Mechanism of Caking of Ammonium Nitrate (NH₄NO₃) Prills

Christer Sjölin[1]

A study has been made with ammonium nitrate prills in order to determine the mechanism of caking. Methods of investigation used were X-ray diffractography, scanning-electron microscopy, and tests in a climate chamber. The results show that caking is mainly caused by the phase transition IV ⇌ III at 32°C and depends on the dissolution and recrystallization of the solid at this phase transition. If no pressure is applied to the sample a porous powder is formed due to the volume increase of the phase transition and the formed salt bridges. If pressure is applied to the sample it will be pressed together, due to mechanical weakness of the prill during the phase transition, resulting in large crystal surfaces in contact with each other, and the dissolution-recrystallization process gives a very hard product. A certain degree of caking may result from recrystallization phenomena on the surface of the prills due to changes in the relative humidity.

Ammonium nitrate is finding increased use as a fertilizer and as an explosive. It is also well known that ammonium nitrate during storage will cake together. The problem of the caking of ammonium nitrate prills has been the subject of a large number of investigations because of its great importance with respect to the handling of ammonium nitrate prills.

This problem has been partially solved by adding inorganic additives in an amount of 1-2% and sometimes also by treating the prills with a surface active agent in order to prevent contact between the prills and surrounding humidity. Although good results have been reached by these methods, no unitary mechanism of the caking has been presented. An important factor is the particle size and the shape of the particle. It is known that crystallized ammonium nitrate will cake easier than prilled ammonium nitrate.

It is known that ammonium nitrate is a very hygroscopic salt, which has sometimes been suggested as being the reason for caking. Some authors consider that the hygroscopicity is of no importance and that the reason for caking is the phase transition IV ⇌ III. This transition takes place at 32°C and involves a change in volume of 3.6% (Nagatani et al., 1967). Most producers refrigerate the ammonium nitrate to about 28°C after drying in order to prevent caking during storage (Kazakova et al., 1967). The purpose of this work is to describe the mechanism of caking of ammonium nitrate prills.

Lowry and Hemmings (1920) have proposed that caking depends on recrystallizations on the surface of the ammonium nitrate crystals. Due to the phase transition IV ⇌ III at 32°C cracking takes place and the retained water in the crystals will be released and can thus take place in the recrystallization process. They have also shown that very carefully dried ammonium nitrate will not cake. This latter statement has been confirmed by Sjölin (1971). Shneerson et al. (1956) has stated that the phase transition IV → III does not cause caking, while the phase transition III → IV is of very great importance for caking. They have also shown that the pressure is of importance. Like Lowry and Hemmings (1920) they stated that it is the water on the surface which, during recrystallization, causes salt bridges to be formed between the different crystals. This is intensified by the increase of free ammonium nitrate surface created by the phase transition III → IV.

Erofeev and Mitskevich (1958) put forward that the phase transition IV ⇌ III itself has nothing to do with caking. The phase transition only loosens the structure of ammonium nitrate, thus causing an increase in the specific volume. Wolf and Scharre (1967) have also reasoned in a similar manner. At the same time, contrary to Shneerson et al., they state that the phase transition IV → III can cause caking. The caking mechanism is stated to merely be due to a difference in solubility of ammonium nitrate at different temperatures. The mass transport of water within and between the crystallites results in salt bridges, thus giving rise to caking. A similar argument has been put forward by Whetstone (1952).

The importance of the water content and its effect on the phase transition temperature for the transition IV ⇌ III (see Figure 1) has been demonstrated by Sjölin (1971) and Griffith (1963). Brown and McLaren (1962) have shown that the phase transition IV ⇌ III only takes place in the presence of water and that the phase transition is a dissolution and recrystallization of the solid ammonium nitrate. This latter theory is supported by the great difference in the structure of phase IV and phase III.

EXPERIMENTAL

The ammonium nitrate prills that have been used in this work are of commercial low-density type produced by KemaNord AB, Sweden. These experimental prills, however, have no additives in order not to disturb the effects of the different treatments.

