ON THE RÔLE OF CALCIUM HYDROXIDE IN HYDRATED LIME-ACID LEAD ARSENATE SPRAYS

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INTRODUCTION

Hydrated lime has been used successfully in many parts of the country to reduce or eliminate injury to tender foliage caused by acid lead arsenate (PbHAsO$_4$). In New Jersey, however, there are on record in the office of the State entomologist at least two authentic instances of severe arsenical injury to foliage caused by hydrated lime-acid lead arsenate sprays. This paper is the result of an attempt to determine what conditions would make possible such unusual foliage injury. The chemical reactions in vitro of the combination spray are considered first, and its possible effect on foliage is then discussed.

THE REACTION BETWEEN CALCIUM HYDROXIDE (Ca(OH)$_2$) AND ACID LEAD ARSENATE (PbHAsO$_4$)

It has been known for many years that ammonium hydroxide (NH$_4$OH) will react with acid lead arsenate (PbHAsO$_4$) to form a basic lead arsenate. It follows by analogy that calcium hydroxide (Ca(OH)$_2$), or any other base, would likewise tend to convert acid lead arsenate to a more basic compound. Robinson (10) believes that the following reaction takes place in acid lead arsenate-lime sulphur mixtures containing an excess of calcium hydroxide: 3PbHAsO$_4$ + Ca(OH)$_2$ → Pb$_3$(AsO$_4$)$_2$ + CaHAsO$_4$ + 2H$_2$O. This supposition is the only reference to the reaction which the writer has been able to find.

A few semiquantitative experiments on the foregoing reaction were performed by William Moore and the writer, of which the following will serve as an example: Two grams of acid lead arsenate were suspended in 400 c. c. of distilled water containing a few drops of phenolphthalein indicator, and 10 c. c. of a saturated solution of calcium hydroxide were added. The flask was stoppered and shaken until the red color which resulted from the addition of the calcium...
hydroxide disappeared. Another 10 c. c. portion of the calcium hydroxide solution was immediately added to the contents of the flask, and the shaking was resumed until the color again disappeared. In the same manner 12 more 10 c. c. portions of the base were added before the color remained permanently, which occurred 55 minutes after the beginning of the experiment. This experiment was analogous to an acidimetric titration. The amount of calcium hydroxide used was considerably greater than that required by Robinson's equation, indicating the formation of more basic compounds. Since an excess of ammonium hydroxide will convert acid lead arsenate to basic lead arsenate \( \text{Pb}_4\text{PbOH (AsO}_4)_2 \), \( (6,7) \), it is not unreasonable to assume that calcium hydroxide in excess would do likewise; so, for the purpose of discussion, the reaction may be represented by the equation: \( 5\text{PbHAsO}_4 + 3\text{Ca(OH)}_2 \rightarrow \text{Pb}_4(\text{PbOH})_2(\text{AsO}_4)_2 + 3\text{Ca}_3(\text{AsO}_4)_2 + 5\text{H}_2\text{O} \). The reaction was completed sooner by the addition of 10 c. c. portions of the calcium-hydroxide solution than by the addition of 50 c. c. portions, apparently in contradiction to the law of mass action. The particles of acid lead arsenate must have been less susceptible to hydrolysis in higher concentrations of calcium hydroxide.

EFFECT OF CALCIUM HYDROXIDE ON "SOLUBLE ARSENIC" IN HYDRATED LIME-ACID LEAD ARSENATE SUSPENSIONS

A comparison was made between the amounts of soluble arsenic in filtrates from suspensions of acid lead arsenate and in filtrates from suspensions of hydrated lime-acid lead arsenate. Two grams of acid lead arsenate, or 2 gms. acid lead arsenate plus calcium hydroxide in considerable excess of the amount required to complete the reaction were shaken at intervals for an hour in 1-liter flasks with 400 c. c. of water. The suspensions were then filtered and the filtrates analyzed for water-soluble arsenic by the analytical part of the method of the Association of Official Agricultural Chemists \( (1) \). About 50 analyses were made, for which different brands of acid lead arsenate were mixed with hydrated and freshly slaked lime in both tap and distilled water. In every case the amount of soluble arsenic from acid lead arsenate was substantially increased by the addition of the lime. Some characteristic results are shown in Table I. These are in contradiction to the tradition that "lime takes care of soluble arsenic." It is not asserted, however, that the relative amounts of soluble arsenic in suspensions of acid lead arsenate with and without the lime would have been the same if the suspensions had been agitated for a period longer than one hour. Cook and McIndoo \( (2, p. 17) \) have shown that in acid lead arsenate-Bordeaux combinations soluble arsenic decreases as the period of agitation increases, the converse being true for suspensions of acid lead arsenate alone. This may be true of calcium hydroxide-acid lead arsenate combinations also. It is maintained, nevertheless, that these results indicate the probability of the existence of a higher concentration of soluble arsenic in a spray tank containing the combination spray than in one containing only acid lead arsenate.
Calcium Hydroxide and Lime and Lead Arsenate Sprays

