

ture. This is reasonable since the 4.6% average ammonia content at the start of the run did not permit a large increase of the over-all degree of ammoniation.

Fertilizer Mixtures Ammoniated. A comparison was made between three superphosphate fertilizers at 180° F. using a gas mixture containing 8% ammonia and with a relative humidity of 13%. The results of these runs indicate that the ammoniation characteristics were quite similar. Probably, the results of the present investigation should apply relatively well to all typical superphosphate fertilizers.

An ammoniation run was made at 130° F. using a uniform mixture of closely sized particles that consisted of 55.6% (by weight) of triple superphosphate and 44.4% potassium chloride. No experimental difficulties were experienced, and the ammoniation results (based on the triple superphosphate fertilizer present) were essentially identical to those without potassium chloride. The potassium chloride seemed to act essentially as an inert solid.

Degree of Ammoniation. The degree of ammoniation (the amount of ammonia reacting with a given superphosphate) is obviously affected by a large number of variables. The single most important variable is the length of time of the run. In all cases, even after 120 minutes of operation, ammoniation reactions were still continuing, but at a

relatively low rate. Based on results (7) in which up to several weeks were required before an equilibrium free moisture content could be determined, similar times would probably be required for transfer of the ammonia to the center of each fertilizer particle in order to complete the ammoniation reactions.

Table II indicates the degree of ammoniation obtained in some 120-minute runs. These results probably give quantitative comparisons of the ultimate degree of ammoniation that could readily be obtained when superphosphate fertilizers are contacted with ammonia for long periods of time. The degree of ammoniation increased with increased ammonia concentrations plus increased relative humidities—i.e., with increased free moisture contents for the fertilizer. In general, the degree of ammoniation obtained for these relatively long runs also increased with low temperatures. Higher temperatures might logically be detrimental to high degrees of ammoniation because of decreased ammonia solubility in the liquid phase and because of partial decomposition of the ammoniated phosphates.

Phosphate Reversion. The phosphate analyses of the ammoniated and unammoniated fertilizers of this investigation indicate that only about 1.3 to 1.8% of total P (3 to 4% of total P_2O_5) was converted on a relative basis to a citrate-insoluble form during ammonia-

tion. The reversion that did occur was, however, apparently not dependent on the degree of ammoniation, temperature, or ammonia concentration. The present results are similar to those found earlier in the fluidized-bed reactor at lower temperatures (7).

Acknowledgment

The assistance of P. L. Chueh, E. D. Scholl, O. W. Ford, and C. Loyal W. Swanson and the financial support of Texaco, Inc., are gratefully acknowledged.

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Received for review August 26, 1963. Accepted November 26, 1963. Division of Fertilizer and Soil Chemistry, 145th Meeting, ACS, New York, September 1963.

FERTILIZER TECHNOLOGY

Ammoniation of Triple Superphosphate Fertilizers with Gaseous Ammonia and with Nitrogen Solutions

AMMONIATION of superphosphates is an important operation in the production of high analysis fertilizers, and a continuous rotary-drum reactor similar to that developed by the Tennessee Valley Authority is often employed (9). In this method, the ammonia or nitrogen solution is introduced and distributed under a rolling bed of fertilizer. Frequently, the ammoniated fertilizer is granulated either in the ammoniator or a subsequent rotary-drum granulator.

Previous investigators (4, 5) have also used a rotary-drum reactor to investigate the factors affecting the ammoniation of superphosphate. Temperature, particle

size, and initial moisture content of the fertilizer were found to be important operating variables. More recent investigators (7, 6), using a fluidized-bed reactor, have given further information on the ammoniation reactions between triple superphosphate fertilizers and gaseous ammonia. The ammoniation reactions almost certainly occur in the liquid phase associated with the fertilizer particles. Although considerable work has been done on the ammoniation process, more information is needed to solve the problems of nitrogen losses and phosphate reversion. Both of these losses can occur during or possibly after the ammoniation process (3, 7, 8). These difficulties become more severe with an increased degree of ammoniation—that is, increased amount of ammonia absorbed per unit weight of P_2O_5 .

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In the present ammoniation investigation, a rotary-drum reactor was used. The quantitative effects of several important operating variables were investigated using both gaseous ammonia and nitrogen solutions. The results support the theory that the ammoniation reactions occur in the liquid phase present on the fertilizer particles.

Experimental Details

Experiments with Nitrogen Solutions. Figure 1 illustrates the ammoniation equipment used for runs with nitrogen solutions. The stainless steel rotary-drum reactor was 14 inches in diameter and 6 inches long and could be rotated at 22, 32, or 40 r.p.m. Four inlet or outlet lines constructed of 1/8-inch i.d. stainless steel tubes entered the

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A rotary-drum reactor has been successfully used for the ammoniation of triple superphosphate fertilizers with both anhydrous gaseous ammonia and nitrogen solutions. Temperature, partial pressure of ammonia, free moisture content of the superphosphate fertilizer, particle size, and speed of the drum rotation have all been found to be important operating variables which affect the rate of ammonia absorption by the fertilizer, regardless of the ammoniating agent used. Phosphate reversion was less than 3% for all of the runs in the present investigation. Several improvements in reactor design and operation are suggested.

