

# Thermal Decomposition of High-Analysis Fertilizers Based on Ammonium Phosphate

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The thermal stability of high-analysis fertilizers based on ammonium phosphate was studied. Laboratory tests show that significant nitrogen losses can occur during drying and storage. These losses were greater from grades formulated with diammonium phosphate and urea than from ammonium nitrate and monoammonium phosphate.

THE TREND in granular fertilizer is toward a higher plant food content with ammonium phosphate as the formulation base. Thermal stability of these high-analysis fertilizers is essential since it is often not possible to assure a particular grade by overformulation, higher nitrogen grades are likely to have a higher vapor pressure of ammonia, and economics dictate a high nitrogen recovery.

Previous investigators have studied nitrogen losses from superphosphate fertilizers which contain mono- and dicalcium phosphates. Bridger and Burzlafl (3) studied drying of ammoniated superphosphate and found appreciable nitrogen losses occurring at 93° to 110° C. (200° to 230° F.). Increased losses, even at lower temperatures, were obtained when potassium chloride was added. Alfrey and Bridger (7) showed that in mixed granular fertilizers, ammonium chloride fumes were evolved over a range of 141° C. (296° F.) for a 10-4.3-8.3 (10-10-10) grade to 265° C. (506° F.) for a 15-13.1-12.5 (15-30-15) grade. Borland and Schall (2), in studying nitrogen loss from 12-5.3-10 (12-12-12), found a decrease in stability when NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, H<sup>+</sup>, and NO<sub>3</sub><sup>-</sup> ions were present together. The absence of any one of these ions increased the stability considerably. Gaseous products were found to be nitrogen and nitrous oxide. Commercial fertilizers had a sufficiently low hydrogen ion concentration at pH 5.0 to be stable. Development work at the Tennessee Valley Authority (9) has shown that the sulfuric acid feed rate affected ammonia loss in manufacturing 12-5.3-10 (12-12-12). This loss occurred as free ammonia and as the decomposition products of ammonium nitrate. They have also studied (6) urea hydrolysis in 12-5.3-10 (12-12-12) fertilizer in storage. Jensen (5) showed that urea hydrolyzed during long continued hot storage. Conse-

quently, 12-5.3-10 (12-12-12), using urea, must be cooled before storage. Also, Waters and Ziegler (10) studied 8-2.6-3.3 (8-6-4) and 10-2.6-3.3 (10-6-4) grades and found that the urea content decreased when stored at 50° C.

The ammonium phosphates and the vapor pressure of ammonia in these systems have been discussed by Pratt (7). The recommended conditions for the manufacture of diammonium phosphate using the vacuum crystallization process were ammoniation of H<sub>3</sub>PO<sub>4</sub> to pH 6.5, with a maximum dryer temperature of 80° C. The properties of the diammonium phosphate fertilizers have been investigated by Thompson *et al.* (8). Young, Hicks, and Davis (11) reported ammonia loss from 18-20-0 (18-46-0), during drying, of 2 to 3% at 82° C. (180° F.) and 4% at 99° C. (210° F.). Also, Caro and Marshall (4) have studied the stability of mono- and diammonium phosphates in the development of a vacuum oven method for the determination of moisture.

This investigation was undertaken to determine losses occurring in the drying and storage of the following high-analysis ammonium phosphate fertilizers: 18-20-0 (18-46-0), 15-13-13 (15-30-15), 12-11-10 (12-24-24), 20-4.3-8.3 (20-10-10), and 30-4.3-0 (30-10-0). These are based on mono- and diammonium phosphate, urea, ammonium nitrate, potassium chloride, and potassium nitrate as principal ingredients. The commercial ammonium phosphates were prepared by ammoniating wet-process phosphoric acid. Laboratory conditions selected were somewhat more severe than normal plant operating conditions to emphasize areas of possible plant losses. It also appeared desirable to investigate alternative formulations as a means of improving thermal stability. The recent commercial availability of fertilizer-grade potassium nitrate presents the possibility of eliminating ammonium chloride loss by replacement of chloride with the nitrate ion. Also, the stability of the polyphosphates was studied as a poten-

tial source of high nutrient fertilizer,

## Apparatus and Procedure

Representative samples were obtained by riffing approximately 50 grams of granular fertilizer from a 2-kg. sample. It was then ground in a mortar to approximately 100 mesh and mixed. No drying was attempted because of possible loss of volatiles other than water. Reasonable precautions were taken during handling and storage in order to maintain essentially the same moisture content as originally present.

