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THE CAKING OF GRANULATED FERTILIZERS DURING STORAGE, WITH PARTICULAR REFERENCE TO SUPERPHOSPHATE

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The caking during storage of superphosphates and compound fertilizers made from it has been known as a highly undesirable phenomenon since the beginning of our industry. As B. Raistrick (1) said in the introduction to his excellent paper on "Good Quality Granular Fertilisers", we too expected that the introduction of granulation would not only improve the handling and efficiency of our fertilizers, but would also eliminate completely the unfortunate hardening during storage. This hope has, on the whole, not been confirmed even though a certain improvement of the storage properties has been achieved.

In the meantime, we have become so accustomed to the fact that granulated products cake also that we regard it almost as natural that curing should be done in a heap for months before despatch, that the heaps should be broken down with heavy machinery and sometimes even with explosives, that the hard lumps obtained should be crushed, the granules be again classified, and lastly the fines formed by crushing should be regranulated. This being so, we should try to imagine what would happen if there were actually no caking: we should not require any curing and could bag and despatch the material immediately after manufacture if necessary. We should store our fertilizers not in heaps but in silos from which they could be despatched without curing, without crushing, without screening and -last not least - without the losses which all these processes involve. Everyone can work out for themselves how their despatch costs would be reduced by this!

In view of the importance which the caking problem has for our industry it can be assumed that probably everyone present at this Meeting has dealt with it more or less thoroughly. If we have decided to take part in the discussion of this important problem, it is not because we believed that we had acquired new knowledge or had even achieved special practical results in this field. We have rather to confess that we are still far removed from a satisfactory solution. We hope, however, to come perhaps nearer to this target if we initiate a detailed discussion of the problem in our circle. We shall, therefore, examine critically the more recent literature and then report our own observations and results.

CAUSES OF CAKING

There is probably agreement that the development of crystal bridges between the individual granules has to be regarded as the cause of caking. From microscopic and X-ray examinations W.A. Mitchell (2) came to the conclusion that in the case of NPK fertilizers these crystal bridges consist of ammonium chloride which is formed by reaction of KCl with $(\text{NH}_4)_2\text{SO}_4$. He thought that the NH_4Cl sublimes during drying and accumulates at the surface of the granules increasingly so as the drying temperature is increased. Under the influence of moisture growth of the NH_4Cl crystals continues during storage until bridge formation between the particles occurs.- This view, which by the way is shared also by other authors, is certainly not quite correct. Because many NPK fertilizers are made without any drying, by mixing superphosphate with potassium and nitrogen salts, ammoniating the mixture during granulating and cooling the granules in rotary drums. Although no sublimation occurs in these cases, the products often harden during storage to an even greater extent than dried products. Another objection to the NH_4Cl theory is that other completely chlorine-free compound fertilizers cake just as strongly, e.g. Ansupka 8x8x14, which is made with potassium sulphate, or the potash-free Ansup 11x11x0, etc.

Turbett and McArthur (3) pointed out that the degree of caking is connected, among other things, especially with the NH_4NO_3 content of the ammoniating solution. This agrees with our own experience in so far as we also generally find that those NPK fertilizers cake most which were made with a maximum of ammoniating solution. At the same time, it is generally known that our compound fertilizers used to harden in store like concrete even before any ammoniating was used.

In a very interesting paper Silverberg, Lehr and Hoffmeister (4) examined microscopically the mechanism of caking and its prevention. They came to the same conclusion as Mitchell that crystal deposits on the surface of the granules are responsible for caking, but they mention several salts other than NH_4Cl , e.g. KNO_3 , MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$. Very beautiful microphotographs show how these salts surround the granules like a prickly coating. The formation of the crystal films is ascribed to diffusion and efflorescence effects which are assisted by a higher moisture content and curing.

