FERTILIZER AMMONIATION

Effect of Particle Size upon the Ammoniation of Superphosphate

CHARLES E. WATERS,
WILLARD W. ARNOLD[1],
and WILLIAM H. PAYNE

Nitrogen Division, Allied Chemical and Dye Corp., Hopewell, Va.

In the modern manufacture of mixed fertilizers, such high ammoniation rates are frequently attempted that the limiting factor is the ability of the superphosphate to absorb ammonia. This paper describes a laboratory study of effect of particle size. Mixtures of screened, normal superphosphate, potassium chloride, and sand were ammoniated at three different rates with a commercial ammonium nitrate–ammonia–water solution. Absorption of ammonia was judged by the disappearance of ammonia from the air in the ammoniator, and by analysis of the products. Excepting some irregularities, the data show that the finer the particle size, the more rapid and complete is the absorption of ammonia.

THE TREND TOWARD HIGHER ANALYSIS in mixed fertilizers, and the increasing availability of nitrogen solutions, have led to the use of higher and higher rates of ammoniation (3). Although it was formerly the practice to limit the ammoniation rate to about 3 pounds of neutralizing ammonia per 20-pound unit of phosphorus pentoxide, rates as high as 7 pounds per unit are not uncommon at present. In some cases the rates of ammoniation approach the capacity of the superphosphate for ammonia, and lead to incomplete absorption. Any considerable evaporation of ammonia is a direct loss. Worse still, it may set up an intolerable concentration of ammonia in the air, so that operations must be suspended.

Among the conditions that may influence the amount of ammonia absorbed by superphosphates are particle size, density, structure, and free acid and moisture content of the superphosphates, temperature of ammoniation, and period of contact with ammonia. Moreover, normal superphosphate has a considerably greater capacity per unit of phosphorus pentoxide than triple superphosphate. A study of the influence of these factors upon the absorption of anhydrous ammonia was presented by Kumagai, Rapp, and Hardesty (4).

The work described here was confined to a study of the ammoniation of particles of different sizes by means of a nitrogen solution containing 65% of ammonium nitrate and 21.7% of ammonia. Complete fertilizers were made by laboratory ammoniation of mixtures of potassium chloride, sand, and fractions obtained by screening commercial normal superphosphate. An effort was made to minimize variations in factors other than particle size. In each series of experi-

[1] Present address, Nitrogen Division, Allied Chemical and Dye Corp., Indianapolis, Ind.

ments the fractions were all from a single lot of normal superphosphate, and they were adjusted to comparable moisture contents. The conditions of ammoniation were as nearly uniform as could be achieved practically.

Possible phosphate reversion was not considered in this study, and the availabilities of phosphorus pentoxide in the products were not determined.

Equipment and Procedure

The ammoniation equipment was similar to that described by Datin, Worthington, and Poudrier (2). The apparatus consisted of a drum of stainless steel, 4 inches deep and 13 inches in inside diameter, fitted with a gasketed cover held in place by springs. A single spray nozzle was used in place of the perforated central tube. A half-inch hole was drilled in the cover, and fitted with a quickly removable plug through which gas samples

could be taken from the drum during the ammoniations. During the ammoniations, the sides of the drum were hit with a rubber mallet to prevent caking of the product. The drum was rotated at approximately 25 revolutions per minute.

The nitrogen solution, containing 65% ammonium nitrate and 21.7% ammonia (40.6% nitrogen), was taken from storage in a 50-gallon drum and measured in a calibrated section of glass pipe with a capacity of 220 ml. Nitrogen gas pressure was used to spray the solution directly into the rotating drum.

Except where otherwise noted, a total reaction period of 3 minutes was allowed. From 40 to 42 seconds were required for spraying the solution; the remainder of the 3 minutes was used for mixing. Air samples were taken from the drum by means of previously evacuated 250-ml. gas sampling tubes, 1, 2, and 3 minutes after the beginning of ammoniation. The drum was stopped during the 10-

Table I. Analysis of Superphosphate A and Fine and Coarse Material Screened from It

Material	Original Material	Fine Fraction	Coarse Fraction
Total P_2O_5, %	..	19.82	23.33
Citrate-insol. P_2O_5, %	..	0.80	0.83
Free acid as P_2O_5, %	1.29	1.14	0.90
Moisture (5 hr. in 100° C. oven), %	8.74	9.04	7.17
Moisture, adjusted, %	..	...	9.00

