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SOME CONSIDERATIONS ON THE MANUFACTURE OF PHOSPHORIC ACID FROM DIFFERENT PHOSPHATES.

by Mm. Beetz et Jadot
(Ste. Ame. Metallurgique De Frayon).

I. GENERAL

For a long time the manufacture of phosphoric acid by the wet process was considered very difficult: its physical chemistry was not well understood, handling and filtration were thought to be tiresome, and there was a lack of materials which were resistant under the required working conditions.

To-day, these difficulties have been overcome, and a plant can be set up capable of producing a phosphoric acid rich in P_2O_5 under completely profitable economic conditions.

Having for many years been interested in the manufacture of phosphoric acid, we have been led by the geographical position of our country, to use phosphates of very different origins.

We propose to discuss the characteristics of the three phosphates most often used: Kola, Casablanca and Florida phosphates, which differ widely from each other both in their analysis and their behaviour during the manufacture of phosphoric acid.

Kola phosphate, which is an apatite with no trace of carbon, occurs in the form of a hard rock quite difficult to decompose.

Casablanca phosphate, a soft sedimentary rock, is rich in calcium carbonate but contains very little Fe_2O_3 and Al_2O_3 .

The Florida land pebble, a sedimentary rock like the Casablanca, contains a little less calcium carbonate and more Fe_2O_3 and Al_2O_3 .

II. DESCRIPTION AND FUNCTIONING OF OUR PROCESS

A Manufacturing process

The process is to react the phosphate with sulphuric acid at a temperature at which the calcium sulphate crystallises as $CaSO_4 \cdot 2H_2O$. This temperature is maintained by cooling the slurry, which is effected by the evaporation under vacuum of much of the water which it contains, thus helping to raise the P_2O_5 concentration of the acid produced. It is in fact an improved

version of the dihydrate process, called by us "dihydrate process with auto-concentration of the acid produced."

B Constructional principles

1. We are dealing with a mixture of liquid and solid, so the handling must be designed to avoid any points at which the two could become accidentally separated and cause a blockage.

Requirements:

- (a) To reduce to the absolute minimum the un-agitated volumes
 - (b) That the piping system should be of ample dimensions while maintaining sufficient speed to avoid decantation of the slurry.
- That they should have a considerable gradient.
That they should be made as straight as possible.

2. If CO₂ is evolved, it is necessary to bring the frothing under control and to avoid having gassy solutions.

Requirements:

- (a) To provide adequate foam control in the tanks.
- (b) To use a dense slurry.

C Layout and Description of the Process

The decomposition is carried out in two large tanks divided into eight smaller ones.

In the first, the mixture is prepared for reaction: the recycled cooled slurry is mixed with phosphate. Depending on the phosphate used, the phosphoric acid produced by the washings of the gypsum on the filter, together with the sulphuric acid, are introduced wholly or in part into compartments 1-4 depending on the reaction temperature, the frothing produced, etc.

The slurry thus produced proceeds from tank to tank without ever being removed from the action of the agitators, a very important point since it facilitates easy handling of a dense slurry, without deposits, stoppages or other troubles well known in the older types of plant, also

- a constant conditioning of the slurry, giving complete utilisation of the whole volume to be reacted,
- an effective removal of gases where a phosphate rich in carbon is being used (calcium carbonate or organic matter).

Reaction is carried out in tanks 1 to 6 at a temperature of 65 to 70° C. A volume of 2 cubic metres per ton of P₂O₅/24 hours is assumed.

At this point is placed an apparatus which has a fundamental part in the dihydrate process. The slurry, which has taken up most of the heat produced by the reaction, is pumped into an apparatus in which it is placed under vacuum. an evaporation of water occurs, thus cooling the slurry and facilitating:

- (1) the stabilisation of the slurry by a crystallisation of dihydrated calcium sulphate which is completed in the digestion tanks 7 and 8.
 - (2) control of the reaction temperature by means of the considerable flow of slurry returning to the first reaction tank.
- In addition, the evaporator offers the two following advantages:

- (1) It ensures complete removal of gas from the slurry, facilitating its moving by centrifugal pumps, which is very difficult with a gassy slurry.
- (2) It removes a considerable amount of water from the material, thus allowing the production of a more concentrated acid.

Thus, recycling of the cooled mass to the start of the reaction circuit plays a triple role, namely that of:

- initiating crystallisation of the gypsum by bringing seed particles into the zone where the calcium sulphate is formed;
- controlling the reaction temperature, which can be adjusted at will;
- homogenising the reaction conditions through bringing about a considerable circulation of material.

