FERTILIZER DRYING

Nitrogen Loss in Drying of Ammoniated Superphosphates and Mixed Fertilizers

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Laboratory experiments were carried out on drying of ammoniated superphosphates and mixed fertilizers to determine under what conditions loss of nitrogen and potassium and reversion of available phosphorus pentoxide would occur. Both storage-cured and quick-cured superphosphate were used for ammoniation. Sources of nitrogen included aqueous ammonia, ammonium nitrate, ammonium sulfate, and ammoniating solution. Drying was carried out at various temperatures in a laboratory dryer. With ammoniated superphosphate prepared with aqueous ammonia at an ammoniation rate of 5 pounds of ammonia per unit of available phosphorus pentoxide nitrogen loss during drying became appreciable at product temperatures in the range 200° to 230° F. at inlet air temperatures of 300° to 600° F. Product temperature had a much greater effect on nitrogen loss than inlet air temperature. When potassium chloride was added, nitrogen loss became appreciable at lower product and inlet air temperatures. Use of ammonia–ammonium nitrate solution at the same rate of free ammonia did not increase nitrogen loss; addition of ammonium sulfate increased nitrogen loss only slightly, and addition of potassium chloride did not increase nitrogen loss at all. There was no appreciable potassium loss in any of the experiments, and only slight occasional reversion of available phosphorus pentoxide. Quick-cured superphosphate was as satisfactory for ammoniation as storage-cured superphosphate. The results point to the importance of careful choice of drying temperatures for mixed fertilizers prepared in various ways. Nitrogen losses of 15 to 20% were encountered under some conditions, but can be avoided by proper drying temperatures.

MANY NEW FERTILIZER PROCESSES include steps for heat drying of fertilizer ingredients or mixed fertilizers containing nitrogen, phosphorus, and potassium compounds. Nitrogen compounds are subject to sublimation and decomposition at temperatures that might be employed in drying. The decomposition pressures of certain nitrogen compounds that are important in fertilizer manufacture are shown in Figure 1. Available phosphorus compounds are subject to reversion to unavailable forms at high temperatures. Potassium compounds are not so easily sublimed as nitrogen compounds, but it is conceivable that temperatures might be reached in drying that would cause appreciable loss of potassium.

The present study was carried out to determine under what drying conditions nitrogen loss, phosphorus pentoxide reversion, and possibly potassium loss would be encountered for some typical fertilizer compositions. The study was by no means exhaustive. Much further work would be necessary to include all of the commercially important fertilizer compositions. A second objective was to demonstrate that quick-cured superphosphate prepared by a process previously developed in this laboratory (3) was suitable for ammoniation and mixing with other fertilizer ingredients.

Materials and Procedure

The superphosphates were prepared from Florida phosphate rock containing 34.0% phosphorus pentoxide (74.2% bone phosphate of lime dry basis) and ground to 91% – 100 mesh and 61% – 200 mesh by mixing it with sulfuric acid containing 55% H_2SO_4 in the proportion of 1.80 pounds of H_2SO_4 per pound of phosphorus pentoxide. The storage-cured superphosphate was made by permitting the fresh material to stand for at least 90 days with occasional loosening and turning over in an open container at room temperature. The quick-cured superphosphate was prepared by drying the fresh material in a laboratory Roto-Louvre dryer; this material was also 90 days old at the time of its use. Both superphosphates were milled to –10 mesh before use. The compositions of the two materials were:

	Quick-Cured, %	Storage-Cured, %
Total P_2O_5	19.8	17.1
Citrate-insol. P_2O_5	1.3	0.0
Available P_2O_5	18.5	17.1
Moisture	4.5	14.8

