ammonium nitrate crystals and recycle fines by an air jet impinging on the falling stream. The sulfuric acid and the remainder of the phosphoric acid are fed on top of the bed through separate distributors. The material from the mixer is discharged into a rotary ammoniator-granulator, 8 feet in diameter by 12 feet long, which rotates at 12 r.p.m. It is divided into a 3-foot ammoniating section and a 9-foot granulating section by a 12-inch retaining ring. There also is a 12-inch retaining ring at the feed end. Ammoniation and agglomeration occur in the ammoniating section where ammonia is added through a drilled pipe under the bed. The agglomerates are hardened in passing through the granulating section.

The granules are dried to a moisture content of about 0.3% in a cocurrent rotary dryer. The discharge from the dryer (220° F.) is screened at 6 and 16 mesh. The oversize is crushed in a chain mill and returned to the dryer. The fines, estimated to be 60 to 70% of the throughput, are recycled to the ammoniator. The product is passed through a rotary cooler and coated with 3% by weight of a calcined fuller's earth. The product is shipped in bulk or in bags. Typical analysis of the plant product is given in Table X.

In earlier operation, the preneutralizer was not used. The first drum was divided into a 5-foot mixing section and a 3-foot ammoniating section using a 14-inch retaining ring. Ammonium nitrate crystals. recycle fines, phosphoric acid, and sulfuric acid were mixed in the first section; ammoniation and granulation occurred in the second section. There was a considerable amount of caking in

Table X. Typical Analysis of Plant Products

Chemical Composition, Wt. %							Screen Analysis, Cumulative, % Retained on Tyler Screen				
N		P₂O₅			Water-						
Total	NH₃	Total	W. S.	SO₃	insoluble	Moisture	6	8	10	16	20
30.4	17.2	10.2	10.2	2.0	3.4	0.35	3	30	86	97	98

the ammoniator. With the preneutralizer, the amount of caking was reduced substantially. Also, the product has a higher degree of ammoniation (7.5 vs. 5.5 pounds of NH_3 per unit of P_2O_5), since the preneutralizer is operated in the pH range that results in crystallization of diammonium phosphate.

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TRACE ELEMENTS IN FERTILIZERS

Solubility Status of Zinc Carriers Intermixed with N–P–K Fertilizers

W. A. JACKSON, N. A. HEINLY, and J. H. CARO

U. S. Fertilizer Laboratory, U. S. Department of Agriculture, Beltsville, Md.

The degree of water solubility of zinc, added to mixed fertilizers as basic zinc sulfate or zinc sulfate monohydrate, depends chiefly upon the pH of the fertilizer system. Ammoniated mixed fertilizers having a pH range of 4.6 to 6.1 showed a larger capacity for fixing zinc than nonammoniated fertilizers having a pH range of 3.6 to 4.2. Water-soluble zinc recovery was greater at pH 6.1 to 6.6 than at the intermediate pH levels, indicating the formation of soluble zincates. The results show that chelated zinc remains water soluble in N–P–K fertilizers which otherwise have a large capacity to immobilize free zinc ions.