In the digestion tanks 7 and 8 the slurry, coming from the evaporator where its temperature is adjusted to about 60°C, becomes stabilised; that is, the liquid phase, supersaturated in calcium sulphate, allows the latter to precipitate in the form of gypsum crystallising on the seed particles present; thus a physical-chemical equilibrium is reached, corresponding to the temperature of the slurry, and crystallisation is completed. The same phenomenon occurs with sodium fluosilicate.

Thus conditioned, the mass is filtered by a continuous and automatic rotary vacuum filter with a vertical axis. This filter is divided into a certain number of parts individually connected with a central vacuum chamber. The compact nature of the latter allows it to be cooled to hold a vacuum higher than 700 mm Hg without failure.

The feeding of the slurry, the counter-current washing of the gypsum cakes and the discharge of the exhausted cakes are carried out automatically and continuously. We operate three counter-current washings, bringing about an excellent degree of exhaustion of the cakes (extraction yield greater than 99%) with the introduction of a very limited quantity of water; this gives very concentrated washing liquids, a matter of fundamental importance if it is desired to produce an acid rich in P_2O_5 ; in actual fact, the product of the last washing is re-fed into the reaction, and it is this product which determines the P_2O_5 concentration of the initial reaction medium.

We are thus able to carry out the reaction with sulphuric acid of a concentration favourable to a good yield, and to produce an acid containing 32% of P_2O_5 .

D Important details of the process - carrying them into effect.

1. Conditioning of the slurry

The preparation of a well-conditioned slurry, that is, dense and fluid, is absolutely necessary to ensure the steady development of the chemical phenomena (reaction of the phosphate) and the physical phenomena (crystallisation of the gypsum). With this end in view, we designed a system of tanks and agitators bringing about a vigorous mixing capable of making completely homogenous the dense slurries met with in this case.

2. Pumping the slurry

The density of the mass, and the corrosion and abrasion which it causes, led us to develop, in close co-operation with a Belgian Founder and Engineer, a type of pump perfectly adapted to the problem. It is a centrifugal pump with a vertical axis, with an immersed rotor, and all parts which come into contact with the liquid are of non-oxidisable alloys selected for good resistance to the conditions they have to meet. The interest of this pump lies in the fact that it can be immersed in the agitated mass; thus the suction pipe is eliminated, together with the usual troubles resulting from blockages of this pipe; further, the pump can be started as soon as it is immersed, thus avoiding the always tedious starting manoeuvres. This pump makes it possible to keep the flow constant, a matter of the first importance in a manufacturing process of this sort, in which constant load conditions are an absolute necessity.

For the centrifugal pumps to work properly, the slurry must be sufficiently de-gassed; the evaporator, which de-gases the recycled mass at the head of the circuit, allows us to meet this condition.

3. Temperature control

In the gypsum process, temperature control is fundamental; it is well known that gypsum is the stable crystalline form of calcium sulphate only below a certain limiting temperature; which moreover, falls as the P_2O_5 content of the liquid phase in equilibrium is greater.* For example, it is about $80^\circ C$ for a liquid phase containing 30% of P_2O_5 . Now, when it is desired to produce gypsum crystals easy to separate out by filtration, it is necessary to keep below this limit temperature. If a more or less concentrated acid is to be produced, the working temperature must be strictly controlled. Our evaporator facilitates this control, and offers also the considerable advantage of concentrating the liquid phase, since it evaporates about 1000 kg of water per ton of P_2O_5 treated. This quantity varies, depending on the phosphate.

4. Filtering and washing.

In producing phosphoric acid by the wet method, reaction and filtration form a limit: they are interdependent. First, the reaction provides the slurry for the filter; we have just seen how, by a judicious concept and disposition of the apparatus, a good slurry can be prepared, that is:

- well conditioned: both dense and fluid
- well stabilised: the solid and liquid phases are in physico-chemical equilibrium at a temperature at which calcium sulphate crystallises perfectly in the form of gypsum.

Therefore: good filtrability
long life of the filter tissues.

Then, the filter washing solutions are returned to the reaction. We consider that the volume and P_2O_5 concentration of these solutions are fundamental factors in the method of carrying out the phosphate decomposition.

