Understanding Caking Phenomena in Industrial Fertilizers: A Review

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Review
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One of the most important problems of the fertilizer industry is that fertilizers show caking tendency during transportation and storage. Caking occurs as a result of interaction at the contact points formed between solid fertilizer particles. These interactions, also called contact mechanisms, are activated by a number of properties that fertilizers have and by environmental conditions. Prevention of caking mechanism is a substantial research subject that directly affects the quality and financial value of the final product and ensures its applicability. Fertilizer in good quality can provide ease in agricultural applications, and directly affect plant nutrition and crop productivity. At this point, there are various promoter practices for obtaining the free-flowing property in fertilizers that can be maintained or suggested during or after production, both in industry and in R&D studies. In order to develop new process control points in the industry, it is important to understand the factors that cause caking and the mechanism of physicochemical interactions that progress depending on these factors. In addition, it is essential to improve the storage conditions of the fertilizer, as well as to maintain its quality until end-use. This paper focuses on the caking behavior of fertilizers in detail, giving brief information about the prevention of caking and various types of anticaking agents.

Key words:
caking, particle contact mechanisms, granular fertilizers, anticaking agents

Introduction

The rising demand for food due to increasing world population requires significant improvements in agriculture and its related industries.[1] Higher agricultural yields are needed to meet the food demand of growing population, which is expected to reach 9 billion by 2050.[2] It is expected that the global food demand will rise by 15 % by 2030, resulting in an increase in fertilizer demand.[3] One of the most important parts of a healthy and sustainable food chain is efficient plant nutrition. Plants need essential nutrients to grow, and each nutrient has specific effects in plant development.[4] Therefore, the demand for fertilizers has increased significantly due to the growth in food production.[5] According to the United Nation's Food and Agriculture Organization (FAO) report, total nitrogen, phosphorus, and potassium demand in the world will reach 200,919 thousand tons by 2022.[6] It is presented that fertilizer industry plays a key role in the world's future. Like many other industries, fertilizer industry is faced several challenges in the quality of products related to handling and efficiency.[7]

Among fertilizer types, the use of NPK compound fertilizers containing basic plant nutrients is quite common. Today, China is the world's largest producer and consumer of NPK compound fertilizers. Approximately 4,000 companies and facilities manufacture NPKs in the country, with a total capacity of about 204.0 million metric tons in 2018.[8] NPK fertilizers are produced in various formulations with different compositions for the substantial needs of plants. They are basically mixtures of nitrogen, phosphorus, and potassium-containing crystalline salts. These salts bring specific features to fertilizers with their natural physicochemical properties.[9] In compound granular fertilizers, the problems related with the physical properties of the fertilizer, such as caking, dusting, poor fluidity, segregation, and excessive hygroscopicity are more common than the chemical composition of the product.[10–12] This review focuses on crystalline granules due to their common use. Although the manufacture of powder fertilizers was frequent before 1950, granulation process allowed granular fertilizers to become widespread.[11] In addition, unlike relatively fine powders or small crystals, granular fertilizers are simply particle size controlled fertilizers. In recent years, powder fertilizer production has decreased after granular fertilizers have led to improvements in dust formation. Granular fertilizers are easy to apply due to their fixed particle size distribution, and usually have better storage and han-

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dling properties when compared with powder fertilizers. However, they can tend to cake significantly, although not as much as powder fertilizers.[10,11]

Bulk materials such as fertilizers, inorganic salts, and chemicals in different sectors often become rigid and cake during storage and handling, owing to the fact that the free-flowing particles turn into lumps.[13] The most prominent case of bulk materials, which is marked as the agglomeration of particles after production, causes industrial and commercial problems. The physical quality of granular fertilizers is very critical in terms of agronomic applicability as well as transportation and storage.[14] Caked solids usually have low flowability, which adversely affects their handling properties.[15] Also, caking of the solid particles causes a great negative impact on the quality of fertilizer products leading to additional costs.[16] A fertilizer with suitable characteristics provides the consumer a relatively easier, faster, more homogeneous, and inexpensive application. In addition, the handling from the production to the final use of fertilizers has basically become more of an issue in the sense of safe working conditions. Produced fertilizers are stored in bulk or bags in the stock areas for a period from one month to several years until its application depending on supply and demand. During storage, fertilizer must remain completely free-flowing or caking must be at an acceptable minimum.[11] These products must be transported from the manufacturer to the end-user by ship, train, or truck as a bulk material or packaged in bags. During transportation, the fertilizer product is often exposed to different external factors, such as variations in temperature and humidity levels, which strongly influence the product's caking.[16,17]

Unlike chemical compositions, the physical properties of fertilizers are often not controlled by regulations. The physical condition of fertilizers is usually dependent on the requirement of a special agreement between the buyer and the supplier. Furthermore, over the years, some traditional methods have been specified for measuring and evaluating the physical properties of fertilizers.[11,18] Measurement methods and control parameters affecting the caking have developed a number of studies to overcome the caking problem. While the methods such as drying, cooling, dust minimization, and moisture-resistant packaging are being applied in the attempt to reduce caking, this issue still requires improvement.[12,19]

This review includes the phenomenon of caking in crystalline fertilizers based on particle contact mechanisms, internal and external factors causing caking, hypothetical analysis methods that can be interpreted as caking, and industrial precautions to be taken regarding this phenomenon. The interactions between the fertilizer characteristics, which are affected by the storage/transportation conditions and the contact mechanisms of fertilizer particles, and their effects on caking mechanism are investigated in detail. Thus, the data obtained from small-scale quality and R&D studies, as one of the most important purposes of the study, may be interpreted in a useful way in industrial practice, that is, on a large scale. In addition, this study is very critical in terms of providing the basic information required in R&D and product development studies in the fertilizer industry. Particular attention has been paid to gathering key information for optimization of both the physicochemical properties of fertilizers and storage conditions. Thus, this study will help the industry to understand the parameters that control the caking tendency in fertilizers, and to establish measurement methods for the properties of the fertilizer and determine the specific storage conditions related to decreasing caking tendencies. Similarly, information is given on the improvement of fertilizers and the measures to be taken against the phenomenon of caking due to the nature of the solid particles and the commercial products that can be applied.

Caking mechanism

One of the most challenging problems of solid materials such as fertilizers is their structure that tends to clump together and cake. Caking is simply defined as an agglomerated appearance due to the contact points formed between the fertilizer particles or granules.[11] It can also be defined as the formation of undesired agglomerates during storage.[20] The described contact points are where some reactions arising from the internal structure of the fertilizer take place, and which are also triggered by environmental factors during the storage period. With the growth of these contact interactions between particles, the caking structure starts to form dramatically.[11] Caking is fundamentally caused by the formation of liquid and solid bridges due to capillary condensation, continuing chemical reactions, dissolution, and molecular attractions in the fertilizer structure, as presented in Fig. 1.[21]

Structural properties of solid materials such as crystallinity/amorphism along with ambient humidity and temperature are the primary factors determining the main mechanisms of caking. Caking in amorphous materials is defined as viscous sintering and explained with a glass transition mechanism where the glassy materials become rubbery at temperatures above their glass transition temperature so they can mobilize as a flow with high viscosity.[15] The present review focuses on the formation of crystalline bridges, and the caking mechanism can be mainly explained in four stages: I) moisture sorption and diffusion, II) capillary condensation or

