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in mineral resources, metallurgy and chemical industry

Review of phosphoric acid market in the CIS

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CONTENTS

Annotation.....	9
Introduction	10
I. Technolgy of phosphoric acid manufacture and industrial raw material	12
I.1. Technology of phosphoric acid manufacture	12
I.2. Principle suppliers and supply channels.....	16
II. Production of phosphoric acid in Russia and in the CIS countries	21
II.1. Output quality	21
II.2. Pruduction of phosphoric acid by the CIS countries in 1997-2007.....	23
II.2.1. Pruduction of phosphoric acid by Russia in 1997-2007.....	25
II.2.2. Pruduction of phosphoric acid by Ukraine in 1997-2007.....	28
II.2.3. Pruduction of phosphoric acid by Kazakhstan in 1997-2007.....	30
II.2.4. Pruduction of phosphoric acid by Uzbekistan in 1997-2007.....	32
II.2.5. Pruduction of phosphoric acid by Byelorussia in 1997-2007.....	35
II.3. Key producers of phosphoric acid in the CIS countries	36
II.4. Current status of phosphoric acid producers in the CIS	37
II.4.1. OJSC "PhosAgro".....	37
II.4.1.1. OJSC "Ammophos" (Cherepovets, Vologda Regoin, RF).....	38
II.4.1.2. LLC "Balakovo Mineral Fertilizers (VMU)" (Balakovo, Saratov Region, RF).....	43
II.4.2. OJSC "MChP "Eurochim".....	47
II.4.2.1. LLC "Eurochim-Belorechensk Mineral Fertilizers" (Belorechensk, Krasnodar Krai, RF)	50
II.4.3. LLC "Voskresensk Mineral Fertilizers" (Voskresensk, Moscow Region, RF).....	54
II.4.4. OJSC "Gomel Chemical Plant" (Gomel, Byelorussia)	61
III. Expot-and-Import of phosphoric acid	63
III.1. Phosphoric acid export-and-import by Russia in 1997-2007.....	63
III.2. Phosphoric acid export-and-import supply trends and piculiarities in RF.....	64
III.3. Key channels of phosphoric acid export-and-import supplies in RF	67
III.4. Volume and key channels of phosphoric acid export-and-import supplies by Ukraine in 2003-2007.....	70
III.5. Volume and key channels of phosphoric acid export-and-import supplies by Kazakhstan in 2004-2007.....	72
III.6. Volume of phosphoric acid export-and-import supplies betwin Russia and Ukraine in 2003-2007.....	73
IV. Posphoric acid price review	74
IV.1. Posphoric acid domestic prises	74

IV.2. Dynamics of export-and-import prices in RF.....	75
IV.3. Dynamics of export-and-import prices in Ukraine	77
IV.4. Dynamics of export-and-import prices in Kazakhstan.....	78
IV.5. Dynamics of export-and-import prices in Byelorussia	79
V. Phosphoric acid consumption in the CIS	80
V.1. Phosphoric acid utilization balance in Russia	80
V.2. Phosphoric acid utilization balance in Ukraine	82
V.3. Phosphoric acid utilization balance in Kazakhstan	83
V.4. Structure of phosphoric acid consumption in Russia	84
V.5. Phosphoric acid principle fields of application	86
<i>V.5.1. Chemicals industry. Manufacture of phosphate mineral fertilizers</i>	<i>86</i>
<i>V.5.2. Chemicals industry. Manufacture of sodium tripolyphosphate</i>	<i>89</i>
V.6. Consumers of phosphoric acid in Russia.....	92
<i>V.6.1. OJSC "Middle Ural copper mill" (SUMZ, Revda, Sverdlovsk Region, RF)</i>	<i>92</i>
<i>V.6.2. CJSC "Memchem" (Volkhov City, Leningrad Region, RF)</i>	<i>96</i>
VI. Phosphoric acid output forecast till 2015 in Russia	99
<i>V.6.1. OJSC "Middle Ural Copper Mill» (SUMZ, Revda city, Sverdlovsk</i> <i>Region, RF).....</i>	<i>94</i>
<i>V.6.2. CJSC "Metachem» (Volkhov city, Leningrad Region, RF).....</i>	<i>98</i>
Appendix: Phosphoric acid producer and consumer ventures address book...	100