DETERMINATION OF THE MECHANISM OF THE PHASE TRANSITION IV ⇌ III

The X-Ray Investigations. If the mechanism of the phase transition IV ⇌ III is a dissolution and recrystallization of the solid ammonium nitrate, as stated by Brown and McLaren (1962), who noticed the large increase in electrical conductance at the phase transition, this could be studied by X-ray diffractography. During repeated transitions there is no reason to believe that the same nucleating center will be the seed of the recrystallization at each transition and, therefore, different crystal planes will be over- or under-represented in the sample each time the phase transition takes place, resulting in very different diffracted beam intensities each time. Ammonium nitrate is easy to grind and usually gives no orientating effects.

The X-ray specimen holder was made of copper and the temperature could be changed by pumping water from a
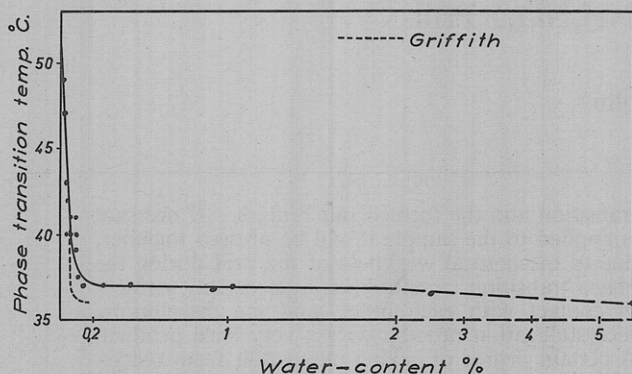
Figure 1. The phase transition temperature IV→III as a function of the water content for ammonium nitrate prills

Table I. The Relative Intensities of the Diffracted Beam after Cycling over the Phase Transition IV ⇄ III

| Water content, % | Cycling no. | Intensity[a] | | | |
| | | Phase IV | | Phase III | |
		100 peak[b] (111)	75 peak[b] (020)	100 peak[b] (220)	75 peak[b] (120)
1.88	0	100	100	100	100
	1	5	1	50	500
	2	20	20	10	100
	3	40	150	120	80
	4	100	20	20	200
	5	50	50	0	50
	6	10	0	...	...
0.81	0	100	100	100	100
	1	80	50	10	120
	2	50	20	190	60
	3	20	175	...	...
0.05	0	100	100	100	100
	1	20	50	80	100
	2	50	10	100	80
	3	50	20	50	150
	4	75	20	90	150

[a] Intensity = % of line intensity for the initial phase IV and % of line intensity for the initial phase of that phase III which is obtained after the first phase transition. [b] By "100 peak" and "75 peak," respectively, is meant the peak with the highest intensity and 75% of the intensity of the highest peak, respectively, according to ASTM Index No. 8-499 for phase III and No. 8-452 for phase IV.

thermostated bath through small channels (loops) in the holder. The temperature was measured with a thermocouple (Cu–constantan) placed in the middle of the ammonium nitrate.

The experiments were made in the following ways. The sample was carefully ground and a diffractogram was registered (for Cu Kα angle $2\theta = 35-25°$) to study the initial phase. In all experiments the intensities of the different peaks in the initial diffractogram were in good agreement with those given in the ASTM Index. The sample was then heated until the phase transition IV → III took place and a diffractogram was registered (angle $2\theta = 41-20°$) in order to determine the intensities of the different peaks of phase III. Similarly, the sample was cooled again and the intensities of the peaks of phase IV were studied. By thus cycling over the phase transition temperature several times, the variations of the intensities could be studied. Samples with different water content were studied.

