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A new slow-releasing iron fertilizer

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ABSTRACT

This paper describes the development of an environment-friendly, slow-release fertilizer of the micronutrient iron. The compound is water insoluble, and is based on a polymeric phosphate structure. Kinetics and solubility of products in the goethite [FeO(OH)]–H_3PO_4 and [FeO(OH)]–MgO–H_3PO_4 systems were studied at 170–300 °C. Polymerization patterns were complex. The presence of Mg as additive, improved product properties. The fertilizer was prepared by polymerization of goethite, magnesium oxide and phosphoric acid to an optimized chain length at 200 °C, followed by neutralization with magnesia. The fertilizer was soluble in citrate and DTPA. A significant increase in the yield of wheat and uptake of iron was observed at a dosage of 2 kg/ha Fe as the slow-release fertilizer.

1. Introduction

Slow-releasing fertilizers have long been recognized as the best solution to the various environmental problems caused by traditional water-soluble fertilizers. With slow-release fertilizers, dosage requirements are lowered, fertilizer use efficiency is improved and environmental pollution problems are practically negligible. Slow-release fertilizers are of various types depending on the mechanisms of slow-release. Control mechanisms in slow-releasing fertilizers may be categorized as: (i) Hydrolysis control, where bonds are broken by hydrolytic cleavage to release nutrients into solution e.g., metaphosphates, glass frits, ureaforms, etc. [1,2]. The limitation of such materials is that hydrolysis rates are affected by soil pH, water content, temperature, etc., and consequently nutrient release rates may not match the rate of uptake by the plant. (ii) Diffusion control, where soluble nutrients are encapsulated in a membrane or held in polymer gels such as polyacrylamide. Here, the ions diffuse out slowly through the membrane or gel [3,4]. Coating thickness, porosity of the membrane, environmental factors that affect porosity, are all controlling factors in nutrient availability. Therefore, different types of crops and soils require customized coatings to deliver the required rates of nutrient release. (iii) Surface area control, where the size of the particles is increased to slow down solubilization, e.g., super granules [5,6]. Supergranules have not been very successful because highly localized nutrient application and improper distribution. (iv) Chelate reaction control (bio-release) where nutrients are released from an insoluble compound by organic acid chelates [7–9].

A perfect slow-release fertilizer would be one in which the nutrient release would not be controlled by hydrolysis or diffusion but by the dissolution activities of the root itself. A water-insoluble molecule that can be actively dissolved by plant roots by ion-exchange with the root hairs or by extracellular organic acid secretions that extract nutrients by chelation would be an ideal slow-release fertilizer. This category of slow-release fertilizers has, therefore, been designated as ‘bio-release fertilizer’.

Such bio-release fertilizers have been developed for zinc, copper, molybdenum and iron-manganese in combination [7–11]. They are partially polymerized linear chain phosphates in which the phosphate chain functions as a cation exchange backbone. Although the compounds are water insoluble, they are soluble in organic chelates like citrate and DTPA. Solubility in such chelates ensures high availability of the plant nutrients, i.e., high bio-availability [12,13].

A major problem in the synthesis of fertilizers based on such partially polymerized linear polyphosphates is their hygroscopicity and stickiness. Due to the wide distribution of chain lengths [14], polyphosphates contain short, water-soluble chains together with long, water insoluble chains. It is, therefore, virtually impossible to produce a heavy metal polyphosphate, which has low water solubility but is also highly soluble in organic acids. However, Ray et al. [7] succeeded in overcoming these problems to produce, for the first time, a slow-release micronutrient fertilizer of Zn based on the short-chain polyphosphate structure. Subsequently Cu, Mo and Fe–Mn compounds were also produced. All these compounds were very effective at 1/5 to 1/10 the normal

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dosages and produced yield increases of 25–80%. In view of the promising results of such slow-release formulations, the extension of this concept to other micronutrients is necessary. Although, a combined iron-manganese compound has been synthesized [9], a compound containing only iron (without manganese in the structure) is also desirable. This would improve its applicability and versatility to agro-environments which may not require manganese and also for blending into various formulations in mixtures.

The chemistry of iron polyphosphates was clearly different from the iron–manganese compound and mere absence of manganese could not produce a slow-release iron fertilizer. Therefore, compound development had to be done from the initial stages.

