

Sulfuric Acid

Process Technology (including Chamber and Double Absorption Contact Routes), Production Costs, and Regional Supply/Demand Forecasts are presented.

PERP07/08S8

Report Abstract

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CHEMSYSTEMS PERP PROGRAM

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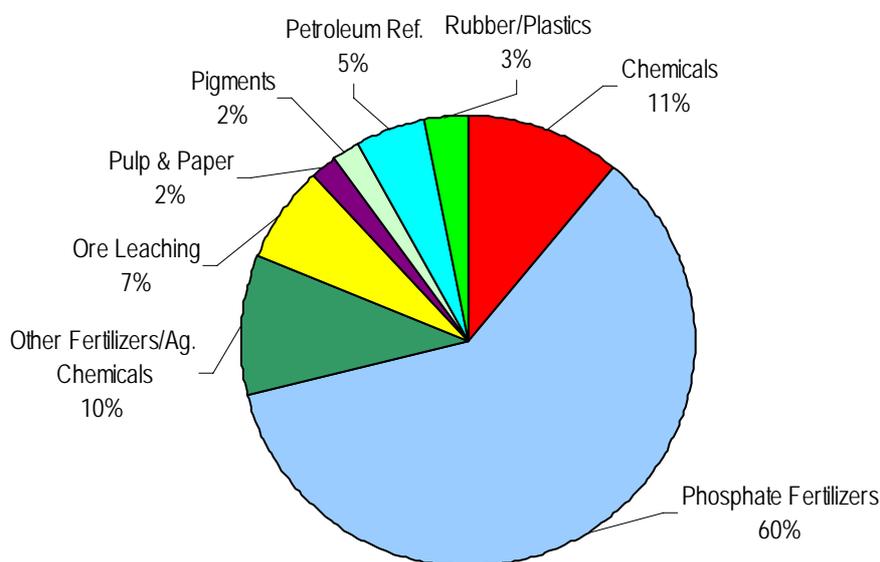
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INTRODUCTION

Sulfuric acid has many applications, and is generally considered the chemical with the highest total annual production quantity globally. Principal uses of sulfuric acid include ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis.

However, there are so many uses of sulfuric acid that any detailed listing of them is likely to be incomplete or include aggregate categories. A common description of sulfuric acid demand according to the primary uses is shown in the figure below.

Global Sulfuric Acid Demand by Application



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Despite the diverse and seemingly endless uses for sulfuric acid, its use in phosphate fertilizers represents approximately half or slightly more of the total sulfuric acid used worldwide. In recent years with increased demand for phosphate fertilizers, this has grown to about 60 percent, as the population growth worldwide and upgrading of diets in a number of large countries has increased the intensity of agricultural practices. Another contributing factor is the demand for fertilizer caused by biofuels production.

Sulfuric acid is a strongly acidic, oily liquid that may be clear to cloudy in appearance. Concentrated acid is both an oxidizing and a dehydrating agent. Many grades are available ranging from electrolyte grade (33 weight percent) for batteries, to 93 weight percent (66 deg Baume), 98 weight percent, and 20-22 weight percent fuming oleum containing excess dissolved sulfur trioxide. The grade most often shipped is 93 weight percent, since this concentration offers a low freezing point (about -30 °F).

In the environment, sulfuric acid is a constituent of acid rain, since it is formed by atmospheric oxidation of sulfur dioxide in the presence of water. Atmospheric sulfur dioxide is generated by combustion of sulfur-containing fossil fuels such as coal and oil. In theory, there is sufficient sulfur dioxide to supply all the world's sulfuric acid needs in combustion offgases from power stations and large industrial boilers. Although it is possible to recover such sulfur dioxide by regenerative flue-gas desulfurization processes, or to convert it directly into sulfuric acid, these options are typically at an economic disadvantage compared to non-regenerative pollution control techniques. Such non-regenerative techniques usually convert the sulfur dioxide to gypsum, which then can become a secondary pollution problem if the quantity produced exceeds market needs, at least on a local or regional basis.

Sulfuric acid was once known as oil of vitriol, coined by the 8th century Arabian alchemist Jabir ibn Hayyan after his discovery of the chemical. It was prepared by Johann Van Helmont in the 1600s by destructive distillation of green vitriol (ferrous sulfate) and by burning sulfur. The word vitriol derives from the Latin vitreus, "glass", referring to the glassy appearance of the sulfate salts (which also carried vitriol in their common names). Burning sulfur with saltpeter (potassium nitrate) was first used to prepare sulfuric acid in the 17th century. By the mid-17th century, John Roebuck had invented the lead chamber process which used nitrogen oxides as oxidant. The contact process, wherein the oxidation of sulfur dioxide to sulfur trioxide is performed by oxygen (air) over a catalyst, was originally developed about 1830 by Peregrine Phillips in England.

An important distinction that occurs in sulfuric acid production is between discretionary and non-discretionary production. In discretionary production, the mining of sulfur or sulfur-bearing minerals (pyrites) is the sole objective, based on the voluntary mining of discrete deposits to obtain maximum economic recovery. In non-discretionary production, sulfur or sulfuric acid is recovered as an involuntary by-product, the quantity of which is subject to demand for the primary product alone.

