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Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

RECENT DEVELOPMENTS IN THE PAN GRANULATION PROCESS.

Per Stokka
Norsk Hydro Research Centre
Porsgrunn, Norway

1. SUMMARY.

The Norsk Hydro High Temperature Pan Granulation Process has been in commercial operation for nearly 20 years. Originally developed to make non–dusting, coarse (4–11 mm) ammonium nitrate (AN) granules for aerial spreading, the process has been developed to produce AN and CAN (2–4 mm), urea (2–4 mm) and urea supergranules (1, 2 or 3 grams), calcium nitrate (2–4 mm) and NP and NPK fertilizers. Plants with unit capacity up to 1500 MTPD are in operation.

The process is based on granulation of melts containing from less than 0.5 to 16 % water. In spite of the difference in melt composition, the granulation can be described for all different melts by a model based on melt chemistry.

The pan process is also compared technically with other granulation processes.

2. INTRODUCTION

In the Norsk Hydro Nitrophosphate NPK process evaporated NP melt with less than 0.5 % water is mixed with potassium salt and thereafter solidified in a prilling tower. It is not necessary to dry the prills from the tower. The prilling process is specially suited for large, single train production units. The limitation of the process is the amount of potassium salt that can be added to the mixer. To increase the flexibility of the Norsk Hydro nitrophosphate NPK process, the Norsk Hydro High Temperature Pan Granulation Process (HTPG) has been developed to handle super evaporated nitrophosphate NP melts for NPK production.

Our development within particle forming processes based on evaporated melts have given us some know–how in this field. In our development work we have found that the best results are obtained when know how can be linked to know why. A more fundamental understanding of the actual melt system is important when dealing with processes involving solidification of melts.

3. MELT GRANULATION

The first NPK melt granulation process was patented by former FISONS FERTILIZERS Ltd (now Norsk Hydro Fertilizer Ltd) (1). NP melts consisting of AN and MAP with a water content less than 2.0 %, were fed to a drum granulator and sprayed on a bed of recycled material and potassium cloride. A commercial plant was built in 1968, but changed its production from NPK to NP after some time of operation.

The Norsk Hydro High Temperature Pan Granulation Process was originally developed to produce forest grade (4 – 11 mm) AN from melts with 0.5 % water. The process was later developed to produce 2 – 4 mm AN, CAN, Urea and Urea supergranules (1, 2 or 3 grams), all produced from melts with less than 1,0 % water. These developments and the main principles and general concepts of the process have been published on several occasions (2,3,4). The process for all these types of fertilizer can be described in a general process flow diagram as shown in figure 1.

4. WHAT IS MELT GRANULATION ?

In general the term melt is used for liquids with a low water content that solidifies when cooled to room temperature. This is a practical, but not a correct term. Norsk Hydro melt granulate Calcium nitrate (CN) where the melt contains 16 and the final product 15 % water. The solidification is not a problem since the water in the product is bounded as crystal water. In our work we have found that the following definition of melt granulation is valid:

- In melt granulation the correct liquid / solid ratio is obtained by crystallization from the added melt. For a given melt system this ratio corresponds to a temperature depending on the melt composition.

- The recycled material acts as a heat absorber.

4.1. Granulation Curves.

According to the definition one can predict granulation temperatures as the composition changes for a melt system if the following is known:

- The liquid / solid ratio to have good granulation, given as % liquid phase.

- The phase diagram for the melt system to be granulated.

For the system AN – Water the phase diagram is known, see figure 2.

From phase diagrams one can for different given compositions, calculate how the liquid / solid ratio changes as the temperature is reduced. In figure 3 the results from pilot plant pan granulation of AN with varying water content in the melt are plotted. Also shown is a calculated granulation curve representing 20 % liquid phase (80 % crystals). This curve is a iso–liquid content curve.

Similar curves can be made for Urea – Water, Calcium nitrate – AN – Water, AN – MAP – Water and other fertilizer melts of interest. For these systems pan granulation takes place with 20 to 30 % liquid phase in the granulating mass. The % liquid phase for optimum granulation varies with the melt system. For two component systems like AN – Water the phase diagram can easily be made from available solubility data. The number of published phase diagrams for three and four component systems of interest for fertilizer melt granulation are rather limited. In addition to the granulation curve (iso liquid), a simple diagram like the one in Figure 4 will for any composition within the diagram give:

- The starting temperature for crystallization (at equilibrium) and which component that starts to crystallize.
- The liquid / solid ratio and the composition of the liquid and solid phase at any temperature during the crystallization.
- The temperature of which the last liquid crystallizes.

4.2. Recycle ratio.

According to our definition of pan melt granulation, the recycled material acts as a heat absorber. The most important parameters deciding the recycle ratio are:

- Heat of crystallization.
- The percentage of the melt that crystallizes during granulation.
- Heat capacity (Cp) of melt and recycled material
- Difference in granulation – recycled material temperature.
- Difference in granulation – melt temperature when the melt hits the recycled material.

The evaporation of water from the granulator and heat loss from the surface of the granulator have significant, but minor effects (low water content melts).

Looking at Urea and Ammonium nitrate, typical pan granulation temperatures are 127 and 140 ^{o}C. With approx. 80 % of the added melt crystallized during granulation of AN and approx. 70 % for Urea, the energies released are:

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Urea granulation: 242.0 kJ/kg x 0.70  = 169 kJ/kg melt
AN        "     :  77.5 kJ/kg x 0.80  =  62   "    "
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Where 242 and 77.5 kJ/kg are the heat of crystallization for Urea and AN. With recycled material added at a temperature of 30 ^{o}C, 1 kg of recycled material will for Urea and AN absorb 160 and 260 kJ/Kg. The average recycled material is normally heated to a temperature appr. 10 ^{o}C below the granulation temperature.

