LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Degree Programme in Chemical and Process Engineering

Henri Lappalainen

Identification of granule setting factors and measurements

Examiners: Professor Satu-Pia Reinikainen

M.Sc. Jarkko Roivainen

Abstract

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Identification of granule setting factors and measurements

Master's Thesis

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Examiners: Professor Satu-Pia Reinikainen

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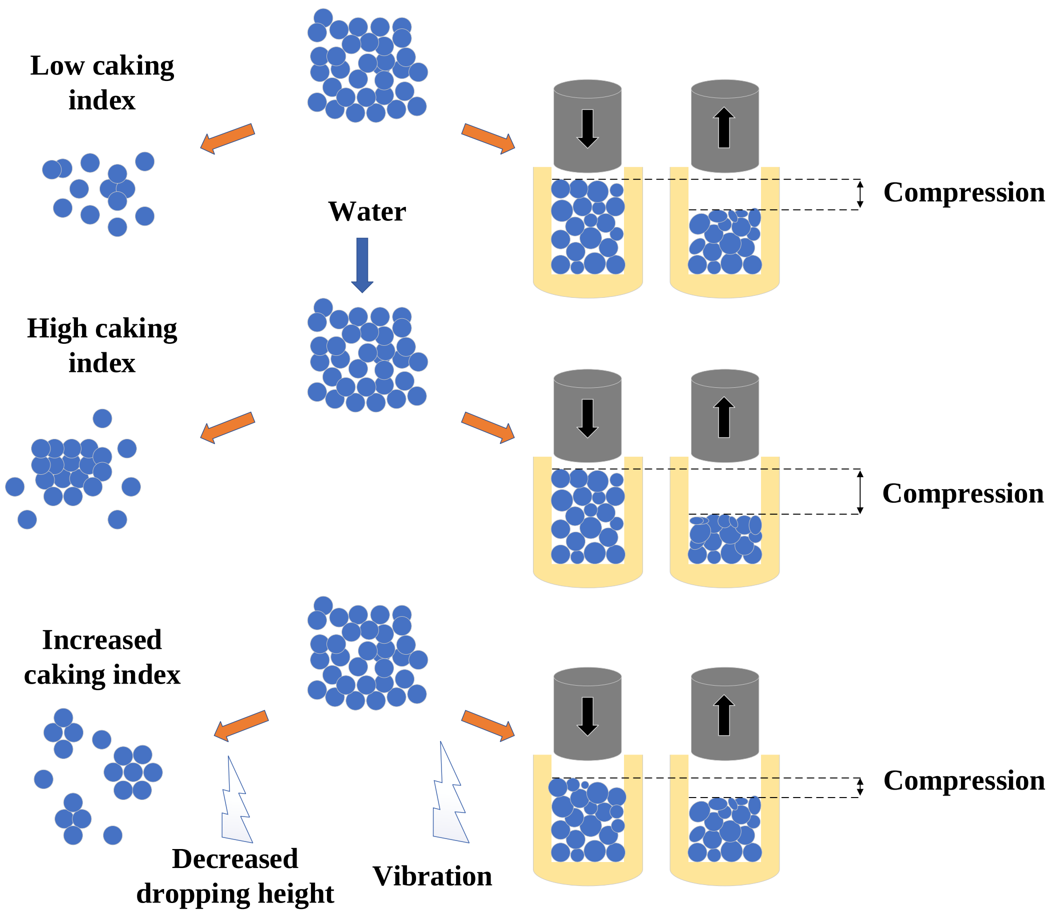
Keywords: setting, granulated solids, compression, caking index

Agglomeration of granulated particles, also known as setting, severely decreases the handling characteristics of the material. In the literature part, factors effecting the setting of inorganic granules are examined. Moisture, temperature, chemical composition as well as the physical structure of the granule were identified as the main factors in particle agglomeration.

In the experimental part measurements based on the compression of granule bed and agglomeration of the granules were studied. The effect of the factors identified in the literature part was examined. The goal was to identify measurements error sources, increase the reliability and improve the predictive power of the measurements. The measurements showcased that the moisture content and the temperature have a clear impact on setting. In particle bed compression the packing density has significant effect. In the agglomeration measurement the most effective way to increase the predictive power was to decrease the dropping height of the samples.

Graphical abstract



Tiivistelmä

Lappeenrannan-Lahden teknillinen yliopisto

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Kemiantekniikan koulutusohjelma

Henri Lappalainen

Rakeiden asettumistaipumuksiin vaikuttavien tekijöiden tunnistaminen ja mittaaminen

Diplomityö

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Tarkastajat: Professori Satu-Pia Reinikainen

FM Jarkko Roivainen

Ohjaaja DI Henri Pitkänen

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Hakusanat: asettuminen, rakeinen kiintoaine, painuma, paakkuuntuvuus

Rakeisessa kiintoaineessa rakeiden yhteen kasvaminen eli asettuminen vaikeuttaa huomattavasti materiaalin käsittelyä. Työn kirjallisessa osassa tarkastellaan epäorgaanisten rakeiden asettumisen ja paakkuuntumisen laukaisevia tekijöitä. Kosteus, lämpötila, raemateriaalin kemia ja rakeen fysikaalinen rakenne ovat vaikuttavia tekijöitä rakeiden yhteen kasvamiseen.

Kokeellisessa osassa tarkasteltiin raepatjan painuman sekä rakeiden yhteen tarttumiseen perustuvia mittauksia. Kirjallisuusosassa tarkasteltujen tekijöiden vaikutusta tarkkailtiin. Tavoitteena oli tunnistaa mittaustapoihin liittyviä virhelähteitä, parantaa mittausten luotettavuutta ja kasvattaa asettumisen ennustuskykyä. Mittaukset vahvistivat kosteuden ja lämpötilan merkityksen asettumisessa. Painuman mittauksessa raenäytteen irtotiheydellä on merkittävä vaikutus. Rakeiden yhteen tarttumisessa mittauksessa tehokkain keino lisätä mittauksen ennustuskykyä oli vähentää näytepussien pudotuskorkeutta.

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List of symbols

A	thickness of the coating layer	m
A_w	water activity	-
B	drum rotation speed	rpm
C	compression	%
d	granule diameter	m
d_{p0}	particle size of the recycle	m
E^*	Average modulus of elasticity	Pa
E	Young's modulus	Pa
F_{el}	elastic contact force	N
Fr	Froude number	-
g	gravitational acceleration	m/s^2
h	height	m
m	mass	kg
M	mass flow of the sprayed slurry	kg/s
P	pressure	Pa
P_v	water vapor pressure of the material	Pa
P_w	vapor pressure of pure water	Pa
r	radius of a sphere	m
R	ideal gas constant	kJ/K mol
R	radius of sphere	m
r_k	Kelvin radius	m
t_c	contact time of particles and slurry spray	s

T	temperature	K
V_0	volume of 1 mol of saturated solution	m^3
z_0	contact distance	m
γ	surface energy of sphere	J/m^2
μ	parameter for model choosing	-
ε	average voidage of the particle bed	-
θ	wetting angle	∘
σ	surface tension	N/m
τ	particle residence time in drum	s

List of abbreviations

AN	Ammonium nitrate
AS	Ammonium sulphate
CN	Calcium nitrate
CAN	Calcium ammonium nitrate
CRH	Critical relative humidity
DAP	Diammonium phosphate
FIBC	Flexible Intermediate Bulk Container
IFA	International Fertilizer Industry Association
KF	Karl-Fischer
KN	Potassium nitrate
K2	Solid solution of AN dissolved in $KNO_3 - II$
K3	Solid solution of AN dissolved in $KNO_3 - III$
MAP	Monoammonium phosphate
MOP	Muriate of potash
NKS	Solid solution, ammonium potassium sulphate, $(NH_4, K)_2SO_4$
NPK	Nitrogen, phosphorus, potassium fertilizer
N3	Solid solution of KNO_3 dissolved in AN-III
NK	Nitrogen, potassium fertilizer
NP	Nitrogen, phosphorus fertilizer
N	Nitrogen fertilizer (saltpeter)
PLM	Polarized light microscope
RH	Relative humidity

SEM-EDX	Scanning electronic microscope with energy dispersive X-ray
SOP	Sulphate of potash
XRD	X-ray diffraction

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1. Introduction

Fertilizers are the cornerstone of modern agriculture. The use of fertilizers has increased the crops harvested per given area up to 30-50% (Stewart et al., 2005). Therefore, the farmers were able to meet the demand of rising populations. For the targeted crops it is important that the fertilizer has the promised proportions of the nutrients. Nowadays, also the physical quality of the granulated fertilizers has become more important. To ensure safe and easy use of bagged fertilizer the content of each bulk bag has to be loose and dust free. In caking and setting the individual fertilizer granules attach to one another, forming large chunks of fertilizer inside the bag. The formed chunks of fertilizer can blockage or damage the spreading equipment and in worst case cakes can cause a health hazard by falling on a person. Therefore, the caking is highly unwanted phenomenon.

The caking tendency of the fertilizer in the production phase is measured multiple times to ensure good physical characteristics. Recently the amount of reclamations about the physical quality, especially setting and caking have risen. However, according to the quality control, the caking tendency of fertilizer has stayed on an acceptable level. From here rises the problem for this thesis. The current methods of the setting and caking measurements are unable to recognize all of the cases when fertilizers tend to form lumps and cake. For some type of fertilizers, the current methods provide accurate results, but for some the results do not correspond with the product delivered to the customer. Therefore, the task of this work is to enhance the current measurement techniques in order to detect caking tendency in the production phase for all different types of granulated fertilizers. Well before the product is packaged and delivered.

1.1 Research objectives

The purpose of the research is to improve the physical quality control measures to have more predictive power if the fertilizer granules have an increased tendency to agglomerate. The research was further targeted to mainly improving the already used methods, but also scoping for alternative methods if found suitable for detecting problems in the physical quality. To achieve the goals, answers to the following research questions are pursued.

- What are the root causes of caking?
  - Why the caking occurs and how it is monitored in tests?
  - Are the measurements effected by uncontrolled parameters?

- What factors affect the measurement of caking tendency
  - Evaluating the effect of individual measurement parameters
  - Identifying the most important parameters

- How to increase the predictive power of the measurements?
  - How the measurement parameters, conditions, and procedures should be altered to increase the predictive power?
  - Is there major sources of uncertainty in the measurement process?

1.2 Structure of the thesis

The literate part is divided into four sections, chapters 2-4. The second chapter is about the basics of fertilizers and fertilizer industry. The process used in the production unit where this thesis is made is presented in chapter 3. The main point of focus is to concentrate on process phenomena related to the physical quality of the product. The fourth chapter is about the caking and setting mechanism of fertilizers and which parameters have found to have an effect. In the fifth part the different types of caking measurement techniques are reviewed. The experimental part contains chapters 6-10. Chapter 6 focuses on the sampling and handling of granulated fertilizer. The experiments and the results are presented in parallel to help the reader as the amount of different measurements is vast. Chapter 7 focuses on the compression measurements and chapter 8 to the caking index measurement.

Chapter 9 contains additional measurements. The results are further discussed in chapter 10 and the conclusions and the recommendations are given in chapter 11.

2. NPK fertilizers

Due to the harvest the soil loses nutrients thus decreasing the growth potential of the future harvests. Therefore, there is a need to add nutrients to the soil as a form of fertilizers. The use of fertilizers dates back thousands of years when ash, (Pollini 2014), animal manures (Bogaard et al., 2013) and other organic materials were used to improve the growth of crops. Justus von Liebig created the foundation of the inorganic fertilizer industry through his work on studying the plant nutrient needs (Liebig, 1855). The use of mineral fertilizers started in the beginning of 1800s when the production of superphosphates from bones mixed with sulfuric acid began. The use of potassium minerals-based fertilizers started in 1860s. Nitrogen production in large scale began in the beginning of 20th century when the Haber-Bosch process was developed, which opened the possibility for N fertilizer. (Russel & Williams, 1977). In the 1950s the granulated compound fertilizers were developed to respond to the growing demand of cake free products (Brummit, 1998).

The nutrients plants need to grow can be divided to macro and micronutrients based on the amount needed (Kosegarten et al., 2001). The different elements can be further divided into macro, primary and secondary nutrients, and trace elements, which corresponds to microelements, this division is visualized in Figure 1. Carbon oxygen and hydrogen are macronutrients, which plants can acquire from water and carbon dioxide, so they are typically dismissed when discussed about fertilizers. In case of fertilizers the most important elements are the three primary nutrients: nitrogen, phosphorus, and potassium. The term NPK is derived from the chemical sign of the primary nutrients. Sulfur, magnesium, and calcium are the secondary nutrients. Typically, the amount needed is smaller than for the primary nutrients. The elementary nutrients are also vital for the crops, but the amount needed is on much smaller scale. The division is visualized in Figure 1

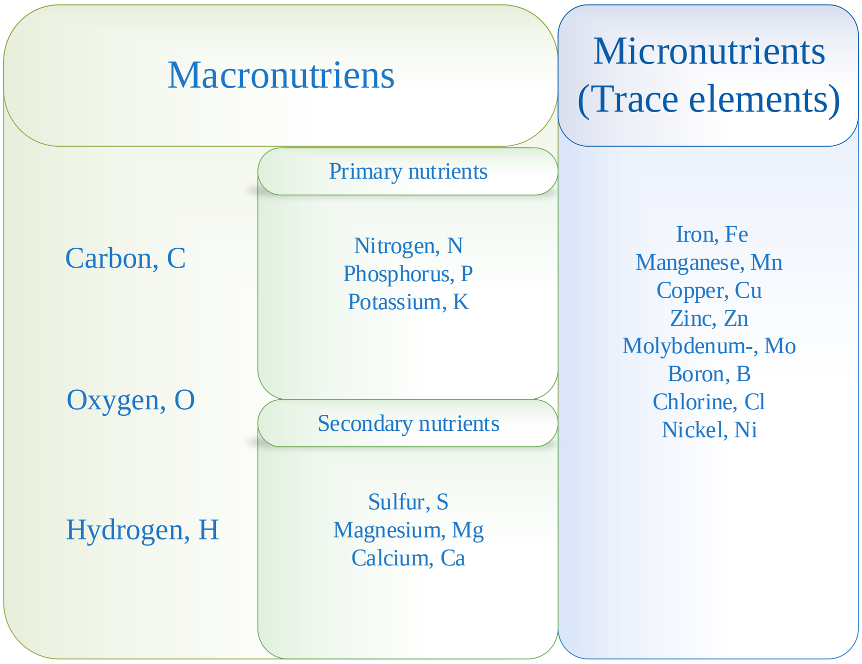

Figure 1 Categorization of nutrients

The naming of fertilizers is typically done by using the primary nutrient content. For example, name 21-6-12 means that the fertilizer contains 21 % nitrogen, 6 % P_2O_5 and 12 % K_2O. Sometimes the amount of secondary nutrients is also given in the name such as 22-7-7-2 Mg, which means that the fertilizer also contains 2 % of elemental magnesium. (Roy, 2007)

3. Manufacturing process

For understanding the possible root causes of the fertilizer caking and setting, understanding the fundamentals of the fertilizer process is needed. Many of the process parameters have been identified to have direct effect on the physical quality of the final product. A mixed acid process with two spherodizer granulator lines is used in the studied plant. Simplified flow diagram of the process is displayed in Figure 2. The process can be divided into the reactor part, the granulation cycles and to cooling and coating.

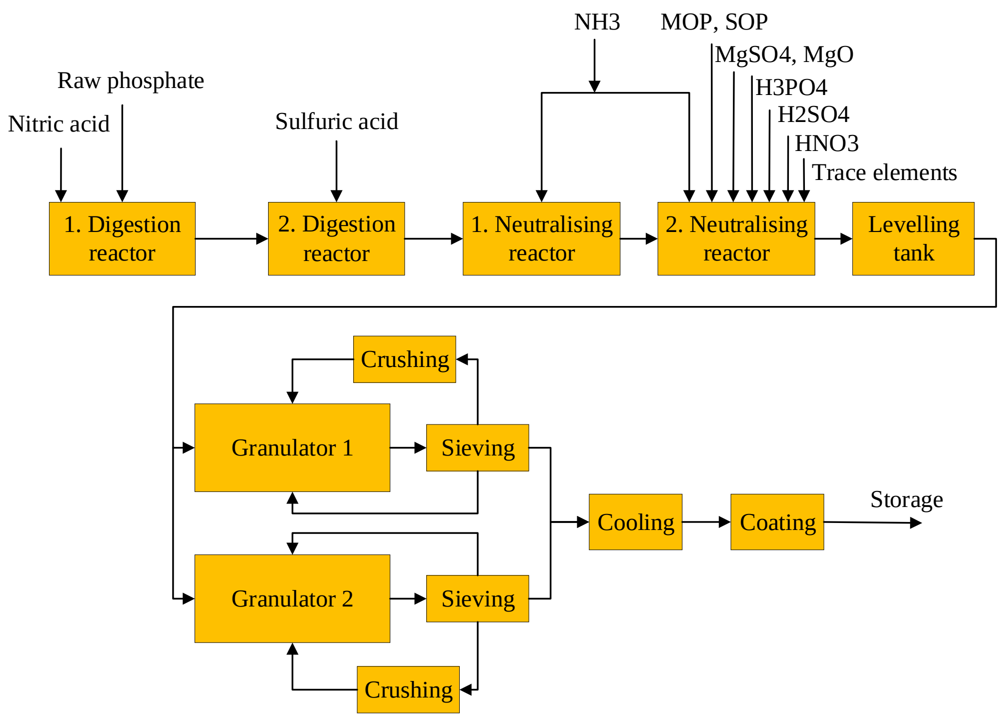

Figure 2 Block chart of the fertilizer process

3.1 Raw materials

Fertilizers with different requirements have different raw materials. The nutrient composition of the fertilizer has the biggest effect which raw materials are used. Other important factors are the raw materials price and compatibility to the process especially to the safety. There can be also other requirements such as no chlorine, which restricts the possible raw materials. The most used raw materials of the studied process are shown in Table 1.

Table I List of the main raw materials of the fertilizer process

Raw material	Nutrients gained	Chemical formula
Nitric acid	Nitrogen	HNO_3
Ammonia	Nitrogen	NH_3
Calcium fluorapatite	Phosphorus, Calcium	$Ca_{10}F_2(PO_4)_6$
Phosphoric acid	Phosphorus	H_3PO_4
MOP	Potassium, Chloride	KCl
SOP	Potassium, Sulphur	K_2SO_4
Magnesium sulphate	Magnesium, Sulphur	$MgSO_4$
Magnesium oxide	Magnesium	MgO
Sulfuric acid	Sulphur	H_2SO_4
Calcium sulphate	Calcium, Sulphur	$CaSO_4$
Biotite	Potassium, Magnesium	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$

A significant amount of water is carried to the process with the acid feeds. Also, water from the scrubber system is recycled back to the reactors. Most of the water is evaporated during neutralizing phase of the reactor cascade. The rest is removed during the granulation. In the final product the water content is lower than 1 %, typically lower even than 0,5 %.

There can be also some impurities present which have an effect on the physical quality of the product. These are not covered in detail in reaction paths in chapter 3.2 and 3.3, instead a quick review is given. The raw phosphate can contain metallic impurities such as iron, aluminum, and magnesium. Iron and aluminum form iron (III) hydrogen phosphates and aluminum hydrogen phosphate in the reactors, which can bind crystal water. Crystal water binding increases the viscosity of the fertilizer slurry and can cause problems to the process. (Toivanen 2008) Ability to bind water of crystallization by the metallic impurities improves the physical quality of the final product. (Hauskaviita & Kiiski 1990) The metal impurities of iron and aluminum are still unwanted, because they act as catalyst for AN deformation, thus creating a safety hazard. (Oluwoye et al., 2020), (Oxiey, et al., 1992)

3.2 Digesting reactors

Digesting of the raw phosphate is the first step of the reactor part of fertilizer process. Nitric acid and raw phosphate are mixed in the first digestion reactor. There is two reaction routes for the digestion depending on the amount of the nitric acid used. When using higher amounts of nitric acid, the fluorapatite reacts to phosphoric acid and calcium nitrate. The fluoride of the raw phosphate creates hydrogen fluoride, Equation 1. (Hignett 1985)

$$Ca_{10}F_2(PO_4)_6 + 20\ HNO_3 \rightarrow 6\ H_3PO_4 + 10\ Ca(NO_3)_2 + 2\ HF \qquad (1)$$

When the amount of nitric acid is lower the phosphate could ether be reacted into monocalcium or dicalcium phosphates (Lutz & Pratt 1967)

The formed slurry is lead to the second digestion reactor as an overflow. In the second digestion sulfuric acid is added. This causes the calcium nitrate to precipitate as calcium sulphate and also forms nitric acid, shown in reaction 2. (Lutz & Pratt 1967)

$$Ca(NO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2HNO_3 \qquad (2)$$

The precipitation of calcium nitrate to calcium sulphate is important, because the calcium nitrate has found have a big negative effect on the physical product quality. (Lutz & Pratt 1967) Even the small amounts of calcium nitrate present in fertilizer increase its hygroscopicity, which causes the final product to adsorb more water (Latham, Geissler, 1968).

3.3 Neutralizing reactors

In the first neutralizing reactor the overflow of the second digestion reactor is neutralized using ammonia. Depending on product requirements the pH can increased in one or two steps. The pH of the neutralizing reactors has a big effect, which reactions take place thus having major impact to the chemical composition and the physical quality of the final product.

Calcium nitrate that has not precipitated to calcium sulphate reacts with ammonia and phosphoric acid. Depending on the level of neutralization ether reactions 3 or 4 is dominant. In reaction 3 products are monocalcium phosphate, dicalcium phosphate and ammonium nitrate. In reaction 4 dicalcium phosphate is formed with ammonium nitrate and monoammonium phosphate, Equations 3 and 4 (Hignett 1985)

$$3\ Ca(NO_3)_2 + 5\ H_3PO_4 + 6\ NH_3 \rightarrow 2\ Ca(H_2PO_4)_2 + CaHPO_4 + 6\ NH_4NO_3 \quad (3)$$

$$Ca(NO_3)_2 + 2\ H_3PO_4 + 3\ NH_3 \rightarrow\ CaHPO_4 +\ NH_4H_2PO_4 + 2\ NH_4NO_3 \quad (4)$$

Nitric acid and ammonia react to ammonium nitrate, Equation 5. (Kiiski 2009)

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \quad (5)$$

The phosphoric acid reacts with ammonia to MAP, Equation 6

$$H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4 \quad (6)$$

The MAP can react with ammonia to DAP, Equation 7, (Utomo et al., 2010)

$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4 \quad (7)$$

The slurry in the second neutralizing contains both MAP and DAP, and the ratio is based on the pH value.

To the second neutralizing reactor nitric, phosphoric, and sulfuric acids with ammonia for neutralization can be added as well as MOP, SOP, secondary- and micronutrients. Nitric acid and ammonia react to AN as shown in Equation 7. Sulfuric acid reacts with ammonia producing ammonium sulphate, Equation 8. This reaction can also happen in the first neutralizing reactor if surplus sulfuric acid is added to the second digestion reactor for the precipitation of calcium sulphate.

$$H_2SO_4 + 2\ NH_3 \rightarrow (NH_4)_2SO_4 \quad (8)$$

MOP reacts with AN, Equation 9 (Gorbovskiy 2017)

$$KCl + NH_4NO_3 \rightarrow NH_4Cl + KNO_3 \quad (9)$$

MOP also reacts with phosphate compounds, Equations 10 and 11 These reactions can cause a decrease of MOP conversion. The KH_2PO_4 formed in Equation 11 has is less water soluble than MAP. This causes the KH_2PO_4 to precipitate on the MOP crystals surface thus preventing the reaction in Equation 9 to take place. (Kiiski 1994)

$$KCl + NH_4H_2PO_4 \rightarrow NH_4Cl + KH_2PO_4 \qquad (10)$$

$$NH_4H_2PO_4 + KH_2PO_4 \rightarrow (NH_4K)H_2PO_4 \qquad (11)$$

SOP reacts with AN, Equation 12 (Lutz & Pratt 1967).

$$K_2SO_4 + 2\ NH_4NO_3 \rightarrow 2\ KNO_3 + (NH_4)_2SO_4 \qquad (12)$$

The overflow of the second neutralizing reactor is lead to buffer tank where the possible concentration differences of the previous reactors are levelled. The fertilizer slurry is pumped from the buffer tank to the granulators.

3.4 Granulation cycles

Granulation is a size enlargement process, where small particles are combined to larger ones. The granulation can occur by multitude of mechanisms. Agglomeration and layering are two typical mechanisms that take place. Tardos et al. (1997) have further divided these mechanisms. This is visualized in Figure 3, The particle agglomeration can take place ether in nucleation, part (a) or coagulation, part (b). In nucleation the primary particles have attached one another by the layer of binder. The difference to nucleation in coalescence is that the agglomeration takes place between larger particles. Due to collisions and binder saturation the particles are able to form bonds. In the layering the growth of particles can either be caused by the attachment of fine particles on the granules surface or to drop of binder. (Tardos et al. 1997)

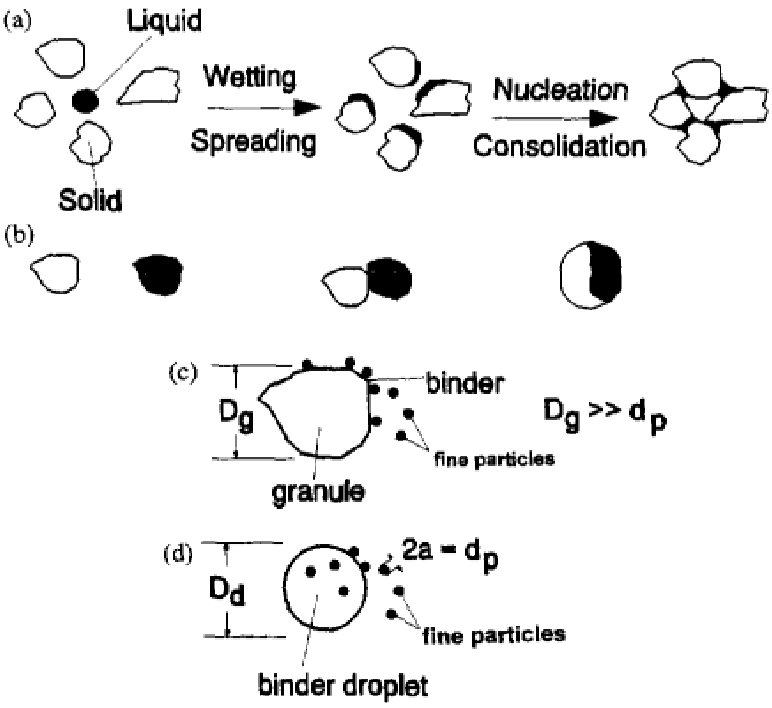

Figure 3 Visualization of granulation mechanisms (Tardos et al., 1997)

In the studied process two spherodizer drums are used for the granulation. In this type granulator the coating mechanism is the dominant, type (c) in Figure 3. The fertilizer slurry from the buffer tank is atomized using pressurized air and sprayed to the rotating seed granule curtain. The granules grow in size when the liquid binder in this case the slurry, solidifies on the surface of the seed granule (Villa et al., 2016). Forming granule can be referred as an onion type granule because the cross section of the granule resembles the one in onion. This is visualized in Figure 49, where section of granule is analyzed by a polar light microscope. During the granulation some granules are formed by agglomeration, but it only a side mechanism.

