### ZINC CARRIERS FOR CROPS

# Influence of Slowly Soluble, Soluble, and Chelated Zinc on Zinc Content and Yield of Alfalfa

**E. R. HOLDEN and J. W. BROWN**
**U. S. Fertilizer Laboratory, Soil and Water Conservation Research Division, U. S. Department of Agriculture, Beltsville, Md.**

The results obtained with growth of alfalfa on two widely different soils under greenhouse conditions show that slowly soluble zinc carriers must be at least as fine as 200-mesh for satisfactory performance. Low applications of zinc glasses, though having less effect on zinc content of the crop, increased yield more than a fine crystalline form of zinc sulfate. Zinc ammonium phosphate powder supplied adequate zinc, but not when granulated with clay. Hemimorphite ($2\ ZnO.H_2O.SiO_2$) dissolved at a satisfactory rate in a neutral Florida sand, but not in a western calcareous loam. Willemite ($2\ ZnO.SiO_2$) supplied only very low levels of zinc, and sphalerite (ZnS) had no effect on the crop. Zn EDTA increased zinc content of the crop twice as much as zinc sulfate in neutral soil and up to six times as much in calcareous soil. The influence of the zinc chelate on crop zinc was relatively stable over a 9-month period.

Crops have been grown many years without adding zinc to replace the amounts taken from the soil and the incidence of zinc deficiency is increasing. This situation and the growing use of irrigated lands deficient in available zinc have led to greater use of zinc in fertilizer programs. On some soils, the addition of zinc has become standard practice for growing corn, beans, nut and fruit trees, vegetables, and other crops (*20, 21*).

Zinc deficiency is most commonly corrected by use of zinc sulfate, a water-soluble material. The much less soluble oxide, phosphate, and carbonate often produce results comparable to those obtained with zinc sulfate (*5, 17*). Zinc from these compounds is relatively immobile in the soil (*3, 6*), so that surface and other placements not distributed satisfactorily in the root zone are often ineffective. Consequently, application levels are frequently higher than would be necessary with efficient utilization of the applied zinc.

Large applications of soluble zinc on some coarse-textured soils increase leaching losses (*18*) and may be toxic to crops. Crop nutrition may also be affected by certain unfavorable interactions between zinc and other nutrients. The application of zinc tends to lower phosphorus uptake, and fertilization with phosphorus can reduce zinc uptake to deficiency levels (*4, 8*). The inhibiting effect on phosphorus uptake is more likely to occur when zinc is mixed with a phosphate fertilizer (*2*). Under some conditions, soluble zinc, as well as copper or manganese, can induce iron chlorosis and reduce root growth (*7, 19*). These circumstances suggest that slowly soluble carriers or chelates might be useful in controlling active concentration of the applied zinc.

With view to determining the properties and effects of carriers that release zinc slowly in soils, experimental sodium-zinc silicate glasses were developed. Relative performance of these glasses, commercial micronutrient glasses, zinc minerals with low solubilities, zinc ammonium phosphate, and disodium zinc(ethylenedinitrilo)tetraacetate (Zn EDTA) was determined in a greenhouse experiment, using zinc sulfate as the standard of comparison. Ranger alfalfa (*Medicago sativa* L.) was grown on Lakeland sand, a coastal soil subject to much leaching, and on Sagemoor very fine sandy loam, a western zinc-deficient soil. The effectiveness of the test materials was followed by means of yield and zinc content data of consecutive harvests.

## Materials and Experimental Procedure

**Soils.** The Lakeland soil, obtained from central Florida, contained mostly quartz sand with small amounts of bronzite, tourmaline, zircon, and rutile, but little or no phosphate or clay minerals. Dithizone-extractable zinc (*16*) in the soil was 1.1 p.p.m. The Sagemoor soil, obtained from Prosser, Wash., contained some calcium carbonate particles, weathered lava, and many basaltic minerals. X-ray diffraction pattern of the clay fraction indicated a large amount of montmorillonite and a small amount of kaolinite. Titratable alkalinity of the soil was 2.4 meq. per 100 grams and hydrochloric acid–extractable zinc, 1.4 p.p.m. (*14*). Other characteristics of the soils were:

| | *Lakeland Soil* | *Sagemoor Soil* |
|---|---|---|
| Exchange capacity, meq./100 g. of soil | 2.4 | 15.2 |
| pH | 4.4 | 7.8 |
| Organic carbon, % | 0.6 | 0.3 |
| Moisture capacity between tension of 0.1 and 15 atm., % | 3.7 | 24.7 |

