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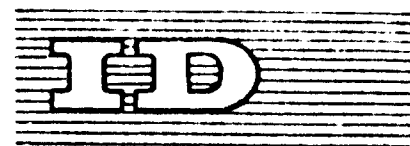
Second Interregional Fertilizer Symposium

Kiev, USSR, 21 September – 1 October 1971
New Delhi, India, 2 – 13 October 1971

Agenda item III/1i

SUMMARY

PRESENT STATE OF THE TECHNOLOGY FOR THE INDUSTRIAL

PRODUCTION OF PHOSPHORIC ACID[1]/

by

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The growing demand for mineral fertilizers throughout the world entails the development of the production of phosphoric acid, which is one of the main sources of such fertilizers in concentrated form.

Phosphoric acid can be produced in industry by the wet-process and the furnace process. Nature of these processes and differences between them, chemical and physico-chemical principles governing the production of phosphoric acid, quantity of acid produced.

Characteristics of raw materials for producing phosphoric acid by the wet-process, effect of impurities, fineness of grinding, etc. Methods of obtaining the acid by the dihydrate and hemihydrate processes, advantages and disadvantages of each; diversity of the hemihydrate process and prospects for its development.

Need to concentrate wet-process phosphoric acid and methods of doing so.

Characteristics of raw materials for producing elemental phosphorus and acid from it. Methods of obtaining furnace-process phosphoric acid by circulation and circulation

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evaporation systems.

Advantages and disadvantages of each system. Possibility of obtaining polyphosphoric acid directly from phosphorus.

Technical and economic aspects of the production of wet-process and furnace-process phosphoric acid.

Cost of raw materials and processing and production cost of the acid. Ways of reducing the cost of production.

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PRESENT STATE OF THE TECHNOLOGY FOR THE INDUSTRIAL PRODUCTION OF PHOSPHORIC ACID [1]/
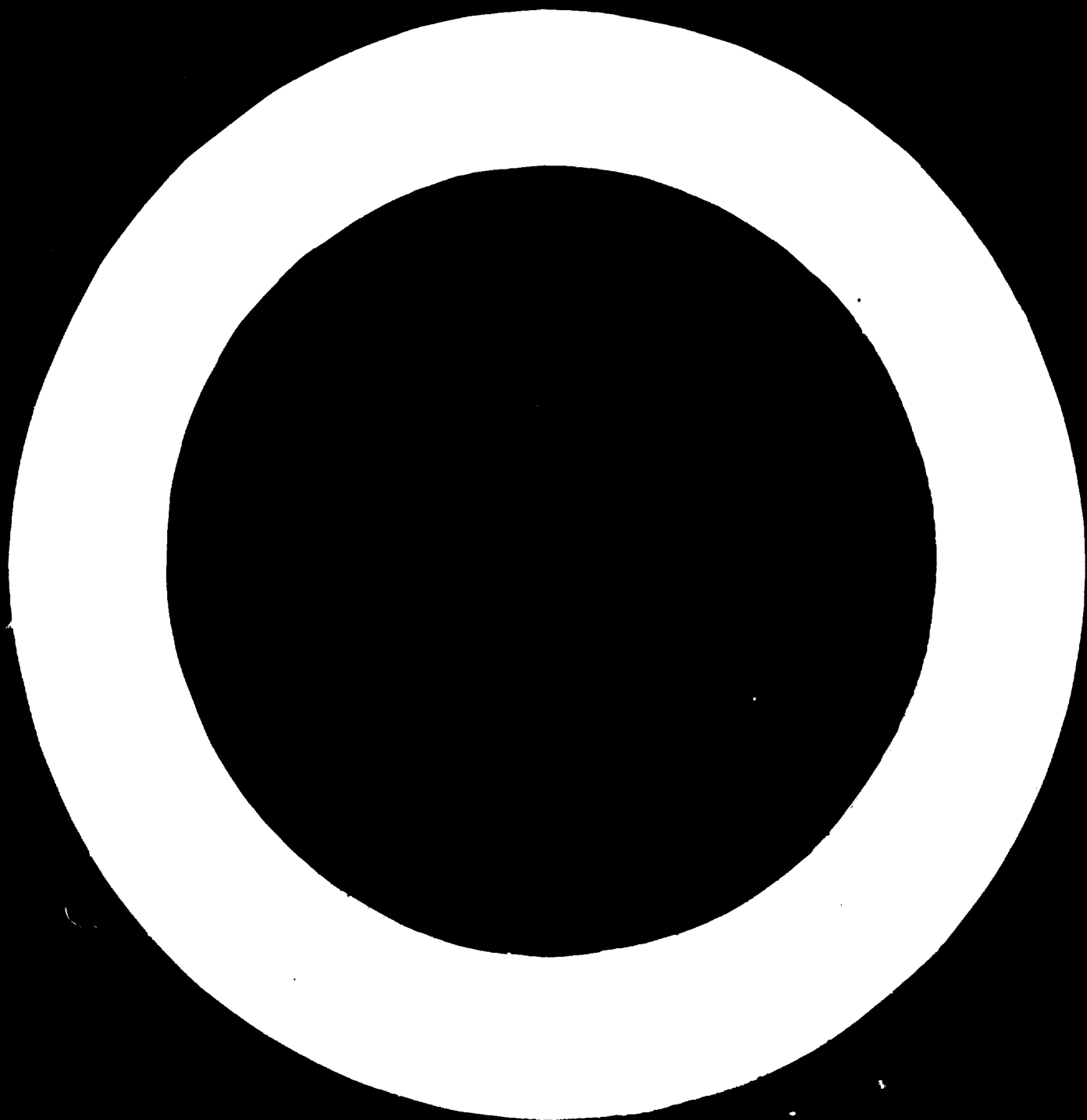
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A portion of composite and concentrated phosphoric ferti-
lizers in the world production is gradually increasing. Accor-
ding to the forecasts for the next 10-15 years ca. 85% of all
the fertilizers in this kind will be produced on the basis of
phosphoric acid (1). There are essentially two different pro-
cesses of phosphoric acid production - wet-process and thermic,
the acid produced having the coincident designation. Every
process is characterized by the method of phosphoric component
extraction from phosphate rock. In the first case it is extrac-
ted by sulphuric acid ("suphuric acid" or "wet" process), in
the second - elemental phosphorus sublimation in electrical sub-
liming furnaces followed by its oxydation and hydratation into
phosphoric acid. Differences in wet and thermic processes of
phosphoric acid production cause a sharp discrepancy in acid
quality (2) (see Table 1) and cost price, which fact will be
discussed later.

Wet-process phosphoric acid quality depends to a great
extent on the raw material composition, as phosphate rock impu-
rities pass over partly or totally into acid. The thermic pro-
cess permits to obtain high concentrated acid with low impurity
level containing 62-69% P_2O_5, from any kind of raw materials.
However, because of high electric power consumption in the
phosphoric acid production, as well as of its high commercial

Table 1

PROPERTIES OF WET-PROCESS AND THERMIC PHOSPHORIC ACID PRODUCED IN THE USSR

Raw materials	Content, %									Total impurity content % not more than
	P_2O_5	SO_3	Fe_2O_3	Al_2O_3	MgO	CaO	F	Pb	As	
Not concentrated wet-process acid										
Apatite concentrate	25–30	1,8–2,8	0,8–1,1	0,5–1,0	–	0,2–0,4	1,5–1,8	0,03	0,05	7,1
Tshulaktaus Phosphorite (main pack)	20–22	3,2–3,5	0,8	1,2	3,0–3,2	–	1,5–1,7	–	–	10,4
Concentrated wet-process acid										
Apatite concentrate	55–57	4,5	2,0	1,5	–	0,6	0,4–0,5	0,05–0,2	0,1–0,4	9,3
Tshulaktaus Phosphorite	33–35	5,0	1,9	1,9	5,0	–	–	–	–	13,8
Thermic phosphoric acid from any kind of raw materials										
Two-staged process	62–69	0,2	0,02	0,002	abs. traces	abs. traces	0,002	0,002	0,003	0,4

Table 2

Chemical composition of various phosphorite deposits in the U S S R

Deposit	Content, %							
	P_2O_5	CaO	Fe_2O_3	Al_2O_3	CO_2	MgO	F	SiO_2
Kolskij apatite concentrate	39,4	52,0	0,2	0,5-0,9	-	0,1-0,2	2,8-3,1	0,7
Kara-Tau (rich)	27,5	43,7	1,3	1,3	5,5-9,0	3,2-4,1	2,1-2,8	11-13
Kara-Tau (ordinary)	23,1	38,7	1,4	1,94	6-9,0	3,07	2,5-2,8	20,2

price, the thermic acid cost price in the USSR exceeds considerably till yet that of wet-process acid.

The phosphoric acid production growth is due both consumer demand increase and application area broadening.

On a phosphoric acid consumption scale the fertilizer industry is in the lead, the second being salt production. At present 13-15% of overall phosphoric acid delivery falls on that of thermic one.

Thermic phosphoric acid owing to high quality and low impurity level is mainly used for technical salt production, such as sodium tripolyphosphate or pyrophosphate, ammonium phosphate and others; just a small portion is consumed in the fertilizer and cattle-breeding feeding-stuff production (3).

As far as phosphoric industry is developed and phosphorus cost price is reduced, the outlined tendency will be gaining strength to produce concentrated, composite fertilizers on the basis of phosphoric acid.

Wet-process phosphoric acid is used for the fertilizer and cattle-breeding feeding-stuff production.

Nowadays phosphoric acid of elevated concentration is in great demand, consumed in the production of high-concentrated, composite as well as liquid fertilizers.

Polyphosphoric wet-process and thermic acids are obtained in the same manner as corresponding ortophosphoric acid when adding the evaporation stage if wet-process polyphosphoric acid is produced, and decreasing the water percentage on hydrating phosphoric anhydride if thermac acid is aimed.

On phosphate rock reserves the Soviet Union is among the leaders in the world. In the first line - Kolskij apatite, a

pay ore of top world quality. Apatite flotation concentrate is characterized by a high P_2O_5 content (39,4%), minimum $CaO:P_2O_5$ (1,31) ratio, low impurity level, high enrichment factor for primary rock (4) and so on. The very apatite properties are at the bottom of the fact that in the USSR a main portion of wet-process phosphoric acid is produced from apatite concentrate. Major phosphorite reserves are in the South Kazakhstan (Kara-Tau) and in the Estonia. These phosphorites have similar chemical composition, but in contrast to apatite, a higher impurity level, mainly magnesium carbonate and minerals containing iron and aluminium.

Table 2 represents the chemical composition of some commercial phosphorites (3).

Soviet scientists have made a considerable contribution to the development of the foundation of wet-process phosphoric acid production. In works of Soviet scientists (4,5,6,7) the phosphorite and apatite decomposition kinetics, calcium sulphate crystallisation, impurity effect on these processes and a great deal of other questions were elucidated in detail. In the publications mentioned were shown, that whereas the apatite concentrate reprocessing does not offer any essential difficulties, the $MgO : P_2O_5$ ratio does not exceed 8-10% and the $Re_2O_3 : P_2O_5$ ratio amounts to 10-12% (4).
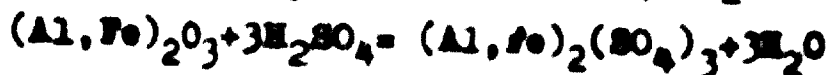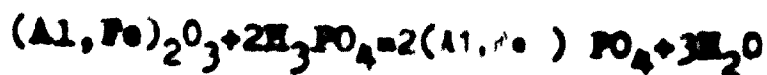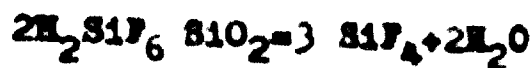
Flow diagrams for the apatite and phosphorite reprocessing are identical, the difference concerning processing parameters only.

