



**TECHNICAL PAPER:
PHYSICAL-CHEMICAL CHARACTERISTICS AND FACTORS AFFECTING WATER
SORPTION AND CAKING OF NPK 10-20-20 MOP (BAGFAS) FERTILIZER**

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Introduction

One problem frequently observed during storage and marine transportation of fertilizers is the formation of agglomerated caked product. This phenomenon is dependent on the moisture content of the product along with other factors that could enhance the problem.

In this paper the water sorption characteristics of NPK 10-20-20 MOP (Bagfas) fertilizer were determined, and the critical moisture content to prevent caking during storage or transportation was estimated, along with other physical-chemical parameters. The factors affecting caking were also addressed.

Product Hygroscopicity

Compound fertilizers use to present elevated hygroscopicity. Hygroscopicity is defined as the tendency of a fertilizer to adsorb (or release) water, usually from the atmosphere around the product.

Hygroscopicity of a fertilizer depends on many factors but mainly in chemical composition, chemicals involved in the formulation, particle size, temperature, use of preventive coatings, etc.

Once the fertilizer is exposed to air with a determined relative humidity (%RH), it will adsorb or release moisture from or to the air depending on the moisture content and its corresponding water activity (equilibrium relative humidity of the fertilizer/100). Water activity at a given temperature

is mathematically defined as the fraction between the partial pressure exerted by water in the product and the vapour pressure of water at that temperature. If the equilibrium relative humidity (%R_{Eq}) of the product is below the external air relative humidity (%RH) then, the product will adsorb moisture from air. The opposite will occur if the equilibrium relative humidity of the product is higher than the relative humidity of the external air.

Factors Affecting Agglomeration/Caking of Fertilizers

Caking is caused by the individual particles in a mass of fertilizer becoming cemented together during storage, in a way that the free flowing properties are lost. There are various degrees of caking ranging from a lightly set mass, which usually breaks up when applying slight force, to very compact caking resembling stone texture. Caking is normally caused by re-crystallization of soluble material between particles of fertilizer. Several factors can cause or enhance the caking process: moisture, pressure, presence of fines or dust in the product, temperature, etc. The following factors have been found to affect caking of mixed fertilizers:

a) Moisture

There is unanimous acceptance of the fact that caking is directly related to the moisture content of the fertilizer. A moisture level of 0.5-1% moisture has been recommended as the safe maximum to prevent caking in fertilizers containing ammonium nitrate and urea in a ratio of nitrogen to phosphorus (as P₂O₅) greater than 1:1. Fertilizers with a lower ratio of nitrogen to phosphorus (as P₂O₅) (< 1:1) not including ammonium nitrate and urea as source of nitrogen in their formulation could have higher safe moisture content (1.5-2.0%). This criterion does not necessarily apply to fertilizer formed from other constituents. It has been pointed out that the activity of the liquid phase in the fertilizer is most important than its absolute quantity and for granular fertilizers, a 30% equilibrium relative humidity or less is required for safe storage of most of them.

The relationship between the moisture content of a fertilizer and its equilibrium relative humidity (defined in physical chemistry as water activity or *a_w*), can be determined through its sorption isotherm at a given temperature.

Sorption isotherms are useful to establish the critical moisture level for safe storage, to understand product caking and moisture adsorption from external air.

The form and characteristics of the sorption isotherms depend on the constituents of the fertilizer and on their relative amounts in the formulation. The information regarding sorption isotherms of fertilizers is scarce in the technical literature. Since the values given by isotherms depends on the fertilizer composition, two NPK 10-20-20 fertilizers with different constituents in its formulation would have different isotherms. The sorption isotherms at different temperature can be determined in the laboratory.

b) Pressure and Temperature

It has been found that if caking occurs at all, an increase in compression pressure greatly increases the degree of caking. A pile of fertilizer of about 8.5 meters high will induce a pressure in the product stowed in the bottom of about 12 psig (pounds per square inch gauge). Caking tests recommended by the USDA suggested this pressure for 7 days at 30 °C.

A temperature level of 30-32 °C tends to favor caking, especially in mixtures containing ammonium nitrate, due to the change in the crystallization pattern (transition IV → III) that could induce caking. The same is true if temperature fluctuations take place.