The various nitrogen materials used were aqua ammonia containing 27% NH_3, Barrett No. 2A ammoniating solution containing 22.0% NH_3, and 40.6% total nitrogen, fertilizer grade ammonium nitrate, and fertilizer grade ammonium sulfate.
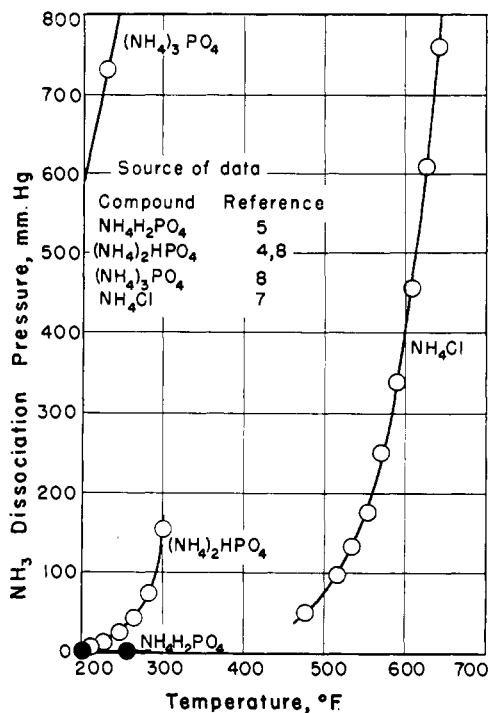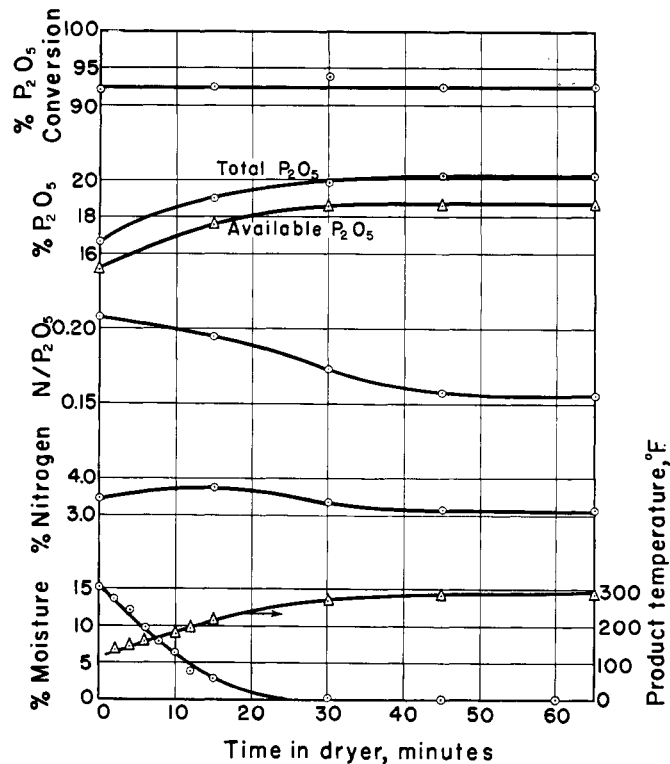
The potassium chloride used was com-

Figure 1. Decomposition pressures of various nitrogen compounds

Source of data

Compound	Reference
$NH_4H_2PO_4$	5
$(NH_4)_2HPO_4$	4,8
$(NH_4)_3PO_4$	8
NH_4Cl	7

mercial muriate containing 62% K_2O.

Ammoniation and mixing were carried out in a slurry phase similar to that used in the Martenet process (6). A sufficient amount of water was added so that a slurry would be formed at the tempera-

tures developed by the ammoniation reactions and solidification and granulation of the mass would occur as it cooled. Mixing was carried out in an open pan 7 inches in diameter with close-fitting agitator blades which rotated at 97 r.p.m. In making a mix the dry materials were introduced first and thoroughly mixed, then any necessary water was added and mixed, and finally the aqua ammonia or ammoniating solution was added from a pressurized calibrated vessel. There was usually a small loss of free ammonia during mixing. In all of the mixtures except those made with aqua ammonia, a thin slurry was obtained which set up to a granular product on cooling. With the aqua ammonia it was not possible to obtain a slurry which would set up on cooling.

The granular wet product from the mixing step containing 12 to 18% moisture was passed through a $1/4$-inch screen and dried in a laboratory Roto-Louvre dryer operated batchwise (3). This type of dryer is designed for drying of heat-sensitive materials. The inlet air temperature was held constant throughout a run, and the product temperature, which increased gradually as drying progressed, was measured by a thermometer inserted into the bed of product, which was in constant agitation due to the rotation of the dryer. Samples of product were withdrawn at various intervals.

Losses of nitrogen and potash and phosphorus pentoxide reversion were measured by comparing the composition of the dryer feed with those of the various samples taken throughout the drying cycle. For example, nitrogen loss was calculated from the initial and final ratios of nitrogen to total phosphorus pentoxide as follows:

$$\% \text{ nitrogen loss } = \left(\frac{\text{initial } N/P_2O_5 - \text{final } N/P_2O_5}{\text{initial } N/P_2O_5}\right) \times 100$$

The nitrogen loss thus calculated is that encountered in the drying step only and does not include loss in the mixing step.

