

# Caking in Ammonium Phosphate Fertilizers

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An experimental study was undertaken to determine the relationship between caking of ammonium phosphate fertilizer grades 13-5.7-10.8 (13-13-13) and 12-7-13.3 (12-16-16) and the titration mole ratio ( $\text{NH}_3/\text{H}_3\text{PO}_4$ ) and moisture content of the fertilizer. Work was also done toward identifying the bonding-phase material causing caking. The caking tendency of 13-5.7-10.8 grade decreases as the mole ratio increases from 0.9 to 1.16; further increase causes an increase in caking to a mole ratio

of about 1.28. Caking of the 12-7-13.3 grade decreases as mole ratio increases from 0.9 to 1.05; further increase to 1.08 causes caking to increase. If the mole ratio is increased above the values of 1.28 and 1.08, caking decreases. A salt complex of the general formula  $\text{K}_{(2-z)}(\text{NH}_4)_z\text{SO}_4 \cdot z\text{H}_2\text{O}$  is credited with causing caking in the fertilizer grades tested near the critical mole ratio (1.16 for 13-5.7-10.8 and 1.05 for 12-7-13.3).

**B**oth the fertilizer industry and the consumer are plagued by the caking of commercial fertilizer. Numerous investigators have attempted to discover the causes of caking and to eliminate them. As yet, no entirely satisfactory solution to the caking problem has been found and, in fact, the causes of caking have not been completely ascertained. It has been found, however, that caking occurs in mixed fertilizers because of bonding between the individual particles of fertilizer. Neither the exact mechanism of bonding nor the constituents of the bond have been determined for all types of fertilizers.

According to Lawrence (1945), Mitchell (1954), and Silverberg *et al.* (1958), caking is the result of bonding together of fertilizer granules by a salt bridge. This bridge, formed at the point of contact between adjacent granules, actually welds the particles together with a bond which at times is physically stronger than the granule itself.

Composition of the bridge is, of course, dependent upon composition of the mixed fertilizer involved. Hignett *et al.* (1958) and Sauchelli (1955) have shown the bridge to be composed of water soluble salts. X-ray crystallographic and optical methods have shown that in instances where ammonium and chloride containing compounds (*e.g.*, ammonium nitrate and potassium chloride) are present in the raw materials, ammonium chloride and potassium nitrate are the prime constituents of the salt bridge. In fertilizer formulation of this type, the following double decomposition—credited to Sauchelli (1955)—may take place:



When the number of ammonium ions present is greater than the number of chloride ions, all chloride in the final crystals will appear as ammonium chloride.

Several hypotheses have been suggested for the mechanism by which the crystal bridge forms. Under certain conditions, an aqueous solution of ammonium chloride surrounds the contact points of the fertilizer granules and crystallization of the ammonium chloride takes place from the solution. Mitchell (1954) and Sauchelli (1955) believe that ammonium chloride diffuses to the surface by sublimation

during the drying process. Others believe that saturated salt solutions which are contained within crevices in the fertilizer granule migrate to the surface while the fertilizer is cooling from the drying to the storage temperature. Probably both mechanisms contribute to the increase in concentration of certain salts at the granule surface. Once the solution is present, capillary action draws a portion of it into the contact points of adjacent granules. If the ions remain in the solution, no caking takes place, but recrystallization from the solution forms a rigid bridge between the particles.

According to Hardesty and Kumagai (1952) free moisture content is the most important single factor influencing caking. If no water is present in the final product, aqueous salt solutions cannot form. Many investigators have proved the importance of free moisture and Raistrick (1956) even states that drying the entire production to a maximum moisture content of 1% is necessary.

The objectives of this investigation were: (1) to determine the relationship between caking and the mole ratio and moisture content of two common fertilizers. The mole ratio is defined as ratio  $\text{NH}_3/\text{H}_3\text{PO}_4$  in the fertilizer, determined by titration. (2) to identify the bonding phase of commercial 13-5.7-10.8 (13-13-13) and 12-7-13.3 (12-16-16) ammonium phosphate fertilizers. A bonding phase was identified by optical and X-ray studies of the fertilizer granule and bonding phase. The effect of mole ratio and moisture content on caking was determined by preparing, granulating, caking, and breaking fertilizer samples of known mole ratio and moisture content.