The results from these experiments are shown in Table I. It is obvious that when the phase transition IV → III has been passed, the different crystal planes are no longer statistically
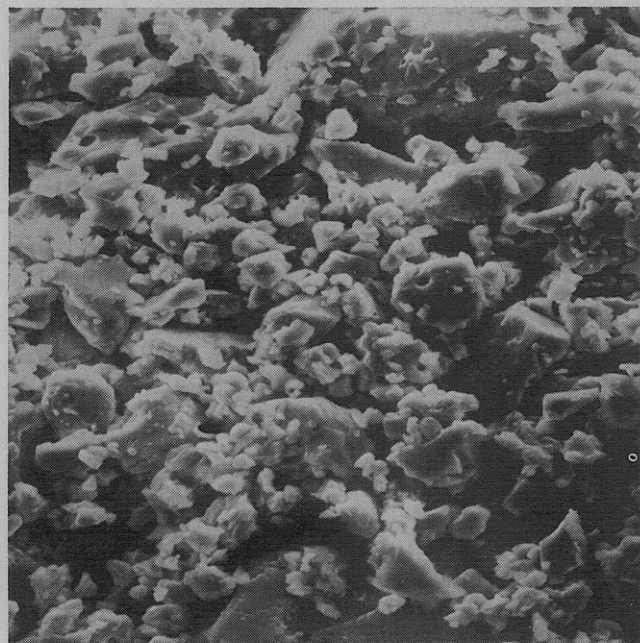

Figure 2. Ground prills (300×)

represented and the changes are much greater than can be expected by a common order–disorder phase transition. The same phenomenon takes place by the phase transition III → IV. No correlation or trend in the diffracted beam intensities of the different spectral lines was observed during repeated cycling through the phase transition. This indicates that different nucleating centers initiate the phase transition each time, as was predicted.

As may be seen in Table I, samples of different water content were used, and as long as the phase transition IV ⇄ III takes place, no difference dependent on the water content can be observed. The water content must be <0.01% to eliminate this phase transition (Sjölin, 1971). Also, samples with additives were tested and they behaved exactly in the same way as soon as the water content was high enough to give a phase transition IV ⇄ III (e.g., 1.09% for an additive of 2% of $Mg(NO_3)_2$; Sjölin, 1971).

These results, together with the knowledge that small amounts of water must be present, indicate that Brown and McLaren's (1962) theory, based on the increase in electrical conductance at the phase transition IV ⇄ III, is correct and the mechanism of the phase transition IV ⇄ III is a dissolution and recrystallization of the solid.

The Scanning-Electron Microscope Investigations. With the scanning-electron microscope it was possible to observe a sample before and after a rapid cycling over the phase transition IV ⇄ III. Because of its great depth of focus, this microscope is very suitable for investigations of this type. The most common magnifications used were 300× and 1000×. The scanning-electron microscope used was a Jeol JSM-2.

With the scanning-electron microscope pictures were taken of a ground sample before and after the phase transition IV ⇄ III. The sample with a water content of 0.2% was divided into two parts, one being cycled through the phase transition temperature and the other kept as a reference sample. The results are shown in Figures 2, 3, 4, and 5.

The photographs show very clearly that the ground crystals have grown together after having passed the phase transition IV ⇄ III. This phenomenon is not due only to a recrystal-
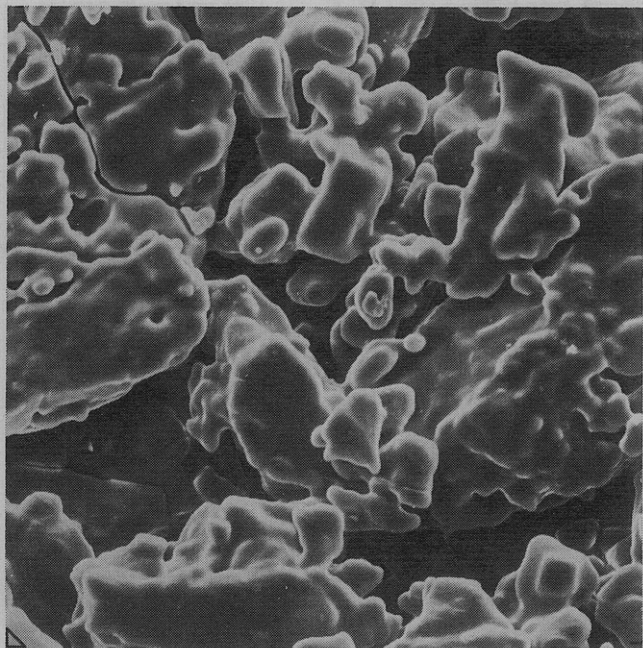
Figure 3. The same sample as in Figure 2 after the phase transition (300×)

