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RESEARCH PROJECT INITIATION

Date: **September 26, 1974**

Project Title: **Fertilizer Seed Mulch Formulation**

Project No: **E-19-630**

Principal Investigator **G. L. Bridger**

Sponsor: **Georgia Institute of Genetics (thru the Board of Regents)**

Agreement Period: From **8/1/74** Until **9/30/75**

Type Agreement: **Grant**

Amount: **$30,000**

Reports Required: **Semi-Annual Progress**
Annual Progress

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Assigned to: **Chemical Engineering**

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SPONSORED PROJECT TERMINATION

Date: _November 9, 1979_

Project Title: _Fertilizer Seed Mulch Formulation_

Project No: _E-19-630_

Project Director: _Dr. G. L. Bridger/Dr. W. R. Ernst_

Sponsor: _Georgia Institute of Genetics (thru the Board of Regents)_

Effective Termination Date: _9/30/77_

Clearance of Accounting Charges: _9/30/77_

Grant/Contract Closeout Actions Remaining: _None_   TER~~MINA~~TED

- _ Final Invoice and Closing Documents
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

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CA—4 (1/79)

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ATLANTA, GEORGIA 30332

SCHOOL OF
ICAL ENGINEERING

October 24, 1979

MEMORANDUM

TO: Mr. Odis Rogers - Photolab

FROM: Dr. W. Ernst - Ch.E. $W.\mathcal{E}$

SUBJECT: G.I.T. Project No. E-19-630

I understand this project has never been closed out. Enclosed are two copies of an article which describes the work that was completed. The article should serve as the final report.

WRE/jc

Enclosure

DISTRIBUTED ON 29 Oct 79
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Slow Release Fertilizer Materials Based on Magnesium Ammonium Phosphate. Pilot-Plant Granulation Studies

Peter H. Peng, William R. Ernst,* G. L. Bridger, and Edwin M. Hartley

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Continuous pilot-plant production of magnesium ammonium phosphate based fertilizers from a finely divided dry feed of magnesium oxide, monoammonium phosphate, and optionally potassium and micronutrients has been investigated in a pan granulator. The reaction, $MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 + H_2O$, was not complete throughout the granule because the water added as a fine spray was held to the minimum amount to ensure a dry, free-flowing, non-caking, granular product with high crush strength. These properties were mainly due to the elimination of most of the free water by the formation of magnesium ammonium phosphate hexahydrate. The raw materials for this process are easily stored and handled, in contrast to the raw materials for slurry feed granulation processes (i.e., phosphoric acid and ammonia, which are hazardous and corrosive). Typical formulas produced from monoammonium phosphate (13-52-0) were 8-32-0-11 (N–P$_2$O$_5$–K$_2$O–Mg) with product designation MNP, and 7-29-7-9 with product designation MNPK.

Background

Because of a growing world demand for fertilizer and the limitation of raw material supplies, the importance of fertilizer as a component of the cost of planting is expected to increase. Because many ordinary fertilizer materials are soluble, a significant fraction of the nutrients may be leached very rapidly from the soil. This problem has been discussed in several agronomical papers (see, for example, Englestad and Russell, 1975; Kilmer, 1974). Some nutrient losses are related to the high solubility of fertilizer materials. Burning of seeds, roots, or leaves, low efficiency in phosphorus assimilation, losses by nitrification–denitrification sequences, leaching and short-term fertilization effects make highly soluble forms of fertilizer inadequate for a number of uses or for some methods of application. Growing awareness that reserves of minerals and fossil fuels are limited has directed a significant part of fertilizer research in the last two decades toward the development of new, more efficient sources of plant nutrients and toward finding ways to improve the efficiency of known sources. One important research area has been the study of materials with low water solubility as nutrient sources.