Table I. Phosphate Analyses of Fertilizers

Run Na.	Super-phosphate Type	Temp., °F.		Degree of Ammoniation, Lb. NH ₃ per Unit P ₂ O ₅	P ₂ O ₅ in Superphosphate, %			Total P (P ₂ O ₅)	Availability, %
		Initial	Final		Water-soluble	Citrate-soluble	Citrate-insoluble		
...	A	0.00	35.1	12.0	0.9	20.9 (47.7)	98.1
...	B	0.00	41.2	6.2	0.3	20.7 (47.0)	99.2
7	A	85	135	3.83	18.2	13.4	1.5	14.9 (33.9)	95.6
9	A	70	139	2.48	19.9	16.5	0.7	17.0 (38.7)	98.1
8	B	75	136	2.48	22.4	14.2	1.4	16.9 (38.4)	96.3
11	B	93	183	4.48	17.5	14.0	0.9	14.9 (33.9)	97.3
13	B	87	183	3.23	18.8	16.4	0.7	15.6 (35.4)	98.0
14	B	88	200	3.73	17.3	14.4	0.9	14.3 (32.6)	97.1

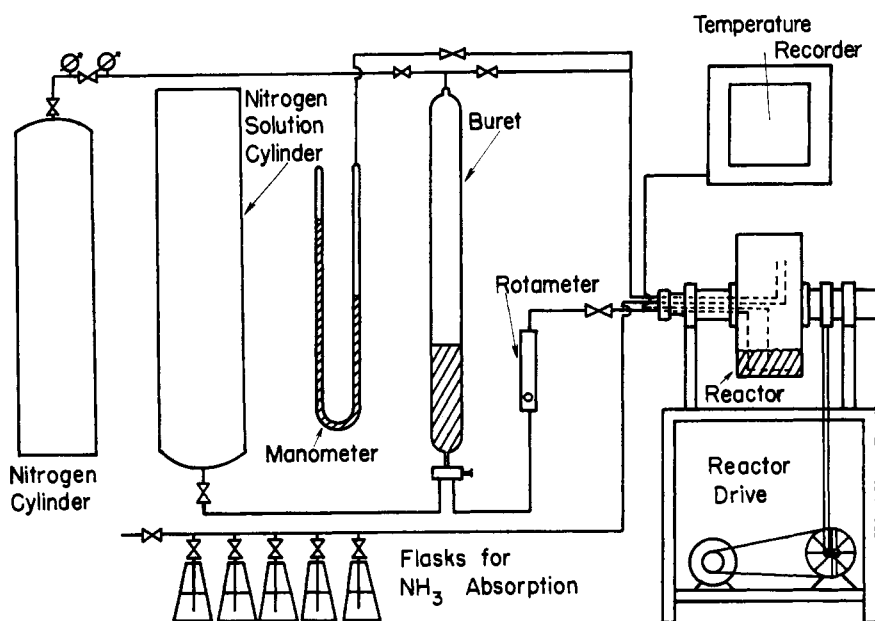


Figure 1. Schematic diagram of ammoniation equipment

reactor at its axis through a gastight Teflon seal. The first tube supplied the nitrogen solutions to the drum. A distributor was connected to the end of this tube and was located close to the bottom of the drum, about 1.5 or 2.5 inches below the surface of the fertilizer. The distributor was constructed of a short length of 1/8-inch stainless steel tubing, closed at one end and with several 1/16-inch holes drilled in it. The second tube extended into the gas space of the reactor, and on the outside it was connected to a mercury-filled manometer. The third line also extended into the gas space of the reactor and served as an exhaust. It was connected to a series of flasks containing sulfuric acid, which were used to absorb

exhaust ammonia from the reactor. The fourth line entering the reactor served as a thermocouple well, and it was positioned below the surface of the fertilizer in the reactor. The flow rate of the nitrogen solution to the reactor was measured by means of a ball-type rotameter. The total amount of nitrogen solution to be used during a run was measured in a buret. In most runs, no attempt was made to control the temperature in the reactor. A Bunsen burner was used in two runs to preheat the reactor plus contents to about 200° F. In addition, the bottom portion of the drum was immersed in a water bath in several runs.

Two types of triple superphosphate fertilizer were used. The first, type A,

Table II. Analyses of Nitrogen Solutions

Composition	Weight, %	
	Solution 1	Solution 2
Free NH ₃	18.2	23.7
Ammonium nitrate	75.2	71.3
Total nitrogen	41.4	44.5
Water	6.6	5.0

was a hard, granular product produced from wet-process phosphoric acid. The second (type B) was a soft, porous type produced from wet-process phosphoric acid. Type B is generally called "run of the pile" material in the industry and is normally used for commercial ammoniation. Table I gives the phosphate analyses of these two fertilizers. Two nitrogen solutions were used, and the analyses of these are shown in Table II.

