, going into the sediment. It is obvious, also, that the amount of sulphur that combines with lime is not affected by the amount of water present. These results indicate that the most economical proportion of lime and sulphur to use is 1:2.25; with these proportions there is least possible waste in the process, since the chemical reaction appears to be complete under these conditions.

CONDITIONS FAVORABLE TO FORMATION OF SEDIMENT IN LIME-SULPHUR SOLUTIONS.

Our experiments have all helped to some extent to indicate the conditions under which sediment is formed in the manufacture of lime-sulphur solutions. It may be useful here to call special attention, by way of a summary, to the different conditions that affect the formation of sediment or insoluble matter. The causes of formation vary and also the character and composition of the sediment. The principal facts may be briefly stated, as follows:

(1) *Calcium sulphite.* In the usual method of making lime-sulphur mixtures, some calcium sulphite ($CaSO_3$) is always formed from calcium thiosulphate as an unavoidable part of the chemical changes taking place, and this compound, being insoluble, appears as sediment. It is formed in larger amounts by long-continued boiling, as when (a) a dilute solution is made more concentrated, or (b) by the ordinary amount of boiling (1 hour) when too little water is used in proportion to lime and sulphur, or (c) when the mixture becomes too concentrated in the kettle as a result of evaporation during boiling. *Plenty of water*

and avoidance of too long boiling reduce to a minimum the amount of sediment due to calcium sulphite.

(2) *Impurities in lime and sulphur.* Compounds present in lime and sulphur, which do not take any part in the chemical changes that result in the formation of the sulphides of calcium (CaS_4 and CaS_5), form part of the sediment. Of the compounds most apt to occur in quicklime or lump-lime, the following may be mentioned: Carbonate of lime, compounds of magnesium, iron, aluminum, etc. Sulphur can easily be obtained that is practically free from impurities, usually being over 99 per ct. pure; but when any insoluble impurities are present in the sulphur used, they contribute to increase the amount of sediment.

(3) *Lime used in excess.* When lime is used in amounts larger than can combine with the amount of sulphur present to form soluble compounds, the excess of lime appears as part of the sediment. Generally speaking, when we use more than one part of lime for two parts of sulphur, the amount of lime used above this proportion is unchanged and remains insoluble as part of the sediment, especially if enough water is used. This fact readily accounts for the large amounts of sediment formed when some of the old formulas were used, in which the amount of lime equalled or exceeded that of sulphur. Any lime that, through lack of complete slaking, is allowed to remain in lumps and fails to take part in the lime-sulphur reaction, goes into the sediment.

(4) *Sulphur used in excess.* Theoretical considerations, in harmony with actual experiments, indicate that when we use sulphur in proportions greater than 2.25 parts for 1 part of lime, the excess of sulphur remains unchanged, appearing in the sediment as free sulphur. For example, when we use 3 parts of sulphur for 1 of lime, 30 to 40 per ct. of the sulphur used is found in the sediment. When the ratio of sulphur to lime is 2.25 (or less) :1, we find only 1 to 5 per ct. of the sulphur in sediment and this is there not as free sulphur but as calcium sulphite, having been taken into solution and changed again to an insoluble form. Sulphur in finely powdered form easily gathers into little

lumps which are not easily penetrated by water and which may remain unchanged, passing as free sulphur into sediment. It is essential that the lime-sulphur mixture be constantly and thoroughly stirred during the process of making so as to break up as completely as possible all lumps of sulphur or of lime.

EFFICIENCY OF LIME-SULPHUR SOLUTIONS IN RELATION TO CHEMICAL COMPOSITION.

In what particular manner the lime-sulphur solution acts as an insecticide and fungicide, no one has yet clearly demonstrated. What specific compounds are directly responsible for the effects produced we are not yet certain. It is held, as the result of some experimental work, that the effect of the lime-sulphur mixture is not due to the direct action of calcium pentasulphide (CaS_5) or of calcium tetrasulphide (CaS_4), but is due rather to compounds that are formed from these, either calcium thiosulphate (CaS_2O_3), or free sulphur, or both. If the directly effective substance is calcium thiosulphate, then the amount that can be formed from the lime-sulphur solution is directly dependent upon and proportional to the amount of calcium pentasulphide or tetrasulphide in solution. If the sulphur set free from the pentasulphide, tetrasulphide and thiosulphate is the effective agent, then the amount of compounds in solution capable of furnishing the largest amount of free sulphur directly determines the value of the solution. Calcium pentasulphide is capable of furnishing more free sulphur by decomposition than the tetrasulphide and this more than the thiosulphate. If the free sulphur is the material desired, then the solution containing the largest amount of pentasulphide is the most valuable. It is now commonly believed, whether correctly or not, that the solution containing most pentasulphide is most effective, at least in connection with destruction of scale insects. Whatever may prove to be the facts in relation to the manner of action of the lime-sulphur solution, it is obvious that its efficiency stands in some close and direct relation to the amount of sulphide compounds contained in it, or, in other words, to the chemical composition of the solution.

KEEPING-POWER OF LIME-SULPHUR SOLUTION ON STANDING.

