Ammoniation of Fluidized Triple Superphosphate Fertilizers

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A fluidized bed reactor is a useful experimental tool for the ammoniation of triple superphosphate fertilizers at temperatures up to 300° F. The degree of ammoniation was found to increase at higher ammonia concentrations and relative humidities in the gas phase. Initial reaction rates increased with increasing temperature, ammonia concentration, and relative humidity. The loss of availability of P_2O_5 was always very small (maximum of 2.4%). A fluidized bed reactor can be operated to ammoniate triple superphosphates to 7 to 8.5% ammonia by weight in 10 to 15 minutes or less under easily controlled conditions.

The importance of several operating variables for the ammoniation of superphosphate fertilizers has been previously discussed by several investigators (*1, 2, 5*). Further information at high temperatures is desirable since high localized temperatures sometimes occur in rotary-drum reactors, such as those developed by TVA (*6*). High temperatures may be a factor in phosphate reversion plus nitrogen losses; however, the time that the fertilizers are at such temperatures in the reactor may be rather short.

A fluidized bed reactor has been used recently (*1, 4*) for the ammoniation of granular superphosphate fertilizers with ammonia. A fluidized bed allowed relatively good temperature control for batch ammoniations. If this type of reactor were used on a continuous flow basis, even more uniform temperatures could undoubtedly be maintained. Previous investigations in such a reactor were limited to temperatures ranging from about 80° to 180° F. Higher initial rates of ammoniation occurred as a result of higher temperatures, higher relative humidities of the fluidizing gas, smaller particle sizes, and increased ammonia concentrations. Less than 2% P (4% P_2O_5) was usually converted to the citrate-insoluble form. Relative humidity in the gas stream was kept at about 30% to maintain a significant ammoniation reaction at 130° F. Previous results (*1*) clearly indicate that the ammoniation reaction occurs in the liquid water phase present on the surface of the particles. The ammoniated salts then crystallize from this liquid phase (*3*).

The present investigation was made as a continuation of the earlier investigations with the fluidized bed reactor. Temperatures up to 300° F. were employed in the present study, and gas mixtures with higher ammonia concentrations and higher relative humidities were used.

Experimental Procedures

The apparatus used was similar to that built earlier (*1*), but it was modified so that temperatures up to 300° F. were obtainable in the reactor. A clear mineral oil was heated to high temperatures in an auxiliary bath, and this oil was then circulated through the jacket surrounding the reactor. As in the previous investigation (*1*), the air, steam, and ammonia were each metered, heated in a constant-temperature bath, mixed, and passed through a fritted disk to fluidize the fertilizer particles in the glass reactor.

Three triple superphosphates were used in this work. One was manufactured using phosphoric acid of the electric furnace process, and the other two using phosphoric acid of the sulfuric acid process. One of the latter fertilizers had also been used earlier (*1*). All three fertilizers had similar analyses, and contained approximately 22% P (50% available P_2O_5). The superphosphate fertilizers were crushed and then screened to obtain a fraction between 20 and 28 Tyler standard mesh, which was used in all the experiments of this work.

Relative humidities were calculated by using the ideal-gas law approximation to find the partial pressure of the water in the fluidizing gases, and dividing by the vapor pressure of pure water at the same temperature. Initial moisture contents of the phosphate particles were obtained by preconditioning the fertilizer for about 90 minutes with a fluidizing stream of air of the same relative humidity as that used during the run. A batch size of 250 grams of fertilizer and a total gas flow rate of 148 standard cubic feet per minute per square foot of cross-sectional area were used.

The analytical procedures employed for nitrogen and phosphorus were those specified by the Association of Official Agricultural Chemists. Nitrogen analyses are considered accurate to about ±0.1% based on ammonia. The phosphates were analyzed by the Purdue Biochemistry Department; the experimental uncertainty was estimated to be ±0.5% P_2O_5 for the soluble and total fractions and ±0.1% P_2O_5 for the citrate-insoluble fraction. The free moisture of fertilizers was determined by placing the samples in a vacuum dessicator over magnesium perchlorate for 4 days. These analyses are considered to be accurate to within ±0.5% on an absolute basis.

