New Slow-Releasing Molybdenum Fertilizer

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This paper describes a new water-insoluble molybdenum compound that has been developed as a slow-release fertilizer. The compound is an inorganic polymer formed by inclusion of molybdenum within a long-chain polyphosphate structure. It was designed by a process of "reverse engineering" of the molecule. Synthesis involved reaction of phosphoric acid with magnesium oxide, molybdenum trioxide, and sodium carbonate at 275 °C. Kinetics of reaction revealed complex multistage processes. X-ray diffraction patterns showed a crystalline nature with short-range as well as long-range ordering. The magnesium sodium polymolybdophosphate had ideal slow-release characteristics; it had low water solubility and high citrate solubility and was powdery, free flowing, and nonhygroscopic. Field testing showed an 80% increase in yield of green gram at a low dose of 0.04 kg/ha Mo. Nodulation increased by over 161%, and N content of gram increased by 20%. The slow-release fertilizer would provide an effective, low-cost, and environmentaly friendly alternative to Mo fertilization.

KEYWORDS: Micronutrient; molybdenum; slow release; fertilizer; polyphosphate; green gram; field test

INTRODUCTION

Slow-release fertilizers provide an effective means of overcoming the high waste, very low use-efficiency, and environmental problems associated with the use of water-soluble fertilizers. Although slow-release fertilizers are essentially water-insoluble, all insoluble materials are not necessarily good fertilizers. Insoluble compounds can be effective fertilizers only if rates of release of nutrient ions can match plant requirements throughout the growth period. Existing slow-release formulations have been mainly developed for the macronutrients (N, P, and K). These have release rates mainly controlled by diffusion or hydrolysis. Membrane-coated materials (*1, 2*) are characterized by diffusion-controlled release; hydrolysis-controlled release is characteristic of polymeric materials such as urea formaldehydes, phosphate glasses, and metaphosphates (*3–6*). However, none of such materials have had very significant commercial success, due to the inherent problems of controlling nutrient release rates to provide for a wide variety of crop requirements and soil conditions.

Conceptually, a perfect slow-release fertilizer would be one in which the nutrients mimic the natural forms of available nutrients in soils, such as in exchangeable or chelate-extractable positions (*7*). In such materials, nutrient release would not be controlled by hydrolysis or diffusion but by the dissolution activities of the root itself. Thus, plant roots are able to "digest" certain insoluble compounds by ion exchange with the root hairs or by extracellular organic acid secretions that extract nutrients by chelation (*8*). A water-insoluble molecule that can be actively dissolved by plant roots by such processes would be an ideal slow-release fertilizer. This category of slow-release fertilizers has, therefore, been designated "biorelease fertilizers" (*9–11*).

A group of such compounds with novel slow-release characteristics have been developed (*7, 9–13*). These compounds have low water solubility and high solubility in citrate and diethylenetriaminepentaacetic acid (DTPA). They are powdery, nonhygroscopic, crystalline, short-chain polymeric phosphates. Slow-release fertilizers of Zn, Cu, Fe, and Fe−Mn have been developed. Plant growth trials show very good response at low doses of these fertilizers (*7, 12, 13*).

Encouraging results obtained with cationic slow-release compounds prompted us to develop a slow-release fertilizer of the anionic micronutrient molybdenum (*9*). Molybdenum is essential for leguminous crops due to its requirement in nitrogen fixation. It also improves yields of vegetables of the *Brassica* family (*14*). Presently, ammonium molybdate is popularly used for Mo fertilization. Being water soluble and anionic it can be readily leached out. Consequently, fertilizer use-efficiency is low, and in many regions it may not be economically viable for leguminous food crops such as pulses and vegetables. Thereby, yields are limited due to insufficiency of Mo; N content of pulses may also be affected.

Improved Mo fertilization by the use of slow-release forms would reduce Mo dosages, improve Mo usage, and consequently improve yields. In this investigation we report the development of a novel compound of molybdenum. This is a "designed"

