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Novel Slow-Releasing Micronutrient Fertilizers. 1. Zinc Compounds

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A new concept for slow-releasing micronutrient compounds is proposed, based on the short-chain polyphosphate framework. The development of a zinc fertilizer, the first of such compounds, is described. Kinetic studies indicate that zinc phosphates polymerize in several linear stages. The polyphosphates are, in general, extremely water soluble and hygroscopic; moreover, those with lower solubility contain a high proportion of unavailable Zn^{2+}. Initially, it was not possible to obtain a zinc polyphosphate having low water solubility and high nutrient availability. Solubility and hygroscopicity were attributed to free acid groups on the polyphosphate chain; neutralization of these groups indeed removed these undesirable characteristics. The fertilizers formulated have an average chain length of 2.35, contain some crystalline phases, have low water solubility, and are almost completely soluble in dilute HCl, citrate, diethylenetriaminepentaacetate, etc. Plant experiments indicate that the zinc polyphosphate is either equivalent to or better than $ZnSO_4$.

1. Introduction

In view of the alarming environmental hazards and low utilization efficiency associated with the use of soluble salts as fertilizers, the major emphasis in fertilizer research, at present, is on the development of new materials which have low water solubility and consequently are not readily removed from the soil by leaching. Such *slow-release* or *controlled-release* formulations must, however, fulfill the basic requirement that the nutrient ions in them be available for plants in spite of their sparingly soluble character. Most of the sparingly soluble inorganic salts are, for this reason alone, not suitable for use as slow-release fertilizers. The three main categories of slow-release formulations include (i) organic-based compounds such as the urea–formaldehydes and resin chelates, (ii) membrane-coated compounds, and (iii) phosphate glasses (frits) and metaphosphates (Roberts, 1975; Sauchelli, 1964, 1967, 1969; Silverberg et al., 1972; Volfkovich, 1972). Although they possess suitable properties, the major drawback of most of these formulations, is their cost which makes them uneconomical for use, except for high-value crops.

Phosphate glass frits are being used to some extent as slow-releasing sources of micronutrient ions (Roberts, 1973, 1975, 1977). Such glasses are usually produced by fusing $NH_4H_2PO_4$ or NaH_2PO_4 with the oxides of the micronutrient ions at temperatures between 800 and 1400 °C and then rapidly quenching the melt. However, the drawback to large-scale utilization of such products is the highly corrosive reaction conditions which necessitate the use of expensive materials for furnace construction thereby increasing the cost of product. This difficulty may be overcome by producing long-chain metaphosphates which require much lower operating temperatures (around 500 °C) and do not involve corrosive melts. Poly- and metaphosphates of the macronutrients like K^+ or NH_4^+ are well-known and have been intensively studied (Fleming, 1969; Huffman and Newman, 1970; Sauchelli, 1967). Micronutrients may sometimes be included in such compositions by adding the appropriate ions prior to reaction (Ray, 1972; Volfkovich, 1972). However, most such proposed compounds are essentially macronutrient fertilizers which contain a small proportion of micronutrient ions. Apart from this, the major disadvantage of the micronutrient-incorporated metaphosphates is their very slow rate of dissolution and consequent poor availability of the micronutrient ions to plants.

In spite of the existing limitations of the phosphate glasses and the metaphosphate compounds, slow-releasing micronutrient fertilizers based on the polyphosphates appear to be the most promising from both the economic and the chemical points of view. The ability of phosphoric acid to form a linear polymeric chain (Van Wazer, 1966) provides a convenient long-chain backbone on which the heavy metal cations can be complexed. Moreover, one may visualize the formation of compounds of varying solubility by controlling the chain length of the phosphate polymer. Therefore, in principle, it is possible to synthesize fertilizers having any desired solubility characteristic. Generally, solubility decreases with increasing chain length (Thilo, 1962). Solubilization is also aided by hydrolytic cleavage of P–O–P bonds (Ohashi, 1964). Another unique feature of the polyphosphate-based fertilizer is that this concept is not only applicable to the all the macro- and micronutrient cations (Ca^{2+}, Mg^{2+}, NH_4^+, Zn^{2+}, Cu^{2+}, Fe^{2+}, etc.) but also the two important micronutrient anions, viz., B^{3+} and Mo^{6+}, can also be included in it. This is because during the polymerization of phosphate the borate as well as molybdate ions can copolymerize forming polyborophosphates and polymolybdophosphates (Van Wazer, 1966). Thus, by utilizing a single technique, fertilizers of almost any of the micronutrient ions can be prepared. This concept admits a great deal of flexibility, both in the composition of the product and in the solubility and availability of the nutrient ion.

In spite of this apparently simple approach, today no satisfactory slow-releasing micronutrient fertilizers are available for widespread use. The phosphate-based compounds, which have the distinct advantage of low-cost raw materials, have yet to make any significant impact. This is mainly because only two categories of polyphosphates are presently available, viz., the phosphate glass frits and the metaphosphates, both of which have their limitations as mentioned earlier. It appears that if a third type of polyphosphate could be synthesized which would show greater solubility (and plant nutrient availability) than the metaphosphates but at the same time would avoid the very high temperatures as required for producing phosphate frits, a comparatively inexpensive slow-releasing micronutrient fertilizer may be developed. Perhaps the main reason why this has not yet been possible is due to the difficult nature of the polyphosphates themselves. We

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have observed, in preliminary trials, that if the solubility of a metal polyphosphate is attempted to be increased by decreasing the chain length, the sample becomes hygroscopic and a large fraction of it becomes water soluble. If the amount of the water-soluble polyphosphates is decreased by increasing the degree of polymerization, then the amount of the nonavailable nutrient fraction increases. This observation may be ascribed to the fact that in any polyphosphate compound there is a very wide distribution of chain lengths; consequently, there is also a very wide variation in the properties. Thus, in any such polyphosphate, a certain proportion of the components would be short chain and water soluble whereas another portion of it would be long chain, water insoluble, nonexchangeable and also unavailable to plants. Both these properties are deleterious to the ideal fertilizer. It is not possible to obtain compounds in which the soluble polyphosphate fractions are not present and, at the same time, to limit the size of the long-chain-length fractions so that the micronutrients remain in an available form. This problem is particularly acute with the transition metal polyphosphates for which there is a very marked change in properties with even small variations in chain length. Another problem of a more practical nature is that most of the polyphosphates, except the very long chain metaphosphates, are extremely hygroscopic. Such hygroscopic compounds will not be acceptable as fertilizers. It is probably for this reason alone that almost every attempt so far has been to synthesize long-chain metaphosphates rather than short-chain polyphosphates. Such compounds, consequently, contain unavailable nutrient forms and are not completely satisfactory fertilizing agents.

Investigations were undertaken by us in an attempt to develop effective slow-releasing micronutrient fertilizers based on the alternative short-chain polyphosphate concept proposed above. The work involved, first, formulating a suitable compound. Here, the problem was to synthesize compounds in which the nutrient ions will remain available but will have low water solubility and will be dry and nonhygroscopic. After the synthesis routes were established, the compounds were characterized and assessed by studying their chemical and crystal nature, solubility in various media, and plant-growth responses. This article presents a report of the first of a series of such micronutrient fertilizers which have been developed. A slow-releasing zinc fertilizer is described here under three subsections which include (i) kinetics of polymerization of zinc phosphates and studies on some properties of the products with a view to assessing the suitability of the various compounds as potential fertilizers; (ii) formulation of the fertilizer compound, after modification of the chosen polyphosphate, to minimize its undesirable characteristics; and (iii) characterization and assessment of its fertilizing potential.