The Lakeland soil was limed with high-purity calcium carbonate and magnesium oxide in amounts equivalent to 2400 and 800 pounds of calcium carbonate per acre (2,000,000 pounds of soil), respectively. After the Lakeland soil had equilibrated 3 weeks with the liming materials, both soils were fertilized with reagent grade chemicals, which had been analyzed and found to contain only negligible amounts of zinc. In chemical form, the compounds were ammonium nitrate, monocalcium phosphate, sodium molybdate, ferric chloride, boron trioxide, or normal sulfates. The levels of application in pounds per acre (weight basis) were: nitrogen, 200; phosphorus, 131 (phosphorus pentoxide, 300); potassium, 166 (potassium oxide, 200); sulfur, 72; copper, 1.5; manganese, 5.0; iron, 5.0; molybdenum, 0.2; boron, 1.5; cobalt, 0.01. Following the second and third harvests, supplemental fertilizer was added at the pound per acre levels of: nitrogen, 75; potassium, 62.2 (potassium oxide, 75); sulfur, 25. Following the fifth harvest, the Sagemoor soil also received the equivalent of 62.2 pounds of potassium (75 pounds of potassium oxide) and 25 pounds of sulfur per acre.

**Zinc Carriers.** The chemical composition of the test materials is given in Table I. Glasses 3476 and 3473 were prepared with the necessary compositions of the general formula $Na_2O.SiO_2.30\%$ ZnO for nutrient release rates in the range previously found optimal for boron (*12*). The other carriers were obtained from commercial sources, and the U. S. National Museum. Sieve analyses of glass and mineral composite samples—i.e., materials not classified with respect to particle size—are shown in Table II. All of the carriers were mixed thoroughly with 7.75 pounds of each soil at the level of 3 p.p.m. of zinc and in triplicate, except zinc sulfate which was added at 0, 1.5, 3, and 6 p.p.m. with two sets of triplicate pots at 0 and 3 p.p.m. The treated soil was placed in undrained No. 10 plastic-coated cans, further protected

### Table I. Chemical Composition of the Experimental Materials

| Material | Zinc Content, % | Other Constituents, % |
|---|---|---|
| Zinc sulfate, heptahydrate | 23.39 | S 11.60 |
| Glasses | | |
| 504A[a] | 24.93 | Al 4.97; B 0.75; Ca 7.88; Cu 0.34; Fe 2.52; K 2.41; Mg 0.28; Na 5.01; Si 14.99 |
| 3476[b] | 23.80 | Na 16.20; Si 22.68 |
| 3473[b] | 23.60 | Na 14.76; Si 23.70 |
| 502[a, c] | 5.27 | B 2.8; Cu 2.0; Fe 3.9; Mn 9.7; Mo 0.13 |
| 501[a, c] | 5.26 | B 2.0; Cu 2.0; Fe 12.25; Mn 4.9; Mo 0.13 |
| Zinc ammonium phosphate, powder[d] | 36.76 | N 7.74; P 17.28 |
| Zinc ammonium phosphate, granular containing about 60% clay[d] | 13.47 | N 3.14; P 7.07 |
| Hemimorphite, Sterling Hill, N. J.[e] | 54.49 | Fe 0.03; Si 10.68 |
| Willemite, Franklin, N. J. | 55.95 | Fe 0.77; Mn 0.8; Si 12.06 |
| Sphalerite, Cherokee County, Kan.[f] | 60.99 | Fe 0.24; S 29.88; Si 3.37 |
| $Na_2$ Zn EDTA[g] | 9.59 | |

[a] Sample supplied by Ferro Corp., Cleveland, Ohio.

[b] Melt made at National Bureau of Standards, Washington, D. C.

[c] Values under "other constituents" are "guaranteed analysis" provided by manufacturer. Glass also contains a relatively large amount of Si and lesser amounts of Al, Ca, K, Mg, and Na.

[d] Sample supplied by W. R. Grace and Co., Clarksville, Md.

[e] National Museum sample 101991.

[f] National Museum sample 63702.

[g] Versene Z supplied by Dow Chemical Co., Midland, Mich.