Basic processing steps are: reagent dosage, phosphate raw material decomposition in extractors, calcium sulphate

crystallization, extraction slurry separation by filtration followed by countercurrent washing off calcium sulphate on filters and gas cleaning to eliminate fluorine.

The necessity to follow such an order of processing steps is dictated by the mechanism of reactions between phosphorite and sulphuric acid represented in Fig.1.

Fig. 1. Reactions between apatite and sulphuric acid.

$$Ca_5(PO_4)_3 + 5H_2SO_4 + H_2O = 3H_3PO_4 + 5(CaSO_4 . 2H_2O) + HF$$

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O$$

$$2H_2SiF_6 + SiO_2 = 3 SiF_4 + 2H_2O$$

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2$$

$$MgCO_3 + H_3PO_4 = MgHPO_4 + H_2O + CO_2$$

$$(Al,Fe)_2O_3 + 2H_3PO_4 = 2(Al,Fe)PO_4 + 3H_2O$$

$$(Al,Fe)_2O_3 + 3H_2SO_4 = (Al,Fe)_2(SO_4)_3 + 3H_2O$$

Impurities present in phosphorites react with sulphuric acid or phosphoric acid formed hindering extraction and impair its quality.

Actually the phosphate rock decomposition is carried out by a mixture of phosphoric and sulphuric acids. Relatively low-dissociated phosphoric acid goes over into the solution, calcium sulphate being precipitated. The impurity decomposition proceeds simultaneously with that of the basic material.

Detail investigation of the mechanism and decomposition kinetics fulfilled by the Soviet scientists (Voskresenski, Bruskus, Posin, Ionass and others) on pure products and phosphorites of different deposits have permitted to find regularities in decomposition processes, the most principal being as following:

1. Flotation apatite decomposition proceeds much slower than that of phosphorite.

2. Decomposition rate for both kinds of raw materials is the highest at the initial stage of decomposition, but phosphorite decomposition rate gradient exceeds significantly that of apatite.

3. Temperature effect on the apatite decomposition is much more indicative as compared to that for phosphorite. Phosphorites, e.g., undergo the essentially complete decomposition during a period of 1,5-2 hours at 20-30°C while in the case of apatite the temperature 70-80°C is needed to maintain the same decomposition period. The effect of sesquioxides, especially that of iron, on phosphorite decomposition and phosphoric acid composition has also been studied. Minerals, containing iron and aluminium, are lightly decomposable by acids. Ferric phosphates are precipitated because of low solubility in phosphoric acid, what results in a decrease in the P_2O_5 extraction into solution. Iron and aluminium remaining in solution impair the phosphoric acid quality, when reducing its activity as a consequence of the partial neutralisation of the first hydrogen ion. In addition, fertilisers produced from such an acid contain a marked part of P_2O_5 in the water insoluble and little assimilable form. It is unsuitable, therefore, the phosphate rock reprocessing, when the iron oxides: P_2O_5 ratio exceeds 8-10%, as it was mentioned above.

The phosphate rock decomposition was noted to result in formating the calcium sulphate precipitate being low-soluble under these conditions.

Calcium sulphate is known to exist in three crystalline

modifications: hypsum $(CaSO_4 \cdot 2H_2O)$, semihydrate $(CASO_4 \cdot 0,5H_2O)$, anhydrite $(CaSO_4)$. The calcium sulphate crystalline hydrate solubility in phosphoric acid solutions was studied by Belopolski, Tapero, Shulgina, Voskresenski and others (4,5,6).

Investigation of mutual transformations of calcium crystalline, hydrates as temperature and concentration functions showed, that:

1. At isothermic equilibrium in the system $CaO-SO_3-P_2O_5-H_2O$, at $80^{\circ}C$, over the concentration interval of 0-60% P_2O_5 the stable form is anhydrite. Semihydrate and hypsum are metastable under these conditions.

2. Over the concentration interval of 0-33% P_2O_5 hypsum is more stable than semihydrate. At the P_2O_5 concentration higher than 33% semihydrate is the most stable modification.

When the temperature is decreased to $60^{\circ}C$, the regularities remain to be unchanged as relative to those at $80^{\circ}C$, but the equal solubility point for hypsum and semihydrate corresponds to the 40,9% P_2O_5.

In Fig. 2 polyterms are represented for mutual transformations of calcium sulphate crystalline modifications in phosphoric acid solutions.

At a constant temperature the transition rate of semihydrate into hypsum is reversely proportional to P_2O_5 concentration. The transition rate of semihydrate into anhydrite becomes appreciable just at elevated concentrations and temperatures. The diagrams make it possible to predict (for pure solutions) the conditions of dehydrate, semihydrate and anhydrite processes.

It is seen from the diagram, e.g., that when the reactor residence time for phosphorite is 8 hours at $80^{\circ}C$, the maximum

P_2O_5 concentration, at which the semihydrate recrystallization into hypsum achieves the completeness, amounts to 25-26%. The process will proceed as a dehydrative one. If the acid concentration is 30% or more under the same conditions, the semihydrate first precipitated will not be able to further hydratation because of its low transition rate and will precipitate as a solid phase on filter, the process being semihydrative. Further hydrating calcium sulphate into hypsum would be required 13-14 hours in lieu of 8.

The production of phosphoric acid containing 27-28% P_2O_5 would proceed under the most unsuitable conditions. In this case the period of semihydrate recrystallization into hypsum exceeds somewhat the phosphorite residence time in the reactor, so that the recrystallization may complete on filters, in pipelines and communications resulted in the obstruction thereof with solid hypsum precipitations and in process ceasing.

As one may conclude from the findings above, the knowledge of transition rates for transformation of semihydrate into hypsum and that of its temperature dependence is of great importance, especially by the present of impurities, contained always in phosphate raw materials.

Investigations along these lines have shown, that impurities do not influence the crystallization sequence of calcium sulphate modifications, but at the same time they cause the changes (sometimes considerable) in transformation rates. For example, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+} ions retard the transformation of semihydrate into hypsum and anhydrite (?).

The effect of free sulphuric acid concentration on transformation rate for different calcium sulphate modifications in

phosphoric acid solutions is shown in Fig.3.

As it follows from this Figure, an increase in the free sulphuric acid concentration results in a decrease in the P_2O_5 concentration and temperature, at which hypsum transforms into semihydrate. The transition rate for the transformation into hypsum is vigorously affected by the presence of crystalline hypsum priming, which eliminates the crystallisation induction period and enhances the recrystallization rate. Under these conditions the dehydrative process ($CaSO_4.2H_2O$) is possible to be carried out at 70-75°C while obtaining wet-process phosphoric acid, containing 32% P_2O_5.

The mechanism of the impurity effect on the phase transitions is not yet quite clear.

The completeness of the P_2O_5 extraction from phosphorite into solution, as well as the filtration apparatus operating conditions are strongly affected by the crystall kind, their size and filtration properties relative to mother liquors and production solutions.

The larger hypsum crystalls are, the more lightly extraction is carried out and highest yields of phosphoric acid are attained.

Crystallization is provisionally to divide into 3 stages, followed by each other.

The first stage is a period of latent crystallization (induction period), when crystall seeds are formed; the second one is a period of prompt crystallization, during which the solute concentration drops sharply; the third is a period of elimination of remanent oversaturation, when the solute concen-

tration is slowly decreased approaching the equilibrium one. This is graphically illustrated by the diagram in Fig.4, the curves being plotted in coordinates "solubility - temperature". The lower curve shows the solubility variation, the upper - a conditional boundary line of oversaturated solution, over this line the crystallization starting instanteneously.

It is obvious, that to obtain large crystalls with minimum surface area the crystallization has to be carried out under the conditions of some oversaturation and at relatively low rate. The vigorous slurry agitation is necessary to eliminate local oversaturations in the apparatus. In order to grow good crystalls under the operating conditions the crystallization is carried out with some excess of sulphuric acid.

Crystall shape and size are affected by impurities present in the solution, in the first line those of F^- and Al^{3+} (8), but this question is not quite clear.

The P_2O_5 amount passing over from rock into acid is one of the processing efficiency criteria. The deviations in the amount are caused by the P_2O_5 losses with solid phase.

Three kinds of P_2O_5 losses with solid phase are distinguishable. The first kind includes losses with undecomposed starting phosphorite (calcium fluorine apatite), depending on the grist fineness, decomposition duration and suphuric acid excess in the slurry liquid phase. The values amounts generally to 0,1-0,2% P_2O_5.

The second is connected with uncomplete phosphogypsum washing on filter, the value depending on the crystall character, filtration effectivity, filtration surface area and washing water consumption.

The third involves losses arised from the P_2O_5 coprecipitation or with calcium sulphate crystalls due to the isomorphic substitution of SO_4^{2-} ions by $H_2PO_4^{-}$ ions because of the proximity of their ionic radii.

At present the majority of wet-process phosphoric acid is produced by the dehydrative process. Multiple-stirring extractors of large capacity 1400-800 m^3 are used; the phases are separated on vacuum- filters of different designs with active filtration surface area of dozens square meters. As a rule, phosphoric acid with 30-32% P_2O_5 is obtained. The process is carried out at 70-80°C, followed by slurry cooling in a vacuum-evaporator or by air purging over the slurry surface in the extractor. The dehydrative process flow diagram for the wet-process phosphoric acid production is shown in Fig. 5.

In the Soviet Union standard units on wet-process phosphoric acid production are those of operating efficiency of 110 or 55 t/year. They are provided with extractors with effective volume of 740 and 400 m^3 and turret- type vacuum - filters with effective filtration surface area of 80 and 40 sq.m., relatively.

Operating characteristics of some Soviet plants, reprocessing apatite concentrate (39,4% P_2O_5), are represented in Table 3.

Table 3

Main processing parameters for wet-process
phosphoric acid production

Phosphoric acid concentration (P_2O_5)	30-32%
Apatite concentrate decomposition, %	98
Acid washing off effectivity on filters,%	98-99
P_2O_5 processing yields, %	96

Productivity, kg P_2O_5 /hour per m^3 of reactor volume   20

P_2O_5 consumption in phosphorite per t of P_2O_5 in

                     acid, t   1,04

Sulphuric acid consumption per t of P_2O_5

                    in acid, t   2,41

SO_3 content in acid, %   2,5

F content as fluorine acids, %   1,7-1,9

Kara-Tau phosphorites reprocessing results in a P_2O_5 decrease in the acid by 2-3% and an increase in the sulphuric acid consumption by 20%. This starting material, however, is cheaper and, while taking into account high P_2O_5 content (28% and more), Kara-Tau phosphorite reprocessing is advisable from the economical point of view.

As advantages of the dehydrative process should be mentioned:

1. A rather full knowledge on the mechanism, what permits flexible process running and adjusting against new types of raw materials.

2. Favorable heat conditions (at temperatures as low as 70-80°C) make it possible to select corrosion resistant materials for the apparatus.

3. Dehydrative process admits some fluctuations of the processing parameters without disrupting essentially operating conditions.

As disadvantages one should note:

1. Low acid concentration, so that the additional concentration by evaporation is sometimes required.

2. Low phosphogypsum output per 1 m^2 of filtration surface area. Last years the investigations were intensified in a number

of countries concerning the concentrated wet-process phosphoric acid production (40-50%) without evaporating on the method of calcium sulphate crystallization in the forms of semihydrate and anhydrite. The anhydrite process has not lied outside experimental works, while the semihydrative one is already operated on a large commercial scale. In the field of the semihydrate production a lot of theoretical works have been published, devoted to comprehensive studying the conditions of semihydrate existence, the mechanism of semihydrate stabilization and so on.