Model created by Degrève et al. (2006) describes the particle growth of the layering mechanism in Equation 13.

$$\frac{3A}{d_{p0}} + \frac{12A^2}{2d_{p0}^2} + \frac{12A^2}{3d_{p0}^3} = \frac{30M(1-\varepsilon)t_c}{R\tau} \tag{13}$$

Where	A	thickness of the coating layer	[m]
	d_{p0}	particle size of the recycle	[m]
	M	mass flow of the sprayed slurry	[kg/s]
	ε	average voidage of the particle bed	[-]
	t_c	contact time of particles and spray	[s]
	τ	particle residence time in drum	[s]

The target for the granulation is to produce granules with desired particle size. Other desired properties include narrow particle size distribution, granule roundness and hardness. Narrow particle size distribution decreases the need for sieving and the crushing of oversize particles, when the d_{50} is within specification.

For operating the granulators, the control between the temperature and the moisture content of the slurry is vital. Figure 4 shows the typical granulating zone of NPK fertilizer. When the moisture content of the fertilizer is too low there is not enough binder liquid to bond the solid material thus leading under-granulation, which means that the produced granules have a small particle size. When the moisture content is even more decreased no granules are formed and the solids are in the powder form. Increasing the temperature increases the particle size. However, if both moisture content and temperature are too high the formed granules are too large. In even higher moisture contents, the granules are too soft and will turn into mud.

The chemical composition of the granulated fertilizer has an effect on the suitable granulation zone. Fertilizers containing high amounts of nitrogen tend to over granulate. Spherodizer drums are not suitable for granulating fertilizers with low nitrogen content.

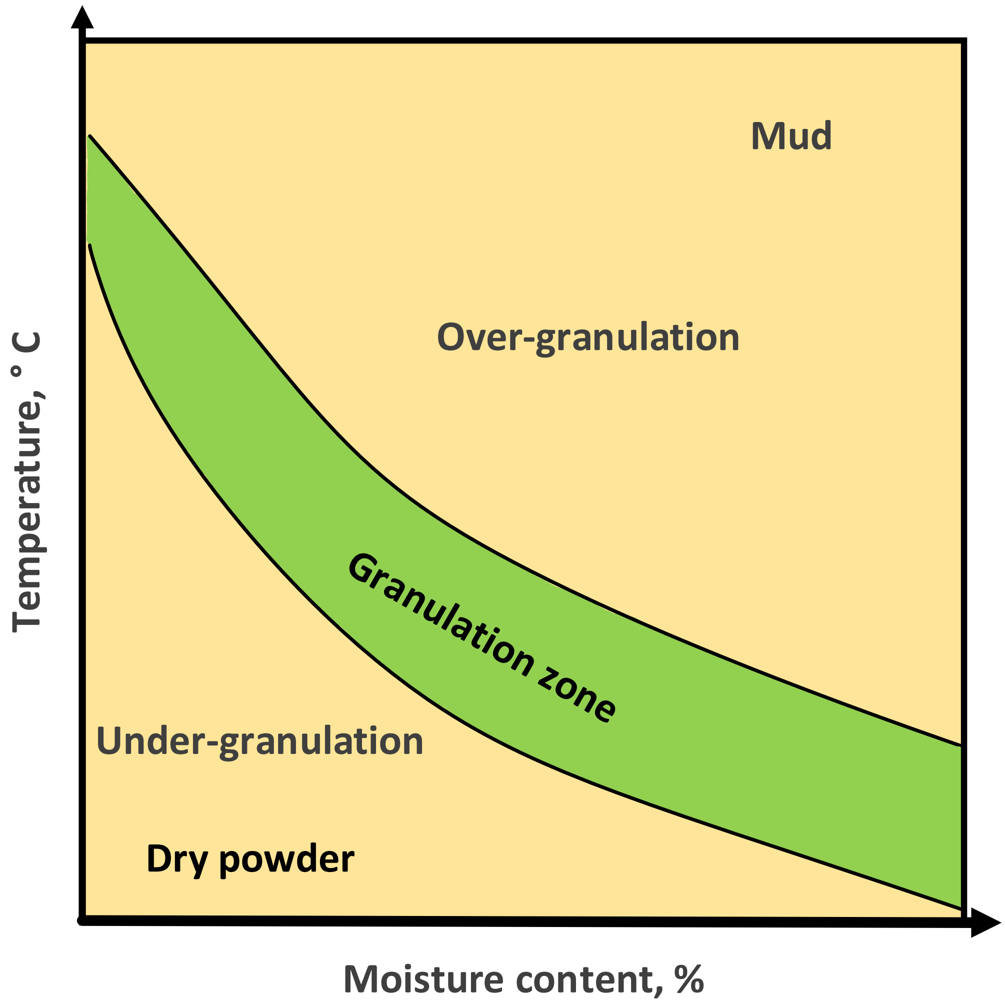

Figure 4 The combined effect of temperature and moisture content on granulation, based on (Toivanen 2020)

The rotating speed of the granulator has a great effect on the successfulness of the whole granulation process. Density of the seed granule curtain is important, for growing the granules, but also for keeping the equipment clean. If the seed granule curtain is too thin part of the slurry is sprayed on the walls of the spherodizer. Depending on the rotating speed, the fertilizer particles have different transverse bed motions. The motions can be divided into slipping, cascading and cataracting motions. A Froude number and the filling degree of the drum can be used as a guideline for estimating, which type of transverse bed motion is taking place, Equation 14. When the Froude number equals 1 the particles are assumed to be in centrifuging transverse bed motion. In granulation the Froude number is typically between 0.4-0.6. (Rodrigues et al., 2017) The properties of the moving particles effect the Froude number needed for cataracting motion (Mellmann, 2001).

$$Fr = \frac{N^2 D}{g} \tag{14}$$

where,	Fr	Froude number	[-]
	N	Drum rotation speed	[RPS]
	g	gravitational acceleration	[m/s^2]

The drums used in the process have flights to lift granules. This increases the amount of airborne particles and lowers rotating speeds needed for the particles become fluidized, which increases the overall efficiency of the granulation. (Huang et al., 2009)

Rodrigues et al. (2017) studied the effect of single superphosphate granulation process variables on the granulation efficiency and the granule hardness. A pilot size drum granulator was used in the experiments. It was found that the decrease of the liquid phase and increase of the drum hold up increased the hardness of the formed granules. The hardening of the granules was explained by the reduction of porosity. When the amount of liquid phase is high the pours are saturated by filling mechanism, which in the drying causes the salts to migrate towards the surface, thus leading into porous structure. (Rodrigues et al., 2017)

In the studies conducted by Iveson et al. (1996) it was found that the porosity of the granule was reduced by increasing the rotational speed of the drum. The effect of the amount and viscosity of the binder liquid were also studied. Water and glycerol were used as the binders and glass ballotini as the particles. It was found that the porosity of the granule decreases when the amount of low viscosity binder is increased but increases when higher viscosity binder amount is increased. (Iveson et al., 1996)

Walker et al. (2003) studied the effect of process parameters of granulation on the crushing strength of fertilizers. The increase of liquid phase led to harder particles while also increasing the roundness of the granules. Due to the increase of liquid phase larger liquid bridges are created, which then form larger crystal bridges when the granules are dried. (Walker et al., 2003)

In the spherodizer drum the granulation and drying of the granules is done simultaneously. The drying is done by blowing concurrently hot air through the drum. Drying is vital step for reducing the caking and setting tendency of the fertilizer, this is further discussed in section 4.1. The drying efficiency in rotating drum depends on the movement of the particle inside the drum, and transfer of heat and mass inside the particles (Abbasfard et al., 2013).

The drying rate is highest near the inlet of the spherodizer. However, the rate is quickly reduced because of the poor heat transfer of fertilizers. For example, the thermal conductivity of AN is generally under 0,5 W/ m K according to El-Sharkawy et al., (1991) Also most of the moisture is inside the fertilizer granules. Therefore, a diffusion of the water to the surface has to occur before the evaporation. It is possible that the surface of the granule is dry, but there is still moisture inside the particle, which will then migrate to the surface and cause caking (Hero, 1984).

After exiting the spherodizer, the granulates are sieved. Sieving is done in two steps. First the oversize granules are separated and directed to crushing. In the second step the fines are removed from the product fraction. The crushed oversize particles, undersize granules and a fraction of the product size particles are recycled back to the spherodizer where they act as the seed layer for the layering and grow in size.

3.5 Cooling and coating

The fertilizer has to be cooled to slow down any of the still ongoing post reactions before storage (Kiiski 1994). High temperatures also increase the solubility of the fertilizer salts thus increasing the amount of dissolved salts within the granule (Kant & Kafkafi, 2013) This increases the tendency of setting and caking. On the other hand, even if the fertilizers are well cooled the possible supercooling can cause problems to the product quality. Supercooling occurs when the salt crystals weren't able to change their structure during the cooling and remained in a form stable at high temperature. The transformation to stable phase takes place then during the storage. (Kiiski 1994)

The product size granules are cooled in two steps. In the first step a cooling drum is used, where counter current air is used to transfer heat from the granules. The cooling drum also has flights to increase fluidization of the particles. The final cooling is done in a fluidized heat exchanger, where particles collide with the heat exchanger bed where cold water is pumped through. After the cooling a polishing sieve removes the formed agglomerates and shattered particles.

The coating is vital for ensuring the good physical quality of fertilizers during storage. Rutland (1991) has collected a comprehensive list of different ways the coating agents prevent caking. The coating agents can be used to prevent interparticle contacts of saturated solutions, to spread the phase that is going to crystallize to larger surface area. The coating agents can also be used to modify the crystallization by decreasing the crystal size or otherwise hindering the crystallization. (Rutland 1991) The reduction of hygroscopicity is also presented in Rutland's list but also in studies conducted by Sigtryggsson et al. (2020). The coating agents can also hinder the caking caused by capillary adhesion. In more severe cases the coating agents can act as a drying agent on the granules surface or decrease the strength of the formed solid bridge (Rutland, 1991)

For coating both inert dusts and liquid coating agents can be used (Rutland, 1998). The function of the inert dust is to act as a physical barrier between the granules. The inert dust can also be used to control the possible liquid phase in the particles surface by spreading, adsorbing, or making it otherwise inactive. In case of caking and setting the inert particles decrease the strength of the bridges between particles. Possible options for the inert dust consist of clay, diatomaceous earth, or talc. (Rutland, 1998)

Liquid coating agents can be divided into non-surface active and surface-active agents. Non-surface-active agents form a layer that will repel moisture from entering the fertilizer. Oils, paraffin waxes and synthetic polymers can be used as non-surface-active coating agents. (Rutland, 1998)

The surface-active agents change the surface tension between the granules and the liquid phase. The effect of the surfactants can vary from crystallization modifier, moisture barrier, to hamper liquid film distribution and bridging strength. (Rutland, 1998) The surfactants have a bipolar structure. A long hydrocarbon chain acts as a hydrophobic and the polar or ionic group as hydrophilic. Surfactant molecules can be further divided into anionic, cationic, or nonionic based on the polar group. Surfactants such as alcohols, acids, and amines with a hydrocarbon tail between 12-22 molecules can be used for reducing the hygroscopicity of AN. (Elzaki et al., 2020).

In contrary to the effect of coatings acting as hydrophobic barriers Hansen et al. (1998) found that the coatings did not have an effect on the enthalpy of water sorption of MOP. The samples that were coated and the samples that weren’t coated had the same sorption behavior. Despite this the coated fertilizers did not cake but the uncoated fertilizers did. This was argued to be caused by the coating agents by preventing the formed saturated solutions from joining one another. Other possible explanation was given to be the coating agents effect on the crystallization behavior. (Hansen, et al., 1998)

In the studied process talc powder and amine containing coating oil are used. The coating agents are applied in a coating drum, where the fertilizer granules are rolled to create the coating.

3.6 Storage and packaging

The fertilizers are stored in concrete bins before packaging or transport. The finished fertilizer is dropped with a moving sledge from the conveyor to ensure even filling of the bin. The fertilizer is given couple days of time to finish all the possible post reactions. These can cause increase of the temperature of the pile. The post reactions consist from the conversion of the raw materials as well as other types of post reactions such as crystallization. Double salt and solid solution formations can also take place. The post reactions conversion is monitored by taking samples from the bin. These post reactions are presented in depth at section 4.2.

The storage time in the bins varied from couple days up to a month during the time of this thesis. During this time the fertilizer is subjected to the conditions of the warehouse. The humidity of the warehouses is monitored and controlled by blowing dry air. The relative humidity must be kept at low to avoid the water adsorption of the fertilizer. However, in very humid weather the RH inside the warehouse has increased to levels where the water adsorption takes place. The adsorption is mostly affecting the surface of the pile.

When packaging the fertilizers are removed from the surface of the silo using kratzer-crane type reclaimer. Before the packaging, the fertilizer is sieved one more time to remove all the small and large particles that may have been formed during the storage or came from the production.

The fertilizer is mostly packed to 700 kg bulk bags also known as, FIBC which are then stacked to 3 or 4 layers. The force applied to the bottommost bag is then roughly from 14 kN to 21 kN. This corresponds 21 to 32 kPa of pressure respectively when the surface area of the bad top is estimated to be 0,64 m^2

The storage time of the fertilizer in the bag can vary from days to over a year (Kohonen 2006). Therefore, the fertilizer has to withstand a variety of conditions without setting or caking. Most of the caking takes place during the first couple weeks inside the bulk bag. But the caking could also take place if the packed fertilizer is subjected into unfavorable conditions such as high temperatures (Hero, 1984). Punctures to the bags will also give the moisture an entrance to the fertilizer. Therefore, during the storage, the fertilizer bags should be sheltered from rain and sunlight and raised from the ground.

4. Caking and setting of fertilizers

Caking and setting are unwanted phenomena, in which the individual fertilizer granules attach to each other. The formation of lumps causes blockages to the spreader equipment and silos thus leading loss of time and work. The cakes also cause uneven spreading distribution of fertilizers, thus affecting the fields nutrition. Especially equipment with narrow slits where the fertilizer is spread are sensitive to even slightest setting, for example in a seeder. Figure 5 shows examples of fertilizer cakes formed in the bags.

Figure 5 Severe caking of bagged fertilizer

It is important to recognize the difference between caking and the setting of the fertilizers in the perspective of the farmer. Fertilizer that has setting occurred can be used when small amount of force is applied to break the loosely contacted lumps. Fertilizer that has caked is unusable or requires excessive amounts of force to break the lumps. However, no clear value of where the setting is described to be caking is available.

There are multiple different ways of defining caking phenomena. According to the Chen et al. (2019) caking is defined to be agglomeration on free-flowing material into lumps. However nowadays the definition has grown to include that the free-flowing material has to have a low moisture content. The material forms lumps, which further agglomerate to solids thus lowering the product value. (Chen et al., 2019)

Rumpf and Schubert (1974) have collected different mechanisms for the adhesion between particles. The mechanism can be divided into material and non-material bridges. The non-material bridges can be formed by to the van der Waals, electrostatic or magnetic forces. The material bridges can further be divided into liquid, viscous or solid bridges. (Rumpf, Schubert, 1974) Steric interlocking is also described to be cause of setting (Samain et al., 2019). Hauskaviita & Kiiski (1990) have divided fertilizer caking mechanisms into crystal growth and capillary adhesion, which both are also mentioned by Rumpf and Schubert (1974).

Interparticle bonds formed by magnetic forces are the weakest followed by the bonds formed by electric and the Van der Waals forces (Zafar et al., 2017). The magnetic forces are not considered due to the fact that fertilizers do not possess magnetic properties. Electric forces are presented in some studies to be linked with the tendency of setting and caking, due to the piezoelectric properties of some of the salt crystals (Kiiski, Hauskaviita 1993) Liquid bridges are weaker than solid ones (Zafar et al., 2017).

Specht (2006) argues that the only the formation of solid bridges causes caking. The liquid bridges, van der Waal, and electrostatic adhesion can increase the cohesive strength within the particles, which then increases the formation of solid bridges. (Specht 2006) This is also confirmed by Hartman & Palzer (2011) who argue that the before caking the adhesion forces between particles have to increase.

There is a multitude of ways why the agglomeration of fertilizer granules occur. The main causes are comprised in Figure 6. Time, pressure, time, and moisture are needed for the agglomerates to form. The mechanisms of caking can be roughly divided into water, particle deformation or post reaction based. It should still be noted that all the mechanisms are tightly entwined to one another and do not act as separate entities.

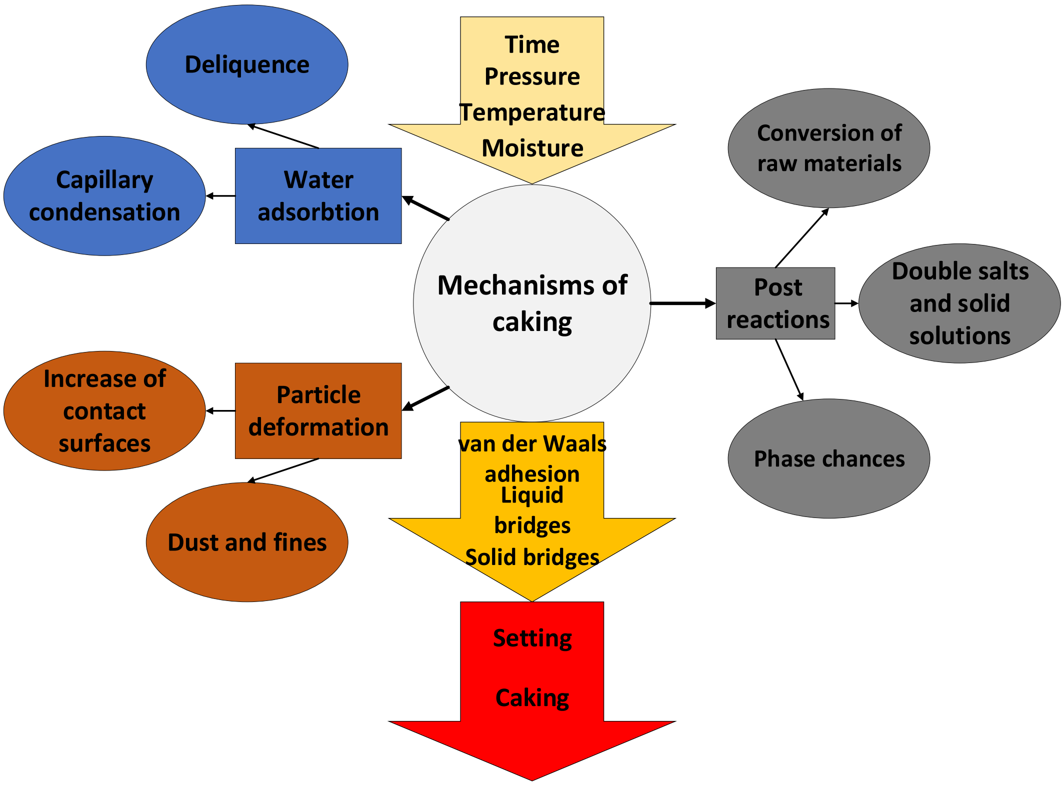

Figure 6 Collection of caking mechanisms

4.1 Moisture caking

The moisture content of the fertilizer has been identified to be the one if the most important quality affecting factor. Dissolution recrystallization phenomena and the post reactions both need water to take place. During the production, some water is retained inside the fertilizer granules. Fertilizers can contain water in forms of water of crystallization, bound water, and free water. (BS EN 13466-1:2001) Water of crystallization is water that is bound directly to the crystal structure for example in $CaSO_4 * 2H_20$. Bound water describes water that's movement is hindered by the solid surfaces (Mohamed, Paleologos, 2018). Free water can move freely inside the granule. External pressure can cause the liquid phase to move to surface, which then causes recrystallization related caking. (Kiiski 2010). Fertilizers by the default are hygroscopic so they will absorb water from the surrounding air. The air's relative humidity, RH and the fertilizers critical relative humidity control the amount of moisture the fertilizer absorbs. Therefore, formation of solid crystal bridges in fertilizers can be caused by both external and internal root causes.

In the case of external moisture caking, water is adsorbed on the granule surface, which causes the solid phase to dissolve. The dissolution can happen either in capillary condensation or deliquescence. (Chen et al., 2020) In the low RH values the water adsorption is due to the capillary condensation, but when the RH is over the CRH the adsorption of water increases rapidly due to deliquescence. Fertilizers which have higher enthalpy of solution are more hygroscopic due to the vapor pressure being smaller. (Sigtryggsson et al., 2020). Different types fertilizers CRH behavior is shown in the Figure 7. For example, calcium nitrate will adsorb water at 30 % relative humidity, but urea will not until the RH surpasses 70 %.

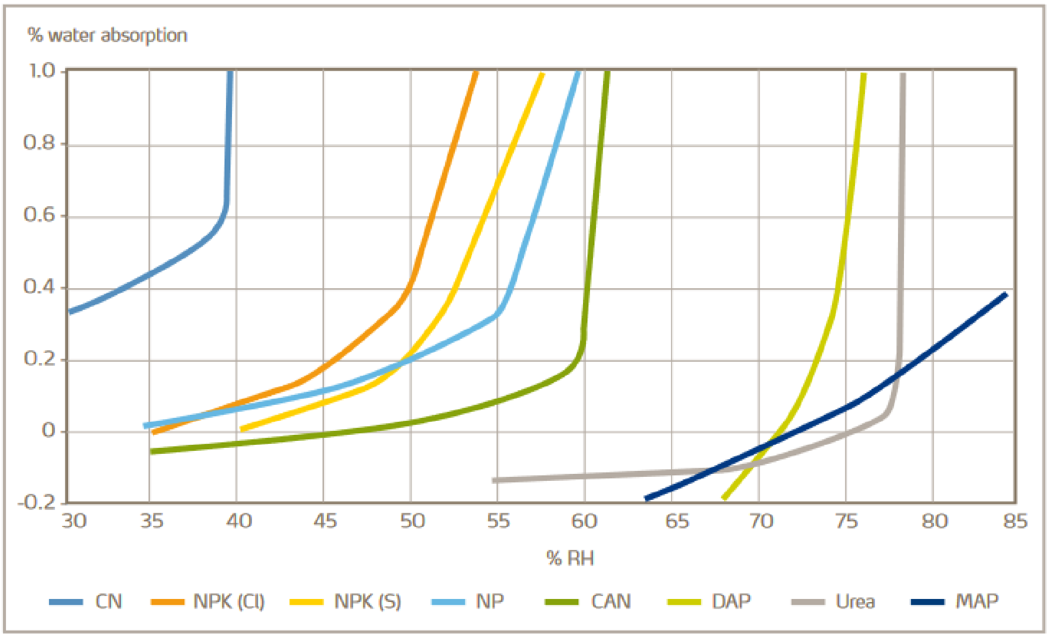

Figure 7 Water adsorption behavior of fertilizers at 25 ºC (Yara 2015)

In lower RH values the salt dissolution takes place in the contact points of the crystals known as capillary condensation. In the capillary points the air pressure is lower, this causes condensation, even if the RH of the surrounding air is under 100 % (Billings, et al., 2006). The relative humidity value where the capillary condensation starts is noted as RH_{cc}. (Chen et al., 2018) The condensation of water creates a liquid phase of saturated solution. (Langlet et al., 2013) The liquid bridges are then formed by the capillary pressure and tensile forces (Sun, Sakai, 2018). The decrease of the relative humidity causes the water in the liquid phase to evaporate. This causes the dissolved salts to recrystallize, thus creating a solid bridge (Langlet et. al., 2013).

The Kelvin equation can be used to determinate the Kelvin radius in which the capillary condensation will take phase, Equation 15. When the Kelvin radius is larger than the capillaries between particles a solution forms to fill the capillary. (Billings et al., 2006)

$$A_w = \frac{P_v}{P_w} = e^{\left(\frac{-2\sigma \cos(\theta)\, V_0}{r_k RT}\right)} \tag{15}$$

where,	A_w	water activity	[-]
	P_v	water vapor pressure of the material	[Pa]
	P_w	vapor pressure of pure water	[Pa]
	r_k	Kelvin radius	[m]
	θ	wetting angle	[°]
	σ	surface tension	[N/m]
	V_0	volume of 1 mol of saturated solution	[m^3]
	R	ideal gas constant	[J/K mol]
	T	temperature	[K]

The relation of the values of Kelvin equation between ideal particles is shown in Figure 8 (Chen et.al. 2018) The Kelvin radius equals to half of the secant at the condensed phase endpoint in circle defined by the surface curvature of the condensed liquid. It can be seen from the figure that if the particles are compressed together the while the Kelvin radius stays the same, the area of capillary condensation increases thus then causes more severe caking and setting

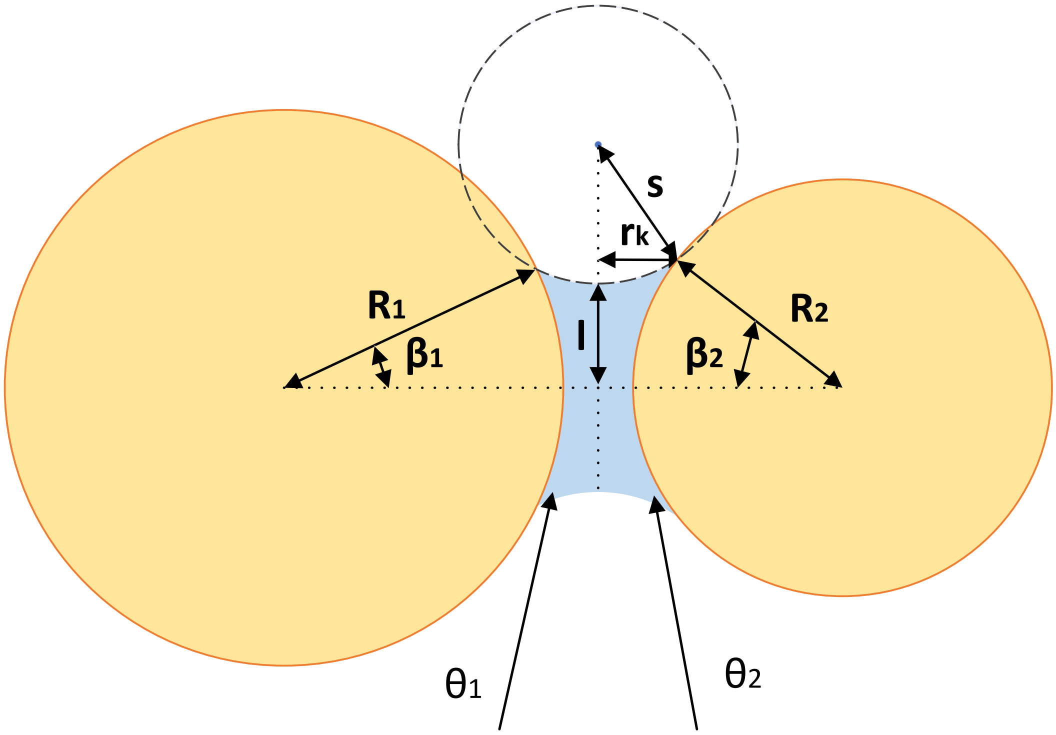

Figure 8 Formation of capillary condensation based on (Chen et.al. 2018)

The dissolution-recrystallizing cycle can take place multiple times if the relative humidity alters between high and low values (Chen et al., 2020). This would occur when the temperature rises and decreases, because the relative humidity is dependable on the temperature (Pei et al., 2021). Also, the fertilizers CRH cycles with the temperature. In higher temperatures the fertilizers CRH is lower. (Lachance et al., 2018) In higher temperatures the relative humidity of the surrounding air decreases. Therefore, the tendency of caking is linked to the relation between the fertilizers characteristic CRH and the surrounding air's RH in different temperatures. On every temperature cycle the solid bridge grows, thus increasing the severity of the caking. Especially in sealed off containers the dissolution recrystallization phenomena can cause severe problems when the excess moisture cannot exit the system. This, is for example the could case in the bulk bags used for fertilizers. The conclusion of this is that the humidity of the bag must not exceed the value even for the RH_{cc} or otherwise, there will be some amount of capillary condensation.

