CHEMICAL AND PHYSICAL PROPERTIES OF ZINC FERTILIZER THAT AFFECT THEIR AVAILABILITY IN NEUTRAL OR CALCAREOUS SOILS[1]

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The widespread incidence of zinc deficiency has resulted in marketing of many zinc-containing fertilizers having a wide spectrum of chemical and physical properties. Boawn (1966) reviewed research on the agronomic effectiveness of many materials used in the Northwest, and discussed factors affecting their abilities to supply zinc to plants. Mortvedt and Cunningham (1971) reviewed the literature dealing with the production, marketing, and use of micronutrient fertilizers. The different zinc fertilizers marketed, their composition, and the agronomic effectiveness and source of supply for some of them have been presented by Diamond (1972). In general, results have shown that almost all materials marketed are satisfactory sources of zinc when finely powdered and well mixed with the soil. Consequently, properties that increase the number of fertilizer particles in a unit volume of soil or increase the effective size of the particles in the soil enhance zinc availability.

The purpose of this paper is to discuss the chemical and physical properties of zinc fertilizers affecting zinc availability when applied to field crops growing on neutral or calcareous soils.

In neutral or calcareous soils, zinc is considered to be an immobile element. Thus, satisfactory zinc fertilization requires bringing adequate fertilizer into close contact with the root system or placing it where eventual root growth will bring roots and fertilizer particles into close proximity. Any property of the fertilizer or manipulation of it that increases the chances of root-fertilizer contact enhances the availability of the fertilizer.

For nutrient absorption to occur, roots and nutrients must come in contact with each other. According to Parrish (1971) this can happen in three ways: (a) mass flow of soil water carrying dissolved nutrients to the roots, (b) diffusion across concentration gradients, or (c) root interception. For an immobile element such as zinc applied to neutral or calcareous soils, mass flow is generally not important; thus zinc

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is supplied via diffusion and root interception. Appreciable diffusion occurs only over small distances; therefore, root interception and, consequently, root size and distribution are important in supplying zinc to the roots.

ROOT SIZE AND DISTRIBUTION

Roots are primarily confined to soil pores larger than 0.15 mm in diameter, although smaller roots have been reported. In many soils, pores larger than 0.15 mm in diameter represent less than 10% of the total pore space in the soil. Pores smaller than this diameter generally contain water and air. Some of the pores larger than 0.15 mm may not contain roots because they are constricted in some portion or may be inaccessible voids. Root hairs greatly enlarge the effective volume and surface area of roots. Dittmer (1938) determined the roots of a rye plant to be 0.12 to 0.25 mm in diameter, with root hairs 0.7 to 0.8 mm long. Thus, the overall root diameter, i.e., roots plus root hairs, was about 2 mm. Even though the root systems of plants may appear extensive, they actually contact only a small fraction of the total soil. Wiersum (1962) estimated that roots of fully grown field-grown crops explore less than 5% of the total volume of soil within their root system. The root systems of seedlings and young plants would be much smaller than those of fully grown plants and, consequently would explore a much smaller volume of soil. Russell (1961) presents data showing the different characteristics of root systems for several different plant species. He also emphasizes the tremendous part root hairs play in furnishing surface area to contact the soil, increase root interception, shorten diffusion paths, and thereby enhance nutrient absorption.

The entire root system of plants is not equally effective in absorbing nutrients at a given time. Along each primary and secondary root, the most active absorption area is found a few millimeters behind the root tips, where root hairs develop, and extends toward the base of the root. The older root hairs drop as the root enlarges, matures, and becomes covered with corky or waxy material. Absorption of water and nutrients decreases in this older tissue, but does not cease. Thus, it is advantageous not only to have the zinc fertilizer particles near the roots, but also to have them near the regions of most active absorption.

NUMBER OF PARTICLES

The number of particles applied per unit area is proportional to rate of application, and inversely proportional to zinc concentration, density and size of fertilizer particles. Table 1 shows the effect of zinc concentration and particle density on the resulting number of particles for four particle sizes applied at 10 lb of zinc per acre as three different carriers.

Table 1. The number of fertilizer particles per unit area, resulting from application of 10 lb of zinc per acre, as affected by zinc concentration, particle density, and particle size.

