5

Novel Slow-Releasing Micronutrient Fertilizers. 2. Copper Compounds

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The development of a new type of slow-releasing copper fertilizer which is based on a short-chain polyphosphate structure, is described. Kinetics of polymerization of cupric phosphate at various Cu:P ratios and temperatures were studied, and the products were characterized. The desired fertilizers were formulated by selecting the appropriate copper polyphosphates and then neutralizing them to improve their properties. The fertilizers were analyzed by chemical methods, IR, XRD, solubility studies, and plant growth experiments. They were observed to have short-chain P–O–P linkages and contain amorphous as well as crystalline phases. Their water solubility was <5%, but in organic complexants, like citric acid or diethylenetriaminepentaacetic acid, solubilities were >90%, thereby indicating excellent plant availability. Plant growth experiments showed that copper calcium polyphosphate is an efficient source of copper, comparable to $CuSO_4$; however, lower dosages are required with the former than with the latter.

Keywords: *Fertilizer; micronutrient; slow-releasing; copper; polyphosphate*

1. INTRODUCTION

Various environmental and economic drawbacks associated with the use of soluble salts as micronutrient fertilizers make it imperative that these be replaced, as far as possible, by slow-releasing compounds. However, the large-scale use of such compounds is even now, very limited. This may be attributed to the fact that very few types of slow-releasing micronutrient fertilizers are commercially available. The more notable of these, the phosphate glass-frits, are rather expensive; consequently, their use is mostly confined to the high-value crops. Moreover, the availability of nutrient ions varies with the soil type and is, therefore, not always satisfactory (Reuter, 1975). This is because the solubilization of ions from phosphate glasses occurs by hydrolytic cleavage of P–O–P bonds, which in turn is affected by various soil factors, such as pH, temperature, ionic nature of solution, etc. (Van Wazer, 1966).

At present, two categories of polyphosphate-based slow-releasing fertilizers are known. These are (i) the glassy phosphates which are prepared from melts and involve fusion temperatures, between 800 and 1400 °C (Krems Chemie, 1975; Ranney, 1978; Roberts, 1977), and (ii) the metaphosphates which are crystalline or amorphous products obtained at below-fusion temperatures, usually <500 °C (Lyons et al., 1971; Sauchelli, 1967; Volfkovich, 1972). Although the problems arising from the highly corrosive reaction conditions associated with the production of glass frits are negligible during the production of metaphosphates, the suitability of the latter compounds for micronutrients appears to be doubtful. Whereas potassium metaphosphates show good fertilizing potential (NDC, 1968; Volfkovich et al., 1975), a purely micronutrient metaphosphate (e.g., those of Zn, Cu, Fe, Mn, etc.) may not perform well since metaphosphates of heavy metals are highly insoluble compounds (Thilo, 1962). In fact, a purely micronutrient metaphosphate fertilizer does not appear to have been synthesized yet, the only exception being boron phosphate, BPO_4 (Volfkovich, 1972). All other compounds suggested (Lyons et al., 1971; Volfkovich, 1972) are essentially macronutrient (K or N) fertilizers in which small quantities of micronutrients are incorporated as additives.

We attempted to develop another category of slow-releasing micronutrient fertilizers which will overcome the major limitations of the two earlier types (Ray et al., 1993). These compounds are short chain polyphosphates of the respective metal ions; such materials do not appear to have been previously recommended for use as slow-releasing micronutrient sources. This may be due to some inherent handicaps in the chemical makeup of short-chain metal polyphosphates. Short-chain compounds, which are produced by heating the respective acid phosphates, contain a large proportion of water soluble components; they are highly acidic and extremely hygroscopic. Solubility as well as hygroscopicity may be reduced by further heating, to form longer chain polyphosphates. However, by this treatment, a considerable amount of insoluble components are also formed, in which the nutrient ions may be unavailable for plants. This phenomenon is due to the fact that any polyphosphate produced by heating always contains a wide range of P–O–P chain lengths (Van Wazer, 1966); the shorter chains are water soluble, whereas longer chains not only may be insoluble in water but also in organic complexants. Hence, heating to reduce short chain compounds also results in an increase of long chain forms. Moreover, even highly polymerized polyphosphates contain water soluble components and become sticky when exposed to the atmosphere.

Recently, it has been possible to overcome these hurdles to produce slow-releasing micronutrient fertilizers based on the short-chain polyphosphate concept. As the first of a series of such compounds, a zinc polyphosphate fertilizer was developed (Ray et al., 1993). In this work, the development of another such fertilizer containing copper, has been described. There

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are, broadly, three stages in this study. First, the kinetics of polymerization of cupric phosphates have been investigated and the nature and solubility of the polyphosphate products determined. On the basis of these studies, a suitable polyphosphate has been selected for formulation of the slow-releasing fertilizer. Finally, this fertilizer compound has been characterized by various techniques and assessed for its fertilizing potential.