The American papers quoted give the impression that caking can occur only when secondary crystallizations develop on the surface of the granules. In our own examinations of caked granules we regret to have to admit that we could not discover much of crystal films, although we should have been pleased to illustrate the present paper with a few nice microphotographs.- An argument against the "crystal film theory" is the generally known fact that all pure salts cake with time when stored in a heap - you need only think of your stores of muriate of potash, sulphate of ammonia or ammonium nitrate.- To elucidate the caking problem we found it

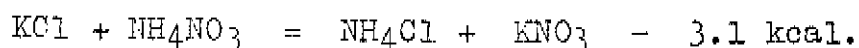
necessary to consider a little more closely the causes of the formation of crystal bridges.

- 1.) The ultimate reason for the caking of pure salts is, in our view, a thermodynamic one. As fine crystals have higher energies than coarse crystals, they always tend to become coarser. In the case of salts with a high vapour pressure, e.g. the ammonium salts, crystal growth can occur via the gas phase even at drying temperatures. In general, however, the moisture film of the crystals will be the medium for the growth process: as many salts have a higher solubility with increasing temperature, and also as the rate of crystallization likewise increases with temperature, crystal growth is accelerated by higher temperatures. Adjacent crystals in a suitable position can then crystallize together as they grow, and the probability of this will be all the greater, the more densely the crystals are packed: hence the positive effect of pressure on caking which we would specially emphasize here. This consideration of pure salts indicates that the three principal factors are: moisture, temperature and pressure.
- 2.) In the case of pure salts, crystal growth which is controlled purely energetically is important, but frequently allotropic modifications also occur. The numerous conversion points of ammonium nitrate at 125.2° , 84.2° , 32.2° and -18° and of sodium sulphate at 250° , 217° , 210° and 147° are well known. If these salts are made at a high temperature with cooling in a heap during storage, hardening is generally particularly severe when crystal transformation occurs. Moisture also acts as a catalyst in these transformations. It is a well-known fact that sodium sulphate which is made in the sulphate-hydrochloric acid process at approx. 500° , remains loose and powdery for weeks during cooling in store, but when it is despatched, it generally sets to rock-like masses, - under the catalytic influence of atmospheric moisture during loading. This example shows that, in principle, all crystallization processes which occur during storage produce hardening.
- 3.) In our industry we have to reckon with various crystallization processes which may produce hardening during storage: If granules are put into store warm, with an elevated moisture content, the salts dissolved in the liquid phase will later crystallize out as the heap cools, the most readily soluble salts being the last to do so. As the drying of granules proceeds from the surface to the interior, a moisture gradient from the interior to the surface exists immediately after the drying process is completed. With slow cooling of the heap, therefore, liquid will diffuse from the interior of the granules to the surfaces. Since in NPK compounds, which have been studied most, NH_4Cl is the most readily soluble salt, it will precipitate by diffusion preferentially at the surface of the granules. This process is evidently the basis of the "crystal film theory".

Conditions, however, are quite different when crystallizations during storage proceed with absorption of water of crystallization. For instance, when superphosphate cakes, the hydration of the calcium sulphate is of major importance, as we shall discuss later in detail. Finally, particularly in our industry, one of the chief factors is that compound fertilizers are made largely by mixing various salts. As the individual components are used in a fairly coarse form (superphosphate!), as mixing is generally less than complete, and lastly as several reagents, such as the

calcium sulphate anhydride of the superphosphate, are less reactive, the reactions between the components, in spite of granulation, are not yet completed when the granules are deposited on the heap. It is obvious that precisely those chemical reactions which continue in the heap must produce caking.

In this context there is one further point which deserves attention. The reactions between the mixture components are exothermic processes, one example being the well known reaction:



It gives approx. 20 kcal per kg of the stoichiometric mixture, a quantity of heat which would raise the temperature of the pure mixture by approx. 70°.- In the case of the usual NPK fertilizers several other reactions naturally occur also, but the heat of reaction should have an order of magnitude roughly in this region. If the reactions occur partly only in the heap, heat of reaction will be liberated there also. The observation that large heaps cool off only very slowly is connected, therefore, not only with the impeded conduction of heat, but also with the subsequent evolution of heat. The particularly severe hardening in large heaps is evidently due not only to the higher static pressure, but according to our observations, also to the additional pressure increases produced by heat evolution in the interior.