One sample of lime-sulphur solution was examined after it had been standing for a month in a warm room in a stoppered bottle. There was a slight deposit of free sulphur. The total amount of sulphur in the fresh solution was 13.74 per ct.; at the end of a month, the sulphur in solution was 13.66 per ct., essentially the same as in the fresh solution.

ANALYSIS OF CRYSTALS FORMED IN LIME-SULPHUR SOLUTIONS.

In a barrel of concentrated lime-sulphur solution, there were deposited, after standing some months, large reddish-brown crystals. An analysis of these crystals showed them to consist of calcium sulphides with a very small amount of calcium thiosulphate. The crystals consisted chiefly of a mixture of about equal parts of calcium pentasulphide (CaS_5) and calcium tetrasulphide (CaS_4).

In an experiment, in which we used only 15 gallons of water for 50 pounds of lime and 100 of sulphur, and, after boiling, diluted to 50 gallons, needle-shaped crystals separated. The ratio of calcium to sulphur in these crystals was found to be 1:3.31, which indicates that the crystals are nearly all calcium tetrasulphide (CaS_4). The remaining solution after the removal of the crystals contains larger amounts of pentasulphide, the ratio of calcium to sulphur being 1:3.60.

RELATION OF DENSITY OF SOLUTION TO PERCENTAGE OF SULPHUR AS A BASIS FOR DILUTION.

The relation of density of lime-sulphur solutions to the percentage of total sulphur in solution is a matter of fundamental importance, because in orchard practice the extent of dilution is made to depend upon the density as measured by specific gravity, which is preferably expressed in degrees Beaumé on account of simplicity. The method of dilution of lime-sulphur solutions is based upon the supposition that one degree, Beaumé, corresponds to the same percentage of sulphur, whether in dilute or in concentrated solutions. Previously, we have had insufficient data upon which to base reliable statements in regard to the ratio of density to sulphur content of solutions. On the basis of a few data, the statement was made in Bulletin No. 319 (p. 415) that, in general, one degree, Beaumé, corresponds approximately to 0.76 per ct. of sulphur in concentrated solutions within the limits of density indicated by 25° to 33° B. As we shall see this general statement needs some modification in the interest of accuracy. For the purpose of making as careful and complete a study as possible of the relations of density to percentage of sulphur in lime-sulphur solutions, we have brought together in Table X the results of sixty-two analyses of samples, the history of which is known to us in each case. In the fourth, fifth, ninth and tenth columns are given some additional data, to which reference will be made later.

We will now consider in detail (1) the relation of density of solution to percentage of sulphur, (2) the adoption of definite values expressing such relations, as a basis for diluting lime-sulphur solutions and (3) an application of the method of dilution to cases of known composition for the purpose of testing the accuracy of the proposed dilutions.

The percentage of sulphur corresponding to 1°B. is obtained simply by dividing the percentage of sulphur in solution by the number representing the density of that solution in Beaumé degrees.

TABLE X. — RELATION OF DENSITY OF SOLUTION TO PERCENTAGE OF SULPHUR.

Density	Percentage of sulphur in solution	Percentage of sulphur for 1° B.	Percentage of sulphur in diluted solution	Sulphur in 1 gall. of diluted solution	Density	Percentage of sulphur in solution	Percentage of sulphur for 1° B.	Percentage of sulphur in diluted solution	Sulphur in 1 gall. of diluted solution
Degrees, Beaume	*Per ct.*	*Per ct.*	*Per ct.*	*Ozs.*	*Degrees, Beaume*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
11.9	7.18	**0.60**	......	.....	29.9	21.31	**0.71**	3.34	4.62
16.7	10.14	**0.61**	3.16	4.37	30.0	21.19	**0.71**	3.32	4.57
17.8	11.47	**0.64**	3.36	4.67	30.4	20.22	**0.67**	3.18	4.40
20.0	12.78	**0.64**	3.36	4.67	30.4	21.17	**0.70**	3.33	4.60
21.0	13.74	**0.65**	3.44	4.74	30.4	22.75	**0.73**	3.58	4.94
21.4	14.18	**0.66**	3.56	4.91	30.4	23.28	**0.77**	3.66	5.07
21.5	13.64	**0.63**	3.43	4.73	30.9	23.55	**0.76**	3.51	4.83
21.6	14.66	**0.68**	3.50	4.82	31.1	22.75	**0.73**	3.40	4.70
21.9	16.33	**0.75**	3.90	5.40	31.2	23.72	**0.76**	3.54	4.89
22.3	16.50	**0.74**	3.95	5.47	31.2	24.32	**0.78**	3.63	5.00
23.7	15.06	**0.64**	3.32	4.57	31.2	24.34	**0.78**	3.64	5.02
24.1	16.61	**0.70**	3.50	4.82	31.4	22.87	**0.73**	3.43	4.73
24.2	15.28	**0.63**	3.22	4.44	31.4	23.36	**0.74**	3.50	4.82
24.5	16.14	**0.66**	3.41	4.71	31.5	23.15	**0.73**	3.47	4.78
24.5	16.53	**0.68**	3.46	4.76	31.8	24.47	**0.77**	3.57	4.92
24.5	17.45	**0.71**	3.68	5.10	31.9	24.70	**0.77**	3.60	4.97
24.7	16.48	**0.67**	3.20	4.41	32.0	24.52	**0.76**	3.58	4.95
24.7	15.43	**0.62**	3.00	4.13	32.2	21.83	**0.68**	3.20	4.41
26.8	18.73	**0.70**	3.30	4.54	32.7	25.68	**0.78**	3.57	4.92
26.8	19.68	**0.73**	3.46	4.76	33.0	25.72	**0.78**	3.58	4.94
26.9	19.78	**0.74**	3.48	4.80	33.0	25.60	**0.77**	3.56	4.91
27.1	19.80	**0.73**	3.48	4.80	33.5	25.48	**0.76**	3.56	4.91
27.2	19.79	**0.73**	3.49	4.81	33.5	26.05	**0.78**	3.64	5.02
27.4	19.91	**0.73**	3.52	4.85	33.6	25.66	**0.76**	3.50	4.82
27.9	19.30	**0.70**	3.30	4.55	33.9	26.49	**0.78**	3.62	4.99
28.5	22.39	**0.78**	3.84	5.30	34.0	25.93	**0.76**	3.54	4.89
28.6	21.02	**0.73**	3.38	4.68	34.2	25.81	**0.75**	3.53	4.87
29.0	19.90	**0.69**	3.21	4.43	34.3	26.03	**0.76**	3.57	4.92
29.0	21.00	**0.73**	3.39	4.69	34.5	25.43	**0.74**	3.50	4.82
29.2	19.98	**0.70**	3.22	4.44	35.7	26.65	**0.75**	3.43	4.73
29.8	22.35	**0.75**	3.50	4.82	36.0	27.82	**0.77**	3.58	4.94