Table II. Ammoniation of Superphosphate A

| Mesh Size and Other Data | Ammonia in Air, Vol. % | | |
	1 min.	2 min.	3 min.
Original product through 4-mesh	8.96	0.16	0.00
Repeat	8.64	0.16	0.00
Fine fraction through 50-mesh	0.48	0.00	0.00
Repeat	0.32	0.16	0.00
Coarse fraction retained on 50-mesh	43.04	4.48	2.40
Repeat	42.40	20.64	14.56
Same as preceding, but ground in mill	1.28	0.16	0.00

50-mesh sieve approximately equivalent to Tyler 48-mesh sieve.

Table III. Analysis of Superphosphate B and Screen Fractions from It

Fraction[a]	Original	4–16	16–30	30–40	40–50	50–60	60–100	Through 100
Weight from approx. 195 lb. original, lb.		48	27	18.5	18	20.5	20.5	39
H_2O (5 hr. in 100° C. oven), %	9.0	7.55	6.5	6.0	6.4	6.4	5.8	6.1
H_2O adjusted, %		7.8	8.3	8.3	6.9	7.0	7.4	7.5
P_2O_5 (before H_2O adjusted), %								
Total	20.88	20.00	20.93	23.28	24.68	22.75	21.28	18.62
Available	19.98	18.98	19.98	22.22	23.92	21.54	20.40	18.44
Citrate-insoluble	0.90	1.02	0.95	1.06	0.76	1.21	0.88	0.18
Free acid	1.74	1.18	1.06	0.82	0.74	0.71	0.72	0.81

[a] Sieves used for preparing these fractions were somewhat different from Tyler series; comparison is stated in text.

second period required for the taking of each sample.

At the end of 3 minutes the fertilizers produced were exposed to the air to permit the escape of unreacted ammonia. Samples were then taken for the determination of Devarda and ammoniacal nitrogen. The difference between these percentages was considered to represent the nitrate nitrogen, and the difference between the percentages of nitrate and ammoniacal nitrogen was considered to represent nitrogen introduced as free ammonia. Standard methods of analysis of the Association of Official Agricultural Chemists (7) were used for determinations of nitrogen, moisture, and phosphorus pentoxide. Free acid was determined by extraction with acetone and titration of the extract with alkali.

The gas samples were bubbled through a Bowen potash bulb containing a saturated aqueous solution of boric acid, and the solution was titrated with hydrochloric acid to determine the ammonia. The result was calculated as percentage of ammonia by volume in the drum atmosphere.

All ammoniations were done when room temperature was between 20° and 30° C., with an over-all average of 24.4°. When the ammoniator was opened at the end of each run, a thermometer was thrust into the product, and the maximum indicated temperature was recorded. The fact that the temperatures of the 1-minute ammoniation products were higher than those of the corresponding 3-minute products indicates that the maximum temperature of ammoniation was attained quickly, certainly in less than 3 minutes, and possibly in the first minute. This is shown in Table IV. There is no evident relationship between the temperature and either particle size or ammoniation rate.

Materials and Data

The superphosphates used in this study were commercial products made by acidulation of Florida phosphate rock. These were ordinary superphosphates containing approximately 20% of avail-

able phosphorus pentoxide, and showed only minor differences from each other. All superphosphate, even that referred to as unscreened, was passed through a 4-mesh sieve before ammoniation or further screening.

The preliminary work was done with sample A. An 80-pound portion of this was screened on a 14 × 14 inch, 50-mesh sieve, 45 pounds being retained and 35 pounds passing through. Table I gives data on the original superphosphate and the two fractions. A portion of the coarse material was adjusted to 9% moisture content before use, so that it would correspond more closely to the fine fraction. There was a very noticeable difference between the phosphorus pentoxide contents of the fine and coarse materials. This difference was considered in formulating, so that the phosphorus pentoxide contents, and thus the rates of ammoniation, were equalized. In this series of experiments, a 5–10–10 formulation was used, with an ammoniation rate of 5.33 pounds of neutralizing ammonia per unit of phosphorus pentoxide.

