



2006 IFA Technical Symposium

25-28 April 2006, Vilnius, Lithuania

Technical Research Paper no. 24

Potash in Complex Fertilizers: Inert or Complex

presented by

Harri Kiiski
Kemira GrowHow Oyj, Finland



About the IFA Technical Committee

The IFA Technical Committee encourages the development and adoption of technology improvements that can lead to greater production efficiencies and reduced emissions, as well as better health and safety standards throughout the fertilizer industry. Our mission is to actively promote the sustainable development of efficient and responsible production, storage and transportation of all plant nutrients. The Technical Committee accomplishes these objectives through a variety of channels, including:

- Technical and policy-oriented information materials. The committee regularly conducts surveys and produces reports on key industry metrics, including the IFA Energy Efficiency and CO₂ Emissions Report, the IFA Safety Report, and the IFA Emissions Report. This work enables member companies to assess their operations over time, make comparisons with similar facilities on an established level of performance, determine the need for technology improvements and identify good industrial and management practices.
- Regular exchange of information on technology developments and industrial practices. A key role of the IFA Technical Committee is to encourage ongoing technical innovation in the fertilizer industry through the development, compilation and exchange of technical information between members, researchers, engineers, equipment suppliers and other industry associations. To this end, the committee organizes a Technical Symposium every other year to examine progress in the production technology of fertilizers. Each Symposium traditionally features the presentation of 30-40 new technical papers from member companies worldwide, providing members with information on the latest technological developments. In the intervening years, the committee holds a variety of meetings to assess current industrial practices and standards, with an eye toward identifying key developments of interest to members.
- Technical and educational workshops and special events. The IFA Technical Committee provides workshops designed for engineers working in the fertilizer industry, particularly those who have recently assumed new responsibilities, and for new engineers to increase their technical knowledge. These workshops (e.g. concentrating on nitrogen and/or phosphate fertilizer production) are designed to improve the participants' skills and broaden their vision and understanding of the entire industry, including technology, economics, energy use, safety and environmental stewardship. Workshops also provide engineers with an opportunity to exchange ideas, solve specific problems and improve plant operations and profitability.
- Education and advocacy. The IFA Technical Committee recognizes that customers, markets and regulatory environments are best served by clear and concise information on the fertilizer industry and its practices and products. Because the knowledge and expertise found within the fertilizer industry is the best source for this information, the Technical Committee endeavours to educate policymakers, standardization bodies, customers and the public on industry achievements, technological advances, voluntary initiatives and best practices. The committee also encourages universities and development centres to conduct research on fertilizer product development and production processes.

(as provided by the author for distribution in Vilnius)

Potash in Complex Fertilizers: Inert or Complex

Abstract

Potash is an essential raw material for manufacturing NK, NPK and PK fertilizers. It reacts with the other raw materials such as ammonium nitrate and ammonium phosphate. These reactions may cause unexpected surprises during the lifecycle of the product. Depending on the degree of conversion potash continues to react during storing and distribution thus creating caking. The degree of conversion depends on the characteristics of the potash such as size distribution, coating, and content of impurities. This paper summarises the test methods related to selection of potash such as wettability, Enslin test, rate of dissolution, and conversion in ammonium nitrate melt. The test results are correlated with typical potash characteristics such as the size distribution and organic coating. The hindering effect of phosphorous on potash conversion in ammonium nitrate melt was tested and probable reasons are presented along with the effects of kinetic parameters such as moisture content, residence time and reaction temperature. Findings from laboratory scale experiments were confirmed in continuous bench scale tests for selection of the right processing parameters. All studies confirm the behaviour of potash to be complex in complex fertilizers.

Contact details:

Kemira GrowHow Oyj
Mechelininkatu 1a, P.O. Box 900, 00181 Helsinki, Finland
Tel: +358 10 215 2557 - Fax: +358 10 215 2531
E-mail: harri.kiiski@kemira-growhow.com

All papers and presentations prepared for the IFA Technical Symposium in Vilnius
will be compiled on a cd-rom to be released in June 2006.

Potash in Complex Fertilizers: Inert or Complex

Summary

Potash is an essential raw material for manufacturing NK, NPK and PK fertilizers. It reacts with the other raw materials such as ammonium nitrate and ammonium phosphate. These reactions may cause unexpected surprises during the lifecycle of the product. Depending on the degree of conversion potash continues to react during storing and distribution thus creating caking. The degree of conversion depends on the characteristics of the potash such as size distribution, coating, and content of impurities. This paper summarises the test methods related to selection of potash such as wettability, Enslin test, rate of dissolution, and conversion in ammonium nitrate melt. The test results are correlated with typical potash characteristics such as the size distribution and organic coating. The hindering effect of phosphorous to potash conversion in ammonium nitrate melt was tested and probable reasons are presented along with the effects of kinetic parameters such as moisture content, residence time and reaction temperature. Findings from laboratory scale experiments were confirmed in continuous bench scale tests for selection of the right processing parameters. All studies confirm behaviour of potash to be complex in complex fertilizers.

1. Introduction

In the normal fertilizer production process the different processing stages may influence the final quality of the product. The normal fertilizer production process consists of the following stages:

Raw material handling is not only to feed the raw materials into the process. It consists of all the steps from purchasing to deliveries and finally to the feeding operations. The impurities, quality and size of the raw materials are important parameters affecting the final product quality.

The **processing** stage in the most commonly used nitrophosphate process consists of the dissolution of phosphate rock with acids in a digestion reactor. The formed calcium nitrate is treated by means of separation (Odda- process), or conversion to calcium phosphates with phosphoric acid (phospho- nitric process), and to calcium sulphates with sulphuric acid. In Kemira NPK process the phosphate solution is ammoniated by ammonia in a two-step process. In the first ammoniation reactor a pH of ca 2.5 is achieved. The second ammoniation is continued until a pH of about 5- 6 is achieved. Trace elements and potash are added to the ammoniated slurry in the third (fourth) reactor. In this stage all of the raw materials have normally completely reacted if the conditions and reaction kinetics are favorable.

The NPK slurry is **granulated** by means of a drum or blunger granulator. Here, granules are formed by a process of agglomeration. Seed material is obtained from the sizing operation. In the granulation stage the reacted components become solidified when mixed together with the recycling solid materials. To have proper granulation there must be a sufficient liquid phase. Sometimes a granulation promoter is needed. This is the stage where the solid solutions are formed from the melt containing approx. 5- 15 % water. In addition to agglomeration process accretion in e.g. spherodiser can be used.

The water content in the obtained granulates is between 1 and 5 %. The granulates are **dried** by means of, e.g., rotary driers. The product temperature in the outlet of the dryer is between 80 and 105 °C. The final moisture content of the product depends on the formulation and can vary between 0.2 and ca 1 %. In the **sizing of the product** to a fraction between 2 and 5 mm, the fraction above 5 mm is crushed and returned to the granulator together with the fraction below 2 mm.

The product fraction is cooled in a **cooler** (e.g. fluidized bed) to a temperature between 30 and 45 °C. During drying and cooling the conversion reactions are slowed down or completely stopped due to the reduction of the liquid phase. If these stages are not efficient enough, the remaining, even minute, amounts of moisture may cause a continuation of the chemical reactions. Even if the dryer is working efficiently, moisture absorption may occur during the cooling step, especially if the relative humidity of the air used is too high.

In the temperature range from ambient to 150 °C there are many different types of phase transitions, which normally result in changes of volume. The dry recycling material especially may go through these transitions several times. The volume changes may result in a weakening of the physical parameters of the product. After cooling, phase transitions may occur during storage.

The cooled product is **coated** with, e.g. hydrophobic coating agents. The surface is **powdered** with, e.g. silicates such as talc to form a smooth, inert surface. The above mentioned operations are needed to improve the storage properties of the product. During storage there can be ongoing post reactions, especially if there is enough moisture to accelerate the reactions. The other phenomena that can occur is that the product may be super cooled, and therefore the unstable crystals will change to stable form as time goes by. The ongoing reactions will result in a weakened physical quality resulting in an increased caking tendency, disintegration, high abrasion, increased dustiness, low crushing strength, etc.

To evaluate the properties of commercial potash a systematic study was performed. Normally used potash contains impurities which are known to act as crystal modifiers. On the laboratory scale it is impossible to cover them all and therefore natural potash samples were chosen for the experiments. To obtain a full potash conversion, the processing parameters are very important; with such parameters as moisture content, residence time and potash reactivity, an almost complete conversion may be assured. To achieve a full potash conversion we may exclude its effect on the physical quality and concentrate on the effects of the solid solutions. The laboratory scale experiments were followed by a small continuous process. It was developed to come close to meeting the requirements of a product made on an industrial scale.

2. Production and properties of Potash

Froth flotation of potassium chloride from sylvinitic ores accounts for 80 % of the potassium chloride produced in North America and for ca 50 % of the potassium chloride produced in Europe and the former USSR.