The lead chamber process has now been almost completely superseded by the contact process in the industrial production of sulfuric acid. Much of the acid produced by the lead chamber process is utilized in the making of fertilizers, since the acid is relatively dilute. In contrast, the contact process can make acid of any desired concentration.

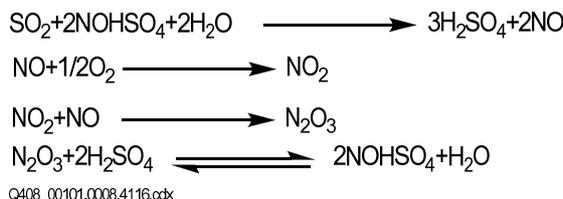
Contact process plants fed sulfur dioxide made from burning sulfur are simpler than those processing sulfur dioxide from metals smelting operations, in that special purification of the feed gases is not required. Cooling and heating of the feed gases are minimized, improving energy recovery. When by-product sulfur dioxide from smelter gases is used, extensive purification is required to remove impurities such as fluorides and arsenic which can damage the catalyst carrier. There are also secondary sources of sulfur such as hydrogen sulfide and spent sulfuric acids.

This report provides the background of sulfuric acid manufacture, an overview of the lead chamber process, and a detailed discussion of the contact process (focusing on the double-absorption version). A cost of production estimate is presented, along with sensitivities to sulfur price, plant investment, and capacity. Sulfuric acid pricing trends are discussed, and a commercial analysis discusses end uses and supply/demand/trade data for the United States, Western Europe, and East Asia, including a global summary.

TECHNOLOGY

Chamber Process

Sulfuric acid is formed by a complex series of reactions the details of which are not fully understood to this day. Nitrogen oxide processes are based on oxidation of sulfur trioxide in the liquid phase. The overall course of the reaction can be described as follows:



with the net reaction being:



Sulfur dioxide is absorbed in the aqueous phase and oxidized there by nitrosyl hydrogensulfate, NOHSO_4 (“nitrosylsulfuric acid”) in a medium of about 70 percent sulfuric acid.

Among the developments that helped keep the process competitive with the increasingly popular contact process (to be discussed below) was the introduction by Peterson in 1923 of an improved process that replaced the lead chambers themselves with acid-irrigated towers. In 1910, plants using nitrogen oxides to produce sulfuric acid accounted for about 80 percent of production in North America and Western Europe. This figure dwindled to 20-25 percent by 1950 and to almost nil by 1980. Presently, the only interest is for the processing of gases with extremely low sulfur dioxide content.

Contact Process

Sulfuric acid production is dominated by the contact process which permits the direct production of pure acid ranging from dilute solutions to super-concentrated solutions containing over 100 percent sulfuric acid (oleum, a.k.a. “fuming” acid). The name contact process comes from sulfur dioxide being oxidized to the trioxide by oxygen (in air) while passing over a catalyst bed (“contact mass”).

The following aspects of the Contact Process are discussed in the report:

- Process Chemistry.
- Catalysts.
- Sulfur Burning Process plants (Gas drying, Catalytic conversion of sulfur dioxide to the trioxide, Absorption of sulfur trioxide, and Product acid cooling).
- Sulfuric acid plants based on metallurgical off-gases.
- Haldor-Topsoe Wet Sulfuric Acid (WSA) Process.
- Spent Acid Regeneration.
- Tail-Gas Treatment.
- Storage and Handling.

RECENT DEVELOPMENTS

Some examples of recent sulfuric acid-related patents summarised in the report include:

- The use of ruthenium catalysts for the final bed of a contact sulfuric acid plant.
- The use of certain metals for constructing heat recovery equipment for use in the acid-making circuit of a sulfuric acid plant.
- Claimed improvements in the materials of construction in handling the acid.
- Claimed improvements in dealing with spent acid.
- Removing organic impurities from sulfuric acid with liquid or supercritical carbon dioxide.
- Process for manufacturing sulfuric acid from a gas containing sulfur dioxide and steam.

ECONOMIC ANALYSIS

Cost of Production Estimate of Sulfuric Acid (98% Product, on 100% Basis) via the Sulfur Burning, Double Absorption Process has been evaluated for various scenarios as follows:

- Cost of production estimates have been calculated over a range of plant capital costs.
- Cost of production estimates have been calculated over a range of sulfuric acid production capacities.

The base case sulfur price used for fourth quarter 2007 represents a historic high up to that date in time, and sulfur prices have been extremely volatile over the last two years. The price of sulfur has a major impact on the cost of sulfuric acid. Accordingly, the price of sulfur has been parameterized over a range of prices.

COMMERCIAL ANALYSIS

Sulfuric (or sulphuric) acid, H_2SO_4 , is a strong mineral acid that is the most common acid used in industry and commerce. It is soluble in water at all concentrations and although hazardous if handled carelessly, can be used and shipped safely with attention to standard precautions and a focus on detail and safety procedures.

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production has been a reasonably good indicator of its industrial strength for the last century or so.

In order to understand the sulfuric acid market, one needs to also address the markets for phosphate rock and phosphate fertilizers. This, as well as sulphuric acids relationship to the sulphur market, are discussed in the report.

- Sources of sulfuric acid supply vary by region and to some extent by time. Supply/demand data globally as well as for the specific cases of North America, Western Europe, and East Asia are given in the report.
- The fairly complicated relationship between sulfuric acid production and energy markets/industry is briefly discussed.



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