

ISMA* Technical Conference

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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

Introduction

In the production of phosphoric acid as a basic material for fertilizer manufacturing, preference is for economical reasons given to the wet phosphoric acid process. As is well known, this process implies a reaction of rock phosphate with sulphuric acid, the resulting calcium sulphate being separated by filtration. Depending on the reaction temperature and the phosphoric acid concentration, the calcium sulphate is precipitated as dihydrate, hemihydrate or anhydrite.

The objective aimed at in the production of phosphoric acid is to achieve the maximum possible yield. This means on the other hand that phosphoric acid production will in this case result in a very pure calcium sulphate. In this connection it has to be taken into consideration that environmental protection problems resulting from possible gypsum deposits resp. the disposal of gypsum slurry in water ways have to be surmounted particularly in those cases where the calcium sulphate contains impurities. These environmental problems may in certain circumstances become so great that the authorities will prohibit the operation of phosphoric acid plants without any further phosphoric acid gypsum processing. Apart from the quality of the products, it is imperative for the phosphoric acid process to achieve optimum operational conditions also with a view to investment and operation cost. This implies reaction spaces that should be as little complicated as possible, easily filtrable meshes requiring only small filters for filtering off the calcium sulphate, low consumption of energy and water as well as materials guaranteeing reduced corrosion and, consequently, low maintenance cost.

With a view to the resulting products, a wet phosphoric acid process, therefore, has to center on the following targets:

I) Phosphoric acid

- a) Maximum yields from phosphate inputs and low sulphuric acid consumption.
- b) Maximum F_2O_5 concentration, as all phosphoric acid is processed, which requires subsequent evaporation of the water present in the acid.
- c) Maximum degree of purity for the phosphoric acid only in those cases where the acid is destined for non-fertilizer uses. If it is employed for fertilizer manufacturing, normal impurities do not constitute any impediment, unless they reach a concentration apt to reduce the nutrient content of the fertilizer.

II) Calcium sulphate

If at all serving for any further purpose, the calcium sulphate resulting from the phosphoric acid process is used in the construction or cement industry. Apart from the exceptional case of a production of sulphuric acid and cement according to the Müller-Kühne process, the following $CaSO_4$ utilization possibilities may be envisaged:

- 1) As an aggregate for the cement industry (setting retarder). Input approx. 4 - 5 % $CaSO_4$ on the basis of the finished cement.
- 2) For the production of plaster (plaster powder).
- 3) For the manufacturing of plaster partition walls or plaster slabs.
- 4) For the production of sandwich type plaster boards.

Quality standards for the calcium sulphate resulting from a phosphoric acid process have consequently to be set in accordance with the above utilization possibilities with the objective of obtaining a product that can be directly processed without any further purification implying additional cost as well as polluted waste water.

The most valuable form of calcium sulphate is the hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, provided it is sufficiently pure. Without any further treatment and additional drying or calcination cost this material can be directly used for the manufacturing of plaster slabs or sandwich type plaster boards. Owing to its granular structure, the hemihydrate is less suitable for other purposes, as e. g. the production of plaster for facing. In this case, a recrystallization into dihydrate should definitely precede any practical use. During this process the water still present in the calcium sulphate following scrubbing of the phosphoric acid is bound as crystal water, so that the resulting dihydrate is completely dry and has very good flowing properties.

Dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a less valuable calcium sulphate form. Even if produced with a high degree of purity, it has, in comparison with the hemihydrate, always the disadvantage of a considerably higher water content, so that before any kind of utilization the material has to be dried or calcinated. Impure types of gypsum, as obtained during the normal phosphoric acid dihydrate process, can be used in the construction industry only after costly purification operations and, possibly, additional calcination in order to eliminate acid traces occluded in the gypsum crystal.

At present, no technical use is made of phosphoric acid processes involving the precipitation and filtration of anhydrite which, because of its poor reactivity, is used

for purposes of the construction industry only in exceptional cases (cast plaster floors).

Phosphoric acid processes

The following phosphoric acid manufacturing processes are commercially used:

- 1) Normal dihydrate process (single-stage)
- 2) α -hemihydrate process (single-stage)
- 3) Hemihydrate/dihydrate process (double-stage)
- 4) Dihydrate/hemihydrate process (double-stage).