INCORPORATING zinc carriers into mixed fertilizers, a procedure sometimes followed in the fertilizer industry, is recognized as an economical means of applying this element to soil (8, 72). In this practice, the zinc carrier may react with the components of the fertilizer during storage prior to use, thus affecting the solubility, and hence the nutrient status, of the trace element. Nikitin and Rainey (9) conducted an investigation of reactions between trace elements and fertilizer salts in which zinc was limited to one carrier, applied at one rate to a single grade of mixed fertilizer, and evaluated after aging for one specified time period. Expansion of each of these variables should provide additional useful information. The present investigation pertains to the effects of a wide variety of mixed fertilizers on the water solubility of three zinc carriers: basic zinc sulfate, zinc sulfate monohydrate, and a zinc chelate.
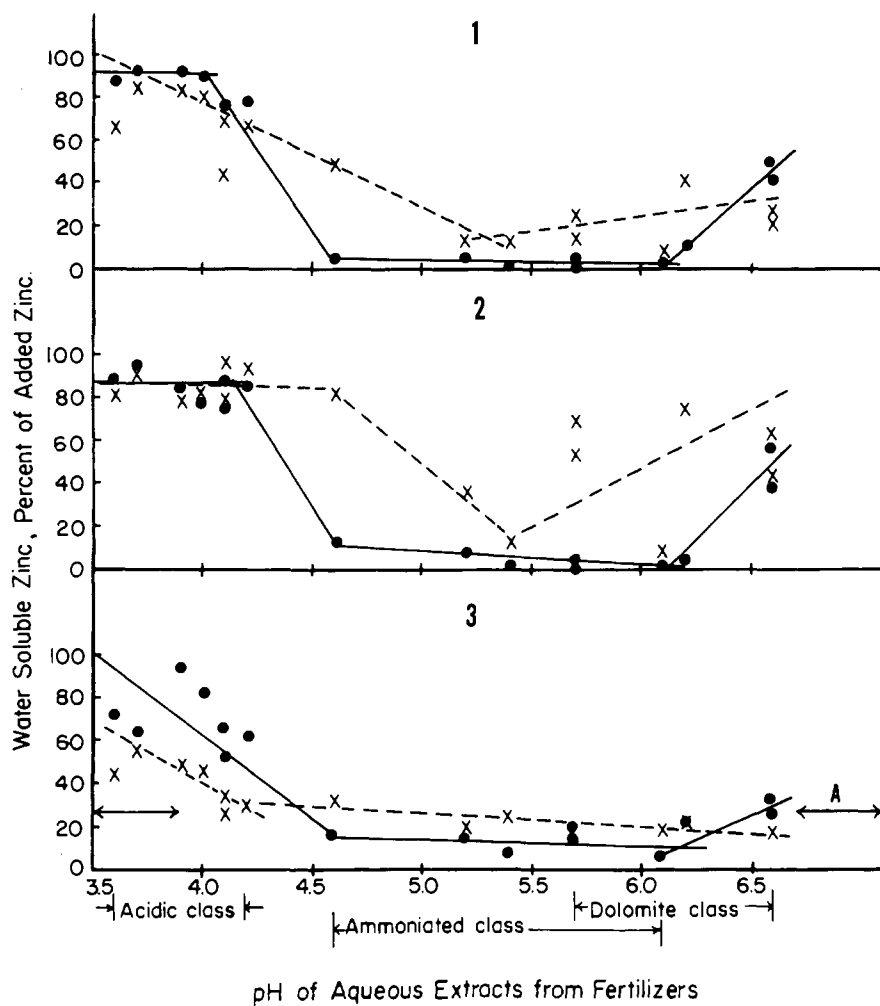
Figure 1. Relationship between water soluble zinc content and extract pH of mixed fertilizer systems

Zinc applied at the rate of 1 pound per ton x-----x No aging; ●————● 8 weeks' aging
1. Basic zinc sulfate $ZnSO_4 \cdot 4Zn(OH)_2$
2. Zinc sulfate monohydrate $ZnSO_4 \cdot H_2O$
3. Zinc chelate $Na_2ZnEDTA$
A. Dithizone extraction value of chelate = 27%

Preparatory Investigations

Analytical Procedure. Inasmuch as the proposed work plan for the zinc N–P–K aging tests called for as many as 108 zinc determinations per week, an assay method was sought that would eliminate many of the time-consuming features of known procedures. The adopted technique is a modified mixed-color dithizone procedure based on previous methods (10, 11). Details of the procedure are as follows:

Dissolve 200 grams of ammonium citrate in 800 ml. of water, adjust the pH to 8.6 with aqua ammonia, and dilute to 1 liter and extract the heavy metals with successive portions of 0.01% solution of dithizone in CCl_4 (10).

