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NEW EXPERIENCES WITH THE KAMPKA NITRO

PROCESS

By

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For nearly 4 decades the Odda process, developed by Erling B. Johnson, Norway, has been the basis of fertiliser production techniques which allow the production of NP or NPK fertilisers in conjunction with straight nitrogen fertilisers, without the use of additional phosphoric acid and, hence, sulphuric acid. As the nitric phosphate processes involve the adjustment of the CaO/P_2O_5 ratio by the addition of phosphoric acid, they are related to the price of sulphur. The Odda process and its variations will become popular again in periods of sulphur shortage.

A basic diagram of the Odda process is given in Figure 1. A few years ago, the use of the Odda process was limited by the P_2O_5 water solubility obtainable in the fertiliser, i.e. the degree of the calcium-nitrate tetrahydrate (KS) separation. Recently, a series of process modifications has been developed which make it possible to produce fertilisers with a higher content of water soluble P_2O_5 without the addition of phosphoric acid. These are processes which achieve a higher degree of KS separation by deep freezing the slurry, the processes of Norsk Hydro or of Severoceske Chemicke Zavody (SCHZ), Lovisice CSSR, for example, and processes which also operate without additional phosphoric acid but precipitate the remaining calcium up to the required water solubility by means of a sulphate cycle or in some other way. Depending on the formulation required, the bound CaO is removed from the process or remains as ballast in the slurry after a more or less high degree of KS separation.

A diagram of a sulphate recycle process is shown in Figure 2. The range of formulations, based on potassium chloride, varies from 20-20-0 to 23-23-0 with the 1 - 1 - 0 type and with the 1 - 1 - 1 grades, from 15-15-15 with 27 per cent water soluble P_2O_5 to 17-17-17 with more than 85 per cent water soluble P_2O_5. The working up of the mother liquor yielded is not a typical characteristic of the Odda process. Normal granulation methods are used. Whereas the traditional form of the Odda process necessarily yields a straight nitrogen

fertiliser, it is profitable for many industries to operate the acidulation stoichiometrically; the ammonium nitrate (AN) is thereby recycled into the fertiliser slurry. Depending on the fertiliser formulation, however, this also inevitably leads to a more or less high yield of straight nitrogen fertiliser. At first glance, plants based on the Odda process and its modifications seem to be more expensive in investment costs, compared with a normal nitrophosphate plant based on the phosphoric acid/nitric acid process, as they need at least an additional crystallization unit and perhaps a nitrogen fertiliser plant also. On the other hand, however, the cost of additional phosphoric acid or of plants for the production of phosphoric acid and sulphuric acid is not incurred.

KAMPKA NITRO PROCESS

The Kampka Nitro process, described in some detail in this paper, is a modification of the Odda process and has been in operation for about ten years. It is a significant development of the Odda process in this respect: there is a minimum yield of straight nitrogen fertiliser, i.e. minimum input of nitric acid. The general diagram of this process is shown in Figure 3. There are three obvious stages of the process:

(a) minimum HNO_3 input (stoichiometry)

(b) AN recycle and

(c) additional acidulation.

If no straight nitrogen fertiliser is produced, these three stages do not ensure that the process is completely without additional phosphoric acid. It will seem obvious that phosphate rock with the lowest possible CaO/P_2O_5 mole ratio for the acidulation and a soft phosphate rock quality for the additional acidulation should be used. Test results are available for all current phosphate rock qualities; for the highest requirement in respect of the $CaCO_3$ yielded, Kola phosphate (85 BPL) is preferred. The acidulation takes place with a slight excess of nitric acid, compared with stoichiometry (6.9 - 7 mol H/P_2O_5). This excess of nitric acid is necessary to avoid the crystallisation of monocalcium phosphate in the crystallisation stage which would have a devastating influence on the quality of the centrifuged salt. On the other hand, the crystallisation of KS takes place at higher temperatures. A corresponding group of curves is shown in Figure 4.

The concentration of the acid should be between 55 and
60 per cent when the degree of acidulation achieved
amounts to 99 per cent, using a specific acidulation
volume of 5.2 m^3/t.h. P_2O_5. By means of special
installations in the vessels, any phosphate rock can be
acidulated without serious disturbance by foam. The
only condition is that the phosphate rock should have
a fineness of 0.25 mm or less. The acidulation can
reasonably take place at temperatures lower than $55^{\circ}C$
in order to eliminate, as far as possible, interference
by waste gas. Nevertheless, an intensive scrubbing is
subsequently carried out. Following acidulation,
insoluble solids are separated from the slurry in a
decanting station. In this way, the conditions of
crystallisation are improved and the corrosive effects
and clogging in the centrifuges are avoided. At the
same time, the removal of the insoluble solids from
the acidulation slurry makes it possible to increase
the concentration in the fertilisers as this inert
material is ballast. For KS-crystallisation two
completely continuous processes are available:

(a) a traditional crystallisation in vessels equipped
with cooling coils, operating fully controlled
and allowing the cleaning of the coils without
interrupting the flow of slurry.

(b) a crystallisation system, developed by Chemoprojekt/
SCHZ, working by direct cooling without cooling
surfaces in the slurry. The cooling effect takes
place by mixing the slurry with undercooled media
which are not soluble in the acidulation solution.
This process has several advantages compared with
other traditional procedures.

In a subsequent stage of the process the crystallised
calcium nitrate is centrifuged, washed with cold nitric
acid, (recycled to acidulation) and is then available for
further processing.

A typical granulometry of the calcium nitrate after
centrifuging is given in Table 1.

TABLE 1

Granulometry of $Ca(NO_3)_2 4H_2O$

Crystal size, mm	% Proportion of Total	Cumulative %
>2.5	1.4	100.0%
2.5 - 2.0	3.1	98.6%
2.0 - 1.5	5.6	95.5%
1.5 - 1.0	20.0	89.9%
1.0 - 0.5	49.2	69.9%
<0.5	20.7	20.7%

Depending on the requirements of the products made from
this calcium nitrate, purification may be necessary
before subsequent processing. The object of the purif-
ication stage in the process is to separate insolubles
collected at the centrifuges as well as associated
impurities. This takes place in a fully automatic con-
trolled precipitation stage. The impurities, especially
fluorine and P_2O_5, are precipitated in accordance
with the exact reaction conditions. The precipitate is
easily filterable. The purification of the calcium
nitrate is a necessary condition for obtaining a pure,
white $CaCO3$. Economic considerations and the proposed
use of the carbonates are the deciding factors. In this
way, nitrate solutions which are completely free of P_2O_5
are yielded.

At the same time the content of insolubles is zero. The
fluorine content, expressed as the F-factor $\frac{F}{CaO}$, decreases
from 2.4×10^{-3} to 2×10^{-4}. The precipitated P_2O_5 is
recycled into the fertiliser process. It is present as
calcium apatite in the filtration sludge, is very reactive
and, therefore, easily acidulated again. The purifying
procedure is shown in Figure 5.

Ammoncarbonising

The system of $CaCO_3$ production used by Chemische Fabrik Kalk operates in the liquid state with purified as well as unpurified calcium nitrate solution. In our plants the conversion of CO_2, NH_3 and $Ca(NO_3)_2$ takes place jointly in one vessel and leads to an easily filterable $CaCO_3$. The heat produced is dissipated by cooling water. The typical analysis of calcium carbonate is shown in Table 2.

TABLE 2

$CaCO_3$ Analysis

Characteristics	
$CaCO_3$, %	99.09
CaO (DRY PRODUCT), %	55.48
H_2O %	0.1
N %	0.2 - 0.7
F, ppm	65
As, ppm	<1
Pb, ppm	2
Fe, ppm	4
WEISSGRAD (570mu) %	99.0

TABLE 3

Granulometry

Granulometry, microns	%
<100	98
< 80	96
< 60	91
< 40	85
< 30	51
< 20	0

The grain range can be varied within certain limits by modification of the process conditions. The data apply to CaCO3 from Kola phosphate.

