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# MICA - THE KEY TO BETTER QUALITY IN GRANULAR FERTILIZERS

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## 1. SUMMARY

**The requirements for improving the physico-chemical quality of products continue to increase year-by-year. At the same time, numerous regulatory aspects influence the types of products and raw materials applied in the market. These requirements make it more challenging to cost-effectively produce better products. It is no longer possible to improve just one parameter at a time, as the whole lifecycle of the product must be considered.**

**At Kemira GrowHow an innovative solution for several problem areas was found through extensive research and development. Although implementation of the quality enhancement process is currently in its initial phase, the stage is set for its introduction as an invaluable tool for the next decade.**

## 2. INTRODUCTION

The fertilizer industry has gone through significant restructuring since the 1980’s. The number of manufacturing companies has decreased significantly while overall capacities have continued to follow a slightly downward trend. The global demand for fertilizers, however, continues to increase.

This restructuring trend has also been reflected in the IFA Technical Conferences over the past few years. The conference proceedings were once a valuable information source for newcomers to the industry. In the last 10 years, however, the scope of the papers has changed. The general impression is that of an industry that is not developing or is becoming increasingly inward-looking as the number of players decreases. In response to this, a paper on quality enhancement has been compiled to encourage companies to embrace new innovations and increase openness.

The market demands continuous improvement in the quality of granulated N, NK and NPK fertilizers. The most recent demands have been related to Product Stewardship, i.e. management of the whole lifecycle of the fertilizer from raw material to consumer. As no existing manufacturer operates in full isolation all HSE aspects related either to production or the products are therefore shared common knowledge.

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Environmental requirements have reduced permissible phosphorous content levels, especially in Europe, thus resulting in an increasing need for V-type fertilizers. In addition to these requirements further regulatory requirements are soon to be introduced for lower levels of heavy metals, e.g. cadmium, per kilo $P_2O_5$ which will require the increased use of pure phosphates. This will not, however, improve the quality of the final fertilizer products as certain phosphate rock impurities actively improve granulation and further the physical properties of the end product.

Kemira GrowHow, as committed to the Food Chain Partnership, has recognized the current needs and fully supports the European development. Through extensive Research and Development activities the factors affecting physico-chemical characteristics have been understood and solutions to impending problems have already been found. This presentation highlights possible solutions to further improve physico-chemical properties through cheap and innovative utilization of commonly available minerals.

## 3. MICA, A PRODUCT STRAIGHT FROM NATURE

### 3.1 Introduction

In Finland, the Siilinjärvi ore belongs to the igneous type of rock phosphate deposit. These deposits are often associated with carbonatives and alkaline intrusions. The ores are typically low grade as e.g. Siilinjärvi ore contains 3.5 to 5.5% $P_2O_5$. Common minerals associated with alkaline intrusions include nepheline, alkali feldspars, micas (biotite, muscovite), pyroxenes and amphiboles.

Mica is a common mineral and includes numerous sub-classifications of minerals.

The type of mica extracted from the Siilinjärvi mine is phlogopite/biotite.

The low grade igneous apatite deposits consist, on average, of the following:

| | |
|---|---|
| 65% | phlogopite $[K(Mg,Fe)_3AlSiO_3O_{10}(OH,F)_2]$, |
| 19% | calcite, |
| 4% | dolomite, |
| 10% | apatite and |
| 5% | other silicates. |

Quantities (metric tons) of materials annually extracted from the mine:

| | million t/a |
|---|---|
| Total mining | 12.5 |
| Grinding and flotation | 9.1 |
| Flotated sand, mainly mica | 8.1 |
| Apatite | 0.9 |
| Mg containing limestone | 0.075 |
| Mica production | |
| biotite | 0.07 |
| mica for other purposes | 0.01 |

## 3.2 The beneficiation process

Crushing, screening, blending, grinding and conditioning are needed to prepare ore for flotation. The ore slurry is 35% below 74 µm. A selective phosphate collector is used to separate the apatite concentrate which is further reduced to a moisture content of 6–8% by pressure filters. The typical composition of the apatite concentrate is presented in Table 1.

In the beneficiation plant calcite concentrate is also produced along with mica as a by-product. The majority of the flotated sand is pumped in slurry form into a natural pond. Apatite is used for phosacid and fertilizer production and dolomite/limestone is used as a soil conditioning agent. A proportion of the mica is used for fertilizer production and special purposes.

Table 1: Chemical composition of apatite and mica concentrates

| | Apatite concentrate | Mica concentrate |
|---|---|---|
| $P_2O_5$ | 35.5% | 1–1.5% |
| $K_2O$ | 0.03% | 7–9% |
| MgO | 1.95% | 18–20% |
| CaO | 53 % | 18–22% |
| $Na_2O$ | 0.09% | 0.5% |
| $SiO_2$ | 0.5% | 30–34% |
| $Fe_2O_3$ | 0.6% | 8–9 % |
| $Al_2O_3$ | 0.6% | 7–8 % |
| $CO_2$ | 6.5% | 5–10% |
| $H_2O$ | 8% | 12% |

The composition of mica can vary due to fluctuations in the ore and due to the flotation process. As it contains up to 12% moisture, further drying is performed to avoid dosing problems. Drying is typically performed to a moisture content of 5% $H_2O$.