2. Methodology

The materials used for kinetic studies were ZnO (R May & Baker) and H_3PO_4 (AR BDH). In all experiments, the acid was diluted to a concentration of abour 46.4% P_2O_5. The exact strength of acid used was determined by pH-metric titration (Van Wazer et al., 1954); standardization was done at 3-day intervals (Varadachari, 1992).

All reactions were carried out in a platinum crucible. In the preweighed crucible, 0.5 g of ZnO was taken and moistened with 0.4 mL of water; water is necessary to avoid the vigorous reaction and spattering losses which otherwise occurs on addition of H_3PO_4. Finally the required quantity of H_3PO_4 was pipetted in. Weights were recorded at each stage. The crucible was then placed in a muffle furnace maintained at 150 °C (±0.5 °C) and heated for 30 min. This was done in order to remove most of the excess water which causes spattering at higher temperatures. The crucible was kept in a desiccator (over fused $CaCl_2$), and the furnace temperature was increased to 300 °C (±1 °C), 350 °C (±1 °C), or 400 °C (±1.5 °C). After the furnace temperature stabilized, the crucible was placed in it and heated for the required period of time. It was then cooled in a desiccator (over P_2O_5) and weighed. The contents of the crucible were finally washed, filtered, and made to volume. The residue on the filter paper was dried and stored [details in Varadachari, (1992)].

From the known weight and concentration of H_3PO_4 solution initially taken, the actual amount of H_3PO_4 (excluding all the water) was calculated; this quantity is henceforth designated as $[H_3PO_4]$. The weight loss of the reaction system per gram of $[H_3PO_4]$ was then calculated from the initial weight of ZnO + $[H_3PO_4]$ minus the final weight after heating. The range of error in these values is about ±0.1%. The ratio R of the reacted product (ZnO + H_2O)/P_2O_5 mole ratio, which is an index of the degree of polymerization, was also similarly determined. The composition of the polyphosphate residue consists entirely of ZnO, H_2O, and P_2O_5; since total weight = weights of (ZnO + H_2O + P_2O_5) and since weights of ZnO and P_2O_5 are known quantities (amounts initially added), the weight of H_2O in the residue can be easily determined. Consequently, the value of R can be deduced. It may be noted that the H_2O evaluated here is only the structural component of the acid polyphosphates such as in $H_4P_2O_7$ ($P_2O_5{\cdot}2H_2O$) or $Zn(H_2PO_4)_2$ ($ZnO{\cdot}P_2O_5{\cdot}2H_2O$).

The solutions obtained after washing the reaction products with water were analyzed for Zn^{2+} and P; Zn^{2+} was determined (Rush and Yoe, 1954) by the zincon method (±0.005 ppm). For the analysis of P (±0.02 ppm), the samples were first depolymerized to the orthophosphate by heating in 0.1 N HCl at 100 °C for 96 h; the P in solution was then determined as the chlorostannous reduced molybdophosphate blue complex in HCl medium (Jackson, 1973). Analysis of the insoluble portion of the reaction residue was done by dissolution in 5 N HCl prior to Zn^{2+} determination as the zincon complex; P was determined as stated above after fusing of the residue with NaOH and dissolution in HCl solution.

The reaction products were also subjected to the following qualitative solubility tests, viz., solubility in 0.1 and 1.0 N HCl, 0.33 M citric acid (GR SM), and 0.02 M ethylenediaminetetraacetate (EDTA) (AR BDH). If the sample dissolved in an excess of the reagent within 20 min (without heating), it was taken to be *soluble*; if a few particles remained even after 60 min, it was termed *slowly soluble*; if no significant dissolution was observable even after 60 min, then it was termed *insoluble*.

Number-average chain length ($\bar{n}'$) was determined by dissolving the sample in 0.1 N HCl, adding $K_4[Fe(CN)_6]$ (GR SM) (25 mg for 5 mg of Zn^{2+}), to complex Zn^{2+}, and then titrating with NaOH, first without and then with the addition of $AgNO_3$ (AR BDH) (Van Wazer et al., 1954).

Chemical analysis of the fertilizer compounds for Zn^{2+} and P was done as described earlier for the insoluble residual products of reaction. In addition, Ca^{2+} was determined by atomic absorption spectrometry in the solution obtained by dissolving the sample in 1.0 N HCl; NH_4^+ was determined after distillation of the sample with NaOH and absorption in H_2SO_4 (Black, 1965).

IR spectra of the samples were recorded on a Perkin Elmer Model 577 spectrometer, with the scan range of

4000–200-cm^{-1} resolution (±5 cm^{-1}) using pellets containing KBr as matrix. X-ray diffraction (XRD) was recorded on a Philips PW 1140 X-ray diffractometer using Ni-filtered Cu Kα radiation at a scanning speed of 1° 2θ/min (precision in 2θ, ±0.1°).

Solubility of the fertilizer compounds in the following reagents was noted, viz., in 0.1 N HCl, 0.33 M citric acid (GR E. Merck), 1.0 N ammonium citrate (pH 8.5), 0.005 M diethylenetriaminepentaacetate (DTPA) (AR Ferak-Berlin), 0.5 N ammonium oxalate (AR BDH) (pH 8.5), and a mixture of 0.5 N ammonium acetate (AR IDPL) and 0.02 M EDTA (AR BDH) (pH 4.65). These reagents are popularly used for extracting and evaluating available forms of micronutrients from soils (Black, 1965; Cox and Kamprath, 1972). To 0.1 g of the fertilizers 20 mL of the reagent was added and agitated for 2 h. The solution was then filtered, washed, and made to volume. Soluble Zn^{2+} was determined by atomic absorption spectrometry (AAS) with a precision of ±0.01 ppm Zn. Here the zincon method described earlier was not used because citrate and oxalate were observed to cause interference in color development.

The rate of solubilization of Zn^{2+}, from the fertilizers, in water was also studied: 0.1 g of the compounds was taken and 10 mL of water was pipetted into each. The solutions were agitated for 2 h each day and then allowed to stand. After 24, 48, 72, 96, and 120 h of contact time, the solutions were filtered, washed, and made to volume; Zn^{2+} in these solutions was determined as before, by the zincon method.