Taking no other factors into consideration, the estimated recycle ratio will be:

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Urea granulation : 169 / 160  = 1.05 kg/kg
AN        "      : 62  / 260  = 0.23   "
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Observed values for the given temperatures are:

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Urea granulation : 0.95 kg/kg  (Pilot plant)
AN        "      : 0.45   "    (Commercial Plant)
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The results indicate that there is a factor that has not been taken into consideration, and that this factor is more important for AN than Urea. This factor is the melt temperature. Cooling the melt down to the granulation temperature releases energy that must be absorbed by the recycled material. The energies released when cooling the melt to the granulation temperatures are:

Urea granulation : 7 x 2.0 = 14 kJ/kg
AN " : 35 x 2.0 = 70 kJ/kg

Where 2.0 kJ/°C*kg is the Cp value for both Urea and AN in the liquid state (% $H_2O < 0.5$). Taking these energies into account, the recycle ratio can be estimated to:

Urea granulation : 183 / 160 = 1.14 kg/kg
AN " : 132 / 260 = 0.51 "

All the parameters mentioned above have now been taken into consideration. The deviation between observed and calculated recycle ratio is mainly caused by not having taking into account heat loss from the granulator surface, and the evaporation of water. With an increasing amount of water in the melt, the evaporation of water during granulation will have a significant effect in reducing the recycle ratio. For a given melt system, the results of the calculations are normally given as variation in recycle ratio as a function of temperature of the recycled material.

For melt systems where the phase diagram, heat of crystallization, heat capacities and phase transformations are known, granulation curves and heat and mass balances can be made. The necessary liquid phase to enable granulation must be estimated, and the granulation curves are based on equilibrium conditions. The results must be verified in the pilot plant, but the number of tests needed are reduced. When scaling up, using a reliable model for heat and mass balances reduces the uncertainty linked to changes in the recycle ratio.

In cases with complex systems such as NPK, the use of thermodynamic data can be used to explain and estimate. As examples the pan granulation of nitrofosphate NP / NPK, and drum granulation of NP / NPK are shown (1). The melt used by the former FISONS FERTILIZERS Ltd. consisted of AN + MAP, and KCl as the potassium source. The data for the drum granulation process is taken from the patent application.

The water content of all the melts were less than 2,0 %. The AN content varied from 60 to 80 % and the MAP content from 10 to 40 % (deviation from 100 % because of some inert in the nitrophosphate NP melt). The heat of crystallization is for AN and MAP respectively 77.5 and 118 KJ/kg. This results in a deviation in crystallization energy per Kg melt of 82 + 12 KJ. Without salt, the NP recycled material has only small variations of Cp, typical value about 1,7 KJ/Kg. With an increased amount of salt, the Cp values of the recycled material decrease. To absorb the same amount of heat of crystallization from the melt, more recycled material is needed. On the other hand, increased addition of salt means increased production at constant melt load. The result is therefore only minor changes in the recycle ratios.

Granulating NP / NPK with N / P_2O_5 varying from 1.0 to 3.7 and K_2O from 0 to 23 % at the same granulation temperature, and with the same melt and recycle temperatures, one should not expect any big deviations in recycle ratios.

In figure 5 the recycle ratio is given as a function of granulation temperature with the variations in product grades given above. The melt, salt and recycle temperature were for all tests respectively 170 + 5, 95 + 15 and 50 + 10 °C. Even this wide variation in product grades gave almost the same recycle ratios at a given granulation temperature. With increasing granulation temperature the recycled material absorbs more energy and the recycle ratio decreases.

5. PARTICLE GROWTH MECHANISMS

When granulating melts in the pan process, the particle growth is dominated either by layering (onionskin) or agglomeration. As the recycled particles acts as an heat absorber, the amount of energy that one particle can absorb is proportional with its size and inversely proportional with its temperature. With the classifying ability of the pan, recycled particles will grow to a certain size before they leave the granulator. If the recycled particle is too small (or hot), the melt load will result in a too high energy absorption demand. As a result, the recycled particle is not able to crystallize enough of the added melt. The liquid phase of the particle will be too high resulting in a sticky surface. The small particles will then form agglomerates or stick to bigger particles, resulting in coarser granules from the pan than one will have with layering as the only growth mechanism.

Figure 6 shows cumulative screen size analysis for Calcium nitrate pan granulation. The recycled material has a low amount of small particles, and the particle growth mechanism is close to a 100 % layering.

Figure 7 shows how deviation from pure layering varies with the amount of too small particles in the recycled material. The temperature of the recycled material is 20 to 40 ^oC. The deviation is determined for the d_{50} obtained versus the d_{50} calculated

$$\% \text{ Layering} = (d_{50} \text{ cal.} / d_{50} \text{ obt.})^3 * 100$$

The limit for too small particles in the recycled material varies with the melt system, and is typically for a recycle temperature of 20 – 40 ^oC from 1.0 to 1.5 mm.

6. PROCESS DEVELOPMENT.

In the 1980's the Norsk Hydro High Temperature Pan Granulation Process (HTGP) has been developed to granulate Calcium nitrate. A commercial plant started operation in 1987 and has demonstrated a single train capacity of 1500 t/d. To obtain the heat balance a part of the product fraction is recycled. To minimize the amount of small particles in the recycled material, the finest fraction of the product sized material is recycled uncrushed.

For AN and CAN, the process has been linked to the use of magnesium nitrate as an additive (stabilizer). Granulation with Aluminum sulfate as an additive to obtain a less hygroscopic product has been demonstrated.