Three groups of semihydrate processes of phosphoric acid production are known:

1. Initial semihydrate crystallization and its recrystallization into dehydrate before filtration.

2. Initial dehydrate crystallization followed by its recrystallization into semihydrate.

3. Semihydrative processes.

The first two of these have not evolved in the Soviet Union.

Recently in the Soviet Lnion the process was developed for the production of wet-process phosphoric acid, containing 43-48% P_2O_5 from apatite concentrate and Kara-Tau phosphorites when using dehydrative process equipment in a direct semihydrative variant. The characteristic features of the process are: 1) method of semihydrate stabilization; 2) transformation more than 50% of F introduced with starting materials into fluorsilicic acid.

In this process the precipitate amount enhances up to 1600 kg/m^2 of filtration surface area, instead of 600-700 kg/m^2 in the dehydrative one.

The replacement of processing conditions on operating units from dihydrative to semihydrative makes it possible to increase the acid concentration and productivity by 25-30%. On building new units the capital costs are reduced by 40%, the phosphoric acid cost price is decreased by 13-15% and the operating efficiency is increased. Per 1 t P_2O_5 one may produce 50 kg 100% H_2SiF_6; the consumption of steam, electric power and water is diminished by 15, 55 and 85%, relatively. Thereby the productive capacity is increased by a factor of 1,5, specific filtration efficiency - by a factor of 1,6 - 1,9.

To obtain concentrated wet-process phosphoric acid (50-53% P_2O_5) extractors are used, operating under vacuum or atmospheric conditions. The most widespread apparatus is that of bubbling type. In the Soviet Union bubblers are developed permitting relatively easy and with minimal expenses to concentrate wet-process phosphoric acid from 22-23 to 54-57% P_2O_5. In Fig.6 a bubbler design is shown to concentrate wet-process phosphoric acid.

In a bubbler with the useful capacity of 3 m^3 it is possible to reproduce up to 1300 kg/hour of phosphoric acid, while evaporating up to 300 kg/hour of water (calculated on I m^3 of apparatus volume) or up to 450 kg/hour (calculated on 1 m^2 of evaporation table). Flue gas temperature is usually maintained about 1000°C, specific heat consumption for evaporation amounts to 850-970 kcal/kg of water.

Other evaporator types are not considered because of their constructive similarity or of low occurrence (vacuum apparatus).

The Soviet and foreign scientists have made an appreciable contribution to the theory of phosphorus oxidation by oxygen and

subsequent anhydride hydratation by water (11,12,13,14,15).

Phosphorus oxidation by atmospheric oxygen is a typical chain reaction. The overall equation is derived as it follows:

$$P_4 + 5\ O_2 = P_{.}\ O_{10}$$
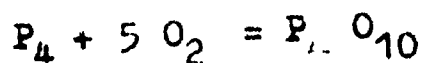
Virtually the reaction above is a multi-staged one, which does not go to compleness under some conditions, resulted in the formation, along with P_2O_5, lower phosphoric oxides. The yellow phosphorus oxidation by atmospheric oxygen was extensively studied in the Soviet Union by Postnikov et al. They showed that for obtaining the maximum of phosphorus oxidation as P_2O_5 anhydride the optimal processing parameters were phosphorus combustion temperature - at least $600^{\circ}C$, air excess by the oxidation - at least 25%, reagent contacting time - 2-3 sec. Phosphorus oxidation is the first stage of the phosphoric acid production.

It is known, that lower phosphoric oxide percentage in combustion products (oxidation products) is decreased as the temperature of phosphorus-oxyged reaction is increased.

Fig. 7 represents basic calculated coefficients for the phosphorus combustion (gas content, P_2O_5 percentage therein, theoretical temperature etc.)

The phosphoric anhydride, the main product formed on phosphorus combusting, is the second stage of thermic phosphoric acid production.

The products of the multi-staged phosphoric anhydride hydratation are:

1. Metaphosphoric acid $P_2O_5 + H_2O = 2HPO_3$

2. Pyrophosphoric acid $P_2O_5 + 2H_2O = H_4P_2O_7$

3. Ortophosphoric acid $P_2O_5 + 3H_2O = 2H_3PO_4$

Conversely,   pyro- and metaphosphoric acids are obtained from
heating ortophosphoric acid which is dehydrating thereby.

The phosphoric acid formation through other phosphoric
oxide hydratation (such as P_2O_3 etc.) is not discussed here, for
their yields are low at high temperatures of phosphorus oxidation.

Thus, composition and concentration of phosphoric acids
depened on temperature and partial water pressure. Much emphasis
has been placed on the question of phosphorus oxidation and an-
hydride hydratation (16,17).

The phosphoric acid hydratation occurs on the mechanism
above when its absorption takes place by acid (water) or phospho-
ric anhydride vapors react with steam. In the last case phospho-
ric acid vapors formed are absorbed by an absorbent present (18).
In Fig. 8 and 9 absorption degree is plotted vs. gas and acid
temperature, density and acid concentration for the absorption
of phosphoric anhydride from vapors.

Phospheric anhydride and acid vapor absorption is seen
to increase sharply with recycle acid concentration, spray
density and temperature. If anhydride is absorbed by water, the
absorption degree is decreased to 30%. When phosphoric anhydride
is absorbed by water or acid the phosphoric acid fog is formed
in some regions of the absorption zone in the apparatus, entrai-
ned poorly because of its high dispersion degree. The latter
proved to be adjustable by air supply to phosphorus oxidation.
To enlarge fog drops, the phosphorus combustion should be car-
ried out with a minimum air excess.

A most suitable apparatus for the phosphoric acid fog
entrainment are electrostatic precipitators.

The investigations above have laid the foundation of thermic acid production on a commercial large-scale based on the scheme of elemental phosphorus oxidation with atmospheric oxygen followed by hydrating phosphoric anhydride formed by acid (water) and trapping the latter in liquid and "fog" form in the appropriate apparatus.

Some other processes have been developed in which phosphoric acid is produced on combustion of phosphoric gases formed in phosphoric or blast furnaces, by the phosphorus oxidation with steam or water etc. However, by different reasons they have not received much recognition. On this account we omit the description of these processes.

The development in the thermic phosphoric acid production has been started on a large-scale actually simultaneously in a number of countries.

At present there exists a number of commercially realised flow sheets for the thermic phosphoric acid production. The gas may be cooled by water evaporating, injected into hot gases, by heat transfer to acid circulated inside the apparatus, followed by its cooling, by cold air admixing etc.

On the method of gas cooling phosphoric acid systems may be divided into three groups:

1. Evaporation systems in which gas is cooled via water evaporation.

2. Circulation systems in which gas is cooled by means of acid circulation inside the apparatus.

3. Heat exchange type systems where heat is eliminated through the wall by circulated water.

4. Combined systems.

The evaporation system is exemplified by the flow diagram in Fig. 10.

According to this scheme phosphorus is supplied on a heated pipeline to a burner and combusted in a chamber. Oxidation products formed enter a hydratation tower through vertical and horizontal gas conduits, in the tower a part of acid being concentrated, and then pass to an electrostatic precipitator to be separated finally from gases.

Gas inlet temperature in the hydratation tower amounts to $850-900^\circ C$, in the electrostatic precipitator - $180-200^\circ C$. 30% of acid is produced in the tower, the remaining - in the electrostatic precipitators. Acid concentration - 60% P_2O_5. There are similar systems with preliminary phosphorus sublimation and that operating under pressure.

The circulation systems are now of most commonly usage, one of them being represented in Fig. 11.

As it is seen from this Figure, heat elimination liberated on phosphoru combustion, and phosphoric anhydride absorption are carried out simultaneously by water running down the inner walls of the phosphoric acid reactor. The latter is cooled in an exterior cooler and recycled. Phosphorus combustion and gas cooling proceed in the same apparatus. 75% of phosphoric acid is produced in the tower, 25% - in the electrostatic precipitator, where the gases are finally purified. Final acid concentration 70-35% H_3PO_4.

Consumption coefficients per 1 t of 100% H_3PO_4

Yellow phosphorus, t	0,33-0,34
Water , m^3	200
Electric power, kw-hour	65,5

compressed air, m^3 370

spray acid, m^3 150

As a disadvantage of the system, first of all, the necessity should be noted to use the phosphoric acid circulation for cooling. On domestic plants spray coolers were replaced by that of higher operating efficiency - shall-and-tube and plate coolers, the burner number was decreased in the combustion chamber. In some systems Venturi tubes were employed for gas purification from phosphoric acid instead of electrostatic precipitators, what was resulted in a considerable decrease in capital costs.

In the Soviet Union the combined domestic systems have gained wide distribution of the thermic phosphoric acid production developed in the "Scientific Institute of Fertilizers and Insecticides and Fungicides - SIFIF" and "Scientific Research State Institute of Projection in Chemical Industry (Leningrad)".

Such a circulation-evaporation system is shown in Fig.12.

Principal elements are two towers in the first one phosphorus is combusted, in the second-phosphoric anhydride formed and reaction heat are absorbed by acid spraying the inner walls of the tower (on the circulation scheme above). In the second tower the remaining P_2O_5 and after-heat are absorbed by acid injected into it.

A further evaporation-heat exchange system is developed and building up ("SIFIF"), in which acid production is carried out in the steel apparatus with water jackets (Fig. 13).

In such a system one succeeds in the production of both orto- and polyphosphoric acid (up to 110% H_3PO_4). A combustion reactor is made up from special steel and provided with a water jacket to eliminate the phosphorus combustion heat. The second

tower is provided for hydrating by injected water.

The calculations showed, that in the combustion chamber it is possible to eliminate up to 40% of heat liberated in the course of phosphorus combustion. Building expenses are reduced in this case by 30-40% as compared to conventional systems with lined towers.

Operating experience and technical-economical calculations have led to the conclusion, that for systems with operative capacity of 200 kg/hour (calculated on phosphorus combusted) flow sheets, based on the evaporation processes, are preferable, while for enlarged units (more than 200 kg phosphorus combustion per hour) circulation systems are recommended. A combined variant (circulation with evaporation or evaporation with heat exchange) is the most suitable in the case of units of high operating efficiency (3-5 t of phosphorus combustion per hour).

Thermic polyphosphoric acid is usually produced when using a circulation flow sheet and polyphosphoric acid as a sorbent of phosphoric anhydride, which is fed into the combustion chamber to the inner walls thereof.

In Fig. 14 the flow diagram is represented (SIFIF - process) for the polyphosphoric acid production.

The system is provided with a chamber where phosphorus is combusted under highly intensified conditions. Polyphosphoric acid produced contains up to 86% P_2O_5. Polyphosphoric acid supplied for spraying into the cooling- hydrating tower is cooled ir plate coolers. The technical-economical calculations on estimating the cost price of various processes of the wet-process and thermic phosphoric acids production based on flow sheets and raw materials employed in the Soviet Union have revealed an appreciable diffe-

rence of each other.

The cost price of 1 t P_2O_5 in wet-process phosphoric acid produced from apatite concentrate (39,4% P_2O_5) is estimated as high as 120-150 rubles, from Kara-Tau phosphorites (28% P_2O_5) - 150- 170 rubles.

The cost price of 1 t P_2O_5 in thermic phosphoric acid produced from Kara-Tau poor phosphorites (24% P_2O_5) is ca. 300 rubles.

In both cases the cost of starting material reprocessing amounts to about 20% of the total production costs.