PREVENTION OF CAKING

In his paper mentioned earlier B. Raistrick recommends "thorough drying" as a sure measure for preventing the subsequent caking of fertilizers. The upper moisture limit which is regarded as critical for the storage properties is defined by the relative humidity being as to 30% in equilibrium with the given fertilizer. This means, as a rule, a moisture content of less than 1%.

We have checked this statement in a series of laboratory experiments and in two experiments on a technical scale, and have found that this drastic drying is obviously the most effective of all measures available to us. We, too, found that hardening does not continuously become less with decreasing moisture content, but that there is a sharply defined lower limit which it is essential to observe.

However effective the measure recommended by Raistrick may be, it has important disadvantages: Drastic drying increases the load on the drying plant with a resulting fall in output and increased fuel consumption.

It is true that according to Raistrick, the initial fall in output from 6.5 to 4.5 tons per hour has been made good by improved granulation and more regular loading of the dryer, and it has been possible even to increase the output to 7.5 tons per hour. He gives a figure of 45 kg coal per ton of material to be dried as fuel consumption. As the dryer is the bottleneck in our granulating plant, it is not possible for us to carry out more intensive drying in practice. To increase output by increasing the gas exit temperature is also not feasible because our NPK fertilizers always contain nitrates and are, therefore, quite temperature-sensitive.

Silverberg et al. (4) summarize their experiments on the prevention of caking as follows: "The data show that it was possible to prevent or reduce caking of these fertilizers by one or a combination of the following treatments prior to bagging: reducing moisture content, curing in a pile for 7 days, and coating with a conditioning agent such as kaolin clay or kieselguhr."

They, too, place drying first in order of importance.- Their further recommendation of curing for 7 days is certain to be very effective because the reactions can go to completion during this period. From a practical point of view, however, this limited curing is hardly practicable because it would mean that a week's production (1000 to 2000 tons) would have to be handled a second time in store in view of the fact that despatch never synchronizes with production. If the material is left for any length of time, however, the conditions are exactly the same as usual: caking proceeds, and the known difficulties occur when the heap is broken down.- The third recommendation is coating, and this requires to be considered in greater detail.

Silverberg et al. used 2.5% kieselguhr and kaolin clay as powdering agents. They explain the action of the coating in that the formation of the crystal films is not prevented, but the film remains below the coating layer, and individual crystals penetrate only seldom through the layer of the coating agent. According to these authors, the effect of the coating agent is that the crystal film is distributed more uniformly over the granule and the growth of single large crystals which could form a bridge is prevented. The more uniform distribution of the crystals on the surface is explained by the coating layer having a kind of nucleation effect.

Like all who are concerned with the caking problem, we too have examined a very wide variety of coating agents in the laboratory and on a technical scale, and there is no doubt that this coating is an effective measure. A good coating agent has to meet the following specification: it must be fine and adhere well to the surface of the granules; above all, it must not react with the fertilizer, otherwise its effectiveness will soon be lost. For this reason chalk and gypsum which have been variously recommended are quite unsuitable. Kieselguhr and certain very finely ground clays have proved useful also in our case, but our experiments in this respect are not yet completed. On the whole, however, our observations show that coating is not a panacea. The action is, in particular, limited in time unless coating is preceded by a good drying of the granules. In the event of a high moisture content the readily soluble salts diffuse through the powder layer, the latter thus losing its effectiveness.- The disadvantage of coating is that it reduces the nutrient value of the fertilizer, that it frequently impairs the appearance of the granules (by discoloration) and - last, but not least - that good coating agents are fairly expensive.

Summarizing our experience of preventing the caking of granulated NPK fertilizers, we can say that drying helps, that curing helps, that cooling helps and that coating helps. The unsatisfactory aspect of the matter is that none of these measures taken singly is adequate and that, when used together, they are quite expensive, so expensive in fact that we doubt whether our existing method of curing for several months and then crushing and classifying is not more economical.

