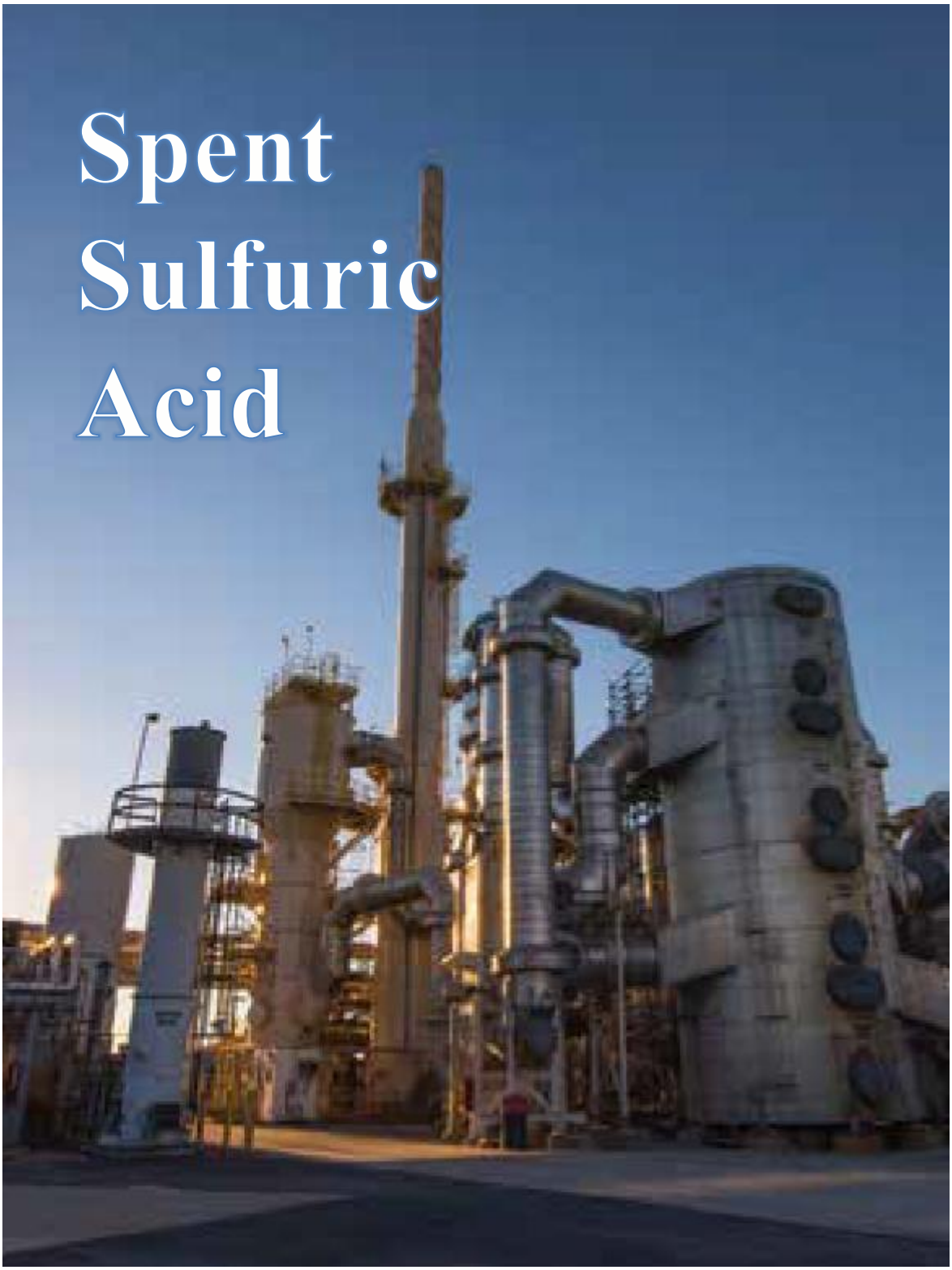
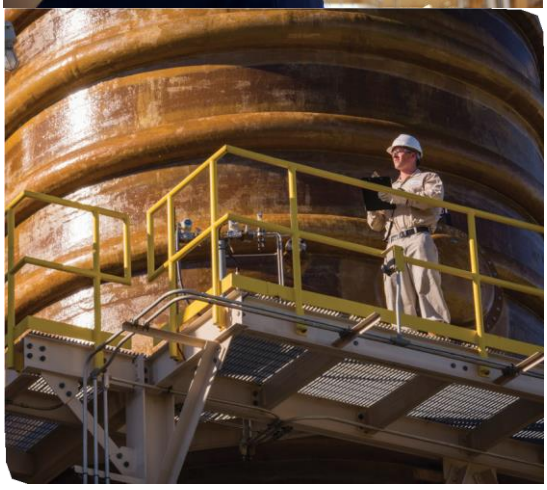
NEXPERA



