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OPERATING EXPERIENCE FROM THE
MODERNISED NORSK HYDRO ODDA NPK PROCESS

By :

Olav Haug and John O. Pande
Norsk Hydro a.s.,
Norway.

Summary

The Norsk Hydro NPK process is a technologically advanced version of the Odda process. Only nitric acid is used for processing of the phosphate rock and no sulphur is needed.

Some of the experience, obtained during the 36 years since production was started, is presented, mainly from an operating point of view.

Raw materials, the various production steps, regularity and losses, grade switch, product control etc. are discussed.

1. INTRODUCTION

The original Odda Process was invented in Norway in 1928 by Erling Johnson.

Norsk Hydro was the first company to exploit the process. Commercial production of NPK was started in 1936 at the Eidanger works at Herøya. In 1955 a second plant for pugmill-granulated NPK was built in Glomfjord, situated north of the Arctic Circle.

Meanwhile the process was extensively studied and developed by our research group. For instance the concentrations of nutrients and water-soluble P, were increased by the introduction of "deep-cooling". In 1965/66 a 500 tons per day combined production and pilot plant for prilling of NPK was erected as part of the old plant. Based on the operating experiences from this plant, a new plant, with a capacity of 500,000 to 600,000 metric tons per year was built and put on stream in 1967.

This NPK plant is probably one of the largest one-string NPK plants in the world, and it proved so successful that Norsk Hydro decided to license its NPK process on the world market. A 900 short tons per day NPK plant was built and put on stream in 1969/70 by Wellman-Lord for Farmers Chemical A.I. in Tunis, N.C., U.S.A. In this case a $\text{Ca}(\text{NO}_3)_2$ -conversion was added to the process. Norsk Hydro is still selling all of their $\text{Ca}(\text{NO}_3)_2$ by-product as "Nitrate of Lime".

In a new plant to be built in Hungary using Norsk Hydro technology, by-products calcium nitrate ("Nitrate of Lime") or ammonium nitrate limestone can be made optionally in the same plant. The capacity of the NPK-plant will be about 750 000 tons a year, whereas about 400 000 tons of by-products can be made.

The object of this paper is to present some of the operating experience obtained during these years, without releasing vital know-how.

2. BRIEF DESCRIPTION OF THE PROCESS

The Norsk Hydro NPK process has been presented in various papers (see references). It is a technologically advanced version of the original Odda process. The main advantage of the Odda process is that it needs no sulphur, as only nitric acid is used for the processing of phosphate rock.

It is assumed that the main principles and chemistry of the Odda process are known, but as a background for the information to be presented, a very brief description of the process will be given (see fig. 1).

Phosphate rock is dissolved in nitric acid of about 60% strength in the digestion step. The heat of solution raises the temperature about 45° C. The warm solution is cooled in crystallizers where $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ is crystallized. The crystals are separated from the mother liquor on tandem filters. In the second filtration stage the crystal cake is washed with nitric acid and a small amount of water before it leaves the process as a by-product. The wash acid is returned to the rock digestion step.

The mother liquor is neutralized with ammonia in neutralizers. Ammonium nitrate solution is added to obtain the desired N:P₂O₅ ratio. The water content of the NP liquor is reduced to about 0.5% in specially designed evaporators. This NP melt is mixed with a potassium salt, recycled fines and, if desired, other additives, and the mixture is prilled in an air-cooled tower.

The prilled product is cooled, screened and coated before it leaves the plant as finished NPK complex fertiliser. Oversize

product is crushed and returned to the screens. The fines are recycled to the mixer.

The by-product $\text{Ca}(\text{NO}_3)_2$ can either be processed to Nitrate of Lime, utilized in nitrogen solutions, or converted to NH_4NO_3 and CaCO_3 .

3. GENERAL CHARACTERISTICS OF THE OPERATION

NPK production is "mud chemistry" and there are generally rough operating conditions.

Nitric acid combined with fluorides is very corrosive, especially when erosive particles damage the protective oxide film on stainless steels. The neutralized process liquors are slurries with 10-60% suspended particles. They tend to plug the equipment, since ammonium nitrate and especially monoammonium phosphate (MAP) will crystallize on cooling. If not kept dry, NPK solids and dust will stick to surfaces in chutes, pipes, drums, conveyors, elevators etc. Everyone who has worked in the fertiliser industry is probably familiar with the art of making a plant run well, and the difficulties involved in applying scientific methods.

Every piece of equipment (valves, pumps, strainers, pipes, chutes, diverters, inspection ports, etc.) should be of special design and construction in order to give good performance. Very often things can be done in many ways, and the problem is usually not the idea in itself, but how to make a practical design that will work properly.

It often seems difficult to get this message through to the research and design people. Many things may look good on paper, but you cannot tell how they will work until they have actually been built and been in operation for some weeks. Generally, equipment should be of simple design but high quality. Too sophisticated things seldom work.

We think that a lot of our process know-how consists of how to make details work. Through the years many different ideas have been tried out and there have been many improvements :

- Equipment for sampling and controlling of pH in liquors etc
- Techniques for quick and easy cleaning of dry handling equipment.
- Flow meters and control valves that can withstand attack by acidic liquors, or are not affected by the plugging tendency of neutralized liquors.
- Manual valves that are not blocked by solidified liquor.

Most of the mechanical equipment, e.g. crystallizers, filters, evaporators, mixing/prilling equipment and some of the process control equipment have been designed and constructed at Norsk Hydro's own workshops. As construction material and process control equipment have improved, there has been a trend towards large single-string units, and the number of operators has been reduced.