Figure 5. The same sample as in Figure 4 after the phase transition (1000×)

Figure 4. Ground prills (1000×)

lization on the surfaces due to temperature differences, because in that case the sharp edges of the initial sample would remain, which is not the case. During these experiments no pressure was put on the sample and, therefore, the porous structure remains.

The passage of the phase transition temperature was made within 10 min. The initial sample was also investigated 1 month later and no effect of the storage could be seen in the scanning-electron microscope. Another sample which had passed through the phase transition very slowly showed the same appearance as that which had passed through rapidly. It is, therefore, obvious that it is the cycling over the phase
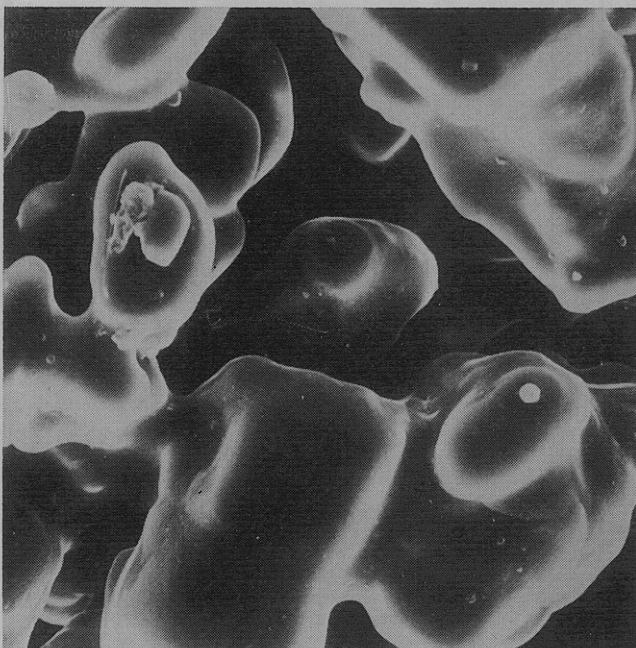
transition IV ⇌ III that has caused the change (caking) of the ammonium nitrate.

TESTING IN THE CLIMATE CHAMBER

In order to study further the two main hypotheses of caking mechanism, i.e., passing of phase transition IV ⇌ III and the hygroscopicity of ammonium nitrate, experiments were performed in a climate chamber.

The samples were commercial 25-kg sacks of ammonium nitrate prills which were piled up 0.5-m in height. The following three tests were carried out.

A. The sample was cycled eight times over the phase transition IV ⇌ III by heating at 40 and 20°C every alternate day. The relative humidity in the sacks during the whole experiment was below 50% (under this humidity ammonium nitrate does not take up moisture according to Ross et al., 1946). The water content was measured before and after the experiment in order to study if mass transport of water exists.

B. The sample was cycled at a temperature under 32°C (between 28 and 15°C) and at a relative humidity under 50% for 26 days. The sacks were perforated in order to allow contact between the prills and the surrounding atmosphere. The water content was measured before and after the experiment.

C. The sample was cycled eight times over the critical relative humidity (66% at 15°C and 62% at 25°C according to Ross et al., 1946) by changing the relative humidity between 35% (at 20°C) and 85% (at 15°C). Again, the sacks were perforated and the water content was measured before and after the experiment.

The results from these investigations are shown in Table II and in Figure 6, 7, and 8.

