InfoMine research group

The association of independent consultants
in mineral resources, metallurgy and chemical industry

Review of phosphoric acid market in the CIS

Sample PDF

Moscow
August 2008

Internet: www.infomine.ru
e-mail: info@infomine.ru

CONTENTS

Tables

Figures

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^oC the substance would transform to a dense oily fluid; at-121^oC it forms glassy aggregation. Orto-phosphoric acid crystals fusion temperature stands at +42.3^oC, density is 1.88 g/sm^3.

However such acid is very rare. More often one could find semi hydrate ($H_3PO_4 \cdot 0,5H_2O$) 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 29.3C^o.

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^oC 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 hearting the phosphoric acid loses water with formation of consistently piro - and metaphosphoric acids:

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7 + 71.17 \text{ kilojoule/mole}$$
$$H_4P_2O_7 \rightarrow H_2O + 2HPO_3 + 100.46 \text{ kilojoule/mole}$$

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 dehydratation, 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.

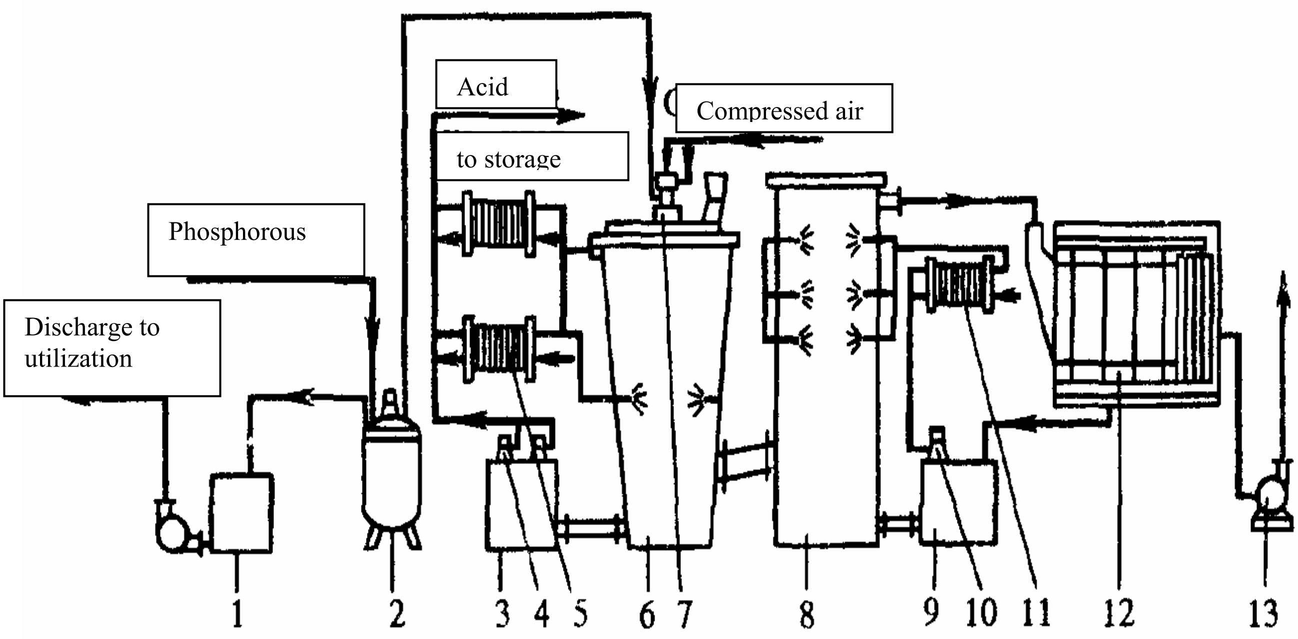
The vaporizing systems based on heat elimination by means of water evaporation or of phosphoric acid dilution, are the most primitive ones from the point of view of instrumental design. However, due to rather huge volume of exhausted gases, application of such systems is viable with aggregates of small 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 – Hydrotation tower; 9 - Circular collector; 10 - Submersible pumps; 11 - Lamellar heat exchangers; 12 – Electrical filter; 13 – Ventilator.

Source: Review of scientific-technology literature

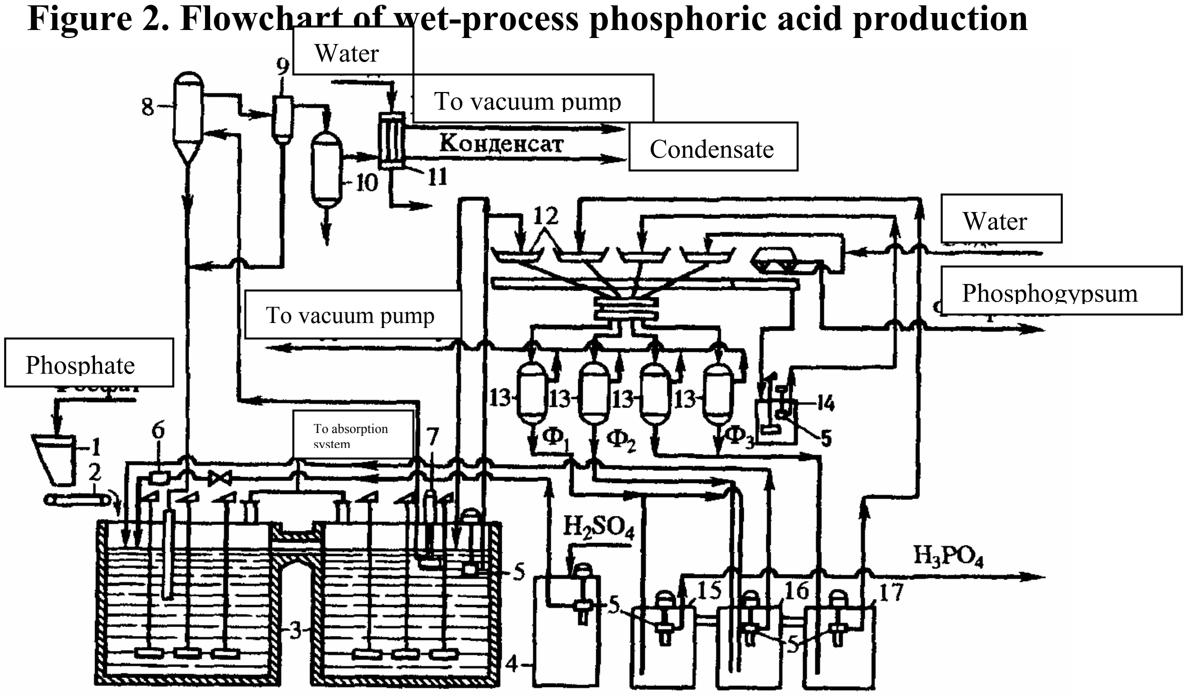
The **extraction method** for phosphoric acid generation is considered to be more economic. This method is based upon disintegration of natural phosphates with acids – mostly with sulfuric acid, to a lesser extent with nitric and, insignificantly, with hydrochloric acid.

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 $CaHPO_4 \cdot 2H_2O$).

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 $CaSO_4$ - H_3PO_4 - H_2O 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 row 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.