Introduction

Sulfuric acid with the chemical formula $\mathbf{H_2SO_4}$ is a highly important industrial product, widely used in numerous applications in the chemical industries. Its production can be considered the foundational industry of mineral chemistry. The production of sulfuric acid already exceeded 10 million tons (Mt) at the beginning of the 20th century, reached 38 Mt in 1955, 160 Mt in 1990, and has now reached 180 Mt.

1. Properties of Sulfuric acid

Anhydrous sulfuric acid is a colorless, odorless liquid, more or less viscous depending on its concentration, with a specific gravity of 1.83 at +15°C. It solidifies at +10.35°C and forms several hydrates with the general formula H_2SO_4, nH_2O (where n = 1, 2, 3, 4, 6). The solidification temperature varies significantly with the degree of hydration. It boils at 320°C, containing about 98% pure acid. Commercial solutions are commonly used: one is **66°**Baumé acid, containing approximately **98%** acid, and the other is **26°**Baumé acid, which contains about **30%** acid.

2. Production of Sulfuric Acid

Sulfuric acid is primarily produced from sulfur dioxide (SO_2), which is one of the main gases produced by the combustion of fossil fuels or mineral processing. There are mainly two industrial processes for producing this acid:

2.1. Lead Chamber Process

This is an older method that involves passing gases containing sulfur dioxide through lead chambers, where sulfur dioxide is oxidized into sulfur trioxide by the air. The sulfur trioxide is then absorbed into water to produce sulfuric acid. This method is less common today.

2.2. Contact Process

This is the most commonly used method for large-scale sulfuric acid production. It relies on the oxidation of sulfur dioxide (SO_2) into sulfur trioxide (SO_3) using a vanadium-based catalyst. This process occurs at high temperatures and produces a gas that is then absorbed into a water solution to form sulfuric acid.

3. Raw Materials for Sulfuric Acid Production

The production of sulfuric acid requires several essential raw materials for its manufacturing process. The main raw materials used in sulfuric acid production are:

1. ***Sulfur (S)***

- Sulfur is the primary raw material used in sulfuric acid production. It is often extracted from natural deposits or industrial by-products (such as petroleum and natural gas).
- Sulfur is burned to produce SO_2 (sulfur dioxide), which is the first step in the production process.

2. ***Oxygen (O_2)***
   - Oxygen is essential for the oxidation of SO_2 into SO_3 (sulfur trioxide) in the second step of the process. It is usually obtained from ambient air, and in the contact process, oxygen is used to enhance the efficiency of the SO_2 oxidation reaction.
3. ***Water (H_2O)***
   - Water is used in the final step of the process, where SO_3 is absorbed in water to form sulfuric acid (H_2SO_4). The absorption of SO_3 in water is an exothermic reaction that releases heat.
4. ***Vanadium-based Catalyst (V_2O_5)***
   - In the contact process, a vanadium-based catalyst is used to accelerate the oxidation reaction of SO_2 to SO_3. Vanadium pentoxide (V_2O_5) is used as the catalyst to increase the efficiency of the reaction without being consumed in the process.

4. The Contact Method

The sulfuric acid productio process primarily consists of three phases: combustion, oxidation, and absorption.

First Step : Production of Sulfur Dioxide (SO_2)

Sulfur dioxide (SO_2) is a colorless gas with a pungent odor. It is primarily produced industrially by the combustion of sulfur or sulfur-containing minerals. Here are the main methods of production :

4.1.Production by Sulfur Combustion

In this stage, sulfur dioxide (SO_2) is produced through the combustion of elemental sulfur is in the presence of oxygen at. This process occurs at temperatures ranging from **900 to 1100°C**. The liquid sulfur is sprayed into fine droplets inside excess dry air to ensure complete combustion and prevent any unburned sulfur. This means that sulfur fully reacts with oxygen, leaving no unreacted sulfur. This reaction is highly exothermic (releases heat).