As it was noted by us earlier, a considerable rise in price for thermic phosphoric acid in comparison with that of wet-process one arises from the high electric power consumption and its high commercial price.

Cutting down the prices on electric power by a factor of two, the cost price differences will be negligible and thermic phosphorus acid shall find application in the field of production of high-concentrated and top-quality fertilizers.

In this short communication we were able to outline just main landmarks of the recent development in the phosphoric acid production. From a wide variety of flow sheets for the wet-process and thermic acid production we have chosen those of great commercial importance and possessed by characteristic features of all the process types. We have also attempted to view briefly the foundations of physico-chemical processes allowed to realize the production of phosphoric and polyphosphoric acids on a commercial scale and to contemplate the ways of its perfecting.

While chhosing a flow sheet variant one should take into

account as a main factor starting material (phosphorite, apatite) properties as well as acid potential application areas.
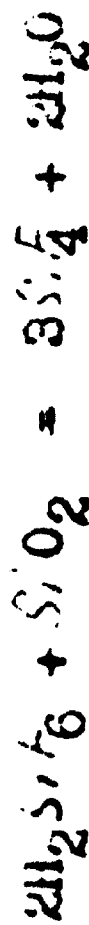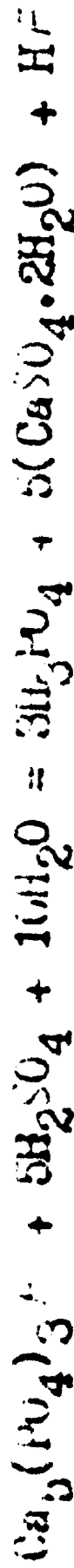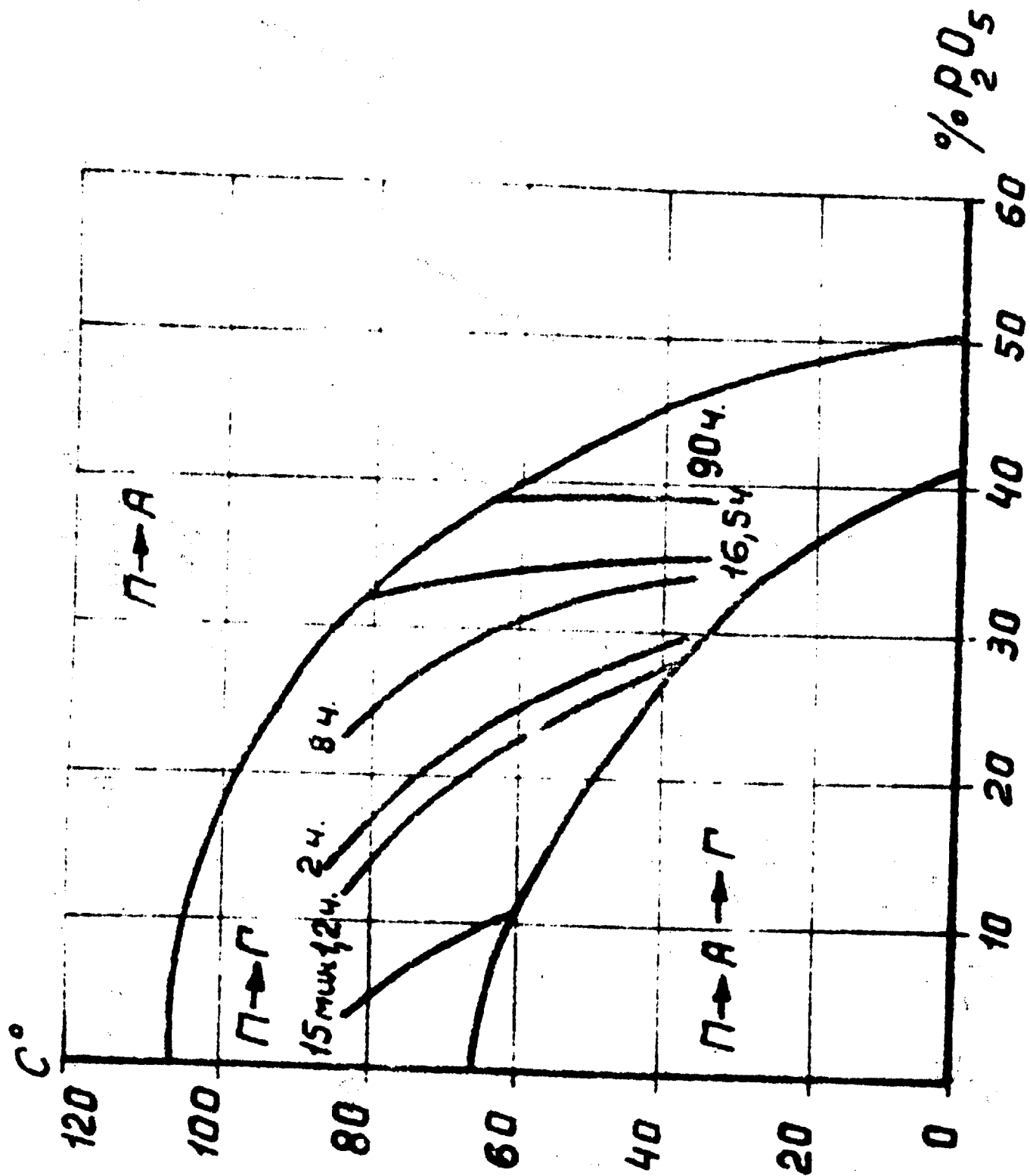
Рис 1.

-24-

Реакции взаимодействия апатита

с серной кислотой

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O = 3H_3PO_4 + 5(CaSO_4·2H_2O) + HF$$

$$CaF + SiO_2 = H_2SiF_6 + 2H_2O$$

$$2H_2SiF_6 + SiO_2 = 3SiF_4 + 2H_2O$$

$$M_2CO_3 + H_2SO_4 = M_2SO_4 + H_2O + CO_2$$

$$M_2CO_3 + H_3PO_4 = M_2HPO_4 + H_2O + CO_2$$

$$(Al,Fe)_2O_3 + 2H_3PO_4 = 2(Al,Fe)PO_4 + 3H_2O$$

$$(Al,Fe)_2O_3 + 3H_2SO_4 = (Al,Fe)_2(SO_4)_3 + 3H_2O$$

Рис 2

C°

120
100
80
60
40
20
0

П → А

П → Г

П → А → Г

90ч.

16,5ч.

8 ч.

2 ч.

15 мин. 1 ч.

% P$_2$O$_5$

0 10 20 30 40 50 60

Рис 3.
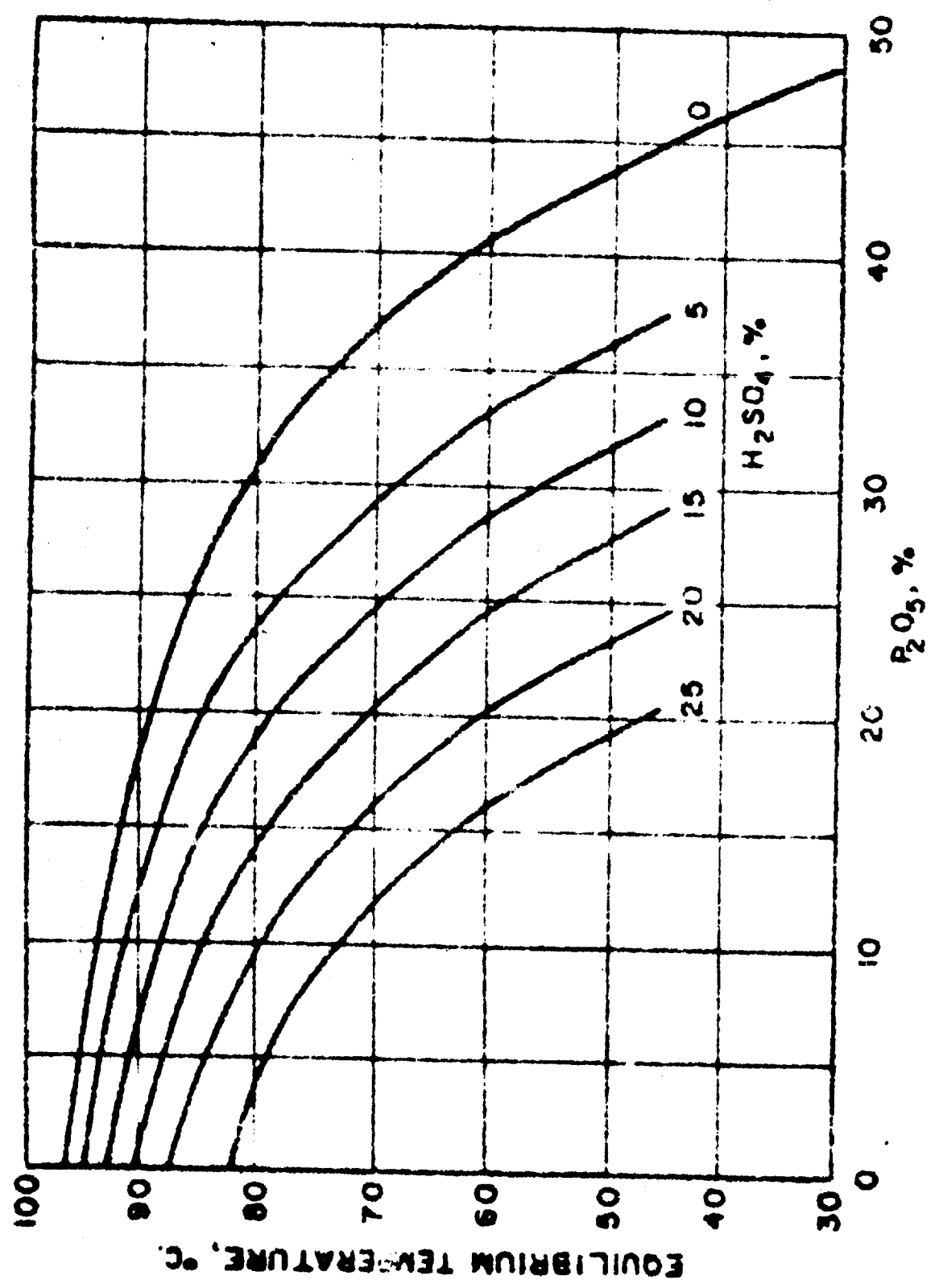
The metastable equilibrium dihydrate–α–hemihydrate* in phosphoric acid-
sulfuric acid solutions. [From Ikeno et al. (10).]