2. METHODOLOGY

Cupric hydroxide was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (AR BDH) in water and neutralizing the solution with NH_4OH (AR BDH) till a pH of 8–9 was attained. The precipitate was washed, dialyzed, dried at 80 °C, and stored in a desiccator. Cu^{2+} content of this sample was determined by dissolving in 6 N HCl and recording the color of the zincon complex (sensitivity ±0.005 ppm) formed at pH 6.1 (Rush and Yoe, 1954). Briefly, to a solution of Cu^{2+} in 25 mL volumetric flasks was added 5 mL of a buffer solution at pH 6.1 (this was prepared by mixing 100 mL of 0.2 N sodium acetate (AR, BDH) and 3 mL of 0.2 N acetic acid (AR BDH)). Finally 1.5 mL zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene, E. Merck) solution (prepared by dissolving 0.0325 g of zincon in 0.5 mL of 4% NaOH and diluting to 25 mL) was added. The solutions were made to volume, and the color intensity recorded at 620 nm (Rush and Yoe, 1954). Adsorbed water (H_2O^-) and total water (H_2O^+) were determined from the weight loss at 105 and 1000 °C, respectively. The composition of the compound, thus obtained, was as follows: CuO, 67.13%; H_2O^+, 30.56%; H_2O^-, 2.31%.

Cupric hydroxide, $Cu(OH)_2$, was reacted with H_3PO_4 (AR BDH) solution diluted to 46.4% P_2O_5 (w/w). Standardization of the acid was as described by Van Wazer et al. (1954). Weighed amounts of $Cu(OH)_2$ and H_3PO_4 were taken in a platinum crucible to obtain Cu:P ratios of 1:2 or 1:3. The mixture was then placed in a muffle furnace at 150 °C (±0.05 °C) for 90 min to remove most of the free water, which causes spattering losses at higher temperatures. Finally, it was heated at 300 °C (±1 °C), 350 °C (±1 °C), or 400 °C (±1.5 °C) for the desired period of time, cooled in a desiccator over P_2O_5, and then weighed. Further experimental details of this reaction stage may be obtained from Varadachari (1992). The reacted samples were washed to separate the soluble portion and the insoluble residue, both of which were stored for analysis.

Dehydration parameters were calculated. These include (i) weight loss per unit weight of H_3PO_4 actually present (obtained from the known strength of phosphoric acid solution, w/w, and the known weight of solution taken for reaction; error range ±0.1) and (ii) the value of R ($CuO + H_2O/P_2O_5$) for the reaction product, which is an index of the degree of polymerization. This is obtained from the known weights of CuO and P_2O_5 (amounts initially added) and the calculated weight of H_2O, which is equal to the total weight of product minus the weight of CuO + P_2O_5 in it (details in Ray et al., 1993).

Solutions, obtained by washing the reaction products with water, were analyzed for Cu^{2+} as the zincon complex (Rush and Yoe, 1954). Total P was determined in depolymerized solutions obtained by heating an aliquot containing 0.1 N HCl at 100 °C for 96 h followed by colorimetric analysis (±0.02 ppm) as the molybdenum blue complex (Jackson, 1973). For analysis of the insoluble residues, the same aforementioned colorimetric procedures were adopted except that the samples were dissolved in 6 N HCl prior to Cu^{2+} analysis and were fused in NaOH for the determination of total P.

The residues were also qualitatively assessed for their solubility in various reagents. These were, 0.1 and 1.0 N HCl (AR BDH), 0.2 M EDTA (AR BDH), and 0.33 M citric acid (GR E. Merck). To a small amount of sample in a test tube (about 20 mg) was added 5 mL of the reagent; the suspension was allowed to stand, and its nature was examined at periodic intervals. As in our previous study (Ray et al., 1993), if a it was termed *soluble*. If a few particles remained even after 60 min, it was described as *slowly soluble* and if no significant change was observed even after 60 min, it was termed *insoluble*.

Average chain length of polyphosphate ($\bar{n}'$) was determined by dissolving the sample in 0.1 N HCl, removing Cu^{2+} from the solution by oxine extraction and finally titrating with standardized NaOH, as described in detail by Van Wazer et al. (1954).

Fertilizer samples were prepared by reacting $Cu(OH)_2$ with H_3PO_4 (Cu:P = 1:3) at 150 °C, as described previously. Subsequently, it was heated at 300 °C for 60 min, when a weight loss of 0.047 g/g of H_3PO_4 was obtained. The reacted mass was cooled, made into a paste with water, and $CaCO_3$ [illegible] or dilute (1:1) desiccator, ground, and stored. The equation representing the neutralization reaction may be represented as $Cu_{0.19}H_{1.97}P_{0.58}O_{2.62} + 0.51\ CaCO_3 \rightarrow Cu_{0.19}H_{0.95}Ca_{0.51}P_{0.58}O_{[illegible]} + 0.51\ H_2CO_3$.

Chemical analysis of the fertilizers, copper calcium polyphosphate and copper ammonium polyphosphate, was done by the same process described earlier for the reaction residues. In addition, Ca^{2+} (±0.05 ppm) was determined by AAS and NH_4^+ (±0.2 mg) by Kjeldahl distillation (Jackson, 1973). IR spectra of these compounds were recorded on a Perkin Elmer model 577 instrument within a scan range from 4000 to 200 cm^{-1} using pellets containing KBr as matrix. XRD was recorded on a Philips PW 1140 X-ray diffractometer using Ni-filtered CuKα radiation at a scanning speed of 1°2θ/min.

Solubilization of Cu^{2+} from the fertilizers, (0.1 g in 10 mL of water) was noted after 0, 24, 48, 72, 96, and 120 h (with [illegible] h agitation each day) and the Cu^{2+} analyzed as the zincon complex (Rush and Yoe, 1954). In addition, the amounts of Cu^{2+} solubilized by 0.1 N HCl, 1.0 N ammonium citrate (pH 8.5), 0.33 M citric acid, and 0.005 M DTPA (AR Ferak-Berlin) were also determined; the solutions obtained on shaking 0.[illegible] g of sample in 20 mL of the reagent and filtering, were analyzed for Cu^{2+} as before.

