



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

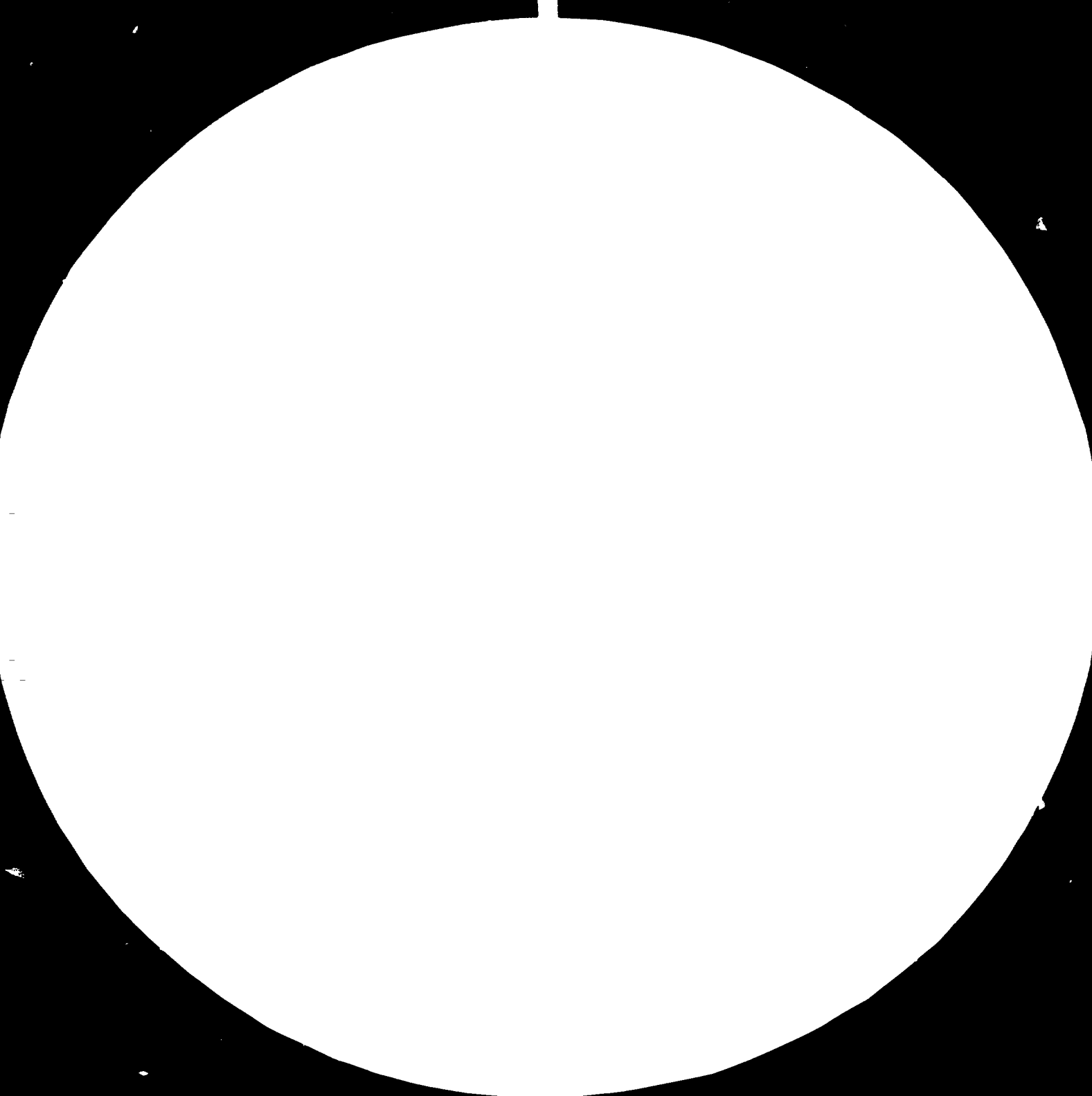
FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org





3.2



MICROCOPY EDITIONS AVAILABLE FROM

UNIVERSITY MICROFILMS INTERNATIONAL, 300 N. ZEEB RD., ANN ARBOR, MI 48106

11072

UNITED NATIONS INDUSTRIAL
DEVELOPMENT ORGANIZATION

Distr.
LIMITED
UNIDO/IO.464
19 November 1980
English

ASSISTANCE TO THE NITROPHOSPHATE
FERTILIZER INDUSTRY
TS/PAK/80/001
PAKISTAN

Terminal report

Prepared for the Government of Pakistan by the
United Nations Industrial Development Organization

Based on the work of Paul Catana^v, fertilizer expert

Explanatory notes

The following abbreviations have been used in this report:

| | |
|------|----------------------------------------|
| AN | ammonium nitrate |
| CAN | calcium ammonium nitrate |
| CN | calcium nitrate |
| DAP | diammonium phosphate |
| MAP | monoammonium phosphate |
| NFC | National Fertilizer Corporation |
| NFDC | National Fertilizer Development Centre |
| NP | nitrophosphate |
| rpm | revolution per minute |
| WS | water soluble |

The following exchange rates are used in the conversion of country currencies to United States dollars:

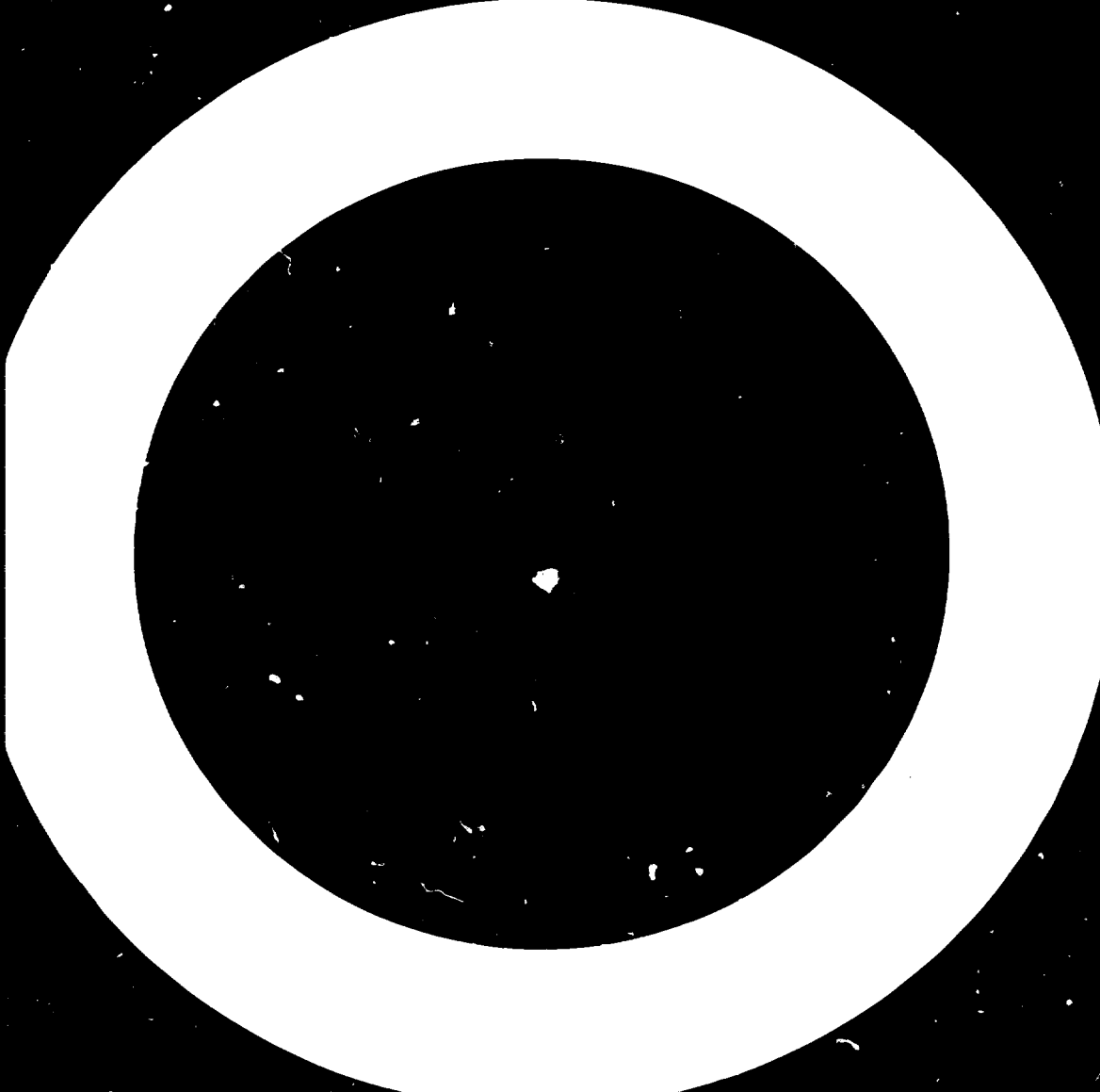
| <u>Country</u> | <u>Currency</u> | <u>Exchange rate per US dollar</u> |
|-----------------------------|----------------------|----------------------------------------|
| Federal Republic of Germany | Mark (DM) | 1.92 |
| Pakistan | Pakistan rupee (PRs) | 9.90 |

The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries.

Mention of firm names and commercial products does not imply the endorsement of the United Nations Industrial Development Organization (UNIDO).

ABSTRACT

The project entitled "Assistance to the nitrophosphate fertilizer industry" (TS/PAK/80/001) was requested by the Government of Pakistan in March 1980, and was approved by the United Nations Industrial Development Organization (UNIDO) in April 1980. The project's objective was to assist the PAKARAB Fertilizer Company in correcting problems in its nitrophosphate fertilizer plant with regard to increasing the water solubility of the product and to advise on filtration problems for the calcium carbonate by-product. The five-week mission took place in September and October 1980, and was designed to evaluate a proposal to rectify the situation and to suggest additional technical recommendations. The technical data provides the basis for the necessary improvements.