Lately the process has also been developed to handle evaporated nitrophosphate melts. By adding potassium salt on the pan, NPK grades are produced. As potassium sources, both KCl and K_2SO_4 have been tested with good results. The produced grades are well rounded with a high mechanical strength, low dusting and have good storage properties.

7. COMPARISON WITH OTHER GRANULATION PROCESSES.

The basis for the following comparative evaluation is to have 97.5 to 98% melt available at battery limit of the pan granulation plant.

- The operating conditions ensures no need for high quality steel in the equipment.
- The process flexibility also allows standard equipment selection, enabling choice at the most competitive market prices.
- These conditions coupled with a low recycle ratio and minimum equipment for pollution control, leads to low investment cost compared to other granulation processes.

The budget investment figure for a single train plant of 1500 MTPD producing AN (33.5% N or 34.5% N) would be 9 mill. US$. The figure do not include engineering services. By incorporating the limestone crushing unit, such a plant would be directly able to produce CAN (e.g. 27.5% N). The price of the crushing unit is not included in the above figure.

The low recycle ratio and limited need of high pressure drop scrubbing, results in a very low electric power consumption of about 18 to 20 kWh/ton product.

The steam consumption would be limited to the reconcentration of any solution recycled back to the wet part of the process and would be only 5 kg steam/ton product. With 95% solution at 140 ^{o}C as a basis (AN granulation) the total requirement including evaporation to 98.5 %, would be about 80 kg per ton of product. Consequently the amount of cooling water needed would also be negligible. The requirement for process water or process steam condensate is also low i.e. 40 kg per ton of product.

With the low amount of air requiring high pressure drop scrubbing, the increasingly stricter environmental regulations can be met at reasonable costs by the pan granulation process. This means that within the investment cost stipulated above, it would be possible to meet a requirement of maximum 15 mg/Nm^3 dust in the vent air when producing 34.5% N. For production of 33.5% N or 27.5% N which requires addition of solid material to the pan, the dust level in the air from the plant would be about 40 mg/Nm^3. As a consequence of these low effluent levels the efficiency of raw materials consumption would be very good.

8. REFERENCES

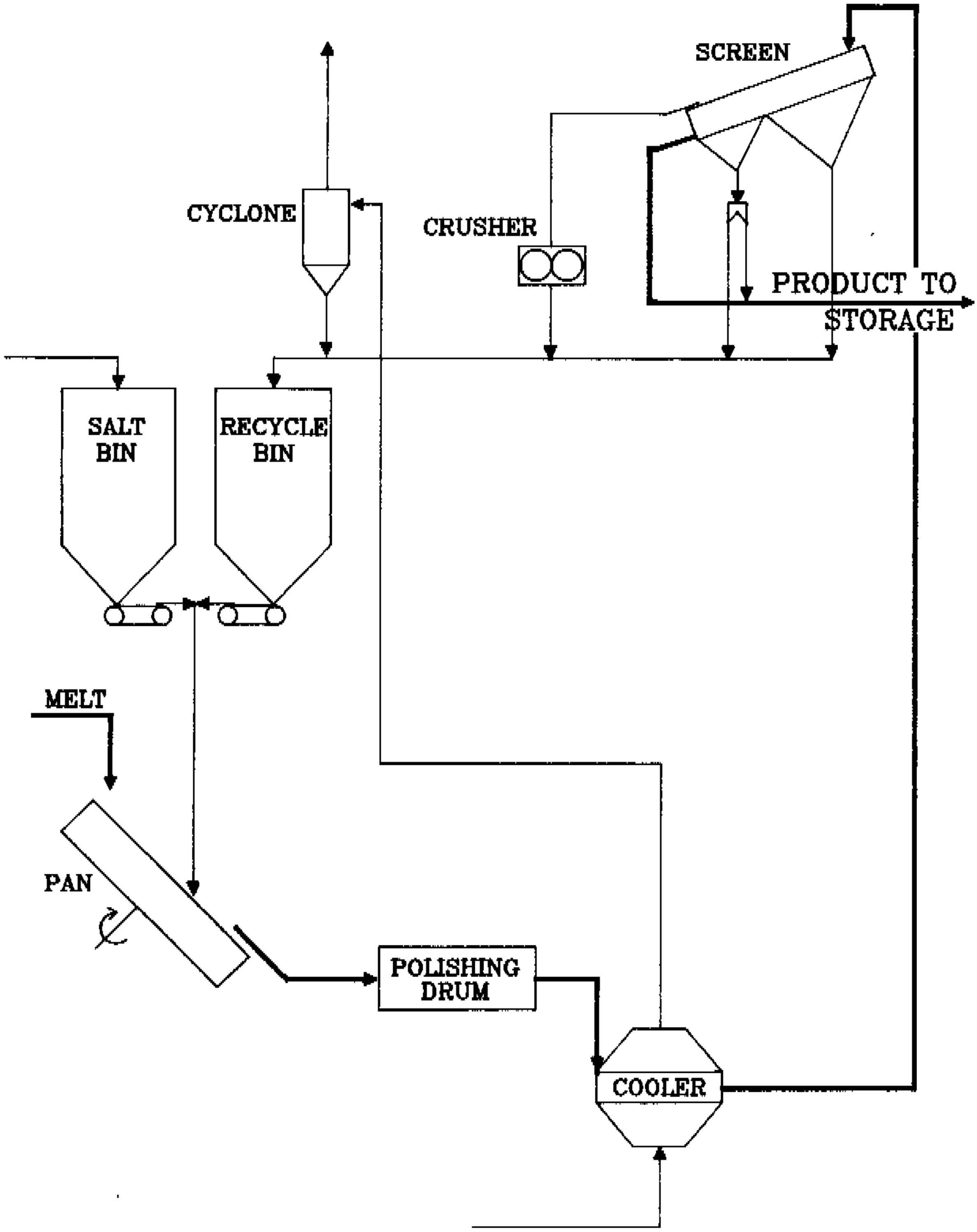
(1) FISONS FERTILIZERS Ltd, Danish patent application, 7.1.1966.