In view of this, some degree of caking shall be expected in stowed bags or product in bulk stowed in a tall pile or in a ship's hold, particularly in the zone near the bottom of the stowed product that support more pressure. If the moisture content of the product is low enough and below the critical level, caking shall be of the loosely held agglomeration type, not affecting the product quality. Loosely held agglomeration or caking is normally removed when bags are dropped from a height of 60-90 cm several times or by physically moving the product in bulk by mechanical means. Assessment of caking in bagged fertilizers include dropping the bags from a height of 90 cm four times, twice on each flat side followed by screening through standard sieves.

c) Time of Storage

There is evidence that caking increases little after storage for 4-6 weeks and most of it occurs in the first 10 days of storage.

d) Particle Size, Shape and Hardness

The size of granules has little effect on caking when the size is within normal dimensions found in granulated fertilizers (1-4 mm). The presence of considerable amount of fines and small particles tends to induce caking specially in fertilizers formulated with urea and ammonium nitrate. The difference in shape does not have a large effect in caking. However, better results are obtained with particles presenting smoother granules (i. e. spherical form). Mechanical weakness of granules usually promotes caking, since under storage pressure they tend to deform increasing the contact area. In general terms a hardness of more than 3 kg is recommended to reduce caking.

e) Composition

The components present in mixed fertilizers have an important role in the caking tendency of the product. Therefore, fertilizers composed of different materials could present different caking tendencies. Therefore, sorption equilibrium data varies for different fertilizers depending on its composition and formulation.

It is known that the presence of ammonium nitrate in a mixture would make the degree of caking more severe and its reduction in formulation will decrease this tendency. The solubility relations

of ammonium nitrate enhance caking by two mechanisms: it has high solubility in water and any evaporation therefore deposits a large amount of crystals in the surface; on the other hand, it has a large temperature coefficient of solubility in such a way that when warm fertilizer is cooled after manufacturing, a large quantity of crystals is formed out of the solution. Other compounds such as the superphosphates are virtually non-caking and this beneficial property is to some extent conferred to mixtures containing it in high proportion.

Fertilizers containing ammonium nitrate, urea, mono-ammonium phosphate, ammonium sulphate, potassium nitrate and double salts show a propensity to crystallize out of the solution. Ammonium chloride has been found to be the principal bonding phase in fertilizers based on ammonium sulphate, superphosphate and potassium chloride. Propensity to caking has been found in fertilizers containing potassium chloride and ammonium nitrate that react in the liquid phase to form ammonium chloride that has been pointed out to enhance caking.

f) Curing

A curing period after manufacturing is usually recommended to reduce the caking tendency of granular fertilizers. An increase in the curing period from 1 to 8 days was found to reduce caking strength of granular material in 45%. Pile curing of granular fertilizers for 7 days has been found helpful in reducing caking. Cooling after manufacturing is perhaps the most important factor in these cases.

g) Additives to prevent caking

Additives acting as coating agents in granular fertilizers have proved to be effective in preventing caking at low moisture contents. Several coating materials and methods are available, including: hydrated silica, synthetic calcium, magnesium silicates and diatomaceous earth among others. The coating applied in the granule surface prevents the granules from interacting from each other, avoiding, therefore, re-crystallization and adherence between them. The use of hydrophobic films has proved also to be effective. Hydrophobic films consist in mixtures of oils and waxes sprayed onto the surface of granules. Typical substances include petrolatum rosin-paraffin mixtures. In the case of granular fertilizers including ammonium nitrate it has been found that they could be effectively coated with 0.5-1.0% of the above mentioned mixture. It has to be pointed out that the effectiveness of most coating agents disappears at high moisture content.

Mineral oil can also be used as anticaking agent. It has been reported the use of minor amounts of mineral oil in addition to calcium lignosulfate to avoid caking in granular fertilizers. Other compounds reported for the same purpose are aliphatic amines, resol type phenol, talc and organic acids.

Determination of the Water Sorption Isotherm of NPK 10-20-20 MOP (BAGFAS) Fertilizer and Estimation of Critical Moisture for Agglomeration/Caking

As indicated previously the knowledge of the sorption isotherm of a fertilizer like NPK 10-20-20 MOP (BAGFAS) (muriate of potash) is required to establish critical level of moisture to avoid

caking and to determine the moisture of the product associated to exposure to atmosphere with a given relative humidity.

