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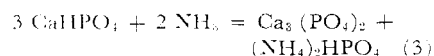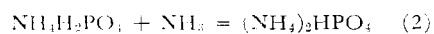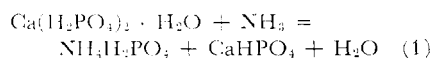
# FERTILIZER TECHNOLOGY

# A Study of Ammoniation Reactions in a Fluidized Bed of Superphosphate

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Superphosphate fertilizers were ammoniated with anhydrous ammonia in a fluidized-bed reactor over wide ranges of operating variables to obtain products containing up to 9.7% (by weight) ammonia. The results show that the chemical reactions are probably occurring predominantly in the liquid phase present in or on the fertilizer granules. Free moisture contents of the fertilizer of about 0.6 to 15% are preferred; lower contents result in slow ammoniation and higher amounts cause agglomeration. Phosphate reversion was very low and relatively independent of operating conditions.

AMMONIATION of superphosphates is one of the most important operations in the fertilizer industry. Much of its commercial success has resulted from the pioneering work done by the Tennessee Valley Authority, which developed the drum-type ammoniator for industrial application. Ammoniation is a highly complex process, and some of the observations and difficulties arising during operation are not easily explained. At the present time, two of the principal problems are the reversion of phosphates, i.e., the formation of insoluble phosphorus compounds, and the loss of nitrogen during ammoniation and possibly subsequent storage. These difficulties become more severe with increasing degree of ammoniation, i.e., increasing amount of ammonia absorbed per unit mass of superphosphate (7).

The principal reactions occurring during ammoniation of triple superphosphate are as follows (9):

$$Ca(H_2PO_4)_2 \cdot H_2O + NH_3 =$$
$$NH_4H_2PO_4 + CaHPO_4 + H_2O \quad (1)$$

$$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4 \quad (2)$$

$$3 \ CaHPO_4 + 2 \ NH_3 = Ca_3 (PO_4)_2 + (NH_4)_2HPO_4 \quad (3)$$

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Several side reactions may also occur involving impurities such as fluorides, sulfates, plus iron and aluminum salts. The reactions appear to be ionic in character, but little or no discussion has been found in the literature on the mechanism of these reactions.

The rate and extent of the chemical reactions are governed chiefly by tem-

perature, activity of the ammonia, porosity and particle size of the superphosphate, and moisture content. Kumagai et al. (1) have studied the effects of these variables on the ammoniation of superphosphate fertilizer in a small, drum-type reactor. Rotating drums are currently used in the great majority of all commercial ammoniating
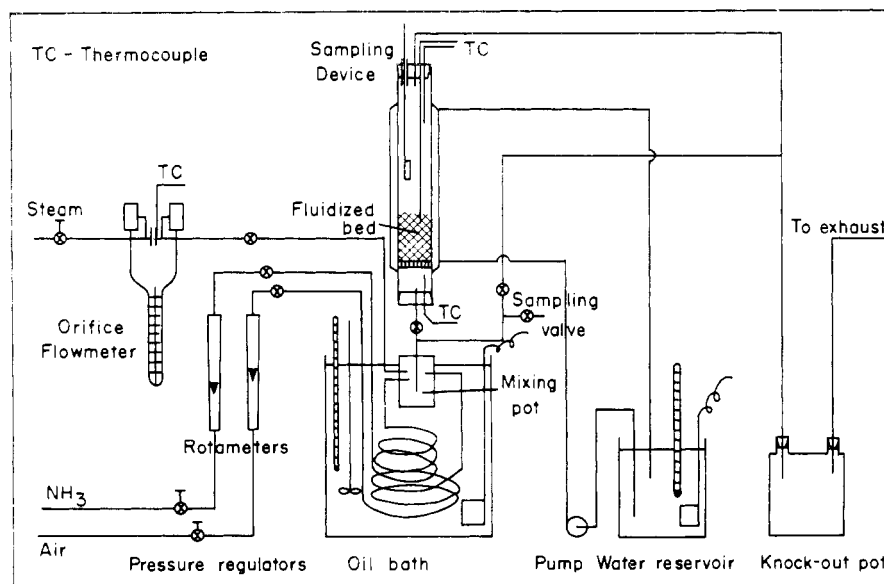


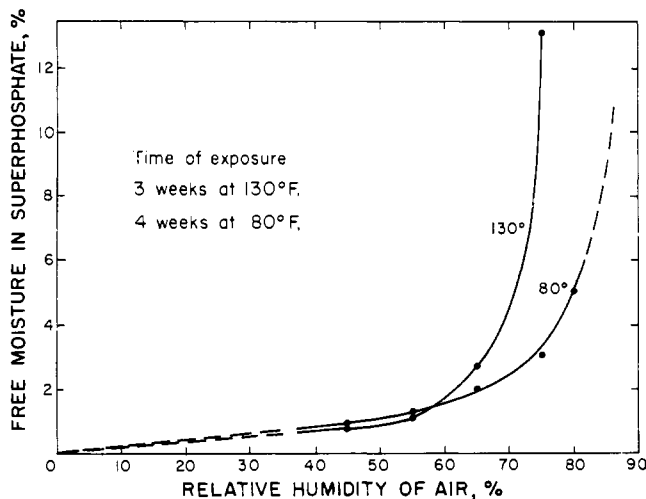Figure 1. Flowsheet for fluidized-bed ammoniator