Ammoniation runs were made at various combinations of the following conditions for up to 180 minutes: temperatures—130°, 180°, 250°, and 300° F.; relative humidity of gas mixtures—0 to 55%; and ammonia concentration of gas mixture—3, 8, 15, 30, and 56%. Variations in the operating conditions caused some uncertainty in the data reported in this work. The ammonia concentrations and the humidities of the fluidizing gas were estimated to be

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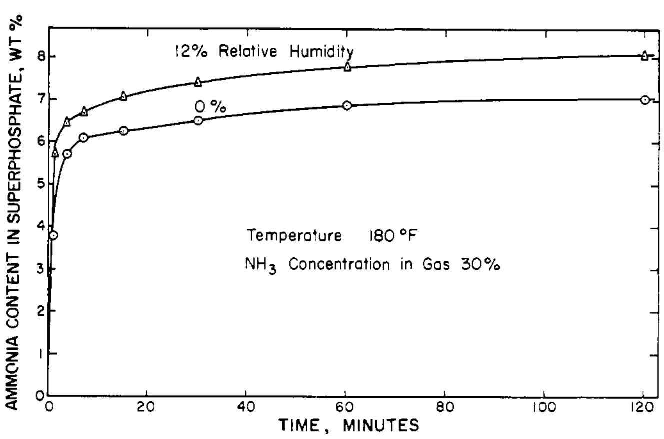

Figure 1. Effect of relative humidity of gas phase on ammoniation of triple superphosphate at 180° F.

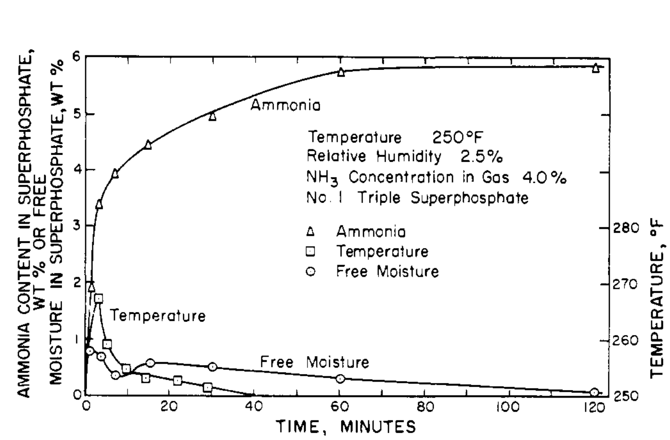

Figure 2. Ammonia pickup, temperature, and free moisture during run at 250° F.

accurate to within 2 and 10%, respectively, on a relative basis.

Results and Discussion

Free Moisture Content of Fertilizer. The present investigation clearly indicates that relatively dry fertilizers can be ammoniated at temperatures from 180° to 300° F. Earlier results (*7*) had shown that no significant ammoniation would occur at 130° F. unless some free moisture was initially present on the fertilizer. Conditioning of the fertilizers with dry gases for at least 1 hour resulted in fertilizers with low moisture contents; however, some moisture was undoubtedly still present especially in the interior of the particles. When the ammonia and fertilizer were initially contacted in the fluidized bed, significant ammoniation reactions occurred as indicated by sharp increases in the temperature. For runs at 180° F., a peak temperature ranging from 224° to 264° F. was obtained during the first 2 to 3 minutes of the run. The temperature rises were roughly proportional to the rates of ammoniation. The 250° F. runs had peak temperatures up to 325° F., and the 300° F. run peaked at 351° F. Within about 7 minutes after the start of the run, the temperature had leveled off to within about ±1° F. of the desired operating temperature; this temperature was maintained for the remainder of the run.

During the initial stages of the ammoniation run, the fertilizer particles generally appeared quite moist. The particles sometimes became so moist and sticky that serious agglomeration occurred, stopping the fluidization. If fluidization stopped, the run was discontinued and the fertilizer quickly removed from the reactor; otherwise the fertilizer tended to "set up" so that removal from the reactor was difficult. The initial ammoniation reaction at 180° F. or higher apparently released sufficient water of hydration to create a liquid phase for the succeeding ammoniation reactions.

