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THE BASF ODDA NPK PROCESS

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SUMMARY

BASF started in the 50's with the production of nitrophosphate fertilizers using the Odda process. In the meantime the process has been extensively studied in our research laboratories working in close conjunction with the production plants.

The purpose of this paper is to give a review of the improved production techniques contributing to a real product optimisation which has enhanced the attractiveness of the BASF Odda NPK process.

Raw material consumption in the various production steps, energy balances and by-product assessment are discussed.

Particular attention is paid to the processing of NP solutions to NPK fertilizer and the conversion of calcium nitrate to calcium-ammonium nitrate.

The choice of corrosion-resistant materials is of special interest and is described in detail.

1. INTRODUCTION

The first nitric phosphate process which was developed into a commercially successful plant was based on the inventions of E.B. Johnson, Odda, Norway, around 1930. BASF Ludwigshafen was involved in the development of the (so-called) Odda Process from a very early date. With its operating plants, Ludwigshafen, Chemische Fabrik Kalk and later BASF Antwerpen N.V., BASF has carried out extensive development work to improve production techniques and the product quality of fertilizers produced by the nitric acid route.

Increasing attention is being paid by the world fertilizer industry to the nitrophosphate route and the main features of the various processes have been extensively described elsewhere [1, 2, 4].

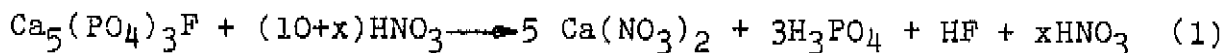
The BASF Odda NPK process today is the culmination of nearly 40 years' experience.

The results of these efforts have been incorporated in the plant producing 3000 tons per day of NPK fertilizers at Ludwigshafen. A second plant with a capacity of 2500 tons per day will be going on stream at BASF Antwerpen in 1985.

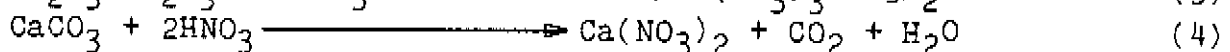
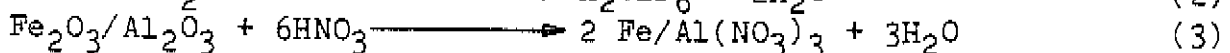
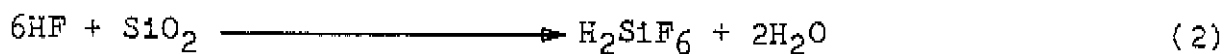
Basic equipment must be adapted to the problems associated with the quality of the rock phosphate. Only improved production technology used in conjunction with a continuous analysis of the main process parameters permit optimal adjustment of the various production steps. Details of the process chemistry will be given in cases where a direct relation between this and the processing equipment or product quality has been found.

2. PROCESS DESCRIPTION "SURVEY"

The Odda process is based on the principle of complete conversion of phosphate rock by nitric acid to phosphoric acid and calcium nitrate.



Hydrogen fluoride reacts with the silica resulting from the decomposition of minerals accompanying phosphorite, and the nitrates of metals present as sesquioxides pass into solution. An additional amount of HNO_3 is also required to decompose the CaCO_3 in the phosphate rock



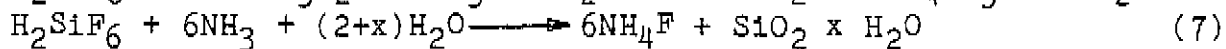
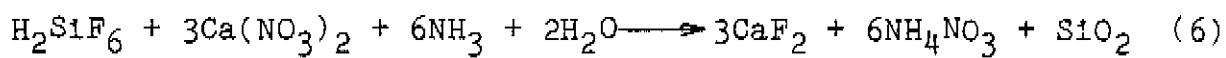
In order to achieve a high nutrient content and water solubility of the final NPK fertilizer, at least 60-80% of the total calcium in the digestion liquor must be removed after crystallisation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Heat of crystallisation: 142 KJ/kg salt).

The mother liquor from the separation unit is then neutralized with ammonia, evaporated and, after addition of potassium salts and traces of nutrients, granulated to NPK fertilizers (s. Figure 1).

The main reaction:



Side reactions



Iron and aluminium phosphates are also precipitated, and complex salts with ammonium phosphates may be formed.

The calcium nitrate crystals removed from the NP slurry are converted with ammonia and CO_2 to ammonium nitrate, which can be used to adjust the nitrogen content of the main product or combined with the precipitated CaCO_3 to produce CAN fertilizers.

3. PROCESS DETAILS

Almost all the chemical reactions in the processing of fertilizers using the nitric acid route are in fact relatively simple, although the parameters affecting the stoichiometry of nitric acidulation have not all been defined exactly.

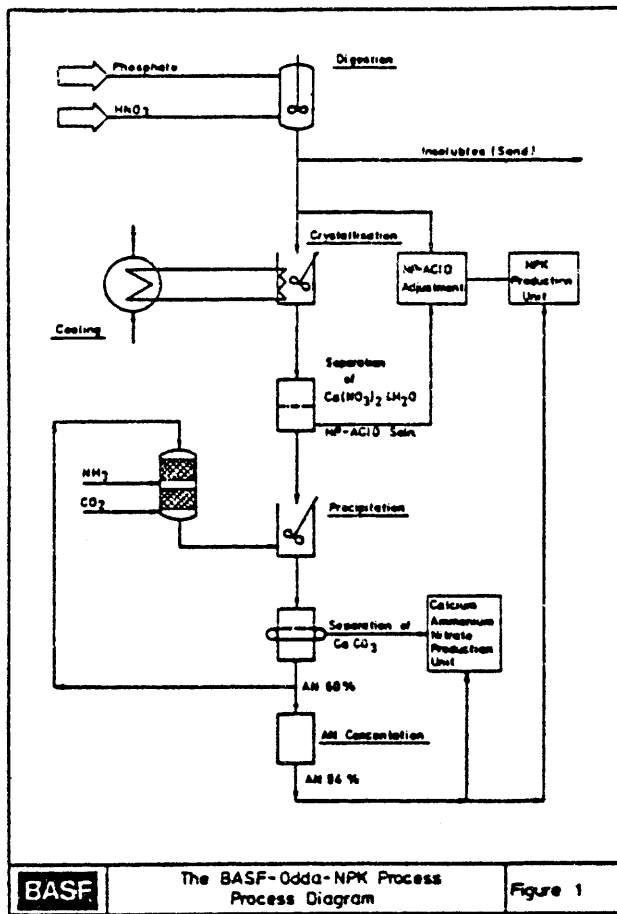
The major difficulties occur in manufacturing and are of a technical nature. The development of nitrophosphate fertilizers mainly involves the various techniques used for solving problems associated with the removal of calcium and insoluble residues.

The main problem, in brief, is the high solubility of the calcium nitrate in the phosphoric acid product resulting from attack by the rock phosphate.

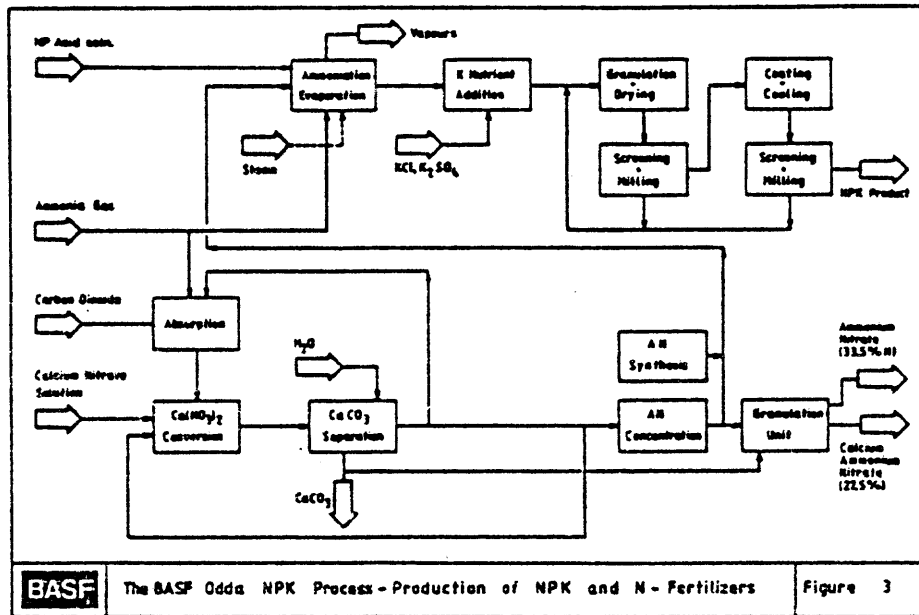
The economic efficiency of the BASF Odda NPK process depends strictly on the quality of the NP acid produced in the "wet" part of the plant. The next sections analyses various technical designs suitable for solving a given chemical or physical problem. Process flow-sheets are shown in Figures 2 and 3.