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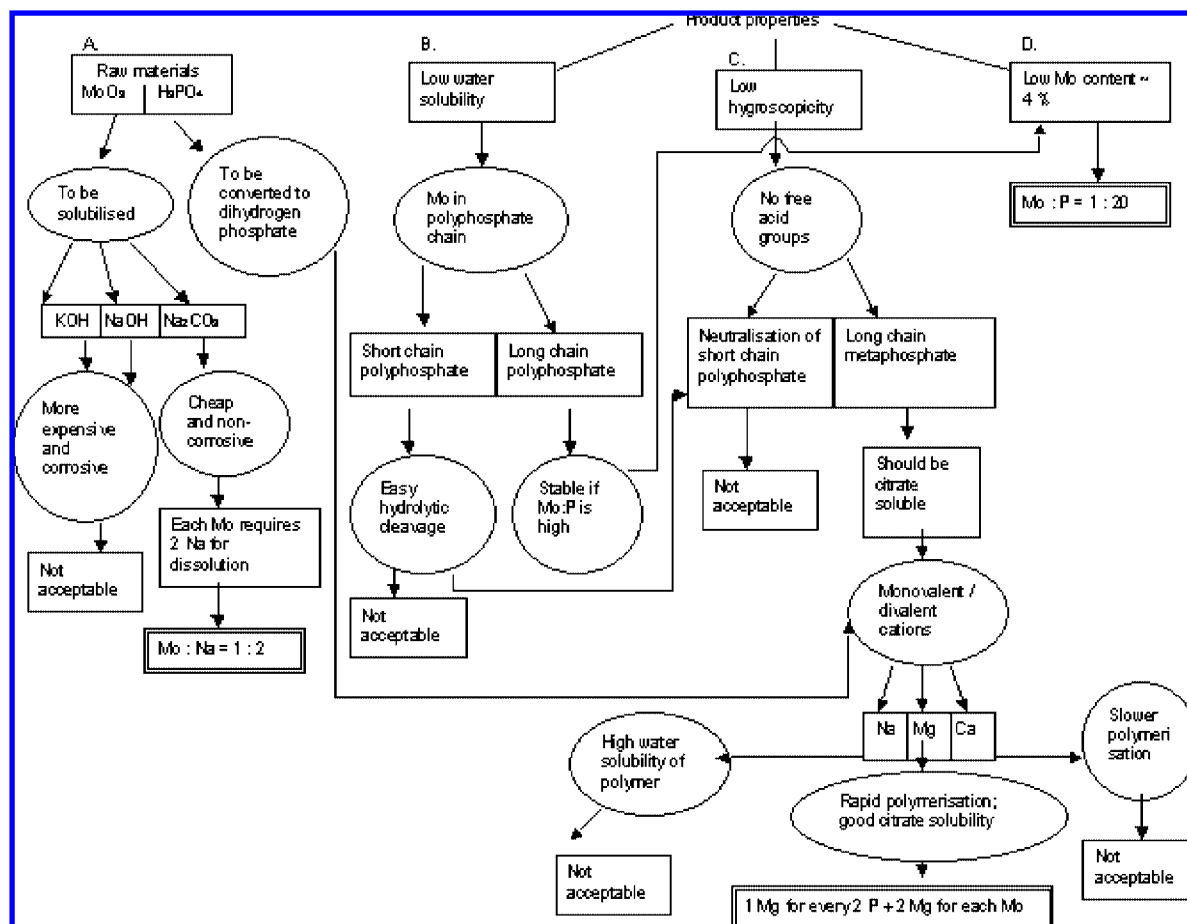[§] University of Calcutta.

Figure 1. Logic diagram for deriving composition of Mo fertilizer.

molecule formulated from a knowledge of polyphosphate chemistry. Subsequently, we experimentally verified and selected the optimized composition, studied the kinetics of the polymerization reaction, and characterized and tested the material. The compound appears to be a very promising slow-release Mo fertilizer.

MATERIALS AND METHODS

Formulation. Formulation of a new Mo-containing compound was done by broadly following a process of "reverse engineering". From the existing knowledge of reactions and properties of polyphosphates (*7, 12–16*) we formulated a compound having a set of essential properties. The logical stages as presented in the flow sheet (**Figure 1**) are as follows: We start with the premise that the fertilizer is to be made from molybdenum trioxide and orthophosphoric acid (input A). The product will have low water solubility and low hygroscopicity (inputs B and C) and also low Mo content to enable small Mo doses to be better distributed over the soil; an optimized composition should contain around 4% Mo (input D). By following a logical sequence, we obtained the following logical output: MoO_3 should be solubilized (to enable faster and more homogeneous reaction) by conversion to the sodium salt (Na_2MoO_4) by reaction with Na_2CO_3; the required molar ratio of Mo/Na should be 1:2. Phosphoric acid should be converted to a dihydrogen phosphate. A Mg salt is preferred because our requirement is a nonhygroscopic, long-chain metaphosphate that is citrate soluble. Therefore, a Mg/P molar ratio of 1:2 is required. A Mo atom in a polyphosphate chain would have two bonds with P—O groups on either side of the chain and four single-bonded oxygens, of which two are bonded to Na^+. The remaining two oxygens need to be neutralized to prevent hygroscopisity in the product. Two Mg^{2+} are, therefore, required for every Mo so that the reactive Mo compound is of the form $Na_2Mg_2MoO_6$ (Mo in octahedral coordination). This is in addition to the Mg required for neutralization of phosphoric acid. To ensure water