% Zn	Sp. Gr.	Particle Size		No. Particles	
		Sieve No.	Diameter mm	Per Sq. Ft.	Per Cubic In. 1/
78	6.0	10	2.00	5	0.004
		18	1.00	40	0.03
		35	0.50	340	0.3
		60	0.25	2,700	2
36	2.8	10	2.00	25	0.02
		18	1.00	200	0.2
		35	0.50	1,600	1.4
		60	0.25	12,700	11
15	2.0	10	2.00	80	0.07
		18	1.00	650	0.6
		35	0.50	5,100	5
		60	0.25	42,500	37

1/ On the basis of uniform mixing with 8 inches of soil

Rate of Application

Zinc fertilizers are generally applied at rates of about 10 lbs of zinc per acre. As the application rate decreases, the number of particles applied per unit area decreases proportionately. A 50-percent decrease in the number of particles may not be serious for the low-analysis, low-density material applied as 0.25-mm particle size, but it may seriously reduce the availability as a result of the decrease in the number of particles applied as 2.00-mm particles of high-analysis material. Boawn and Rasmussen (1971) have shown that extremely high rates of zinc may be applied safely to many crops grown on neutral or calcareous soils, but application of 10 lbs of zinc per acre adequately corrects the deficiency and usually does so for 3 or more years. Consequently, application of higher rates is not recommended simply as a means for increasing the number of particles applied per unit area.

Particle Density

The specific gravity of different materials may range from less than 2.0 to near 6.0. The number of particles applied at a given level of zinc increases as particle density decreases. For a high-density material such as zinc oxide, the number of particles of the same size is less than half the number applied under the same conditions as from zinc sulfate, even if both materials contained the same zinc percentages. Thus, the number of particles applied per unit area for different carriers may differ as much as threefold simply as a result of particle density.

Zinc Concentration

Zinc-containing fertilizers marketed today commonly contain from 10 to 80% zinc. Based solely on zinc content, the number of particles applied at a given rate may vary as much as eightfold. In addition to supplying adequate numbers of particles, material with low concentration probably provides greater uniformity when fertilizer is broadcast alone as a dry material. Applying 10 lbs of zinc per acre as a 10% zinc material requires application of 100 lbs of dry material per acre; most spreaders are capable of satisfactorily applying this amount of material. At the same rate of zinc fertilization, however, using 80% material requires spreading uniformly only 12.5 lbs of materal per acre; not many spreaders have this capability.

Particle Size

For a given material, the number of particles increases eightfold as the particle diameter is halved. Consequently, as particle diameter is decreased from 2.00 to 0.25 mm, the number of particles in the same amount of material is increased by a factor of 512. Applying finer material is the most direct way of increasing the number of particles per unit area. Because of difficulty in spreading fine powders, their application may not be suitable under field conditions. Attempts have been made to incorporate many small particles of zinc fertilizer in macroelement fertilizer (Giordano and Mortvedt, 1966) at low zinc concentration, and thereby take advantage of the increased number of particles and any acidulating or complexing properties of different carriers. The results of pot experiments indicate that, with some carriers, reactions occur with the soil or carrier that offset advantages ordinarily resulting from increasing the number of particles when the zinc fertilizer is applied alone. Concentrated superphosphate containing zinc at 0.5, 2.0, and 8.0% was shown to be a good carrier for zinc, whereas ammonium nitrate was not. The availability of zinc mixed with NPK fertilizers decreased as the percentage ammoniation of the concentrated superphosphate increased.

It is not possible to determine how many fertilizer particles or sites are needed to supply adequate zinc to a crop growing on a low zinc soil. The number required depends on many factors such as (a) the severity of the zinc deficiency, (b) the size of the particle, (c) the concentration and solubility of the zinc in the dissolved granule, (d) the concentration gradient surrounding the particle, and (e) the age of the root and its efficiency of absorption. Many of these single factors are part of the process that determines the rate of absorption by the plant. The rate of absorption must be adequate so that it does not restrict the growth rate of the plants. The statements made here apply to a single-season's effect. The effect of subsequent tillage on zinc particle distribution is not known. Mixing, however, is expected to enhance zinc availability by improving zinc-enriched particle distribution within the tilled layer.