Other phosphates can be carbonized just as well but, in many cases, a slight yellow tinge in the product is to be expected. The conversion of the calcium nitrate reaches 99 - 100%. The ammonium nitrate discharged is of about 50% concentration and is accordingly largely free of unconverted KS. It is concentrated in an evaporator and added to the fertiliser slurry as far as possible. The surplus is discharged. The filter wet CaCO3 has less than 10% water. The waste gas from the carbonisation contains a fairly high loss of ammonia so that acid scrubbing is indispensable. The wet carbonate is dried from a maximum of 10 to 0.1% water.

The granulation unit of the Kampka Nitro process operates according to the recycle procedure. The flow is shown in Figure 6. The adjusted NP slurry, coming from the Odda part of the plant, is fairly completely ammonised in one stage by gaseous ammonia before potash addition. By exact selection of the vessel dimension and special layout of the agitator, the losses of ammonia are not significant (smaller than 0.1%). Solubility is not affected. A small amount of ammonia is added during granulation. In addition to a final neutralisation of the grains, surface heating takes place, thus promoting the drying of the granule surface. The ammoniation capacity is high. About 1200 tonnes per day of 13-13-21 are run through a vessel with 12 m³ effective volume. The ammoniated slurry reaches the evaporator where evaporation, started in the ammoniation stage, is continued. Evaporation is carried out here by heat at normal pressure. A forced circulation system is employed in the evaporation stage giving a service life of many weeks before thorough cleaning is necessary. The subsequent addition of potash is effected either in a potash mixing vessel or immediately in the granulator; adding in the potash mixing vessel yields a more homogeneous product and is to be preferred if possible. The granulation of the NPK slurry takes place in double shaft mixers. For economic reasons and for reasons of flexibility we prefer this system to all other granulation methods. The capacity of one granulator is about 600 tonnes per day of 13-13-21. The granulation is carried out with recycle which is added in measured quantities from a silo. Fines from the screening devices, broken oversize and recycled and broken production grains are used as recycle in this process. This is necessary, as the output from the granulation stage has more production grains than can be taken from the

circulation. The procedure needs a recycle ratio of about 1 : 2.5 which is, however, known to be very dependent on the raw material used. After drying in a drum, the material is hot screened.

A characteristic sieve analysis at the dryer discharge is given in Table 4. The sieving takes place here to avoid undue disturbance of the final drying and cooling. To obtain the storage properties of the fertiliser, conditioning is carried out and this must be adjusted to local requirements. At Chemische Fabrik Kalk the fertiliser is stored in warehouses, without air-conditioning, 12m. high.

TABLE 4

NPK Granulometry after first drying drum

Size, mm	NPK 15-15-15 % of total		NPK 13-13-21 % of total		
6.3	5.9)		10.9)		)
5.0 - 6.3	2.6)	13.6	7.6)	18.5	) Over-size
4.0 - 5.0	5.1)				)
3.1 - 4.0	11.8)		17.1)		)
2.5 - 3.1	18.9)	60.3	24.5)	61.2	) Prod. size
2.0 - 2.5	29.6)		19.6)		)
1.5 - 2.0	15.6)		17.1)		)
1.0 - 1.5	6.7)		)	20.3	)
0.75- 1.0	2.1)	26.1	3.2)		) Fines
0.5 - 0.75	1.2)				)
0.5	0.5)				)
	100.0		100.0		

Investment Costs and Consumption Data

The investment costs (based on 1971 prices) for a complete NPK fertiliser plant, intended for production of 1000 m.t.d. of 16-16-16 with 80% water soluble P_2O_5 are summarised in Table 5. This plant also yields 380 m.t.d. CaCO3 as well as 1330 m.t.d. AN as 50% AN solution. The crystallisation process, developed by SCHZ, with direct cooling by super-cooled white spirit, is used with subsequent fertiliser production and ammoncarbonisation according to the Kampka Nitro process. The calculation is based on prices for the manufacture of plants in West Germany. The layout of the plant was tested on a model and the process

runs without KS purification. The raw material require-
ments are summarized in Table 6 and utilities consumpt-
ion in Table 8.

TABLE 5

Cost - Model NPK Plant
(1000 mtd 16-16-16 product, 380 mtd $CaCO_3$ and
1330 mtd AN 50%)

Plant Unit and Capacity	Investment Costs million DM	% of total
Acidulation 160 mtd P_2O_5		
Crystallisation	9.50	25.00
Fertiliser Unit 1000 mtd 16-16-16 Ammoniation Granulation Dryer, etc	6.90	18.15
AN-concentration 1330 mtd AN 50 to 95%	3.25	8.55
Carbonisation	4.85	12.76
$CaCO_3$ Dryer 380 mtd	0.50	1.32
Cost of Plant, FOB	25.00	65.78
Buildings, Mountings and starting up	13.00	34.21
Turnkey Price	38.00	100.00

TABLE 6

Requirements per tonne of 16-16-16 Product

Materials	
Morocco Phosphate 77/79 BPL, kg P_2O_5	166.5
Nitric Acid kg $N-NO_3$	149.8
Ammonia, kg $N-NH_3$	178.5
Potassium Chloride, kg K_2O	160.7
CO_2, kg CO_2	199.4
Conditioner, kg	10.0
Ballast kg	6.5
Water m^3	1.4

TABLE 7

Production Rates per Day

NPK 16-16-16	1000t
CaCO3	380t
AN 50%	1330t

TABLE 8

Utilities per Tonne of 16-16-16 Product

Utilities	
Steam, kg	609
Fuel Oil, kg	24.8
Electricity, kwh	103
Cooling Water, m^3	36.7
Losses of white spirit, kg	1.61

Besides 16-16-16, a small 375 mtd plant is also used for
the production of 12-12-24 and 12-24-12 products. Since
12-12-24 is the main product of this plant, the costs of
the production of 16-16-16 shown in Figure 7 can only be
regarded as approximate values. The curve demonstrates
the total production costs in relation to the capacity
of the plant. The indications of this curve are, however,
only relative as many subsidiary conditions have signif-
icant effects on the costs and vary from plant to plant.

For the ammoncarbonisation stage the data are listed
separately in Tables 9, 10 and 11. Here, examples with
and without KS-purification are compared. The invest-
ment costs for two corresponding plants with and without
KS-purification are shown in Table 9. What is remarkable
is the great difference with regard to the KS quality
used. Here, a salt with a high P_2O_5 content is deliber-
ately brought into the process. The lower limit of

operation in the purifying stage is at 0,8 - 0,9%
P_2O_5 in the salt, as the filtration properties of the
sludge are dependent on the P_2O_5 concentration. The
investment costs refer to a plant free German border,
without buildings, mounting and starting up. The plant
comprises the following plant units: KS-purification,
ammoncarboniser, filtration, and drying. The consumpt-
ion data for utilities are given in Table 11.

TABLE 9

Investment Costs KS Conversion

	Without KS-Purification	With KS-Purification
Capacity, mtd KS	1056	1056
KS analysis,		
P_2O_5 %	0.3	1.2
CaO %	23.2	23.2
N-NO$_3$%	11.7	11.7
Investment Costs, million DM	5.23	7.36

TABLE 10

Production Rates: KS Conversion

		Without KS-purification	With KS-purification
Production Rates			
CaCO$_3$ (Dry)	mtd	450	390
AN-N (50%)	mtd	267	265
Sludge N	mtd	-	8.4
Output			
N-NO$_3$	%	98	98
N-NH$_3$	%	96	96
Raw Materials			
NH$_3$	mtd	166	170
HNO$_3$	mtd	60	66.5
CO$_2$	mtd	255	205

TABLE 11

Utilities Consumption in KS Conversion

	Without KS-Purification	With KS-Purification
Cooling Water, m^3 p.d.	7,600	7,600
Process Water, m^3 p.d.	540	500
Steam 4atm t.p.d.	127	129
Electricity	27,000	30,500

References.

1. Second Interregional Fertiliser Symposium, Kiev, Ukrainian SSR. September 1971. "Nitrophosphate process using direct cooled continuous crystallisation".