Determination of Water Sorption Isotherms. A standard technique to determine sorption isotherms in the laboratory of Universidad Simón Bolívar, Caracas, was followed. Seven desiccators containing over saturated solutions of different salts giving characteristic equilibrium relative humidity in the air inside the desiccators were prepared. The desiccators were placed in a room at 25 °C. The salts used and their corresponding equilibrium relative humidity are presented below:

Over saturated salt	a_w or % Equilibrium relative humidity/100 25 °C
LiCl	11.3
MgCl ₂	32.8
K ₂ CO ₃	42.8
Mg(NO ₃) ₂	52.9
NaNO ₂	65.0
KI	70.0
NaCl	75.3

Langley, Handbook of Physics and Chemistry

The samples of fertilizer were grinded, placed in plastic dishes and allowed to equilibrate in the desiccators for 37 days. After this period the moisture content was determined by triplicate using the vacuum oven method (50 °C for 2 hours at 475-500 mm Hg of vacuum). The agglomeration tendency of the fertilizer was also assessed in a qualitative visual manner. For this purpose a layer of fertilizer of about 5 cm deep, was placed in a test tube that was introduced in the desiccators with the saturated solutions (this test does not take into account the effect of pressure in caking). The results obtained are presented here:

Moisture Content (g water/100g dry solid)	Water activity (a_w)**	Qualitative agglomeration observed*
0.0853	0.113	-
0.2604	0.328	-
0.3992	0.428	-
0.6059	0.529	-
1.0900	0.650	-
9.8676	0.700	+
---	0.750	++

*: - not observed/ agglomeration/caking: + slight /++ medium /+++ heavy
 **Equilibrium relative humidity (%)= a_w 100

The sorption isotherm of the NPK 10-20-20 MOP (BAGFAS) fertilizer is shown in Figure 1