AOAC methods of analysis were used (1), except that a colorimetric phosphorus pentoxide determination developed in this laboratory (2) and a flame photometric method for potash were used.

Results of a typical experiment are shown in Figure 2. In this run quick-cured superphosphate was ammoniated with aqua ammonia at a rate of 5.4 pounds of ammonia per unit of available phosphorus pentoxide; this rate and subsequent ones are based on analysis of the dryer feed material. The dryer was operated with an inlet air temperature of 500° F. As drying proceeded, the moisture content of the product decreased to almost zero in 25 minutes and the product temperature increased

Figure 2. Typical primary data for drying of ammoniated superphosphate

Aqua ammonia at 5.4 pounds of ammonia per unit of available phosphorus pentoxide. Inlet air temperature 500° F.

Figure 3. Effect of product temperature on nitrogen loss and phosphorus pentoxide conversion at various inlet air temperatures

Aqua ammonia at 5.4 pounds of ammonia per unit of available phosphorus pentoxide

Product moisture

⑩	10%
⑤	5%
③	3%
①	1%
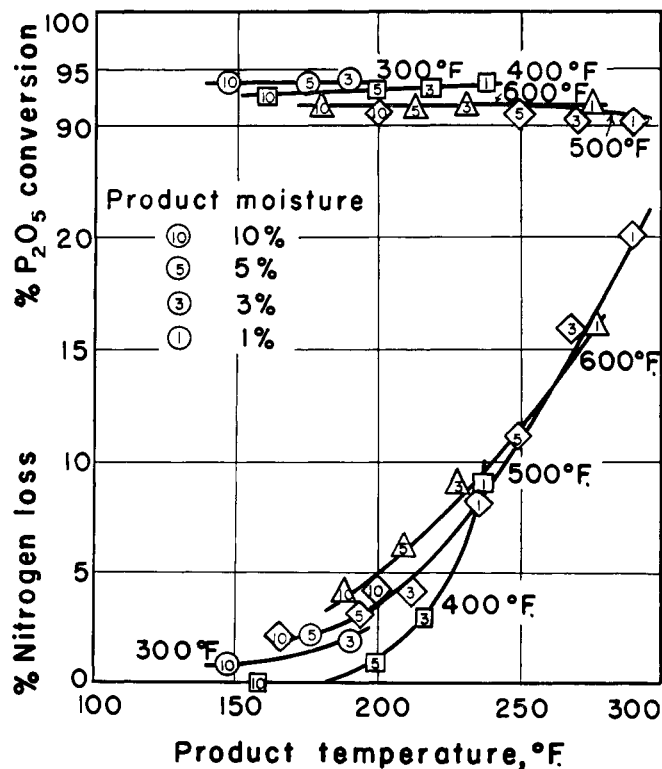
rapidly at first and then became almost constant at 290° F. Nitrogen content increased during the first 15 minutes, owing to moisture removal, and then decreased gradually. Total and available phosphorus pentoxide content increased considerably. The ratio of nitrogen to phosphorus pentoxide decreased steadily, indicating a definite loss of nitrogen. Phosphorus pentoxide conversion was constant throughout the entire drying cycle.

In comparing the results of various experiments, it is necessary to choose data at the same drying times, moisture contents, or product temperatures. Comparison at the same product temperature gave better correlation than comparison at either constant time or constant moisture content. Consequently it was assumed that product temperature is the controlling variable with respect to nitrogen loss, although it is recognized that drying time and product moisture content must also have some influence.

Effect of Temperature

Experiments were made in which quick-cured superphosphate was ammoniated with aqua ammonia at a rate of 5.4 pounds of ammonia per unit of available phosphorus pentoxide and

Figure 4. Effect of product temperature on nitrogen loss and phosphorus pentoxide conversion at various inlet air temperatures

