

GENERAL RESEARCH

Development of a Novel Slow-Releasing Iron–Manganese Fertilizer Compound

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Development of a new slow-release micronutrient fertilizer of iron–manganese is described. Studies include formulation, synthesis, kinetics, characterization, and testing. The compound is a partially polymerized, iron–manganese–magnesium polyphosphate, which is produced at 200 °C by reaction of iron, manganese, and magnesium oxides with phosphoric acid, followed by neutralization to pH 5.6. Polymerization is optimal at 21.2% with an Fe/Mn/Mg/P molar ratio of 1:0.51:1.15:7.33. Condensation kinetics show multistage processes with plateau formation at the end of each stage. The compound is crystalline with new XRD patterns indicative of a regular arrangement of polyphosphate chains. ESR spectra reveal Mn predominantly in the IV state. The product has ideal slow-release characteristics of low water solubility but high citrate and DTPA solubility, indicating high bio-availability of the micronutrients. Plant trials with chilli show a 45.6% increase in yield, at Fe 2 kg/ha–Mn 1 kg/ha as the slow-release fertilizer. The compound appears to be a promising, environmentally friendly alternative for Fe–Mn fertilization.

Introduction

The use of soluble salts as micronutrient fertilizers is a cause for serious environmental concern. Dosages far exceed plant uptake and could lead to a buildup of these metal ions in soils. Leaching losses of anionic micronutrients and chelated forms may cause groundwater contamination. High wastage and very low use-efficiency are major economic drawbacks. Consequently, micronutrient fertilizer application has not been popularized to the extent necessary and essential in many regions of the world. The solution, to both the environmental and economic problems associated with the widespread use of water-soluble fertilizers, is in the development of cost-effective slow-release compounds. For a water-insoluble compound to function as a fertilizer, nutrients may either be released slowly into the solution by hydrolysis or diffusion or they may be present in forms that are extractable by plant roots. The majority of slow-releasing fertilizers developed to date belong to the first category, that is, either hydrolysis or diffusion controls the release of nutrients to the plants, as in urea formaldehyde, via membrane-coated fertilizers or glass frits, and so forth.^{1–3} The other category of slow-release fertilizer is that in which nutrients are present in exchangeable or chelate-extractable positions. These mimic the natural forms of available nutrients in soils. Synthetic ion-exchange-resin-based fertilizers⁴ belong to this category as well as the more recently developed phosphate-polymer-based compounds.^{5,6} Those in the latter group are superior because release rates in hydrolysis and diffusion-controlled mechanisms may not match rates of plant uptake, and thus such fertilizers are not always effective. Furthermore, fertilizers with incorporated heavy-metal micronutrients are

highly insoluble and have not proved to be successful. Compounds developed for Zn and Cu^{7,8} have overcome some of the major drawbacks associated with earlier slow-release formulations. Uniquely, these are short-chain polyphosphates in which problems of hygroscopicity, stickiness, and water solubility inherent to such partially polymerized linear polyphosphates can be successfully overcome to produce very effective fertilizers.^{5,6} The nutrient ions in these compounds have low water solubility but are potentially plant-available by virtue of their high solubility in organic acids such as citrate, and so forth, which are excreted by plant roots (hence solubility in organic acids can be used as an index of nutrient availability⁹). Thus, nutrient availability from such compounds is not controlled by hydrolysis rates but by active extraction by the roots.

In view of the promising characteristics of this type of slow-release formulation, the next step must be to extend this concept to the development of fertilizers of other micronutrient cations. Iron and manganese are two other important micronutrients widely used as fertilizers. They are used mostly in the form of sulfates or EDTA salts, both of which are water-soluble. Dosages for ferrous or manganous sulfate fertilization are necessarily high (10–50 kg/ha) because of rapid transformation in the soil.⁹ Fe-EDTA salts are more efficient but are expensive and, therefore, not widely used for cereals and low-value crops. Development of effective and relatively inexpensive slow-release iron and manganese fertilizers could improve usage of iron and manganese, particularly in cereals and vegetables grown in developing countries. This would improve crop yields in these densely populated regions and also provide more iron nutrition in the diet.

Here, we report the development of a novel slow-releasing iron–manganese compound based on a short-chain polyphosphate structure. The study involved three stages, namely, (i) formulation and synthesis of a slow-release compound with desired properties, (ii) fundamental studies (including reaction

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kinetics) in the iron–manganese–(magnesium)–phosphate system, and (iii) characterization and testing of the compound developed.