CONTENTS

| <u>Chapter</u> | <u>Page</u> |
|---------------------------------------------------------------|-------------|
| INTRODUCTION | 6 |
| CONCLUSIONS AND RECOMMENDATIONS | 7 |
| I. DESCRIPTION OF THE PROCESS | 8 |
| II. MAINTENANCE, OPERATING TIME, OPERATING STAFF | 13 |
| III. ANALYSIS OF CONTRACTOR'S ALTERNATIVES | 17 |
| IV. SUGGESTIONS FOR IMPROVEMENTS | 19 |
| NP plant..... | 19 |
| CN/CAN plant..... | 22 |
| V. PROJECT FINDINGS | 24 |
| <u>Annexes</u> | |
| I. Material balance tables - NP plant | 27 |
| II. List of people with whom the expert held discussions | 37 |
| Figure. Flow diagram (NP/CN/CAN process) | 9 |

INTRODUCTION

The PAKARAB Fertilizer Company, Multan, a National Fertilizer Corporation (NFC) unit, is producing nitrophosphate (NP) complex fertilizers. The plant has both NP and calcium ammonium nitrate (CAN) sections. Though the plant was designed to produce NP with 80% solubility and 23% nutrient content, these levels could not be reached. Instead, products with solubilities varying between 62% and 73%, averaging 67%, and a nutrient content not exceeding 21.7% were obtained. The supplier, who was asked to rectify this situation, submitted a proposal on 23 July 1980.

The Government of Pakistan sought advice on the proposal, and Paul Catana, Fertilizer Expert, was assigned to the work under UNIDO project TS/PAK/80/001. The expert arrived in Multan on 14 September 1980 and began work at PAKARAB on 15 September. The original assignment of three weeks was later extended to five weeks.

The problems of PAKARAB are summarized as follows:

- (a) Plant operating below capacity;
- (b) P_2O_5 water solubility less than 80%;
- (c) Low nutrient (N and P_2O_5) content in the final product;
- (d) Poor filterability of calcium carbonate suspension in the calcium nitrate (CN) plant;
- (e) Evaluation of plant suppliers (Stamicarbon of the Netherlands (licencee) and Unde of the Federal Republic of Germany (contractor) and their suggestions and recommendations for improving plant operation;
- (f) Plant management is interested in increasing P_2O_5 citrate solubility in the final product and decreasing nitrochalk (CAN) caking.

The expert spent four weeks visiting all sections of the plant and held numerous discussions with the plant management, senior engineers and staff members (see annex II).

CONCLUSIONS AND RECOMMENDATIONS

Under the present conditions the nitrophosphate plant, at Multan, Pakistan, cannot achieve its planned capacity and the end-product is of poor quality.

The contractor's proposals made on 23 July 1980, cannot result in an improvement of the situation.

From the calculation formulas for P_2O_5 in the soil as indicated by the National Fertilizer Development Centre (NFDC), Islamabad, it is envisaged that the plant can only be improved by investing about DM 7 million in order to yield the required P_2O_5 capacity and an 80% P_2O_5 solubility in water.

It is recommended that inert separation is practised by using hydrocyclons; by enlarging crystallization, refrigeration stations and centrifuging; by modifying the crystals discharge system from the centrifuge in order to increase the size of tetrahydrate calcium nitrate crystals (as well as the increase of recycled calcium nitrate quantity); and ensuring a CaO/P_2O_5 molar ratio of 0.64 in the mother liquor.

A buffer vessel needs to be provided between crystallization and centrifuging stages.

In order to increase the citrate soluble P_2O_5 content, the neutralization system should be provided with two pre-neutralizers.

To guarantee the plant's annual output it is recommended that an increase of 10% be made in the capacity indicated in the expert's or the contractor's proposals.

I. DESCRIPTION OF THE PROCESS

The nitrophosphate process involves the digestion of phosphate rocks with nitric acid and the separation of the formed calcium nitrate crystals from the system by cooling and filtration. This is generally done following the Odda process which has been in operation since 1928.

Plants using the Odda process throughout the world differ from each other in some of their engineering aspects at various steps of the process. In comparing today's processes with the initial Odda process, the procedure of using calcium nitrate as a by-product has been changed; the conversion of calcium nitrate to ammonium nitrate and calcium carbonate is practised. The various steps are given in the figure.

At PAKARAB, the following process is presently applied at the NP plant:

(a) Digestion of imported phosphate rock is made in two vessels provided with agitators. The volume of the vessels dictates a retention time of approximately 45 minutes. The reaction is carried out at 65°C. The process takes place according to the equation: $\text{Ca}_5\text{F}_4(\text{PO}_4)_2 + 10\text{HNO}_3 \rightarrow 2\text{H}_3\text{PO}_4 + 5\text{Ca}(\text{NO}_3)_2 + 4\text{HF}$;

(b) Crystallization is conducted in four streams of crystallizer lines each having nine crystallizers. NP solution from the digestion steps is fed into the crystallizers in series, while the brine solution, as the cooling agent, is fed in parallel. By using a brine solution as the cooling agent at a temperature of -7°C in the jacket of the crystallizers, the temperature in each of the following crystallizers decreases gradually and the final crystallizer's temperature is maintained at +4°C. When the temperature of the NP solution is decreased, crystals of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ appear;

(c) Separation of the crystals from the NP suspension is carried out by centrifuges. The mother liquor containing NP equilibrium solution and a quantity of NP crystals which escapes screening is then mixed with the proper quantities of ammonium nitrate solution;

(d) The NP solution is then neutralized with ammonia gas in a process specified to take place at pH = 3.5, but in practice pH = 4.5 is applied. This is to enable the following chemical reactions to take place:

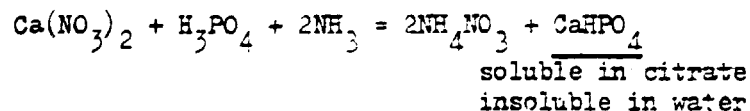
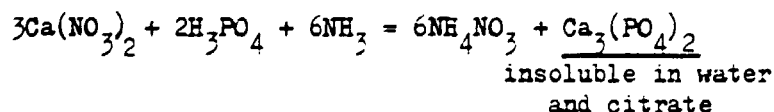
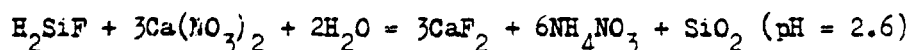
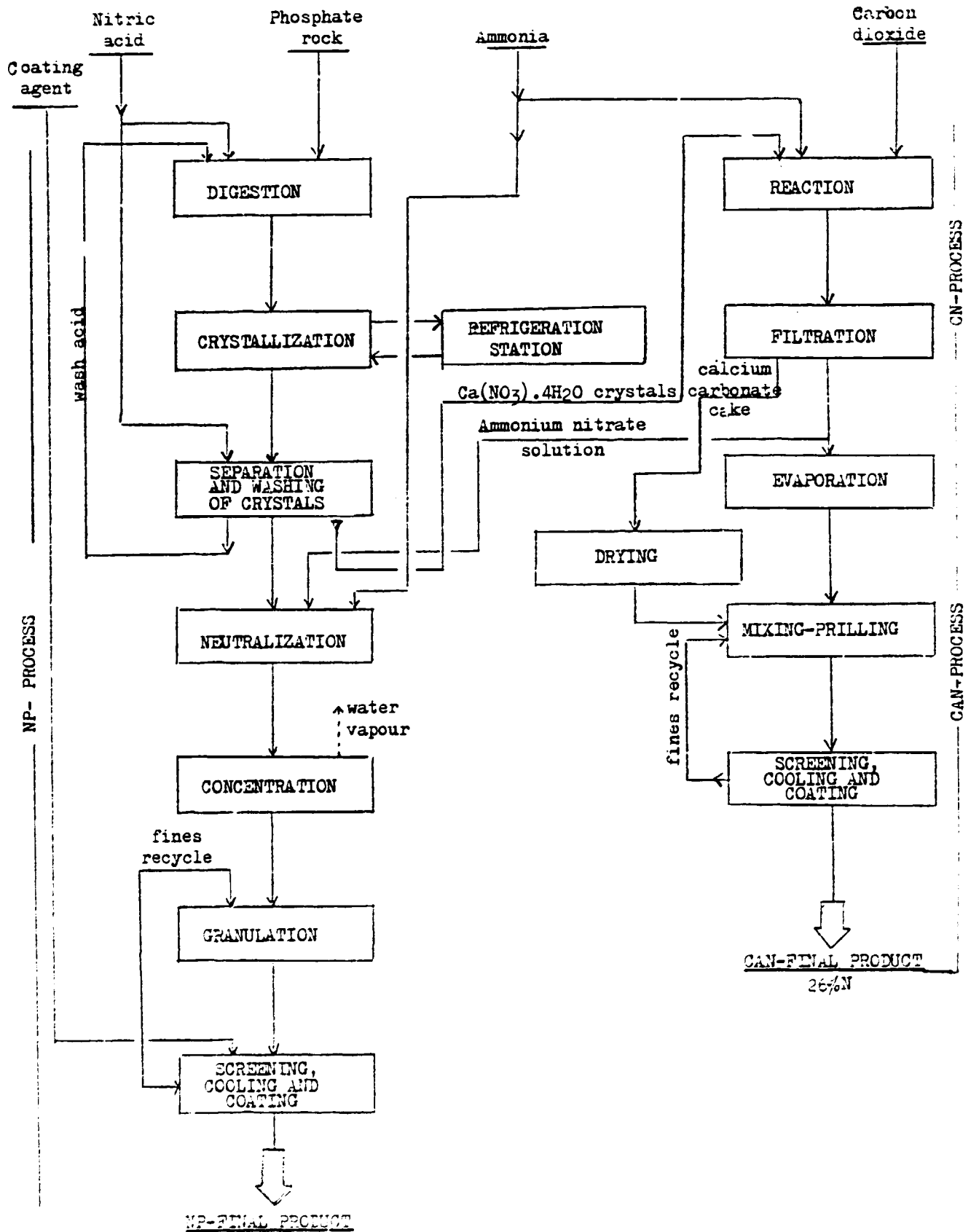
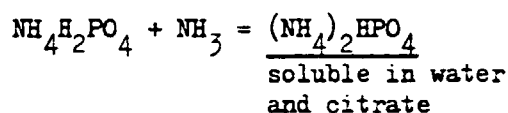
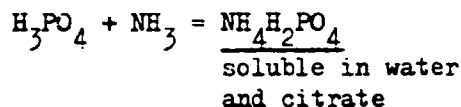
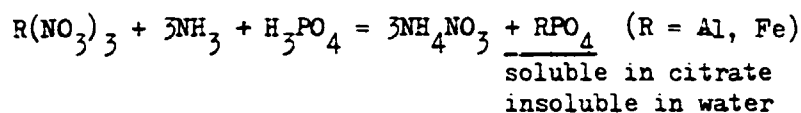