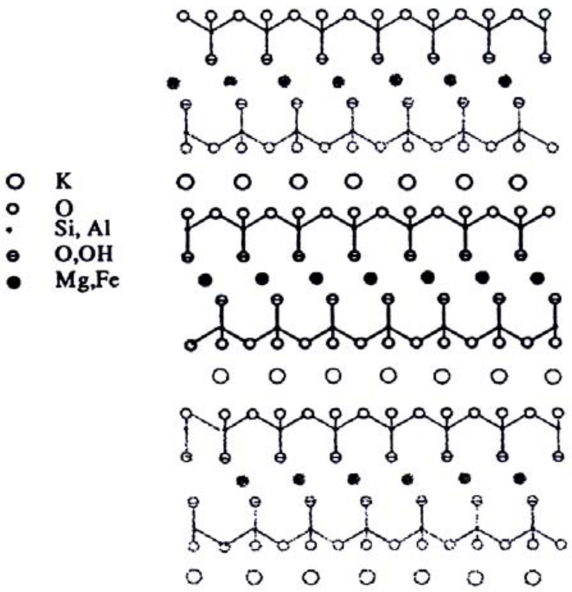
## 3.3 Mica

Biotite is a common rock-forming mineral which is present to at least some degree in most igneous and both regional and contact metamorphic rocks. The typical black to brown color of biotite is characteristic although it is difficult to distinguish brown biotite from dark brown phlogopite. The two are actually at opposite ends of a series which is dependent on the percentage of iron content. Phlogopite is iron-poor and biotite is iron-rich. The darker color and density increase in line with increased iron content. Biotite tends to form in a wider range of conditions than phlogopite, which is limited mostly to ultramafic rocks and magnesium-rich marbles and pegmatites.

Phlogopite is a rarer member of the mica group and is lesser known even among mineral collectors. It has been mined however for its heat and electrical insulating properties which are considered superior to other micas. The typical light brown color of phlogopite is characteristic although it is difficult to distinguish brown biotite from dark brown phlogopite.

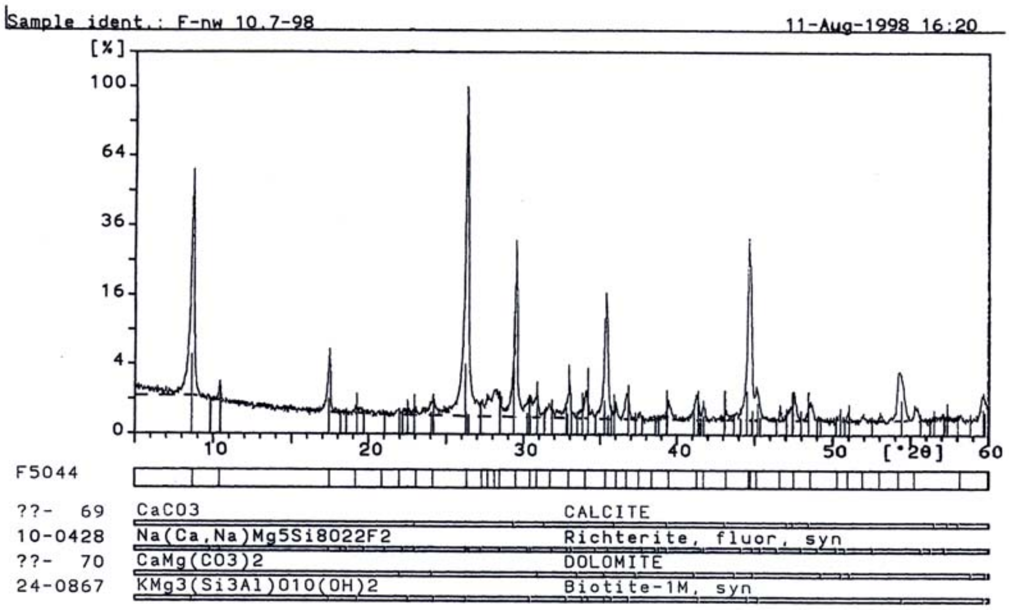
Phlogopite and biotite, like other micas, has a layered structure of (iron) magnesium aluminum silicate sheets weakly bonded together by layers of potassium ions. These potassium ion layers produce perfect cleavage. Weathered tiny crystals of biotite can appear golden yellow with an attractive sparkle producing a "fool's gold" that has, indeed, fooled many.

Figure 1: The crystal structure of mica



Mica has a plate-type structure which partly opens upon acid treatment when K, Mg and some Fe are dissolved from the structure. Water and certain other ions can replace these in the fertilizer thus introducing a water binding effect. A typical X-ray diffraction pattern is presented in Figure 2.

Figure 2 : An X-ray diffraction pattern from untreated mica



# 4. IMPORTANT QUALITY ASPECTS OF FERTILIZERS

The numerous handling, transport and storage steps usually involved between production and application demands that a fertilizer material is free-flowing (non-caking), non dusty, and able to withstand exposure to atmospheric humidity.

The fertilizer material is applied in many different ways around the world. While European farmers use machinery, their colleagues in Asia spread fertilizer manually. It is clear therefore that different properties are important in different market areas. Fertilizers should always be free of air-borne dust during handling to ensure healthy working conditions in all bulk handling areas.

The demands of the market continue to increase year-by-year. Physical properties that were acceptable 10 years ago would not sell today. The physical properties are monitored daily at the production plants, but also yearly comparisons between plants are made and products from the various plants are ranked according to their total quality performance and action taken in case of any deviations.