In flotation, the first stage involves agitating the de-slimed ore with a clay depressant or slime binder to deactivate clay particles that are entrained in the washed ore flowing from the hydraulic de-sliming operation. Suitable depressants include starches, guar gum, carboxymethyl cellulose and polyacrylamides. Depending on the amount of entrained clay and the type of depressant used, dosage rates are 50- 500 g of depressant per metric ton of ore being processed.

Reagents, including a collector, that are required for the flotation are added in the second stage. An extender is added if the ore contains relatively large percentages of coarse KCl crystals, i.e., > 15 wt- % of 0.8- 1.7 mm crystals. An extender makes the amine- coated surfaces more hydrophobic, thereby enabling the particles to float readily in the flotation cells. Commonly used extenders are No 5 and No 6 fuel oils.

Collectors are primary amines derived from beef tallow. Commercially available amine is a homogeneous mixture of palmetyl-, stearyl-, and oleylamines. Longer chain amines (archidyl-behenyl) are used in special cases in which brine temperatures exceed 35 °C. At temperatures higher than ambient, normal tallow amine tends to dissolve, and is therefore unavailable to coat the surfaces of the potassium chloride crystals. Amine consumption is from 50 g/ton of high grade ore (40 wt- % KCl) to 150 g/ton of low grade ore (20 wt- % KCl). Tallow amines contain small amounts of short chain compounds from the octyl, lauryl and myristyl (C₁₄) groups. These amines usually produce enough froth for flotation. Small quantities (20- 40 g/ton ore) of methyl isobutyl carbinol (MIBC) or normal hexanol are frequently added to the flotation system to supplement the natural frothers.

The obtained product crystals are dried at ca 175 °C to reduce the moisture content to less than 0.1 wt- %. At higher moisture contents during storage, the potassium chloride tends to cake. Amine remaining on the product is beneficial in that it acts as anticaking reagent, thereby preventing pile set. In other processes that are used to separate potassium chloride from sodium chloride and that do not require amine, the product crystals are treated with amine salts at a 110- 180 g/ton rate to prevent pile set.

To ensure the free-flow property during transportation potash may also be treated with:

- fatty amines $\text{CH}_3\text{-(CH}_2\text{)}_n\text{-NH}_2$
- fatty acid
- palmitic acid $\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-COOH}_{1/2}$
- stearic acid $\text{CH}_3\text{-(CH}_2\text{)}_{16}\text{-COOH}_{1/2}$
- octanediol $\text{CH}_2\text{OH-(CH}_2\text{)}_6\text{-CH}_2\text{OH}$
- mineral oil
- potassium prussiate
- modified montan waxes

The feed quantity of oils and amines varies between 100 and 500 g/ton. With quantities more than 300 g/ton, the wettability and the dissolution behaviours of the potash component are very much reduced. Furthermore, there is a risk of organic matter being evaporated with rising temperature after the chemical conversion, and the materials therefore become deposited in heat exchangers or filters which can give rise to failure of the operation. As mentioned in ref. 1 the amine quantities should be limited to 150 g/ton.

The amine content varies as a function of the particle size. In Table 1 this variation is summarized. The variation can be explained by the larger surface in smaller fractions.

Table 1. Variation of oil and amine content as a function of sieve fractions.

Fraction μm	Amine g/ton	Oil %
< 88	228	0.07
88 - 125	164	0.05
125 - 177	132	0.05
210 - 297	112	0.03
297 - 420	123	0.03

In the commercially available potash materials the potassium (60.1- 60.6 % K_2O) and chloride (46.9- 47.2 % Cl) content is relatively constant. Sulphates and chlorides, such as magnesium, sodium and calcium, are also present as impurities. Potash may also contain impurities which act as crystal modifiers. In ref. 10 the following trace elements are mentioned: Pb, Fe, Cu, Ni, Cr, Mo, V and Ti. The trace element content may, in special cases, affect to the reactivity especially if the content is high. The amount depends on the origin of the potash.

3. Experimental methods

The wet granulation studies indicated that the wettability and solubility properties of potash are critical quality parameters in the production process. In the slurry process the potash is normally added during the 2nd ammoniation. The available reaction time for the chemical reaction is between 2 and 6 hours. When the potash is added to the granulator the reaction time is reduced to a few minutes. A complete conversion reaction is needed to avoid ongoing post reactions after manufacturing. Therefore it is essential to know the reactivity of the used potash. The published reactivity tests have been compared and the major factors which have an effect on the reaction have been studied. These results are presented in this chapter.

3.1. Wettability

Wettability is measured with a simple test. Into a 50 cm³ beaker ca 70 g of potash is poured to fill the beaker to a depth of ca 1 cm from the top. The surface is tamped to form a smooth surface. With pipette 5 cm³ of water is added to the beaker and the time taken for the water disappearance is measured starting from the moment water emerges from the pipette.

3.1.1. *Moisture absorption*

An Enslin test is used to estimate the moisture absorption properties. The measuring equipment consists of a fritted glass filter with U- tube attached to it. Under reduced pressure the apparatus is filled with ion-exchanged water. Reduced pressure is used to avoid the formation of air bubbles. The surface of the filter is dried with filter paper. Five grams of potash is weighed out and placed on the glass filter. The volumetric amount of water taken up by the salt in a fixed period of time (5 min) is measured with a final time of 50 minutes.

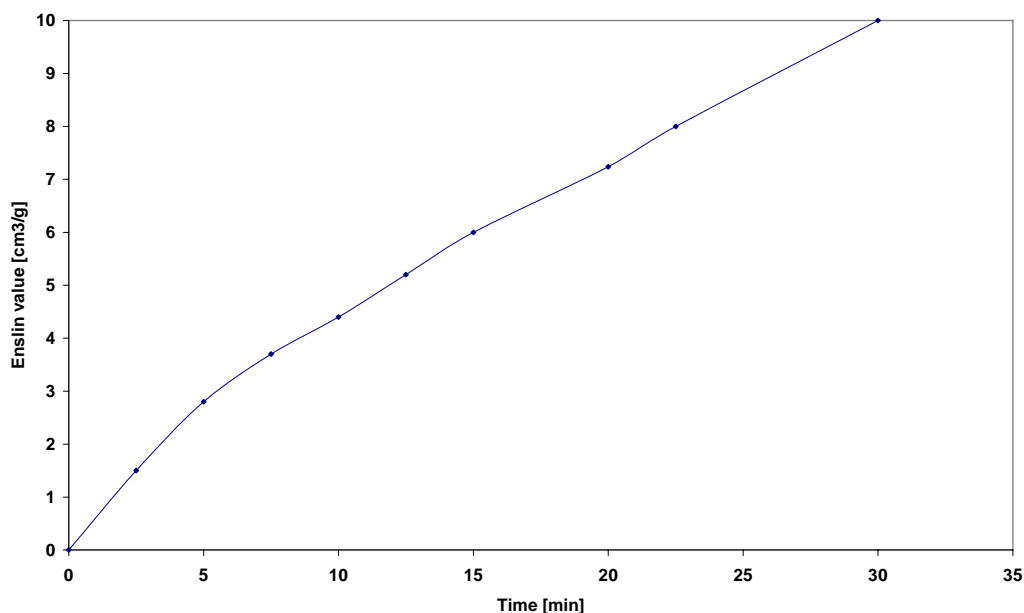
The volumetric amount of water taken up as a function of time is called the Enslin value and is expressed as cm³/g:

Equation 1
$$E = \frac{V}{m} * 100$$

where V= the volume of absorbed water [cm³]
m= the amount of the sample [g]

A typical moisture absorption curve is presented in Figure 1. The Enslin value is presented as a function of time.

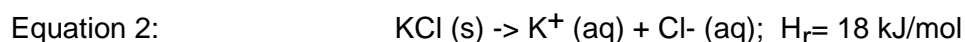
Figure 1. Enslin value as a function of time for sample KR1.