## MATERIALS AND PROCEDURE

The laboratory-prepared fertilizers, 13-5.7-10.8 and 12-7-13.3, were made from concentrated ammonium hydroxide (C.P.), sulfuric acid (98% C.P.), wet process phosphoric acid (30%  $\text{P}_2\text{O}_5$ ) and coarse grind muriate of potash (KCl).

**Sample Preparation.** Fertilizer grades 13-5.7-10.8 and 12-7-13.3 were prepared in the laboratory by neutralizing a mixture of 30%  $\text{P}_2\text{O}_5$  phosphoric acid and 98% sulfuric acid with concentrated ammonium hydroxide to the desired mole ratio ( $\text{NH}_3/\text{H}_3\text{PO}_4$ ). Coarse potash was added to the slurry and the mixture was allowed to air dry to approximately 8% moisture. The "dry" material was charged in small portions to the small-scale granulator shown in Figure 1. Granules thus prepared were dried in a rotary bench-scale dryer to a 0 to 5% moisture content range, screened to a range of 1.68-4.76 mm., and stored at room temperature in plastic freezer bags until ready for subsequent tests.

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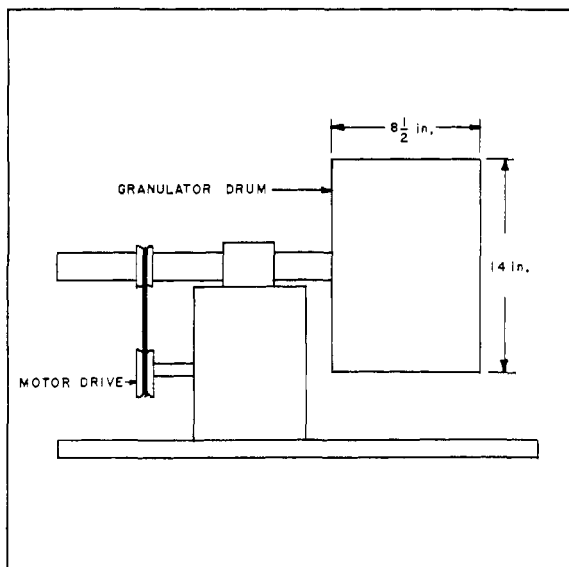


Figure 1. Fertilizer granulation apparatus

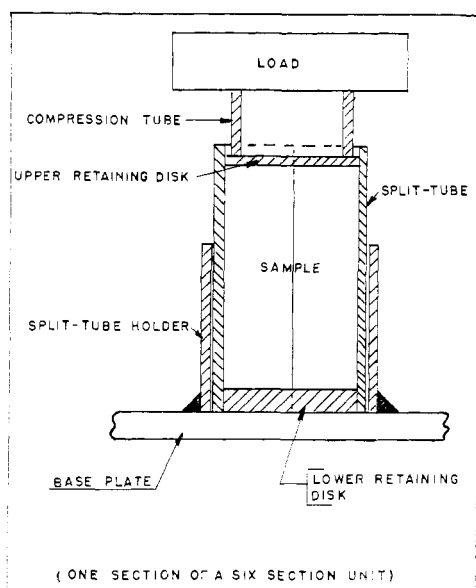


Figure 2. Detailed view of caking apparatus

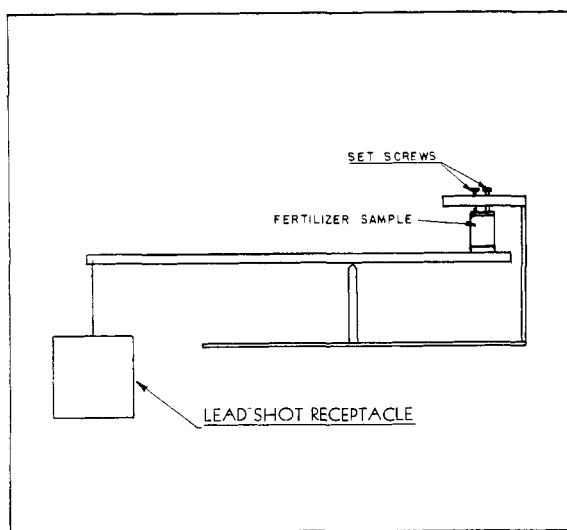


Figure 3. Breaking strength apparatus

Table I. Quantities of Material Used to Formulate Grade 13-5.7-10.8 [13-13-13]<sup>a</sup>