Thermograms were obtained with a Deltatherm Model D2000 basic unit and a Model D4000 thermobalance (Technical Equipment Corp., Denver, Colo.). A 10-mg. sample was weighed into an open quartz space pan and heated from ambient temperature to 300° C. at the rate of 4° C. per minute. Weight losses were recorded on the 0 to 4 mg. (0.4 mg. per inch of recorder chart) scale.

The urea content of samples was determined using the potassium bromide pressed plate technique of sample preparation and measurement of the carbonyl band at 1670 cm.<sup>-1</sup> with a Perkin-Elmer Model 450 infrared spectrophotometer. Sample size was adjusted to obtain an instrument transmittance in the range of 15 to 70%. For samples containing 2 to 15% urea, the desired concentration was obtained by pulverizing 5 mg. of sample with 0.5 gram of spectral grade potassium bromide in a Wig-L-Bug (Spex Industries, Metuchen, N. J.), and 0.2 gram of the mixture pressed into a plate for absorbance measurements. For other concentrations the initial quantities were varied accordingly.

Absorbance values were calculated using a base line technique and the urea content was determined by calibration with reagent urea.

The nitrate nitrogen content of the fertilizers was determined by measurement of the ultraviolet absorbance of the nitrate ion in aqueous solution at 261 and 300 mμ with a Perkin-Elmer Model 350 spectrophotometer.

## Results

The thermal decompositions of reagent grade fertilizer components, as measured with the thermal balance, are shown in

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Figure 1. For diammonium phosphate, the weight loss shown is primarily ammonia, with conversion to the monoammonium salt at 170° C. and loss of 12.9% as indicated by the plateau on the dashed curve. Loss begins below 100° C. and is significant at 121° C. (250° F.), the approximate temperature of the inlet gases in a commercial dryer. Monoammonium phosphate is stable up to 200° C. and then decomposes similarly to diammonium phosphate above this temperature. Ammonium sulfate is stable up to 250° C. and the curves for potassium nitrate and potassium chloride show that these compounds are stable.

Urea and ammonium nitrate are relatively stable up to about 120° C., but above this temperature decompose completely within a relatively short temperature range. Urea is the most unstable of these high nitrogen fertilizer materials at temperatures above 130° C. At 121° C., the comparative weight losses were: ammonium nitrate, 0.6%; urea, 1.2%; and diammonium phosphate, 2.3%. Thus, in this temperature range diammonium phosphate was the more unstable compound. This is also shown in the thermograms in Figure 1, where urea loss also increases rapidly above 130° C.

Figure 2 shows the thermal decomposition of 18-20-0 (18-46-0) and compares two commercial grades to a laboratory formulation from reagent chemicals. This grade is essentially diammonium phosphate in which wet process phosphoric acid has been ammoniated to an ammonia-phosphoric acid mole ratio of 1.85 to 1. A product 2 to 1 mole ratio is obtained by inclusion of ammoniated sulfuric acid. The 170° C. plateau of conversion of diammonium to monoammonium phosphate is evident in the laboratory preparation but is less distinguishable in the commercial grades. The curves show the same general trend in shape; however, the commercial grades are somewhat more unstable in the lower temperature regions.

Figure 3 shows the thermal stability of a commercial and a laboratory preparation of 15-13-13 (15-30-15) formulated from diammonium phosphate, urea, and potassium chloride. In addition, two experimental formulations are included for comparison—a diammonium phosphate potassium nitrate, and a potassium polyphosphate from TVA furnace acid and ammonium nitrate.