In examining the third and eighth columns in Table X, we notice that the percentage of sulphur corresponding to 1°B. shows a general tendency to become higher as the density increases. Below 25°B., each degree represents in most cases less than 0.70 per ct. of sulphur; in solutions testing above 25° B., each degree corresponds to about 0.75 per ct. of sulphur.

Another point to which attention should be called is the evidence of some marked irregularities; there are some cases in which solutions having the same density contain variable percentages of sulphur, as, for example, three solutions testing 24.5° B. but varying in sulphur ratio from 0.67 to 0.71, and, again, four solutions testing 30.4° B. but varying in sulphur ratio from 0.67 to 0.77. The irregularities observed are probably about as extreme as are apt to occur and, indeed, much greater than occur in the case of properly managed home-made washes. In view of the irregularities observed in the relation of density, expressed in degrees, Beaumé, to the percentage of sulphur, the question arises as to whether we can devise any method of meeting this condition, in order that we may make use of the density in degrees Beaumé as a basis for diluting lime-sulphur solutions to the proper degree required for different purposes.

Adoption of values as basis for diluting lime-sulphur solution. In making dilutions of lime-sulphur solutions for application to trees, it is desirable that the diluted solutions contain as nearly as possible the same amount of sulphur when used for a given purpose, if it is expected to obtain uniform results. It is necessary to have the following data as a basis: (1) The amount of sulphur which a gallon of dilute solution should contain for a specific use; (2) the percentage of sulphur that is necessary to allow for each degree, Beaumé; and (3) the rate of dilution for each degree, Beaumé, which shall make the diluted solutions contain the same percentage of sulphur, or, expressed in another way, the same number of ounces of sulphur in one gallon of diluted solution.

Mr. P. J. Parrott has furnished the following information bearing on the first point: In treating San José scale, each gallon of diluted lime-sulphur solution should contain about 4.75 ounces of sulphur. This dilution is obtained approximately by diluting one gallon of lime-sulphur solution testing 33° B. with 8 gallons of water, making 9 gallons of diluted solution. In spraying for blister-mite, one gallon of solution (33° Beaumé) is diluted with 11 gallons of water; and, for fungicidal work on foliage, the dilution is 40 gallons of water for one gallon of lime-sulphur solution (33° B.). On the basis of these statements, we readily learn by making the proper calculations that one gallon of diluted solution prepared for San José scale should contain 3.45 per ct. of sulphur; that one gallon of solution prepared for blister-mite should contain about 3.56 ounces of sulphur, which is equivalent to 2.60 per ct.; while as a fungicide, each gallon should contain 1.04 ounces of sulphur, which is equivalent to 0.775 per ct. of sulphur.

In assigning a sulphur value for each degree, Beaumé, the figures given in the second column of Table XI were adopted as making the closest practical approximation to actual facts and involving the least error. It is observed that, starting at 36° B., the sulphur value is 0.75 and that this is made gradually to decrease as the density decreases, until at 20° B. and below the value of 0.65 is given. These values have been so selected that, as will be seen later, any deviation from normal will nearly always be in the direction of diluted solutions a little above required strength, instead of more or less below.

The rate of dilution is based upon the density in degrees, Beaumé, in such a way that the diluted mixture contains the same percentage of sulphur or the same number of ounces in a gallon. The data for the calculations are given in the table below. Where the number of gallons of water to be added to one gallon of solution involves a fraction, the quarter nearest the exact figure is used for convenience; this does not impair appreciably the accuracy of the dilution, as shown by the percentage of sulphur in each diluted mixture. The details in Table XI are given for the benefit of those who desire to know upon what data the figures are based for making the different dilutions.