insolubility, a long-chain polyphosphate is to be produced. Such a chain will be stable toward hydrolysis only if Mo/P ratios are high because Mo—P bonds would be more readily cleaved. A product with a low Mo content of around 4% and a high Mo/P ratio can be obtained within a compound with Mo/P = 1:20. The derived molar ratio of the product is, therefore, as follows: Mo/Na/Mg/*P* = 1:2:12:20.
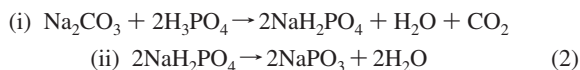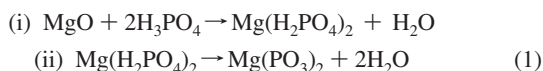
Synthesis. For the synthesis experiments, commercial grade chemicals were used. These were first analyzed. MoO_3 (0.1 g) was fused with 1.5 g of NaOH beads and extracted into 500 mL of 0.2 N HCl. Mo was determined spectrophotometrically as the thiocyanate complex (*17*). Commercial H_3PO_4 was analyzed for P content as the blue phosphomolybdate (*18*). Soda ash (Na_2CO_3) and calcined magnesite (MgO) were analyzed for Na^+, Mg^{2+}, and Ca^{2+} by dissolving 0.1 g in 1 N HCl followed by analysis by atomic absorption spectroscopy (AAS). Si^{4+} in all solids was determined by fusing 0.05 g of the sample with 1.5 g of NaOH beads and extraction into 0.2 N HCl followed by spectrophotometric analysis as the blue silicomolybdate (*19*). For synthesis experiments, 0.5 g of MoO_3 (99% MoO_3) was taken in a 100 mL borosilicate beaker and dissolved in 1 M soda ash (68% Na_2CO_3, 32% H_2O) so that the molar ratio of Mo/Na was 1:2. A diluted solution of H_3PO_4 (1:1) was prepared from commercial H_3PO_4 (80.8% H_3PO_4), and its P content was determined again as the blue phosphomolybdate (*18*). A predetermined amount of this solution was pipetted into another beaker (to give a Mo/P molar ratio of 1:20), and 2.41 g of calcined magnesite (69.2% MgO, 23.1% SiO_2, and 1.0% Fe_2O_3) was added. A small excess of acid (3 times the molar amount Fe) was added to compensate for P consumption by Fe impurities. The solution of the molybdate was then added to it with stirring. The beaker was placed in a furnace preheated to 150 ±1 °C for 30 min to remove excess water and avoid spattering at higher temperatures. It was then taken out and kept in a desiccator. Then the furnace temperature was increased to 275 ±1 °C, and the sample was placed in it again and heated for 30

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min. It was observed from preliminary trials that under these conditions, the sample solidified and became dry. It was ground and sieved through a 100 mesh.

The process was repeated at four other ratios, nameily, Mo/Na/Mg/P = 1:4:10:20, 1:4:5:10, 1:4:15:30, and 1:0:14:20. Products were exposed to room humidity for a day and examined visually for their hygroscopicity and stickiness. Weight increase was also noted. Solubility in water, 0.1 M HCl, and 0.33 M citric acid was assessed by visual examination.

Reaction Kinetics. Experimental details for the kinetic studies were essentially as described under Synthesis. However, instead of commercial grade chemicals, analytical grade reagents (AR/GR) were used. Also, preheating at 150 °C was not done, and samples were directly heated to 250, 275, and 300 °C for 5−75 min. The weight of the beaker was recorded at regular intervals until the product solidified and weight loss almost plateaued. These studies (in triplicate) were conducted for the system Mo/Na/Mg/P = 1:2:12:20. This particular ratio of reactants yielded the best product as observed under Synthesis. Weight loss in the system was calculated as the amount of MoO_3 + Na_2CO_3 + MgO + $[H_3PO_4]$ taken, minus the weight after heating, and is expressed as g/g $[H_3PO_4]$, where $[H_3PO_4]$ is the actual amount of H_3PO_4 (excluding water) in the system. This calculation excludes the free water present initially in the system and, therefore, negative values of weight loss are recorded as long as free water is not evaporated.

