Guidelines EN-G06: Sulfuric Acid Works

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1. Introduction

Sulfuric acid (H_2SO_4) is a strong mineral acid. It is soluble in water at all concentrations. It was once known as oil of vitriol. Sulfuric acid has many applications, and is one of the top products of the chemical industry. Many proteins are made of sulfuric acid-containing amino acids such as cysteine and methionine which produced sulfuric acid when metabolized by the body.

Sulfuric acid is a constituent of acid rain which is formed by atmospheric oxidation of sulfur dioxide in the presence of water – i.e. oxidation of sulfurous acid. It is the main byproduct produced when sulfur-containing fuels such as coal or oil are burned.

It is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. The major use (60% of total production worldwide) for sulfuric acid is in the "wet method" for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as trisodium phosphate for detergents. Sulfuric acid is used for a variety of other purposes in the chemical industry. It is the usual acid catalyst for the conversion of cyclohexanoneoxime to caprolactam, used for making nylon. It is used for making hydrochloric acid from salt via the Mannheim process. Much H_2SO_4 is sued in petroleum refining, for example as a catalyst for the reaction of isobutene with isobutylene to give isooctane, a compound that raises the octane rating of gasoline (petrol). Sulfuric acid is important in the manufacture of dyestuffs solutions and is the "acid" in lead-acid (car) batteries. It is also used as a general dehydrating agent in its concentrated form.

Although sulfuric acid is non-flammable, contact with metals in the event of a spillage can lead to the liberation of hydrogen gas. The dispersal of acid aerosols and gaseous sulfur dioxide is an additional hazard of fires involving sulfuric acid. Sulfuric acid is not considered toxic besides its obvious corrosive hazard and the main occupational risks are skin contact leading to burns and the inhalation of aerosols. Exposure to aerosols at high concentrations lead to immediate and severe irritation of the eyes, respiratory tract and mucous membranes: this ceases rapidly after exposure, although there is a risk of subsequent pulmonary edema if tissue damage has even more severe. At lower concentrations, the most commonly reported symptom of chronic exposure to sulfuric acid aerosols is erosion of the teeth, found in virtually all studies: indications of possible chronic damage to the respiratory tract are inconclusive as of 1997. In the United States, the permissible exposure limit (PEL) for sulfuric acid is 1 mg/m^3.

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Interestingly, there have been reports of sulfuric acid ingestion leading to vitamin B12 deficiency with subacute degeneration. The spinal cord is most often affected in such cases, but the optic nerves may show demyelination.

Rhodia Eco Services is the world's largest producer of sulfuric acid made from sulfur.

These notes apply to the manufacture of sulfuric acid by the double-contact process and to the production of sulfur trioxide for use in chemical processes.

2. Sampling, Measurement of Emissions and Monitoring

- As part of proper supervision, the owner shall make tests and inspection of the process. Tests shall normally be taken not less than once per day from each exit and adequate facilities shall be provided on chimneys and ducts.

- Continuous monitors for emission of sulfur dioxide shall be installed, with sufficient range to cover start-up conditions.

- The Reich test or an agreed alternative shall be used to determine the sulfur dioxide (SO_2) content of the strong gas fed to the first catalytic converter. Allowance shall be made for the use of quench or additional air.

3. Emission Sources

The primary sources of sulfuric acid emissions are the industries that manufacture it or use it in production. Some of the industries that use it in production are the metal smelters, phosphate fertilizer producers, oil refiners, the chemical industry, battery manufacturers, manufacturers of fabricated metal products, electronic components and measuring and controlling devices. These are emissions to the air unless there is a spill to water or land. Sulfuric acid spill to land or water may result in emissions of the acid to air. Other possible emitters of sulfuric acid are home and larger pool treatment, the disposal of automobile batteries, electroplating facilities, electronics, semiconductor and circuit board production, potato growers and water and waste water treatment. These emissions may be to the soil, water or air. Sulfuric acid may be also produced as a result of sulfur dioxide reacting

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with other chemicals in the air. It naturally occurs in volcanic gases. Although sulfuric acid is not found in motor vehicle exhaust, it may be produced by the reaction of sulfur dioxide in the exhaust with other chemicals. Hard surface cleaners, metal cleaners, pool chemicals, car motorcycle, truck and boat batteries may contain sulfuric acid.