3.1 DIGESTION UNIT

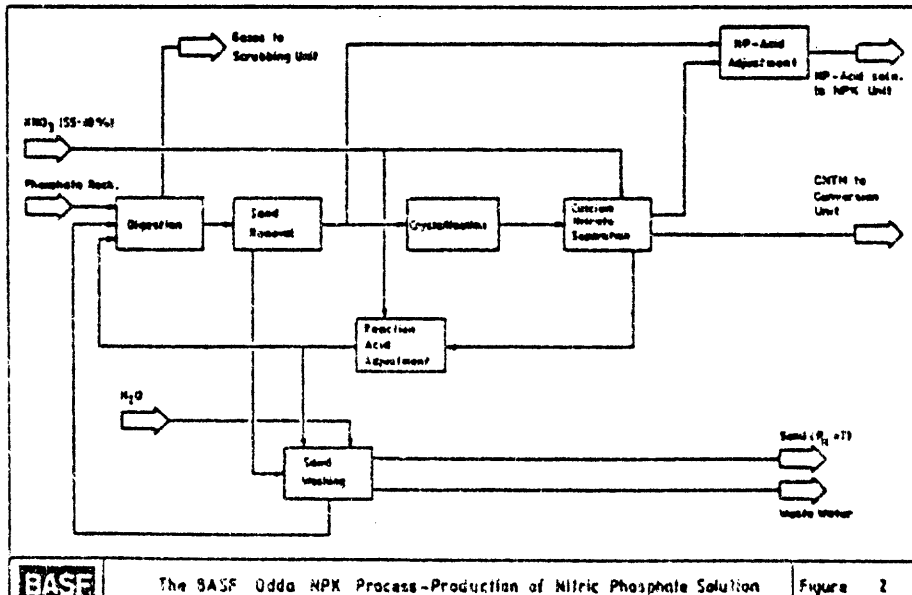
The kinetics of the decomposition of apatite of igneous origin (Kola phosphate) with concentrated nitric acid has been extensively studied in the past ten years [5,6]. The factors governing the equilibrium of the exothermic reaction (1) can be approximated by means of a graphical analysis of the $\text{CaO-P}_2\text{O}_5\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ system [2].



BASF The BASF-Odda-NPK Process Process Diagram Figure 1



BASF The BASF Odda NPK Process - Production of NPK and N-Fertilizers Figure 3



BASF The BASF Odda NPK Process - Production of Nitric Phosphate Solution Figure 2

Marine phosphorites such as Florida Pebble or Morocco phosphate consist, however, of phosphate of sedimentary organic origin and account for about 90% of the phosphate rock consumption in Western Europe (Figure 4).

Except for the problems posed by carbonates, which cause foaming, and by the presence of insolubles and impurities affecting the final product grade, the applicability of the simple kinetic equation (8) can be verified under industrial conditions

$$r = k \cdot S \cdot c_{H^+} \quad (8)$$

k rate constant of the reaction

S surface area of the apatite particles

c_{H^+} hydrogen ion concentration in the reactive solution.

It has been shown [5] that almost all the hydrogen ions result from the dissociation of nitric and fluorosilicic acids, so that a high nitric acid concentration accelerates the decomposition of the phosphate.

(S) is related to the fineness of grinding and the nature of the phosphate ore. Figure 5 shows typical particle size distributions for the various phosphates used in our plants. Coarse phosphate rock with a particle size up to 4 mm can be employed without prior milling. Other factors affecting the kinetics of the decomposition process are the mixing rate in the digestors (diffusion-dependent conditions), temperature and the presence of a high content of insolubles (SiO_2).

An urgent requirement for a large industrial plant is to achieve the maximum use of raw material. To ensure a complete reaction, i.e. a phosphate conversion of above 99.95%, an excess of HNO_3 (12-18%) is maintained. The remaining excess acid is checked after reaction of lower oxides of iron, aluminium and also of organic substances.

On-line measurement of the so-called "free acid value" increases the stability, the performance of the plant and integrates the following additional process variables:

- the plant does not generally use only one sort of phosphate rock
 - HNO_3 is recycled from the various recovery and separation units.
- The concentration of the reaction acid is therefore not constant (55-58 weight%).

The reaction is carried out continuously in a cascade of stirred vessels (2 to 4). The number of vessels required to achieve a given conversion can be easily determined by a simplified straight run method given in Figure 6.

The average residence time of the suspension in the reactors does not exceed 120 min and the temperature is maintained below 70°C to avoid excessive corrosion. Stirrers are a very important feature, particularly in the first reactor. Special stirrers are used in conjunction with antifoaming agents to prevent difficulties arising from the formation of carbon dioxide. The power of agitation should not be lower than 1.4 KW/m³ suspension.

3.2 REMOVAL AND WASHING OF INSOLUBLES

Some phosphates contain up to 8% of insolubles, mainly sand. Efficient separation of the insoluble residue remaining after acidulation is of prime importance for the efficient operation of the downstream process units. The main problem is the erosion caused to pumps, pipes, valves and stirrers. The removal of the sand also increases the nutrient content of the NP acid product.

The sand can be separated from the reaction product by means of a hydrocyclone, a concentrator or a centrifuge. A washing drum or a belt filter may be used for washing the sand mash that is obtained. It is not necessary to dewater the washed sand since the water runs off during storage or intermediate storage. After being washed to a pH of 7 the sand is used in the building materials industry.

Figure 7 shows the industrial alternatives used in BASF plants. The particle size of the remaining insolubles in the reaction mixture does not exceed 60µm, which is extremely important for minimizing the effects of erosion.

3.3 CRYSTALLISATION OF $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

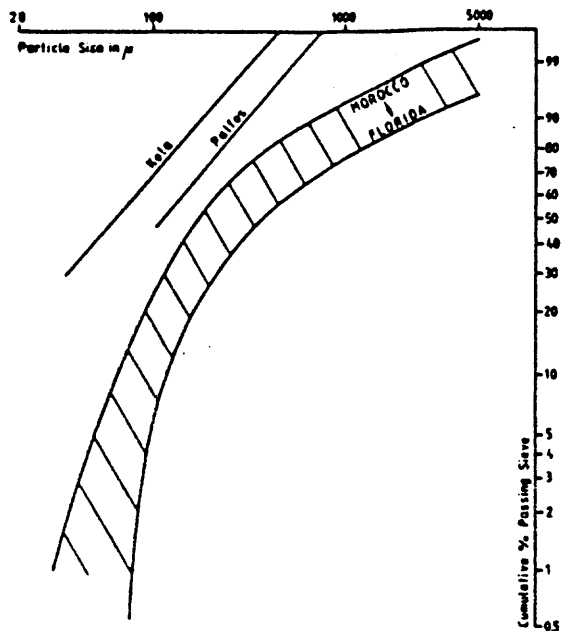
Crystallisation and removal of the calcium nitrate tetrahydrate are the characteristic steps of the Odda process. The amount of calcium to be removed depends on the required water solubility of P_2O_5 in the final product. The "freezing out" of calcium nitrate in the $\text{CaO}-\text{P}_2\text{O}_5-\text{N}_2\text{O}_5-\text{H}_2\text{O}$ system has been extensively investigated by BASF under industrial process conditions. An example of a solubility curve and practical extraction grades of CaO are shown in Figure 8. It is well known that, on cooling, the precipitate salt forms an encrustation on the cooled surface of the crystallizer, gradually decreasing heat transfer coefficients, i.e. increasing the energy required for cooling.