SOLUBILITY

The solubilities of zinc fertilizers marketed today range from very sparingly soluble materials, such as zinc oxide and zinc carbonate, to extremely soluble $Na_2ZnEDTA$ and zinc chloride. In neutral and calcareous soils, high solubility of zinc fertilizers is desirable. Solubility enhances the movement and, consequently, the effective size of the particles applied. Soluble material absorbs water from the soil and forms essentially a saturated solution. This solution then diffuses away from the center of the particle, thereby increasing its effective size. Assuming that the resulting affected soil retains its spherical shape, enlargement of the diameter by a factor of 2, enlarges the volume by a factor of 8. A sparingly soluble material such as zinc oxide, on the other hand, enlarges very little when placed in a neutral or calcareous soil. Indeed, it is likely that the surface of the particle becomes coated with other soil constituents. The solubility of zinc oxide is so low that very little zinc can move into the surrounding soil. Because of the low solubility of the material, the high concentration of zinc in the particle remains ineffective in enlarging the zinc-containing volume of the soil. However, sparingly soluble materials are not unsuitable as fertilizer. They may have a longer lasting effect than the more soluble materials through less fixation by the soil. For such materials to be effective when first applied, they must be finely divided or the rate of application increased to supply adequate zinc for growing crops.

SPECIAL PROPERTIES

Acidulation

Because of the immobility of zinc in neutral and calcareous soils, fertilizer having acid properties or being placed in the soil in an acid environment may enhance the uptake of zinc. In a calcareous system, carbonates control the pH and, consequently, the movement of inorganic zinc and the effective enlargement of fertilizer particles. Acidification may be more beneficial on neutral than on calcareous soils because of the extreme buffering capabilities of free lime and the very large amounts present in some soils. Thus, acidulation may occur only in localized zones immediately surrounding the fertilizer particle. Acidulation may result from hydrolysis of zinc salts containing the anion of a strong acid, hydrolysis of macronutrient fertilizer such as concentrated superphosphate, oxidation of N or S contained in fertilizer or amendments, or the direct application of acid.

Acidity of saturated solutions of the zinc fertilizer does not always control zinc availability. Mortvedt (1968) shows a decrease in fertilizer effectiveness from adding zinc sulfate to various ammoniated NPK fertilizers even though saturated solutions of these materials were near pH 3.5 to 4.0. The water solubility and the agronomic effectiveness decreased as a result of ammoniation of the concentrated superphosphate contained in the materials. Concentrated superphosphate without N and K proved to be an effective carrier of zinc, whereas ammoniated superphosphate was not. Saturated solutions of these materials in water had pH's of 2.8 and 5.4 to 5.9, respectively. Reactions of zinc with dissolved soil or fertilizer constituents that accompany or result from acidulation may further immobilize fertilizer zinc and prevent effective particle enlargement in the soil. Moreover, the stability of zinc chelates increases with pH, and the advantage of chelation may be lost when these materials are placed in an acid environment.

Chelation

Chelation is a special property whereby zinc and several other cations may be complexed and held very strongly by organic anions or ligands. Some ligands are synthetic, e.g., EDTA, HEEDTA, DTPA; some occur naturally, such as polyflavonoids. Ligands are polyvalent and the attraction between ligand and metal cations is stronger for some valences than others. For example, when zinc is chelated by EDTA the following reaction occurs in aqueous solution:

$$2Na^+ + H_2EDTA^= + Zn^{++} \rightleftarrows ZnEDTA^= + 2Na^+ + 2H^+$$

The bonding between the Zn and EDTA is so strong that very little dissociation occurs. The result is that the Zn cation essentially loses its identity and takes on the properties of the anion. Thus, it moves more freely in soil water than it did as a cation because it has very little attraction for the negatively charged soil particles. The dissociation of the zinc chelate is very slight and is related to the stability of the chelate, which differs for different pairs of ligands and cations; for a given ligand, the stability differs with various cations. The release of zinc from the chelate is dependent on pH and concentrations of other cations in the system and relative stabilities of the chelates formed. Generally, Fe^{+3} forms more stable chelates than does Zn^{+2}, which in turn forms more stable chelates than does Ca^{+2}. The stability of chelates is greatest near neutral pH. Thus, when these materials are added to soil, part of the zinc remains chelated and does not react immediately with the soil. The importance of chelation in the movement of zinc fertilizer was shown by the greater mobility of chelated vs nonchleated zinc (Elgawhary et al., 1970). In this work the apparent diffusion coefficients were increased by a factor of 25 as a result of chelation. The increased mobility results in particle enlargement in the soil and enhanced diffusion from fertilizer particle to plant root.