The formulation using potassium nitrate had a somewhat better thermal stability from 150 to 250° C. than the pure grade based on potassium chloride and urea. However, at lower temperatures it was essentially the same. The formulation showing the greatest stability was based on potassium polyphosphate, 0-24-25 (0-55-30), which was blended with diammonium phosphate and ammonium nitrate to make a 15-13-13 (15-30-15) material. It showed

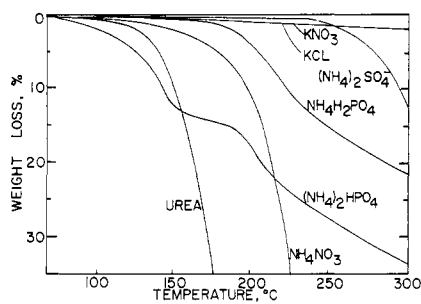


Figure 1. Thermal decomposition of reagent grade fertilizer components

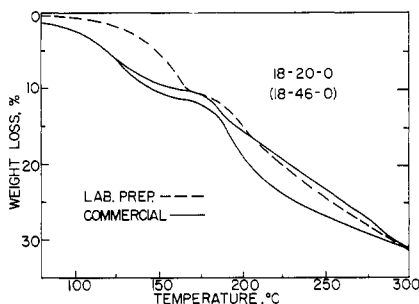


Figure 2. Thermal decomposition of 18-20-0 (18-46-0)

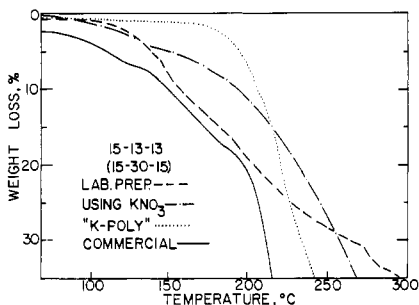


Figure 3. Thermal decomposition of 15-13-13 (15-30-15)

very little loss up to about 175° C.

The thermal decomposition of another DAP-urea-KCl fertilizer, 12-11-20 (12-24-24), is given in Figure 4. The top curve is a laboratory preparation using potassium nitrate and monoammonium phosphate with no urea. The composition changes increased the thermal stability of the grade. However, other results in this study indicate that substitution of potassium nitrate for potassium chloride did not cause the improved stability.

Unfortunately, neither of the potassium nitrate grades of 15-13-13 (15-30-15) nor 12-11-20 (12-24-24) can be made with potassium nitrate and wet-process phosphoric acid because of impurities present primarily in the wet acid. Consequently, for maximum potash fertilizer formulations, potassium chloride is preferable to potassium nitrate. Commercial potassium chloride contains 60% K<sub>2</sub>O while potassium nitrate contains 44% K<sub>2</sub>O and 13% N.

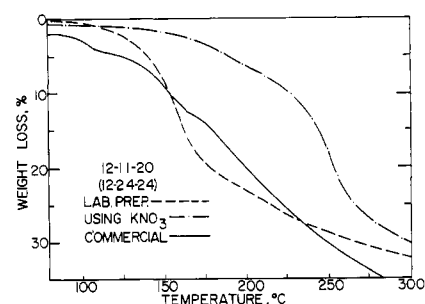


Figure 4. Thermal decomposition of 12-11-20 (12-24-24)

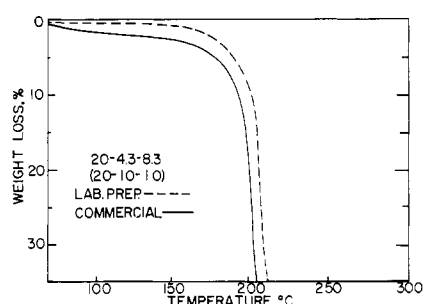


Figure 5. Thermal decomposition of 20-4.3-8.3 (20-10-10)

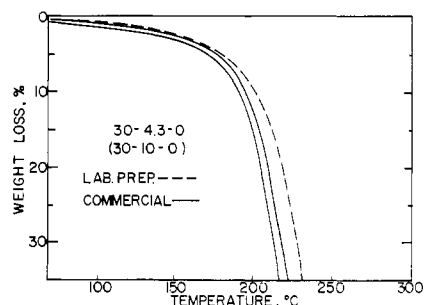


Figure 6. Thermal decomposition of 30-4.3-0 (30-10-0)

Figures 5 and 6 are the thermal stability curves for ammonium phosphate-ammonium nitrate grades. The 20-4.3-8.3 (20-10-10) is essentially an ammonium nitrate-monoammonium phosphate formulation and shows the greater thermal stability of these compounds below 200° C. Figure 6 shows 30-4.3-0 (30-10-0), which is primarily ammonium nitrate with about 15% diammonium phosphate. This curve follows closely the data for ammonium nitrate and shows that 30-4.3-0 (30-10-0) is considerably more stable than diammonium phosphate grades. These last two grades are stable to approximately 50° C. higher temperatures than the previous grades shown. Consequently, these data indicate that ammonium nitrate and monoammonium phosphate formulations have greater thermal stability than diammonium phosphate and urea formulations.