The capillary condensation causes the capillary adhesion. The liquid bridge applies an attraction force between the particles. The force is combined from two parts. The first part of the force is caused by the adhesion in the interface between the gas, liquid, and solid phases. The second force is based on the pressure difference between the liquid phase and the gas phase. (Rondeau et al., 2003)

When the RH value of the air is over the CRH of the fertilizer deliquescence will take place. The water is absorbed throughout the crystals surface. This is visualized in Figure 9, where NaCl crystals are exposed to different RH environments for prolonged time. The CRH of the NaCl is around 73-65 %. It can be seen that there is no salt dissolution happening in the cases where the RH is under the CRH. When the RH is between 80-83 % the salt starts to dissolve. The dissolved salt formed bridges between separate salt crystals, thus causing caking. (Hartmann, Palzer, 2011) Similar results were found by Lachance et al. (2018) who studied the caking of MOP. The biggest cause for the caking was the conditioning of the MOP at high RH values due to the hygroscopicity. (Lachance et al., 2018)

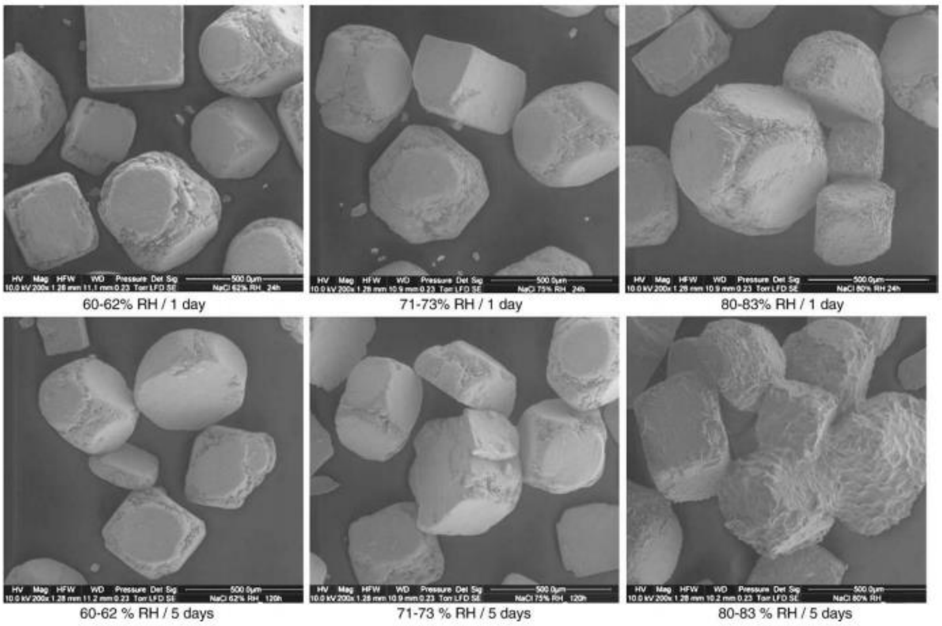

Figure 9 Deliquescence of NaCl particles at different RH values (Hartmann, Palzer, 2011)

4.2 Post reactions

Post reactions have long been identified as one of the key attributes of caking. The principle path of post reactions caused caking are presented in Figure 10. The different types of post reactions are further presented in this chapter.

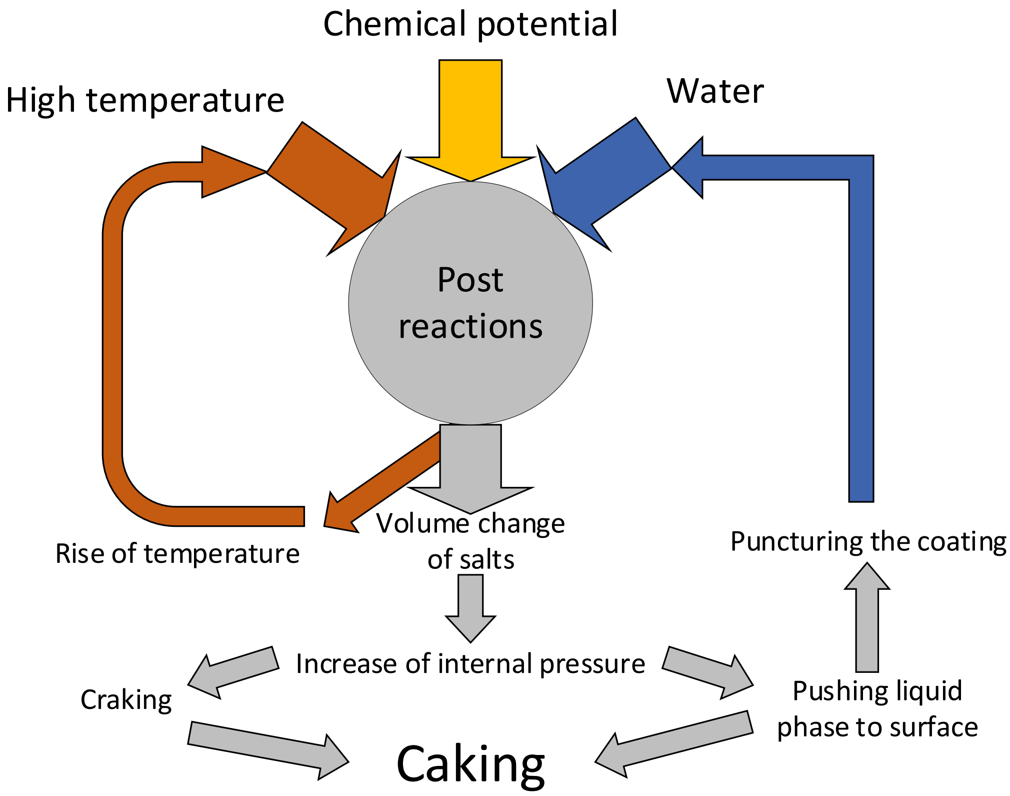

Figure 10 Flowchart of post reaction related to caking

Post reactions are reactions that take place during the storage of the fertilizer. Depending on the chemical composition of the fertilizer the number of different post reactions is vast. The root cause for post reactions is the salt system inside the granules not being in thermodynamic equilibrium. This could be caused by too short retention times in reactors or granulation cycles. It is also possible that a layer of insoluble salt has formed on the surface of salt crystal thus preventing from further reacting. This is for example in case of reaction in Equation 10. All the post reactions need free water to take place, therefore they could be prevented by perfect drying. However, this has been found uneconomical and unpractical (Hauskaviita & Kiiski 1990). The post reactions change the volume of the salt crystals. This causes an internal pressure to the granule, which then pushes the liquid phase on the surface. On the surface the water evaporates, and the dissolved salts recrystallize. The post reaction can cause other physical quality deteriorating effects such as decrease of granule strength, dust formation, and decrease of water solubility of the nutrients. (Kiiski 2010)

Some post reactions occur because of small conversion of raw materials. such as MOP and SOP which will react with AN according to Equations 8 and 9. Other possible post reactions are the formation of solid solutions and double salts. The solid solution and double salt formation begins in the granulation cycles but can continue also during the storage. (Kiiski 1994). According to Bassani (2005) solid solutions can be formed by two ways. The solid solution can be formed by substitution when the volume and chemical behavior of the substituting and original atom are close to one another. In interstitial solid solution there is a difference in volume over 15 % between solute atoms. This causes the size of the solvent unit cell to increase. The ratio between the components can vary (Galsin, 2019). In double salts there are two different cations and or anion, but when dissolved a solution of two different salts forms (Daintith, Martin 2010). In double salts the ratio is fixed (Kiiski & Hauskaviita 1992). The solid solutions and double salt can further react to create even more complex substances as seen in the following reaction equations such as 21 and 22 where solid solutions form Montan salts.

Based on the temperature and pressure pure ammonium nitrate obtains 6 crystal structures. The most relevant for fertilizers are the tetragonal AN-II, orthorhombic AN-III, and orthorhombic AN-IV. For pure ammonium nitrate the change of the crystal structure between AN-III and AN-IV is at 32,3 ℃. The change of the crystal structure changes the volume of the crystal which has caused problems such as swelling and lose of structural integrity especially when the temperature cycles around the phase change temperature. This can be prevented by additives such as potassium salts. (Kiiski, 2009)

The ammonium nitrate and potassium nitrate form solid solutions based on the ratio of NH_4^+ and K^+ ions. Equations 16, 17 and 18 showcase the estimation of composition of the three most relevant of the solid solutions. The phases are named based on the crystalline structure of AN and KN. In N3 the KN is dissolved in AN-III, in the K3 AN is dissolved in KN-III phase and in K2 AN is dissolved in KN-II phase. (Kiiski 2009) Figure 11 contains the phase diagram between the NH_4NO_3 and KNO_3. The drying and the cooling temperatures have a major effect on the phase composition of the final product. Fertilizer dried in high temperature will have a higher concentration of K3 than fertilizer dried in lower temperatures. (Kiiski 1994) This finding is supported by the Figure 11 phase diagram. The amount of K3 is largest in fertilizers which have NH_4NO_3 and KNO_3 ratio around 0.6 (Kiiski 1994), which can be seen in Figure 11.

The ratio between the in the studied fertilizers varied between 0.4 and 0. Some of the fertilizers with the highest amounts of reclamations had the AN-KN in the zone where the K3 phase was stable at 100 C. This could also be one of the reasons, why V-shape fertilizers are judged to have problems with the physical quality.

$$70\%\ NH_4NO_3 + 30\%\ KNO_3 = N3 \tag{16}$$

$$50\%\ NH_4NO_3 + 50\%\ KNO_3 = K3 \tag{17}$$

$$90\%\ KNO_3 + 10\%\ NH_4NO_3 = K2 \tag{18}$$

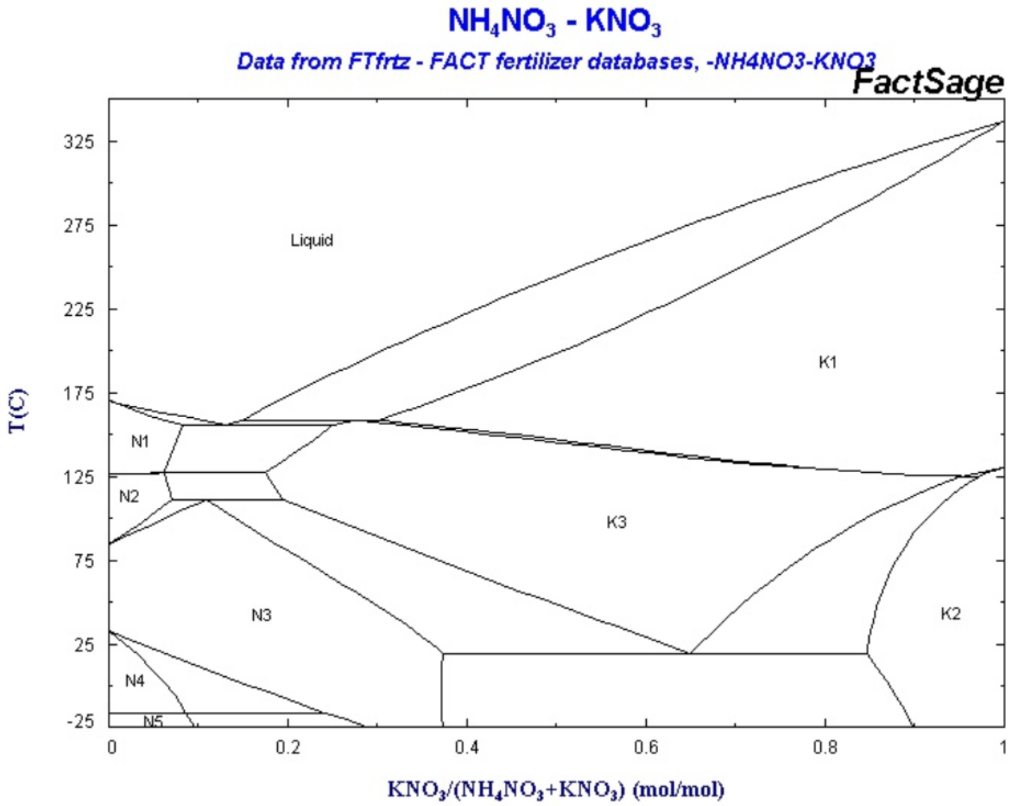

Figure 11 Phase diagram between NH_4NO_3 and KNO_3 (Bale et al., 2016)

K2 and N3 are stable, but K3 is unstable in the storage conditions. Based on Figure 11 it is seen that the K3 phase under 23 ℃ is unstable. In the presence of water, the K3 will disproportionate into K2+N3 phases. This reaction causes the volume of the salts to increase up 5 % if the conversion is complete. The change of volume weakens the structure of the granule and forces the solid solution to the granule surface which both increases the cake formation tendency. (Kiiski 1994)

The presence of ammonium sulphate crystals has been linked to severe caking. The post reactions of AS also cause of change of volume (Gezerman & Corbacioglu, 2011) To prevent the caking the related to AS the amount of the AS has to be minimized. The post reactions between ammonium nitrate and ammonium sulphate can form two different double salts, Equations 19 and 20 (Gorbovskiy et al., 2017)

$$(NH_4)_2SO_4 + 2\,NH_4NO_3 \rightarrow\ (NH_4)_2SO_4 \cdot 2NH_4NO_3 \qquad (19)$$

$$(NH_4)_2SO_4 + 3\ NH_4NO_3 \rightarrow (NH_4)_2SO_4 \cdot 3NH_4NO_3 \qquad (20)$$

Figure 12 shows the phase diagram between AN and AS. Fertilizers produced in the studied process contain only a minute amount of AS, therefore the granules contain mainly mixture of double salt 3 $NH_4NO_3 * (NH_4)_2SO_4$ and some of the AN crystalline structures based on the temperature. In the drying the composition is most likely AN-II + phase A and in the storage conditions the composition could be ether AN-III+AN-IV+A or AN-IV + A depending on the amount of AS. From the phase diagram it also should be noted that there is not a single point, where AS and AN coexist in storage temperatures. Therefore, if AS and AN are connected in the fertilizer granule there will be post reactions. Most likely the AN and AS will react as shown in Equation 19.

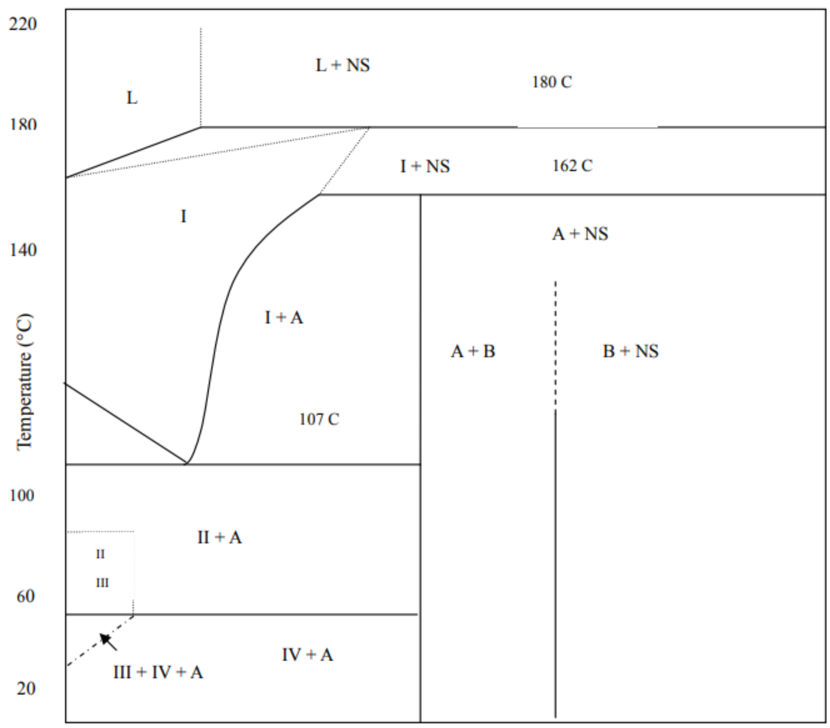

Figure 12 AS-AN phase diagram, $I = AN - I$, $II == AN - II$, $III = AN - III$, $IV = AN - IV$, A=3 $NH_4NO_3 * (NH_4)_2SO_4$, $B = 2\ NH_4NO_3 *$

$(NH_4)_2SO_4$, $NS = (NH_4)_2SO_4$, L=liquid (Gezerman & Corbacioglu, 2011)

Montan salts can be formed by three different mechanism from the solid solutions of ammonium potassium nitrate and ammonium potassium sulphate. The formation of montan salts increases the pile temperature during storage. Equation 21 reaction decreases of 1.4 % of the salts volume and Equation 22 reaction increases 3.2 %. The reaction 23 should not theoretically cause any change in salt volume (Kiiski 2010) The presence of montan salts in the fertilizer granule increases the elasticity of the fertilizer particle thus increasing the fertilizers tendency to cake (Kiiski 1994).

$$K3 + (NH_4, K)_2SO_4 \rightarrow 2(NH_4, K)NO_3 \cdot (NH_4, K)_2SO_4 + K2 \qquad (21)$$

$$2N3 + (NH_4, K)_2SO_4 \rightarrow 2(NH_4, K)NO_3 \cdot (NH_4, K)_2SO_4 \qquad (22)$$

$$2\ N3 + K3 + (NH_4, K)_2SO_4 \rightarrow 2\ (NH_4, K)\ NO_3 \cdot (NH_4, K)_2SO_4 + K2 \qquad (23)$$

Figure 13 contains phase diagram of KNO_3, NH_4NO_3, K_2SO_4 and $(NH_4)_2SO_4$ at system when the sample is first heated to 150 °C and then rapidly cooled to 25 °C. Figure 14 displays the same system, but now the components are in stable form the at 25 °C temperature.

When comparing Figures 13 and 14 the major difference is the of the presence of K3 phase. When cooled quickly to ambient temperature the K3 phase has not disproportioned into 2 $NH_4NO_3 * (NH_4)_2SO_4$ and KNO-II which form the stable composition in the room temperature with the solid solution NKS. However according to the Figure 15 at AS-AN ratio below 0,35 and KN-AN ratio under 0,9 there is zone where K3 is still stable. This can be interpreted so that small amounts of sulphates can improve the stability of the K3 phase, which is the case in the studied fertilizers.

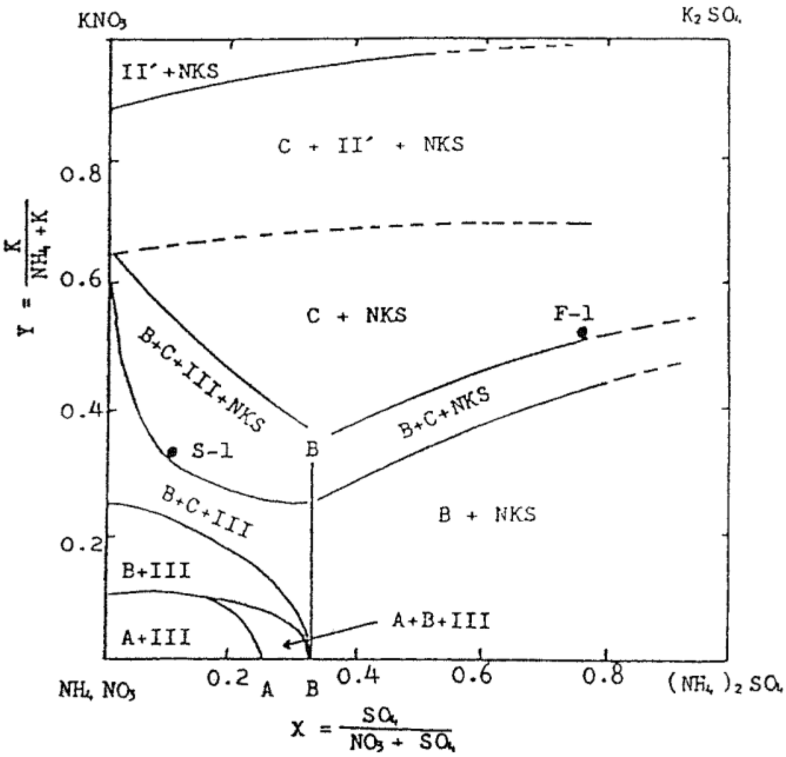

Figure 13 AN-AS-KN-SOP system cooled rapidly from 150 °C to 25 °C $III = AN - III$, A=3 $NH_4NO_3 * (NH_4)_2SO_4$, $B = 2\ NH_4NO_3 * (NH_4)_2SO_4$, $II' = KNO_3 - II$, $C = K_3$, $NKS = (NH_4, K)_2SO_4$ (Kiiski 1992)

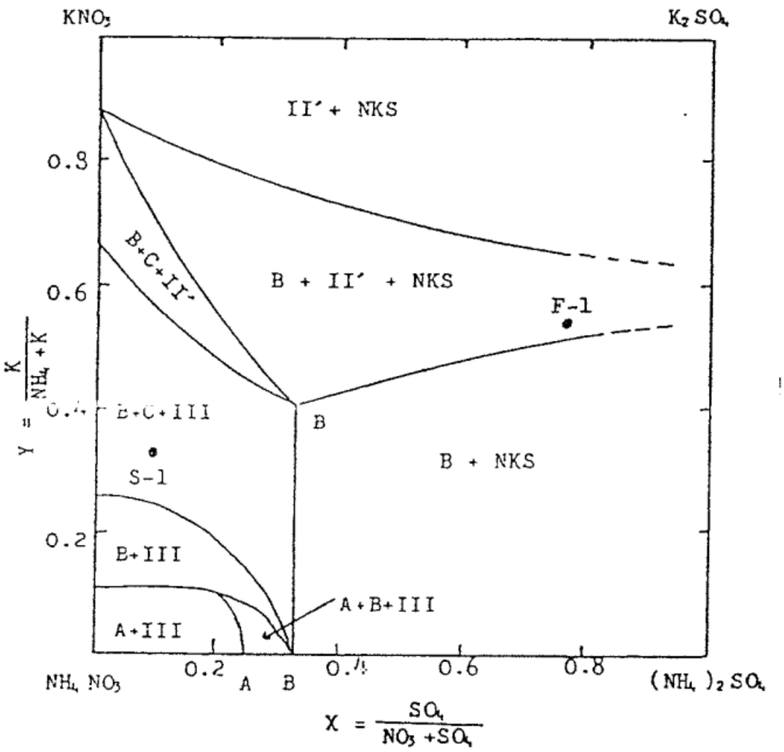

Figure 14 AN-AS-KN-SOP system stable at 25 °C $III = AN - III$, A=3 $NH_4NO_3 * (NH_4)_2SO_4$, $B = 2\ NH_4NO_3 * (NH_4)_2SO_4$, $II' = KNO_3 - II$, $C = K_3$, $NKS = (NH_4, K)_2SO_4$ (Kiiski 1992)

The magnesium and calcium sulphates form double salts with other sulphates. Magnesium sulphate can react with AS and SOP into Tutton's salts, Equations 24 and 25. (Kiiski 2010)

$$MgSO_4 + (NH_4)_2SO_4 + x\ H_2O \rightarrow MgSO_4 \cdot (NH_4)_2SO_4 \cdot xH_2O \qquad (24)$$

$$MgSO4 + K_2SO_4 + x\ H_2O \rightarrow MgSO_4 \cdot K_2SO_4 + xH_2O \qquad (25)$$

In studies conducted by Kiiski and Hauskaviita 1993 calcinated $MgSO_4$ was mixed with different combinations of AN, AS and KN to create slurry containing 5 % of water. In the test it was found that initially the there was no or only a small amount of Tutton salt formation. When the samples were moistened Tutton salts were formed.

When mixing the calcined $MgSO_4$ with dry AN, AS and KN there was no formation of Tutton's salts. When water was added to the mixture Tutton's salts were formed. When Epson salt, $MgSO_4 * 7H_2O$ was mixed with the AN, AS and KN mixture the Tutton's salts were formed within 48 hours. Therefore, it was concluded that the $MgSO_4$ has to adsorb water to become $MgSO_4 * 7H_2O$ which then reacts to Tutton salt. The most likely route for Tutton salt is the reaction between Epsom salt and potassium rich montan salt. (Kiiski & Hauskaviita 1993)

Figure 15 showcases the removal of the magnesium sulphates water of crystallization measured by thermogravimetric analysis by (Chipera et al. 2006) The heating was done at a rate of 10 °C/min and a dry N_2 was used to purge the evaporated water. In the perspective of fertilizer production, the most important area is from 25 to 150 °C. The epsomite will deposit one of its crystal waters when the temperature reaches 50 °C. In temperatures under 100 °C water of crystallization is removed only from the $MgSO_4 * 7\ H_2O$ and $MgSO_4 * 6\ H_2O$. This is around the temperature which the fertilizer reaches in the drying. In the reactor temperatures only the kieserite, and anhydrous magnesium sulphate have retained their masses. Therefore, it could be thought that the magnesium sulphate which is fed to the reactors as kieserite do not adsorb large amounts of water unless the temperature decreases to around 100 °C.

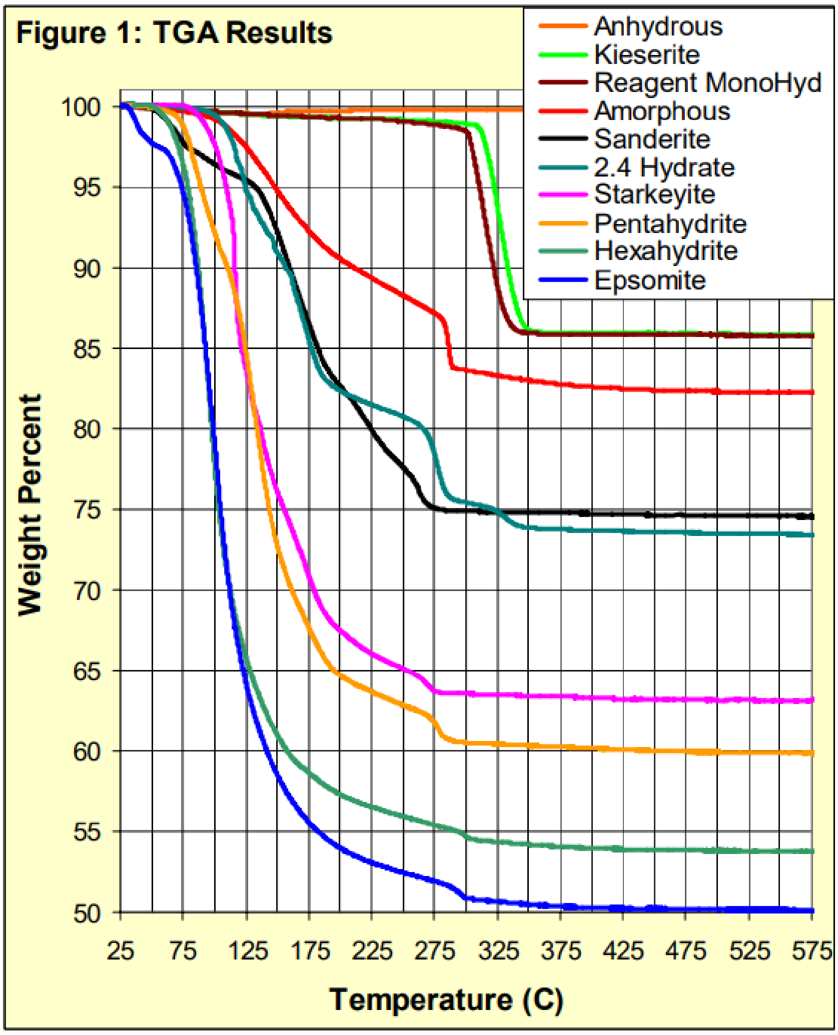

Figure 15 Dehydration behavior of magnesium sulphate (Chipera et al. 2006)

4.3 Particle deformation

The fertilizer granules have to be strong enough to withstand the stresses posed to them during the storage and transportation. The loss of shape increases the contact surface area between the fertilizer particles thus increasing the possibility of the caking. Crumbling particles form dust and fines which also increase the connecting surface area between particles. Dust can also be created by abrasion of the particles.