Mole Ratio	NH <sub>3</sub> (Lbs.)	40% <sup>o</sup> H <sub>3</sub> PO <sub>4</sub> (Lbs.)	98% <sup>o</sup> H <sub>2</sub> SO <sub>4</sub> (Lbs.)	Potash (Lbs.)	Filler (Lbs.)
0.97	0.80	2.2	1.76	1.09	0.08
1.05	0.80	2.2	1.72	1.09	0.14
1.16	0.80	2.2	1.65	1.09	0.23
1.28	0.80	2.2	1.61	1.09	0.35
1.47	0.80	2.2	1.50	1.09	0.50

<sup>a</sup> Formulation basis was 5 pounds of product at 2.5% final moisture.

Table II. Quantities of Material Used to Formulate Fertilizer Grade 12-7-13.3 [12-16-16]<sup>a</sup>

Mole Ratio	NH <sub>3</sub> (Lbs.)	40% <sup>o</sup> H <sub>3</sub> PO <sub>4</sub> (Lbs.)	98% <sup>o</sup> H <sub>2</sub> SO <sub>4</sub> (Lbs.)	Potash (Lbs.)	Filler (Lbs.)
0.91	0.735	2.8	1.69	1.35	0
0.94	0.735	2.8	1.63	1.35	0
1.02	0.735	2.8	1.55	1.35	0
1.07	0.735	2.8	1.49	1.35	0
1.13	0.735	2.8	1.43	1.35	0

<sup>a</sup> Formulation basis was 5 pounds of product at 2.5% final moisture.

Tables I and II show the components used in preparing each fertilizer grade. It should be noted that the composition of all the fertilizers prepared was based on a final moisture content of 2.5%; adjustment of the moisture content was performed during the drying operation.

**Accelerated Caking.** The special unit shown in Figure 2 was fabricated to permit caking six samples simultaneously. Approximately 50 grams of sample was placed in each section. Weight was added to the samples which simulated a loading force which would be experienced by a bag of fertilizer at the bottom of a 25-bag stack (approximately 4 pounds per square inch of sample cross-section).

The caking unit was then placed in an oven at 135° F. for 48 hours. This temperature was high enough to give good evaporation but was not so high as to promote chemical decomposition. At the end of this period, the apparatus was removed from the oven, allowed to stand at room temperature with the weight in place for an additional 24 hours. When the cooling cycle was complete, the sample was removed and broken as described below.

**Breaking Strength.** Sample breaking strength is the axial force required to fracture a cake sample. A cylindrical caked sample of fertilizer was placed on the apparatus as shown in Figure 3. Lead shot was added to the balance arm (after the unit had been balanced) until the cake fractured. The weight of shot required for breakage was then used to calculate the sample breaking strength. Samples were analyzed for moisture and mole ratio after breaking.

**X-ray Diffraction Study.** X-ray analysis was chosen for this investigation because it is accurate, much less time-consuming than chemical analysis, and nondestructive to the sample. Also, the minute size of some of the samples would virtually prohibit chemical analysis with any degree of accuracy. To identify the constituents of the fertilizer and to determine if any change had taken place in the fertilizer during the caking process, an X-ray diffraction analysis was made of both caked and uncaked samples of 13-5.7-10.8 and 12-7-13.3 fertilizer (both laboratory and commercial

material). These samples had been prepared near the critical  $\text{NH}_3/\text{H}_3\text{PO}_4$  mole ratio. A small portion of the sample to be tested was ground to a fine powder, packed lightly in an aluminum powder-sample holder, and placed in position in the diffraction unit. Analysis of the resulting diffraction patterns was done by first indexing each pattern—*i.e.*, labeling each “peak” on the pattern with its  $d$ -spacing (in Angstrom units). By using the X-ray powder data file, identification of the material in the fertilizer which produced the various peaks in the X-ray pattern was made.