The small sample size used in thermal analysis is inadequate for further chemi-

cal analysis, so nitrogen loss was determined at constant temperature with varying times, using 2-gram samples. The temperatures used were 121° C., corresponding to a typical dryer temperature, and 50° C., an approximate high storage temperature. Table I shows weight losses resulting from heating reagent chemicals in an open dish at 121° C. for 30- and 90-minute intervals. At this temperature, diammonium phosphate loss is considerably greater than the other compounds, with urea next in amount of loss.

**Table I. Total Weight Losses of Reagent Chemicals after Open Dish Heating at 121° C.**

Reagent	Weight Loss, %	
	30 min.	90 min.
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	6.2	10.9
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0.1	0.1
Urea	1.7	5.4
NH <sub>4</sub> NO <sub>3</sub>	0.2	4.4
NH <sub>4</sub> NO <sub>3</sub> (90%) + KCl (10%)	0.2	0.7
NH <sub>4</sub> NO <sub>3</sub> (75%) + KCl (25%)	0.2	0.7
Urea (90%) + KCl (10%)	1.6	10.1

Table II shows weight losses for the fertilizers under the same conditions, as well as open dish weight losses at 50° C. for 19 and 30 days. The weight losses at 50° C. (122° F.) for 30 days approximate the results for heating at 121° C. for 30 minutes. The weight losses do not duplicate corresponding thermal balance data but show the same relative order of stability of fertilizer compounds.

**Table II. Total Weight Losses of Fertilizer Grades after Open Dish Heating at 50° and 121° C.**

Fertilizer	Weight Loss, %			
	50° C.		121° C.	
	19 days	30 days	30 min.	90 min.
18-20-0 (18-46-0)	7.8	8.5	7.0	9.6
12-11-20 (12-24-24)	4.2	5.1	6.8	10.0
15-13-13 (15-30-15)	5.6	6.4	6.5	9.2
20-4.3-8.3 (20-10-10)	1.3	1.7	1.9	2.8
30-4.3-0 (30-10-0)	1.1	1.2	1.5	2.1

The chloride and nitrogen contents were determined on the grades before and after heating at 50° C. for 30 days. These results are presented in Table III on the basis of the per cent by weight of original sample. Nitrogen loss is also calculated as weight per cent of the total nitrogen originally present. This varies from a high of 36% of the original nitrogen lost from 18-20-0 (18-46-0) to a low of 3% for 30-4.3-0 (30-10-0). There

was no indication of any chloride loss from the three grades containing potassium chloride.

Table IV compares nitrogen losses at 50° C. for 30 days to the grades expressed as components—namely, 18-20-0 (18-46-0) for diammonium phosphate from wet-process acid, and 11-21-0 (11-48-0) for monoammonium phosphate. The 18-20-0 (18-46-0) had the greatest weight loss, with 36%. The actual total nitrogen content was 11.5% based on the original sample and 12.6% on the dried sample at the conclusion of the test, so it approached the monoammonium phosphate composition of 11-21-0 (11-48-0). In the 121° C. temperature studies, loss after heating for 90 minutes corresponded to 50° C. for 30 days with a final nitrogen content of 12.4%. The 30-4.3-0 (30-10-0) grade, with the largest amount of ammonium nitrate, had the lowest loss—namely, 3%.

Table V shows the urea content of two grades. The 15-13-13 (15-30-15) reportedly had 11.3% urea added during formulation, yet three different production runs contained 3.9, 5.9 and 8.1%. Even with the urea loss, the total nitrogen content was within grade acceptance limits. Similar data are shown for the 12-11-20 (12-24-24), but with better agreement with calculated analyses.

A comparison of data in the last column in the table with the original urea content shows that over half of the urea had hydrolyzed in 30 days at 50° C. The data also show that heating for 90 minutes at 121° C. exhibits essentially the same loss.

The nitrate contents of the 20-4.3-8.3 (20-10-10) and 30-4.3-0 (30-10-0) grades were determined and are presented in Table VI. No nitrate losses were observed in heating at 121° C. for 90 minutes or 50° C. for 30 days.