Plant-growth experiments were carried out in porcelain pots. Soils (0–15 cm) were collected from (i) Pusa, Bihar, India, and (ii) Mal, West Bengal, India. Both these soils are reported to the responsive to Zn^{2+} fertilization (Kanwar and Randhawa, 1978). Characteristics of these soils are as follows. (a) Pusa: Old alluvium; Haplaquept; pH 8.75; organic carbon, 0.60%; available Zn^{2+} (0.005 M DTPA), 0.79 ppm. (b) Mal: Terai (near Himalayan foothills) alluvium; Haplaquept; pH 4.85; organic carbon, 1.46%; available Zn^{2+} (0.005 M DPTA), 0.88 ppm. In each pot, 1 kg of soil was weighed. The soils were then treated with superphosphate (100 mg of P_2O_5/kg). Here, an excess of superphosphate fertilizer was added so that the plant's requirement of nutritional P would be completely met; response to additional P in the insoluble polyphosphate fertilizer would be of relatively little consequence. Zinc was added as $ZnSO_4 \cdot 7H_2O$ as well as zinc calcium polyphosphate at the rates of 0, 2.025, 4.05, 8.10, 12.15 ppm Zn^{2+} which are equivalent to 0, 5, 10, 20, and 30 kg/ha of $ZnSO_4$, respectively. All fertilizers were mixed with the soil 4 days prior to transplanting. Paddy (IET 4094) was grown in a nursery bed and transplanted when the seedlings were 3 weeks old. Each pot contained one plant for the Pusa soil and two plants for the Mal soil; the former was grown as a summer crop and the latter as a winter crop. At each fertilizer level, four replicates were performed. After harvesting, grains were separated from the straw and then grain weight and straw weight were recorded after drying at 60 °C. The straw was cut into small chips (with stainless steel scissors) and analyzed for Zn^{2+} after digestion with triacid mixture (Jackson, 1973). In this case again the zincon method was unsuitable because of interference; hence analysis was done by AAS. Results of these experiments were thereafter statistically analyzed.

3. Results and Discussion

3.1. Kinetics of Zinc Phosphate Polymerization and Nature of the Reaction Products. Rate curves for dehydration of the system ZnO + H_3PO_4 in which Zn:P = 1:2, 1:2.16, and 1:1.58, are shown in Figures 1–3 at reaction temperatures of 300, 350, or 400 °C. In Figure 1, the initial reacting species is $Zn(H_2PO_4)_2$ (since Zn:P = 1:2). Therefore, the reaction may be represented as Zn-

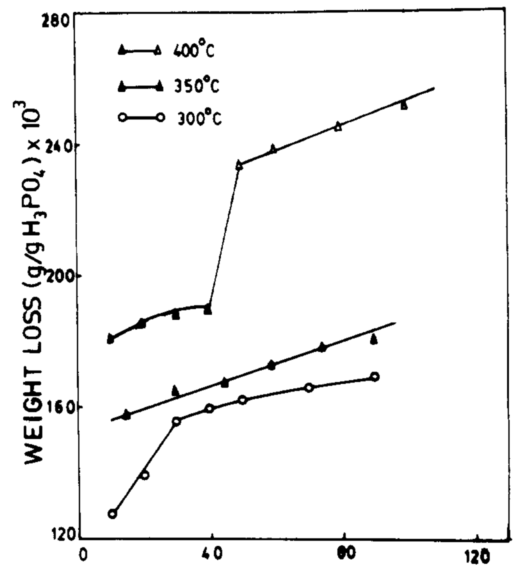

Figure 1. Kinetics of dehydration in the system ZnO–H_3PO_4 (Zn:P = 1:2).

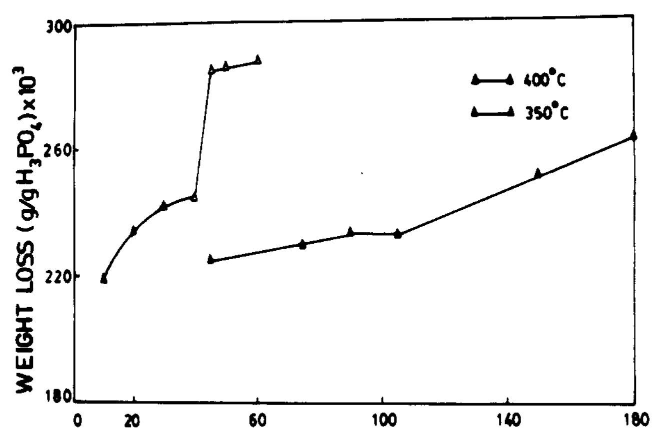

Figure 2. Kinetics of dehydration in the system ZnO–H_3PO_4 (Zn:P = 1:2.16).

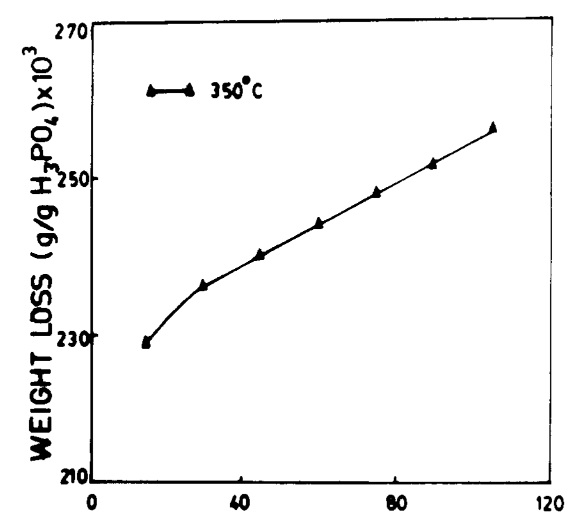

Figure 3. Kinetics of dehydration in the system ZnO–H_3PO_4 (Zn:P = 1:1.58).

$(H_2PO_4)_2 \rightarrow Zn(PO_3)_2 + 2H_2O$. The formation of the metaphosphate $Zn(PO_3)_2$, thus, involves the elimination of 2 mol of H_2O for every mole of $Zn(H_2PO_4)_2$.

Compounds which are less polymerized (the polyphosphates) are not completely condensed and hence lose less water. For the compounds shown in Figure 1, the theoretically maximum possible water loss corresponding to complete polymerization is 0.2756 g/g of $[H_3PO_4]$. Here, none of the reaction products are completely dehydrated indicating the formation of polyphosphate rather than the metaphosphate. This is also evident from the fact that none of the curves show plateau formation which reveals the attainment of an equilibrium state.

An unusual aspect of these curves (Figures 1–3) is the apparent lack of similarity between nature of dehydration kinetics (as seen from the curve shapes) at 300, 350, and 400 °C. Any reaction of a particular order n is normally expected to have similar curve shapes at different temperatures since the value of n which determines the nature of the curves (defined by the kinetic equation $dc/dT = kc^n$) does not change with temperature. However, closer inspection reveals interesting features which could explain this apparent abnormality. Thus, at 300 °C, Figure 1 shows two linear regions: one at the $(127–155) \times 10^{-3}$ g/g of H_3PO_4 and the other at the $(160–169) \times 10^{-3}$ g region. At 350 °C (Figure 1), only a single straight line is obtained covering the region $(158–182) \times 10^{-3}$ g. By overlapping the data for 300 and 350 °C, it can be seen that whereas the region at $(160–169) \times 10^{-3}$ g (for the sample reacted at 300 °C) is a straight line, this region is also a straight line for the sample reacted at 350 °C. Other regions, however, are not common for both samples, and therefore, their natures cannot be compared.