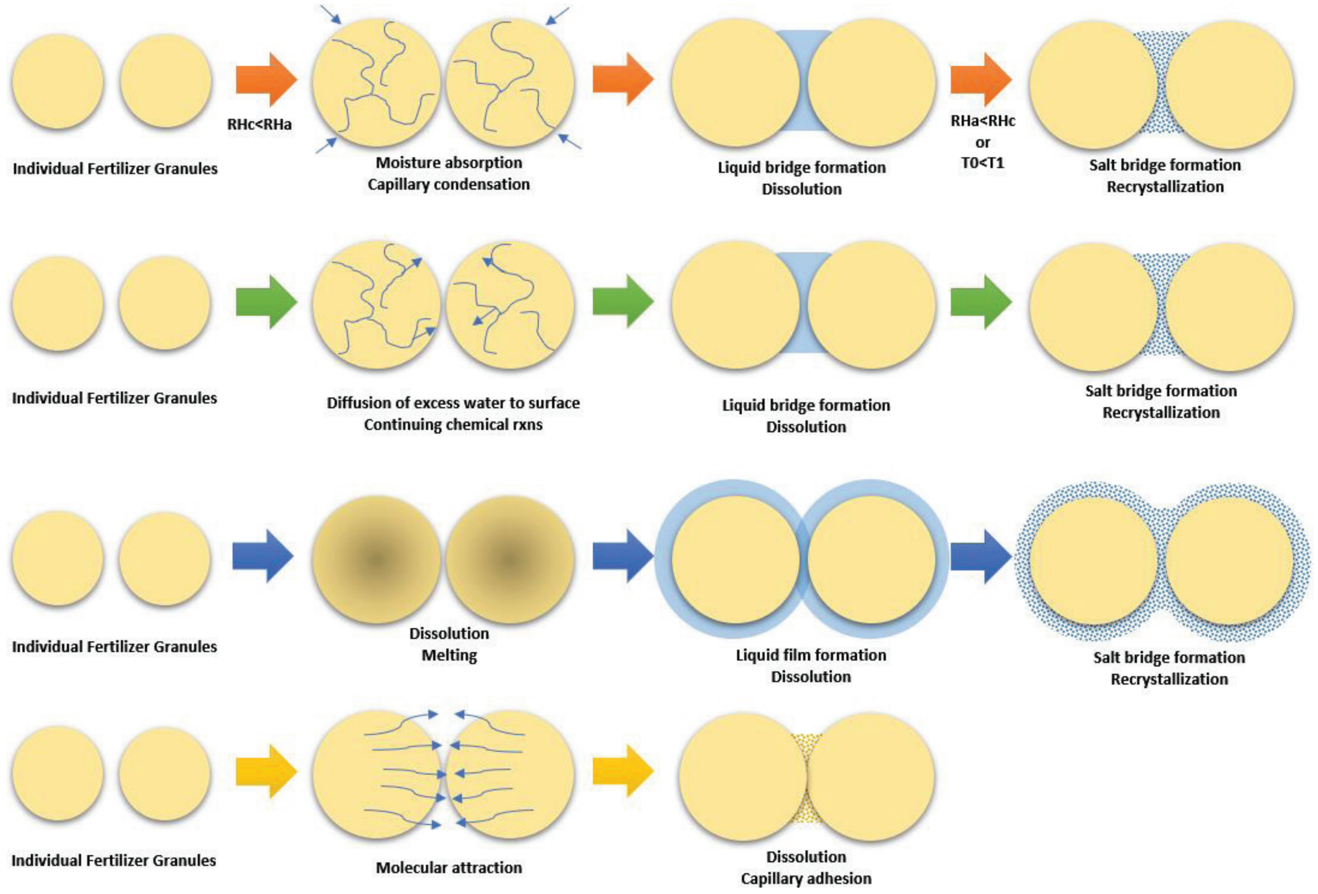

Fig. 1 – *Illustration of contact mechanisms between solid particles*[22]

dissolution, III) liquid bridge or film forming, IV) solid bridge forming by recrystallization. Caking starts with continuous moisture sorption, which causes water diffusion into the fertilizer structure.[23] Moisture can be present due to remaining excess water during the production of fertilizer by complications in process control or it can be directly absorbed from the environment depending on Critical Relative Humidity (CRH) of fertilizer. Moisture diffusion into the fertilizer structure leads to water-solid interactions such as capillary condensation, dissolution, or melting.[24] Salt crystals dissolve into an aqueous solution with diffusing water, which can be formed as liquid bridge at the contact points. Liquid film is formed when water content is increased in the structure continuously, and finally results in a total dissolution of solid.[16] Liquid bridge or film formation is the other important stage of caking, which creates a capillary force and surface tension.[17,25] Low-viscosity liquid bridges are one of the most important adhesion parameters in agglomeration phenomena. Low-molecular weight water-soluble crystalline materials generate liquid bridges by adding water droplets when they are agglomerating.[27] According to the storage conditions when the water content has vaporized, liquid bridges or films thermodynamically turn into crystal form[16] and a solid bridge occurs. These are also called salt bridges, which greatly increase the agglomeration of bulk solids. Crystallization enhances during storage due to the continuing chemical reactions usually related with the storage temperature or humidity.[25] Fig. 2 shows a caked granular NPK fertilizer sample after laboratory-scale testing.

As a practical view at caking configurations from strongest to weakest, they can be grouped as follows: a) salt bridges; b) liquid bridges; c) plastic deformation; d) capillary adhesion; e) electrostatic force; f) magnetic force.[23] Caking can also occur due to molecular attractions by capillary forces (adhesion), electrostatic forces, and magnetic forces between particles. Capillary adhesion occurs due to interaction between molecules at contact point.[20] Capillary forces, which lead the agglomeration mechanisms, appear as a result of Van der Waals forces, magnetic forces, and electrostatic forces.[20,23,25] Capillary adhesion is a solid-solid phenomenon that occurs when a number of particles come together and stick.[27] Adhesion force, which leads to agglomeration of particles is directly dependent on the material structure, thus the interaction between water-soluble solids and water, vapor, or aqueous binder solutions are important parameters for adhesion

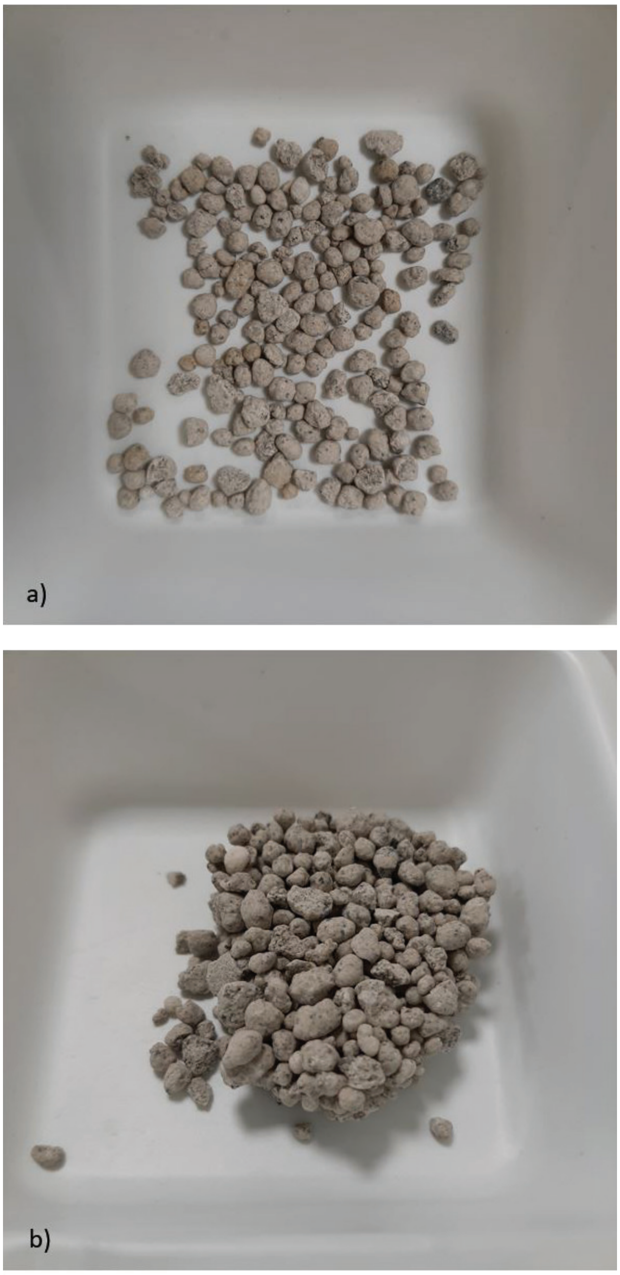

Fig. 2 – *Granular NPK fertilizer: (a) not caked (b) caked*[26]

mechanism. An increase in adhesion force between particles is the key factor for any desired or undesired agglomeration process. Once a stable agglomerate is formed, the caking mechanism is triggered in the structure.[28]

Plastic deformation occurs when there is a constant stress level affecting the fertilizer for a certain time, and it causes caking and dusting in solid materials.[17,25] On the other hand, there is not much evidence that electrostatic forces can cause caking, because the electrical force between particles usually disappears much faster than the time it takes for caking to occur. It is stated that electrostatic forces are 10 times smaller than Van der Waals forces.[27] However, although typically a weak interaction, an electrical attraction between molecules has been studied as one of the mechanisms that can lead to caking. For example, mechanical stress on the surface can initiate a charge polymerization known as a piezoelectric effect in crystallization, which increases the tendency to caking. Temperature differences occurring in the structure that has started to crystallize may increase caking, and finally, when this product enters an electrical field that can cause a difference in the electrical potential, agglomeration called ferroelectric caking may occur.[23,30] Briefly, caking occurs as a result of the natural tendency to come together with the mentioned gravitational forces, moisture absorption character, and crystal structure.