Transfer an aliquot of the test solution, containing 0 to 15 μg. of Zn, to a 125-ml. separatory funnel, dilute to 25 ml. with twice-distilled water, and add 10 ml. of the purified buffer solution, one

drop of 1% phenolphthalein solution (pink color indicates proper pH), and 10 ml. of a 0.002% solution of dithizone in CCl_4. Shake vigorously for 1 minute, allow phases to separate, and determine the transmittance of the colored organic layer with a spectrophotometer at 535 mμ for aliquots containing 0 to 5 μg. of Zn, or at 620 mμ for aliquots having 5 to 15 μg. For calibration, carry a blank and a set of three samples prepared from a standard zinc solution along with each set of test solution.

Mixing Techniques. Prior to the principal experiment, a brief study was undertaken to determine the efficiency of a number of mixing techniques. Basic zinc sulfate was added to 200-gram lots of a 10–10–10 mixed fertilizer at rates of 1 to 10 pounds of zinc per ton, and the composites were mixed for 10 minutes using one of four blending techniques: hand mixing, in which the material contained in a 500-ml., wide-mouth jar was

turned and tumbled by hand; end-over-end mixing, in which the material was tumbled in a mechanical device at a rate of 50 r.p.m.; twin shell blending, involving mechanical tumbling at 30 r.p.m. in a Y-type device; and, rotary pan mixing in which the material was blended in an upright cylinder rotating at 200 r.p.m. with fixed vertical internal blades. After the material had been mixed, it was poured into a conical pile, and six samples were scooped from different points around the pile and placed in individual jars. The contents of each jar were thoroughly mixed, and portions were taken in duplicate for assay of water-soluble zinc content.

The results showed that hand mixing and twin shell blending were superior to the other two procedures tested. The coefficients of variation of the six determinations made for each method of mixing at the 1- and 10-pound rates, respectively, are: hand mixing, 2.27 and 4.12%; end-over-end, 4.47 and 7.35%; twin shell blender, 2.84 and 3.81%; and rotary pan, 6.46 and 4.42%. Since the twin shell blender gave more reproducible results, it was used in the subsequent zinc–N–P–K aging test.

Materials and Method

Aging Tests. Sixteen mixed fertilizers, representing a variety of grades and formulations (Table I), were prepared from finely-ground, commercial-grade materials in 2000-gram lots, stored for 6 months at room temperature, and ground prior to inclusions in the tests. Grades were chosen from those in actual manufacture so that high-N, high-P, high-K, and 1–1–1 ratio grades, and two common filler materials, dolomite and diatomaceous earth, would be represented.

Zinc was contained in three carriers: basic zinc sulfate, $ZnSO_4 \cdot 4Zn(OH)_2$, 52.27% Zn; zinc sulfate monohydrate, $ZnSO_4 \cdot H_2O$, 35.07% Zn; and a zinc chelate, disodium zinc ethylenedinitrilo-tetraacetate, 9.45% Zn. Zinc content of the carriers was determined by the potassium ferrocyanide titration method (6).

Each carrier was added to 200-gram lots of each of the 16 fertilizers at rates of 1 and 10 pounds of zinc per ton of material, a total of 96 combinations. Each combination was mixed in the twin-shell mixer, transferred to an 8 × 12 inch plastic bag and brought to about 5% moisture, to promote possible chemical reaction, by adding 10 ml. of distilled water to each bag and kneading by hand until the water was uniformly distributed throughout the material. After removal of samples for the determination of immediate water-soluble zinc content and extract-pH, the mixtures were transferred to fruit jars, sealed, and stored at room temperature. Samples were taken

for analysis of water-soluble zinc content after aging periods of 1, 3, and 8 weeks. Solutions for analysis were prepared by leaching 0.5- to 1-gram portions of the samples with about 240 ml. of twice-distilled water and diluting the leachate to 250 ml. The zinc found was corrected for the initial zinc content of the fertilizers, determined by the proposed procedure. In the work schedule that was followed, the 96 combinations were arranged in eight groups, each containing four fertilizers and three zinc carriers, and each group of 12 mixtures were handled as a unit. The schedule was designed for overlapping of work on separate units so that a uniform analytical program was achieved.