Through the introduction of the prilling process, solids handling was greatly reduced. There is less than 10% recycle. The product leaving the prilling tower contains very little fines. No drying drum with oil burners and large air flows is needed. As a result, the vent air contains only small amounts of dust. Bag filters are no longer required, as a couple of cyclones normally will give sufficient cleaning of the air. The water content in prills is about 0,5 %, and they are easier to handle than granules. The dust problem and clogging of the equipment has thus been greatly reduced, and the operation simplified.

In the granulation strings we had to flush the crushers and screens every 1-3 days, and the pugmill and drying drum every 1-3 weeks. With the prills, however, the screens, crushers and cooler can be operated for weeks and months without cleaning, provided that moisture is kept out.

One operating experience is the importance of good house-keeping. We think it pays off to spend some money on "operators' convenience". Good access to equipment, easy-to-open inspection ports, funnels for feeding in material on all floors, curbs and covers to simplify cleaning and flushing of floors and equipment, "waste trays" below stuffing boxes on, for instance, pumps etc. Operators appreciate a clean working place and there is less work involved in cleaning when standards are high, and the cleaning is done at once. Once a part of the plant has become untidy, things start to accumulate and people tend to give up. Therefore, we stick to the rule that the shift operators themselves do all the cleaning, and we no longer have extra people on day-time.

We used to say as a joke that everything in a NPK plant - including the engineers and operators - had to be SSS-proof, that is (in Norwegian or German), acid-, sledgehammer- and water proof. We feel, however, that in our new NPK plant the operating conditions have been so much improved and the plugging and leaking problems so much reduced that this joke is not true any more, and that the plant and process now is more like any other chemical industry.

4. PHOSPHATE ROCK QUALITY

In principle, any quality of phosphate rock can be used as phosphate raw material, but for practical and economical process

performance there will be certain limitations.

Apatite of igneous origin, as for instance Russian Kola phosphate, is generally well suited to the process.

About 85% of the world's phosphate rock production, however, consists of phosphate of sedimentary organic origin. In those types, minor quantities of organic material still remain. In the dissolution step, these will act as a foam stabilizer and cause vigorous foaming in connection with the formation of carbon dioxide. By calcination of the sedimentary phosphates organic matter is destroyed and carbon dioxide driven out, thus reducing the foaming tendency.

Generally, high-grade non-foaming types, such as Kola rock, give higher production rates with less equipment and labor.

Low-grade ores are less expensive, but especially uncalcined types are troublesome in operation due to foam, larger amounts of acid insolubles and $\text{Ca}(\text{NO}_3)_2$ which have to be removed, higher viscosity of the liquors after neutralization, more impurities affecting the product grade, etc.

Considerable work has been done in the research lab. and by test runs in the plants in order to try out phosphate rocks from all over the world.

With suitable equipment design, antifoaming agents and some training, most of the low grade ores can be mastered, but the general experience is that a high grade rock always gives higher production with the same equipment. It will therefore be a question of an overall economic optimization of the market situation and the plant capacity to select the best rock type in every specific case and for every grade.

Due to corrosion, chlorine containing material must not be allowed to enter the digesters. We have found, however, that a chlorine content of up to 0.1% can be tolerated without destroying the passivity of CrNiMo 18-12-3 stainless steel.

If the rock contains much insoluble matter, this has to be removed in a sand trap. The insolubles are mainly silica, and tend to cause erosion-corrosion on equipment such as pumps and valves.

High contents of other acid-soluble impurities such as iron, aluminium, magnesium or sulphur, should be avoided, as these components cannot easily be separated and may cause process difficulties.

Compared to wet-process phosphoric acid production, the Norsk Hydro process can utilize a much coarser phosphate rock.

The bulk of the material should preferably have a particle size below 1 mm, but a small amount of coarser particles can be allowed. For that reason we do not have any facilities for grinding the rock on the plant site.

5. CRYSTALLIZATION AND SEPARATION OF $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

The warm digestion liquor is cooled batchwise in a number of crystallizers. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ starts crystallizing at about 25° c. The terminal crystallizing temperature determines the degree of calcium removal, which in turn determines the level of water-soluble P_2O_5 and nutrients in the finished product.

Previously, we cooled to 17 to 12° C and a product with a Ca:P ratio of 1.1 to 0.7 was obtained, corresponding to 25-50% water-soluble P_2O_5 . In 1967 we introduced deep cooling.

Theoretically, 85 to 90% water-soluble phosphorus can be obtained without use of a supplementary step for calcium removal. However, cooling costs money and takes time as the crystallizing curve for $\text{Ca}(\text{NO}_3)_2$ flattens out towards the end, there must be a limit beyond which a further increase is uneconomical. When the cooling brine is cooled by vaporizing ammonia, -5 to 0° C seems to be a practical limit, as long as the ammonia vapor must have sufficient pressure for the neutralization step. Our operating experience indicates that 75 to 85% water solubility of phosphorous can be obtained from most phosphate rocks.

The advantages of batchwise crystallizing are the following:

1. The cooling surface is cleaned between every cycle, because the crystal deposits dissolve in the new warm digestion liquor.
2. Crystal formation and growth are closely controlled, and large crystals of uniform size are obtained.
3. By cooling more crystallizers in series, a maximum overall heat transfer and optimum temperature difference between coolant and liquor can be obtained.

The filtration takes place in tandem filters, designed and constructed by Norsk Hydro to suit the particular requirements of the process. The filters have proved to be very reliable "work horses" which can be operated continuously for months without any maintenance. Before this type was introduced in 1966, we also tried a commercial filter, but experienced breakdowns and high maintenance costs due to erosion/corrosion.

6. NEUTRALIZATION AND EVAPORATION

The mother liquor, along with fine undissolved particles which have passed through the 0.5 mm mesh filter cloth, is then neutralized with gaseous ammonia in the neutralizers. Dicalcium phosphate and various impurities of calcium, fluorine, iron, aluminium, etc. are precipitated, while ammonium nitrate and phosphate remain in solution.