Plant growth experiments were carried out in porcelain pots. Soils (0–15 cm) were collected from (i) Pusa, Bihar, India (old alluvium; Haplaquept; pH 8.75; ECe 0.68 dS/m; organic C, 0.60%; available Cu^{2+}, 0.005 M DTPA, 3.00 ppm) and (ii) Mal, West Bengal, India (Himalayan Terai alluvium; Haplaquept; pH 4.85; ECe 0.33 dS/m; organic C, 1.46%; available Cu^{2+}, 0.005 M DTPA, 4.95 ppm). Each pot contained 1 kg of soil and was treated with a basal dose of superphosphate (100 mg of P_2O_5/kg). It may be noted that an excess of phosphate fertilizer was added so that the plant's requirement of nutritional P would be completely met; response to additional P in the polyphosphate fertilizer would thus be of little consequence. Copper was added as $CuSO_4 \cdot 5H_2O$ as well as the copper calcium polyphosphate at the rate of 0, 1.00, 2.00, 4.00, and 8.00 ppm Cu^{2+}, which are equivalent to 0, 2.5, 5.0, 10.0, and 20.0 kg of $CuSO_4$/ha, respectively. Urea was added whenever necessary. Paddy (IET 4094) was transplanted to the pots as 3 week old saplings at the rate of one plant per pot for the Pusa soil and two plants per pot for the Mal soil. At each fertilizer level, four replicates were performed.

After harvesting, grains were separated from the straw and grain weight was recorded. Straw, dried at 60 °C, was digested with triacid, $HClO_4 + HNO_3 + H_2SO_4$, mixture (Jackson, 1973), and the Cu^{2+} was determined by AAS. Finally, the results were statistically analyzed.

3. RESULTS AND DISCUSSION

3.1. Polymerization Kinetics of Cupric Phosphates and Nature of Products. The rate curves for dehydration polymerization at Cu:P = 1:2 are shown in Figure 1. At this ratio of Cu:P, $Cu(H_2PO_4)_2$, is formed initially (at 150 °C) which then condenses with loss of water. Thus, the formation of metaphosphate may be represented by the reaction $Cu(H_2PO_4)_2 \rightarrow Cu(PO_3)_2 + 2H_2O$. In the intermediate stages of polymerization, polyphosphates are formed in which some of the O ions

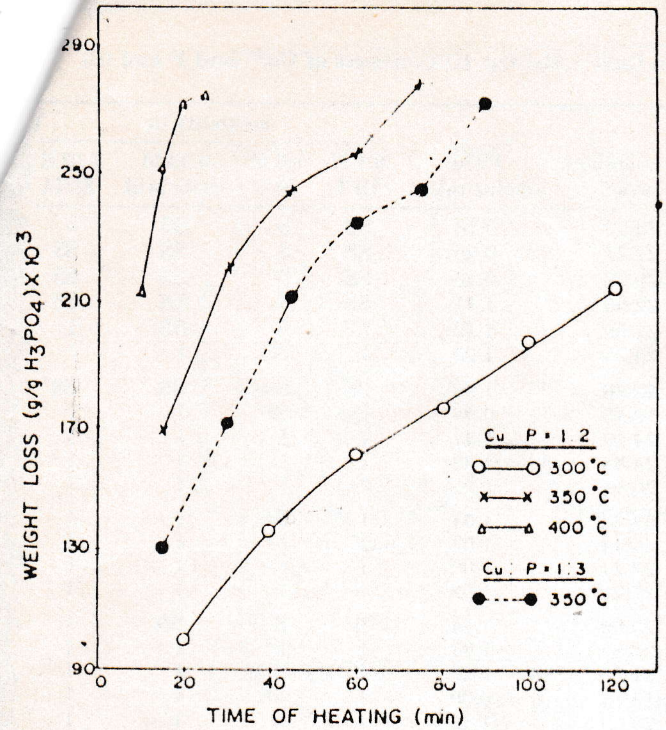

Figure 1. Kinetics of dehydration in the system CuO-H_3PO_4 at Cu:P = 1:2 and Cu:P = 1:3.

Table 1. Kinetics of Water Loss in the Reaction CuO + H_3PO_4 and the Corresponding *R* Values

Cu:P (molar ratio)	reaction temperature (°C)	time of heating (min)	weight loss (g/g H_3PO_4)	*R* (CuO + H_2O/P_2O_5)
1:2	300	20	0.0990	2.96
		40	0.1351	2.55
		60	0.1609	2.28
		80	0.1775	2.08
		100	0.1976	1.86
		120	0.2139	1.69
	350	15	0.1666	2.20
		30	0.2196	1.62
		45	0.2439	1.35
		60	0.2548	1.24
		75	0.2776	0.99
	400	10	0.2129	1.70
		15	0.2523	1.26
		20	0.2709	1.05
		25	0.2737	1.03
1:3	350	15	0.1302	1.92
		30	0.1708	1.48
		45	0.2106	1.04
		60	0.2342	0.79
		75	0.2452	0.67
		90	0.2721	0.38

