SULFURIC ACID

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1.0 SCOPE

This document provides loss prevention recommendations for sulfuric acid and oleum manufacturing facilities. The manufacturing methods covering in this data sheet are sulfur burning, metallurgical, and spent acid regeneration processes.

1.1 Hazards

The main hazards in this occupancy are:

- Corrosive environments
- Weak acid generation
- Hydrogen gas explosions
- High temperature and pressure conditions
- Plastic equipment and piping (FRP)
- Explosions in electrostatic precipitators

1.2 Changes

October 2024. Interim revision. The following changes were made:

A. Reorganized recommendations in Section 2.0 to provide clearer guidance regarding application of recommendations to specific sulfuric acid manufacturing processes (sulfur burning, metallurgical and spent acid regeneration).

B. Removed Section 2.4.1, Gas Cleaning Plants. New guidance was developed in the process overview section (3.2) for metallurgical and acid regeneration plants.

C. Included clarification for blower recommendations on surge detection systems and prevention/detection for condensate acid ingress.

D. Clarified recommendation for sulfuric acid storage tanks venting protection.

E. Added clarification to sulfur burner furnace recommendation regarding autoignition temperature and interlocks.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Construction and Location

2.1.1 For the construction of the plant, use building materials that are compatible and that will resist the environmental and process conditions. Document and maintain throughout the lifecycle of the plant the required materials of construction for all piping, process vessels, gaskets, etc. Include any alloy changes in a management of change program.

2.1.2 Use a positive material identification (PMI) program for all piping and vessels requiring high alloy services. Materials should be verified using alloy analysis tools (e.g., x-ray fluorescence) during construction and all repair and modification activities.

2.1.3 Locate plastic equipment using spacing distribution to prevent equipment from being concentrated in a single area. Ensure plastic equipment is located away from areas in which potential acid leakage could damage the integrity and proper function of the equipment.

2.1.3.1 Label or identify plastic equipment using placards or other means to alert people about the fire risk if activities such as hot work (cutting and/or welding) are performed on or near the equipment.

2.1.4 Install plastic ducts so they are not exposed to potential fires from equipment with oil fire hazards and/or combustible storage. For additional guidance refer to Data Sheet 7-78, *Industrial Exhaust Systems*.

2.1.5 For steam turbine generators (STGs), follow the recommendations for construction and location in Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*.

2.2 Process Safety

2.2.1 Establish a formal process safety program in accordance with Data Sheet 7-43, *Process Safety*. Place emphasis on process and equipment integrity (mechanical).

2.3 Protection

2.3.1 For the protection of stacks with plastic liners, follow the recommendations in FM Property Loss Prevention Data Sheet 7-78, *Industrial Exhaust Systems*.

2.3.2 Follow recommendations for protection of steam turbine blowers and generators in FM Property Loss Prevention Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*.

2.4 Equipment and Processes

Equipment, including accessory or utility equipment, should be designed, constructed, installed, operated, protected, and maintained in a way that minimizes the risk of failures, while providing process reliability. Selection of building construction materials for equipment is paramount in this occupancy due to harsh environmental and process conditions.

2.4.1 Fuel Fired Equipment

2.4.1.1 Provide all fuel-fired equipment, including sulfur burners, gas heating systems, and pre-heaters, with combustion safeguards and interlocks in accordance with FM Property Loss Prevention Data Sheet 6-10, *Process Furnaces*.

2.4.2 Blowers

2.4.2.1 Select blower building materials according to compatibility and process conditions. Ensure a slight over-design is provided to account for normal levels of corrosion and wear expected over the life of the unit.

2.4.2.2 For blowers taking suction after the drying tower, ensure that measures are implemented to prevent or limit the ingress of condensate acid to the blower.

2.4.2.3 Ensure blowers with the potential to experience surge conditions are provided with a surge protection system. An interlock to open a recycle line that discharges back to the inlet of the drying tower may be used. See FM Property Loss Prevention Data Sheet 7-95, *Compressors*, for additional guidance on surge detection and anti-surge control systems.

2.4.3 Heat Exchangers

2.4.3.1 Install a detection system interlock after each acid cooler heat exchanger to detect any acid/water leaks and shutdown the flow to prevent weak acid damage to heat exchangers and downstream equipment. Steam quality, conductivity, or some other detection means may be used.