After neutralization, a liquor with a $N:P_2O_5$ ratio of 0.70 to 0.90 is obtained, depending on the Ca:P ratio and the acid:rock ratio used. With such low $N:P_2O_5$ ratios, very strict pH control is necessary, in order to avoid thickening of the slurry and formation of citrate-insoluble P_2O_5 .

With $Ca:P \approx 1.0$ most of the phosphorus is precipitated as $CaHPO_4$, and a rather viscous slurry of solids in an ammonium nitrate-water solution is obtained.

With $Ca:P = 0.3$ to 0.4 only 15 to 20% of the phosphorus is precipitated, and the rest remains as ammonium phosphates in solution. The liquor is normally thin, but as MAP tends to crystallize, the liquor requires more careful control of pH and temperatures, handling in pipes, evaporators, etc.

7. MIXING AND PRILLING

The almost water-free NP melt can be prilled as such, making for instance 23-23-0, or mixed with a potassium salt and other additives as $MgSO_4$ and Borax.

Very thick liquor may form during mixing and cause difficulties. These difficulties have been overcome by special equipment design.

It is in the nature of the prilling process that the cost of the prilling tower is nearly independent of the capacity. Thus the advantages of the prilling process increase with the size of the plant. Only the future can show the economical upper limit for a one-string prilling tower. We have obtained more than 80 tons per hour to date.

Traditionally potassium chloride (50% K) is used, except for certain crops which are sensitive to chlorine ions. It is well known, however, that the self-sustaining decomposition of some grades of nitrophosphate is catalysed by chlorine ions, and that this effect is increased by the presence of copper ions. In 1967 Norsk Hydro decided to replace the KCl by K_2SO_4 in some grades, mainly those containing copper, in order to make them stable.

As K_2SO_4 is made from KCl , either by conversion with H_2SO_4 or Na_2SO_4 , the cost of K_2SO_4 is approximately 30% (50% per ton K) more than KCl , and the cost of the product is increased. However, wherever there is a sulphur shortage and sulphur is needed, this is an excellent fertiliser. K_2SO_4 (42% K) gives a slightly higher nutrient level in the product than KCl + elemental sulphur. Operating experience has shown that although K_2SO_4 gives a thicker prilling slurry, it leads to maximum production and a product with a good appearance. If copper is present, the chlorine content must be below 0.1 to 0.4% in order to eliminate the catalyzing effect of chlorine ions on decomposition. Especially when switching grades, overlapping of copper and KCl must be avoided.

As only a limited amount of oversize and fines can be recycled, it is important to have screens which cut off the fractions sharply.

For instance, some vibrating screens tend to leave some fines in the product, while some of the product goes into the oversize. The material leaving the prill tower normally contains 92 to 96% between 1 and 4 mm.

The final product consists of spherical balls, free flowing and easy to handle. The most common grades have a bulk density of 1.2 tons/m³ and an angle of repose of about 25°.

8. UTILIZATION OF THE CALCIUM NITRATE BY-PRODUCT

The calcium nitrate by-product is a common feature of all versions of the Odda Process. In Norsk Hydro this is used in the production of Nitrate of Lime. The company is the world's largest producer of this product with about half of the world's total production capacity.

Calcium nitrate fertiliser contains 15.5% nitrogen, of which 14.5% is in the nitrate form and 1% of water-soluble calcium. For special agronomic purposes, this is an excellent product. It is hygroscopic, but in a good silo or in tight bags it can be stored for years without caking and without requiring any conditioning agent. This is due to its ability to take up and bind water in the crystal lattice and still behave like a completely dry product.

If a product with a higher N-content is desired, the calcium nitrate can be converted into ammonium nitrate and calcium carbonate by means of ammonia and carbon dioxide. These products can be used separately, or calcium ammonium nitrate with 26% N can be produced. Norsk Hydro has also developed a commercial process for such production, and the previously mentioned NPK plant built in the U.S.A., based on the Norsk Hydro process, is using this alternative.

A third possibility for utilizing the calcium nitrate is to make a nitrogen solution. A solution containing 34 % calcium nitrate and 32 % ammonium nitrate in water will have a nitrogen content of 17 % and a crystallization point of 4° C. It can be stored and transported in carbon steel tanks.

9. LOSSES.

Approx. 1 % of the phosphorus is lost with the $\text{Ca}(\text{NO}_3)_2$ by-product, if it is not recovered through precipitation and recycling.

Depending on the production rate, some NH_3 will not be absorbed in the neutralizers, but these small amounts are normally not recovered.

During evaporation in the prilling process, or evaporation/drying in the granulation process, the pH is somewhat reduced, from approximately pH 5.7 to pH 4.7, because of release of ammonia.

Other losses stem from temporary leaks in stuffing boxes, cleaning of equipment and floors, overflow, plugging, or mistakes by the operators.

Generally 97 to 99 % of the raw materials going into the plant will end up in the warehouse as fertilizer.

10. SELF-SUSTAINING DECOMPOSITION.

Not all formulations of NPK have the capability of self-sustaining decomposition. A major part of the grades that Norsk Hydro produce today are thermo-stable. This was obtained either by the formulation, change from ca:P = 0.70 to Ca:P = 0.40 or by replacement of KCl by K_2SO_4 (see reference No.2).

Before this change, decomposition of NPK happened occasionally in the drying drums or crushers of the granulation strings. When starting the prilling plant, we were in the beginning somewhat afraid of the high temperatures (150 to 180° C) involved, but there have been practically no incidents of this at all, except some fumes from the mixing tank a couple of times.

Decomposition is always a potential hazard, however, and strict rules for welding and cutting are maintained in the plant and storage buildings. For the same reason, all the conveyor belts were made of fire resistant materials.