Table 2. Water Solubility of the Reaction Products of the Reaction CuO + H_3PO_4

Cu:P (molar ratio)	reaction temperature (°C)	time of heating (min)	Cu^{2+} (% soluble) [w/w]	P (% soluble) [w/w]	P:Cu (molar ratio)
1:2	300	20	10.16	49.49	9.99
		40	16.20	51.95	6.58
		60	27.03	54.44	4.13
		80	24.12	53.28	4.53
		100	21.44	53.14	5.08
		120	9.64	43.82	9.28
	350	15	21.21	54.76	5.30
		30	26.10	52.42	4.12
		45	16.16	37.12	4.71
		60	18.96	37.23	4.03
		75	1.35	4.30	6.53
	400	10	30.60	51.60	3.46
		15	15.53	28.88	3.81
		20	9.63	15.74	3.35
		25	7.61	15.91	4.29
1:3	350	15	59.19	77.52	2.69
		30	61.99	80.45	2.66
		45	68.05	78.60	2.37
		60	68.05	83.50	2.52
		75	39.62	63.13	3.27
		90	1.26	25.82	42.03

by Cu^{2+} ions. The maximum weight loss per unit H_3PO_4 that is theoretically possible for these systems is 0.2756 g/g H_3PO_4 [since 1.5 mol or 27 g of H_2O is lost from 1 mol or 97.975 g of H_3PO_4 in accordance with the reactions $CuO + 2H_3PO_4 \rightarrow Cu(H_2PO_4)_2 + H_2O$ and $Cu(H_2PO_4)_2 \rightarrow Cu(PO_3)_2 + 2H_2O$]. Therefore, it appears that the system reacted at 400 °C for 25 min tends to approach complete dehydration, whereas at 350 °C with a reaction period of 75 min, complete dehydration occurs with the formation of ultraphosphate. At lower temperatures, polymerization is certainly far from complete.

Shapes of the dehydration curves apparently suggest complex reaction kinetics. Similar behavior has also been observed for zinc polyphosphates (Ray et al., 1993). In the sample containing an excess of phosphoric acid (Cu:P = 1:3), the nature of the dehydration curve (Figure 1) is similar to that of the Cu:P = 1:2 sample at the same temperature.

The *R* values of the products which indicate the extent of polymerization or chain length are shown in Table 1. Values close to 3.0 indicate unpolymerized orthophosphate, $Cu(H_2PO_4)_2$ [CuO = 1; H_2O = 2; P_2O_5 = 1, hence CuO + H_2O/P_2O_5 = 3.0]. Values close to 1.0 indicate a very long chain metaphosphate, $Cu(PO_3)_2$ [CuO = 1; P_2O_5 = 1, hence CuO + H_2O/P_2O_5 = 1]. It is seen that compounds with *R* values approaching 1.0 are formed only at 400 or 350 °C. Compounds having intermediate values of *R* (between 3.0 and 1.0) are acid polyphosphates in which some of the H^+ ions are substituted by Cu^{2+} (Van Wazer, 1966). Successive increases in the length of the chain may occur by condensation of terminal OH groups. The products are thus essentially twin P–O–P chains, the two units of which are connected by Cu atoms. The product contains terminal OH groups which account for the H_2O component of *R* (CuO + H_2O/P_2O_5).

Solubility of the polyphosphates formed are shown in Table 2. In general, there is a trend of decrease in solubility with increased period of heating although haphazard trends are also evident particularly at 300 °C. Thus, at this temperature, the solubility of Cu^{2+} is initially low; it rises to a maximum and decreases again. Similar behavior is also observed at 350 °C. The unusual solubility data suggest that hydrolysis of the soluble cupric phosphates to the insoluble cupric hydroxide probably has an important effect particularly in less polymerized compounds. It may be observed that even compounds having *R* values close to 1.0 contain soluble Cu^{2+} (Table 1). This shows the wide variations in chain lengths in the polyphosphate product. The trend in the data for % P solubilized is similar to that for % Cu. The molar P/Cu ratios are very high, suggesting that acid polyphosphates are mainly being solubilized.

The composition of the residues and their P/Cu molar ratios are shown in Table 3. Here, too, the high content of Cu suggests selective dissolution of acid polyphosphates leaving a residue which is richer in Cu^{2+} than P. Thus, the residues which remain insoluble are

Table 3. Water-Insoluble Residue of the Products of the Reaction CuO + H_3PO_4: (i) Contents of Cu^{2+} and P and (ii) Solubility[a]

						solubility in			
Cu:P (molar ratio)	reaction temperature (°C)	time of heating (min)	Cu^{2+} (% soluble) [w/w]	P (% soluble) [w/w]	P/Cu (molar ratio)	0.1 N HCl	1.0 N HCl	0.33 M citric acid	0.02 M EDTA
1:2	300	20	52.94	20.22	0.78	SS	S	SS	S
		40	52.16	21.77	0.86	SS	S	SS	SS
		60	52.94	20.22	0.78	SS	S	SS	SS
		80	41.67	22.56	1.11	SS	S	SS	SS
		100	41.37	22.56	1.12	SS	S	SS	I
		120	38.88	23.33	1.23	I	SS	I	I
	350	15	43.53	22.56	1.06	SS	S	SS	SS
		30	40.75	19.45	0.98	I	SS	I	I
		45	36.07	24.10	1.37	I	I	I	I
		60	38.56	24.88	1.32	I	I	I	I
		75	30.47	26.44	1.78	I	I	I	I
	400	10	47.26	23.33	1.01	I	SS	I	I
		15	35.45	26.44	1.53	I	I	I	I
		20	34.83	27.21	1.60	I	I	I	I
		25	32.96	27.21	1.69	I	I	I	I
1:3	350	15	42.50	25.69	1.24	S	S	SS	I
		30	41.45	21.58	1.07	S	S	I	I
		45	40.59	21.58	1.09	S	S	I	I
		60	42.50	18.52	0.89	I	SS	I	I
		75	36.32	25.69	1.45	I	I	I	I
		90	28.78	23.65	1.69	I	I	I	I