3.1.2. The rate of dissolution

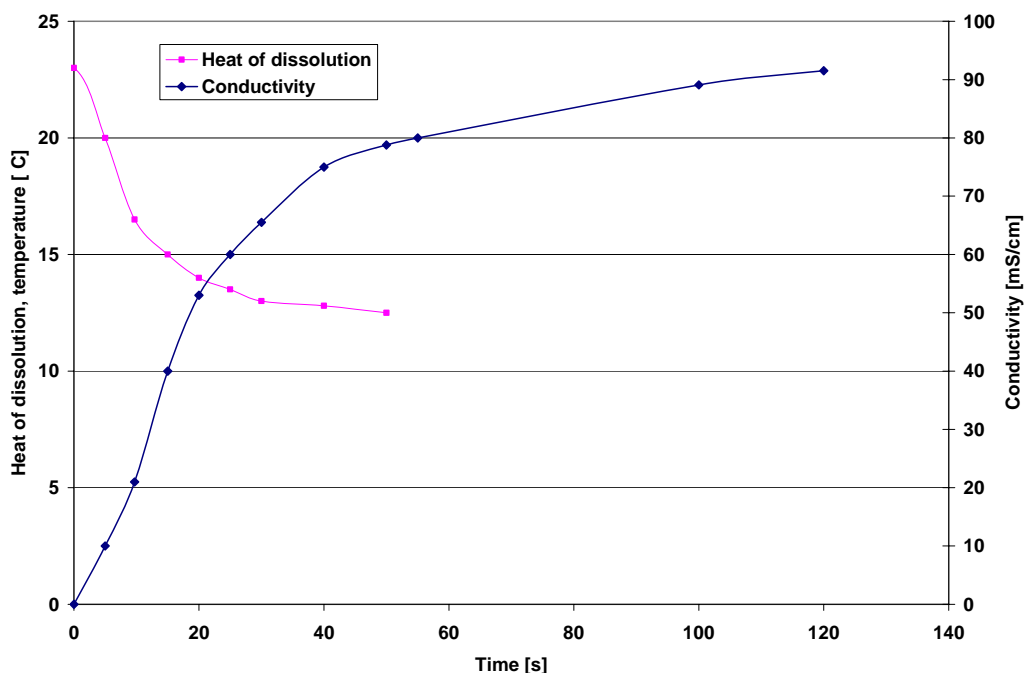
The rate of dissolution can be determined by either measuring the heat of dissolution or by measuring the change in conductivity.

When potash dissolves into water the temperature decreases. With a ratio of 1:4 (20 wt-% KCl) the decrease is ca 14 °C for the endothermic equation:



In one experimental method, 25 g of potash is added with constant agitation to 100 cm³ of ion-exchanged water in a Dewar jar. The initial temperature is ca 20 °C. The decrease in temperature is measured as a function of time from the period starting with the introduction of the sample and ending with the maximum change in temperature, as illustrated in Figure 2 a.

Figure 2. Rate of dissolution determined by a) the heat of dissolution and b) conductivity as a function of time for sample KR12.



In the other experimental method 15 g of potash is added with intensive agitation to 200 cm³ of ion-exchanged water at 20 °C. The change in the conductivity is measured as a function of time. A constant measured value indicates the complete dissolution of the sample. The analysis covers the period starting with the dissolution of the sample and ending with a constant measured value.

Typical rate of dissolution curves for both of the methods are presented in Figure 2. The end-point has been evaluated from the onset point.

3.2. Determination of the reactivity with an ammonium nitrate melt

Approximately 10 g of anhydrous ammonium nitrate is weighed in a crucible and heated in a sand bath by a hot- plate. A stoichiometric quantity of the potash salt is added to the clear ammonium nitrate melt and the resulting slurry is subjected to intensive agitation for 10 minutes. The molten ammonium nitrate- potash mixture is cooled to ambient temperature in a crucible and the solidified mixture is reduced in size. On the basis of Least Square Quantitative X-Ray Diffraction (LSQX) analysis the degree of conversion (c) is calculated according to equation 3.

Equation 3

$$c = \frac{(x_{\text{KCl}} + x_{(\text{NH}_4,\text{K})\text{Cl}} * y_{\text{KCl}}/100)}{x_{\text{K}}} * 100$$

where x_{KCl} is the amount of potassium in the unreacted potassium chloride, $x_{(\text{NH}_4,\text{K})\text{Cl}}$ is the amount of solid solution $(\text{NH}_4,\text{K})\text{Cl}$, y_{KCl} is the amount of potassium in the solid solution $(\text{NH}_4,\text{K})\text{Cl}$ and x_{K} is the total potassium content in the mixture.

4. Reactivity studies

4.1. Comparison of different test methods

The results from the different reactivity tests are included in Table 1. In the wettability test the obtained results were between 7 (KR11) and 26 131 s (KR7). By this method the potash samples can be separated from each other. In some samples water penetrates into the potash within a few seconds. In the results there was no correlation to oil and amine content. The penetration time was dependent on the physical properties of the potash. Parameters, such as the hydrophobic properties, hardness, number and size of voids, impurities and the density of the potash, all influence water penetration. These properties were not studied.

Sample KR11 was easily wetted in the water drop test. In contrast, the moisture absorption was low. The Enslin tests described how much and how rapidly the water was absorbed into the potash sample. The obtained Enslin values were relatively low. Few samples (KR30, KR31) absorbed high quantities of water in this test. There was no correlation with the other measured properties. This method correlates most probably with such physical parameters as specific surface area, hydrophobic properties and the number and size of the voids.

The two above mentioned test methods are most likely connected to the storage and transportation properties of the potash. Therefore they should not be regarded as reactivity tests.

Two different methods were used to estimate the rate of dissolution. With the method based on conductivity the measured values were between 12 and 180 s. Results from the other method (heat of dissolution) varied between 42 and 100 s. This method is practical when the rate of dissolution into water is an important parameter. It depends both on the particle size distribution of the potash, and the quantity and quality of the coating. The method provides an indirect means for determining the amount of coating agents for potash samples from the same origin. The method was simple to use. For both methods it was difficult to decide which value represents the end value. The method cannot be applied in the determination of potash reactivity in the NPK- process.

The best estimation of the potash reactivity is to measure the amount of the unreacted potassium chloride after the reaction between ammonium nitrate and potash. To be more accurate the estimation should be made with the particular NPK- slurry. As the potash is used for many different NPK grades, a number of tests are needed. The result obtained from the reactivity test correlated with the amount of the coating when the same coating agents were used and the potash was from the same origin. A clear correlation with particle size was obtained. This correlation will be further discussed. There was no correlation in the values obtained with the other test methods.

Table 2. Results of different potash reactivity tests.

Sample	Water drop [s]	Rate of dissolution by conductivity [s]	Rate of dissolution by heat [s]	Enslin test [cm ³ /g]	Degree of conv [%]	Amines [g/ton]	Oil [g/t]
KR1	1973	150	65	7.51/11.44	97.5	10	697
KR2	9621	180	95	0.12/ 0.26	96.0	112	221
KR3	912	150	80	0.10/ 0.20	87.1	106	124
KR4	6603	180	75	0.35/ 0.45	83.2	88	107
KR5	804	180	85	0.39/ 0.68	90.5	81	186
KR6	54	150	100	<< 0.5	92.8	146	92
KR7	26131	21	75	0.0 /0.0	87.7	185	192
KR8	20	13	35	9.57/9.75	93.0	185	192
KR9	58	100	100	<< 0.5	85.6	216	135
KR10	20	70	42	0.65/ 0.75	96.0	216	135
KR11	7	12	55	0.69/ 0.89	77.1	18	96
KR12	12	18	40	0.31/ 0.50	90.8	18	96
KR34	829	150	80	0.32/ 0.46	84.5	nm	nm
KR35	19	12	40	1.85/ 2.00	98.7	nm	nm
KR36	31	50	65	2.02/ 2.21	96.1	nm	nm
KR37	16	18	25	0.76/ 2.00	98.1	nm	nm

nm= not measured

4.2. The effect of particle size

In the reactivity tests there was a correlation in the results with the particle size of the potash. This item was further studied. Different sieve fractions were collected by sizing with sieves. The results from the tests are presented in Table 3.

Water easily penetrated the potash when the particle size was increased. This was seen in the values obtained from the water drop test. The rate of dissolution was practically at same level in all sieve fractions. The chemical composition in the different sieve fractions was assumed to be constant due to the high K₂O content of the sample (no space for impurities).

Moisture absorption was dependent on particle size. The Enslin value increased as a function of the sieve fractions. Low moisture absorption values were obtained from sieve fractions between 36 and 71 µm. Water slowly penetrated into the sample. The highest values were obtained for the sieve fractions between 224- 280, and 280- 355 µm. Between these fractions there were suitable voids for the moisture to penetrate. The moisture absorption value decreased when particles above 355 µm were tested. At this size the particles were loosely packed and the open voids between the particles were too large for the water to penetrate. The penetration has to occur along the crystal surface. Most likely there was no capillary suction. This could occur if the potash surface were porous. The porosity was not determined.