Magnesium ammonium phosphate is a rather insoluble compound which has been shown to be a long-lasting, non-burning, slow-release fertilizer (see, for example, Bridger et al., 1962). It forms two hydrates, the monohydrate and the hexahydrate. Below 57 °C, the hexahydrate is the stable form. It has the unusual feature that all of its elements are necessary plant nutrients. In a finely divided form (e.g., in a slurry) it may be used efficiently in foliar application (see Bridger and McCullough, 1963). As a granule, magnesium ammonium phosphate can be expected to be a long-lasting fertilizer (Bridger, et al.,

1962). Magnesium ammonium phosphate has been produced commercially in the United States only to a very limited extent partially because of the high cost of manufacturing.

Most granulation methods that have been reported are slurry granulation methods, i.e., those in which a wet feed coats dry recycled particles inside of granulation equipment. Usually the recycle ratio is high as is the moisture content to be driven off the product. In the preparation of slurry feed for granulating magnesium ammonium phosphate, the choice of raw materials has been restricted mainly to combinations of the following: sources of nitrogen such as anhydrous ammonia, ammonia solutions and urea; phosphoric acid solutions as the source of phosphate; and sources of magnesium such as magnesia, magnesium hydroxide, magnesium carbonate, magnesium silicates, magnesium sulfates, and dolomite. Any combination of these feeds must be slurried for their contact to be sufficiently intimate to obtain complete reaction.

A slurry feed preparation method for metal ammonium phosphates is described in the patent of Salutsky et al. (1964). The preparation method has two basic steps. In the first step, a finely ground suitable magnesium or other metal compound was slurried and reacted with phosphoric acid at 175–225 °F and with vigorous agitation. The pH after digestion ranged from 4.0 to 6.0. The reaction for the magnesium compound was postulated to be

$$MgO + H_3PO_4 + 2H_2O \rightarrow MgHPO_4 \cdot 3H_2O \quad (I)$$
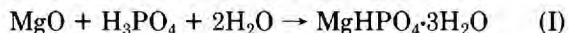
In the second step the magnesium phosphate was ammoniated to pH 7–9 by bubbling ammonia through the slurry. The slurry was then digested (75 to 225 °F), filtered, washed, and dried. Two stable hydrates of mag-

nesium ammonium phosphate could be prepared. The monohydrate was formed at high digestion temperatures. The preparation is expensive although suitable to a wide range of magnesium sources.

With small variations other reported methods are similar to the one described above. As a rule they were developed to make use of some particularly available feed (see Varshavskii et al., 1969; Taborsky et al., 1974; Kowalsky and Bodzek, 1970; Kim, 1972; Loeblich, 1970; Mazaeva, 1969).

The magnesium ammonium phosphate prepared according to any of the cited methods would be a suitable feed for the granulation method patented by Bridger and Alfrey (1964). In that process, a 70% water–30% magnesium ammonium phosphate slurry was fed onto a bed of dry recycle in a granulator. The magnesium ammonium phosphate in the slurry feed and in the recycle were reported to be in a 1:1 ratio. The process required a considerable amount of drying. The granules were not particularly strong although it was reported that the granule strength increased after application to the soil.

A departure from this granulation process was offered by Hudson (1969). He described a slurry process in which anhydrous ammonia and a phosphoric acid solution in stoichiometric amounts were sparged beneath a rolling bed of recycled solids while simultaneously a 35% solids magnesium hydroxide slurry was sparged on the top of the bed. Thus successive layers of monoammonium phosphate and magnesium hydroxide coated the recycle; reaction between the layers yielded magnesium ammonium phosphate. Alternatively, the $Mg(OH)_2$ slurry was fed in a second section of the drum, separate from that in which acid and ammonia were reacted. The recommended recycle ratio was 4:1. The drying requirement for the product, as it can be inferred, was considerable.

In another process, Legal and Mobley (1967) reacted ammonia, magnesium hydroxide, and phosphoric acid in a reactor–granulator along with recycle product to yield a 7–9% N, 42–45% P_2O_5 fertilizer. Product drying and cooling were necessary. The recycle ratio was not disclosed. The process was extended by Legal and Schindler (1969). This process also included aqueous urea solution and KOH solution as feed to the reactor–granulator. Product composition was reported to be 7% N, 40% P_2O_5, and 6% K_2O. Yoshita (1971) described a similar process in which urea alone was the source of nitrogen.