2. Phosphorus and Potassium No. 21, 18-16 (1966), "Nitrophosphate processing and Kampka-Nitro process".

3. ECAFE Fertiliser Conference, Bombay 1963.

5. Proc. of the ISMA Technical Conference Edinburgh/Scotland September 1965.

DISCUSSION

DR. KURT TESCHE (Chemische Fabrik Kalk, GmbH, Germany). The KAMPKA Nitro Process is a modern process for the production of NP or NPK fertilisers and bears the typical features of any Odda process:

1) No use of raw materials or intermediate products which are produced by the direct or indirect use of sulphur.

2) Manufacture of the phosphoric acid required in the process by cooling the acidulation solution and separating the crystallised calcium nitrate tetrahydrate.

The purpose of this process is to produce only the minimum inevitable amount of straight nitrogen fertiliser or, in other words, to make do with the minimum possible nitrate input per ton NPK. This is achieved by three stages:

1) Minimum, virtually stoichiometric, input of nitric acid in the acidulation stage.

2) Recycle of ammonium nitrate.

3) Additional acidulation with crude phosphate to utilise the residual acidity in the centrifuge mother liquor.

A few supplementary details on this point:

The extent of additional acidulation is more than 10% of the total crude phosphate content. The diagram (slide 17) shows a comparison of a classic Odda process with the KAMPKA Nitro process without additional acidulation, with AN recycle only and the variant with additional acidulation. The diagram shows in simplified form the molar quantities used, in relation to 1 mol P_2O_5. While the classic Odda process operates with a big excess of nitric acid without AN recycle, and has already set the final ratio of N $3/P_2O_5$ in the centrifuge mother liquor, the KAMPKA Nitro process manages practically with the stoichiometric nitric acid quantity. The recycle, which this makes possible, of a considerable quantity of AN results in a saving of about 25% of the total quantity of the ammonising ammonia. If the process is operated with additional acidulation, it is immediately evident that, as a result of the addition of crude phosphate, the nitrate/P_2O_5 ratio drops while the $CaO/P2O5$ ratio increases slightly. The amount of ammonia used in the

ammoniation drops from 75 to 64% as a result of the
increased AN recycle which is then made possible,
as now an AN recycle of 36% in relation to the
ammonia is possible. This is a great advantage
afforded by this process. The residual ammoniation
of the fertiliser slurry takes place in one stage,
without drawbacks with regard to solubility.

The lower part of the table shows how the nitric
acid input is distributed over single and NPK
fertilisers. With a full nitric acid input we find
only 54% of the nitrate in NPK fertilisers as opposed
to 46% in single fertilisers. In the KAMPKA Nitro
process it is immaterial whether the production is
carried out with or without additional acidulation.
66% of the NO_3-N is present in NPK fertilisers and
only 34% in single fertilisers. This fraction must
be removed from the process. If one balances the
total quantity nitrate against P_2O_5, it is clear that
it is possible to achieve an acidulation of 6.5
H/P_2O_5 without the quality of the salt crystallisation
being affected, as the correction only takes place
after the cooling stage. A soft phosphate rock
which breaks down readily is recommended for the
additional acidulation.

Whereas the crystallisation was formerly a costly
part of all Odda processes, it is now possible to
reduce investment costs considerably, as we are in
a position to offer, in combination with our Fertiliser
Production Technology Department, the crystallisation
system which has been developed by Chemoproject. The
diagram shows you a plan of this crystallisation
system. (Slide 18). It operates without the use of
cooling surfaces in the slurry by the direct cooling
of the acidulation solution with undercooled benzene
with a flash point of about 40°. This provides high
yields with minimum outlay. After the traditional
sand separation, crystallisation takes place in one or
more stages, according to whether or not it is
necessary to achieve high degrees of water-solubility.
The centrifuged salt is really clean after the usual
washing and corresponds to normal requirements. With
figures of 1 and 2 kg the benzene loss is extremely
low. The spec. output of this crystallising system
is more than 1.5 t P_2O_5 per m3 per day. That is
much higher than the m3 yield of other types of
crystallisation systems. It shows at once that the
investment required is much lower than in other types
of crystallisation plant. Here in Spain, in the
meantime, the first plant with this combined process
has been put into production in Valladolid; grades
produced: 12/24/12, 16-16-16, 12-12-24. The plant
is fulfilling expectations.

MR. O.H. LIE (Norsk Hydro a.s., Norway.)
I would like, first, to congratulate the author on a
most interesting presentation.   Coming from a
company which is convinced of the virtues of the
nitrophosphate technology - even at very low sulphur
prices - and has been using and constantly refining
its own version of the Odda-process, I find it of
particular interest to learn how others design and
operate the various process steps.   My comments and
questions to the author are listed below:

1. Acidulation.   It is stated that the use of
    only a slight excess of HNO_3 in the digestion is
    a new twist so to speak in the Odda process.
    I disagree with this.   The use of only a
    slight excess of nitric acid compared to
    stoichiometry is one of the fundamental features
    of the Odda Process.   I think out of pure self
    interest any user of the process will keep the
    acid excess to the lowest possible level in
    order to achieve maximum calcium-nitrate (CaN)
    removal at minimum cooling.   At the same time
    and for the same reason, the nitric acid
    concentration should preferably not be much
    below 58%.

2. Decanting.   The use of a decanting station
    is primarily to protect the downstream
    centrifuges.   Could you tell us the type of
    equipment employed for this purpose, the "cut
    size" of the particles removed, how much water
    the washing of the insolubles introduces into
    the process, and the P_2O_5 and N losses here?

3. Crystallisation.   Crystallisation by direct
    cooling of the decanted slurry by means of
    white spirit is in my opinion the most
    interesting aspect of this process.
    Unfortunately, but perhaps understandably, the
    author has chosen to divulge few details in
    this area.   To obtain a high heat transfer
    rate, the two phases must be intimately mixed.
    This may lead to the formation of emulsions
    which may be hard to break and may require an
    excessive residence time for separating.
    Could you tell us whether emulsion formation is
    a problem, and if so, how you solve it?

    Is it necessary to use a series of crystallisers
    in series to obtain satisfactory particle size
    distribution of the CaN crystals and high heat
    transfer rates?   How many?

    In table 8, you state that the consumption of
    white spirit is 1.6 kg/ton 16-16-16.   What is
    the fate of the consumed white spirit?   Is

there any long term degradation of the white
spirit in the cooling cycle?   Does the use
of the white spirit require any particular
safety precautions as to plant lay-out and
operating procedure?

4.   Centrifuging.   What types of centrifuges are
used, and what is the capacity per centrifuge?
How much of a problem is erosion/corrosion of
the centrifuges?

5.   Additional acidulation.   Additional acidulation
in the mother liquor from the CaN separation
is a convenient way of reducing the NO_3-N/P_2O_5
ratio of the Odda-process.   One should however,
keep in mind that the reduction is achieved at
the expense of the water solubility of the P_2O_5
in the final product.

6.   Neutralization.   Could you tell us the pH and
water content of the slurry after neutralization?

7.   Evaporation.   How far is the evaporation
carried (%H_2O)?   Is ammonia recovery required?

8.   Purification of the CaN-melt.   The purification
of the CaN melt - by precipitation of the
P_2O_5 and most of the other impurities/filtering
and recycling to the NPK process - is desirable
since it completely eliminates any systematic
P_2O_5 loss from the Odda-process.   At the same
time the quality of the $CaCO_3$ formed in the
conversion of the CaN (ammon-carbonization)
is improved and commercial opportunities for this
material are enhanced.

From our own experience, I know that conditions
during the precipitation of impurities are
critical and must be strictly adhered to in order
to insure the formation of filtrable crystals.
It would be interesting to know how much of the
CaN-melt is contained in the filter cake from
the purification step and being thus recycled to
the acidulation step in the NPK plant.   If the
amount of CaN recycled is considerable, this
would, of course, reduce the net output of the
front end of the NPK plant (acidulation through
centrifuging).