**Figure 2.** Free moisture content of triple superphosphate as a function of relative humidity of air in static experiment
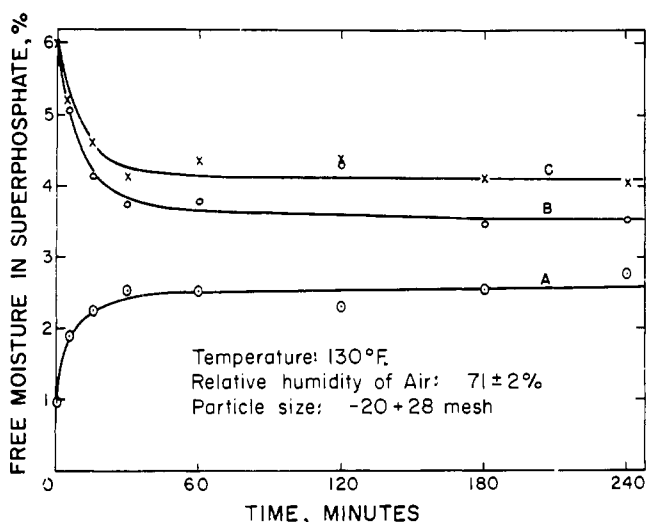


**Figure 4.** Effect of contact time and of pretreatments on the free moisture content of triple superphosphate in the fluidized bed

(A) Untreated material; (B) material stored 16 hours at 130° F. after addition of 5% H₂O; (C) material stored 33 days at 130° F. after addition of 5% H₂O
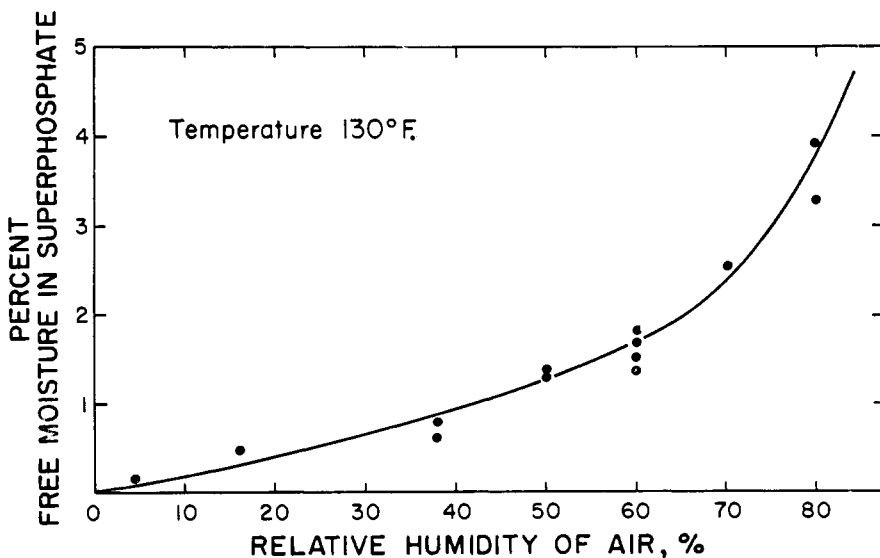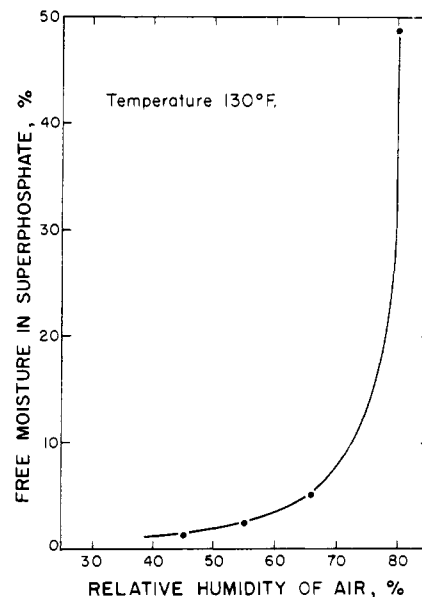


**Figure 3.** Free moisture content of ammoniated triple superphosphate (8.34% NH₃) as a function of relative humidity of air in static experiment

facilities. They are, however, not completely satisfactory for detailed investigations of the ammoniation process because local conditions—in particular, temperature and ammonia concentration—vary widely throughout the bed of superphosphate. A bomb-type reactor with a mechanical agitator was used by White, Hardesty, and Ross (9), who avoided excessive temperature rises by keeping the rate of ammoniation very low.

A fluidized bed has been reported to give excellent results in air-drying of superphosphate fertilizer (2). Trojan, Jara, and Vanacek (6) describe the use of a fluidized-bed reactor for the ammoniation of superphosphate. Only a very low degree of ammoniation was obtained, but the claim was made that a fluidized bed could be operated more economically than the drum-type ammoniator. However, those authors failed to present any quantitative arguments, and furthermore, they neglected to give such essential information as reactor temperature and composition or type of superphosphate used.

Fluidized-bed reactors probably would give good temperature control. In addition, the possibility of using mixtures of ammonia with an inert gas offers an additional degree of freedom over conventional designs. Such a reactor system was employed in this investigation, which was undertaken for the purpose of gaining new information on the ammoniation reaction.