### Table II. Fineness of Composite Materials

| | Material Retained between Mesh Sizes, % of Total | | | | |
|---|---|---|---|---|---|
| | +28 | 28 to 48 | 48 to 100 | 100 to 200 | −200 |
| Glasses | | | | | |
| 504A | 0.03 | 0.9 | 8.8 | 22.7 | 67.2 |
| 3476 | | 5.0 | 20.0 | 25.0 | 50.0 |
| 3473 | | 5.0 | 20.0 | 25.0 | 50.0 |
| 502 | | 0.1 | 4.9 | 23.7 | 71.4 |
| 501 | | 0.1 | 0.4 | 9.8 | 89.7 |
| Hemimorphite | | | 30.3 | 22.6 | 47.0 |
| Willemite | | | 34.9 | 23.1 | 41.9 |
| Sphalerite | | | 36.3 | 22.6 | 41.1 |
| Zinc sulfate | 10.4 | 48.5 | 32.5 | 5.9 | 2.7 |

against contamination by use of polyethylene liners.

**Crop.** Ranger alfalfa was planted with inoculated seed and later thinned to 12 plants per can. Five harvests, cut at the half-bloom stage, were grown from the Lakeland soil and six from the Sagemoor soil. Soil moisture was maintained by adding distilled water about twice daily. The amount of zinc added as an impurity of the distilled water (0.004 p.p.m. of zinc) was approximately 0.1 p.p.m. of zinc per season. Yields and zinc contents of the crop were determined on the oven-dry basis (65° C.).

**Analytical Methods.** The plant material was ignited at 500° C. and analyzed for zinc by the single-extraction dithizone method, as described by Sandell (*15*). The carriers were brought into solution by appropriate methods, after which zinc was determined by titration with potassium ferrocyanide (*13*), iron by dichromate titration, calcium and magnesium by Versenate titration (*9*), copper and aluminum by weighing the oxides, boron by methyl borate distillation and titration, and other elements by ASTM standard methods (*1*). Relative reactivity of the carriers was determined by extracting 16 hours with ammonium acetate of pH 4 (*12*) and titrating zinc in the extracts with potassium ferrocyanide. Interference during titration of zinc was avoided by evaporating the extracts with 1.7 ml. of sulfuric acid to remove ammonium acetate, and by extracting the residue with cupferron and chloroform to remove iron, copper, molybdenum, and manganese (*10*).

## Crop Response to Zinc

The Lakeland soil was not zinc-deficient and the application of zinc did not affect yield. The Sagemoor soil was borderline with respect to zinc deficiency in alfalfa. Visually, the crop was the same whether or not zinc had been added to the soil. Well-defined differences in yield were obtained in the first harvest, but significant differences in yield were less frequent in the next two harvests and there were none in subsequent harvests. Yield response was lost as the result of a decrease in soil pH, which increased the availability of soil zinc. Root confinement to low soil volume greatly hastens base removal by the crop. With five and six harvests being taken, soil pH dropped from 7.1 to about 5.8 in the Lakeland and from 7.8 to 6.9 in the Sagemoor soil.

## Glass Carriers

**Influence of Particle Size.** Yield on the Sagemoor soil and zinc content of the crop on either soil (Table III) varied with sieve fineness of each glass consistently in the first harvest. The coarse 28- to 48-mesh glasses had no effect on the crop. The 48- to 100-mesh glasses increased yield and zinc contents slightly but not significantly. At 100- to 200-mesh, differences between 504A and the control with no added zinc were still nonsignificant, but those for glass 3476 were usually significant at the 1% level and those for glass 3473 were usually significant at the 5% level. When fineness was increased to −200-mesh, all of the glasses increased yield from the Sagemoor soil and zinc contents of the crop on either soil significantly at the 1% level.

Ammonium acetate–extractable zinc varies directly with zinc uptake, as affected by fineness of a particular glass. However, it does not predict uptake satisfactorily when more than one glass composition is involved. For example, the 48- to 100-mesh material of glass 504A with 94.1% extractable zinc had no effect on the crop, while the −200-mesh material of glass 3473 with only 39.5% extractable zinc produced highly significant increases in uptake and yield. Hence, no matter how rapidly zinc is released, slowly soluble zinc carriers must be at least as fine as 200-mesh for efficient use of the applied zinc.