All these processes are assumed to be well known to the participants.

Whilst the single-stage processes result in an impure calcium sulphate, the calcium sulphate obtained from the double-stage processes is pure and can, generally, be used for construction purposes. Moreover, the double-stage processes permit a better phosphate utilization which makes it possible to achieve yields of approx. 98 %, whilst with the single-stage processes yields do in general not exceed 94 %.

In comparison with the single-stage processes, the double-stage types are, however, bound to imply the drawback of higher investment and operation cost. It is most probably for this reason that the single-stage processes, in particular the normal dihydrate process, still hold a predominant position.

The VEBA phosphoric acid process

As results from the above survey, the more or less ideal phosphoric acid process should, if possible, have the following characteristics:

- a) Maximum possible simplicity of plant layout, single-stage, one filtration only.
- b) CaSO_4 to be separated as hemihydrate and to be as pure as to be directly and without any further treatment suitable for the construction industry.
- c) Operation at moderate temperatures to reduce corrosion and tail gas problems.
- d) Purity of the phosphoric acid is of a comparatively lesser importance if the acid is to be used for fertilizer purposes.

The phosphoric acid process developed by VEBA-CHEMIE at Embsen has largely reached the above targets. It operates as follows (Illustration 1):

In a single tank and at operation temperatures of 80 - 95° C rock phosphate is attacked by a mixture of sulphuric acid/nitric acid, the calcium sulphate being precipitated as hemihydrate (Illustration 2). Under reaction conditions that have to be strictly observed, well-shaped hemihydrate crystals are obtained that have excellent filtration properties. In addition, the viscosity of the phosphoric acid/nitric acid mixture is relatively low so that a total of only 50 - 75 % of the normal dihydrate process filtering surface is required. The admixture of nitric acid accelerating and improving the phosphate attack, approx. 50 % of the attack volume required for the dihydrate process are sufficient. This means that thanks to the VEBA hemihydrate process phosphoric acid plants of an identical size can reach performances that are 1.5 to 2 times higher than with the dihydrate process. Investment

and operation cost are reduced accordingly. The corrected phosphoric acid concentration reaches 30 - 40 % P_2O_5 . In this context "corrected" means: after deduction of the input of nitric acid which does not react as such but, in the end, exerts an influence by its mere presence. Phosphoric acid manufactured according to the VEBA phosphoric acid process may e. g. have the following composition.

P_2O_5	26 %	=	H_3PO_4	=	36 %
			HNO_3	=	18 % = 30 % HNO_3 60 %
			Other substances	=	4 %
			Water	=	42 %

As nitric acid was in this case used as HNO_3 60 %, this quantity has to be deducted in order to determine the corrected P_2O_5 content, i. e. following deduction of 30 parts of nitric acid, 70 parts of acid contain 26 % P_2O_5 . 100 parts of acid consequently contain:

$$26 : 7 \times 100 = 37 \% P_2O_5$$

This means in other words: If 30 parts of a 60 % nitric acid are added to 70 parts of a 37 % P_2O_5 phosphoric acid to be used for fertilizer production, e. g. according to the nitrophosphate process, the resulting acid has the above composition.

In the VEBA process, sulphuric acid may wholly or partially be replaced by sulphates, e. g. ammonium or potassium sulphate, which makes it e. g. possible to use ammonium sulphate obtained e. g. as a by-product in the plastics industry. This economizes a corresponding quantity of sulphuric acid in the phosphoric acid plant and of ammonia in the connected fertilizer unit.

The following sulphuric acid quantities may be substituted by ammonium sulphate when using the produced acid for the manufacturing of fertilizers having the following composition:

<u>N : P₂O₅ ratio of fertilizer</u>	<u>Maximum (NH₄)₂SO₄ input as sulphuric acid substitute - in % -</u>
2 : 1	100 %
1 : 1	50 %
1 : 2	20 %

Thanks to low temperatures in comparison with other hemihydrate processes, there is a limited amount of corrosion. The presence of nitric acid reduces corrosion occurring with normal stainless steel. Caking of sodium or potassium salts of the hydrofluosilicic acid happens less frequently than with normal phosphoric acid processes and does not cause any problems.