Significantly different from slurry feed processes are the dry feed processes. Since monoammonium phosphate became available as a commercial fertilizer, it has been considered for a number of processes where originally ammonia and phosphoric acid were the reactants. The main advantages of using monoammonium phosphate are in the storage and handling operations. While acid and ammonia are corrosive and hazardous, monoammonium phosphate is a trouble-free granular solid. Monoammonium phosphate and magnesia, in the presence of water, react according to the equation

$$MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 + H_2O \quad (II)$$
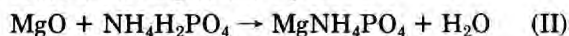
Diammonium phosphate which is usually an impurity in fertilizer grade monoammonium phosphate reacts with magnesia in the presence of water as follows

$$MgO + (NH_4)_2HPO_4 \rightarrow MgNH_4PO_4 + NH_4OH \quad (III)$$
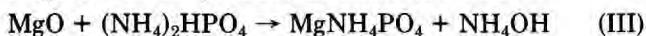
Kawamoto and Kubota (1971) and Stevenson (1968) described processes based upon reaction II. Both used premixed powdered dry feed. The Kawamoto–Kubota process used $Mg(OH)_2$ and $NH_4H_2PO_4$ which were fed to a rotary drum granulator along with water and steam.

Preheating the dry mix was recommended and a granular $MgNH_4PO_4$ product was reported. In the Stevenson process, a magnesium compound, either magnesium oxide, hydroxide, or carbonate, and crystalline monoammonium phosphate were premixed and then granulated in either a rotating drum or pan granulator, with sufficient water to effect granulation. The operation was batchwise and the products were dried and cooled. After the first pass, the fines and crushed oversize were recycled. A 90% granulation efficiency was reported.

There are several other processes which make use of reaction II (see Akiyama and Takaoka, 1971; Christoffel and Strother, 1968; Ushioda et al., 1973).

This report discusses a continuous dry feed process based upon reaction II that has been developed and demonstrated at pilot plant scale at Georgia Tech (Peng, 1977). In this process a finely pulverized mixture of sea water magnesia, monoammonium phosphate, and optionally other ingredients is fed and granulated continuously in a pan granulator. A fine water spray provides the liquid phase necessary for granulation. The major objective of this project was to establish the best operating conditions for the pan granulator so as to effect granulation with the smallest amount of water possible in order to maintain a high nutrient analysis in the product and avoid the need for drying.

The report also discusses an X-ray diffraction study that was conducted with the objective of identifying products of reaction in the product granules and determining extent of reaction.

Experimental Section

a. Description of Pilot Plant. The pilot plant consisted of a 24-in. diameter pan granulator fabricated at Georgia Tech, equipped with variable speed of rotation, variable inclination, and variable bed depth. Feeding was provided from feed hoppers and controlled through Syntron Vibra Flow Model F-TO feeders. A fine water spray feed was produced by means of a hydraulic spray nozzle (Teejet Model 11001 by Spraying Systems Co.). Photographs showing overall and detailed views of the pilot plant are presented in Figures 1 and 2.

b. Raw Materials. The magnesium source used in the process was sea water magnesia (Magox 98 HR by Basic Chemicals, Inc.) which is a highly reactive form (98%, –200 mesh) precipitated from sea water and calcined at low temperature. Two fertilizer grades of monoammonium phosphate, namely 13-52-0 by Gardinier and 11-52-0 by Agrico, were used. Both are granular (–6 to +16 mesh) forms. The potassium chloride used was soluble grade, 62% K_2O, –20 mesh crystals. A finely divided potassium sulfate (50% K_2O) was used when a chloride-free grade product was made. Micronutrients, when used, were metal sulfates, except for ammonium molybdate and sodium borate. All micronutrients were in the form of fine powders. A stoichiometric ratio of MgO and monoammonium phosphate was used in all runs.