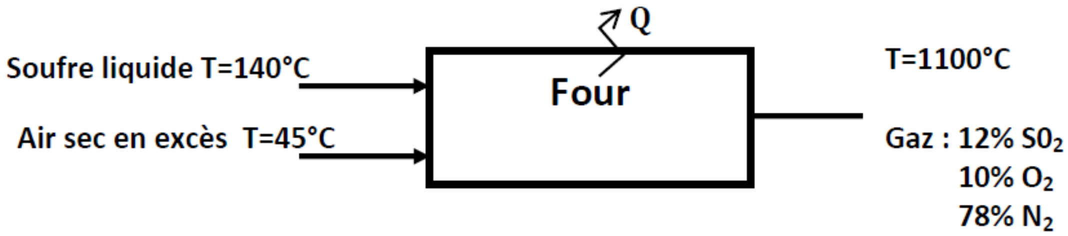
$$\mathbf{S(l) + O_2(g) \rightarrow SO_2(g)} \quad \Delta H°r,\ 298K = -\ 297\ kJ/mole$$

After the reaction is complete in the furnaces, the composition of the exiting gases is as follows

12% SO_2: The percentage of sulfur dioxide produced.

10% O_2: The percentage of remaining oxygen.

78% N_2: The percentage of nitrogen that does not react.



1. *Production from Sulfur-containing Minerals*

Sulfur dioxide can be produced by roasting sulfur-containing ores, mainly pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$).

Oxidation of pyrite : $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

Oxidation of zinc sulfide : $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO2$

Oxidation of chalcopyrite : $CuFeS_2 + 4O_2 \rightarrow Cu + 2FeO + 2SO_2$

2. *Production by Sulfate Reduction*

Some processes allow the production of SO_2 by reducing metallic sulfates with carbon :

$$Na_2SO_4 + C \rightarrow Na_2S + 2CO_2 + SO_2$$

This method is less common and is mainly used in some chemical industries.

3. *Production by Recovery from Industrial Gases*

SO_2 is also a by-product of various industrial processes, including :

- **Non-ferrous metallurgy** (extraction of copper, lead, zinc).
- **Combustion of sulfur-containing fossil fuels** (coal, oil).
- **Oil refining**.

In these cases, SO_2 is often recovered and converted into sulfuric acid via the contact process.

Second Step : Conversion of SO_2 to SO_3 (Thermodynamics, Kinetics, and Converter Calculations)

The conversion of SO_2 to SO_3 is an oxidation reaction that occurs in the sulfuric acid production process using the contact process**.** This reaction requires a catalyst**,** usually vanadium oxide (V_2O_5), and takes place at high temperatures**.**

1. Thermodynamics

The reaction between SO_2 and O_2 to form SO_3 is exothermic, meaning it releases heat during the reaction. The **ΔH°r** for this chemical equation is negative, indicating that the reaction generates heat as it proceeds.

$$\mathbf{SO_2 + 1/2\ O_2 \rightleftharpoons SO_3 \quad \Delta H°r,\ 298K = -99\ kJ/mole}$$

Equilibrium is achieved at high temperatures, which helps maximize the production of SO_3.

2. Kinetics

Kinetics depends on several factors, such as concentration**,** temperature, and the presence of the catalyst. The rate of the reaction is highly dependent on temperature and the available oxygen. At high temperatures and with the presence of vanadium oxide as a catalyst, the reaction occurs much faster.

3. Calculations in Converters

In contact process converters, the conversion rate of the reaction is measured, which is the ratio of the number of SO_3 molecules formed to the number of SO_2 molecules available in the incoming gas. The conversion rate can be calculated using the following equation :

$$\mathbf{Conversion\ Rate = X = (SO_2\ (inlet) - SO_2\ (outlet)) / (SO_2\ (inlet)) \times 100\ (\%)}$$

$$\textit{Taux de conversion } X = \frac{SO_2(\textit{Entrée}) - SO_2(\textit{Sortie})}{SO_2(\textit{entrée})} \times 100 \qquad (\%)$$

Where :

- **SO_2 (inlet) :** The concentration of sulfur dioxide in the incoming gas to the converter.
- **SO_2 (outlet) :** The concentration of sulfur dioxide in the gas exiting the converter after the reaction.
- The conversion rate represents the ratio of SO_3 molecules formed to SO_2 molecules in the incoming gas.

These calculations are used to determine the efficiency of the converter and to adjust operating conditions such as temperature and gas pressure to achieve the optimal conversion rate. For example, temperature can be adjusted to accelerate the reaction, or pressure can be increased to improve the conversion rate and increase the production of SO_3.

Third Step : Absorption of SO_3

After sulfur trioxide (SO_3) is formed in the contact process converters, it is absorbed in water or an aqueous solution to produce sulfuric acid. This process involves absorbing the gas containing SO_3 into cold water or an aqueous solution containing sulfuric acid, where SO_3 reacts with water to form sulfuric acid (H_2SO_4) according to the following chemical equation :

$$\mathbf{SO_3 + H_2O \rightarrow H_2SO_4}$$

At this stage, the gas containing SO_3 is cooled after being absorbed by water or the aqueous solution. The heat generated from the previous reaction is used to accelerate the absorption process.