Figure. Flow diagram (NP/CN/Can process)





According to the above chemical reactions and depending on the calcium nitrate content in the solution, it is possible to obtain larger or smaller quantities of phosphorus compounds soluble in water or ammonium citrate solutions. From the above chemical reactions it is obvious that the presence of fluorine compounds partially block various quantities of calcium. This leads to an increased P_2O_5 solubility in the final product. The tricalcium phosphate formed, $Ca_3(PO_4)_2$, is insoluble in water and citrate; it is an undesirable product.³ The extent of its formation largely depends on the ratio Ca/P in the mother liquor. Similarly, its formation may be also due to improper working techniques, particularly in the neutralization reactors where improper mixing is carried out. Once this compound is formed it cannot be retransformed into water or citrate-soluble compounds;

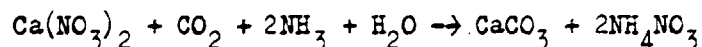
(e) The crystals are washed with nitric acid at $0^\circ C$. Both the residual mother liquor and the nitric acid are then separated from the washed crystals;

(f) NP neutralized solution is concentrated by vacuum evaporation ($175^\circ C$ and 0.3 bar) by applying thermosiphon circulation;

(g) Granulation of the product is carried out by prilling, using a rotation prilling bucket. The NP melt is passed to the prilling stage at a temperature of $175^\circ C$;

(h) The screening, cooling and coating operations (grades 1:1:0 do not need coating) are conducted in the normal equipment generally used in the fertilizer industry. For cooling of prills, a fluid-bed cooler is used;

(i) The CN crystals obtained from centrifuging, with a maximum P_2O_5 content of 0.26%, are melted at $75^\circ C$ and passed to the CN/CAN unit for conversion to ammonium nitrate and calcium carbonate in accordance with the chemical reaction:



Before being pumped to the conversion reactor, the CN solution is pre-neutralized with ammonia gas until the pH becomes 4.5 (in practice 1.4-2.4). The purpose of this step is to allow the precipitation of fluorine and phosphorus compounds as apatite. The amounts of NH_3 and CO_2 which are fed to the bottom of the precipitation column are controlled to obtain the following conditions for the suspension at the bottom of the reactor: pH = 7.8-8.1, evolution of free CO_2 (fizz test) and Ca soluble, less than 0.04%. Within the column a proper cooling system has been provided regarding heat exchangers;

(j) Separation of suspended CaCO_3 from ammonium nitrate is done by filtration. The filtrate contains 63% ammonium nitrate. Residue is washed CaCO_3 cake. Water condensate is used for washing of CaCO_3 . Some parts of the ammonium nitrate solution are pumped to the neutralization stage in the NP unit and the rest is fed to the evaporation stage;

(k) The evaporation system has a multiple effect, resulting in a melt of ammonium nitrate (AN);

(l) For the preparation of the CAN product (nitrochalk 26.5% N), the AN melt is mixed with the proper quantities of dry CaCO_3 ;

(m) The CaCO_3 powder is obtained from CaCO_3 cake by drying with hot gases in the pneumatic column;

(n) The mixture of AN and CaCO_3 solid is granulated by prilling;

(o) The CAN prills are passed through the screens, cooled at 45°C and coated with kieselguhr and amine (300 ppm).

Since the most difficult problems were connected with the NP unit, special attention was paid to it. This unit had the following parameters:

Design capacity: 1,015 t/d (100%) NP
fertilizer 23:23:0

Working time: 300 d/a

Designed quality of fertilizer:

P_2O_5 22.6 ± 0.4%

N 22.6 ± 0.4%

P_2O_5 water solubility 80% min

P_2O_5 citrate solubility unspecified

Operating capacity: approximately 60% of design capacity

Achieved quality:

P_2O_5 about 21%

N about 21%

P_2O_5 water solubility (WS) 60%-73%

P_2O_5 citrate solubility 88%

PAKARAB is interested in producing a complex fertilizer with the highest possible water solubility for the P_2O_5 and achieving at the same time maximum production capacity. Therefore, the management of the complex has established

the lowest permissible limit for the quality of the fertilizer provided in the plant, i.e. 60% water solubility. Steps were taken to obtain the maximum production capacity under these conditions.

It should be recorded that when the present plant facilities tried to produce 80% water solubility, operating capacity dropped to approximately 30% of design capacity.

II. MAINTENANCE, OPERATING TIME, OPERATING STAFF

After 20 months of operation, the general impression of the plant compared with similar ones elsewhere is that it is clean and well kept.

From a mechanical point of view it can be said that the major difficulties arise from:

Decanters. There is a strong corrosion effect on rotating equipment. From time to time (average two weeks) one of the three decanters is dismantled for welding a new surface with stellite (approximately 12 kg of metal).

Booster, compressor and turbine. These were out of order for most of the time the expert spent in the plant. This indicated problems in the sealing-oil circuit which fed steam to the turbine.

Under present conditions this equipment can be by-passed so it would not remain a major factor affecting the NP plant capacity. It will, however, create problems for CN/CAN plant capacity.

Separating centrifuges. The slot screens which are installed on the centrifuges are worn out and must be replaced every five weeks. Corrosion leads to an increase in the quantities of crystals passing through the screens together with the mother liquor.

The temperature originally set for crystallization is likely to rise due to increased quantities passed to the crystallizer. It therefore becomes necessary to decrease the temperature of the crystallizer further in order to cope with the new situation. This has its limitations and will not help in achieving the final water solubility required. The needed quantity may be obtained at the cost of quality.

Venting ducts. Corrosion was noticed, especially in ducts carrying gases from CN and NP melting tanks. This is to be expected in view of the gas composition (HNO_3 , SiF_4 , NH_4 and HF) and its high temperature (75° - 175°C). Internal cooling of the ducts is needed to decrease the temperature and the corrosion effect. This is usually done by introducing water-spraying nozzles. A trial was begun to prove this during the mission. The temperature of the CN melting tank was decreased, a follow-up of the extent of corrosion is being made.

Leakage of steam under pressure. The steam pipes made from carbon steel are operating under pressure and relatively high temperatures. These fail to withstand corrosion under stress in the operating environmental atmosphere. For this reason it is recommended to change the carbon steel (only in the NP plant area) to stainless steel. If this cannot be done immediately, it is advisable to do it whenever there is a need to change any of the pipes. The present losses in production as a result of plant stoppages due to corrosion justify the use of the more expensive stainless steel pipes.

There is no doubt that eliminating such problems and applying adequate preventative maintenance measures with the use of the proper materials, a large operational burden will be removed and the technical staff will be able to concentrate on controlling the main production processes.

Centrifugal pumps. The pump for the NP melt before prilling is creating serious problems. In some plants, this pump is eliminated by installing the evaporators above the prilling system. The prilling system is fed by free-flowing melt rather than by being pumped. At the same time there are plants where the pH of the NP melt is maintained at a higher value than at the Multan plant. It is well known that the solubility of monoammonium phosphate is maximal when the molar ratio of NH_3 to H_3PO_4 is 1.5 (in the Multan plant this ratio is 1). This explains the present tendency in the NP unit to apply a higher pH than that established by the contractor. It is felt that at a higher pH the pump operates better. In fact, the plant was not designed for such a high pH, which results in supplementary losses of ammonia in the evaporators.

It is difficult to locate the evaporators above the prilling system. Hence it is necessary to drain and steam-wash immediately after the NP melt pump is stopped. Before reswitching the pump for a new operation, the pump must be reheated. It is possible that the cause of the pump cracking is due to the strain created as a result of thermal expansion and mechanical vibration. It is necessary to check all the pipes and NP melt pumps in the system and to install flexible connecting pipes.

It should be mentioned that these pumps are costly and any other suggestion to prolong their life would be worth exploring.

Compressors. The compressors used for the refrigeration system create problems, especially at the bearings which result in axle displacement. When the compressor stops, the working capacity of the refrigeration unit drops, which in turn results in lower operating capacity and P_2O_5 water solubility in the final product.

Perforated plate of the fluid-bed cooler. The blocking of the perforated plate appears frequently and requires time for it to be cleared. The plant has thus to be stopped for 10 hours every two months.

In the expert's opinion this unwelcome phenomenon is a result of the low size of prill: from the prilling tower. Since the fan used for blowing air from under the perforated plate is out of order, the plant operators were forced to work with only one other fan, which is used for the induced air from the upper part of the cooler. The pressure above the fluid bed must be maintained at zero (i.e. the same as atmospheric pressure). It is clear that both fans have to be in operation to obtain the zero level.

Prill bucket. Quite often the holes of the prill bucket are blocked by inert particles. It is recommended that the holes be enlarged and double the number of holes be made in each row. If the melt temperature is decreased and the viscosity of the melt is increased along with the increase in the dimensions of the holes, larger prills will be obtained. As mentioned earlier, the fluid-bed cooler would work better under such conditions. If the melt temperature is decreased, recycling must be increased. To increase the recycling, a system for the transport of the recycling to the top of the tower must be employed.

It should be noted that the NP unit along with the CN/CAN is the last element in the chain of the integrated complex, for example, ammonia \rightarrow nitric acid \rightarrow NP or CN/CAN, and that all these plants need utility services. Normally, all the faults that appear in the first part of the chain or in the CN/CAN plants or utilities are transferred to the NP plant, and the plant will cease operating or reduce output. This situation convinced the expert to seek the main causes which forced the plant into this situation.

The expert discovered that during the three months (July-September 1980), 2,208 hours should have been worked at the plant, but the plant was stopped for 476 hours as follows:

| | (hours) |
|------------------------------|------------|
| Mechanical failure | 242 |
| Absence of utilities | 57 |
| Difficulties at other plants | 177 |
| Total | <u>476</u> |

Outside conditions permit the plant to operate for only 78.5% of the time. In the expert's opinion this percentage is too low. It should not fall below 90%. One possibility of decreasing the lost time is to reduce mechanical failures when other problems appear, and use that time for preventative mechanical maintenance. This would reduce the amount of lost time by one half (238 hours instead of 476 hours). The expert also recommends increasing the number of personnel in the mechanical team (i.e. more personnel to be equally divided at the plants, so that each plant has a certain number of available mechanics). The teams should also have sufficient spare parts for their equipment.