Рис 4

Растворимость L

Область лабильных растворов

B

A

Область метастабильных растворов

B

A

Область ненасыщенных растворов

L_2

L_1

0

T

$T_c^\bullet$

Рис 5
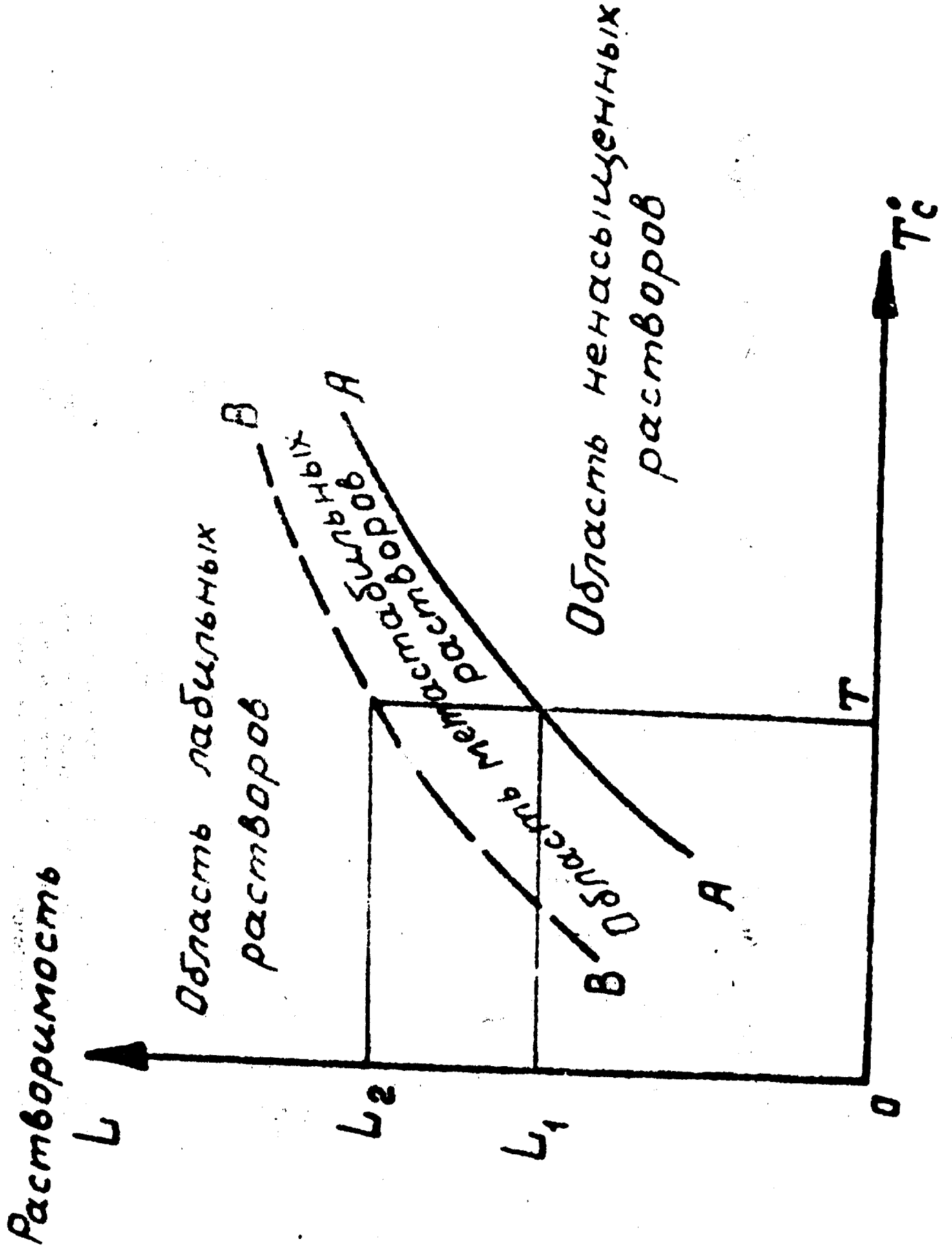
ТЕХНОЛОГИЧЕСКАЯ СХЕМА ПРОИЗВОДСТВА
ЭКСТРАКЦИОННОЙ ФОСФОРНОЙ КИСЛОТЫ ПО ДИГИДРАТНОМУ ПРОЦЕССУ
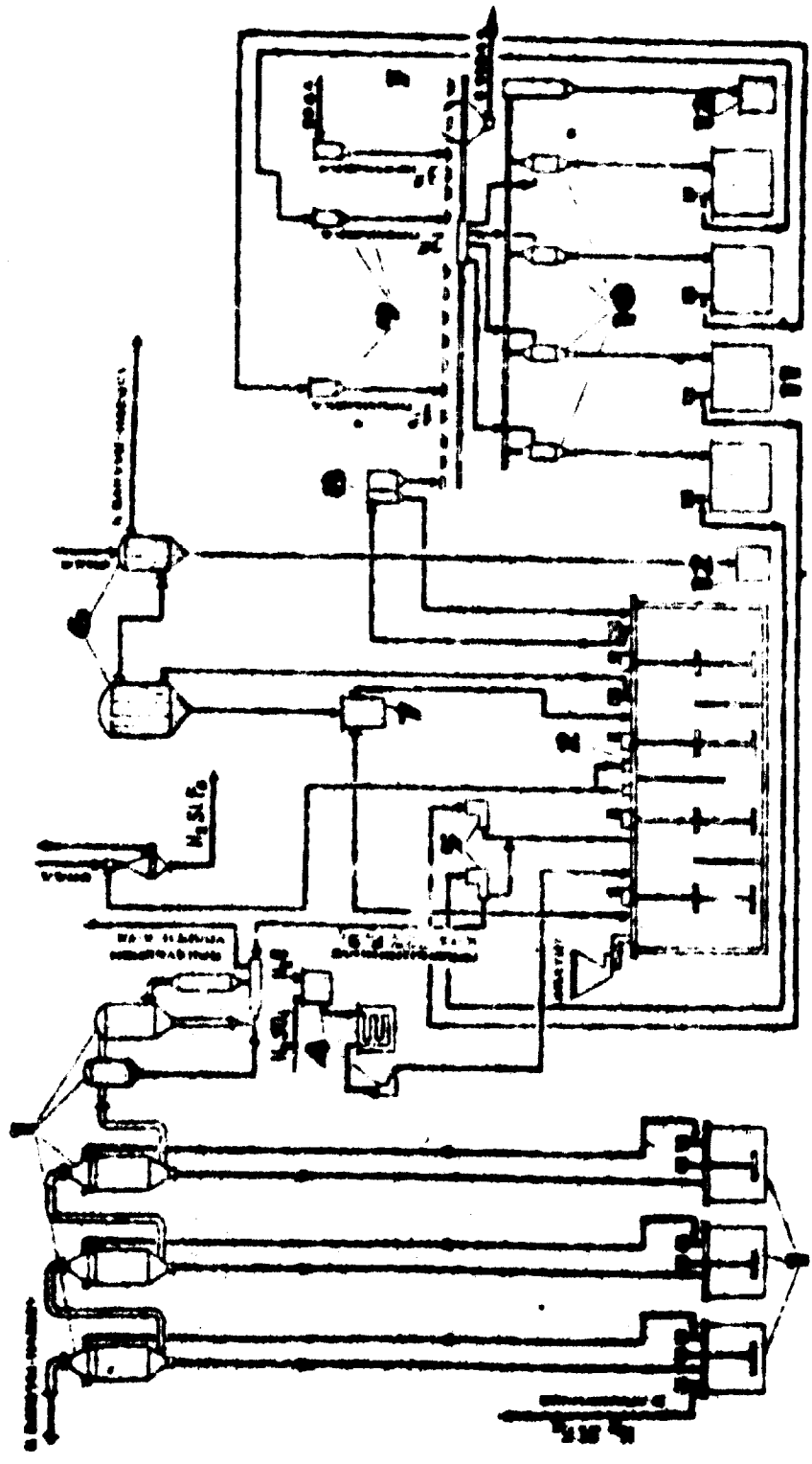
H_2SiF_6

Таблица № 3

Основные технологические показатели работы заводов
экстракционной фосфорной кислоты

Концентрация фосфорной кислоты (P_2O_5)	-	30-32%
Разложение апатитового концентрата,(%)	-	98
Отмывка осадка от кислоты на фильтрах,(%)	-	98-99
Технологический выход P_2O_5, (%)	-	96
Съем P_2O_5 с $м^3$ реактора , (кг/час)	-	20
Съем P_2O_5 с $м^2$ поверхности фильтра, (кг/час)	-	200
Расход P_2O_5 в фосфорите на 1 т. P_2O_5 в кислоте, (т/т)	-	1,04
Расход серной кислоты на 1 т P_2O_5 в кислоте, (т/т)	-	2,41
Содержание SO_3 в кислоте , (%)	-	не выше 2,5
Содержание F в виде фтористых кислот,(%)	-	1,7-1,9

Рис 6

Рис. Эжекторой аппарат
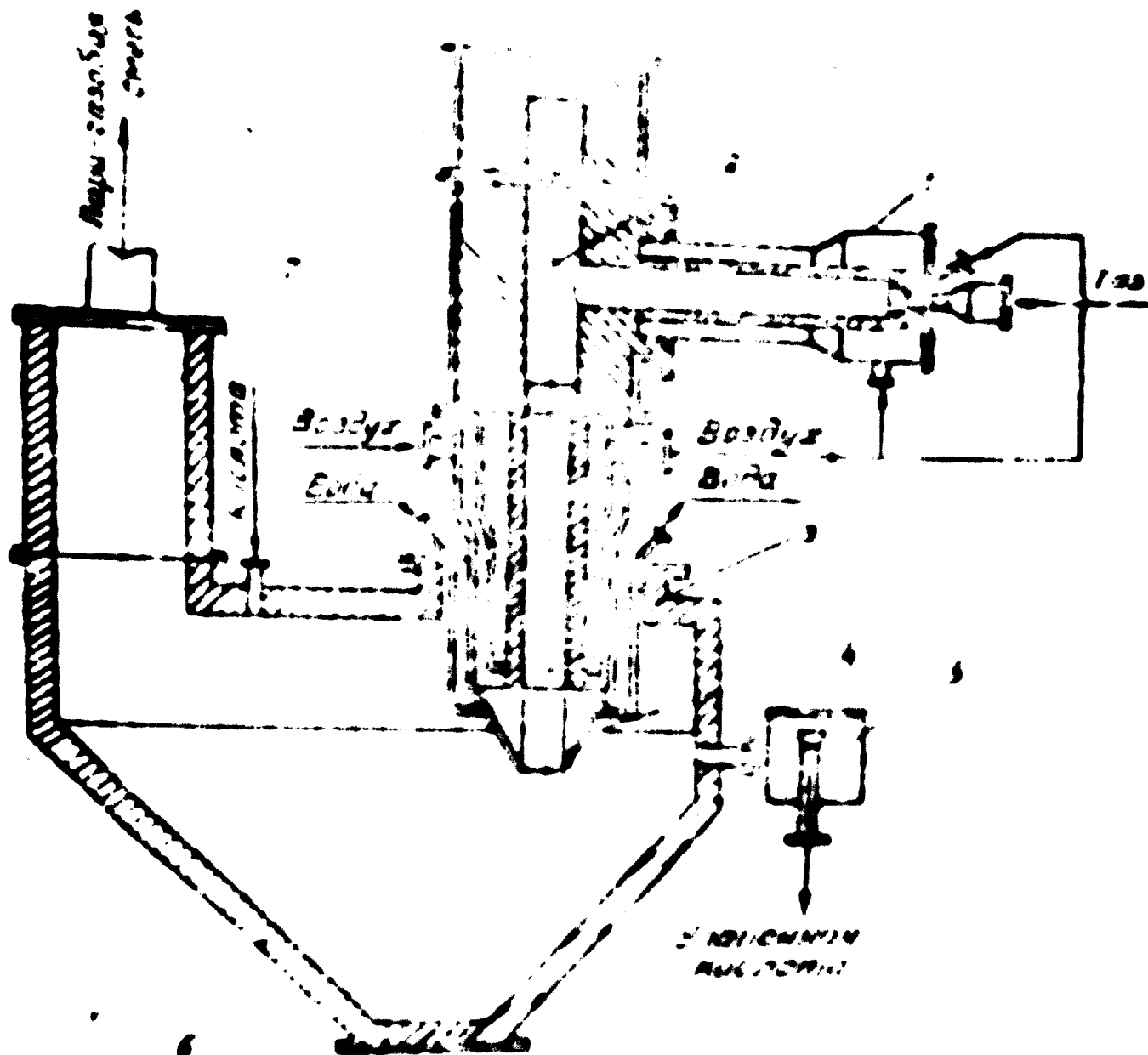
1 - топка; 2 - газовод; 3- барботажная труба;
4 - охлаждающий водой наружная барботажной трубы;
5 - регулятор уровня; 6 - корпус аппарата; 7 - финогазоочистка