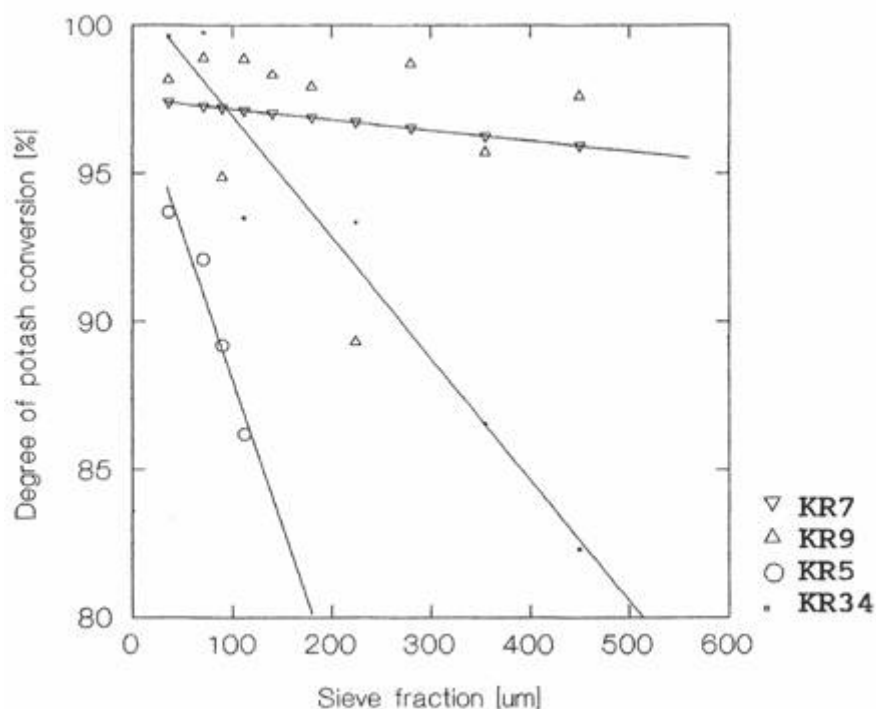
The degree of potash conversion was affected by particle size when measured by the reaction between ammonium nitrate and potash. The degree of potash conversion was increased from 69 % to approx. 94 % as a function of a decrease in the sieve fraction. The results are presented in Table 18. The degree of conversion was slightly improved when the sieve fractions were decreased from 90- 110 to 36- 71 µm. The largest difference was seen when the fractions > 355 and 112- 224 µm were compared. Between these fractions the degree of conversion was improved from 69 to 86 %.

Table 3. The results of the reactivity tests involving different sieve fractions

Sample	Sieve fraction [μm]	Water drop [s]	Rate of dissolution by conductivity [s]	Rate of dissolution by heat [s]	Enslin [cm ³ /g]	Degree of conversion [%]
KR46	36 - 71	20	19	25	3.0/ 3.3	93.7
KR47	71 - 90	17	20	50	5.6/ 6.7	92.1
KR48	90 – 112	21	30	140	4.4/ 4.0	89.2
KR49	112 – 224	23	20	35	11.9/12.0	86.2
KR50	224 – 280	9	38	35	18.5/18.5	76.7
KR51	280 – 355	6	20	40	16.4/17.4	
KR52	> 355	6	32	95	9.0/10.3	69.3

The effect of the sieve fraction was determined further for samples KR5, KR7, KR9 and KR34. The degree of potash conversion linearly decreased as a function of the sieve fraction. The larger the particle size was, the lower the degree of potash conversion. The conversion was not only dependent on the particle size, but also on the origin of the potash. The samples KR7 and KR9 were from Eastern Europe, KR34 from Great Britain and KR5 from Germany. Samples KR7 and KR9 were very reactive. The decrease of the particle size influenced the degree of potash conversion by a few percent. In sample KR5 the particle size had a remarkable effect on the degree of potash conversion. Although the particle sizes were lower than 200 μm the degree of potash conversion was below 90 %. In the fraction below 36 μm the degree of potash conversion was not above 95 %. This potash can be regarded as non-reactive. In sample KR34 the effect of the particle size was clearly seen. The degree of potash conversion increased from ca 83 % to 99 % when the particle size was decreased from ca 450 μm to 36 μm. On the basis of these results it is essential to know the reactivity of the potash from various sources. This should be a parameter for a continuous follow-up if the potash raw materials are variable. The results are presented in Figure 3.

Figure 3. Degree of conversion as a function of the sieve fraction.



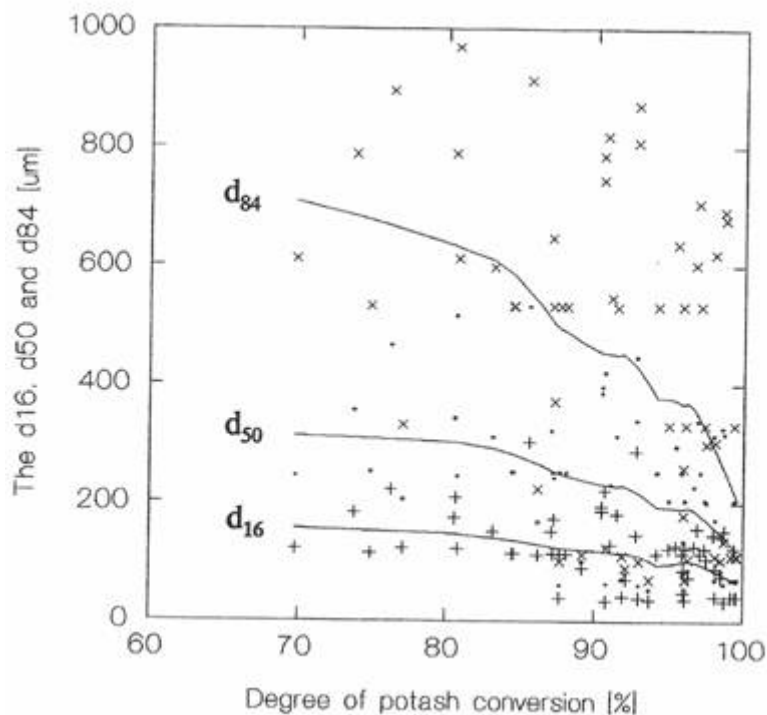
A particle size analysis was done for most of the samples. From the analysis, the representative d_{50} -, d_{16} - and d_{84} - values were calculated. The d_{50} - value represents that there are 50 % larger and smaller particles than the given value. These values were calculated according to equation 4.

Equation 4
$$d_x = Z_n - \frac{(x - C_n) * (Z_n + Z_{n+1})}{F_{n+1}}$$

where x is the parameter 16, 50 or 84, d_x is the equal size distribution parameter, C_n is the cumulative percentage retained on the n^{th} sieve, Z_n is the sieve size for which the cumulative percentage retained (C_n) does not exceed x %, Z_{n+1} is the sieve size for which the cumulative percentage retained (C_{n+1}) exceeds x %, and F_{n+1} is the percentage retained on sieve Z_{n+1} .

The degree of conversion was dependent on the d - values as presented in Figure 4. There was a clear trend towards a higher degree of conversion with a decrease in the average particle size. The highest slope was in the d_{84} - value. When the d_{84} was lowered from ca 800 μm to 600 μm the degree of potash conversion increased from 70 to 85 %. Further decrease in d_{84} to ca 300 μm increased the degree of potash conversion to close to 100 %. The decrease in d_{50} - value from ca 350 to 200 μm increased the degree of potash conversion from ca 70 to 95 %. The least slope was obtained for the d_{16} - value. When it was decreased from 180 to 120 μm the degree of conversion increased from 77 to 96 %.

Figure 4. The d - values as a function of the degree of potash conversion.



Further studies were made from samples where the particle size was reduced by crushing. Some samples were crushed with an ultra-centrifugal laboratory mill (Retsch). The results are presented in Table 4. For all samples the degree of conversion was increased after crushing.

The d_{50} - value of R18 was decreased 17 μm by additional crushing. This reduction in size resulted in a 2 % (abs) increase in conversion. The d_{50} - value of R22 was decreased from ca 530 to 83 μm . As a result the degree of conversion was increased by 10 %. Extra crushing reduced the particle size of the original potash but also broke down the amine / oil coating. This allowed a faster and more complete reaction with the ammonium nitrate melt.

Table 4. The effect of particle size reduction on the degree of conversion.

Sample	Crushed	d_{50} [μm]	d_{16} [μm]	d_{84} [μm]	Degree of conv. [%]
R18		70.9	42.0	109.5	96.1
R19	crushed R18	53.9	36.8	71.1	98.1
R6		251.8	114.1	531.9	84.5
R17	crushed R6	63.6	33.7	135.5	98.7
R59		227.5	127.0	601.8	96.7
R60	crushed R59	86.4	75.6	104.4	98.5
R57		230.6	129.2	546.0	91.1
R58	crushed R57	86.5	73.9	104.5	96.3
R20		172.8	90.2	302.9	87.7
R21	crushed R20	61.8	40.3	102.0	93.0
R22		532.3	302.7	913.4	85.6
R23	crushed R22	82.5	47.7	178.5	96.0
R24		205.5	123.4	330.9	77.1
R25	crushed R24	63.8	34.0	123.7	90.8