The fraction of this superphosphate that passed through the 50-mesh sieve absorbed ammonia more rapidly than unscreened material, which in turn absorbed more rapidly than the fraction

that was retained on the sieve. However, when part of the coarse fraction was ground in a sample mill, it too absorbed ammonia rapidly, showing that particle size influences ammonia absorption independently of other factors. The results of these tests are listed in Table II. The duplicate tests shown in the table indicate the degree of reproducibility that was attained. The results were generally least reproducible when the efficiency of absorption was poor, probably because large and variable amounts of ammonia escaped from the ammoniation drum.

The remaining tests were carried out with superphosphate B. A quantity of the superphosphate was passed through a standard 4-mesh sieve, and then divided into seven fractions by means of six successively finer screens. The following list shows the designations of these screens, the sizes of the openings, and the numbers of the most nearly corresponding sieves of the Tyler series:

Mesh	Opening, Mm.	
16	1.12	Finer than Tyler 14
30	0.56	Finer than Tyler 28
40	0.35	Tyler 42
50	0.30	Close to Tyler 48
60 (twill weave)	0.19	Between Tyler 65 and Tyler 80
100	0.14	Close to Tyler 100

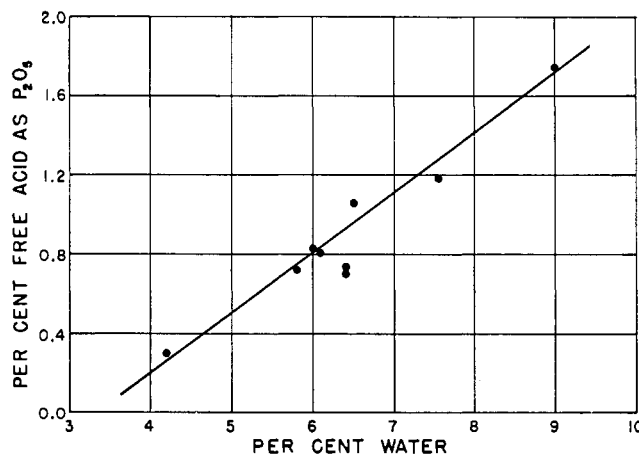**Figure 1. Relation between free acid and moisture content of superphosphate**

Table III gives data on the original material and the various fractions. The variations of total and available phosphorus pentoxide with particle size are very noticeable, both values reaching maxima in the 40- to 50-mesh fraction. These differences were taken into account in formulating the mixtures.

The low moisture contents of the fractions show that some drying oc-

Table IV. Ammoniation of Superphosphate B Product and Gas Analyses

Ammoniation Rate and Formula	Superphosphate Mesh Range[a]	Ammoniation Time, Min.	Temp. Change, °C.	Per Cent Nitrogen in Product				Ammonia in Air, Vol. %		
				Total	Ammoniacal	Nitrate	Free NH$_3$	1 min.	2 min.	3 min.
7.17 lb. NH$_3$/unit P$_2$O$_5$	4–16	3	24.4	4.24	2.83	1.41	1.42	55.04	45.28	41.44
(5–7.5–10)	16–30	3	26.2	4.68	3.14	1.54	1.60	46.56	31.36	23.04
	16–30	1	31.0	4.01	2.82	1.19	1.63	38.56	...	...
	30–40	3	28.4[b]	4.80	3.39	1.41	1.98	41.60[b]	21.76[b]	14.88[b]
	40–50	3	26.8[b]	4.94	3.59	1.35	2.24	40.16[b]	26.24[b]	15.52[b]
	50–60	3	27.8[b]	5.05	3.70	1.35	2.35	39.68[b]	23.36[b]	12.72[b]
	60–100	3	28.2	5.09	3.71	1.38	2.37	35.04	13.60	7.20
	Through 100	3	26.3	5.07	3.53	1.54	1.99	13.44	1.76	0.48
	Through 100	1	37.4	4.76	3.55	1.21	2.34	21.26	...	...
	Original product	3	27.8	4.81	3.53	1.28	2.25	45.92	26.24	15.52
	Original product	1	37.1	4.55	3.33	1.22	2.11	43.88	...	...
5.33 lb. NH$_3$/unit P$_2$O$_5$	4–16	3	25.0	4.67	3.22	1.45	1.77	50.08	27.04	14.24
(5–10–10)	16–30	3	25.4[b]	4.90	3.27	1.63	1.64	28.64[b]	4.80[b]	0.96[b]
	16–30	1	34.0	4.38	3.05	1.33	1.72	28.50	...	...
	30–40	3	26.1	4.94	3.55	1.39	2.16	20.32	0.96	0.16
	40–50	3	25.0	5.03	3.54	1.49	2.05	15.36	0.32	0.00
	50–60	3	25.4	5.09	3.62	1.47	2.15	9.44	0.16	0.00
	60–100	3	25.8	5.11	3.71	1.40	2.31	4.16	0.00	0.00
	Through 100	3	23.5	5.09	3.62	1.47	2.15	0.16	0.00	0.00
	Through 100	1	32.2	4.97	3.46	1.51	1.95	3.52	...	...
	Original product	3	30.5	4.98	3.59	1.39	2.20	16.96	0.96	0.16
	Original product	1	37.1	4.96	3.59	1.37	2.22	22.44	...	...
4.13 lb. NH$_3$/unit P$_2$O$_5$	4–16	3	28.3	4.84	3.51	1.33	2.18	21.28	2.08	0.32
(5–13–10)	16–30	3	26.5	4.95	3.21	1.74	1.47	7.68	0.00	0.00
	16–30	1	39.3	4.79	3.44	1.35	2.09	24.32	...	...
	30–40	3	28.3	5.03	3.64	1.39	2.25	4.64	0.00	0.00
	Through 100	1	36.9	4.96	3.74	1.22	2.52	0.21	...	...
	Original product	3	23.6	5.19	3.76	1.43	2.33	0.80	0.00	0.00
	Original product	1	36.1	4.86	3.65	1.21	2.44	1.55	...	...