In this work, we report the development of a slow-releasing iron polyphosphate compound. Briefly, we studied the fundamental reaction chemistry (polymerization kinetics and product properties) in the iron-phosphate system. We also studied the effect of additives on the polymerization reaction, with a view to improving product properties. Based on these studies, a suitable polyphosphate was formulated and methods developed to convert it to a slow-release fertilizer. The fertilizer compound was then characterized by chemical and physical techniques and assessed for its fertilizing potential.

2. Experimental

Studies on reaction kinetics were done with the following materials: (i) goethite [α-FeO(OH)] which was synthesized by slow hydrolysis of Fe^{3+} solutions [15], (ii) orthophosphoric acid (analytical grade) and (iii) MgO (analytical grade). In all experiments, a diluted phosphoric acid (about 40% P_2O_5) was used. The exact strength of the acid was determined by spectrophotometric analysis as the blue molybodophosphate complex [16]. Standardization of the acid was done at weekly intervals.

Reactions were carried out in a platinum crucible. To a preweighed crucible, 0.1 g goethite was added followed by a measured volume of H_3PO_4 to give a Fe:P molar ratio = 1:3; the weight of crucible and contents were recorded. In another set of experiments, MgO was also added at a Fe:Mg:P molar ratio of 1:3:5. Preliminary experimentation showed that this level of Mg was necessary to produce a compound of desired solubility properties. The crucible with the reactants was preheated in a muffle furnace at 150 °C (±0.5 °C) for 60 min to remove excess water and avoid spattering of the contents at higher temperature. It was then stored in a desiccator (over fused $CaCl_2$) and the furnace temperature raised to 170, 200 (±0.5), 250 or 300 °C (±1.0). The crucible was placed in it for the required period, then cooled in a desiccator (over P_2O_5) and weighed. The reaction product was subsequently washed with 0.1N HCl, filtered and stored. More details of this methodology are available elsewhere [17].

For each reaction system, the actual amount of H_3PO_4 (excluding all the water) was calculated from the known weight and concentration of H_3PO_4 solution initially taken; this quantity is designated as $[H_3PO_4]$. Weight loss in the reaction system was obtained from the initial weight of $FeO(OH) + [H_3PO_4]$ minus the final weight after heating. Range of error in these values is about ±0.1%. Theoretical H_2O loss for complete polymerization (100% polymerization) to metaphosphate was evaluated according to the reaction:

$$FeO(OH) + 3H_3PO_4 \rightarrow Fe(PO_3)_3 + 5H_2O$$

Thus, for every 91.975 × 3 mg H_3PO_4 in the system, 5 × 18 mg weight loss corresponds to 100% polymerization. Therefore, the degree of polymerization of a system containing p mg H_3PO_4 having a weight loss of q mg is $[(100 \times 97.975 \times 3 \times q)/(5 \times 18 \times p)]$%.

In systems containing MgO (at Fe:Mg molar ratio of 1:3), the value of % polymerization is obtained from the two reactions corresponding to 100% polymerization, viz.,

$$FeO(OH) + 3H_3PO_4 \rightarrow Fe(PO_3)_3 + 5H_2O$$

$$3MgO + 6H_3PO_4 \rightarrow 3Mg(PO_3)_2 + 9H_2O$$

As shown above, the degree of polymerization for a system containing p mg P having a weight loss of q mg would be $[(100 \times 97.975 \times 9 \times q)/(14 \times 18 \times p)]$%.

Amount of $Fe^{3+/2+}$ in the reaction product, solubilized by 0.1N HCl, was determined by spectrophotometric analysis of $Fe^{3+/2+}$ in the solution as the *o*-phenanthroline complex [18]. Number average chain length ($\bar{n}$) of the polyphosphate was determined by dissolving it 1N HCl, removing $Fe^{3+/2+}$ and Mg^{2+} interference by solvent extraction as the 8-hydroxyquinoline followed by titrimetric analysis [19].

Chemical analysis of the fertilizer for total $Fe^{3+/2+}$ content was done by dissolving in 1N HCl and analyzing as the *o*-phenanthroline complex [18]; Mg^{2+} was determined by AAS. For the analysis of P, the compound was fused with NaOH, dissolved in dilute HCl, made to volume and P determined as the reduced molybophosphate complex [16]. Adsorbed water (H_2O^-) was determined by heating to constant weight at 100 °C. Structural water (H_2O^+) was determined by heating to constant weight at 800 °C and subtracting the weight of adsorbed water.