(2) Ø.Skauli — Pan Granulation of Ammonium Nitrate and Urea. (ACS Annual Meeting, Atlantic City, USA, Sept.,1974). Norsk Hydro's fertilizer technology symposium in the USSR in october 1975.

(3) Ø.Skauli and O.H.Lie — "The pan granulation process". Paper read before the Fertilizer Society of London, 13.12.1979.

(4) U.Nylund — "The Norsk Hydro high temperature pan granulation (HTPG) process for nitrogenous fertilizers". The Ammonium Nitrate Pollution Study Group Meeting in Edmonton, Canada. 23.9.1985.

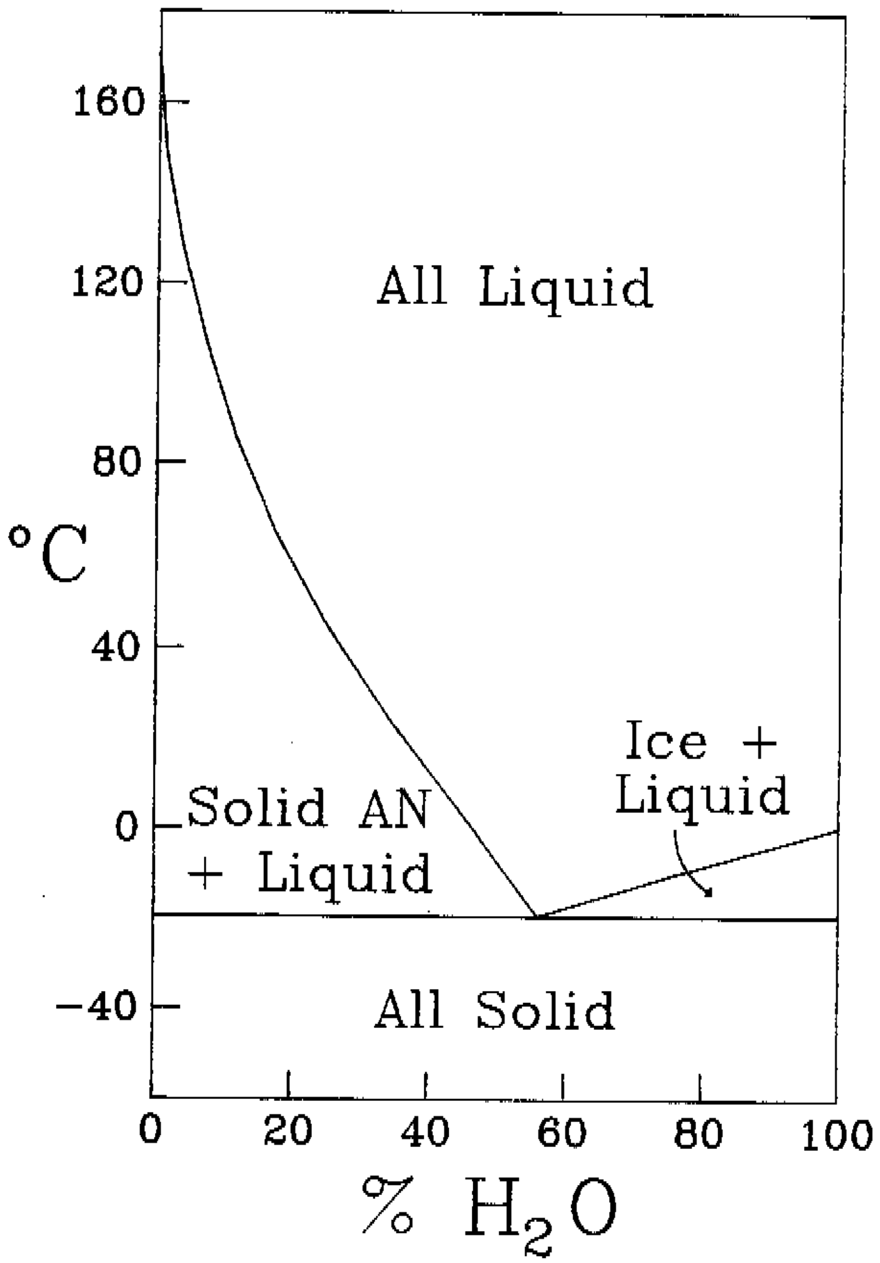
THE NORSK HYDRO HIGH TEMPERATURE PAN GRANULATION PROCESS (HTPG)