Because of the microscopically small amounts of the bonding phase found on the fertilizer granules, a powder camera method of analysis had to be substituted for the goniometer method of examination of the bonding phase. Samples of the bonding phase approximately the size of the head of a pin were placed on a glass slide and a drop of collodion added. When the collodion had dried, it was rolled into a cylindrical configuration. With the samples thus suspended in the collodion cylinder, it was mounted in the camera unit and exposed to X-rays for a period of three hours.

## RESULTS AND DISCUSSION

**Effect of Titration Mole Ratio and of Moisture Content on Caking of Laboratory-Prepared Fertilizer.** The effect of moisture content and titration mole ratio on caking was ascertained by preparing controlled fertilizer samples, causing them to cake by an accelerated method, and measuring the force necessary to fracture the caked mass, as described above. Two grades of ammonium phosphate fertilizer were prepared: 13-5.7-10.8 and 12-7-13.3. Samples of each grade were prepared at five mole ratios and at five moisture contents for each mole ratio. Each sample was treated in triplicate. Breaking strength data (force necessary to break fertilizer cake) was correlated with moisture content and titration mole ratio of the fertilizer in an attempt to discover the cause of caking.

As expected, there is a general increase in the sample breaking strength with increase of moisture content at a constant mole ratio. For a given grade, however, samples of different mole ratios exhibit different rates of increase in breaking strength; some increase rapidly while others increase gradually.

Figures 4 and 5 were prepared by plotting breaking strengths *vs.* mole ratio with per cent moisture as the parameter. From these curves, it may be seen that the mole ratio has a marked effect upon caking. For grade 13-5.7-10.8, the breaking strength of the cake drops off sharply as the mole ratio increases from 0.91 to about 1.16. At 1.16, the breaking strength abruptly increases and then decreases with continued increase in mole ratio. This pattern of behavior is consistent for the five moisture contents used. Fertilizer grade 12-7-13.3 shows a similar behavior but with a shift in the critical mole ratio from between 1.16 and 1.28 to 1.05.

Dashed lines were used to connect points across the critical mole ratio because the exact points of inflection for the curves are not known. There is a span of 0.05 mole ratio units with respect to the critical mole ratio for 12-7-13.3 which is considered sufficiently small to allow assumption of a critical mole ratio value of 1.05. In 13-5.7-10.8, however, the span is 0.12 mole ratio units; therefore, an assumption of the precise critical mole ratio is not justified. An intuitive estimate of 1.2 for the critical mole ratio of 13-5.7-10.8 is probably near the correct value.

The critical mole ratio is considered to be a point of discontinuity in the breaking strength-mole ratio curve, with a finite

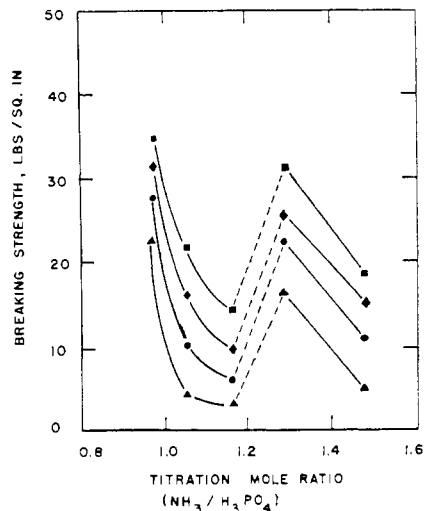


Figure 4. Breaking strength curve for 13-5.7-10.8 [13-13-13]