Methodology

1. Formulation and Synthesis. Preliminary experiments were conducted working on the premise that the end product should possess the desired properties of low water solubility and high citrate/DTPA solubility.^{5,6} The following materials were used: (i) synthetic goethite [α -FeO(OH)], (ii) manganese dioxide (GR, E Merck), and (iii) orthophosphoric acid (GR, E Merck). Goethite was analyzed for Fe content after digestion in concentrated HCl followed by spectrophotometric determination as the *o*-phenanthroline complex.¹⁰ The Fe content of goethite was 62%.

The Fe/Mn weight ratio used was fixed at 2:1 (molar ratio of 1:0.51) based on an average ratio of iron and manganese contents observed in normal leaf tissues of a large number of plant species.⁹ Sufficient H_3PO_4 was added to convert all cations to the dihydrogen phosphates; therefore, molar ratios were Fe/Mn/P = 1:0.51:5.04. Reactants were taken in a borosilicate glass beaker and placed in a muffle furnace at 200 °C. Samples were taken at regular intervals, neutralized with ammonia to pH 5.6–6. This pH range was experimentally obtained for optimum product properties. (Details are given in the Results section). Neutralized products were tested for solubility in 0.33 M citric acid and 0.005 M DTPA. The objective was to obtain a compound which was almost completely soluble in citrate and DTPA since solubility in these reagents may infer plant availability.^{5,9} Weight loss in the system was recorded at periodic intervals.

Characterization of the Fe–Mn system showed that products with desirable properties could not be obtained. Notably, all of the products had low solubility in citrate and DTPA. It was envisaged that addition of a bivalent cation could result in the formation of cross-linked chains that would be more susceptible to cleavage. Thus, some $\text{P}-\text{O}-\text{M}^{2+}-\text{O}-\text{P}$ cross-linkages could be added which would induce some weak points in the crystal and make the structure more soluble. Following preliminary trials with Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , we observed the best results with Mg^{2+} . Another set of experiments was, therefore, conducted with MgO (GR, E Merck) as an additive. Here, Mg content was varied from Fe/Mg = 1:2.3 to 1:0.29 with sufficient H_3PO_4 added to convert the cations to the dihydrogen phosphates.

Bench-scale studies were then repeated with potentially promising raw materials: (i) iron ore or red oxide of iron (hematite), (ii) manganese ore (pyrolusite), (iii) roasted magnesite, and (iv) commercial phosphoric acid. Hematite (0.1 g) was digested¹⁰ in a mixture of 10 mL of concentrated HF and 3 mL of concentrated HClO_4 (GR, E Merck) on a hot plate, and the solution was analyzed for $\text{Fe}^{2+/3+}$ and Al^{3+} , with $\text{Fe}^{2+/3+}$ determined as the *o*-phenanthroline complex as described above and Al^{3+} determined as the calcium aluminum alizarin Red S complex.¹⁰ Si^{4+} in all the ores was determined as the blue silicomolybdate after fusing the sample with NaOH beads and extracting into dilute HCl.¹⁰ Pyrolusite was analyzed after dissolving the sample in 10 mL of concentrated H_2SO_4 with dropwise addition of 3 mL of 30% H_2O_2 followed by heating.¹⁰ Mg^{2+} and Ca^{2+} contents of magnesite were determined by AAS after dissolution of the sample in 6 M HCl. P content of H_3PO_4 was determined as the blue phosphomolybdate.¹⁰ Results of chemical analysis data were as follows: (a) hematite: 46.28% Fe, 4.33% Al, 8.99% Si; (b) pyrolusite: 49.31%

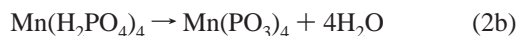
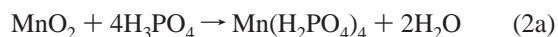
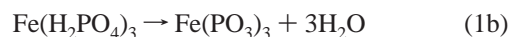
Mn, 1.08% Al, 2.21% Fe, 1.94% Si; (c) magnesite: 41.72% Mg, 0.71% Fe, 11.56% Si; and (d) commercial phosphoric acid: 25.54% P.