It is apparent from Table II that no great differences in physical data were obtained compared with the results reached with the commonly used laboratory tests for ammonium nitrate prills. This is due to the fact that when the sample is stored in a sack the available space for the volume
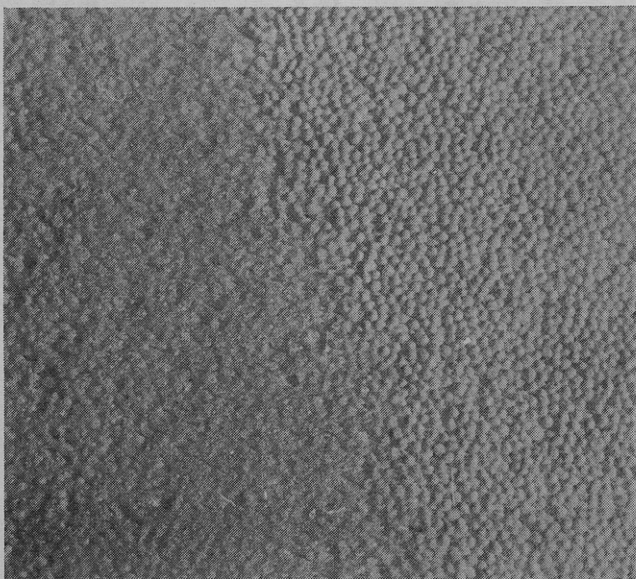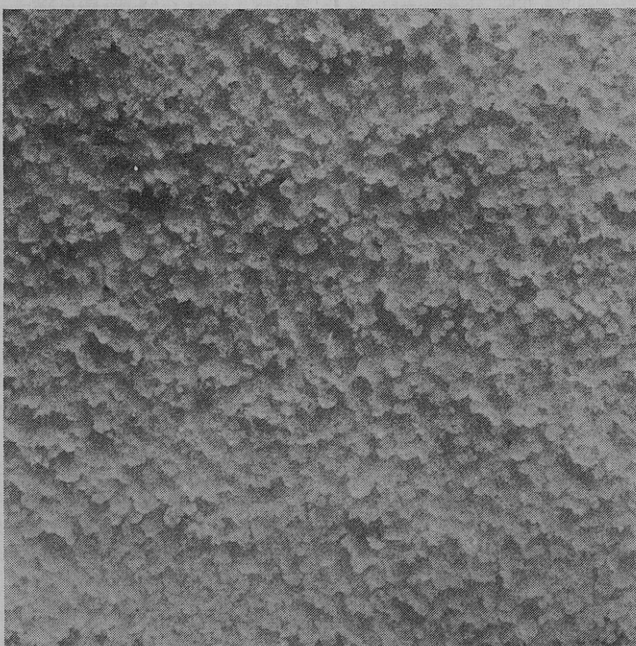
Figure 6. The caking zone in a sack (1×)

Figure 8. Prills cycled over the critical relative humidity (1×)
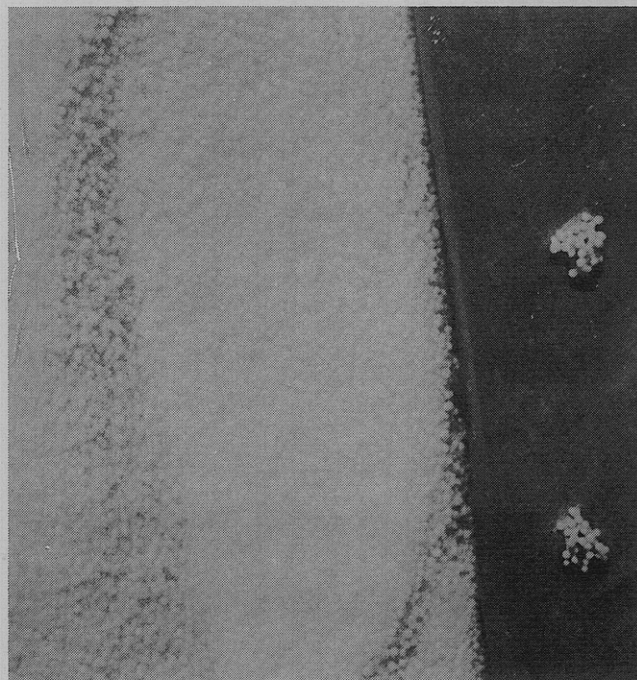