Aqua ammonia at 5.4 pounds of ammonia per unit of available phosphorus pentoxide. Potassium chloride at 1 unit of potassium oxide per unit of available phosphorus pentoxide
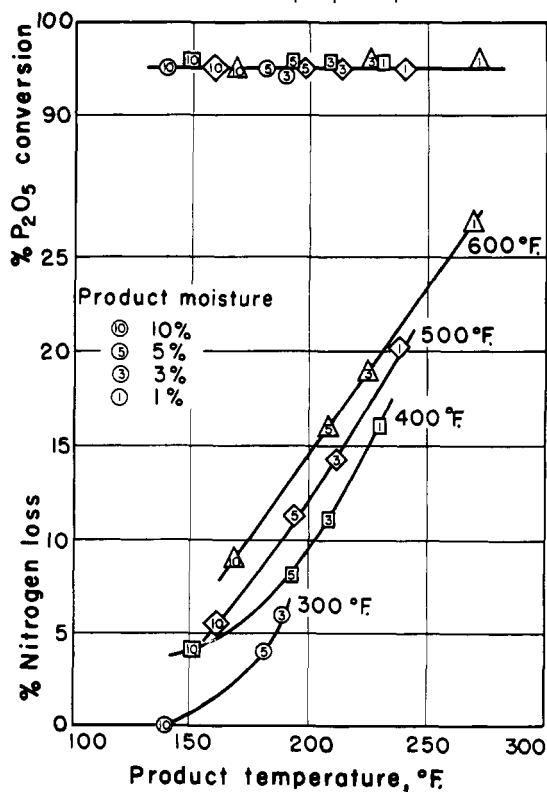
dried at inlet air temperatures of 300°, 400°, 500°, and 600° F. The results are shown in Figure 3. The points indicated on this curve are those at the 1, 3, 5, and 10% moisture levels, which were read from curves similar to Figure 2. Two different runs were made with inlet air at 500° F.; the specified moisture levels were attained at different product temperatures for the two runs, probably because of differences in the physical condition of the fresh ammoniated superphosphates. However, correlation on the basis of product temperature was good.

Nitrogen losses became appreciable at a product temperature of about 200° F. and were pronounced at 240° to 290° F., reaching as high as 20% of the initial nitrogen in one case. The higher inlet air temperatures usually produced higher nitrogen losses at a given product temperature, doubtless because of the greater chance for local overheating of the surface of the particles.

One experiment was carried out with an ammoniation rate of 2.9 pounds of ammonia per unit of available phosphorus pentoxide at an inlet air temperature of 500° F. (not shown in Figure 3). Nitrogen loss was negligible at temperatures up to 260° F., and there was no phosphorus pentoxide reversion.

Experiments similar to the above were carried out, in which potassium chloride was mixed with the quick-cured superphosphate just prior to the ammoniation. The proportion of potassium chloride was approximately one unit of potassium oxide for each unit of available phosphorus pentoxide. An ammoniation rate of 5.8 pounds of ammonia per unit of phosphorus pentoxide was used.

The results of these experiments are shown in Figure 4. The presence of potassium chloride increased nitrogen losses markedly. The effect of inlet air temperature was more pronounced than when no potassium chloride was used. At a product temperature of 200° F. nitrogen losses ranged from 8 to 14%, and at a product temperature of 270° F. and an inlet air temperature of 600° F. the nitrogen loss was 27%. Under these conditions it would be necessary to operate a dryer with an inlet air temperature of 300° F. and dry to a moisture level of only 3 to 5% in order to avoid serious nitrogen losses.

Effect of Source of Nitrogen

Experiments were made in which the nitrogen was derived from ammonium nitrate, ammoniating solution containing free ammonia and ammonium nitrate, and a combination of ammoniating solution plus ammonium sulfate for comparison with the results with aqua ammonia. The ammonium nitrate was added at a rate of 5.2 pounds of total nitrogen per unit of available phos-
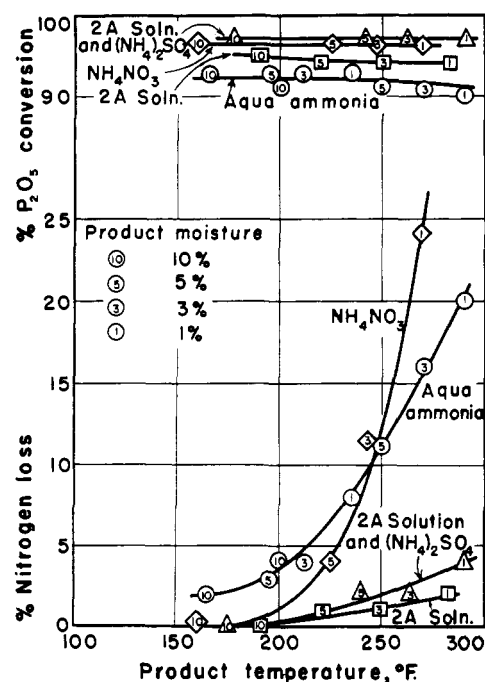