The triple superphosphate which was to be used was generally sieved to obtain a -8-mesh fraction with a Tyler standard sieve; this fraction contained an appreciable quantity of particles that were -200 mesh. A calculated amount of water was added and carefully mixed with the fertilizer to obtain the desired free moisture content. The batch was then stored at room temperature in a wide-mouthed bottle with the lid tightly closed for at least 24 hours prior to the run. Just before the run, the sample was poured from the bottle, any lumps were broken, and the whole batch was carefully mixed to ensure uniform free flowing particles. The reactor was then loaded with the superphosphate through a small opening on the periphery of the reactor. This opening was then sealed by a small door to produce an essentially

Table III. Ammonia Losses in Runs where Nitrogen Solution 2 and Type B Superphosphate Were Used

Run No.	Raw Material		Average Feed Rate for Nitrogen Solution, Cc. per Min.	Temp., °F.		Reactor Pressure, Inches Hg	% Total NH ₃ Feed Lost after Following Lb. NH ₃ Added per Unit P ₂ O ₅				Fertilizer Sticking to Reactor Drum, %
	Type, mesh	Initial moisture, %		Initial	Final		2.0	3.125	3.7	4.27	
16	-10 ^a	4.0	300	88	216	0-4	0.07	0.08	0.12	0.97	20
17	-10	4.0	550	87	207	0-10	0.12	0.18	0.37	2.53	55
STOPCOCKS WITH LARGER OPENINGS INSTALLED IN LAST TWO ABSORPTION FLASKS											
18	-10	1.7	265	204	265	0-4	1.45	1.13	1.53	2.92	50
19	-10	0.5	271	85	224	0-6 and -6-4.5	2.27	1.44	1.39	3.28	40
20	-10	8.0	295	83	208	0-4	0.04	0.10	0.42	1.22	60
21	-10	3.9	280	89	218	0-4	0.02	0.08	0.65	3.36	50
22	-10 plus 41.5% KCl	2.0	278	87	172	0-9	0.03	0.15	0.97	4.40	5
23	+10	4.6	270	90	188	0-14	0.89	3.61	7.3	15.2	5
24	-10	1.3	270	203	274	0-5	0-35	0-85	2.31	...	5

^a -10 mesh material contains 18.6% of -10+28 mesh; 29.5% of -28+48 mesh; 34.0% of -48+100 mesh; and 17.9% of -100 mesh fractions.

gastight reactor. The reactor was then rotated.

For runs using nitrogen solutions, no attempt was made to flush the air out of the reactor. The buret was filled with the desired amount of solution, and the beginning of the run was considered to have occurred as soon as the flow of nitrogen solution was started. The flow rate was quickly adjusted to a constant rate. In general, these runs were so short, requiring only 1.5 to 5 minutes, that no attempt was made to obtain fertilizer samples during the run. However, at predetermined levels of nitrogen solution in the buret, the flow of exhaust gases from the reactor was switched to a different sulfuric acid flask.

The pressure was read at frequent intervals during the run. After the flow of nitrogen solution was stopped, the reactor exit gases were allowed to flow into the last absorption flask until the pressure inside the reactor returned to atmospheric pressure; about 10 seconds were usually required. The reactor drum was rotated for another 3 minutes, and the outside of the drum was lightly tapped to disengage any fertilizer which may have been loosely stuck to the drum walls. The drum was then emptied of all of the loose fertilizer. A rough estimate was made of the amount of fertilizer still stuck to the walls. After the drum was completely emptied, the large lumps of fertilizer were crushed, and the fertilizer was mixed well and a sample taken. The amount of ammonia absorbed in each sulfuric acid flask was determined by back-titration with a standard caustic solution.

Experiments with Gaseous Ammonia. The reactor system for the ammonia runs was identical to that for the other runs except for modifications in the connecting lines. Ammonia metered by the rotameter entered the reactor through the first tube. Ammonia could

also be introduced into the gas space of the reactor through the second tube. Since the third tube still acted as an exhaust, air inside the reactor could then be flushed out of the gas space. The bottom portion of the reactor was sometimes immersed in a water bath for temperature control.

Five-pound batches of fertilizer (type A) were used for each run. For most of the runs, some of the air initially in the reactor was first flushed out. During flushing, the exhaust gases were passed through a sulfuric acid flask to absorb all ammonia present, and the unabsorbed air was vented. At the end of the flushing period, the gas flow to the sulfuric acid flask was stopped, and a gas sample was drawn to an Orsat analyzer to determine the ammonia concentration in the gas phase of the reactor.

The run was started by admitting ammonia under the bed of superphosphate through the distributor and beginning the rotation of the drum. Almost immediately the pressure inside the reactor decreased below atmospheric pressure because the initial reaction rate was fast and because the exhaust line was closed. The ammonia flow rate was increased until the system pressure was approximately atmospheric, and for the remainder of the run, the rate was frequently adjusted to maintain a pressure inside the reactor of approximately 0-1.0 inch of mercury above atmospheric.

Fertilizer samples were taken several times during the run, which usually lasted at least 1 hour. In sampling, the reactor was stopped for about 40 to 50 seconds with the sample hole near the bottom. The sample was allowed to flow into a weighing bottle which was then closed. The sample hole was then closed, and the rotation of the drum started again. Gas samples from the reactor were also analyzed several times during the run.