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

Table 4. Chemical Composition, Formulas, and Chain Length of the Copper Polyphosphate Fertilizers

	copper calcium polyphosphate	copper ammonium polyphosphate
% CuO	15.03	17.22
% P_2O_5	41.43	47.49
% CaO	28.59	
% NH_4^+		20.26
% H_2O	8.57	12.63
% H_2O^-	7.90	2.70
total	101.52	100.30
formula	$Cu_{0.19}H_{0.95}Ca_{0.51}P_{0.58}O_{2.62}$	$Cu_{0.22}H_{1.40}(NH_4)_{1.13}P_{0.67}O_{3.16}$
chain length ($\bar{n}'$)	2.77	2.77

mostly hydrolysis products. With longer periods of heating, the % Cu in the residue decreases with a subsequent increase in the P/Cu molar ratio.

3.2. Formulation of the Copper Fertilizer. Solubility characteristics of the polyphosphate residues are shown in Table 3. It may be observed that copper polyphosphates, prepared at Cu:P = 1:2 ratios, have low solubility in most reagents. Thus, at 300 °C with a 20 min heating period, the product is slowly soluble in 0.1 N HCl and is completely dissolved only by 1.0 N HCl. Even in 0.33 M citric acid, the compound is insoluble although it does dissolve in 0.02 M EDTA. In fact, even a compound obtained on reacting a Cu:P = 1:2 mixture at 150 °C has insoluble character which is comparable to those obtained at higher temperatures. With Cu:P = 1:3 mixtures at 350 °C, except for the first compound (Table 3), all others are insoluble in both complexants. However, on lowering the reaction temperature to 300 °C, it was observed that a Cu:P = 1:3 mixture when heated for 60 min (water loss 0.047 g/g of H_3PO_4) has the desirable solubility properties. It is soluble in all of the aforementioned reagents except 0.33 M citric acid, in which it slowly solubilizes overnight. However, when the compound was neutralized with $CaCO_3$ to a pH of 3.0 and then dried, ground, and tested, the solubility characteristics showed an improvement. It solubilized more rapidly in all reagents including 0.33 M citric acid (within 30 min).

Other polyphosphates were then prepared at 300 °C with Cu:P = 1:3.5 and Cu:P = 1:3 which were dehy-

However, the solubility of these compounds in th complexants was poor. Therefore, it appeared that th product showing a weight loss of 0.047 g/g of H_3PO_4 wit Cu:P = 1:3, possessed the optimum properties. Th value of this product is 2.83 and the number avera chain length ($\bar{n}'$) of the polyphosphate chain is 2.77

The copper phosphate proposed above is, howeve both hygroscopic and acidic. It has earlier been o served (Ray et al., 1990, 1993) that hygroscopicity and acidity of the polyphosphates is due to the presence o free acid groups. Therefore, if these are suitabl neutralized, both drawbacks may be easily overcom Subsequently, the desired quantities of the fertilize were prepared as described in the methodology sectio

3.3. Characteristics of the Fertilizer Com pounds. Chemical composition and structural formu lae of the fertilizers are shown in Table 4. It may b noted that although the average number of P−O− groups per chain is 2.77, in reality the product contain chains much larger as well as much smaller than thi

IR spectra of the calcium and ammonium forms of th copper polyphosphates are shown in Figure 2. Ther is an overall similarity in the spectra of the two compounds except for the strong absorption at around 1400 cm^{-1} due to the NH_4^+ ion. Both compound contain considerable amounts of H-bonded water mol ecules, as shown by the very strong absorptions at 3000 cm^{-1}. The presence of short chain P−O−P compounds is also indicated by the absorptions at 1150−1050 cm for longer-chain metaphosphates, these absorption

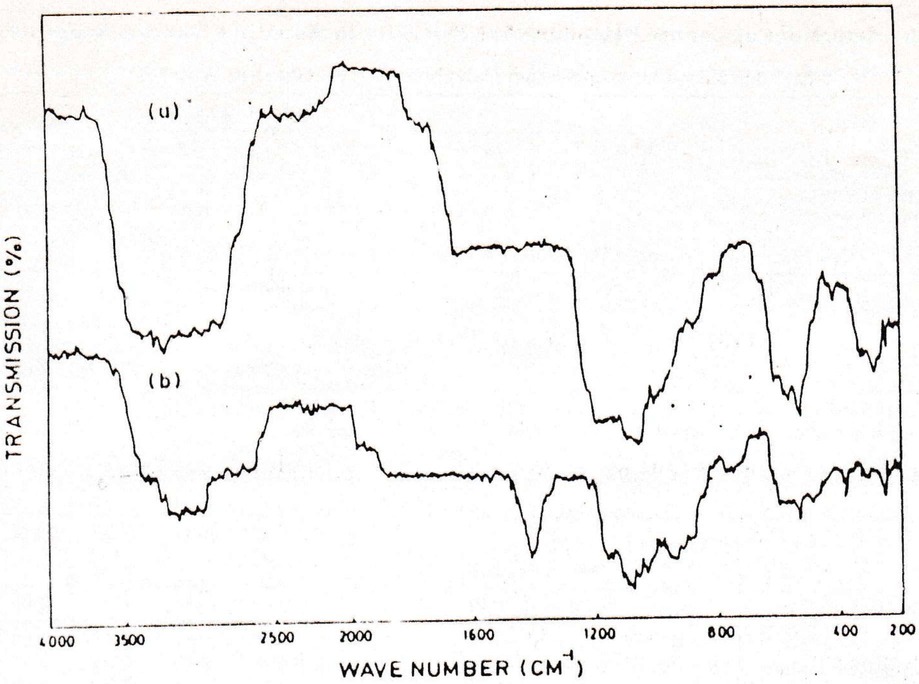

Figure 2. Infrared absorption spectra of (a) copper calcium polyphosphate and (b) copper ammonium polyphosphate.

and Lowe, 1954). Stretching vibrations of P–O–P groups are observed at 950 and 700 cm^{-1}.