Maximum possible weight loss corresponds to 100% polymerization. This was calculated by considering that weight loss is due to loss of all structural water from H_3PO_4 and CO_2 from Na_2CO_3. The reactions may be represented by eqs 1,2,3:

$$\text{(i)} \quad MgO + 2H_3PO_4 \rightarrow Mg(H_2PO_4)_2 + H_2O$$
$$\text{(ii)} \quad Mg(H_2PO_4)_2 \rightarrow Mg(PO_3)_2 + 2H_2O \qquad (1)$$

$$\text{(i)} \quad Na_2CO_3 + 2H_3PO_4 \rightarrow 2NaH_2PO_4 + H_2O + CO_2$$
$$\text{(ii)} \quad 2NaH_2PO_4 \rightarrow 2NaPO_3 + 2H_2O \qquad (2)$$

$$Na_2CO_3 + MoO_3 \rightarrow Na_2MoO_4 + CO_2 \qquad (3)$$

Initially dihydrogen phosphates are formed (reactions i) followed by formation of metaphosphates (reactions ii). Therefore, each mole of H_3PO_4 gives out 1.5 mol of H_2O (2 mol of the acid gives 3 mol of H_2O as in eq 1 or 2). This corresponds to a weight loss of 0.2756 g/g of $[H_3PO_4]$. Moreover, each mole of Na_2CO_3 gives 1 mol of CO_2. Therefore, to calculate the actual weight loss due to polymerization, loss of weight due to CO_2 was subtracted from the total weight loss. The amount of CO_2 was obtained from the weights of Na_2CO_3 added. Thus, the maximum weight loss for complete polymerization for this system was evaluated as 0.2986 g/g $[H_3PO_4]$. Percent polymerization was then obtained as follows: [observed weight loss of sample (excluding CO_2)/0.2986] × 100.

Characterization and Testing. A sample was prepared from commercial materials, as described under Synthesis, by reaction at 275 °C with a molar ratio of Mo/Na/Mg/P = 1:2:12:20. Chemical analysis of the sample was done as follows: 0.1 g was dissolved by heating with 0.1 N HCl, and the solution was analyzed for Na and Mg by AAS. For the analysis of Mo and P, the sample was brought into solution by fusing 0.1 g with 1.5 g of NaOH beads and extracting into 0.2 N HCl. Mo and P were determined spectrophotometrically as described above.

For analysis of solubility of the compound in water, 0.1 g of the compound was added to 50 mL of water, agitated for 10 min, filtered, and analyzed for Mo and P. Solubility in 0.1 N HCl and citrate was determined by mixing 0.1 g of the fertilizer with 50 mL of 0.1 M HCl or 0.33 M citric acid. The suspensions were agitated in a horizontal shaker for 30 min, filtered, washed (with about 75 mL of deionized water), made to volume, and analyzed for Mo as described earlier (under Synthesis). For analysis of hydrolysis rates in water, 0.1 g of the compound (in multiple sets) was taken and 50 mL of water was added to it. The suspensions were allowed to stand. After 3, 6, 9, 12, 15, 18, and 21 days of contact time, the solutions were filtered, washed (with 30 mL of deionized water), made to volume, and analyzed.

Infrared (IR) spectra of the powdered sample were recorded on a Perkin-Elmer Fourier Transform Infrared (FTIR) RX1 instrument with
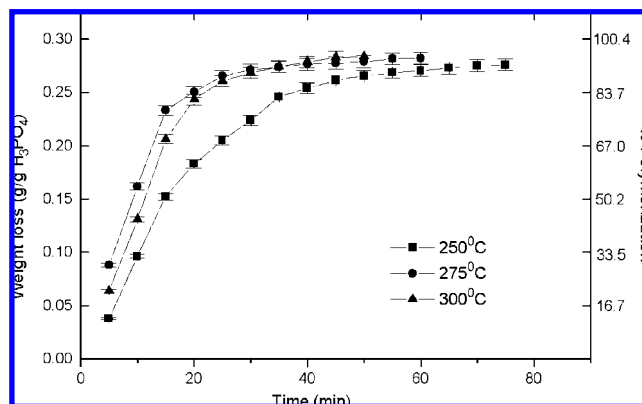

Figure 2. Kinetics of polymerization at various temperatures.

the scan range of 4500–450 cm^{-1} (resolution $\pm$ 5 cm^{-1}) using KBr pellets. X-ray diffraction (XRD) was recorded on a JDX-8030 X-ray diffractometer using Ni-filtered Cu Kα radiation at a scanning speed of 2° 2θ/min. The electron spin resonance (ESR) spectrum was recorded at room temperature with powdered samples using a JEOL (model JES-RE1X) spectrometer. The ESR spectrum was recorded at low temperature (liquid nitrogen) in a Varian E-112 spectrometer.