The paper states the necessity of deliberately
employing CaN-melt high in P_2O_5 content to obtain
filtrable crystals in the purification step.   By
the use of Table 9 and the assumption that about
85% of the CaO in the phosphate rock appears in
the CaN-melt it is possible to estimate the amount
of P_2O_5 present in the CaN-melt.   About 6% of
the P_2O_5 in the phosphate rock follows the
CaN-melt.   This P_2O_5 is precipitated as apatite

and recycled to the acidulation step,
resulting in an increase of about 6% in the
NO_3-N requirement of the process besides
reducing the net output of the front end
of the NPK-plant (acidulation through
centrifuging). It seems to me to be a
worth while incentive to adjust/optimize the
conditions during the precipitation of the
impurities to permit the use of the higher
quality CaN-melt in Table 9, thus practically
eliminating the undesired effects described
above.

9. <u>Investment</u>. Could you specify the battery
limits applicable to the investment numbers
in Table 5?

DR. TESCHE. Mr. Lie has asked a number of
questions which I shall be glad to try and answer.
Some of the questions, however, touch on the knowhow
of the process so that I shall not be able to give
precise figures in all cases. With regard to the first
question, on the acidulation process, we are doubtless
all of the opinion that the most economic method is
maximum stoichiometric input of nitric acid at the
acidulation stage, with crystallisation in mind. On
the other hand, the concentration range of nitric
acid with which it is possible to operate is relatively
restricted. With an acid concentration of less than
55-56% the dilution is so great that the crystallisation
temperatures have to be reduced appreciably. This
makes the crystallisation process more expensive.
With higher concentrations, from about 60%, we are
moving into the range in which the viscosity of the
slurry has a disturbing effect on crystallisation
and on the separation of the salt from the mother
liquor.

To move on to your second question, the
decomposition solutions obtained in this way are
decanted. For this, we use specially equipped
centrifuges with a high grade casing which has a
life of three months and more. The separation of
the fines in the acidulation solution depends upon
the type and grade of phosphate rock used; among
other factors, the viscosity of the slurry plays a
very important part at this stage. It is therefore
very difficult to estimate in advance. We operate
our plant so as to separate off about 75-85% of the
insoluble fraction, reintroducing it, if the
fertiliser composition permits, into the slurry again
as far as possible after crystallisation. If the
ballast is discarded, the losses occurring should be
disregarded, the washing water goes back into the
process, the intended application determining the

quantity.   As the process used is an expulsion wash
on the centrifuges, the quantity of water is extremely
low.   The quantity of water is also determined by
the possible uses of the washing water, i.e. whether
you can take it back into the process, whether you
must discard it or whether you have other uses for
the P_2O_5 acid washing water.   The questions you
raised with regard to crystallisation come up in all
discussions.   The idea that the white spirit loss
of 1-2 kg, given here as 1.6 kg/t 16-16-16, is enriched
during the process is without foundation.   It has not
yet been possible to detect this white spirit fraction
in the fertiliser process.   Any interference with
the ammoniation, granulation, the production of $CaCo3$
or any other part of the process can also be disregarded.
At the low temperatures prevailing in the crystall-
isation section, the vapour pressure of the white
spirit is so low that there is normally no risk of
explosions occurring as a result of its blowing out.
Nevertheless, it is advisable, which is also an
advantage of the process, to construct this crystall-
isation unit out-of-doors.   It is so simply
constructed, that there is a clear case for operating
the unit out of doors, just as the cooling of the
white spirit should also be carried out in the open.
As you will have seen from the diagram, the upper
section of the crystallisation unit, which widens
considerably, acts as a stabilising and separation
vessel, the discharged white spirit fraction running
over a small separator inserted in order to catch any
acid droplets it may have carried along.   The
insertion of a crystallisation cascade is not necessary
with calcium nitrate precipitates which produce
fertilisers with water solubilities of the order of
16-50%, because the crystallisation unit is operated
so that only coarse crystallate is drawn off and the
fines remain in the unit.   With slurries with high
water solubilities it is expedient to crystallise in
two stages and also to centrifuge in two stages
because the high proportion of salt present in the
slurry would cause unnecessary difficulties during
separation.   At the same time the ensuing relatively
high viscosity of the mother liquor makes matters more
difficult.   We have various types of centrifuges at
our disposal for separating the salt.   We use first
sliding/oscillating centrifuges and then screen worm
centrifuges.   The output of the machines is between
8 and 10 tons salt separation per hour.   The size of
the machine makes surprisingly little difference and
it is immaterial whether you use a machine with a
diameter of 1 m or one with a diameter of 80 cm; the
greater outlay is not justified.   The life of the
screens - they are specially designed slot or round
screens, with special plating - is between 3 and 6
months.   Erosion therefore presents no problem in
this case.

I think that your question number 5 on additional acidulation has been sufficiently answered by the diagram already shown. The additional acidulation is, of course, restricted by the acidity available. To what extent the reduced NO_3/P_2O_5 ratio can be boosted again by ammonium nitrate depends, of course, on the required fertiliser formula. It would be wrong to carry additional acidulation so far that it might lead to definite impairment of the water-solubility of the fertiliser. The necessary correction of the freshly introduced calcium should be made at the outset in the crystallisation stage and with greater effect. With regard to your questions concerning the neutralisation and evaporation, the following may be said: The pH value is dependent on the phosphate rock used and on the slurries which may be recycled. As we are all aware, the thickening points in the slurry during ammoniation dictate the range of only a few tenths in the pH value in which the plant may be operated. In our ammoniation processes we introduce about 90% of the ammonia still necessary after the ammonium nitrate has been recycled. The remaining 10% is added during granulation. Scrubbing of the waste gas is unnecessary as the ammonium losses in the waste gas are in the order of 0.2 g per m3 waste gas. The introduction of a scrubbing process at this point would require an extensive condensation of the expelled water vapour, which is very costly, as the quantities of water expelled during evaporation are considerable. In addition, the ammonium content of the waste gas contains not only free ammonia, but also vapourized ammonium salts which are not easy to remove even with a scrubbing process.
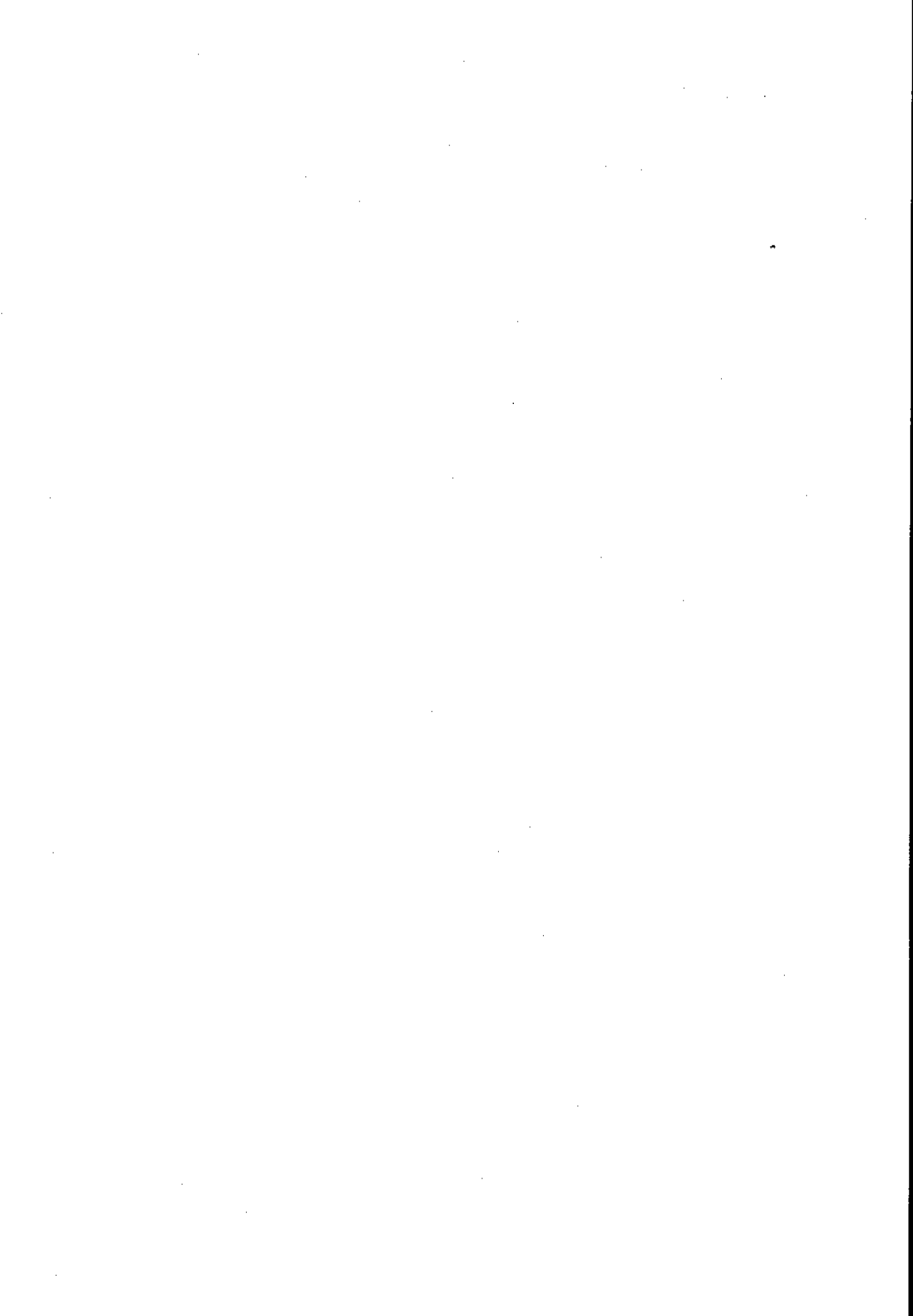
As to the water content of the slurry, the same applies basically as for the pH value. The evaporation units are operated with controlled temperatures and with forced rotation in such a way that at the end of the ammoniation/evaporation chain after granulation a precisely defined water content, specifically determined for the individual fertiliser type, is obtained. To give you an idea of the course of water balance during ammoniation and granulation: about 30% of the water present in the slurry is expelled in the ammoniation process, about 50% of the remaining water is expelled by evaporation. These figures apply to average potassium contents.