c. Pilot Plant Procedures. Granular or crystalline feed materials were pulverized to a desired screen size in a mix-muller. All dry powdered ingredients including MgO, magnesium ammonium phosphate, KCl or K_2SO_4, and occasionally micronutrient sources, were mixed in a closed drum, set on rollers. Five minutes of rotation provided a uniform mixture; premixing of the dry feed was essential for granulation. Feeding components separately did not produce satisfactory granules. The feed hopper for the pan granulator was then charged with the dry mix while undersize product granules collected from previous runs were charged to a smaller recycle hopper. The
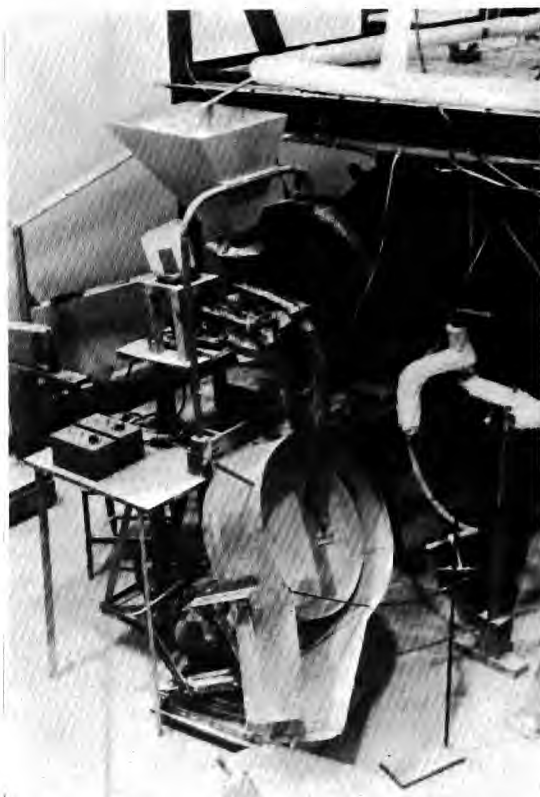
Figure 1. Overall picture of pan granulation pilot-plant.

Figure 2. Detail of operation: sizing action in pan can be observed.

purpose of this recycle was to provide seeds for granulation and to help control production. The arrangement is shown in Figure 1.

The duration of most runs was 2–6 h. An extended run was conducted continuously for 5 days during which about one ton of product granules was produced for agronomical experiments. The feed formulation for the production run is shown in Table I.

d. Product Characterization. X-ray diffraction was used to identify reaction products in the granules. The apparatus used was a Phillips Electronic Instruments Type 12215/0 X-ray diffractometer with Norelco Type 42273/1θ:2θ goniometer.

The powder diffraction patterns of the product samples were compared with the powder diffraction patterns of standards. By observing relative intensities of peaks from a sample, together with those of a standard, it was possible to judge if the compound was present as a major constituent, in substantial quantity, or as a trace constituent. Some constituents could not be positively identified due to overlapping of their most prominent peaks with peaks

Table I. Dry Feed Formulation

	wt, lb
MgO (sea water magnesia)	400
MAP (11-52-0)	1200
K_2SO_4 (0-0-50)	264
$MnSO_4$	30
$CuSO_4 \cdot 5H_2O$	30
sodium borate	10
$FeSO_4 \cdot 7H_2O$	40
$ZnSO_4$	30
ammonium molybdate	2
total	2006

of conspicuously present compounds. Diffraction patterns for standards were obtained from the Powder Diffraction File (1972).

All samples were ground in a Fisher mortar-grinder for 45 min. Powder diffraction patterns were obtained by scanning the samples at a rate of 1° 2θ/min, from 5° 2θ to 2θ. Cu Kα radiation was used (γ 1.5405 μm). Intensities were measured as peak heights above background.

Samples chosen for X-ray analysis were commercial magnesium ammonium phosphate, experimental products MNP and MNPK.

X-ray diffraction was also used to determine the percentage of $MgNH_4PO_4 \cdot 6H_2O$ in a sample of product MNP. An internal standard technique (Klug and Alexander, 1954) which used tungsten trioxide orthorhombic (WO_3) as the internal standard was employed.