Field trials were done in Behrampur, West Bengal, India. The characteristics of this soil are as follows: Typic Haplustept (old Gangetic alluvium), pH 7.2, EC_e 0.99 dS/m, and organic carbon 4.06 g/kg. Randomized block design (RBD) was used for the field trials. There were seven treatments, which consisted of (i) a control (where only NPK fertilizers but no Mo fertilizers were added), (ii) three different levels of Mo (0.02, 0.04, and 0.06 kg/ha Mo) as the slow-release fertilizer, and (iii) the same three levels of Mo as ammonium molybdate. Each treatment had six replicates. Each microplot measured 3 × 3 m^2. All plots were equalized for additions of N, P, K, and Mg by calculated additions of urea, diammonium phosphate (DAP), KCl, and $MgSO_4$. The fertilizers were thoroughly mixed with soil in a bag and placed in bands in the rows before sowing. Green gram (*Phaseolus aureous* Roxb.) was grown as the test crop. It is a popular leguminous pulse and a good source of protein. After harvesting, gram was removed from the pods and weights were recorded. Nodules were also removed from roots and their weights recorded. N content of gram in all treatments and replicates was analyzed. Grains were first powdered in a grinder, digested in concentrated H_2SO_4 with $CuSO_4$/Na_2SO_4, and distilled with 60% NaOH. The distillate was collected into standard 0.1 N HCl and titrated with standardized 0.1 N NaOH using methyl red as indicator (20). All data were statistically analyzed.

RESULTS AND DISCUSSION

Formulation and Synthesis. Products synthesized at different ratios of the raw materials showed that (i) the product formed with higher ratio of Na at Mo/Na/Mg/P = 1:4:10:20 was rapidly solubilized within an hour, (ii) product formed with a higher P ratio (Mo/Na/Mg/P = 1:4:15:30) was sticky and hygroscopic, (iii) at a lower P ratio (Mo/Na/Mg/P = 1:4:5:10), the product had low solubility in 0.1N HCl and 0.33 M citric acid, (iv) in the absence of Na (Mo/Na/Mg/P = 1:0:14:20), polymerization was slower and the product was sticky, hard, and insoluble in citrate, and (v) with Mo/Na/Mg/P = 1:2:12:20, the product polymerized well, was dry, powderable, and nonhygroscopic, and was insoluble in water and soluble in 0.1 N HCl and 0.33 M citric acid. These results, therefore, revealed that a ratio of Mo/Na/Mg/P = 1:2:12:20 produced the best results. This corroborates the composition we formulated by the "reverse engineering" route and substantiates the logic sequence in its formulation.

Reaction Kinetics. Polymerization kinetics for a reaction system with the ratio Mo/Na/Mg/P = 1:2:12:20 at 250, 275, and 300 °C are depicted in **Figure 2**. From these curves, it
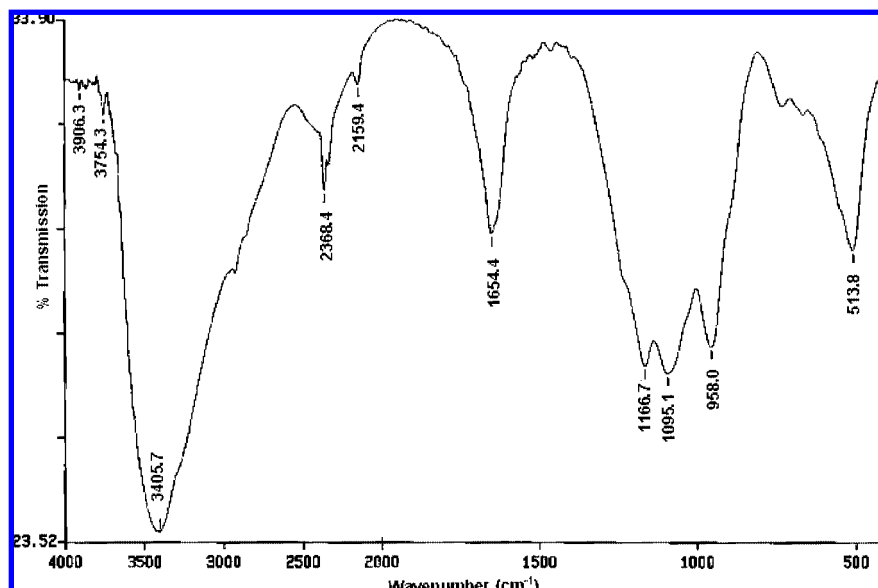
Figure 3. Structural representation of magnesium sodium polymolybdophosphate.

appears that the optimum reaction temperature could be 275 or 300 °C. Reaction at 250 °C is too slow. At all temperatures, a multistage condensation behavior is evident. There are three linear stages at 250 °C. At 275 and 300 °C, there is a single linear weight loss at the initial stage followed by a curvilinear stage that reached a plateau. The initial linear stage is a zero-order reaction, which could be attributed to the removal of 1 mole of H_2O from every 2 molecules of dihydrogen phosphate with the formation of polyphosphates of various chain lengths. Because of the large concentration of P—OH groups for the condensation reaction, the reaction is, as expected, of zero order. With the formation of polyphosphates of intermediate chain lengths, the concentration of P—OH groups available for polymerization is reduced and the reaction slows. This middle stage could continue to be linear if the temperature is sufficiently low, so that reaction rates are slow and are not limited by the concentration of P—OH groups. However, at higher temperatures when rates of reaction are faster, reduced availability of P—OH could limit the reaction rate and the reaction would show first-order features. This could explain the observed differences in kinetic curves at different temperatures. Plateau formation corresponds to nearly complete reaction, that is, 100% polymerization forming the metaphosphate.