In the designed capacity for the same period, the plant was supposed to produce 21,113 t of P_2O_5 , but it only produced 8,922.6 t. The deficit in capacity can be calculated as follows:

$$\left(1 - \frac{8,922.6 \times 90 \times 330}{78.5 \times 300 \times 21,113}\right) \times 100 = 46.7\%$$

where:

- 78.5% = present working time
- 90% = expected working time
- 300 = working days per year
- 330 = number of days per year with interruptions when plant is operating

As a result there is a need to increase the capacity in some stages of the plant by at least 46.7%, assuming that the efficiency of the personnel is 100%.

In the short period the expert worked at the plant he was in contact with process-operating personnel, and recognized that the team was of good quality.

III. ANALYSIS OF CONTRACTOR'S ALTERNATIVES

In order to remedy the situation of the NP unit in Multan, concerning the capacity and quality of the final product, specialists from both the contractor and licensor carried out tests in the plant and the laboratory. The results were issued on 25 January 1980 as an alternative study and a final report came out on 23 July 1980.

In analysing the proposals the expert encountered a number of difficulties. There were insufficient data in the final report (type of rock used, condition of the screen slots of the centrifuges etc.). The presence of the blocking elements for calcium (F, SO_4) was not taken into account, and the quantity of crystals which passed the centrifuges was not given.

It was realized that the screens of centrifuges were relatively new. The tests were carried out over a period of two months using five sets of screens, although in practice screens are changed every five weeks. In the alternative study it was concluded that there were three possibilities for improving the capacity (up to design capacity) with a different product quality, and different investment and utility consumption figures. The alternatives were:

1. Provide eight supplementary crystallizers and to decrease crystallization temperature to $0^{\circ}-2^{\circ}C$ using supplementary refrigeration; this creates the conditions necessary for obtaining a final product with ~~70%~~-73% P_2O_5 water solubility. For this alternative a supplementary investment of DM 2.81 million is needed.
2. A new stream of crystallizers (nine items) are required in addition to the 36 crystallizers in operation at present. Working temperature of the crystallizers would be $0^{\circ}-2^{\circ}C$ and a fourth centrifuge would be required.

This alternative expects to obtain 100% design capacity and P_2O_5 water solubility of ~~70%~~-73%. The investment needed is DM 3.32 million.

3. This alternative requires inputs of two new streams of crystallizers ($2 \times 9 = 18$), and a crystallizer final temperature of $-4^{\circ}C$, increasing of refrigeration station capacity with 4.10^6 kcal/h (17 GJ/h) and installing two new centrifuges. This is anticipated as achieving 100% design capacity and ~~75%~~-77% P_2O_5 water solubility. The investment cost for equipment only is estimated at DM 5.17 million.

None of these alternatives guarantees a contract quality of the final product (80% P_2O_5 water solubility).

An analysis of the method used to establish these possibilities is as follows:

(a) The molar ratio CaO/P_2O_5 in the final report is too high for the equivalent P_2O_5 water solubility for each alternative if it is required to obtain at the same time a P_2O_5 citrate solubility of 98%.

(b) On a practical basis the proposals do not appear to reveal any qualitative changes; the dimensions of the crystals remain the same so that the efficiency of separation in the centrifuges is the same. If it is thought that as time goes on the efficiency of separation decreases in this type of centrifuge, the expert considers that the proposals will not result in achieving the figures shown in the final report as far as the capacity and the water solubility plus citrate solubility for P_2O_5 are concerned.

It should be mentioned that from the total content of P_2O_5 in fertilizer, plants utilize only that which is soluble in citric acid.

At present the product (as indicated in the second alternative) has 88% citrate solubility; this is too low to be acceptable. If the neutralization step could be improved and made to work properly, the citrate solubility would increase to 96%-98% and the water solubility for P_2O_5 would drop.

When taking into consideration the costs which would necessarily have to be spent and the uncertain results which can be expected, the expert considers that each of the proposed alternatives would only obtain 85%-90% of the yearly capacity, and the P_2O_5 water solubility which would be guaranteed in the final product will be 5% lower than the figures indicated in the final report under conditions when the plant should be achieving 97%-98% P_2O_5 citrate solubility in the final product.

IV. SUGGESTIONS FOR IMPROVEMENTS

NP plant

The process requires that the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ separated from the system by crystallization and centrifugation be of such quality that the remaining NP solution has the correct ratio between CaO and P_2O_5 .

In the neutralization step an amount of Ca is blocked as CaF_2 (some parts are already blocked as CaSO_4) so that the final result obtains compounds insoluble and soluble in citrate, and P_2O_5 which is still free to react with ammonia to obtain water soluble phosphates as MAP and DAP.

In cases where the CaO to P_2O_5 ratio is around 0.55, the water solubility in the final product will be 85% P_2O_5 . If the ratio were 0.64 the water solubility of P_2O_5 in the final product would be approximately 80%, and for 0.86, 70%. In these final products, P_2O_5 citrate solubility is around 97-98%. At the same time the quantities of $\text{Ca}(\text{NO}_3)_2$ which are in the mother liquor are determined by the equilibrium composition of the mother liquor. There are also some crystals that have passed through the centrifuge screens.

Using equilibrium diagrams (Jenecke-type) for the systems $\text{Ca}_3(\text{PO}_4)_2$ - HNO_3 - H_3PO_4 - $\text{Ca}(\text{NO}_3)_2$ for different temperatures, it was possible to establish the equilibrium composition of the mother liquor, and for a ratio of 0.64 to be established, what was the maximum quantity of crystals that could be allowed to pass the centrifuges in the mother liquor. For this reason it was necessary to control (and thus decrease) the quantity of crystals which pass the centrifuges.

The only solution is to increase the dimensions of the crystals and to maintain for a longer period the correct space between the centrifuge screen slots. It is recommended that the dimensions of the crystals be doubled.

It should be mentioned that in installed-type crystallizers it is difficult to treat crystals. The stainless-steel stirrers suffer from corrosion, especially under the effect of the inert material at the same time as the crystals. It is normal to suppose that if the stirrers were affected, so would the crystals be affected.

In this type of crystallizer the speed of revolution should be reduced, and this would decrease the heat-transfer coefficient. In this respect it would have a mild effect on the crystals and at the same time achieve the heat transfer necessary for working with a maximum stirrer speed of 30-40 rpm.

It would also compensate the heat transfer so as to increase the surface thermal transfer and in addition, a larger volume of crystallizers.

When decreasing the speed of agitators, the power consumption will also decrease (it is proportional to the cube of the rotational speed), so that in time the saving of energy will compensate for the equipment's initial larger cost.

Another way of increasing the dimensions of the crystals is to prolong the retention period when the systems approach equilibrium. This parameter begins to become important after a long retention period. This would result in a much greater volume of crystallizers. However, this method is uneconomical.

The concentration of $\text{Ca}(\text{NO}_3)_2$ in the system is another factor which can influence the crystal dimensions. In the equilibrium diagrams (Jenecke-type), in each composition of the NP dissolving solution there is a precisely located point.

At the moment when the temperature of the solution begins to decrease the initial point moves (beginning with 23°C) on the straight line connecting the initial point with the co-ordinate point for $\text{Ca}(\text{NO}_3)_2$. The point changes its position on the straight line until it meets the contact point between the straight line and the equilibrium curve representing the separation between $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, HNO_3 and $\text{Ca}(\text{NO}_3)_2$ in the solution. For each final temperature there is another position of the equilibrium curve in the diagram.

A larger quantity of crystals will be separated from the system at the same temperature when the initial point is closer to the original point for $3\text{Ca}(\text{NO}_3)_2$.

The normal dilution of the solution from the digestion of phosphate rock with nitric acid should take into consideration the sub-cooling effect; crystallization begins at 23°C and the system stabilizes at 28°C . When the temperature of the NP solution decreases to below 28°C the number of crystals from the system remains theoretically constant. For this reason the supplementary quantity which is separated from the solution must be crystallized on the crystals which are already in suspension. It is insufficient just to decrease the temperature any further (below 5°C , the quantity of $\text{Ca}(\text{NO}_3)_2$ which passes into the solid form is too low). Therefore, it is important that an initial solution of the $\text{Ca}(\text{NO}_3)_2$ must be at a sufficient level so that when the crystallizers are finished, crystals of the proper dimensions are obtained.

Increasing the initial concentration of $\text{Ca}(\text{NO}_3)_2$ in the solution before crystallization will not change the final temperature of crystallization because a larger initial amount of $\text{Ca}(\text{NO}_3)_2$ means better efficiency of crystallization for the same temperature. Increasing the initial quantity of $\text{Ca}(\text{NO}_3)_2$ means in fact, the necessity of increasing the heat-transfer surface and the need for a larger capacity refrigeration unit. The expert therefore proposes to stop cooling the nitric acid for washing the crystals in the centrifuges, and to use directly HNO_3 at $30^\circ\text{-}35^\circ\text{C}$. This will dissolve more crystals and be recycled with the washing acid to the digestion unit.

To operate the centrifuges correctly, even if the crystals obtained are doubled in size, the maximum admissible distance between screen also is 0.4 mm after corrosion. The most important effect of corrosion on the screens appears as a result of the system of crystal discharge from the filtration and washing zones of the centrifuges.

The centrifugal force in the equipment keeps the crystals "sticky" on the screens. At the same time there is movement of the crystals as a result of the effect of the discharge pulsation system of the centrifuge; the solid materials (crystals and inerts) have a scraper effect on the screen.

A new system for discharge of the centrifuges is necessary; the expert proposes that a blow-air discharge system be located on the upper part of the centrifuges. The centrifuges only must work in one stage which includes filtration, washing and discharge.

The life of the centrifuges will be prolonged. Additionally, the new system of discharge is recommended because the suspension fed to the crystallizers contains a lower quantity of inert material. Under such conditions, the use of hydrocyclones instead of decanters (or both systems in series), makes it possible to reduce the quantity and size of the particles that remain in the solution. It is preferable that the maximum dimensions of the inert particles be no greater than $50\ \mu\text{m}$. It must be emphasized that hydrocyclones will not completely solve the problem because they will be strongly corroded; however, it is easier to change a bottom cone in a hydrocyclone than in a decanter.