Factors influencing caking

Most types of fertilizers have a tendency to cake during storage. The severity of caking can be affected by various parameters involved in a number of physicochemical properties of fertilizer and the environmental conditions during storage.

Internal factors

The basic properties of solid fertilizers, e.g., moisture content, chemical composition, CRH, particle size, etc., should be evolved for the prevention of caking.[16] The moisture content is considered to be the most effective parameter that determines the tendency toward caking of a fertilizer. In many agglomeration mechanisms, the primary reason for caking is excess water in the fertilizer structure. Ordinarily, high operating temperatures during the production process are applied to avoid free water content in the fertilizer. Fertilizer samples, which cannot be dried sufficiently, retain a certain amount of excess water in their structures, resulting an increased risk of caking.[25] The drying process has a great effect on the inactivation of the caking mechanism, and the degree of drying varies with the physicochemical features of desired fertilizer. Alternative test methods are used to determine the moisture content in fertilizer. It should be taken into account from calculations that it will include hydrate water, which normally does not participate in the tendency to cake as a result of drying in an oven or analyzing the moisture with Karl Fischer titration and dioxane.[11] As well as the free water content, ions dissolved in this water also have an effect on the caking tendency. Dissolved ions in high relatively concentrations cause caking by forming crystalline bridges on granular surfaces.[12] On the other hand, different crystal ions contained in the main liquid affect particle behavior, such as some liquids demonstrate repulsion contrary to water, and this repulsion decreases particle contacts.[16] In many studies, high caking tendency has been observed in fertilizers rich in ammonium and chloride ions. This is because ammonium and chloride ions react on the granular surface to form ammonium chloride salt. Commonly, the proportion of fertilizer compounds in crystalline bonds differs from the total fertilizer formulation. Capillary adhesion occurring between the granules increases with the free water content in the fertilizer, which also causes caking by enhancing the surface tension and contact area between the granules.[12]

The hygroscopic nature of the fertilizer can have an effect on the severity of caking. The CRH of the fertilizer is defined as the humidity of the atmosphere, where the material begins to naturally absorb moisture from the atmosphere on its surface, and below which it will not hold atmospheric moisture. All soluble salts, including fertilizer salts, have specific CRH[10,11], and the moisture absorption is faster when ambient humidity exceeds CRH of fertilizer.[16] This humidity feature decreases when the fertilizer contains impurities or as different fertilizer salts come together. As a result of moisture absorption, the mechanism of caking in fertilizers is activated. When fertilizer is exposed to moisture prolongedly, caking can become more severe.[25] In some cases, fertilizers that consist of various salt crystals, which have different CRH values among each other, may trigger a reaction, such as the equation below, after enough water has been absorbed by the fertilizer.[11]

$$KCl + NH_4\,NO_3 \rightarrow KNO_3 + NH_4Cl^{11}$$

Because CRH varies depending on the structural properties, the amorphism or crystallinity gives important information about the caking tendency. Especially amorphous materials have a higher tendency to cake due to environmental conditions affecting the capillary condensation. Amorphous hydrophilic substances behave differently and start to absorb more amounts of water when they are present in increased humidity. In addition, the water molecules can be stored easily into an amorphous matrix of the structure.[29] The presence of amorphism and impurities can create a more sensitive surface to moisture sorption, which triggers caking.[31]

The chemical composition of fertilizer has an effect on the tendency to form lumps. Ammonium nitrate and urea-based NPK fertilizers have a significantly greater caking tendency than that of ammonium sulfate and ammonium phosphate-based NPK fertilizers. Also, the impurities in the composition may affect all chemical and physical properties of fertilizer, and thus the caking tendency.[25] The formation of ammonium chloride is considered one of the major causes of caking, since saturated ammonium chloride solution evaporates on the outer surface of the fertilizer granule and forms salt bridges with its neighboring components. The source of salt bridges causing caking is easily identified by XRD analysis on fertilizer compounds.[12]

The size, shape, and uniformity of particles are important parameters for contact mechanisms because they directly affect the specific surface area. If the fertilizer has a good granule structure such as limited size distribution and relatively large dimensions, the contact surface area will decrease as will the risk of caking.[16,25] Relatively large fertilizer particles reduce caking tendency, because the contact points between the particles are decreased. Knowing this effect, the production of granular fertilizers with larger particle size is preferred instead of powder fertilizers or fertilizers of smaller particle size.[11] Surface roughness is another parameter affecting the particle interactions and caking tendency, since it is related to the contact area and the nature of the asperity contact between particles. Additionally, it can influence the stress acting at the contact and capillary condensation therein.[23] In order to understand the surface profile of fertilizer, microscopic imaging is of great importance. Fig. 3 presents an image of the morphological characteristics of a granular NPK fertilizer sample magnified 1000x and 10000x, showing the sample as a highly rough surface. Some holes and irregular structure may be observed at high magnification. Water molecules can be easily absorbed and diffused in the cracks and pinholes on the surface, and resulting in caking.

The mechanical strength or hardness of the fertilizer particles is essential for the caking tendency. Weak granules may break down and be crushed under stack or pile due to exerting pressure or during handling by abrasion. Therefore, the size of granules can become finer and the contact area between the particles can increase.[12,14,22]

The temperature of the fertilizer during storage is the other feature that affects the caking tendency. Therefore, newly manufactured products must be cooled adequately before being stored in warehouse as pile or in bags. High temperatures can increase chemical reactivity, causing evaporation of water in the fertilizer structure, crystallization of salt solutions, and formation of solid crystal bridges. In addition, the high temperature of the product increases the severity of plastic deformation when under stock pressure. This deformation causes crystal bridge formation and capillary adhesion.[22] As a result, the internal factors that cause caking are the parameters that affect the moisture sorption on the surface, dissolution, and recrystallization of salts in fertilizer composition. Moisture sorption capacity is