11. CAPACITY-REGULARITY.

The operating experience with our large NPK-plant at Herøya indicates considerable flexibility in production of different products. Initially designed for production of a limited number of NP- and NPK-grades, the plant has up to now produced more than 20 different products. As this plant was designed for operation with a $N:P_{25}$ -ratio of about 1.4, different bottlenecks have naturally been encountered for different products.

For grades with a lower $N:P_{25}$ ratio, the wet part of the plant is production limiting, but this part normally has an on-stream factor of 90 % or higher. Any increased down time in the prilling part of the plant will normally not affect the overall production rate because a slurry surge tank of 100 m capacity serves as buffer. For grades with higher $N:P_{25}$ ratios and much salt, the prilling/prills-handling part is the bottle-neck, but now less cleaning is required, and the onstream time is still 90 % or higher. For grades with an extremely high N-content, like NPK 25 - 7 - 11, the evaporation step should be the bottle-neck, but as the heat transfer is increased beyond design due to the low viscosity, the NP liquor flow can be increased accordingly provided that the steam supply and vapor receiving capacity is sufficient. Thus the wet part, the evaporation step and the prilling/prills handling part were in good balance with each other and high production rates could be obtained for the different grades produced to date.

In order to obtain a flexible plant with a high overall production rate, it is therefore important to estimate the capacity of the different production steps for all the various grades to be produced, and to provide sufficient buffer capacity between the critical production steps.

12. SWITCHING OF GRADES.

Because of the many different grades and frequent switching of grades, a NPK producer sometimes feel like manoeuvring a battleship in a narrow sound, but the necessary techniques of doing it with a minimum of down time and without any off-specification material have been developed.

An advantage with the prilling process is that there is less than 10 % recycle. On stops, the dry handling parts are continued until after 30 minutes all material is in the warehouse except a few tons of fines in a recycle bin.

If merely the liquid/salt ratio is to be changed, the new grade can be started again as soon as the position in the warehouse

has been changed. If the composition e.g. the $N:P_2O_5$ ratio of the liquor is different, correction and control analysis of the buffer tank is necessary. If for instance copper as micronutrient is to be added as scrap metal to the digesters, and at the same time the potash silo has to be emptied in order to switch from KCl to K_2SO_4 , quite a lot of coordination is necessary in order to avoid contamination of e.g. the chlorine product with copper. Normal practice is to accumulate a list of mechanical changes and maintenance and take a full day's stop combined with the switch. Then it is possible to make a fairly "clean cut" switch with only a few tons of off-specification material which is spread either on top of the old pile or in the bottom of the new one.

13. PRODUCT CONTROL.

One troublesome area of plant operation is keeping the NPK on analysis. Over-formulation is expensive. Under-runs are also expensive either as reruns or bulk mixing, not to mention the possibility of penalties and lost reputation. These problems are not specific to nitrophosphates, however, as they apply to all sorts of multicomponent fertilizers.

Normally the composition of the raw materials, e.g. phosphate rock, ammonium nitrate and potash is very stable. The ratios of the individual nutrients are determined within the plant and normally expressed by the $N:P_2O_5$ and salt:NP ratios. The $N:P_2O_5$ ratio is again determined by the acid:rock-, Ca:P ratio and ammonium nitrate addition.

Once a grade is specified, the nutrient level (the sum of N, P and K) will remain fairly constant, and can only be changed by the degree of calcium removal or through addition of magnesium sulfate or a cheap "filler". A complication is the citrate solubility of the phosphorus, which normally is 97 to 99 % but sometimes shows unpredictable drops. Attention should also be drawn to the fact that different methods, e.g. AOAC and PETERMAN, give different values and that also the ratio of P_2O_5 in the sample to the amount of citrate solution during analysis is of importance.

It is thus in the nature of the process that the nutrient level is fairly easy to keep constant, whereas keeping the individual components within certain tolerances is more difficult. However, a deficiency in one nutrient will normally always be accompanied by an excess of another component.

For that reason, we feel that in the long run it would be advantageous both for producer and customer to specify the mean content of each individual nutrient together with limits between which one nutrient may vary, as long as it is compensated by

the two other nutrients. As things are now, over-formulation and extra work are necessary in order to be able to guarantee the amounts of each nutrient in samples from shipments of down to 50 tons.

The production is checked from hour to hour by samples sent to the laboratory. For shift analysis simplified and expedient methods have been developed. Experience is that even with the best flow-meters, the analyses are always more reliable for controlling the ratios.

An automatic analyser has been tried out extensively in the laboratory and will be put on stream in the NPK plant this summer. The impression so far is that the analyser is no "cure-all", but that it will be a valuable tool when properly cared for and followed up by conventional analyses.

Humans are often poor "controllers". Quite a lot of work has been involved in training the operators and developing graphs and routines for evaluating the analyses and calculating the necessary adjustments in order to keep to product specifications. An advantage of the prilling process is that there is very little delay in the system. The full effect of an adjustment of the salt:NP ratio can be determined in a sample taken from the prilling tower 5 minutes after the adjustment. In the granulation process, the full effect will take hours to develop, due to the large amounts of material recycling.

14. CONCLUSION

As an operating company, Norsk Hydro tries to optimize the total result of investments and operation. Traditionally conservative, we have a tendency to build our own plants and equipment heavier and larger than actually necessary, calculating a long life and leaving room for changes and expansion.

In the contracting business, however, there seems to be a tendency to pare the investment costs to a minimum, due to competition and the fact that customers often seem to over-emphasize the initial costs and under-estimate the effect of equipment quality on operating costs.

When offering the Norsk Hydro NPK process on the world market, all the improvements and simplifications are incorporated. It has also been a challenge to cut investment costs to a minimum and at the same time maintain the operability of the process.