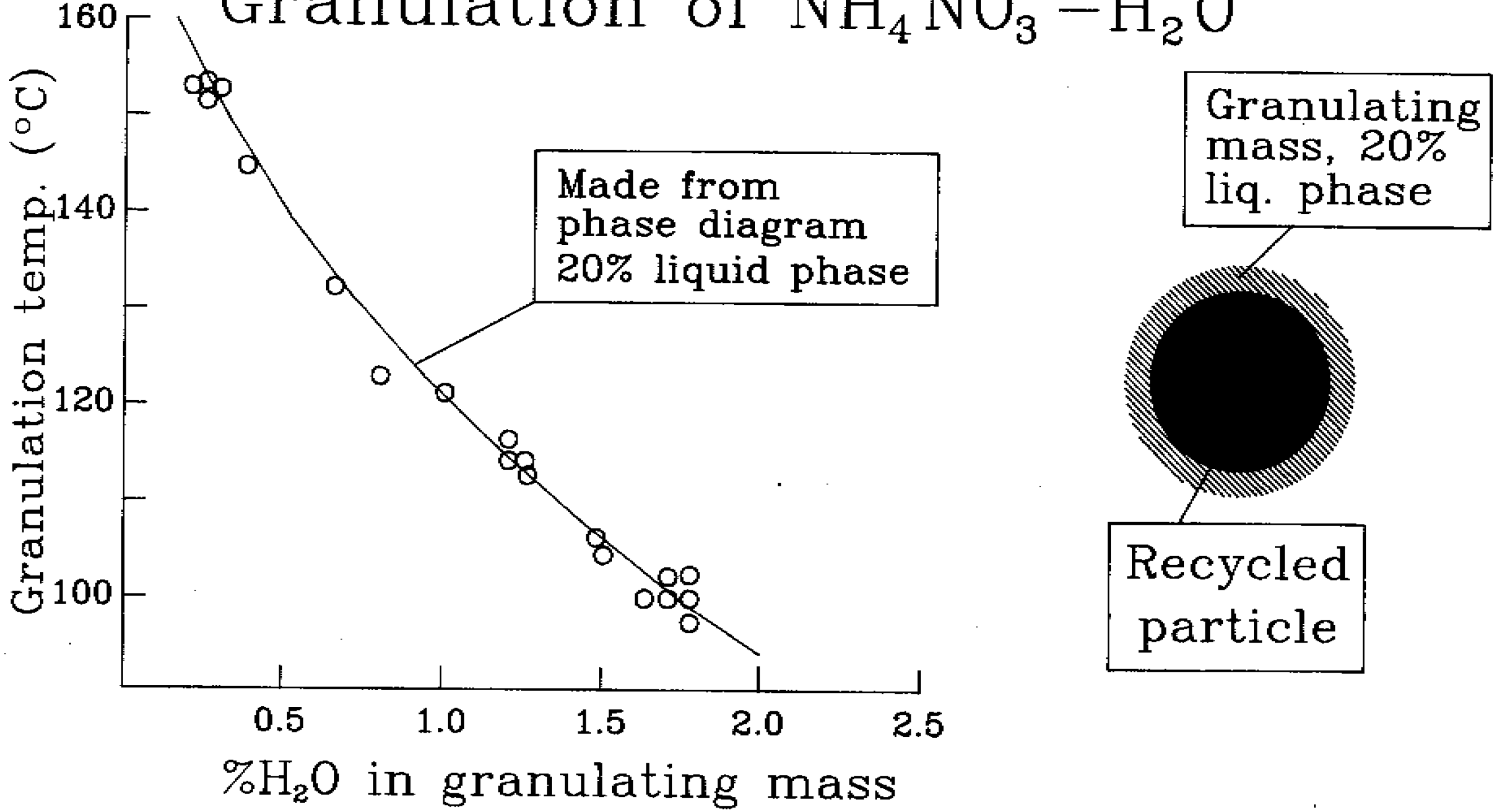
GENERAL PROCESS FLOW DIAGRAM

HYDRO RESEARCH

PHASE DIAGRAM $NH_4NO_3-H_2O$



Granulation of $NH_4NO_3-H_2O$



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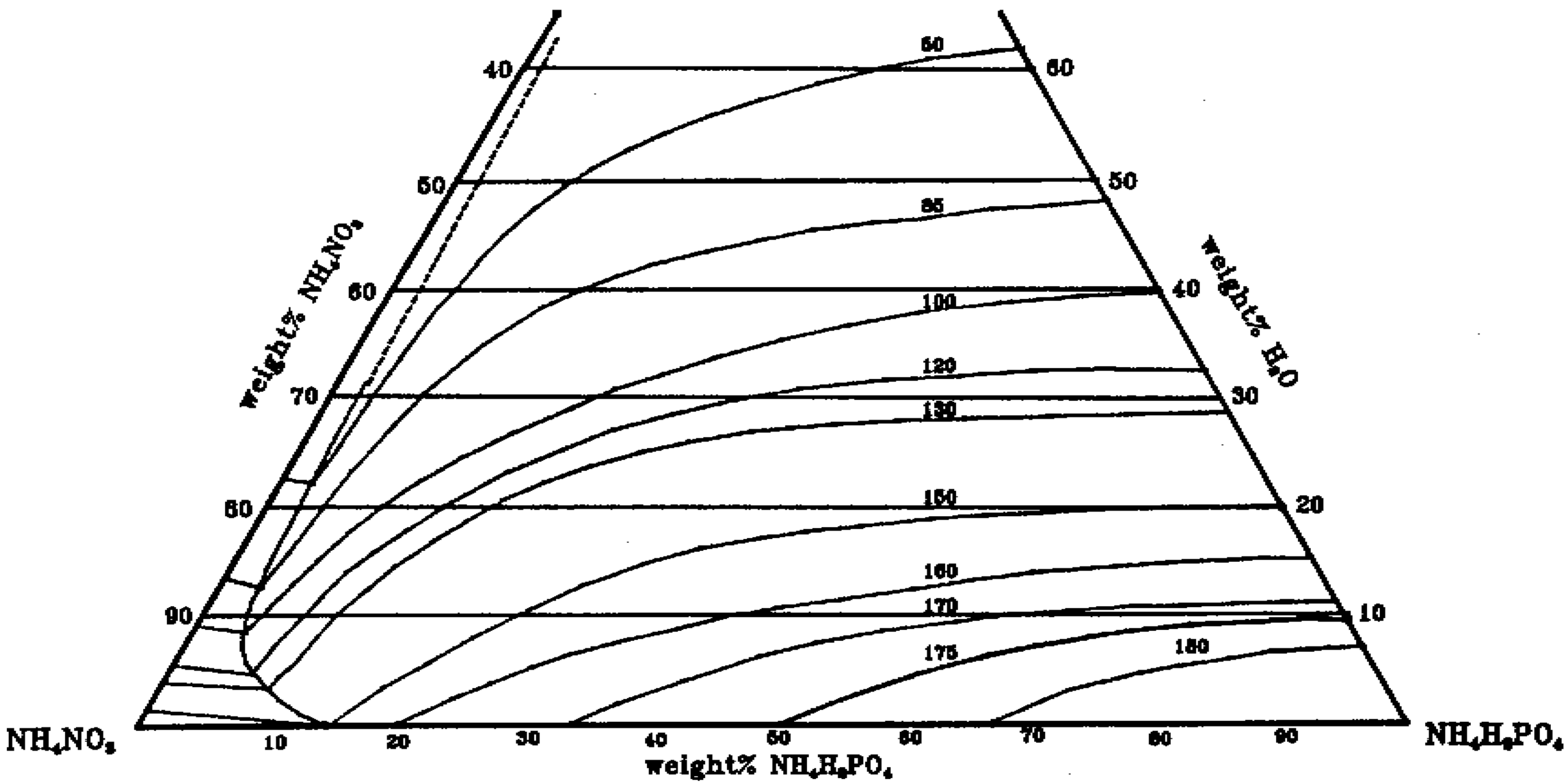
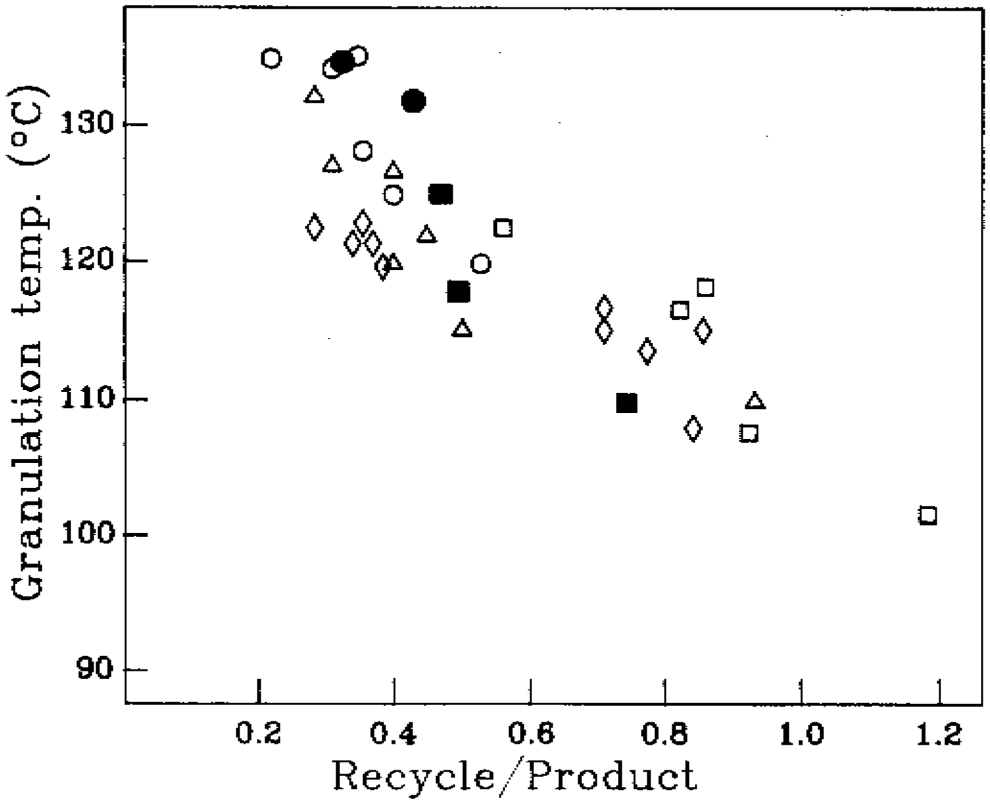
The Phase diagram of Map–NH_4NO_3–H_2O



HYDRO RESEARCH

PAN GRANULATION OF NP – NPK

Temperature of recycled material: 40 – 60 °C
Salt temperature: 80 – 110 °C



○ NP Granulation

△ NPK Granulation
K as K_2SO_4

□ NPK Granulation
K as KCl

◇ NPK Granulation
K as $KCl+MgSO_4$

FISONS (now NHFL)