NOTE: Pressure of time did not allow Dr. Tesche to answer Mr. Lie's remaining questions, Nos. 8 and 9 during the discussion. They have been answered subsequently in writing and are as follows:

Question 8. We carry out the purification of the calcium nitrate in a solution and not in a melt.

As a result the calcium nitrate content of the precipitate is low. The slurry produced is added to the process after the subsequent decomposition stage. This is possible as the precipitated apatite is still very reactive and makes no claims on the concentration of the acids still present. The CaO correction according to the calcium content of the slurry is effected accordingly during the crystallisation stage. If this is not feasible because of the water-solubility required, the objection that correspondingly more nitric acid must be used, is justified, and the slurry must be returned to the acidulation stage. In this case the P_2O_5 content of the salt should be kept as low as possible or further purification should be dispensed with.

Question 9. The investment costs quoted are "turn-key" prices exclusive of outside storage. Only small intermediate tanks with storage capacity for a maximum of 8 hours in the production unit are included.
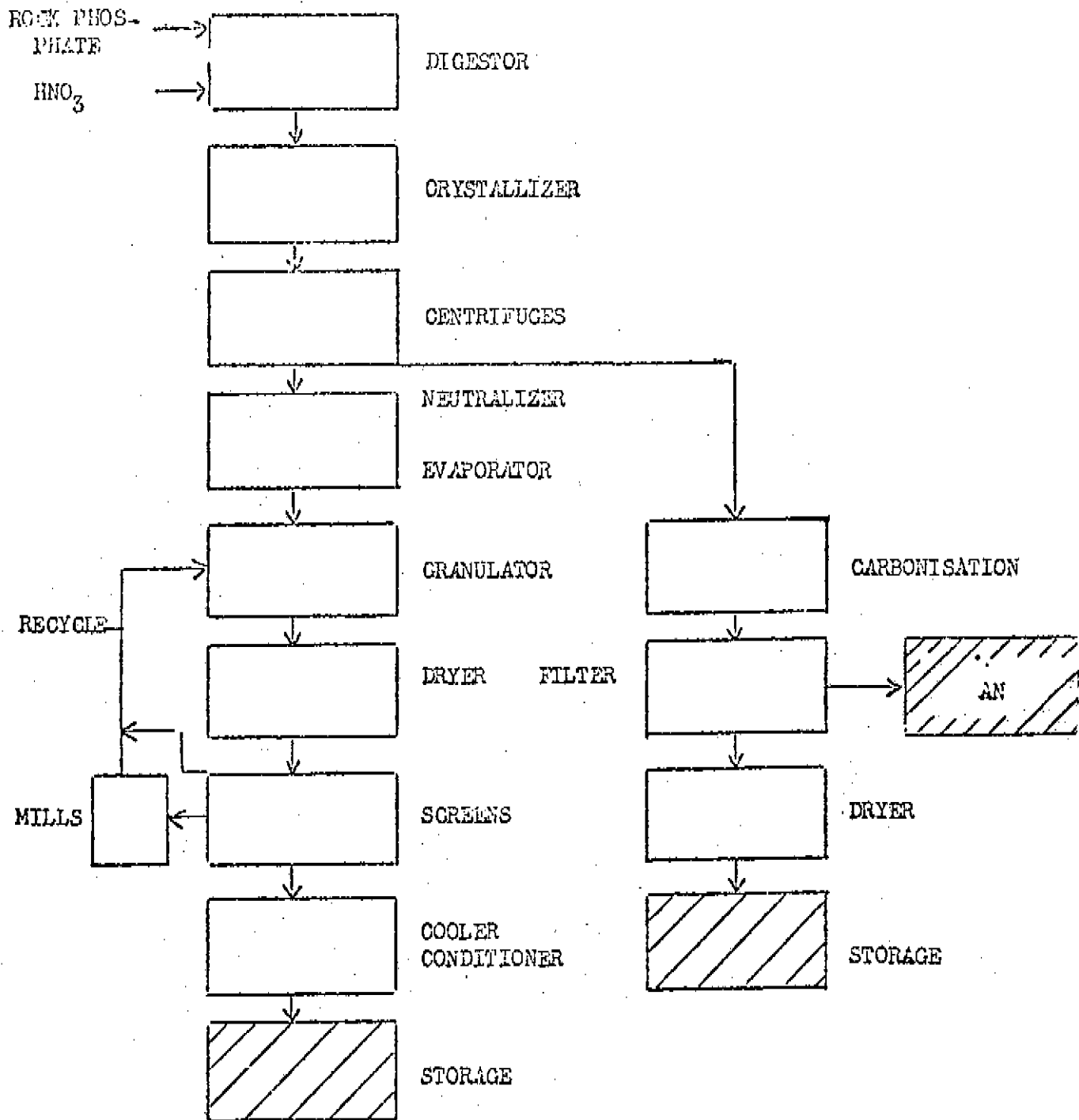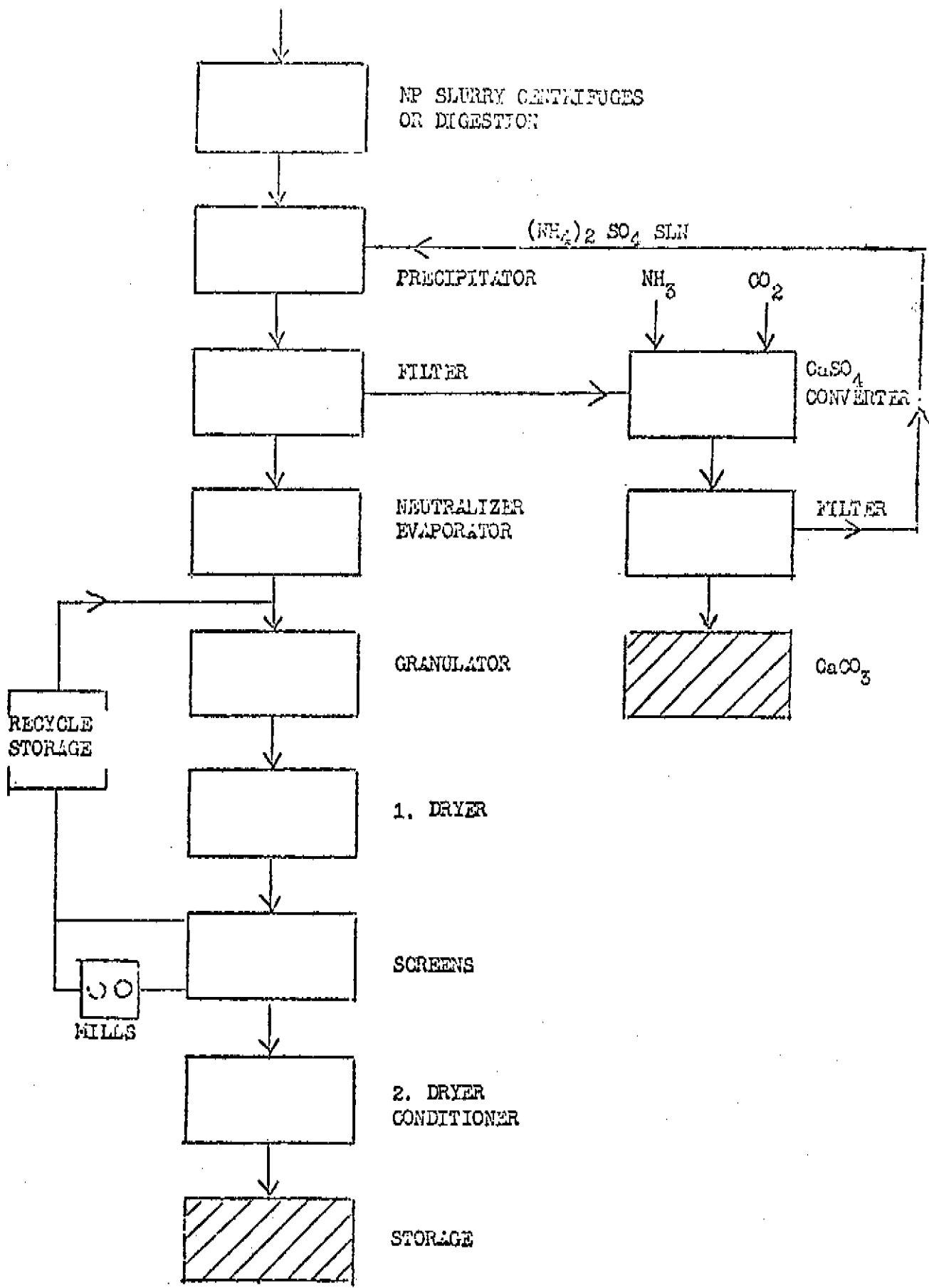
ROCK PHOS-
PHATE → →□ DIGESTOR