Studies with $ZnO + H_3PO_4$ mixtures containing different proportions of Zn:P also reveal such behavior. Thus, in Figure 2 (Zn:P = 1:2.16), the linear region at $(225–232) \times 10^{-3}$ g for the sample reacted at 350 °C is also shown by the sample reacted at 400 °C; the other linear region at $(242–262) \times 10^{-3}$ g is similarly present in the sample reacted at 400 °C. Figure 3 (Zn:P = 1:1.58) shows a single straight line from 232×10^{-3} to 255×10^{-3} g. The interesting feature here is that common linear regions can be observed not only within samples containing the same Zn:P ratios but also between samples having different Zn:P ratios. For example, the region at $(225–232) \times 10^{-3}$ g which is linear for the Zn:P = 1:2.16 sample reacted at 350 °C (Figure 2) is also linear for the Zn:P = 1:2 sample reacted at 400 °C (Figure 1) and the Zn:P = 1:2.16 sample reacted at 400 °C (Figure 2). Moreover, the linear region at $(232–262) \times 10^{-3}$ g for the Zn:P = 1:2.16 sample reacted at 350 °C (Figure 2) is also shown by samples at Zn:P = 1:2 reacted at 400 °C (Figure 1) as well as Zn:P = 1:1.58 at 350 °C (Figure 3) and Zn:P = 1:2.16 at 400 °C (Figure 2). In fact, the break in the curve occurs in the same position, viz., at 232.5×10^{-3} g, in the first three samples mentioned above.

The implications of these observations are as follows: The reaction of ZnO and H_3PO_4, in which polymerization occurs by the elimination of water, is kinetically a zero-order process as evidenced by the straight-line shapes of the curves. However, breaks in these lines suggest that polymerization occurs in linear stages, each stage being characterized by the degree of weight loss (i.e., degree of polymerization). Once a particular degree of polymerization is reached (i.e., polyphosphates of a particular average chain length are formed), then a quasi-equilibrium stage results. After a period of time, polymerization begins once again at a rate different from the former one. This process continues as before until another breakpoint

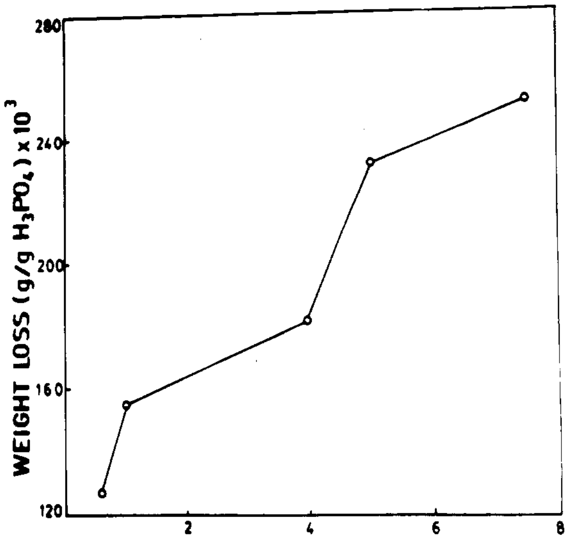

Figure 4. Empirical dehydration curve for the system $ZnO–H_3PO_4$.

(characterized by the degree of polymerization) is reached, whereupon a further change in the rate of polymerization occurs. The nature of polymerization of the zinc phosphates may, thus, be represented by the empirical curve in Figure 4. An initial dehydration up to 155×10^{-3} g is followed by another of slower rate up to 180×10^{-3} g; then a sharp rise occurs which continues up to 232×10^{-3} g and followed by a slower rate until polymerization is complete. On increase of the reaction temperatures from 300 to 400 °C, only the slopes of the lines will increase; apart from this, other features of the curves, particularly the boundaries of the breakpoints, will remain unaltered even with changes in reaction conditions.

Table I gives values of R for the reaction products. R, which is an index of the degree of polymerization, equals 3.0 for the unpolymerized orthophosphate and reaches a limiting value of 1.0 for the infinite linear chain metaphosphates; values lower than 1.0 indicate cross-linked ultraphosphates (Van Wazer, 1966). Here, it is seen that R values are greatest at Zn:P = 1:2 ratios (i.e., polymerization is lowest) as compared to higher or lower Zn:P ratios under identical heating conditions. At Zn:P = 1:2.16, the presence of free H_3PO_4 is probably responsible for increasing condensation. In samples deficient in H_3PO_4 (Zn:P = 1:1.58), the initial amount of structural H_2O is itself less, and hence even if the same amount of water is removed by reaction, the R value $(ZnO + H_2O/P_2O_5)$ will be lower than that of the Zn:P = 1:2 residue.

Amounts of water-soluble Zn^{2+} and P in the polyphosphate products obtained from the aforementioned kinetic studies are shown in Table II. Products from Zn:P = 1:2 reaction mixtures at 300 and 350 °C contain a very high proportion of water-soluble components; only at 400 °C after 50-min reaction do the samples become sparingly soluble. However, at all temperatures, solubility trends are irregular. This irregularity is probably due to the fact that the polyphosphates hydrolyze rapidly, and therefore, during the period of filtration and washing, some insoluble compounds may be hydrolyzed to the soluble forms. Therefore, the solubility data reflect only an average picture. They are, however, useful for assessing the overall trend in the solubility characteristics. It is also interesting to note that even the highly polymerized compounds, with R values around 1.0, contain significant amounts of water-soluble components (Tables I and II). This indicates a very wide distribution of the chain length such that

Table I. Kinetics of Water Loss in the Reaction ZnO + H_3PO_4 and Corresponding *R* Values

Zn:P (molar ratio of reaction mixture)	reaction temp (°C)	time of heating (min)	wt loss (g/g of H_3PO_4)	*R* (M_2O/P_2O_5)
1:2	300	10	0.1267	2.62
		20	0.1388	2.49
		30	0.1556	2.31
		40	0.1594	2.27
		50	0.1620	2.23
		70	0.1659	2.19
		90	0.1690	2.16
	350	15	0.1581	2.28
		30	0.1651	2.20
		45	0.1672	2.18
		60	0.1728	2.12
		75	0.1786	2.07
		90	0.1802	2.04
	400	10	0.1807	2.04
		20	0.1864	1.98
		30	0.1884	1.95
		40	0.1894	1.94
		50	0.2333	1.46
		60	0.2389	1.40
		80	0.2446	1.34
		100	0.2516	1.27
1:2.16	350	45	0.2244	1.16
		60	0.2313	1.09
		75	0.2296	1.10
		90	0.2327	1.07
		105	0.2328	1.07
		150	0.2514	0.86
		180	0.2627	0.74
	400	10	0.2189	1.22
		20	0.2340	1.06
		30	0.2421	0.97
		40	0.2418	0.97
		45	0.2844	0.51
		50	0.2863	0.49
		60	0.2875	0.47
1:1.58	350	15	0.2284	1.78
		30	0.2359	1.70
		45	0.2401	1.63
		60	0.2439	1.62
		75	0.2477	1.58
		90	0.2515	1.53
		105	0.2559	1.49

Table II. Water Solubility of Reaction Products of the Reaction ZnO + H_3PO_4

Zn:P (molar ratio of reaction mixture)	reaction temp (°C)	time of heating (min)	Zn^{2+} (% soluble) (w/w)	P (% soluble) (w/w)	P/Zn (molar ratio of solution)
1:2	300	10	52.29	79.18	3.20
		20	67.23	82.76	2.60
		30	65.36	85.55	2.76
		40	72.21	81.78	2.39
		50	68.48	82.60	2.55
		70	73.46	84.85	2.44
		90	65.74	82.96	2.66
	350	15	69.41	86.94	2.64
		30	70.67	83.83	2.50
		45	70.03	83.58	2.52
		60	66.61	78.01	2.47
		75	61.94	74.96	2.55
		90	57.58	72.06	2.64
	400	10	77.19	91.15	2.49
		20	79.06	91.00	2.43
		30	68.48	81.66	2.52
		40	59.76	70.14	2.48
		50	7.47	14.11	3.99
		60	6.23	12.67	4.29
		80	3.32	5.50	3.50
		100	1.62	2.92	3.80
1:2.16	350	45	63.13		
		60	66.88		
		75	61.26	81.48	2.81
		90	55.00	86.44	3.32
		105	56.25	84.82	3.18
		150	30.00	59.33	4.17
		180	20.75	30.70	3.12
	400	10	57.50	89.23	3.28
		20	63.75		
		30	49.37	76.93	3.29
		40	55.00	86.21	3.31
		45	4.73	11.96	5.34
		50	5.00	12.29	5.19
		60	5.55	16.20	6.16
1:1.58	350	30	44.81	59.34	2.80
		45	28.32	47.54	3.54
		60	47.30	55.25	2.47
		75	37.34	45.35	2.56
		90	27.69	31.39	2.39
		105	28.32	30.18	2.25

although the average value is very high (low *R*), a small proportion of short-chain compounds are also present which remain soluble.