The 15-13-13 (15-30-15) and 12-11-20 (12-24-24) grades were studied for loss of chloride as ammonium chloride, as reported by Bridger, Alfrey, and Burzlaff (7, 3). The temperatures studied, 110° C. (230° F.) and 300° C. (572° F.), correspond to product and dryer air temperature used in their investigation, and at which appreciable nitrogen losses also occurred. Analyses before and after heating are shown in Table VII. Less than 10% of the nitrogen loss at 110° C. can be accounted for by ammonium chloride, based on the chloride loss. Also, less than 25% of the nitrogen loss at 300° C. could be accounted for as ammonium chloride.

In addition to heating fertilizers to study nitrogen loss as ammonium chloride, reagent chemicals were tested using

**Table III. Effect of Elevated Temperatures on Nitrogen and Chloride Contents of Fertilizers**

Fertilizer	Weight of Original Sample, %						Weight % Loss of Total Nitrogen
	Original Sample			After 30 Days at 50° C.			
	Nitrogen		Chloride	Nitrogen		Chloride	
18-20-0(18-46-0)	17.88	17.58	...	11.51	11.28	...	36
12-11-20(12-24-24)	11.64	8.48	17.2	8.39	5.32	17.7	28
15-13-13(15-30-15)	15.79	12.08	9.6	12.19	8.25	10.0	23
20-4.3-8.3(20-10-10)	21.33	9.76	11.2	19.28	9.64	11.2	10
30-4.3-0(30-10-0)	29.57	16.30	...	28.70	15.44	...	3

**Table IV. Effect of Elevated Temperatures on Nitrogen Constituents of Fertilizers**

Fertilizer	Nitrogen Constituents				Loss, %
	Present, %				
	Urea	18-46-0	11-48-0	NH <sub>4</sub> NO <sub>3</sub>	
18-20-0(18-46-0)	..	100	..	..	36
12-11-20(12-24-24)	22	78	..	..	28
15-13-13(15-30-15)	18	58	24	..	23
20-4.3-8.3(20-10-10)	..	..	32	68	10
30-4.3-0(30-10-0)	..	14	..	86	3

**Table V. Effect of Elevated Temperatures on Urea Contents of Fertilizers**

Sample	Fertilizer	Urea, %			
		Calcd.	Before heating	90 min. at 121° C.	30 days at 50° C.
A	15-13-13(15-30-15)	11.3	3.9	1.9	1.9
B		11.3	5.9	0.9	0.9
C		11.3	8.1	2.3	3.6
D	12-11-20(12-24-24)	6.7	4.3	2.6	1.2
E		6.7	5.8	1.2	1.4
F		6.7	5.1	1.4	1.1

ammonium nitrate-potassium chloride and urea-potassium chloride mixtures. Table VIII shows no loss of nitrogen or chloride from heating an ammonium nitrate-potassium chloride mixture at 121° C. for 90 minutes. Loss is shown from urea-potassium chloride mixtures, with nitrogen loss being greater than chloride. This suggests that the primary loss is as ammonia rather than as ammonium chloride.

The effect of potassium chloride upon the thermal stability of the nitrogen-containing compounds is also shown in Figure 7. Thermograms were obtained for the pure compounds and with 10% additional potassium chloride. Curves from both conditions closely parallel each other, indicating little effect by the potassium chloride on decomposition. Monoammonium phosphate, with the addition of potassium chloride, shows an increase in thermal decomposition above 200° C., presumably with the formation of ammonium chloride as found by Bridger, Alfrey, and Burzlaff (1, 3). However, this temperature should be far outside any reasonable temperature found in fertilizer drying. Diammonium phosphate and potassium chloride show no interaction in the diammonium phosphate range below 170° C. However, above 170° C., in the monoammonium phosphate range, the same increased loss occurred as was shown for monoammonium phosphate.

These data do not show ammonium chloride to be a major source of nitrogen loss in the ammonium phosphate grades. This apparent anomaly with the work of Bridger, Alfrey, and Burzlaff can easily be resolved by comparing the grade studied. They studied calcium phosphate fertilizers, which are more acidic than ammonium phosphate fertilizers. The pH's of all the fertilizers studied in this investigation were between 6.1 and 6.7.