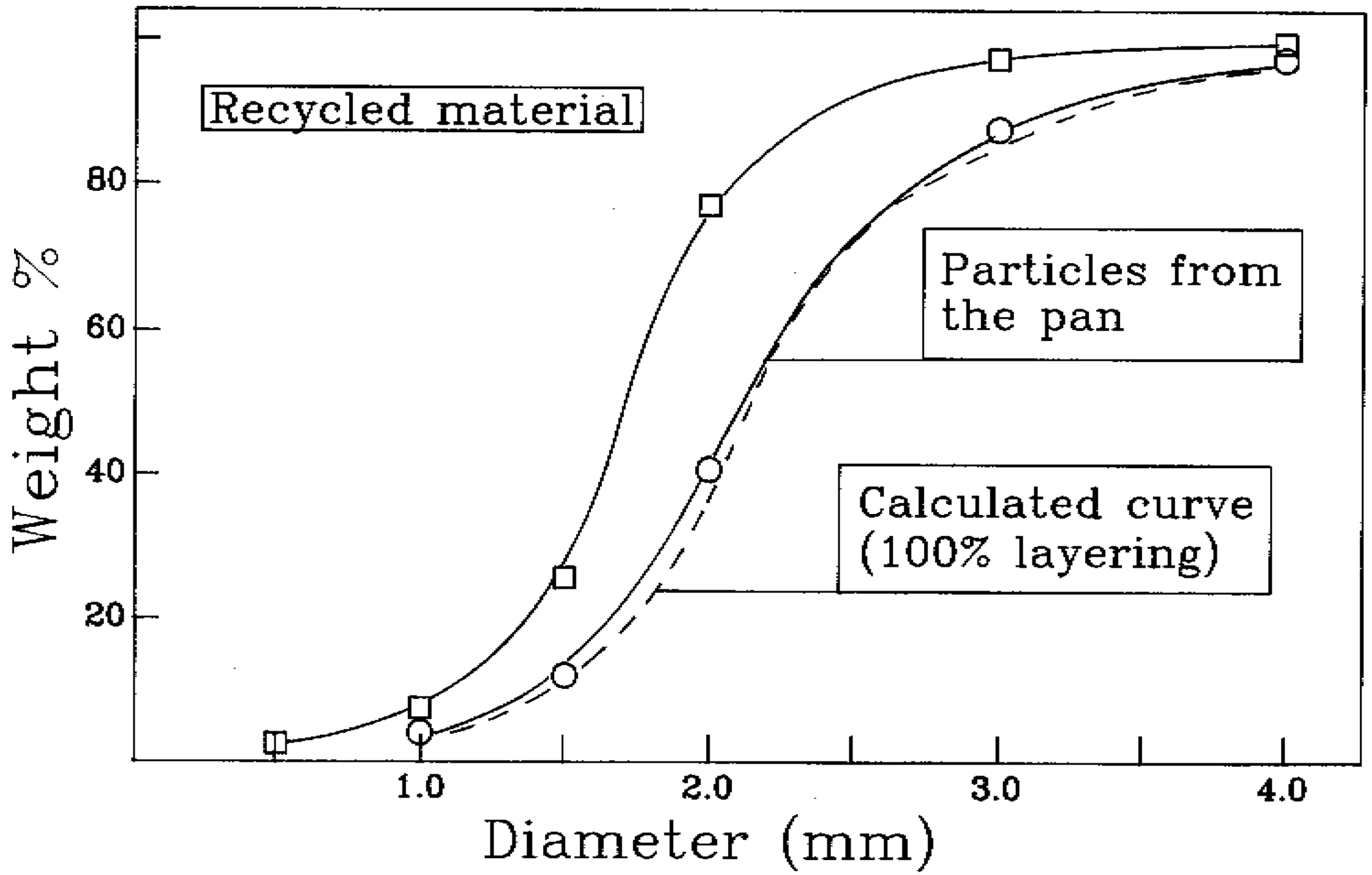
● NP Gran. ■ NPK Gran (KCl)

For NP – NPK,
N/P_2O_5 from 1.0 to 3.7
For NPK, K_2O from 7 to 23%

HYDRO RESEARCH

PARTICLE GROWTH

Cumulative screen size analysis, Calcium Nitrate



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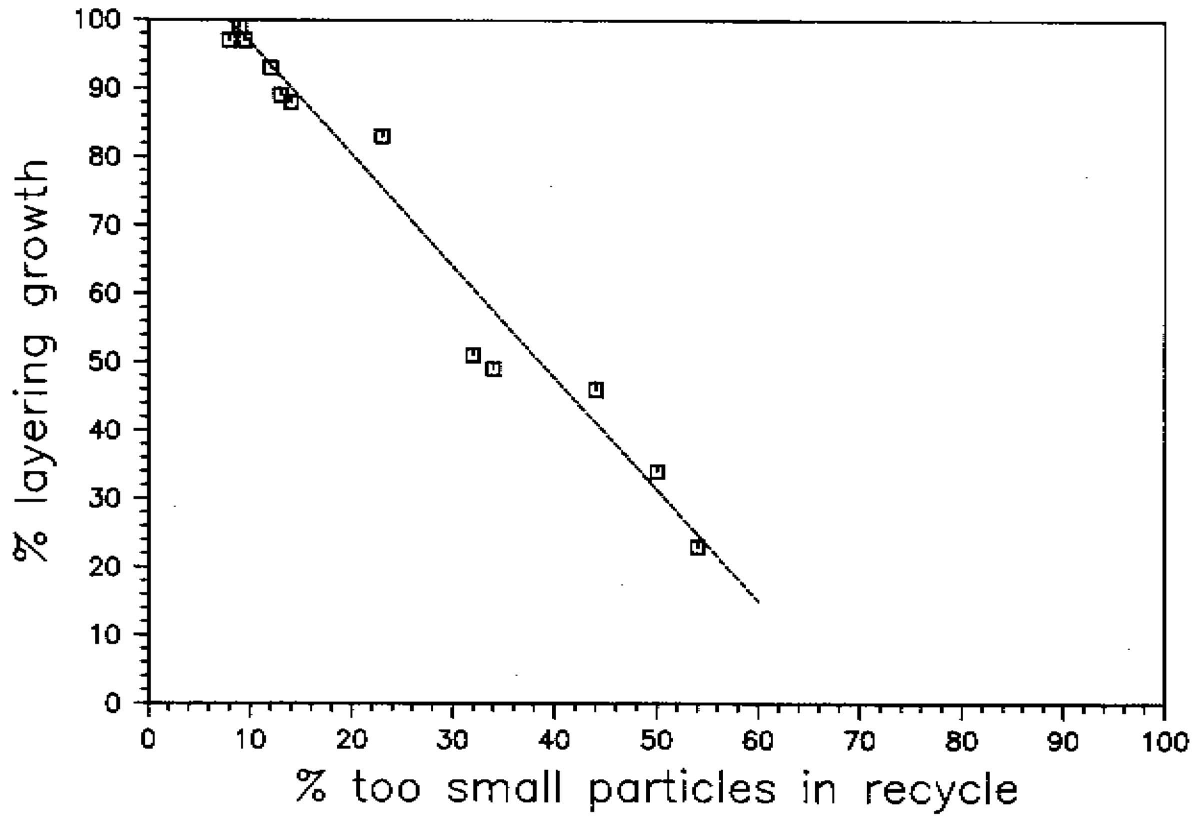
GROWTH MECHANISM