HNO₃ → →□

CRYSTALLIZER

CENTRIFUGES

NEUTRALIZER

EVAPORATOR

CARBONISATION

RECYCLE GRANULATOR

DRYER   FILTER

MILLS

SCREENS

DRYER

AN

COOLER
CONDITIONER

STORAGE

STORAGE

FIGURE 1 : NITRIC PHOSPHATE ODDA PROCESS

NP SLURRY CENTRIFUGES
OR DIGESTION

$(NH_4)_2 SO_4$ SLN

PRECIPITATOR

NH_3 CO_2

FILTER $CaSO_4$
              CONVERTER

NEUTRALIZER   FILTER
EVAPORATOR

GRANULATOR $CaCO_3$

RECYCLE
STORAGE

1. DRYER

SCREENS

MILLS

2. DRYER
CONDITIONER

STORAGE

FIGURE 2 : SULPHATE RECYCLE PROCESS
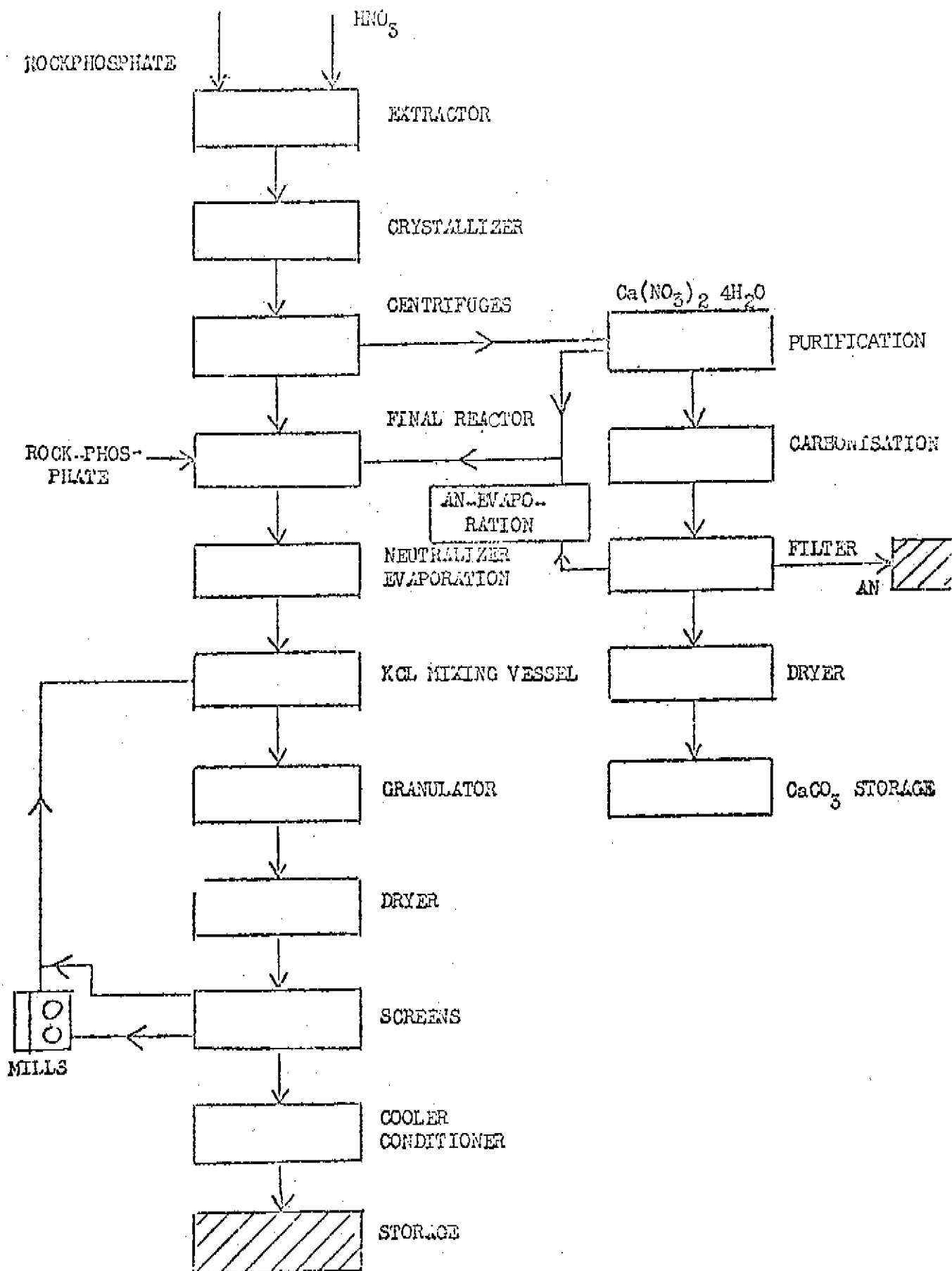
FIGURE 5 : NITRIC PHOSPHATES
KAMPKA NITRO PROCESS
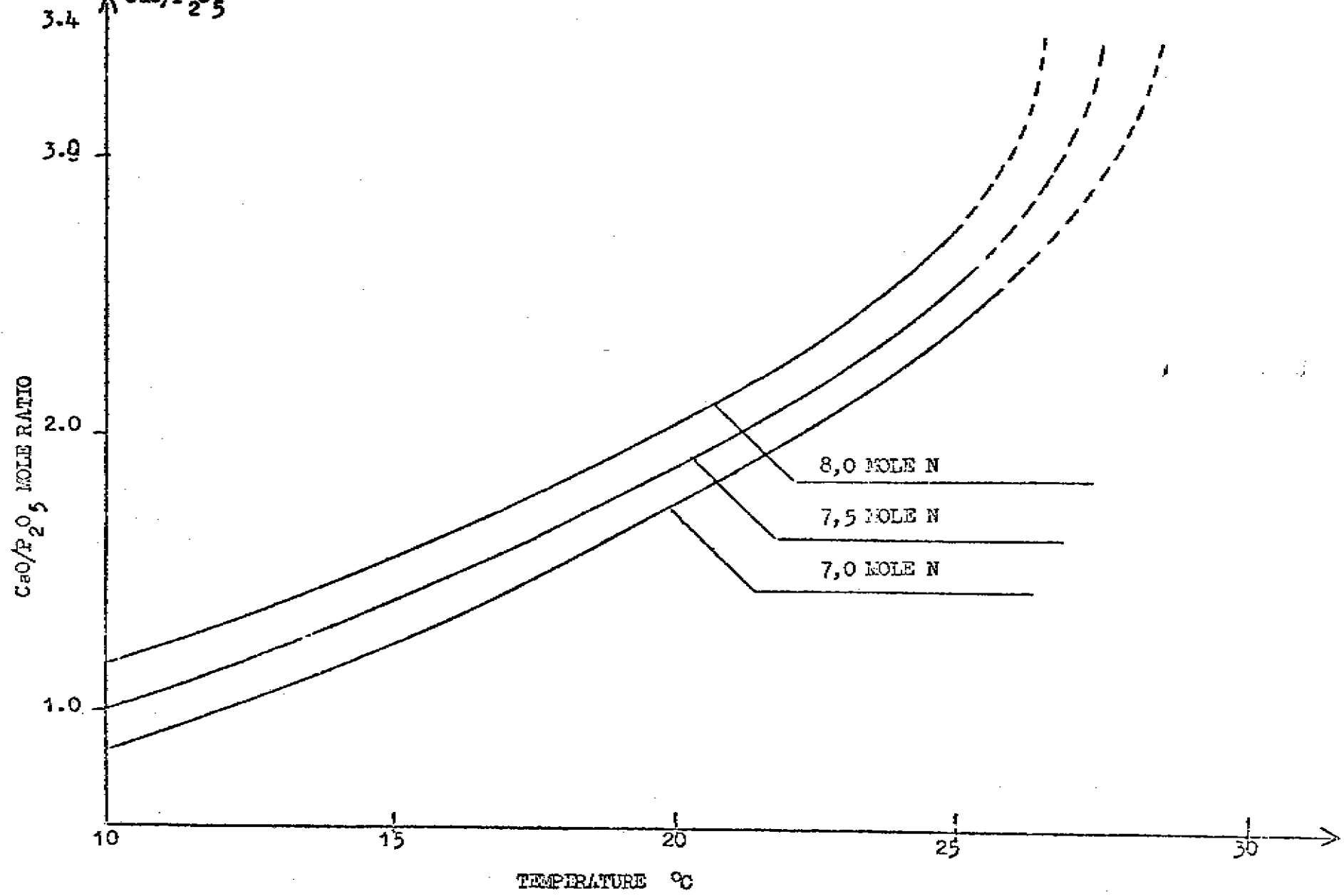
FIGURE 4 :   Ca(NO$_3$)$_2$ 4H$_2$O   CRYSTALLIZATION CURVES