Figure 7. Caked prills from a sack (2×)

Table II. Test Results from the Climate Chamber Experiments

	Water content[a]		Prill breakage %[b]		Density, g/cm³	
Sample	Before[c]	After[c]	Before[c]	After[c]	Before[c]	After[c]
Original sample	0.22		18		0.84	
A top bag[d]	0.20	0.16	18	24	0.84	0.72
A bottom bag[e]	0.20	0.15	18	21	0.84	0.74
B top bag[d]	0.22	0.23	17	16	0.85	0.85
B bottom bag[e]	0.22	0.22	17	18	0.85	0.85
C top bag[d]	0.24	0.22	18	18	0.84	0.84
C bottom bag[e]	0.24	0.23	19	18	0.84	0.85
Common laboratory tests cycling eight times[f]	0.22	...	19	69	0.84	0.57

[a] By gravimetric methods. [b] % of total amount prills crushed after shaking for 30 min. [c] Values obtained before and after the experiment in question. [d] Top bag = average values of samples from the outer part of a top bag in the pile. [e] Bottom bag = average values of samples from the outer part of a bottom bag in the pile. [f] For one cycle, prills have been heated to 40°C and then cooled to 15°C; time per cycle 2.5–3 hr.

increase (due to the phase transition IV ⇌ III) is limited.

Since different pressures are applied to the sacks according to position in the store pile, samples were taken from both bottom and top layer sacks. The temperature was measured and registered during the whole experiment, both in the middle and in the outer parts of the bags. Because of the endothermic phase transition IV → III the temperature profile has a plateau at about 33°C, and as ammonium nitrate is a bad thermal conductor, the transition temperature was passed only in the outer regions (about 10 cm thick) of the sacks. This is the reason why the samples were taken from these parts.

Experiment A. The results from this experiment show (Table II) that caking has taken place in all bags. During the experiment the water content is somewhat diminished due to the low relative humidity. The bags from the lower layer

have not decreased so much in density because the pressure limits the volume increase. The remaining volume increase is due to the fact that when the phase transition IV → III takes place the crystallites in the prills break up and salt bridges are formed. There is no reason why the prills which have expanded in this way should decrease in volume in exactly the same way by taking their initial positions when passing back through the phase transition III → IV. Thus, the dissolution–recrystallization process gives rise to new salt bridges between the crushed crystallites, and the volumetric density decreases. In Figures 6 and 7 photographs are shown

from these experiments. Figure 6 shows clearly how deeply into the sack the phase transition has taken place. This is in good agreement with the temperature measurements. Figure 7 shows how the individual prill in the caked zone has nearly lost its identity.

If the bags are exposed to so great a pressure that the crushed prills are pressed together, the result will be large crystal surfaces in contact with each other and the dissolution–recrystallization process can take place over the whole ammonium nitrate bulk, resulting in a very hard caked product.

An experiment was carried out with a sack which was set under a pressure of 0.55 kp/cm^2 and passed up and down through the phase transition once. As a result the density increased from 0.85 g/cm^3 to 0.86 g/cm^3 and the sack contents were very hard and were only crushed with difficulty to smaller pieces. The prilled structure of the ammonium nitrate was almost completely lost.

Experiment B. As may be expected, the results here show (Table II) that no caking at all has taken place. The prills were in exactly the same condition after the experiment as before.

Experiment C. The results here show (Table II) that no caking has taken place. This is also evidence on the photograph in Figure 8 where it is obvious that the prills are in the same condition as before cycling over the critical relative humidity. In Figure 8 it is, however, seen that the prills in direct contact with the vents in the sack are somewhat caked. This is due to recrystallization on the surface of these prills, but in this case the identity of the prills as such remains.