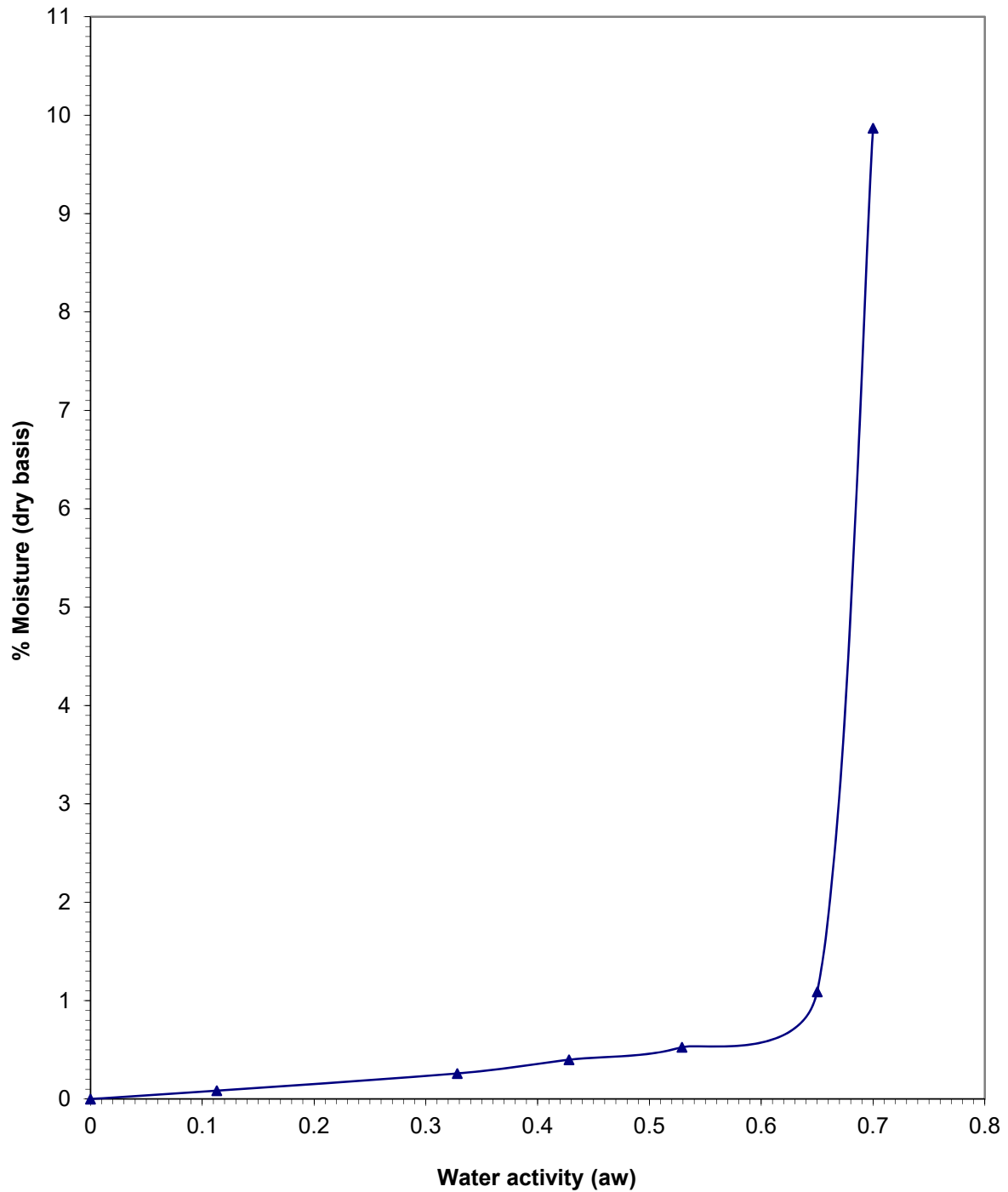


Figure 1. Experimental sorption isotherm (25 °C) of the NPK 10-20-20 MOP (BAGFAS) Fertilizer.

Sorption data was adjusted to various models using a linear regression program, being the best plot to predict moisture of product as a function of the equilibrium air relative humidity (%RHeq) obtained for:

a) Range of $a_w < 0.50$. The best fit was for the Khun model:

$$M = -0.434425 / \ln a_w - 0.118655 \quad (\text{regression coefficient} = -0.998)$$

b) Range of $a_w > 0.50$. The best fit was for the Harkins-Jura model:

$$\ln a_w = -0.35045 - 0.10428 / M^2 \quad (\text{regression coefficient} = -0.999)$$

where:

M= moisture in dry basis (g water/100 g dry solids)

a_w : water activity (equilibrium relative humidity/100)

Estimation of Critical Moisture for Agglomeration/Caking

Critical moisture was determined by the method indicated by (Sauchelli, 1960). Sorption data showing equilibrium relative humidity below 40% ($a_w < 0.40$) was adjusted to the known B.E.T. equation (Brunauer, Emmett and Teller) in order to determine the amount of water adsorbed in the monolayer:

$$a_w / (V (1-a_w)) = (1/(V_m C)) + ((C-1)/(V_m C)) a_w$$

Where, a_w : water activity (equilibrium relative humidity/100)

V: volume of water adsorbed isothermally by the fertilizer (g water/100 g dry fertilizer)

V_m : monolayer water adsorbed isothermally by the fertilizer (g water/100 g dry fertilizer)

C: Product constant related to the heat of adsorption of water (dimensionless)

The monolayer water is referred as a mono molecular layer of water that is adsorbed and attached to chemically active sites in the surface of particles in the fertilizer.

It has been reported in the technical literature that the moisture content of product at which agglomeration first becomes noticeable is usually in the range of a_w from 0.20 to 0.30. The sorption capacity of the water bounded in the monolayer is usually completed when its a_w is around 0.18. Above this level, moisture becomes sufficiently active to bring ions from the surface of particles of fertilizer to form a saturated solution by dissolving the ions in the granules and forming a liquid bridge between granules that can cause caking of granules by re-crystallization.

The data was adjusted to the linearized BET equation presented above, using statistical software with a linear regression program, and the following values calculated (regression coefficient = 0.951):

Water adsorbed in the monolayer: $V_m = 0.374$ g water/100 g dry fertilizer (0.38 % in wet basis), with $C=1.94707$.

The monolayer water corresponds to a relative humidity in equilibrium according to Khun equation of about 41% ($a_w=0.41$). This figure is higher than the range reported for starting of agglomeration of most fertilizers (a_w between 0.20 and 0.30). As pointed out in the technical literature, when the moisture content of the fertilizer is greater than that of the water in the monolayer value (in this case 0.38% wet basis), moisture adsorbed in excess of the monolayer quantity becomes sufficiently active to bring ions from the surface of fertilizer particles into a form of incipient solution that could cause agglomeration and caking by re-crystallization.

The monolayer water content for this particular NPK fertilizer (about 0.38% in wet basis), represents the maximum moisture content of the fertilizer for safe long term storage without agglomeration and caking. In this sense, the tolerance of 1.0% moisture given by local receivers seems to be too high to guarantee safe storage, especially if the product is to be stored under pressure.

Risks of agglomeration start at a_w values above this figure. Observing the sorption isotherm, the range of a_w from 0.41 to 0.60 (0.38% to 0.82% moisture wet basis) represents a zone with positive agglomeration risks, but above $a_w > 0.60$ (moisture content above 0.82% wet basis) the amount of water adsorbed increases dramatically being the risks of agglomeration severe.