The filter used answers perfectly to the requirement: thanks to its high vacuum and to an efficient use of the filtration surface it is capable, in three counter-current washings, of washing the gypsum cake with a recovery of more than 99%, at the same time giving a very concentrated washing solution. This performance is achieved with a flow of 5 t. of P_2O_5 per sq. metre of filtration surface/per 24 hours, corresponding almost to one ton of gypsum per sq. metre per hour. Further, all the parts of the filter have been designed taking into account the fact that the solutions cool down in the circuit under vacuum, causing the precipitation of dissolved salts: this allows the time of stoppages for cleaning to be reduced to about one hour in fifteen.

E Running the plant

This installation is intended to be run by one qualified worker with one assistant. Once normal flow is reached, it is necessary only to control the free sulphuric acid at the end of the reaction to ensure the correct proportion of reagents. All operations are continuous and automatic.

F Economics of the process

1. Cost of plant

The moderate conditions of acidity and of temperature occurring in this process and the reduced volume of the tanks and of the filtration surfaces have enabled us to build the plant fairly cheaply.

* Communication of Mr. Nordengren to the Milan Technical Reunion in October 1949.

Waggaman - Phosphoric Acid, Phosphates and Phosphatic Fertilizers. Fig. 5, p. 184

2. Cost of production.

The continuity, flexibility and automatic nature of the process make it possible to attain an economic cost, since

- labour is reduced,
- maintenance is reduced,
- almost any phosphate can be used,
- an acid rich in P_2O_5 is produced,
- a high yield is obtained.

III. COMPARISON OF RESULTS OBTAINED WITH DIFFERENT PHOSPHATES

We have drawn together into one table, for each of these three phosphates

- a typical analysis of the raw phosphate
- an average analysis of the phosphoric acid and the gypsum obtained in our plants for each phosphate rock used.

A further table gives, for each of these three phosphates, the flow of reagents and the amounts of water removed by the evaporation per ton of P_2O_5 treated.

A N A L Y S E S

	K O L A			C A S A B L A N C A			F L O R I D A		
	Phosphate (dry)	Acid	Gypsum (dried at 150°C)	Phosphate (dry)	Acid	Gypsum (dried at 150°C)	Phosphate (dry)	Acid	Gypsum (dried at 150°C)
P ₂ O ₅	39.5	31.3	1.14	34.1	32.0	1.0	34.3	32.2	1.1
CaO	50.6	0.20	39.5	51.0	0.28	39.1	49.4	0.16	39.1
SO ₃	0.05	1.57	55.8	1.77	1.40	53.2	0.90	1.90	51.4
Fe ₂ O ₃	0.60	0.40	0.08	0.26	0.26	0.05	0.90	0.90	0.12
Al ₂ O ₃	0.40	0.35	0.02	0.20	0.15	0.03	0.40	0.50	0.09
MgO	0.40	0.02		0.20	0.32	0.01	0.50	0.10	
SiO ₂	5.10	0.60	3.02	1.92	0.04	0.45	4.90	0.90	3.7
F	3.35	2.28	0.29	4.2	2.01	1.52	4.15	1.95	1.47
Na	0.16	0.02	0.10	0.92	0.09	0.56	0.86	0.03	0.45
K	0.08	0.02	0.03	0.08	0.02	0.06	0.02	0.01	0.01
CO ₂				4.1			2.62		

PHOSPHORIC ACID - Figures per ton of P₂O₅ treated.

Reagents	KOLA	CASABLANCA	FLORIDA
Phosphate	2,540 kgs	2,960 kgs	2,900 kgs
Sulphuric Acid 60 Bé	1,750 litres	1,980 litres	1,900 litres
Water of dilution	1,250 litres	1,500 litres	1,400 litres
Quantity of water evapor- ated in evaporator	850 kgs	1,010 kgs	975 kgs

The figures in this table derive from the previous one; the CaO/P₂O₅ ratio of the Kola is lower than for the other two phosphates; it is this which causes it to have a lower H₂SO₄ consumption and a smaller surplus of calories per ton of P₂O₅ treated.

The yield of phosphoric acid given by our installation can thus be calculated for the different phosphates.