### Experimental Details

**Equipment.** The flowsheet for the ammoniator is shown in Figure 1. The fluidized-bed reactor was constructed
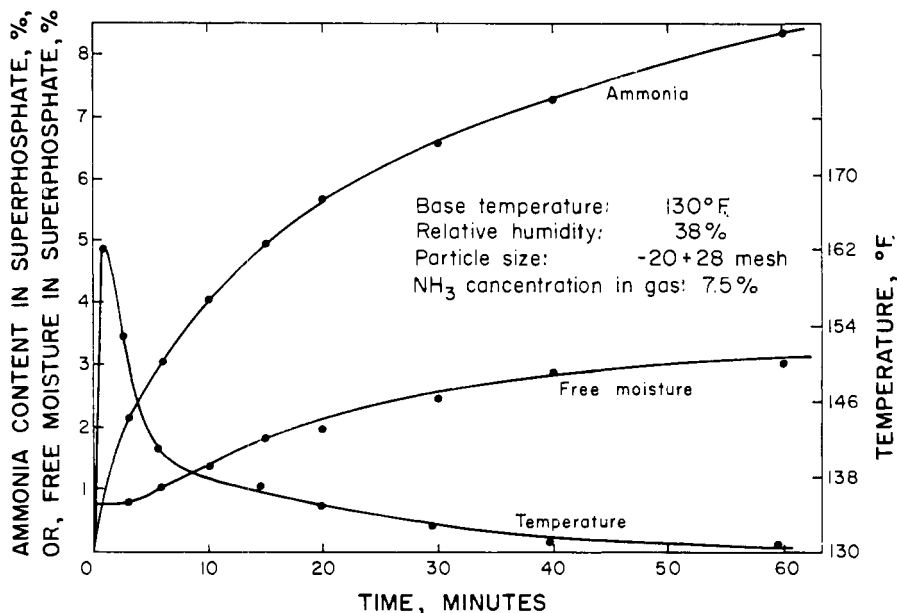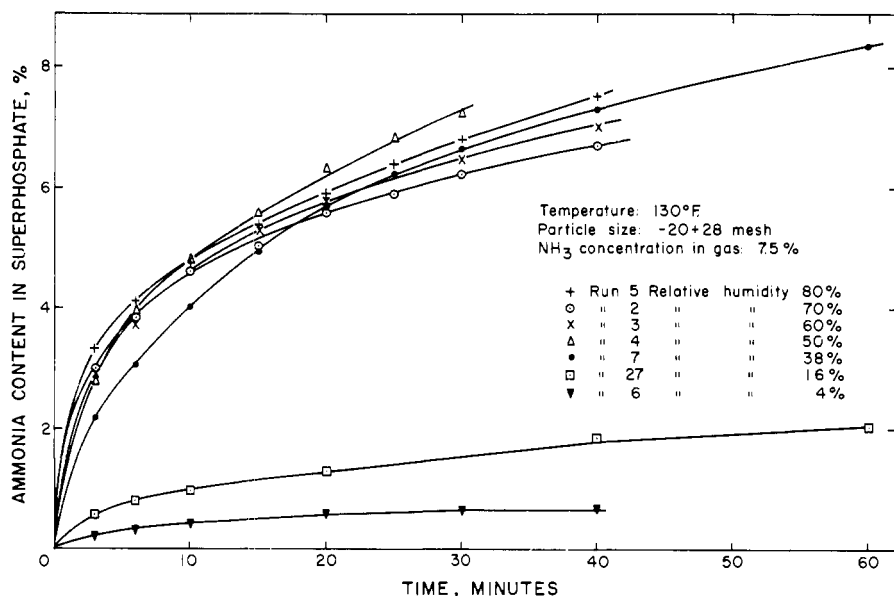


**Figure 5.** Free moisture content of triple superphosphate as a function of relative humidity of air in the fluidized bed after at least 1 hour contact time

**Figure 6.  Ammoniation run 7**



**Figure 7.  Effect of relative humidity of gas phase on ammoniation at 130° F.**

$Fe_2O_3$, 3.2%; free $H_2O$, 1.0%. It had been manufactured from Florida phosphate using wet-process phosphoric acid, and was of the dense, granulated type. The fertilizer was crushed and screened to obtain $-14+28$, $-16+20$, $-20+28$, $-28+48$, and $-28+60$ Tyler screen sizes. Commercial-grade anhydrous ammonia was used in all ammoniation runs.

**Operation.** A total of 200 to 600 grams of superphosphate was used for each batch run. In the first phase of the project, no steam was used in the ammoniator. Instead, a calculated amount of water was added and thoroughly mixed with the superphosphate. The mixture was placed in a closed jar and kept for at least 20 hours in an oven maintained at the temperature at which the reactor was to be run. For startup, the temperature in the oil bath and the water jacket plus the flow rates of the air and the ammonia were adjusted to the desired level before the fertilizer was introduced into the fluidizing column. Temperatures were recorded and several samples were taken during the run.

In the second phase of this research, the superphosphate was placed directly in the reactor without adding any water. It was then fluidized with humidified air (prepared by mixing line air and steam) for at least 1 hour. This time was found to be sufficient to establish an apparent equilibrium between the humidity of the air and the free moisture in the superphosphate. Just prior to the start of the ammoniation, a sample of the fertilizer was taken. When the flow of ammonia was started, the relative humidity of the gas mixture was kept constant by decreasing the air flow slightly to compensate for the ammonia flow.

**Analysis.** All ammoniated samples were analyzed for free moisture and for ammoniacal nitrogen, and, when desirable, for total, water-soluble, citrate-soluble, and citrate-insoluble $P_2O_5$, using the methods specified by the Association of Official Agricultural Chemists. Free moisture content in the fertilizer was obtained by drying at room temperature over magnesium perchlorate in a vacuum desiccator for at least 48 hours. Water vapor and ammonia in the fluidizing gas stream were determined by absorption on magnesium perchlorate and in sulfuric acid, respectively.