The selection of the process to be used in a new or modernized installation is a difficult and complex problem. Nitrophosphates and the Norsk Hydro prilling process have their advantages and limitations. As with most other developments, they do not

represent a universal solution to all the problems in the industry, but they do appear to have a place.

We who have our daily work in Norsk Hydro feel that our NPK plants have become very successful, and that the economical and technological justification of the NPK prilling process has been fully demonstrated.

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DISCUSSION

Mr. J.O. PANDE (Norsk Hydro, Norway) : As you know, our process is based on the original Odda process, invented in Norway in 1928 by Erling Johnsen. You will be able to see a part of our new NPK plant on your visit to Herøya the coming Friday. This plant has a capacity of 5-600,000 tons per year of NPK, and was put on stream three years ago.

In principle, any quality of phosphate rock can be used as phosphate raw material, but for practical and economical process performance there are certain limitations.

About 85% of the world's phosphate rock production consists of phosphate of sedimentary organic origin. Minor quantities of organic material which still remain act as foam stabiliser. Vigorous foaming may therefore arise during dissolution, in connection with the formation of carbon dioxide. By calcination of the rock, however, organic matter is destroyed and carbon dioxide driven out, thus reducing the foaming tendency.

Low-grade ores may be troublesome in operation due to foam, acid insolubles and larger amounts of $\text{Ca}(\text{NO}_3)_2$ which have to be removed, higher viscosity of the liquor after neutralisation, and more impurities affecting the product grade etc.

Due to corrosion, chlorine containing material must not be allowed to enter the digesters. We have found, however, that a chlorine content of up to 0.1% can be tolerated without destroying the passivity of CrNiMo stainless steel.

If the rock contains much insoluble matter, this has to be removed. The insolubles are mainly silica, and tend to cause corrosion on equipment such as pumps and valves, because the protective oxide film on the stainless steel is damaged by the erosive particles.

The phosphate rock is dissolved in nitric acid of about 60% strength in the digestion step. The heat of solution raises the temperature about 45° C.

The warm digestion liquor is cooled batchwise in a number of crystallisers of our own design. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ starts crystallising at about 25° C. The terminal crystallising temperature determines the degree of calcium removal, which in turn determines the level of water-soluble P_2O_5 and nutrients in the finished product.

With deep cooling, theoretically a very high water-solubility of the phosphorus can be obtained, without the use of any supplementary step for calcium removal. However, cooling costs money and takes time. As the crystallising curve for $\text{Ca}(\text{NO}_3)_2$ flattens out towards the end, there must be a limit beyond which a further increase is uneconomical. When the cooling brine is cooled by vaporising ammonia -5°C seems to be a practical limit, as long as the ammonia vapour must have sufficient pressure for the neutralisation step. Our operating experience indicates that 75 to 85% water solubility of phosphorus can be obtained from most phosphate rocks.

The advantages of batchwise crystallising are the following :

1. The cooling surface is cleaned between each cycle, because the crystal deposits dissolve in the new, warm digestion liquor.
2. Crystal formation and growth are closely controlled, and large crystals of uniform size are obtained.
3. By cooling more crystallisers in series, a maximum overall heat transfer and optimum temperature difference between coolant and liquor can be obtained.

The filtration takes place in rotating drum filters, designed and constructed by Norsk Hydro to suit the particular requirements of the process. The filters have proved to be very reliable "work horses" which can be operated continuously for months without any maintenance. Before this type was introduced 4 years ago we also tried a commercial filter, but experienced break-downs and high maintenance costs due to erosion and corrosion.

In the second filtration stage the crystal cake is washed with nitric acid and a small amount of water before it leaves the process as a by-product. The wash acid is returned to the rock digestion step.

The mother liquor, along with fine undissolved particles which have passed through the 0.5 mm mesh filter cloth, is then neutralised with ammonia vapour in the neutralisers. Dicalcium phosphate and various impurities of calcium, fluorine, iron, aluminium, etc. are precipitated, while ammonium nitrate and phosphate remain in solution.

By addition of ammonium nitrate, the $\text{N}:\text{P}_2\text{O}_5$ ratio can be increased to any level desired.

The NP liquor is then pumped to specially designed evaporators.

The almost water-free NP melt can be prilled as such, making for instance 23-23-0, or mixed with a potassium salt and other additives such as $MgSO_4$ and Borax.

The prilled product is cooled, screened and coated before it leaves the plant as finished NPK complex fertiliser.

Oversize product is crushed and returned to the screens. The fines are recycled to the mixing/prilling step.

The final product consists of spherical balls, free flowing and easy to handle. The most common grades have a bulk density of 1.2 tons/m^3 and an angle of repose of about 25° .

The calcium nitrate by-product is a common feature of all versions of the Odde Process. In Norsk Hydro this is used in the production of Nitrate of Lime. The company have also developed a conversion process for making ammonium nitrate and calcium carbonate. The NPK plant in U.S.A. is using this alternative. A third possibility is to make N solutions.

One troublesome area of plant operation is product control, keeping the NPK on analysis. Over-formulation is expensive. Under-runs are also expensive either as re-runs or bulk mixing, not to mention the possibility of penalties and lost reputation. These problems are not specific to nitrophosphates, however, as they apply to all sorts of multicomponent fertilisers.

Once a grade is specified, the nutrient level, the sum of N, P and K, will remain fairly constant, and can only be changed by the degree of calcium removal or through addition of magnesium sulphate or a cheap "filler". But a complication is the citrate solubility of the phosphorus, which is normally 97 to 99% but sometimes shows unpredictable drops. Attention should also be drawn to the fact that different methods, AOAC and PETERMAN, give different values and that the ratio of P_2O_5 in the sample to the amount of citrate solution during analysis may also be of importance.

It is thus in the nature of the process that the nutrient level is fairly easy to keep constant, whereas keeping the individual components within certain tolerances is more difficult. However, a deficiency in one nutrient will normally always be accompanied by an excess of the other components.