## 4.1 Product Stewardship

Product Stewardship is defined as follows: the responsible and ethical management of the health, safety and environmental aspects of a product throughout its total life cycle. In other words Product Stewardship is Responsible Care© applied to products. After several accidents occurred in the fertilizer industry during 2001–2003 the importance of covering the whole lifecycle of the fertilizer is becoming ever more essential as present-day manufacturers can no longer operate in complete isolation.

Product Stewardship is an essential aspect of the producer’s responsibility in the development of new fertilizers or processes utilizing new raw materials. It covers the whole lifecycle of the product from raw material to consumer. The critical issues are related to production safety as well as to product safety, e.g. the product must be free from risk of detonation or self-sustaining decomposition hazards, but issues related to occupational (industrial) hygiene and to health and environmental issues must also not be overlooked, especially when trace elements are applied.

## 4.2. Chemical quality

Chemical quality is clearly defined by laws, requirements, or agreements. The chemical methods used to control the nutrient content in fertilizers are based mainly on official methods of analysis. Analytical methods in relation to export are based on the OFFICIAL METHODS OF ANALYSIS from the AOAC (Association of Official Analytical Chemists). The methods for controlling fertilizer analysis in Europe are based on the Regulation (EC) No: 2003/2003. Several ISO standards also exist for chemical analysis of fertilizers. In all methods the sampling and preparation of the sample is essential. If not done correctly the results may differ significantly. To avoid any problems arising from manufacturing, sampling and analytical inaccuracies, tolerances are defined to match different laboratories and methods together.

## 4.3. Physical quality, product quality

Product quality is normally associated with what is seen and experienced by the customer. There are several properties which affect the storage, spreading and transport characteristics of a fertilizer, the main parameters being described in Table 2.

Table 2: The most common physical properties

| | Property |
|---|---|
| STORAGE | Caking tendency |
| | Crushing strength |
| | Angle of repose |
| | Hygroscopicity |
| | Self-sustaining thermal decomposition |
| | Volume expansion |
| SPREADING | Flowability |
| | Dust |
| | Bulk density |
| | Roundness |
| | Sieve analysis |
| TRANSPORT | Abrasion |
| | Shattering resistance |
| INTERNAL STRUCTURE | Porosity |
| | Structure |

Unfortunately, physical quality is not well defined as many producers have their own self-developed methods. Kemira actively participates in the standardization program among European producers to achieve common agreement on the methods to be used. The methods used in Kemira are based on internationally accepted and published procedures.

### 4.3.1. Caking and setting

The standard cause for caking of most fertilizers is the growth of crystal bonds between fertilizer particles. These crystals develop during storage either as a result of continuing internal chemical reactions or thermal effects that result in the deposition of crystals from minute quantities of salt solutions present in the fertilizer. As a rule, fertilizers must be free-flowing after production.

Several solutions exist to achieve a free-flowing product:

- ➜ change the chemical composition
- ➜ change the raw materials
- ➜ change the production conditions
- ➜ extend drying to very low moisture content
- ➜ cool the product down further
- ➜ longer curing time i.e. storage period
- ➜ apply an anticaking treatment
- ➜ limit the storage time
- ➜ move the product several times, and
- ➜ prevent moisture uptake

Although all these solutions help to achieve free-flowing products, customer requirements in this respect continue to grow day-by-day. A common current problem, especially in markets where big bags are applied, is setting. The cakes (lumps) which result from setting tend not to be hard and are easily breakable, often from the slightest touch, but they are visible and provide farmers with additional work.

### 4.3.2. Dust

Dusty fertilizer is normally also subjected to hard caking. Breaking down the cakes, piles and lumps requires a considerable amount of labor. Furthermore, the fertilizer material disintegrates to a complete dust or wet powder when in contact with high humidity.

Dustiness is primarily an occupational hygiene issue. The presence of dust also creates problems such as weakening bag seals, causing extensive corrosion in humid conditions and scorching plant leaves.

Dust can be controlled using the following solutions:

- process conditions
- formulation
- raw materials
- drying
- curing time
- polishing screening
- antidusting treatment

The limits for Total Inhalable Dust are between 2 and 10 mg/m$^3$, especially if the dust contains airborne talc.

### 4.3.3. Other quality aspects

Important product properties include:

- flowability and spreading
- roundness of granules
- smoothness of granules
- hardness (static strength of granules)
- color

Customers demand consistency of product quality from the manufacturer. Cost-driven customers also tend to return to quality fertilizers after realizing the additional costs incurred by lower qualities.

# 5. UTILIZATION OF MICA IN FERTILIZER PRODUCTION

## 5.1. Research and development

A great deal of Research and Development has been undertaken concerning mica. The quantities mined annually had the potential to satisfy the domestic requirements for potassium and so the initial objective was to extract potassium and use it as a raw material in fertilizer production. Similar thoughts were applied to the extraction of other valuable elements such as magnesium.

Due to these efforts entirely new solutions for the utilization of mica were found. Typical applications included pearl tone in paints and additives in plastics and cosmetics. Although the solutions were novel the production volumes for such products remained small.

In the 1980's the requirements for improved thermal stabilization of high nitrogen products were raised. Several years of fundamental research led to the idea of utilizing the stabilization agents from mica and as a result an entirely new product – FinnCAN was launched. The improvements in physical properties that were achieved spurred the application of mica also in NK and NPK fertilizers.