Figure 5. Effect of source of nitrogen on nitrogen loss and phosphorus pentoxide conversion

Inlet air temperature 500°F.

phorus pentoxide. The ammoniating solution was added at a rate of 5.5 pounds of total nitrogen per unit of available phosphorus pentoxide which corresponds to 3.0 pounds of ammonia per unit of available phosphorus pentoxide. The combination of ammoniating solution and ammonium sulfate was added at a rate of 9.9 pounds of total nitrogen per unit of available phosphorus pentoxide, of which 2.6 pounds was free ammonia.

The results are shown in Figure 5. The nitrogen losses when ammonium nitrate was used were high, owing to decomposition of the ammonium nitrate by the free acid of the superphosphate, which was evident from the nitrogen oxide fumes that were evolved. When the ammoniating solution was used, the nitrogen losses were about the same as when aqua ammonia at the same rate of free ammonia was used, and are considered negligible. When the combination of ammoniating solution and ammonium sulfate was used, nitrogen loss increased slightly but was only 4% at a product temperature of 290° F.

These results indicate that the nitrogen losses are due primarily to compounds formed from free ammonia and that losses of ammonium nitrate and ammonium sulfate are negligible, providing the free acid of the superphosphate has been neutralized.

Experiments similar to the above were carried out in which potassium chloride at the rate of about one unit of potassium oxide per unit of available phosphorus pentoxide was added. The results are

shown in Figure 6. Nitrogen losses were negligible when ammonium nitrate, ammoniating solution, and ammoniating solution plus ammonium sulfate were used. The presence of potassium chloride prevented decomposition of the ammonium nitrate by the free acid of the superphosphate.

Comparison of Quick-Cured and Storage-Cured Superphosphates

Storage-cured superphosphate was ammoniated with the ammoniating solution at a rate of 5.5 pounds of total nitrogen per unit of available phosphorus pentoxide corresponding to 3.0 pounds of ammonia per unit of available phosphorus pentoxide both with and without potassium chloride at a rate of about one unit of potassium oxide per unit of available phosphorus pentoxide for comparison with similar results with quick-cured superphosphate.

The results are shown in Figure 7. When no potassium chloride was used, nitrogen losses from the ammoniated storage-cured superphosphate were higher than those from the ammoniated quick-cured superphosphate, reaching about 6% at a product temperature of 200° F. When potassium chloride was used, nitrogen losses were negligible in all cases.

Phosphorus Reversion And Potassium Loss

In most of the experiments there was no phosphorus pentoxide reversion on drying the products to 1% moisture, and in a few a reversion of about 1% was

Figure 6. **Effect of source of nitrogen on nitrogen loss and phosphorus pentoxide conversion**