The free moisture content of the fertilizer was related to the relative humidity of the fluidizing gas (*7*). Figure 1 shows the results for two runs at 180° F. with a gas containing 30% ammonia. Each run had a similar initial rate of ammoniation although the relative humidities varied from 0 to 12%. After 3 to 5 minutes, however, the degree of ammoniation for the run with 12% humidity became significantly greater than that for the other run. A series of runs was also made at 180° F. in which the gas mixture contained 8% ammonia and the relative humidities varied from 0 to 55%. Results of this latter series of runs also indicate, as did previous comparable results (*7*), that increased moisture content promotes a higher degree of ammoniation. Decreasing the ammonia concentration from 30 to 8% in these two series of runs decreased the degree of ammoniation.

Figure 2 shows the degree of ammoniation (expressed as weight per cent ammonia in the dried ammoniated material), the free moisture content, and the temperature in the fluidized bed, respectively, as a function of time for a run at 250° F. The rate of ammoniation (amount of ammonia absorbed per unit weight of superphosphate per unit time) was highest at the start of the reaction. This high rate caused a rapid increase in the ammonia content, a sharp initial temperature rise, and also a sharp initial increase in the free moisture content. The free moisture content then decreased slowly for the remainder of the run.

At 250° F., the agglomeration of the fertilizer particles during the initial stages of the reaction limited operation to relatively low concentrations of ammonia in the gas plus low relative humidities. The actual concentrations of steam in the gas at higher temperatures were often high even though the relative humidities were low. Two runs at 250° F. with a 4% ammonia concentration indicated that changing the relative humidity from 0 to 2.5% had little effect on the ammoniation as seen in Figure 3. Actually the run with 0% humidity indicated a higher initial rate of reaction probably because the liquid phase formed offered less resistance to mass transfer of the ammonia in solution. Figures 1 and 3 indicate that the degrees of ammoniation at the ends of the runs were significantly higher for the 180° F. runs than for the 250° F. runs.

Ammonia Concentration in Fluidizing Gas Mixture. Two series of runs were made to determine the effect of the ammonia concentration in the fluidizing gas mixture. At 180° F. and with a relative humidity of 12%, both the rates of reaction and the degrees of ammoniation for 120-minute runs increased as the ammonia concentration was raised from 8 to 30% ammonia. The degree of ammoniation varied from 6.3 to 8.1%. At 250° F. and with a relative humidity of 0%, increasing the concentration of ammonia from 4 to 8% had a similar significant effect on the rate; the degree of ammoniation increased from 5.6 to 6.7%.

Limits of Fluidization. When the ammonia concentration was held constant during the entire run, the approximate limits of fluidization without agglomeration were as shown by the dashed lines in Figure 4. The limits decreased significantly with increased temperature, relative humidity, and ammonia concentrations. Each of these factors caused high initial rates of ammoniation and hence high release rates for the water of hydration. Batch runs passed through an initial critical stage; if fluidization could be maintained during this critical stage, the fertilizer then tended to "dry" and became less sticky during the final stages of the run. One method of successfully passing through this initial stage without agglomeration was to start at low ammonia concentrations, relative humidities, and/or temperatures, and to increase at least one of the above gradually throughout the run. Figure 5 indicates the results of such a run at

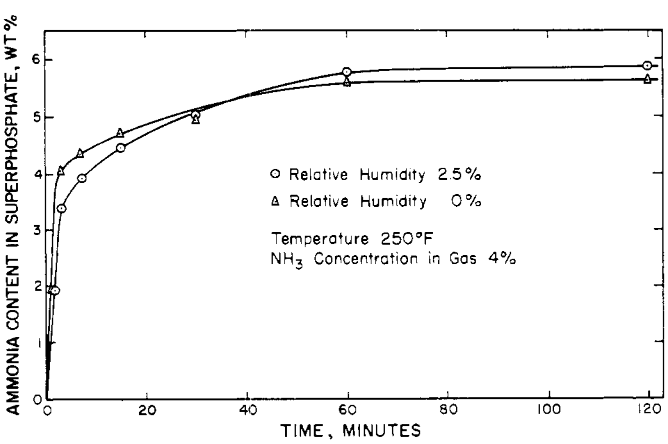

Figure 3. Effect of relative humidity of gas phase on ammoniation of triple superphosphate at 250° F.