- 3% moisture
- ◆ 2.5% moisture
- 2% moisture
- ▲ 1.5% moisture

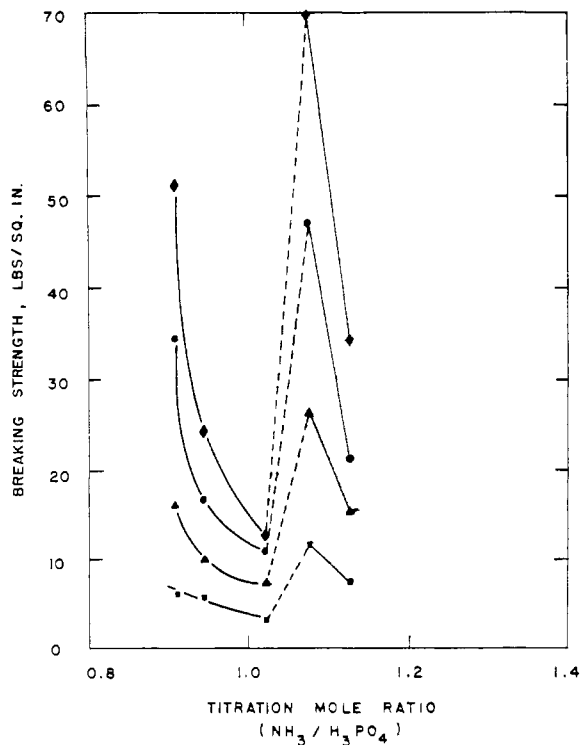


Figure 5. Breaking strength curve for 12-7-13.3 [12-16-16]

- ◆ 2.5% moisture
- 2% moisture
- ▲ 1.5% moisture
- 1% moisture

jump in breaking strength occurring at the critical mole ratio. A study of Figure 6 in which mole ratio is plotted *vs.* pH shows that the critical mole ratios for both 13-5.7-10.8 and 12-7-13.3 lie in the rapidly changing region of the curve. Slight variation in mole ratio within this region results in a marked change in the pH of the fertilizer sample. For this reason, it is believed that the pH is a factor in causing the fertilizer granules to cake. Based on the X-ray diffraction

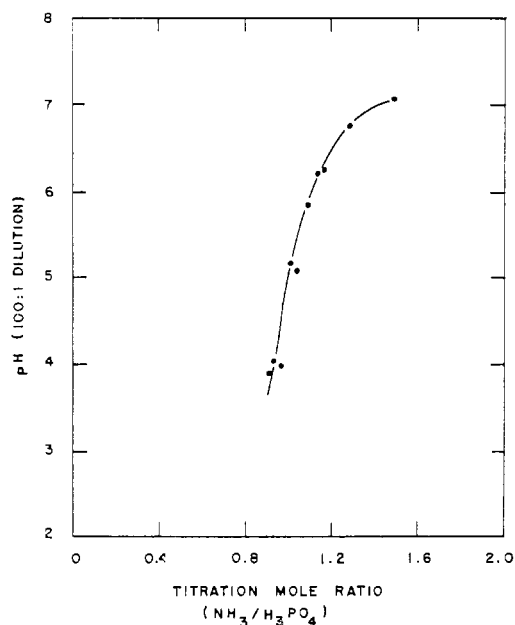


Figure 6. Titration mole ratio vs. pH of fertilizer

studies, it would be reasonable to postulate that either the crystallinity or the structure of the ammonium-potassium sulfate complex is some function of the pH of the fertilizer.

**Identification of Bonding Phase.** To aid in determining the fertilizer composition, standard diffractograms were prepared by analyzing pure samples of ammonium sulfate, mono-ammonium phosphate, ammonium chloride, 60% muriate of potash (KCl), and gypsum and comparing the resulting pattern with those of the fertilizer.

Further aid in compound identification was obtained by neutralizing two separate samples of the wet process phosphoric acid with ammonium hydroxide without the addition of any sulfuric acid. One sample was ammoniated to a mole ratio of 0.95, the other to a mole ratio of 1.06. By X-ray analyses the presence of di-ammonium phosphate could be detected; comparison of X-ray patterns of the two samples show that they are identical and that the amount of di-ammonium phosphate produced at a mole ratio of 1.06 is negligible when compared to the amount of mono-ammonium phosphate. All peaks obtained on the two patterns were for mono-ammonium phosphate.

A large amount of pure ammonium sulfate was added to a portion of the neutralized acid and X-ray patterns were made on the mixture. The result is a superposition of the mono-ammonium phosphate and ammonium sulfate diffractograms. The individual peaks are well resolved and indicate that no reaction had taken place between the mono-ammonium phosphate and the ammonium sulfate.