Compositions of the insoluble residues (Table III) also show haphazard trends. This may be attributed to hydrolysis as well as simultaneous precipitation (of insoluble ortho- or pyrophosphate) reactions that are unavoidable during residue recovery.

3.2. Formulation of the Fertilizer. Solubility characteristics of the various polyphosphates are shown in Table III. It may be observed that the products obtained at 300 °C with Zn:P = 1:2 are all soluble in 0.1 N and 1 N HCl and in 0.33 M citric acid. However, all these samples are extremely hygroscopic and become sticky when exposed to the atmosphere for a few minutes. At 350 °C, the samples remain soluble in these reagents till a *R* value of 2.12 (Table I) is reached; beyond this stage the products become much less soluble. In fact, products with *R* values <1.4 are insoluble even in 1 N HCl. The only apparent advantage with such compounds, obtained at 400 °C, is that they are less hygroscopic, and more powdery than the more soluble products obtained at 300 or 350 °C.

With samples prepared at Zn:P = 1:2.16 ratios, solubility decreases further. This is to be expected, in view of their higher chain lengths (vide *R* values, Table I). The compounds prepared from Zn:P = 1:1.58 are likewise less soluble than the Zn:P = 1:2 compounds. Both the Zn:P = 1:2.16 and 1:1.58 compounds are initially fairly dry, but after exposure to the atmosphere for a few hours, stickiness appears and the powders are no longer free flowing.

From this brief survey of the characteristics of the polyphosphates, it would seem that none of them is completely suitable for use as a fertilizer material. Most of the compounds are hygroscopic; those which are more dry are far too insoluble. However, even compounds which are less sticky and fairly well polymerized contain a significant fraction of water-soluble Zn^{2+}. In compounds in which the water soluble fraction is reduced to <10% the solubility in 0.1 N HCl is also very low; such compounds are, therefore, not acceptable. On the other hand, the products obtained at 300 °C with Zn:P = 1:2 contain >80% Zn^{2+} in water-soluble forms; moreover, they are not only very hygroscopic but also acidic, with a pH of around 2.

At this stage, the problem appeared to be insurmountable. Although investigations on the effect of decreasing as well as increasing the amount of P were made specifically to observe if the problem of hygroscopicity and water solubility could be avoided, this approach was not successful. Apparently the chain length distribution pattern of the zinc polyphosphates is too wide to permit synthesis of a compound low in water-soluble forms as well as unavailable forms. As this is an inherent characteristic of the polymerization process itself, the only solution would

Table III. Water-Insoluble Residue of the Products of the Reaction $ZnO + H_3PO_4$: Contents of Zn^{2+} and P and Solubility[a]

Zn:P (molar ratio of reaction mixture)	reaction temp (°C)	time of heating (min)	Zn^{2+} (%) (w/w)	P (%) (w/w)	P/Zn (molar ratio of residue)	solubility in 0.1 N HCl	solubility in 1.0 N HCl	solubility in 0.33 M citric acid	solubility in 0.02 M EDTA
1:2	300	10	39.06	25.70	1.39	S	S	S	S
		20	38.04	20.22	1.12	S	S	S	S
		30	38.65	25.36	1.38	S	S	S	S
		40	39.47	26.73	1.43	S	S	S	S
		50				S	S	S	S
		70	39.88	24.33	1.29	S	S	S	S
		90	37.69	18.84	1.06	S	S	S	SS
	350	15	35.77	25.70	1.52	S	S	S	S
		30	34.75	24.67	1.50	S	S	S	S
		45	36.39	22.62	1.31	S	S	S	SS
		60	36.39	20.56	1.19	S	S	SS	SS
		75	32.90	25.05	1.61	I	S	I	I
		90	34.11	22.69	1.40	I	SS	I	I
	400	10	40.30	14.39	0.75	S	S	SS	I
		20	35.77	21.07	1.24	S	S	SS	I
		30	34.95	34.44	2.08	SS	S	I	I
		40	36.96	27.45	1.57	I	S	I	I
		50				I	SS	I	I
		60				I	SS	I	I
		80	29.02	28.37	2.06	I	I	I	I
		100	27.79	28.19	2.14	I	I	I	I
1:2.16	350	45	37.31	19.35	1.09	S	S	SS	SS
		60	46.64	22.26	1.01	S	S	SS	SS
		75	42.76	24.29	1.20	S	S	SS	SS
		90	35.34	25.83	1.54	SS	S	I	I
		105	39.40	23.46	1.26	I	S	I	I
		150	33.92	27.55	1.71	I	I	I	I
		180	34.05	28.48	1.77	I	I	I	I
	400	10	41.59	19.75	1.00	S	S	SS	SS
		20	45.10	21.34	1.00	S	S	SS	SS
		30	33.43	27.96	1.77	SS	S	I	I
		40	37.31	31.25	1.77	I	S	I	I
		45	29.93	39.89	2.81	I	I	I	I
		50	36.54	39.98	2.31	I	I	I	I
		60	30.32	21.10	2.17	I	I	I	I
1:1.58	350	30	45.23	17.83	0.83	S	S	SS	I
		45	35.99	6.84	0.40	S	S	SS	I
		60	47.30	7.53	0.34	SS	S	SS	I
		75	42.37	6.18	0.31	SS	S	I	I
		90	42.76	20.56	1.01	I	SS	I	I
		105	39.08	21.90	1.18	I	SS	I	I

[a] Abbreviations: S, soluble; SS, slowly soluble; I, insoluble.

be to find out some other means of overcoming the solubility problem.

Since most of the zinc polyphosphates are not completely dehydrated, they are expected to contain free acid groups. This is supported by the fact that the pH of the polyphosphates is usually <2. It was conjectured that the high water solubility of these polyphosphates could be due to the presence of such free acid groups on the chain and that reducing the free acid group content would also reduce solubility. To test this hypothesis, a sample was prepared at 300 °C by heating for 60 min with a Zn:P = 1:2; a small amount of water was added to form a suspension and then it was neutralized with $CaCO_3$ (R May & Baker) until the pH increased to 3.7. The suspension was then dried in a vacuum desiccator over fused $CaCl_2$. When tested, the water solubility of this compound was observed to decrease to about 1% Zn^{2+} from the original value of 70% Zn^{2+} for the unneutralized sample. The compound was also observed to retain its solubility in 0.1 N HCl, 0.33 M citric acid, and 0.02 M EDTA. Moreover, it was also nonhygroscopic and powdery. In short, it possessed all the properties of an ideal slow-releasing fertilizer. This experiment confirmed the fact that free acid groups are responsible for both high water solubility and hygroscopicity of the polyphosphates.