The main challenge in the mica dissolution process is to achieve partial dissolution of the $K^+$ and $Mg^{++}$ ions, thus opening the plate-type structure to achieve open, electrically charged zones and capillary surfaces. The process is highly demanding as the residence time and related temperature must be in balance with stable acid concentration and mica composition. If the reaction does not take place in the right conditions (Figure 4) either no positive effect is achieved or the process becomes problematic.

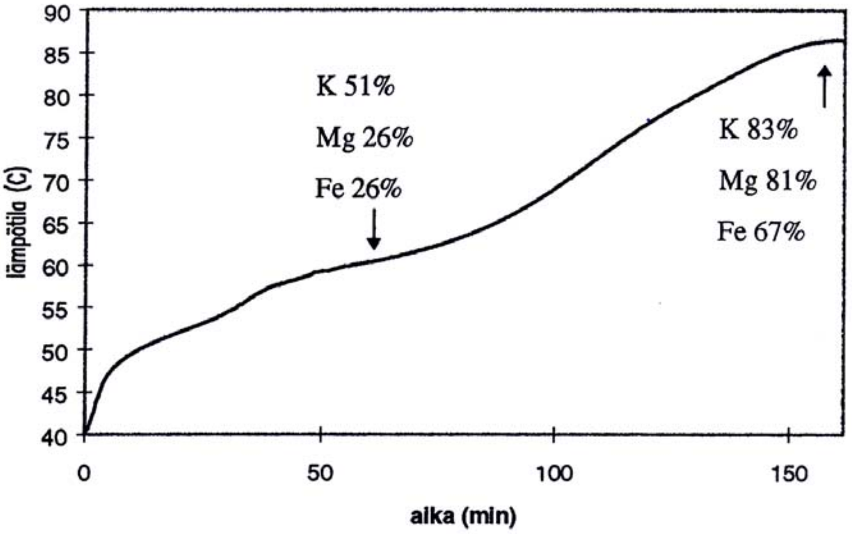


Figure 3: Dissolution curve of mica as a function of temperature [°C] and time [min]. The figures represent the percentage of different ions in solution.

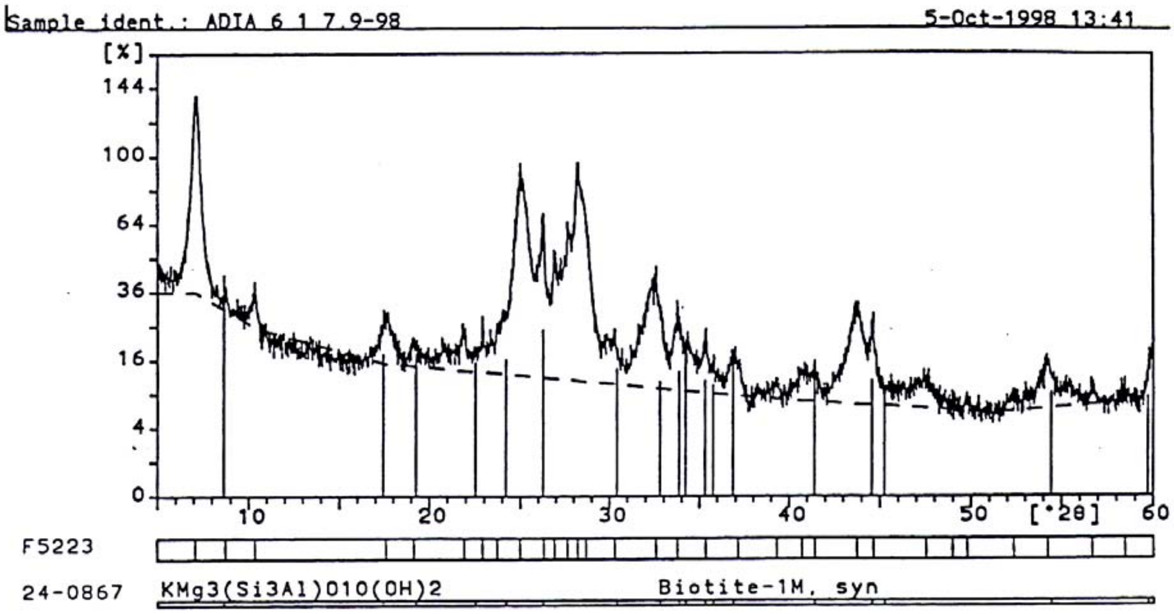


Figure 4: An X-ray diffraction pattern obtained after proper treatment of mica to achieve required physical quality improvements.