Tables

- Table 1. Manufacture of phosphates by Russia in 1999-2007 (in terms of 100% P₂O₅), 000 ton
- Table 2. Supplies of apatite concentrate to wet-process phosphoric acid producers in the CIS, 2004-2007, (in terms of 100% P₂O₅), 000 ton
- Table 3. Yellow phosphorus output dynamics at "New-Djambul phosphorous plant" in 1998-2007, 000 ton
- Table 4. Performance requirements to caloric phosphoric acid (GOST 10678-76)
- Table 5. Performance requirements to wet-process phosphoric acid desulphated (TU 113-08-5015 182-105-95)
- Table 6. Performance requirements to wet-process phosphoric acid made at OJSC "Sumychimprom" (Ukraine) (TU 6 05766356.037-98)
- Table 7. Wet-process phosphoric acid output dynamics in the CIS, 1997-2007, (in terms of 100% P₂O₅), 000 ton
- Table 8. Caloric phosphoric acid output dynamics in the CIS, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Table 9. Commercial phosphoric acid output by Russia in 1998-2007 (000 ton in terms of 100% P₂O₅)
- Table 10. Commercial phosphoric acid output by Ukraine in 2003-2007 by enterprises, ton (in terms of 100% P₂O₅)
- Table 11. Phosphoric acid major producers in the CIS countries, 2003-2007, 000 ton (in terms of 100% P₂O₅), %
- Table 12. Russian consumers of phosphoric acid manufactured at LLC "Balakovo mineral fertilizers" in 2003-2007, 000 ton
- Table 13. Foreign consumers of phosphoric acid manufactured at LLC "Eurochim-BMU" in 2004-2007, 000 ton, \$/t
- Table 14. Russian consumers of phosphoric acid manufactured at "Eurochim-BMU" in 2004-2007, 000 ton
- Table 15. Russian consumers of phosphoric acid manufactured at OJSC "BMU" in 2002-2007, 000 ton
- Table 16. Foreign consumers of phosphoric acid manufactured at OJSC "BMU" in 2003-2007, 000 ton, \$/t
- Table 17. Financials of operational activity at OJSC "BMU" in 2003-2007 and 1Q of 2008
- Table 18. Wet-process phosphoric acid output dynamics at OJSC "Gomel chemical plant" in 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Table 19. Phosphoric acid exports by Russian companies in 2001-2007, 000 ton, %
- Table 20. Russian consumers of imported phosphoric acid in 2001-2007, ton
- Table 21. RF made phosphoric acid importer countries in 2001-2007, ton
- Table 22. Phosphoric acid exporter countries to Russia in 2001-2007, ton
- Table 23. Ukraine made phosphoric acid importer countries in 2003-2007, ton
- Table 24. Phosphoric acid exporter countries to Ukraine in 2003-2007, ton
- Table 25. Kazakhstan made phosphoric acid importer countries in 2004-2007, ton

- Table 26. Phosphoric acid exporter countries to Kazakhstan in 2004-2007, ton
- Table 27. Average annual prices for phosphoric acid made at OJSC "Voskresensk mineral fertilizers" in 2006-2007, ruble/ton excluding VAT
- Table 28. Current prices for phosphoric acid made at OJSC "Ammophos"
- Table 29. Prices for phosphoric acid made at OJSC "Sumychimprom", \$/t excluding VAT
- Table 30. Average annual export prices for made in RF and supplied to different countries in 2001-2007, \$/t
- Table 31. Average annual phosphoric acid import prices due in RF, 2001-2007, \$/t
- Table 32. Average annual phosphoric acid export prices in Ukraine bound to foreign countries in 2003-2006, \$/t
- Table 33. Average annual phosphoric acid import prices due in Ukraine, 2003-2007, \$/t
- Table 34. Average annual phosphoric acid export prices in Kazakhstan bound to foreign in 2004-2007, \$/t
- Table 35. Average annual phosphoric acid import prices due in Kazakhstan, 2004-2007, \$/t
- Table 36. Phosphoric acid consumption balance in Russia, 1997-2007 (in terms of 100% P₂O₅)
- Table 37. Phosphoric acid consumption balance in Ukraine, 2003-2007 (in terms of 100% P₂O₅)
- Table 38. Phosphoric acid consumption balance in Kazakhstan, 2004-2007 (in terms of 100% P₂O₅)
- Table 39. Phosphoric acid consumption structure in Russia by sectors in 2006-2007, 000 ton (in terms of 100% P₂O₅), %
- Table 40. Production of phosphoprous-containing fertilizers in Russia, 2004-2007, 000 ton (in terms of 100% P₂O₅) and the share of its enterprises in total output, %
- Table 41. Sodium tripolyphosphate output dynamics in Russia by enterprises in 1997-2007, 000 ton

