Sulfuric Acid Production, Market and Forecast in Kazakhstan

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e-mail: info@infomine.ru
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Annotation

The report is devoted to investigation of the current standing of the sulfuric acid market in Kazakhstan and a forecast of its development for the period up to 2020. The report consists of 6 chapters, contains 74 pages, including 24 figures, 17 Tables and an Appendix.

This work is a desk study. As information sources, data of the Statistics Agency of Kazakhstan, the United Nations database, the Federal Customs Service of Russia were considered, as well as materials of industrial regional press, web-sites of producers and consumers of the product.

The first chapter of the report presents brief characteristics of the production technology of sulfuric acid, the data on raw materials used in Kazakhstan, costs and profitability of the production.

The second chapter is devoted to production of sulfuric acid in Kazakhstan. It presents data on volumes of release in the 2000-2011, the structure of production, and the current status of the largest manufacturing enterprises. It also provides information about ongoing projects on construction of new sulfuric acid plants.

The third chapter presents an analysis of the market prices for sulfuric acid. The dynamics of prices in the domestic market of Kazakhstan, as well as the export-import prices in 2005-2012 years are given. In addition, the forecast of the price of sulfuric acid in Kazakhstan for the period up to 2020 is presented.

The fourth chapter of the report analyzes foreign trade operations with sulfuric acid in Kazakhstan in 2005-2011. It discusses statistical data on the volume of foreign trade, the regional structure of exports and imports of the reagent.

The fifth chapter analyzes the consumption of sulfuric acid in Kazakhstan in 2007-2011. This section provides a supply-demand balance, evaluates a sectoral structure of consumption, and describes the current state of end-uses and largest enterprises-consumers of sulfuric acid.

The sixth, final chapter of the report presents a forecast of development of the market of sulfuric acid in Kazakhstan for the period up to 2020.

The Appendix contains contact information for the largest enterprises-producers and consumers of sulfuric acid in Kazakhstan.
Introduction

Sulfuric acid exists in nature as a separate chemical compound (H\textsubscript{2}SO\textsubscript{4}), as well as its aqueous solutions (H\textsubscript{2}SO\textsubscript{4}·H\textsubscript{2}O, H\textsubscript{2}SO\textsubscript{4}·2H\textsubscript{2}O, H\textsubscript{2}SO\textsubscript{4}·4H\textsubscript{2}O).

Pure sulfuric acid, referred to as monohydrate, is a colorless and odorless oily liquid of the density of 1.83 g/cm\textsuperscript{3} (at 20°C). The substance has a deleterious effect on the plant and animal tissues, depriving them of water, so that they are charred. Pure sulfuric acid melts at 10.31°C, and at 279.6°C it boils with decomposition, forming vapors of sulfur trioxide.

With water and sulfur trioxide the substance is mixed in all proportions, and when it is diluted with water a strong warming occurs, accompanied by a spray of a liquid.

Sulfuric acid is one of the strongest acids. In aqueous solution, it is almost completely dissociates into ions H\textsuperscript{+} (or rather, H\textsubscript{3}O\textsuperscript{+}) and SO\textsubscript{4}\textsuperscript{2–}. In general, the physical properties of aqueous solutions of sulfuric acid, such as density, temperature of crystallization and boiling points, depend on their composition. Thus, the boiling point of aqueous solutions of sulfuric acid increases with its concentration and reaches a maximum at 338.8°C, forming an azeotropic mixture of 98.3% of H\textsubscript{2}SO\textsubscript{4} and 1.7% of H\textsubscript{2}O.

Solutions of SO\textsubscript{3} in sulfuric acid, forming two compounds (H\textsubscript{2}SO\textsubscript{4}·SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}·2SO\textsubscript{3}), are called oleum. The boiling point of oleum decreases with the increasing content of SO\textsubscript{3}.

Sulfuric acid is a relatively strong oxidant, which is manifested most clearly at its heating. The compound oxidizes many metals (Cu, Hg, etc.), carbon - to CO\textsubscript{2}, sulfur - to SO\textsubscript{2}, as well as HI and HBr - to free halogens. At this process, sulfuric acid itself is reduced to SO\textsubscript{2}, and by the most powerful reducing agents - to S and H\textsubscript{2}S.

Concentrated H\textsubscript{2}SO\textsubscript{4} is partially reduced by hydrogen (H\textsubscript{2}), and because of that it can not be applied for its drying.

Dilute sulfuric acid reacts with all metals, which are located in the electrochemical series to the left of hydrogen. Oxidizing properties are not typical for dilute sulfuric acid.