IR spectra of the samples were recorded on a PerkinElmer instrument (FTIR RX-1) with the scan range of 4000–400 cm^{-1} using pellets containing KBr as matrix. XRD of the slow-releasing iron fertilizer was recorded on a Philips diffractometer (PW 1140) using Ni-filtered Cu Kα radiation at a scanning speed of 2° 2θ/min.

Solubility of the fertilizer compound in the following reagents was determined: 0.1 M HCl, 0.33 M citric acid and 0.005 M DTPA. To 0.05 g of the fertilizer, 50 ml of the reagent was added and the suspension agitated in a horizontal shaker for 30 min; it was then filtered, washed, made to volume and analyzed for $Fe^{3+/2+}$ as described above. To study rates of solubilization of the fertilizer in water, 0.05 g of the compound was taken in conical flasks and 10 ml water was added to 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, made to volume and analyzed for $Fe^{3+/2+}$ as described above.

Plant growth experiments were carried out in pots. Surface soil from a black soil (Vertisol: very fine montmorillonitic, hyperthermic, Udic Chromustert) was collected from the State Government Farm, Gundkheri, Nagpur, Maharashtra, India. Characteristics of this soil are as follows: pH 7.95, EC_e 0.155 dS/m, organic carbon 0.74%, available $Fe^{3+/2+}$ 1.80 ppm after extraction by 0.005 M DTPA and exchangeable Mg^{2+} 11.84 cmol kg^{-1}. In each pot, 2 kg of soil was weighed. The treatments consisted of a control (where only NPK fertilizers but no Fe fertilizers were added), slow-release Fe fertilizer at four different dosages (viz., 2.01, 4.02, 6.03, 8.04 kg/ha Fe) and ferrous sulphate at the same four levels of Fe. Each treatment had 5 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 mixed into the soil before planting. Paddy (*Tulsi*) was grown in seedbeds and transplanted into the pots (at the rate of 2 seedlings/pot) when they were three weeks old. After harvesting, grain was separated from the straw and weight of grain and straw were recorded. Grain and straw were oven dried, ground separately in a grinder and digested in tri-acid mixture [16]. Fe^{3+} 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 5% level.

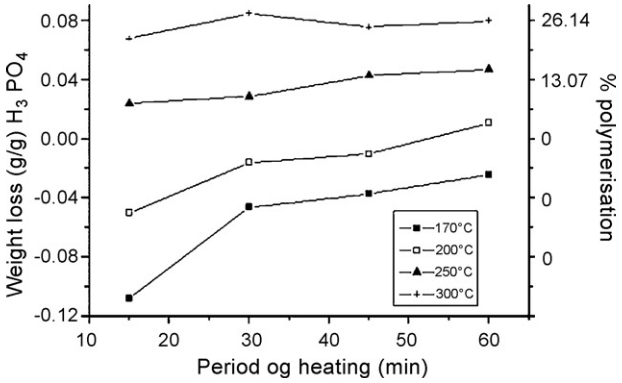

Fig. 1. Kinetics of polymerization in the system FeO(OH)–H_3PO_4.

3. Results and discussion

3.1. Kinetics of polymerization and nature of reaction products

Rates of condensation in the system FeO(OH)–H_3PO_4 were studied at 170, 200, 250 and 300 °C at a Fe:P molar ratio of 1:3 (Fig. 1). Preliminary heating at 150 °C converted the system to a clear viscous liquid containing $Fe(H_2PO_4)_2$ and sorbed water. Table 1 shows that at 170 °C, polymerization did not begin even after 60 min and only sorbed water was eliminated. At 200 °C, polymerization barely started after 60 min resulting in a product that had 3.6% polymerization. Products formed at 250 and 300 °C were all polyphosphates. Polymerization of products obtained at 300 °C was much higher than those formed at 250 °C; they ranged from around 22–26% polymerization for the former and 7–15% polymerization for the latter. Neither of these condensation curves fitted into a first or second order kinetic equation. Earlier studies on dehydration polymerization of phosphoric acid [17] and Zn, Cu, Fe–Mn phosphates [7–9] also revealed unusual kinetic curves. Since polymerization and elimination of water would occur as a consecutive reaction, complex reaction kinetics is to be expected. The reaction may be represented as:

$$n\mathrm{FeO(OH)} + 3n\mathrm{H_3PO_4} \rightarrow n\mathrm{Fe(H_2PO_4)_3} + 2n\mathrm{H_2O}$$

$$n\mathrm{Fe(H_2PO_4)_3} \rightarrow \mathrm{Fe}_n\mathrm{H}_{(4n+2)}\mathrm{P}_{3n}\mathrm{O}_{(11n+1)} + (n-1)\mathrm{H_2O}$$
$$\rightarrow \mathrm{Fe}_n(\mathrm{P}_n\mathrm{O}_{3n})_3 + (3n)\mathrm{H_2O}$$

Here the dihydrogen phosphate polymerizes, by elimination of 1 mol of water between two P–OH groups of adjacent ferric phosphates, forming linear polyphosphates with –P–O–P– linkages. Condensations of small chains would produce successively large chains. However, this could occur in a random manner. Thus a diphosphate ($n = 2$) could condense with another diphosphate or orthophosphate to produce a tetraphosphate ($n = 4$) or a triphosphate ($n = 3$) respectively [9]. In such a system the reactant species would be very heterogeneous. This would account for the complex reaction kinetics in the iron polyphosphates.

Relationships between the solubility of the products in 0.1N HCl and their degree of polymerization are shown in Table 1. It appears that the reaction temperature influences the solubility of a product. Lower temperatures of synthesis produced more acid soluble polyphosphates than higher temperatures. Another feature particularly relevant here, is that all the polyphosphates had low solubility in HCl probably due to strong cross-linkages. Insolubility in dilute HCl is a very undesirable property for a slow-release polyphosphate fertilizer. A product which is not soluble in 0.1N HCl would be too tightly bound and would not be available to plants. It was, therefore, envisaged that in order to produce polyphosphates with improved solubility properties, an additive would be needed. Preliminary trials with Mg, K and Na showed that Mg was the most suitable. Accordingly, reaction kinetics and product solubility were studied for the system FeO(OH)–MgO–H_3PO_4 corresponding to $Fe(H_2PO_4)_3$–$3Mg(H_2PO_4)_2$. Dehydration curves at 200, 250 and 300 °C are shown in Fig. 2. The curves suggest a multiple stage reaction, as observed earlier with cupric phosphate [8].

Table 1
Kinetics of condensation and Fe solubility in the reaction system I (FeOOH + H_3PO_4) and system II (FeOOH + MgO + H_3PO_4).

System I					System II			
Reaction temperature (°C)	Period of heating (min)	Weight loss (g/g H_3PO_4)	% Polymerization	% Fe soluble (0.1 M HCl)	Period of heating (min)	Weight loss (g/g H_3PO_4)	% Polymerization	% Fe soluble (0.1 M HCl)
170	15	−0.108	–	32				
	30	−0.046	–	29				
	45	−0.037	–	25				
	60	−0.024	–	8				
200	15	−0.050	–	18	15	−0.084	–	48
	30	−0.016	–	6	30	−0.021	–	81
	45	−0.010	–	7	45	0.002	0.70	100
	60	0.011	3.60	7	60	0.011	3.85	100
					75	0.034	11.89	94
					90	0.048	16.79	88
250					10	0.023	8.05	89
	15	0.024	7.84	6	20	0.034	11.90	100
	30	0.029	9.48	7	30	0.038	13.30	94
	45	0.043	14.06	11	40	0.042	14.70	88
	60	0.047	15.36	7	50	0.037	12.95	88
					60	0.049	17.15	83
					70	0.057	19.94	81
300					5	−0.019	–	88
					10	0.056	19.59	94
	15	0.068	22.22	4	15	0.078	27.29	96
	30	0.085	27.78	3	20	0.087	30.44	90
	45	0.076	24.84	3	25	0.086	30.09	88
	60	0.080	26.1	3	30	0.086	30.09	81