- Let: A = the P₂O₅ content of the dry phosphate
 B = " CaO " " " " "
 C = " P₂O₅ " " " acid produced
 D = " CaO " " " " "
 E = " P₂O₅ " " " gypsum dried at 150°C
 F = " CaO " " " " " " "

X = the ratio $\frac{\text{weight of gypsum dried at 150}^\circ\text{C}}{\text{weight of corresponding phosphate}}$

R = the yield $\frac{\text{P}_2\text{O}_5 \text{ acid}}{\text{P}_2\text{O}_5 \text{ phosphate}}$

$$\text{Then } X = \frac{B - D \times \frac{A}{C}}{F}$$

$$R = \frac{A - (E \times X)}{A}$$

which gives:

	Kola	Casablanca	Florida
X	1.27		
R	96.2		

It appears thus that a flexible process of this kind can be adapted to quite different phosphates, to treat them under very satisfactory technical conditions, and to give a good yield:

Yield of decomposition ± 97%	} Overall yield ± 96%
Yield of filtration + 99%	

Though the results obtained are very similar, the methods used and the acid produced differ a little.

It should be noted:

1. While the Kola is a hard rock and requires a particularly careful decomposition and crystallisation, the Casa and the Florida give off an abundance of CO_2 which causes extremely troublesome frothing in the reaction tanks and produces, unless special measures are taken, gassy slurries unfavourable to the reaction and impossible to pump. This is avoided by decomposing a dense slurry and fitting the size of the tanks to this condition. It is as well to be equipped for de-frothing so as to control frothing which may occur if something accidentally goes wrong.

In changing over from the treatment of one phosphate to another, the factors mentioned earlier need to be kept in mind; it is done by a simple adaptation of the distribution of the supply of weak phosphoric acid and especially of sulphuric acid (see pages 1 and 2).

2. Importance of the fineness of grinding.

Concentrated Kola of about 39.5% of P_2O_5 is treated without further grinding. In order to treat the other phosphates with a reaction volume of $2\text{m}^3/\text{ton}$ of $\text{P}_2\text{O}_5/24$ hours, they are ground in a Peittemill, to a fineness such that 90% passes a 100 mesh A.S.T.M. sieve.

If the phosphate is coarser than this, production has to be reduced in order to obtain a unit reaction volume greater than $2\text{m}^3/\text{ton}$ of $\text{P}_2\text{O}_5/24$ hours.

On the other hand, if it is finer than this, the reaction is faster and the related phenomena more intense: rise of temperature, evolution of CO_2 , etc.

3. Crystallisation (see photomicrographs x 132.)

The crystalline form of gypsum produced is characteristic of the original phosphate used. Kola gives long crystals whose length/breadth ratio is about 4. The typical size is $160 \cdot x 40$. However, larger ones occur, together always with a small percentage of small crystals which slow up the filtration.

Casablanca gives wider, shorter crystals: length/breadth = ± 2.5 . Average size $150 \cdot x 60$. Smaller ones occur which hardly affect filtration because of their squat shape.

Florida gives crystals with an intermediate ratio: length/breadth = 3 to 3.5. They are composed of agglomerated fragments welded into a crystal of regular shape and of good filtrability.

4. The distribution, between the acid and the gypsum, of the fluorine derived from the phosphate, varies considerably with the phosphate.

Percentage of F passed into the	Kola	Casa	Florida
Acid	88	50	52
Gypsum	11	47	45

This distribution is determined by the values of the ratios SiO_2/F and Na/F in the phosphate. In fact, the precipitated F is in the form of Na_2SiF_6 .

Requirements for its precipitation are:-

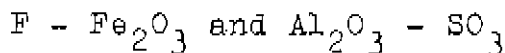
- (1) that the substances required to form it are present in the phosphate
- (2) that the slurry should attain its physico-chemical equilibrium at the temperature of filtration.

Ratios	Na ₂ SiF ₆	Kola	Casablanca	Florida
$\frac{SiO_2}{F}$	0.525	1.52	0.46	1.18
$\frac{Na}{F}$	0.403	0.048	0.22	0.206

If this table is compared with the preceding one, it may be concluded that about 90% of the Na₂SiF₆ capable of forming in the reacting mass is precipitated with the gypsum.

	Kola	Casa.	Florida
Percentage of F passed in to the gypsum	11	47	45
$\frac{Na/F \text{ of the phosphate} \times 100}{Na/F \text{ of the Na}_2SiF_6}$	12	55	51.5

5. For some purposes a fairly pure acid is needed. The main impurities present in phosphoric acid produced by the wet process are:



How are they eliminated?

F - As we have just seen, the distribution of the F between the acid and the gypsum varies greatly from one phosphate to another, according to the ratios $\frac{SiO_2}{F}$ and $\frac{Na}{F}$.