The inert separation method still remains a problem, and the expert recommends the following:

(a) The use of a material balance process (as shown in annex I) which when compared with the material balance issued initially by the contractor, increases the amount of $\text{Ca}(\text{NO}_3)_2$ recycled by washing acid (five times higher), the increasing free HNO_3 in the dissolving solution and decreasing the final crystallization temperature to -7°C so that the molar ratio $\frac{\text{CaO}}{\text{P}_2\text{O}_5}$ in the mother liquor reaches 0.64;

(b) The use of eight crystallizers of large capacity, each having a heat-transfer surface of 200 m^2 with a low stirrer speed in order to obtain an overall heat-transfer coefficient of $85 \text{ kcal h}^{-1} \text{ m}^{-2} \text{ }^\circ\text{C}^{-1}$ ($360 \text{ kJ h}^{-1} \text{ m}^{-2} \text{ }^\circ\text{C}^{-1}$);

(c) Providing the refrigeration station with additional capacity of 4 Gcal/h (17 GJ/h) so that it has a total capacity of 10.2 Gcal/h (42.7 GJ/h);

(d) Providing two additional centrifuges with air-blowing systems for discharge purposes;

(e) A buffer tank between the crystallizers and the centrifuge should be provided; this guarantees the possibility of working with any stream of crystallizer from any of the centrifuges;

(f) Installing in the neutralization stage two new pre-neutralizers designed properly for the system. The pre-neutralizer proposed by the licensor did not have sufficient capacity for this work;

(g) For cooling the fresh nitric acid for digestion, a heat exchanger should be installed which enables the recovery of the refrigeration capacity of the mother liquor before neutralization;

(h) The diameter of the holes in the prilling basket should be doubled.

CN/CAN plant

To improve the CaCO_3 filterability, and to prevent the blocking of evaporator tubes for ammonium nitrate solution and for improving the CAN quality (removing the tendency to cake and sufficient mechanical strength for prills) the following steps are recommended:

(a) Strict control for P_2O_5 content in the CN solution;

(b) Pre-neutralization carried out at the pH value which was already established;

(c) Precipitation of CaCO_3 carried out at a pH and temperature lower than indicated by the contractor. At the same time, the excess of the CO_2 in suspension before filtration should be continuously checked;

(d) After administration of $(\text{NH}_4)_2\text{SO}_4$ in the AN solution before evaporation, it is necessary to insert a control filter system under the pumped pressure;

(e) Retention time and the temperature in the mixing vessel should be decreased;

(f) Recycle stage to the mixer should be transported pneumatically and not with an AN melt;

(g) Prills should be cooled up to 30°C before coating;

(h) The pressure for the amine pump should be increased, and it will be necessary to use the correct nozzles, properly installed in the coating drum.

V. PROJECT FINDINGS

The NP plant with its present equipment can produce only 40%-50% of the designed capacity with a final product being 60%-65% P_2O_5 water soluble and approximately 88% P_2O_5 citrate soluble.

The contractor's suggestions dated 23 July 1980 cannot guarantee either the realization of the capacity or the quality of the final product. Neither will any of the proposed alternatives.

It is important to begin experiments for the replacement of decanters with hydrocyclones.

Since a large area of the agricultural soil in Pakistan contains a high calcium content, a reasonable proportion of the water soluble P_2O_5 is likely to be converted into insoluble form after being incorporated in the soil for a short time.

The general formula for phosphate uptake by the soil can be expressed as follows:

$$Y = 50 + 0.5 X^{1/}$$

where Y is the uptake and X the percentage of P_2O_5 water solubility.

For fertilizer obtained under contract conditions

$$Y (80\%) = 50 + 0.5 \times 80 = 90\%$$

For 100 kg NP fertilizer containing 22.6% P_2O_5 and having 80% solubility in water, the quantity of P_2O_5 taken up by plants = $100 \times 0.226 \times 0.8 \times 0.9$
= 16.3 kg.

If instead of the pre-designed 90% P_2O_5 water solubility in the NP fertilizer, a fertilizer with 60% water solubility is used in the soil, we have

$$Y (60\%) = 50 + 0.5 \times 60 = 80\%$$

and the quantity of P_2O_5 taken up by plants =

$$100 \times 0.21 \times 0.8 = 16.8 \text{ kg}$$

In principle (because the soil has the capacity to recover partially some residual P_2O_5 which is in insoluble form), additional fertilizer quantities

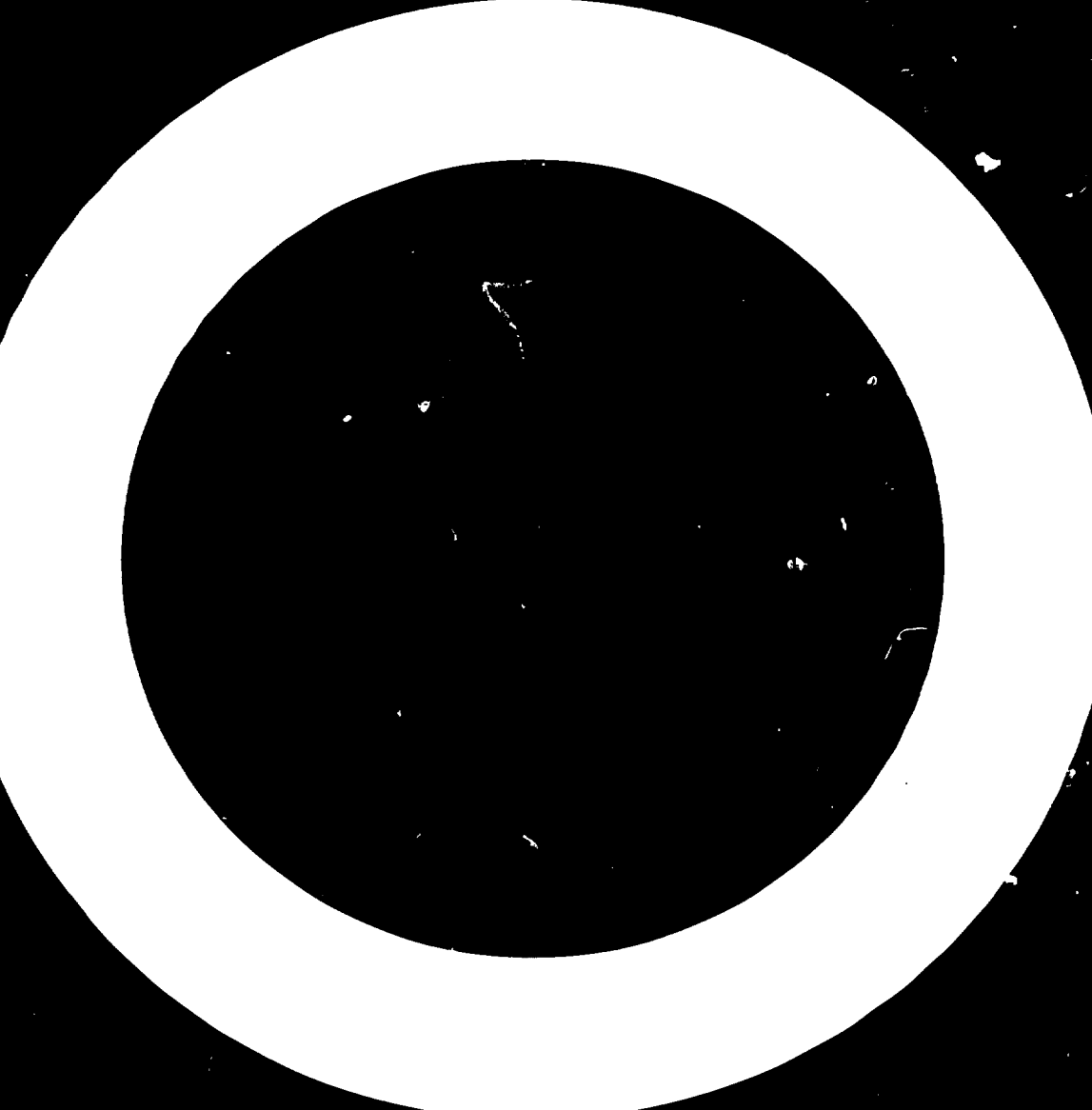
^{1/} Reference D. Koole and T. Saleem, NFC, Islamabad.

must be incorporated into the soil. This complementary quantity = $\left[\left(\frac{16.3}{10.1}\right)-1\right]$ x 100 = 61.4%. If this formula is strictly applied there is no doubt that it will be necessary to make an effort to obtain the proper quality of the NP product. It will be more economic compared with the investment cost suggested for the first alternative in chapter III. In one year the supplementary cost will be recovered.

NP outputs from Multan consist of approximately 30% of the overall present consumption of phosphate fertilizer in Pakistan. It is not feasible to avoid using the PAKARAB product with 60% P_2O_5 water solubility in areas with a high calcium content in the soil. However, the accuracy of the figures must be checked before any final decision is made.

This report reflects the technical viewpoint of the expert. Within the limited time of the mission it was not possible either to check all the figures or to check the feasibility of introducing some of the proposals. This often requires laboratory and pilot tests before making a decision for an alternative scheme. Examples can be illustrated in the suggestions to improve crystallizer and centrifuge performance, and to increase their refrigeration and neutralization capacities. The key to the operational problem lies with the dimensions of the crystals.

Before any proposals are implemented, it would be necessary to add 10% to the capacities as a safety factor, despite the 300 days per year presently worked.