**Equilibrium Moisture Tests.** A series of static moisture tests were made to determine the true equilibrium between the moisture content of the superphosphate and the relative humidity of the surrounding atmosphere. For this purpose, samples of $-28+48$-mesh superphosphate fertilizers were stored for several weeks at constant temperature (80 or 130° F.) in sealed jars over sulfuric acid of known water vapor pressure, and changes of the sample weight were recorded as a function of time.

from a borosilicate glass tube, 2.5 inches in diameter and 30 inches long. A sintered-glass insert for dispersing the gas uniformly in the bed was positioned near the bottom of the reactor. The reactor was jacketed for about 2 inches below the sintered glass and for 16 inches above. Water from a constant-temperature water reservoir was circulated through the jacket. The fluidizing gas was a mixture of air, ammonia, and in some cases steam; these gases were metered by either rotameters or orifice flowmeters. The ammonia and air were preheated in coils immersed in an oil bath before being mixed in the mixing pot which was positioned just under the

reactor. A gas by-pass around the reactor and a gas sampling valve were also provided. Gas lines were heated where necessary to prevent condensation of moisture. Temperature in the fluidized bed and in the gas space above it were measured with thermocouples (TC). Superphosphate samples were taken by pushing a glass thimble through a gas-tight seal into the fluidized bed.

**Materials.** The triple superphosphate used was purchased locally, and its composition was: total $P_2O_5$, 48.5%; water-soluble $P_2O_5$, 39.4%; citrate-soluble $P_2O_5$, 8.8%; citrate-insoluble $P_2O_5$, 0.3%; CaO, 21.6%; $SO_3$, 2.5%; F, 2.6%; $Al_2O_3$, 1.8%;

## Results

**Preliminary Runs.** All sizes (−14+ 28- to −28+60-mesh) of dry super-phosphate were fluidized satisfactorily with air flow rates of 4.5 standard cubic feet per minute (scfm) or more, equivalent to at least 110 scfm per square foot of reactor cross section. A mixing test indicated that colored fertilizer particles were well mixed with uncolored ones within 5 to 10 seconds. No segregation with respect to size or shape was observed. At free moisture contents of about 15% or higher, agglomeration became serious, causing poor fluidization and mixing. Attrition was negligible.

Initial ammoniation runs were made with superphosphate containing up to 15% free moisture and with mixtures of air and ammonia; this fluidizing gas mixture had a relative humidity of less than 5% in all cases and had an ammonia concentration of 8.15% by volume. Initial rates of ammoniation during a run were quite high, and during this initial period, temperature rises of about 10° to 15° F. were recorded. The reaction then slowed down rapidly and practically stopped after 20 minutes; during this time, the temperature returned to the starting value. The ammonia pickup by the superphosphate in a run was higher at low temperatures and with fertilizers that initially contained more free moisture. The maximum pickup obtained during these runs was only about 5.0% (by weight) ammonia in the final product. In all cases, the free moisture content of the fertilizers had decreased during the batch runs to essentially zero.

These preliminary results clearly indicated that the moisture content of the fertilizer was most important for ammoniation. The ammoniation in a dry fluidizing gas was accompanied by rapid drying (aggravated by the heat release from the exothermic chemical reactions). When the solid material dried out, the ammoniation reaction became very slow and perhaps even stopped completely. A special run was then made at 110° F. to demonstrate the necessity of having moisture present in the superphosphate. At the end of each 20-minute period, more water was added to give a moisture content of 12%. In 60 minutes of ammoniation, the material had picked up 7.65% ammonia.

**Equilibrium Moisture Content of Triple Superphosphate.** Since fluidization with dry gas mixtures causes dehydration of the superphosphate, humid gas was considered as a means of preventing or at least minimizing the drying. Hence tests were made to determine the equilibrium moisture content of the fertilizer as a function of temperature and of the relative humidity of the contacting air. Three to 4 weeks were required to establish the equilibrium. The results of these static tests are shown
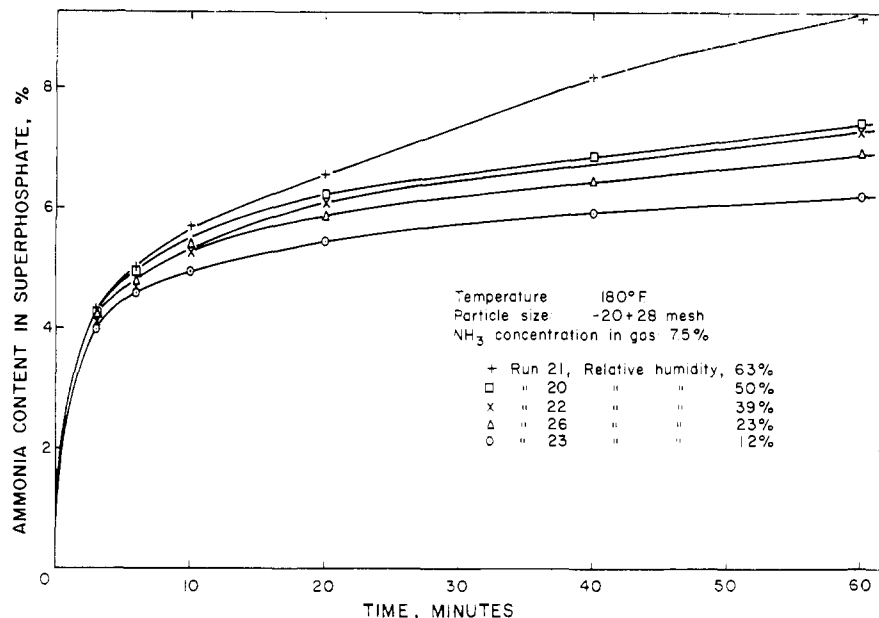