In this procedure, 1 g of pulverized $MgNH_4PO_4 \cdot 6H_2O$, produced from technical grade MgO and $(NH_4)_2HPO_4$, and 1 g of pulverized product MNP were each mixed with 0.2 g of WO_3. Selected peaks for both samples, (200) for WO_3 and (130) for $MgNH_4PO_4 \cdot 6H_2O$, were scanned at the rate of $1/_8$° 2θ/min. The WO_3 peak was scanned from 26.800° to 24.675° 2θ. The $MgNH_4PO_4 \cdot 6H_2O$ peak was scanned from 26.800° 2θ to 27.30000° 2θ. An Ortec System 400/700 peak analyzer was used to record the number of X-rays detected.

Free water analyses of granular products were determined by placing a known sample weight in a vacuum desiccator which contained a strong dehydrating agent (i.e., phosphorus pentoxide). The desiccator was evacuated to 520–570 mmHg and sealed. After 16–18 h, the sample was weighed. The percent loss in weight represented free water content.

Total water content was not determined; however, as will be discussed, loss of weight upon heating product to 105 °C for 3 h was shown to be due to transition of magnesium ammonium phosphate hexahydrate to the monohydrate.

The crushing strength of granules was defined as the resistance to fracture of individual granules subjected to a force applied by a plunger (T.V.A., 1970a). A small kitchen balance was used to measure fracture force.

Bag storage tests were conducted on dry feed and product granules. The test conditions were equivalent to those in the bottom bag of a twenty 50-lb bags stack (T.V.A., 1970b).

A very sensitive, qualitative test was developed to detect the loss of ammonia during storage. The test consisted of introducing a test tube, which had its top (rim) wetted with HCl solution, inside a bottle containing the fertilizer granules, making sure that the granules were not in direct contact with the HCl solution. The bottle was then tightly closed. Any ammonia release that occurred could be observed as the formation of NH_4Cl at the top of the tube.

Results and Discussion

a. Granulation. Operating variables which affected granulation included bed depth, angle of pan with hori-

Table II. Summary of Operation Data for the Pan Granulator

diameter of the pan: 24 in.
depth of the pan: 4 in.
angle with horizontal: 65°
speed of rotation: 36 rpm
solid feed rate: 90 g/min
liquid feed rate: 18 to 30 cm³/min[a]
approximate area of rolling bed of granules: 60 in.²
approximate area covered by spray water: 18 in.²
approximate area in which dry feed is placed: 3 in.²
approximate retention time: 5 min
temperature of the bed: ca. 60 °C

[a] 18 to 22 cm³/min when KCl was source of K_2O; 22 to 30 cm³/min when K_2SO_4 was source of K_2O.

zontal, speed of rotation, dry feed and liquid flow rates, position of dry feed and liquid feed with respect to the pan, solid feed particle size, and fines recycle rate. Some of the observations made during pilot plant operation are qualitative in nature and would be difficult to quantify. Therefore, those results will be discussed in general terms.

Rotational speed, angle of pan with horizontal, bed depth, solid and liquid feed rates, and placement were all critical for the granulation. A proper rotation speed and proper angle of pan with horizontal were necessary to produce a rolling bed of granules in the pan. Moisture of the bed and position of the scraper are also critical for the proper bed condition. Recycle of fines did not greatly affect granulation; in fact, satisfactory product could be produced without recycle. Table II summarizes typical run conditions that were found to produce granules with desirable properties—good spherical appearance, few fines, and high crushing strength. Figure 3 shows schematically the placement of dry feed and water. The pan granulator provided a sizing action, which can be seen in Figure 2. During start-up of each run, the water spray was moved to several different positions over the rolling bed and then fixed at the position which produced granules of a good spherical appearance. The dry powdered materials were fed onto the rolling bed in such a way as to coat just recently wetted particles.