Bench-scale studies with ores were done in borosilicate beakers. The optimum molar ratio of Fe/Mn/Mg/P determined by trials was 1:0.51:1.15:9.9. Here, excess H_3PO_4 was added to compensate for impurities (such as Al^{3+} , Ca^{2+} , Si^{4+}), which may consume the acid. Each batch consisted of 8 g of hematite, 3.76 g of pyrolusite, 4.44 g of roasted magnesite, and 79.57 g of phosphoric acid. All components were taken in a preweighed beaker and placed in a muffle furnace at three test temperatures: 175, 200, and 250 °C. Condensation kinetics was studied by recording the weight at regular intervals. Product characteristics were evaluated by taking samples at periodic intervals, neutralizing them with ammonia to pH 5.6, and then testing them for solubility in 0.33 M citric acid. The sample produced a nearly colorless solution within 30 min when at the optimum polymerization stage. The polyphosphate liquid was then neutralized with ammonia solution (10% NH_3), and its weight was recorded. It was dried in an oven at 80 °C, and the weight of the sample was recorded once more. The sample was ground and sieved through 150 mesh. Several batches of fertilizer were produced for analysis and testing.

2. Reaction Kinetics. Kinetics (laboratory-scale) was studied using synthetic goethite, manganese dioxide, magnesium oxide, and orthophosphoric acid. Here, H_3PO_4 was diluted to about 40% P_2O_5 to make it easier to pipet. The exact strength of the acid was determined by spectrophotometric analysis as the blue molybdophosphate complex.¹⁰ Standardization of the acid was done at weekly intervals.

Details of the reaction studies were described earlier.^{5,11} Briefly, reactions were carried out in preweighed platinum crucibles containing weighed amounts of FeO(OH), MnO_2 , MgO, and H_3PO_4 in the molar ratio Fe/Mn/Mg/P = 1:0.51:1.15:7.33. This ratio was observed to be best-suited for fertilizer formulation. After addition of the reagents, the weight of the crucible and its contents were recorded. The crucible was then preheated in a muffle furnace at 150 °C (± 0.5 °C) for 30 min to remove excess water and to avoid spattering of the contents at higher temperature. It was stored in a desiccator, and the furnace temperature was raised to 165, 175, 200, and 225 °C (± 0.5 °C). After the required period of heating, the crucible was cooled in a desiccator and weighed.

The actual amount of H_3PO_4 (excluding water), designated as $[\text{H}_3\text{PO}_4]$, was calculated for each system from the known weight and concentration of H_3PO_4 solution initially taken. Weight loss in the reaction system was obtained from the initial weight of $\text{FeO(OH)} + \text{MnO}_2 + \text{MgO} + [\text{H}_3\text{PO}_4]$ minus the final weight after heating. Range of error in these values is about $\pm 0.2\%$. Theoretical H_2O loss for complete (100%) polymerization to metaphosphate was evaluated according to the following three pairs of reactions :





Since the molar ratio of Fe/Mn/Mg in our system is 1:0.51:1.15, the total water loss for complete polymerization is $(5 \times 1) + (6 \times 0.51) + (3 \times 1.15) \text{ mol} = 11.51 \text{ mol} = 207.18 \text{ g}$. This system contains 7.33 mol of H_3PO_4 . Thus, a weight loss of 0.104 g/g [H_3PO_4] in the system corresponds to the formation of dihydrogen phosphate, and a weight loss of 0.288 g/g [H_3PO_4] corresponds to 100% polymerization. The degree of polymerization (expressed as a percent) of a system with a recorded weight loss of $\theta \text{ g/g H}_3\text{PO}_4 = [(\theta - 0.104)/(0.288 - 0.104)] \times 100$.

Amount of $\text{Fe}^{3+/2+}$ solubilized by 0.33 M citric acid, from the polyphosphate, was determined by spectrophotometric analysis as the ferrous *o*-phenanthroline complex.¹⁰ It was experimentally determined that the solution was required to stand for 24 h after addition of reagents in order to overcome the inhibiting effect of citrate ion on color development.