[a] Sieves used for preparing these fractions were somewhat different from Tyler series; see text.
[b] Average of duplicate ammoniations.

curred during the long periods required for screening. Because the moisture contents were low and differed so widely, they were adjusted before use, so that all fractions had moisture contents in the range 6.9 to 8.3%. At this fairly high level, differences in moisture content within the range are believed to have but little effect upon the speed of ammonia absorption. Comparison of the ammoniations of the 30- to 40- and 40- to 50-mesh fractions at the highest rate appears to show a slight effect. The 30- to 40-mesh fraction at 8.3% moisture absorbed ammonia somewhat better than the 40–50 fraction at 6.9% moisture. At the medium ammoniation rate the 40–50 fraction absorbed better than the 30–40 fraction in spite of the difference in moisture contents. The 40–50 fraction was not ammoniated at the low rate.

A relation between moisture and apparent free acid is likewise shown in Table III by the fact that the original superphosphate showed a greater percentage of free acid than did any of the fractions, and that when the unscreened superphosphate was dried to 4.35% moisture content the apparent free acid content dropped to 0.28%. Figure 1, based on data in Table III, indicates that the apparent free acid is roughly a linear function of the moisture content. While all other factors were not held constant, they were held within narrow limits, and all points on the graphs were

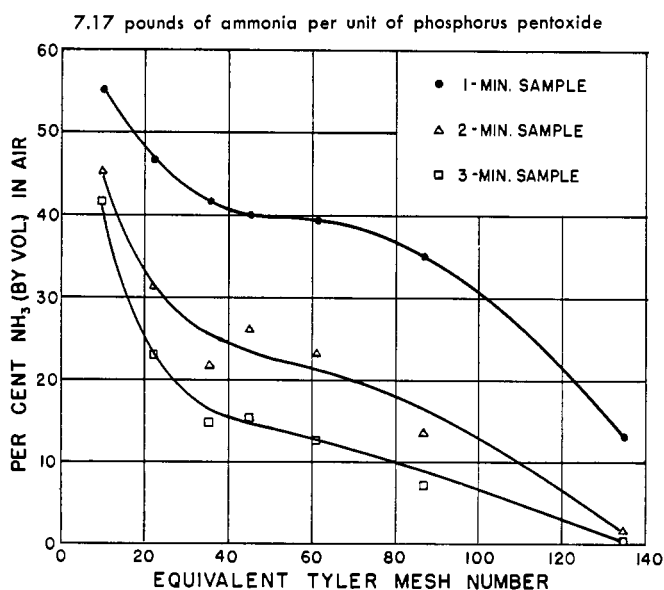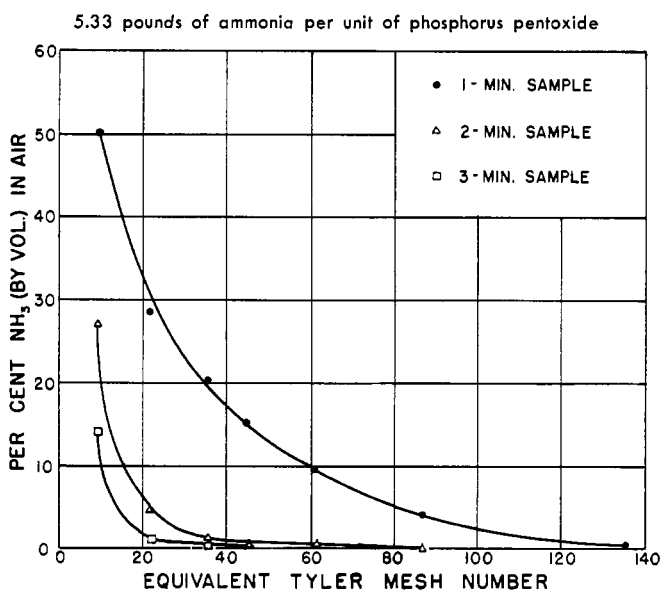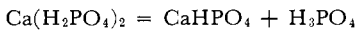Figure 2. Influence of particle size on percentage of ammonia in air