The percentages of sulphur in the diluted solution can be obtained by dividing the number of pounds of sulphur in one gallon of solution before dilution by the weight of the whole mixture after dilution. The number of ounces in one gallon of diluted mixture is found by dividing the number of ounces of sulphur in one gallon, before dilution, by the total number of gallons after dilution.

TABLE XI.— DATA FURNISHING A BASIS FOR DILUTING LIME-SULPHUR WASH.

Density of solution in degrees, Beaumé	Percentage of sulphur equal to 1° B.	Percentage of sulphur in solution	Weight of one gallon of solution.	Sulphur in one gallon of solution	Dilution for San José scale: For 1 gall. lime-sulphur solution	Sulphur in one gallon of diluted solution	Dilution for blister-mite: For 1 gall. lime-sulphur solution	Sulphur in one gallon of diluted solution	Dilution for summer spray: For 1 gall. lime sulphur solution	Sulphur in one gallon of diluted solution
	Per ct.	*Per ct.*	*Lbs.*	*Lbs.*	*Galls. water*	*Ozs.*	*Galls. water*	*Ozs.*	*Galls. water*	*Ozs.*
36	0.75	27 00	11.08	2.99	**9**	4.78	**12½**	3.54	**45**	1.04
35	0.75	26.25	10.98	2.88	**8¾**	4.73	**12**	3.54	**43¼**	1.04
34	0.75	25.50	10.88	2.77	**8¼**	4.79	**11½**	3.58	**41½**	1.04
33	0.75	24.75	10.78	2.67	**8**	4.75	**11**	3.56	**40**	1.04
32	0.74	23.70	10.69	2.53	**7½**	4.76	**10½**	3.52	**37¾**	1.04
31	0.74	22.95	10.60	2.43	**7¼**	4.72	**10**	3.53	**36¼**	1.04
30	0.73	21.90	10.51	2.30	**6¾**	4.75	**9½**	3.50	**34¼**	1.04
29	0.73	21.15	10.42	2.20	**6½**	4.70	**9**	3.52	**32¾**	1 04
28	0.72	20.15	10.32	2.08	**6**	4.75	**8½**	3.50	**31**	1.04
27	0.72	19.45	10.23	1.99	**5¾**	4.72	**8**	3.54	**29½**	1.04
26	0.71	18.45	10.15	1.87	**5¼**	4.79	**7½**	3.52	**27¾**	1.04
25	0.70	17.50	10.07	1.76	**5**	4.70	**7**	3.52	**26**	1.04
24	0.69	16.65	9.98	1.65	**4½**	4.80	**6½**	3.52	**24¼**	1.04
23	0.68	15.65	9.90	1.55	**4¼**	4.72	**6**	3.54	**22¾**	1.04
22	0.67	14.75	9.82	1.45	**3¾**	4.88	**5½**	3.57	**21¼**	1.04
21	0.66	13.85	9.74	1.35	**3½**	4.80	**5**	3.60	**19¾**	1.05
20	0.65	13.00	9.67	1.26	**3¼**	4.74	**4¾**	3.51	**18¼**	1.05
19	0.65	12.35	9.59	1.18	**3**	4.72	**4¼**	3.60	**17**	1.04
18	0.65	11.70	9.51	1.11	**2¾**	4.77	**4**	3.55	**16**	1.04
17	0.65	11.05	9.44	1.04	**2½**	4.75	**3¾**	3.50	**15**	1.04
16	0.65	10.40	9.37	0.97	**2¼**	4.77	**3½**	3.44	**14**	1.04
15	0.65	9.75	9.30	0.90	**2**	4.70	**3**	3.60	**12¾**	1.05

It will be observed in columns 6, 8 and 10 that the dilutions have been so arranged that where fractions of a gallon are called for, quarters are used (¼, ½, of ¾), so that the figures really represent gallons and quarts, an arrangement much more convenient than having several different kinds of fractions calling for fractions of quarts. This method of using uniform fractions does not involve any appreciable error, as can be shown by examining the seventh, ninth and last columns in Table XI, in which we give the number of ounces of sulphur in each gallon of diluted solution corresponding to each density (Beaumé degrees). For example, in the seventh column, each gallon, in case of absolute uniformity of dilution, would contain 4.75 ounces; the widest variation below this is 0.05 ounce, in which case the number of ounces is 4.70 instead of 4.75; and the widest variation above is

0.13 ounce, in which case the number of ounces is 4.88 instead of 4.75. In the former case the solution is slightly weaker and, in the latter, slightly stronger, than the regular amount. Such variations are insignificant and could have no influence upon practical results. In the case of solutions for blister-mite, where the dilution is somewhat greater than for San José scale, the slight error is still smaller; and, in the case of solutions diluted for fungicide, the variation of sulphur in a gallon is less than 0.01 ounce.