Control of the granulation process was a major problem. Small disturbances in the operating conditions could very quickly cause imbalances in the granulation, setting the process out of control. Automatic controllers would be a requirement for a large-scale commercial operation based on this process.

It was found that water requirement for good granulation decreased with magnesium ammonium phosphate particle size. The use of coarse feed even at high water feed rate did not produce satisfactory granulation mainly because MgO tended to granulate separately from the monoammonium phosphate. Consequently, with coarse feed a product was formed in which analysis varied from granule to granule. The product had a very noticeable ammonia odor and low crushing strength. Because the
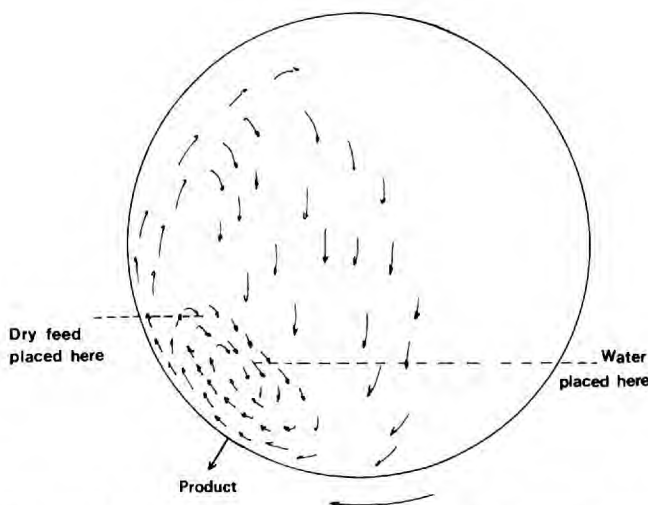

Figure 3. Schematic description of placement of feeds on rolling bed of granules in pan granulator.

difference in density and particle size between the sea water magnesia and the coarse monoammonium phosphate was very large, segregation in the pan occurred. It was therefore concluded that since the difference in density cannot be overcome, a close particle size distribution should be observed in order to produce an intimate mixture of the reactants which would rapidly produce the cementing reaction II needed for the granulation. Table III shows the size distributions that were tested and includes observations about the product granules and process. The "fine" material was used in most of the work, instead of the "extrafine" (which produced the best granules) mainly because there was less dusting with the "fine" material. In using the "fine" material, the optimum water feed rate 25 to 33% of the dry feed rate for production of MNP and MNPK (with K_2SO_4) and 20 to 25% for production of MNPK (with KCl). Granulation with less water generated a dusty process and product; on the other hand, when too much water was present, the granulation bed did not roll adequately.

b. Product Characterization. Analyses of granular products varied depending upon analyses of monoammonium phosphate employed, the source of K_2O, the water feed rate, and the amount of micronutrients. Typical analyses of MNP and MNPK products, made from monoammonium phosphate (13-52-0), in which micronutrients were not incorporated, were respectively 8-32-0-11 (N-P_2O_5-K_2O-Mg) with 23% total water and 2.78% free water and 7-29-7-9 with 22% total water and 2% free water. When micronutrients were incorporated, the percentages of macronutrients decreased. During the extended production run in which monoammonium phosphate (11-52-0) was used and micronutrients were incorporated, product analysis was 5-25-5-9, with 20% total water and 2% free water.

Table III. Particle Size Distribution of Feeds and Effect on Granulation

| feed materials | % retained on screen (mesh sizes) | | | | | | | observations |
	42	65	80	100	150	200	325	
Magox 98HR	–	–	–	–	–	–	2	
KCl (sol.)	10	35	60	90	93	–	–	
monoammonium phosphate:								
extra coarse	92	93	94	–	96	98	–	unsatisfactory granulation
coarse	60	–	80	82	87	89	–	unsatisfactory granulation
medium	20	–	45	54	60	70	–	unsatisfactory granulation
fine	2	17	25	–	44	55	–	satisfactory
extra fine	–	–	–	2	10	22	55	best granulation, but dusty process