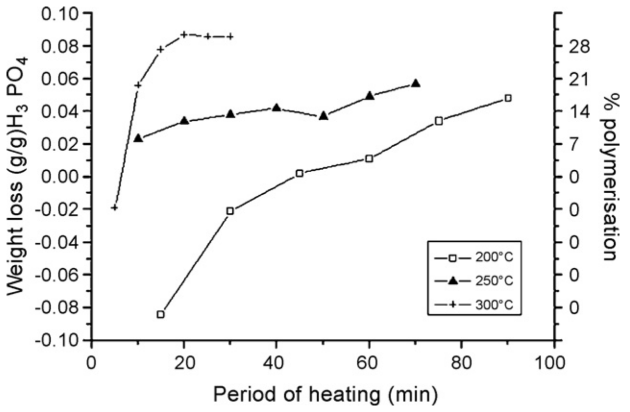

Fig. 2. Kinetics of polymerization in the system $FeO(OH)–MgO–H_3PO_4$.

The reaction with Mg included in the system, may be represented as

$$nFeO(OH) + 3nMgO + 9nH_3PO_4$$
$$\rightarrow nFe(H_2PO_4)_3 + 3nMg(H_2PO_4)_2 + 5nH_2O$$

$$nFe(H_2PO_4)_3 + 3nMg(H_2PO_4)_2$$
$$\rightarrow Fe_nMg_{3n}H_{3(4n+2)}P_{9n}O_{3(11n+1)} + 3(n-1)H_2O$$
$$\rightarrow Fe_nMg_{3n}(P_{9n}O_{27n}) + (6n+3)H_2O$$

Product solubility *versus* degree of polymerization relationships (Table 1) show that with the introduction of Mg into the structure, solubility of the polyphosphates improved significantly to about 80–100%. Introduction of Mg^{2+} provides weak cross linkages that are susceptible to solubilization by acids. As Mg^{2+} is removed, the structural breakdown occurs and the compound solubilizes. Polyphosphates of high acid solubility (≈100%) had much lower degrees of polymerization when produced at lower temperatures, rather than at higher temperatures. Thus at 200 °C, polyphosphates with near 100% solubility in dilute HCl had 0.7–3.8% polymerization whereas at 250 °C, high HCl solubility was shown by a polyphosphate with 11.9% polymerization; at 300 °C, the highest attainable solubility of about 96% was shown by a polyphosphate with 27.3% polymerization. This behaviour exhibited by the polyphosphates is somewhat contrary to expectation since products with similar degrees of polymerization would be expected to show similar solubilities. Further, a polyphosphate of 88% solubility in 0.1N HCl was about 30.1% polymerized when produced at 300 °C whereas it was 14.7% polymerized when produced at 250 °C. It would appear from the observations above, that polyphosphates formed at different temperatures are structurally different even if they have similar degree of polymerization, i.e., they differ in their degrees and nature of cross-linking.

A schematic diagram of the polyphosphate is shown in Fig. 3.

3.2. Formulation of fertilizer

At the first stage, we needed to select a polyphosphate with optimized chemical properties. Polyphosphates produced with only goethite and phosphoric acid as the starting materials showed high insolubility in 0.1N HCl. This will not yield a satisfactory material since much of the Fe^{3+} would remain in a non-available form for plants. On the other hand, in systems with added Mg, products of high 0.1N HCl solubility could be obtained. Therefore, the basic formulation must necessarily be an iron-magnesium polyphosphate.

We then attempted to select the most appropriate iron magnesium polyphosphate for formulation of the fertilizer. Data on polymerization rates and solubility characteristics showed that polyphosphates produced at 250 and 300 °C would be more appropriate than those at 200 °C, since rates of polymerization at 200 °C were much too slow.

However, like all short chain polyphosphates, the iron–magnesium polyphosphates produced at 200 and 300 °C were very hygroscopic and rapidly become sticky when exposed to atmosphere. Such stickiness was due to free acid (H^+) groups on the polyphosphate chain; neutralization of these groups not only removed hygroscopicity but also reduced the water solubility of the compound [7]. Therefore, an iron-magnesium polyphosphate (250 °C, 20 min) was selected and neutralized with NH_4OH to