Of all the polyphosphate residues studied, only the compounds formed at 300 °C at Zn:P = 1:2 show good solubility in 0.1 N HCl, 0.33 M citric acid, and 0.02 M EDTA (and thereby contain Zn^{2+} in completely available forms). Taking other ratios of Zn:P does not appear to be of any particular advantage. On the contrary, with an excess of H_3PO_4 (Zn:P > 2), more free acid groups will have to be neutralized, whereas with a mixture deficient in H_3PO_4, there is a chance of unreacted ZnO remaining. Therefore, a reaction mixture containing Zn:P = 1:2, appears to be most suitable.

Tables II and III show that the products obtained at 300 °C (Zn:P = 1:2) are all extremely soluble in water as well as in 0.1 N HCl and 0.33 M citric acid. However, solubility in 0.02 M EDTA decreases below a R value of 2.16 (Table I). In order to obtain a compound with high solubility in all these reagents, a residue with a R value slightly higher than 2.16 appeared to be optimum. Thus, a zinc polyphosphate with a Zn:P ratio of 1:2 and a R value of 2.19 was chosen as the polyphosphate base which would be subsequently modified by neutralization to produce the fertilizer. The number-average chain length ($\bar{n}'$) of this polyphosphate (as determined by titrimetric analysis) is 2.35.

Small amounts of the proposed fertilizer were then prepared. Mixtures of ZnO and H_3PO_4 (Zn:P = 1:2) were reacted as described in section 2, at 300 °C for 60 min; the final weight loss recorded was 0.166 g/g of [H_3PO_4]. This corresponds to a R value of 2.19. The product was then

$ZnO + H_3PO_4$

↓

Heat at 150°C

↓

$Zn(H_2PO_4)_2$

↓

Heat at 300°C

↓

Zn^{2+} - polyphosphate

↓

Add water and mix to form a slurry

↓

Add $CaCO_3/NH_4OH$, mix and allow to stand for 6 hours

↓

Dry and grind

Figure 5. Flow chart for the production of zinc polyphosphate fertilizer.

cooled to room temperature and made into a slurry with water. To this, 1.02 g of $CaCO_3$ or 16.2 mL of 0.5 N NH_4OH (AR BDH) (per 1 g of ZnO) was added, and the mixture was stirred and allowed to stand for 6 h. It may be mentioned that, in addition to $CaCO_3$, NH_4OH solution may also be successfully used as the neutralizing agent. Since neutralization reaction is slow, sufficient time has to be allowed for the reaction to complete. This entire process has been depicted in the flow chart shown in Figure 5. Several such batches were prepared to obtain a sizable quantity for further studies.

3.3. Characterization of the Fertilizer Compounds. Chemical composition (in percent) of the zinc calcium polyphosphate is ZnO, 26.99; P_2O_5, 44.93; CaO, 14.15; H_2O^+ (structural), 6.93; H_2O^- (adsorbed), 6.60. This corresponds to the formula $Zn_{0.33}H_{0.77}Ca_{0.25}P_{0.63}O_{2.54}$. For the zinc ammonium polyphosphate, the chemical composition is as follows: ZnO, 29.57; P_2O_5, 52.84; NH_4^+, 6.62; H_2O^+, 5.64; H_2O^-, 4.70; its formula is $Zn_{0.36}H_{0.63}(NH_4)_{0.37}P_{0.74}O_{2.71}$.

IR spectra of the compounds are shown in Figure 6. The two compounds reveal almost the same absorption behavior except in the region around 1400 cm^{-1}. The NH_4^+ ion absorbs strongly around 1400 cm^{-1}; $NH_4H_2PO_4$ has twin absorptions at 1450 and 1400 cm^{-1} which coalesce to a single peak at 1450 cm^{-1} for $(NH_4)_2HPO_4$. However, the latter shows an additional absorption at 1715 cm^{-1} (Corbridge and Lowe, 1954; Nyquist and Kagel, 1971). The spectra recorded here (Figure 6) reveal broadening of the absorptions in these regions; this could arise due to the presence of ammonium polyphosphates in addition to the orthophosphates. Stronger absorptions at 3000 cm^{-1} for the ammonium fertilizer may be attributed to NH stretching in addition to the OH stretching of H-bonded water molecules. Absorptions due to P–O ionic stretching and deformation at 1180–1050 and 560 cm^{-1}, respectively (Corbridge and Lowe, 1954), are also evident in the spectra of both compounds (Figure 6). The position of the P–O–P absorption which is centered at 1100 cm^{-1} indicates short-chain units of the tripoly type rather than the longer chain polymers; in the latter type of compounds, such absorptions

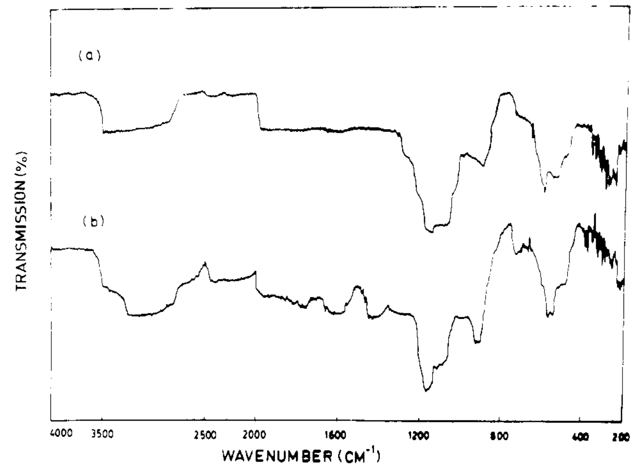

Figure 6. Infrared absorption spectra of (a) zinc calcium polyphosphate and (b) zinc ammonium polyphosphate.

are usually centered at longer wavelengths of around 1250 cm^{-1} (Corbridge and Lowe, 1954). This conclusion is also supported by the chain-length analysis data wherein a $\bar{n}'$ of 2.35 was obtained.

X-ray diffraction analysis (Table IV) of the samples reveals some interesting features. Both compounds show a broad diffraction band around 6×10^{-1} nm indicating an amorphous phase and strong sharp lines suggesting crystalline phases, too. The strongest diffraction is at $(2.03–2.04) \times 10^{-1}$ nm. Numerous other bands are also common to both compounds. These may, therefore, be attributed to the basic zinc polyphosphate structure which is the same for both. It may be mentioned that a cupric polyphosphate fertilizer which was studied also showed an identical strong peak at $(2.03–2.04) \times 10^{-1}$ nm together with many other diffractions (unpublished; Ray, 1991) which are common with those of the zinc salts. Here, such lines which are common to the polyphosphates of both zinc and copper have been tentatively assigned to the basic polyphosphate skeletal structure (Table IV).