2.4.3.2 For heat recovery boilers, see the guidance in Data Sheet 6-14, *Heat Recovery Boilers*.

2.4.4 Sulfuric Acid Storage Tanks

2.4.4.1 Provide atmospheric acid storage tanks with adequate venting to protect the tank from vacuum or pressure caused by filling/emptying operations and atmospheric temperature changes. This recommendation is also important for carbon steel tanks to vent the hydrogen created by normal corrosion rates.

2.4.4.2 Provide acid storage tanks with high level alarms and high-high level interlocks.

2.5 Operation and Maintenance

2.5.1 Operation

2.5.1.1 Establish operational procedures for all operation modes, including normal startup and shutdown, process upsets, emergency shutdown, and restart, that include activities to prevent conditions such as weak acid generation or hydrogen formation and explosions.

2.5.1.2 Ensure updated procedures exist for fuel-fired equipment with all the activities/instructions to be followed for cold start and hot restart operations.

2.5.2 Maintenance

2.5.2.1 Establish and implement an asset integrity monitoring program in accordance with FM Property Loss Prevention Data Sheet 9-0, *Asset Integrity*.

2.5.2.2 Inspect, test and maintain safety controls, alarms and interlocks according to Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks*.

2.6 Sulfur Burning Process

2.6.1 General

2.6.1.1 Locate the outdoor sulfur pile storage in an area that is not subject to prevailing winds. If necessary, provide wind barriers, water spray or coating with molten sulfur (long term storage) if there are no natural barriers present.

2.6.2 Protection

2.6.2.1 Provide automatic sprinkler protection for elevated conveyors and combustible buildings handling or storing solid or molten sulfur. For additional information see Data Sheets 7-11, *Conveyors*, and 3-26, *Fire Protection for Nonstorage Occupancies*.

2.6.3 Equipment and Processes

2.6.3.1 Sulfur Burner Furnace

2.6.3.1.1 Interlock the sulfur burner furnace to prevent molten sulfur from entering the chamber if the temperature of the chamber is below the sulfur autoignition temperature. Ensure safety margins are considered when establishing the trip temperature for the interlocks.

2.6.3.2 Molten Sulfur Storage Tanks

2.6.3.2.1 Provide molten sulfur storage tanks or pits with temperature monitoring devices to ensure temperature is maintained in the range of 250-280 °F (120-140 °C) to prevent overheating and fires.

2.6.3.2.2 Provide an inert atmosphere of storage tanks or pits to prevent potential fires using one of the following options:

A. An inert gas system to maintain an inert atmosphere in the tank head space. See Data Sheet 7-59, *Inerting and Purging Vessels and Equipment*, for additional information.

B. Steam snuffing at a delivery rate of 4-8 lb/min per 100 ft^3 (0.64 to 1.3 $kg/min/m^3$) of enclosure volume, interlocked to be activated when the molten sulfur exceeds safe temperature limits.

2.6.3.2.3 Maintain atmospheric vents clear of sulfur build-up.

2.7 Metallurgical and Acid Regeneration Processes

2.7.1 Protection

The protection recommended in this section applies to plants where abundant fiberglass reinforced plastic [FRP] ducts and equipment can normally be found at the gas cleaning sections.

2.7.1.1 Provide directional water spray protection for important plastic equipment and ductwork. Focus on concentrations where large ducts cross over each other, or multiple vessels are positioned side-by-side. Design the system to provide a discharge pressure of 20 psi (1.4 bar) for open sprinklers or nozzles greater than or equal to 1/2 in. (13 mm) or 30 psi (2.1 bar) for smaller nozzles.

2.7.1.2 Institute a policy that ordinary combustibles are not to be staged or stored below long run ducts.

2.7.1.3 Install automatic sprinkler protection inside scrubbers in accordance with Data Sheet 7-78, *Industrial Exhaust Systems*.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

FM client losses to this occupancy from 1977 to 2019 are presented in Figure 3.1-1, where the three largest categories of loss by peril were explosion, natural hazards, and equipment breakdown.