Granular product with few fines was produced even when a low recycle ratio was used. For example, in one run in which 24 lb of MNPK with KCl was produced, only 2.5% of the product was −32 mesh. In another run in which 1000 lb of MNPK was produced with K_2SO_4 about 2.5% was −32 mesh, 24% percent was −16+32 mesh, and 66% was −6 to +16 mesh, the rest being +6 mesh. No appreciable dry feed segregation occurred in the feeder or pan granulator except during the previously mentioned runs in which coarser monoammonium phosphate was used. Thus, N, P_2O_5, K_2O, and Mg analyses (dry basis) were almost identical for all of the granule particle sizes produced. Water content varied with particle size. Smaller mesh sizes contained a higher percentage of water than larger sizes. Deviations in water concentration were usually less than 20% of the average water concentration for the total product.

X-ray diffraction studies identified the major reaction products in MNP and MNPK as magnesium ammonium phosphate hexahydrate. The monohydrate was not found in either product. The species $MgKPO_4 \cdot 6H_2O$ was present in significant quantity in MNPK. A sample of MNP that had been dried for 3 h at 105 °C, upon X-ray diffraction analysis, showed the monohydrate as the major constituent but no trace of the hexahydrate. These results proved that all of the bound water in products MNP and MNPK was present in the hexahydrate and that heating of the product caused the following reaction to take place

$$MgNH_4PO_4 \cdot 6H_2O \rightarrow MgNH_4PO_4 \cdot H_2O + 5H_2O \quad (IV)$$

These results suggested that percent conversion for reaction II could be determined by measuring weight loss after heating MNP or MNPK at 105 °C for 3 h or more.

In order to test this method a sample of MNP was subjected to X-ray diffraction analysis to determine the amount of hexahydrate that was present. The MNP had a nutrient analysis of 8-32-0-11, a free moisture content of 2.78%, and a weight loss after heating at 105 °C for 3 h of 23.09%. The amount of hexahydrate in the sample was 55%. Percent conversion (P.C.) was computed from both X-ray data (eq 1) and weight loss data (eq 2). There

$$P.C. = \frac{\%P_2O_5 \text{ in hexahydrate}}{\%P_2O_5 \text{ in product granules}} \times$$

$$\% \text{ hexahydrate in product granules} = \frac{31.02}{32} \times 55 = 53.3\%$$

$$(1)$$

$$P.C. = \frac{\%P_2O_5 \text{ in hexahydrate}}{\%H_2O \text{ loss in converting pure hexahydrate to pure monohydrate}} \times$$

$$\frac{\% \text{ wt loss} - \% \text{ free water}}{\%P_2O_5 \text{ in product granules}} = \frac{31.02}{36.73} \times$$

$$\frac{23.0 - 2.78}{32} = 53.6\% \quad (2)$$

is good agreement between the two methods of determining percent conversion. Thus eq 2, which requires easily obtainable weight loss data, was used throughout the remainder of the work.

Typical percent conversions for MNP and MNPK products computed from weight loss measurements are listed in Table IV.

Some ammonia loss during granulation was evident as determined by changes in N/P_2O_5 ratio between feed and product granules. The losses varied from run to run and

Table IV. Typical % Conversions for MNP and MNPK Products

product	analysis	wt loss, 3 h at 105 °C	free water	P.C.
MNP	8-32-0-11	23	2.78	53.6
MNPK	7-29-7-9	22	2.00	58.2
MNPK	5-25-5-9	20	2.00	60.8

Table V. Crushing Strength of MNP and MNPK Granules during Curing

	crushing strength, lb	
time, h	MNP (−4 to +6 mesh)	MNPK (−4 to +6 mesh)
1	1-3	1-3
3	1-3	2-4
16	2.5-4.5	3-5
72	4-7	6-8
96	6-7	6-9

Table VI. Crushing Strength of MNP and MNPK Granules after Curing, Compared to Commercial Magnesium Ammonium Phosphate[a]

	crushing strength, lb		
granule size, mesh	MNP	MNPK	comm. $MgNH_4PO_4$
+4	8-16	8-16	14-22
−8 to +12	4-6	4-8	4-14
−12	2-3	2-3	3-4