Water Solubility of Intermixed Zinc

Changes effected in the water solubility of zinc intermixed and aged with the test fertilizers are shown in Table II. The data are interpreted below with respect to the differences between classes of fertilizers, individual fertilizer formulation, trace nutrient carriers, and rates of zinc application.

Classes of Mixed Fertilizers. Nikitin and Rainey (9) found that the retention of zinc was less in acidic mixtures than in those neutralized with ammonia or lime. The latter two could be differentiated by the fact that zinc retention in ammonia-neutralized mixtures decreased in the high pH range. The mixtures in the present investigation are divided into similar classifications in Table II. The first seven fertilizers at each rate of application are comprised of unneutralized, acid-forming mixtures; the center four fertilizers are more basic, and contain dolomite in three cases; and the last five are ammoniated mixtures.

The highest recovery of water-soluble zinc is from the nonammoniated, acidic class of fertilizers which has a pH range from 3.6 to 4.2. Except in scattered instances, interaction of zinc with the fertilizer was substantially complete within the first week of aging. In general, zinc solubility was less in the ammoniated class than in the dolomitic mixtures. The relationship between water-soluble zinc and the pH of aqueous extracts of different mixed-fertilizer systems is shown in Figure 1. These results are in accord with the well-established fact that the availability of zinc declines as the pH of the system rises (1, 2, 9). The increase in zinc solubility above pH 6.1 (Figure 1) indicates the formation of a soluble zincate (1, 2).

Differences Within Classes of Fertilizers. In the acidic class of fertilizers, there is very little reaction with zinc within the 8-week aging period. A substantial decrease in zinc solubility is, however, indicated in mixture 7 (Table II) when the trace nutrient is carried as the basic sulfate. The decrease is

Table I. Percentage Composition of Mixed Fertilizers

No.	Grade	Normal Super-phosphate	KCl	Triple Super-phosphate	(NH4)2-SO4	NaNO3	Urea	Anhydrous NH3	NH4NO3	Dolomite	Diatomaceous Earth
1	0- 9-27	45.0	43.6	....	...	...	...	...	...	...	11.4
2	0-30-15	22.7	24.2	53.1	...	...	...	...	...	...	...
3	10-10-10	26.3	16.2	9.9	47.7	...	...	...	...	...	...
4	10-10-10	50.0	16.6	...	...	...	21.8	...	...	...	12.0
5	6-18- 6	41.6	9.7	20.2	28.6	...	...	...	...	...	...
6	0-20-20	44.8	32.3	23.0	...	...	...	...	...	...	...
7	10-10-10	0.9	16.2	20.5	...	62.5	...	...	...	...	...
8	12- 0-10	...	16.2	...	57.1	...	...	...	...	...	26.7
9	12- 0-10	...	16.2	...	57.1	...	...	...	...	26.8	...
10	8- 0-24	...	38.8	...	38.1	...	...	...	...	23.2	...
11	6- 6-18	30.0	29.0	...	28.6	...	...	...	...	12.4	...
12	15- 5- 5	25.0	8.1	...	65.8	...	...	1.2	...	...	...
13	8-32- 0	...	...	61.6	31.8	...	...	1.7	...	...	4.9
14	17- 7- 0	35.0	...	...	44.9	...	...	1.7	18.5	...	...
15	10-10-10	50.0	16.2	...	...	...	...	2.5	23.6	7.9	...
16	15-15- 0	13.8	...	25.5	57.1	...	...	3.7	...	...	...