Inlet air temperature 500° F. Potassium chloride at 1 unit of potassium oxide per unit of available phosphorus pentoxide
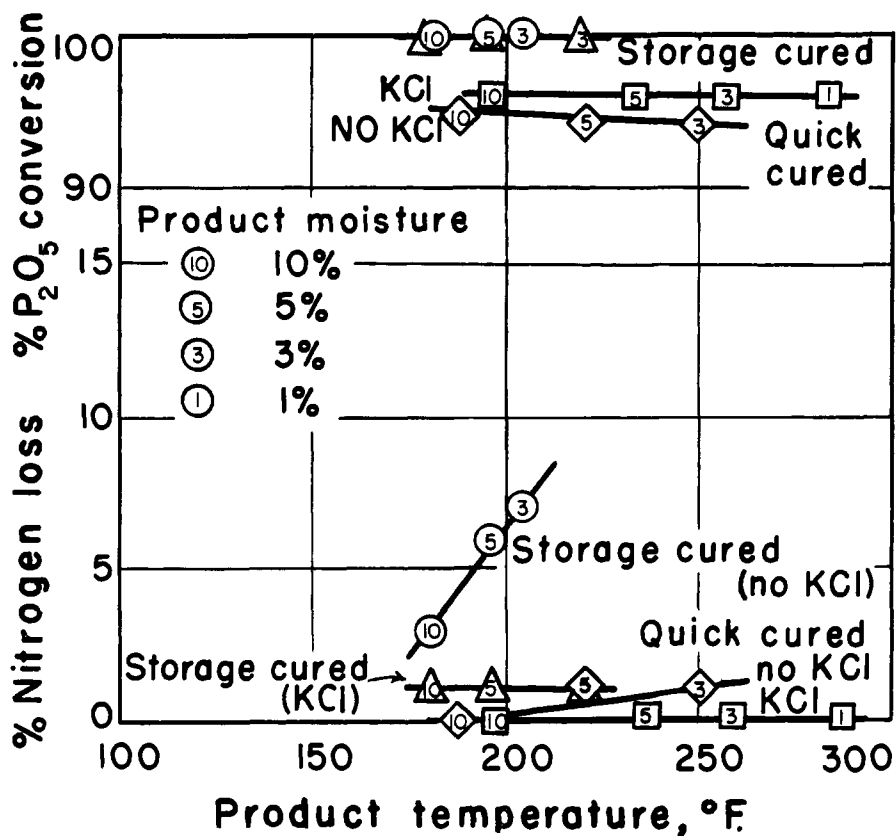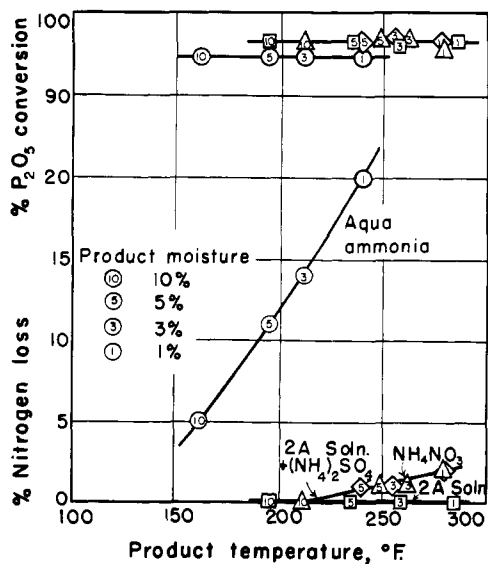

Product temperature, °F

Figure 7. **Comparison of quick-cured and storage-cured superphosphates for ammoniation**

Ammoniating solution at 3.0 pounds of free ammonia per unit of available phosphorus pentoxide. Potassium chloride at 1 unit of potassium oxide per unit of available phosphorus pentoxide in 2 runs

found. In a few instances in which drying was continued to lower moisture contents and product temperatures greater than 300° F., phosphorus pentoxide reversions of 3 to 4% were found.

In most of the experiments there was no potassium loss, as indicated by K_2O/P_2O_5 ratios. Occasionally there was an indicated loss of 1 or 2%, but the experimental precision was not good enough to be sure of this.

Conclusions

Nitrogen losses during the drying of ammoniated superphosphates and mixed fertilizers containing ammoniated superphosphates can be substantial under some conditions. The principal factor influencing nitrogen loss is product temperature, but inlet air temperature of the dryer is also important. Under some conditions, losses of nitrogen can be greater than 20% at inlet air temperatures of 500° F. and product temperatures of about 250° F. By proper control of these temperatures, nitrogen losses can be made negligible. These conclusions may not hold quantitatively for dryers other than the Roto-Louvre dryer; in dryers not designed for heat-sensitive materials, nitrogen losses may be greater.

Quick-cured superphosphate was as satisfactory as storage-cured superphosphate for ammoniation and mixing.

Literature Cited

(1) Assoc. Offic. Agr. Chemists, "Methods of Analysis," 7th ed., 1950.
(2) Bridger, G. L., Boylan, D. R., and Markey, J. W., Anal. Chem., **25**, 336–8 (1953).
(3) Bridger, G. L., and Kapusta, E. C., Ind. Eng. Chem., **44**, 1540–6 (1952).
(4) Britzke, E. V., Dunaev, A. P., and Pokhvalinskaya, E. P., Trans. Sci. Inst. Fertilizers (U.S.S.R.), No. **51**, 5–83 (1928).
(5) Curtis, H. A., "Fixed Nitrogen," pp. 409–66, New York, Chemical Catalog Co., 1932.
(6) Martenet, S. J., Agr. Chemicals, **9**, No. 4, 46–8, 138–41 (1954).
(7) Smith, A., and Calvert, R. P., J. Am. Chem. Soc., **36**, 1363–82 (1914).
(8) Warren, T. E., Ibid., **49**, 1904–8 (1927).