MATERIAL BALANCE TABLES - NP PLANT

Amounts in kg/h

| PROCESS STREAM | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------------------------------------------|-------------------------------------------|---------------------------------------------|--------------------------------------|------------------------|--------------------------------------------|---|---------------------------|
| DESCRIPTION | Rock phosph to dissolving vessel | HNO ₃ to dissolving vessel | HNO ₃ to centrifuge | Wash acid return | Dissolving solution to filter pot | | Solid from decanter |
| COMPONENTS | | | | | | | |
| HNO ₃ | | 28166,6 | 12340 | 10800,8 | 4533,7 | | 14,1 |
| H ₃ PO ₄ | | | | 5484,2 | 19103,7 | | 59,5 |
| H ₂ O | 415,3 | 18777,7 | 8226,7 | 14977,0 | 34808,1 | | 108,4 |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | 21541 | | | | | | |
| CaHPO ₄ | | | | | | | |
| NH ₄ H ₂ PO ₄ | | | | | | | |
| FePO ₄ | | | | | | | |
| AlPO ₄ | | | | | | | |
| Ca(NO ₃) ₂ | | | | 13588,5 | 56631,0 | | 176,4 |
| Ca(NO ₃) ₂ ·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | | | | | |
| Fe(NO ₃) ₃ | | | | 89,4 | 311,2 | | 0,6 |
| Al(NO ₃) ₃ | | | | 112,8 | 392,9 | | 1,1 |
| CaF ₂ | 2244,0 | | | 63,0 | 219,6 | | 0,7 |
| CaSiF ₆ | | | | 98,2 | 341,8 | | 0,8 |
| CaCO ₃ | 2965,3 | | | | | | |
| CaSiO ₃ | 325,0 | | | | 169,7 | | 169,7 |
| R ₂ O ₃ - Fe ₂ O ₃ | 73,3 | | | | | | |
| Al ₂ O ₃ | 67,1 | | | | | | |
| Mg(NO ₃) ₂ | | | | 134 | 466,7 | | 1,2 |
| H ₂ SiF ₆ | | | | 212,1 | 738,8 | | 2,1 |
| NO _x as NO ₂ | | | | 4 | 14 | | |
| Inert + SiO ₂ | 1672,6 | | | 29,1 | 1261,3 | | 1159,8 |
| Coating agent | | | | | | | |
| Oil - amine | | | | | | | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Na ₂ SiF ₆ | | | | 152,3 | 855,5 | | 306,5 |
| CaSO ₄ | 702,3 | | | 982,3 | 1413,9 | | 86,4 |
| MgCO ₃ | 189,3 | | | | | | |
| Na ₂ SO ₄ | 343,8 | | | | | | |
| TOTAL | 30539 | 46944,3 | 20566,7 | 46127,7 | 121241,9 | | 2087,3 |
| | 23,5 | 35 | 15,3 | 34,2 | 78,2 | | |
| Temperature °C | amb | | ~35 | ~10 | ~65 | | ~65 |
| Pressure Kg/cm ² a | | | | | | | |
| Density Kg/m ³ | 1200 | 1340 | ~1340 | 1350 | 1550 | | |
| pH | | | | | | | |
| % (w) P ₂ O ₅ | 32,31 | | | 8,61 | | | |
| % (w) CaO | 50,4 | | | 10,56 | | | |
| % (w) N-NO ₃ | | | | 10,37 | | | |
| % (w) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | ~1,6 | | | molar 3,1 | | | |
| N / P ₂ O ₅ | | | | molar 6,1 | | | |

Amounts in kg/h

| PROCESS STEAM | 9 | 10 | 11 | 11A | 12 | 14 | 15 |
|---------------------------------------------------------------|------------------------------------|---------------------------------|---------------------------------|----------------------------------|-----------------------------|-------------------------|------------------------------------|
| DESCRIPTION | Dissolving solution to buffer tank | Dirty cooling water to scrubber | Dirty cooling water to scrubber | Gases from digestion to scrubber | Dissolving solution to pump | Cooling water to cooler | Dissolving solution to head vessel |
| COMPONENTS | | | | | | | |
| HNO ₃ | 4519,6 | | | 58,3 | | | 4519,6 |
| H ₃ PO ₄ | 19044,2 | | | | | | 19044,2 |
| H ₂ O | 34699,7 | | | 433 | | | 34699,7 |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | | | | | | | |
| CaHPO ₄ | | | | | | | |
| NH ₄ H ₂ PO ₄ | | | | | | | |
| FePO ₄ | | | | | | | |
| AlPO ₄ | | | | | | | |
| Ca(NO ₃) ₂ | 56454,6 | | | | | | 56454,6 |
| Ca(NO ₃)·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | | | | | |
| Fe(NO ₃) ₃ | 310,6 | | | | | | 310,6 |
| Al(NO ₃) ₃ | 391,8 | | | | | | 391,8 |
| CaF ₂ | 218,9 | | | | | | 218,9 |
| CaSiF ₆ | 341,0 | | | | | | 341,0 |
| CaCO ₃ | | | | | | | |
| Mn(NO ₃) ₂ | 465,5 | | | | | | 465,5 |
| R ₂ O ₃ -Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | 44,8 | | | |
| H ₂ SiF ₆ | 736,7 | | | | | | 736,7 |
| NO _x as NO ₂ | 14 | | | 430,8 | | | 14 |
| Inert + SiO ₂ | 101,5 | | | | | | 101,5 |
| Coating agent | | | | | | | |
| Oil-amine | | | | | | | |
| Cooling water | | 60.000 | 60.000 | | | ~368.000 | |
| Brine | | | | | | | |
| Na ₂ SiF ₆ | 529 | | | | | | 529 |
| CaSO ₄ | 1327,5 | | | | | | 1327,5 |
| CO ₂ | | | | 1403,4 | | | |
| TOTAL | 119154,6 | 60.000 | 60.000 | 2368,3 | 119154,6 | ~368.000 | 119154,6 |
| Temperature °C | 76,8 | 60 | 60 | 65 | 76,8 | 368 | 76,8 |
| Pressure kg/cm ² a | 65 | 34 | 36 | 65 | 65 | 34 | 65 |
| Density kg/m ³ a | 1550 | 1000 | 1.000 | | 15,50 | 1000 | 1550 |
| pH | | | | | | | |
| % (W) P ₂ O ₅ | 11,6 | | | | | | |
| % (W) CaO ₃ | 16,8 | | | | | | |
| % (W) N-NO ₃ | 9,1 | | | | | | |
| % (W) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | mol cr 3,67 | | | | | | |
| N/P ₂ O ₅ | mol cr 3,99 minimum | | | | | | |

Amounts-in kg/h

| PROCESS STREAM | 17 | 18 | | 20 | 5 | 21 | 22 |
|---------------------------------------------------------------|--------------------------------------|---------------------------------|--------------------------------|--------------------------------|------------------------|-------------------------|--------------------------|
| DESCRIPTION | Dissolving solution from head vessel | Mother liquid from recycle pump | Slurry crystals to centrifuges | HNO ₃ to centrifuge | Wash acid to digestion | ML to intermediate tank | Crystals to CN melt tank |
| COMPONENTS | | | | | | | |
| HNO ₃ | 4519,6 | 6780 | 5197,6 | 12360 | 10.800,8 | 3855,3 | 2881,5 |
| H ₃ PO ₄ | 19044,2 | 2848,1 | 21889,3 | | 5484,2 | 16.194,7 | 2134 |
| H ₂ O | 34699,7 | 1396,0 | 12627,8 | 8226,7 | 14977,0 | 7.937,8 | 2036,5 |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | | | | | | | |
| CaHPO ₄ | | | | | | | |
| NH ₄ H ₂ PO ₄ | | | | | | | |
| FePO ₄ | | | | | | | |
| AlPO ₄ | | | | | | | |
| Ca(NO ₃) ₂ | 56454,6 | 1640 | 3640 | | 13.588,5 | 3640 | 41,3 |
| Ca(NO ₃) ₂ ·4H ₂ O | | 824,3 | 77746,7 | | | 4886 | 53437 |
| NH ₄ NO ₃ | | | | | | | |
| Fe(NO ₃) ₃ | 310,6 | 46,4 | 357 | | 89,4 | 264,1 | 3,5 |
| Al(NO ₃) ₃ | 391,8 | 58,4 | 450,2 | | 112,8 | 333,0 | 4,4 |
| CaF ₂ | 218,9 | 32,7 | 251,6 | | 63 | 186,2 | 2,4 |
| CaSiF ₆ | 341,0 | 57 | 392 | | 98,2 | 290 | 3,8 |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ -Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| Mg(NO ₃) ₂ | 463,5 | 69,6 | 535,1 | | 134 | 395,9 | 5,2 |
| H ₂ SiF ₆ | 736,7 | 110,1 | 846,8 | | 212,1 | 626,4 | 8,3 |
| NO _x as NO ₂ | 14 | 2,1 | 16,1 | | 4 | 12,1 | |
| Inert+SiO ₂ | 101,5 | 15,1 | 116,6 | | 29,1 | 86,1 | 1,1 |
| Coating agent | | | | | | | |
| Oil-amine | | | | | | | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Air | | | | | | | |
| Na ₂ SiF ₆ | 529 | 79,1 | 608,1 | | 152,3 | 449,4 | 5,9 |
| CaSO ₄ | 1327,5 | 198,1 | 1525,6 | | 382,3 | 1128,4 | 14,9 |
| TOTAL | 119.134,6 | 7050 | 126.204,6 | 20.566,7 | 46.127,7 | 47.087,5 | 58.659,2 |
| | 76,8 | 4,7 | | 15,3 | 34,2 | 26,7 | 31,9 |
| Temperature °C | 65 | -7 | -7 | ~35 | ~10 | -9 | -7 |
| Pressure kg/cm ² a | | | | | | | |
| Density, kg/m ³ | 1550 | 1500 | 1550 | ~1340 | ~1550 | 1500 | 1840 |
| pH | | | | | | | |
| % (W) P ₂ O ₅ | | | | | | | 0,28 |
| % (W) CaO | | | | | | | |
| % (W) N-NO ₃ | | | | | | | |
| % (W) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | | | | | | |
| N/P ₂ O ₅ | | | | | | | |