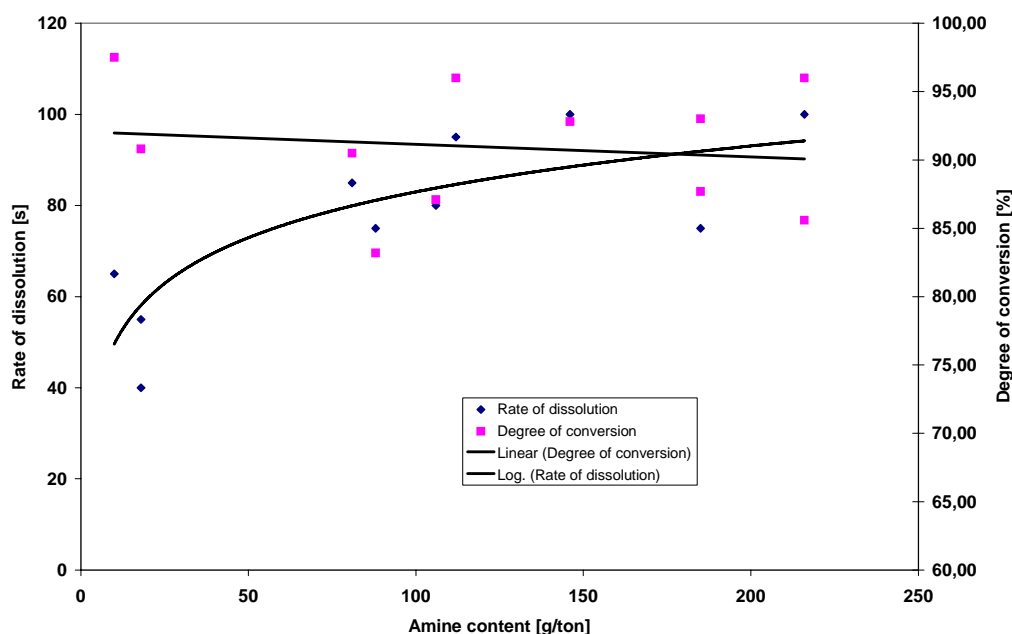
4.3. The effect of organic coating

The effect of the amine content on the degree of potash conversion was studied. When the reactivity of potash was measured by the rate of dissolution, a clear correlation with the amine content was achieved (fig. 5).

In the literature^{1,2} it is mentioned that the amine content should be limited to 150 g/ton to achieve an almost complete conversion of potash. From the graph in Fig. 5 it may be concluded that for potash with amine content lower than 100 g/ton the degree of conversion is above 80 %, depending on the origin. The poor correlation ($r= 0.45$) was partly explained by the different origin and particle size of the potash. When the third variable, i.e. d_{50} values, was added, the correlation was even weaker ($r= 0.35$). With this result the amine content seemed to have no effect on the conversion at all. When potash is added to the reactors, this assumption is most likely valid. Amines are destroyed by the reactor conditions (pH, temperature). If the potash is added to the recycle then the amine content has an effect on the surface of the potash particles. The liquid phase which contains ammonium nitrate does not have enough time to dissolve the coating layer or to penetrate through the layer as the water is simultaneously evaporated. With low amine content, the surface is broken and the reactions will continue. The granulation can be destroyed if there are amines in the recycling material.

In Table 1 the amine content for different sieve fractions was presented. In the smaller fractions the degree of potash conversion should be affected by the amine and oil content. In the described experiments the degree of conversion was higher for the smaller particle sizes than the larger (Table 3). The degree of potash conversion was more strongly dependent on the particle size than on the content of oils and amines. The origin of the potash was also an important parameter.

Figure 5. The rate of dissolution and the degree of conversion versus amine content.

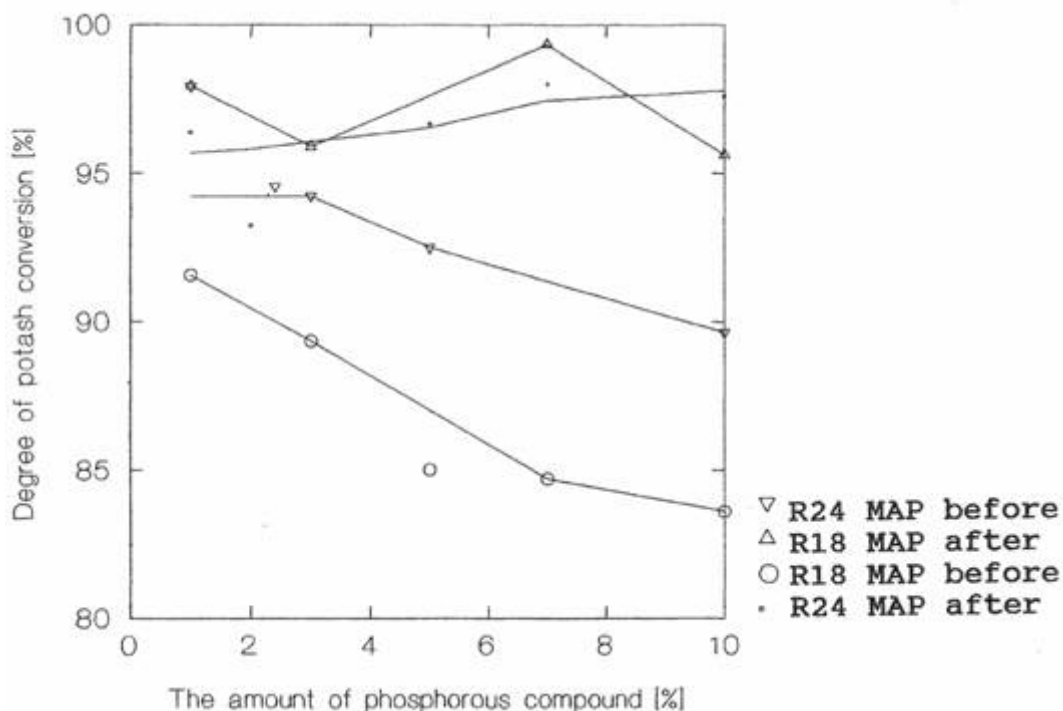


4.4. The hindering effect of phosphorus compounds

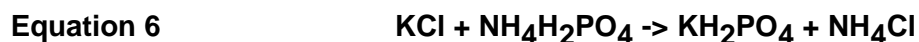
It has been understood that H_2PO_4^- hinders the conversion reaction (4). This item was studied with potash R18 (high degree of conversion) and with potash R24 (low degree of conversion). Ammonium nitrate was melted in a sand bath, and potash with known amounts of pro-analysis monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ (MAP), diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ (DAP), monopotassium phosphate KH_2PO_4 (MKP) and rock phosphate was added. The percentage amount of phosphorus compounds added was 1, 2, 3, 4, 5, 7.5 and 10 %. In these experiments the phosphorus compounds such as MAP had no hindering effect. If any conclusions should be drawn, the MAP may in fact be seen to increase the degree of conversion, especially with potash R24. This is shown in Figure 6.

When the phosphorus compounds were added to the melt before the addition of potash, the decreasing effect of MAP and DAP was clearly seen. The results are presented in Figure 6. The degree of potash conversion was depressed more in sample R18 than in R24.

Figure 6. Degree of conversion versus the percentage amount of added phosphorus compounds.



The importance of the order of the addition order confirms that the H_2PO_4^- ions were needed to prevent the conversion reaction. When MAP was added the following reactions occurred:



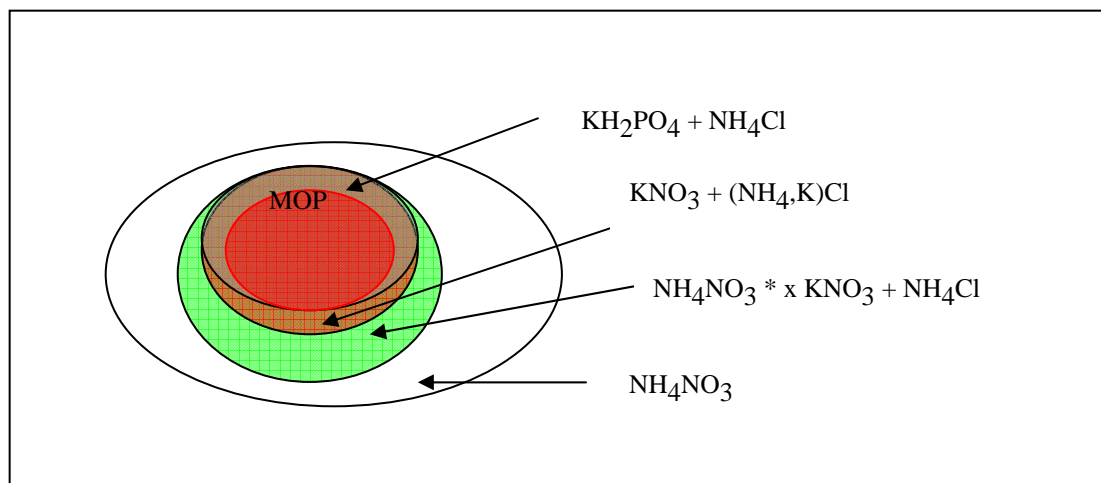
The solid solution $(\text{NH}_4, \text{K})\text{H}_2\text{PO}_4$ was formed. When diammonium phosphate was added it was partly decomposed to monoammonium phosphate, with a release of ammonia. As a function of formed solid solution the degree of potash conversion was decreased.