Analytical Procedures. Fertilizer samples were stored in glass-stoppered bottles for at least 2 days before analyses. Samples were analyzed for water-soluble, citrate-soluble, and citrate-insoluble P₂O₅ by standard A.O.A.C. techniques (2). Nitrogen analyses were performed using the standard Kjeldahl technique. Free moisture content was determined by weighing the samples before and after exposure to a vacuum for at least 48 hours.

Results

Experiments with Nitrogen Solutions. Preliminary experiments indicated that the temperature increased rapidly and significantly (75°-125° F.) whenever the nitrogen solution was added to either type A or B triple superphosphate. In addition, the pressure increased steadily during the run. Part of the increased pressure was caused by the higher temperatures of the gas phase. However, the higher pressure resulted more importantly because part of the ammonia in the nitrogen solutions flashed off into the gas phase. The volume of gases that exhausted through the vent lines to an absorber flask was of course dependent on the total pressure in the reactor plus the dimensions of the exhaust lines. The amount of ammonia exhausted was dependent on the composition of the gas phase, which initially was pure air but toward the end of the run was primarily ammonia. As large quantities of nitrogen solution were added to the fertilizer, the total pressure in the reactor increased, and the amount of ammonia lost or vented increased rapidly especially after about 3.5 to 4.0 pounds of ammonia had been added per unit P₂O₅. The present results, although quantitative for the reactor used, indicate qualitatively what would happen for similar reactors. Ammonia losses de-

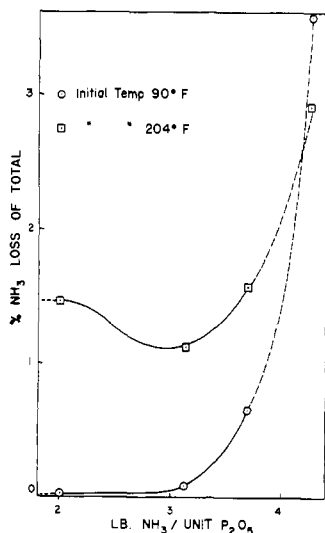


Figure 2. Effect of initial temperature on ammoniation

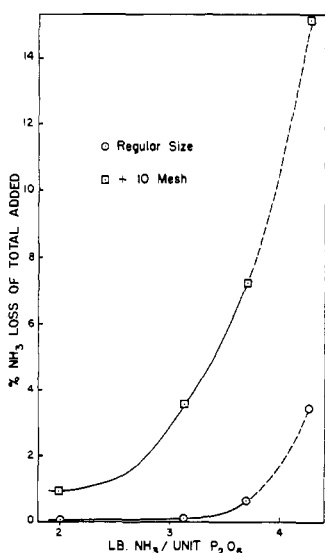


Figure 3. Effect of particle size on ammoniation

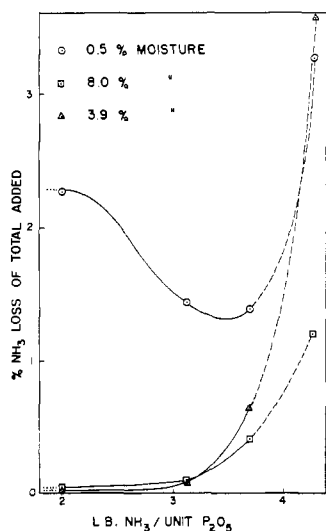


Figure 4. Effect of initial moisture on ammoniation

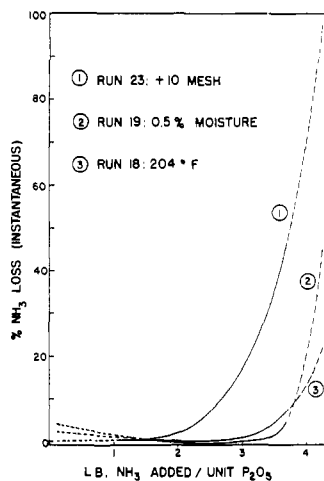


Figure 5. Instantaneous ammonia loss during ammoniation

pended on the pressure drop through the exhaust lines and undoubtedly on the depth of the fertilizer bed in the drum. In commercial ammoniators, there are generally no significant pressure differentials between the drum and the surroundings; however, the depth of the bed in the drum is considerably greater than in the present unit.

In all runs, the fertilizer remained relatively free flowing until sufficient nitrogen solution had been added to approximate 3.75 to 4.00 pounds of ammonia per unit P_2O_5 . In one run, approximately 20% more nitrogen solution was added, and a considerable number of fertilizer balls of approximately $\frac{3}{8}$ -inch diameter were formed. In addition, significant superphosphate stuck to the walls of the reactor. The fertilizer which stuck to the walls of the reactor when analyzed had a somewhat lower nitrogen content than that which remained free flowing. The free flowing fertilizers immediately after most runs gave the appearance of moist sand. In several other runs, rather significant amounts of fertilizer also stuck to walls of the reactor.