A portion of the mixture of mono-ammonium phosphate, and the ammonium sulfate was wetted, allowed to air dry, and then examined with the X-ray unit to determine the effect of moisture addition. Ammonium sulfate peaks at  $2\theta$  angles,  $17^\circ$ ,  $20.3^\circ$ , and  $29.3^\circ$ , which were well resolved in the pattern of the dry mixture, were shifted into adjacent peaks by the addition of water. This indicates that water is entering the ammonium sulfate lattice to form some type of hydrate. The formation of the hydrate must be, however, influenced by the presence of mono-ammonium phosphate since X-ray analyses indicated no hydrate is formed with pure ammonium sulfate and water. No hydrate of mono-ammonium phosphate was indicated by the diffractograms.

An important observation was also made upon comparing the patterns for the mixture of mono-ammonium phosphate/-ammonium sulfate and those of the fertilizer samples. Resolution of the ammonium sulfate doublet (a double peak between  $20.2^\circ$  and  $20.6^\circ$ ,  $2\theta$ ) was not obtained in the fertilizer, indicating the presence of the hydrate. But of even more interest, the single peak had shifted from an angle of  $20.5^\circ$  to an angle of  $20.8^\circ$  in the fertilizer. This represents a change in the  $d$ -spacing for this particular diffracting plane of from  $4.32 \text{ \AA}$  to  $4.27 \text{ \AA}$ ; a change which is consistent in all of the fertilizer samples tested. No shift may be seen in either the dry or wetted mixture of neutralized phosphoric and ammonium sulfate.

A small amount of muriate of potash (potassium chloride) was added to the dry mixture of mono-ammonium phosphate and ammonium sulfate and was examined with the X-ray. No reaction was indicated. When the sample was wetted and allowed to air-dry, however, X-ray analysis showed a great change had taken place in the mixture. Potassium chloride peaks which had been well defined at  $28.4^\circ$  and  $40.6^\circ$  on the pattern of the dry sample disappeared upon addition of water and new peaks at  $30.7^\circ$  and  $32.75^\circ$  were formed. The peak at  $32.75^\circ$  was identified as the major peak for ammonium chloride and the one at  $30.7^\circ$  as a peak for either potassium sulfate or a potassium-ammonium sulfate complex.

A drastic alteration of the major ammonium sulfate peak also appeared. It changed from a sharp single peak and shifted approximately  $0.6$  degrees to a higher  $2\theta$  angle (smaller  $d$ -spacing). The mono-ammonium phosphate peaks remained unchanged. This is sufficient evidence to suggest the formation of a new substance.

Formation of ammonium chloride, change in the ammonium sulfate, and no change in the mono-ammonium phosphate indicated that one, or both, of the following reactions take place in the wetted mixture.



Upon examination of the shifted ammonium sulfate peak and consideration of the reactions above, it was found that the ammonium sulfate peak shifts toward the major peak of a complex having the form  $\text{K}_{[2-x]}[\text{NH}_4]_x\text{SO}_4$  [ $X = 0.35$ ]. Combining this information with the fact that the ammonium sulfate peaks remain very prominent in fertilizer diffractograms (no large formation of potassium sulfate), reaction 1 appears to be the more likely. To confirm that all ammonium ions forming ammonium chloride come from ammonium sulfate, a small sample of potassium chloride was added to mono-ammonium phosphate, wetted, allowed to air-dry, and then analyzed with the X-ray. The result indicates that no reaction between potassium chloride and mono-ammonium phosphate took place since all peaks are well resolved, and appear at the proper angles.

X-ray photographs were taken of the bonding phase between granules to verify the presence of a complex. After studying many photographs, the conclusion was reached that the bonding phase is composed mainly of an ammonium-potassium sulfate complex. Other compounds, such as mono-ammonium phosphate, ammonium chloride, and potassium chloride were also found to be present in many samples of the bonding phase. Because of the minute size of the bridge and its intimate contact with the granule, it was difficult to separate the bonding phase so as to exclude any granule surface material. For this reason, it could not be

ascertained whether the bridge was one definite salt or a combination of several salts. It is thought, however, that the bonding phase is composed primarily of the ammonium potassium sulfate complex for fertilizers with  $\text{NH}_3/\text{H}_3\text{PO}_4$  mole ratio near the critical. Tables III and IV give data on bonding phase photographs.