In order to test that the critical relative humidity was actually reached in the climate chamber, an evaporation basin was filled with prills and left in the climate chamber. After the experiment it was observed that the upper layer of the prills had recrystallized and the individual prills had entirely lost their identity (caking). The caked layer was about 5 mm thick but under this layer quite unaffected prills could be found. This indicates that the mechanism is such that the ammonium nitrate prills primarily exposed to high relative humidity will take up moisture until a saturated solution is formed before the moisture can be forced further into the ammonium nitrate bulk. This is in good agreement with Ross *et al.* (1946), as the equilibrium state for ammonium nitrate at the critical relative humidity is a saturated solution. This explains why the prills at the vents had caked somewhat but the rest of the prills in the bag had not done so.

THE MECHANISM OF CAKING

From the above results it is apparent that the mechanism of caking is as follows. When ammonium nitrate prills pass the phase transition IV → III at 32°C the bulk ammonium nitrate volume increases and during the dissolution–recrystallization process salt bridges are formed between the crystallites. During the phase transition III → IV the bulk ammonium nitrate volume decreases but the different crystallites cannot take their initial positions because of the newly formed salt bridges. If the phase transition IV ⇌ III is passed several times this volume increase continues, resulting in a more or less powdered product where the original prill structure is entirely lost.

If, on the other hand, the sample is subjected to a higher pressure the prills cannot expand freely but will be pressed together because of their reduced strength at the phase transition due to the dissolution–recrystallization mechanism.

Consequently, there will be large ammonium nitrate crystal surfaces in contact with each other and large opportunities for the dissolution–recrystallization process to take place between the different crystals resulting in a very hard ammonium nitrate lump.

Another piece of evidence in support of this theory is that caking is obtained as soon as the sample has passed the phase transition IV ⇌ III. The water content is not important as long as the critical amount (more than about 0.05%) is present. Whether the water is located on the surface or in the ammonium nitrate bulk is of no principal importance. On the other hand the phase transition in reality will start on the surface of a prill and, therefore, the water at the surface can be of greater importance.

Although the phase transition IV ⇌ III is the main reason for caking, the changes in the relative humidity may cause slight caking. This type of caking is only due to a recrystallization on the surface of the prills and cannot in reality cause the great problems in handling ammonium nitrate prills which are caused by the caking proper.

If ammonium nitrate prills with a higher water content (in reality, *e.g.*, 0.2–0.35% H$_2$O) are stored in moisture-proof bags, this water will give raise to the humidity in the bags, thus giving caking due to recrystallizations on the prill surfaces even if the temperature never exceeds 32°C. Changes in temperature below 32°C will give the necessary changes in the relative humidity.

It is obvious that caking cannot be the time-dependent mass transport of water, as suggested by Wolf and Scharre (1967). Furthermore the recrystallization of the surfaces of the prills suggested by Whetstone (1952) and Shneerson *et al.* (1956) cannot be the only reason for caking in reality since the experiment with cycling over the critical relative humidity did not give such severe caking as the passage of the phase transition IV ⇌ III. This process is also time-dependent, since the relative humidity does not change rapidly.

In many other cases this theory of the caking of ammonium nitrate prills will explain results earlier presented in the literature.

CONCLUSIONS AND RECOMMENDATIONS

From the results it is obvious that in order to eliminate the caking of ammonium nitrate prills it is necessary to eliminate the phase transition IV ⇌ III. This can be done by keeping the water content low enough to prevent the phase transition or by adding additives as Mg(NO$_3$)$_2$ and Al$_2$(SO$_4$)$_3$ (described by Sjölin, 1971) in order to diminish the water content in the ammonium nitrate bulk, thus preventing the phase transition IV ⇌ III. It is also necessary to keep the relative humidity sufficiently low so as to eliminate recrystallization on the surface of the prills. This latter effect is relatively unimportant when the particle size is uniform and the number of contact points is small, as is the case for the prilled ammonium nitrate.