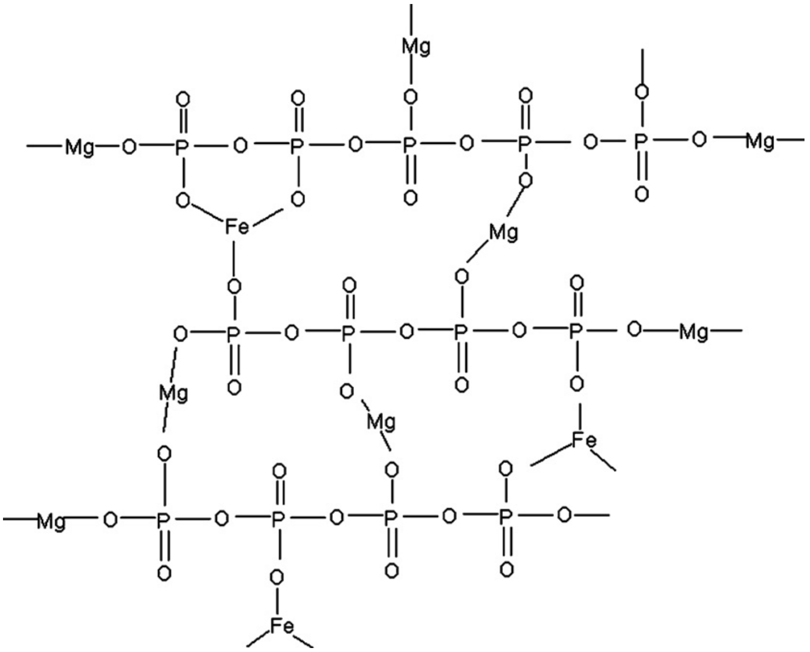

Fig. 3. Schematic structure of the iron magnesium polyphosphate.

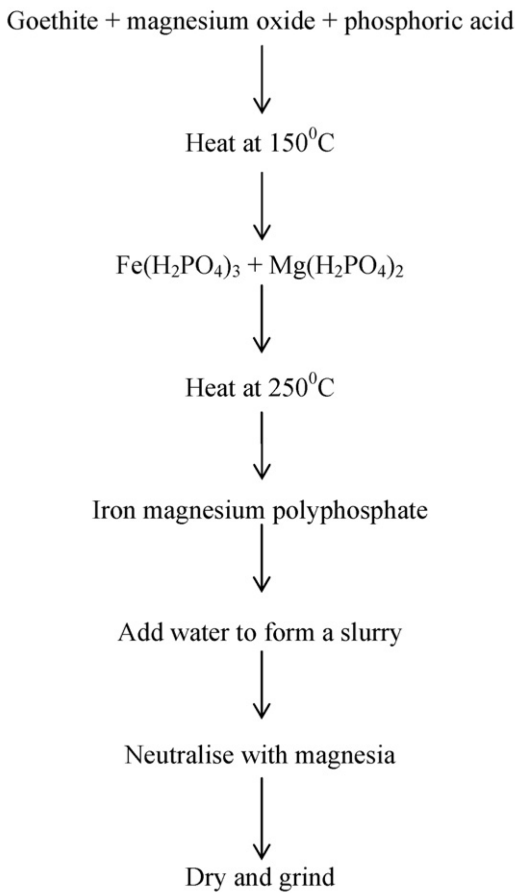

Fig. 4. Flow chart for synthesis of slow-release iron fertilizer.

various pH. The products, in general, showed high water solubility, which is not a desirable characteristic of a slow-release fertilizer. Solubility was low only at pH 5.6 but this increased sharply with a pH change of ±0.1. More polymerized products also showed an increase in water solubility. An alternative treatment was, therefore, attempted using MgO instead of NH_4OH. Products showed overall, a remarkable improvement in solubility properties. All products neutralized to a range of 4.6–6.1 had <1.3% Fe solubility. The lowest solubility was shown at a neutralization pH of 5.6.

The optimum conditions derived for the formation of the fertilizer were, therefore, as follows: FeO(OH), MgO and H_3PO_4 in the molar ratio Fe:Mg:P = 1:3:5 was heated at 150 °C for 30 min and then at 250 °C for 20 min to obtain a product with 11.9% polymerization. This was then made to a paste with water and neutralized with MgO to pH 5.6. The product was dried and ground to a powder. A flow-sheet for the process is shown in Fig. 4.