The F present in the acid produced can be precipitated by adding Na⁺ ions, which form sodium fluosilicate which can be separated by filtering. The Na₂SiF₆ can thus be precipitated in the decomposition mass itself by artificially adjusting the SiO₂/F and Na/F ratios.

Fe₂O₃ and Al₂O₃ - The amounts of these impurities are very variable, depending on the phosphates treated. Elimination may be done in various ways, depending on the use to be made of the acid.

SO₃ - Inevitable with the wet process. The content should be reduced to the minimum compatible with a good yield. It is easily precipitated by Ca⁺⁺ or Ba⁺⁺ ions. The choice of the reagent is a matter of convenience.

6. On determining the unreacted P₂O₅ in the gypsum, using the customary method (total P₂O₅ in gypsum minus water-soluble P₂O₅ determined on a 5 g sample of gypsum in suspension in 500 cc of water) a certain value will be obtained.

If, when analysing water-soluble P₂O₅, the sample receives

sufficient water to dissolve all the gypsum, at the same time a part of the P_2O_5 which is usually taken as insoluble enters into solution:

15%	in the case of	Kola
60%	" " " "	Casa
80%	" " " "	Florida

Various explanations have been put forward for this. It has been suggested

- either that the P_2O_5 is present as mono-calcium phosphate occluded on the gypsum,
- or that this P_2O_5 occurs in mixed salts of crystallization isomorphous to that of gypsum.

IV. C O N C L U S I O N S

For a long time, phosphoric acid was an expensive product whose uses were severely limited. Its production came up against serious difficulties:

- Difficulties of conditioning and handling the slurry.
- Difficulties of filtration.
- High cost of maintenance both in spare parts and labour.
- Production of a very dilute acid requiring subsequent concentration at high cost.
- Intermittent operation.

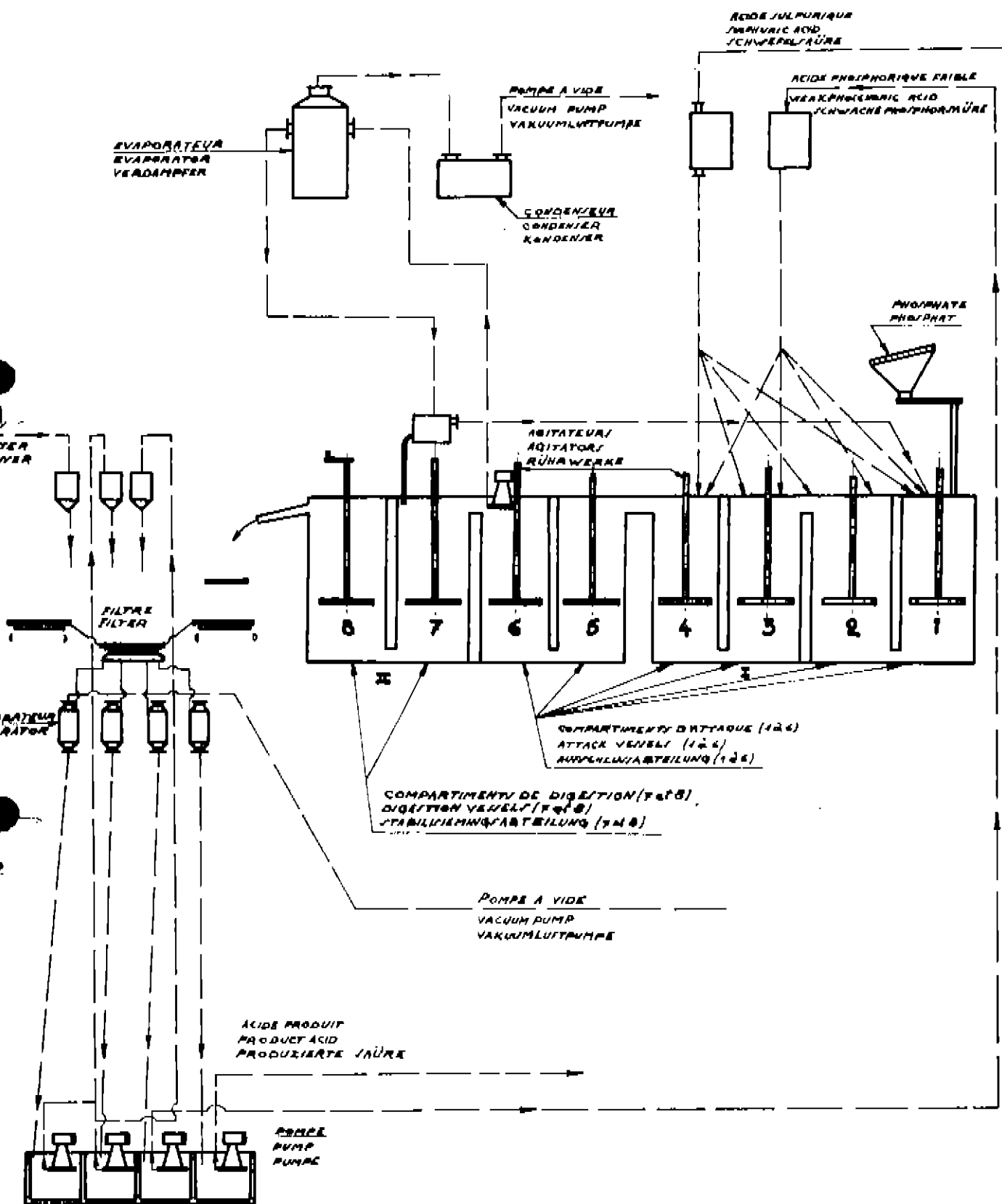
To-day this process of manufacture has made tremendous advances in the general direction of higher production at lower cost. We had only to get a clear idea of the real difficulties of the problem, then to leave the beaten tracks and boldly design equipment specially adapted for the operations envisaged, making use of the constant progress in the production of more and more resistant materials. In these conditions, it is now possible to produce a phosphoric acid containing 32% of P_2O_5 with a yield of 96%, at an economic cost, whatever the phosphates used.