COMBINATION OF FACTORS

Seldom, except for adjusting the zinc rate, is only one factor affecting the number of fertilizer particles changed. Usually when zinc fertilizer practices are changed, different materials are used. Thus, two or more of the physical and chemical properties are changed simultaneously. The relative effects of doubling each of four factors, alone or in combination, are given in Table 2. Of the four factors listed, zinc rate operates in opposition to the other three, i.e., doubling the zinc rate doubles the number of particles, whereas doubling the particle density or zinc concentration halves the number of particles applied per unit area of soil.

Table 2. The relative number of fertilizer particles applied as influenced by doubling the values for each of four fertilizer properties singly and in combination

Zinc Rate	Particle Density	Zinc Concentration	Particle Size	Relative No. Particles
1	1	1	1	100
1	2	1	1	50
1	1	2	1	50
1	1	1	2	12.5
1	2	2	1	25
1	2	1	2	6
1	1	2	2	6
1	2	2	2	3
2	1	1	1	200
2	2	1	1	100
2	1	2	1	100
2	1	1	2	25
2	2	2	1	50
2	2	1	2	12.5
2	1	2	2	12.5
2	2	2	2	6

The data in Table 1 show more dramatically the effects of changing more than one factor on the number of fertilizer particles applied per unit area of soil. Here the factors have been changed by more than twofold. Particle size clearly has the largest individual effect; decreasing diameter by one-half for each material increases the number of particles applied eightfold. For the 2-mm size materials, application of 10 lb of zinc per acre results in 5, 25, and 80 particles per square foot for the 78, 36, and 15% material, respectively. However, the major differences arises when the 2-mm size, 78% material is compared with the 0.25-mm size, 15% material. In this comparison, the number of particles applied per unit area differs by a factor of 8,500.

The effects of solubility, acidulation, and chelation are not tabulated because of the uncertainties relating to the solubility of the fertilizer and reaction of the zinc with soil or other fertilizer constituents. The main effects of these properties involve effective particle enlargement after the fertilizer is mixed with the soil and diffusion from particle site to a nearby root. If we assume spherical particles, doubling the radius increases the effective particle volume eightfold. But because of density and zinc concentration differences for the materials as they are applied, the volume of the 15% material is already 15 times as large as that of the 75% material. Thus, if the particle radius of the 15% material enlarges by twice as much as the 78% material, the effective particle size is increased eightfold again, and the relative volume of soil affected becomes 120 times as large for the 15% as for the 78% material. The condition imposed here for the above comparison is probably extremely conservative.

In Table 3, three materials are compared on the basis of some of these properties. Zinc oxide is a good source of zinc when applied as a fine powder and well mixed with neutral or calcareous soils. It has no special properties to enhance its availability. Di-sodium zinc EDTA, on the other hand has not only high solubility and chelation to enhance its availability, but also low zinc concentration and low particle density to increase the number of particles applied. At the same particle size and rate of application, the number of particles increases by a factor of 17 for zinc EDTA as compared with zinc oxide and by a factor of 4 as compared with zinc sulfate; this is without counting the effects of special properties. Thus, materials such as this have many properties that enhance their availability to plants.

Table 3. Some physical and chemical properties of three zinc fertilizers.

Zinc Fertilizer	Percent Zinc	Particle Density	Solubility	Special Properties
Zinc oxide	75	6.0	Very low	None
Zinc sulfate	36	2.8	High	Acidulation
$Na_2ZnEDTA$	14	1.8	Very high	Chelation

SUMMARY

Because of limited exploration of soil by roots, and the immobility of zinc in neutral and calcareous soils, it is necessary to apply some zinc fertilizers as finely divided material in order for them to effectively prevent zinc deficiency. Physical and chemical properties that increase the number of particles applied enhance the availability of the zinc contained therein. Properties that increase the number of fertilizer particles applied per unit area of soil at a given application rate are low zinc concentration, low particle density, small particle size, high solubility, and special properties such as acidulation and chelation. Thus, when sparingly soluble materials such as zinc oxide or zinc carbonate are applied their effectiveness increases as smaller particles are used. These materials also have high zinc concentrations, high particle density, and possess no special properties.

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