In view of the above physical-chemical data, agglomeration of this product cannot be avoided when shipped with moisture content above 0.82%, particularly if it would be stowed under pressure in deep piles. As a matter of fact, agglomeration would take place when stored under pressure with moisture between 0.38 and 0.82%. This explains the agglomeration/caking found in the vessel's holds and warehouses, with declared moisture content in the Quality Certificate in origin of 0.97%. Obviously as moisture increases above the critical level agglomeration/caking also increases.

Agglomeration tests showed positive for product stored without pressure for 37 days with moisture equilibrated with ambient relative humidity of 70-75% ($a_w = 0.70-0.75$)

It has to be pointed out that the sorption isotherm for this NPK 10-20-20 MOP (BAGFAS) resulted very similar in shape and moisture levels to the reported in the literature for potassium chloride / muriate of potash, present in this product in a fraction of about 20%.

Further Remarks about this Product

This granular product has free flowing characteristics and is highly hygroscopic particularly when exposed to high relative humidity as evidenced in the data presented before. Caking risk starts at relatively low moisture content (0.38%) and severe agglomeration at above 0.82%. Due to its nature this product gains moisture when exposed to air and particularly when relative humidity is high. Moisture affects the product when it is above a critical value (in this case the tolerance established by local receivers was 1.0%, but the actual physical-chemical tolerance for safe long

time storage is 0.38%) by dissolving the salts in the surface of granules, forming a saturated solution between granules that join one granule with the others in its vicinities forming a continuum, resulting in loss of free flowing characteristics and caking/compactness of product.

Due to its hygroscopic nature, this product must be stored in warehouses or silos as hermetic as possible in order to reduce exposure to external humid air. When an optimal warehouse is not available, one of the forms to delay deterioration by exposure to humid air is to cover the piles of stored product with tarpaulins or plastic sheeting to act as a barrier to delay moisture adsorption.

Exposure of product to high air relative humidity results in the formation of a caked layer in the surface of the stored product. Its appearance and thickness would depend on the relative humidity to which the product was exposed and to the time of exposure. When product is exposed to high relative humidity the top layer gains moisture immediately and the thickness starts to grow deeper from the product surface in a progressive way. In the beginning the rate of increase in thickness is fast but it tends to diminish as thickness increases. On the other hand, if time is enough the surface layer could liquefy as mud and the liquid phase diffused downward to produce further compactness. The caked layer could affect the rest of the product basically in two ways: the product directly involved in the cake layer has high moisture content. Secondly, when the product is manipulated with a pay-loader or bulldozer, the layer is normally broken and tends to mix with sound product inside the pile and then the overall product could get contaminated with pieces of compacted layer and also increasing its moisture in a variable degree (not significant, minimal or high depending on the case). The caked layer developed in the vessel holds tends to have a no significant role due to the relatively low surface (S) to volume (V) ratio (S/V). If the product is stored in non-hermetic horizontal warehouses or silos, the role is more significant since the height is less and the surface area is more, increasing the ratio S/V and having the surface layer a larger proportion of the whole product stored.

This product is affected by contact with free water immediately, because free water acts dissolving the granules, forming a continuum and a solid block of compact product. While high relative humidity tends to damage the product progressively, direct contact with free water (for instance rain or seawater) induces immediate damage in the product. When large pieces of compact product disaggregate, tend to produce smaller hard pieces and dust and fines.

Usually this fertilizer is used in mechanized agriculture where the seed and fertilizer are applied at the same time by the use of mechanical equipment. The presence of hard pieces of compacted product clogs the lines of this equipment causing problems and delays. Dust and fines adsorb atmospheric moisture faster, and induces caking/compactness of the stored or bagged product in storage. Product contaminated with hard pieces normally retains its chemical composition as fertilizer (NPK content) since this contamination is a physical problem, affecting granulometry and the way the fertilizer can be applied.

Another important point to consider is the lack of uniformity in lab methods to determine moisture content. While methods clearly state the oven temperature and drying time, they are not explicit about the granulometry of the fertilizer. It was found that some labs use the whole granulated fertilizer of eventual different sizes for the moisture test while others grind the fertilizer for this



determination. It was found in lab tests done by the undersigned that the moisture content obtained using the same drying temperature and time, was different for granulated and grinded samples, being significantly lower for the former.

Bibliography Consulted

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