In comparison with the phosphate input, yields reach approx. 98 %. Grinding of the phosphate is generally not necessary but fractions exceeding 1.5 mm have to be separated by screening. Nitric acid losses are very small, as the acid lost during air cooling of the process is recuperated by a scrubber connected to the reactor. The calcium sulphate hemihydrate still contains a small amount of nitrate (approx. 0.03 % NO₃-N). This negligible quantity of nitrate does not, however, impair the processing of the calcium sulphate; under certain circumstances it may even be helpful.

The quality of the resulting calcium sulphate hemihydrate corresponds more or less to that achieved by the double-stage dihydrate/hemihydrate process. Without any further purification the calcium sulphate hemihydrate can be directly processed into building materials. With most phosphates, the phosphoric

acid process leads to a very white calcium sulphate hemihydrate, e. g. Kola phosphate, Bucraa phosphate (Sahara), Negev phosphate; Florida Pebble phosphate results in a yellowish hemihydrate.

Depending on the phosphate used, recrystallization of the hemihydrate into dihydrate occurs at different moments (Illustration 3). Whilst it is very rapid with Moroccan and Negev phosphates, it takes longer with other phosphate types, e. g. Kola phosphate. Addition of calcium hydroxide makes it, however, possible to accelerate recrystallization of the slow-reacting hemihydrates to such an extent that they recrystallize into dihydrate in the shortest possible time.

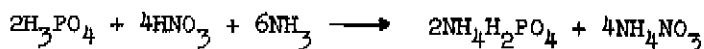
Hemihydrate analysis (basis Kola, input 80 % H_2SO_4 ,
20 % ammonium sulphate)

P_2O_5 (total)	0.20 %
P_2O_5 (water-soluble)	0.03 %
Na_2O	0.2 %
F	0.2 %
NO_3-N	0.03 %
NH_3-N	0.03 %
H_2O (total)	19 %
Crystal water	6.3 %

It is in general more difficult to operate phosphoric acid plants according to the α -hemihydrate process than on the basis of the normal dihydrate process. This is a. o. due to the fact that the recrystallization of the produced α -hemihydrate into dihydrate may imply indurations. We do, however, have sufficient command of the process technology to achieve an operating time of 90 %.

If repairs should become necessary, the reactor need not be emptied, because even during a several days' stoppage no re-crystallization of the hemihydrate into dihydrate will take place in the strongly acid mash.

Utilization of the phosphoric acid produced according to the VEBA process is restricted to fertilizer manufacturing, as the acid still contains some nitric acid. Particularly for the so-called nitrophosphate process this is, however, of no importance, as this process uses nitric acid e. g. according to the following equation:



Comparison of the VEBA phosphoric acid process with the classical dihydrate process

The following table gives a comparison of the VEBA phosphoric acid process with the normal phosphoric acid/dihydrate process. In both cases the feedstock consisted of Kola phosphate with 39 % P_2O_5 and sulphuric acid with 96 % H_2SO_4 . The reactor capacity amounts to 200 m^3 , the filter size (Giorgini-filter) to 20 m^2 . Plants of this size, when operated according to the normal dihydrate process, permit the production of 100 t p. d. P_2O_5 , whilst the VEBA phosphoric acid/hemihydrate process makes it possible to manufacture in the same type of plant 200 t p. d. P_2O_5 .

Dihydrate process	VEBA phosphoric acid process
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All quantities per ton P_2O_5 production in the form of phosphoric acid

Rock phosphate (Kola 39 % P_2O_5)	2.73 t	2.61 t
H_2SO_4	2.55 t	2.45 t
Process water	6 m ³	3 m ³
Vapour	0.6 t	0.3 t
Electric energy	100 kWh	60 kWh
<hr/>		
Reaction space (24 hrs. operating time)	2 m ³ /t p. d. P_2O_5	1.0 m ³ /t p. d. P_2O_5
Filtering surface (24 hrs. operating time)	0.20 m ² /t p. d. P_2O_5	0.10 m ² /t p. d. P_2O_5
<hr/>		
HNO_3 losses	-	2 kg HNO_3 -N