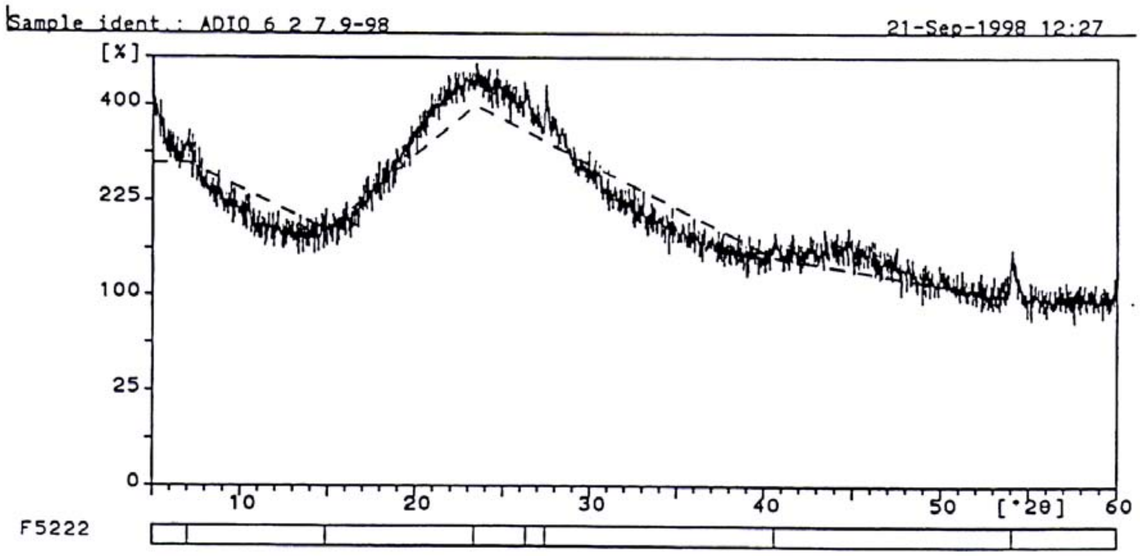


Figure 5: X-ray diffraction pattern of mica which has undergone excessive process treatment resulting in non-favorable effects.

## 5.2. Applications of Mica

### 5.2.1. Straight Nitrogen Products

The need for improved CAN quality first arose in the 1980's. Knowing that the dolomites and calcites in Finland would not fulfill the requirements of the CAN definition the alternatives were kept open. The soil requirements for sulfur were increasing and it was therefore decided during the early stages to include sulfur in the form of calcium sulfate. The successful production runs revealed surprisingly good stabilization against thermal cycles. Typical complaints related to CAN quality at this time were due to breakdown caused through incorrect storage. The Kemira mixed acid manufacturing process with spherodizer was subsequently introduced. The final product was 26-0-1, containing 0.02% B and 0.001% Se.

The characteristics of the product are presented in Figure 5. Comparison across 12 different CAN products indicates that most of the products have reasonable strength properties (>30 N) although some poor performers (or extended storage periods) do exist. The crushing strength of FinnCAN direct from production is typically as high as 100–120 N. The FinnCAN sample from South-east Asia was taken several months after delivery and had passed through an extreme number of thermal cycles. It is worth noting that the typical water content of the product is between 1 and 2.5% $H_2O$, whereas in the past less than 0.1% $H_2O$ was required for good quality.

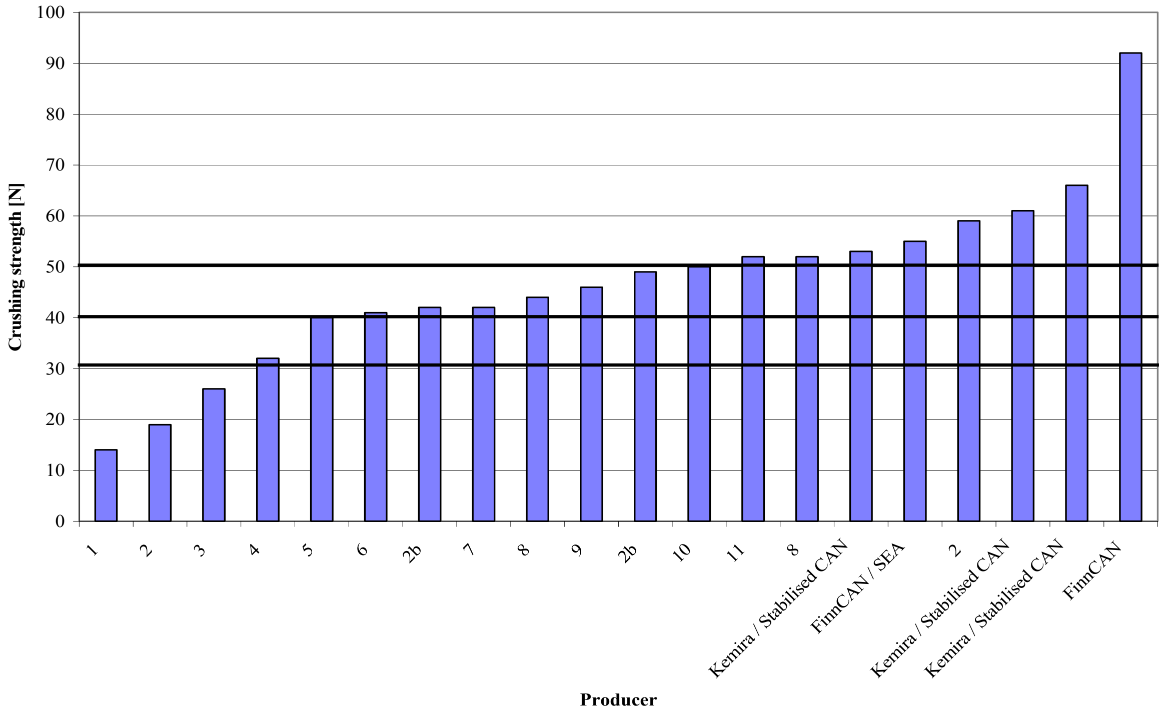


Figure 6: Crushing strength of some commercially available CAN products (12 producers). The majority of products have reasonable hardness (>30 N), the average being around 45 N.