		N-Africa Phosphate	Russian Phosphate	USA Phosphate
P ₂ O ₅	%	31	39	32
CaO	%	51	50	47
SiO ₂	%	2	3	6
Fe ₂ O ₃	%	0.2	0.4	1.5
Al ₂ O ₂	%	0.4	0.7	1.5
MgO	%	0.6	0.1	0.4
F	%	3.7	3.0	3.6
Cl	ppm	75	130	20
CO ₂	%	6	—	3
105° Weight loss		1.25	0.3	2.1
Insolubles 45 μ		1	0.5	5

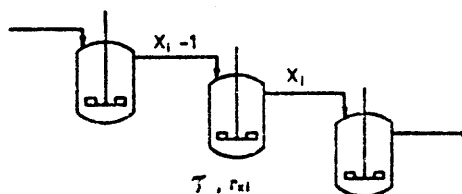
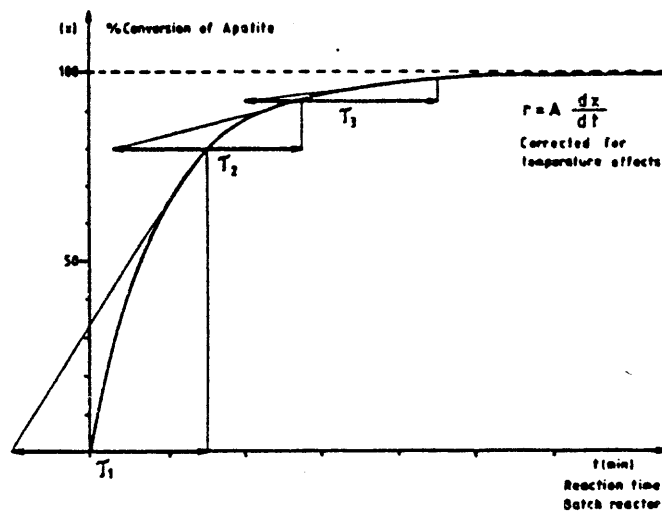
Weight %

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Average Composition of standard Phosphates Figure 4



BASF Sieve Analysis of Phosphate Rock Samples Figure 5



$$\frac{X_i - X_{i-1}}{T_i} = \frac{r_{xi}}{A} = \frac{dx}{dt}$$

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Decomposition of Apatite by Nitric Acid Test Run under conditions of Batch Operation

Figure 6

Our plants are equipped with a battery of vessels in which a cooling medium is circulated through the coils. A special stirrer design minimizes energy consumption at low temperatures (max. 0.5 KW/m³ slurry at 4°C). The cooling procedure is fully automated. A control system regulates the course of the individual cooling stages and the frequency of coil cleaning.

The average particle size of the crystals in the suspension (min. 400µm) is primarily a function of the nitric acid concentration, phosphate rock impurities and level of sub-cooling of the solution. Furthermore there is a close correlation with any given phosphate between the free-acid concentration and the amount of CNTH to be extracted at a given viscosity of the slurry.

A favourable condition for crystal growth is first of all gradual cooling in a weakly supersaturated solution.

Crystallisation in BASF plants is conducted either continuously or discontinuously. Arrangements used in production units are shown in Figure 9.

Crystals adhering to the cooling surface are periodically removed with hot reaction mixture or by brief injection of warm medium into the cooling coils. In this way a maximum overall heat transfer can be achieved. After heat exchange in the crystallizers, the cooling medium is recycled in a battery of ammonia evaporators, or when ammonia consumption in NPK neutralisation and calcium-nitrate conversion units is low, the cooling brine is passed to a freon evaporator. In plants using a batch cooling procedure, buffer tanks for brine have been installed in order to reduce variations in the temperature of the cooling medium, which cause pressure disturbances in the ammonia gas system.

Reliable temperatures for the cooling medium are -8 to -14°C and the circulation rate is about 1 to 2 m³ per m³ NP solutions per hour.

3.4 SEPARATION OF Ca(NO₃)₂ · 4H₂O (CNTH)

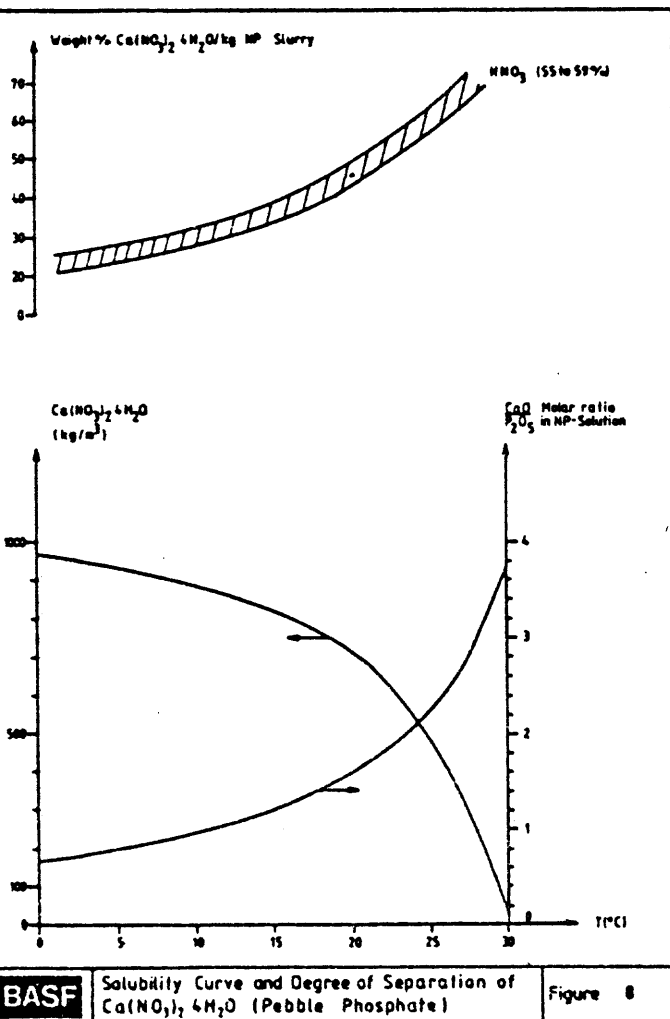
The removal of calcium nitrate tetrahydrate was, up to ten years ago, the critical step of the process. In order to achieve high water solubility in NPK products, separation of crystals from the mother liquor must be as complete as possible. A limit is posed by the solubility of the salt at the separation temperature and by the size of filter openings allowing good filtrability of viscous NP slurry. If extremely low CaO/P₂O₅ ratios are required, fractional filtration and at least two cooling stages will be necessary.