**Table I.**—Relative weights of arsenic oxide (As₂O₃) made soluble in a suspension of acid lead arsenate and in suspensions of acid lead arsenate plus calcium hydroxide

<table>
<thead>
<tr>
<th>Added to 2 gms. acid lead arsenate and 400 c. c. distilled water</th>
<th>Weight of arsenic oxide found in filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nothing.</td>
<td>0.0004</td>
</tr>
<tr>
<td>1 gm. hydrated lime.</td>
<td>0.0022</td>
</tr>
<tr>
<td>2 gms. hydrated lime.</td>
<td>0.0039</td>
</tr>
<tr>
<td>1 gm. freshly slaked lime.</td>
<td>0.0017</td>
</tr>
<tr>
<td>2 gms. freshly slaked lime.</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

**THE EFFECTS OF Ca(OH)₂+PbHAsO₄ SPRAY ON FOLIAGE**

If a combination spray contains more soluble arsenic than an acid lead arsenate spray, the former must cover the foliage with a higher concentration of soluble arsenic than the latter, at least while the spray is drying. But the probability of foliage injury is supposed to be directly proportional to the concentration of soluble arsenic on the leaf surface, and the combination spray is known to be safer than the acid lead arsenate. The problem is, therefore, to reconcile these apparently incompatible facts.

If the reaction between acid lead arsenate and calcium hydroxide be borne in mind, it will be evident that the compound forming the soluble arsenic of the combination spray will not be the same as that forming the soluble arsenic of the acid lead arsenate spray. In the former case it should be a solution of acid calcium arsenate (CaHAsO₄) or tricalcium arsenate (Ca₃AsO₄·2H₂O); in the latter case a solution of arsenic acid (H₃AsO₄), which, according to McDonnell and Graham (8), results from the hydrolysis of acid lead arsenate. Moore suggested that equal weights of arsenic in arsenic acid and in the calcium arsenates might have a greater toxicity in the former compound than in the latter. If such be the case, soluble-arsenic determinations, without a knowledge of the soluble compounds concerned, would fail to serve as indices of the phytotoxicity of arsenical sprays, and the low toxicity to foliage of PbHAsO₄ + Ca(OH)₂ sprays as compared with that of PbHAsO₄ sprays might be explained.

Moore's suggestion was tested experimentally by the writer in 1924 at Rutgers University. Neutral solutions of the arsenates of sodium, potassium, calcium, and barium were prepared by partial neutralization of identical volumes of arsenic-acid solution by the hydroxides of the four metals. The end points were determined by the usual colorimetric hydrogen-ion methods. Each solution was diluted with the volume of water requisite for an arsenic concentration of 0.184 gm. per liter. In neutral solution, of course, all the arsenates were present as acid salts. Young Black Valentine bean plants were sprayed in a greenhouse, temperature 30° C., with each of the foregoing solutions and with a solution of arsenic acid of the same arsenic concentration. Both surfaces of the leaves were sprayed, the pot soil being covered by a towel to catch the drippings. Large drops hanging from the leaf tips after spraying were jarred off. The results of this experiment are outlined in Table II.
TABLE II.—Effect of five arsenate solutions on Black Valentine bean foliage (arsenic concentration 0.184 gm. per liter)

<table>
<thead>
<tr>
<th>Hours after spraying</th>
<th>Hydrogen</th>
<th>Potassium</th>
<th>Sodium</th>
<th>Calcium</th>
<th>Barium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Losing turgidity</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>4</td>
<td>Losing turgidity</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>8</td>
<td>Completely flacid</td>
<td>Completely flacid</td>
<td>Completely flacid</td>
<td>Losing turgidity</td>
<td>Losing turgidity</td>
</tr>
<tr>
<td>24</td>
<td>Shriveled and dry</td>
<td>Shriveled and dry</td>
<td>Shriveled and dry</td>
<td>Shriveled and dry</td>
<td>Terminal leaves slightly curled</td>
</tr>
<tr>
<td>48</td>
<td>Shriveled and dry</td>
<td>Shriveled and dry</td>
<td>Shriveled and dry</td>
<td>Terminal leaves slightly curled</td>
<td>Terminal leaves slightly curled</td>
</tr>
</tbody>
</table>

Arsenic acid was most toxic to bean foliage. The arsenates of sodium and potassium were almost as toxic as the acid and were about equal in their effects. There was a wide difference in the high toxicity of the foregoing arsenates and in the almost complete innocuousness of the arsenates of calcium and barium. The former group killed the plants, whereas the latter merely caused a slight curling of the terminal leaves. Moore's supposition that arsenic in calcium arsenate might be less toxic to foliage than arsenic in arsenic acid was thus strikingly verified.