7.17 pounds of ammonia per unit of phosphorus pentoxide

Figure 3. Influence of particle size on percentage of ammonia in air

5.33 pounds of ammonia per unit of phosphorus pentoxide

obtained with one superphosphate, B. Perhaps this is caused by a shifting of equilibrium in the equation

$$Ca(H_2PO_4)_2 = CaHPO_4 + H_3PO_4$$

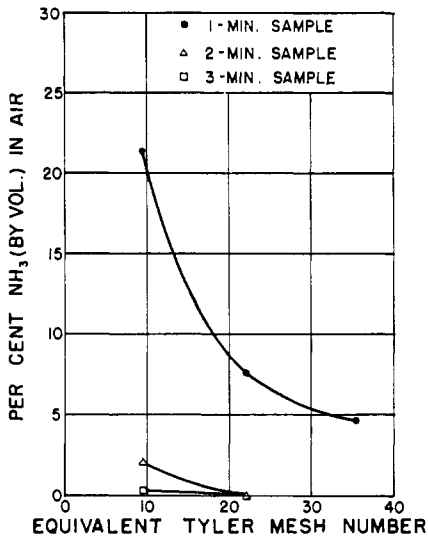which occurs in the presence of water in variable amounts.

Figure 4. Influence of particle size on percentage of ammonia in air

4.13 pounds of ammonia per unit of phosphorus pentoxide

Superphosphate B and all fractions were ammoniated as described above, to yield complete fertilizers. Each batch of fertilizer was calculated to weigh 2000 grams, and to be made with 340 grams of potassium chloride (approximately 60% potassium oxide equivalent) and 251 grams of the nitrogen solution. As the quantity of ammonia was held constant, the ammoniation rate was varied by changing the number of units of phosphorus pentoxide—that is, by varying the proportion of superphosphate in the batch. The rate was increased by using less superphosphate, and decreased by using more. the total weight being held constant by adjusting the amount of inert filler (sand). Three different formulas were used: 5–7.5–10 for a 7.17-pound ammoniation rate; 5–10–10 for a 5.33-pound rate; and 5–13–10 for a 4.13-pound rate. The series at the 4.13-pound rate was discontinued before all fractions had been ammoniated, for only the very coarsest left any free ammonia in the drum atmosphere at

the end of 2 minutes. Analyses of the drum atmosphere and the fertilizers produced are reported in Table IV.

To simulate commercial operations more closely, a series of ammoniations was performed, allowing only a 1-minute reaction period. Analyses of the drum atmospheres were consistent with those obtained at the end of 1 minute in previous ammoniations, but the total nitrogen contents of the products were consistently lower, showing incompleteness of absorption. These results are also in Table IV.