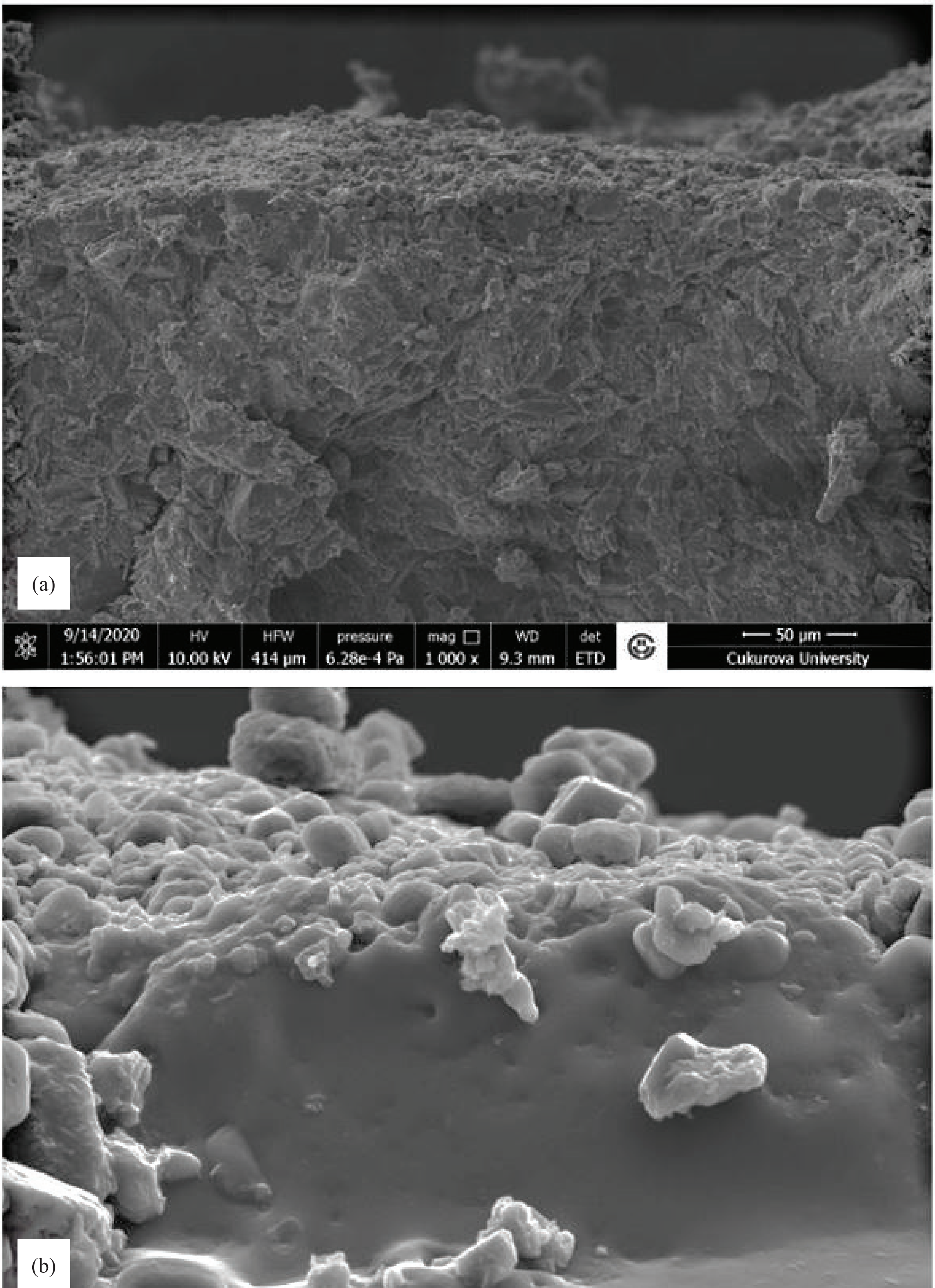

Fig. 3 – *SEM imaging of NPK fertilizer granule: (a) 1000x (b) 10000x*[26]

characterized by the physical surface properties of fertilizer granules such as porosity, roughness, and granule morphology, i.e., its shape, size, and size distribution. On the other hand, dissolution and recrystallization of salt crystals are mostly affected by properties such as chemical composition, critical relative humidity, moisture content, and crystal / amorphous structure. In addition, the temperature and mechanical strength of the fertilizer are among the features that trigger the caking mechanisms.

Environmental factors

Bulk solids are stored both by manufacturer and customer for different time periods and under various types of physical conditions. Besides storage, transportation of these bulk solids is carried out in big bags or sacks, which are affected by different temperature and humidity levels during day-night cycles.[17] Maintenance of the physical/chemical conditions of bulk solids in which they were manufactured is an important phenomenon in many industries, because even after a long storage time, the bulk solids should not solidify partly or completely. If caking happens, quality problems also arise besides deagglomeration procedures, incurring extra costs to both the manufacturer and the customer.[17]

High storage temperature increases the caking tendency in some fertilizers, because higher temperatures decrease the CRH of fertilizer and thereby increase its hygroscopicity.[22] The maximum recommended storage temperature for granular fertilizers containing ammonium nitrate is about 54 °C (130 °F). Similarly, urea-based fertilizers made with non-ammonia or partial ammonia super-phosphates need to be cooled to this temperature in order to prevent hydrolysis of urea and decreased water solubility of P_2O_5. On the other hand, diammonium phosphate and granular sulfate-based or urea-ammonium phosphate products usually only need to be cooled to about 71 °C (160 °F). Prilled and granular urea are also less sensitive to temperature than ammonium nitrate. Studies have shown no increase in the tendency to cake even at storage temperatures up to 82 °C (180 °F). These storage temperatures are for products that have undergone a good drying process.[11]

The humidity of the environment in the warehouse also influences the caking substantially. If fertilizer is placed in an atmosphere with humidity above its critical humidity, it begins to absorb the moisture and the caking mechanism is activated. The length of storage affects caking tendency in most cases, especially at the bottom of a stack or pile.[16] Usually, a fertilizer starts to show caking in the first few weeks after its production, and caking increases with longer storage time. However, if the fertilizer has no tendency to cake, the length of storage has no influence on its caking mechanism.[22] In the case of fertilizers with high caking tendency, it is necessary to take notice of the pressure on fertilizer particles exerted during long storage, because the pressure can increase the granule contact area by increasing breakages in the fertilizer.[16] Limiting the number of bags stacked or the height of bulk pile might reduce the pressure. The pressure on the bottom of a bag stack is calculated by measuring the contact area between the bags and dividing the weight of the stack by this area. In fertilizer industry, a reference pressure value of 0.28 kg cm^{-2} is used in small or large bag tests, and this pressure effect is achieved by placing 20 bags of fertilizer on top of each other, and placing 60 kg on the top bag. According to this calculation, the average height of a fertilizer heap should be 20 bags. However, if the fertilizer is resistant to caking, prolonged pressure causes no caking.[11,16,22]

The nature of caking is related to the diffusion of moisture from the outer surface of the fertilizer material towards the particle center during the storage process. Therefore, as the storage period increases, the possibility of diffusion of moisture into the fertilizer center increases. This situation causes an increase in caking tendency.[32] The degree of caking varies according to the moisture absorption rate of the fertilizer. The most important factor affecting caking kinetics is the difference between the ambient humidity and the CRH of the fertilizer. The surface morphology of a fertilizer, such as pore structure, porosity, and water holding capacity are essential features for the penetration rate of moisture.[22] Also, the rate of movement of the moisture absorbed by the fertilizer particle towards the particle center, and the evaporation rate of the nitrogen concentration in the storage medium are directly related. Especially, in fertilizers with high nitrogen concentration, the most important parameter affecting the relevant kinetics can be considered as nitrogen concentration, since the moisture movement towards the fertilizer particle center is maximum. In this sense, the problem of caking can be expressed as the adhesion of fertilizer particles to each other due to movement of moisture within the fertilizer particles and the reduction of nitrogen concentration as a result of this adhesion, and the reduction of breaking strength and tendency of the fertilizer to degrade.[32] Environmental factors affect caking depending on internal factors. While internal factors can be controlled during manufacturing, environmental conditions can be provided by climate-control of storage areas and arrangement of stocking systems. Ambient humidity especially is slightly more effective than other environmental parameters, and needs to be studied.

Measuring the caking tendency

There are revenant properties that must be considered to determine caking tendency, such as adhesion, amorphous content, moisture sorption, particle size, and many others.[30] In addition, environmental factors that influence caking directly, such as temperature, relative humidity, pressure, should be focused on in order to determine the caking tendency. Many caking test methods have been performed to interpret the caking tendency by measuring these parameters. The approaches of these specific test methods change from simple, such as small bag experiment, to more complex methods, such as shear cell testing.[33] In general, methods for evaluating the caking tendency of fertilizers can be classified as micro- and macro-scale tests. The macro-scale experiments, such as large-bag storage tests, small-bag storage tests, and accelerated caking tests, provide an observation for cake formation and they are mostly preferred in modern fertilizer industry. In large-bag storage test, caking tendency is determined under a certain pressure for a length of time similar to the actual storage time and using standard-size bags. The disadvantages of this test are that it requires a large quantity of material, a large working area, and a lot of labor. Another method that works on a similar principle but at smaller scale is the small-bag storage test. An illustration of the experimental set-up used in small-bag storage test is shown in Fig. 4. While small packages simulate the stacked fertilizer bags, a 60-kg load is placed on the top bag at a height of 1.5 m. The small packages are kept in a temperature- and humidity-controlled environment for a certain time shorter than actual storage time, and the caking tendency is determined over the caked amount.[11,12]

Accelerated caking tests, such as shear cells and uniaxial tester, are mostly preferred in the modern fertilizer industry, in order to determine the caking tendency of the fertilizers. Cake formation is observed by applying pressure on a fertilizer sample with the help of a press.[12,17,19,33,34] Shear cells are used for accelerated test to investigate caking tendency of solid materials under controlled temperature and humidity ambiance. Flow properties, such as caking tendency, internal friction, time consolidation, wall friction, etc., can be measured using shear cells. For measuring time consolidation, a filled shear cell is removed from the tester after the pre-shear procedure and the sample is then sheared. Unconfined yield strength (kPa) before and after time consolidation is calculated from measured yield and time yield loci by Mohr stress circles.[17,31,35,36] The uniaxial tester is also typically developed for investigating caking behavior of solids, and its mechanism is presented in Fig. 5. The compressive pressure is applied for a predetermined time at constant temperature and relative humidity.[12,19,31,34,37] Another instrument is ICI caking tester, which has been developed to eliminate the deficiencies that may be encountered in the pressure distribution of uniaxial testers. In the ICI caking tester, the sample is placed in a polyethylene-lined mold and pneumatic pressure is used.[31,38,39] Creep testing is used for investigation of the effect of load pressure and time comparing creep rates to predict caking of the material.[12,38]