An automatic analyser has been tried extensively in the laboratory and is now being put on stream in the NPK plant.

Humans are often poor "controllers". Quite a lot of work has been involved in training the operators and developing graphs and routines for evaluating the analysis and calculating the necessary adjustments in order to keep to the product specifications.

An advantage of the prilling process is that there is very little delay in the system. The full effect of an adjustment of the salt:NP ratio can be determined in a sample taken from the prilling tower 5 minutes after the adjustment. In the granulation process, the full effect will take hours to develop, due to the large amounts of material recycling.

Another advantage of the prilling process, is that switching of product grades can be done quickly and easily.

As an operating company, Norsk Hydro tries to optimise the total result of investments and operation. Traditionally conservative, as you will see when visiting our plant tomorrow, we have a tendency to build our own plants and equipment heavier and larger than actually necessary, calculating with a long life and leaving room for changes and expansion.

Mr. KAASENBROOD (Stadtsmijnen, Netherlands) : Reading through the paper by Messrs. HAUG and PANDE, I realised that, although the problem is easily formulated, it is not at all easy to make an NPK plant run well. When the authors speak in their section 3 of NPK production as mud chemistry, they give a good representation of the conditions in which the work in the plants has to be done. The control of materials and chemical reactions in these plants involves dealing with large quantities of material forming multi-compound systems so that gases are evolved and solids precipitated or transformed in a simple and dependable way. Success in this is always the outcome of troublesome work, with complex practical situations.

The paper deals with these practical situations. It tells about corrosivity, especially when erosive particles are present, about plugging of pipes, the required quality of phosphate rock, the best way to use crystallisers. It tells about the practical difficulties in the successive stages of production. It attempts to formulate the problems met in such a way as to give those not directly concerned with the plant an idea of the extent of the work done.

I think the authors have succeeded in doing this. Though I am one of the "non-understanding" research people mentioned on page 3, line 27 of the paper, I agree with the postulation that good housekeeping may be more important than saving, on paper, some utility and investment costs.

As several sections of comments in the papers invite further discussion, I am very glad to have the opportunity to narrow the gap between the needs of the staff of an NPK plant and the activities of its research chemists by posing the following questions.

1. The first question deals with the recycle of fines to the mixer situated before the prilling tower.

We all know that recycle of fines is essential because they are present at the bottom of the prilling tower. But is this the only reason why they are fed back? Or does suspended solid matter of the same chemical composition as the end product favour the crystallisation of the liquid droplets and give prills with better physical properties?

2. Concerning the quality of phosphate rock, it is stated that a high content of acid soluble impurities such as aluminium, iron, magnesium and sulphur should be avoided. Does this not require exclusion of certain types of phosphate rock in the NPK process described?
3. The third question deals with the mixing of potassium salts in the NP melt before prilling. As is stated, the difficulties caused by the formation of very thick liquids have been overcome by special equipment. But it is not clear whether this design prevents the formation of these liquids, or makes it possible to handle them.
4. Next an international problem concerning the self-sustaining decomposition of a rather wide variety of ammonium nitrate and potassium chloride containing fertilisers.

As is stated in the paper, not all the grades Norsk Hydro produces are thermostable. But would it not be desirable to manufacture only thermostable products, now that there is an internationally recognised test for determining thermostability?

5. Though it is a troublesome operation to keep the NPK on analysis, it is proved to be possible between certain limits. A complication seems to be, however, the citrate solubility of the phosphorus which is normally 97 to 99%.

but sometimes shows unpredictable drops.

Would it be possible, in the future, to measure and control the responsible variables in an effective way, so that the last technological imperfection of the Norsk Hydro NPK process is removed ?

Mr. PANDE :

1. As mentioned in the paper, approximately 10% of the fines are recycled back to the mixing/prilling step. The reason for this is to eliminate oversize and fines in the NPK product.

The crystallisation of the melt has been investigated in our research laboratory. So far, we have not found any significant effect of the recycled fines on the crystallisation of the prills.

2. Normally, a new grade of phosphate rock is first tested in our pilot-plant in the research laboratory. Its behaviour in the various process steps is investigated and the optimal process parameters established. For instance, the foaming tendency, the pH during neutralisation and the viscosity of the liquor are of importance.

Eventually we get an estimate of what production rates can be obtained, and what product grades can be produced. If this looks promising, we will make a test run in the plant. Our experience is that there is fairly good correlation between the pilot-plant results and behaviour in the production plant.

So far, we have no means of removing soluble impurities.

3. This problem has been attacked both from the chemical and mechanical sides. We try to keep the prilling slurry as free-flowing as possible and to design the equipment to handle as thick slurry as possible. Of course, there is a limit to the amount of solids which can be mixed into the liquor. So far, we have produced grades with up to 50% potash salt and other solid additives.

4. It is the intention of our company to produce thermostable products only. So far, all the NPK grades we produce for the Scandinavian market are thermostable according to the official, Perbal trough test.

Occasionally, customers want other formulations, especially for overseas markets, and therefore we have made

limited amounts of NPK products which cannot be regarded as thermostable.

One main advantage with "deep cooling" is that the range of stable products is substantially increased, as Ca is removed. Many grades were made stable, which would have been unstable with the conventional Odde process.

5. The citrate solubility of the phosphorus has been extensively studied in our research laboratory. We know about certain parameters influencing citrate insolubility.

When there is a drop in the citrate solubility of the phosphorus, we are usually able to track it down to some process disturbances, for instance a deviation in the pH during neutralisation. This is the reason why we used the term "unpredictable drop". When such a deviation occurs, we have to adjust the ratio of nitrogen to phosphorus for some time in order to get a sufficient amount of available phosphorus in the product.