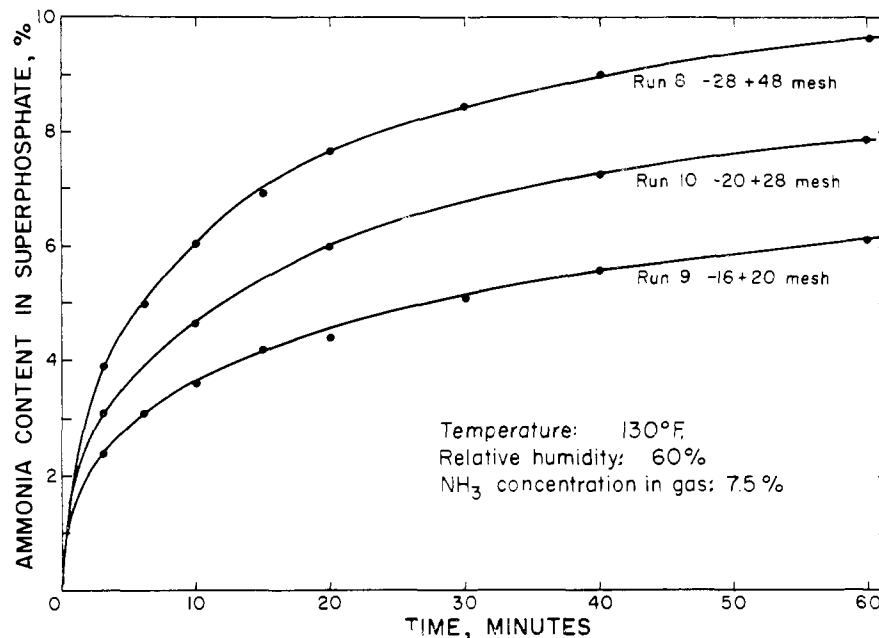Figure 8. Effect of relative humidity of gas phase on ammoniation at 180° F.



Figure 9. Effect of particle size on ammoniation

in Figure 2. Sharp increases of the free moisture content of the solids were noted at relative humidities above 60%. The location of the critical humidity, where deliquescence sets in, was not ascertained, but it is evident that with increasing temperature, this critical point would be displaced towards lower relative humidities.

Static moisture tests were also made with an ammoniated fertilizer (8.3% NH₃) at 130° F. This material had somewhat higher equilibrium moisture contents than the unammoniated superphosphate, as indicated by Figure 3.

The moisture content of the unammoniated fertilizer was next determined in

the fluidized bed as a function of time, temperature, and humidity of the air. After 1 hour, the free moisture content had usually reached what appeared to be a constant value. However, these values varied, depending upon the initial moisture content and pretreatment of the superphosphate. For example, Figure 4 shows how three samples pretreated to various moisture contents before fluidization behaved when treated under the same conditions in the fluidized bed. The free moisture contents obtained after 1 to 4 hours of fluidization obviously do not represent true equilibrium values. Mass transfer or diffusion of the moisture to or from the interior of the particle is

without question a slow process. as the static tests had also indicated. Conditioning the fertilizer in the fluidized bed for several hours probably allowed the outer surfaces of the particles to come to equilibrium with the humid air even though the interiors of the particles were not at equilibrium.

**Ammoniation with Humid Gas Mixtures.** The variables studied in the second phase of the project were temperature (130° and 180° F.), relative humidity of the fluidizing gas (0 to 80%), ammonia concentration in the gas (3.6, 7.5, and 15%), and particle size (−16+20-, −20+28-, and −28+48-mesh). The highest relative humidities at which agglomeration did not interfere with fluidization were 80% at 130° F. and 63% at 180° F. Ammonia pickup was reproducible for duplicate runs within about 5% (on a relative basis); however, the final free moisture contents varied by as much as 25%.

The moisture contents of several fertilizer samples used in ammoniating runs, taken after 1 hour of conditioning with humid air and just before the start of the ammoniation, are plotted in Figure 5. Although there is some scatter of the data, a comparison with Figure 2 indicates that the moisture contents obtained by the fluidizing technique using originally dry superphosphate were significantly lower than those resulting from the static tests.

Figure 6 shows how the degree of ammoniation, temperature, and free moisture content changed with time in the course of a typical ammoniation run. The absorption of ammonia at first proceeded rapidly; the accompanying heat release caused the temperature to rise by 30° F., until the rate of heat transfer to the fluidizing gas and to the reactor walls was greater than the rate of heat generation. After passing through a well defined maximum, the temperature in the bed decreased again and approached that of the incoming gas. At the end of 60 minutes, the rate of the ammoniation reaction was still appreciable, but much lower than at the start. The free moisture content increased somewhat after the first few minutes, during which the initial temperature rise counteracted the change in chemical composition which would favor the absorption of moisture. As already mentioned above, ammoniated superphosphates have a higher equilibrium moisture content at a given relative humidity than unammoniated materials. Also, water of hydration was liberated by the chemical reaction.

Figures 7 and 8 for 130° and 180° F., respectively, show that the initial rate of ammoniation increases with increasing relative humidity of the fluidizing gas. i.e., with increased free moisture content of fertilizer. At 130° F., and at humidities above about 38%, no obvious cor-
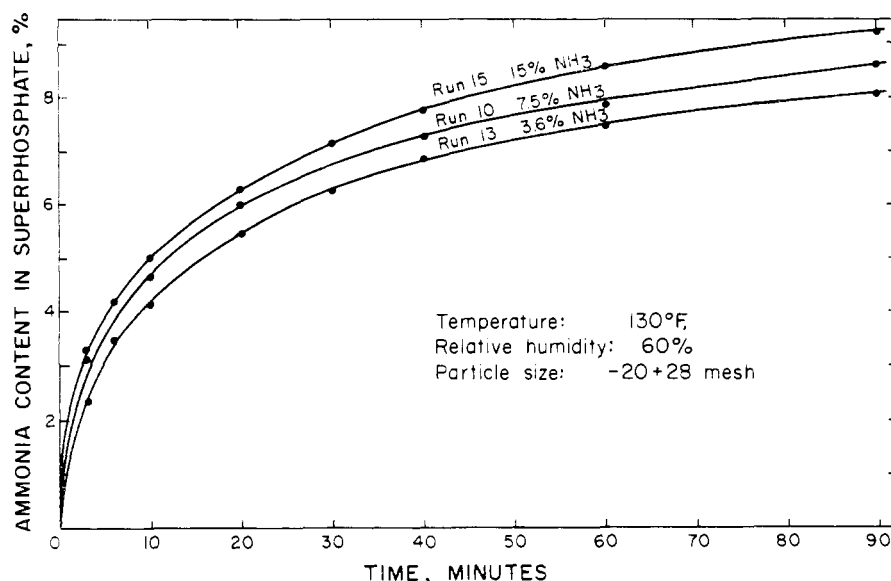
relation exists for rates of ammoniation after about 20 minutes. At 180° F., however, the rates of ammonia pickup seem to remain consistently higher for more humid gas mixtures. Use of the relatively dry gas (4% humidity) at 130° F. clearly shows that moisture is important during ammoniation.