Due to pressure individual particles can have an elastic or plastic deformation. In elastic deformation the particle returns to its original shape after the pressure is released. Plastic deformation occurs when the change of shape is permanent. Hertz equation can be used to describe the connection between the deformation and the elastic contact force, Equation 26 (Antonyuk et al., 2005)

$$F_{el} = \frac{2}{3} E^* \sqrt{\frac{d}{2} \Delta h^3} \tag{26}$$

where,	F_{el}	elastic contact force	[N]
	E^*	Average modulus of elasticity	[Pa]
	d	granule diameter	[m]
	Δh	displacement	[m]

Figure 16 showcases the effect of increasing the pressing force on plastic particles. The a)-corresponds to low force situation when the contact point pressure is lower than the yield pressure. When the contact point pressure surpasses the yield pressure the contact points began to expand, part b). The expansion takes place so long as there is some pours inside the granule structure part c). (Kendall, 2001) It should be noted that the increase of the contact surface area decreases the pressure, so therefore the system balances itself and the contact point pressure and the yield pressure reach equilibrium.

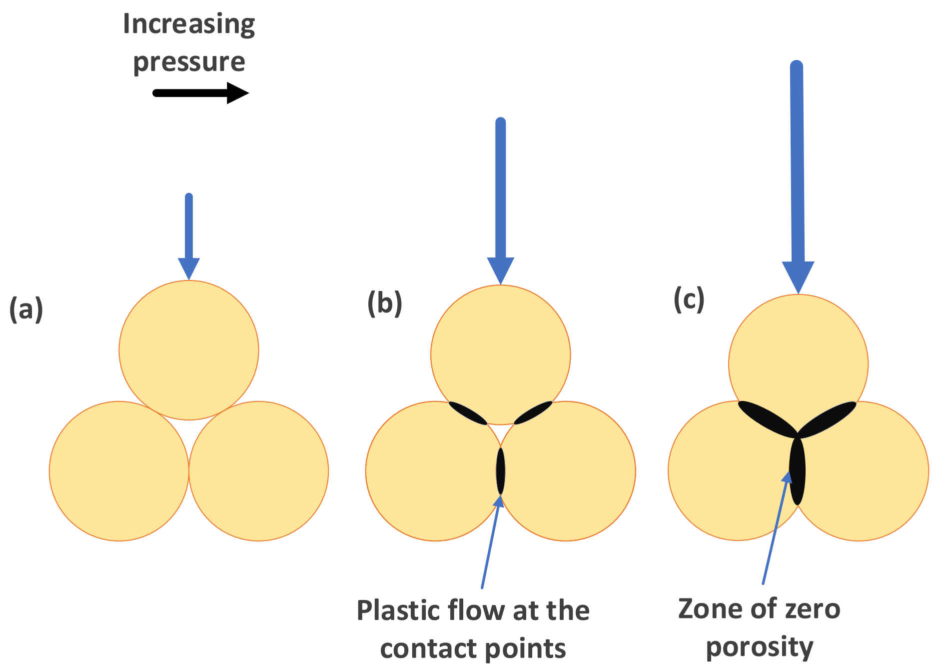

Figure 16 The effect of compaction in plastic particles, based on (Kendall, 2001)

Kalman, (2020) has described the behavior of granular material under compression. When pressing a bed of granules, an array of different mechanisms are present. The granules are compacted, and a network of force chains is formed inside the particle bed. At the same time the weakest of particles break and form dust and fines. The particles can create bonds and if even more pressure is added tableting is occurring. (Kalman, 2020)

Force chains mean phenomena in which the compressive pressure is directed through only a part of the particles of the granule bed. Therefore, the particles part of the force chain under are larger pressure than the rest of the particles. This causes extra stress to the particles, which can then break, thus altering the route of the force chain through the particle bed. The formed fine particles and the dust reduce the stress on the bed by filling the gaps between the particles. (Kalman, 2020)

Kalman (2020) also describes the relation between the breaking and bonding of granules. The studied showed that the part of the particles has to break before the bonding. This was explained by the fact that the fines created by granule degradation were needed to strengthen the bonding. (Kalman 2020). The pressures used varied from 1 MPa up to 16 MPa, which are much higher than are subjected to fertilizers. Therefore, this kind of setting and caking could take place if there is excessive force used in the handling of the fertilizer.

The plasticity of the granules are effected by the chemical composition and water content. As for example NP fertilizers deform significantly more compared to regular NPK. The increase of free water naturally increases the deformability of the granules. The impurities of the raw phosphate decrease the plasticity as told in the chapter 3.1.

The deformation of the particle surfaces can lead into sintering between particles. The driving force behind the sintering process is the particle system's tendency to reduce the surface free energy. This is accomplished by decreasing the surface-area. The decrease of surface area can be achieved in crystalline particles by multiple different means of diffusion, such as surface, lattice, and grain boundary diffusion. (Zafar et al., 2017).

The compression of plastic particles increases the van der Waals forces between the particles. Li et. al. (2006) have comprehensively detailed the effect of van der Waals adhesion on particles. JKR and DMT models of particle adhesion are compared. JKR model is suitable for particles, which are large soft and have a high surface energy. The DMT model suits better for particles which are small, hard and have a low surface energy. Parameter μ can be used in evaluating which model should be used, shown in Equation 27. If the μ is larger than 1 the JKR should be used, otherwise the DMT is better. Both models are only applicable to smooth particles. (Li, et al., 2006)

$$\mu = \frac{32}{3\pi}\left[\frac{2R\gamma^2}{\pi E z_0^3}\right]^{\frac{1}{3}} \tag{27}$$

where	μ	parameter for model choosing	[-]
	R	radius of the sphere	[m]
	γ	surface energy of the spheres	[J/m^2]
	E	Youngs modulus	[Pa]
	z_0	contact distance	[m]

A quick estimation was done based on parameters found on literature to find out which model suits best for the fertilizers. The surface of the granule is estimated to be talc, which has surface energy of 217,31 mJ/m^2 according to Helmy et al. (2005) The contact distance is estimated to be 4 nm, the smallest possible distance according to Li et al. (2006) is 0,4 nm. The radius of the sphere is approximately 1,5 mm and the Young's modulus can be calculated from the Bulk modulus by Equation 28. The bulk module, 22 MPa, and the Poisson ratio, 0,3, of AN-V is used in the estimation based on the calculations of Materials Project database (de Jong et al., 2016).

$$E = 3K(1 - 2\vartheta) \tag{28}$$

where	K	bulk modulus	[Pa]
	ϑ	Poisson ratio	[-]

In this estimation the parameter for the model choosing turned out to be 28, which indicates that JKR model should be used. When the contact distance was increased to 4000 nm μ decreased under one.

The force between particles based on the JKR model is shown in Equation 29 (Li et al., 2006). For fertilizer particle with radius of 1,5 mm the force based on the JKR model should be around 3 N.

$$F = 3\pi R\gamma \tag{29}$$

4.4 Surface area and particle shape

As in the setting and the caking the particles are joined on the surface the amount of surface area and contact points are major factors in determining the caking and setting tendency of fertilizers.

The specific surface area increases when the particle size decreases. Especially dust has a lot of surface area compared to its volume. The decrease of particle size also increases the amount of contact points between particles thus increasing the setting and caking tendency (Kiiski, Hauskaviita 1990). The increase of surface area also increases the water adsorption, which increases the setting and caking tendency. (Carpin et al., 2017)

The size of the granules is given as the d_{50} median size which roughly corresponds to the sieve mesh size where half of the particles have been retained. The Equation 30 shows the general form of determine the particle size (Kiiski & Hauskaviita 1990).

$$d_n = \frac{d_a - d_b}{L_a - L_b} * (n - L_a) + d_a \tag{30}$$

where d_n size of n:th size particle [m]

d_a	mesh size of flow through over 50 %	[m]
d_b	mesh size of flow through under 50 %	[m]
L_a	flow through percent	[%]
L_b	flow through percent	[%]

The uniformity index is used to describe the particle size distribution of the fertilizer. It is calculated from the d_5 and d_{90} values, according to Equation 31. Higher values indicates narrower particle size distribution. Value of 1 indicates perfectly uniform particle size. (Kiiski & Hauskaviita 1990)

$$UI = \frac{d_5}{d_{90}} * 100\ \% \tag{31}$$

where UI uniformity index

Also, the irregular shape increases the overall surface area of the granules. The effect of shape on the caking tendency of trisodium phosphate has been studied by Chen et al. (2016). As the results particles with more circular shape had smaller caking tendency. This was caused by the smaller contact area between the particles. (Chen et al., 2016)

The shape of the particles can be expressed by circularity and sphericity. These are typically mixed with one another. They are meant to describe different aspects of the particle. The sphericity describes the ratio of the surface area and the circularity the perimeter of perfectly round particle to measured particle. (Grace & Ebneyamini, 2020) Roundness on the other hand is defined to be the ratio between the sum of the corners radius curvatures and the amount of curves and the largest possible fitting circle. (Bullard & Garboczi, 2013) All of these values describing the shape of the particles are between 0 and 1.

5. Measuring the fertilizer tendency to cake

There are plenty of different approaches for testing the caking tendency of crystalline material. Chen et al. (2018) have compiled measurements, which are divided into mechanical, morphological, and statistical indices. The mechanical testing can be further divided into compression and cake strength measurements. The morphological indices are based on shape of the particles, such as circularity. The statistical indices are determined by using the distributions of the other indices' types. Also, the caking index is categorized to be statistical indices. (Chen et al., 2018) The caking index measurement is further presented in section 8. Undirect measurements are also used for detecting the caking tendency. This includes measuring the water content of fertilizer and the value of critical relative humidity. Also, more advanced measurements such as XRD and polarized light microscopy can be used to detect compounds and particle structures that could cause caking.

5.1 Mechanical strength measurement

The mechanical strength of fertilizers can be measured with variety of methods. The measurement can be made from individual particles as well as from particle beds. Compression, cake strength, hardness and abrasion are typical parameters that are measured.

Järveläinen et al. (2016) describe the granule bed compression taking place in four different stages. In the first stage the particles packing density increases due to the rearrangement and elastic deformations. In the second stage the structure of the granule fails, and cracks began to form. Initially the particle bed compaction slows down, due to the end of rearrangement of the granules. When the pressure is further increased the granules break down. In the third stage the fractured particles and formed fines and dust are packed more densely. The fourth stage is reached when the porosity of the particle bed is zero. Particle size, shape, porosity, as well as the friction between the particles themselves and with the die walls effect the compression process. (Järveläinen et al., 2016)

The four stages of compression are visualized in Figure 17. Kaolinite granules are used as the sample. In the first stage on the relative density grows slowly linearly. Because the sample was tapped before the measurement there was no major rearrangement of particles. In the stage 2 the packing density starts to increase due to the breaking of the particles. In the third stage the particle bed density increases again steadily. The average particle strength can be then estimated from the crossing of linear part asymptotes. (Järveläinen et al., 2016)

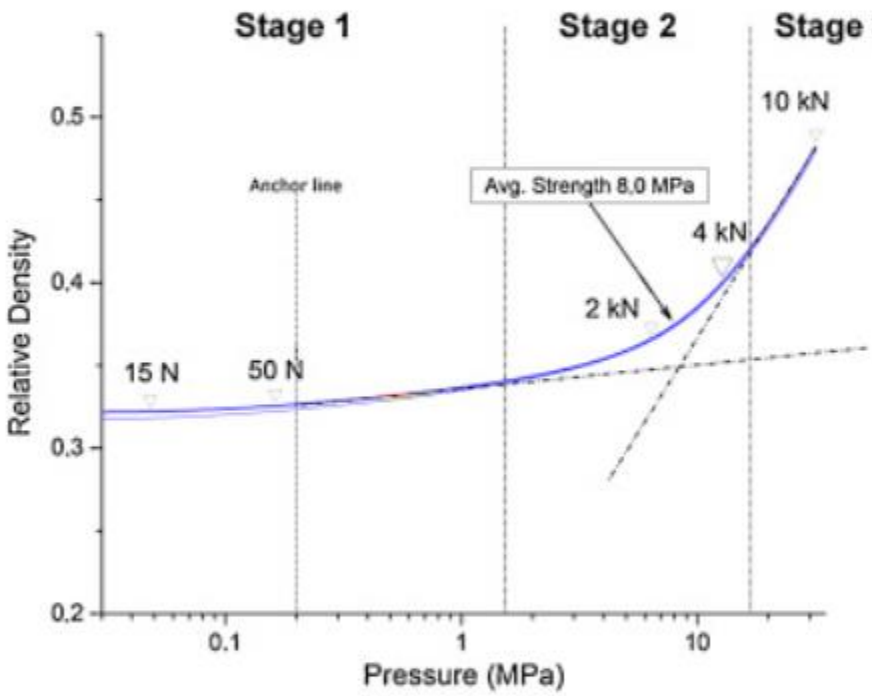

Figure 17 Compression curve of kaolinite showcasing 3 stages of compression (Järveläinen et al., 2016)

Models have been created to connect the particle bed compression to the mechanical properties. Uniaxial compression can be described by the Kawakita equation, Equation 32. The compression parameter 1/b corresponds to the failure stress of individual particle. (Adams, McKeown, 1996) The parameter a corresponds to the maximum engineering strain. (Nordström et al., 2008)

$$C = \frac{h_0 - h_p}{h_0} = \frac{abp}{1 + bP} \tag{32}$$

where,	C	compression	[-]
	h_0	initial height	[m]
	h_p	height under pressure	[m]
	a	compression parameter	[-]
	b	compression parameter	[1/Pa]
	P	pressure	[Pa]

In further studies conducted by Nordström et al. (2008) it was discovered that the Adam's parameter describes better the failure stress of the particles than the inverse of the compression parameter b. The Adam's parameter is defined in Equation 33. (Nordström et al. 2008)

$$\ln(P) = \ln\left(\frac{\tau_0}{\alpha}\right) + \alpha\varepsilon + \ln\left(1 - e^{(-\alpha\varepsilon)}\right) \tag{33}$$

where	τ_0	Adams parameter
	α	friction coefficient
	ε	natural strain

Typically, as the bed of fertilizer granules is compressed a cake is formed. This phenomenon is used in the accelerated caking tests. The acceleration can be achieved by increasing the pressure. The mechanism of caking in pressure accelerated caking tests is assumed to be the capillary adhesion. (Walker et al., 1998) The relative humidity and temperature can also be used in accelerating the caking process. In this case the caking can also be caused by the formation of solid bridges due to dissolution-recrystallization cycle. (He et al., 2019)

The strength of the formed cake can be used indicating the fertilizer tendency for caking. The strength of the cake can be measured in multiple ways. When comparing compression, tensile or shear cake breaking of tests on sucrose the shear breaking test was found to be most consistent (Samain et al., 2019) The Acap easy uses the compression breaking test, which was found to be least repeatable method of the three.

The problem of the uniaxial compression test was the variation between measurements varied the most. However, the samples studied were wide and short so when the cake breaks part of the cake is probably under pressure. In the Acap easy the shape is the opposite when break occurs also the contact with the press breaks.

The caking tendency can also be determined by measuring individual particle contacts. Wahl et al., (2008) have studied the caking tendency of urea prils. They have used a device where two particles are glued in the points of two opposing pins. One pin is stationary and other is moved to apply the pressure. The schematic of the device is shown in Figure 18. (Wahl et al., 2008)

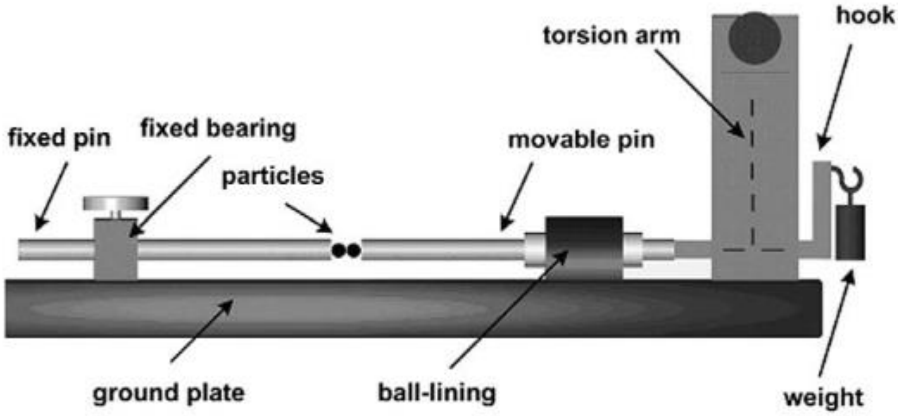

Figure 18 Sketch of the device used for pressing individual particles (Wahl et al., 2008)

The pressing of the individual particles is done in environmental chamber, which humidity conditions were well under the critical relative humidity of the urea. The measurements showed that the solid bridge diameter increased only slightly, but the tensile strength increased significantly when the pressing time is increased. This was explained that initially the crystal bridge is hollow but is filled when the time increases. (Wahl et al., 2008) The results showed same kind of crystal growth as visualized in Figure 8.

Walker et al., (1997 have conducted comprehensive tests about the crushing strength of individual particles. The principle is to measure the force needed to break the granule. Typical stress-strain plot of fertilizer granule is shown on Figure 19. The peak A) corresponds to the force needed to break the particle. The stress-strain plot does not have a single slope value. This is caused by the deformations of the sub particles within the granule. (Walker et al., 1997)

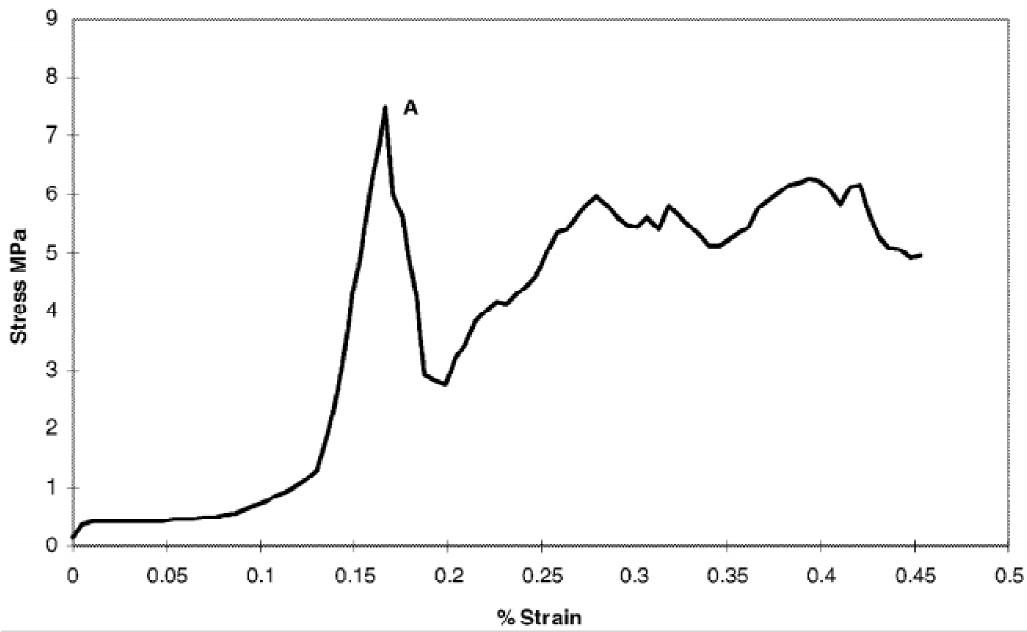

Figure 19 Typical stress-strain curve of individual fertilizer particle (Walker et al., 1997)

Walker et al. (1997) also showed that the crushing strength is depending on the size of the granule. Larger granules have a higher crushing strength, However, when taking the surface area into account there is no big difference between the pressure needed to break the granule. The increase of humidity decreased the crushing strength of the particle significantly, but the strain value where the break occurred stayed relatively stable. The relation between the caking and crushing strength were also studied. The particles that showcased caking had also smaller crushing strength. (Walker et al., 1997)

5.2 Morphological measurements

The properties related to the particle size distributions, roundness and dustiness are measured from the fertilizer samples. The poor performance in these measurements can increase the tendency, because of the increased surface area. The values are also important for the good spread ability of the product (Kohonen 2006)

Fertilizers particle size distributions can be measured by sieve analysis but also with optical methods. Kiiski and Hauskaviita 1990 have explained the typical sieving process of the fertilizers. In the sieve analysis a sample fertilizer is placed into set of standard sieves. When choosing the mesh sizes, the particles should get divided so that single sieve does not retain more than 50 % of the granules. Also, the bottom should not contain less than 10 % of the granules. The results containing information from the particles d_{50} size as well as the uniformity index can be calculated as shown in Equations 30 and 31 based on the amount of granules retained on each sieve. (Kiiski & Hauskaviita 1990).

The particle shape and size can also be measured using optical measurements. Dynamic image analysis is based on taking pictures of falling particles against a backlight. To ensure accurate measurement the particles must be applied separately to the imaging. An image processing software is used to analyze the particle size and shape. (Wilms, et al., 2019)

5.3 Moisture content measuring

Fertilizers can contain water in forms of free water, bound water, and water of crystallization. Moisture content of the fertilizer can be measured by using Karl-Fischer titration. The method is based on a chemical reaction, shown in Equation 34. The solution containing HI is colorless, but if there is unreacted I_2 in the solution it turn into dark red brown. This indicates that all the water is consumed. The amount of water can then be calculated from the amount of I_2 added. This can also be monitored electrically. (IFA 2014)

$$2\,H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2\,HI \tag{34}$$

The KF-method is suitable for detecting the free water and a variety of water of crystallization. However, there is still restrictions. Table II contains water of crystallization which can be detected using KF method. Based on the Table II there are some important water of crystallization that cannot be analyzed mainly the other waters of crystallization of the $MgSO_4$. The methanol solvent detects much greater amount of water of crystallization than the 2-propanol. This could at first hand to thought as bad thing. But according to Kiiski (1994) the problems related to the water content occur when the water is not bound as water of crystallization. Therefore, the use of 2-propanol could give more insight to the water content of bound and free water.

Table II Water of crystallization detectible (BS EN 12366-1:2001)

Substance	Methanol	2-propanol
$Ca(NO_3)_2 * 4H_2O$	Yes	Yes
$CaHPO_4 * 2H_2O$	Yes	No
$CaSO_4 * 2H_2O$	Yes	No
$CaSO_4 * 0{,}5H_2O$	Yes	No
$MgSO_4 * 7H_2O$	Yes	Yes
$KCl * MgSO_4 * 2{,}75H_2O$	Yes	No
$K_2SO_4 * MgSO_4 * 6H_2O$	Yes	No
$K_2SO_4 * CaSO_4 * H_2O$	Yes	No
$KCl * MgCl_2 * 6H_2O$	Yes	Yes
$(Mg(NO_3)_2 * 6H_2O$	Yes	Yes

Other possible method is to use gravimetric measurements. The water can be removed by temperature and vacuum. The conditions have to be carefully planned in order to avoid to loss of other volatile components such as ammonia. For the phosphate or potassium chloride fertilizers the gravimetric can be a viable option in disputed cases. (IFA 2014)

5.4 Critical relative humidity measuring

The critical relative humidity of fertilizers can be measured in multiple different ways. Conventionally the CRH value can be measured either using the powder moisture absorption or the saturated solution methods. The drawback of those methods is that they are complex and time consuming. (Zhan et al., 2010) Figure 20 contains typical measurement curves of determining the CRH of the fertilizer. The (a)-plot is measured by the moisture absorption method and the (b)-plot by saturated solution method.

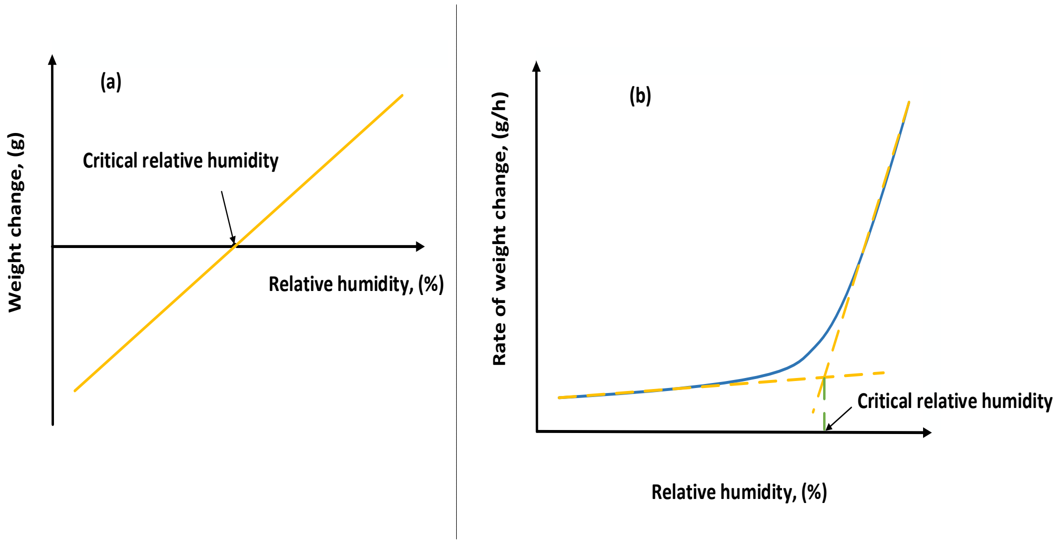

Figure 20 Moisture absorption and saturation method result curves, based on (Zhan et al., 2010)

Zhan et al. (2010) have showed that accurate results can be obtained by measuring the air humidity of the equilibrium system of air and saturated solution. The schematic of the measurement setup is shown in Figure 21. The measurements are done by adding a saturated sample into airtight container. An adsorbent paper is added to increase the evaporation area. The humidity sensor placed and sealed on the top. The whole system is kept in standard temperature and enough time has to be given for equilibrium to form. (Zhan et al., 2010)

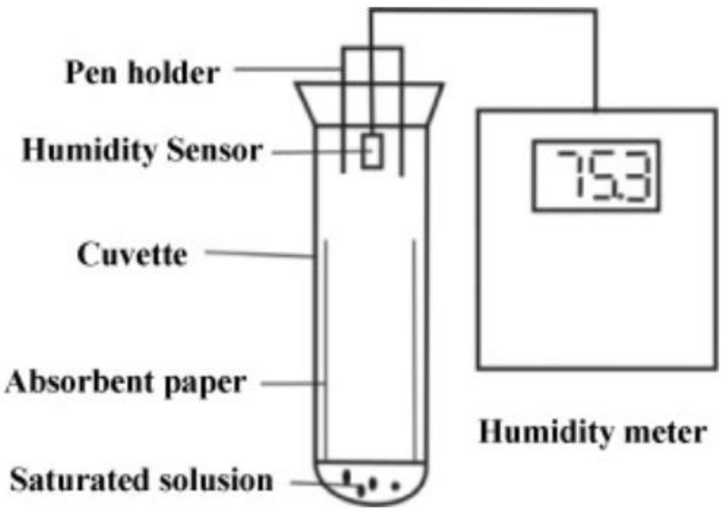

Figure 21	Test system for measuring fertilizers CRH (Zhan et al., 2010)

5.5 Optical measurements

Optical measurements provide a way to analyze the internal structure of the fertilizer granule. Kiiski and Hauskaviita have listed some of the possible methods for analyzing the structure and composition of fertilizers optically. The possibilities contain the polarized light microscopy, XRD measurements as well as SEM-EDX. The optical measurement are useful tools when studying the possible post reactions because the chemical composition stays the same. (Kiiski & Hauskaviita, 1992)

The working principle of polarization microscope is based the polarization of light. Light that is polarized vibrates only in one direction, compared to the natural light, which has infinite amount of vibration directions. (Kiiski & Hauskaviita, 1992)

In polarization microscope the light passes through of polarizer, which lets through light which vibrates only in one direction. Depending on the structure of the sample, part of the light could be twisted 90°. The second polarizer is in 90° angle compared to the first polarizer. This means that only the light which has twisted in the contact with the sample will pass through. Magnification part of the microscope is similar to the ordinary microscopes. (Ockenga, 2011) The working principle is visualized in Figure 22.