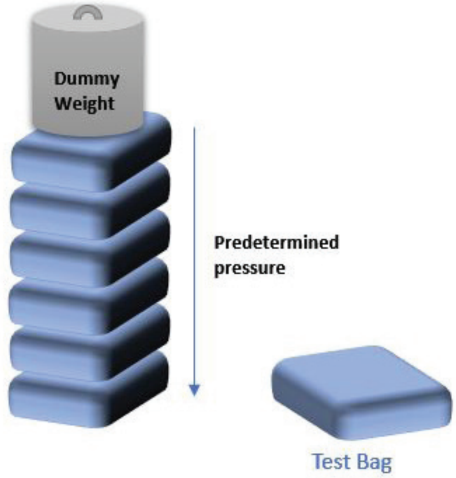

Fig. 4 – *Small-bag accelerating caking test*[11]

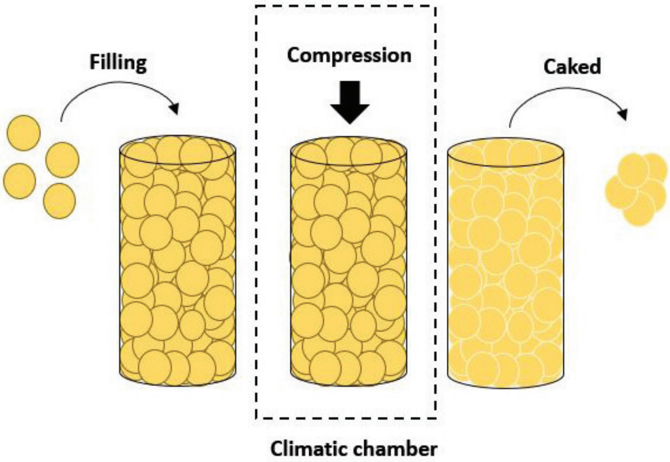

Fig. 5 – *Experimental scheme of uniaxial test*[17]

In addition to macroscale tests in which caking tendency of fertilizer is directly observed, there are several analysis methods that give estimation on the agglomeration in microscale.[12,17,19] An experimental procedure determines the effect of capillary forces on the crushing strength of the sample.[20] Another method utilizes the effect of relative humidity on interarticular forces.[17,36,40] Measurements of the growth of crystal bridges can be performed with microscale experiments, such as XRD and X-ray microanalysis[12] to investigate the geometry of the contact area, the particles can be viewed as images by a microscope, i.e., SEM-EDX analyzer.[17,39] Also, the meaning of the crystal bridge size and strength measured in the two-particle system can be carried out determined.[41] Interactions between solid particles have been theoretically evaluated by benefiting with analytical models, and additionally using adhesion measurements. The adhesion interactions have been investigated for several years and many adhesion models have been presented, such as the Johnson-Kendall-Robers and Derjaguin-Muller-Toporov models.[27] Since the mechanical strength of the fertilizer granules also give important information on the caking tendency, the crushing strength test should be applied in fertilizers with an agglomeration problem, since the low strength of the granules makes them easily deformed. This increases the contact surface area of the fertilizer, while increasing the caking tendency, and at the same time, causes dusting by crushing. Crushing of fertilizer granules also removes the effect of used anticaking substances on the surface.[12,17,19] The relationship between sorbed vapor and a solid can be basically demonstrated by a vapor sorption experiment. Dynamic vapor sorption (DVS) is a gravimetric analysis, which measures the amount of water sorbed by the sample. The analysis is performed as the measurement of the difference in sample weight at different humidity levels, data is then used to set sorption isotherms, and can be used to give information about the moisture sorption of fertilizer.[36,42] Many methods used in industry and research studies are listed above that basically give an assumption of caking tendency by compaction or dominance of the fertilizer under controlled climate.

Anticaking agents

A number of approaches, of which many are found applicable in the industry, have been proposed to solve the fertilizer caking problem. Powder fertilizers were used commonly before development of the granulation process. Additives with large particle sizes, such as vermiculite, perlite, cottonseed shells, sawdust, corncob, tobacco stalks, rice shells, peat, inert powders were used to prevent caking. Today, granular fertilizers are commonly used, and the anticaking agents vary accordingly.[25]

Using anticaking agents is one of the most effective and most common methods to improve the granular structure of a fertilizer.[11,12,24,25,43] The effect of anticaking agents varies according to their functional groups, and various alternative materials have been evaluated both in industry and research projects.[46,47] In general, an anticaking agent prevents crystallization reaction of the salt solutions on the fertilizer surface. It can also prohibit moisture absorption by creating a hydrophobic surface on the fertilizer, while insulating capillary adhesion that would occur between the particles.[12,25] However, some of them have disadvantages which are associated with effectivity and handling, i.e., oil-based materials tend to vaporize or be absorbed into fertilizer structure and loose anticaking property.[44,45]

Anticaking agents are mainly categorized by their application method as coating agents and internal conditioners, as shown in Fig. 6.

Coating agents are divided into inert powders and liquid coating agents. Inert powders such as diatomaceous earth, clay, and talc are applied in the range of 1–4 % by weight in a coating drum. In the application of powder additives, the size and operation of the coating drum is very important for obtaining a good coating on the fertilizer. It is also common practice to use a suitable oil-based product in small quantities (0.2–0.5 %).[11,25] Inert powders usually neutralize the salt solution on the fertilizer surface and act as mechanical barrier between fertilizer granules.[11] Clay additives are extremely fine (90 % <10 µm, 50 % <1 µm) inert powders, and therefore generally have good adhesion properties.

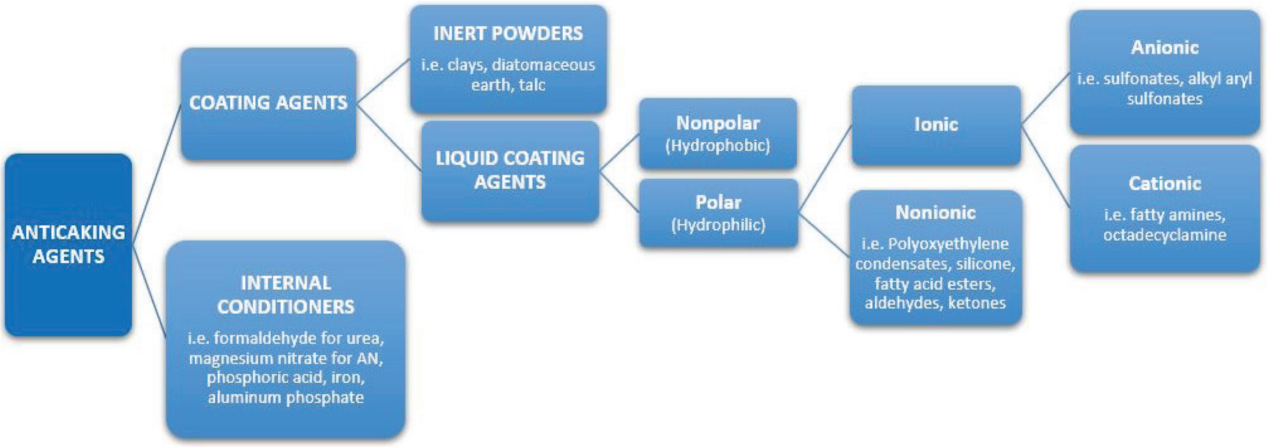

Fig. 6 – *Types of anticaking agents*[11]

Kaolin clays are widely used and relatively inexpensive compared to other substances, thus they are economically feasible. They can be applied alone or with organic additives such as hydrophobic amines on the fertilizer, especially AN.[25] Diatomaceous earths (kieselguhr) are rougher than clays (90 % <20 µm, 50 % <3 µm), making adhesion lower.[11]