A remarkable quality improvement was also obtained in relation to stability against thermal cycling. In CAN type products there are no legal requirements for stabilization. This is clearly visible in Figure 7. The initial bulk density of FinnCAN can be as high as 1100 kg/$m^3$ and remains close to 1000 even after 30 thermal cycles. Hardness remains on a constant level versus the thermal cycles whereas normal CAN deteriorates after 15 cycles, thus losing the bulk handling characteristics and creating fines and off-spec. properties.

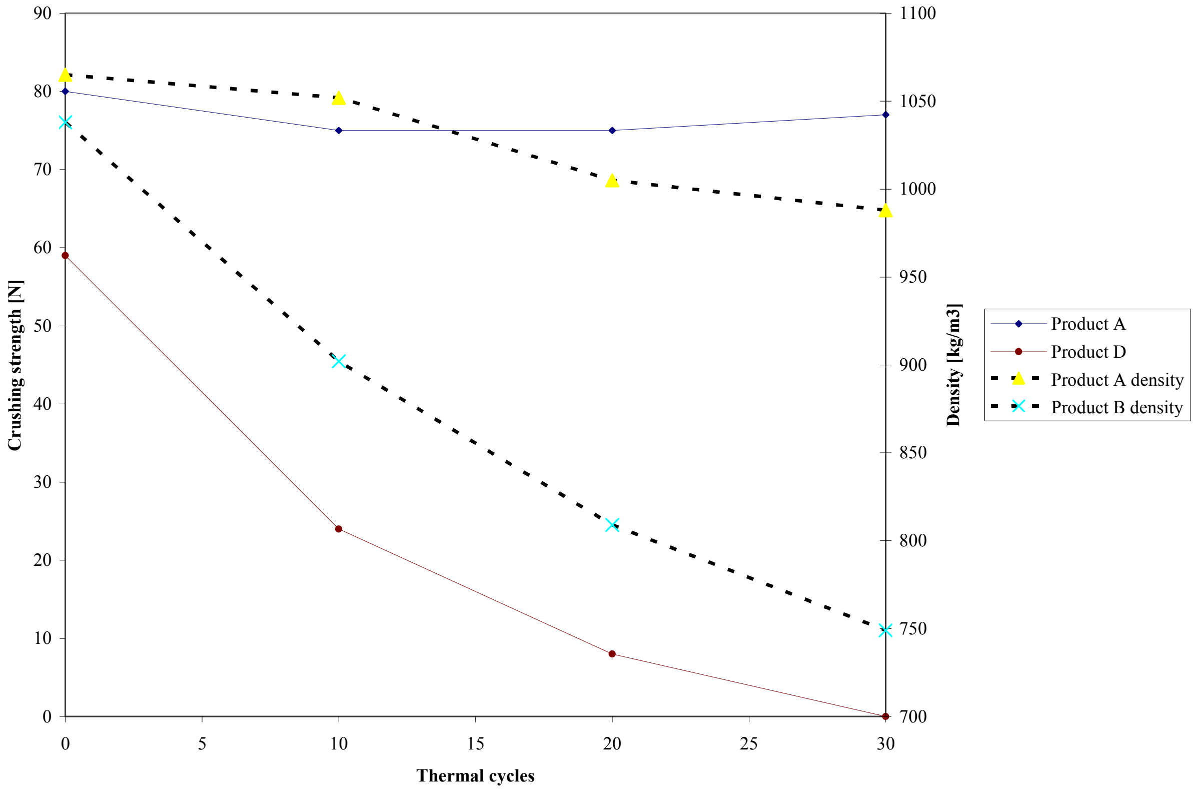


Figure 7: The effect of thermal cycling on crushing strength (Y1 axis) for standard CAN (product D) and FinnCAN (product A), and on bulk densities (Y2 axis) for ordinary CAN (Product B) and FinnCAN (product A).

### 5.2.2. NPK fertilizers

The requirements for reducing the heavy metal content of fertilizer products are on the increase. A high concentration of these metals in the soil can cause toxicity to plants and pose a hazard to both animal and human health. Unfortunately the requirements also lead to the use of phosphoric acid and/or phosphates which are in some cases "too pure", thus causing elasticity and caking problems in the final product as well as difficulties in granulation. The acid used nowadays typically contains only <1% impurities.

The solutions outlined in chapters 3.3.1. and 3.3.2. are not sufficiently effective to improve the physical properties of the fertilizer grades. Mica has therefore been applied as a quality-enhancing additive in quantities ranging from 30 to 100 kg/ton. Typical grades are 23-7-6+7$SO_3$, 22-12-5+7$SO_3$, 20-7-10+7$SO_3$, and 20-5-15+7$SO_3$. These grades also contain sulfates known to cause problematic post reactions causing caking, elasticity and dust formation. The N:$K_2O$ ratios are also important as double salts or solid solutions of $NH_4NO_3$*x$KNO_3$ are formed. Such combinations normally require extreme drying and extensive cooling in order to avoid such reactions. Even minor moisture uptake can easily destroy storage and transport properties.

In Figure 8 the bulk densities of 70 different products from around the world are presented. The grades are manufactured by 19 different producers at several production sites. The figure indicates a wide span in bulk densities. The products in which mica was utilized as a quality enhancer rank among the top 25%.

