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## Caking Processes in Granular NPK Fertilizer

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This investigation into the caking of granular NPK fertilizer examines three specific areas, namely, accelerated caking tests, the role of unbound water, and the effect of ammonium chloride on caking. The caking propensity of granular fertilizer was characterized by two accelerated caking tests, with the caking propensity being correlated with the tensile properties of the fertilizer granules and the theory of capillary adhesion. The concentration of saturated fertilizer salts in free water found within the granules was determined and gave a good correlation with the caking propensity as determined by the accelerated caking tests. It also indicated that high levels of ammonium and chloride ions were found in the free water within fertilizer granules. X-ray diffraction analysis revealed that high concentrations of ammonium chloride were found on the surface of fertilizer having a high caking propensity. A further investigation using X-ray microanalysis indicated complete conversion of potassium chloride to ammonium chloride within fertilizer granules.

### Introduction

International demand for fertilizers is continually increasing, forcing the fertilizer industry to respond by offering a wide range of high-quality grades. A modern fertilizer plant has stringent quality controls on its products, including NPK and particle size analyses; however, it is the caking propensity of granular fertilizer product which, in many cases, causes greatest concern. Most fertilizer production plants employ a number of features to prevent caking, such as drying, cooling, dust minimization, and product storage in moisture-proof bags. Although these measures significantly reduce fertilizer caking, they do not completely alleviate the problem. This work identifies physical and chemical techniques which can be used to compare caking and noncaking granular fertilizers and to identify factors which contribute to fertilizer caking. The physical analyses used include accelerated fertilizer caking tests; compressive testing of granules, and estimation of the free water content of the fertilizer. Further chemical analysis on the fertilizer utilized the following techniques: X-ray diffraction of fertilizer compounds, X-ray microanalysis, and chemical analysis of unbound water. The NPK analysis of the granular compound fertilizer investigated in this work is made up from ammonium nitrate, mono- and diammonium phosphate, and potassium chloride.

### Results and Discussion

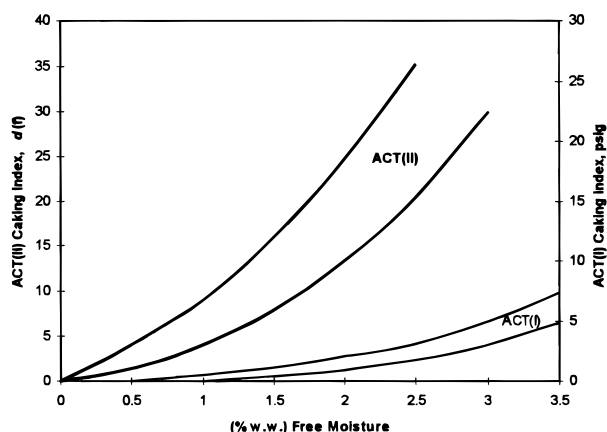
**(i) Accelerated Caking Tests.** The use of accelerated caking tests to characterize the caking propensity of granular product is widespread within the modern fertilizer industry due to the rapid determination of the

caking propensity compared to the bag caking test (Thompson, 1972). This rapid determination means that accelerated caking tests can be used as a quality control analysis on fertilizer production lines and therefore can be used as an aid in the study of factors that influence fertilizer caking. Fertilizer quality, in this study was characterized using two accelerated caking tests in which pressure is applied to a fertilizer sample for a predetermined time in a cylindrical press resulting in cake formation (Bloom and Sharpe, 1963).

In the first accelerated caking test used in this work (ACT(I)), a known weight of fertilizer is subjected to a pressure of 30 psig in the cylindrical press for a predetermined period of time and uses the level of pressure required to shear the resultant cake as an indication of caking propensity. If the sample requires a pressure of > 1 psig to shear the cake, the fertilizer is considered to be of poor quality and is liable to "caking" in storage. A fertilizer that is said to be "caking" correlates to product that after 12 months of storage is less than 99% (w.w.) free flowing product after a standard 50 kg bag has been dropped once from waist height. This accelerated caking test has been shown by experience to be an excellent indicator of the future caking propensity of granular compound fertilizer, with virtually no fertilizer having a ACT(I) value < 1 psig, caking in storage.