The liquid coating agents consist of organic surface-active agents (surfactants) and nonsurface active agents. The surfactants act on the surface tension between the solid and liquid phase, preventing the mechanisms of caking, such as moisture absorption, dissolution, and crystallization. Liquid coating agents can be classified according to the polar (hydrophilic) and nonpolar (hydrophobic) content of the surfactants. Polar molecules are categorized as cationic if the charge is positive or anionic if the charge is negative, according to the polarity of the charge carried by the active part. Cationic surfactants generally consist of fatty amines such as octadecyclamine.[11,25] Sulfonates are one of the common examples of anionic surfactants. There are also nonionic neutral surfactants such as paraffin wax, synthetic polymers, or oils. They can also be used with an inert powder.[46–48]

Apart from the coating agents that interfere with the granule surface, internal conditioners that are included in the chemical composition of the fertilizer are also used for the anticaking effect. These products increase granule resistance, prevent water diffusion to the surface, and improve storage properties. Several anticaking substances classified as internal additives are added to fertilizer formulations before granulation, i.e., formaldehyde for urea fertilizer, magnesium nitrate for AN (ammonium nitrate) fertilizer, phosphoric acid and iron for fertilizer blends.[11]

The best results are generally achieved with high viscosity oils, which are highly paraffinic. Paraffin is a petroleum-based product, a mixture of saturated hydrocarbons containing 80–90 % of linear chains with an average of 20–30 carbons.[50] However, since the demand for green materials continues to increase, paraffin is not an appropriate coating material because it is non-biodegradable, non-recyclable, and unsustainable.[47,48] Additionally, low-viscosity oils are easily absorbed by the fertilizer, and cannot function properly. On the other hand, the application of oil to ammonium nitrate- or nitrate-rich fertilizers is unacceptable due to the risk of flammability and explosion. However, some tests have shown that NP granules containing less than 60 % ammonium nitrate contain up to 3 % oil without risk.[11,25]

There are several studies of anticaking agents introducing new formulations that lessen the potential negative impacts of these coatings on human health and the environment. European authorities have made efforts to minimize the release of microplastics in all types of chemical industries, including fertilizer industry. Insoluble heavy polymers will be affected by the new arrangements in EU regulation in the near future. For the case of the fertilizer industry, it targets polymers having an insoluble heavy molecule used as anticaking coatings or control releasing additives. Polymer products have high stability at high temperatures due to their hydrocarbon structure, and ease in application even at low dosages due to their high melting points. Although their application is feasible from a technical point of view, their disadvantage is that they tend to be non-biodegradable. Optimization of new formulations with low eco-toxicity and bioaccumulation, having low-melting point to reduce CO_2 emissions associated with production, transport, and application of these polymers is also the topic of many studies. These eco-friendly anticaking agents are promising in line with current products; however, further tests are required of long-term efficiency and stability of these new formulations. In order to develop eco-friendly anticaking products, understanding of the crystallization reactions and contact mechanisms that take place in the fertilizer structure is essential.[49] It should be ensured that anticaking materials are evaluated in terms of both chemical efficiency and environmental sensitivity for industrial practices. In order to use suitable anticaking material, it is essential to understand in detail the caking mechanisms and its parameters.

Relationship between caking and dusting

The dusting of fertilizer is another physical problem that cannot be considered apart from the caking. Cake formation leads to difficulties during storage and handling, whereas dust formation causes material loss, air pollution, and health problems.[44,50] Fertilizers generally have a tendency to form dust during manufacture and transportation due to their physical structure, especially in the case of bulk fertilizers.[11] Among the reasons for dust formation are mechanisms such as mechanical abrasion, ongoing chemical reactions, and moisture loss. Mechanical abrasion can occur between the fertilizer particles during handling and transportation.[51] Additionally, dusting is usually formed due to low mechanical strength, disagreeable particle sizing, incorrect coating material, and poor surface structure similar to caking. The use of inappropriate anticaking agent may also create dusting on the surface due to the incompatibilities experienced by this additive.[11]

As caking and dust formation have a strong relationship, the studies aiming to solve the caking problem are also interested in dusting of fertilizer.[52–54] Also, granulation is an important process to reduce fertilizer dust, and to manufacture fertilizer products in similar size. In order to decrease dust content in fertilizers, their endurance should be enhanced by additives to prevent caking or improve mechanical strength. However, in some cases, anti-dust agent usage is required additionally. The effect of anti-dust agents is mostly based on adhering of dust particles on the surface by spraying the liquid coating agents on the granule surface. The most frequently used liquid agents are 0.2–2 % petroleum, but they are not used in ammonium nitrate and high-nitrogen fertilizers due to their organic content, resulting in risk of explosion. Oils with high paraffin content are also very effective in reducing dusting. The application of coating oils is carried out by spraying on a rotating bearing. In addition to oils, liquids containing lignin sulfonate are also applied for dust control.[11] As a result, the problem of dusting in fertilizer cannot be considered separately from the caking tendency, so it is an issue that needs to be studied together.

Theoretical studies on caking phenomenon

There are many research studies on caking of solid substances, most of which are based on analytical observations, and some of these studies are in given the following section. Walker *et al.*, characterized caking behavior of granular NPK fertilizer by performing accelerating caking tests, and microscopic investigation of caked parts in terms of the role of free water and the effect of ammonium chloride was performed by XRD and X-ray microanalysis. The rapid determination of caking tendency was performed using two method types. In first method, granules were subjected to a pressure of 30 psig in a cylindrical press for a predetermined time, while in the second test, a pressure of 60 psig was applied to granules for a longer time than in the first method. It was stated that crystal bridges in the fertilizer structure attained a high caking tendency in ACTs. Also, the crushing strength of fertilizer granules which were 2–3 mm in diameter were determined by a material testing machine in the same study. It indicated that there is a direct relationship between tensile strength and caking tendency of granules. In addition, the formation of ammonium chloride, which may be linked with caking was observed by XRD analysis. According to X-ray microanalysis of free water in fertilizer granules, the distribution patterns for K and Cl were determined. A high effective correlation between free water concentration and caking tendency was found.[12] In another study, caking of NPK fertilizers was observed by performing an ICI equipment under 4–60 psig for 6–72 h.[38] Röck and Schwedes presented a macroscale study on the caking behavior of bulk solids such as ammonium chloride with almost spherical particles by simulating real climatic conditions for transport and storage. Unconfined failure strength for ammonium chloride was measured at stress level between 3.5 and 11.5 kPa in a uniaxial test in dependence on consolidation time, relative humidity, and consolidation stress. Relative humidity and consolidation time mainly affected caking tendency. The influence of stress level during consolidation was comparatively small.[17] In a different study, several samples of fertilizers coming from various industrial partners were investigated by the principle of uniaxial testing. The caking behaviors of solids were found strongly dependent on consolidation stress, consolidation time, ambient temperature, and humidity, similar to previous studies.[34] Albadarin *et al.*, aimed to understand the caking performance of a commercial fertilizer (POLY4) as a single fertilizer and as an additive in NPK blend. Positive results were found, i.e., POLY4 reduced caking tendency within NPK blend by performing crushing strength test, DVS, and ACTs. The sample with the highest rate (50 %) was recorded to have the longest estimated storage time of about 300 months.[19] Hartmann and Palzer analyzed the caking mechanisms in the crystalline and amorphous structures. The viscosity property was found to depend on the kinetics of sintering solid bridge in amorphous materials. Likewise, it is stated that the agglomeration of crystal substances was associated with physical phenomenon, such as dissolution and recrystallization, when the ambient humidity temporarily exceeds the critical relative humidity of the substance.[29] Similarly, Fitzpatrick *et al.*, investigated the influence of moisture content and storage conditions on the caking of dairy powders using shear testing methods. The results suggested that storage environment had great influence on powder caking, as well as moisture content of material.[35] In another study, the flowability behaviors of some pharmaceutical solids in various formulations were analyzed at different relative humidity levels by shear tester.[36] Weigl *et al.*, also studied powder caking by using uniaxial tester, and a standard test procedure was developed to measure the crushing strength of caked products.[37] Calvert *et al.*, carried out an investigation of caking propensity in various environmental conditions by a new developed uniaxial caking tester. The tester works with conditioning air that passes through the solid material to rapidly change the environmental condition of the sample.[33] Lloyd *et al.* used simple test methods to determine the caking behavior of amorphous lactose solids in the principle of uniaxial testing. Also, NMR analysis (Nuclear Magnetic Resonance) was performed to measure the onset glass transition, and the deformed surfaces of the lactose particles were observed using SEM.[39] Wahl *et al.* focused on crystal bridges which were formed due to unsuitable ambient humidity. It is stated that the crystal bridge strength distribution in the simulation used was important.[41] In a recent study, vacuum tower asphalt extender was used as a coating agent for dust control and/or anticaking fertilizer during storage and transportation.[44] In another study, a mixture of wax, mineral oil, an elastomer and a resin were used for producing of a coating agent, which would allow a decrease in moisture uptake and dust formation in fertilizers.[52] Another study suggests a method for improving the crushing strength and reducing the tendency of dusting and caking by introducing a carbohydrate and polyvinyl compound to fertilizer salt.[55] The mentioned theoretical studies aimed to examine the phenomenon of caking in different types of solid materials. The agglomeration of solids is interpreted by specific approaches. Detailed understanding of caking behavior is possible with the accelerated tests at high-pressure by supporting microanalysis methods.