Amounts in kg/h

| PROCESS STREAM | 23 | 26 | 27 | 28 | 31 | 32 | 33 |
|---------------------------------------------------------------|---------------------------------|--------------------------------------|---------------------------|-----------------------------------|------------------------------|--------------------------------------------|---------------------------------------------|
| DESCRIPTION | Wash liquid to wash liquid tank | Mother liquid from intermediate tank | AN solution from CN-plant | Process condensate from CAN-plant | Mother liquid to neutralizer | NH ₃ liquid for NP/CN CAN-plant | NH ₃ gas from refrigeration unit |
| COMPONENTS | | | | | | | |
| HNO ₃ | | 3177,3 | | | 3177,3 | | |
| H ₃ PO ₄ | | 13346,6 | | | 13346,6 | | |
| H ₂ O | | 7720,5 | 7502 | 3314,3 | 7720,5 | 87,3 | |
| NH ₃ | | | | | | 17435,7 | 17435,7 |
| Ca ₃ (PO ₄) ₂ | | | | | | | |
| CaHPO ₄ | | | | | | | |
| NH ₄ H ₂ PO ₄ | | | | | | | |
| FePO ₄ | | | | | | | |
| AlPO ₄ | | | | | | | |
| Ca(NO ₃) ₂ | | 5683,6 | | | 5683,6 | | |
| Ca(NO ₃)·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | 12773,7 | | | | |
| Fe(NO ₃) ₃ | | 217,7 | | | 217,7 | | |
| Al(NO ₃) ₃ | | 274,6 | | | 274,6 | | |
| CaF ₂ | | 153,5 | | | 153,5 | | |
| CaSiF ₆ | | 239 | | | 239 | | |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ -Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| Mg(NO ₃) ₂ | | 326,3 | | | 326,3 | | |
| H ₂ SiF ₆ | | 516,3 | | | 516,3 | | |
| NO _x as NO ₂ | | 10 | | | 10 | | |
| Inert + SiO ₂ | | 71 | | | 71 | | |
| Coating agent | | | | | | | |
| Oil-amine | | | | | | | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Air | | | | | | | |
| Na ₂ SiF ₆ | | 370,8 | | | 370,8 | | |
| CaSO ₄ | | 930,3 | | | 930,3 | | |
| TOTAL | 46127,7 | 33037,5 | 20275,7 | 3314,3 | 33037,5 | 17523 | 17435,7 |
| Temperature °C | | 22,1 | | | 22,1 | | |
| Pressure kg/cm ² a | | -7 | | | ~+6 | | |
| Density kg/m ³ | | 1500 | | | 1500 | | |
| pH | | | | | | | |
| % (W) P ₂ O ₅ | | 29,3 | | | | | |
| % (W) CaO | | 7,6 | | | | | |
| % (W) N-NO ₃ | | 5,54 | | | | | |
| % (W) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | molar ~ 0,64 | | | | | |
| N P ₂ O ₅ | | molar ~ 0,46 | | | | | |

Amounts in Kg/h

| PROCESS STREAM | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
|----------------------------------------------------------------|------------------------------------|-------------------------------------|----------------------------|-----------------------------|-------------------------------|----------------------|-----------------|
| DESCRIPTION | NH ₃ gas to neutralizer | NH ₃ gas to CN/CAN plant | brine to cold brine vessel | brine to refrigeration unit | brine from refrigeration unit | brine to cristalizer | brine to cooler |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | | | | | | | |
| NH ₃ | 4165,7 | 13270 | | | | | |
| Ca ₃ (PO ₄) ₂ | | | | | | | |
| CaHPO ₄ | | | | | | | |
| NH ₄ H ₂ PO ₄ | | | | | | | |
| FePO ₄ | | | | | | | |
| AlPO ₄ | | | | | | | |
| Ca(NO ₃) ₂ | | | | | | | |
| Ca(NO ₃) ₂ ·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | | | | | |
| Fe(NO ₃) ₃ | | | | | | | |
| Al(NO ₃) ₃ | | | | | | | |
| CaF ₂ | | | | | | | |
| CaSiF ₆ | | | | | | | |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ - Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | | | | |
| H ₂ SiF ₆ | | | | | | | |
| NO _x as NO ₂ | | | | | | | |
| Inert + SiO ₂ | | | | | | | |
| Coating agent | | | | | | | |
| Oil - Amine | | | | | | | |
| Choling water | | | | | | | |
| brine | | | | | | | |
| air | | | | | | | |
| steam | | | | | | | |
| TOTAL | 4165,7 | 13270 | | | | | - |
| m ³ /h | | | 3395 | 3395 | 3395 | 3160 | - |
| Temperature °C | | | ~ -8,2 | -8,3 | -12 | -12 | |
| Pressure kg/cm ² a | | | | | | | |
| Density kg/m ³ | | | | | | | |
| pH | | | | | | | |
| %(w) P ₂ O ₅ | | | | | | | |
| %(w) CaO | | | | | | | |
| %(w) N-NO ₃ | | | | | | | |
| %(w) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | | | | | | |
| N/P ₂ O ₅ | | | | | | | |

Amounts-in kg/h

| PROCESS STREAM | 41 | 42 | 43 | 44 | 45 | 46 | 47 |
|----------------------------------------------------------------|-------------------|---------------------------|-----------------------|-------------------------------|---------------------------|------------------------|--------------------------|
| DESCRIPTION | brine from cooler | brine to hot brine vessel | brine from brine pump | SL- Steam to hot brine vessel | NP solut from neutralizer | Vapor from neutralizer | NP Solution to separator |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | | | | | 14069,1 | 4370,4 | 14069,1 |
| NH ₃ | | | | | | 10 | |
| Ca ₃ (P O ₄) ₂ | | | | | 631,9 | 1,2 | 631,9 |
| Ca HPO ₄ | | | | | 2546,8 | 5,1 | 2546,8 |
| NH ₄ H ₂ PO ₄ | | | | | 12261,3 | 24,5 | 12261,3 |
| Fe P O ₄ | | | | | 135,5 | 0,3 | 135,5 |
| Al P O ₄ | | | | | 157 | 0,3 | 157 |
| Ca (NO ₃) ₂ | | | | | | | |
| Ca (NO ₃) ₂ · 4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | | | 23230,8 | 141 | 23230,8 |
| Fe (NO ₃) ₃ | | | | | | | |
| Al (NO ₃) ₃ | | | | | | | |
| CaF ₂ | | | | | 940,7 | 1,8 | 940,7 |
| Ca Si F ₆ | | | | | | | |
| Ca CO ₃ | | | | | | | |
| Ca Si O ₃ | | | | | | | |
| R ₂ O ₃ - Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| Si F ₄ + HF | | | | | | 5 | |
| (NH ₄) ₂ Si F ₆ | | | | | 94,1 | 0,2 | 94,1 |
| NO _x as NO ₂ | | | | | | 10 | |
| Inert + Si O ₂ | | | | | 272,8 | 0,5 | 272,8 |
| Coating agent | | | | | | | |
| Oil-A mine | | | | | | | |
| Cooling water | | | | | | | |
| brine | | | | | | | |
| (NH ₄) ₂ HPO ₄ | | | | | 279,2 | 0,5 | 279,2 |
| Na ₂ Si F ₆ | | | | | 370,1 | 0,1 | 370,1 |
| Ca SO ₄ | | | | | 928,5 | 1,8 | 928,5 |
| NH ₄ Mg P O ₄ | | | | | 301,5 | 0,6 | 301,5 |
| TOTAL | — | UHDE balance → | | | 56219,3 | 4573,9 | 56219,3 |
| Temperature °C | — | | | | | | |
| Pressure kg/cm ² a | | | | | | | |
| Density kg/m ³ | | | | | | | |
| pH | | | | | | | |
| % (w) P ₂ O ₅ | | | | | | | |
| % (w) CaO | | | | | | | |
| % (w) N-NO ₃ | | | | | | | |
| % (w) N-NH ₃ | | | | | | | |
| Ratio Ca O/P ₂ O ₅ | | | | | | | |
| N / P ₂ O ₅ | | | | | | | |

Amounts-in kg/h

| PROCESS STREAM | 48 | 49 | 50 | 51 | 52 | 53 | 54 |
|----------------------------------------------------------------|----------------------|---------------------|-----------------------------------------|----------------------------------------------|-----------------------------------------|----------------------------------------------|-----------------------------|
| DESCRIPTION | Vapor from separator | dirty cooling water | dirty cooling water to direct condenser | dirty cooling water to condenser seal vessel | dirty cooling water to mixing condenser | dirty cooling water to condenser seal vessel | NR. Solution from separator |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | | | | | | | 213 |
| NH ₃ | 13836,9 | | | | | | |
| Ca ₃ (PO ₄) ₂ | 1,2 | | | | | | 630,7 |
| CaHPO ₄ | 5,1 | | | | | | 2541,7 |
| NH ₄ H ₂ PO ₄ | 24,9 | | | | | | 12479,7 |
| FePO ₄ | 0,3 | | | | | | 135,2 |
| AlPO ₄ | 0,3 | | | | | | 156,7 |
| Ca(NO ₃) ₂ | | | | | | | |
| Ca(NO ₃)·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | 141,0 | | | | | | 23089,8 |
| Fe(NO ₃) ₃ | | | | | | | |
| Al(NO ₃) ₃ | | | | | | | |
| CaF ₂ | 1,8 | | | | | | 938,9 |
| CaSiF ₆ | | | | | | | |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ - Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | | | | |
| H ₂ SiF ₆ | | | | | | | |
| NO _x as NO ₂ | | | | | | | |
| Inert + SiO ₂ | 0,6 | | | | | | 304 |
| Coating agent | | | | | | | |
| Oil - Amine | | | | | | | |
| Cooling water | | 1266 000 | 206 000 | | 1060 000 | | |
| brine | | | | | | | |
| NH ₄ F | 117,4 | | | | | | |
| Na ₂ SiF ₆ | 0,7 | | | | | | 369,4 |
| CaSO ₄ | 1,8 | | | | | | 926,7 |
| NH ₄ MgPO ₄ | 0,6 | | | | | | 300,9 |
| TOTAL kg/h | 14132,6 | 1266 000 | 206 000 | 210 300 | 1060 000 | 1074 200 | 42086,7 |
| m ³ /h | | 1266 | 206 | 210,3 | 1060 | 1074,2 | 26,3 |
| Temperature °C | 175 | 34 | 34 | ~46 | 34 | ~43 | 175 |
| Pressure kg/cm ² a | 0,3 | | | | | | 0,3 |
| Density, kg/m ³ | 0,143 | 1000 | 1000 | 1000 | 1000 | 1000 | 1600 |
| pH | | | | | | | |
| %(w) P ₂ O ₅ | | | | | | | |
| %(w) SiO ₂ | | | | | | | |
| %(w) N-NO ₃ | | | | | | | |
| %(w) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | | | | | | |
| N/P ₂ O ₅ | | | | | | | |