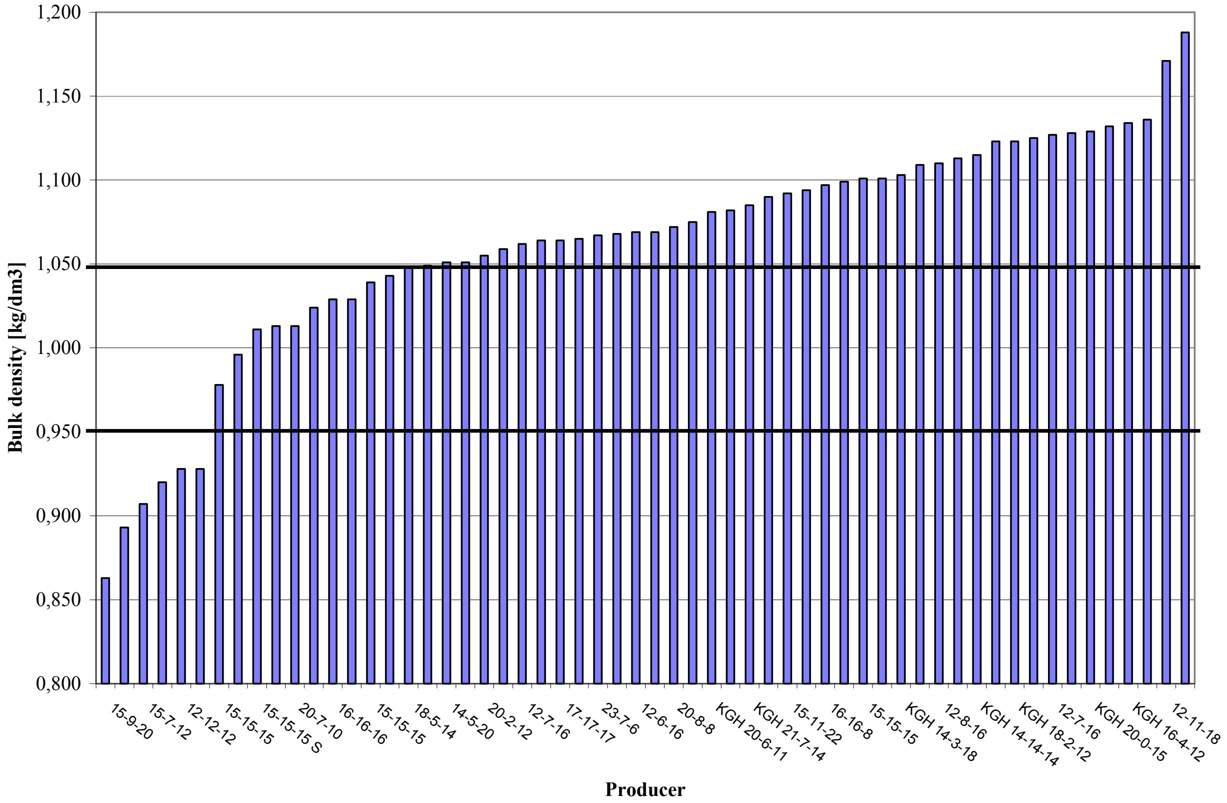


Figure 8: The bulk density [kg/dm3] of different products from around the world (70 grades, 19 producers).

### 5.2.3. Sodium-containing products

NPKs with *sodium* are difficult to produce and in many cases the physical properties of the final products are so weak that they cannot tolerate handling or bulk storage. During the manufacturing process sodium chloride reacts readily with ammonium nitrate according to equation 1:

$NaCl + NH_4NO_3 \rightarrow NaNO_3 + NH_4Cl$ Equation 1

The formed sodium nitrate is extremely hygroscopic. The final products are similarly highly sensitive to moisture. The dependency of caking on moisture content in figure 9 indicates the need for a very low final moisture content of the product (Note! The acceptance level in Kemira GrowHow is max. 2% cakes in the u-bag test method). Moisture absorbed from air penetrates deep into the pile within the space of a few days. Moisture absorption in the TVA- test is typically around 400 mg/cm$^2$ with high moisture penetration. The moisture absorption characteristics are almost twofold when compared to CAN products. The CRH values are around 30%.