However, if the vast majority of fertilizer manufactured at a process plant is of significant quality as to be considered "noncaking" (i.e., ACT(I) < 1 psig), the ACT(I) test is of little use for quality control analysis. We have therefore developed a second accelerated caking test, ACT(II), for determining the effect of specific factors on caking. In this case a pressure of 60 psig is applied to the granules for a longer period of time than with the ACT(I) test, with the voidage of the resultant cake, the particle size distribution of the granular sample, and the surface tension of any coating oils used

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**Figure 1.** Comparison of accelerated caking tests with variation in free water content.

also measured. The advantage of the ACT(II) test is that it always gives a "positive caking" result; i.e., a cake that can be sheared is always produced. The results from this test are inputs to eq 1 (Newitt and Conway-Jones, 1958), with  $\delta(f)$  being regarded as a definitive caking propensity for process control purposes (Walker et al., 1997a).

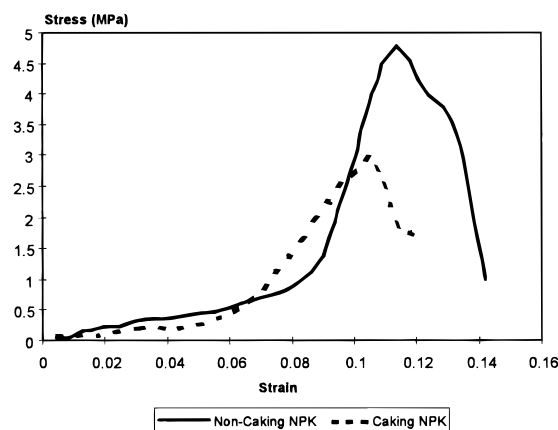
$$i = 2.8 \left( \frac{1 - \epsilon}{\epsilon} \right) \frac{\sigma}{X \delta(f)} \quad (1)$$

Figure 1 shows how these two tests compare for variation in fertilizer free water content (AOAC 2.013; the effect of free water content on caking is detailed in a subsection of this paper). It indicates that the ACT(I) test is insensitive to noncaking fertilizer having a low free water content of less than 0.5% w.w., but the ACT(II) test resulted in a positive value of  $\delta(f)$ , a better correlation with free water content. This plot illustrates a band of values for both accelerated caking tests due to variations in caking propensity with NPK formulation.

It is considered that the caking mechanism in these short-duration accelerated caking tests is capillary adhesion; i.e., the attractive forces between granules can be described by the pressure deficiency ( $p$ ) beneath a meniscus of radius,  $r$ , where  $\lambda$  is the surface tension of the liquid and  $\theta$  the contact angle (see eq 2). As water and saturated fertilizer salts have significantly higher surface tensions than most oils used for coating purposes, it is advantageous that water and saturated solutions are absent from granule surfaces and contact points.

$$p = \frac{2\lambda \cos \theta}{r} \quad (2)$$

In a microscopic investigation of the cakes formed in the two accelerated caking tests, no evidence was found of crystal bridging with this ascribed to the short duration of the tests. However, if a material attained a high caking propensity in the ACT(I) test, i.e., > 5 psig, some evidence of crystal bridging can be found in the fertilizer after 3 months under normal storage conditions (approximately 4 psi). It follows therefore that the water, at the granule-granule interface, associated with capillary adhesion may become saturated with diffusing fertilizer salts and over time form crystal bridges upon evaporation.



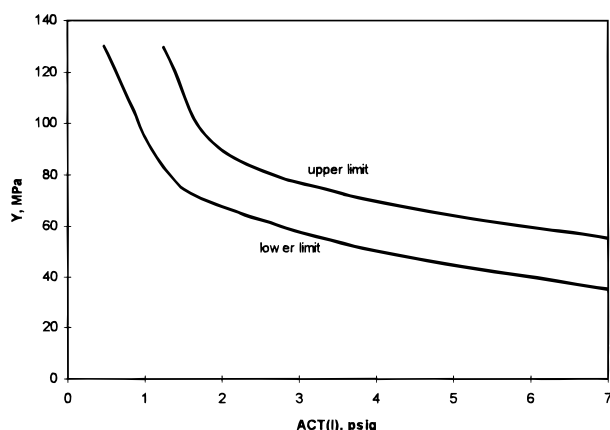
**Figure 2.** Tensile stress versus tensile strain of caking and noncaking fertilizer particles (high-nitrate NPK).