With the imposition of the high fineness requirement, the range of optimal reactivity is roughly defined by the results with the −200-mesh size of glasses 3473 and 3476. Ammonium acetate–extractable zinc for these materials was 39.5 and 92.4%, respectively, and substantially the same range of release as found optimal for boron glasses (*12*). Boron glasses differ in that a high degree of fineness is not essential, but release rate for best performance is the same for the two micronutrients.

The need for fineness, or large numbers of carrier particles, relates to low rate of diffusion of the dissolved zinc, not to total amount released from the carrier. Zinc uptake was no greater with application of the most reactive glass, No. 504A, than with the least reactive glass, No. 3473, at equal fineness. With the slowness of diffusion, size of the sphere of influence surrounding a glass particle is very small and limits chance of root contact. At the critical level of 200-mesh fineness, the number of glass particles in the soil would be approximately 600 per cubic inch and, if equally spaced, distance between particles would be about $^1/_8$ inch. Thus, zinc was supplied to the crop most effectively when the fertilizer zinc was distributed with close spacing between particles, as provided by 200-mesh or higher levels of fineness.

## Table III. Effect of Zinc Carriers on Zinc Content and Yield of Alfalfa

| Carrier | Mesh Size | Ammonium Acetate, pH 4, Extractable Zinc, % of Total | Zinc Added to Soil, P.P.M. | Crop on Sagemoor Soil | | | | | | Crop on Lakeland Soil$^{a}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Harvest 1 | | Harvest 2 | | Harvest 3 | | Harvest 1 | Harvest 2 | Harvest 3 |
| | | | | Zn content, p.p.m. | Yield, g./pot | Zn content, p.p.m. | Yield, g./pot | Zn content, p.p.m. | Yield, g./pot | Zn content, p.p.m. | Zn content, p.p.m. | Zn content, p.p.m. |
| None | | | | 12.7 | 5.63 | 11.8 | 5.95 | 14.2 | 5.51 | 34.0 | 32.9 | 30.4 |
| Zinc sulfate | | | 1.5 | 17.3$^{b}$ | 6.19$^{c}$ | 13.8$^{c}$ | 5.89 | 17.5$^{c}$ | 5.73 | 45.5$^{b}$ | 36.7 | 42.3$^{b}$ |
| | | | 3 | 20.3$^{b}$ | 5.97 | 16.0$^{b}$ | 6.15 | 22.6$^{b}$ | 5.82 | 52.3$^{b}$ | 46.2$^{b}$ | 45.5$^{b}$ |
| | | | 6 | 24.3$^{b}$ | 6.35$^{b}$ | 18.7$^{b}$ | 6.30 | 25.5$^{b}$ | 5.74 | 64.0$^{b}$ | 62.1$^{b}$ | 66.0$^{b}$ |
| Glasses | | | | | | | | | | | | |
| 504A | −200 | 99.8 | 3 | 18.0$^{b}$ | 6.32$^{b}$ | 14.3$^{b}$ | 6.18 | 19.2$^{b}$ | 6.15$^{c}$ | 45.1$^{b}$ | 44.2$^{b}$ | 46.5$^{b}$ |
| | 100 to 200 | 99.5 | 3 | 12.2 | 6.02 | 11.6 | 6.15 | 13.1 | 5.69 | 36.0 | 37.5 | 28.0 |
| | 48 to 100 | 94.1 | 3 | 11.5 | 5.66 | 13.0 | 6.15 | 14.5 | 5.72 | 34.2 | 34.4 | 29.9 |
| 3476 | −200 | 92.4 | 3 | 17.7$^{b}$ | 6.43$^{b}$ | 15.9$^{b}$ | 6.37$^{c}$ | 21.6$^{b}$ | 6.04$^{c}$ | 54.8$^{b}$ | 49.2$^{b}$ | 50.8$^{b}$ |
| | 100 to 200 | 62.8 | 3 | 13.6 | 6.22$^{b}$ | 14.8$^{b}$ | 5.98 | 18.0$^{b}$ | 5.55 | 41.7$^{b}$ | 43.3$^{b}$ | 45.7$^{b}$ |