Sulfuric acid forms several types of salts: medium (sulfates) with the anion SO\textsubscript{4}\textsuperscript{2–}, acid (hydrogen sulfates) with the anion HSO\textsubscript{4}\textsuperscript{–}, and basic, containing, along with the anion SO\textsubscript{4}\textsuperscript{2–}, the OH\textsuperscript{–} groups; and also esters, among which dialkyl (diaryl) sulfates (RO)\textsubscript{2}SO\textsubscript{2} (esters), and acid esters ROSO\textsubscript{2}OH are distinguished.

Sulfuric acid is one of the major large-tonnage chemical products. It is used in various sectors of the economy, because it has a complex of special properties that facilitate its technological use. Sulfuric acid does not fume, has no color and smell; at ordinary temperatures it is a liquid; in concentrated form it does not corrode ferrous metals. At the same time, sulfuric acid is one of the strong mineral acids, it forms numerous stable salts, and it is unexpensive.
The industry produces technical, battery and reactive sulfuric acid. These types of acids differ in purpose and the content of the main component and impurities.

Sulfuric acid is used in the manufacture of fertilizers; as an electrolyte in lead-acid batteries; for obtaining various mineral acids, salts; as well as fibers, dyes, explosives, and smoke-generating substances; in the oil, metal, paint, textile, leather and other industries. It is used in the industrial organic synthesis in the reactions of dehydration (production of various esters), hydration (the manufacture of ethanol from ethylene), sulfonation (detergents and dyes), alkylation (the production of isoctane, caprolactam, and polyethylene glycol), etc. (Figure 1).

**Figure 1. Areas of application of sulfuric acid**

- Production of sulfates of Na, K, Fe, Cu, Zn, Al etc.
- Production of K$_2$Cr$_2$O$_7$ and Na$_2$Cr$_2$O$_7$
- Explosives
- Synthesis of alcohols, esters and other organic substances
- Organic dyes
- Production of molasses and glucose
- Chemical fibers, textile industry
- Mineral fertilizers
- Ammonium sulfate
- Etching of metals
- Metallurgy: Al, Mg, Cu, Hg, Co, Ni, Au
- Mineral acids HF, H$_3$PO$_4$, H$_3$BO$_3$
- Mineral pigments
- Refining of petroleum and mineral oils

*Source: review of the technical literature*

Sulfuric acid is produced at enterprises of the non-ferrous metallurgy, at plants for the production of phosphate fertilizers and plants manufacturing sulfuric acid. The world production of sulfuric acid now exceeds 200 million tons per year.

**The largest consumer of sulfuric acid in the world is the production of mineral fertilizers.**

The production of phosphate fertilizers and means of chemical defense of plants uses about 70-75% of sulfuric acid, produced around the world. The release of
chemical products and leaching of ores consume 10% of monohydrate each. Also, large consumers of monohydrate are the manufacture of rubber products and the pulp and paper industry, each consuming about 5% of the reagent.

Sulphuric acid and oleum are very aggressive substances. They affect the respiratory tract, skin, mucous membranes, causing shortness of breath. MPC (a maximum permissible concentration) of the aerosol of sulfuric acid in the working area is 1.0 mg/m³, the average in the air - 0.1 mg/m³, and the maximum single concentration - 0.3 mg/m³. An aerosol of sulfuric acid can be formed in the atmosphere from emissions of the chemical and metallurgical industries, containing oxides of sulfur, and they fall as an acid rain.
1. Technology of production of sulfuric acid and raw materials used in Kazakhstan

The raw material in the manufacture of sulfuric acid may be elemental sulfur and various sulfur-containing compounds, which can be used to obtain sulfur or directly sulfur (IV) dioxide. Natural deposits of native sulfur are small, although its clarke is 0.1%. Most often, the sulfur in the nature occurs in the form of metal sulfides and sulfates, and is part of the oil, coal, natural gas and associated gas. Significant amounts of sulfur in the form of sulfur oxides are contained in flue gases and the waste gases of the non-ferrous metallurgy and in the form of hydrogen sulfide, released during clean-up of flammable gases.

Thus, primary sources of raw materials for the production of sulfuric acid are quite diverse, although for a long time as a raw material mainly elemental sulfur and iron pyrites were used. A limited use of such raw materials as flue gases of thermal power plants and gases of the copper production was due to the low concentration of sulfur (IV) oxide in them. However, in the last decade due to the tightening of requirements for the content of sulfur dioxide in emissions of the gas industry, the need to capture SO₂ and convert it to sulfuric acid increases the proportion of exhaust gases in the balance of raw materials for the manufacture of H₂SO₄. An increasing amount of this product in the world is produced on the basis of flue gases of the non-ferrous metallurgy and gases formed during the processing of oil, while pyrite is virtually not used anymore.