Number-average chain length (n) of the polyphosphate was determined by dissolving the sample in 0.5 M H_2SO_4 and removing Fe^{3+} , Mn^{4+} , and Mg^{2+} interference by solvent extraction as the 8-hydroxyquinoline complex followed by titrimetric analysis.¹²

3. Characterization and Testing. Sufficient fertilizer (iron–manganese–magnesium–ammonium polyphosphate) was produced at the bench scale using commercial hematite, pyrolusite, roasted magnesite, and phosphoric acid (as described in section 1). This was done by mixing raw materials in the molar ratio Fe/Mn/Mg/P = 1:0.51:1.15:9.9 and heating at 200 °C for 70 min, corresponding to a weight loss of 0.144 g/g [H_3PO_4] in the system. The polyphosphate was neutralized with ammonia solution (~10% NH_3) to pH 5.6, dried at 80 °C, and ground and sieved through 150 mesh. Samples were dissolved in concentrated HCl and analyzed for $\text{Fe}^{3+/2+}$ and Mg^{2+} contents, while Mn^{4+} was analyzed after dissolving the sample in $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ as described earlier.

Solubility of the compound in water, 0.33 and 0.104 M (2%) citric acid (GR, E Merck), and 0.005 M DTPA (AR, Ferak-Berlin) was determined. To 0.05 g of the fertilizer, 50 mL of 0.33 M citrate, 150 mL of 2% citrate or 150 mL of 0.005 M DTPA was added, and the suspension was agitated in a horizontal shaker for 30 min, after which samples were filtered (Whatman 42), washed (with about 75 mL of deionized water), made to volume, and analyzed for $\text{Fe}^{3+/2+}$, Mn^{4+} , and P as described above, after digestion with triacid ($\text{HClO}_4\text{--HNO}_3\text{--H}_2\text{SO}_4$)¹³ to oxidize chelates. To study rates of solubilization of the fertilizer in water, 0.05 g of the compound was taken, and 10 mL of water was added to each. The suspensions were allowed to stand. After 3, 6, 9, 12, 15, 18, and 21 days of contact time, the solutions were filtered (Whatman 42), washed (with 30 mL of deionized water), made to volume, and analyzed for Fe^{3+} .

IR spectra of the sample were recorded on a Perkin-Elmer FTIR RX1 instrument with the scan range of 4500–450 cm^{-1} (resolution $\pm 5 \text{ cm}^{-1}$) using KBr pellets. XRD was recorded on a JDX-8030 X-ray diffractometer using Ni-filtered Cu K α radiation at a scanning speed of 2° 2 θ /min. The ESR spectrum was recorded at room temperature with powdered samples using a JEOL (model JES-RE1X) spectrometer.

Plant growth experiments were carried out in pots using the iron–manganese–magnesium–ammonium polyphosphate. Surface soil from a black soil region (Vertisol) was collected from

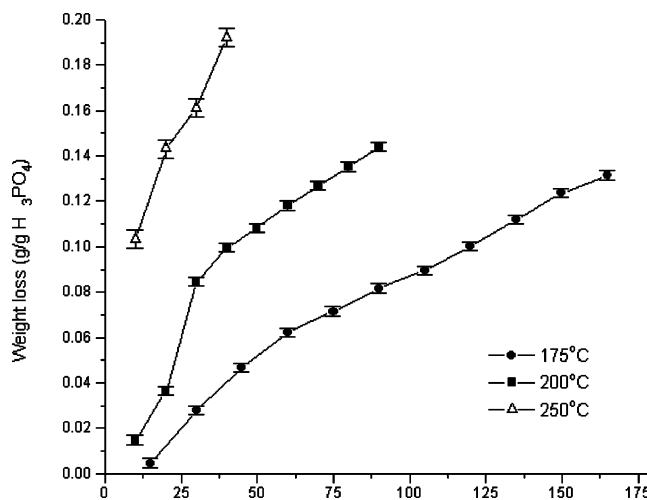


Figure 1. Rates of reaction at different temperatures (bench-scale studies with commercial materials).

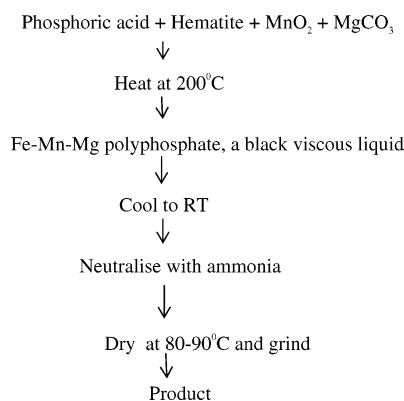


Figure 2. Schematic diagram of the process of production of slow-release iron–manganese fertilizer.