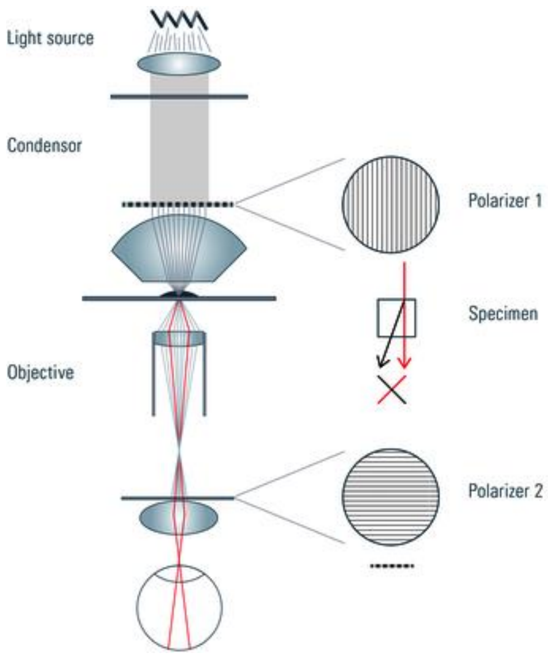

Figure 22 Working principle of polarization microscope (Ockenga, 2011)

The study of fertilizer is based on the effect of individual salt crystals on the light. If light has no change of direction the crystals are isotropic. Of the salts found in fertilizers the MOP and NH_4Cl are isotropic. Anisotropic crystals alter the direction of the polarized light. Typical anisotropic crystals found in fertilizers are $(NH_4)_2SO_4$, K_2SO_4 and $CaSO_4$. (Kiiski & Hauskaviita, 1992)

The images taken from the polarized light microscope can be used in the detection of post reactions. Post reactions can be seen from the surface between a crystal and the surrounding fertilizer matrix. Sharp lines means that no post reaction have taken place. When borderline contains black spots, it is an indication of post reactions. (Kiiski & Hauskaviita 1992). Pictures taken by polarized light microscope are shown in Figure 49 and in Figure 50.

XRD analysis can be used when the structure of crystalline materials is studied. XRD stands for X-ray diffraction. The principle of XRD measurement is to shoot the studied sample with monochromatic X-rays. The crystal structure of the sample causes interference to the reflecting X-rays. This pattern of interference is used to analyze the structure of the crystal. (Alderton, 2021)

Typical way the measure the X-ray diffraction is to have a setup where the sample of powder and the X-ray detector are coupled. so that the rotational angle of the detector increases 2x compared to the sample. Resulting diffraction pattern showcases the intensity of the X-rays on the detector compared to the angle of diffraction. (Patience, 2018) An example the XRD diffraction pattern is shown in Figure 52, where dust of 22-0-14 fertilizer is analyzed.

In studying fertilizers, the XRD can be used for determining the presence of solid solutions. Kiiski and Hauskaviita (1992) showcase that XRD can be used in estimating the composition of solid solutions formed by AN and KN. Also, the size of the crystals can be estimated. (Kiiski & Hauskaviita 1992)

6. Sampling

For the overall accuracy of the measurements the sample taking is the foundation on which the rest of study is built on. If the sampling method is faulty so will be the results as well. Therefore, the importance of well thought sampling process cannot be exaggerated.

Bun (1989) has presented a group of factors that has to be considered when creating plan for sampling fertilizers.

1. What is the subject of the measurement?

2. What properties are studied, chemical or physical?

3. What kind of knowledge is targeted, averages or the properties range?

4. How homogeneous is the sample?

5. How the sample is taken?

Samples are at the moment taken in four different locations during the production and storage. The random samples are taken from a conveyer belt after the coating drum. Daily collection sample is also taken after the coating drum, but automatically. Pile samples are taken from the storage bins and bagging samples are automatically taken by the bagging process.

The random samples are used for the quick compression test and for the laboratory analysis. A designated sample scoop is used to the laboratory sample, which covers the whole conveyer cross area. Showcased in Figure 23 (b). In contrary the compression samples are typically taken by coffee cup. This can cause the sample to be biased, because of the segregation of the fertilizer granules by the size differences. The larger granules rise to the surface of the material stream due to the conveyor vibrations and the smaller granules sink to the bottom due to particle rearrangement (Yen, et al., 1997). However, there is some studies suggesting that the particles can be quite well blended by transfer to the final conveyer belt, because of the close proximity to the outlet of the coating drum (Ilic et al., 2020). The need of improving of the sample taking can be analyzed more closely when studying the effect of the particle size on the caking measurements. Other effects of the sample taking device can be assessed more comparing the compression results with different sample taking methods.

Particle size segregation also takes place in the storage bins. The larger particles are enriched on the sides of the pile while the smaller particles are more concentrated on the center. The different size particles can also form layer structures to the pile. Combinations of these structures are possible. The bin filling type, height, and the ratio of the particle size effect the segregation result. (Benito et al., 2013)

The pile samples are taken in both ends of the bin. A sampling spear is pressed to the pile by hand to take sample. Slight cone shape in the tip of the spear holds the fertilizer when the spear is lifted from the pile. The sampling tools are shown in Figure 23.

Figure 23 Sampling spear (a) and the conveyor sampler (b)

The sampling is only the first part of the chain of sample handling. In the case of fertilizers, it is important to keep the sample in airtight containment in order to prevent the water adsorption which could affect the results. In the study this was achieved by storing the fertilizers in closed plastic bags. All the samples were stored in room temperature to ensure the temperature history of the samples to be as similar as possible.

The particle segregation also takes place during the storage. This means that if the primary sample is divided into sub samples without mixing or using predesigned dividers the samples will have deviations in particle size distributions. In order to reduce the effect of the measurer related errors the sample taking was mainly done by two persons. The sample handling was done by one person and the measurement procedure mainly by two people. In the measurements made by the laboratory there was more variation on the persons conducting the measurements.

7. Acap Easy measurement

Acap Easy measurement device is used in the fertilizer plant to measure caking tendency of the fertilizer during the production. In a standard procedure a sample is taken from the final product conveyor belt. 45 ml of the sample is measured to the sample cup. The sample cup is inserted to the measurement device. The amount of compression is measured by pressing a piston to the sample cup with predesignated force. The pressing time is also determined before measurement. The device measures the initial height of the pressing piston and final height after the pressing. The initial length is measured when the force sensor detects over 30 N of force. The result given is the percentual compression of the sample, Equation 35.

$$C = \frac{h_0 - h_p}{h_0} * 100 \tag{35}$$

where,	h_0	initial height	[m]
	h_p	final height	[m]

During the compression measurement the fertilizer in the sample cup forms a cake. After measuring the compression, the breaking force of the sample is determined. The device turns the pressing base and then uses the pressing piston to push the sample cup down. The formed cake stays on top of the pressing base, which is turned back to the original position. The pressing piston then pushes the formed cake to determinate the breaking strength of the cake. The cake strength is determined by the software to be the maximum force before the amount of force decreases 40 %. The results were found to be highly inaccurate and might have caused the unexplainable results in the study conducted by Keipi (2011). The measurements can also be done without the cake breaking strength measurement. This leaves the formed fertilizer cake intact for visual inspection. The sketch picture of the Acap Easy device is shown in Figure 24

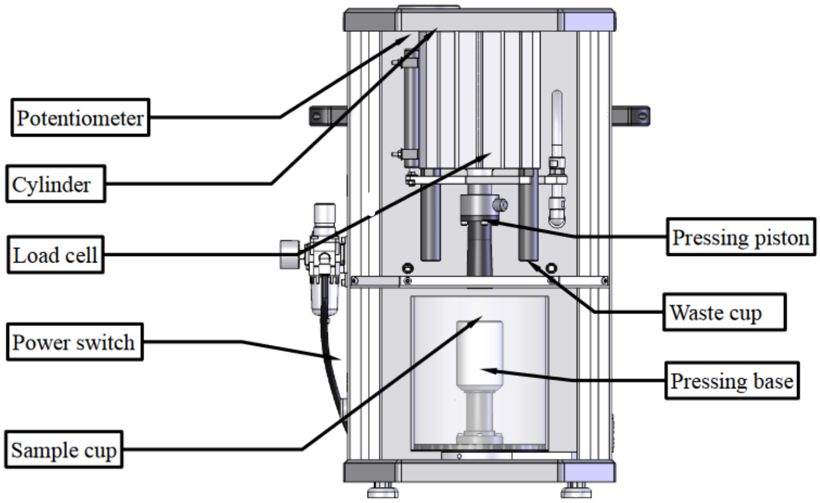

Figure 24 Sketch of the Acap Easy measurement device (AMT-Systems 2011)

Figure 25 showcases the measured force at different measurement points. The red line corresponds to the position of the pressing piston and the black line to the force detected by the sensor. The position of the piston lowers steadily as seen in the red line. The slope of the red line becomes horizontal when the piston has reached the pressing base.

The line of the force measurement seems to be stable until reaching the measuring point of 4000. However, the measurement of the crushing strength has taken place already approximately in measurement point 1000. This is barely visible in the Figure 25. The values which the software gives quite often disregard the real force needed to break the formed cake. Instead the force given by the software corresponds to spikes on the force line around measurement point 4000. These spikes correspond to the breaking strength of the fertilizer granules that have stayed on top of the pressing vase after the cake has broken. The wrong measurement values are due to small force needed to break the cake. The reliability of values given by the software are better when the force needed for breaking the cake is high.

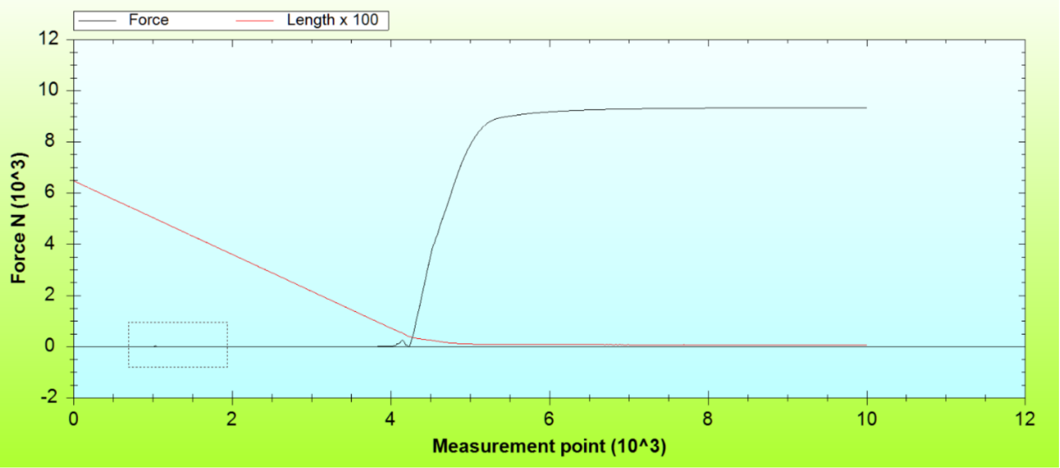

Figure 25 Force plot of the Acap Easy

The measurements of Acap Easy are divided into three sections. The first measurements focus on the sample taking and the overall accuracy and reliability of the Acap easy instrument. The second section focuses on the measurement parameters of the instrument and the last section on the effect of the fertilizer properties on compressibility results.

7.1 Reliability of the Acap Easy measurements

There are several factors that can cause both random and systematic errors to the measurements. One of biggest factors is that the measurement is not operated by a single person, but a whole group of operators. Therefore, the way the sample is taken, divided, and analyzed creates a lot of factors affecting the results of the measurements, which have not been accounted.

During the measurements there is errors linked to the length and force measurements which have a direct impact on the results given by the device.

Pressing time has a undirect impact and it is controlled by computer, so it is not included as an error source. The laboratories air temperature and relative humidity were regularly monitored and noted if the values differed significantly.

The first step for analyzing the accuracy of the Acap Easy measurement was to study how the sample taking and handling affects the results. This was done by taking individual samples from the production line using the official method and the unofficial method of using coffee cup as the sampling tool. The measurements were done so that every other sample was the official method and every other the unofficial to reduce the effect of the inevitable changes in the process. Still, the samples were taken from steady state production in order to minimize the effect of process variables.

For the coffee cup measurement every measurer took a sample as they pleased from the moving conveyor. The sample was then immediately moved to the laboratory to measure the compress. The samples taken by the official sampler were taken from the same location. The sample was poured to plastic bag where it was mixed to reduce the particle size segregation. Coffee cup size sample was taken from the bag and it was also measured instantly.

The personal bias between different operators was studied at the same time. At total three different measurers made the same 2+2 measurements and one made 1+1. The different measurers represented different experience level from the expert to newcomer. Control test were made using sample taken from an opened bulk bag. This eliminates the effect of process variables and time factor because the post reaction have already taken place.

The standard deviation of the Acap Easy measurement and the average difference were calculated with a dataset gathered from another fertilizer plant. The measurement time and the pressing force were equal, but the amount of the sample differed slightly. Dataset includes only measurements where the compression exceeds 8 %. A total of 3703 measurements were used to determinate the overall reproducibility of the measurement.

The total accuracy of the instrument and the need of calibration were tested by pressing empty cup. A total of 17 measurements were made. The effect of compaction between uncompressible particles was studied using 3 mm ball bearing. 45 ml of ball bearings was added to the sample cup. The press measurement was used. The first measurement was 15 min at 596 N to simulate the used method. Based on the finding that the height level remains stable after the initial pressing the pressing time was reduced to 1 min. The sample was mixed between measurements to rearrange the bearings to pouring packed bed density. In three measurements no mixing was done and in three measurements the sample was vibrated as showcased in Chapter 7.2.

The comparison of the personal effect indicated that the hand mark of the individual measurer is small but can be improved by using the official sampling tools. Therefore, for further sampling the official sampling methods were used instead of the operator driven traditional methods.

Table III contains statistical analysis of Acap Easy measurements done in other manufacturing site. It is the benchmark of accuracy from which the results are compared. The calculated values clearly indicate that the accuracy of the method without standardization of the measurement procedure is good enough to see the rough image of the products compressibility. Similar results were found in the initial testing of the onsite Acap Easy, which standard deviation between measurements was 0.66. These also correspond to the measurements of Keipi (2011), where the uncertainty of the measurements were evaluated to be around 5 %.

Table III Pairwise statistical analysis of repeated Acap Easy measurements

Year	Number of datapoints	Average diffence between measurements	Standard deviation of the difference	Average of the relative difference, [%]
2019	387	0.55	0.42	6.52
2018	621	0.64	0.57	7.77
2017	531	0.55	0.49	6.87
2016	998	0.46	0.37	6.09
2015	1166	0.49	0.38	6.37
Tot	3703	0.538	0.446	6.72

The measurements done with empty sample cup and with the 3 mm ball bearings showcased the presence of small errors. Measuring the empty sample cup showcased the base of the waste cup giving in 0,1 mm. Which was inevitable and deemed to be insignificant. In the steel ball bearing measurements, the most typical compression value was around 0,8 %. However, there was some deviation caused by the bearings flying out of the cup as pressed. Similar behavior was occasionally observed for the fertilizer samples as well. This could explain why some measurements showcase higher compression values.

7.2 Effect of the measurement parameters

Pressing force, pressing time and the size of the sample are the measurement parameters that can be altered. Other possible parameters include the sensitivity of the force sensor, which affects the height of surface detection in the beginning of compression, however this was not studied, because changing the sensitivity would always require a new calibration of the instrument.

In the manufacturers manuals the amount of sample was intended to be 45 ml. It was noticed that when using volume as the base for measuring the size of the sample there was some deviation in the mass of the sample. This is caused by the fluctuations of the particle bed density of the poured sample. Therefore, it was decided to also measure the mass alongside the volume instead of using the volume as the sole base of the measurements. The mass can also be measured more accurately compared to volume measurement which had to be done by the eye. Keeping the mass of the sample fixed works best when analyzing samples of same fertilizer product. However, there is some deviation of the bulk densities between the different types of the fertilizers which has to be taken account when comparing the results of different products. Therefore, a compromise was made by measuring the first sample by the volume and the remaining samples by the mass of the first sample.

Two measurements were done about of the size of the measured sample. The first measurement was done using 25-7-7 fertilizer taken from the opened FIBC. The pressing force was 3500 N and the time 5 min. The mass varied from 28.45 to 54.84 g and the volume from 30 to 55 ml. The volume was measured using a measuring cylinder. Each measurement was done twice to increase to statistical credibility. In the second measurement a sample of 22-0-14 taken from an opened FIBC was used. At this time the volume of the sample was discarded, and the size of the sample was wholly based on the mass. The mass was varied from 34.5 to 45.5 g. Two compression measurements were done from each measured mass.

Figure 26 displays the results of the first mass variation measurement. There is slight decrease of compression as the mass is increased, but not a very significant. The outlier of 60.6 g sample is caused by the sample cup being filled to top, so the granules have more space to slide under the pressing piston causing increase of compression values.

Similar behavior is seen in Figure 27 .The trend is somewhat decreasing but there is no clear relation between the mass of the sample to the compress. Based on these findings it seems that the size of the sample has a limited effect on the results of the measurements. However, the size of the samples was kept fixed in the further studies to reduce to amount of possible variables.

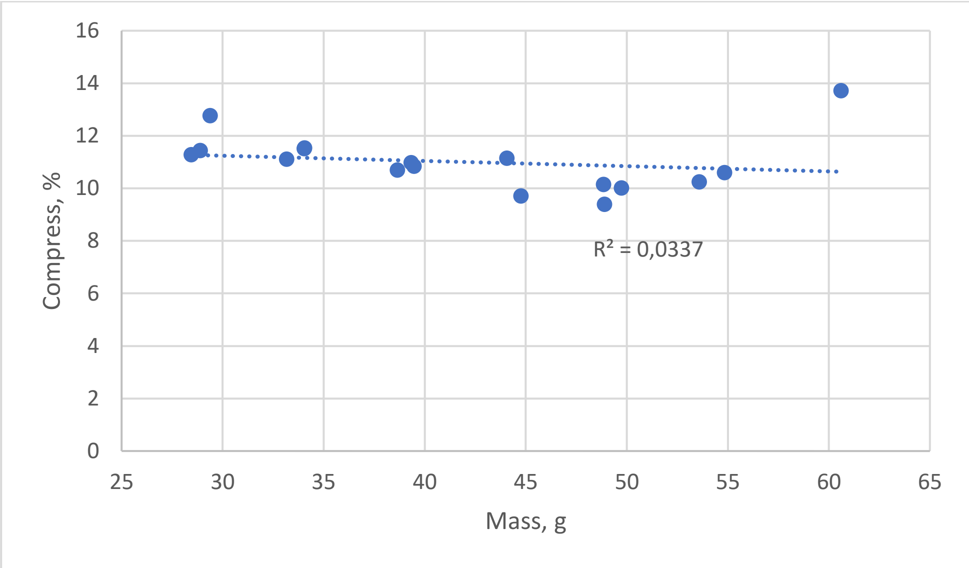

Figure 26 Compress at different mass samples, 3500 N, 5 min

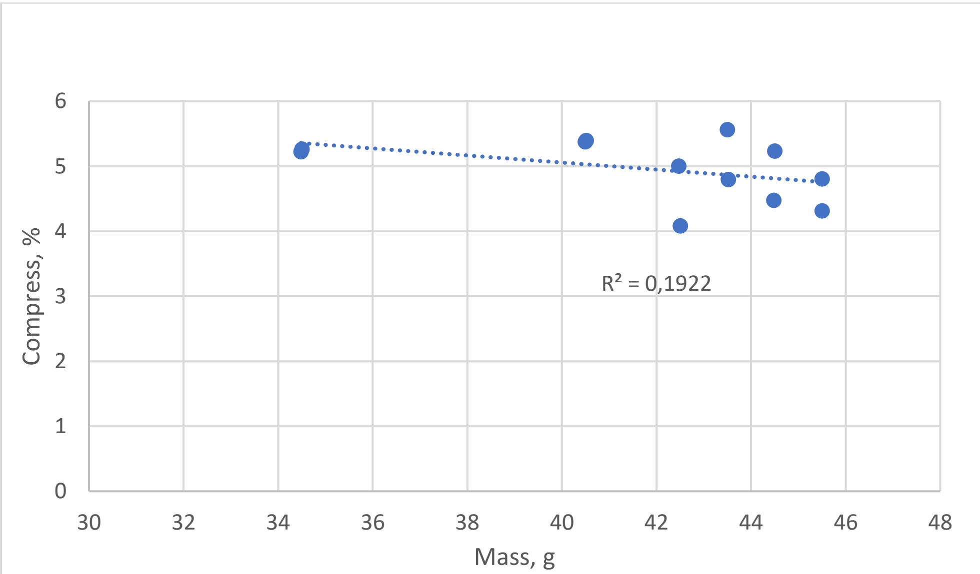

Figure 27 Compress at different mass samples, 596 N, 15 min

The effect of the pressing force was tested throughout the span of measurements to have insight how the different types of fertilizers behave in higher pressures. The most common measurement was made from the bin samples. The comparison was done using the recommended 596 N force and 3500 N force. In these measurements the time for 596 N was 15 min and 3500 N 5 min.

More comprehensive measurements were made from 20-5-15 fertilizer. The sample was taken from the packaging sample. The pressing time was 15 min and the mass of the samples 44 g. The force was changed from 300 to 8000 N which corresponds 0.34 to 9.11 MPa of pressure respectively.

The relation of the particle bed compression and the pressing force is linear as seen in the Figure 28. When comparing this finding to the theory of Järveläinen et al. (2016) in section 5.1 the bed compression is still in the 1st stage or in the earlier 2nd stage. The fertilizer granules do not break, but instead deform steadily as the pressure is increased. It was seen from the formed cakes that the particles were deformed, and small cracks formed when higher pressing forces were used indicating the shift towards the 2nd. stage. The force of 8000 N corresponding to 9,11 MPa of pressure is not enough to reach the stage 3 or 4. The intersection point of the linearization is not 0. This most likely is caused by the rearrangement of the granules within the sample cup, as the error related to the instrument was insignificant and the ball bearings also indicated some compression.

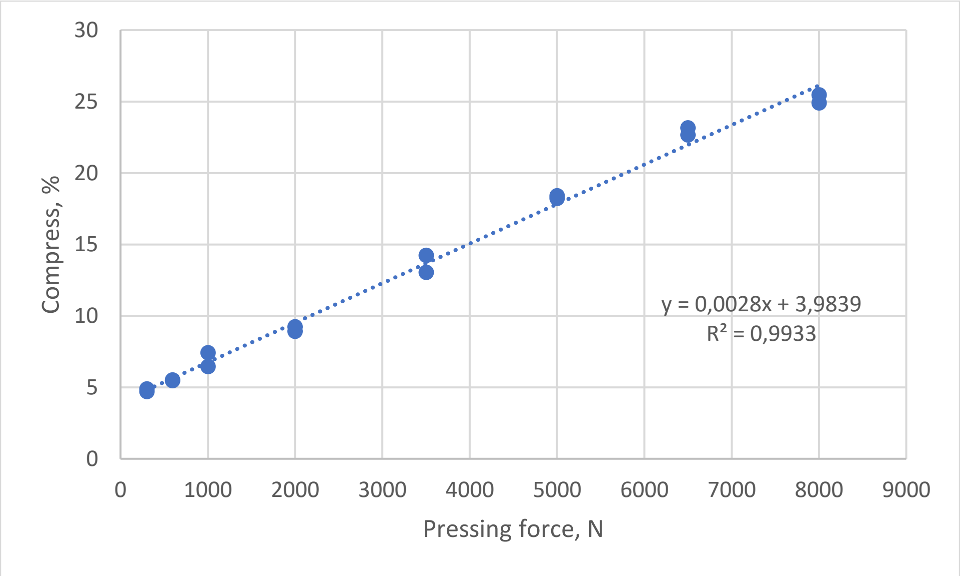

Figure 28 The compress as a function of pressing force

In Figure 29 the compression values of the same sample measured with 596, 15 min and 3500 N, 5 min of pressing force are compared. The relation between the compress values showcases is linear relation even if the measured fertilizers varied from measurement to measurement. This relation makes possible to evaluate the acceptable level of compression in different pressing forces. In a regression test the ANOVA F-value was 4e-7 indicating great significance,

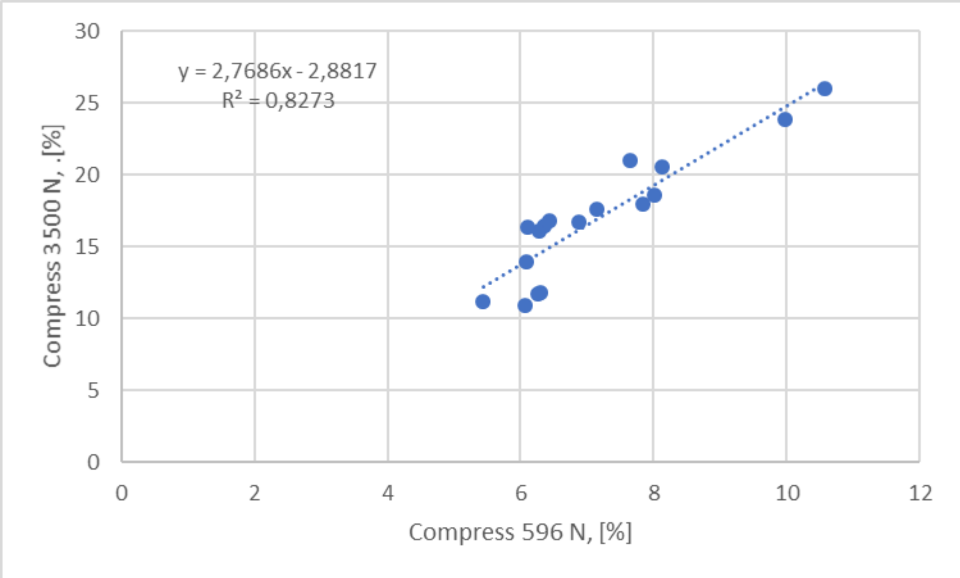

Figure 29 Comparison of fertilizer compress in 596 N and 3500 N

The increase of the pressing force also increased the crushing strength value of the formed caked, indicating increase of interparticle adhesion forces. The relation is quite linear as seen Figure 30. The values however, had to be collected manually from the measurement data as the ACAP Easy could not accurately determinate the low crushing strength values. This is most likely the reason why Keipi (2011) has announced the ACAP Easy crushing strength values to be useless in evaluating the caking tendency. In a regression analysis the ANOVA test indicated 5,5e-7 significance.