The nitrogen losses shown are of sufficient magnitude that any fertilizer plant operating under the conditions should have cause for concern. The laboratory tests differ from actual plant conditions by utilizing small samples, with an abundance of free surface exposed to air

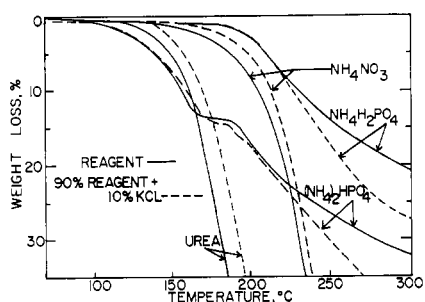


Figure 7. Effect of potassium chloride upon thermal stability of reagent grade fertilizer components

Table VI. Effect of Elevated Temperatures on Nitrate Contents of Fertilizers

Fertilizer	Before heating	Ammonium Nitrate, %			
		After Heating			
		121° C.		50° C.	
		30 min.	90 min.	19 days	30 days
20-4.3-8.3(20-10-10)	49	49	50	50	52
30-4.3-0(30-10-0)	69	71	72	69	72
30-4.3-0(30-10-0)	77	76	79	78	77

Table VII. Effect of Elevated Temperatures on Nitrogen and Chloride Contents of Fertilizers

	15-13-13		12-11-20	
	(15-30-15)		(12-24-24)	
WEIGHT LOSS, %				
At 110° C. for 8 hr.	12.6	10.5		
At 300° C. for 1 hr.	29.7	28.9		
NITROGEN % OF ORIGINAL				
Before heating	14.39	11.67		
At 110° C. for 8 hr.	7.0	5.9		
At 300° C. for 1 hr.	1.5	1.7		
CHLORIDE % OF ORIGINAL				
Before heating	11.80	18.28		
At 110° C. for 8 hr.	11.1	16.9		
At 300° C. for 1 hr.	5.7	13.7		

in a manner such that equilibrium conditions are maintained. The tests are reproducible and permit comparison between samples, but do not necessarily reproduce plant conditions.

Reference has been made to loss at dryer temperatures of 121° C., corresponding to 250° F. It is expected that a more realistic over-all product temperature would be 75° to 95° C., corresponding to 170° to 200° C. Loss would be less at the lower temperatures; however, localized overheating, even to temperatures higher than dryer temperatures, could be a potential source of major nitrogen loss and it is for this reason that actual dryer temperatures were studied.

All variables which affect nitrogen loss have not been discussed, particularly economic and marketing factors. Rather, an attempt has been made to establish certain process criteria in evaluating various formulations. Other factors, such as granulating characteristics, also help determine the composition of a particular grade.

### Conclusions

Significant nitrogen losses can occur during drying and storage of ammonium phosphate fertilizers. Nitrogen losses occur primarily from grades containing high nitrogen-phosphorus ratios from diammonium phosphate and urea. Thermal decomposition data indicate that fertilizer dryer temperatures can be approximately 50° C. higher when monoammonium phosphate and ammonium nitrate are used in place of the

Table VIII. Effect of Elevated Temperatures on Nitrogen and Chloride Contents of Ammonium Nitrate-Potassium Chloride and Urea-Potassium Chloride Mixtures

	90% NH <sub>4</sub> NO <sub>3</sub> + 10% KCl	90% Urea + 10% KCl
	Weight loss, % at 121° C. for 90 min.	0.8
Nitrogen, % of original		
Before heating	30.3	41.2
After 121° C. for 90 min.	30.9	39.2
Chloride, % of original		
Before heating	5.20	5.37
After 121° C. for 90 min.	5.07	4.69

former materials. Ammonium chloride evolution and ammonium nitrate decomposition were not found to be major sources of loss from ammonium phosphate fertilizers at normal temperatures. The use of potassium nitrate in the formulation gives a slightly increased thermal stability, but some formulations are not possible. Use of potassium polyphosphate and ammonium nitrate produces a high-analysis mixed fertilizer with substantially greater thermal stability than found in the other formulations studied. Overheating is a potentially serious cause for nitrogen loss, and the curves indicate a maximum temperature allowable for each formulation.