CENTRIFUGES
WASHING

PRECIPITATION

FILTER

NP-SLURRY

STORAGE TANK
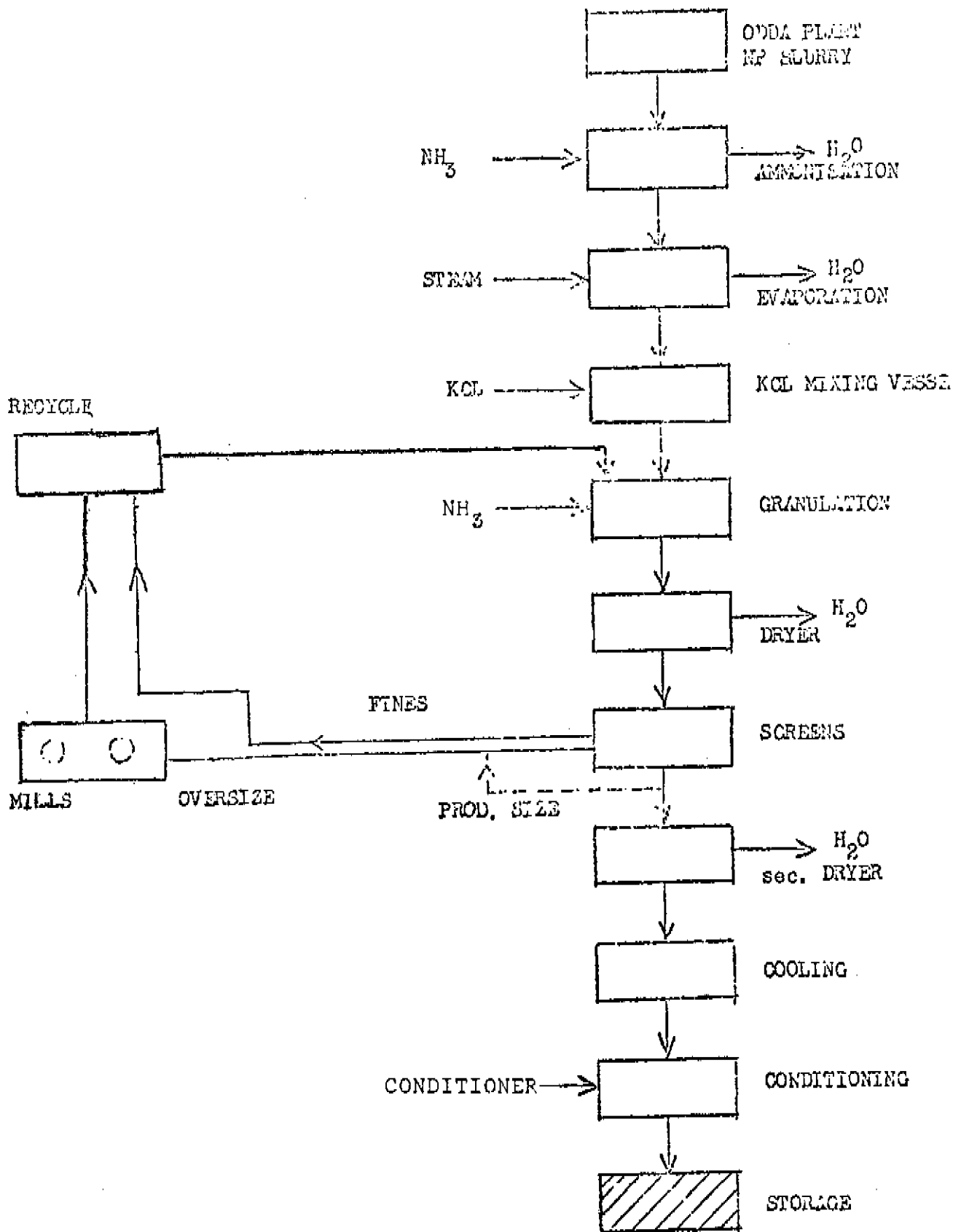$Ca(NO_3)_2$ SOLUTION
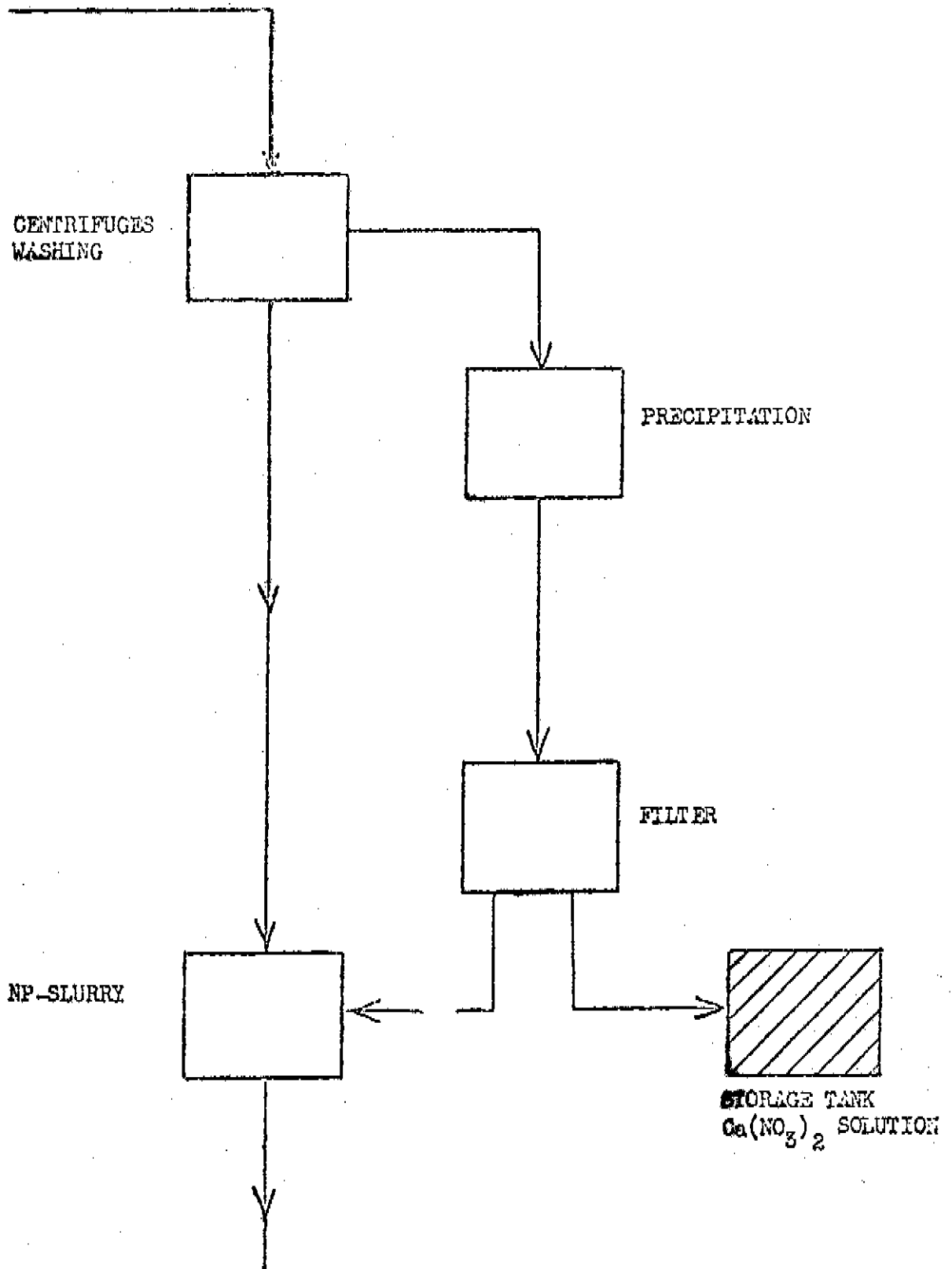