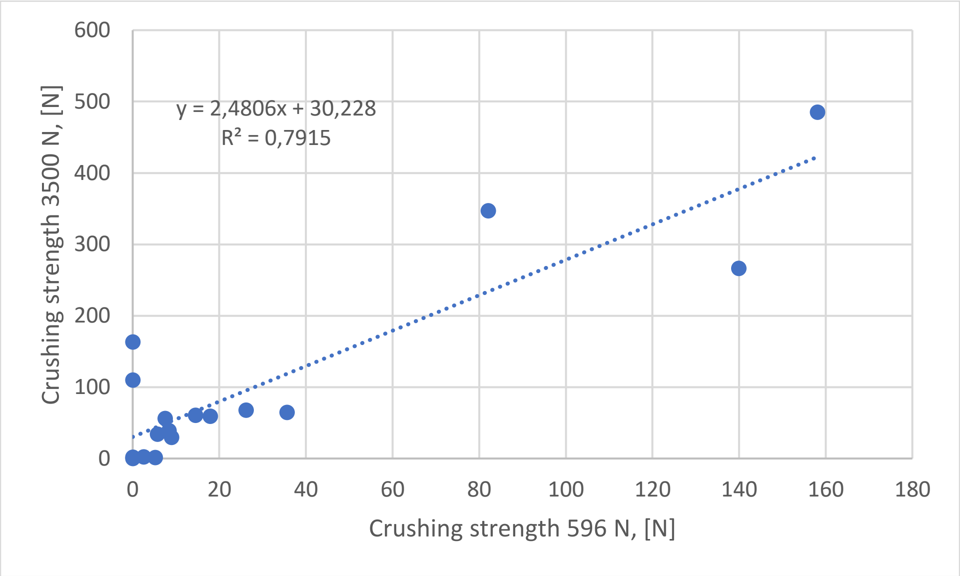

Figure 30 Comparison of fertilizer crushing strength in 596 N and 3500 N

For determining the effect of the pressing time for the compress values of the Acap Easy a set of 8 measurements was conducted. A sample of 27-5-4 fertilizer was used taken from the bin sample. The pressing time was varied between 1 and 90 minutes. The force and the amount of the sample were kept constant at 596 N and 42.3 g.

The beginning of the pressing was further examined. The samples were 22-0-14 taken from the bin sample. The pressing force was 596 N. A total of two measurements were conducted. The measurement was done by filming the height values of the piston displayed by the software. The height values were then recovered from the video. In the beginning the height was recorded from every second. The time between recorded values was increased step by step all the way to 1 min.

The effect of pressing time on the compress is shown in Figures 31 and 32. The pressing force is kept at 596 N. Figure 31 indicates the formation of force equilibrium in the particle bed. This means increasing the pressing time do not increase the compression after the equilibrium is reached.

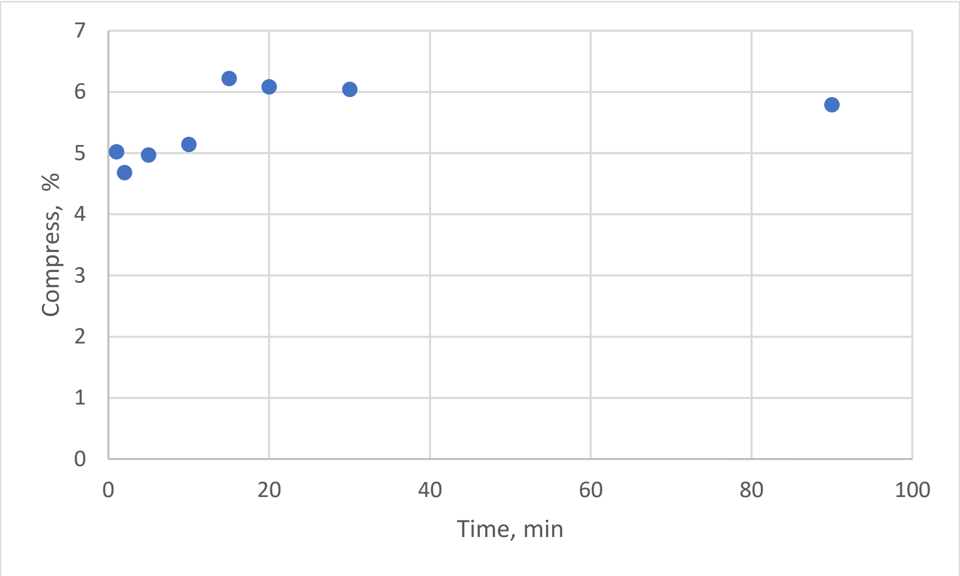

Figure 31 Compress as a function of time, 596 N

The press height of two measurements were monitored and the results are displayed in Figure 32. It was found that the majority of the compression takes place in the first second of the measurement, after which the press height steadily decreases thus steadily increasing the compression. This is caused by the increase of pressing force from the 30 N threshold limit to the compression pressure target value. The rate of compression is almost identical in both measurements.

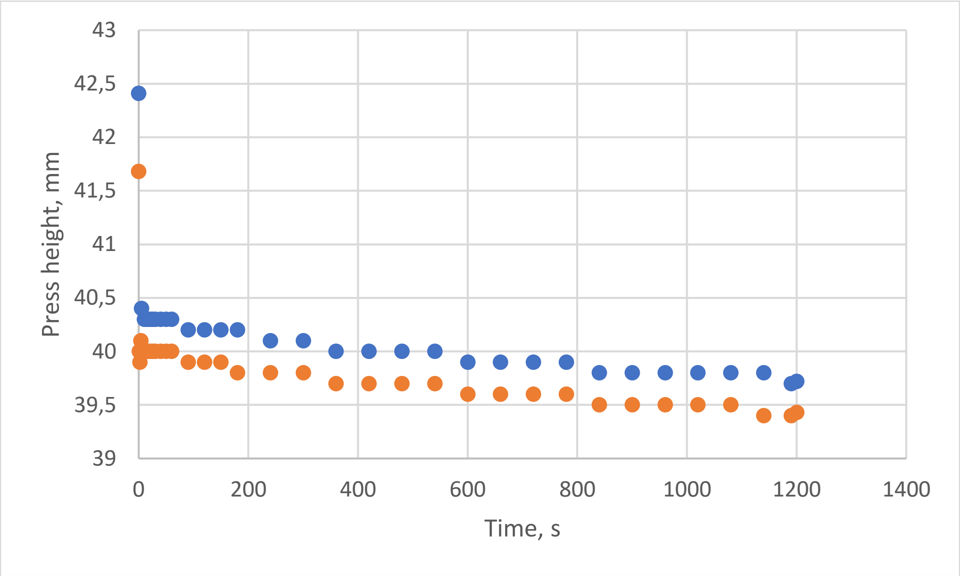

Figure 32 Rate of compression, 596 N

It was noticed that the volume which the fertilizer granules occupy decreases significantly when comparing sample at the pouring packaging density and a sample in compacted density. The Acap Easy measurement is dependent on the height which the piston reaches the surface of the sample, therefore the packing density of the fertilizer granules effect the measurements. The packing density of the fertilizers was altered by vibrating the samples in rig shown in Figure 33. The vibration were created by repurposed process sieve vibrator, which had a cup made on for the waste cup. The intensity of the vibrations were controlled by altering the current.

In the measurements the pressing force was 596 N, time 15 min and the mass of the sample 43.5 g. The studied fertilizer was 22-0-14. The sample was poured to the sample cup as normally and then the whole sample cup, waste cup rig was taken to the vibrator. Vibration insensitivity was varied from 20 to 60 % of the maximum current plausible and the vibration time was between 5 to 30 s. Most of the measurement points were done twice to decrease the uncertainty of the measurements.

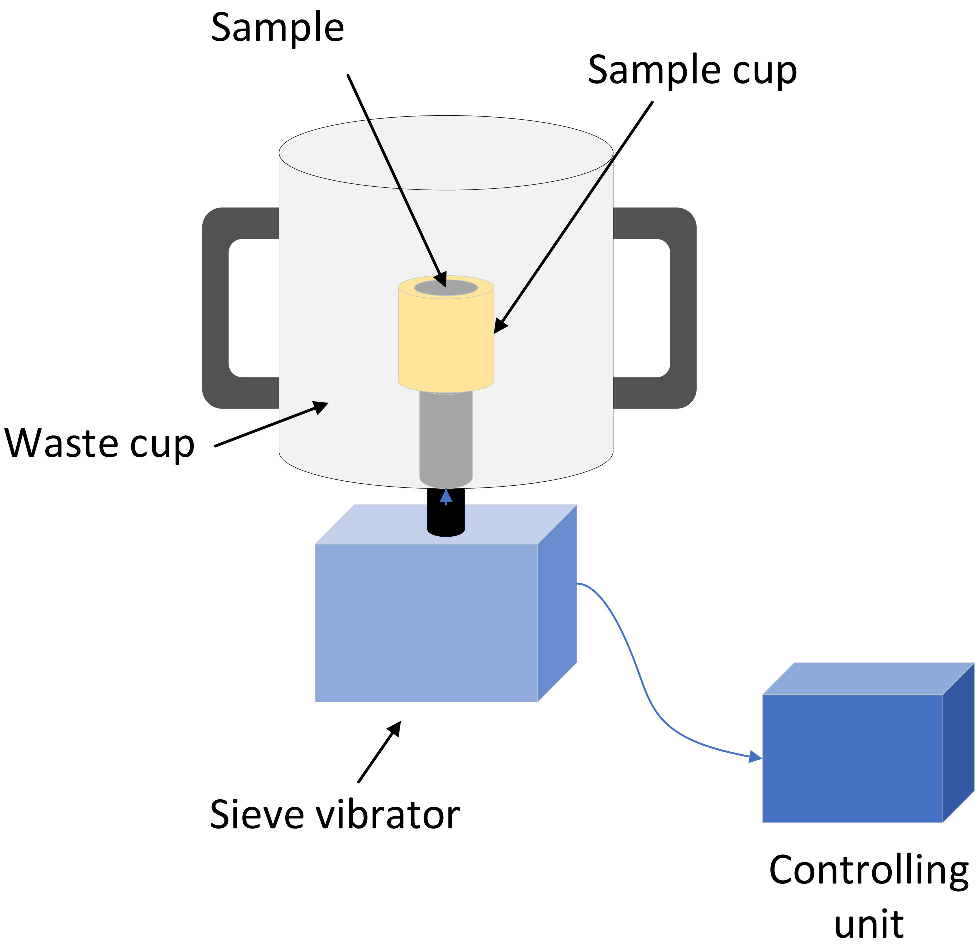

Figure 33 Vibrator rig used in the particle bed compaction

The optimal level of vibration was searched by altering the insensitivity and the duration of the vibration. Increasing both was found to decrease the compress values as seen in the Figure 34. Based on the datapoints the maximum particle bed density is achieved when the time*intensity reaches 1200.

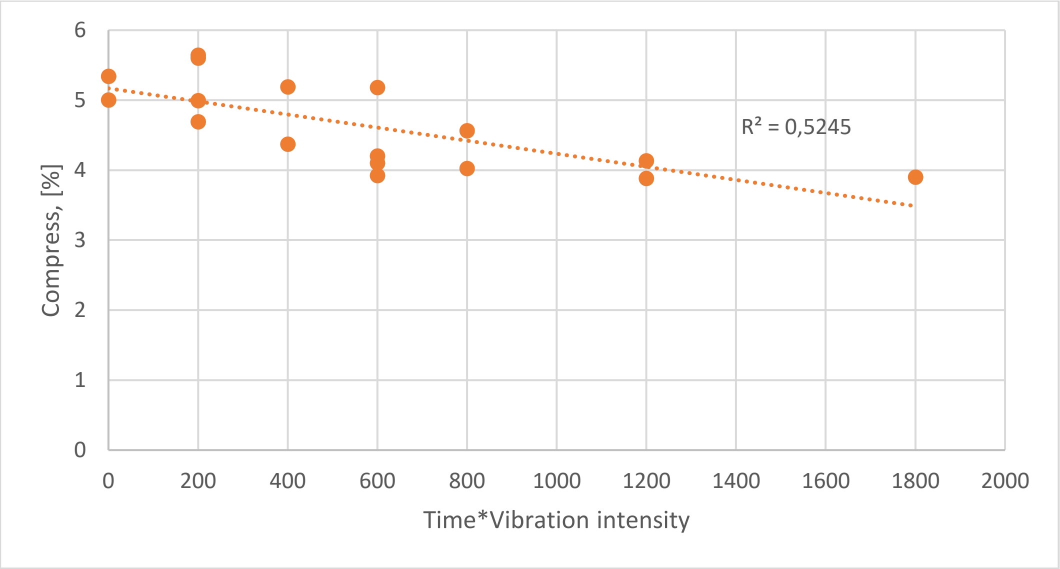

Figure 34 Effect of vibration time and intensity on the compression

The effect of the measurement starting length on the compression are presented in Figures 35 and 36. Figure 35 describes the relation between the compression value and the measurement starting length when the mass of the fertilizer sample is varied. The relation between the mass and the initial height of the measurement is linear with R^2 value of 0.992. The measurement is described in page 65. Figure 36 visualizes the effect when the starting length is modified by vibration. The conclusion from these figures is that the changing the fertilizer mass do not affect the compression value, but vibrating the sample does in some extent. Also, the vibration has its limits as seen in the Figure 36. The compression value does not decrease after the packing density of the fertilizer granules has reached its maximum.

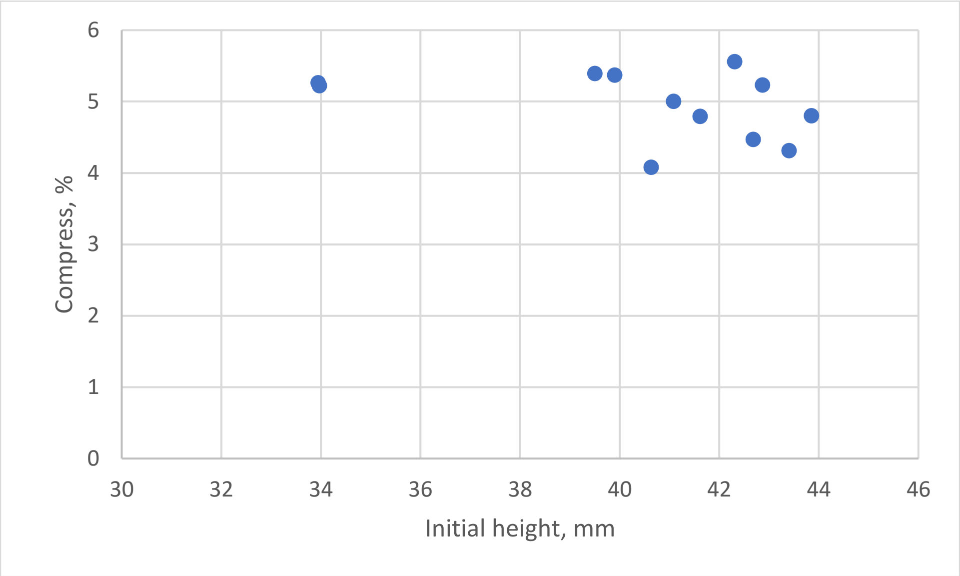

Figure 35 Compress as a function of initial length for different mass samples

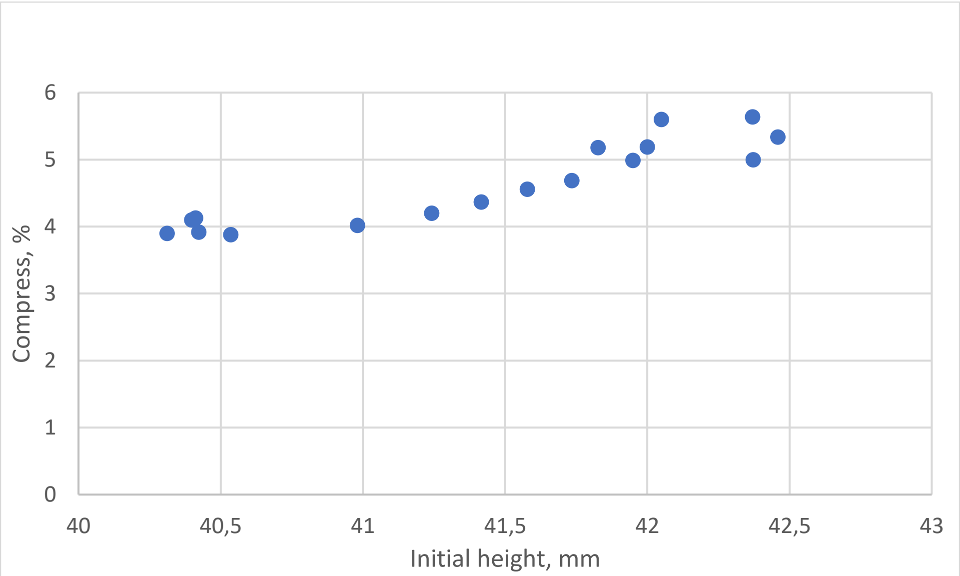

Figure 36 Compress as a function of the initial length of fibrate sample

The effect of vibrating the sample on reproducibility is visualized in Figure 37. There is clear level difference between the vibrated and ordinary measurements. The standard deviation between vibrated samples was 0.19 when the for the ordinary measurements it was 0.4. Therefore, by vibrating the sample the reproducibility of the measurements can be increased.

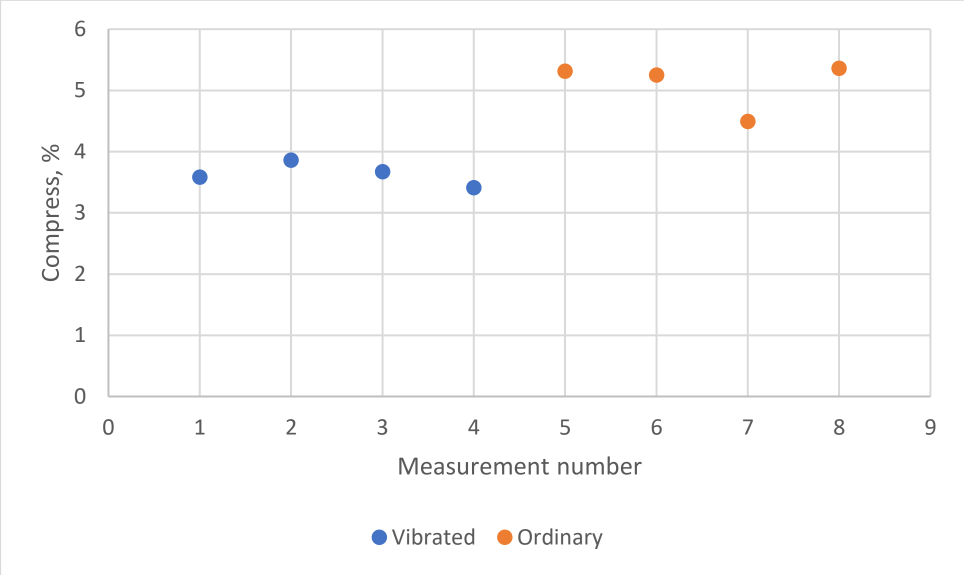

Figure 37 Comparison of vibrated and non-vibrated samples on the reproducibility of the measurements

7.3 Effect of fertilizer properties

The temperature, size and the moisture content were mentioned several times in the literature to have an effect on the caking tendency of granules. Therefore, the effect of those parameters on the results of the Acap Easy was studied. Also, the chemical composition has a major effect on the result. It is not studied directly, however the during the measurements its importance came imminent.

The effect of the temperature of the final product and the coating were studied. The effect of the temperature was measured both by heating and cooling the sample. The heating was done with hot air blower. The temperature was measured with infrared instrument. One sample was placed in a freezer to cool it down and the temperature was measured to be around -4 C before the measurement. These measurements were more focused on the effect rather than the actual numbers because during the measurement the temperature couldn’t being kept at a stable level. Also, the infrared instrument is only capable measuring the surface temperature. Therefore, the temperature inside the granules was left unknown. The measurements conducted showcased the increase of temperature resulting slightly higher compression values. The room temperature compression of the sample was around 7.4 and heating to 35 and 30 ℃ resulted the compression to increase 7.8 and 8.9 respectively. Cooling to -4 ℃ decreased the compression into 7 %.

For analyzing the effect of the particle size on the Acap Easy a sample of 22-0-14 was sieved into 5 fractions. The sample was taken from the final product conveyor using the standard sampling procedure. The sample was sieved by hand using standard hand sieves with sieve sizes of 4 mm, 3.2 mm, 2.8 mm, and 2 mm. The different fractions were collected into separate plastic bags. The amount of particles in fractions under 2.8 mm was too small to be measured.

In the compress measurements force of 596 N and time of 15 min were used. The mass of the sample was 44.75 g. Two sets of measurements were done. The first was done right after the sieving with the standard procedure. In the second set the sample was first vibrated as in the section 7.2.

The relation of particle size of sieved fertilizer on the compression is showcased in Figure 38. The relation is somewhat mixed. Sieved granules with smaller particle size have a larger compress, but when 20 s of high intensity vibration is applied the largest particles have the highest compression. For the largest particles the effect of the vibration is the smallest, but it is still unclear if it is about the measurement accuracy or do the larger granules pack themselves tighter when poured to the sample cup.

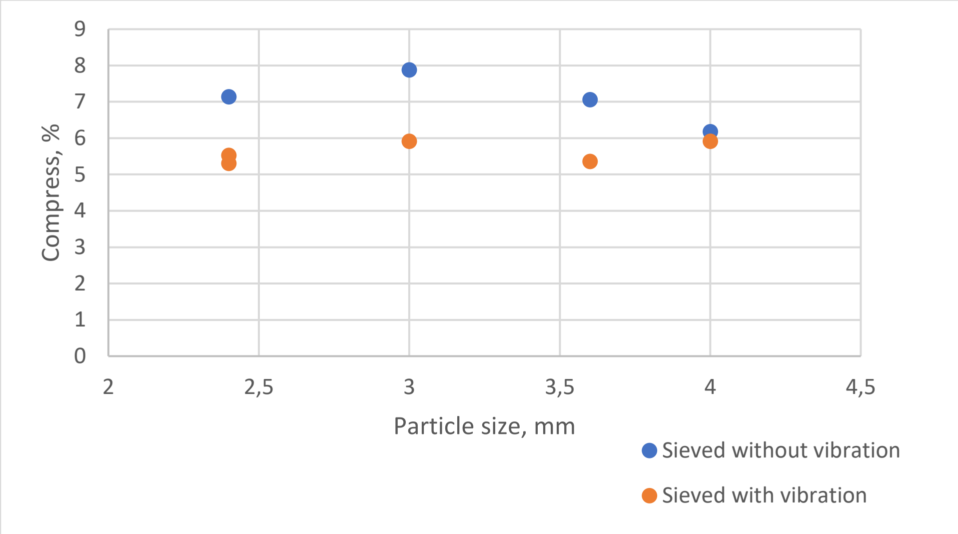

Figure 38 Particle size effect on compress.

To study the effect of moisture on the results of the Acap Easy samples of fertilizer were subjected to high relative humidity conditions. The primary sample was divided into six 500 ml plastic bottles after thorough mixing. Roughly 1 mm holes were punched to the sides of the bottles to let the moisture to have more entry points to the sample. The mass of empty bottles was measured before filling. The bottles were filled with fertilizer so that the combined mass of each bottle was the same. A small amount of water was put at the bottom of a bucket. The sample bottles were then placed at bucket, the water level was monitored to ensure no water reaches the height of the pierced holes. The bucket was sealed with plastic

A FLIR EM54 humidity meter was used to measure the relative humidity inside the bucket. The humidity was measured by punching a small whole to the plastic cover and inserting the humidity meter through. The humidity meter took a long time to settle to a value, therefore the values were estimated from the meter readings at first. When the meter was left to for longer periods of time to measure stable values were gained. Figure 39 shows the test setup with the relative humidity measured.

Figure 39 Testing equipment for fertilizer moistening

After measuring the humidity, the cover of the bucket was removed, and the mass of the samples were weighed. Before weighing the outside of the bottles were carefully dried to ensure the difference of mass is related only the amount of water adsorbed by the fertilizer. One of the samples was taken for analyzing the compress, KF-moisture content and the 16-hour caking tendency. The compression was taken immediately. The KF samples were done within a day and the 16 h measurements were done collectively when last of the bottles was removed. The samples were stored in plastic bags avoid any moisture loss.

The effect of the moisture was measured twice. In the first measurement a sample of 22-0-14 was taken from the final product conveyor. The combined weight of the bottle and the sample was measured to be 630 g. In the measurements four out of the six bottles were uncapped. The uncapped bottles were removed at a moistening time of 4, 21, 28 and 45 h. The caking index measurement was done after the 45 h sample was removed from the moistening. The remaining 2 bottles which had caps on were 1 week in the moistening. The relative humidity inside the bucket was between 90 to 100 %.

In the second measurement the sample was 23-7-10 taken from the final product conveyor. This time the amount of the holes in the bottles was doubled and all the bottles were capped. Five of the bottles were placed in the bucket to adsorb moisture and one was left at room conditions to act as reference. The mass of the bottles and the RH in the bucket was measured daily. The relative humidity was around 90 to 100 %. Samples were taken to further analysis on after 2 and 4 days of moistening. The caking index measurement was done on the fourth day.

The increasing moisture content was seen as increased compression values. The results are presented in Table IV The relation between the increase of compression and the increase of the water content of the sample is not uniform between the measurement. In the measurement 2 the slight increase of water content caused much larger increase in compression. This might be due to the difference in the chemical composition of the samples.

Table IV Results of the moisture effect on compress, 596 N 15 min

Moistening time, h	Sample mass, g	Compress, %	KF-moisture, %
Measurement 1			
0	630	7.49	0.4
4	630.16	7.57	0.5
21	630.85	7.62	0.6
28	631.05	7.08	0.5
45	631.86	8.17	0.6
Measurement 2			
0	639,85	4.32	0.2
48	640,85	10,43	0.3
96	641,85	11.37	0.5

The effect of the coating was measured by taking a sample of 22-0-14 before the coating drum and comparing the results of the measurements made from the coated granules. In the comparison of the uncoated and coated fertilizer compression, it was found that the coated fertilizer had slightly higher compression values, this is in line with findings of Walker (1997). The cake crushing strength of the uncoated samples was significantly higher than of the coated ones. This means that the coating successfully prevents the particles to join one another during the compression.

8. Laboratory measurements

In the current laboratory measurements, the caking tendency of the fertilizer is measured by holding the fertilizer under pressure and then measuring the formed agglomerates. Laboratory measurements are made from the daily collection, bin, packaging, and shipment samples.

The procedure of the laboratory measurement is following. A well-mixed and cooled 90 ml sample of fertilizer is put to a small plastic bag. The bag is sealed, and two small holes are punched to each end of the bag. Five sample bags are put to the pressing device. A metal plate is placed between each bag and covering plates are put on the top. A steel ball is placed between the covering plates and the lever. Weight is added to the end of the lever to create the pressure to the sample bags. The samples are kept approximately 16 h under pressure.