Discussion

Analyses of the air in the drum show that at the 7.17-pound ammoniation rate there was a high concentration of ammonia even at the end of 3 minutes, for all the size ranges except the very finest. Even with the material that had passed through a 100-mesh sieve, the final concentration was 0.48% by volume. Curves representing the concentrations of ammonia in the drum atmosphere after reaction periods of 1, 2, and 3 minutes are shown in Figure 2. (In this graph and the succeeding ones, the abscissas are mesh numbers of equivalent Tyler sieves, and not the numbers of special screens. Points are plotted at the average values of the limiting sieve numbers of the respective fractions. The higher

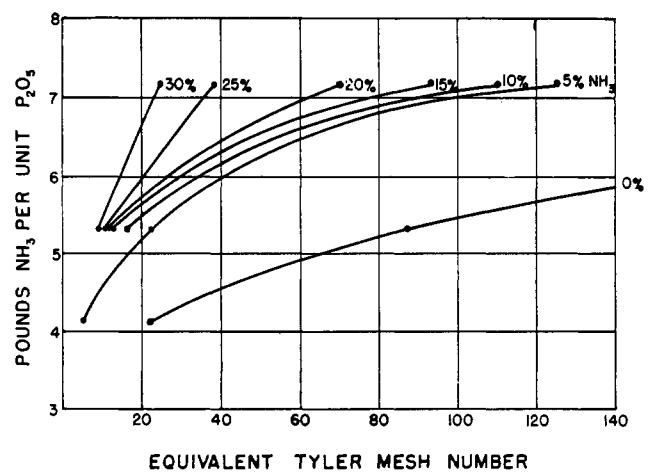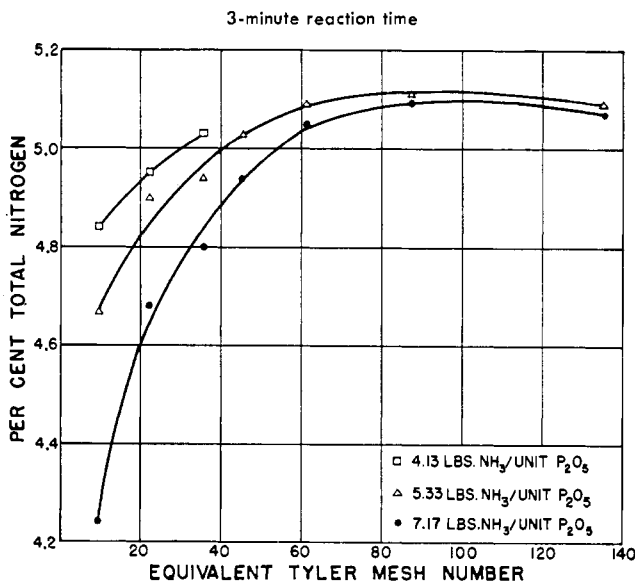**Figure 5. Influence of particle size on nitrogen content of fertilizer product**

3-minute reaction time

EQUIVALENT TYLER MESH NUMBER

Figure 6. Ammoniation rate for given percentages of ammonia by volume in air

2-minute reaction time

limiting sieve number for the −100 fraction was arbitrarily taken as 170, giving an average of 135.)

At the medium rate, 5.33 pounds of ammonia per unit of phosphorus pentoxide, the absorption of ammonia was incomplete at the end of 3 minutes with the 30- to 40-mesh or coarser fractions, but was complete in 3 minutes or less with the 40–50 or finer fractions. Curves for this ammoniation rate are given in Figure 3. At the 4.13-pound rate, even the 16- to 30-mesh particles were fine enough to absorb all of the ammonia in 2 minutes, as shown in Figure 4. These results again demonstrated the correctness of the premise that finer particles absorb ammonia more readily than coarser ones.

The effect of particle size upon the total nitrogen content of the ammoniated product is illustrated in Figure 5. These curves show that fine particle size and low ammoniation rate—i.e., higher phosphorus pentoxide content for the same amount of nitrogen solution—combine to give a high nitrogen content in the product. The curves become almost horizontal as the theoretical 5.1% nitrogen content is attained; otherwise the nitrogen content increases regularly with the mesh number of the superphosphate used. These curves indicate almost complete absorption by the 30- to 40-mesh fraction at the low rate, by the 40- to 50-mesh fraction at the medium rate, and by the 50- to 60-mesh fraction at the high rate.

In Figure 6, which is based on Figures 2 to 4, ammoniation rates at which definite percentages of ammonia would be left in the drum atmosphere at the end of 2 minutes are plotted against equivalent Tyler mesh numbers. The curve for zero ammonia in the air is an approximate indicator of the maximum rate at which each size range could be ammoniated in 2 minutes without loss of ammonia.