In the overall scheme of the sulfuric acid production the first two stages are essential - a preparation of raw materials and their incineration or burning. These operations and their hardware design depend strongly on the nature of raw materials, which largely determines the complexity of the technological production of sulfuric acid.

The cost of sulfuric acid is determined, essentially, by three elements: the cost of sulfur-containing raw materials; the cost of their delivery to the sulfuric acid plant; and the cost of processing of raw materials into sulfuric acid. Thus, the cost, above all, depends on the type of feedstock, as the cost of sulfur in different materials varies.

In general, the production of sulfuric acid from sulfur-containing materials includes several chemical processes, in which the degree of oxidation of raw materials and intermediate products changes. This can be represented by the following scheme:

\[
\begin{align*}
\text{S}_\text{d}^6 & \xrightarrow{\text{Fe[S}_\text{2}^\text{2}]} \text{S}^\text{+4} \xrightarrow{\text{H}_\text{2}[\text{S}_\text{2}^\text{2}]} \text{S}^\text{+6} \\
\text{FeS}_\text{2}^\text{2} & \xrightarrow{\text{H}_\text{2}[\text{S}_\text{2}^\text{2}]} \text{S}^\text{+4} \xrightarrow{\text{O}_\text{2}} \text{S}^\text{+6}
\end{align*}
\]
where I - is the stage of obtaining the furnace gas (sulfur (IV) oxide),
II - is the stage of the catalytic oxidation of a sulfur (IV) oxide into sulfur (VI)
oxide and its absorption (conversion to sulfuric acid).

In the real production the following processes are added to these stages: the
preparation of raw materials, cleaning of furnace gas, and other mechanical and
physico-chemical operations. In general, the production of sulfuric acid can be
expressed as follows

Raw materials $\rightarrow$ their preparation $\rightarrow$ burning (roasting) of raw
materials $\rightarrow$ cleaning of furnace gas $\rightarrow$ contacting $\rightarrow$ adsorption of the
contacted gas $\rightarrow$ SULFURIC ACID

The need for the first stage disappears when exhaust gases are used as raw
materials, as in this case, the roasting of sulfides is one of the other stages of the
process. Therefore, the cost of sulfur in the flue gases of the metallurgical industry is
not taken into account; moreover, the costs of transportation of raw materials are
eliminated.
1.1. Production of sulfuric acid from flue gases of the enterprises of the non-ferrous metallurgy

The specific technological scheme of production of sulfuric acid, as already mentioned, depends on the type of feedstock, the characteristics of the catalytic oxidation of sulfur (IV) oxide, a presence or absence of the stage of absorption of sulfur (IV) oxide. Depending on how the process of oxidation of SO$_2$ to SO$_3$ occurs, there are two main methods of obtaining of sulfuric acid: the contact and the nitrous.

In the contact method of obtaining sulfuric acid the oxidation of SO$_2$ to SO$_3$ is performed on solid catalysts. Then sulfur trioxide is converted into sulfuric acid in the final stage of the process - the absorption of sulfur trioxide, which can be represented with simplifications by an equation of the reaction:

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$

In carrying out the process by the nitrous (tower) method nitrogen oxides are used as carriers of oxygen. The oxidation of sulfur dioxide is carried in the liquid phase and the end-product is sulfuric acid.

Currently, in the industry the contact method of producing sulfuric acid is mainly employed, because it allows using process units with greater intensity.

To date, the performance of standard production lines of sulfuric acid by the contact method is 180 thousand tons per year. Their replacement with lines of the performance of 360 thousand tons of acid per year can reduce capital costs of the sulfuric acid production by 30%, and production costs by 20%.

In Kazakhstan the technology of production of sulfur from flue gases of the non-ferrous metallurgy by the contact method is implemented at enterprises PLC «Kazakhmys Corporation» and PLC «Kazzinc».
1.2. Production of sulfuric acid by combustion of sulfur

The general scheme of the production of sulfuric acid from sulfur is presented in Figure 2.

Figure 2. Technological scheme of the production of sulfuric acid from sulfur

Source: review of the technical literature

The industrial production of sulfuric acid from sulfur can be divided to the following main stages:
1. Reception of lump sulfur and its placement in storage.
2. Storing the bulk and the lump sulfur.
3. Melting of lump sulfur, its filtering and delivery to burners of the oven. Since the melting point of lump sulfur is relatively low, by settling, followed by filtration, solid mechanical impurities can be easily separated from liquid sulfur, which provides raw materials of a sufficient purity.
4. Preparation of dry air and combustion of liquid sulfur in the furnace to produce SO₂ (sulfur dioxide). For burning molten sulfur two types of furnaces - nozzle and cyclone - are used. Both classes of equipment include a spray of liquid sulfur in order to achieve its rapid evaporation and to ensure a good contact with the