It may reasonably be hoped that this process, given appropriate plant, will produce a still more concentrated acid. Up to the present one factory producing on these principles is giving an acid with more than 33% of P_2O_5 .

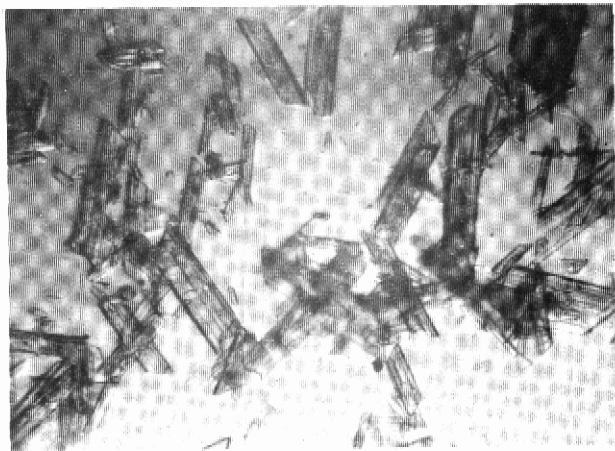
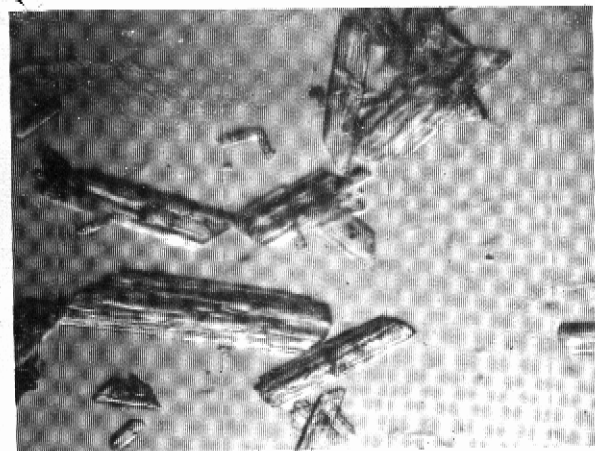
For completeness, it should be made clear that the difficulties inherent in the concentration of phosphoric acid have been overcome. It is now possible to take this acid, under very satisfactory economic conditions, up to the concentrations required for the various manufacturing processes.

Phosphoric acid, produced easily and inexpensively in large amounts, will become in the near future a basic chemical product; this is a very important fact, capable in coming years of causing powerful changes in the industries using it, notably in the fertilizer industry, where it has come at the right time now that the aim is to produce more and more concentrated fertilizers; enriched superphosphate, double superphosphate, triple superphosphate and ammoniated phosphates will be able to rely on a cheaper raw material which will open wide prospects before them.