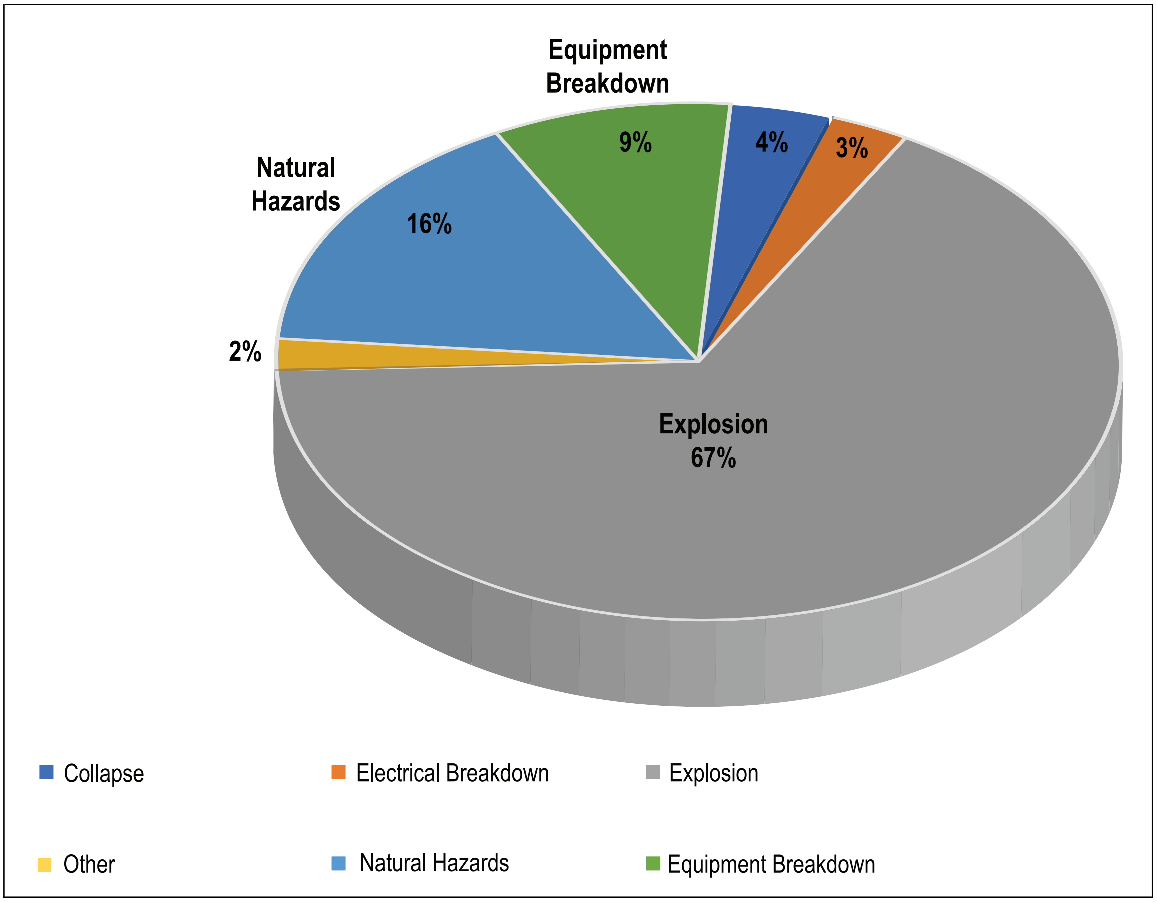

Fig. 3.1-1. FM client losses by peril from 1977 to 2019

The largest losses in sulfuric acid plants were related to explosions in which electrostatic precipitators and furnaces were involved.

Natural hazards occupied the second place with 16% of the total losses during this period, with flood being represented the main cause for these losses.

Heat exchangers and coolers were the main equipment driven the equipment breakdown losses. One of the largest losses in this category involved a weak acid scenario, where sulfuric acid corroded the heat exchanger tube bundle, allowing higher pressure water to enter process stream and reduce concentration to corrosive levels, with ensuing damage to multiple pieces of equipment.

3.2 Process Overview

Sulfuric acid is an extremely important industrial chemical, probably one of the most important in the world. In 2015, about 250 million tons of sulfuric acid were produced worldwide, with a forecast production for 2021 of 278 million tons. The leading producers in the world are China, United States, India, and Russia, which together contribute with more than 60% of the global production of sulfuric acid.

Sulfuric acid is used in a wide variety of industries and processes around the world. Approximately 60% of the sulfuric acid produced is used to manufacture fertilizers (i.e., superphosphate of lime and ammonium sulfate). In the chemical industry, it is used to manufacture chemicals such as hydrofluoric acid, nitric acid, sulfate salts, synthetic detergents, dyes and pigments, explosives, and drugs. Sulfuric acid is also used for metal processing and in petroleum refining to wash impurities out of gasoline and other refinery products. Some other industries include pulp/paper and fiber.