Figure 9 demonstrates that the rate of ammoniation was also a function of particle size. Smaller particles offered greater surface area for mass transfer and thereby favored the absorption of ammonia. One would expect, however, that the curves for all particle sizes would approach a common upper limit with increased time of ammoniation.

The rate of ammoniation was also accelerated slightly by increased ammonia concentration in the gas; this is illustrated in Figure 10 for runs at 130° F. with a gas humidity of 60%. Runs at 38% humidity indicated that differences in the ammonia concentration of the gas were somewhat more important with the drier gas mixture.

Figures 11 and 12 show the results of runs at 130 and 180° F., respectively, in which the ammoniation was twice interrupted by conditioning periods during which the partly ammoniated superphosphate was treated with ammonia-free air at the same relative humidity as the ammoniating gas mixture. The ammonia content of the fertilizer decreased somewhat during these conditioning periods, especially at 180° F. However, the ammonia content increased rapidly at the beginning of each ammoniation period. The free moisture content also changed significantly as the run progressed, but not in the same manner at 130° and at 180° F. The maxima that occurred at 180° F. cannot be explained at present. Figures 11 and 12 also indicate how the phosphate

analyses varied during the run. The formation of insoluble phosphates occurred in both runs primarily during the initial portion of the reaction.

Table I reports the analyses of several fertilizer samples obtained in this investigation. The most significant data are those referring to the phosphate availability. The proportion of unavailable $P_2O_5$ was practically constant at about 2%, even though a wide range of operating conditions was covered and the degree of ammoniation ranged from 2.16 to 9.68% ammonia in the final product, i.e., from 0.9 to 4.3 pounds ammonia per unit of $P_2O_5$. (One unit of $P_2O_5$ equals 20 pounds.)

### Discussion of Results

The effects of temperature, moisture content, and particle size are in general agreement with the observations reported by Kumagai, Rapp, and Hardesty (3). When reaction rates are compared, it must be remembered that in the present investigation, relatively coarse superphosphate was used. Much finer material could undoubtedly be ammoniated in a fluidized bed by modifying the design and flow rates.

The ammoniation reaction is obviously a very complex process, but most of the observations can be explained by assuming that the actual chemical reactions occurred primarily in an aqueous liquid phase. Rader (7) in 1948 had given information on the existence of such a phase. The reaction presumably must consist of at least the following steps:

Solution of ammonia in the liquid phase. Some ionization would occur at this stage.