XRD of the two polyphosphates are shown in Table 5. The presence of an amorphous phase is conspicuous by a broad reflection at 6–7 Å. There are also numerous strong peaks indicating crystalline phases, which appear to be more predominant in the ammonium form rather than in the calcium form. The copper calcium polyphosphate contains compounds such as $Ca_{1.5}HP_2O_7 \cdot 2H_2O$ and $CaHPO_4 \cdot 2H_2O$ (JCPDS, 1978); these are probably formed during the neutralization of free acid by $CaCO_3$. Apart from these, certain reflections are common to both compounds and may be attributed to the polyphosphate network. In fact, such "polyphosphate skeletal" reflections are also shown by zinc polyphosphates (Ray et al., 1993). The ammonium compound contains $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ (Table 5). Other unidentifiable ammonium polyphosphates are also present which are common to the ammonium forms of both copper as well as zinc polyphosphates (Ray et al., 1993). In fact, the spectrum of the copper ammonium salt is extremely complex; the heterogeneity of the sample together with a lack of sufficient reported data, makes it difficult to interpret the spectrum in detail.

Solubility of the two fertilizers in water at various periods of time is shown in Table 6. The calcium form is observed to be less soluble than the ammonium form, probably due to cross-linking of adjacent chains by Ca^{2+} ions. Increase of solubility with time is also low, indicating slow hydrolysis of polyphosphate chains. In fact, solubility patterns are rather complex because solubilized Cu^{2+} may revert to insoluble forms in combination with ortho or pyrophosphate forming $Cu_3(PO_4)_2$, $Cu_2P_2O_7$, etc.

In dilute acid (0.1 N HCl) as well as in all the organic complexants that were tested (Table 6), the fertilizers show very high solubility (90–100%). Solubility of the fertilizers in various extractants indicate that the Cu^{2+} in these compounds would be readily available to plants. Under various environments, one or more of the extractants such as HCl, EDTA, DTPA, etc. are used for evaluating available Cu^{2+} in soils (Black, 1965; Cox and Kamprath, 1972; Lindsay and Norvell, 1978; Ponnamperuma et al., 1981). Considering the fact that all such extractants, which are used for determining avail-

Table 5. X-ray Diffraction Characteristics of the Copper Calcium and Copper Ammonium Polyphosphates[a]

copper calcium polyphosphate			copper ammonium polyphosphate		
d (Å)	*I*	assignment	*d* (Å)	*I*	assignment
10.05	24	CaPy	9.51	28	Pp
9.12	11	Pp	6.81(b)	40	Pp
7.76	22	CaP	6.23	24	
6.81	73	Pp	5.61	45	DAP,APp
4.27	24	CaP	5.34	60	MAP
3.164	35	CaPy	5.04	41	DAP
3.058	18	CaP	4.67	20	Pp (?)
2.978	33	Pp	4.40	13	APp
2.940	24	CaP	3.869	5	
2.849	4	CaPp (?)	3.770	36	MAP,DAP
2.636	13	CaPy,CaP	3.648	5	
2.550	7		3.453	19	APp,DAP
2.508	7	CuPp (?)	3.232	7	DAP,Pp (?)
2.356	11	Pp	3.089	80	MAP,Pp
2.181	4	CaP	3.018	5	APp
2.103	7	CuPp (?)	2.885	28	CuPp (?)
2.040	100	Pp,CaPy	2.814	16	CuPp (?)
1.982	4	CuPp (?)	2.800	11	APp
1.918	7	CuPp (?)	2.667	18	
			2.536	5	DAP,CuPp (?)
			2.417	9	Pp (?)
			2.350	27	Pp
			2.326	5	
			2.141	9	CuPp (?)
			2.032	100	Pp
			2.018	20	MAP,CuPp (?)
			1.926	7	CuPp
			1.888	4	
			1.852	7	
			1.7776	4	
			1.7156	3	
			1.6750	4	
			1.6104	3	

[a] Abbreviations: APp, ammonium polyphosphate; CaP, $CaHPO_4 \cdot 2H_2O$; CaPy, $Ca_{1.5}HP_2O_7 \cdot 2H_2O$; CuPp, copper polyphosphate; DAP, $(NH_4)_2HPO_4$; MAP, $(NH_4)H_2PO_4$; Pp, polyphosphate framework.