The reaction sequence may be represented as follows:

(i) $Na_2Mg_2MoO_6 + 10\ Mg(H_2PO_4)_2 \rightarrow Mg_{12}Na_2H_{40-2n}$-
$P_{20}MoO_{86-n} + nH_2O$

(ii) $Mg_{12}Na_2H_{40-2n}P_{20}MoO_{86-n} \rightarrow Mg_{12}Na_2Mo_6(PO_3)_{20} +$
$(20-n)H_2O$

In the first step, a molybdate salt copolymerizes with dihydrogen phosphate with the formation of a polymeric phosphate chain (16); Mo could be incorporated into this chain by virtue of its ability to form bonds with phosphates (16). Further reaction leads to condensation of all OH groups forming very long chain compounds. In this polymolybdophosphate chain, cations neutralize charges on the oxygens. Divalent cations such as Mg^{2+} cross-link different chains and thus stabilize the structure.

The compound would, therefore, have a structure as presented in **Figure 3**).

Characterization and Testing. The new compound may called a magnesium sodium metamolybdophosphate in view of its chemical nature. It is a dry, free-flowing, white powder. Chemical analysis (**Table 1** showed a Mo content of 4.08% (6.13% MoO_3), which was within the level envisaged (**Figure 1**). The molar ratio of the ionic constituents (Mo/Na/Mg/P = 1:1.8:12.3:21) shows small deviations from the ideal ratio due to impurities in raw materials and also due to excess acid added for impurity compensation. The compound had a water solubility of 6.6%. Solubility increased slowly with time, and in 3 weeks 48% of Mo was solubilized by hydrolysis. Solubilities in 0.1 N HCl and 0.33 M citric acid were very high and in the range of 95–99% (**Table 1**).

The infrared (IR) spectrum of the compound (**Figure 4**) revealed characteristic absorptions of polyphosphates at 514, 958, 1095, 2368, and 3406 cm^{-1}. The P—O ionic stretching at around 1000 cm^{-1} shifts to longer wavenumbers with an increase in the length of the P—O—P chain (21). Thus, in pyrophosphates, absorptions occur at 1045–970 cm^{-1}, whereas the metaphosphates have absorptions at 1300–1205 cm^{-1}. Absorption bands of the sample in the region of 1100 cm^{-1}, therefore, suggest the presence of metaphosphates. Absorption at 514 cm^{-1} corresponds to the P—O deformation mode and the weaker band at 2368 cm^{-1} to the P—OH stretching vibrations of acid salts (21). The presence of H-bonded water molecules is also suggested by the absorption at 3405 cm^{-1}.

The XRD pattern of the polyphosphate (**Figure 5**) confirmed the crystalline nature of the sample. Because the compound is new and its crystal structure is yet not known, band assignments are possible only by comparison with XRD of similar compounds studied earlier (7, 12, 13). XRD of zinc, copper, and iron—manganese polyphosphates (7, 12, 13) show broad similarities. A sharp band at 7.26 Å seen here in the Mo compound was present as a broad band in Cu and Zn polyphosphates (12, 13). This band suggests a long-range order probably arising from adjacent polyphosphate planes cross-linked by cations. Another band at 3.08 Å is shown by all polyphosphate salts including Zn (12), Cu (13), and Fe—Mn (7) as well as this Mo compound. This has been attributed to the short-range order of the P—O—P chain (7). Another reflection due to the P—O—P chain is at 2.35 Å. Bands at 4.37, 3.88, 3.76, 3.55, and 2.79 Å may be ascribed to molybdophosphate.

The ESR spectrum at liquid nitrogen temperatures showed a strong and fairly broad signal (0.082 g) centered at 1.924 g. Complexes of Mo in the +5 and +3 states have ESR signals at around 1.9 and 2.0 g, respectively (22). Some reduction of Mo from the +6 to the +5 state is, therefore, suggested by the data. Broadening and absence of splitting suggest Mo is in variable chemical environments.