Application of the method of dilution to solutions of known composition.— The preceding discussion of the data embodied in Table XI should make clear the fact that the dilutions given in the table for each degree (Beaumé) have been so adjusted as to give accurate results and make sure that each gallon of diluted solution will have the same number of ounces of sulphur, when the Beaumé degrees and the sulphur value are those given in Table XI. But we have seen in Table X that there is considerable variation in the relation of density to percentage of sulphur, and the question arises as to whether the adjustment of density to the percentage of sulphur, as given in Table XI is sufficiently accurate for practical purposes. We can test the question readily by applying to all the results in Table X the degrees of dilution given in Table XI and then ascertaining how closely the amount of sulphur which should be in the diluted solution agrees with the amount found by applying our method of dilution. We have made comparison only in case of the dilution for San José scale, because any discrepancies would be more marked than in the case of solution for blister-mite and fungi, when the dilution is greater. The results of our comparison are given in Table X in the fourth, fifth, ninth and tenth columns. The figures in these columns give both the percentage of sulphur in the diluted solution and the number of ounces of sulphur in one gallon of diluted solution. If the solutions in the sixty-two cases whose composition and density are given in Table X, were diluted on the basis of their actual content of sulphur, each gallon of diluted product would contain 3.45 per ct. of sulphur, equal to 4.75 ounces per gallon. The figures for these values given in Table X represent the results obtained by applying the method of dilution given in Table XI, just as if we knew nothing about the actual composition of the solution except as estimated in that table on the basis of density in Beaumé degrees. Bearing in mind that the figures in the fourth and ninth columns should, if absolutely accurate, be uniformly 3.45 per ct., we notice that in about fifty of the sixty-two cases the variation is not more than 0.2 per ct. from 3.45. The lowest value is 3 per ct., or 0.45 per ct. low; the highest value is 3.95 per ct. which is 0.50 per ct. high. Expressed in ounces of sulphur per gallon of diluted solution, we can state the results as follows: If the solutions were accurately diluted, each gallon would contain 4.75 ounces of sulphur; but diluted on the basis of composition, as dependent upon density shown by Beaumé degrees, each gallon contains an amount of sulphur varying more or less from the correct figure (4.75). In the lowest case, one gallon of solution contains 4.13 ounces of sulphur or about one-half ounce too little of sulphur. It is doubtful if this deficiency in sulphur would appreciably affect the destructive power of the wash when applied to San José scale. In six cases, the diluted wash was one-third of an ounce below the specified amount, while in seven cases the amount was below only to an inappreciable extent. In the remaining cases, the amount was practically as required, or else more or less in excess, varying from 4.76 up to 5.47 ounces, being, in the highest case, nearly three-fourths of an ounce in excess. The values in Table XI have, in general, been so adjusted as to obtain solutions after dilution with more, rather than with less, sulphur than the required amount. It is safe to say that methods in previous use have obtained, with solutions varying widely in density, nothing like the accuracy possible with the method given in Table XI, which is based upon all the data available for making the needed calculations. The method gives most excellent results when applied to concentrated commercial mixtures and also to home-made preparations that are properly handled during the operation of boiling.

A comparison of methods of dilution was made with two samples of lime-sulphur solution; one tested 21.6° B. and the other 33.6° B. Each one was diluted in two ways, (1st) by the method given in Table XI, and (2nd) by the method given in Bulletin No. 320, the diluted solution being made to have a density of 4.5° B. Solutions of proper strength should, after dilution, contain about 3.45 per ct. of sulphur or 4.75 ounces of sulphur per gallon. The results are indicated in the following tabulated statement:

TABLE XII.—COMPARISON OF RESULTS BY DIFFERENT METHODS OF DILUTION.

Results by old method					Results by new method		
Density of original solution	Amount of dilution	Density of diluted solution	Sulphur in diluted solution	Sulphur in diluted solution per gallon	Amount of dilution	Sulphur in diluted solution	Sulphur in diluted solution per gallon
Deg. B.	*Sol'n : Water Gals.*	*Deg. B.*	*Per ct.*	*Ozs.*	*Sol'n : Water Gals.*	*Per ct.*	*Ozs.*
21.6	1 : 4½	4.5	3.03	4.17	1 : 3¾	3.50	4.82
33.6	1 : 8½	4.5	3.44	4.69	1 : 8¼	3.50	4.82

These results show that in case of the weaker solution, dilution to 4½° B. gives too weak a spraying mixture, containing only 3.03 per ct. of sulphur, instead of 3.45, and 4.17 ounces of sulphur per gallon instead of 4.75, while dilution by the new method gives a solution of strength slightly higher than required (3.5 per ct. of sulphur or 4.82 ounces per gallon). In case of the concentrated solution, dilution by either method gives nearly the same results. It would appear, therefore, that in case of home-made mixtures, the old method of diluting to a density of 4½° B. is apt to give too weak solutions.

EFFICIENCY OF DIFFERENT FORMULAS USED IN MAKING LIME-SULPHUR WASH.

Under this head we wish to bring together various facts of interest and consider them briefly in their bearing on the advantages and disadvantages of using different proportions of lime, sulphur and water. The best combination of proportions of these constituents will meet the following conditions:

(1) *The proportions of lime and sulphur* should be such that there will be just enough of each to combine with the other without leaving any uncombined lime or sulphur to go into the sediment. This condition works for efficiency in bringing into solution all lime and sulphur, so that when fairly pure materials are used, practically no sediment is formed and never any that requires removal or other attention. The proportions of lime and sulphur which meet this condition should be, according to the results of our experiments, not less than 2 nor more than 2.25 parts of sulphur for 1 part of lime.