Most of the sulfuric acid is produced by sulfur-burning plants. The next most important producer would be metallurgical smelters, whose production ranges between 10% and 15% worldwide. Sulfuric acid can also be produced by a spent acid regeneration (SAR) process. These last two processes are commonly used as an option to minimize air pollution or dispose of unwanted by-products.

The sulfuric acid process is based on the following chemical equations:

$S + O_2 \rightarrow SO_2$

$SO_2 + O_2 \leftrightarrow SO_3 + \text{Heat}$

$SO_3 + H_2O \rightarrow H_2SO_4 + \text{Heat}$

In the scope of chemistry, none of these reactions are overly complex. However, controlling these relatively simple reactions is far from simple. Sulfur dioxide and sulfuric acid are corrosive and difficult to handle, sulfur trioxide intermediate is highly reactive and far from stable, and the amount of heat generated by these exothermic reactions requires special consideration.

As mentioned above, sulfuric acid can be produced using the following processes:

- Sulfur burning (see Figure 3.2-1)
- Metallurgical (see Figure 3.2-2)
- Spent acid regeneration (see Figure 3.2-3)

Basically, the main difference between these three processes is the type of raw materials used, and the cleaning or production process required to obtain the necessary SO_2 that will be transformed by catalytic oxidation into SO_3 in the converter. The catalytic oxidation of SO_2 to SO_3 is a highly exothermic reaction and converters are commonly designed as multistage adiabatic units with gas cooling between each stage.

The sulfur burning process use horizontal brick-lined combustion chambers with dried air and atomized molten sulfur introduced at one end. Atomization can be achieved by pressure spray nozzles or by mechanically driven spinning cups, the degree of atomization being a key factor in producing efficient combustion. Plants using this process produce considerable heat from the sulfur combustion, which can be used to produce steam and generate power via turbines.

Burners used for spent acid can have some similarities with those used for sulfur burning. Very high temperatures are reached in the combustion chamber that can also be used to generate steam or power.

Gases coming from metallurgical processes need to be cleaned prior entering the contact section of the acid plant to prevent plugging of catalyst beds and other effects on equipment such as corrosion. Typical cleaning methods include gravity settling chambers, cyclone collectors, wet scrubbers, filters and electrostatic precipitators. The main purpose of the gas cleaning section is to eliminate undesired gases, moisture, and particulates to produce an optically clear SO_2 gas. The method chosen to treat and clean the gas will depend on the specific composition of the gas and the impurities present. Acid regeneration plants also require a gas cleaning system downstream of the combustion chamber and boiler.

The gas cleaning section operates under vacuum, created by the main acid plant blower. Gas is drawn from the gas source generally at just below atmospheric pressure. The pressure of the gas continuously decreases as it passes through the equipment and reaches its lowest pressure at the blower suction.

The catalytic oxidation of SO_2 to SO_3 takes place in the contact section of the converter and is a highly exothermic reaction. Converters are commonly designed as multistage adiabatic units with gas cooling between each stage.

Gas leaving the converter is normally cooled to improve SO_3 absorption in the absorption towers. The process gas is not cooled below certain temperature ranges to avoid the possibility of corrosion from condensing sulfuric acid originating from trace water in the gas stream. In some cases, a gas cooler is used instead of an economizer.

Once the SO_3 stream is cooled, it goes to packed absorption towers, where SO_3 is absorbed and converted to H_2SO_4. Concentrated sulfuric acid circulates in the tower and cools the gas to within a few degrees of the acid inlet temperature. Acid temperatures rise within the tower due to the exothermic reaction that is produced when sulfuric acid is generated. The hot product acid leaving the tower is cooled in heat exchangers before being recirculated or pumped into storage tanks.