Gundkheri, Nagpur, Maharashtra, India. Characteristics of this soil are as follows: Udic Chromustert, pH 7.95, EC_e 0.155 dS/m, organic carbon 0.74%, available Fe and Mn 1.80 mg/kg and 3.3 mg/kg, respectively (determined by 0.005M DTPA extraction),¹⁹ and exchangeable Mg^{2+} 11.84 $\text{cmol}(\text{p}^+)/\text{kg}$ (determined by AAS). Each pot contained 2 kg of soil. The treatments consisted of the following: (i) a control (where only NPK fertilizers but no Fe–Mn fertilizers were added), (ii) four different levels of Fe–Mn micronutrients as the slow-release fertilizer, and (iii) the same four levels of micronutrients as ferrous sulfate and manganous sulfate. Each treatment had 6 replicates. All pots were equalized for additions of N, P, K, Mg, and SO_4^{2-} by calculated additions of urea, DAP, KCl, MgSO_4 , and K_2SO_4 . The fertilizers were thoroughly mixed into the soil before planting. Chilli (*Capsicum frutescens*) was grown as the test crop. Chillies were harvested and their weights recorded. Due to pest attack some plants were damaged, and this also introduced more error in statistical analysis of the data. Vitamin C was analyzed by extracting 0.5 g in 4% oxalic acid followed by titrimetric analysis using 2,6-dichlorophenol indophenol.¹⁵ Samples were also oven-dried, ground, and digested in the triacid mixture. $\text{Fe}^{3+/2+}$ in the extract was determined as described above. Results of the experiment were statistically analyzed for the significance of the differences in the mean values at 1% and 5% levels.

Results and Discussion

1. Formulation and Synthesis. Trials with the Fe–Mn–P system showed that citrate (0.33 M) solubility of all products

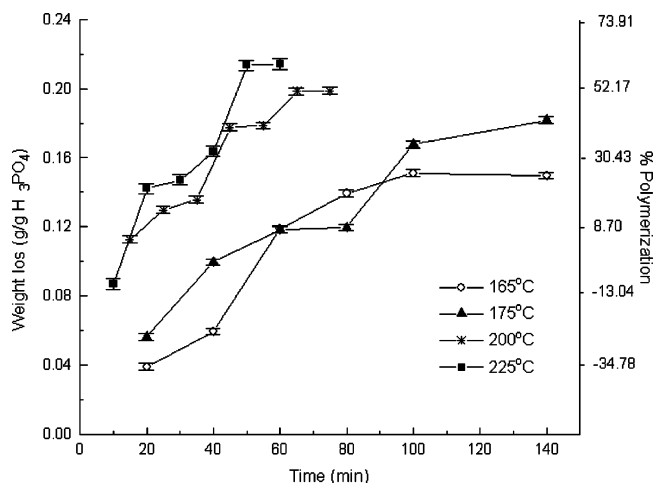


Figure 3. Reaction kinetics and degree of polymerization at different temperatures (laboratory-scale studies with pure compounds).

was low; no product could be synthesized which had good solubility in citrate. Low solubility could be attributed to the fact that Fe^{3+} and Mn^{4+} form very strong cross-linkages between adjacent P–O–P chains, and thereby a very stable structure is formed which cannot be made soluble by breaking of P–O–P–Fe/Mn–O–P– bonds. Therefore, Mg^{2+} was introduced into the structure to provide weak points susceptible to solubilization. The products formed with Mg as an additive were more promising. At the lowest Fe/Mg molar ratio of 1:0.29, there was a significant improvement in solubility; even so, some citrate-insoluble residue was observed in all products. With further increase in the Fe/Mg ratio to 1:1.15, an improvement in solubility occurred. The product obtained at 200 °C with 45 min heating produced a clear solution with citrate (0.33 M). The mechanism of dissolution is essentially due to chelation of

the cations, which are removed from the structure by citrate or DTPA leaving behind a polyphosphate chain. By addition of Mg^{2+} , weaker linkages are introduced. The initial dissolution of Mg^{2+} by chelation exposes the structure to further breakdown and facilitates solubilization. Lower levels of heating yielded products that left a whitish insoluble residue in citrate. Over-polymerized products, on the other hand, produced a black residue on citrate treatment. Weight-loss data showed that the optimum level of polymerization corresponds to a weight loss of 0.143 g/g H_3PO_4 or 21.2% polymerization.