(2) *The proportions of lime and sulphur* should be such as to furnish the largest amount of the soluble compound containing most sulphur, calcium pentasulphide (CaS_5). This condition, as well as the one preceding, is met most completely in our experiments by using lime and sulphur in the ratio of 1:2.25.

(3) *The proportions of water to lime and sulphur* should be such as to enable the chemical changes to take place quickly and to form as concentrated a solution as possible, while utilizing with least loss the lime and sulphur. The proportion of water which we have found most effective for all purposes is about 3.5 parts for 1 part of lime and sulphur, although good results may be obtained when the water is not lower than 3 to 1 of lime and sulphur. The chemical reaction between the lime and sulphur can not take place completely unless the particles of lime and sulphur are kept in a finely divided condition and this can be accomplished satisfactorily only when the amount of water is sufficient. When the proportion of lime and sulphur to water is large, the particles

compact in masses more easily and are more difficult to break up, resulting in the formation of lumps that remain unchanged and help increase the amount of sediment. We have noticed also that when smaller amounts of water are used, the soluble thiosulphate is changed into insoluble sulphite; the amount of sediment is thereby increased, while the amount of lime and sulphur in solution is decreased.

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The combination of constituents that appears best to meet the largest number of desirable conditions is the following, stated in round numbers:

36 pounds of lime (pure lime, CaO, used as basis).

80 pounds of high-grade, finely-divided sulphur.

50 gallons of water.

In connection with this formula, it is necessary to call attention to the kind of lime and sulphur to be used and also to certain details in the operation of making the preparation.

(1) *Kind of lime.* It is desirable *to use only the best kind of fresh commercial quicklime,* commonly called stone-lime, lump-lime, etc., and this means lime containing the highest amount of calcium oxide (CaO). While slaked lime of high purity can be used, the commercial products should be avoided on account of uncertain composition and the larger amount required (at least one-third more). *Air-slaked lime should under no circumstances be used,* because it consists more or less largely of carbonate of lime, which, in experiments made by us, has proved wholly worthless, because no appreciable chemical reaction takes place when it is boiled with sulphur and water. Lime containing more than 5 per ct. of magnesium oxide should not be used, because, as shown in Bulletin No. 319, it causes unnecessary loss of sulphur, produces poisonous hydrogen sulphide, and increases the amount of sediment. It is possible to obtain commercial lime containing 95 per ct. or more of pure lime (calcium oxide, CaO) and this should be used. The use of lime containing less than 90 per ct. of pure lime should be avoided.

When lime containing impurities is used, more than 36 *pounds must be taken in order to obtain* 36 *pounds of pure lime.*

Use 38 pounds of lime containing 5 per ct. of impurities (95 per ct. pure).

Use 40 pounds of lime containing 10 per ct. of impurities (90 per ct. pure).

Use 42 pounds of lime containing 15 per ct. of impurities (85 per ct. pure).

The agricultural law of New York requires that in the case of lime sold for agricultural purposes, the minimum percentage of calcium oxide (pure lime) shall be guaranteed. No one should, therefore, purchase lime for use in making the lime-sulphur wash except under guarantee, *and only lime guaranteed to contain more than* 90 *per ct. of calcium oxide should be used.* For a simple method of determining approximately the purity of lime, see pages 447–449.

(2) *Kind of sulphur.* Sulphur of high-grade purity (over 98 per ct.) and as finely divided as possible, should be used. This can be easily obtained. In our experience, equally good results are given by flowers of sulphur or sulphur flour when in equally fine powder. Ground crystalline sulphur is not usually fine enough to use to advantage, since the coarser particles are not easily dissolved and therefore pass largely into the sediment.

(3) *Some details of making solution.* It is not our purpose to repeat all the well-known details of making the lime-sulphur wash, but simply to call attention to particular features that are essential to the best results in the use of the Geneva formula. Two special precautions are to be observed in addition to those usually mentioned: Keeping up the volume of solution during boiling and making the lime and sulphur as finely divided as possible.

(a) *The level of the mixture during boiling should be kept near the* 50-*gallon mark,* not being allowed to drop more than an inch below; this is accomplished by adding water from time to time in the required amounts. It is preferable to add water in small amounts at more frequent intervals than larger amounts less often, since the boiling is less interfered with. When the boiling is completed, the level of the liquid should be made up to the 50-gallon mark, if not already there. The amount of water necessary to add during the boiling varies with the intensity of the fire under the kettle and also with the temperature of the surrounding air. Larger amounts must be added in warm weather than in cold. When the kettle contains 50 gallons of mixture at the close of boiling, this volume will shrink on cooling to the temperature of the air, so that when cooled there will be only 46 to 48 gallons, according to the temperature to which it is cooled. It should be remembered that the object of keeping the solution from becoming concentrated during boiling is to prevent the conversion of thiosulphate into insoluble sulphite. (b) The completeness with which the lime and sulphur combine depends, other conditions being favorable, upon getting and keeping the lime and sulphur in as finely divided condition as possible. This is accomplished in case of the lime by careful slaking; in case of sulphur, it must be brought about largely by more or less constant stirring of the mixture, especially the sediment at the bottom of the kettle. The larger proportion of water for lime and sulphur makes this easier to accomplish than in the case of formulas in which large amounts of lime and sulphur are used.