4. Emission Limits and Controls

- During normal operation, the production of sulfur dioxide emitted to air shall not exceed 2,000 mg/m^3; including sulfuric acid mist shall not exceed 150 mg/m^3.
- The waste gases shall be substantially free from persistent mist.

5. Operational Controls

- An efficient mist eliminator shall be provided after the final absorber.
- Means for rapid warming of absorber acid feed failure shall be installed.
- Means for indicating the sulfur feed rate and the air flow rate to the sulfur burner shall be installed.
- Means for the early detection of leaks on acid coolers shall be provided.
- When sulfuric acid is being transferred or loaded into tanks, non-splash techniques and bottom loading shall be practiced.
- Adequate preheating facilities shall be provided to enable at least two catalysts stages to “strike” as soon as sulfur dioxide is fed to the system.
- Absorber acid strength and temperature shall be adjusted to optimum before the start-up.
- By careful preparation and control, the duration of abnormal emissions on start-up shall be minimized.

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6. Materials Handling and Storage

- The receipt, handling and storage of powdered raw materials shall be carried out in such a manner as to minimize the emission of dust to the point where there is no significant visible emission. Covered storage shall be provided.

- Gaseous sulfur trioxide shall be kept in a closed system and escapes to air shall be prevented.

- If oleum is produced, storage and tanker-loading facilities shall be fitted with means to prevent the emission of fumes.

7. Chimneys

- Chimneys are an insurance policy against plant breakdown and are determined on the bases of the expected maximum rate of sulfur dioxide emission.

- The minimum height for a sulfuric acid plant shall be as follows:

PLANT RATED CAPACITY *(metric tons / day)*	HEIGHT *(meters)*
up to 400	60
600	75
800	85
1,000	95

- The height may need to be increased to allow for special local circumstances.

- The linear velocity of waste gases in the chimney shall not exceed nine (9) m/s.

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8. Environmental and Health Effects

Sulfuric acid is a corrosive chemical and can severely burn the skin and eyes. It may cause third degree burns and blindness on contact. Exposure to sulfuric acid mist can irritate the eyes, nose, throat and lungs, and at higher levels can cause a buildup of fluid in the lungs (pulmonary edema). Asthmatics are particularly sensitive to the pulmonary irritation. Repeated exposure may cause permanent damage to the lungs and teeth. The International Agency on Cancer – Australia has classified occupational exposures to strong-inorganic-acid mists containing sulfuric acid as carcinogenic to humans.

Sulfuric acid can enter the body if we breathe in contaminated air. While it is not absorbed through the skin, skin contact with strong concentration may cause serious burns.

Consumers are most likely to be exposed to sulfuric acid when using products containing the substance (e.g. some cleaning products or car batteries. Workers in the industries that sue or produce sulfuric acid are at risk of exposure. Consumers can also be exposed to sulfuric acid by exposure to air contaminated by sulfur dioxide emissions.

Sulfuric acid will exist as particles or droplets in the air if released to the atmosphere. It dissolves when mixed with water. It has moderate acute (short-term) toxicity on aquatic life. Sulfuric acid is very corrosive and would badly burn any plants, birds or land animals exposed to it. It has moderate chronic (long-term) toxicity to aquatic life. Chronic effects on plant, birds or land animals have not been determined. Small quantities of sulfuric acid will be neutralized by the natural alkalinity in aquatic systems. Larger quantities may lower the pH for extended periods of time. Industrial emissions of sulfuric acid can produce elevated concentrations in the atmosphere. Sulfuric acid will exist as particles or droplets which may dissolve in clouds, fog, rain, dew or snow, resulting in very dilute acid solutions. In clouds and moist air, it will travel along the air current until it is deposited as wet acid deposition (acid rain, acid fog, etc.). In waterways, it readily mixes with water. It enters the air during production, use and transporting it, in the air it will react with other chemicals present such as ammonia, magnesium, calcium, etc. to form salts, which neutralizes the acid. The acid particles dissolve in clouds, fog, rain or snow resulting in very dilute acid solutions. This may impact the environment as wet acid deposition (“acid rain”).

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