The following variables were examined to determine their effect on ammonia losses when nitrogen solution No. 2 was added to Type B fertilizer: degree of ammoniation, up to 4.27 pounds of ammonia per unit P_2O_5 ; nitrogen solutions feed rates, 46 to 550 ml. per minute; initial temperature, 83° to 204° F.; particle size, -10 mesh fraction and +10 mesh fraction; and initial moisture, 0.5 to 8%. Table III indicates the ammonia losses so determined, and Table I reports the phosphate analyses for several of the ammoniated fertilizers.

DEGREE OF AMMONIATION. The fraction of entering ammonia that was lost (or vented) increased in all cases except two as the amount of nitrogen solution added to the reactor increased. In

these two exceptions (runs 18 and 19) which used a low-moisture fertilizer, ammonia losses were higher in the initial stages of ammoniation than in the intermediate stages. Apparently in these cases, the nitrogen solutions initially did not have a chance to mix with any moisture phase present on the superphosphate particle.

NITROGEN SOLUTION FEED RATES. The rate of addition of the nitrogen solution to the triple superphosphate fertilizer was found to have only a slight effect on the ammonia losses when the feed rate varied from 46 to 300 ml. per minute. A slight increase in the ammonia losses perhaps occurred as the feed rate was increased. With nitrogen solution No. 2, ammonia loss increased significantly as the feed rate increased from 300 to 550 ml. per minute (runs 16 and 17). A larger fraction of ammonia flashing is to be expected when the rate of addition of nitrogen solution was increased, since there would be poorer mixing of the nitrogen solution and the fertilizer particles. A similar but smaller difference was noted when nitrogen solution No. 1 was used; however this solution had a lower ammonia concentration so that less flashing would be expected.

The importance of the resistances to flow in the exhaust lines is demonstrated by comparing runs 16 and 21. Stopcocks with larger openings were used for the last two flasks of run 21, and as a result there was less resistance to flow and more ammonia was absorbed in these two flasks.

INITIAL TEMPERATURE. The results of runs 18 and 21 in which the initial temperature was varied from 90° to 204° F. are shown in Figure 2. As was expected, the ammonia losses at 204° F. were initially considerably higher than those at 90° F. The higher temperature acted to flash off more of the ammonia of the nitrogen solution as it entered the reactor, and also dried the triple superphosphate so that its initial moisture content was low. Apparently until the fertilizer was wet and the phosphate salts had gone into solution, the ammonia could not readily react with these salts. As a result, the ammonia losses were initially high and then passed through a minimum before they again increased at high degrees of ammoniation. The total loss of ammonia in the 204° F. run eventually became slightly less than that in the 90° F. run. Whether this finding is significant is not known.

Run 24 was to be a repeat of run 18; however, the ammonia losses for run 24 did not pass through a minimum. The reason for this difference is not known. Apparently the factor(s) causing the difference is sensitive to small changes in the operating variables. Possibly the distributor for the nitrogen solution had shifted positions in the reactor. For

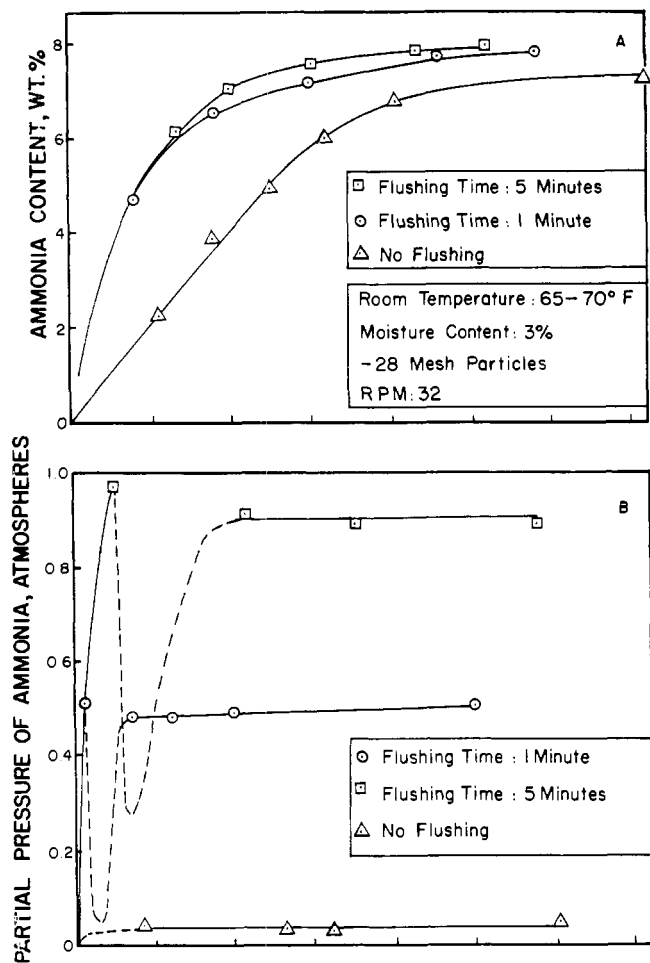


Figure 6. Effect of flushing time on (A) ammonia pickup, (B) partial pressure of ammonia, and (C) temperature