Conclusion

The storage and handling of bulk materials manufactured in various industries, such as chemical, food, pharmaceutical, detergent, and fertilizer, are usually related to physical problems such as caking, dusting, and degrading. Many of these problems, which have a great co-effect on the physical conditions of the products, occur by similar mechanisms running in material structure. Caking and other problems that come with it are the issues that the fertilizer industry has been working on for many years. Although all fertilizer types, which can be powder, crystalline, and granular form, may have a high caking tendency, this review particularly focuses on granular crystalline fertilizers. Caking is a great problem for fertilizer industry; it directly affects product quality and causes extra costs for the rework process. Manufacturers usually store fertilizers in piles or bags for months or years until delivery. Therefore, a product that came out of production in good and suitable quality may then cake during storage or delivery. Complaints may occur about the caking problem months after the fertilizer was produced and shipped to warehouses without caking. As caked fertilizer is deemed certainly unsuitable in the market, the delivery of fertilizer that has caked during storage or transportation, harms the commercial brand profile. Therefore, it is very important to detect and control caking tendency of fertilizers, and to optimize external factors that may cause caking.

Fertilizer particles, like many bulk materials, may have a great tendency for coming together and caking into large and hard lumps. Caking is caused because many types of salt crystals in fertilizer composition naturally have critical properties such as moisture sorption capability, moisture content, critical relative humidity, chemical reactivity, and crystallinity, etc., which lead to particle interactions combined with ambient conditions. Caking fundamentally occurs by particle interactions, including capillary condensation, dissolution, and recrystallization of salt compounds that are normally in the chemical composition of fertilizer. In addition, molecular attractions, which may be caused by Van der Walls or electrostatic forces, lead to phase contacts.

At this point, moisture absorption capability and CRH of fertilizer salt is stated as having the greatest effect on caking tendency. By simply keeping the internal and external parameters influencing the fertilizer caking under control by running required quality tests, provides a clean area to study prevention applications. Therefore, it is essential for the fertilizer industry and material engineering to learn caking mechanisms with the influencing parameters. Prevention of caking comprises many applications of coating granules with anticaking agents. Granule coating is gaining importance in the fertilizer industry because it improves the handling properties of fertilizers. Many coating materials can be used for anticaking effect based on chemical and biochemical compounding, such as mineral oils, waxes, vegetable oils, etc. Alongside coating materials, many additives can be used for the same objectives, which are combined into the fertilizer structure during manufacturing.

Consequently, in order to reduce the caking tendency of fertilizers, there are several focal points that include production process control, coating or internal support agents, and warehouse/transport conditions. Some suggestions, which can be gained from industrial and research studies, can be applied in the fertilizer industry against the caking problem, as follows:

- Applying a sufficient drying step in the manufacturing process enables a low-moisture fertilizer. Thus, moisture content control is ensured and a product with excess water in its structure is avoided.
- An efficient granulation system that separates too small or too large granules is essential for obtaining granular particles of uniform size and shape.
- Sufficient cooling steps need to be added to the process in order to reduce and control the final product temperature prior to packaging.
- Storage at fixed temperature and humidity controlled ambient conditions for a certain length of time and stock height.
- Coating oils or other anticaking materials that can be applied internally in the production pro-

cess of the fertilizer are used according to fertilizer types. To develop the effect of anticaking materials, coating thickness or application rate studies can be performed on these products. Antidust or granulating aids that might act with these products can be used.

References

1. *Alexandratos, N., Bruinsma J.,* World agriculture towards 2030/2050: The 2012 revision, ESA Working paper No. 12-03, FAO, Rome, 2012, pp 1-5.
2. *Charles, H., Godfray, J., Crute, I. R., Haddad, L., Lawrence, D., Muir, J. F., Nisbett, N., Pretty, J., Robinson, S., Toulmin, C., Whiteley, R.,* The future of the global food system, Phil. Trans. R. Soc. B **365** (2010) 2769. doi: https://doi.org/10.1098/rstb.2010.0180
3. *Sexton, S. W.,* Prioritizing personnel safety, World Fertilizer Magazine, March 2017.
4. *Moore, L.,* Measuring sustainability of fertilizer coatings, World Fertilizer Magazine, July 2020.
5. OECD/FAO, OECD-FAO Agricultural Outlook 2020-2029, OECD Publishing, Paris/FAO, Rome. doi: https://doi.org/10.1787/1112c23b-en
6. FAO, World fertilizer trends and outlook to 2022, Rome, 2019.
7. Fertilizer Europe, Feeding Life 2030 Report – The European fertilizer industry at the crossroads between nutrition and energy, 2018.
8. URL: https://ihsmarkit.com/products/npk-compound-fertilizers-chemical-economics-handbook.html (16.09.2020)
9. *Bröckel, U., Wahl, M., Kirsch, R., Feise, H. J.,* Formation and growth of crystal bridges in bulk solids, Chem. Eng. Technol. **29** (2006) 691. doi: https://doi.org/10.1002/ceat.200600066
10. *Kholkute, R.,* Fertilizers storage and handling: Indian perspective, ARAB Fertilizer **64** (2014) 12.
11. *Hignett, T. P.* (Ed.)., Fertilizer manual, Springer Science & Business Media, Alabama, 2014, pp: 284-312.
12. *Walker, G. M., Magee, T. R. A., Holland, C. R., Ahmad, M. N., Fox, J. N., Moffatt, N. A., Kells, A. G.,* Caking processes in granular NPK fertilizer, Ind. Eng. Chem. Res. **37**(2) (1998) 435. doi: https://doi.org/10.1021/ie970387n
13. *Fitzpatrick, J. J., Descamps, N., O'Meara, K., Jones, C., Walsh, D., Spitere, M.,* Comparing the caking behaviours of skim milk powder, amorphous maltodextrin and crystalline common salt, Powd. Technol. **204**(1) (2010) 131. doi: https://doi.org/10.1016/j.powtec.2010.07.029
14. *Fulton, J., Kaylee P.*, Physical properties of granular fertilizers and impact on spreading, Tho Ohio State University–Collage of food, agricultural and environmental sciences (2016). URL: https://ohioline.osu.edu/factsheet/fabe-5501 (16.09.2020)
15. *Kamyabi, M., Sotudeh-Gharebagh, R., Zarghami, R., Saleh, K.*, Principles of viscous sintering in amorphous powders: A critical review, Chem. Eng. Res. Des. **125** (2017) 328. doi: https://doi.org/10.1016/j.cherd.2017.06.009
16. *Chen, M., Wu, S., Xu, S., Yu, B., Shilbayeh, M., Liu, Y., Zhu, X., Wang, J., Gong, J.*, Caking of crystals: Characterization, mechanisms, and prevention, Powd. Technol. **337** (2018) 51. doi: https://doi.org/10.1016/j.powtec.2017.04.052
17. *Röck, M., Schwedes, J.,* Investigations on the caking behaviour of bulk solids—macroscale experiments, Powd. Technol. **157**(1-3) (2005) 121. doi: https://doi.org/10.1016/j.powtec.2005.05.018
18. *Biskupski, A., Schab, S., Myka, A., Dawidowicz, M.*, Physicochemical properties of fertilizers available on market and possibility of production of blended fertilizers, Chemik **66** (2012) 541. doi: https://doi.org/10.1016/j.biosystemseng.2003.09.006
19. *Albadarin, A. B., Lewis, T. D., Walker, G. M.*, Granulated polyhalite fertilizer caking propensity, Powd. Technol. **308** (2017) 193. doi: https://doi.org/10.1016/j.powtec.2016.12.004
20. *Rondeau, X., Affolter, C., Komunjer, L., Clausse, D., Guigan, P.*, Experimental determination of capillary forces by crushing strength measurements, Powd. Technol. **130** (2003) 124. doi: https://doi.org/10.1016/S0032-5910(02)00255-3
21. *Falodun, O. A., Okonkwo, E. M., Meka, N. A.*, Effect of rotational speed of a pan granulator on granular size distribution of a neem-based organomineral fertilizer, Ew. J. Dev. Technol. Manag. **1**(1) (2015) 1.
22. *Chen, M., Zhang, D., Dong, W., Luo, Z., Kang, C., Li, H., Wang, G., Gong, J.,* Amorphous and humidity caking: A review, Chin. Jour. Chem. Eng. **27**(6) (2019) 1429. doi: https://doi.org/10.1016/j.cjche.2019.02.004
23. *Zafar, U., Vivacqua, V., Calvert, G., Ghadiri, M., Cleaver, J. S.,* A review of bulk powder caking, Powd. Technol. **313** (2017) 389. doi: https://doi.org/10.1016/j.powtec.2017.02.024
24. *Li, H.,* Design of amphiphilic anti-caking systems for solid particles, PhD Dissertation, Martin-Luther-Universität Halle-Wittenberg, 2010.
25. *Rutland, D. W.,* Fertilizer caking: Mechanisms, influential factors, and methods of prevention, Fertilizer Research **30**(1) (1991) 99. doi: https://doi.org/10.1007/BF01048832
26. *Ulusal, A., Avsar, C.,* Unpublished report, Toros Agri&Industry, R&D Center Laboratory, 2020.
27. *Petean, P. G. C., Aguiar, M. L.*, Determining the adhesion force between particles and rough surfaces, Powd. Technol. **274** (2015) 67. doi: https://doi.org/10.1016/j.powtec.2014.12.047
28. *Dopfer, D., Palzer, S., Heinrich, S., Fries, L., Antonyuk, S., Haider, C., Salman, A. D.,* Adhesion mechanisms between water soluble particles, Powd. Technol. **238** (2013) 35. doi: https://doi.org/10.1016/j.powtec.2012.06.029
29. *Hartmann, M., Palzer, S.,* Caking of amorphous powders—Material aspects, modelling and applications, Powd. Technol. **206**(1-2) (2011) 112. doi: https://doi.org/10.1016/j.powtec.2010.04.014
30. *Griffith, E. J.,* Cake formation in particulate systems, VCH Publishers, New York, 1991, pp: 18-58 doi: https://doi.org/10.1002/prac.19923340319
31. *Carpin, M., Bertelsen, H., Bech, J. K., Jeantet, R., Risbo, J., Schuck, P.,* Caking of lactose: A critical review, Trnd. Food Sci. Technl. **53** (2016) 1. doi: https://doi.org/10.1016/j.tifs.2016.04.002
32. *Gezerman, A. O.,* Mathematical modeling for prilling processes in ammonium nitrate production, Eng. Rep. **e12173** (2020). doi: https://doi.org/10.1002/eng2.12173
33. *Calvert, G., Curcic, N., Redhead, C., Ahmadian, H., Owen, C., Beckett, D., Ghadiri, M.,* A new environmental bulk powder caking tester, Powd. Technol. **249** (2013) 323. doi: https://doi.org/10.1016/j.powtec.2013.08.037