Solution, accompanied by hydrolysis, of monocalcium phosphate and other



Figure 10. Effect of ammonia concentration in the gas phase on ammoniation

## Table I. Degree of Ammoniation and Phosphate Availability

| No. | Temp. °F. | Humid., % | NH$_3$ concn., % | Particle size mesh | Sample No. | Time, min. | % NH$_3$ | Lb. NH$_3$ per unit P$_2$O$_5$ | % P$_2$O$_5$ Total | % P$_2$O$_5$ Water Soluble | % P$_2$O$_5$ Citrate Soluble | % P$_2$O$_5$ Citrate Insoluble | P$_2$O$_5$ Available % of Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Unammoniated triple superphosphate | | | | | | | 0 | 0 | 48.5 | 39.4 | 8.8 | 0.3 | 99.3 |
| 2 | 130 | 70 | 7.5 | −20+28 | 5 | 15 | 5.02 | 2.1 | 48.4 | 25.3 | 21.5 | 1.6 | 96.7 |
| | | | | | 9$^a$ | 40 | 6.69 | 2.8 | 48.5 | 23.9 | 23.0 | 1.6 | 96.7 |
| 3 | 130 | 60 | 7.5 | −20+28 | 5 | 15 | 5.27 | 2.2 | 48.4 | 25.9 | 20.9 | 1.6 | 96.7 |
| | | | | | 9$^a$ | 40 | 7.01 | 2.9 | 47.9 | 23.8 | 22.4 | 1.6 | 96.5 |
| 4 | 130 | 50 | 7.5 | −20+28 | 5 | 15 | 5.55 | 2.3 | 48.3 | 25.4 | 21.2 | 1.7 | 96.5 |
| 7 | 130 | 38 | 7.5 | −20+28 | 2 | 3 | 2.16 | 0.9 | 48.5 | 32.2 | 15.0 | 1.3 | 97.4 |
| | | | | | 4 | 10 | 4.05 | 1.7 | 48.5 | 27.3 | 19.5 | 1.7 | 96.4 |
| | | | | | 7 | 30 | 6.60 | 2.8 | 47.5 | 25.8 | 19.9 | 1.8 | 96.2 |
| | | | | | 9 | 60 | 8.34 | 3.6 | 46.6 | 25.2 | 19.6 | 1.8 | 96.2 |
| 8 | 130 | 60 | 7.5 | −28+48 | 4 | 10 | 6.06 | 2.6 | 47.2 | 24.9 | 20.5 | 1.8 | 96.2 |
| | | | | | 9 | 60 | 9.68 | 4.3 | 45.5 | 23.0 | 20.8 | 1.7 | 96.3 |
| 9 | 130 | 60 | 7.5 | −16+20 | 9 | 60 | 6.15 | 2.6 | 47.4 | 24.8 | 20.7 | 1.9 | 96.0 |
| 10 | 130 | 60 | 7.5 | −20+28 | 5 | 40 | 7.29 | 3.1 | 46.8 | 24.1 | 21.0 | 1.7 | 96.3 |
| 13 | 130 | 60 | 3.6 | −20+28 | 9 | 90 | 8.08 | 3.5 | 46.9 | 24.7 | 20.4 | 1.8 | 96.2 |
| 14 | 130 | 38 | 3.6 | −20+28 | 8 | 60 | 7.31 | 3.1 | 47.1 | 25.6 | 19.7 | 1.8 | 96.2 |
| 15 | 130 | 60 | 15 | −20+28 | 6 | 30 | 7.16 | 3.1 | 46.6 | 24.5 | 20.2 | 1.9 | 96.0 |
| 16 | 130 | 60 | 7.5 | −20+28 | 4$^b$ | 15 | 5.77 | 2.5 | 46.9 | 24.9 | 20.3 | 1.7 | 96.4 |
| | | | | | 7$^c$ | 75 | 5.65 | 2.4 | 47.6 | 25.6 | 20.2 | 1.8 | 96.2 |
| | | | | | 10$^b$ | 105 | 7.55 | 3.3 | 46.4 | 24.3 | 20.2 | 1.7 | 96.0 |
| | | | | | 12$^c$ | 165 | 7.19 | 3.1 | 46.8 | 24.2 | 20.5 | 2.1 | 95.5 |
| | | | | | 14$^b$ | 180 | 7.96 | 3.4 | 46.8 | 23.8 | 21.0 | 2.0 | 95.7 |
| 21 | 180 | 63 | 7.5 | −20+28 | 4 | 10 | 5.70 | 2.4 | 48.1 | 24.3 | 21.7 | 2.1 | 95.6 |
| | | | | | 7 | 60 | 9.15 | 3.9 | 47.0 | 22.8 | 22.3 | 1.9 | 95.9 |
| 23 | 180 | 12 | 7.5 | −20+28 | 4 | 10 | 4.93 | 2.0 | 48.2 | 24.7 | 21.7 | 1.8 | 96.3 |
| | | | | | 7 | 60 | 6.19 | 2.6 | 47.4 | 23.2 | 22.4 | 1.8 | 96.2 |
| 25 | 180 | 50 | 7.5 | −20+28 | 4$^b$ | 15 | 6.04 | 2.6 | 47.4 | 24.1 | 21.5 | 1.8 | 96.2 |
| | | | | | 7$^c$ | 75 | 5.25 | 2.2 | 48.3 | 26.1 | 20.5 | 1.7 | 96.5 |
| | | | | | 10$^b$ | 105 | 6.92 | 3.0 | 47.3 | 22.8 | 22.7 | 1.8 | 96.1 |
| | | | | | 12$^c$ | 165 | 5.89 | 2.5 | 48.0 | 24.6 | 21.6 | 1.8 | 96.3 |
| | | | | | 14$^b$ | 180 | 7.53 | 3.2 | 47.7 | 22.7 | 23.2 | 1.8 | 96.2 |

$^a$ Dried in reactor.  $^b$ End of ammoniation period.  $^c$ End of conditioning period.

salts in the liquid phase. Water of hydration would presumably be liberated at this point.

Diffusion of the dissolved components or ions in the liquid phase.

Chemical reaction.

Crystallization of the reaction products.

Transfer of water vapor to or from the liquid phase.

Each of these steps proceeds at a certain rate which depends on the local conditions, and therefore on the operating variables of the ammoniator.

The proposed mechanism is supported by several observations. First and perhaps strongest, the rate of ammoniation was very low for dry superphosphate. In addition, the results of the conditioning runs (Figures 11 and 12) demonstrate that ammonia was lost, probably because of desorption of the dissolved, but as yet unreacted, ammonia from the liquid phase during the conditioning periods. When the ammoniation portions of these runs were started, presumably much of the initial ammonia take-up involved merely dissolving ammonia in the liquid. Some of the ammonia losses during the conditioning runs were possibly caused by decomposition of reaction products, such as diammonium phosphate. This salt has a higher decomposition pressure in aqueous solutions than in the crystalline state (5, 8), and therefore reverse

reactions would occur mainly for that fraction of this compound that was dissolved. The formation of water-insoluble di- and tricalcium phosphates is not reversible.

Figure 7 indicates that a relative humidity of at least about 30% is required for obtaining a reasonable rate of ammoniation. This lower limit coincides with that observed for caking of superphosphate fertilizers in storage, which becomes noticeable at the same relative humidity and is commonly thought to be caused by processes involving a liquid phase. Further evidence is seen in the crystallographic identification of the products of the ammoniation reaction (3). The occurrence of fairly well developed crystallites certainly seems to imply that a liquid phase was present.

In the unammoniated superphosphate, the liquid phase would be saturated with respect to the phosphates and other salts present. At the start of the ammoniation, the rate of absorption of ammonia would be high since the initial steps would involve saturation of the solution phase and reaction of the dissolved salt with ammonia. Once the phosphate ions were depleted from the liquid phase, the subsequent steps would probably be much slower. The dissolution of unammoniated salts, as well as the transport of the salts and of ammonia within the liquid

phase, would depend on molecular diffusion and therefore be slow, as was indicated, for example, by the static equilibrium moisture determination. Thus, the concentration of unammoniated salts in the solution phase would decrease during the reaction, and a fraction of the ammonia absorbed by the fertilizer particles would be present in an unreacted form. Figures 11 and 12 show that this fraction may have been quite high after the reaction had progressed for a while. The relatively minor effect of the ammonia concentration in the fluidizing gas, illustrated by Figure 10, indicates that the gas phase resistance to ammonia transfer was not rate determining in the over-all process. The ionic reactions in the liquid should be very fast, and the net rate of reaction must be controlled largely by diffusion and solution processes within the particles.