Рис 7

Содержание P_2O_5 в газах, г/м³

Избыток воздуха, %

Содержание азота %

Количество газа м³ х кг P

Содержание P_2O_5

Теоретическая температура

Количество окисленных газов и содержание в них кислорода

Теоретическая температура сжигания фосфора, °C
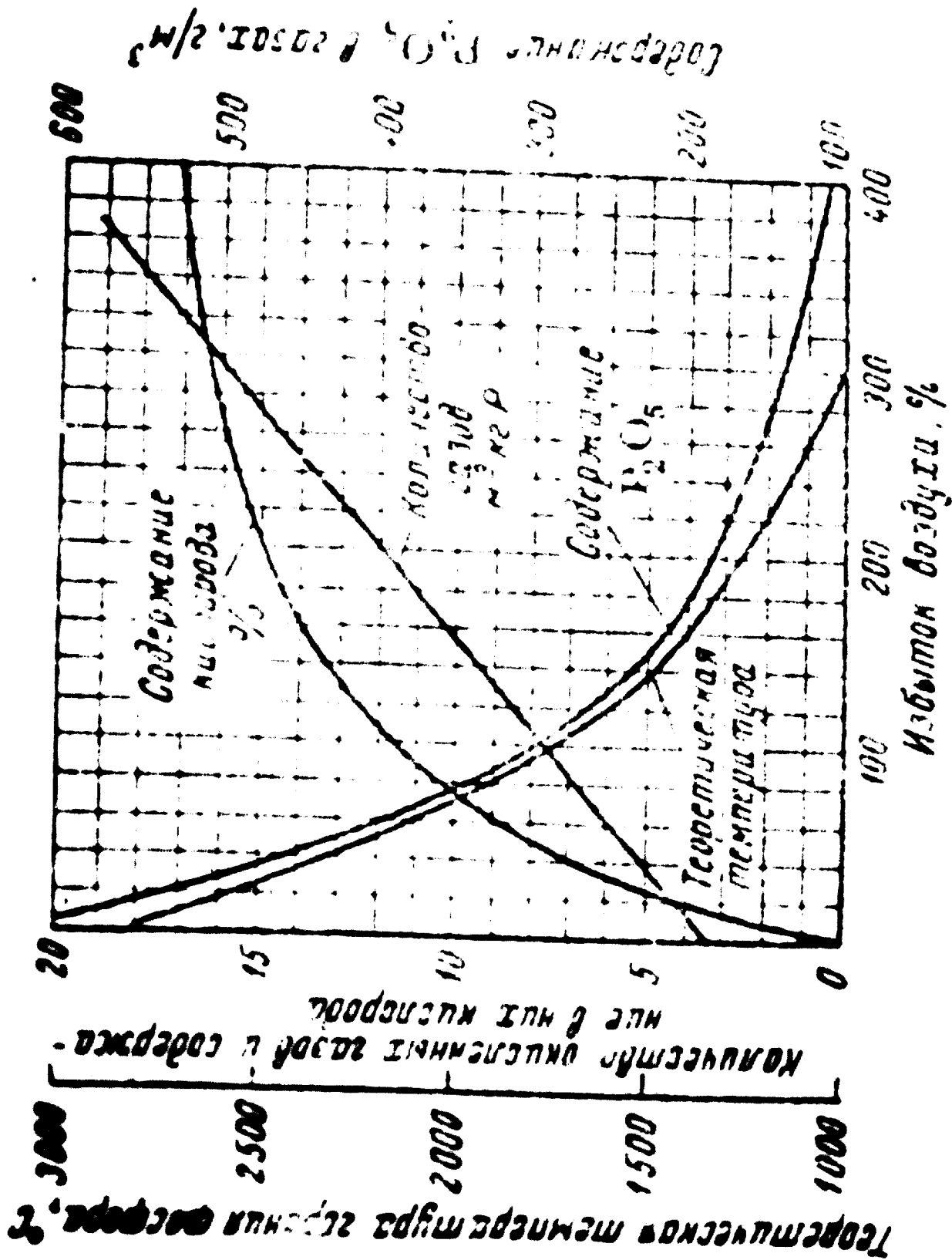
Характеристика процесса сжигания элементарного фосфора.

Рис 8
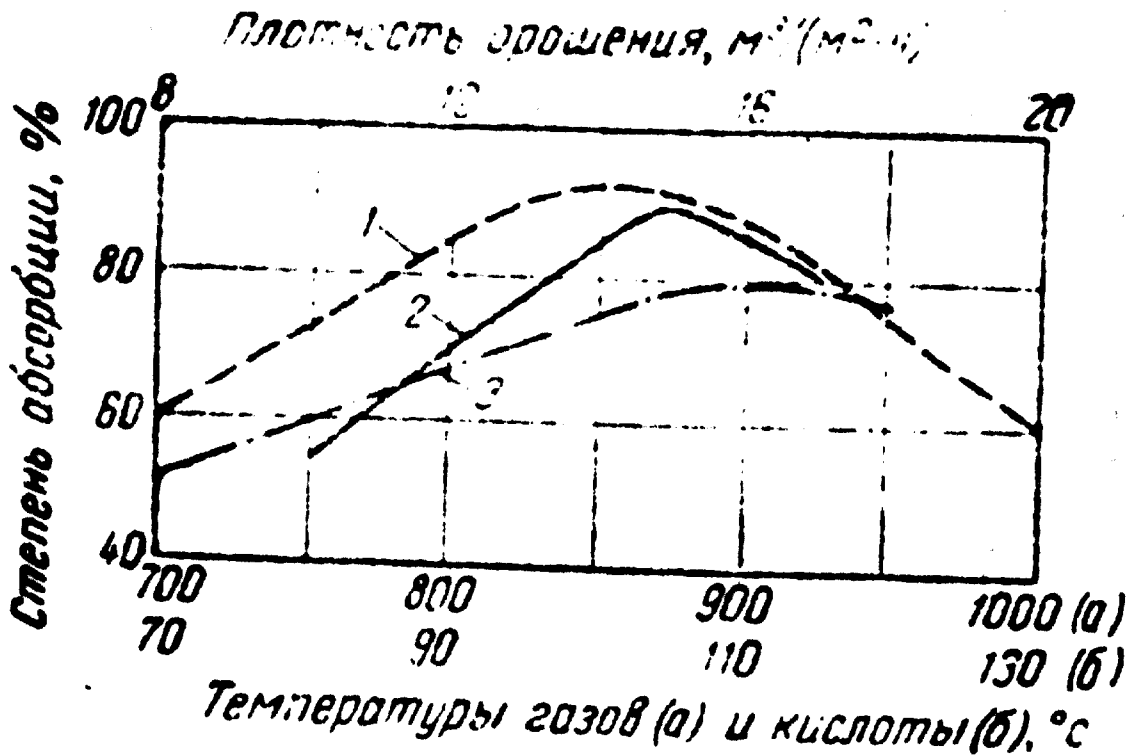
Зависимость степени абсорбции фосфорного ангидрида от температуры газов, поступающих в скруббер (*1*), температуры орошающей кислоты (*2*) и плотности орошения (*3*).

Концентрация кислоты во всех опытах 77% P_2O_5; плотность орошения 12 $м^3/(м^2 \cdot ч)$ (для кривых *1, 2*); температура газов 800—850° С (для кривых *2, 3*); температура орошающей кислоты 100° С (для кривых *1, 3*).

Рис 9
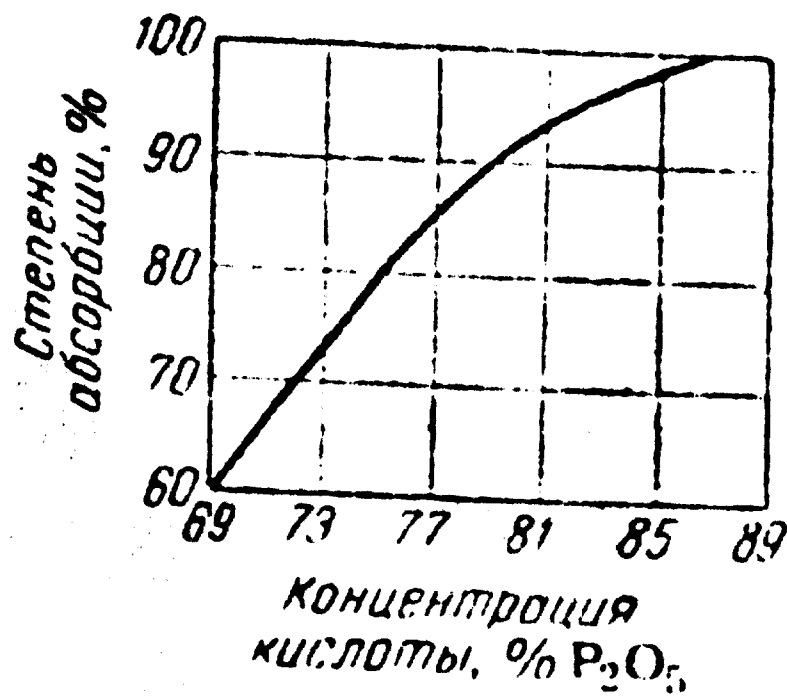
Зависимость степени абсорбции фосфорного ангидрида из газов от концентрации орошающей фосфорной кислоты.

Рис 10.
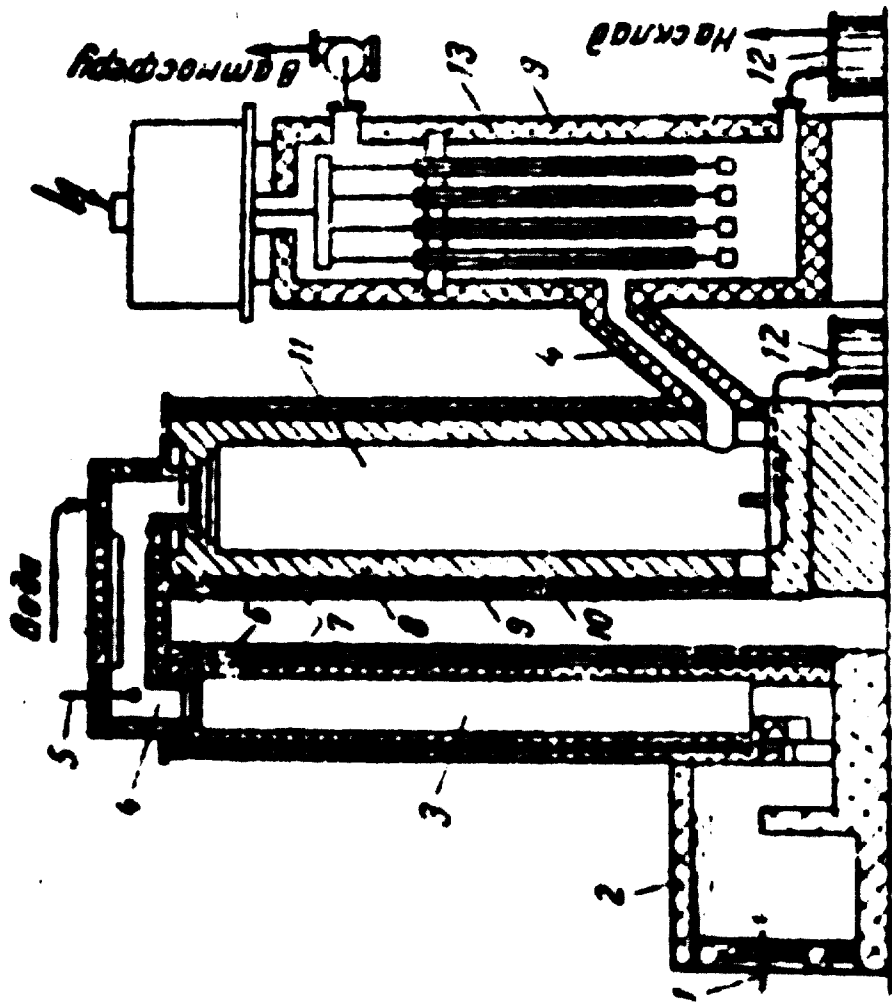
Испарительная система с горизонтальной камерой сжигания и эластичным соединением вертикальной башни охлаждения. и горизонтального газового хода:

1 — форсунка; 2 — камера сжигания; 3 — вертикальный газоход; 4 — соединительный газоход; 5 — термопара; 6 — (изоляционный кирпич); 7 — воздушные прослойки; 8 — угольник; 9 — шамотные плитки; 10 — стальной гуммированный кожух; 11 — башня охлаждения-нейтрализации; 12 — приемник для кислоты; 13 — электрофильтр.