KH_2PO_4 has a lower solubility in water than $\text{NH}_4\text{H}_2\text{PO}_4$. After it has been formed, according to equation 6, it precipitated to the surface of the potash crystals. The water content in the slurry was 5%. Ammonium nitrate liquid and potash particles were therefore separated by the KH_2PO_4 layer. This layer is illustrated in Figure 8. The diammonium phosphate has a pH-value of 8.0 and was not stable in ammonium nitrate-potash mixture. At a higher pH, K_2HPO_4 could be formed.

Figure 7. Solubilities⁴ of different phosphorus compounds.
For comparison the solubilities of KCl and NH₄NO₃.

Compound	g/100 g H ₂ O	pH	Temp. [°C]
KH ₂ PO ₄	33	4.5	25
NH ₄ H ₂ PO ₄	173	4.5	100
K ₂ HPO ₄	167	8.9	20
(NH ₄) ₂ HPO ₄	107	8.0	100
NH ₄ NO ₃	871	-	100
KCl	57	-	100

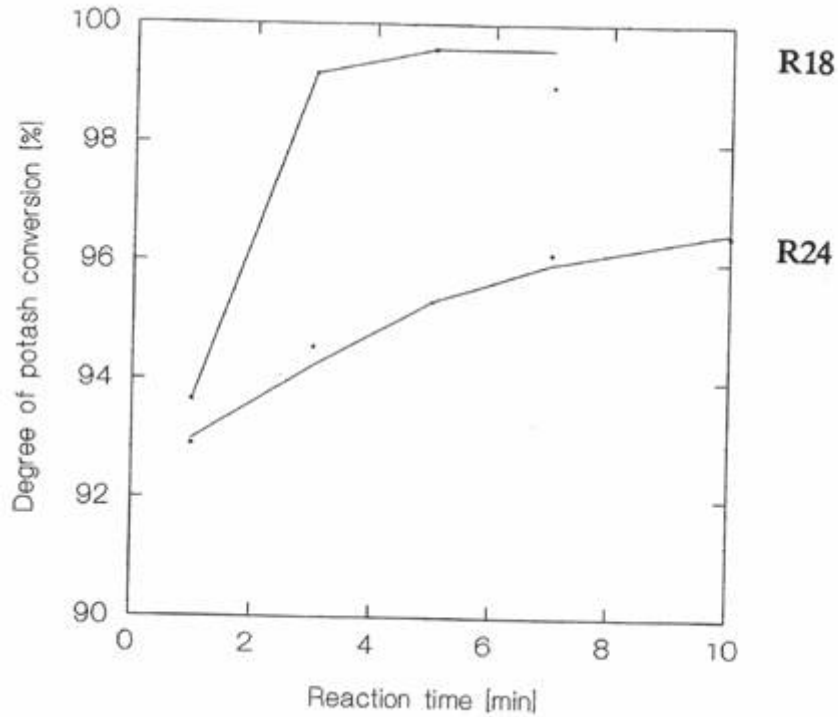
Figure 8. The formation of the KH₂PO₄- layer.



4.5. The effect of kinetic parameters such as moisture content, residence time and reaction temperature

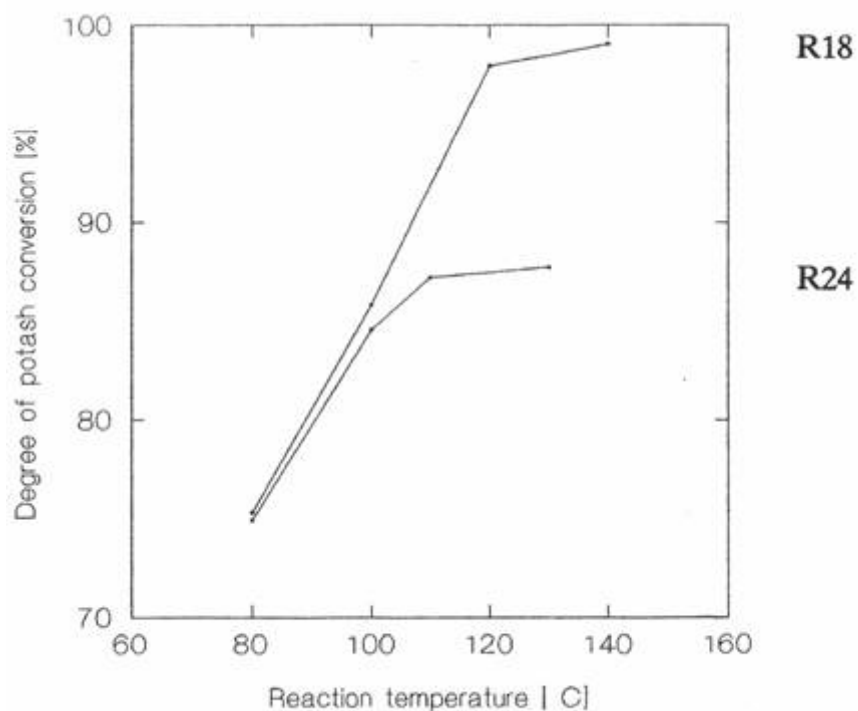
The effect of residence time, reaction temperature and moisture content on the conversion reaction was studied. As a function of reaction time the degree of conversion was increased. The increase depended on the potash type. The degree of conversion of sample R24 slowly increased, whereas sample R18 had an almost complete reaction after 3 minutes. During the first minutes most of the potash had reacted. The degree of potash conversion was even higher than 90 % for reactive potash types. After 10 minutes there was no significant increase in the degree of conversion. All the reactivity tests were therefore performed with a reaction time of 10 minutes. The results are presented in the Figure 9.

Figure 9. The degree of conversion versus reaction time.



The degree of potash conversion was also increased as a function of temperature. Temperatures above 120 °C were needed to almost complete the reaction. The moisture content was not constant in these experiments. At lower temperatures more moisture remained in the solidified product. Therefore the actual degree of conversion (with similar moisture content) would be even lower. The results are presented in Figure 10.

Figure 10. The degree of conversion as a function of temperature.



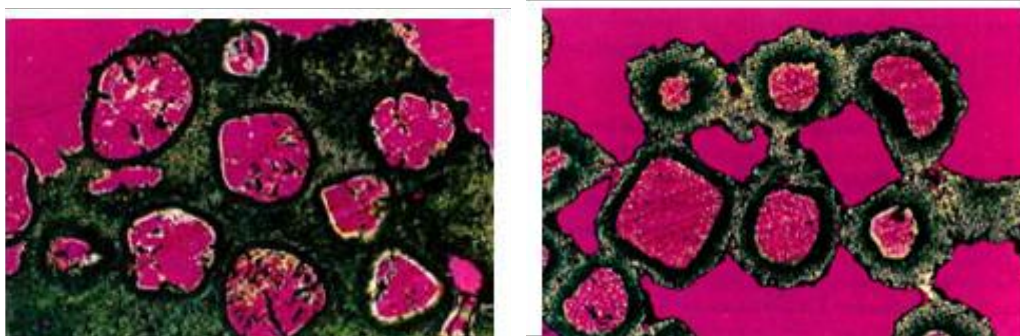
With the described method it was not possible to properly adjust the moisture content. The initial moisture content was always 5 %, and after the reactivity test it ranged from 0.2 to 1.5. Average moisture content in the measured samples was 0.51 ± 0.30 %.

In the reactivity tests moisture content was an important parameter. This is illustrated in the polarized microscope pictures in figures 11 a and b. The reactivity test was made similarly to that mentioned above. The potash particles were larger than $750 \mu\text{m}$. The same quantity of water was added. In the first sample the water rapidly evaporated at ca $120 \text{ }^\circ\text{C}$. In the second sample moisture was left by keeping it at the mentioned temperature for a shorter period of time. Samples were left untouched overnight. A thin layer prepare was made.

In the polarized microscope picture (Fig. 11 a) it can be seen that in the first sample the border line between the potash particles (red crystals) and the surrounding matter is sharp. This indicates that the molten ammonium nitrate has reacted until all of the water has evaporated. No further reactions have occurred because of the sharp, solid border. The element distribution in the scanning electron microscope pictures shows that there is a zone containing separate NH_4Cl and KNO_3 crystals.

In the second sample (Fig. 11 b) the border line is irregular. There has been enough water for the reaction to proceed. The reaction zones surrounding the KCl crystals are wide. In the Cl^- and K^+ distribution it can be seen that larger ammonium chloride crystals are found at the outermost layer. Smaller crystals are seen in the zone located nearest to the KCl crystal.

Figure 11. Polarized light microscope picture of the potash reaction with a) ammonium nitrate melt and b) of the potash reaction with wet ammonium nitrate melt.



The conversion reaction clearly proceeds as long as there is remaining moisture in the samples. From the sharpness of the border line it can be determined whether the conversion proceeded before the evaporation of the moisture, or whether water was present in the final mixture after solidification.

5. Conversion studies in a continuous system

In the laboratory scale tests, described above, it was difficult to maintain constant moisture content. Therefore the reactivity of potash was studied in a continuous system where constant moisture content was kept. In these tests, also the effect of the potash feed points on the degree of conversion was studied.