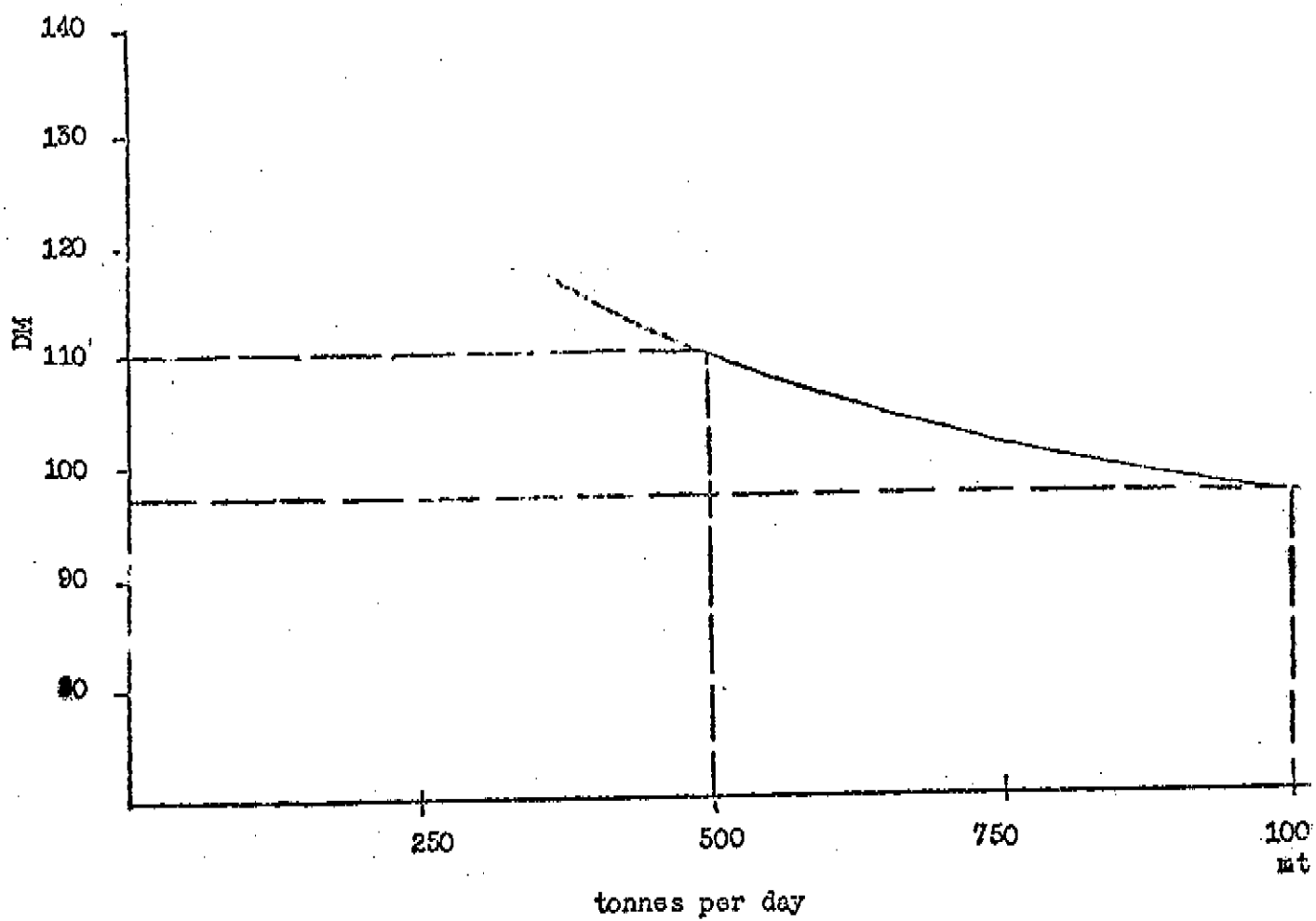
FIGURE 5 : KS-PURIFICATION

FIGURE 6 :   NPK Plant : Granulation Unit

FIGURE 7 :   PRODUCTION COSTS OF NPK 16-16-16