Figures

- Figure 1. Flowchart of caloric phosphoric acid production
- Figure 2. Flowchart of wet-process phosphoric acid production
- Figure 3. Phosphoric acid output dynamics in the CIS, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 4. Phosphoric acid output dynamics in Ukraine, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 5. Phosphoric acid output dynamics in Kazakhstan, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 6. Phosphoric acid output dynamics in Uzbekistan, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 7. Phosphoric acid output dynamics in Byelorussia, 1997-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 8. Sulphuric acid output dynamics at OJSC "Ammophos" in 2000-2007, 000 ton
- Figure 9. Phosphoric acid and ammophos output dynamics at OJSC "Ammophos" in 1997-2007 гг., 000 ton
- Figure 10. Phosphate fertilizers output dynamics at OJSC "Ammophos" (000 ton) and the share of the Company in total volume of manufacture of the product in RF (%)
- Figure 11. Core products output dynamics at LLC "Balakovo mineral fertilizers" in 2000-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 12. Ammophos output dynamics at LLC "Balakovo mineral fertilizers" in 1999-2007, 000 ton (in terms of 100% P₂O₅)
- Figure 13. Phosphoric acid and phosphate fertilizers output dynamics at (000 ton in terms of 100% P₂O₅) at LLC "Eurochim-BMU" and the share of ammophos in phosphate fertilizers manufacture (%)
- Figure 14. Core commercial products output dynamics at OJSC "Voskresensk mineral fertilizers" in 2000-2007, 000 ton
- Figure 15. Phosphoric acid export-and-import dynamics in RF, 1997-2007, 000 ton
- Figure 16. Phosphoric acid RF export geography in 2007, %
- Figure 17. Phosphoric acid foreign trade in Ukraine, 2003-2007, ton
- Figure 18. Phosphoric acid trade between Russia and Byelorussia in 2003-2007, ton
- Figure 19. Average annual phosphoric acid import-and-export prices in Byelorussia, 2003-2007, \$/t
- Figure 20. Phosphoric acid production and consumption dynamics in Russia, 1997-2007, 000 ton
- Figure 21. Phosphoric acid production and consumption dynamics in Ukraine (000 ton) and import's share in consumption (%), 2003-2007
- Figure 22. Phosphoric acid production and consumption dynamics in Kazakhstan, 2004-2007, 000 ton
- Figure 23. Phosphoric acid consumption structure in Russia for 2007 by sectors, %
- Figure 24. Phosphate fertilizers output dynamics in Russia, 1997-2007, 000 ton

- Figure 25. Sodium tripolyphosphate output dynamics in Russia, 1997-2007, 000 ton
- Figure 26. Raw materials supply volume and sodium tripolyphosphate output at OJSC "SUMZ" in 2002-2007, 000 ton
- Figure 27. Raw materials supply volume and sodium tripolyphosphate output at CJSC "Metachim" in 2002-2007, 000 ton
- Figure 28. Phosphoric acid output in Russia and its production (consumption) outlook till 2015, million ton

Annotation

The actual report is devoted to review of phosphoric acid market in the CIS countries. The Report was prepared on the basis of data from Federal State Statistics Service (Rosstat), Federal customs service of the Russian Federation (RF FCS), the branch official statistics of railroad transportation of the Russian Federation, as well as “Infomine” data. The Report consists of six Sections, contains 98 pages, including 41 tables, 28 figures and a supplement.