(c) Density of solution. When the solution is made to the 50-gallon mark at the close of boiling, it will be found when cooled to about 60° F. to have a density of 24° to 25° B.

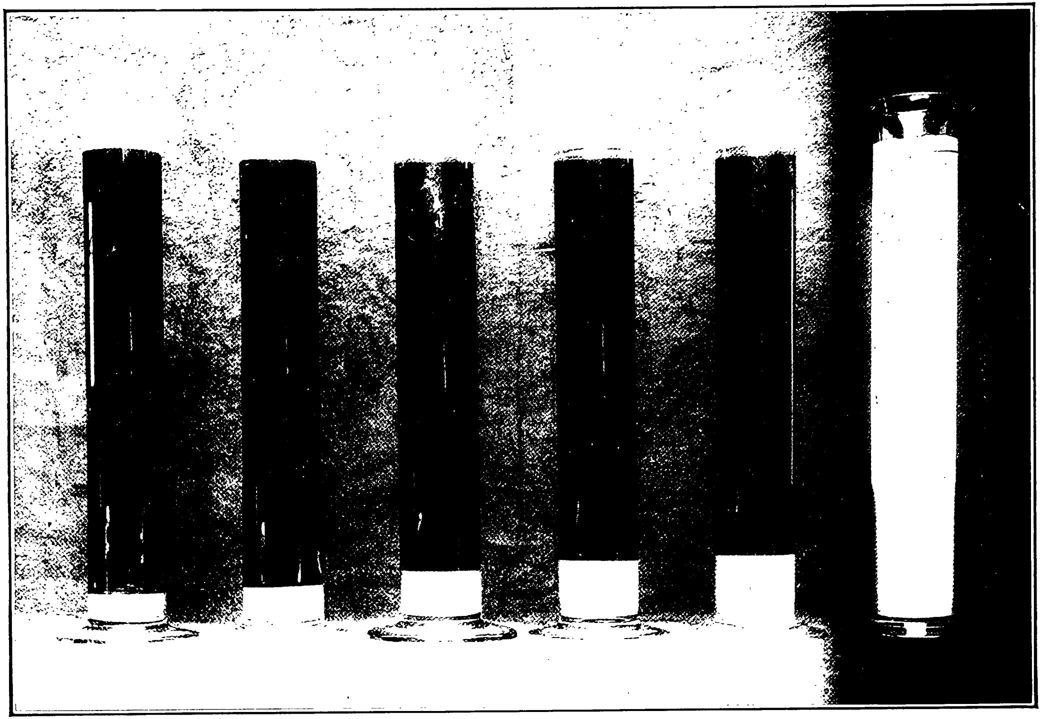
We will briefly call attention to the advantages and disadvantages of the Geneva formula.

Advantages of formula.—(1) The lime and sulphur are in those proportions called for by the usual chemical reactions; the combination is practically complete for both lime and sulphur. (2) The formation of sediment, whether of unused sulphur and lime, or of sulphite formed from thiosulphate, is at a practical minimum; with fairly pure materials, there is practically no sediment. (3) The percentage of sulphur in the form of pentasulphide (CaS_5) is highest. (4) The proportion of solids to water is such as to enable one most effectively to keep the lime and sulphur from forming lumps and therefore in the finely-powdered condition required for complete chemical action. (5) During the boiling, there is less danger of the solution becoming so concentrated as to increase unduly the formation of sulphite from thiosulphate, a condition easily occurring in case of the use of more lime and sulphur in proportion to water.

(6) Solutions made by this formula, when stored, have less tendency to change than more concentrated solutions.

(7) Solutions made at different times by this formula have, in our experience, run very uniform in composition. With other formulas, variable results are obtained at different times when working under conditions as uniform as possible.

Disadvantages of formula.— The only disadvantage that has suggested itself in our experience is the fact that the solution prepared by this formula is less concentrated; on this account, more separate boilings must be made and, if stored, a larger number of containers must be used. In comparison with the formula used by the Station during 1910 (65 pounds of lime, 125 of sulphur, and 50 gallons of water), it would require 150 gallons of the solution made by the new formula to equal 100 gallons made by the other, assuming that sediment and solution can be used or else separated without loss of solution; in other words, the time of making solution and the number of barrels for storage would be increased apparently one-half. To offset this inconvenience, the preparation of solutions by the old formula involved a loss of 32 pounds of material as sediment in comparison with 7 pounds by the new formula; the old mixture is more difficult to keep well stirred. In general, it has been the custom to throw away the sediment in whole or part and with it all the solution adhering to it, so that, of every 50 gallons prepared, considerably less than 50 gallons is actually utilized. The solution prepared by the new formula is largely or wholly pentasulphide; with the old formula, tetrasulphide chiefly was formed, with little or no pentasulphide.



10 20 30 40 50 100

PLATE I.— AMOUNT OF SEDIMENT IN LIME SULPHUR WASH MADE FROM LIME WITH DIFFERENT PERCENTAGES OF IMPURITY.

(White portions in cylinders show sediment; figures below plate indicate percentages of impurity in lime used.)

METHOD FOR APPROXIMATE DETERMINATION OF IMPURITIES IN LIME.