<u>Separation of Insolubles</u>		<u>Washing</u>
Centrifuge	(Batchwise)	Column
Lamella Separator	(Continuous)	Drum
Hydrocyclon	(Continuous)	Bandfilter

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Technical Alternatives to Sand Removal

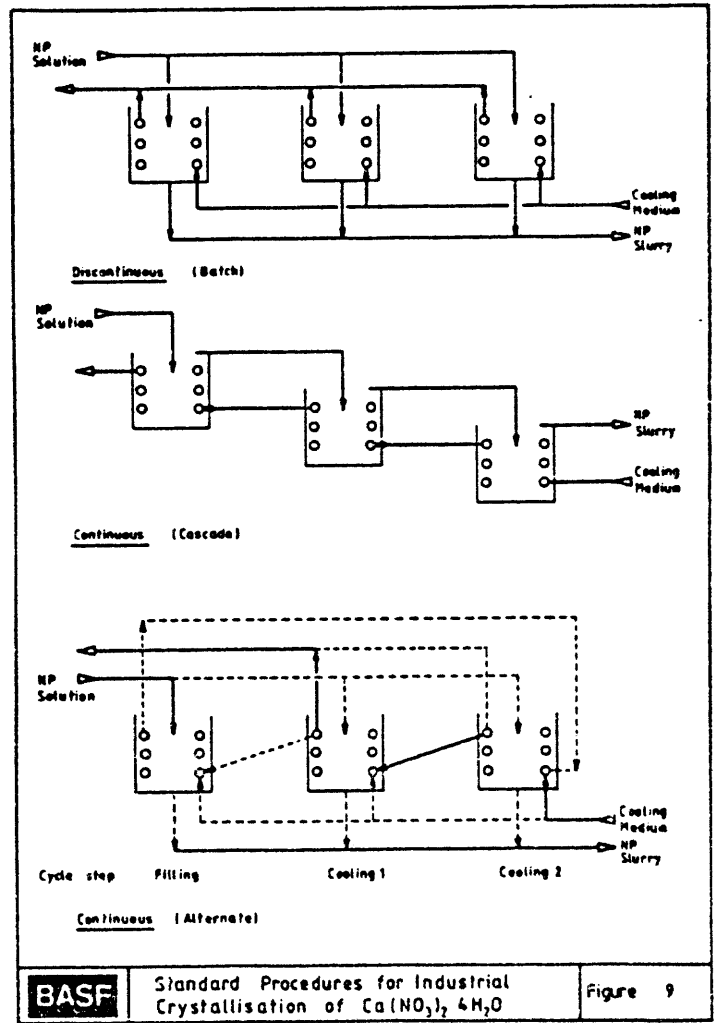
Figure 7



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Solubility Curve and Degree of Separation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Pebble Phosphate)

Figure 8



BASF

Standard Procedures for Industrial Crystallisation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

Figure 9

In consecutive washing, the salt must be freed from traces of adherent nutrients. Concentrated nitric acid is usually employed as the washing agent. In order to reduce calcium nitrate entrainment, the acid temperature is kept at about 10°C. The free acid content of the salt can now be displaced in a second washing zone with a solution of calcium/ammonium nitrate. The percentage of P_2O_5 in the salt is thus kept below 0.12%.

The wash acid is then fed back into the digesters. Overall, we attempt to keep recycle streams to a minimum. A high concentration of calcium salts in the wash acid will decrease the reaction acid concentration (ie. reduce the reaction rate) and increase energy costs in the crystallisation section. Figure 10 shows an example of separation lines at different temperatures and various reaction acid concentrations.

Salt is separated continuously to minimize the buffer capacity of the crystallisation unit.

Centrifugation used to be employed in BASF plants but due to high maintenance costs and low separation efficiency we switched to belt filters. At an experimental stage we had to solve corrosion problems on filter cloths. Another problem concerned the vacuum exhaust gases containing NO_x . The design capacity of the scrubber can be reduced by recycling gases through the filter, and technical arrangements have been proposed by some belt filter manufacturers.

3.5 ANALYSIS AND SPECIFICATION OF THE NP ACID SOLUTION

The amount of calcium nitrate in the mother NP acid solution after separation depends first of all on the crystallisation temperature but also on the free nitric acid concentration in the reaction mixture. Energy considerations in the ammoniation step and the imposed level of nutrients require strict production control for NPK grades with a low $N:P_2O_5$ ratio.

Changes in reaction acid concentration, phosphate ore and switching of grades can occur simultaneously. On-line automatic analysers are valuable tools, which are a substitute for laboratory sampling and may be integrated in process-control systems.

The classical dependence of the water-soluble P_2O_5 content in NPK on the $CaO:P_2O_5$ ratio in the NP acid solution is shown in Figure 11. The dashed lines limit the practical range obtained with various marine phosphorites. Because of the high content of acid-soluble im-

purities present in many types of phosphate rocks we are compelled with some ores to operate with blends. All the dissolved and suspended impurities adversely affect the product grade, but we are able to produce an acid giving NPK's up to 90 % water soluble P_2O_5 .

After chemical characterization in our laboratories, we isolated complex crystalline salts. For example, aluminium and silica tend to complex dissolved fluoride and so alter the distribution of ionic species such as SiF_6^{2-} , AlF_6^{3-} , SO_4^{2-} , Ca^+ . A finely divided salt having the composition $Ca_4(SO_4, AlF_6, SiF_6 OH)_{12} H_2O$ (Chukrovite) precipitate in NP acid instead of simple fluorides or fluoro-silicates.

The removal of this colloidal salt is possible at low concentrations (2 - 4 %) but it is not generally removed for economical and technical reasons.

Another impurity, magnesium, alters the mechanism of fluorine precipitation and can cause process difficulties in the ammoniation step.