Table 6. Solubility Characteristics of Copper Polyphosphate Fertilizer in Water and Various Reagents

Kinetics of Solubility of Copper Polyphosphate Fertilizer in Water

	% Cu^{2+} soluble after *n* hours					
fertilizer	0	24	48	72	96	120
copper calcium polyphosphate	3.38	3.23	3.38	3.84	3.73	8.84
copper ammonium polyphosphate	4.56	5.09	4.69	6.03	5.36	5.76

Solubility of Copper Polyphosphate Fertilizer in Various Reagents

	% Cu^{2+} soluble in				
fertilizer	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
copper calcium polyphosphate	100.00	95.86	91.75	97.44	93.81
copper ammonium polyphosphate	100.00	100.00	100.00	100.00	100.00

Table 7. Average Grain and Straw Yield of Paddy on Application of Copper Sulfate and Copper Calcium Polyphosphate

		dose of Cu^{2+} (ppm)									
		average grain yield (g)					average straw yield (g)				
soil	treatment	0	1.00	2.00	4.00	8.00	0	1.00	2.00	4.00	8.00
Pusa	$CuSO_4$	4.05	4.52	4.62	5.32^a	5.41^a	4.83	4.41	4.85	4.79	4.54
	copper calcium polyphosphate	4.05	5.29^a	4.96	5.25^a	6.05^a	4.83	5.06	5.51	5.48	6.54
Mal	$CuSO_4$	10.08	11.60	11.32	12.42^a	13.45^a	7.88	8.29	8.55	8.69	7.86
	copper calcium polyphosphate	10.08	13.32^a	11.35	12.56^a	13.19^a	7.88	8.88	8.41	7.94	10.41^a

^{a} Significant increase in yield over the control ($LSD_{0.05}$).

Table 8. Uptake of Cu^{2+} by Paddy Straw on Application of Copper Sulfate and Copper Calcium Polyphosphate to Pusa Soil

	dose of Cu^{2+} (ppm)				
	Cu^{2+} content, mg/kg of paddy straw (total uptake, mg)				
treatment	0	1.00	2.00	4.00	8.00
$CuSO_4$	11.00 (53.13)	11.50 (50.72)	13.00 (63.05)	5.25^a (25.15)	6.60^a (27.24)
copper calcium polyphosphate	11.00 (53.13)	4.50^a (22.77)	8.75 (48.21)	7.75 (42.47)	7.50 (49.05)

^{a} Significant decrease over the control ($LSD_{0.05}$).

able Cu^{2+} from soils, can extract >90% of the Cu^{2+} from the fertilizer compounds, it may be inferred that the nutrient ion in the fertilizers is in an almost completely available form. As yet there is no other yard stick to judge the nutrient supplying capacity of insoluble fertilizers, hence techniques used for assessing soils has been applied here, to the fertilizers.

In order to obtain further confirmation of the fertilizing efficiency, plant growth experiments were carried out. Results are shown in Table 7. Overall increase in yields are observed, with the slow-releasing fertilizer, which are statistically significant ($LSD_{0.05}$) at the 1.00, 4.00, and 8.00 ppm Cu^{2+} levels with the Pusa soil. For $CuSO_4$, increases are observed at 4.00 and 8.00 ppm Cu^{2+} levels. Thus, whereas the addition of only 1 ppm Cu as the slow-release fertilizer can significantly increase crop yield, a similar increase is possible only with a much higher dose of $CuSO_4$ (4 ppm Cu). Straw yields do not differ significantly. With an acidic soil (Mal soil) too, the same trend is observed. Here also, the slow-release fertilizer produces an increase in yield at one-fourth the dose of $CuSO_4$. The trials, thus, indicate that even without considering the residual effects and environmental advantages, the slow-releasing fertilizer is an efficient source of Cu^{2+} and is equivalent to $CuSO_4$ in its fertilizing ability; however, dosage requirements for the polyphosphate are much lower than for $CuSO_4$ thereby indicating greater fertilizer-use efficiency of the former material.

Uptake of Cu^{2+} by the plants is shown in Table 8. Here, an unusual trend is observed which is quite contrary to the usually expected behaviour. In most of the plants treated with Cu^{2+} fertilizer, Cu^{2+} content of the straw is either equivalent to or less than that of the control plants. Thus, Cu^{2+} content is significantly less than the control, at 4.00 and 8.00 ppm Cu^{2+} levels for the $CuSO_4$ treatment and at 1.00 ppm Cu^{2+} level for the slow-releasing fertilizer treatment; at other fertilizer levels, the Cu^{2+} contents of control and treated plants are statistically equivalent. Trends in total uptake are similar.

In this connection, one may refer to Loneragan (1975) and Robson and Reuter (1981) wherein numerous similar abnormalities between Cu^{2+} fertilization and Cu^{2+} content of tissues are reported. Thus, leaves of plants given a luxury supply of Cu^{2+} were observed to lose more than 70% of their Cu^{2+} during grain development (Loneragan, 1975). In contrast, leaves of Cu^{2+} deficient plants lost less than 20%. Plants receiving lowest Cu^{2+} doses showed higher Cu^{2+} concentrations than plants receiving higher Cu^{2+} doses. Such a phenomenon has been termed the Piper–Steenbjerg effect (Ulrich, 1952) after it was first reported for Cu^{2+} in oats by Piper (1942) and in barley by Steenbjerg (1950).

Results obtained here for paddy are, therefore, similar to those observed in other plants such as wheat, barley, and oats (Loneragan, 1975; Robson and Reuter, 1981). In fact, the observation that increasing the Cu^{2+} level in the soil decreases Cu^{2+} content of mature leaves may itself suggest that the polyphosphate fertilizer is capable of increasing the available Cu^{2+} content of the soil since the plants show lower Cu^{2+} content in the fertilized than in the control soils.

4. CONCLUSION

In conclusion, it appears that the concept of slow-releasing micronutrient fertilizers based on the short-chain polyphosphate framework can also be utilized for producing copper fertilizers. These compounds have excellent physical and chemical characteristics which suggest that they could be ideal materials for use as a slow-releasing copper source.