The data for 3-minute ammoniations cannot be plotted as readily, but some

estimate can be made of the maximum ammoniation rate for each size without leaving ammonia in the air.

Fraction	Unscreened	−4 +16	−16 +30	−30 +40	−40 +50	−50 +60	−60 +100	−100
Lb. NH_3 per unit P_2O_5	5.7	4.0	5.2	5.7	6.0	6.3	6.6	7.0

The air analysis is evidently a more sensitive indicator than the product analysis. Ten per cent of ammonia in the drum atmosphere represents about 0.51 gram of ammonia, equivalent to 0.42 gram of nitrogen, or only 0.021% of the 2000 grams of product.

If other ammoniation equipment or techniques were used, limiting ammoniation rates would probably differ from those found in this study. These particular limits are thus less important than the general conclusion that fine superphosphate absorbs ammonia better than coarse.

All the superphosphate used in this study, even that designated as original product, had been passed through a 4-mesh sieve. Lumps retained on a 4-mesh sieve would presumably be even poorer absorbers than the 4- to 16-mesh fraction, the coarsest one included in this study.

Acknowledgment

The authors wish to thank H. B. Baird, Jr., for aid in the analytical work.

Literature Cited

(1) Assoc. Offic. Agr. Chemists, Washington, D. C., "Methods of Analysis," 7th ed., 1950.
(2) Datin, R. C., Worthington, E. A., and Poudrier, G. L., *Ind. Eng. Chem.*, **44**, 903–5 (1952).
(3) Frear, G. L., *Comm. Fertilizer*, **81**, No. 3A, 29 (1950).
(4) Kumagai, R., Rapp, H. F., and Hardesty, J. O., *J. Agr. Food Chem.*, **2**, 25–30 (1954).

MINOR PLANT NUTRIENTS

Less-Soluble Boron Compounds for Correcting Boron Nutritional Deficiencies

N. R. PAGE and H. P. COOPER

Agronomy Department, South Carolina Agricultural Experiment Station, Clemson, S. C.

Crop response to annual applications of boron on the coastal plain soils of the southeastern United States is often inconsistent. Fluctuations in the supply of available boron from highly soluble boron compounds is thought to be a predominant reason. Lysimeter studies show that the leaching of moderately soluble boron compounds is less affected by rainfall than leaching of soluble compounds. Availability and crop response to slowly soluble boron compounds are reported. Slowly soluble boron compounds have advantages in preventing toxicity and in the possible elimination of special fertilizer formulations containing boron.

LARGE AREAS in the southeastern section of the United States lack sufficient boron for the maximum production of many crops (1). In the past, these deficiencies have generally been corrected by the application of highly soluble boron compounds.

Most of the soils in this area have a relatively low exchange capacity, are low in organic matter, and are subjected to heavy leaching rains. Under these conditions of soil and rainfall, highly soluble boron compounds may either supply toxic amounts of boron to plants under favorable moisture conditions or be leached by heavy rains to such an extent that an adequate supply of boron is not maintained in the root zone throughout the growing season. These fluctuations in the supply of available boron to the plants are probably a major reason for the often observed inconsistent response to annual applications of boron.

Recently (2, 7, 8) there has been interest in the use of less-soluble boron compounds as a means of minimizing some of the problems encountered in the use of highly soluble sources. By decreasing the seasonal fluctuations in the supply of available boron, these compounds would

Table I. Effect of Three Annual Applications of Equivalent Rates of Colemanite and Fertilizer Borate on Accumulation of Water-Soluble Boron in Soils

Treatments	Water-Soluble Boron, P.P.M.							
	Cecil sl		Dunbar sl		Nosbig fsl		Lakeland s	
	1st year	3rd year	1st year	3rd year	1st year	3rd year	1st year	3rd year
None	0.066	0.057	0.102	0.106	0.083	0.056	0.067	0.053
Colemanite[a]	0.118	0.142	0.162	0.157	0.162	0.130	0.111	0.114
Fertilizer borate[a]	0.147	0.128	0.152	0.143	0.122	0.089	0.085	0.058

[a] Equivalent to 20 pounds per acre of borax.
Soils. Cecil sandy loam, Dunbar sandy loam, Nosbig fine sandy loam, and Lakeland sand.