| | 48 to 100 | 39.7 | 3 | 13.2 | 5.73 | 10.1 | 6.06 | 15.2 | 5.78 | 37.1 | 38.9 | 34.9 |
| | 28 to 48 | 22.1 | 3 | 12.7 | 5.58 | 9.2 | 5.79 | 14.1 | 5.62 | 35.9 | 33.5 | 30.0 |
| 3473 | −200 | 39.5 | 3 | 16.4$^{b}$ | 6.38$^{b}$ | 14.8$^{b}$ | 6.05 | 19.2$^{b}$ | 5.94 | 46.5$^{b}$ | 51.1$^{b}$ | 51.3$^{b}$ |
| | 100 to 200 | 12.7 | 3 | 12.2 | 6.14$^{c}$ | 12.0 | 5.99 | 15.5 | 5.69 | 41.4$^{c}$ | 42.7$^{c}$ | 36.6 |
| | 48 to 100 | 7.3 | 3 | 11.4 | 5.92 | 11.7 | 6.20 | 14.6 | 5.64 | 34.0 | 41.2$^{c}$ | 30.0 |
| | 28 to 48 | 3.8 | 3 | 11.2 | 5.68 | 9.7 | 6.26 | 14.6 | 5.69 | 33.2 | 37.4 | 32.3 |
| 504A | Composite | 94.6 | 3 | 15.4$^{c}$ | 6.33$^{b}$ | 13.7$^{c}$ | 6.23 | 18.1$^{b}$ | 6.15$^{c}$ | 44.3$^{b}$ | 47.9$^{b}$ | 41.5$^{b}$ |
| 3476 | Composite | 67.8 | 3 | 14.5 | 6.57$^{b}$ | 15.1$^{b}$ | 6.43$^{c}$ | 17.5$^{c}$ | 6.12$^{c}$ | 44.5$^{b}$ | 48.3$^{b}$ | 38.0$^{c}$ |
| 3473 | Composite | 23.1 | 3 | 14.4 | 6.28$^{b}$ | 14.2$^{b}$ | 6.20 | 16.6 | 5.82 | 40.8$^{c}$ | 47.2$^{b}$ | 40.7$^{b}$ |
| 502 | Composite | 73.8 | 3 | 14.2 | 6.23$^{b}$ | 12.7 | 6.44$^{c}$ | 16.7 | 5.97 | 37.8 | 39.8 | 35.9 |
| 501 | Composite | 45.8 | 3 | 11.6 | 6.21$^{b}$ | 12.0 | 5.90 | 16.7 | 5.64 | 36.2 | 36.1 | 36.3 |
| Zinc ammonium phosphate, powder | | | 3 | 16.9$^{b}$ | 6.29$^{b}$ | 16.7$^{b}$ | 6.16 | 22.8$^{b}$ | 6.17$^{c}$ | 52.0$^{b}$ | 50.6$^{b}$ | 47.3$^{b}$ |
| Zinc ammonium phosphate, granules | 16 to 35 | | 3 | 15.2 | 6.01 | 12.7 | 6.29 | 15.9 | 6.02$^{c}$ | 33.0 | 32.1 | 32.4 |
| Hemimorphite | Composite | 100.0 | 3 | 12.3 | 5.95 | 11.6 | 6.06 | 16.5 | 5.67 | 41.7$^{b}$ | 40.1 | 36.8 |
| Willemite | Composite | 31.0 | 3 | 9.5 | 5.97 | 10.8 | 5.79 | 14.6 | 5.66 | 35.7 | 39.3 | 30.3 |
| Sphalerite | Composite | 0.0 | 3 | 12.9 | 5.68 | 10.4 | 5.79 | 12.1 | 5.66 | 32.4 | 31.7 | 28.6 |
| Zn EDTA | | | 3 | 40.2$^{b}$ | 6.39$^{b}$ | 28.2$^{b}$ | 6.12 | 33.0$^{b}$ | 6.00$^{c}$ | 71.5$^{b}$ | 73.0$^{b}$ | 58.4$^{b}$ |

[a] Respective average yields in harvests from Lakeland soil were 6.43, 5.22, and 6.29 grams per pot.
[b] Significantly greater, 1% level, than with no added zinc.
[c] Significantly greater, 5% level, than with no added zinc.

**Relationship to Specific Surface of Glass.** The effect of varying specific surface of glass 3476 (calculated for sieve fractions, assuming spheres of mean diameter) on zinc content of the crop is illustrated in Figure 1. In the first harvest from the Lakeland soil, zinc content of the crop increased linearly with surface of the glass (unbroken line), slightly exceeding the level obtained with the equivalent zinc sulfate application (broken horizontal line) at high surface. In the following harvests, an arched curve developed gradually as crop zinc increased at the next to highest level of surface and eventually exceeded that resulting from zinc sulfate in the third and fourth harvests. Little change took place at low surface, but otherwise the pattern of nutrient uptake was much the same as that with boron glasses in a coarse-textured soil (*11*).