Production of phosphoric acid according to the VEBA phosphoric acid process
- Comparison of various phosphate types -

The following table gives a survey of how various types of phosphate may be used:

	Yield	Filtering surface	Reaction space
Kola phosphate with ammonium sulphate (20 %) and sulphuric acid (80 %)	99	1.0	1.0
Kola phosphate without ammonium sulphate with sulphuric acid	98	1.0	1.0
Florida Pebble phosphate, 75 BPL, with sulphuric acid	98	1.0	1.0
Florida Pebble phosphate, 65 BPL, with sulphuric acid	98	1.0	1.0
Bucraa (Sahara) with sulphuric acid	98	1.2	1.0
Togo with sulphuric acid	98	1.5	1.0
Negev with sulphuric acid	98	1.5	1.0
Comparison: Dihydrate process	94	2.0	2.0

Shortcomings of the process

It is, no doubt, a disadvantage inherent in the VEBA phosphoric acid process that it is impossible to manufacture any pure phosphoric acid and that the phosphoric acid obtained always contains some nitric acid. This means that the phosphoric acid can only be used for the manufacturing of ammonium nitrate fertilizers.

In order to eliminate this drawback at least partially it is possible to use the VEBA phosphoric acid process for the manufacturing of ammonium nitrate fertilizers but to produce in the same plant normal phosphoric acid according to the dihydrate process for the manufacturing of other fertilizer types. In this connection it will, however, have to be taken into account that the dihydrate process implies a loss of capacity.

Advantages of the process

In comparison with the normal dihydrate process, the VEBA phosphoric acid process has the following advantages:

- a) Increase of yields
- b) No phosphate grinding required
- c) Increase of capacity
- d) Possibility to opt for the substitution of sulphuric acid by ammonium sulphate
- e) Improved gypsum quality

An assessment of these advantages results in the following economies:

- | | | |
|--------------------------------------------------------------|-----------------------------|--------------------------------------------|
| a) Phosphate | = 0.12 t à DM 125.-- | = DM 15.-- |
| Sulphuric acid | = 0.1 t à DM 40.-- | = DM 4.-- |
| Energy | = 40 kWh à DM .08 | = DM 3.20 |
| Water | = 3 m ³ à DM .50 | = DM 1.50 |
| Vapour | = 0.3 t à DM 15.-- | = <u>DM 4.50</u> |
| | | DM 28.20 |
| ./. HNO ₃ losses | = 2 kg N à DM .60 | = DM 1.20 |
| Profit resulting from reduction of feedstock and energy cost | | = DM 27.--/t P ₂ O ₅ |
- b) Grinding cost economy = approx. DM 10.--/t P₂O₅
- c) The positive effect of the capacity increase may reach an order of magnitude of approx. DM 20.--/t P₂O₅
- d) If ammonium sulphate is used, considerable advantages may be expected from the VEBA process.
- e) Depending on the intended use and on the transport charge up to the processing plant, the value of the calcium sulphate obtained may reach in Central Europe DM 10.-- to DM 40.--, on an average DM 25.--/t CaSO₄ · 2H₂O. In view of the fact that the production of one ton P₂O₅ implies approx. 4 tons CaSO₄ becoming available as CaSO₄ · 2H₂O, total processing of the gypsum results in a profit of DM 100.--/t P₂O₅. This does not take into account possible economies of gypsum disposal cost connected with the dihydrate process. In the absence of natural gypsum deposits, the advantages may become even greater.

Summary

As explained above, the VEBA phosphoric acid process is in any case of economic interest, provided the phosphoric acid is used for the manufacturing of ammonium nitrate fertilizers. The process may be particularly recommended for situations in which

there are either ammonium sulphate availabilities or possibilities to process or sell the resulting calcium sulphate. It is also recommendable for plants located in densely populated areas where gypsum disposal is difficult for environmental protection considerations. In comparison with larger conventional plants, even smaller units do have the possibility of profitably operating according to the VEBA phosphoric acid process because, as against the normal dihydrate process, they may achieve price advantages of DM 100.-- to DM 150.--/t P_2O_5 . The drawback of the presence of nitric acid in the phosphoric acid may partially be avoided by converting the phosphoric acid plant each time no ammonium nitrate fertilizers are manufactured to the classical dihydrate process. There is a possibility of completing existing phosphoric acid plants e. g. by the installation of a new reactor in such a way that phosphoric acid may either be produced with the already existing reactor according to the dihydrate process or with the newly installed reactor following the VEBA phosphoric acid process.