Apart from the crystalline polyphosphates, other crystalline compounds are also evident. In the zinc calcium polyphosphate, calcium pyrophosphate may be present whereas the corresponding ammonium form probably also contains the tripolyphosphate $(NH_4)_4H_2P_4O_{13}$, $(NH_4)_2Zn(P_2O_7)$, and $(NH_4)ZnH_3(PO_4)_2{\cdot}H_2O$ (JCPDS, 1978). In addition to these, there are other reflections which may be due to ammonium polyphosphates and which are also shown by a cupric ammonium salt (unpublished; Ray, 1991).

Solubilization of the zinc fertilizers in water over a period of several days is shown in Table V. After the initial solubilization of 1.25% and 7.50% Zn^{2+} from the calcium and ammonium forms, respectively, further dissolution is practically negligible even after 120 h. It appears that low-molecular-weight fractions contribute to the initial solubility and subsequent hydrolytic dissolution is extremely slow. Hydrolysis is probably inhibited to a large extent due to the cross-linking of chains by the divalent cations, Zn^{2+} and Ca^{2+}, which limits the accessibility of H_2O molecules to the P–O–P groups.

In dilute acids, viz., 0.1 N HCl and 0.33 M citric acid, both fertilizers are completely soluble. Solubilization in 0.1 N HCl may occur by exchange of Zn^{2+} ions on the polymer chains with H^+ ions from solution. In 0.33 M citric acid, however, complexation would be an additional factor of Zn^{2+} solubilization. In near neutral and alkaline media, too, the fertilizers are highly soluble. Such excellent solubility in organic complexants indicates that the Zn^{2+}

Table IV. X-ray Diffraction Characteristics of the Zinc Calcium and Zinc Ammonium Polyphosphates[a]

d (Å)	I	assignment
Zinc Calcium Polyphosphate		
10.05	6	CaPy
9.21	8	Pp
6.71 (b)	19	Pp
4.67	6	CaPy, Pp(?)
4.00	20	ZnCaPp(?)
3.561	12	ZnCaPp(?)
3.255	8	Pp(?)
3.100	19	Pp, CaPy
3.058	4	Pp
2.867	9	ZnO
2.637	8	CaPy
2.607	3	ZnO
2.550	10	CaP
2.481	6	ZnO
2.411	3.8	Pp(?)
2.356	15	Pp
2.232	5	
2.122	10	
2.040	100	Pp, CaPy
1.914	4	Pp(?)
Zinc Ammonium Polyphosphate		
13.4	5	
9.21	24	Pp
7.76	6	Pp(?)
7.25	6	AZnP, AP_4, AZnPy
6.71	8	Pp
6.51	3	Pp
5.98	10	AP_4, AZnP
5.61	10	APp, AZnP
5.40	5	APp
4.79	14	AZnPy
4.44	6	APp
3.480	13	APp, AP_4
3.327	11	AP_4, AZnP
3.198	8	
3.079	5	Pp
2.998	11	APp
2.867	3	ZnO
2.797	8	APp
2.607	8	ZnO
2.481	5	ZnO
2.344	22	Pp
2.036	100	Pp

[a] Abbreviations: AZnP, $(NH_4)ZnH_3(PO_4)_2 \cdot H_2O$; AZnPy, $(NH_4)_2Zn(P_2O_7)_2$; APp, ammonium polyphosphate; AP_4, $(NH_4)_4H_2P_4O_{13}$; CaPy, $Ca_{1.5}HP_2O_7 \cdot 2H_2O$; Pp, polyphosphate framework; ZnCaPp, zinc calcium polyphosphate; ZnO, zinc oxide.

in the micronutrient fertilizers should be readily assimilable by plants. It may be mentioned that the ability of a soil to provide Zn^{2+} for plant growth is usually assessed by the amount that is dissolved by HCl, EDTA, DTPA, or citric acid (Cox and Kamprath, 1972; Jackson, 1973) depending on the soil conditions. Moreover, it has also been observed that water-insoluble zinc fertilizers which readily dissolve in dilute HCl (Jackson, 1973) are all suitable sources of zinc for plants. The fertilizer compounds may, thus, be judged to contain Zn^{2+} in ionic binding sites which are closely comparable to those present in soils; more strongly bound (and less soluble) Zn^{2+} ions would be difficult for plants to assimilate. Consequently, the zinc fertilizers closely simulate natural sources of zinc in the soil which have low water solubility but are available for plant uptake over the entire period of growth.

For a further assessment of the fertilizing action of the polyphosphates, plant-growth experiments were done. Results of the trials carried out with two different types of soils using the zinc calcium polyphosphate as well as zinc sulfate (for a comparative assessment) are shown in Table VI. Grain yields of plants grown on an alkaline soil from Pusa, Bihar, show a definite trend of increase in grain output with the addition of zinc calcium polyphosphate fertilizer. By contrast, soils containing $ZnSO_4$ do not show any such trend probably because of the precipitation of insoluble zinc hydroxides, phosphates, etc. under the highly alkaline conditions which reduce the quantity of Zn^{2+} available. Statistical analysis of the data reveal that increase in yield over the control due to the slow-releasing zinc fertilizer is significant at the 5% level ($LSD_{0.05}$) when the Zn^{2+} dosage is 4.05 and 12.15 ppm. It is also noteworthy that, at three different levels (Table VI), there is a statistically significant increase in yield with the zinc calcium polyphosphate-treated soils over $ZnSO_4$-treated soils.

Experiments with other acidic soil from Mal, West Bengal, also show good response to the slow-releasing zinc fertilizer. Thus, at Zn^{2+} dosages of 8.10 and 12.15 ppm, there is a significant increase ($LSD_{0.05}$) in yield over the control; $ZnSO_4$-treated soils also produce higher grain yields than the control but the increase is significant at only one level (8.10 ppm Zn^{2+}). Yields from $ZnSO_4$-treated and zinc calcium polyphosphate-treated soils are statistically similar at similar fertilizer levels.

On the whole, the results of these trials indicate that the zinc calcium polyphosphate is either as good as or better than $ZnSO_4$ as a fertilizing compound for zinc. The possibility of the phosphorus content of the new fertilizer itself causing an increase in yield was eliminated by adding excess superphosphate to all the pots so that phosphorus hunger would be subsided and response to more phosphorus itself would be poor. To further confirm the fertilizing capabilities of zinc calcium polyphosphate, the straw was analyzed for Zn^{2+} uptake (Table VII). The data reveal a definite increase in Zn^{2+} content of the straws with both types of fertilizers. Increase in the Zn^{2+} concentrations is statistically significant at $LSD_{0.05}$ at three levels with both $ZnSO_4$ and zinc calcium polyphosphate treatments. The overall trend in the data (Table VII) also suggests that Zn^{2+} contents are higher with the plants grown in polyphosphate-treated soils than with those grown in $ZnSO_4$-treated soils. This difference is, however, significant ($LSD_{0.05}$) at only one fertilizer level (4.05 ppm Zn^{2+} dosage).

All the aforementioned results, thus, suggest that the slow-releasing zinc calcium polyphosphate is an effective material for zinc fertilization. The Zn^{2+} in this compound can be taken up by plants as readily as from $ZnSO_4$. Previous chemical data also support this property.

4. Summary and Conclusion

The basic concept of this investigation was to develop novel slow-releasing micronutrient fertilizer compounds based on the polyphosphate framework. Polyphosphates appeared to offer a distinct advantage over other slow-release formulations in view of their low raw material costs. From the chemical angle, too, the polyphosphates appeared to be highly suitable in view of their versatile amenable nature.