Amounts in kg/h

| PROCESS STREAM | 56 | 57 | 58 | 59 | 60 | 61 | 62 |
|----------------------------------------------------------------|--------------------------------|----------------------------------------------|------------------------------|----------------------------|------------------------------------|-----------------------------|----------------------------------|
| DESCRIPTION | SM-steam to NP melt tank | NP-dust from dedusting installation | NP-melt to prill tower | CN-melt to CAN plant | LP-steam to CN melt plant | SM-steam to melt tank | NP-melt to prilling bucket |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | 628 | 12,7 | 225,7 | | 3283 | 150 | 225,7 |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | | 37,6 | 668,3 | | | | 668,3 |
| CaHPO ₄ | | 151,4 | 2693,1 | | | | 2693,1 |
| NH ₄ H ₂ PO ₄ | | 743,7 | 13223,4 | | | | 13223,4 |
| FePO ₄ | | 8 | 143,2 | | | | 143,2 |
| AlPO ₄ | | 9,3 | 166,0 | | | | 166,0 |
| Ca(NO ₃) ₂ | | | | | | | |
| Ca(NO ₃)·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | 1375,2 | 24465,0 | | | | 24465,0 |
| Fe(NO ₃) ₃ | | | | | | | |
| Al(NO ₃) ₃ | | | | | | | |
| CaF ₂ | | 55,9 | 994,8 | | | | 994,8 |
| CaSiF ₆ | | | | | | | |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ - Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | | | | |
| H ₂ SiF ₆ | | | | | | | |
| NO _x as NO ₂ | | | | | | | |
| Inert + SiO ₂ | | 18,1 | 322,4 | | | | 322,1 |
| Coating agent | | | | | | | |
| Oil amine | | | | | | | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Air | | | | | | | |
| Na ₂ SiF ₆ | | 22,0 | 391,4 | | | | 391,4 |
| CaSO ₄ | | 55,2 | 981,9 | | | | 981,9 |
| NH ₄ MgPO ₄ | | 17,9 | 318,8 | | | | 318,8 |
| TOTAL | 628 | 2507 | 44594,1 | 58658,2 | 3283 | 150 | 44594,1 |
| | 84,3 | 2,5 | 28 | 36,6 | 1055 | 30 | 28 |
| Temperature °C | 197 | 45 | 175 | | 158 | 179 | 175 |
| Pressure kg/cm ² a | 15 | | | | 6 | 10 | |
| Density, kg/m ³ | 7,45 | 1000 | 1600 | 1600 | 3,1 | 5,04 | 1600 |
| pH | | | | | | | |
| % (w) P ₂ O ₅ | | | | | | | |
| % (w) CaO | | | | | | | |
| % (w) N-NO ₃ | | | | | | | |
| % (w) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | | | | | | |
| N/P ₂ O ₅ | | | | | | | |

Amounts—in Kg/h

| PROCESS STREAM | 63 | 64 | 55 | 66 | 67 | 68 | 69 |
|----------------------------------------------------------------|----------------------------|------------------------------|-------------------------------|---------------------------------------|-----------------------------|----------------------------|--------------------------------------|
| DESCRIPTION | Air from prill tower | NP product from lump catcher | NP product to bucket elevator | Crushed NP product to bucket elevator | NP product to double screen | NP product to mixing screw | Under sized NP product double screen |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | | | | | | 211,7 | |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | | | | | | 626,6 | |
| CaHPO ₄ | | | | | | 2525,1 | |
| NH ₄ H ₂ PO ₄ | | | | | | 12398,5 | |
| FePO ₄ | | | | | | 134,3 | |
| AlPO ₄ | | | | | | 155,7 | |
| Ca(NO ₃) ₂ | | | | | | | |
| Ca(NO ₃) ₂ ·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | | | | 22938,7 | |
| Fe(NO ₃) ₃ | | | | | | | |
| Al(NO ₃) ₃ | | | | | | | |
| CaF ₂ | | | | | | 932,8 | |
| CaSiF ₆ | | | | | | | |
| CaCO ₃ | | | | | | | |
| CaSiO ₃ | | | | | | | |
| R ₂ O ₃ - Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | | | | |
| H ₂ SiF ₆ | | | | | | | |
| NO _x as NO ₂ | | | | | | | |
| Inert: SiO ₂ | | | | | | 302,0 | |
| Coating agent | | | | | | | |
| Oil - amine | | | | | | | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Air | 6x125000Nm ³ /h | | | | | | |
| Na ₂ SiF ₆ | | | | | | 387,0 | |
| CaSO ₄ | | | | | | 920,7 | |
| NH ₄ MgPO ₄ | | | | | | 208,9 | |
| TOTAL | 750000Nm ³ /h | 44483 | 43583 | 2090 | 16550 | 41842 | 1648 |
| | | 44,5 | 43,6 | 209 | 45,5 | 41,8 | 1,65 |
| Temperature °C | | 95 | 45 | 45 | 45 | 45 | 45 |
| Pressure kg/cm ² a | | | | | | | |
| Density kg/m ³ | | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| pH | | | | | | | |
| % (w) P ₂ O ₅ | | | | | | | |
| % (w) CaO | | | | | | | |
| % (w) N-NO ₂ | | | | | | | |
| % (w) N-NH ₃ | | | | | | | |
| Ratio CaO/P ₂ O ₅ | | | | | | | |
| N/P ₂ O ₅ | | | | | | | |

Amounts - in kg/h

| PROCESS STREAM | 70 | 71 | 72 | 74 | 75 | 76 | 77 |
|---------------------------------------------------------------|------------------------|--------------------|------------------------------|-------------------------------|--------------------------|----------------------------|--------------------------------|
| DESCRIPTION | Dust from dust cyclone | Dust from cyclones | Dust and fines to seal screw | Coating agent to mixing screw | Final product to storage | Oil amine solution to drum | LP steam to oil amine mix tank |
| COMPONENTS | | | | | | | |
| HNO ₃ | | | | | | | |
| H ₃ PO ₄ | | | | | | | |
| H ₂ O | | | 12,7 | | 211,6 | | 10 |
| NH ₃ | | | | | | | |
| Ca ₃ (PO ₄) ₂ | | | 37,6 | | 626,3 | | |
| CaHPO ₄ | | | 151,4 | | 2523,9 | | |
| NH ₄ H ₂ PO ₄ | | | 743,7 | | 12392,5 | | |
| FePO ₄ | | | 8,0 | | 134,2 | | |
| AlPO ₄ | | | 9,3 | | 155,6 | | |
| Ca(NO ₃) ₂ | | | | | | | |
| Ca(NO ₃)·4H ₂ O | | | | | | | |
| NH ₄ NO ₃ | | | 1375,2 | | 22927,6 | | |
| Fe(NO ₃) ₃ | | | | | | | |
| Al(NO ₃) ₃ | | | | | | | |
| CaF ₂ | | | 55,9 | | 932,4 | | |
| CaSiF ₆ | | | | | | | |
| CaCO ₃ | | | | | | | |
| Ca·SiO ₃ | | | | | | | |
| R ₂ O ₃ -Fe ₂ O ₃ | | | | | | | |
| Al ₂ O ₃ | | | | | | | |
| SiF ₄ | | | | | | | |
| H ₂ SiF ₆ | | | | | | | |
| NO _x as NO ₂ | | | | | | | |
| Inert + SiO ₂ | | | 18,1 | | 301,9 | | |
| Coating agent | | | | 436 | 423 | | |
| Oil-amine | | | | | 84 | 84 | |
| Cooling water | | | | | | | |
| Brine | | | | | | | |
| Air | | | | | | | |
| Na ₂ SiF ₆ | | | 22,0 | | 366,9 | | |
| CaSO ₄ | | | 55,2 | | 920,3 | | |
| NH ₄ MgPO ₄ | | | 17,9 | | 298,8 | | |
| TOTAL | 78 | 781 | 2507 | 436 | 42299 | 84 | 10 |
| | 0,078 | 0,781 | 2,5 | | 42,3 | 0,084 | 3,2 |
| Temperatura °C | 70 | 50 | 45 | amb | 45 | 65 | 158 |
| Pressure kg/cm ² a | | | | | | | 6 |
| Density kg/m ³ | 1000 | 1000 | 1000 | | 1000 | 900 | 3,11 |
| pH | | | | | 3,2 | | |
| % (w) P ₂ O ₅ | | | | | 22,61 | | |
| % (w) CaO | | | | | 5,73 | | |
| % (w) N=NO ₃ | | | | | 9,48 | | |
| % (w) N=NH ₃ | | | | | 13,12 | | |
| Ratio CaO / P ₂ O ₅ | | | | | 0,54 | | |
| molar N / P ₂ O ₅ | | | | | 10,14 | | |

Annex II

LIST OF THE PEOPLE WITH WHOM THE EXPERT HELD DISCUSSIONS

Ministry of Production, Government of Pakistan

A. Majid Mufti, Secretary
S. Habeeb Hussain, Additional Secretary

National Fertilizer Corporation of Pakistan

Riaz H. Bokhari, Chairman
Zahid Aziz, General Manager (Technical)
Abdul Manan, Manager (Project)

PAKARAB Fertilizers Company Ltd., Multan

Zahur Ahmad Khan, Managing Director
Mohel Shafi, General Manager (Manufacturing)
M. Nasir Butt, General Manager, Technical and Planning
Abdul Ghafoor, Production Manager
Mahmood Akhgar, Assistant Production Manager
M.S. Chjghtai, Unit Manager, NP plant
Manzoor Ahmad, Assistant Unit Manager, NP plant
M.M. Saeed Bjutta, Unit Manager, CN/CAN plant
S. Mansoor Alvi, Assistant Unit Manager, CN/CAN plant
Zaheer Pervez, Senior Process Engineer, CN/CAN plant
Altaf Jafri, Processing Engineer, NP unit
Abid Hussain, Processing Engineer, NP unit
M.A. Baig, Chief of Laboratory
Waqar Ahmad, Senior Manager
S.A. Mehdi, Chief Accountant

Stamicarbon Company, Holland

J.A. von der Kuyl
L. Weber

National Fertilizer Development Centre

D. Koole, Project Manager
T. Saleem, Deputy Chief

United Nations Development Programme

M.J. Priestley, Resident Representative
M.K. Hussein, SIDFA