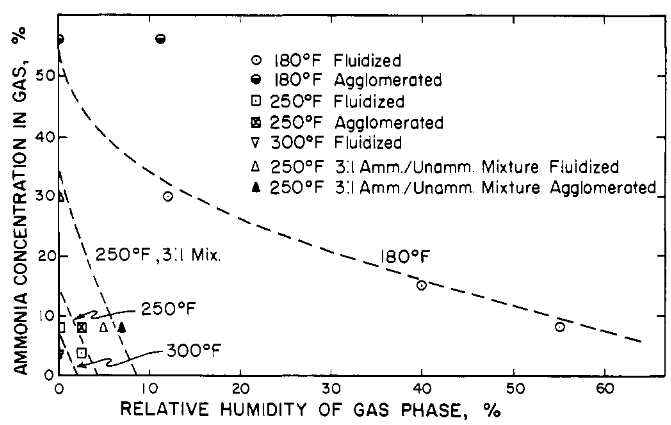

Figure 4. Limits of fluidization of triple superphosphate at various temperatures

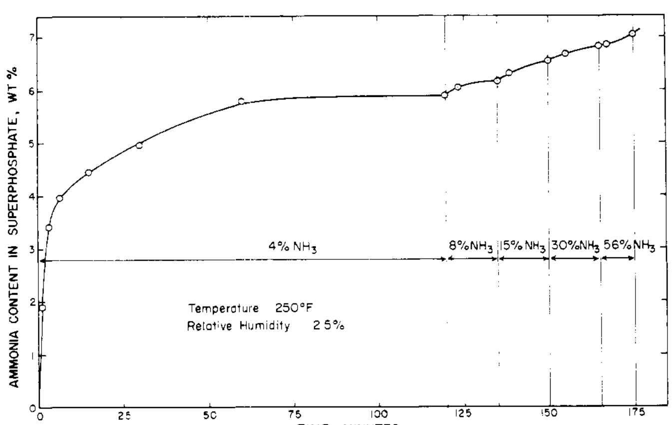

Figure 5. Effect of stepwise increase of ammonia concentration in gas phase on ammoniation at 250° F.

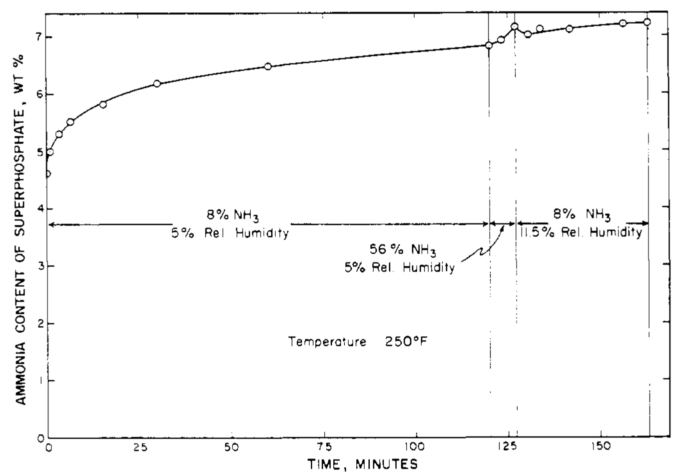

Figure 6. Effect of stepwise increase of ammonia concentration and relative humidity of gas phase on ammoniation of 3:1 ammoniated:unammoniated mixture at 250° F.

250° F. using a gas with a relative humidity of 2.5%. The concentration of the ammonia was increased by steps from 4 to 56%. Each increase of the ammonia concentration resulted in a significant increase of the reaction rate and ammonia pickup. Even at the end of the run, significant ammoniation still occurred.

Another method for preventing agglomeration was to use a mixture of ammoniated and unammoniated materials. Figure 6 indicates the results of a run in which the initial fertilizer mixtures contained 25% of unammoniated superphosphate plus 75% ammoniated (5.8% ammonia content) superphosphate. The limits of fluidization were significantly enlarged at 250° F. by this technique as shown by Figure 4. Presumably they would be enlarged in a similar manner at other temperatures too. Less water of hydration would of course be released for mixtures of this type, and the ammoniated portion of the fertilizer apparently acted as a moisture sink for water that was released. Such mixtures simulate the conditions that would be found in a continuous flow type of fluidized-bed reactor.