The two types of phosphate-based slow-release fertilizers which have been recommended so far are the glass frits and the long-chain metaphosphates. In this investigation, it has been attempted to synthesise a third type of compound which would overcome the major drawbacks of the two earlier types of compounds. In short, these compounds would contain nutrients in available forms and would also be fairly easy to produce.

The first micronutrient fertilizer thus developed was the zinc compound which has been described here. It was hoped that by solving the problem with zinc it would be

Table V. Solubilization of Zinc Polyphosphate Fertilizers in Water and Various Reagents

(i) Kinetics of Solubility of Zinc Polyphosphate Fertilizers in Water

fertilizer	% Zn^{2+} soluble after 0 h	24 h	48 h	72 h	96 h	120 h
zinc calcium polyphosphate	1.25	1.25	1.43	1.48	1.48	1.52
zinc ammonium polyphosphate	7.50	7.50	7.37	7.58	7.32	7.50

(ii) Solubility of Zinc Polyphosphate Fertilizers in Various Reagents

fertilizer	% Zn^{2+} soluble in 0.1 N HCl	0.33 M citric acid	1.0 N ammonium citrate (pH 8.5)	0.5 N ammonium acetate + 0.02 M EDTA (pH 4.65)	0.005 M DTPA	0.5 N ammonium oxalate (pH 8.5)
zinc calcium polyphosphate	100.00	100.00	94.20	94.83	100.00	76.85
zinc ammonium polyphosphate	100.00	100.00	97.81	97.49	99.80	97.81

Table VI. Average Grain and Straw Yields of Paddy on Application of Zinc Sulfate and Zinc Calcium Polyphosphate

soil	treatment	av grain yield (g) at Zn^{2+} dose (ppm) 0	2.025	4.05	8.10	12.15	av straw yield (g) at Zn^{2+} dose (ppm) 0	2.025	4.05	8.10	12.15
Pusa	$ZnSO_4$	3.86	3.77	2.93	2.41	3.59	4.83	4.38	4.84	4.67	4.86
	zinc calcium polyphosphate	3.86	4.96	5.59[a,b]	4.80[b]	6.08[a,b]	4.83	4.60	5.19	5.68	5.39
Mal	$ZnSO_4$	10.08	10.38	11.26	12.33[a]	11.88	7.88	8.09	8.58	8.45	8.98
	zinc calcium polyphosphate	10.08	11.49	11.93	12.90[a]	12.42[a]	7.88	9.11	9.91[a]	8.60	9.67[a]

[a] Significant increase in yield over the control ($LSD_{0.05}$). [b] Significant increase in yield over $ZnSO_4$ ($LSD_{0.05}$).

Table VII. Uptake of Zn^{2+} by Paddy Straw on Application of Zinc Sulfate and Zinc Calcium Polyphosphate to Pusa Soil

treatment	Zn^{2+} content (mg/kg of paddy straw) at Zn^{2+} dose (ppm) 0	2.025	4.05	8.10	12.15
$ZnSO_4$	64.38	85.63[a]	73.50	83.75[a]	86.00[a]
zinc calcium polyphosphate	64.38	89.38[a]	94.63[a,b]	84.38[a]	78.88

[a] Significant increase over the control ($LSD_{0.05}$). [b] Significant increase over $ZnSO_4$ ($LSD_{0.05}$).

possible to gain some understanding of the chemistry of the process which in turn would facilitate development of other micronutrient fertilizer compounds.

Initially, the kinetics of polymerization of ZnO + H_3PO_4 mixtures, at various Zn:P molar ratios and at various temperatures, were studied; the structural water loss and R value (M_2O/P_2O_5 molar ratio) of the products were evaluated. Results of this investigation gave interesting information on the nature of the polymerization process. It was concluded that polymerization of zinc phosphates is a zero-order process which shows linear rates that change with the degree of polymerization. Such a changeover from one rate constant to another is fairly sharp, and the breakpoint is constant regardless of temperature of reaction and, to some extent, the ratio of reactants.

Analysis of the water-soluble Zn and P in these products showed that all of them contained a very high proportion of water-soluble components. Only in the very highly polymerized compounds did the water solubility decrease considerably. On the other hand, the solubility of these polyphosphates in dilute HCl (0.1 and 1.0 N) and in various complexants (0.33 M citric acid and 0.02 M EDTA) showed that whereas the small chain compounds initially formed were soluble, with an increase in chain length the compounds became rapidly insoluble particularly in the complexants. Since solubility in dilute HCl and in complexants may be taken as an index of nutrient availability, the higher chain compounds obviously contain a portion of Zn^{2+} in unavailable forms. Thus, owing to the very high dispersion in chain lengths in the zinc polyphosphates, it was not possible to synthesise compounds having low water solubility but high solubility in complexants. Another problem with the polyphosphates was their extreme hygroscopicity.

Subsequently, it was concluded that the presence of free acid groups was responsible for high water solubility and that this could be reduced simply by neutralizing the acid groups. The desired formulation for the zinc fertilizer was, therefore, developed by choosing an optimum polyphosphate base and then reacting it with a base like $CaCO_3$ or NH_4OH. It was observed that such a treatment also removed the hygroscopicity and resulted in a dry and powdery product. The synthesis routes for these compounds are also very simple.

The fertilizers (viz., the calcium and ammonium salts of the zinc polyphosphate) were then characterized by chain-length analysis, chemical composition, solubility properties, IR characteristics, XRD measurements, and plant-growth experiments. The compounds are short-chain polyphosphates which are sparingly soluble in water but slightly soluble in 0.1 N HCl, 0.33 M citric acid, 1.0 N ammonium citrate (pH 8.5), 0.02 M EDTA, and 0.005 M DTPA. IR spectra also suggest the presence of short-chain polyphosphates. XRD analysis shows an amorphous phase with a broad hump at 6×10^{-1} nm; crystalline phases are also present. The strongest reflection is at (2.03–2.04) $\times 10^{-1}$ nm which could be due to a polyphosphate skeletal structure. The other crystalline phases present include $Ca_{1.5}HP_2O_7{\cdot}2H_2O$, $(NH_4)ZnH_3(PO_4)_2{\cdot}H_2O$, $(NH_4)_2Zn(P_2O_7)_2$, and $(NH_4)_4H_2P_4O_{13}$ in the calcium form and ammonium forms. Plant-growth experiments, carried out with two types of soils, showed statistically significant increases in yield due to the addition of the zinc calcium polyphosphate fertilizer. Zn^{2+} contents of the straw also showed significant uptake of this nutrient. Results indicate that the zinc calcium polyphosphate is either as good as or even better than $ZnSO_4$ as a fertilizing compound.

In conclusion, it may be stated that the concept of a polyphosphate-based compound appears to be well suited for slow-releasing fertilizer formulations. Firstly, the compounds are not only insoluble in water but also contain nutrients in readily available forms. Such a juxtaposition of desirable properties is very rarely observed in slow-releasing materials. This dual characteristic not only reduces drainage losses but also ensures an ever-ready supply of nutrients at any stage of the growth of the plant. Moreover, this supply is not dependent on hydrolysis rates and, therefore, will be much less influenced by soil factors. Secondly, from the commercial aspect, too, the polyphosphate formulation possess certain advantages, viz., cheap raw materials, technically simple synthesis routes, and relatively low operating temperatures.

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