Field trial data of the slow-release Mo fertilizer are presented in **Table 2**. Treatment with this Mo fertilizer at a

Table 1. Chemical Composition and Solubility Characteristics of Molybdenum Polyphosphate Fertilizer

| | | | % of total Mo/P solubilized in | | | | | | | | | |
| | water | | 0.1 M HCl | 0.33 M citric acid | | | % of Mo solubilized with time (days) | | | | | |
chemical composition (%)	Mo	P	Mo	Mo	3	6	9	12	15	18	21	polymerization (%)
MoO_3 = 6.13 MgO = 21.15 Na_2O = 2.40 P_2O_5 = 63.62	6.6	9.9	99	94.9	21.4	23.3	32.7	37.3	44.9	45.9	48.0	94.4

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Figure 4. Infrared spectra of magnesium sodium polymolybdophosphate.
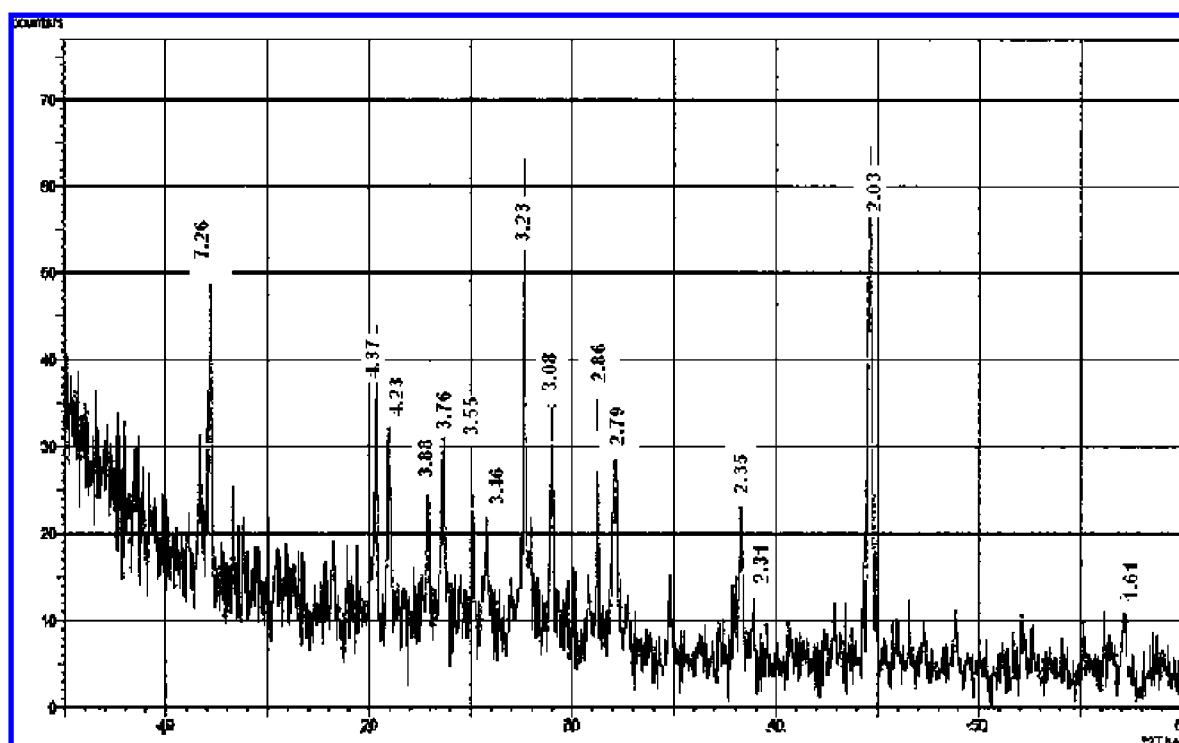

Figure 5. X-ray diffraction of magnesium sodium polymolybdophosphate.

small dose of 0.04 kg/ha Mo significantly improved yield of green gram by 80% over the control. Increases in yield were significant at all levels of the slow-release Mo fertilizer. However, yields obtained with ammonium molybdate were not significant even at the highest tested dose of 0.06 kg/ha Mo. Because the recommended dosages for ammonium molybdate are usually in the range 0.1–0.5 kg/ha Mo, response obtained with the slow-release fertilizer was about $^1/_3$ to $^1/_{10}$ of the normal dosage. Increase in yield over ammonium molybdate treatment was significant at 0.02 and 0.04 kg/ha Mo as slow-release fertilizer. Good response to the slow-release fertilizer may, therefore, be attributed to the fact that sufficient Mo is released at the initial stages of growth (20–50% over 3 weeks; **Table 1**) when the requirement for Mo in legumes is greater and root nodule activity

is higher (*23*). Although requirements are much less in the later half, during the flowering stage, the availability would probably also be sustained up to and beyond this (7 weeks). A repeat application is, therefore, not required. This would also be true for other short duration crops such as those of the *Brassica* family because the biochemical requirement for Mo follows a similar pattern (*23*).