The First Chapter informs of phosphoric acid existing production technologies; their peculiarities; essential raw materials as well as their properties.

The Second Chapter of the Report is devoted to analysis of phosphoric acid production in the CIS countries. This Chapter of the Report provides reglament of existing technical documents in regard of properties of phosphoric acid of different marks, this product output statistics for 1997-2007; it gives valuation of production regional structure, describes principal producers of phosphoric acid.

The Third Chapter analyses phosphoric acid foreign trade operations by RF, Ukraine, Kazakhstan and Byelorussia. It presents data over export-and-import volumes of being assessed product, valuates supplies regional structure, and informs about phosphoric acid delivery volumes by this product exporters and importers.

The Forth Chapter provides data over phosphoric acid price levels in the Russian domestic market as well as analyses export-and-import price movement over the last seven years.

The Fifth Chapter of the Report presents balance of phosphoric acid production and consumption in Russia, Ukraine, Kazakhstan and Byelorussia; valuates regional and industrial consumption structure of the product being assessed; describes principal users of phosphoric acid; analyses factors deciding domestic demand in the acid.

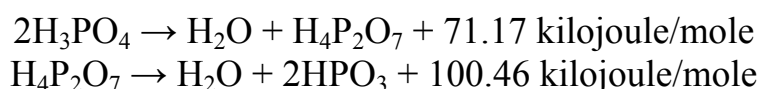
The Sixth Chapter is devoted to forecast of phosphoric acid production development in Russia until 2010.

Introduction

Phosphoric (orto-phosphoric acid) acid H_3PO_4 is the most stable compound among oxygen-containing phosphorus acids. As for physical properties the compound is a colorless hygroscopic crystalloid substance, inclined to overcooling in the fused condition. At temperature $+15^\circ\text{C}$ the substance would transform to a dense oily fluid; at -121°C it forms glassy aggregation. Orto-phosphoric acid crystals fusion temperature stands at $+42.3^\circ\text{C}$, density is 1.88 g/sm^3 .

However such acid is very rare. More often one could find semi hydrate ($\text{H}_3\text{PO}_4 \cdot 0,5\text{H}_2\text{O}$) which precipitates in the form of colorless hexagonal prisms at cooling of the concentrated water solutions of orto-phosphoric acid. The semi hydrate point of fusion stands at 29.3°C .

Under normal conditions the phosphoric acid is low-active and reacts just to carbonates, hydro-oxides and some metals. Thus it forms single, double and triple-substituted phosphates. At heating above 80°C it reacts even to inactive oxides, silica and silicates. At higher temperatures the phosphoric acid is a weak oxidizer for metals. With application to metal surface, the solution of phosphoric acid with additives of Zn or Mn forms a protective film (phosphatization). At heating the phosphoric acid loses water with formation of consistently piro - and metaphosphoric acids:



Orto-phosphoric acid finds wide enough application nowadays. Its principal consumer is ***manufacture of the phosphoric and combined fertilizers***. For these purposes all over the world it has been annually extracted near 100 million ton of phosphorous-containing ores. Phosphoric fertilizers not only promote productivity of various agricultural crops, but also provide the plants with winter sustainability and resistance to other adverse environmental conditions; create conditions for faster crop maturing in areas with short vegetative period. They also favorably affect the soil, promoting its structurization, development of soil bacteria, and change of solubility of other substances contained in the soil as well as suppresses some harmful organic substances.

Orto-phosphoric acid is also consumed by the ***food industry***. The matter is that diluted orto-phosphoric acid has a very pleasant taste and its small additives to fruit jelly, lemonades and syrups considerably improve their flavoring properties. Some salts of phosphoric acid possess the same property also. Calcium hydro phosphates, for example, have been included into baking powders, improving taste of rolls and bread since long ago.

There are also some other scopes of orto-phosphoric acids application in industry

For example, it was noticed that *impregnation of woodwork* with the acid and its salts make timber nonflammable. On this basis they now make fireproof paints, nonflammable phosphor-wooden plates, nonflammable phosphoric polyfoam and other building materials.