### Acknowledgment

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## SOURCES OF NITROGEN AND PHOSPHORUS

# Crop Response to Nitrogen and Phosphorus in Metal Ammonium Phosphates

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MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O, and FeNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O were compared in three granule sizes (-6 +9, -14 +20, and -35 +60 mesh) with NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as sources of nitrogen and phosphorus for two successive crops of corn grown in greenhouse pots. MnNH<sub>4</sub>PO<sub>4</sub>, ZnNH<sub>4</sub>PO<sub>4</sub>, and CaHPO<sub>4</sub> were also compared as sources of phosphorus. Response by crop 1 decreased markedly with increase in granule size of the fertilizers applied as nitrogen sources just prior to planting; after incubation in moist soil for 90 days prior to planting, granule size had only minor effects. Crop 2 showed residual effects only to -6 +9 mesh granules. Granulation of a nitrification inhibitor with MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O significantly decreased recovery of the nitrogen by two crops of corn. Response by both crops to phosphorus in CaHPO<sub>4</sub> and the metal ammonium phosphates increased with decrease in granule size. CaHPO<sub>4</sub> showed the greatest granule size effects and the magnesium compounds the least. FeNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O was the least effective source at all granule sizes.

MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE, MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, dissolves incongruently in water with precipitation of a mixture of di- and trimagnesium phosphates, MgHPO<sub>4</sub>·3H<sub>2</sub>O and Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O (5, 6). In moist soil, a granule of magnesium ammonium phosphate dissolves to give a solution of constant composition corresponding to an invariant point in the system MgO-NH<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O at constant temperature and pressure. At 25° C. this solution is 2.6 × 10<sup>-3</sup>M in Mg, 6.6 × 10<sup>-3</sup>M in P, and 7.7 × 10<sup>-3</sup>M in NH<sub>4</sub>, and has a pH of 7.12. The osmotic pressure of this solution will be no higher than that of the soil solution, and the rate of dissolution of the MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O will be controlled by diffusion of the ions into the surrounding soil and by nitrification of NH<sub>4</sub> ions from the granule. Since both of these processes will be slowed as the area of contact between the granule and the soil is decreased, it is to be expected that crop response to the fertilizer will decrease with increase in granule size.

In contact with water, magnesium ammonium phosphate monohydrate,

MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O, forms the hexahydrate, and the extent of hydration in the soil depends upon the temperature and moisture tension. Bridger, Salutsky, and Starostka (7) showed that the monohydrate is the stable form under dry summer conditions in a surface soil. Under the experimental conditions in this work complete conversion to the hexahydrate is to be expected. Little is known of the solubility of other metal ammonium phosphates.

The present experiments were undertaken to measure the response of corn (*Zea mays*) to the nitrogen and phosphorus in magnesium and other metal ammonium phosphates, as affected by granule size. Corn was grown under nonleaching conditions so that the results could be better related to the known chemical behavior of the compounds.

### Materials and Methods

The compositions of the fertilizers are shown in Table I. All sources were prepared as fine powders and tableted under pressure; the tablets were crushed and screened to -6 +9, -14 +20, and -35 +60 mesh. The samples of metal ammonium phosphates other than Mg-

NH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O (prepared by TVA) were supplied by W. R. Grace and Co.

The soil was Hartsells fine sandy loam (pH 5.2) limed to pH 6.3 with a mixture of 4 parts of CaCO<sub>3</sub> and 1 part of MgCO<sub>3</sub>. Each pot, a polyethylene-lined No. 10 tin can, contained 3 kg. of soil (dry basis). All treatments were made in triplicate. Funk's G-76 hybrid corn was grown in all experiments.

**Nitrogen Source Test (Experiment 1).** One series of nitrogen treatments (150, 300, and 600 mg. of nitrogen per pot) was mixed with the soil and incubated at 18% moisture for 90 days before planting to determine nitrogen release from the fertilizers during this period. The second series was prepared just before planting. In each series, phos-

Table I. Partial Composition of Fertilizers

Source	Total N, %	Total P, %	Total Metal, <sup>a</sup> %
MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	5.6	12.8	9.9
MgNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O	8.9	20.0	15.8
MnNH <sub>4</sub> PO <sub>4</sub>	7.3	16.6	28.7
FeNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O	7.2	16.4	29.4
ZnNH <sub>4</sub> PO <sub>4</sub>	7.8	17.4	35.7
CaHPO <sub>4</sub>	..	22.7	29.4
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	12.2	26.9	..

<sup>a</sup> Mg, Mn, Fe, Zn, or Ca.

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