Рис 11.
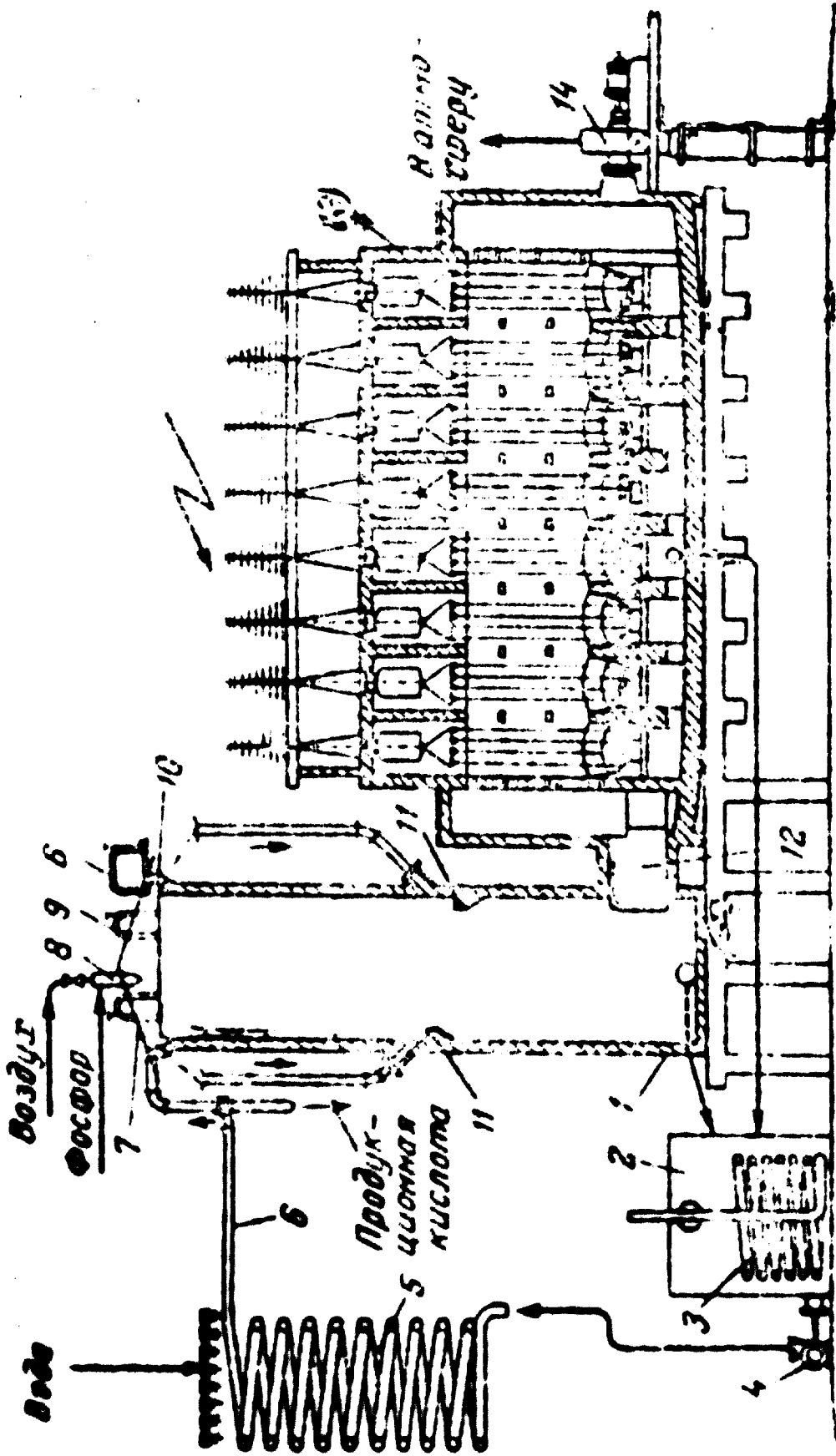
Циркуляционная схема с оросительными теплообменниками:

1 — башня сжигания; 2 — сборник циркуляционной кислоты, 3 — змеевиковый холодильник; 4 — насос; 5 — оросительный холодильник; 6 — кислотопровод; 7 — крышка-решетка; 8 — форсунка; 9 — водопровод; 10 — кольцевой желоб; 11 — кирпичные выступы и кладке; 12 — газоход; 13 — электрофильтр; 14 — штуцеры.

Рис 12.
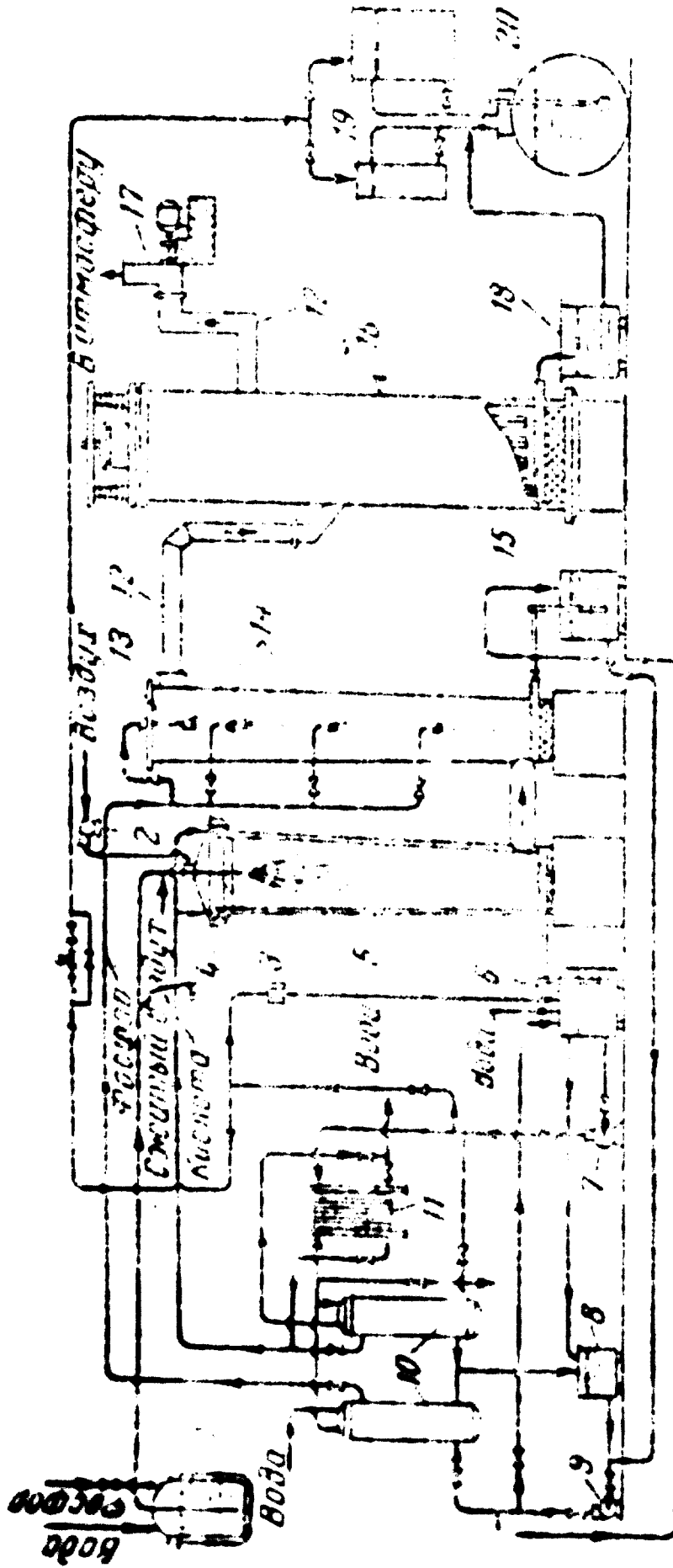
Комбинированная циркуляционно-испарительная система:

1 — хранилище фосфора; 2 — вертикальное горло; 3 — форсунки; 4 — кольцевой желоб; 5 — камера сжигания; 6 — сборник концентрированной кислоты; 7, 9 — насосы; 8 — промежуточный сборник; 10 — воздухотрубные теплообменники; 11 — пластинчатый холодильник; 12 — газоходы; 13 — башня гидратации; 14 — кислотные форсунки; 15 — сборник разбавленной кислоты; 16 — электрофильтр; 17 — вентилятор; 18 — сборник концентрированной кислоты; 19, 20 — цеховое и заводское хранилища кислоты.