% layering of total particle growth,
as a function of too small
particles in the recycled material



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TA/88/5 Recent developments in the pan granulation process by P. Stokka, Norsk Hydro, Norway.

DISCUSSION (Rapporteur P.H. Moscham, Essochemical, Canada)

Q - Mr. A. HORKKO (Kemira Oy, Finland).

What are the NPK grades you have produced with the pan granulator process, and what can you say about the quality of the pan granulated NPK's compares to the spherodizer or drum granulated product ?

A - We have only pan granulated nitrophosphate based NPK, and besides the pure NP grades we have made grades up to 1-1-2 and down to 6% potassium chloride, which is our lower limit on the potassium side. In the nitrophosphate process the limit for the N/P2O5 ratio is 1-1. So we have produced NPKs with potassium from 6-25% (K2O). We have not compared our product with drum or spherodizer produced material, but the quality is equal to that produced in our pugmill granulator at our plant in Northern Norway. Especially the crushing strength is very high and the spreadability is good; it is low in dust and it is not inferior to what is normally on the market.

Q - Mr. L.K. RASMUSSEN (Superfos Fertilizer, Denmark).

1/ What is the turndown ratio of a pan granulation process for AN and CAN ?

2/ For AN without any kind of additives, could you please give us typical values of the following parameters: untapped bulk density, hardness and porosity for the finished product ?

3/ What are the main drawbacks of the pan granulation process compared with the fluidized bed process for AN and CAN ?

A - 1/ We have a 50% turndown ratio, that is we can operate from 50 ton/hr to 25 ton/hr.

2/ For NPK the typical untapped bulk density is 1 kg/l. The hardness (defined between 2.8 - 3.1 mm) is typically 5-7 kg. We have not measured the porosity, but these are very dense particles. For AN, the typical untapped bulk density is also 1 kg/l and the crushing strength 3-5 kg. Again we do not measure porosity.

3/ From the fluidized bed we get a rounder product. I cannot elaborate further on this question.

Q - Mr. P. ORPHANIDES (Duetag, France).

1/ Is the methodology applied to explain and calculate the granulation phenomena also applicable for other melt granulation processes like drum granulation ?

2/ Have you investigated using a pan granulator with a pipe reactor ?

3/ Can you comment on the use of pan granulation for the fattening of prilled AN/urea in comparison with other fattening processes ?

.../.../...

4/ For the production of 26% AN, the amount of powdered CaCO3 is beyond the limits imposed by the mechanism of granule growth by onion type layering. Is the limit for CAN at 28% N for good onion type layering with the pan granulator ?

A - 1/ We have not used this methodology for the drum, but drum and pan granulation is very much the same, and also the results from the Fison test indicate that this can be also used for the drum. I think that the amount of liquid phase necessary to have granulation will be very nearly the same. We have applied this method to pugmill granulation and we have found that 12-15% liquid phase is necessary for our process. In general, when the energy impact increases, the necessary amount of liquid phase decreases.

2/ We have no experience with a pipe reactor.

3/ We have not tried this as a fattening process as such, but we have often used prilled material as start-up material, and this is an excellent starting material. So I think it has possibilities as a fattening process. The only problem will be that you have to satisfy the energy balance and you will need quite a lot of melt.

4/ The 26% CAN is a problem when you have a very low amount of water in the melt. When you increase the amount of water, it is easier to get more dry material into the granules during the granulation. We have not seen any limits to how much dolomite can be used. There is, of course, a practical limit, but we have not elaborated on that, because we are able to obtain the normal quality of material.

Q - Dr. S.K. MUKHERJEE (KRIBHCO, India).

1/ Has there been any commercial experience of pan granulation of 26% N product and, if so, what has been the recycle rate and the scale of operation?

2/ Have you been able to produce pan granulated product with phosphoric acid, ammonia and nitric acid, and could you get a product analysis of 25-25-0 and, if so, what is the character of the product ?

A - 1/ We have not producer 26%, but there is a plant, PFI, in Greece, which has now been operating since 1983. Someone from PFI would be the best to give you the details of the operation of this plant. As far as we know, the plant is operating. There is a problem with the recycle ratio as you mentioned. If you have a cold limestone feed, you have a very low recycle ratio and problems to close the process. It is important to have a good heating system for the lime. With that, I believe that we could operate satisfactorily.

2/ We have no experience with phosphoric acid. As I mentioned at the beginning, all our work on NP/NPK has been done with a nitrophosphate basis.