Under the conditions present in the fluidized bed, reaction 1 probably went to completion. Table I shows that the phosphate reversion was uniformly low and independent of operation conditions. This suggests that reaction 3 did not occur. Impurities, such as fluorides, were presumably responsible for the loss of availability that occurred during the initial stages of ammoniation. The final degree of ammoniation thus appeared to depend primarily on reaction 2.
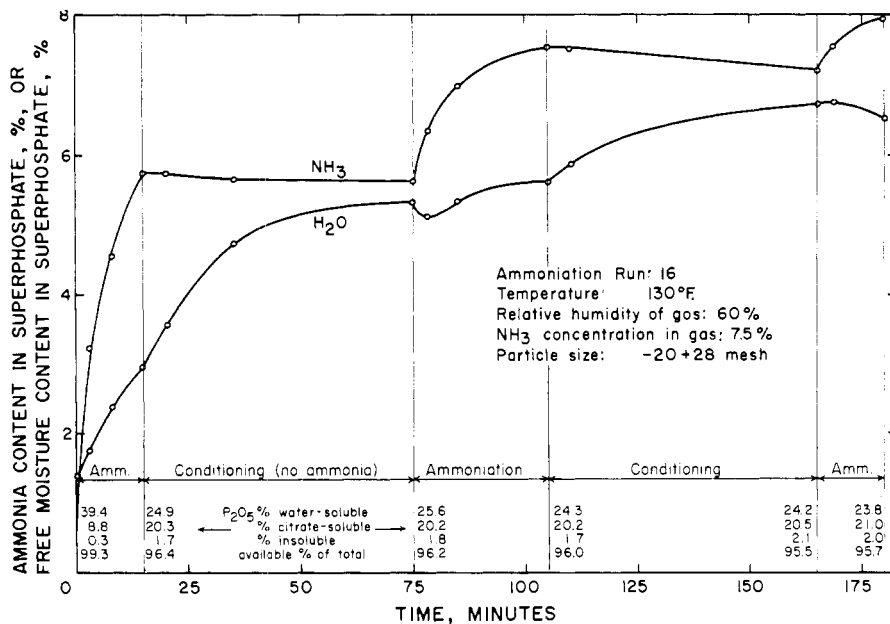
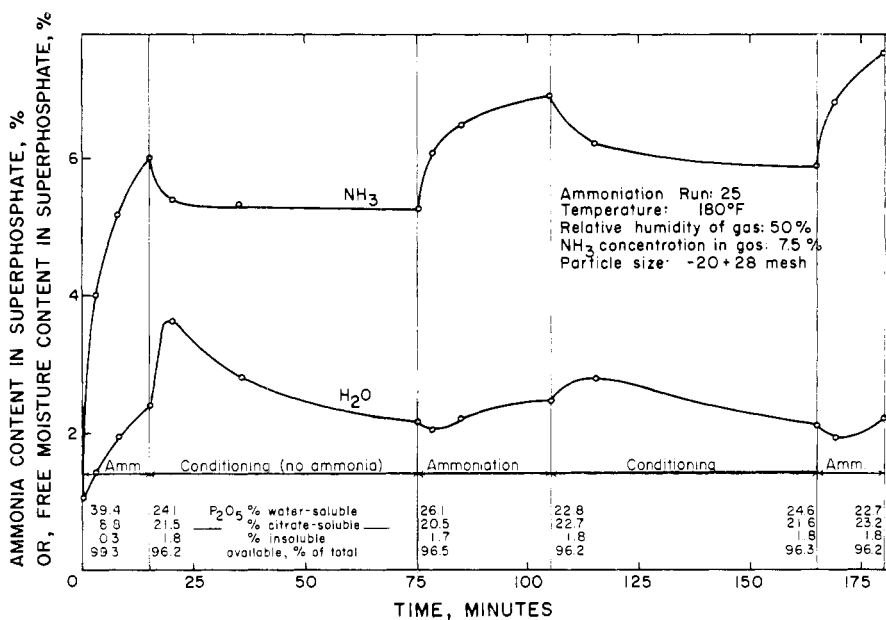Figure 11. Effect of intermittent operation on ammoniation at 130° F., 60% relative humidity



Figure 12. Effect of intermittent operation on ammoniation at 180° F., 50% relative humidity

ammoniated and ammoniated salts in the liquid phase. The rate of crystallization of the ammoniated salts would probably also be temperature dependent.

The ammoniation efficiencies, i.e., the fraction of the ammonia entering the reactor that was absorbed by the superphosphate, were quite low. In the most favorable case, with 3.6% $NH_3$ in the gas at 130° F., efficiency reached 41% during the first 3 minutes. This could undoubtedly be very much improved by suitable modifications of the process. Of course, the unreacted ammonia could also be recirculated. The loss of phosphate availability was lower than that (10) published for TVA-type reactors. Further work is being planned in this area to establish operating factors affecting phosphate reversion.

## Acknowledgment

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Higher temperatures have a complex effect. They accelerate the chemical reactions, but apparently at the same time the final degree of ammoniation that could be attained at a given ammonia partial pressure is lowered, because of the higher decomposition pressure of diammonium phosphate. In addition, temperature would affect the solubilities of ammonia and of the un-