Conditioning the fertilizer before ammoniation was also important in regards to agglomeration. The limits of fluidization as indicated in Figure 4 were determined using fertilizers that had been conditioned prior to the run with air at the same relative humidities as the gas mixture employed for the ammoniation portion of the run. A special run was made in which the fertilizer was conditioned first with dry air at 250° F., then for 90 minutes with air at 250° F. and a relative humidity of 11.8%. The ammonia flow was started to produce a gas mixture containing 0.5% ammonia; later, the ammonia concentration was slowly increased to 30%. A run was successfully performed (without agglomeration) by this technique outside the limits indicated by Figure 4 for 250° F. Presumably the conditioning of the fertilizer with dry air removed some of the water of hydration. Further experiments are necessary, however, before the importance of such a method of conditioning the fertilizer can definitely be determined.

Temperature Effect. The effect of temperature for runs at 0% relative humidity and 4% ammonia concentration in the fluidizing gases is shown in Figure 7. Initial reaction rates were very similar and much higher at 250° and 300° F. than at 180° F. Possibly the release of the water of hydration, necessary to start the reaction at 0% relative humidity, is the rate-controlling step at 180° F. The decreased degree of ammoniation of the fertilizer for these runs as compared with runs at higher relative humidities was apparently caused by a lack of moisture, as was also noted earlier (*1*).

A run was made at 250° F. in which the relative humidity of the fluidizing gases was maintained at 5.4%. The run was divided into 60-minute cycles in which the fluidizing gases contained for the first 30 minutes of the cycle 30% ammonia, followed by 30 minutes with no ammonia. Two and a half cycles were completed. During the ammoniation portion of each cycle, the degree of ammoniation in all three cases reached approximately 7.0%. During the portion of the cycle without ammonia, the ammonia content of the fertilizer quickly decreased to about 5.7 to 5.8% and appeared to level out

Table I. Ammonia Absorption Efficiencies

Run No.	Relative Humidity, %	NH_3 in Gas, %	Efficiency, %
180° F. Starting Temperature			
36	0	4	52
20	0	8	32
18	0	30	12
12	12	11	28
250° F. Starting Temperature			
27	0	4	65
30	2.5	4	69
33[a]	5.0	8	9
35	0	4	82

[a] Run 33 was operated with a 3:1 mixture of ammoniated and unammoniated fertilizer.

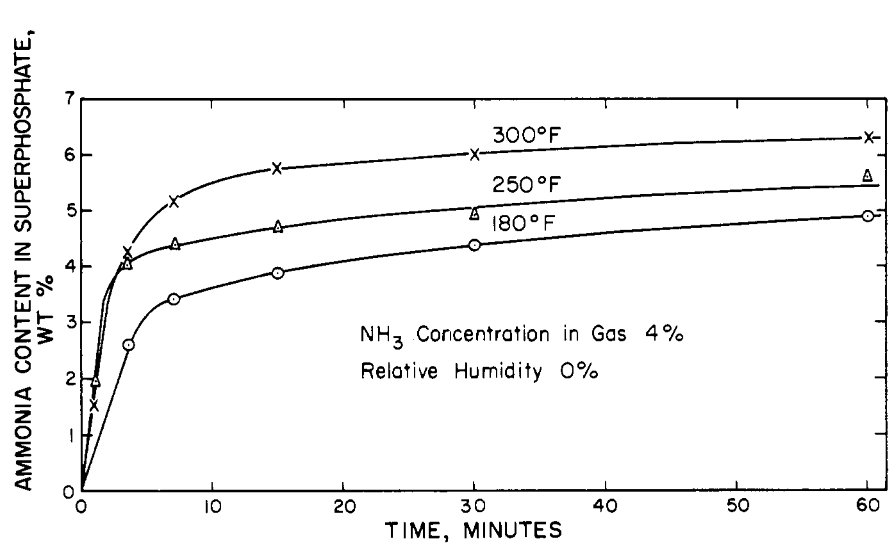

Figure 7. Effect of temperature on ammoniation at 4% ammonia concentration and 0% relative humidity of gas phase