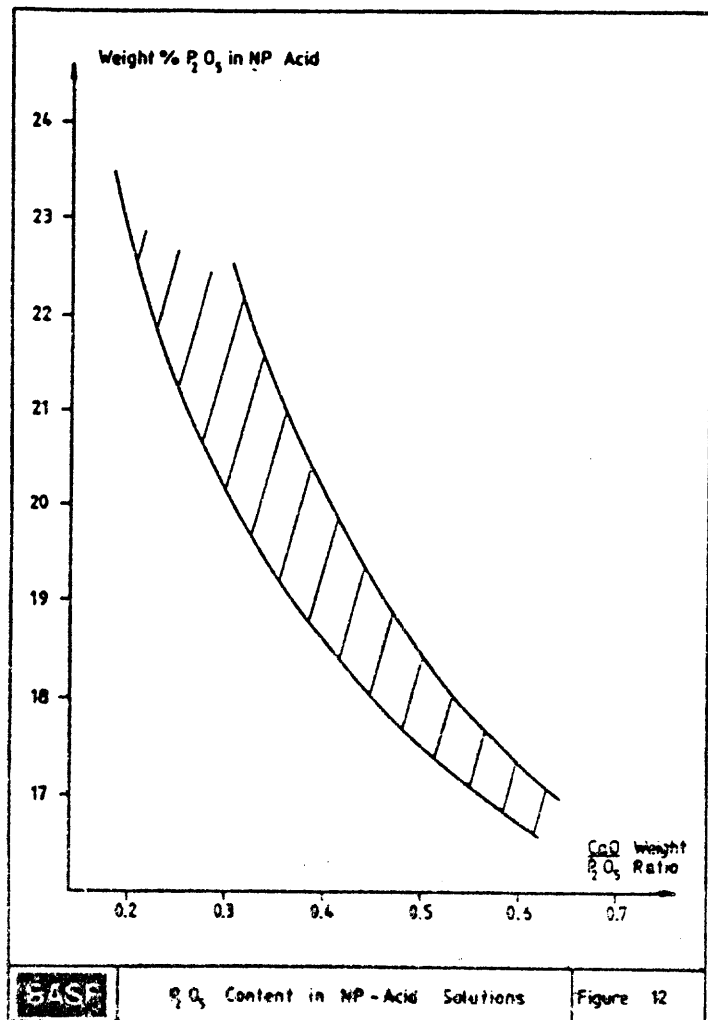
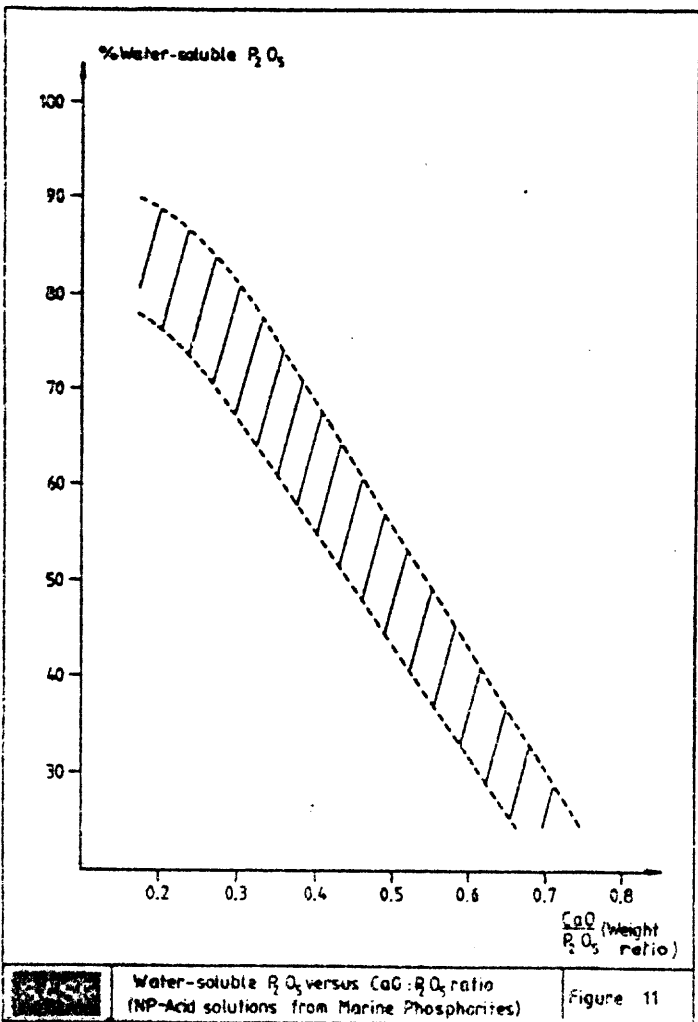
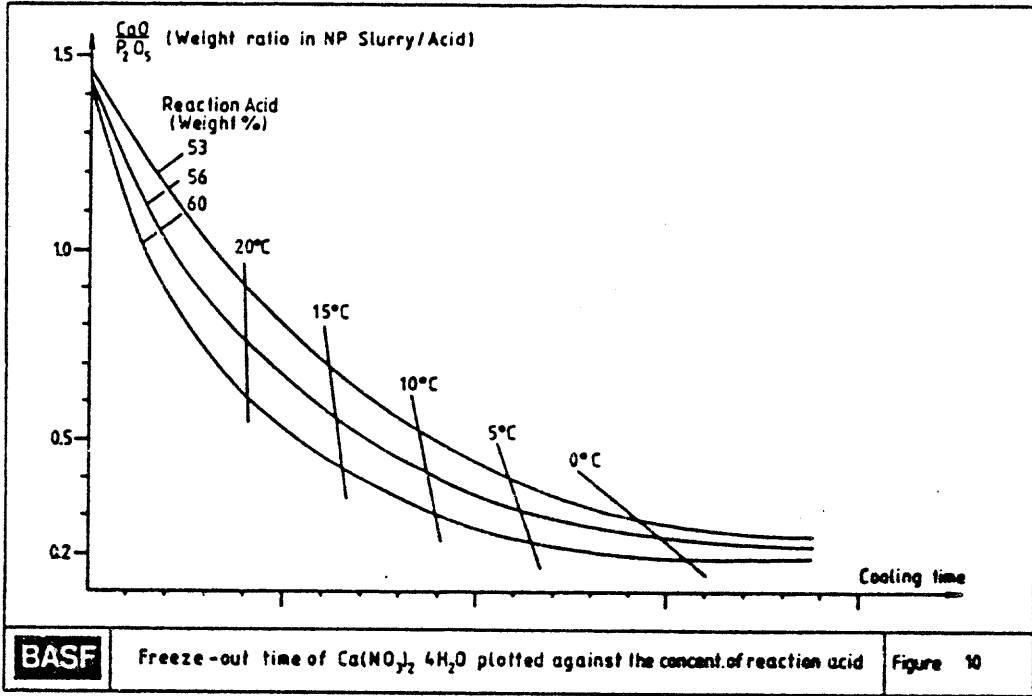
The effect resulting from all the process parameters analysed so far can be summarized in one diagram. Figure 12 shows the range of variation of P_2O_5 content on the $CaO-P_2O_5$ ratio for NP acid solutions produced with various phosphates under different operating conditions.

3.6 CALCIUM NITRATE CONVERSION AND BY-PRODUCT UTILIZATION

The production of an NPK grade such as 16-16-16 necessitates the separation of about 3.4 tons calcium nitrate per ton P_2O_5 . Hydros-copcity and a low nitrogen content are a handicap to its direct employment as a fertilizer.

Conversion to ammonium nitrate and calcium carbonate is an elegant way of solving these two problems. As the degree of calcium removal is a free variable of the process, the capacity of conversion must be adapted to frequent switching of NPK grades. In order to avoid high buffer capacities, ammonia and carbon dioxide are absorbed in, and the conversion reaction takes place in, at least two parallel trains.

-8A-



The content of free ammonia in the absorption solution has to be strictly controlled in order to minimize the amount of ammonia lost. An ammonium carbonate conversion of about 90% and a residence time of 20 to 40 min are selected to precipitate a coarse-grained calcite ($d' 70\mu\text{m}$). After thickening, the calcium carbonate and traces of silica are separated on continuous belt filters.

A two-stage washing step with condensate is necessary for washing out the adherent ammonium nitrate to 0.5%. After decomposition of the 1% of remaining ammonium carbonate and adjustment to $\text{pH} = 5.2$, the 61% ammonium nitrate solution is concentrated to 94-98% in a four-stage evaporation unit.

Calcium carbonate and ammonium nitrate are either processed to calcium ammonium nitrate (27.5% N) or separately to granulated ammonium nitrate (33.5% N) and to wet lime, mainly for the cement industry.

3.7 PROCESSING THE NP ACID SOLUTION TO NPK FERTILIZER

$\text{N}:\text{P}_2\text{O}_5$ ratio of NP acid is first adjusted with concentrated ammonium nitrate (94%) obtained in the conversion of calcium nitrate. The slurry is then ammoniated in at least two stages. On-line pH control is indispensable for minimizing ammonia losses, avoiding local overammoniation and consequently a back reaction of some dicalcium phosphate to citrate-insoluble apatite. If a high water-soluble P_2O_5 is desired, a large amount of ammonium phosphates is present in the neutralized slurry. A strict control of temperature and again of pH is necessary to prevent crystallization.

Temperature in ammoniators depends on the water content of the slurry and is limited to 120-130°C.

Different types of neutralizers and granulators are used in BASF plants so that the moisture level varies, depending on how the slurry is processed into the granulated product. If necessary, the slurry is evaporated at atmospheric pressure in single-stage evaporators with external heaters and forced circulation of the solution. The NPK slurry is finally adjusted in blenders, potassium salts are added and the slurry is injected into granulators.

Granulation processes with a moisture content of the slurry before the granulator of about 15-20% (Spherodizer) allow a low return of fines. The moisture level does not exceed 8% for production lines with separate granulation-drying and high return of fines.

3.8 PROCESS-CONTROL AND ENERGY SAVINGS

Technological improvements in recent years have been concerned also with automation and energy savings.

Strategies for process control are presently being tested in our plant in Ludwigshafen. Our impression so far is that relatively simple simulation models allow the operators to coordinate the various process operations better, avoid mistakes and, last but not least, reduce losses.

The problem of energy saving begins for the BASF Odde NPK process with the concentration level of nitric acid. A strong acid (59-60%) increases the separating efficiency of the calcium nitrate, and the resulting low water content in NP acid reduces evaporation costs.

On the other hand we have recently considerably reduced the indirect introduction of water via pumps and transmitters so that the process has a very good water balance.

The specific consumption of electric energy in a nitrophosphate plant where the same granulation techniques are used, depends on the NPK grade to be produced.

In the "wet" part of the process 70 percent of the electric power is consumed by the separation units. All vacuum levels processed on belt filters were carefully analysed. Mixing energy savings of 30% were achieved by optimizing the geometry of our mixer blades. A distribution scheme for energy consumed is given in Figure 13.