PREVENTION OF CAKING OF SUPERPHOSPHATE

It is surprising that in its literature the caking problem is considered mainly in connection with salts and multi-nutrient fertilizers, whilst, so far as we have been able to ascertain, there is no mention of superphosphate. Unfortunately, however, subsequent hardening occurs time and again precisely with superphosphate, with highly undesirable results, and it is regrettable that here also granulation has not proved to be a method of preventing caking.

It would seem likely that subsequent crystallizations were responsible for caking in storage also in the case of superphosphate. At the ISMA Meeting in Hemburg as long ago as 1937 we had occasion to report on the composition of superphosphate (5) and particularly on the state of the calcium sulphate contained in it. It would take too long to recapitulate this paper in detail, but we are interested at the moment in the statement that calcium sulphate is present mainly as anhydrite and that this anhydrite is converted only extremely slowly and only partially to the dihydrate. Normal superphosphate contains approx. 50% calcium sulphate anhydrite and usually only 1-2% dihydrate. Larger amounts of dihydrate, e.g. 10-15% were found only in samples many years old. It was noticed, however, that hydration proceeded much more rapidly when the superphosphate had been neutralized. It was shown on calcium sulphate anhydrite which had been isolated from superphosphate that it became hydrated more or less rapidly on contact with phosphoric acid, the rate of hydration decreasing as the concentration of the phosphoric acid increased.

In later experiments carried out together with O.B. Jørgensen we tried to ascertain the critical concentration at which water passed from the phosphoric acid to the anhydrite. Although these experiments were eventually extended to one year, we were unable to obtain any result precisely with the anhydrite (similar experiments were made with the semi-hydrate) because equilibrium had still not been reached. At the last ISMA Meeting in Madrid a graph showing the equilibrium between calcium sulphate and phosphoric acid of different concentrations is shown in the discussion of one paper, and is reproduced herewith. The curves indicate that the limiting concentration at which the dihydrate is still stable occurs at normal temperatures (below 30°) between 45% and 50% P₂O₅. The first conclusion which one might draw from this is that the hydration of calcium sulphate in superphosphate can proceed without difficulty, because at a free acid content of approx. 3% P₂O₅ and a moisture content of 8-10% as is in most cases present after 24 hours, the concentration of phosphoric acid in the liquid phase is only approx. 30-35%. The monocalcium phosphate which is dissolved in the liquid phase of the superphosphate further reduces the vapour pressure of the solution so that this shifts the equilibrium further to the side of the anhydrite. Unfortunately, we do not know of any relevant measurements. We carried out once also hydration experiments in the presence of monocalcium phosphate dissolved in phosphoric acid and noticed that in this case hydration still proceeded very much more slowly than in the presence of phosphoric acid only. It is generally known that phosphoric acid tends to form a supersaturated solution at higher concentrations. The fact that dissolved monocalcium phosphate produces a further delay in the reaction can be connected, on the one hand, with a substantial increase in the viscosity of the liquid phase and, on the other hand, with a noticeable reduction in the solubility, and consequently in the rate of dissolution, of the calcium sulphate when calcium ions are present in the liquid phase.

Summarizing these investigations, it can be said that the calcium sulphate anhydride contained in the superphosphate can certainly take up water from the aqueous phase and thus be converted to the dihydrate. This conversion depends on the temperature and the concentration of the phosphoric acid in the liquid phase; it is sharply retarded in the presence of concentrated phosphoric acid and dissolved monocalcium phosphate so that equilibrium evidently occurs only after several years of storage.

In order to examine these matters under practical conditions, a large-scale test was made in our granulating plant. Pebble phosphate 75% was reacted in the Moritz-Standaert plant in the usual manner with 31% sulphuric acid of 60° E and dish-granulated with the addition of approx. 10% sand immediately after being cut out from the den. We use the drying drum of the granulating plant as a cooling drum when granulating superphosphate and thus achieve a cooling of the granules to 30-35°, depending on the outside temperature. This produces a certain hardening and drying of the granules so that they can be screened and put into store in a classified form. In the large-scale experiment the fresh granules from each working day were coated with 1% phosphate rock dust from the Bath filter of the crushing plant, and with 1% basic slag phosphate so that each heap of 250-300 tons of coated fertilizer was available for further investigations in addition to the normal uncoated fertilizer. The state of hydration of the calcium sulphate in the heaps was followed for a period of six months, and the degree of hardening observed also. After six weeks 5 tons of each were bagged in 50 kg paper bags, the latter being stacked in stacks 10 bags high.