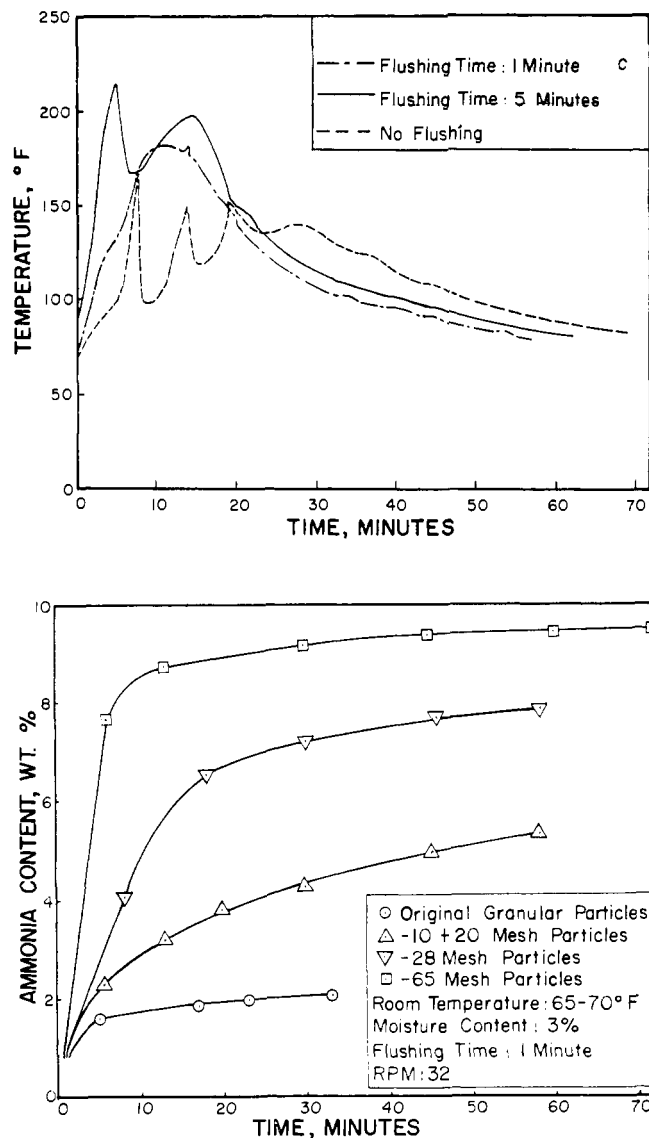


Figure 7. Effect of particle size on ammoniation

example, a deeper depth of the distributor in the bed had earlier been found to result in lower ammonia losses.

PARTICLE SIZE. Figure 3 indicates that ammonia losses with +10 mesh particles (run 23) were approximately four to five times as great as those with -10 mesh (regular) particles (run 21). Diffusion of the ammonia to the center of the fertilizer particles in these ammoniation runs was obviously of extreme importance just as it was in runs with gaseous ammonia.

INITIAL MOISTURE. The importance of the initial free moisture content of the superphosphate was noted in runs 19, 20, and 21. For moisture contents of 4 to 8%, there were no large differences in the amount of ammonia lost until 3 or more pounds of ammonia were added per unit of P_2O_5 (Figure 4). However, when the pounds of ammonia added per unit of P_2O_5 were higher, appreciably less ammonia was lost for an 8% moisture fertilizer. The results with dry (0.5% free moisture) superphosphate fertilizer indicated high initial ammonia losses; the minimum losses occurred at approximately 3.5 pounds of ammonia added per unit of P_2O_5 . The results of this run hence are similar to those of

high temperature run. These results support the hypothesis that the ammoniation reaction occurs in the liquid phase.

MISCELLANEOUS VARIABLES. No significant differences in the ammoniating characteristics of type A or type B fertilizers were noted in several comparative runs. Run 22 was made in which potassium chloride was added to the superphosphate fertilizer. This run gave increased ammonia losses at all levels of nitrogen solution added. The potassium chloride apparently acted as an inert, and since the nitrogen solution was partially wetting the potassium chloride, there was less available surface for reaction of the ammonia with the phosphate ions. This run then indicates a possible advantage when preparing mixed fertilizers in mixing the potassium chloride with the superphosphate after ammoniation rather than before.

The somewhat higher ammonia losses

for nitrogen solution 2 were undoubtedly caused by the fact that it contained a higher percentage of ammonia and had a higher partial pressure than nitrogen solution 1.

Several runs were also made to evaluate the effect of equipment design on the ammonia losses. The use of flights inside the reactor tended to increase the amount of fertilizer sticking to the inner curved surface of the drum especially after the addition of relatively large amounts of nitrogen solution. As a result, higher ammonia losses were obtained in those runs than in comparable runs in which baffles were not used. Initially no insulation was used on the reactor drum. The use of insulation resulted in a general increase in the reactor temperature. Although no direct comparison was made for runs with and without insulation, the higher temperature seemed to produce slightly higher ammonia losses.