In *chemical industry*, the phosphoric acid, the condensed acids and dehydrated phosphates serve as catalysts in processes dehydration, alkylation and polymerization of hydrocarbons.

Besides, phosphoric acid is used for generation of fodder phosphates, synthetic washing and softening means. In metal-processing industry, phosphoric acid is applied in phosphatization, in textile – for treating and dyeing of wool, plant and synthetic fibers. Phosphoric acid and its derivatives are used also for preparation of chisel suspensions at oil extraction; for manufacture of various marks of special glass. In addition, phosphoric acid finds application in photography – for manufacture of photosensitive emulsions; in pharmaceutical industry – for manufacture of some kinds of medicines and tooth cements.

I. Technology of phosphoric acid manufacture and industrial raw material

I.1. Technology of phosphoric acid manufacture

Phosphoric acid was discovered by R. Boyly with the help of indicators. Burning phosphorus and dissolving the formed white product in water, it had received acid unknown to chemists. Under initial substance he named it phosphoric.

Technically phosphoric acid for the first time was obtained over 100 years ago by decomposition of low grade phosphorites containing significant amounts of compounds of trivalent metals, diluted (5-10 %) with sulfuric acid, in which ferrous compounds and especially aluminum compounds transform to solution in insignificant degree. A solution containing 8-10% of P_2O_5 was subject to evaporation until approximately 40% of P_2O_5 . At decomposition of phosphoric rock with more concentrated (30-40%) sulfuric acid there being generated needle-shape gypsum. It arrests significant amount of a liquid phase and is hard to wash out. Thereof, losses of P_2O_5 are huge.

A significant step forward in manufacture of phosphoric acid was adoption of continuous action installations and dilution of 75% - 93% sulfuric acids not with water or weak bottling waste waters, but with a solution of phosphoric acid, i.e. transformation to a process with application of solution for dilution. These conditions generate gypsum rhombic crystals, which are well filtered and washed.

The **basic industrial methods of phosphoric acid manufacture** for today are **thermal** and **extraction** ones, with the former one providing the most refined product.

The **thermal method** includes the following basic stages: burning (oxidation) of elemental phosphorus in excess of air, hydration and absorption of obtained P_4O_{10} , and condensation. There are two methods for P_4O_{10} generation – oxidation of liquid phosphorus in the form of drops or a film and oxidation of phosphorus steams (in industry this method is rare).

All stages of phosphoric acid manufacture with thermal method can be combined in one device, except for catching of fog, which is always made in separate device. The industry usually applies schemes with two or three basic devices combined.

Depending on gas-cooling principle there are three ways for fabrication of caloric phosphoric acid: vaporizing, circular-vaporizing and heat-exchange-vaporizing.