According to literature there are several possibilities to improve potash conversion:

- to feed potash through reactors;
- to feed milled potash through reactors³;
- to pre-mix ammonium nitrate and potash in a separate vessel;
- to pre-mix ammonium nitrate and crushed potash in a separate vessel;
- to use crushed potash⁵;
- to modify the processing conditions, such as moisture content, temperature and residence time;
- to use pre-heated potash.

In the bench scale trials three different feeding points were used: potash to the recycle, to buffer tank (M4) and to ammoniation reactor (M5) (Fig. 12). At each feeding point two different moisture levels were used. In these tests the influence of residence time, milling and moisture content were studied.

5.1. Procedure

In the bench scale granulation tests the ammonium nitrate was prepared by neutralizing nitric acid with ammonia. The obtained ammonium nitrate liquid was kept in a batch reactor (volume 50 litres). The moisture content in the batch reactor was kept at ca 20 %. Liquid ammonium nitrate was pumped into the first overflow reactor (M4). The moisture content was reduced to the needed level. Both of the reactors had volumes of 2.5 litres. The second reactor (M5) was also acting as a buffer tank.

From reactor M5 the slurry (NH_4NO_3 or $\text{NH}_4\text{NO}_3 + \text{KCl}$) went to the blunger as an overflow. The recycle came from a screw feeder located on a balance to obtain a steady recycle feed. The temperature in the blunger was kept between 118- 120 °C with steam in the heating jacket covering the blunger. The heating jacket was used to prevent heat loss during the granulation. The process layout is presented in Figure 12.

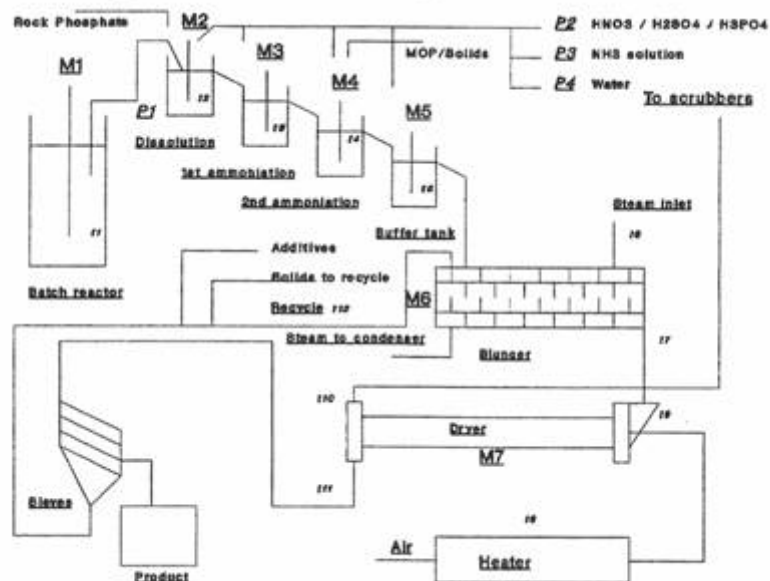
The K_2O content in the potash used was 61.0 % and Cl content 47.3 %, and the degree of potash conversion 68.2 ± 4.6 %, and when crushed, 89.0 ± 0.5 %.

In the first trial the potash was fed into the blunger. The moisture content was thereafter kept at ca 0.8, 1.2 and 2.0 %, with different moisture contents in the slurry.

In the second trial the potash was fed into, reactor M5. The moisture content in the reactor was kept at ca 5, 10 and 15 %. Moisture content was kept constant by pumping water into the reactor.

In the third trial the potash was fed into the reactor M4 to increase the residence time. Moisture content was kept at 5, 10 and 15 % by pumping water into the reactor. Samples were taken from the outlet of the blunger. These samples were dried in a heatable oven at temperatures 80, 100 and 120 °C. Drying time was 1 hour. One sample was kept overnight at 50 °C.

Figure 12. Lay-out of the bench scale granulation trials.



5.2. Results

By feeding the potash into the recycle, the degree of potash conversion varied between ca 40 and 60 %. In the final product the degree of conversion was further improved when potash was fed into the reactors. When fed into buffer tank the degree of conversion increased to ca 75- 90 %. The best results were obtained when potash was fed into ammoniation reactor. The degree of conversion was then between 86 and 91 %. The results are presented in Figure 13.

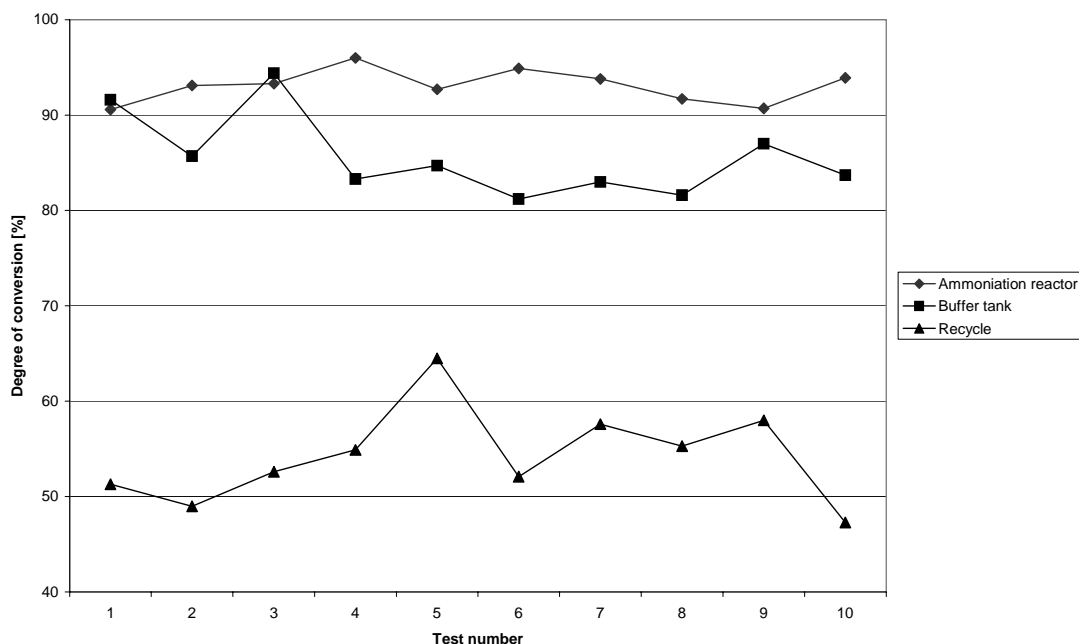
The longer the residence time, the higher was the degree of potash conversion. The variation in the degree of conversion values was lowest when the potash was fed into ammoniation reactor. The highest variation was obtained when the potash was fed into the recycle.

With the polarized light microscope it was possible to identify the unreacted KCl crystals. When potash was fed into the recycle there were clearly a large number of unreacted KCl crystals in the product. These crystals were surrounded by darker reaction zones. This means that the conversion reaction continued after the granules were formed. When the potash was added to ammoniation reactor there were only a few remaining KCl crystals in the thin layer photographs. Thus, the reaction has continued in a part of the crystals after granule formation. As there was a solid border line between the crystal and surrounding surface, no post reactions were expected.

Granulation related to the temperature and moisture content. In these studies the temperature was kept as constant as possible. Therefore it was possible to change the moisture content only in a relatively narrow range. Even a small increase in the moisture content improved the degree of potash conversion.

Drying temperature slightly affected the degree of conversion. In these trials the samples were dried in an oven (after collection in a Dewar jar). In a continuous system the cooling rate may have a large effect on product quality. For example, drying of ammonium nitrate below 32 °C will reduce the caking tendency.

Figure 13. Degree of potash conversion versus feed point.



The results given in Table 5 show that the higher the degree of potash conversion, the higher the amount of calcium and magnesium nitrates. These compounds are highly hygroscopic, as was given earlier. Surprisingly, the moisture absorption decreased as a function of increasing Ca- and Mg- nitrate content. This phenomenon was explained as follows: when Ca- and Mg- nitrates took up some water a layer was formed where the water vapor prevented further absorption of water. The moisture content, given in parentheses, showed that there was a higher moisture content in the last two samples with lower moisture absorption values. The formation of these nitrates could be prevented by adding a small quantity of sulphuric acid to bind these cations to sulphate form.

The nitrates from the impurities in the potash, such as Mg, Ca and Na, were formed as the degree of potash conversion increased. The conversion of the potash has therefore occurred first. The formation of the nitrates occurred after most of the potash had reacted. The impurities were located inside the KCl crystals. Naturally the nitrates were formed after the impurities were liberated from the crystal.