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Phosphate Movement from an Agricultural Watershed During Two Rainfall Periods

Harry M. Kunishi,* Alan W. Taylor, Walter R. Heald, William J. Gburek, and Richard N. Weaver

The distribution of available phosphate between dissolved and adsorbed forms carried by stream water and sediments was measured at two sampling stations on a stream draining an agricultural watershed during high water flows. During an intense summer storm at the watershed the total available phosphate carried by the stream was 0.762 g per ha. In a less intense spring storm the loss was 0.028 g/ha. Changes in phosphate concentration during the storms were interpreted in terms of the adsorption isotherms of the sediments, which show that material derived from subsoils and stream banks has a large adsorption capacity. Concentrations of about 200 ppb (P) in water from fertile topsoil were reduced to less than 15 ppb as it moved downstream. Detailed prediction of phosphate concentrations in moving streams depends on adequate knowledge of the quantity, chemical characteristics, and origin of the sediment carried by the stream.

The rate of flow of streams draining water from the land shows wide variation with time, depending upon seasonal and local precipitation, soil characteristics, and other factors. The amount of nutrients carried by stream water must therefore show similar variation, depending both on the concentration of nutrients and on the rate of water discharge. During a 4-year study of the amount of nutrients carried by streams draining farmland in central Ohio, Taylor *et al.* (1971) found that essentially all the phosphate removal occurred during the periods of highest water flow, usually in the late winter and early spring. Sediment production is also a sporadic process, dependent upon the energy of moving water which is, in turn, related to stream flow. The rate of removal of phosphate either in solution or in adsorbed forms carried by sediments must therefore be estimated on the basis of measurements during periods of high stream flow. Since the conditions in streams at high flow stages may differ considerably from those under low flow conditions, and high flow conditions only occur for relatively short periods of time, estimates of long-term "average" rates of phosphate loss should be calculated only over long periods of time, preferably several years.

This paper reports a study of the amounts and forms of phosphate carried by two streams within the Mahantango watershed in east-central Pennsylvania during two periods of high flow. The watershed was chosen because of the availability of hydrologic data in a predominantly agricultural area having a limited input of urban sewage and industrial wastes. About 60% of the total land area is under cultivation and the remainder is made up of mountains, forests, meadows, and small towns. Corn is the major crop, with smaller acreages of tomatoes, barley, oats, and rye. Chickens for egg production, dairy cattle, and beef cattle are raised in scattered parts of this watershed. Taylor and Kunishi (1971) presented a detailed description of the Mahantango watershed.

EXPERIMENTAL

Samples were taken at two locations within the watershed during two separate storms. The first, occurring in July 1970, was a short duration high-intensity thunderstorm. The second, in May 1971, was a late spring rainfall of lower intensity but longer duration. The two sampling stations are designated Pillow and Malta after the towns near which they are located. Runoff passes the Pillow station from the 26-square-kilometer (10-square-mile) watershed of Little Deep Creek before entering the main channel. The Malta station is a U.S. Geological Survey gauge 6 miles downstream from Pillow, measuring all the water which drains from the 420-square-kilometer (162-square-mile) Mahantango watershed, including the Little Deep Creek region.

Stream gauge heights were recorded every 15 min at the Pillow station and at 60-min intervals at the Malta station. Suspended sediment concentration samples were taken at the same time. In addition, at four times during each event, approximately 19 l. of sample were taken from each location for determination of soluble phosphate on a clarified extract and for determination of available phosphate on the suspended material. Soluble phosphate in stream water was determined using the stannous chloride reduced molybdophosphoric blue color method (Jackson, 1958). The procedure [Taylor and Kunishi (1971)] which includes incineration at 500°C for 4 hr of a residue obtained by evaporating to dryness a clarified stream water extract, measures both organic and inorganic phosphates. All phosphate concentrations in water are expressed in ppb of P.

Suspended material was concentrated using a continuous