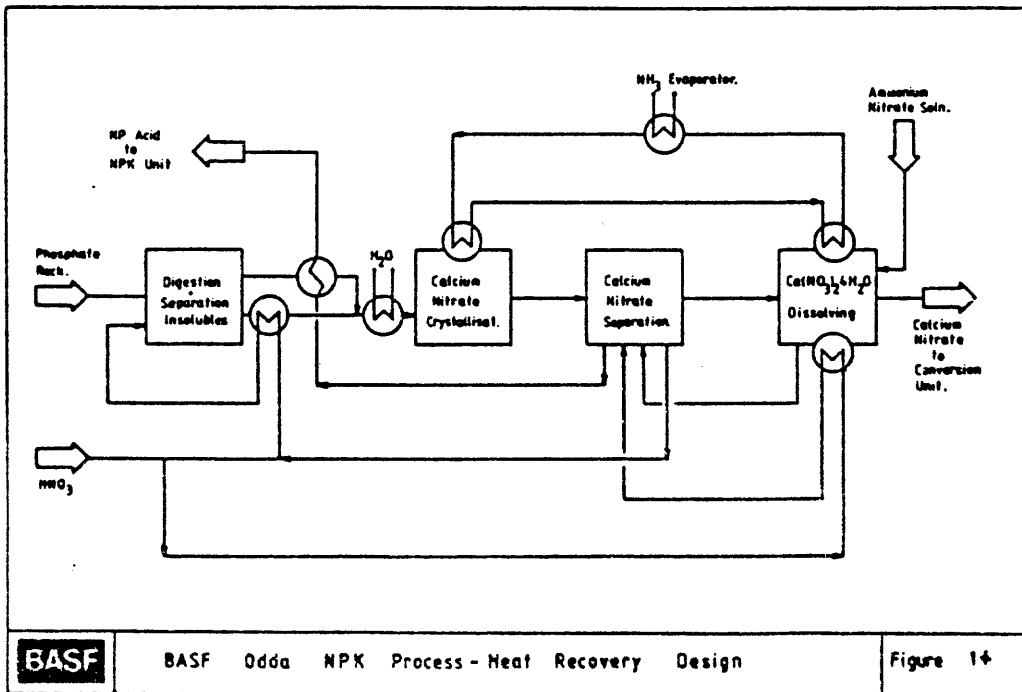
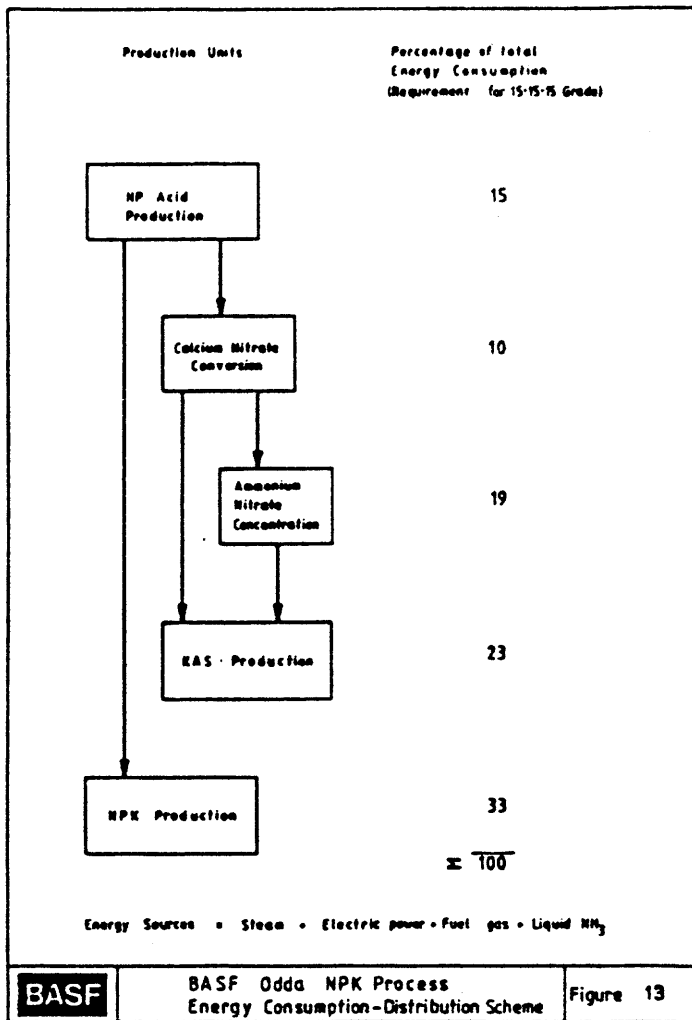
Systematic analysis of process heat exchange systems furthermore furnish designs for best energy recovery and almost always improved payback times in plant modifications. Control systems ensure a coordination of production steps and also contribute to reducing energy losses.

The example of heat recovery design for the acidulation and calcium nitrate separation units is shown in Figure 14.

3.9 ENVIRONMENTAL PROTECTION

BASF was involved from a very early date in the development of anti-pollution methods and the company is one of the leaders in practical experience.

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The fertilizer industry must face the problem of both gaseous and liquid wastes and the production of NPK fertilizers by the Odda route is no exception. As already mentioned in the previous section, potentially emissible materials are:

- Dust (bulk handling of phosphate and fertilizers, NPK processing)
- NO_x (waste gases)
- NH_3 (ammoniation and calcium nitrate processing units)

Dust emission resulting from bulk materials handling can nowadays be greatly reduced using standard equipment. Dust produced in drying units is collected in "high-efficiency" cyclones and/ or venturi scrubbers.

The problem of air pollution by waste gases containing NO_x and fluoruous compounds cannot be solved solely by water stripping. BASF is carrying out tests in order to design a process in which NO_x gases are absorbed and oxidized in a solution containing calcium carbonate.

NH_3 losses occurring in the neutralisation section of the plant are very effectively absorbed in a specially designed scrubbing tower where almost all the ammonia is reacted with nitric acid to form ammonium nitrate which is recycled to the process.

Control of all abatement activities that have been described is of course carried out by recording, sampling and checking operating data. All effluent monitoring systems are periodically checked by our Environment Department working in close conjunction with the authorities.

4. CORROSION AND EROSION PROBLEMS IN NITROPHOSPHATE PLANTS

4.1 THE PROBLEMS

Vessels, lines, valves, equipment items etc. in the Odda process must withstand both corrosive and erosive attack.

Corrosion is primarily caused by fluorine-containing compounds which are formed when the raw phosphate is dissolved by means of nitric acid, but also by small quantities of chloride and nitric acid itself. It must be remembered here that the corrosion rate in the gas phase above raw phosphate digestion solutions containing nitric acid can be higher by orders of magnitude than that in the liquid.

Erosion is caused predominantly by silicate constituents (quartz) of the raw material. Whereas corrosion can be kept within limits by the use of suitable materials of construction in combination with a technology providing mild conditions (for example at the lowest temperature level possible), erosion in Odda process plants can often be countered only by largely removing the abrasive constituents of the raw phosphate.

Plant damage, due to corrosion and erosion, and the associated production losses is expensive. Such costs have to be minimized by the use of suitable raw materials, in conjunction with a technology which provides mild conditions, as active protection against corrosion and erosion and by the use and appropriate treatment of suitable resistant materials of construction as a passive prophylaxis.

The question regarding the most resistant material of construction is a continual challenge. It can be satisfactorily answered only by tests and comparisons under real operating conditions. As is known, highly resistant alloys are expensive.

However, it must be considered whether the costs due to more frequent repairs when cheaper materials of construction are used may in the end nevertheless be higher. In this connection, safety should also be taken into account.

4.2 POSSIBLE SOLUTIONS TO THE MAIN PROBLEMS

4.2.1 Protection against corrosion

- Feedstock specifications and operating conditions

The raw phosphate being processed must have the lowest possible chloride content. This condition is met, inter alia, by the North American provenances and Moroccan phosphate. Concentrations of 500 ppm Cl and higher are serious. The problem can be resolved by appropriate pretreatment.

Amongst the process conditions, the digestion temperature plays the most important role. As a general rule, the lower the temperature, the lower the corrosion rate. There are of course limits to this requirement due to the size of the phosphate particles and the residence time. Digestion temperatures above 70°C should, however, be avoided. Regarding the movement of product in lines and vessels, care should be taken that the gas phase volumes are minimized and that condensation is largely prevented.