**Table 1. Fertilizer Ion Concentration in Free Water within Granules (Average of Five Samples of High-Nitrate NPK)**

ion/ water	caking (ACT(I), 7 psig) (mg/L)	noncaking (ACT(I), 0 psig) (mg/L)	formulation (%)
NO <sub>3</sub>	59.40	62.90	58.3
PO <sub>4</sub>	0.15	0.38	6.5
NH <sub>4</sub>	141.26	145.13	20.9
Cl	75	50.5	4.7
K	1.07	0.59	5.2
H <sub>2</sub> O	0.50 (%)	0.37 (%)	>0.5

**Compressive Testing of Fertilizer Granules.** It has been shown that the ACT(II) analysis can be a useful tool for quality control purposes; however, as with all accelerated caking tests, a period of 6 h to 1 week is essential before caking results can be attained, depending on the test being used (UNIDO, 1980). This time lag makes quality control and correlation between caking and process parameters difficult in a continuous process plant. The measurement of the mechanical strength of fertilizer granules (Walker et al., 1997b) offers an instantaneous result that may be correlated to caking propensity and offers a more proactive approach to quality control. The mechanical strength of fertilizer granules is an important factor in relation to caking in that weak granules may deform and fragment, causing increased points of contact with other granules and resulting in an increase in caking propensity and dust formation. The breakup of fertilizer granules also nullifies the effect of anticaking conditioners; furthermore, weak granules which are easily deformed also cause an increase in the contact area with adjacent granules, which also results in an increase in caking propensity.

Compressive testing was accurately determined by an Instron Test System (Model 4411) using NPK fertilizer granules of 2–3 mm diameter. Results indicated that there is a direct link between the tensile strength of the granule and caking propensity, with granules showing high caking propensity in both the ACT(I) and ACT(II) analyses and having a lower tensile strength than granules having a lower caking propensity (see Table 1). A typical stress-strain plot is illustrated in Figure 2, showing a comparison between caking and noncaking granules. The plot indicates a nonlinear, stress-strain relationship which is probably due to plastic creep and stress solution occurring within the granule when under pressure (Thompson, 1972). The average tensile stress



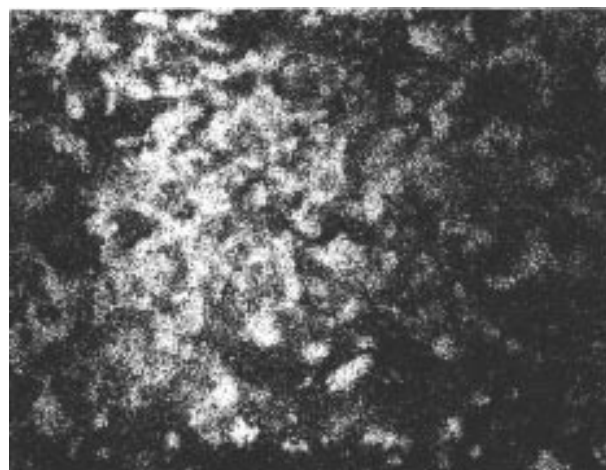
**Figure 3.** Relationship between Young's modulus and caking propensity (ACT(I)) for NPK fertilizer.

and strain values indicate that the break stress for caking particles is lower than for noncaking particles with an increase in percentage strain to break also noted. The decrease in tensile strength of 13% in caking granules compared to noncaking granules correlates well with the hypothesis that weak granules are more susceptible to caking. The modulus of elasticity ( $Y$ ) of the caking granules, calculated as an average to the break point, was found to be approximately 20% lower than that in noncaking granules (Figure 3). It follows therefore that pliable, caking granules, with a low modulus of elasticity, would allow an increase in contact area between granules when stored under pressure.

**(ii) Influence of Unbound Water in Fertilizer Granules.** The role of unbound or free water in the caking of NPK fertilizers is a complex one. The general consensus is that the less free water available, the less likelihood that the fertilizer will cake; indeed any fertilizer that contains zero free water will not cake. The free water content of several samples of fertilizer was analyzed using dioxane and a Karl-Fischer reagent (AOAC technique 2.013; Duncan and Brabson, 1969), with the results correlated to the caking propensity in the accelerated caking tests (see Figure 1). This plot indicates that the fertilizer requires a high level of free water available to promote caking processes. The concentrations of the dissolved fertilizer ions present in fertilizer are also thought to have an effect on caking as high concentrations of fertilizer ions on the surface of the granules may lead to crystal bridging.

A method for the determination of the fertilizer ion concentrations within the free water of granules has been developed which involves packing of a glass column with ground fertilizer and allowing alcohol to pass down through the packed bed. The displaced water forms a wave front which can be tapped off at the bottom of the column. The sample is then filtered, to remove conditioners such as coating talc, and the concentrations of fertilizer ions are determined using standard water analysis.

Results indicate that the caking products have higher fertilizer ion concentration than the noncaking granules. The results illustrated in Table 1 suggest that fertilizers with high levels of ammonium and chloride ions have a higher caking propensity, with ammonium chloride more likely to form on the surface of granules and create crystal bonds. In general, the ratio of fertilizer compounds present in the crystal bonds is usually different from the overall fertilizer formulations (UNIDO, 1980).