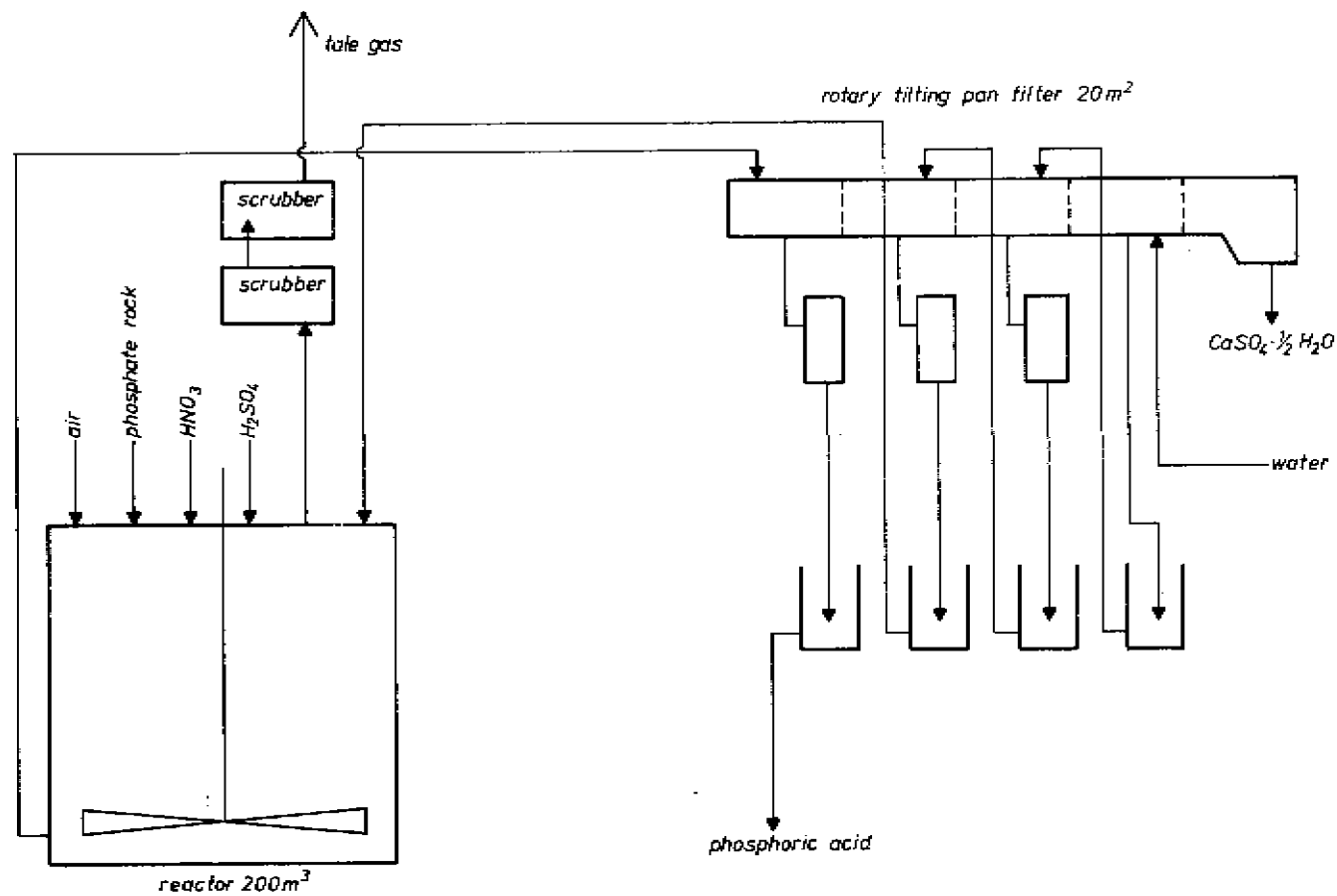


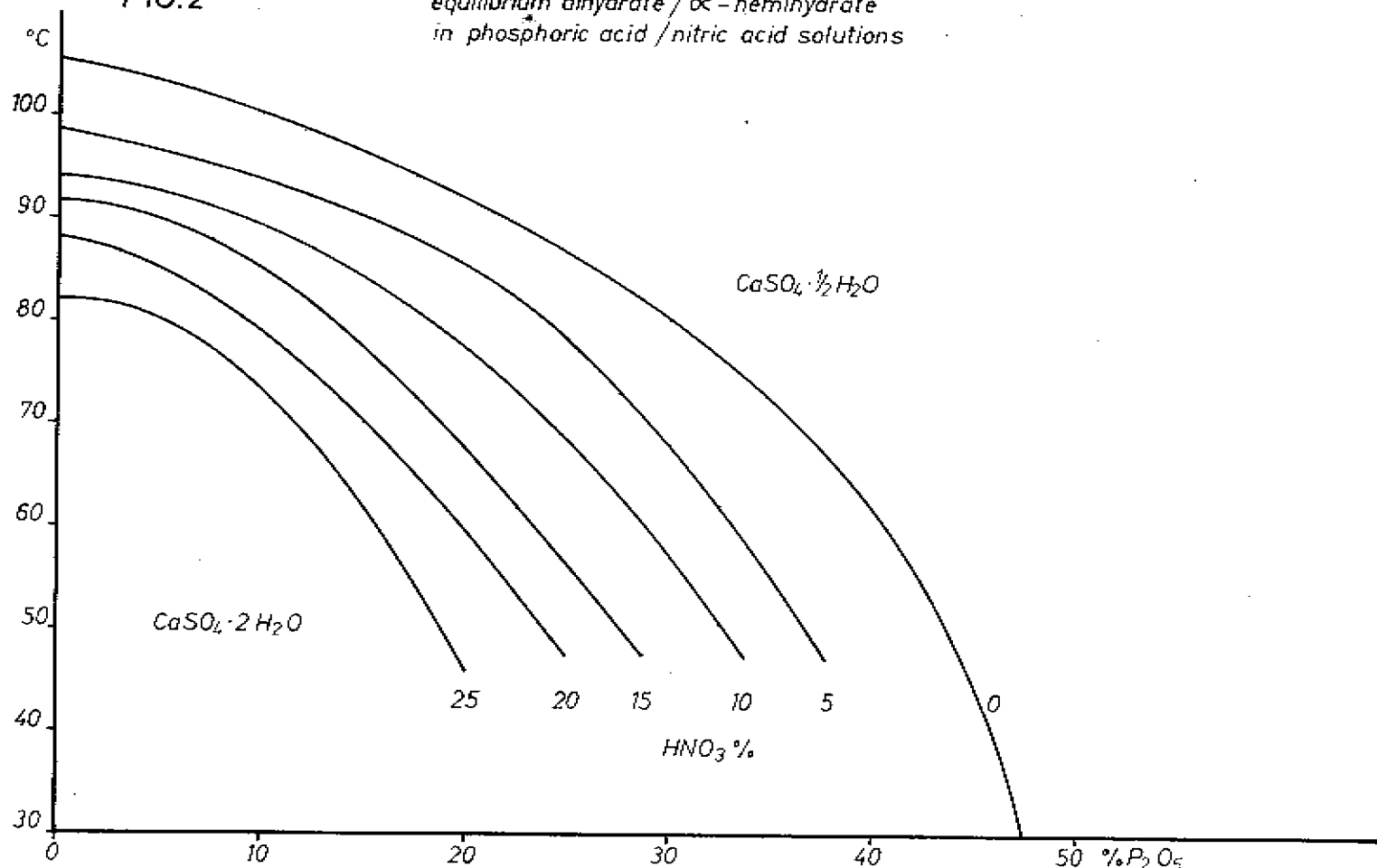
FIG.1

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phosphoric acid plant
200 t P₂O₅/day