In the next stage, the process was upgraded and studied on a bench scale with ore-grade materials. Rates of condensation in this system can be seen in Figure 1. Rates are essentially linear in nature with breaks (slope changes) that indicate a multistage process. Overall, the features are suggestive of a zero-order reaction with phase changes.

Reactions at all three temperatures (Figure 1) have been terminated at the optimum polymerization levels. It is, therefore, interesting to observe that at 175 °C, weight loss for optimum polymerization is lower than that at 200 °C, and weight loss at 250 °C is the highest. Thus, at lower temperatures, although rates of reaction are slower, less polymerization is required to produce the desired materials. Structural differences between polymers obtained at different temperatures may account for this behavior.

For the synthesis of fertilizer, a temperature of 200 °C appears to be optimum; reaction at 175 °C is comparatively slow, whereas at 250 °C reaction control is difficult and over-polymerization is likely. Optimum pH for neutralization of the polyphosphate was studied in the range pH 4–7. Product obtained at pH < 5, on drying, was hygroscopic and sticky. At a neutralization pH > 6, there was a reduction in citrate solubility. High citrate solubility and low hygroscopicity were

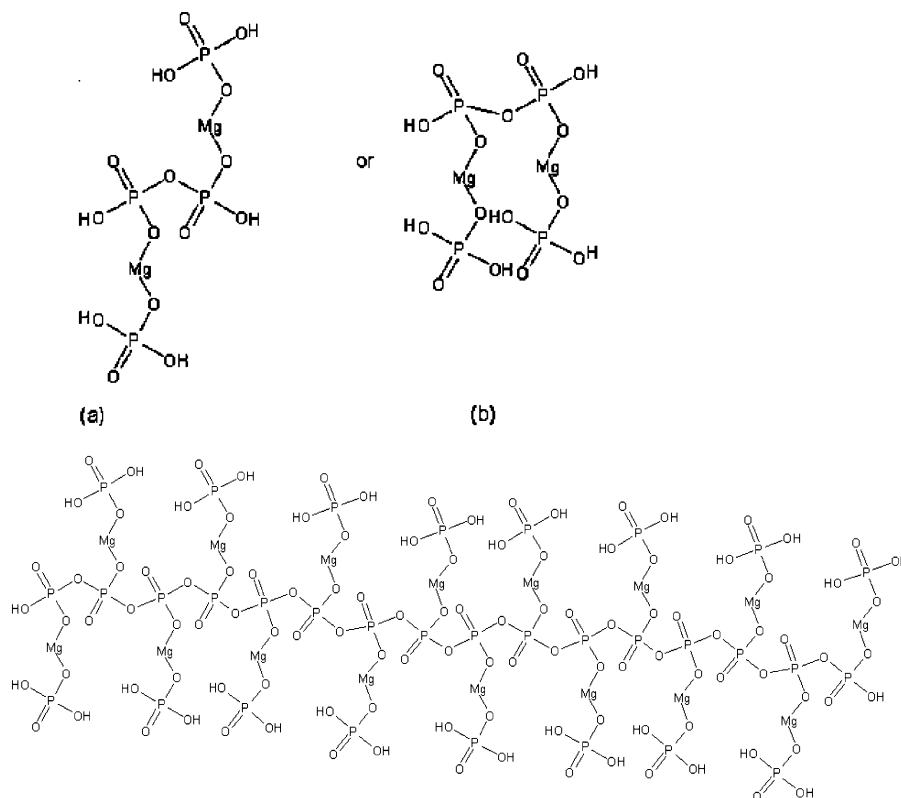


Figure 4. Polymerization steps showing metal tetrphosphate dimer of less-stable (b) and more-stable (a) forms, plus the stable form of a multidimensional polymer (brickwall-like structure). Magnesium is shown as an example of a metal.