This test is based on the fact that when one part, by weight, of pure lime (calcium oxide, CaO) and two parts of sulphur are boiled with plenty of water for one hour, the lime and sulphur go into solution, only slight amounts of sediment being formed. If the lime contains impurities (oxides of magnesium, iron, aluminum, etc., and carbonate of magnesium, calcium, etc.), these do not go into solution but remain as sediment, together with any undissolved sulphur not acted upon because of an insufficient amount of pure lime, caused by impurities in the lime used. The amount of sediment thus formed can be utilized as a measure of the amount of impurities existing in the lime. The method, in brief, consists in making a lime-sulphur mixture on a small scale and measuring the sediment.

The apparatus required consists of (1) a granite-iron-ware deep vessel holding 1½ to 2 quarts, used for boiling the mixture in; (2) a spoon of the same material; (3) a glass cylinder about 2½ inches in diameter, 12 to 15 inches high. A cylinder graduated in cubic centimeters is the most convenient form. A plain cylinder, costing less, can be used but the column of sediment must be measured in inches and the diameter must be very nearly 2½ inches. Such cylinders can be obtained of Bausch & Lomb Optical Co., Rochester; and (4) a stick for stirring and measuring, on which is cut a notch at the point where the surface of the water stands when one quart of water is placed in the dish and the stick placed vertically in the water, one end resting upon the bottom of the dish.

The method of carrying out the test is as follows: Weigh carefully 2 ounces of the lime to be tested, place it in the boiling vessel and slake with water, adding the water gradually and being careful not to smother the lime with too much water. Stir with the spoon until the lime is thoroughly slaked and a thick, uniform paste or milk of lime is formed. Then add water enough to fill to the notch on the stick, after which place over a fire and boil. Weigh 4 ounces of fine, high-grade flowers of sulphur and when the milk of lime begins to boil add the sulphur gradually, stirring in vigorously with the spoon. Allow the mixture to *boil gently* for one hour stirring most of the time to break up any lumps of sulphur, using the spoon or stick or both according to convenience and effectiveness. During the boiling, measure the height of the mixture about once every ten minutes by means of the notched stick and if the level of the liquid has dropped below the notch, add enough hot water to bring the level back to the notch. When the mixture has boiled one hour, let it cool and then, after stirring it up thoroughly with the spoon, pour quickly into the glass cylinder, being careful to get in all the sediment. Allow it to stand over night and then notice the height of the column of sediment by reading the number of divisions (cubic centimeters) at the upper surface of the sediment or by measuring with a rule. The percentage of impurities may be found by consulting the following table. In the third column is given for each percentage of impurity the number of pounds of lime that it will be necessary to use in making the lime-sulphur mixture by the Geneva formula:

Table XII.—Percentages of Impurities for Different Amounts of Sediment, and Amounts of Lime to Use.

Number of cubic centimeters of sediment.	Height of column of sediment in inches.	Percentage of impurities.	Number of pounds of lime to use to contain 36 pounds of calcium oxide
30	½	5	38
50	¾	10	40
70	1	15	42
90	1¼	20	45
105	1½	25	48
120	1¾	30	51

As previously stated, we strongly advise not using any lime that contains over 10 per ct. of impurities. The simplest way is to purchase lime of guaranteed composition, containing not less than 90 per ct. of pure calcium oxide and not over 5 per ct. of magnesium compound. The foregoing test can, however, be made use of whenever one is in doubt in regard to the purity of the lime thus purchased or for testing a sample of lime previous to purchasing.

It is a matter of interest to notice the results obtained by applying this test to mixtures of pure lime (calcium oxide) and known amounts of magnesium oxide and calcium carbonate. The same results were obtained whether we used magnesium oxide or calcium carbonate as the impurity. In each case we used one quart of water and four ounces of sulphur and carried out the test in the manner already described, allowing the mixture to stand sixteen hours before measuring the sediment.

Table XIII.— Relation of Amount of Impurities to Amount of Sediment.

Amount of pure lime used.	Amount of magnesium oxide or calcium carborate used.	Percentage of impurities on basis of 2 ozs. pure lime.	Cubic centimeters of sediment in glass cylinder.	Height of column of sediment.
0 oz.	2 oz.	100	350	5¼ inches.
1 "	1 "	50	180	2¾ "
1.2 "	0.8 "	40	150	2¼ "
1.4 "	0.6 "	30	120	1¾ "
1.6 "	0.4 "	20	90	1¼ "
1.8 "	0.2 "	10	50	¾ "

The results of these experiments are clearly shown in the accompanying illustration, for which the cylinders with their sediments were photographed.

This method can be used also in testing samples of sulphur as to suitability for making lime-sulphur solutions. One solution is made with a sample of sulphur known to be of high grade of purity and finely divided, using lime not less than 95 per ct. pure. A solution is thus made with each of the samples of sulphur to be tested, using the same lime. The test is carried out in each case in the manner described above. The amount of sediment is compared with that obtained in the first case; any increase of sediment over indicates impurities in the sulphur of particles too coarse to dissolve. The sediment should be examined carefully for the presence of coarse, yellow particles of undissolved sulphur which can be readily seen if present in appreciable amount.