Table II. Water Solubility of Zinc Carriers in Mixed Fertilizers

Water-Soluble Zinc, Per Cent of Total Zn Added[b] as:

Fert. No.	pH[a]	$ZnSO_4.4Zn(OH)_2$				$ZnSO_4.H_2O$				$Na_2ZnEDTA$			
		Aging Time, Weeks											
		0	1	3	8	0	1	3	8	0	1	3	8

Zinc Intermixed at Rate of 1 Pound of Zn Per Ton

Fert. No.	pH	0	1	3	8	0	1	3	8	0	1	3	8
1	4.2	64	88	84	78	92	82	90	86	28	50	64	62
2	3.6	64	90	86	88	82	86	88	88	44	74	74	72
3	4.1	70	76	78	76	96	80	78	76	34	52	60	52
4	4.0	80	82	88	90	82	74	80	78	46	62	68	84
5	3.9	82	86	88	92	80	74	84	84	48	86	76	94
6	3.7	86	82	90	92	94	90	90	94	58	62	68	64
7	4.1	44	70	68	72	78	84	84	88	26	56	52	66
Av.	3.9	70	84	84	84	86	82	84	84	40	64	66	70
8	6.2	42	16	12	10	76	18	6	4	22	18	20	22
9	6.6	24	26	34	42	46	14	20	38	20	14	20	26
10	6.6	28	40	42	50	66	38	46	56	20	18	22	34
11	5.7	28	20	4	0	70	24	4	0	26	30	20	14
Av.	6.3	30	26	24	26	64	24	20	24	22	20	20	24
12	5.7	14	8	4	2	58	8	6	2	26	26	12	20
13	4.6	48	10	8	4	82	20	14	12	32	14	24	16
14	5.2	14	8	4	6	36	8	6	8	18	14	18	16
15	5.4	14	2	0	0	10	2	0	0	26	10	12	8
16	6.1	10	0	0	0	14	0	0	0	18	6	10	6
Av.	5.4	20	6	4	2	40	16	6	4	24	14	14	14

Zinc Intermixed at Rate of 10 Pounds of Zn Per Ton

Fert. No.	pH	0	1	3	8	0	1	3	8	0	1	3	8
1	4.2	69	86	89	81	106	91	93	90	38	29	34	28
2	3.6	82	92	87	88	106	93	99	83	40	42	73	48
3	4.1	64	54	48	79	106	82	88	84	31	35	27	43
4	4.0	71	68	76	70	83	84	85	84	29	35	39	47
5	3.9	83	87	79	84	102	96	91	84	26	35	43	45
6	3.7	92	95	84	89	101	94	88	86	28	37	44	44
7	4.1	51	80	80	83	103	102	93	87	27	32	29	38
Av.	3.9	73	81	78	82	101	92	91	86	31	35	41	42
8	6.2	50	44	35	26	97	63	65	57	32	22	23	24
9	6.6	42	44	49	48	80	54	49	43	22	24	22	32
10	6.6	60	58	51	57	91	69	59	57	23	25	22	28
11	5.7	17	15	8	3	86	29	13	3	30	13	12	17
Av.	6.3	42	40	36	34	89	54	47	40	27	21	19	26
12	5.7	23	12	14	12	61	10	13	11	29	16	21	24
13	4.6	51	27	23	21	104	30	31	30	39	26	18	24
14	5.2	21	14	15	14	71	9	14	10	26	16	21	22
15	5.4	12	5	4	3	15	5	5	3	22	14	17	19
16	6.1	10	3	5	4	14	2	3	2	21	9	15	15
Av.	5.4	23	12	12	11	53	11	13	11	27	16	18	20

[a] pH of aqueous extract from fertilizers.
[b] Average of triplicate determinations.

no longer apparent after a week of aging. The cause of this temporary effect is not clear, but is presumably related to the very high concentration of sodium nitrate in the mixture.

Mixtures 8 and 9, identical in all respects except for type of filler material,

react differently with zinc in nonchelated form. A continuing decrease in zinc solubility occurs throughout the 8-week period in mixture 8, which contains diatomaceous earth. No similar effect is apparent in the dolomitic mixture 9. The high surface area of the diatoma-

ceous earth is doubtless the controlling factor (4). This type of reaction is not evident with chelated zinc.