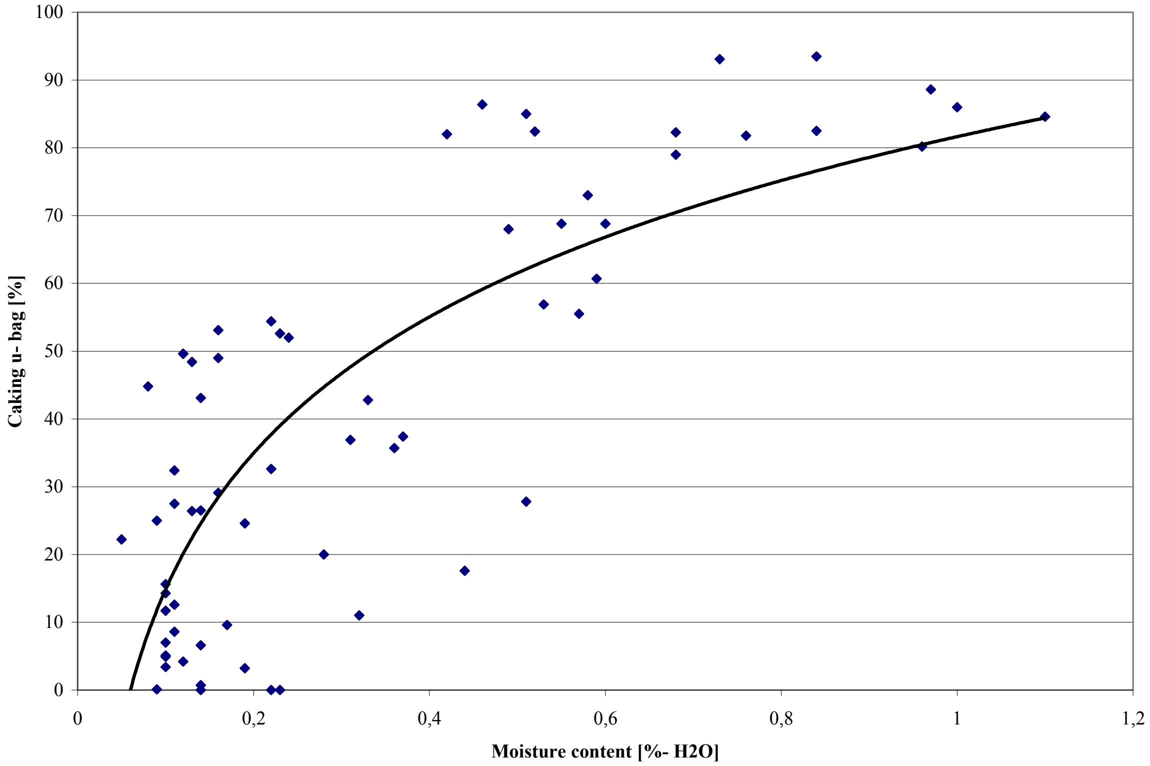


Figure 9: Caking tendency versus moisture content for sodium-containing NPK (25-5-5+5Na).

Addition of 80 kg mica/t enables the product to tolerate up to 15 kg/t water without caking. The product can be stored in open piles for weeks and has a bagged storage life of several years.

Typically produced products are 18-7-5+ 5 Na with good physical and bulk handling properties.

### 5.2.4. NK fertilizers

Another challenging group of products are NK fertilizers. The reaction described in Equation 2 proceeds to completion during storage.

$KCl + NH_4NO_3 \rightarrow KNO_3 + NH_4Cl$ Equation 2

Such post reactions can result in excessive dust formation and caking.

Addition of sulfates to NK fertilizers causes them to become extremely elastic and sometimes subject to high caking. The main chemical reactions proceed according to one of two different reaction routes where

$2\ NH_4NO_3 + (NH_4)_2SO_4 \rightarrow 2\ (NH_4,K)NO_3{*}(NH_4,K)_2SO_4$ Equation 3

is a fast reaction proceeding with a 3.2% expansion in volume. The second reaction proceeds with a 1.4% shrinkage in volume:

$2\ NH_4NO_3{*}xKNO_3 + (NH_4)_2SO_4 \rightarrow 2\ (NH_4,K)NO_3{*}(NH_4,K)_2SO_4$ Equation 4

Both reactions are difficult to control and require very low moisture content in the final product. The moisture uptake characteristics may prevent bulk handling and/or transportation.

Mica has been successfully used to improve physical properties without undergoing the problems described above. This has opened up new possibilities to provide the new products demanded by the customer. Typical NK products are 20-0-18, and sodium-containing 20-0-9 + 5 Na.

Table 3: Physical and chemical properties of sodium- and sulfur-containing NPKs and NKs.

| Property | | 18-7-5+5 Na | NK 20-18 | NK 20-9+5 Na |
|---|---|---|---|---|
| Caking tendency | [%] | 0 | 0 | 0 |
| Moisture content | [%] | 0.6 | 0.7 | 0.6 |
| Dust | [mg/kg] | 50 | 100 | 100 |
| d50 | [mm] | 3.2 | 3.3 | 3.3 |
| Uniformity | [%] | 56 | 54 | 56 |
| Roundness | [%] | 81 | 84 | 70 |
| Hardness | [N] | 71 | 67 | 68 |
| Bulk density | [kg/dm$^3$] | 1100 | 1110 | 1120 |

## 6. CONCLUSIONS

New innovations were once a regular feature at IFA Technical Conferences. Looking back over the past 10 years, however, papers have predominantly concentrated on the ‘status quo’. It is true that, globally, raw materials and fertilizer grades have not changed greatly, but regarding e.g. the European situation, the content of $P_2O_5$ has decreased in most products due to environmental policies. Increasing demands from the customers and policy makers require continuous improvement. This cannot be achieved without fresh innovations.

Kemira’s innovative use of mica as an active raw material provides new, previously virtually unattainable opportunities to achieve good quality in comparison with other products. It is also a cheap source of the valuable nutrients $K_2O$ and MgO. It is important to note that the opportunities experienced in Finland are also likely to exist in a similar form in many other countries.

Traditionally problematic grades have been difficult to produce, store, transport and use. Use of mica as an essential raw material has solved these problems and opened up new opportunities to offer our customers a wider range of premium quality products.

As both existing grades and new grades are now easier to produce, we are better positioned than ever to supply our customers with the latest and best in product quality.

The development does not stop here, however. The major future challenge of the fertilizer industry is the continued development of new, more effective, cheaper and more environmentally friendly fertilizers which, in addition, must be inherently safer. The new applications for mica utilization are just beginning to emerge.

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