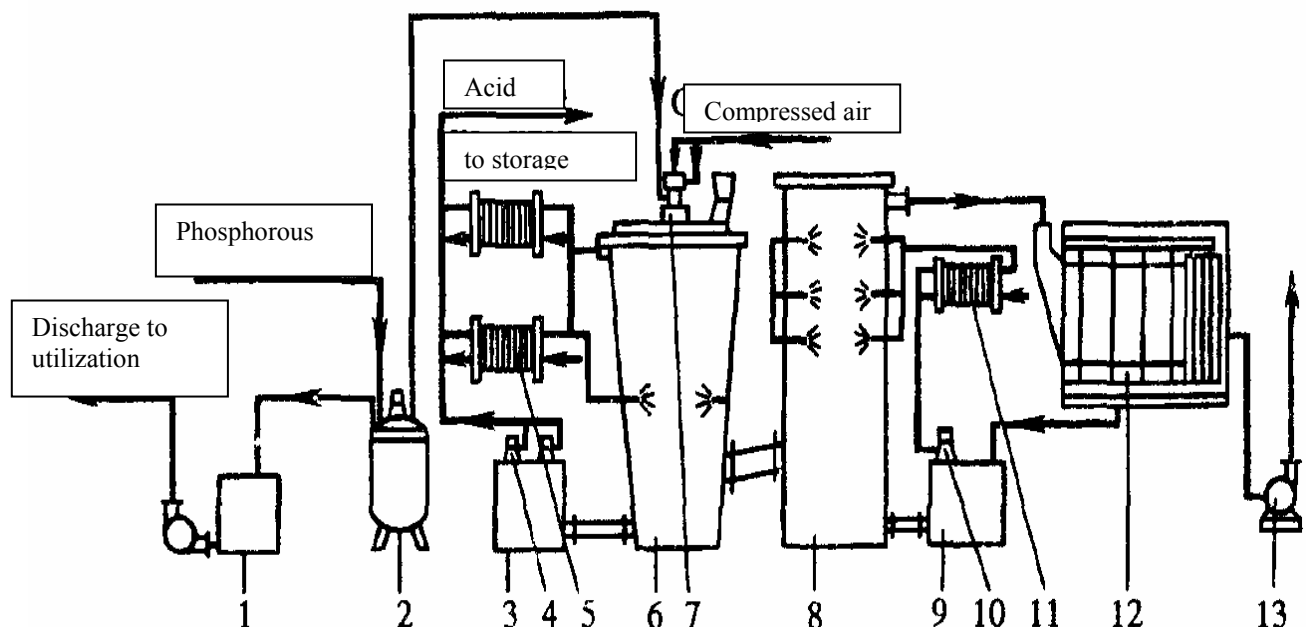
The vaporizing systems based on heat elimination by means of water evaporation or of phosphoric acid dilution, are the most primitive ones from the point of view of instrumental design. However, due to rather huge volume of exhausted gases, application of such systems is viable with aggregates of small unit capacity.

The circular-vaporizing systems allow combination in single device the stages of phosphorus burning, gas phase cooling of circulating acid and hydration P_4O_{10} . The scheme disadvantage lies with need for cooling of acid in large volumes.

The heat-exchange-vaporizing systems combine two ways of heat elimination – through a wall of burning and cooling towers, and also by evaporation of water from its gaseous phase. Essential advantage of this system is absence of acid circulation contours with pump-refrigerating machinery.

Domestic enterprises boast technological schemes that obtain caloric phosphoric acid by means of circular-vaporizing method of cooling (double-tower system). Distinctive features of this system are: availability of an additional tower for gas cooling; use of effective lamellar heat exchangers in circulating contours; application of a high-efficiency atomizer for burning of the phosphorus, providing homogeneous fine dispersion of liquid phosphorus stream and its full combustion without formation of lowest oxides. The flow chart of installation for manufacture of caloric phosphoric acid is presented in Figure 1.

Figure 1. Flowchart of caloric phosphoric acid production



1 – Collector of acid water; 2 – Phosphorous storage; 3 – Circular collector; 4 – Submersible pumps; 5 – Lamellar heat exchangers; 6 – Burning tower; 7 – Phosphorous atomizer; 8 – Hydratation tower; 9 – Circular collector; 10 – Submersible pumps; 11 – Lamellar heat exchangers; 12 – Electrical filter; 13 – Ventilator.