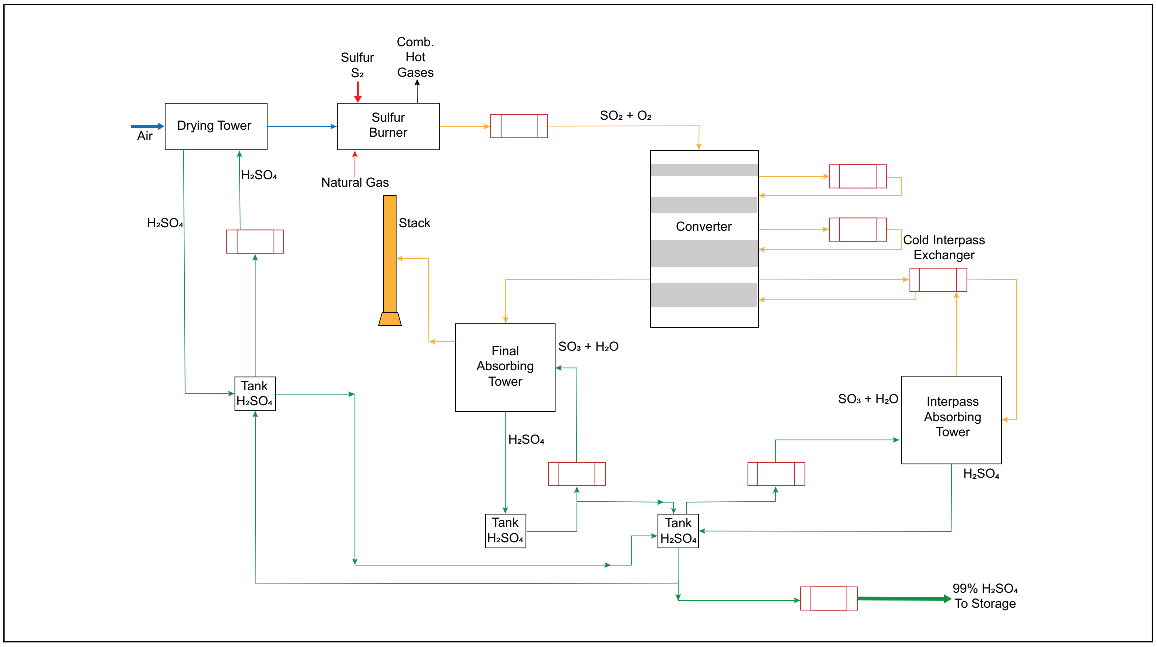

Fig. 3.2-1. Sulfur burning process

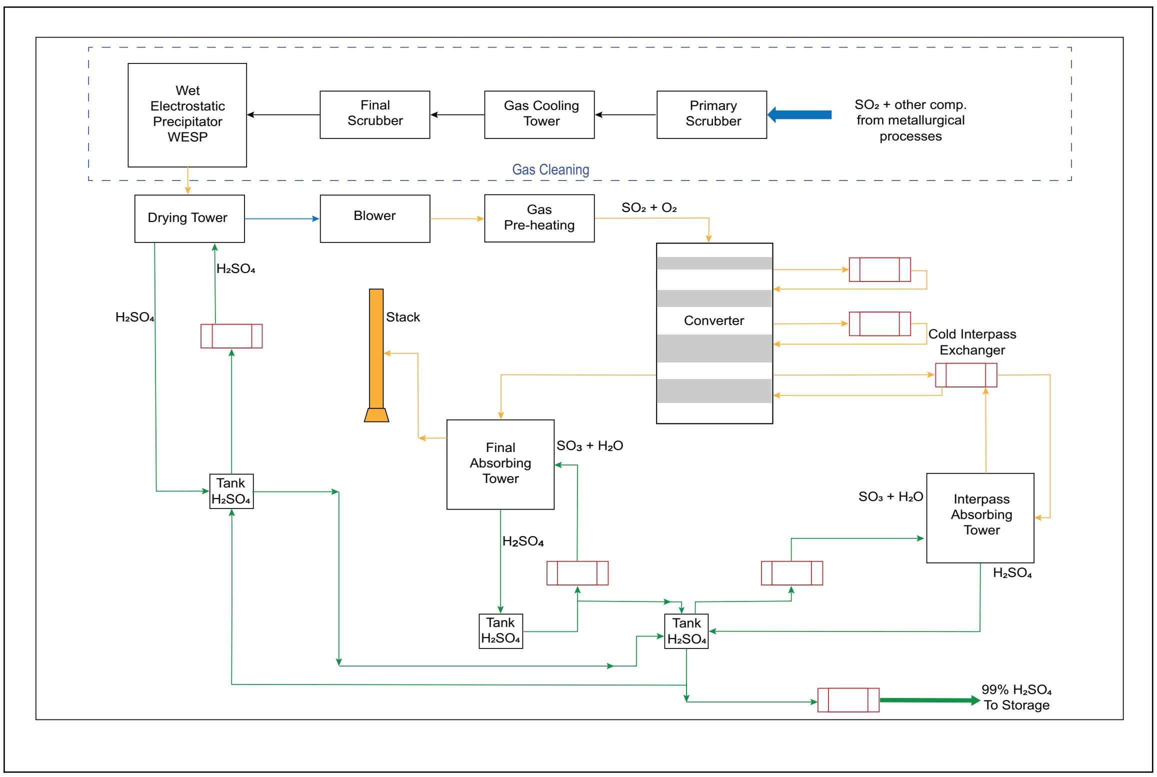

Fig. 3.2-2. Metallurgical process

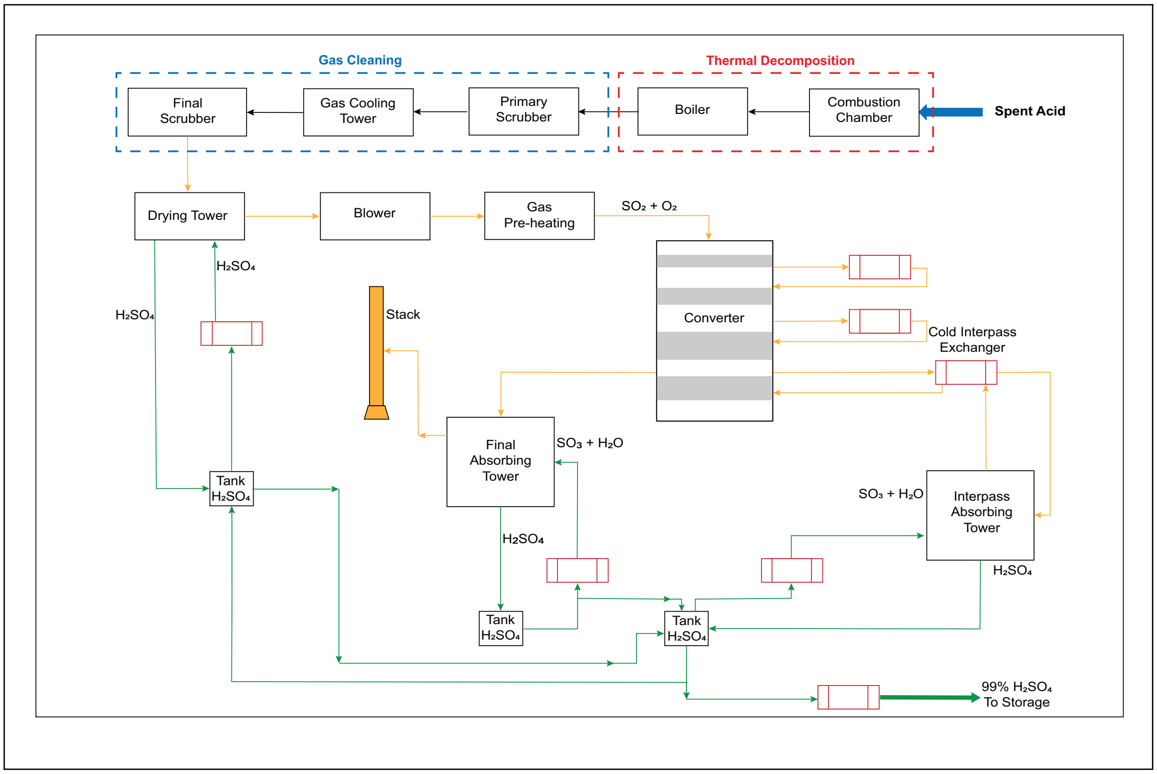

Fig. 3.2-3. Spent acid regeneration process

4.0 REFERENCES

4.1 FM

Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*
Data Sheet 6-10, *Process Furnaces*
Data Sheet 6-14, *Heat Recovery Boilers*
Data Sheet 7-11, *Conveyors*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-45, *Safety Controls, Alarms and Interlocks*
Data Sheet 7-59, *Inerting and Purging Vessels and Equipment*
Data Sheet 7-98, *Hydraulic Fluids*
Data Sheet 7-99, *Heat Transfer Fluid Systems*
Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*
Data Sheet 9-0, *Asset Integrity*

APPENDIX A GLOSSARY OF TERMS

See Data Sheet 7-111, *Chemical Process Industries*.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

October 2024. Interim revision. The following changes were made:

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January 2023. Interim revision. Minor editorial changes were made.

October 2020. This is the first publication of this document.