Zinc content of the crop on Sagemoor soil varied linearly with surface of the glass in the first harvest. A curved relationship developed in subsequent harvests similar to corresponding results with the Lakeland soil. As consecutive harvests were taken, crop zinc tended to approach, but not exceed, levels with equivalent application of zinc sulfate.

**Response to Unclassified Particles.** All five composite glasses increased first harvest yield on the Sagemoor soil (Table III) significantly at the 1% level. Their effect on zinc content of the crop was relatively low. The highest increase in crop zinc obtained with a glass (No. 504A) was 2.7 p.p.m., only 40% as much as with zinc sulfate at equal application.

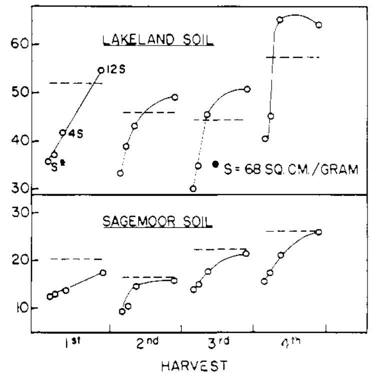

Figure 1. Relationship of initial surface area of optimal glass 3476 to zinc content of alfalfa and to effect of zinc sulfate (horizontal broken lines) at level of 3 p.p.m. of added zinc

The uptake of zinc with multinutrient glasses 501 and 502 was lower than predicted by ammonium acetate extraction values. Extractable zinc was in the same range as that of glasses 3476 and 3473 which contained no micronutrients other than zinc. Yet zinc uptake from the multinutrient glasses was lower on both soils.

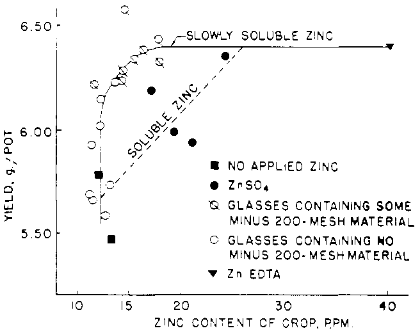

Figure 2. Relationship of yield to zinc content of alfalfa with different types of zinc carriers

First harvest from Sagemoor soil

**Effect of Carrier Type on Zinc Requirement.** Zinc content of the crop was varied by virtue of differences in the reactivity of glass carriers and by varying application of zinc sulfate. The relationship of yield to variation in zinc content of the first harvest from the Sagemoor soil is depicted in Figure 2. The effect of Zn EDTA is also shown in the figure to provide an approximation of yield at full response to zinc. The points, plotted from means of triplicate pots, are satisfactory for constructing the curve for slowly soluble zinc supplied by

### Table IV. Relative Effectiveness of Carriers

| Carrier | Mesh Size | *Ratio of Zinc Sulfate Application to Carrier Application at Equal Response in Zinc Content of Crop* | | | |
|---|---|---|---|---|---|
| | | *Lakeland Soil* | | *Sagemoor Soil* | |
| | | *Early growth*[a] | *Late growth*[b] | *Early growth*[a] | *Late growth*[c] |
| Glasses | | | | | |
| 504A | Composite | 0.67 | 0.98 | 0.37 | 0.77 |
| 3476 | Composite | 0.84 | 0.77 | 0.44 | 0.75 |
| 3473 | Composite | 0.59 | 0.63 | 0.32 | 1.17 |
| 502 | Composite | 0.35 | 0.94 | 0.20 | 0.72 |
| 501 | Composite | 0.26 | 0.46 | 0.08 | 0.64 |
| Zinc ammonium phosphate, powder | | 1.13 | 0.81 | 0.97 | 0.82 |
| Zinc ammonium phosphate, granules | 16 to 35 | 0.01 | 0.26 | 0.21 | 0.50 |
| Hemimorphite | Composite | 0.45 | 0.73 | −0.05 | 0.37 |
| Willemite | Composite | 0.24 | 0.12 | −0.10 | 0.11 |
| Sphalerite | Composite | −0.06 | −0.02 | −0.10 | −0.14 |
| Zn EDTA | | 2.31 | 1.30 | 5.95 | 1.86 |
| $ZnSO_4$ | Composite | 1.00 | 1.00 | 1.00 | 1.00 |

[a] Average ratio of first three harvests.
[b] Average ratio of last two harvests.
[c] Average ratio of last three harvests.

glass carriers. The results for soluble zinc provided by zinc sulfate are represented by the regression of yield on zinc content of the crop (broken line). The deviation of the means from regression is somewhat great, but the variation of individual measurements (not shown) of the population was normally distributed.