Mr. P. BECKER (Compagnie de Gafsa, Tunisia) : Has the process been tried with Tunisian phosphates ?

Mr. O. HAUG : We have not used Tunisian phosphates in the plant for production purposes. We have probably tried them out in the research laboratory but I do not know the results.

Mr. P. MORAILLON :

1. What is the sand trap principle used to remove the insolubles ? How are the removed insolubles washed ?
2. What is the principle of the tandem filters ?
3. Are the evaporators for the NP liquor of the forced-circulation principle ? Do they operate under vacuum or atmospheric pressure ?
4. Can Florida, Moroccan, Senegal and Togo phosphates be used without calcination ?
5. What is the minimum value of the total nitric:P₂O₅ ratio as a function of the nature of the phosphate ?
6. On page 5 "cooling more crystallisers in series" is mentioned. What does the author mean by this phrase ?

7. What is the advantage of filtration of the calcium nitrate relative to centrifuging ?
8. In the case of 1:1:0 and 1:1:1 fertilisers, what are the maximum concentrations obtained, taking into account the impurities of the different phosphates and the addition of coating material ?
9. How are the phosphate impurities divided between calcium nitrate and the NP fertiliser, notably the fluorine ?
10. On page 6 it is indicated that, with a Ca:P atomic ratio of 0.3 to 0.4 in the liquor, 15 to 20% of phosphorus is precipitated during neutralisation.

Theoretically, according to the CaHPO_4 formula, this should be 30 to 40%. Is the difference due to the precipitation of half the CaO as CaF_2 ?

11. What is the type of screens used ?
12. What is the type of mill used ?
13. What is done with the CaCO_3 obtained in the Tunisian and U.S. plant ?
14. What is the fire-resistant material of the conveyor belts ?
15. Why does a lowering below 1.4 of the N:P₂O₅ ratio in the finished product reduce the production capacity of the wet part ?
16. Could one add a filler to the liquor before prilling ? What type of filler ?
17. Can the authors provide information on the investment and costs for example, in the case of the American plant with conversion of the calcium nitrate. In particular, the consumption of steam and kWh.
18. Should one use cooling equipment to complete the cooling effected by the ammonia used in the plant ?

Mr. PANDE :

1. Our sand trap is in principle a settling cone. The removed insolubles are washed with water in a rotating drum. We use countercurrent flow.

2. Our tandem filters consists of two rotating drums in series, operated under a moderate suction. In the first stage, the crystals are separated from the mother liquor. In the second stage the crystals are washed with acid and water.
3. Our NP evaporators are operated under vacuum. We do not use forced circulation.
4. The phosphate rocks mentioned (uncalcined Florida, Morocco, Senegal and Togo) can be used in the process. Due to foaming an antifoaming agent has to be used. Some of these rocks contain substantial amounts of acid insolubles, which have to be removed in order to avoid erosion of the equipment. At present, we mainly use Kola rock, North Carolina rock and uncalcined Togo rock.
5. As a rule of thumb, we can say that the minimum amount of nitric acid required in the digestion step is about 10% more than what is required to convert the rock to phosphoric acid and nitrates, mainly $\text{Ca}(\text{NO}_3)_2$. Norsk Hydro normally prefer, however, to use a somewhat larger excess of nitric acid, as there is a high N content in most of our product grades.
6. The crystallisers are filled batchwise. The cooling medium, however, can be sent through a number of crystallisers in series, countercurrently to their filling sequence.
7. In my opinion, the main advantages with the use of filters instead of centrifuges, is that our filters have proved to be very reliable "work horses". There is very little maintenance and practically no erosion. We get a very stable and steady operation which is beneficial to the operation of the other parts of the plant.
8. To date, we have produced 23-23-0 and 16-16-16. The 23-23 corresponds to a 1:1:1 grade of triple 16.7. In order to make triple 17 somewhat more impurities have to be removed, and a high citrate solubility secured. These values were obtained with Kola rock. With other phosphate rocks a slightly higher or lower nutrient level can be obtained, depending on the amount of impurities which end up in the product. With the North African rocks mentioned, this difference is insignificant.
9. The major part of the soluble impurities in the rock follow the mother liquor into the NPK product, including 80-90% of the fluorine.

10. You are right. We have found that the high water solubility of the phosphorus is caused by the presence of fluorine, as some of the Ca is precipitated as CaF_2 .
11. We are using vibrating screens.
12. We are using hammer mills for crushing of oversize.
13. Farmers Chemical sell their ammonium nitrate. At present they have no use for the CaCO_3 , and it is therefore dumped into a pond. Another possibility would be to mix the CaCO_3 into the AN and make ANL. This alternative will be used in the new plant in Hungary.
14. We use fire resistant rubber belts according to ISO recommendations 340/163 class A.
15. This must be a small misunderstanding.
The capacity of the wet part remains the same concerning phosphorus, independently of the ratio of N to P. However, when the P content in the grade increases, there will remain an overcapacity in the dry part of the plant.
16. It is possible to mix in a limited amount of filler.
Any cheap material can be used, as long as no unwanted side reactions occur in the mixing/prilling step.
17. A couple of years ago, our company made a detailed estimate, and found that the turn-key price for a plant producing 2,000 tons per day of a 1:1:1 grade of high water solubility, Ca conversion included, would be approximately 10 million U.S. \$. This price covers investments within battery limits and includes engineering and licence fee.

The consumption of utilities were estimated at :

- 65 kWh/t of 1:1:1 grade.
- 0.9 t. of steam/t of 1:1:1 grade.

Concerning the production costs, I feel that they are dependent on so many variables, that it would be necessary to go into detailed explanations. For that reason, please excuse that I cannot give you any figures now.

18. We have installed a mechanical refrigeration unit in addition to the ammonium vaporiser for cooling the cooling medium for the crystallisers.