Slow-release Mo fertilizer increased nodulation by 105–161%. Although there is an increase in average weight of nodule weight at the dose P_2 (**Table 2**), this is not significantly higher than either P_1 or P_2. Nodule weight appears to have plateaued from beyond P_1. Mo is present in nitrogenase and nitrate reductase enzymes that are involved in nitrogen fixation in the nodules of legumes (*14*). The increasing weight of nodules, therefore, further affirms the effective Mo fertilizing

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Table 2. Field Trial Data of Molybdenum Fertilizer on Green Gram (*Phaseolus aureus* Roxb.)

treatment[a] (Mo dosage in kg/ha)	av wt of the nodules from each plot (g)	yield of seed (kg/ha)	N content of seed (%)
C(0)	304.8	153	3.20
S$_1$ (0.02)	268.8	214	3.32
S$_2$ (0.04)	276.0	191	3.41
S$_3$ (0.06)	418.8	209	3.38
P$_1$ (0.02)	626.4[c,e]	235[b]	3.65[b]
P$_2$ (0.04)	796.8[c,e]	276[c,d]	3.85[c]
P$_3$ (0.06)	625.2[c]	272[c]	3.92[c,d]
CD(5%)	229.2	80.2	0.45
CD(1%)	310.8	108.7	0.61

[a] C, control; S$_1$–S$_3$, ammonium molybdate; P$_1$–P$_3$, molybdenum polyphosphate fertilizer; CD (5%) and (1%), critical difference at 5 and 1% levels, respectively. [b] Significant with respect to control at 5% level. [c] Significant with respect to control at 1% level. [d] Significant with respect to control and the corresponding dosages of soluble micronutrient fertilizers at 5% level. [e] Significant with respect to control and the corresponding dosages of soluble micronutrient fertilizers at 1% level.

action of the slow-release fertilizer. Yet further evidence of the positive action of slow-release Mo fertilizer is the significant increase in N content of gram. With an application of a low dose of slow-release fertilizer (0.06 kg/ha Mo), the N level in the seed increased by 20% (significant at the 1% level). This implies a corresponding increase in protein content of the gram. The role of Mo in increased protein synthesis and chlorophyll concentrations has been reported (*14*). Also, because of the involvement of Mo in N$_2$ reduction, there is an improvement in total nodule weight and nitrogen fixation and consequently better plant growth and increase in N content (*14*).

The fertilizer contains a small amount of Na. However, because dosages are very low, total addition would be quite small. Mg and P in the fertilizer improve the nutritional quality of the product but again because of small dosages, only a small fraction of total requirement is provided and would not interfere with the overall nutritional balance.

In conclusion, this work reports the successful synthesis of a new slow-release fertilizer compound of molybdenum. The compound, which is a polymeric molybdophosphate, was first formulated on the basis of a "reverse engineering" concept. From the existing knowledge of the chemistry of polymeric phosphates and a sequence of logical steps, we derived the starting materials, reactant ratios, degree of polymerization, and other parameters that would be required to obtain a compound with a desirable set of chemical and physical properties. It was envisaged that the compound would be a long-chain sodium magnesium polymolybdophosphate having a molar ratio of Mo/Na/Mg/P = 1:2:12:20. Subsequently, synthesis experiments at this ratio as well as at other ratios revealed that the theoretically derived ratio gave the best product with all of the desirable characteristics. This product was selected for further studies. Reaction kinetics suggested a multistage reaction with zero-order condensation reaction at the first stage. Subsequently, the availability of P–OH groups may become rate-limiting. IR absorptions confirmed the presence of long-chain P–O–P. XRD showed that it was crystalline with both long- and short-range order corresponding to stacking of P–O–P chains and regularity within the chain backbone. The product had low water solubility (6.6%). High solubility in dilute HCl and citric acid suggested good nutrient availability. Field tests with green gram showed an increase in yield of 80% due to application of slow-release Mo fertilizer at 0.04 kg/ha Mo.

Nodulation in the roots increased by 105%, suggesting enhanced N fixation. At this level of Mo fertilization, N content of the gram increased significantly by 20%.

It may be inferred from our studies that the slow-release fertilizer is an efficient and superior source of Mo. It is effective at $^1/_3$ to $^1/_{10}$ the normal dosage of Mo as ammonium molybdate. Use of this fertilizer would not only give better yields but could also improve soil N levels by improved N fixation. Tropical soils, which are poor in organic matter and N, may, therefore, be particularly benefited. Higher N levels in gram imply higher protein content and better nutrition for people and animals.

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