**Figure 4.** Map of distribution of P by X-ray microanalysis in NPK fertilizer ( $\times 400$ ).

**Table 2. X-ray Diffraction Analysis of the Surface of Fertilizer Products (High-Nitrate NPK)**

caking propensity	count rate at $2\theta = 32.4^\circ$ (ammonium chloride peak) (cps)
caking (5 psi ACT(I))	4.75
noncaking (0 psi ACT(I))	3.50

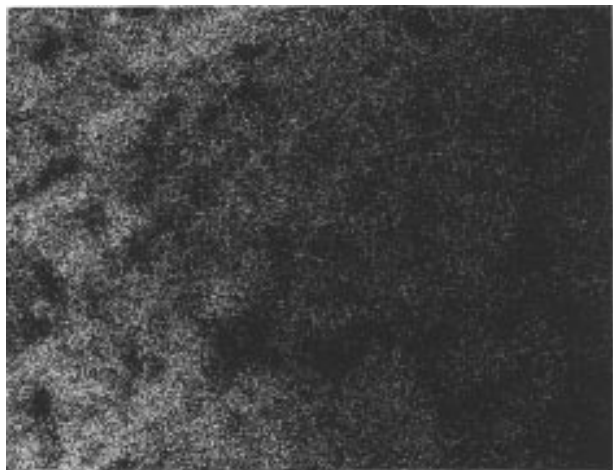
This correlates with data reported in Table 1 in which ion concentrations in the free water vary considerably with the overall formulation.

**Ammonium Chloride and Caking.** The formation of ammonium chloride has been reported by Kuvshinikov et al. (1987) as a major cause of caking in compound fertilizers, because a saturated ammonium chloride solution on the external surface of granules evaporates to form crystal bridges with adjacent particles. Fertilizer compounds can be easily identified using X-ray diffraction analysis. In this case the formation of ammonium chloride is of particular interest because it may contribute to caking. It is formed by the following reaction of ammonium nitrate and potash.



X-ray diffraction analysis (XRD) of the surface of fertilizer granules stored for 3 mo identified ammonium chloride by the characteristic (XRD) peak at  $2\theta = 32.4^\circ$ . A comparison of the X-ray count rates at  $2\theta = 32.4^\circ$  indicated that significantly more ammonium chloride was present in a sample of caking fertilizer as compared to noncaking fertilizer, which suggests that crystal bonds contribute to the caking process (Table 2). A more definitive quantitative X-ray diffraction analysis on granular compound fertilizer proved difficult due to the large number of fertilizer compounds present.

**X-ray Microanalysis.** The elemental distribution pattern obtained by X-ray microanalysis of a cross section of a fertilizer granule, just after production, is illustrated in Figures 4 (P), 5 (K), and 6 (Cl). These indicate that the distribution patterns for K and Cl do not overlap but, in fact, approximate to mirror images of each other, indicating a very low concentration of potassium chloride. As the dark areas in Figure 4 generally represent ammonium and nitrate ions, it can therefore be assumed that most if not all of the KCl has reacted which is clear evidence of the formation of  $\text{NH}_4\text{Cl}$  and  $\text{KNO}_3$  within the fertilizer granule. It must be noted that similar analysis was found for fertilizer



**Figure 5.** Map of distribution of K by X-ray microanalysis in NPK fertilizer ( $\times 400$ ).



**Figure 6.** Map of distribution of Cl by X-ray microanalysis in NPK fertilizer ( $\times 400$ ).

having both high and low caking propensity. It follows therefore that in the case of fertilizer having a high caking propensity that the ammonium chloride formed by reactions within the granule may diffuse as a saturated salt to the granule surface, resulting in crystal formation. This theory correlates with the high levels of chloride and ammonium ions contained in the free water within the granules, which is associated with the high concentration of free water itself.

## Conclusions

It can be concluded from these investigations into caking in three specific areas (accelerated caking tests,

the role of free water, and the effect of ammonium chloride) that these factors are interlinked with free water within fertilizer, the dominant factor for both capillary adhesion and the crystal bridging process. Capillary adhesion forces between granules are increased by high levels of free water in that it causes the granules to be more pliable, which increases the contact area and surface tension between granules. Furthermore, water at these contact points is essential before significant capillary forces can be created, with the diffusion of free water from the core of the granule to the surface the only viable explanation. This investigation shows that, even if the reaction to form ammonium chloride is complete before the product is put in storage, the presence of free water within the granule causes mass transfer of saturated fertilizer salts to the granule surface where solid crystal bridges can be formed upon evaporation.

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