- Choice of appropriate stainless steel

There is no point in using a cheaper material, fairly susceptible to corrosion, in overdesign wall thickness instead of a much more resistant, thinwalled but more expensive material.

In BASF fertilizer plants, most of the vessels, pipes and valves, which are only subjected to the liquid phase, ie. which are exposed almost exclusively to surface corrosion, are still made of austenitic Cr-Ni steel No. 1.4541 (for material lists, see references [7]).

To avoid pitting corrosion, which appears to a greater extent in the gas space above raw phosphate digestion solutions containing nitric acid, or in the gas phase/liquid boundary region, highly corrosion-resistant alloys must be used. These include materials Nos. 1.4464, 1.4465, 1.4311, 1.4439 and 1.4403. The high chromium content (25-28%) guarantees the formation of a stable passivated layer.

Experience shows that steels with added molybdenum are very suitable for avoiding knife-line attack.

Stress corrosion cracking on coolant lines can be effectively prevented only by the use of 1.4541, 1.4550, 1.4571, 1.4311 pipe materials. Pipes of unalloyed steel are inevitably damaged sooner or later by caustic embrittlement.

4.2.2 Protection against erosion

- Raw phosphate handling

The conveyor chains of the chain conveyors consist of an especially resistant hardened steel (42 MnV7), the chains moving on wear rails of hardened manganese steel. The driving and guiding star wheels are provided with a surfacing weld of Gridur 24. The troughs have bottoms lined with fused basalt. For comminution of the coarse raw phosphate material, an impact mill is used, in which the impact bars, impingement plates and wearing walls are made of extremely hard chromium-molybdenum castings.

- Acidulation part

Wearing baffles which are renewed from time to time are fitted in the reactor cascade in the action zone of the stirrer.

Most of the product pumps (casings, wearing walls and impellers) used in the BASF Odda process are made of materials 1.4086, 1.4464, 1.4027, 1.4460 and 1.4138. Heavy wear occurs in pumps which deliver the raw phosphate digestion solution before sand is separated off. Damage can be markedly reduced here by lowering the speed of rotation to the necessary minimum. Generally, the pressure and flow velocity of abrasive media should be matched to the requirements.

In pipes, increased erosion frequently occurs due to the formation of eddies in the vicinity of valves. In this case, conical widenings of cross-section and/or surfacing welds have proved to be very effective.

5. CONCLUSIONS

The BASF Odda NPK process can be considered to be a real improvement in the production of NPK fertilizers by nitric attack of phosphate rock.

As a contractor company BASF is offering on the world market a process that has great feedstock flexibility and meets the highest technical and economic requirements.

The optimized process conception integrates more than 35 years of production experience and satisfies the three following objectives

- High quality products
- Low production costs
- High plant availability.

6. REFERENCES

- [1] Nitrophosphate Processes - Phosphorus and Potassium
(1969) No. 39, 18-23
(1969) No. 40, 29-36
- [2] F.G. Margolis, T.P. Unanyants (1970)
Production of complex fertilizers
Israel Program for Scientific Translations
- [3] S.I. vol'Gkovich, A.A. Sokolovskii
Complex Fertilizers based on the nitric acid decomposition of phosphates
Russian chemical reviews (1974) 43 (3), 224-234
- [4] D.H. Lie
The Odda Process - Possibilities and limitations
Proceedings of the ISMA Technical Conference Brussels
(1968)
- [5,6] A.L. Gol'dinov, O.B. Abramov
"Kinetics of decomposition of apatite concentrate by nitric acid in a continuous process"
Zhurnal Prikladnoi Khimii (1978) 51 (7), 1474-1477
A study of the nitric acid decomposition of apatite
Khim.prom. (1983), 4, 218-219
- [7] C.W. Wegst
Stahlschlüssel
Verlag Stahlschlüssel Wegst GmbH (1983)

TA/84/18 The BASF-ODDA NPK process by A.H. Durocher, L. Diehl & H.J. Eisen, BASF, Germany

DISCUSSION: Rapporteurs L.K. RASMUSSEN, Superfos AS, Denmark & B. PERSSON, SUPRA AB, Sweden

Q - Mr. F. MOSTAD, SUPRA AB, Sweden

Why are you changing from the sulphuric acid route to the nitrophosphate route in the Antwerp plant?

A - Some arguments have already been given. Gypsum deposits are one reason, but switching to the new BASF-ODDA technology by revamping an older plant enables fertilizers to be produced with lower variable manufacturing costs. As you can see from the slide, the manufacturing costs are considerably higher using the mixed acid route, until we reached the practical production limit grade (3x16.7) with the Odda process. These are the main economical reasons.

Q - What are the main improvements in this process compared to the old Ludwigshafen plant?

A - Integration of experience is also sometimes a change in experience and that is the reason why we switched from centrifuges to belt-filter separation technology. Due to erosion/corrosion effects, centrifuges entail higher maintenance costs than belt filters, thus increasing production costs.

Low emissions were also attained, but the main changes were in the separation steps - insolubles and CNTH salt.

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway

You indicate in your paper that 90% water-soluble P2O5 can be achieved by the use of fractional filtrations and several cooling stages.

What is the purpose of fractional filtration, and is this system installed in any commercial plant?

A - By fractional separation we mean a two-step crystallization procedure. There is a limit to crystallization of the NP slurry in one step because a highly viscous solution is obtained which causes problems in the CNTH-separation section. That is the reason why, if we need a NPK grade with 85 to 90% water solubility, we have to recycle the mother liquor, obtained in a first separation step, to cool it to a lower temperature and to re-separate calcium nitrate ballast. We have so far not installed this second step in any of our plants.

Q - What is the design value for water-soluble P2O5 in your new Antwerp plant?

A - We designed the plant for values between 35 and 35%, but there is no need in general in Europe for water solubilities above 50 to 60%.

Q - Mr. R. MONALDI, Fertimont SpA, Italy

Which type of neutralizers of the NP-acid are preferred and, if the slurry evaporates, what is the lowest pH before such an operation?

A - The type of neutralizer depends on the granulation process used in the plant, but in general we preferred loop neutralizers. In fact, this piece of equipment is a standard feature, but the optimization of the neutralizers varies from plant to plant.

Answering your question about the pH, it is 2-3.

Q - Is the coating operation carried out before, during or after cooling?

A - There are only two possibilities: before and during, but not after.

Q - What are the main problems of the scrubbing tower where the NH₃ losses in the neutralization section are absorbed with nitric acid?

A - Problems are related to the presence of steam and high temperatures (about 95°C): steam has to be separated from the ammonia, which is recovered in standard ammonium nitrate scrubbers.

Q - Is this tower on line with the equipment for the NO_x gases where the NO_x gases are absorbed and oxidized in the solution containing calcium carbonate?

A - No, the two units are not on line.

Q - Percent energy consumption in the different units is reported in figure 13. Is it possible to know the absolute value as steam, electric power, fuel gas and liquid ammonia per ton of 15.15.15.?

A - There are a lot of standard answers to this question. Let me say that absolute figures are difficult to give because energy costs change from plant to plant and that is why an answer to this question is not simple.

Q - Mr. J.D. CRERAR, Norsk Hydro Fertilizers Ltd, United Kingdom

What is the minimum ratio of N:P₂O₅ in the final product from the BASF/Odda process?

A - Minimum should be at the moment 0.65:1.

Q - What is the maximum water soluble P₂O₅ proportion?

A - About 85%.

Q - What material is used for the filter cloth for separation of calcium nitrate?

A - We have tested all possible cloths, and have found that

polypropylene cloths are the most suitable ones. In fact the cloth construction needs not be very complicated.

Q - Mr. B.K. JAIN, FAI, India

What percentage increase in operating cost is expected for increasing water soluble P2O5 from 60 to 85%?

A - Between 22-22-0 and 17-17-17. The difference should be 20%.