3.3. Studies on slow-release iron fertilizer

Chain length analysis of the fertilizer showed a number average chain length ($\bar{n}$) of 4.6. Chemical analysis produced the following results: 5.30% Fe_2O_3, 45.45% P_2O_5, 21.55% MgO, 19.20% H_2O^+, 8.50% H_2O^-. This corresponds to a formula $Fe_{0.07}Mg_{0.53}H_{2.13}P_{0.64}O_{2.98}$. Low percentage of micronutrient is a desirable feature of slow-release compounds since this ensures that a small dosage can spread over a large area. Additionally, the product is rich in both Mg and P, which are essential plant nutrients. Therefore, this compound, although functioning as an iron fertilizer, could also provide a supplementary source of Mg and P nutrition.

Infrared (IR) absorption spectra of the slow-release fertilizer showed absorptions at 568, 919, 1120, 1654 and 3422 cm^{-1}. A strong OH absorption at 3422 cm^{-1} may be attributed to OH stretching of H-bonded water molecules [20]. Absorptions due to ionic stretching of –P–O–P– groups occur in the 1180–1050 and 560 cm^{-1} regions [20] and are evidenced as peaks at 1120 and 568 cm^{-1}. Since long chain polyphosphates show shifting of the absorption [20] to around 1250 cm^{-1}, the data suggest that the iron magnesium polyphosphate did not contain long chain P–O–P. Similar absorptions have been observed [7–9] for two other short chain polyphosphates of zinc (at 1100 cm^{-1}), Cu (at 1150–1050 cm^{-1}) and Fe–Mn (at 919–1074). The short chain nature of iron magnesium polyphosphates is supported by chain length analysis data reported above.

X-ray diffraction (XRD) study (Fig. 5) revealed the crystalline nature of the polyphosphate. The major reflections were at 11.04, 6.06, 5.34, 3.23, 3.08 and 2.92 Å (relative intensities being 100, 32, 97, 48, 42 and 39 respectively). Various magnesium phosphates like $Mg(PO_3)_2$ and $Mg(H_2PO_4)_2$ were probably present [21] as seen by reflections at 3.23, 3.08 and 2.92 Å. The iron compound $Fe_4(P_2O_7)_3$ could contribute to the reflection at 5.34 and 3.08 Å [21]. Many of the peaks were common to those shown by the Zn, Cu and Fe–Mn compounds [7–9]. The strongest peak at 11.04 Å could not be matched with any other known compound and may be attributed to the iron magnesium polyphosphate itself. Some reflections also seen here (Fig. 5), viz., at 3.23, 3.08 and 2.32, were common to two zinc polyphosphates and were attributed to the polyphosphate backbone [9].

Initial solubility of the product in water was low (0.21%); it remained low even after 120 h in water (1.99%). Hydrolysis apparently occurred very slowly. On the contrary, solubility of the fertilizer was very high in 0.1N HCl, 0.33 M citric acid, and 0.005 M DTPA (96.1, 95.1 and 89.7% respectively). Reagents like DTPA, citrate, etc. are routinely used for evaluating plant available Fe [13,22]; Fe that is soluble in these reagents may be considered to be plant available. The high extractability of Fe from the slow-release compound thereby indicates ready availability of the nutrient ion. This property of the fertilizer also suggests that Fe^{3+} is present in ionic bonding sides, which are very similar to those present in soils, i.e., it simulates the natural source of available Fe in soils.

Results of the plant experiments are shown in Table 2. Increase in yields of paddy were statistically significant at the P = 5% level at all dosages of Fe as slow-release fertilizer; however, with $FeSO_4$ (the conventional fertilizer), there was no statistically significant

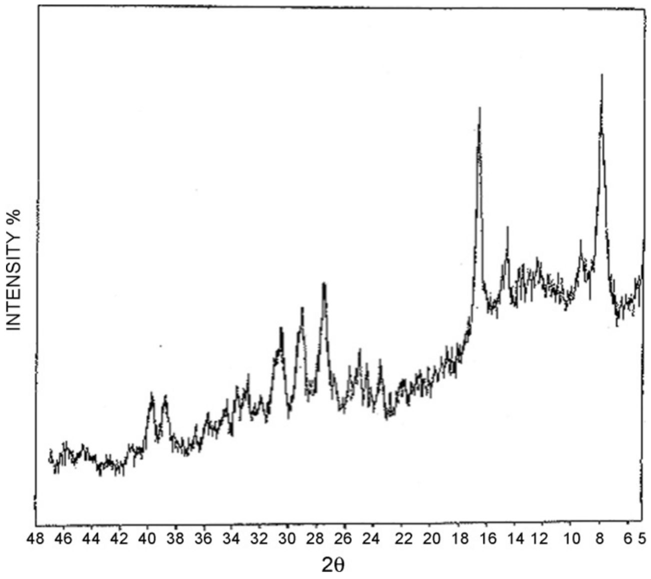

Fig. 5. XRD of slow-release iron fertilizer.