1^{er} A. METALLURGIQUE DE PRAYON

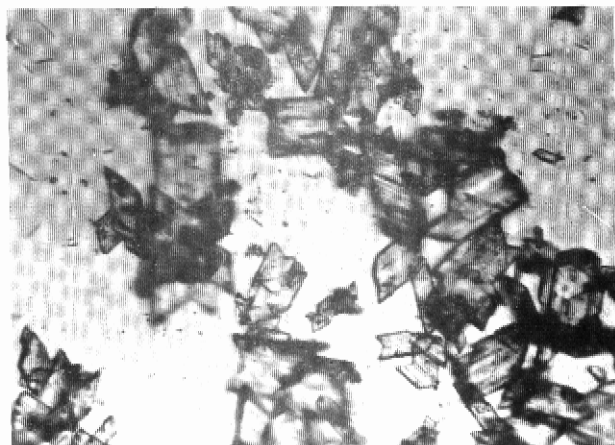
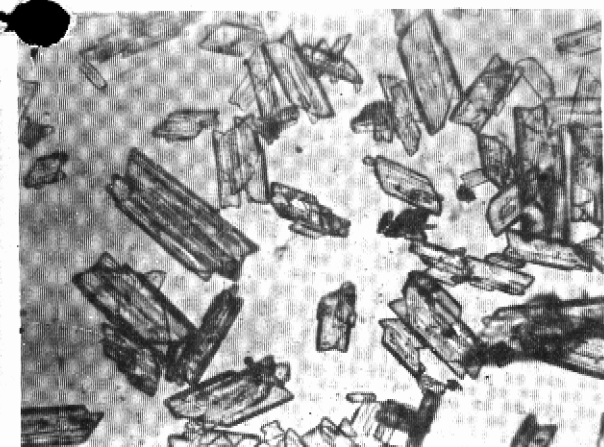


SCHEMA DE FABRICATION D'ACIDE PHOSPHORIQUE
 FLOW SHEET FOR PHOSPHORIC ACID MANUFACTURE
 SCHEMA DER PHOSPHORSÄUREFABRIKATION



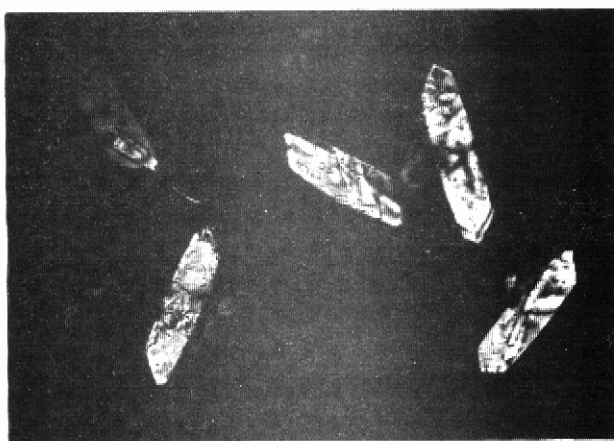
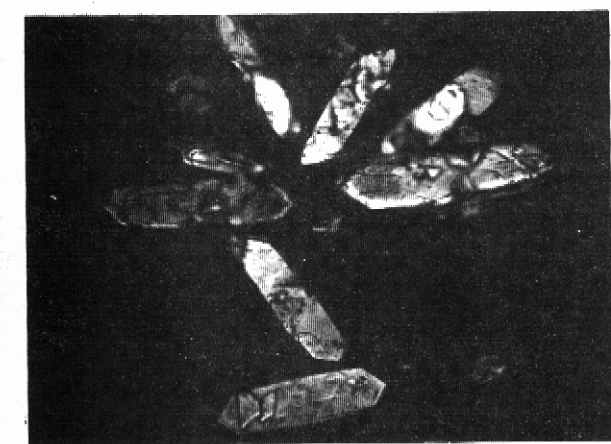
Cristaux de gypse obtenus à partir de phosphate KOLA
Crystals of gypsum from KOLA phosphate
Gypskristalle von KOLA phosphat

(132 x)



Cristaux de gypse obtenus à partir de phosphate CASABLANCA
Crystals of gypsum from CASABLANCA phosphate
Gypskristalle von CASABLANCA phosphat

(132 x)



Cristaux de gypse obtenus à partir de phosphate FLORIDE
Crystals of gypsum from FLORIDE phosphate
Gypskristalle von FLORIDE phosphat

(132 x)