The interaction of zinc with mixture 11 gives some insight into the chemistry by which zinc is rendered insoluble. The fertilizer differs chiefly from mixtures 9 and 10 in the same group in the fact that it contains normal superphosphate (Table I), yet it alone showed a continuing decrease in water-soluble zinc throughout the aging period, completely reverting the zinc in 8 weeks to a water-insoluble form, an action similar to that of the ammoniated class. The explanation lies in the well-known reaction between monocalcium phosphate and ammonium sulfate, both of which are components of mixture 11, to produce monoammonium phosphate and calcium sulfate, the components of ammoniated superphosphate. The 6-month preliminary storage of the fertilizers provided ample opportunity for this reaction to take place so that mixture 11 was more related to the ammoniated group of fertilizers than to the dolomitic group at the time of the aging tests. The inference is that zinc salts react with monoammonium phosphate in weakly acidic or more basic environment to form insoluble zinc phosphates.

Mixtures 15 and 16 in the ammoniated class (Table II) produced a sharp drop in zinc solubility within the first week of aging. Apparently this action is caused by the higher degree of ammoniation as compared to mixtures 12, 13, and 14, which retained a certain amount of water-soluble zinc even after 8 weeks of aging. In mixture 15, the effect is attributable to the dolomite in the fertilizer, which reacts to form diammonium phosphate (5). In mixture 16 also, diammonium phosphate was present, the ammoniation of the superphosphate being carried beyond the point of first-stage neutralization (3). Thus, zinc apparently reacts more rapidly and completely with diammonium phosphate than with monoammonium phosphate.

Differences in Types of Zinc Carriers. The only apparent difference in the action of the two types of zinc sulfate

is shown in Figure 1. A continuing decrease in water-soluble zinc is observed, between pH 3.6 and 5.4, in mixtures containing basic zinc sulfate (dotted line, Figure 1), whereas mixtures containing zinc sulfate monohydrate show a sharp drop in water-soluble zinc at a pH of 4.6 (dotted line, Figure 1). After 8 weeks of aging, the two salts are very similar in their reaction (solid lines, Figure 1). Actually, differences were negligible after only 1 week of aging. The initial effect is attributable to the amphoteric properties of the basic zinc sulfate.

The low values for water-soluble zinc found in mixtures containing the chelated zinc (Figure 1) are misleading, owing to the incomplete extraction of the metal ion by dithizone. Because dithizone is a chelating agent itself, its reaction with the metal ions in solution is complicated by the competitive forces between two chelating agents and a metal (7). The magnitude of the effect can be gauged by the fact that the zinc content of an aqueous solution of the zinc chelate found by the dithizone method was only 27% of the total zinc. Despite this complication, the data yield useful information. Aging and rate of application of the chelate had little effect upon zinc solubility. In contrast to the two forms of sulfate, chelated zinc remains water-soluble irrespective of the type of fertilizer with which it is intermixed. The relatively high percentage recovery of chelated zinc from the acidic class of fertilizers, substantially above the 27% recovery from the chelate itself, indicates that the zinc complex is unstable and dissociates to a greater extent in the acid fertilizer system.

Rate of Application of Zinc. With the zinc sulfates, the percentage recovery of water-soluble zinc was generally higher at the 10-pound-per-ton rate than at the 1-pound rate (Table II). The effect is presumably caused by build-up of the zinc salt on fertilizer particles so that saturation was obtained in local zones. Hence, full reaction with the fertilizer components, accompanied by reduction in zinc solubility, is prevented. Using the same reasoning, one may

rationalize the higher percentage recovery of zinc at the 1-pound rate when added as the chelate and mixed with acidic fertilizers (Table II). The larger amount of the chelate present within the fertilizer would serve to forestall full reaction and hence would decrease the dissociation in the acid environment. Thus, dissociation as a mechanism is supported by two independent observations.

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