Table II. Degree of Ammoniation in 2-Hour Runs Made in Fluidized Bed Reactor

Run No.	Maximum Temp., ° F.	Relative Humidity, %	Initial Free Moisture, %	NH_3 in Gas, %	Degree of Ammoniation, %
130° F. Starting Temperature					
42	...	57	1.8	30	8.8
180° F. Starting Temperature					
21	231	0	0.0	15	6.1
18	253	0	0.0	30	7.0
22	234	12	0.0	15	6.6
23	234	12	0.0	15	6.6
19	264	12	0.05	30	8.1
7	224	13	0.06	8	6.3
24	236	40	0.17	15	8.6
8	225	42	0.28	8	8.2
12	224	55	0.97	8	8.4
250° F. Starting Temperature					
27	296	0	0.0	4	5.6
25	325	0	0.0	8	6.7
30	267	2.5	0.0	4	5.9
38	...	5.8	0.05	30	7.8
40	...	11.8	...	30	8.3
300° F. Starting Temperature					
35a	351	0	0.0	4	6.3[a]
35b	...	0	0.01	30	7.2[b]
35c	...	2.4	0.04	30	7.4[b]

[a] 60-minute run. [b] 60-minute continuation from previous portion of run 35.

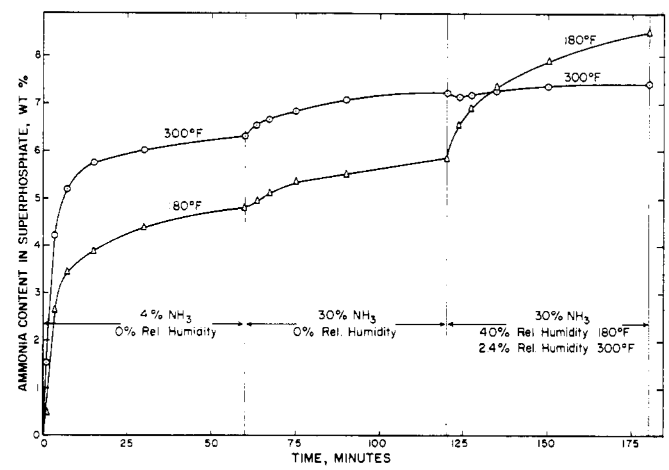

Figure 8. Effect of temperature on ammoniation during stepwise increase of ammonia concentration and relative humidity of gas phase

by the end of the 30 minutes. These results clearly indicate that some of the ammonia was rather easily removed from the fertilizer. It is thought that most of ammonia which was removed was merely dissolved in the liquid phase. Probably not many of the ammoniated phosphate salts which were actually formed and crystallized were decomposed. The present results when combined with previous results at 130° and 180° F. (7) clearly indicate that the "decrease" in the degree of ammoniation is more severe at higher temperatures.

The results of stepwise increases of the ammonia concentration and relative humidity of the gas phase for ammoniation runs at both 180° and 300° F. are shown in Figure 8. The increase of the initial reaction rate because of temperature may be observed in the first period. In the second period, the increase of the ammonia concentration from 4 to 30% at the same relative humidity of 0% gave similar increases of the ammonia content at both temperatures. In the last period, the addition of steam to obtain relative humidities to 2.4 and 40%, respectively, for the 300° and 180° F. runs, significantly increased the rate of ammoniation at 180° F. but not at 300° F. Although the relative humidity was small at 300° F., the steam flow was about one half that for the 180° F. run.

Ammonia Absorption Efficiencies. The absorption efficiencies (fraction of entering ammonia that reacted with the superphosphate) were calculated for runs at different sets of operating conditions. The weight fraction was calculated for the first $3^1/_2$ minutes of a run from the flow rates, the amount of solid material present, and the ammonia content of the fertilizer. The efficiencies found for several runs are given in Table I.

The absorption efficiencies would, of course, decrease for these batch runs as the run progressed beyond the initial $3^1/_2$ minutes. The initial efficiencies were essentially independent of the relative humidity, but increased rapidly with higher temperature and lower ammonia concentrations. The lowest calculated efficiency, 9%, was that of the 3:1 ammoniated: unammoniated mixture. 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 (*1*) 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 ammoniation. 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 (*1*).

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FERTILIZER TECHNOLOGY

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

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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.

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 (*1, 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.

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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