Table 2. XRD, IR, and ESR Data

XRD spectra (A ^a)			XRD spectra (B ^b)			IR absorptions (A)	
<i>d</i> (Å°)	intensity	assignment ^{c,e}	<i>d</i> (Å°)	intensity	assignment ^{c,e}	wavenumber (cm ⁻¹)	assignment ^d
1.67	32	Fe—Mn pp	1.68	33	Fe—Mn pp	3236	OH
			1.80	34		2370	P—OH
1.79	22	App	1.93	35	Mg pp	2344	P—OH
			2.05	33	pp	1687	Mg—O—P
2.00	98	pp	2.20	34		1443	NH ₄
			2.40	45	Mg pp	1404	NH ₄
2.56	21	Fe—Mn pp	2.55	41	Mg pp	1291	P—O
			2.59	57	Fe—Mn pp	1074	P—O
2.63	26	pp	2.73	60	pp	919	P—O—P
			2.88	54	Mg p	541	Fe—O
3.04	100	pp, MAP	3.04	95	pp		Mn—O
			3.10	100	pp		
3.71	40	MAP, DAP	3.46	96			
			4.19	53	Mg p		
5.21	39	App, pp	4.53	50	Mg pp		
			4.62	45	pp		
			4.84	77	Mg pp		
			5.37	56	pp		
			5.94	86	Mg pp		

^a Iron—manganese—magnesium—ammonium polyphosphate. ^b Iron—manganese—magnesium polyphosphate fertilizer. ^c Ref 17. ^d Ref 16. ^e App: ammonium polyphosphate; pp: polyphosphate; MAP: monoammonium phosphate; DAP: diammonium phosphate; Mg p :magnesium phosphates;

Table 3. Results of Plant Experiment with Chilli

Fe—Mn dose (kg/ha)	average yield of chilli pods (g/pot)		total uptake of Fe by fruits (mg/pot)		total uptake of Mn by fruits (mg/pot)		vitamin C (mg/1000 g)	
	water-soluble fertilizers	slow-release fertilizer	water-soluble fertilizers	slow-release fertilizer	water-soluble fertilizers	slow-release fertiliz er	water-soluble fertilizers	slow-release fertiliz er
0–0	2.47	2.47	0.30	0.30	0.12	0.12	2000	2000
2–1	<i>c</i>	6.90 ^a	<i>c</i>	0.50	<i>c</i>	0.24	<i>c</i>	3566
4–2	4.57	<i>c</i>	0.95	<i>c</i>	0.34	<i>c</i>	3566	<i>c</i>
6–3 ^b	7.18 ^a	12.5 ^a	0.85	2.95	0.27	0.61	2573	2710
8–4	6.27 ^a	7.20 ^a	0.68	1.51	0.27	0.32	1791	1959

^a Significant with respect to control at 5% level (LSD_{0.05}); CD at 5% is 3.73; Standard Error is 1.75. ^b Optimal dose. ^c Data not available due to crop failure by pest attack.

order kinetics, that is, a straight line in the kinetic curve. As the structure becomes larger and unstable intermediates are formed, condensation would slow down to allow for structural rearrangements. Polymerization would subsequently continue with the same zero-order kinetics until more unstable structures are formed. Therefore, there would be another slowing down of the rate, resulting in plateau formation.

3. Characterization and Testing of the Compound. Table 1 shows the chemical analysis data, number-average chain length, and solubility characteristics of the iron—manganese compound prepared in the bench scale. The polyphosphate was a short-chain polymer with a number-average chain length of 3.34. Water solubility of Fe or Mn from the fertilizer was too low to be detectable (<0.1%). Solubility over a period of time (0–21 days) showed no further release of cations from the compound. The hydrolysis rate of the polyphosphate appeared to be slow, and the compound was quite stable in water. Solubility of the compound in citrate and DTPA was, however, very high. About 80–90% of the Fe and Mn were solubilized in 0.33 M and 0.1 M (2%) citric acid and 0.005 M DTPA (Table 1). Solubility in these reagents is an index of availability of nutrients to crops,^{9,14} thus the plant availability of the fertilizer Fe and Mn is expected to be high.

Room-temperature ESR spectrum showed a broad band with a *g*-value of 1.986 that corresponds to Fe(III) and Mn(IV). A weak Mn(II) band was also observed at a *g*-value of 2. IR spectrum (Table 2) showed absorptions at 1074 cm⁻¹ that may be attributed to P—O ionic stretching¹⁶ and at 919 cm⁻¹ due to P—O—P vibrations. Whereas long-chain polyphosphates, as reported in the literature, show absorptions at 1250 cm⁻¹, this is shifted to lower wavenumbers for a short-chain polyphos-

phate;¹⁶ the data, therefore, suggest that the iron—manganese polyphosphate contained mostly short-chain P—O—P. Similar absorptions had been observed^{5,6} for two other short-chain polyphosphates of zinc (at 1100 cm⁻¹) and copper (at 1150–1050 cm⁻¹). Weak absorption at 1291 cm⁻¹ however, implies some long-chain P—O—P. The presence of hydrogen-bonded OH groups is also indicated by the strong bands at around 3236 cm⁻¹.