The fact that neutral solutions of the arsenates of sodium and potassium were nearly as toxic as the solution of arsenic acid shows that the difference in hydrogen-ion concentration between arsenic acid and neutral calcium arsenate solution is not the cause of the great difference in toxicity of the two solutions. The writer believes that this difference may be at least partly explained by the difference in solubility of arsenic acid and calcium arsenate. Cell penetration by ions or molecules is partially a diffusion process, the rate of which depends on the concentration gradient between the inside and outside of cells. As the spray dries, the more soluble arsenic acid forms a film on the leaf surface of higher arsenic concentration than does the calcium arsenate solution, already nearly saturated. Of course, differences in percentage of ionization and the specific influence of the cations on cell permeability may also play a part.

EXPLANATION OF THE OCCASIONAL INJURY TO FOLIAGE CAUSED BY Ca(OH)\(_2\)+PbHAsO\(_4\) SPRAYS

The foregoing experiments suggest that a calcium hydroxide-acid lead arsenate spray which throws a trace of calcium arsenate into solution would not be injurious to foliage unless a further chemical change should take place on the leaves—a change which would permit a higher concentration of soluble calcium arsenate to exist on the leaf surface than is present when the spray is applied. As long as calcium hydroxide is present on the leaf surface it will probably repress the ionization of calcium arsenate below a potentially injurious level. But if the calcium hydroxide is converted to calcium carbonate (CaCO\(_3\)) by carbon dioxide (CO\(_2\)) of the air, its protective effect would be lost. Lovett (5) says, "Wherever CaO is present in even slight excess so that Ca(OH)\(_2\) may be found qualitatively in solution, no soluble arsenic will occur," but as for calcium carbonate "this latter material reacts very slowly with the calcium salts and does not prevent the formation of soluble arsenic."
A few experiments were made by the writer to determine how long a heavy coating of calcium hydroxide on a leaf surface would resist total conversion to calcium carbonate. A few drops of a calcium hydroxide solution were added to 200 c. c. of distilled water containing phenolphthalein until the water was barely pink. The flask was shaken until the color disappeared. A normal bean leaf was dropped into the flask, which was again shaken. No color developed. To another 200 c. c. of distilled water similarly treated was added, immediately after it had dried, a bean leaf which had been sprayed on both sides with a freshly slaked lime suspension. The flask was shaken for a few minutes and the contents titrated. The solution required 2.85 c. c. of 0.01 normal hydrochloric acid to decolorize it. Eight days later a solution from three leaves, which bore a heavy white coating, was titrated. Only one drop of the acid was required to decolorize the faintly pink solution. Calcium hydroxide was no longer present. Similar experiments were made on leaves sprayed with a mixture of calcium hydroxide and acid lead arsenate; the former was destroyed within eight days.

In practice, then, one would expect calcium hydroxide to be converted to calcium carbonate within a few days. Then, according to Patten and O'Meara (9), carbon dioxide would react with tri-calcium arsenate and convert it to the more soluble acid calcium arsenate from which foliage injury might result, provided weather conditions were conducive to the penetration of arsenic into the epidermal cells. It is also possible that carbonic acid might react with basic lead arsenate, rendering it more soluble, but no experimental evidence seems to exist for such a reaction, which, therefore, will not be considered. The recent extensive experiments of Morris, Swingle, and Burke (11) and those of Fernald and Bourne (4) have determined the meteorological conditions under which maximum arsenical injury to foliage will occur. High humidity and temperatures over a long period of time are, according to these authors, the optimum conditions for arsenical injury. Visible wetness of foliage is apparently of no importance. It is probable, then, that the cases of arsenical injury to foliage in New Jersey by Ca(OH)₂ + PbHASO₄ sprays were caused by dissolved acid calcium arsenate under hot and humid conditions, which are so likely to occur in that State during the summer.

**SUMMARY**

The following series of reactions probably occur in combination calcium hydroxide-acid lead arsenate sprays:

1. In spray tank and on foliage while there is an excess of calcium hydroxide: $5\text{PbHASO}_4 + 3\text{Ca(OH)}_2 \rightarrow \text{Pb}_4\text{(PbOH)}_8\text{(AsO}_4\text{)}_3 + \text{Ca}_3\text{(AsO}_4\text{)}_2 + 5\text{H}_2\text{O}$

2. On foliage: $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

3. On foliage: $\text{Ca}_3\text{(AsO}_4\text{)}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CaHAsO}_4 + \text{CaCO}_3$

The usual protective effect on foliage of calcium hydroxide in acid lead arsenate combination sprays may lie in the fact that soluble calcium arsenate from such sprays is less toxic to foliage than soluble arsenic acid from sprays of acid lead arsenate alone. Apparently under warm and humid conditions, however, such as often occur in New Jersey, acid calcium arsenate (equation 3) may become present
on foliage sprayed with Ca(OH)$_2$+PbHAsO$_4$, in high enough concentration and over a sufficient period of time to cause severe foliage injury.

LITERATURE CITED