Q - Mr. N. KOLMEIJER, Windmill Holland, Netherlands

The conversion of Ca-nitrate to C.A.N. requires CO2. Are you going to do this in Antwerp? And if so, where do you get the CO2 from?

A - It comes primarily from the ethylene oxide plant.

Q - Mr. E. AASUM, Norsk Hydro, Norway

In your paper you describe that phosphate rocks with more than 500 ppm of Cl are serious for corrosion and that the problem can be resolved by appropriate pretreatment. Do you mean a pretreatment of the rock itself or what other solutions could be foreseen?

A - The word pretreatment is indeed not exactly defined. Pretreatments are possible, but very expensive to say the least. The best pretreatment is to blend the phosphates.

Q - How much NOx and fluorine compounds are released to the air in the waste gases without scrubbing with a solution containing calcium carbonate?

A - Regarding the fluorine content, separation with a normal scrubbing system - water scrubbing - gives rates less than 2 ppm of fluorine and for NOx we do not exceed 100 ppm/m3 in any case.

Q - Mr. P. MORAILLON, CdF Chimie AZF, France

To get a low CaO/P2O5 ratio in the NP acid solution, lower than 0.2 in weight, is it necessary to use more nitric acid than the excess of 12-18% required for a good conversion of phosphate rock?

A - What matters here is the acid concentration and not the excess. The excess of 12-18% is present at all times but what matters at levels below 0.3 is that your acid should be thick enough to promote intensive crystallization; this is why we are using an acid that is very close to 60% by weight.

Q - Mr. S.K. MUKHERJEE, FAI, India

How much production have BASF so far provided to market with water-soluble P2O5 content of 70% and above?

A - The production of such NPK grades is mainly for export and BASF is represented in almost all markets.

Q - Mr. M. SIPILA, Kemira Oy, Finland

What particular method is preferred by BASF for removal and washing of insolubles?

A - Sand removal alternatives depend to a great extent on the type of phosphate you are processing. Kola phosphate does not need sand removal; but centrifuge separation is well suited when processing 68 Pebble phosphate.

Q - What is the typical crystal size distribution?

A - CSD is not a big problem and crystallization procedures do not need to be very sophisticated in our process. Anyway, the average crystal diameter should not be lower than 300 μm .

Q - Mr. L.K. RASMUSSEN, Superfos AS, Denmark

On page 13 you mention concentration of NP-slurry by means of single-stage evaporator. Can you tell us:

. the pH of the slurry?

A - Between 2 and 3.

Q - . the material used for the heat exchanger?

A - Stainless steel n° 1.4541.

Q - . the maximum content of Cl allowed in the slurry?

A - 50 ppm.

Q - Mr. S. ORMBERG, Norsk Hydro, Norway

In washing the Ca nitrate with calcium/ammonium nitrate solution you have the risk of getting some NH_4 ions returned to the dissolution stage. Have you observed any connection between the NH_4 -concentration and the filtrability of the Ca nitrate?

A - The question is not relevant because our AN-CN washing medium is only a displacement wash and no appreciable NH_4 ions are returned to the digestion step.

Q - After conversion of calcium nitrate to AN and CaCO_3 , you concentrate the 61% AN solution to 94-98%. Do you experience scaling in the evaporators?

A - Yes, we do and the evaporators have to be washed from time to time with a special cleaning solution.

Q - Mr. E. HOLTE, Norsk Hydro, Norway

In your 2500 tons per day going on stream in Antwerp in 85 what concentration of CO_2 will you use for converting the calcium nitrate?

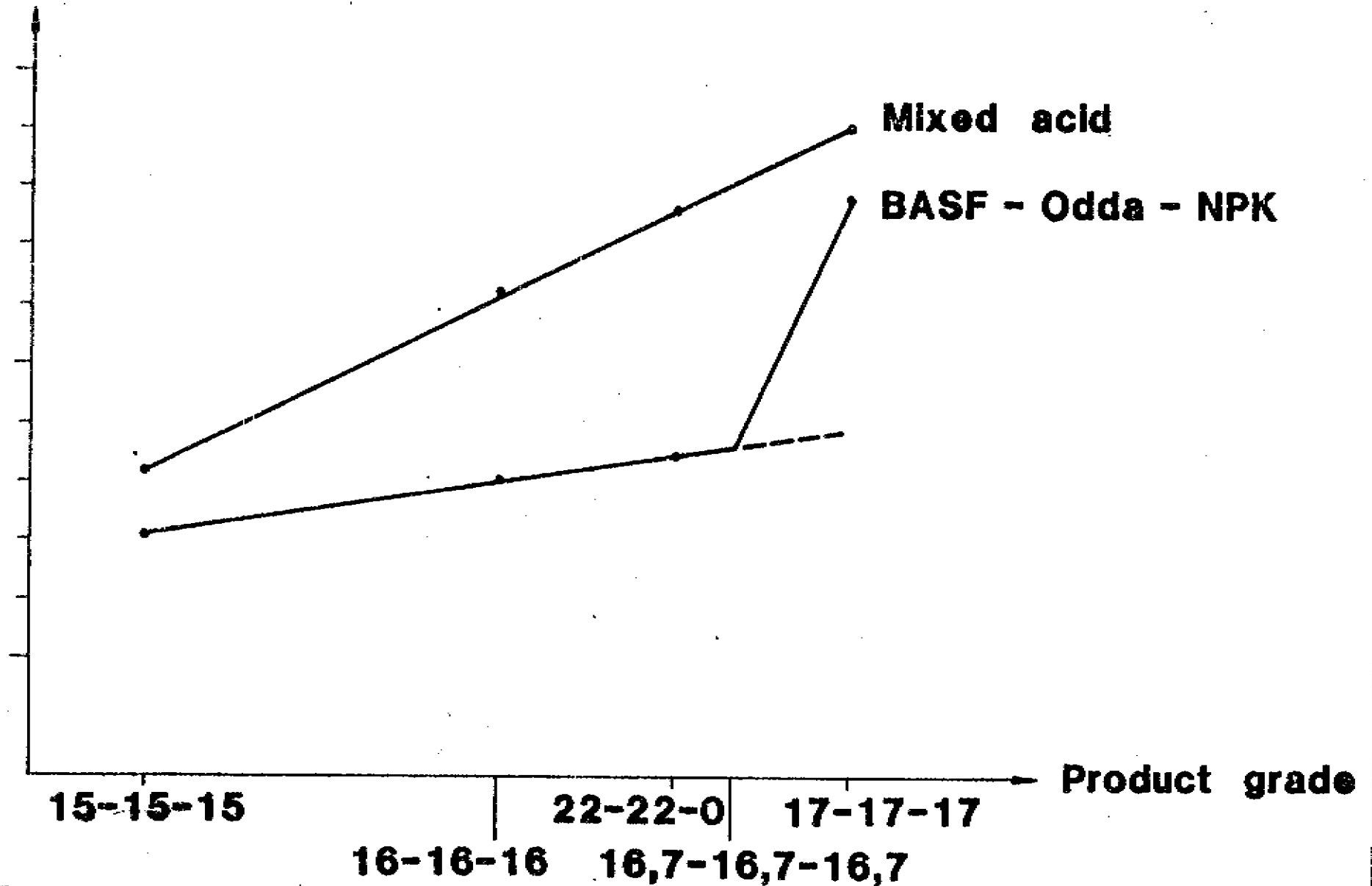
A - Concentrations up to 100%.

Q - Mr. E. AASUM, Norsk Hydro, Norway

Norsk Hydro has in its Glomfjord nitrophosphate plant been operating since 1955 without any equipment for sand removal. Several different phosphates have been used, some with up to 6% acid-insoluble material with size up to 250 micron. The calcium nitrate is filtered off with rotating filters. Would the author comment on this?

A - I would only observe that in this case maintenance costs for pumps, lines, stirrers and the amount of ballast are certainly higher than in our plants using for example phosphate containing up to 6% insolubles. Of course, using Kola phosphate, a plant can be run for 30 years or more without any difficulty.

Variable manufacturing costs



Product grade vs. variable manufacturing costs