#### CONCLUSIONS

The following conclusions are drawn from results of the experimental investigation. The bridge or bonding phase between the caked fertilizer granules of  $\text{NH}_3/\text{H}_3\text{PO}_4$  mole ratio near the critical is a complex salt of the general form:



in which the value of  $x$  is dependent upon both the number potassium ions present and the pH of the fertilizer sample. At a given pH the amount of the complex formed is a function of the amounts of potassium chloride and ammonium sulfate present, and probably to some undetermined extent, the amount of mono-ammonium phosphate present.

Caking is favored both by increase in the amount of the complex present and by the structure of the complex. The greater the value of  $x$  in the structural formula of the complex (the fewer the potassium ions), the greater is the caking tendency of the fertilizer. This is based on an inverse behavior of the amount of potassium chloride reacted to that of the breaking strength with respect to mole ratio or pH of the fertilizer.

The pH has a marked effect on the structure of the complex. It is believed that as the pH of the fertilizer increases slightly from low values of pH of about 3.9, strain in the crystalline structure of the complex is increased. When a given strain in the structure is reached, a change in phase takes place in the structure to relieve the induced strain. Continued increase in the pH renews the straining process. Failure in the structure is believed to occur in crystal faces with  $d$ -spacings less than 3.50 Å as is indicated by X-ray diffractograms of the fertilizer taken on either side of the critical mole ratios. Also, the strain which a crystallite will withstand must be a function of not only the pH but also the value of  $x$  in the structural formula of the complex. This would then explain why the values of the critical pH are different for the two grades of fertilizer investigated. The fact that pH and  $x$  values are so interrelated indicates the necessity for knowing the exact structure of the complex.

The moisture content of the fertilizer, although not so dramatic in its effect as the mole ratio, does have an undisputed role in caking. Figures 4 and 5 show a sizeable increase in breaking strength with increase in moisture content at a constant mole ratio. The effect is believed to be two-fold. First, the ammonium sulfate forms a hydrate upon the addition of water in the presence of mono-ammonium phosphate. No quantitative statement can be made as to the number of water molecules (indicated by  $Z$  in the formula of the complex) present in the structure of the complex. Secondly, the water in the fertilizer acts as a carrier for the complex salt which permits the accumulation of the complex on the surface of the granules where it can bring about the caked state.

Fluctuations in the moisture content would obviously accelerate caking, but caking could also occur at constant moisture content. Natural migration of the highly water-soluble salts to granule surfaces could occur as well as migration due to relieved stresses within the granules. Once the complex has reached the granule surface, capillary action

Table III. Results from X-Ray Photographs of 13-5.7-10.8 [13-13-13] Fertilizer Bonding Phase

Line No.	$2\theta$	$d, \text{Å}$	$I/I_0$ (Visual Estimate)
1	16.85	5.26	70
2	20.70	4.28	100
3	23.40	3.79	60
4	29.25	3.05	80
5	30.60	2.92	30
6	33.15	2.70	30
7	36.35	2.47	10
8	39.95	2.25	10
9	42.45	2.12	10

Table IV. Results from X-Ray Photographs of 12-7-13.3 [12-16-16] Fertilizer Bonding Phase

Line No.	$2\theta$	$d, \text{Å}$	$I/I_0$ (Visual Estimate)
1	17.00	5.21	80
2	20.80	4.26	100
3	23.20	3.83	80
4	29.25	3.05	90
5	33.10	2.70	100
6	35.95	2.49	30
7	39.60	2.27	50
8	42.25	2.13	50
9	45.55	1.99	50
10	47.40	1.91	50

would promote accumulation at points of contact between granules.

The following recommendations are based on the conclusions drawn from results presented and are necessarily restricted to the types and grades of fertilizer investigated.

Since caking has been shown to be extensive at the critical mole ratios, commercial formulation should be controlled so that the product mole ratio is either slightly below or somewhat above the critical mole ratio for that particular grade. Suggested mole ratios for the two grades tested are:

13-5.7-10.8	1.1 or 1.5
12-7-13.3	1.0 or 1.2

The final product should be dried to a moisture content as low as is economically feasible to prevent migration of the complex to the surface of the granules. Bagging of the product should follow immediately after a short cooling period to prevent any uptake of moisture by the fertilizer.

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