It must be stressed that we did not carry out the coating with phosphate rock dust and basic slag phosphate with the intention that these substances should act as separating substances as, e.g. kaolin or kieselsäure. We wanted rather that these additives should neutralize the granules at the surface and hoped to obtain an accelerated crystallizing cap of calcium sulphate dihydrate at the surface. Whilst this would accelerate caking in the heap, it would prevent the subsequent hardening in the bags during storage.

The fresh material contained as much as 1-1½% dihydrate immediately after manufacture. This content increased to 3-4% after 2-3 days. This amount is probably due to the fact that during the reaction or when the freshly made superphosphate is swept out of the den, the material passes also through the region of existence of the semi-hydrate so that a small fraction of the calcium sulphate is precipitated as the semi-hydrate which is much more readily hydratable than the anhydride. The further take-up of water of crystallization or the formation of calcium sulphate dihydrate then proceeded very slowly. After 3½ months the dihydrate content in all three heaps amounted to only 12-13% and no further increase was observed in the subsequent tests. With several samples even slightly lower values, e.g. 10-11% were found. This may have been due to the fact that the last samples were taken rather from the inner core of the partly broken down heap where further cooling had proceeded much more slowly.

With regard to hardening of the heaps, the material which had been coated with basic slag phosphate caked more rapidly at first, whilst the uncoated material after one month in store had caked visibly less. These differences, however, evened out over the period of storage and were later no longer observable.

Material bagged after six weeks in store analysed for dihydrate as follows: 5.3% uncoated, 5.9% with phosphate rock, 8.52% with basic slag phosphate. The storage experiment was terminated after 8 months, when the dihydrate content of the bagged material had risen to the values determined in the heap. However, by feeling the bags it was found that the material had compacted slightly only in the undermost layers, and the material broke up completely when the bags were raised and quite lightly dumped.

Summarizing this experiment, it can be said that there is obviously some connection between the hydration of the calcium sulphate and the hardening. Cooling of the superphosphate before putting it into store was found to be an effective method of bringing about the hydration of the calcium sulphate. Coating the granules with 1% neutralizing substances produced only a slight acceleration.

On the subject of the reason for the caking of superphosphate it can be stated that in principle the same phenomena are present in this case as in the case of the NPK fertilizers. The position, however, is complicated considerably by the fact that the crystallization processes occur here very much more slowly. It is possible that the process of superphosphate manufacture plays an important part in this. It is conceivable that in the case of a superphosphate which is put into store with a higher free acid content and whilst still hot, hydration begins very much later and proceeds more slowly than in our large-scale experiment, because according to our earlier experience it does not appear to occur at all at this stage when more than 3-4% free P_2O_5 is present. Under these conditions it is quite possible that in spite of having been stored for several months, the material will become hard again after delivery to the customer.

It is probable that coating agents can still effect improvements even in the case of superphosphate. Coating, however, is a relatively expensive method. We should, therefore, in this case prefer to bring forward the hydration of the calcium sulphate "at home" to such an extent that no substantial hardening is later possible. If the granules are cooled, a curing of 6-8 weeks appears to be adequate.

Bibliography.

1. Raistrick, B., Good Quality Granular Fertilizers, Fertilizer Society Proceedings 38, March 1956.
2. Mitchell, W.A., J.Sci.Food.Agr., No.5, 455-456 (1954)
3. Turbett, F.L. and McArthur, J.G., J.Agr.Food Chem., 2, 506-513 (1954)
4. Silverberg, J., Lehr, J.R. and Hoffmeister, G., J.Agr.& Food. Chem., 6, 442 (1958).
5. Scheel, K., "Ein Beitrag zur Chemie des Superphosphats", Hamburg, 12th/13th October 1937.