[a] Typical prilled urea has crushing strength (−4+6 mesh) of 2 lb.

ranged between 0 and 20%. The loss was the result of a reaction of MgO with diammonium phosphate, which is generally present in fertilizer grade monoammonium phosphate (see reaction III). The ammonia formed in the reaction was apparently not reabsorbed by the solids but given off as free ammonia. The amount of free ammonia released in this manner would be greater when the 13-52-0 monoammonium phosphate is used as feed than when the 11-52-0 material is used, since the former contains the higher amount of diammonium phosphate. No free ammonia would be produced if pure monoammonium phosphate were used. The release of free ammonia could be eliminated in a commercial operation using fertilizer grade material by adding sufficient phosphoric acid to the spray water to react with the diammonium phosphate as follows

$$(NH_4)_2HPO_4 + H_3PO_4 \rightarrow 2NH_4H_2PO_4 \quad (V)$$

The strength of the granules was related to curing time. While the granules immediately after leaving the pan were noticably wet, weak, and tended to crumble at a firm finger touch, granules that had been aged for about 3 h were dry and had sufficient strength to undergo screening in a Ro-Tap unit without breakage. Table V shows how the hardening of the granules improved with time. Maximum strength was achieved in about 96 h. Table VI compares crushing strength of granules after 96 h of curing with that of commercial magnesium ammonium phosphate and prilled urea.

The increase in crushing strength with curing time is probably a result of a slow transition of magnesium ammonium phosphate from the monohydrate to the hexahydrate form. The temperature of the bed in the pan is about 60 °C due to heat of reaction. Magnesium ammonium phosphate hexahydrate, however, is the stable form below 57 °C, so that the form in the pan was probably

the monohydrate; as the product cooled, the hexahydrate was formed from free water and the monohydrate. Furthermore, it was found that after curing, the granules could be dried easily to the monohydrate, while still retaining most crushing strength. When drying was effected immediately after production, however, the granules remained very weak and did not attain high crushing strength. This observation possibly indicates that reaction II continued even after the granules left the pan as the free water migrated throughout the granules.

In most runs in which MNPK was produced, the feed mixture was prepared so that K_2O content of the product equalled the N content. Because of their density and molecular weight, potassium salts at this level of content corresponded to about 10% of the volume of the dry feed mixture. The MNPK granules that were produced using either KCl or K_2SO_4 were slightly harder, heavier, and somewhat easier to granulate than the MNP.

The MNP and MNPK products when left in an open atmosphere did not absorb moisture but remained dry and hard. This observation was expected since magnesium ammonium phosphate is very insoluble and nonhygroscopic. The dry feed subjected to a bag storage test showed no bag set and no caked lumps after nine months storage.

It was found during four-week tests that granular products were very stable with respect to ammonia losses, as was a finely pulverized feed mixture of monoammonium phosphate and MgO. This indicated that the dry feed mixture would not react in storage. It is recommended, however, that the raw materials monoammonium phosphate and sea water magnesia be stored separately, except for the batch to be immediately used, since any accidental wetting of the mixture would cause reaction to occur.

Conclusions

The process for continuously granulating a finely powdered mixture of sea water magnesia, MAP, and other optional ingredients such as KCl, K_2SO_4, and micronutrients has been developed and demonstrated in a pan granulator pilot plant. The process is well suited for preparing granular products named MNP and MNPK, consisting of unreacted raw materials and reaction product $MgNH_4PO_4 \cdot 6H_2O$ which provides a cementing action and gives strength to the granules. When the fertilizer is used, most of the remaining reactants will react when soil moisture penetrates the granules. Because of the slow-release characteristics of magnesium ammonium phosphate, the products MNP and MNPK might be well suited for plants with long growing seasons, such as trees and ornamentals. The readily soluble, unreacted part of the granule may prove to be advantageous over totally insoluble fertilizer, since it would quickly provide nutrients necessary for early growth and establishment. The limited use of water in this process eliminates the need for drying and cooling.

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