The increase in yield accompanying the rise in zinc content of the crop was more rapid with slowly soluble zinc from glass carriers than with soluble zinc from zinc sulfate. The significance of this relationship was tested by comparing the means for all glasses containing some −200-mesh material (composite and −200-mesh sieve fractions) with the means for zinc sulfate at equal application of zinc (3 p.p.m.). The group comparisons showed that the differences in yield and zinc content of the crop were significant at the 1% level of probability. The group of glasses (24 pairs of observations) was also compared with all values for soluble zinc (18 pairs of observations) by the methods of covariance. The elevation of that portion of the curve delineated by glasses containing −200-mesh material was significantly greater than the regression with soluble zinc at the 0.1% level.

This circumstance relates to the distribution of the applied zinc in the soil and to the amounts of soluble zinc supplied by the carrier. The glasses, being finer than the zinc sulfate (Table II), provided much closer spacing between carrier particles. They also released only part of the applied zinc, reserving the rest for use at later stages of growth. These small but well distributed amounts of zinc were able to correct zinc deficiency with only little effect on zinc uptake. With the wider spacing between particles, zinc sulfate may have increased zinc contents of some plants sharply, while having inadequate effect on the level of zinc in other plants or parts of their root systems.

## *Compounds with Low Solubility*

**Zinc Ammonium Phosphate.** Zinc release from the powder form of zinc ammonium phosphate was adequate for correction of zinc deficiency (Table III). Yield from Sagemoor was increased significantly and zinc contents were increased about as much as with zinc sulfate. Granulation of the compound with about 60% clay reduced effectiveness greatly. In early harvests from the Lakeland soil, the granules had no measurable effect on zinc uptake. On the Sagemoor soil, zinc content and yield of the crop were increased somewhat, but the differences were usually nonsignificant. The inferior results with the granules parallel those of coarse glasses. Zinc is, perhaps, released from the granules at a satisfactory rate, but at only a few points in the soil which provides little chance for root penetration into zones of high zinc concentration.

**Zinc Minerals.** Hemimorphite ($2ZnO.H_2O.SiO_2$) increased zinc content of the crop on the Lakeland soil about as much as suitable glass carriers. These results indicate that a crystalline substance with 100% ammonium acetate–extractable zinc would dissolve sufficiently for use in a neutral or acid soil. However, hemimorphite had little effect on zinc content of the crop on Sagemoor soil, and it failed to increase yield significantly. Willemite ($2ZnO.SiO_2$) with 31% extractable zinc supplied less zinc to the crop, and like hemimorphite it was least effective in the Sagemoor soil. Sphalerite (ZnS) had no detectable effect on zinc content or yield of the crop.

## *Chelated Zinc*

The addition of Zn EDTA at the level of 3 p.p.m. of zinc corrected zinc deficiency of the Sagemoor soil completely. Zinc content of the crop was more than that with zinc sulfate in all harvests from the two soils (Figure 3). Differences between Zn EDTA and the sulfate treatments tended to become smaller in late harvests, especially on the Sagemoor soil. This change is mainly the result of the rise in the absorption of ionic zinc from zinc sulfate with declining soil pH. With some allowance being made for this experimental circumstance, it would appear that Zn EDTA was relatively stable in the soil over a period of 9 months.