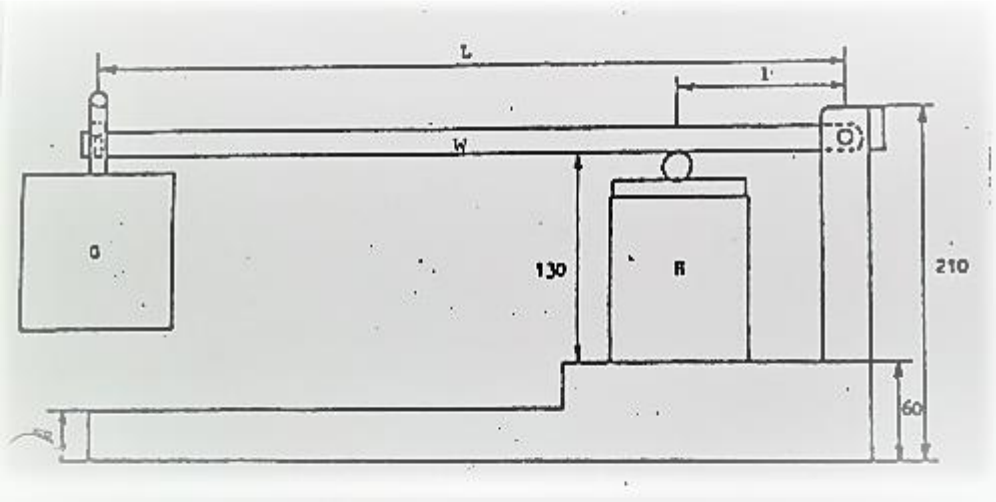

Figure 40 Schematic of the lab measurement pressing device

After applying the pressure, the bags are carefully removed from the pressing device and then dropped twice through dropping tower so that the bag is dropped both of its sides once. The height of the tower is 48 cm. The bags are then opened and poured carefully to 7.1 mm sieve and sieved. The caking index is calculated based on the mass retained on the sieve, Equation 36.

$$Caking\ \% = \frac{m_{over}}{m_{over}+m_{under}} * 100\% \tag{36}$$

where, m_{over} mass retained by the sieve

m_{under} mass under the sieve

It was noticed that usually there was some agglomerates present when the small bags were taken out of the pressure. In most cases they fell apart when the bags were dropped resulting 0 % of caking index. To get a better understanding how often agglomerates formed, the appearance of the bags was evaluated before the dropping. The evaluation was done on a three stage scale. If the bag was completely loose, the appearance is evaluated to be 0. Value of 1 is given when there is some agglomerates visible. If the whole bag has turned into solid agglomerate, it is evaluated as 2.

The 16 h laboratory measurement was modified to simulate better the dimensions of fertilizer stored in 700 kg bulk bags. This was done by replacing the five 90 ml bags with one 400 ml bag, which shape better represented the bulk bag. For studying the effect of compressive pressure to the sample a new pressing rig was designed with a longer lever arm of 75 cm. Eight locations for the weight were made at 5 cm distant to increase the measurement possibilities. Figure 41 shows the modified caking test design. The principle of the caking index measurement stayed otherwise the same in the 400 ml sample bag test.

Figure 41 400 ml samples set under pressure with 75 cm lever arm

Table V and Table VI contain the data of the caking index measurements made from the pile samples done with the 90 ml bag size. Table V contains the appearance values of the caking index measurements before the dropping. The amount where no agglomerates where found was only slightly over one fifth, whereas the majority of the measurements some agglomerates where formed. When comparing appearance values to actual caking index results it can there is striking difference. Only 8 % of the measurements had a caking index over 0 % when 78 % of measurements had agglomerates formed. This means that the dropping of the bags has major significance for the low caking index measurement values.

Table V Appearance of 36 pile sample caking index measurements

Appearance	Value	Amount	Proportion, [%]
No agglomerates	0	8	22.22
Small agglomerates	1	24	66.67
Totally solified	2	4	11.11

Table VI Caking index results corresponding to Table V measurements

Caking index	Amount	Proportion, [%]
0	33	91.67
0>	3	8.33

8.1 Reliability of the laboratory measurement

The reliability of the laboratory measurements was studied by making several parallel measurements from the same sample and keeping the measurement parameters as close as possible.

The results of the normal caking index measurement with 5x90 ml sample and the modified 1x400 ml samples were compared throughout the measurements to get a picture how the two types compare. The 90 ml bags were pressed with the 50 cm arm and the 400 ml bags typically with 75 cm arm.

The post reactions require time to reach equilibrium. It is commonly spoken that the fertilizer has to mature couple days in the storage bin to ensure good physical product quality. This was studied by taking multiple samples from the same pile at consecutive days and measuring the caking index.

8.2 Effect of the measurement parameters

The parameters which could be altered in the measuring device are the pressure applied to the samples, the pressing time, and the dropping height. During the measurements it was also discovered that the tightness of the sample bag effects the results.

The effect of pressure was measured by changing the position in which the weight is on the lever arm. The measurements were done with the 400 ml bag size and the weight position varied from 45 to 75 cm. To further increase the pressure applied one measurement was done with 2 weights added to same lever arm at distance so total distance of the weights was 130 cm.

The results of changing the pressure to the caking index turn out to be somewhat inconclusive on the 400 ml bags. The results are presented in Table VII. There is no linear correlation between the caking index values and the amount of pressure applied to the samples. In the experiments 1 and 2 the sample bags were dropped once at 30 cm height but in experiment 3 no drops were made to reduce the number of possible errors sources. Different sample was used in every experiment. The results showed still a mixed effect. The connection between the pressing force and the caking index is poor. For example, in measurement 3 the caking index rose, when the pressure was increased to 126 kPa, but the 145 kPa measurement indicated much lower caking index value. This indicates the poor reproducibility of the 400 ml sample bag size.

Table VII Effect of the pressing force on the 400 ml caking index measurements

Experiment	Caking index, %	Appearance	Lever length, cm	Pressure, kPa
1	12	1	75	145
1	27	2	65	126
1	1	1	55	107
1	15	1	45	87
2	16	1	75	145
2	24	1	65	126
2	16	1	50	97
2	24	1	130	252
3	40	1	45	87
3	74	2	55	107
3	85	2	65	126
3	48	1	75	145

The effect of time under pressure was tested by both measurement devices. Two samples of 5x90 and 5 samples of 400 ml bags were made. The 90 ml bag tests were pressed 16 and 88 hours. One the 400 ml bags was pressed the normal 16 hours and the time under pressure was increased in 24 h increments up to 112 hours. The test was done in the 400 ml bag with 75 cm lever and the 5x90 ml bag with 50 cm normal lever.

For the 90 ml bags the effect of the time was small. The caking index increased from 0 % to 1 % after the 88 hours. However, the visual inspection showcased that the caking was more severe in the sample bags hold longer under pressure. The increase of the pressing time in the 400 ml bags gave somewhat mixed results, showcased in Figure 42. The overall trend of the caking index is increasing, but the variation between the measurement is large. Especially the sample hold the longest time under pressure indicating the lowest caking index is striking.

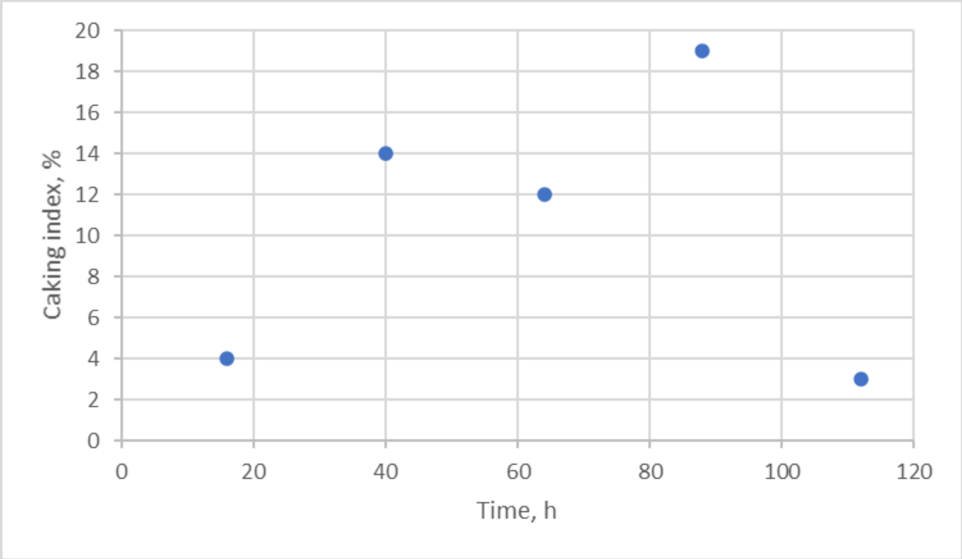

Figure 42 The effect of time under pressure to the 400 ml bag caking index

The effect of the dropping was measured by altering the height and the number of drops. Also, some tests were done without dropping the sample at all. However, this was typically not planned, but being a forced decision based on ruptures found on the small bags. The heights used varied from 50 cm to 24 cm. The bags and bags dropped at lower height or not dropped at all had higher caking index. In the 90 ml bags samples dropped at 48 cm had 8 % caking index. Bags dropped at 24 cm had 16 % caking index. Without dropping the caking index was 32 %.

During the measurements it was found that there is a factor causing errors to measurements of 90 ml sample bags. It was recognized that bags which were tighter caused higher caking index results. This phenomenon was studied by making deliberately some bags as tight as possible and comparing the results to bags which were made significantly looser. The difference between the tight and loose 90 ml bag is demonstrated in Figure 43.

Figure 43 Size of the loose and tight 90 ml sample bag

The bag tightness on the results of the 400 ml bags was also studied by making one bag as tight as possible, one relatively tight and one totally loose bag.

The results of 90 ml bag tightness on the caking index values is presented in Figure 44. Tighter sealing of the bag significantly increases the caking index value of the 90 ml bags. This could be caused by increase of packing density, but also with the decrease of the surface area of the bags thus increasing the pressure applied to the samples. However, in the 400 ml bags there was no such effect to be found.

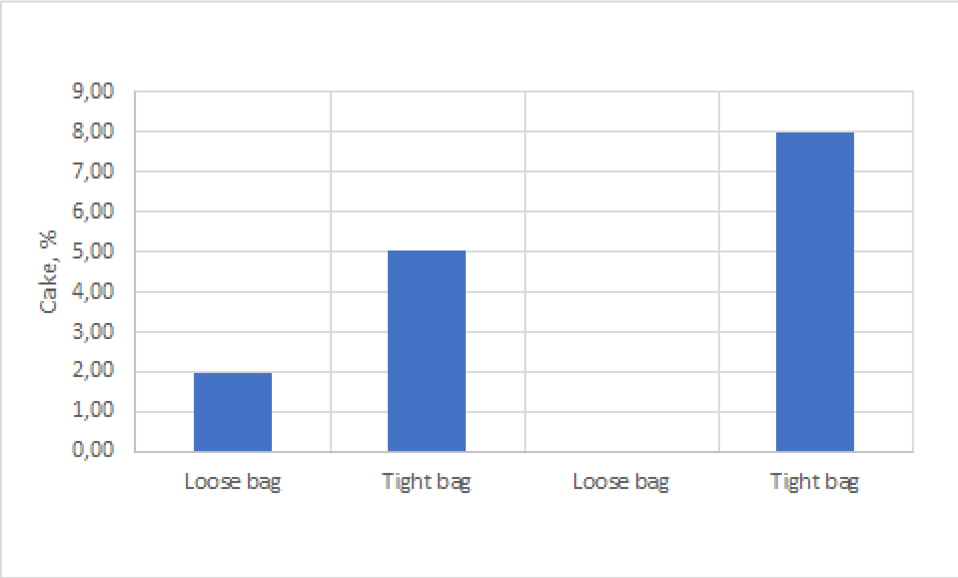

Figure 44 Effect of the 90 ml sample bag tightness of two different measurements on the caking index value

8.3 Effect of fertilizer properties

The effect of temperature, moisture and coating were tested as the in the literature these were found to be major parameters when considering the caking tendency of fertilizers.

The temperature effect was tested by using heating cabinet which temperature was altered. The temperature setting was varied between 30 to 35 °C. Temperature values were also measured by an infrared thermometer. There was difference of couple centigrade, between the bottom and the top part of the samples, but the average temperature was around 35 °C. The difference of temperature was identified to be caused by the heat conduction of the metal parts of the measuring rig from the floor of the heating oven.

Making the caking index test in elevated temperatures caused mixed effect on the results. The measurements done in 90 ml bags showcased similar caking index values in room temperature and in the higher temperatures. Even increasing the pressing time did not made any differences. The 400 ml bag on the contrary showed significant differences. Some grades were not significantly affected by the temperature at all, but 22-00-14 especially was very sensitive to the heat. This is visualized in Figure 45, the fertilizer measured in the 35 °C had compressed significantly and the whole bag was strongly solidified as the sample measured in the room temperature only had minor agglomeration formation. The 22-00-14 was also the only fertilizer that had higher caking index values in the 90 ml bags at 35 °C.

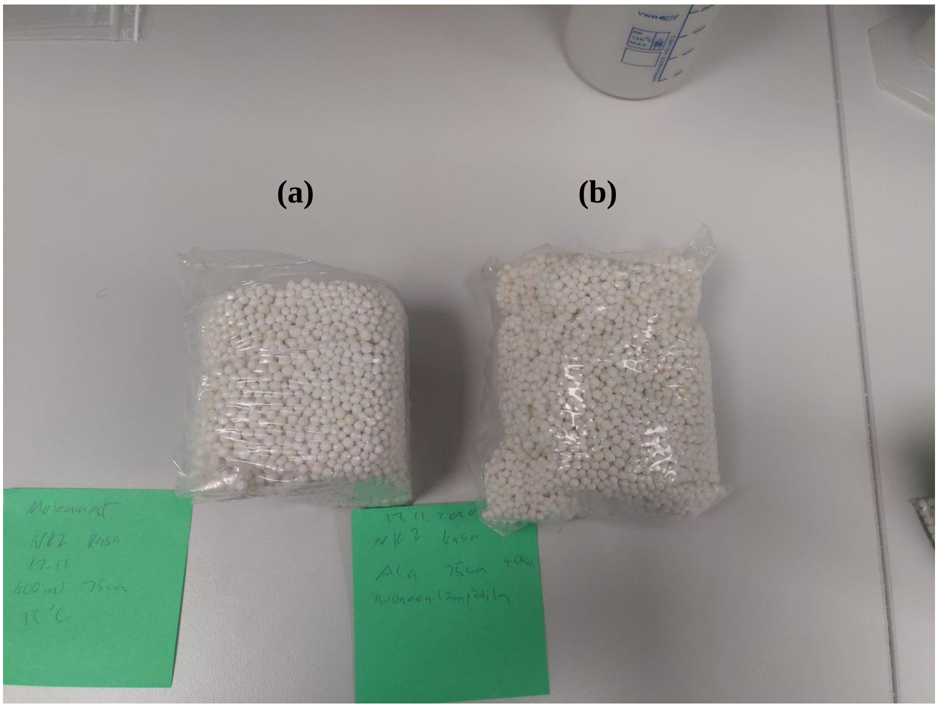

Figure 45 Sample in 35 °C (a), compared to sample in room temperature (b)

Figure 46 contains the results of the measurements done comparing the effect of temperature. Test 1 is 22-00-14 which had completely solidified during the compression. The tests 1-3 were dropped once from 30 cm height and the test 4 and 5 were not dropped.

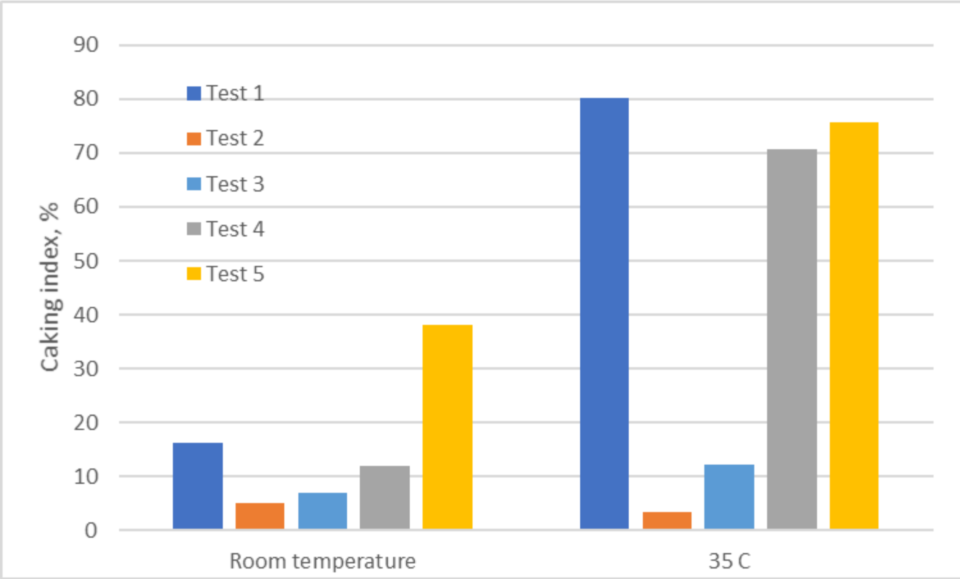

Figure 46 The effect of elevated temperature on 400 ml sample bag caking index

The comparison of the laboratory temperature, packing sample temperature and the pile temperature is shown in Figure 47. The target for laboratory temperature is 21 °C, so it is used as a benchmark in the comparison. The pile and packaging are polynomial fits for the measurement points. Sample temperatures are clearly dependent on the season. During the summer the temperatures in the pile and packaging are higher than on laboratory, but during winter the temperature in the pile is lower. This means that the caking measurements conducted during the summer tend to underestimate the caking tendency, because the samples are cooled to the room temperature. On average the packing and pile temperatures differ couple degrees.

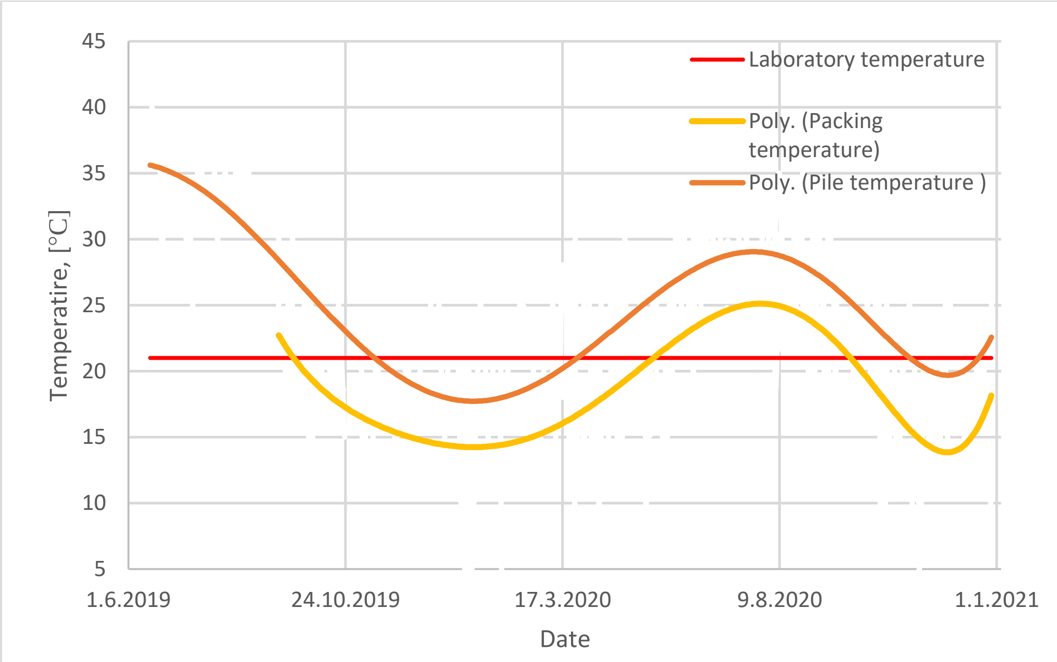

Figure 47 Comparison of the pile, packing and laboratory temperature

The procedure how the samples were moistened is presented in section 7.3 page 77. When testing the caking index, the samples were put into the 400 ml bags and the length of the lever was 75 cm. The bags were dropped once at height of 30 cm.

Measurements of the fertilizers subjected into high relative humidity showcased the degradation of the physical quality. The results are presented in Table VIII. However again in this measurement the repeatably of the 400 ml bags showcases poor performance as the results have a lot of deviation. Still the overall trend of increased caking tendency can be detected in both measurements.

Table VIII Caking index results of the moistened samples, 400 ml bags 75 cm lever

Moistening time, h	Sample mass, g	Caking index, %	KF-moisture, %
Measurement 1			
0	630	-	0.4
4	630.16	28	0.5
21	630.85	22	0.6
28	631.05	6	0.5
45	631.86	79	0.6
Measurement 2			
0	639.85	0	0.2
48	640.85	40	0.3
96	641.85	20	0.5

Brief test of the effect of coating was done from sample of 22-0-14 taken prior the coating drum. Part of the same sample was used in the test done by the Acap Easy. A single bag of 400 ml with 75 cm lever arm was measured and compared to sample which was coated and taken at the same time from the process. The uncoated sample had a caking index of 91 % which was significantly higher than the 56 % of the coated sample.

9. Other measurements

Other measurements were made from the same samples to increase the depth of studies and find correlations between the measurements. These measurements consisted of bulk bag sampling, polarized light microscope and XRD analysis.

9.1 Bulk bag sampling

Random samples were taken from the packaged products to see how the measured values corresponds with the reality. The principle of the random sample was to open the bulk bag and see if there was setting or caking occurred. The fertilizer samples were typically taken from piles which had been packaged two weeks prior to opening. This left some room for caking or setting as the caking mechanisms need some time to have an effect. The bags were mostly from the bottommost row of the stack because it had the highest force pressing the fertilizers. Other rows were also studied if there was a suspicion that there could be setting taking place.

The bag openings were filmed to see the behavior of the fertilizer when bag was opened. Samples were taken from the formed lumps to detect possible causes for the caking and setting. The storage time of the fertilizer in the bag, in the bin and in the surface of the bin were used in determining the history of each packaging batch.

In the bulk bag random sampling a total of 69 bags were opened. The results cannot be used as a direct indication for the quality delivered to the customer as the random sampling was concentrated on packaging runs which were suspected to have setting problems. Also, the bottom row was given an emphasis. Still a clear pattern on the setting and caking tendency and the pressure applied to the fertilizer was seen. The bags placed in the bottommost row are the most prone to cake formation. However, there was occasions when the bottommost row was free flowing, but the middle layer had setting problems. This implies that the pressure is not the sole cause of the setting in the bags. The samples taken from the bulk bags showcased typically good results of physical quality measurements, even if taken directly from the formed agglomerates. In few measurements slight increase of compression and KF-water content was found, indicating fertilizer being adsorbing water.

When comparing the time stored as bulk and in the bag to the found cakes in general interesting relations can be seen. Short storage time in bulk seemed to have connection with the lumps found in the second layer bags, but longer storage time increases the time of cakes found in the 3rd. layer. This relation needs further investigation as the number the random samples was still relatively low. The time stored in the bulk bags seems to increase the amount of cakes found, but still not too harsh conclusions can be made from these results.

Closer inspection of the fertilizer lump found in the bag is showcased in Figure 48. The breaking of the lump has left significant amount of dust and fines in the hand. This was typical when inspecting the formed lumps. This means that the solid bridges between particles have broken during the breaking of the lump as the fertilizer granules themselves did not break. Lump itself was easy to break, therefore even in case of setting the solid bridges are present. Typically, the formed lumps were easy to break and mostly even a slight touch was enough to separate the granules. Visual inspection of the granules typically showed some crystal growth and “lighter spots” in the granules indicating post reactions followed by recrystallization. In the collected videos it was noticed that lumps described to be setting were often located at top of the bag, but when caking occurred the whole bag was solidified.

Figure 48 Breaking a fertilizer lump in a hand

9.2 Polarization microscope

Three samples of 22-0-14 were sent to be analyzed by a polarization microscope. The samples were taken from different bin samples of the same production run. The samples had different results on the caking index measurement. The purpose was look, if the images of the polarization microscope showed any traces of the post reactions.

The sample for the polarization microscope was prepared by carefully grinding the individual granule to wanted thickness using sandpapers sizes from 240 to 2000. First the granule is grinded on one side. When enough material is removed, and the surface is even, the grinded surface is glued on an object glass. The remaining half is grinded after the glue has dried. Grinding is done until the sample is thin enough to surpass light.

The measurement was done using Olympus BH-2 polar light microscope. The light source was a halogen bulb and 530 nm retardation plate was used. Camera used was Deltapix 6EIII and Insight basic software was used. A total of six polar light microscope samples were prepared and analyzed. A comparison sample of 15-15-15 fertilizer was made from product with severe physical quality problems.

Figures 41 and 42 showcase polarized light microscope images. In Figure 49 is shown an image from 22-00-14 fertilizer granule. The image showcases well the onion-type structure of granule formed by layering. There is individual salt crystals mixed to the fertilizer matrix. The borderlines between the crystals and the fertilizer matrix are sharp. This indicates that the crystals have not taken any post reactions. There was no major difference in the appearance of the three samples of the same production run.

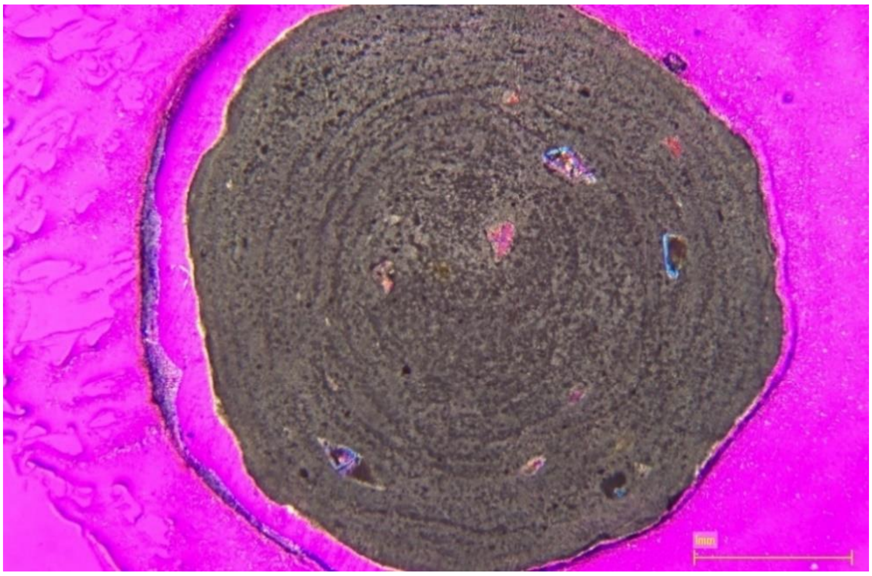

Figure 49 PLM image of 22-0-14 granule

Figure 50 on the other hand showcases an example situation where significant amounts of post reactions have taken place. The image was taken from a customer reclamation sample. The granule has initially had a large amount of crystals in it, which are then reacted, seen as the white spots. Only small amount of unreacted crystal can be identified in the blue spots. Due to the severe post reactions the structure of the granule is compromised. A collection of cracks and pores can be seen.

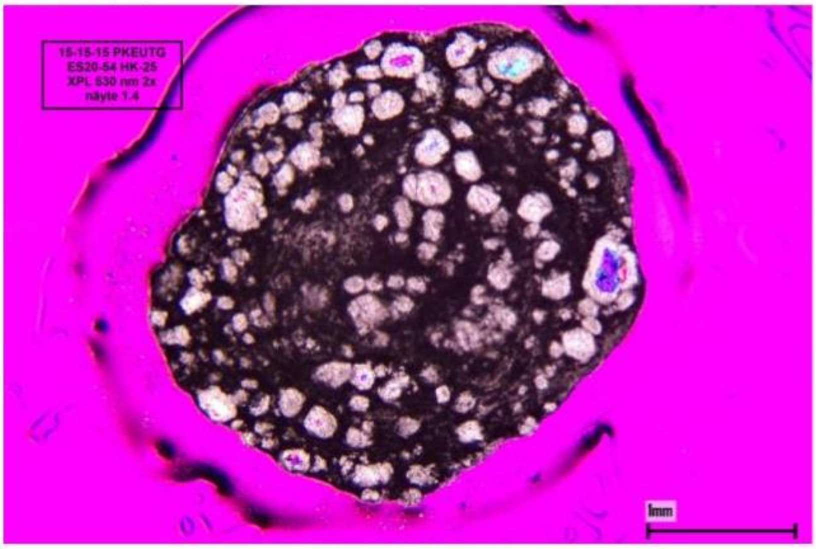

Figure 50 PLM image of 15-15-15 granule with severe caking problem

9.3 XRD measurement

It was noted that the sample bags of 22-0-14 contained significant amount of dust, visualized in the Figure 51. The caking index made from the same sample showcased a tendency of cake forming. Therefore, more advanced measuring methods were used to analyze the chemical composition of the dust. The dust was separated from the rest of the sample by sieving. The total mass of the obtained dust was 2 g. Therefore, only a qualitative analysis was plausible. XRD-cubix3 DY3600 instrument from PANanalytics was used in the analysis.