FIG. 2

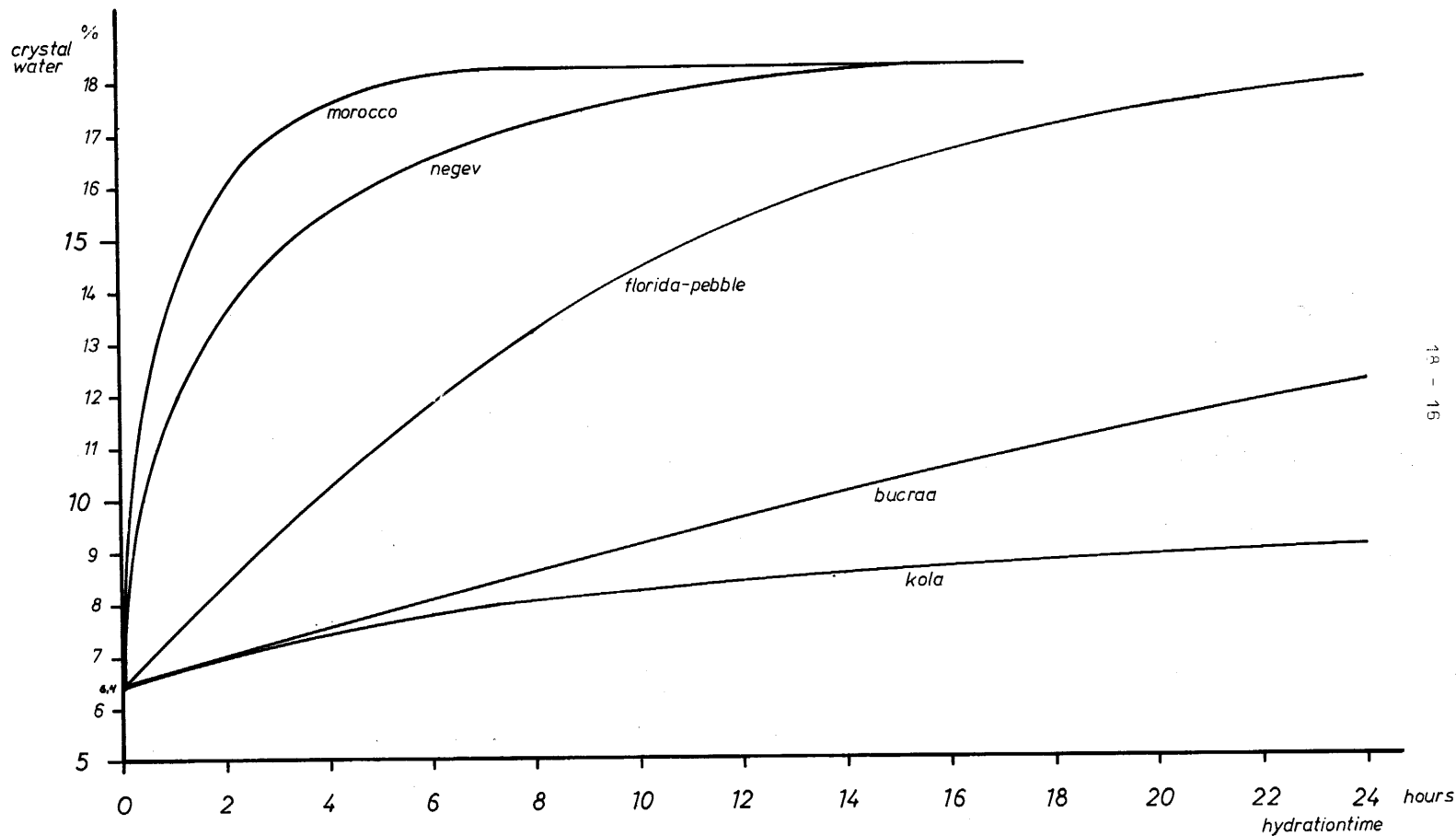
equilibrium dihydrate / α -hemihydrate
in phosphoric acid / nitric acid solutions



50
60

FIG.3

hydration of α -hemihydrate into dihydrate after filtration by use of different kinds of phosphate rock in the Veba phosphoric acid process



14 - 15