34. *Röck, M., Ostendorf, M., Schwedes, J.,* Development of a uniaxial caking tester, Chem. Engin. Technol. **29**(6) (2006) 679.
doi: https://doi.org/10.1002/ceat.200600068

35. *Fitzpatrick, J. J., Barry, K., Cerqueira, P. S. M., Iqbal, T., O'neill, J., Roos, Y. H.,* Effect of composition and storage conditions on the flowability of dairy powders, Inter. Dairy Jour. **17**(4) (2007) 383.
doi: https://doi.org/10.1016/j.idairyj.2006.04.010

36. *Lu, X. Y., Chen, L., Wu, C. Y., Chan, H. K., Freeman, T.,* The effects of relative humidity on the flowability and dispersion performance of lactose mixtures, Materials **10**(6) (2017) 592.
doi: https://doi.org/10.3390/ma10060592

37. *Weigl, B., Pengiran, Y., Feise, H. J., Röck, M., Janssen, R.,* Comparative testing of powder caking, Chem. Engin. Technol. **29**(6) (2006) 686.
doi: https://doi.org/10.1002/ceat.200600083

38. *Walker, G. M., Holland, C. R., Ahmad, M. N., Fox, J. N., Kells, A. G.,* Granular fertilizer agglomeration in accelerated caking tests, Ind. Eng. Chem. Res. **38**(10) (1999) 4100.
doi: https://doi.org/10.1021/ie990204s

39. *Lloyd, R. J., Dong Chen, X., Hargreaves, J. B.,* Glass transition and caking of spray-dried lactose, Int. Jour. Food Sci. Technol. **31**(4) (1996) 305.
doi: https://doi.org/10.1046/j.1365-2621.1996.00352.x

40. *Barreiro, J. A.,* Technical paper: Physical-chemical characteristics and factors affecting water sorption and caking of NPK 10-20-20 MOP (BAGFAS) fertilizer, Cargo Ins. Serv. (2018).

41. *Wahl, M., Bröckel, U., Brendel, L., Feise, H. J., Weigl, B., Röck, M., Schwedes, J.,* Understanding powder caking: Predicting caking strength from individual particle contacts, Powd. Technol. **188**(2) (2008) 147.
doi: https://doi.org/10.1016/j.powtec.2008.04.062

42. *Sheokand, S., Modi, S. R., Bansal, A. K.,* Dynamic vapor sorption as a tool for characterization and quantification of amorphous content in predominantly crystalline materials, Jour. of Pharm. Sci. **103** (2014) 3364.
doi: https://doi.org/10.1002/jps.24160

43. *González-León, J. A., Simon, F., Besson, C., Nicol, P.*, Variables affecting caking on granular phosphorous containing fertilizers, SSRN "SYMPHOS 2019", 5th Int. Symp. Innov. Technol. Phosphate Ind., 2020.

44. *Parker, D. T., Ogzewalla, M., Burrell, Z. T.,* (ArrMaz Products L.-P.), 14 Mar 2019; U. S. Patent No. U. S. 2019/0077723 A1.

45. *Ogzewalla, M. B., Carlini Jr, A. M., Barnat, J.,* (ArrMaz Products L.-P.), 20 Jul 2017; U. S. Patent No. 15/404,348.

46. *Chen, G., Tang, Y., Zhang, J.,* Synthesis and application of polyaminoamide as new paraffin inhibitor from vegetable oil, Chemis. Centr. Journ. **5** (2011) 82.
doi: https://doi.org/10.1186/1752-153X-5-82

47. *Fei, T., Walker, J. A., Vickerman, K. L., Stanley, L. M., Jarboe, D., Wang, T.,* Synthesis and characterization of soybean oil-based waxes and their application as paraffin substitute for corrugated coating, Jour. of Industr. and Engin. Chemis. **58** (2018) 113.
doi: https://doi.org/10.1016/j.jiec.2017.09.015

48. *Sharma, Y. O., Nilkamal, B. A. G., Rao, B. S., Gupta, S., Kiiski, H. T., Sahali-Al, S. A. I. F.* (SABIC Global Technologies B.-V.), 25 Jun 2020; U. S. Patent No. 16/612,635.

49. *Gilgado, I.,* Breaking the caking habit, World Fertilizer Magazine, March 2020.

50. *Vashishtha, M., Dongara, P., Singh, D.,* Improvement in properties of urea by phosphogypsum coating, Inter. Jour. Chem.Tech. Res. **2**(1) (2010) 36.

51. *Ogzewalla, M. B.,* (Perumala Corp. ArrMaz Products L.-P.), 12 Mar 2002; U. S. Patent No. 6,355,083.

52. *Obrestad, T., Tande, T.,* (Yara International A.-S.-A.), 21 May 2019; U. S. Patent No. 10,294,170.

53. *Pettersen, J. M., Obrestad, T., Snartland, S. G.*, (Yara International A.-S.-A.), 18 Feb 1997; U. S. Patent No. 5,603,745.

54. *Hazlett, S.,* (Georgia Pacific L.-L.-C.), 12 Jul 1994; U. S. Patent No. 5,328,497.

55. *Van Belzen, R., Vanmareke, L.,* (Yara International A.-S.-A.), 19 Oct 2010; U. S. Patent No. U. S. 7,816,561 B2.