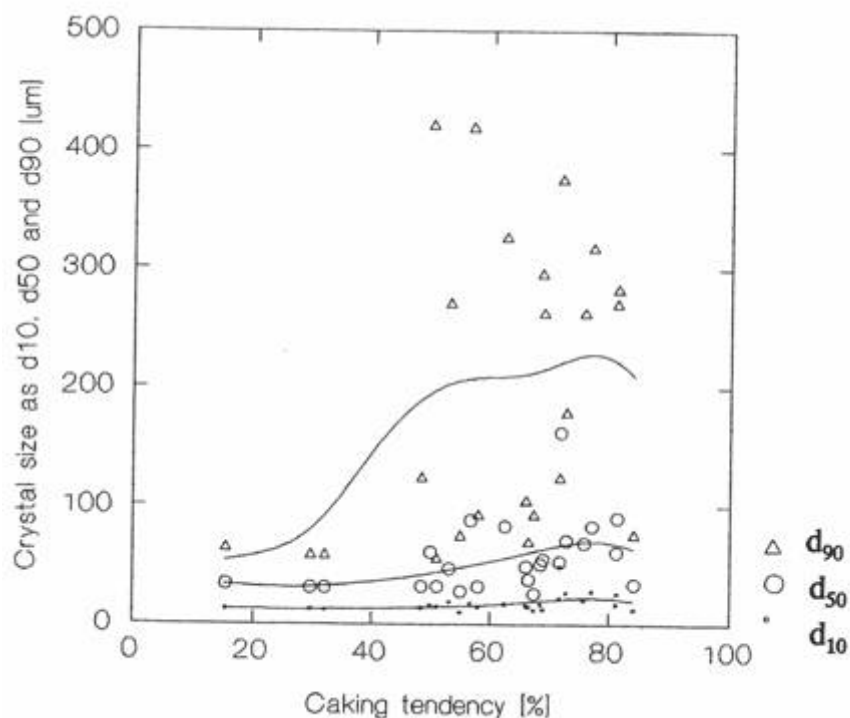
Table 5. Mg and Ca nitrate content in different samples.

	Ca(NO ₃) ₂ [%]	Mg(NO ₃) ₂ [%]	Moisture absorption (initial H ₂ O cont.) [%]
KCl to Recycle - 80 °C	0.013	0.013	9.7 (0.14)
KCl to RII - 50 °C	0.024	0.020	8.1 (0.14)
- 100 °C	0.035	0.041	7.4 (1.40)
KCl to RI - 100 °C	0.043	0.046	6.6 (1.65)

As a result of these conversion experiments a series of samples with different physical properties and degrees of conversion were obtained. The formed solid solutions or degree of conversion was not clearly correlated to, e.g., the caking tendency. Statistically, a relation between the moisture content and caking tendency was found. This is a well known phenomena. Some correlation was found with the contents of phases K3 and K2 with caking tendency.

An assumption was made on the basis of polarized light microscope pictures that the crystal size varies in the samples. Samples were extracted with methanol and isopropanol. The size distribution was then measured with Malvern. The main components in the undissolved matter were potassium nitrate, ammonium chloride and potassium chloride (confirmed by XRD). The only component extracted was therefore ammonium nitrate. Thus the d_{50} was an average size for all the KNO_3 , NH_4Cl and KCl crystals. With high d_{90} value the caking tendency was high. There was a rather wide scatter in the results which was due to the inaccuracy of both methods. Clearly the presence of large crystals resulted in high caking figures. The presence of the large crystals is due to a low degree of potash conversion.

Figure 14. Caking tendency vs d- values of the crystal size distribution.



6. Conclusions

The various methods which are widely used to estimate the reactivity of potash were not comparable. The water drop and Enslin test determined, more or less, the wettability properties of potash. The rate of dissolution correlated with the amine content of the potash when it was from the same origin. The most reliable and practical method was to measure the reactivity in the ammonium nitrate melt. The different reactivity tests were not completely explained by the measured variables. Therefore there were also another or other parameters affecting the reactivity. If further studies are made on the basis of this work, parameters such as the specific surface area, porosity, hardness, and surface

studies of the potash should be included. These parameters were not measured in this work.

For optimum rate of dissolution, the amine content should be lower than 150 g/ton. With this amine content the degree of potash conversion should be above 80 % (depending on the origin).

The highest degrees of potash conversion were obtained when the d- values from the particle size distribution were less than 540 (d_{84}), 250 (d_{50}) and 140 μm (d_{16}). With larger d- values the crushing of the potash improved the degree of conversion. These values depend on the origin of the potash.

A higher moisture content in the slurry tended to increase the degree of conversion. From the point of view of economics, the evaporation of excess water increases the processing costs, but may be used in certain circumstances. Longer residence time increased the conversion; however, processing costs are also increased. Potash conversion was improved by feeding the potash through the reactors. It was not possible to determine the effect of different moisture contents due to the sensitivity of the granulation in the bench scale blunger. When moisture content was increased the granulation came more difficult. This could have been avoided by using higher recycle ratio which was not possible in the installation. Similar problems would occur also in larger scale. The moisture content can be varied only within a limited range.

Obviously the crystal size may have a remarkable effect on the physical properties, especially on the caking tendency, plasticity and hardness. The methods to study precisely the crystal size of the individual compounds from a bulk sample should be developed, to explain the given parameters. The large crystals are an indication of the presence of unreacted potash. These can be determined by the polarized light microscope.

The phosphorus compounds were found to affect on the degrees of potash conversion, if added before potash. Therefore the hindering effect was based on the presence of H_2PO_4^- ions.

From the obtained results a question arises - is 100 % conversion possible? In these laboratory tests the degree of conversion was never 100 %. The potassium nitrate phase contains a small amount of ammonium nitrate in its crystal lattice. As the phase $(\text{K}, \text{NH}_4)\text{NO}_3$ is a stable phase the remaining ammonium nitrate is hardly released from the lattice to react with the remaining potash.

Acknowledgements

Potash and its complex conversion was a very fascinating topic for author. During the studies an excellent mentoring for the science and fiction was given by the following persons whose help is greatly appreciated; Ian Watson, Arie van der Meer, Heikki Hero, Gerald van Dijk, and Arthur van Brempt. Without their valuable contribution during the research a great deal of secrets in potash would never have been revealed.

References

- Rug, H., Kahle, K., *Tailoring potash to suit the application*, Phosph. and Pot., 170 (1990) 23-27.
- Rug, H., Kahle, K., *Tailoring potash to the needs of the fertilizer industry*, Proceedings of the fertilizer society, No 297, 1990.
- Weast, R.C. (ed.), *CRC Handbook of chemistry and physics*, CRC Press, Inc., Florida, U.S.A., 1987.
- Olive, B.M., Hardesty, J.O., *Fertilizer granulation: Effect of particle size of potassium chloride on the granulation of mixed fertilizer*, J. Agr. Food Chem, 12 (1964), 492- 497.
- Gares, L., *Potash mining and production*, Proceedings of the fertilizer society, No 22, 1953.
- Gares, P.L., *Progress in development in the extraction, refining and treatment of potash for use in the fertilizer industry*, Proceedings of the fertilizer society, No 95, 1967.
- Ruping, G., *Potash deposits outside of North America*, Proceedings of the fertilizer society, No. 193, 1980.
- Kirk- Othmer, *Encyclopedia of chemical technology*, 3rd ed., Vol. 18, John Wiley and Sons, 1982.
- Swaine, D.J., *The trace element content of fertilizers*, Technical communication No 52, Commonwealth bureau of soils, Bucks, England 1962.
- Kashtanov, V.M. et al., *Study of the wettability of finely dispersed potassium chloride for optimization of the granular process*, J. Appl. Chem. USSR, 61 (1988) 1168- 1172.
- Olive, B.M., Hardesty, J.O., *Fertilizer Granulation. Effect of particle size of potassium chloride on the granulation of mixed fertilizer*, Agr. Food Chem., 12 (1964) 492- 497.
- Knob, B., et al., *X-Ray diffraction analysis of NPK 12-12-19 fertilizer*, Powder Diffr., 1 (1986) 1, 40-44.
- Hegner, P., Jäger, L., *Hygroscopicity of fertilizer materials*, Research Institute of inorganic chemistry, Czechoslovakia, ISMA Technical Conference, The Hague, The Netherlands, 1976, 115- 127.
- Hignett, T.P. (ed.), *Fertilizer manual*, Developements in plant and soil sciences, Vol 15, Martinus Nijhoff/Dr W. Junk Publishers, Dordrecht, The Netherlands, 1985, 363 p.
- Griffith, E. J., *Cake formation in particulate systems*, VCH Publishers, New York, 1991.
- Barbera, A., Monaldi, R., *Use of chemical and physical data to improve the quality of granular fertilizer production*, ISMA Conference, Vienna, Austria, 1980.
- Akiyama, T., *Chemistry in Production of High Analysis Mixed Fertilizers*, Japan Research institute for phosphate resources, Tokyo, 1986, 187 p.
- Azaroff, L.V., Buerger, H.J., *The powder method in X- ray crystallography*, Mc Graw- Hill Book Company, New York, 1958, pp. 49, 50, 233, 239- 244.
- Lehr, J.R., Brown, E.H., Frazier, A.W., Smith, P.J., Thrasher, R.D., *Crystalline Properties of Fertilizer Components*, Vol 6, 1967.