INSTANTANEOUS AMMONIA LOSSES. The ammonia losses occurring for various ranges of ammoniation were calculated for runs 18, 19, and 23. The results of Table III were used to differentiate graphically and to estimate the instantaneous loss of ammonia as a function of the degree of ammoniation. Figure 5 indicates that the instantaneous ammonia losses became very high for these three runs as the degree of ammoniation approached 4 pounds ammonia per unit P_2O_5 . The instantaneous loss for run 23 approached 100%.

ANALYTICAL RESULTS. The phosphate analyses for those runs using nitrogen solutions are presented in Table I. A loss of phosphate availability was generally low, in the range of 2 to 3%, and did not appear to be a function of any of the variables studied in the present investigation. In several runs using nitrogen solutions, nitrogen balances were calculated to be $\pm 1.7\%$, which is apparently within experimental accuracy.

Experiments with Ammonia. After the superphosphate was loaded to the drum reactor, flow of ammonia to the reactor was started. In most runs, the ammonia was initially introduced to the gas space above the stationary bed of superphosphate to flush air from the system. The partial pressure of ammonia was about 0.5 atm.—i.e., 50% ammonia and 50% air—after 1 minute of flushing, and 0.95 atm. after 5 minutes. During this flushing period, obviously some ammoniation and drying was occurring at and near the top surface of superphosphate bed; it is thought that such ammoniation and drying were small though. At the end of the flushing period, the exit line was closed, ammonia flow was switched to the distributor below the surface of the bed, and rotation of the reactor was started immediately.

Figure 6, *a*, *b*, and *c*, indicates how time of flushing affected ammonia pickup, partial pressure of ammonia, and temperature, respectively, during the course of a run. In these figures, zero time indicates when the flushing of air from the reactor was started. As soon as the reactor was rotated for runs with 1- or 5-minute flushing periods, the total pressure in the reactor dropped well below atmosphere because of the high initial rate of ammonia take-up by the superphosphate fertilizer. The ammonia flow was maintained at a maximum rate as determined by the rotameter, but several minutes were required before sufficient ammonia could be introduced into the reactor for the total pressure inside the reactor to return to approximately 1 atm. The authors assumed that the partial pressure of air inside the reactor remained constant during this initial period of fast ammoniation rates, and the partial pressure of the ammonia was calculated by sub-

tracting the partial pressure of the air from the measured total pressure. Once the total pressure had returned to atmospheric, the gas inside the reactor was analyzed. The slightly lower compositions of ammonia indicated that there had been either small air leakage in the initial periods of reaction when the reactor was at subatmospheric pressures or an inert gas (probably air) was desorbed from the fertilizer. Figure 6*c* indicates, as would be expected, that in the runs with faster rates of ammoniation, the resulting temperatures were higher. The rate of ammonia pickup in the present apparatus is comparable to that in a fluidized bed reactor (7).

Relatively long times were required to complete the ammoniation reaction. At the end of 1 hour, the degree of ammoniation obtained had frequently approached 8% ammonia in the ammoniated product—i.e., almost 4 pounds of ammonia per unit of available P_2O_5 . In one case, a -28 mesh fertilizer with an initial moisture content of 5% was allowed to remain in contact with ammonia for 48 hours. In the period from 2 to 48 hours, the degree of ammoniation increased from 8.4 to 9.8% ammonia. No significant change had occurred during this time in the content of citrate-insoluble P_2O_5 , even in the case of a run at 160° F.

The effect of mixing on the rate of ammoniation was demonstrated by runs at 22 and 44 r.p.m. A slightly higher rate of ammoniation occurred at the higher r.p.m. A relatively small difference in the rate of ammonia pickup was also noted for fertilizer stored for different lengths of time before use. In one case, the fertilizer containing 3% moisture was stored for 1 day and, in the second case, for 30 days prior to use. The longer period of storage undoubtedly allowed more uniform distribution of the moisture throughout the fertilizer and the rate of ammoniation was slightly higher.

Although the effect of particle size in ammoniation has been studied by previous investigators (7, 5), this variable was also investigated here in more detail. Figure 7 indicates that the original granular material, which was relatively coarse in size, picked up the ammonia much slower than material finer particles, especially the -65-mesh particles. One of the significant resistances to ammoniation was obviously the transfer of the ammonia toward the interior of the fertilizer particle. Rapid ammoniation then requires a small particle in which the transfer resistances will be minimized.

The present investigation indicated that the rate of ammonia pickup was slightly higher as the initial free moisture content increased from 3 to 10%. Increasing the temperature of the reaction from approximately room conditions to

about 160° F. also increased the rate of ammoniation. Similar results had been noted previously by other investigators (7, 5).

Phosphate analyses of all the products obtained in runs using gaseous ammonia indicate that the loss of availability of phosphate was less than 2 to 3% in most cases. Phosphate reversion, hence, was not a problem in any of the runs made here, and apparently it would not be a serious factor in ammoniation such as the type employed here. Material balances were made of the entering ammonia versus the ammonia reacted plus that left or exhausted from the reactor. In general, over 99% of the entering ammonia could be accounted for.