LITERATURE CITED

Black, C. A. *Methods of Soil Analysis, Parts 1 and 2*; American Society of Agronomy: Madison, WI, 1965; pp 1078–1089.

Corbridge, D. E. C.; Lowe, E. J. Infrared Spectra of Some Inorganic Phosphorus Compounds. *J. Chem. Soc.* **1954**, 493–502.

Cox, F. R.; Kamprath, E. J. Micronutrient Soil Tests. In *Micronutrients in Agriculture*; Mortvedt, J. J., Giordano, P. M., Lindsay, W. L., Eds.; Soil Science Society of America: Madison, WI, 1972; Chapter 13.

Jackson, M. L. *Soil Chemical Analysis*; Prentice Hall of India: New Delhi, 1973; pp 134–154, 183–204, 272–285, 396–408.

JCPDS. *Powder Diffraction File*; Joint Committee on Powder Diffraction Standards: Philadelphia, PA, 1978; Card Nos. 6-0125, 9-391, 9-77, 12-30.

Krems Chemie, GmbH. Complete Fertilizers Containing Trace Elements. Austrian Patent 326160, 1975.

Lindsay, W. L.; Norvell, W. A. Development of DTPA Soil Test for Zinc, Iron, Manganese and Copper. *Soil Sci. Soc. Am. J.* **1978**, *42*, 421–428.

Loneragan, J. F. The Availability and Absorption of Trace Elements in Soil-plant Systems and their Relation to Movement and Concentrations of Trace Elements in Plants. In *Trace Elements in Soil–Plant–Animal Systems*; Nicholas, D. J. D., Egan, A. R., Eds.; Academic: New York, 1975; Chapter 7.

Lyons, J. W.; Rauh, G. A., Jr.; Vandersall, S. A. Mixed Cation Polyphosphates. U.S. Patent 3574591, 1971.

NDC. *New Fertilizer Materials*; Noyes Development Corporation: New York, 1968; pp 189–194.

Piper, C. S. Investigation on Copper Deficiency in Plants. *J. Agric. Sci.* **1942**, *32*, 143–178.

Ponnamperuma, F. N.; Cayton, M. T.; Lantin, R. S. Dilute Hydrochloric Acid as an Extractant for Available Zinc, Copper and Boron in Rice Soils. *Plant Soil* **1981**, *61*, 297–310.

Ranney, M. W. *Fertilizer Additives and Soil Conditioners*; Noyes Development Corporation: Park Ridge, NJ, 1978; pp 153–154.

Ray, S. K.; Varadachari, C.; Ghosh, K. Process for Producing a Slow Releasing Zinc Fertilizer. Indian Patent 172800, 1990.

Ray, S. K.; Varadachari, C.; Ghosh, K. Process for Producing a Slow Releasing Copper Fertilizer. Indian Patent Application 886/Cal/91, 1991.

Ray, S. K.; Varadachari, C.; Ghosh, K. Novel Slow-Releasing Micronutrient Fertilizers. I. Zinc compounds. *Ind. Eng. Chem. Res.* **1993**, *32*, 1218–1227.

Reuter, D. J. The Recognition and Correction of Trace Element Deficiencies. In *Trace Elements in Soil-Plant-Animal Systems*; Nicholas, D. J. D., Egan, A. R., Eds.; Academic: New York, 1975; Chapter 18.

Roberts, G. J. Micronutrient-Containing Phosphate Glasses. *Natl. Glass Budget*, 1977, July 21.

Robson, A. D.; Reuter, D. J. Diagnosis of Copper Deficiency and Toxicity. In *Copper in Soils and Plants*; Loneragan, J. F., Robson, A. D., Graham, R. D., Eds.; Academic: Sydney, 1981; Chapter 13.

Rush, R. M.; Yoe, J. H. Colorimetric Determination of Zinc and Copper with 2-Carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon). *Anal. Chem.* **1954**, *26*, 1346–1347.

Sauchelli, V. *Chemistry and Technology of Fertilizers*; Reinhold: New York, 1967; pp 10–54, 322–345.

Steenbjerg, F. On the Relative Contents of Plant Nutrients in Crops. *Trans. IVth Int. Cong. Soil Sci.* **1950**, *1*, 254–258.

Thilo, E. Condensed Phosphates and Arsenates. In *Advances in Inorganic and Radio-Chemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic: New York, 1962; Vol. 4, Chapter 1.

Ulrich, A. Physiological Basis for Assessing the Nutritional Requirements of Plants. *Annu. Rev. Plant Physiol.* **1952**, *3*, 207–228.

Van Wazer, J. R. *Phosphorus and Its Compounds*; Interscience: New York, 1966; pp 419–436, 452–459.

Van Wazer, J. R.; Griffith, E. J.; McCullough, J. F. Analysis of Phosphorus Compounds. *Anal. Chem.* **1954**, *26*, 1755–1759.

Varadachari, C. An Investigation on the Reaction of Phosphoric Acid with Mica at Elevated Temperatures. *Ind. Eng. Chem. Res.* **1992**, *31*, 357–364.

Volfkovich, S. I. Polymeric Fertilizers. *J. Appl. Chem. (USSR)* **1972**, *45*, 2479–2487.

Volfkovich, S. I.; Alexandrova, G. G.; Kubasova, L. V.; Cherepanova, A. S. Potassium Metaphosphate–A Highly Concentrated Fertilizer. *Probl. S-Kh. Nauki Mosc. Univ.* **1975**, 236–244.

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