Although the compound was a short-chain polyphosphate, XRD indicated that it was fairly well crystallized (Table 2). In order to determine reflections due ammonium polyphosphates, XRD of a sample containing no ammonium polyphosphate (i.e., a sample neutralized with MgO) was also studied. Thereby, reflection at 1.79 Å could be attributed to ammonium polyphosphate. Other ammonium phosphates were also confirmed by their reflections at 3.71 Å in the ammoniated sample and its absence in the Mg-neutralized sample. On comparison with XRD data for similar short-chain zinc and copper polyphosphates,^{5,6} several common reflections are observed. These reflections at around 3.04 and 2.0 Å are present in all these polyphosphates, and they have been attributed to a periodicity in the polyphosphate chain.^{5,6} Reflections at 5.2 Å could be due to ammonium pyrophosphate and that at 3.7 Å (Table 2) to ammonium hydrogen phosphates.¹⁷ All of the reflections, however, cannot be interpreted since the compound is new and necessary data are not available in the literature.

Chillies (*Capsicum frutescens*) grown on a black soil showed excellent response to slow-release Fe—Mn fertilizer (Table 3). At 2 kg/ha Fe and 1 kg/ha Mn, yield increased by 179% compared to the control (no Fe—Mn fertilization). An increase

in yield of 406% was observed (significant also at $P = 1\%$ level) at a dose of 6 kg/ha Fe and 3 kg/ha Mn. Conventional fertilizers also increased yields, but the extent of increase was less (Table 3). Average Fe uptake by chillies was observed to be higher in slow-release fertilizer treatments. Chillies were also enriched in vitamin C in slow-release fertilizer treatments (Table 3), with an increase of 78% observed at an application rate of 2 kg/ha Fe. Due to large variance caused by pest attack, the data for Fe, Mn, and vitamin C contents did not show significance at the 5% level.

Good fertilizer response obtained with chillies suggests that other crops with high iron or manganese requirements would also be responsive to this slow-release fertilizer.

Conclusion

We were successful in developing a new polymeric compound of iron–manganese that would be an effective slow-release fertilizer material.¹⁸ The compound is a partially polymerized phosphate that is produced by heating a mixture of oxides and phosphoric acid at around 200 °C to an optimum degree of polymerization of around 21%. This is a polycondensation reaction with multistage kinetics and complex reaction routes. The polyphosphate itself is liquid and acidic; neutralization to an optimum pH 5.6–6.0 converts it to a form that can be dried and ground to a fine powder. The final product is free-flowing and nonhygroscopic.

The compound is crystalline and shows XRD patterns that are not characteristic of any known substance. ESR shows Mn in IV and II states and Fe in the III state. Experiments with a test crop (chillies) produced a 179% increase in yield at a dose of 2 kg/ha Fe–1 kg/ha Mn as slow-release fertilizer. This also resulted in increased uptake of Fe and an increase in vitamin C content of the fruit. Considering all performance parameters measured (i.e., yield, Fe uptake, and vitamin C content), an optimum application rate of 6 kg/ha Fe was observed for the fertilizer.

Use of such slow-release fertilizers could drastically cut down micronutrient dosages, which are at present very high because of low use-efficiency of the soluble salts such as ferrous and manganous sulfates. This could also lead to more favorable economics of fertilizer use and thereby encourage micronutrient usage. In view of the simplicity of the synthesis route, attractive chemical properties of the compound (low water solubility and high bio-availability of nutrients), easy application, and apparently good fertilizing efficiency, this slow-release iron–manganese fertilizer could provide an environment-friendly alternative for effective fertilization. Similar compounds could be synthesized on the basis of this concept, to develop slow-release fertilizers for other micronutrients and their combinations.

Acknowledgment

We are grateful to the Department of Science & Technology, Government of India, for financial support. We thank Professor P. Ray, Department of Chemical Engineering, Calcutta University, for his suggestions.

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Received for review June 21, 2006

Revised manuscript received January 9, 2007

Accepted February 12, 2007

IE060787N