Discussion

The results of this investigation are in relatively good agreement when compared with previous results (7, 4, 5). More information has been gained, however, particularly regarding the effect of the low moisture content of the superphosphate, the effect of large particle sizes, and temperature.

The results of this investigation also support the fact that all ammoniation reactions occur in a liquid phase. The following factors are important for the progress of the ammoniation reaction regardless of whether the ammoniation is with gaseous ammonia or with nitrogen solutions:

Uniform distribution of water (or moisture) throughout the fertilizer particle.

Solution of ammonia in the liquid phase. In the case of nitrogen solutions, they must mix to some extent at least with the adsorbed solution of the fertilizer particle.

Solution of unammoniated salts in the liquid phase. Since more liquid phase is available in the case of nitrogen solutions, the rate of solution of the unammoniated salts in the liquid phase should be faster than when gaseous ammonia is used as the ammoniating agent.

Diffusion of ions through the liquid phase.

Ammoniation reactions in the liquid phase. Presumably these reactions will be fast and require little energy of activation.

Diffusion of ammoniated salts back to the solid surface.

Crystallization of ammoniated salts on the solid surface.

Undoubtedly more than one of the above steps could be rate controlling, and the extent to which any of the above steps controls the reaction probably would vary with the operating variables and with the degree of ammoniation.

Results of the present investigation with nitrogen solution should be helpful to the fertilizer industry in designing better reactors. Factors which improve the mixing of the granular particles and

the nitrogen solutions would be beneficial in promoting a more uniform reaction, and would tend to promote faster reactions. The use of baffles may not always be warranted.

Operating variables which should be carefully considered in designing commercial reactors include feed rate, particle size, and free moisture content of the superphosphate. Since ammoniation reactions are hindered by large particle sizes, it is desirable from an ammonia reaction standpoint to minimize granulation during ammoniation. The addition of more than 3.7 pounds of ammonia per unit of P_2O_5 will obviously be difficult if low ammonia losses are to be obtained. Good ammonia absorption might be obtained, however, with some type of counter-current flow of the fertilizer particles with the nitrogen solution. In this

respect, the depth of the distributor below the surface of the phosphate fertilizer would be important. Special consideration of these factors may be necessary at higher feed rates of nitrogen solutions to the fertilizer, the use of nitrogen solutions with higher ammonia vapor pressures, or higher temperatures.

Acknowledgment

Texaco, Inc., sponsored this investigation. C. Loyal W. Swanson of that company offered valuable advice.

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Received for review September 20, 1963.
Accepted December 12, 1963. Division of Fertilizer and Soil Chemistry, 145th Meeting, ACS, New York, September 1963.

FERTILIZER TECHNOLOGY

Segregation Studies of Dry Blended Fertilizer

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A study of the mechanism of segregation in dry blended fertilizers has resulted in the mathematical development of a "friction factor" to predict segregation. The mechanics of determining the friction factor by measurement of the angle of repose of free, conical piles of fertilizer ingredients are discussed; and the use of ingredients with matched friction factors are shown by results of experiments to reduce segregation. For example, the almost complete failure of a blend made from materials of random friction factor to meet chemical and physical tolerances is compared to the marked improvement of a blend made from selected materials. Examples of the variation of friction factor with particle size are given for representative materials.

PHYSICALLY blended fertilizers applied in bulk by truck spreader are an economical and widely used form of plant food. However, after spreading, various components of the mixture do not appear in the same ratio at different points in the field. The raw materials have been physically blended, loaded, transported, and spread; and the deficiencies connected with one or more of these operations will show up in the field. In this paper, the segregating mechanisms are analyzed and the conclusions applied to the improvement of the loading and transporting operations, and assistance in raw material specification determination.

A mixture of materials can be con-

sidered absolutely nongregated only where a crystalline type of structure exists and an elemental pattern is repeated throughout. This situation is impossible in physical mixtures; hence a complete blend is described as a mixture where, for a reasonable volume of material sampled, the chemical composition is independent of the point sampled. The sample size is arbitrary; therefore, the numbers assigned to measure segregation are arbitrary. From taking the total volume of blend (segregation = 0) to taking a unique particle (segregation = 100), there is a complete range of values.

The particles of a blend segregate because the gravitational, vibratory, and resistive forces acting upon them are of different values. The gravitational and vibratory forces relate to the particle's mass, but the resistive depends also on the particle's shape, composition, and surrounding media. This is illus-

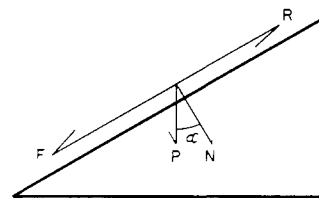


Figure 1. Forces acting on a particle located on an inclined plane

P , gravitational force; α , angle of inclination of the plane; N , component of P normal to the plane; F , component of P parallel to the plane; and R , resistive force

trated by observing the segregation caused by dropping material onto a conical pile and studying the behavior of a particle sliding down the pile (the particle, if rolling, always reaches equilibrium by sliding at the last part of its movement). The gravitational force, P , acting on a particle situated on an inclined surface, can be resolved into

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