The process is typically carried out in absorption towers or special reactors equipped with systems to effectively distribute the gas and liquid, ensuring complete absorption of SO_3 and its conversion into sulfuric acid. Production units can have capacities of up to 2500 tons per day**.**

5. Manufacturing and Environmental Aspects

The manufacturing of sulfuric acid, particularly through the contact process, involves significant chemical reactions that impact the environment. These reactions, which produce SO_2 and SO_3**,** generate heat and contribute to emissions if not properly managed.

5.1. Environmental Aspects of Sulfuric Acid Production

1. **Air Pollution**
    - **SO_2 emissions** : If the process is not properly controlled, sulfur dioxide (SO_2)**,** a significant air pollutant, can be released into the atmosphere. SO_2 is a precursor to acid rain, which harms ecosystems, soil, water bodies, and infrastructure.
    - **Nitrogen oxides (NOx)** : The use of high-temperature processes can lead to the formation of **NOx**, which contributes to air pollution, acid rain, and smog.
2. **Water Usage and Contamination**
    - **Water consumption** : The absorption of SO_3 into water to form sulfuric acid requires substantial amounts of water. This can lead to water scarcity concerns in areas with limited freshwater resources.
    - **Water contamination** : If sulfuric acid production waste or gases like SO_2 are not treated properly, there is a risk of water contamination, impacting local water quality.
3. **Energy Consumption**
    - The process requires high temperatures (around **430-600°C**), making energy consumption a significant environmental concern. The use of fossil fuels to generate this heat can contribute to carbon emissions and climate change.
4. **Waste Management**

- **Solid waste** : The spent catalysts and other residues from the process must be properly managed to prevent contamination. Disposal of hazardous materials can pose environmental risks.

5.2. Mitigating Environmental Impact

1. **Emission Control :** Scrubbers and filters are often used to capture SO_2 and NOx before they are released into the atmosphere, reducing harmful emissions.
2. **Sustainable Practices** : Sulfuric acid production can benefit from improved recycling of sulfur compound and better management of waste products to minimize environmental impact.
3. **Energy Efficiency** : Improving energy efficiency in the production process by using cleaner sources of energy or waste heat recovery systems can help reduce overall environmental impact.

By improving these practices, sulfuric acid production can be made more environmentally sustainable while reducing its impact on the atmosphere, water, and energy consumption.

6. Flow-Sheets

Flow-sheets are graphical representations used to describe industrial processes or chemical reactions in various systems. These diagrams show the sequence of operations and their relationships, using symbols and lines to represent equipment, components, and materials entering and exiting the system.

6.1. Types of Flow-Sheets

1. **Simple Flow Diagram :** Used for processes that require a simple sequence of stages. It shows the incoming and outgoing materials and basic processes like combustion, oxidation, or absorption**.**
2. **Complex Flow Diagram :** Used in large industrial systems or multi-stage processes, where detailed stages such as chemical reactions, catalysts, and temperature are represented. It often includes multiple reactors**,** absorption towers**, or** chemical plants**.**
3. **Process Flow Diagram (PFD) :** Commonly used in chemical engineering, it shows the flow of materials and energy through the system using standard symbols such as vessels, pipes, reactors, and heat exchangers**.**
4. **Piping and Instrumentation Diagram (P&ID) :** Used in mechanical and chemical engineering to represent processes in more detail, including pipes, valves, pumps**,** and industrial equipment. This diagram provides in-depth information about the control systems and instrumentation involved in the process.

6.2. Importance of Flow-Sheets

- **Simplifies Understanding :** They help in understanding complex processes easily.
- **Process Improvement :** Used to identify bottlenecks or weak points in operations.

- **Documentation :** Serve as a method for documenting industrial and chemical systems.
- **Communication :** Facilitate communication between engineers, technicians, and process supervisors.

6.3. Example of a Flow-Sheet for Sulfuric Acid Production

In the sulfuric acid production process, a flow-sheet can represent stages such as :

1. Combustion to produce SO_2.
2. Oxidation using a vanadium catalyst to produce SO_3.
3. Absorption in water or an aqueous solution to produce sulfuric acid.

These flow-sheets show the flow of chemical materials through reactors or towers, as well as operational variables such as temperature and pressure.