Рис 13
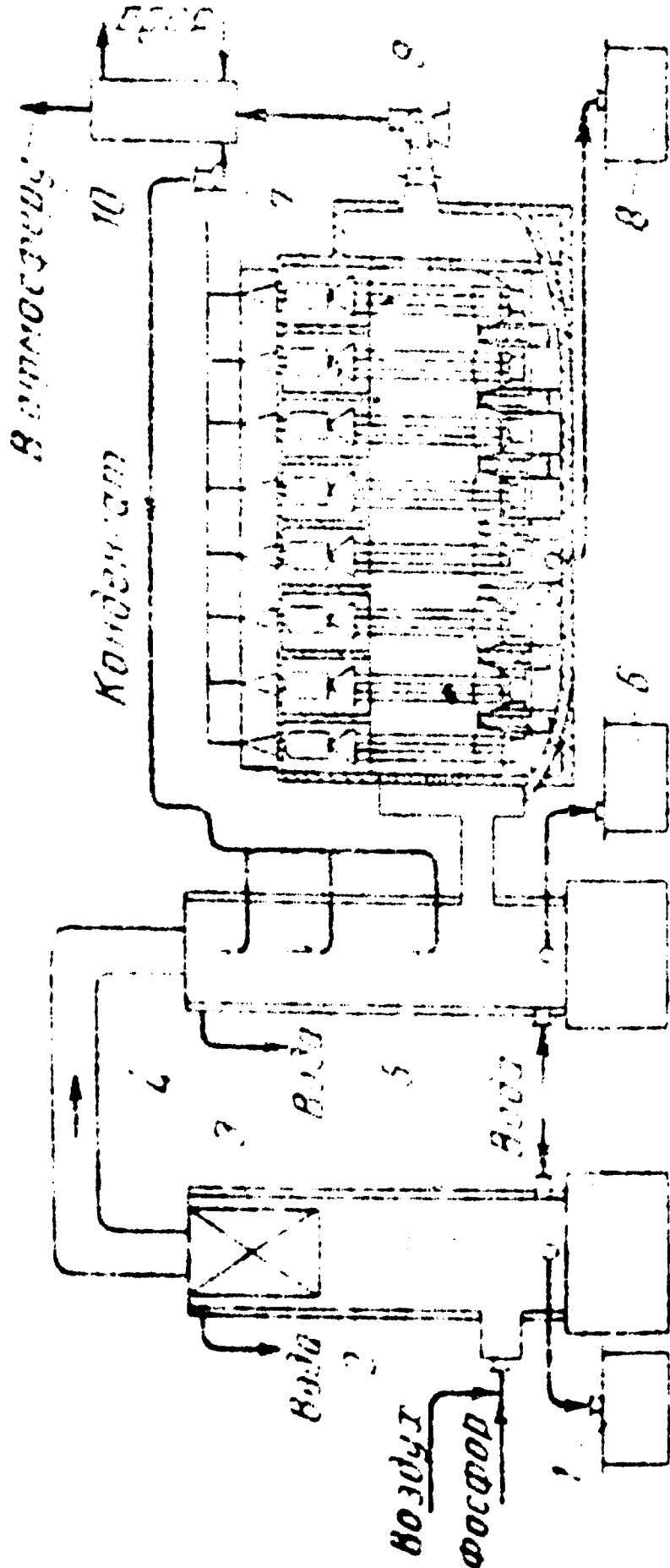
Комбинированная теплообменно-испарительная система для производства термической фосфорной кислоты:

1, 6, 8 — сборники камерной, баппенной и электрофильтрной кислот; 2 — камера сжигания с водяной рубашкой; 3 — газовый холодильник: 4 — газоход; 5 — башня гидратации; 7 — электрофильтр; 9 — вентилятор: 10 — конденсатор паров воды.

Рис 14.
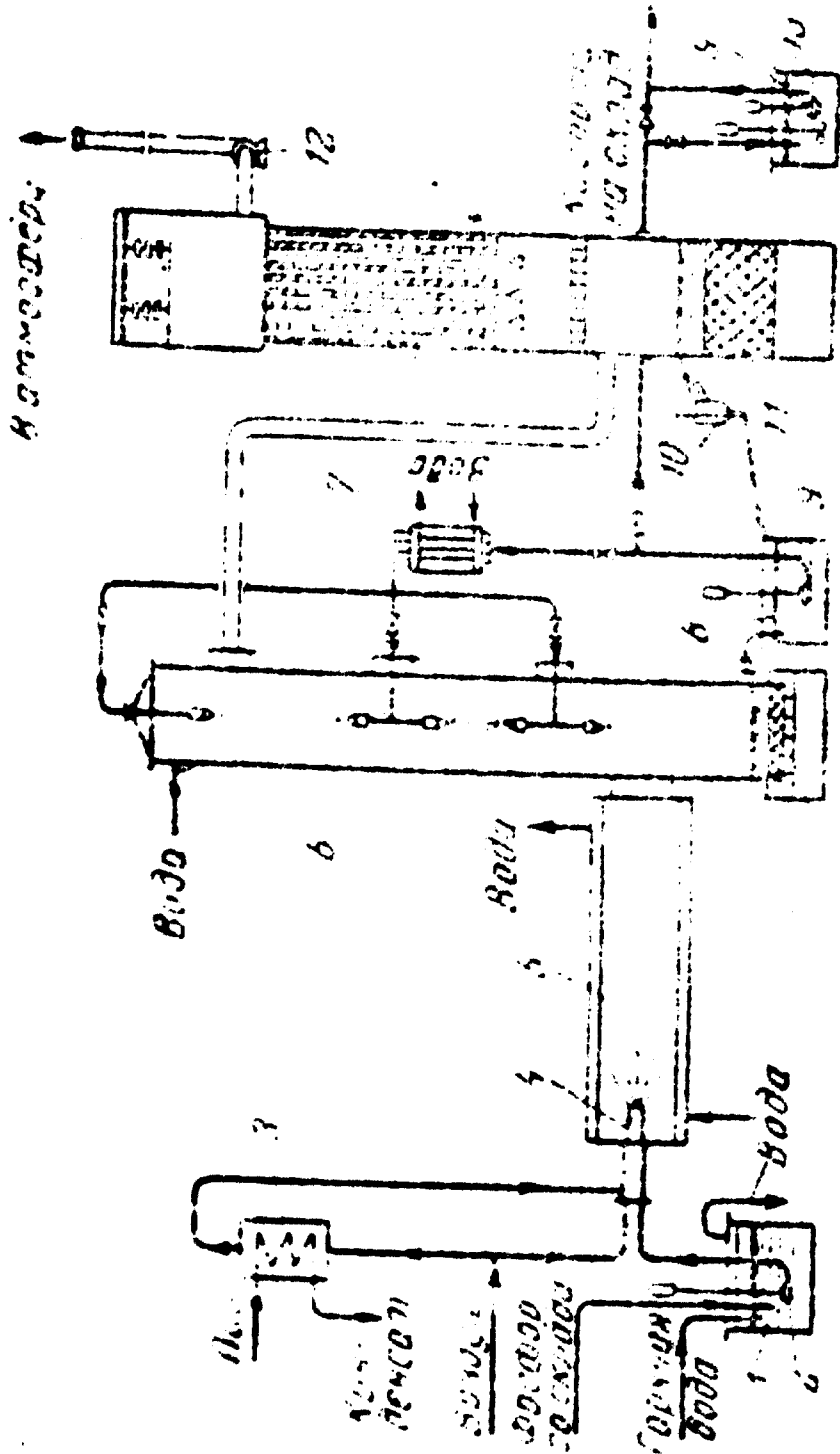
Система производства полифосфорной кислоты, содержащей
до 88% P_2O_5:

1 — бак для фосфора; 2 — погружной насос; 3 — подогреватель воздуха; 4 — форсунка;
5 — камера сжигания; 6 — башни охлаждения-гидратации; 7 — теплообменник; 8 — сбор-
ник; 9 — погружной насос; 10 — приемник кислоты; 11 — электрофильтр; 12 — вентиля-
тор; 13 — сборник кислоты.

C A P T I O N S (on text)

Table 1. quality of thermic and wet-process phosphoric acid produced in the USSR.

Table 2. Chemical composition of phosphorites from different deposits.

Fig. 1. Reaction equations for the interaction of phosphorite with sulphuric and phosphoric acids.

Fig. 2. Polyterms of the transformations of various calcium sulphate modifications in phosphoric acid solutions.

Fig. 3. Effect of free sulphuric acid on transition rate of various calcium sulphate modifications in phosphoric acid solutions.

Fig. 4. Calcium sulphate solubility as a function of temperature.

Fig. 5. Flow diagram for the production of wet-process phosphoric acid in dihydrative process.

Table 3. Main processing data for plants of wet-process phosphoric acid.

Fig. 6. Bubbler for evaporating phosphoric acid.

Fig. 7. Combustion diagram for elemental phosphorus.

Fig. 8. Phosphoric anhydride absorption as a function of gas and acid temperature and of spray density.

Fig. 9. Phosphoric anhydride absorption as a function of spray acid concentration.

Fig.10. Evaporation system of thermic phosphoric acid production.

Fig.11. Circulation system of phosphoric acid production.

Fig.12. Circulation-evaporation system of phosphoric acid production.
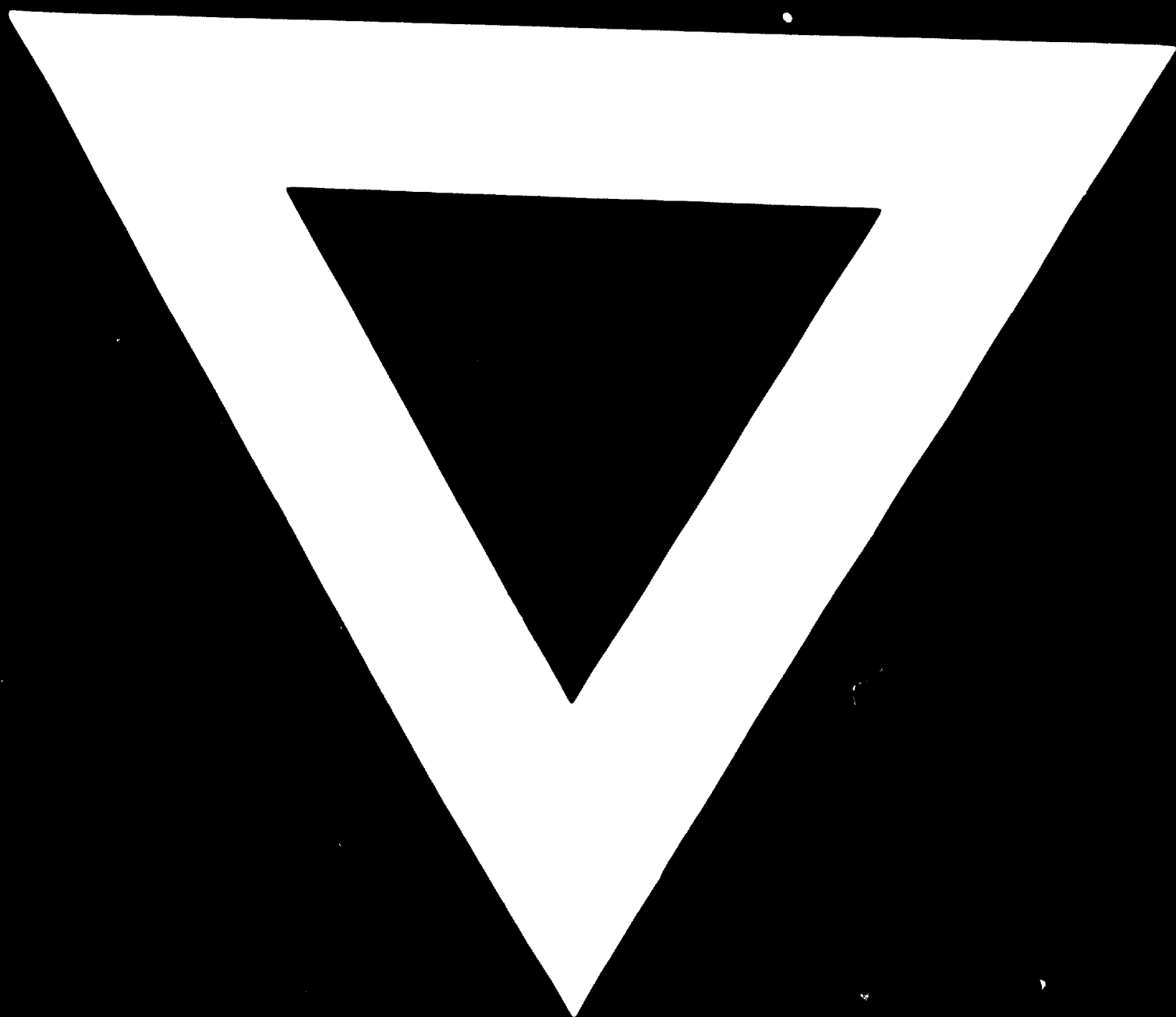
Captions (continued)

Fig. 13. Evaporation- heat exchange system of phosphoric acid production.

Fig. 14. Flow diagram for the production of poly-phosphoric acid containing up to 86% P_2O_5.

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