Table 2
Results of plant growth trials with iron fertilizers.

	Fe dosage (kg/ha)								
	Slow-release iron fertilizer					$FeSO_4$ fertilizer			
	Control	2.01	4.02	6.03	8.04	2.01	4.02	6.03	8.04
Total number of grains	165	225[a]	201	234[a]	228[a]	198	160	200	193
Yield of grain (g/pot)	3.11	4.57[a,d]	4.40[a,d]	4.48[a]	4.46[a]	3.37	2.61	3.70	4.17
Yield of straw (g/pot)	3.67	5.13[a,d]	4.59[d]	3.90	4.42	3.03	2.70	4.57	3.48
Total uptake of Fe by grain and straw (mg/pot)	2.02	5.99[c,d]	4.45[a,b]	8.46[c,d]	4.21	2.28	1.27	2.86	2.90
Total uptake of Mg by grain and straw (mg/pot)	7.57	10.87[c]	10.12[a]	10.32[a]	11.57[c]	8.62	7.84	10.15[a]	9.30

[a] Significant over control at 5% level.

[b] Significant over corresponding $FeSO_4$ treatments at 5% level.

[c] Significant over control at 1% level.

[d] Significant over corresponding $FeSO_4$ treatments at 1% level.

increase, at any level of Fe application. Even very low dosages of 2.01 kg/ha Fe as the slow-release fertilizer, resulted in a 46.9% increase in yield over the control. Yields appeared to have stabilized at these dosages since further application of Fe did not result in any significant yield increase. This is a remarkable feature of the slow-release compound since the usual dosages of Fe application as $FeSO_4$ vary from 20 to 30 kg/ha Fe [22]. Results obtained here also show that $FeSO_4$ treatments did not significantly increase yields even at 8.04 kg/ha Fe application. Total uptake of Fe by the grain and straw can also be seen in Table 2. At 2.01 kg/ha Fe application, there was increased uptake of Fe over control as well as $FeSO_4$ treatments. This increase was significant even at the 1% level. Increases in Mg uptake were also observed at all doses of the slow-release fertilizer. Results suggest that the slow-release fertilizer is an efficient and effective source of Fe and is better than $FeSO_4$ in both these aspects.

4. Conclusion

A polyphosphate based compound was developed to function as a slow-release source of iron. Such an iron polyphosphate compound could be formulated with Fe^{3+} and H_3PO_4 alone; an additive was required to obtained products of desirable properties. For this, Mg^{2+} appeared to be well suited. Thus, whereas iron polyphosphates themselves did not exhibit solubility in dilute acid (regardless of the degree of polymerization), iron magnesium polyphosphates showed good acid solubility over a range of chain lengths. Solubility properties of the polyphosphates were temperature dependent; solubility *versus* degree of polymerization curves showed maxima, which shifted to higher values of % polymerization at higher temperatures. Kinetic curves were complex and suggested multiple stage reactions.

All iron magnesium polyphosphates possessing good acid solubility were only partially polymerized (small chain compounds) and were hygroscopic due to the presence of acidic H^+ of P–OH groups in the –P–O–P– chain. It was possible to eliminate this undesirable property by neutralization of the acidic groups. Neutralization of the polyphosphate with NH_4OH produced compounds with fairly high water soluble Fe^{3+} whereas neutralization with MgO resulted in low water solubility; MgO, therefore, was a preferred neutralizing agent.

The fertilizer compound produced under optimized conditions had a number average chain length of 4.59. Although it had low water solubility yet 90-100% of the Fe^{3+} was in plant available form. Experiments in pots showed that this new fertilizer could increase the yield of paddy by 46.9% at a very low dose of 2.01 kg/ha Fe. Results are indicative of an efficient and potentially promising slow-release iron fertilizer.

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