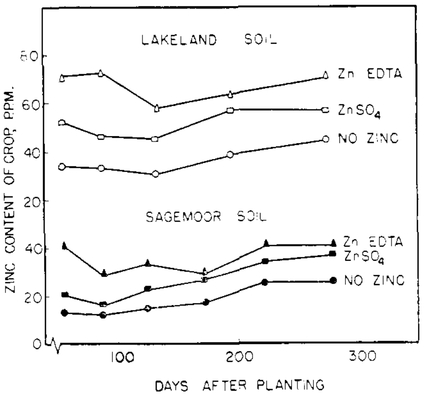

**Figure 3. Effect of Zn EDTA and of zinc sulfate on zinc content of alfalfa at level of 3 p.p.m. of added zinc**

## *Relationship of Carrier Performance to Soil Properties*

The ability of the carriers to supply zinc in the two soils may be compared on a common basis by computing relative effectiveness, expressed as the ratio of zinc sulfate application to carrier application (3 p.p.m. of zinc) at equal response in zinc content of the crop. The average of ratios for harvests during the first 4 months and those for the last 5 months are listed for each soil in Table IV under the heading of early growth and late growth, respectively. The negative values in the table, obtained when uptake was low, presumably indicate relative effectiveness of zero.

The third and fifth columns of the table show that glass carriers were relatively less effective in the Sagemoor soil than in the Lakeland during early growth. Low diffusion rate in the Sagemoor soil temporarily restrains uptake of zinc released from glass (or mineral) carriers. During late growth, there was no consistent difference, and average effectiveness of the glasses as a group was substantially the same in the two soils. Rates of solubilization from the glasses, themselves, were not affected importantly by type of soil, since given sufficient time for diffusion, there was no perceptible difference between soils.

Relative effectiveness of Zn EDTA in the Sagemoor soil was about three times as great as in the Lakeland soil during early growth. With increased uptake from zinc sulfate in late growth, relative effectiveness of the chelate decreased sharply in either soil, but remained greater in the Sagemoor soil. The Sagemoor soil sorbs free zinc ions strongly, as evidenced by the low uptake of applied zinc. The chelate opposes this action by providing anionic zinc, which is not as greatly affected by sorption processes of soils. In view of these conditions, a zinc chelate may be expected to be relatively most effective in a soil having high affinity for cationic zinc.

## Acknowledgment

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**ZINC CARRIERS FOR CROPS**

# Preparation of Zinc Silicate Glasses for Experimental Use in Agriculture

**E. R. HOLDEN and**
**W. R. BONTOYAN**

**U. S. Fertilizer Laboratory, Soil and Water Conservation Research Division, U. S. Department of Agriculture, Beltsville, Md.**

**The influence of method of preparation and composition of 24.1% zinc (30% ZnO) glasses on the release of zinc to ammonium acetate, pH 4.0, was determined. Within the useful range of composition, the release of zinc from frits (unstirred melts) was greater, and less sensitive to differences in composition, than that from homogeneous glasses (stirred melts or remelts). Zinc release from frits was the same whether they were quenched on a dry steel surface or in water. Sodium-zinc glasses of satisfactory reactivity had compositions corresponding to 2 $ZnO \cdot SiO_2$ and $Na_2O \cdot nSiO_2$, where $n = 2$ to 3. The substitution of equimolar amounts of potassium oxide for sodium oxide or alumina for silica had no effect on the reactivity of frits.**

Glass carriers have been utilized in soil treatment to supply micronutrients slowly during growth of crops (*2, 3*). The glasses, like soil minerals, release their micronutrient constituents as they are degraded by weathering. In crop research directed toward the fundamental implications of this natural process, it is essential that rate of dissolution from an experimental glass be neither too slow nor too rapid. Otherwise, the results obtained will cast little, if any, light on the characteristics or potential value of a slowly soluble material.

The use of a glass containing only one micronutrient provides specificity needed in the interpretation of vegetative data. Zinc glasses of this type were made for use in a greenhouse experiment, the results of which have been reported (*7*). The reactivity of these glasses in relation to their method of preparation and composition is described in this article.

## Experimental Procedure

**Preparation of Glasses.** Materials used in making the glasses were quartz flour and finely divided reagent grades of zinc oxide, sodium carbonate, potassium carbonate, and aluminum oxide. The required amounts were formulated to obtain 20- to 25-gram samples of glass containing 24.1% of zinc (30% ZnO). In each of five series, one alkali oxide component was varied at the expense of silica, while other components were held constant. All formulations were mixed thoroughly, placed in a platinum crucible, and melted in a muffle furnace equipped with Globar elements. The temperature of the furnace was increased slowly to a few degrees above the point of fusion (900° to 1600° C.) and held at that temperature for at least one hour.

The following variants in procedure were used in the preparation of a series