Mr. C. BASSELIN (Sté Chimique des Charbonnages, France) :

1. Can the author specify the exact use of the sand trap ?
2. The author indicates on page 6 of the paper the possibility of obtaining nitrate of lime crystals of uniform granulometry. Can he give details ?
3. Concerning neutralisation and evaporation, can he specify the content of MAP and DAP in the liquor leaving the evaporators and the losses of ammonia ?

Mr. HAUG :

1. The purpose of the sand trap is to remove acid insolubles and, of course, it is a question of design of the sand trap as to what size of sand will precipitate and what size will continue in the liquor.

The viscosity of the liquor is also, of course, important for the operation of the sand trap. This is all I can say because it depends on the phosphate rock and on the actual sand trap used. With a sufficiently big sand trap you can remove quite a lot and it is a matter of economics.

2. If you have crystals of uniform size you will get a porous packing of the filters, which lets the mother liquor go through. If the crystals have different sizes the crystal cake will get much tighter and the filtrability will be worse. For that reason we think it is important that the crystals should be of uniform size, and with the way we are operating our crystallisers this is achieved.

Some years ago, I understand, we had trouble with this but in latest years it has operated very satisfactorily.

3. To my knowledge it is mainly monoammonium phosphate and 10, 20 or perhaps 30% diammonium phosphate. The ammonia losses of course are very dependent on the composition of the liquor.

Mr. M. BONGAARD (Windmill, Holland) : Is the location of the cooling drum up stream of the screen essential to your process or is it just accidental ?

Mr. PANDE : I hope I am not wrong when I say it is just accidental. The explanation is that, before we built the plant, we were somewhat afraid that during cooling there would be crushing of prills and dust formation and, for that reason, we wanted to do the cooling before the screening. The operating experience, however, proves that there is very little crushing and, for that reason, we would now place the cooler after the screens.

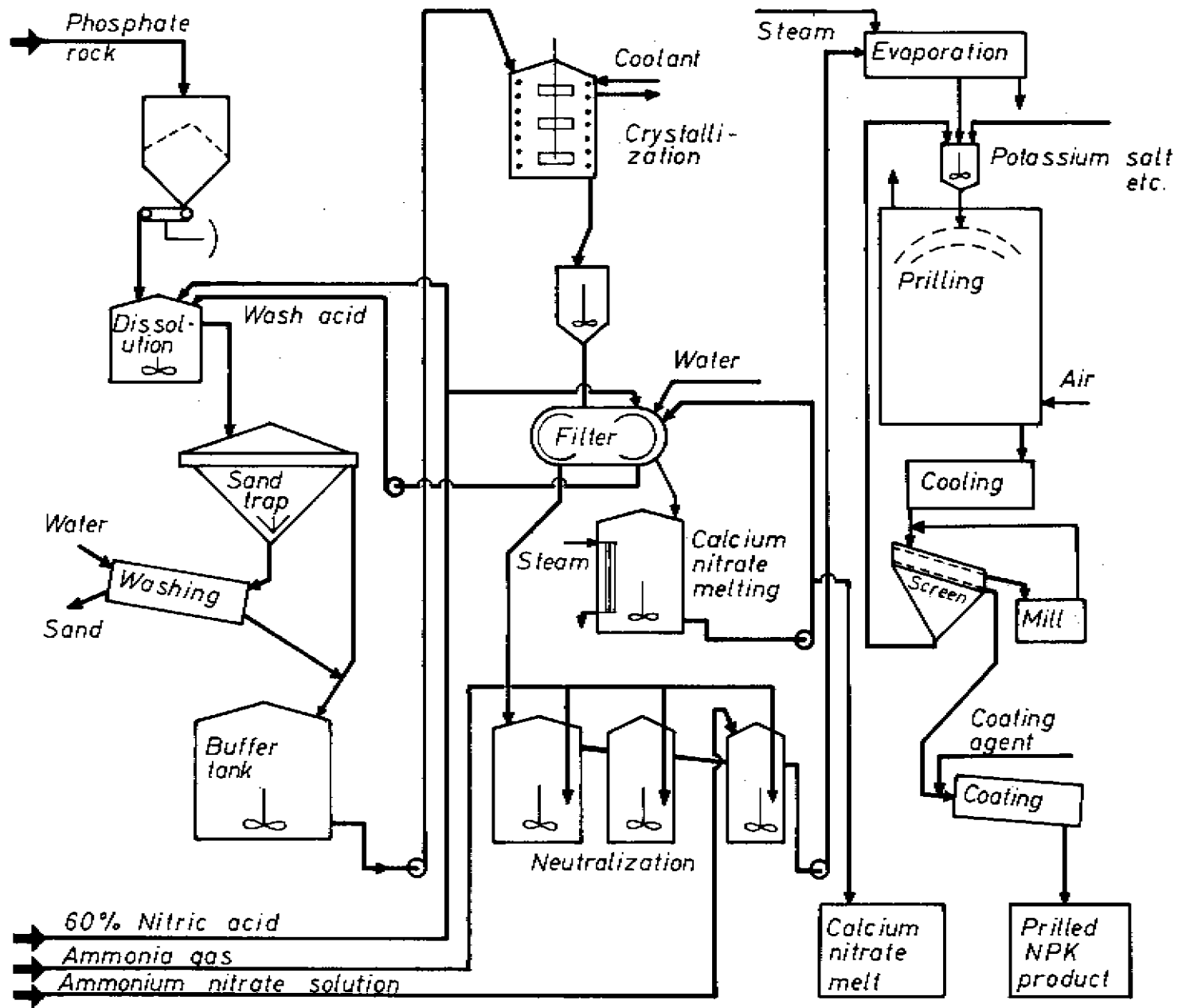


FIG.1. THE NORSK HYDRO NPK PROCESS.