Source: Review of scientific-technology literature

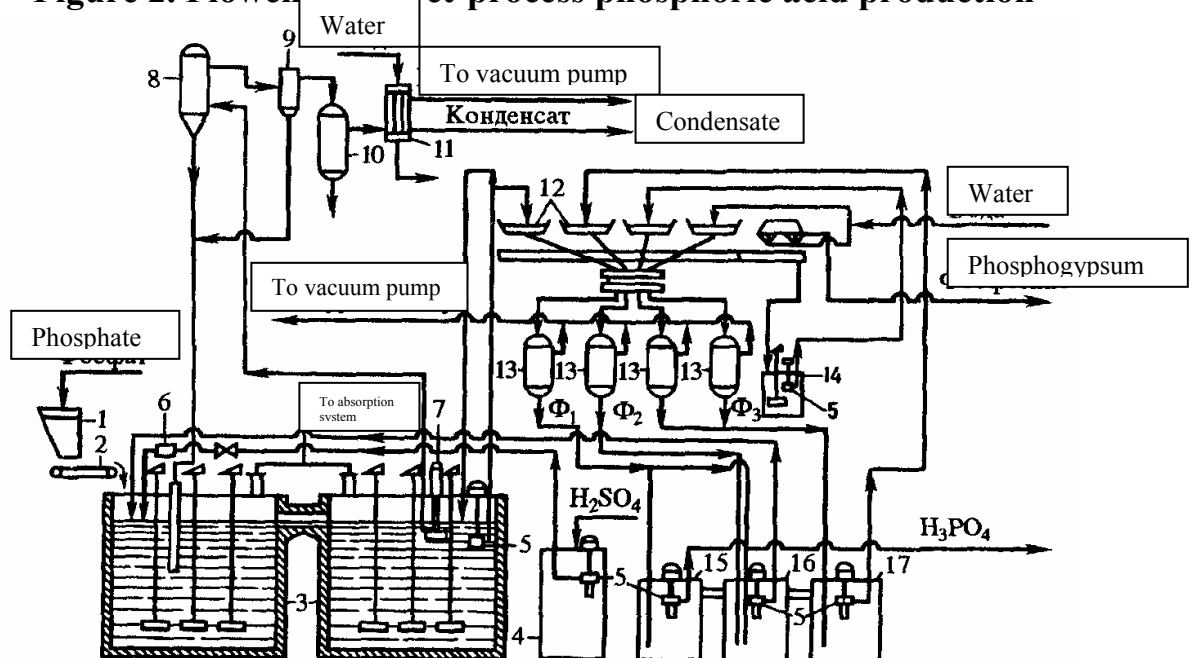
The **extraction method** for phosphoric acid generation is considered to be more economic. This method is based upon disintegration of natural phosphates with acids – mostly with sulfuric acid, to a lesser extent with nitric and, insignificantly, with hydrochloric acid.

The phosphoric solutions obtained by means of disintegration with nitric acid, are processed into composite fertilizers. The phosphoric solutions obtained by means of disintegration with hydrochloric acid, are processed into precipitate (calcium hydro phosphate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

Sulfuric acid disintegration of phosphoric raw materials is the basic method for generation of wet-process phosphoric acid applied at manufacture of concentrated phosphoric and composite fertilizers. The method substance boils down to recovery (extraction) of P_4O_{10} as H_3PO_4 .

Subject to temperature and concentration of phosphoric acid in the system of $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ as dihydrate (gypsum), hemihydrate or anhydrite, accordingly, depending on type of sulfate being precipitated there are three direct methods of wet-process phosphoric acid manufacture: dihydratic, semi-hydratic (hemihydratic) and anhydritic as well as combined: semi-hydrate-dihydratic and dehydrate- semi-hydratic.

Figure 2. Flowchart of wet-process phosphoric acid production



1 – Phosphate raw material bin; 2 – Belt weigh feeder; 3 – Double-tank extractor; 4 – Sulfuric acid storage; 5 – Submersible pump; 6 – Sulfuric acid flow meter; 7 – Circulatory submersible pump; 8 – Evaporator; 9 – Mist eliminator; 10 – Barbotage neutralizer; 12 – Tilting pan filter trays; 13 – Separators; 14 – Suspension interim collector; 15 – Barometric collector for the main filter; 16 – Barometric collector for returnable phosphoric acid; 17 – Barometric collector for washing filtrate

Source: Review of scientific-technology literature

Dihydratic and hemihydratic methods are the most perfected industrial methods in the CIS. The dihydratic method is distinguished by high yield of P_2O_5 (93%-96.5%) into produced acid. However, rather low strength of phosphoric acid requires its subsequent concentration by evaporation. Standard flowchart of wet-process phosphoric acid production is presented in Figure 2.

Hemihydratic process helps to obtain more concentrated phosphoric acid (sometimes at 50% of P_2O_5 without additional concentration by evaporation).

It should be stressed that in the territory of the CIS only a plant in Kazakhstan produces caloric phosphoric acid, the rest of the CIS countries manufacture wet-process phosphoric acid.