Figure 51 Dust found in the sample bag of 22-0-14

Figure 52 represents the XRD measurements results from the dust gathered from the 22-00-14 pile sample bag. The measurements indicate that the dust was mainly formed from boussingaulite and ammonium-potassium nitrate salt. The ratio of the K and the NH_4 is approximately 1/8, which could be N3 phase. Also, small amount of talc powder was found.

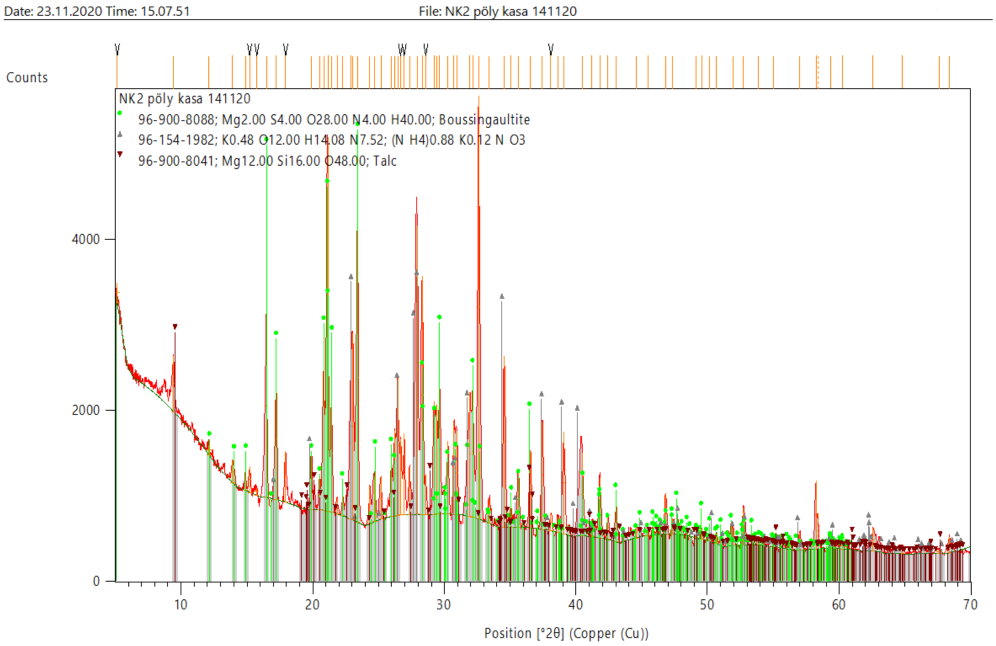

Figure 52   XRD measurement results of the 22-00-14 dust sample

Based on the comparison of the PLR images and the XRD results it can be deducted that the post reactions had taken place within the fertilizer matrix. The small amount of crystals indicates good conversion of MOP and the AS not being crystallized in the reactors. The formation of boussingaulite indicates water adsorption and the potassium-ammonium salt could be caused by the phase change within the granule.

10. Discussion

The data of reclamations about the setting and caking is break down to visualize, the relation of production and packaging. The time fertilizer stored as a bulk and in the bags are also visualized. The data is taken from the reclamations made during summer 2020 and partly from 2019.

The dependence of the bulk bag packaging date on the reclamations is visualized in Figure 53. The amount of reclamations on the fertilizers packed in summer 2019 is significantly higher than on other seasons. There are some spikes on April and December. These represent only single product runs of 24-5-5 product.

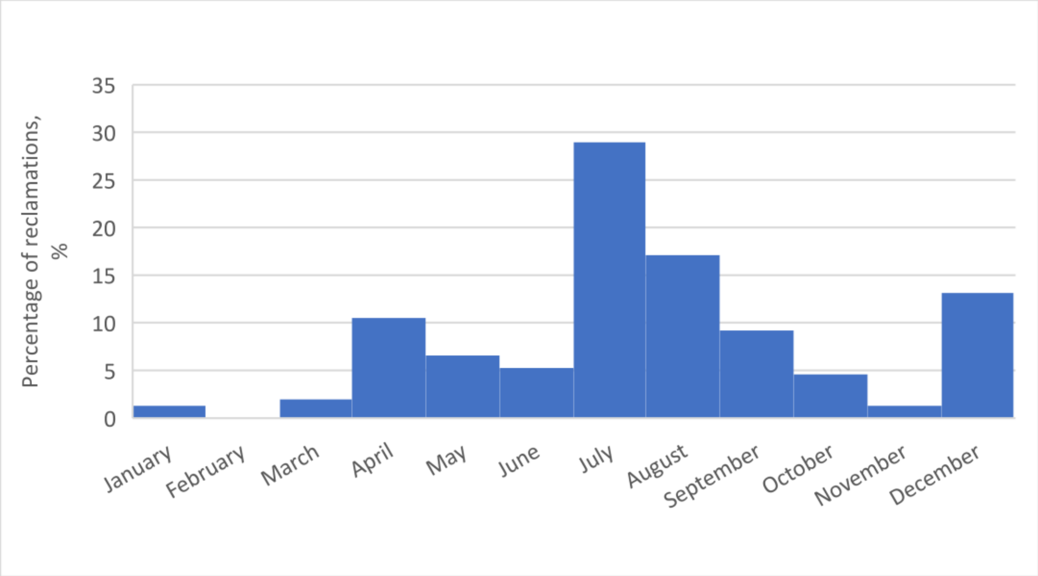

Figure 53 2019 fertilizer setting reclamations per packaging month

Figure 54 displays the relation between the production month and the amount of reclamations. The amount of reclamations is normalized with the monthly production. The figure confirms that the reclamations are mainly done from summertime production runs. The 24-5-5 reclamations were not counted in the figure.

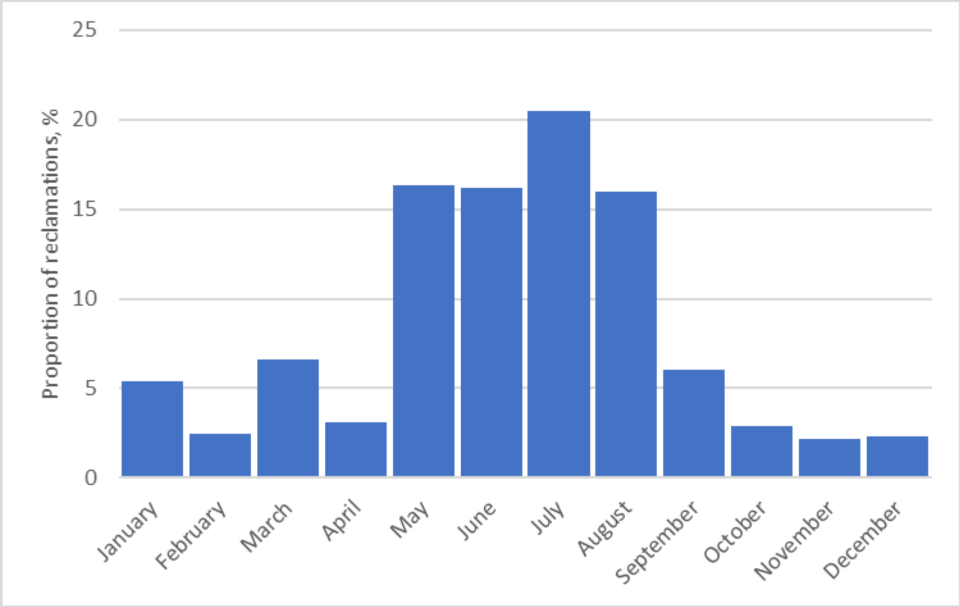

Figure 54 2019 production normalized fertilizer reclamations per production month without the 24-5-5

Comparison on the normalized time stored in the bulk to the amount of reclamations is shown in Figure 55. The normalization is done by taking account the typical duration that fertilizers were stored as bulk. The relation between the time stored in the bulk and the amount of reclamations the gives somewhat mixed results. There is a lot of variation between the different storage time intervals mainly due to the outside variables such as which product was packed and when it was packed. However, it seems that long storage times in bulk do have a negative effect on the fertilizer's quality and at least the long storage time do not improve the quality. The time for the post reactions to reach equilibrium is most likely countered by the humidity from the surrounding air.

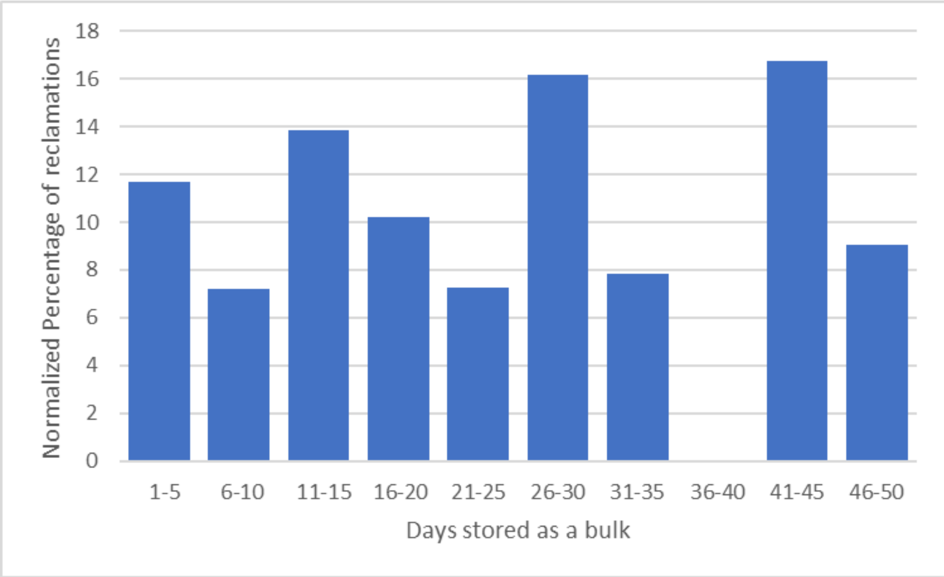

Figure 55 Effect of bulk storage time on the number of setting reclamations

The relation between the time stored in the bulk bag and the amount of reclamations is shown in Figure 56. The time stored in the bulk bag does not have great effect on the amount of reclamations when comparing the amount of reclamations between 0 and 250 days of bulk bag storage. The high values of 250-400 days of storage correspond to production of the previous summer.

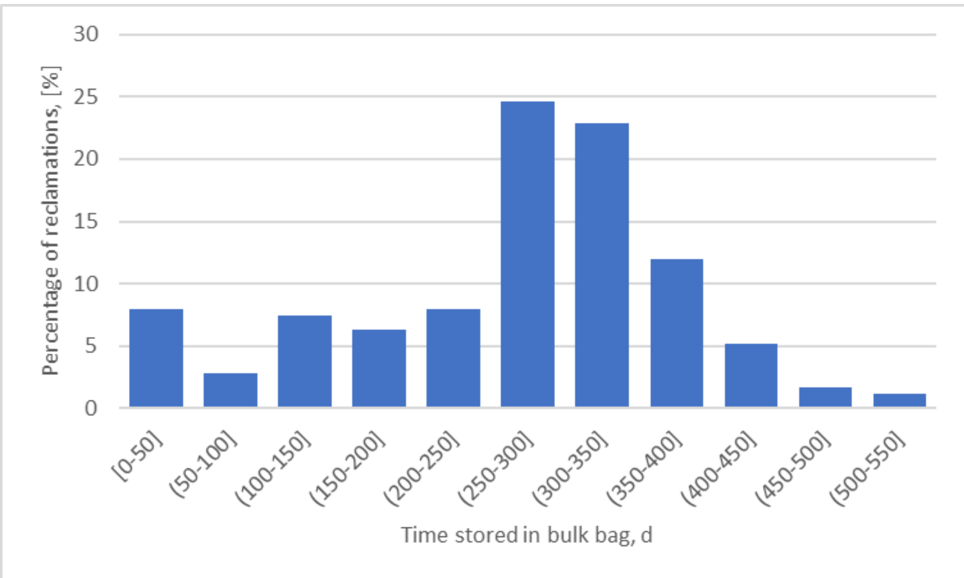

Figure 56 Effect of bulk bag storage time on the reclamations

When comparing the locations where the bagging was done it was found out that 30 % of the reclamations were from fertilizer which was first transferred as a bulk before packing. Most of this is caused by the reclamations made from 24-5-5 as 60 % of the reclamations were made of it. From the total amount of packed fertilizer this corresponded 8%. To make the situation even worse no physical quality testing is done for the packaged product.

Based on this analysis it can be seen that the season of the year has clear effect on the amount of reclamation. Also, the fertilizer that has been transferred in bulk had almost 4 times the reclamation tendency than the fertilizer packaged on site if the 24-5-5 is considered. If not considered the effect on caking tendency of the bulk transport is only slightly higher. The deteriorating effect of transportation in bulk is most likely caused by fertilizer being subjected to moisture. The surface area where the fertilizer can adsorb moisture is significantly increased when comparing the train carts to the storage pile, which increases the amount of fertilizer effected by the moisture. In the moistening tests, samples with more surface area with the humid air gained weight more quickly. Some samples gathered from rail bulk transport showcased very poor physical quality in measurements and significant increase in the water content. This means that the possibility of water contamination during transport is real threat.

The effect of the summer is more complex. The most obvious effect is the change in weather, the temperature and the amount of rain are the highest during the summertime, thus leading into relative humidity conditions decremental to fertilizers. Therefore, preventing the outside air entering the warehouse is needed, otherwise the humid air will be adsorbed by the surface layer of the fertilizer pile.

The high summer temperatures also effect the manufacturing process. The first cooling in the cooling drum uses dried outside air. Therefore, when the temperature of the outside air increases the efficiency of the cooling drum decreases. The second cooling step has to then cool the fertilizer more rapidly. This might cause some supercooling to take place, but it was not studied within this thesis. The more tangible effect is the increase of the final product temperature, the hotter fertilizer will have more post reactions and will have lower CRH, which further increases the tendency for water adsorption. The volume change of the post reactions can puncture the coating of the fertilizer thus even further increase the water adsorption behavior.

The compression results of the ACAP Easy only tell how much the particles deform under pressure, which is only undirect measurement of the setting and caking. Some types of fertilizers possess very high compression values, but no reclamations are made. Although this could also be caused by the reclamations not reaching the production unit. On the other hand, fertilizers with very low compression have still formed cakes. A good example of the compression value giving false security is the results achieved when compressing the uncoated product. The compression values were lower in uncoated than in the coated, even if it is commonly known that uncoated granules will definitely form cakes.

The crushing strength of the formed caked measures directly the strength of the adhesion forces between the particles, but it was not used due to the previous studies conducted from the ACAP Easy. The ACAP Easy instrument does not reliably detect the correct force, due to the formed cakes being so fragile. Typically, the cakes tended to break before the actual measurements. This has caused the measured values to be sometimes orders of magnitude too high as the instrument does not detect if the cake has already broken. The actual values can be manually gathered from the measurement data. However, this works only when the cake was actually broken by the Acap Easy. The real crushing strength values do correlate with the increased caking tendency in comparison of the pressure, time, coating, and the moisture. Especially samples that were subjected to increased levels of humidity showcase high crushing strength.

Deteriorating of the physical quality during storage could partly explain why the measurements are unable to detect the caking tendency. Especially storing the fertilizer long time, makes the initial ACAP Easy and caking index measurements somewhat obsolete as they do not predict the humidity adsorption behavior or even the effect of temperature. However, the caking index measurement done from the packaging samples rarely shows indication of setting. The caking index measurement has the problem of being insensitive, because of the violent dropping of the bags. The other problem lies in the sample taking, as it covers the whole packaging run. The pile surface exposed to the elements is thoroughly mixed with the unexposed good quality fertilizer. And also, as the pile samples are taken from above the bin the quality below the reach of the sampling spear is unreachable and thus not being measured in the 16 h caking tests.

The adsorption of water on the other hand is not the sole cause of the setting and caking. As shown in Figure 57, high nitrogen content increases the water adsorption rate. However, in the reclamations the proportion made from high nitrogen fertilizers was small. Therefore, the water adsorption by itself is not the biggest cause of setting and caking, but the effects it causes to the chemistry of the fertilizers, mainly in form of the post reactions. For the post reactions the water acts as a catalyst, so even the smallest amounts of free water within the fertilizer can cause decrease in physical quality. This was seen in the water adsorption tests where the KF-water content increased only few per mil, but the caking index increased significantly.

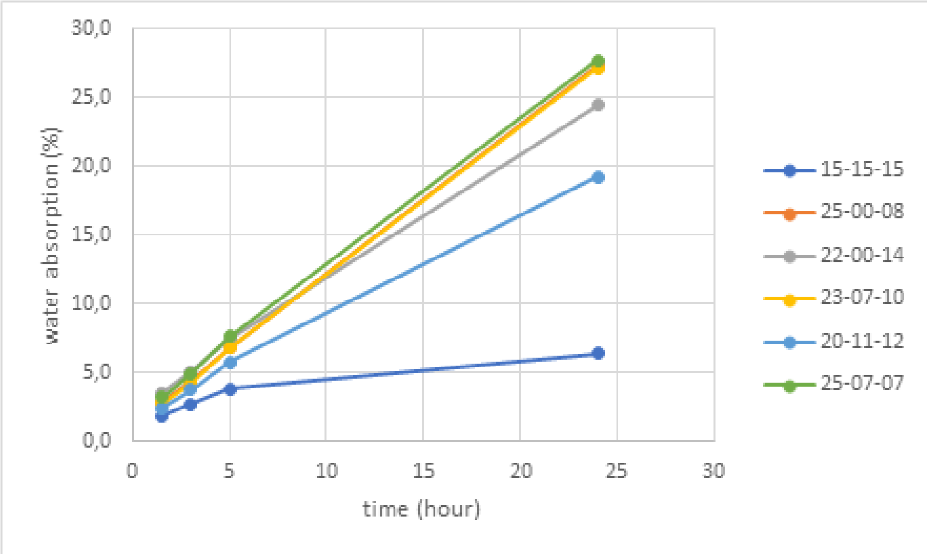

Figure 57 Water adsorption behavior of NPK fertilizers

It is not only the moisture of the summer causing problems, but also the higher temperatures themselves can cause problems at least for some fertilizers. The caking index test made in elevated temperatures showed higher caking tendency, therefore caking, and setting likelihood increases if the fertilizer is packed too hot. The normal laboratory measurement cannot catch this kind of caking as the samples are cooled to the room temperature. Especially the 22-00-14 was found to be highly sensitive to combination of heat and pressure. The caking index measurements showed significant compression and the formed cakes were rock solid.

Increasing the temperature also means that the amount of liquid phase within the granule increases. For example, Epsom salt has completely discarded one of its water of crystallization when the temperature reaches 50 °C visualized in the Figure 15. The pressure applied to the granules forces the liquid phase to surface where it causes setting and caking.

The poor roundness and the small particle size increase the surface area of the particles and the number of contact points. However, the increase of surface area also means that the coating has to cover more area. The amount of coating is applied based on the mass flow of the produced fertilizer instead of the surface area. This could lead poor coating when the granules are small and have irregular shape, but also to overcoating when the granules are round and large.

When studying the more accurately the structure of the granules and the dust caused by the post reactions it was found that the post reactions had taken place in the fertilizer matrix instead of the boundaries of the few crystals found within the granule. Therefore, in that case the formation of AS-crystals or poor conversion of MOP are unlikely to be the driving force of the reactions. Instead the possible driving force to reaction could be linked to the phase changes within the fertilizer matrix. The formation of boussingaulite is an evidence of free water as the reaction route for the boussingaulite requires Epsom salt to be present. Which is formed when the $MgSO_4$ has bound 7 waters of crystallization.

11. Conclusions

As expected, the variety of the variables affecting the fertilizers caking and setting behavior is vast. As most of the reclamations were made from the summertime production runs the temperature of the fertilizers seems to be the biggest root cause. Based on the history, the amount of reclamations had risen when the final product temperature had risen to be the bottleneck for the process. The increase of temperature has connections with higher hygroscopicity, higher free water content thus leading into post reactions and plasticity resulting the individual granules attaching one another. In the summertime the humidity is also a key difference to winter. The relative humidity in the warehouses occasionally surpassed the critical relative humidity of the fertilizer thus leading water adsorption proven by random samples taken from the pile surface. Especially the bin surface will be effected, and the moisture content will reach levels where the caking tendency has significantly increased.

In the random sampling of packaged fertilizers, the mechanism how the granules attach one another was commonly observed to be the formation of solid bridges. This was mainly due to the volume change caused by the post reactions. However very wet granules could form solid bridges by the deliquescence. This type of caking is the most severe. In contrary to the random sampling observations the formation of solid bridges was not observed from the Acap Easy or the laboratory measurements. This means that when applied under pressure the capillary adhesion and the van der Waals forces can be strong enough to hold the granules together. It also means that within the low humidity laboratory conditions the post reactions are suppressed.

The compression measurement of the Acap Easy is only an undirect measurement of the caking tendency. The particle deformation increases the severity of the possible caking, but it does not determinate if it happens. As comparing the results between the Acap Easy and the 16 h measurements showcase. The Acap Easy could predict from two samples which would have higher caking index, but not able to predict the level of the caking index. The sample with higher compression had higher caking index. Packing the bulk bags in four layers could increase the severity of the formed setting and caking as the increase of pressure directly increases the deformation of granules. However, as the four layers was used also during winters it is not the triggering factor. Also, the storage in four layers was initiated well before the emerge of high number of reclamations indicates that the pressure applied to the fertilizers is not the sole root cause.

In both measurements the fingerprint of the different measurers causes the most uncertainty in the measurement. The sampling method of Acap Easy does not represent the whole production as the coffee cup only takes sample from the conveyors surface. The further handling of the Acap Easy sample generally should not cause much difference, if the sample is kept dry. For the 16 h measurements the pile samples only represents the surface layer of the bin, therefore the lower parts of the bin are unmeasured. Also, if the bin surface is not measured separately the effect of the external water adsorption cannot be detected.

In the 16 h measurements the noble intension to standardize the caking measurement process could be the cause why the measurements were unable to notice the caking. The measurements are always done in the room temperature, which makes the measurements comparable with each other, but at the same time losing the predictive power of summertime setting tendency as the fertilizers are packed in higher temperature. However more standardization is needed for the bag tightness and the angle of the lever arm.

In the factors affecting the Acap Easy results, the increase of the pressing force caused linear increase in the compression. The increase of time also increased the compression until the system reached equilibrium. It should be noted that majority of the compression takes place within the first second of the measurement. The size of the sample and the particle size do not have major effect on the result. However, the sample cup must not be filled all the way up as it increases errors. The temperature has slight effect, when considering range between -5 to 40 ℃ as increase of temperature increases the compressibility. The biggest effect on the compression values were on the sample packing density and the humidity. The compression decreased as the sample was subjected to vibration, which increased the granules packing density. The samples with small increase of water content were slightly more compressible, but in high water concentrations the structure of the granules failed completely.

In the 16 h measurements the larger 400 ml bags showcased throughout the measurements higher caking index values compared to the original 5x90 ml procedure, which could make it possible to increase the resolution of the caking index measurement. Similar behavior of lump forming was noted in the 400 ml bags and the random sample bulk bags, which means that the shape of the sample bag is able to simulate the reality. The problem with the 400 ml bag was the poor reproducibility. The original method with five bags evens the differences in the bags, which is not possible with the one 400 ml bag. The handling of the 400 ml bags was also more difficult as the 400 ml bags would be very tight inside the metal cover.

For the 90 ml bag size the effecting parameters were the bag tightness, moisture and to some extent the temperature, which all increased the caking index. However, the most significant factor was the dropping of the bags. The samples in the 90 ml bags most often had some setting occurred when taken under the pressure. The bag dropping was the determining factor for the high amount of 0 % results as the force of impact was higher than the adhesion forces between the particles.

The predictive power of the Acap Easy on the caking is most affected by the fact the compressibility is undirect measurement of the caking. The problems of the measurement were more tied to its poor reproducibility. Initially the standard deviation between the compression measurements was around 0.6 % units of compression. The focus on standardizing the measurement procedure, from reducing the sample size to 45 ml and having a single measurer decreased the deviation to 0.4 % units of compression. The samples that were vibrated further reduced the deviation between measurements to 0.2 %. This corresponds roughly to 0.1 mm of compression. The granules however will still always possess some random behavior in the packaging as the granules size and shape is always slightly different between the samples.

The key to increase the predictive power of the Acap Easy is to take the cake breaking force into account. It measures directly how strongly the individual particles are bound together. The problem of the measurement has been the instrument failing to recognize the correct force of cake breaking due to the cake being typically too fragile to be measured. If corrected the measurement would give during the production an early warning if the granules have easily attached one another, for example in insufficient coating.

11.1 Recommendations for action

- Sampling of the Acap Easy can be improved. There is already an automatic sampler for the analysis of the chemical composition of the fertilizer taking samples to the same laboratory. This sampler should be also be used for the taking the sample for the Acap Easy as it reduces significantly the human errors linked to sample taking hand handling. It makes also possible to further analyze the effect of the product temperature on the compression results as temperature data of the final product is readily available.

- The physical quality should also be measured before packaging when the fertilizer is moved in bulk to another location. This is important to catch the possible water contamination during the transportation.

- Surface pile samples should be reanimated to the sampling procedure at least for the KF-moisture content for all the fertilizers. This gives information both from the actual moisture adsorbed by the sampled fertilizer, but also acts as secondary measurement of the relative humidity conditions of the warehouse. If one product has adsorbed water, it is most likely all the other products have been exposed to high relative humidity.

- In order to get accurate results for the ACAP Easy crushing strength measurements there are two possible options. The first option is to contact the instrument manufacturer to solve the problems in coding of the instrument or increase the pressing force to get the fertilizer granules adhere together more strongly, but this is only a quick fix as if there is no adhesion forces between particles the increase of pressing force does not have an effect.

- The 16 h caking index measurements resolution can be increased most easily by decreasing the dropping height of the bag as the formed agglomerates mostly are broken during the drop. Another improvement could be made by using a ruler for determining the bag tightness so the laboratory technician hand mark could be reduced. Also, the angle of the lever arm can be systemized by implementing clear limits, for example by a ruler. During the summertime the samples should be measured in temperature, which represents the pile and packing temperatures.

- A balance should be kept at the storage time in the bulk. Too short time causes the post reactions to take place in the bag thus causing caking. Also, during the summer, the products temperature can cause caking if the storage time in bulk is short. However, long storage time exposes the fertilizer to the humidity changes and water adsorption, reinitiating the post reactions and decreasing the fertilizers physical quality.

- The relative humidity and the temperature of the air used to keep the bulk bag open during the packaging should be monitored. Any extra water added especially during summertime could cause humidity cycling in the bulk bags thus leading into solid salt bridges and caking.

- The use of 2-propanol as the solvent in the KF-moisture measurements might give a better insight on the amount of loosely bound moisture within the fertilizer than the methanol. This could be useful in detecting the harmful free water, instead of the unharmful water of crystallization.

- The reclamation handling should contain even more accurately the information about the packaging marking, including the packaging time of each bag. This makes it possible to pinpoint if the reclamation are packed at the same time, thus giving on insight if the poor quality bags are packed first, indicating the surface moisture or is there a wave pattern indicating the bag located at the bottom row of the bags during storage.

- The results of the ACAP Easy measurement should be saved into a backup file as the device tends to delete its measurement history. The naming of the measurements should be systemized.

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