Spent Sulfuric Acid

Properties
Usage
Storage

Handling
Technical Information



INTRODUCTION

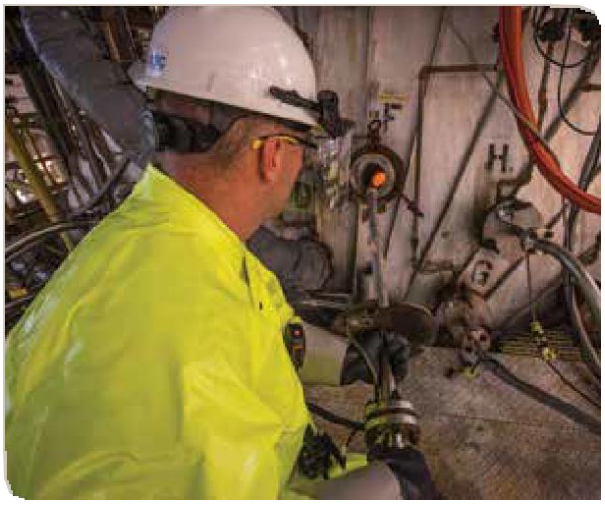
Sulfuric acid is one of the oldest known industrial chemicals. It is a very strong inorganic acid with qualities that make it very useful for a number of industries. More sulfuric acid is produced and consumed than any other chemical in the world. Some of the industries that find sulfuric acid essential include:

- Fertilizers
- Inorganic chemical manufacturing (including chlorine drying)
- Petroleum refining (principally alkylation)
- Pharmaceuticals (sulfonations/sulfations)
- Soaps and detergents (sulfonations/sulfations)
- Pigments and dyes (sulfonations/sulfations)
- Textiles
- Pulp and paper (chlorine dioxide generation and pulp pH control)
- Metals
- Steel (pickling)
- Car batteries/lead-cell batteries (battery acid)

Some synonyms for sulfuric acid include:

- H_2SO_4
- Oil of Vitriol (OV)
- Vitriolic acid
- Hydrogen sulfate
- Oleum (Fuming sulfuric acid, >100% H SO)*

*Oleum is a blend of sulfuric acid and sulfur trioxide. A sulfuric acid concentration greater than 100% refers to a mixture of 100% sulfuric acid and sulfur trioxide (SO_3). The concentration represents the amount of sulfuric acid that would be present if all of the free SO_3 were converted to H_2SO_4. For information about Oleum, refer to the Nexpera Sulfur Trioxide and Oleum "Properties, Uses, Storage and Handling"



Nexpera helps refineries cleanly process sulfur gas and regenerate spent sulfuric acid and caustic which are to the alkylation process. Nexpera manufactures sulfuric acid and high value sulfur derivatives relevant to a broad range of industrial processes. We are committed to providing high-quality services to our customers and operate within a Goal Zero safety culture - focused on continuous improvement toward an overarching goal of zero injuries, zero incidents and zero impacts on the environment.

In August 2024, American Industrial Partners finalized an agreement with Veolia NA to purchase the assets of its Sulfur Products division to operate under the name Nexpera. The asset purchase agreement included 7 operating locations; corporate and functional support teams; and the Acid Technology Center, a dedicated team of engineers who exclusively support the sulfuric acid business. Veolia acquired Sulfur Products from Chemours and previously DuPont, and were widely recognized as global leaders in chemical

manufacturing. DuPont had been involved in the sulfuric acid business since 1865, supplying John D. Rockefeller's first oil refinery (Standard Oil of Ohio) with barrels of sulfuric acid on horse-drawn wagons. The business today, under Nexpera's name, continues to be the benchmark for sulfuric acid plant operations and services. Nexpera operates seven sulfuric acid

“We will work with you to ensure you have the training necessary to safely handle and use Nexpera’s sulfuric acid products. ”

plants throughout the United States. Some of these plants are sulfur-burning plants that use a contact process (refer to “Sulfuric Acid Process, page 3).
Other plants use Spent Acid Regeneration (SAR) processes, where unreacted sulfuric acid that was used in other processes is regenerated for re-use. We can supply a range of sulfuric acid products, varying in strength and quality requirements.

Besides having a strong product base, we are experts in distribution and logistics. We have a variety of means available to us for transporting sulfuric acid, including barges, rail cars and tank trucks. We partner with highly skilled transportation providers to ensure the product gets to you safely and on-time, and we provide them with annual training on the handling and management of sulfuric acid products.

Nexpera is a member of the American Chemical Council (ACC) and is committed to Product Stewardship and Responsible Care®. Our plant operators and personnel are among the best in the world.
We know how to run a safe and environmentally - friendly plant. And we are willing to share our knowledge on the safe handling, use and storage of sulfuric acid with our customers.

Product Stewardship

Nexpera fully endorses American Chemical Council’s (ACC) Responsible Care® seven codes of Management Practice. We encourage customers to thoroughly review their safety management practices in the handling of sulfuric acid. In support of product stewardship, Nexpera is willing to consultant with our customers in the design of unloading and handling facilities, as well as make recommendations for first aid, medical treatment, personal protective equipment (PPE), emergency response, spill mitigation, and materials of construction selection. We will work with you to ensure you have the training necessary to safely handle and use Nexpera’s sulfuric acid products. Nexpera personnel may visit sites before making the first shipment.

Figure 1 below is a typical flow diagram of the contact process for a sulfur-burning plant for sulfuric acid. As you can see, sulfur and air are brought in and burned to make sulfur dioxide (SO_2). The SO_2 goes through a series of gas cooling and heat recovery operations, and then is run through a catalytic converter to make sulfur trioxide (SO_3). The sulfur trioxide is absorbed in sulfuric acid. Water is added to control the sulfuric acid to the desired strength.

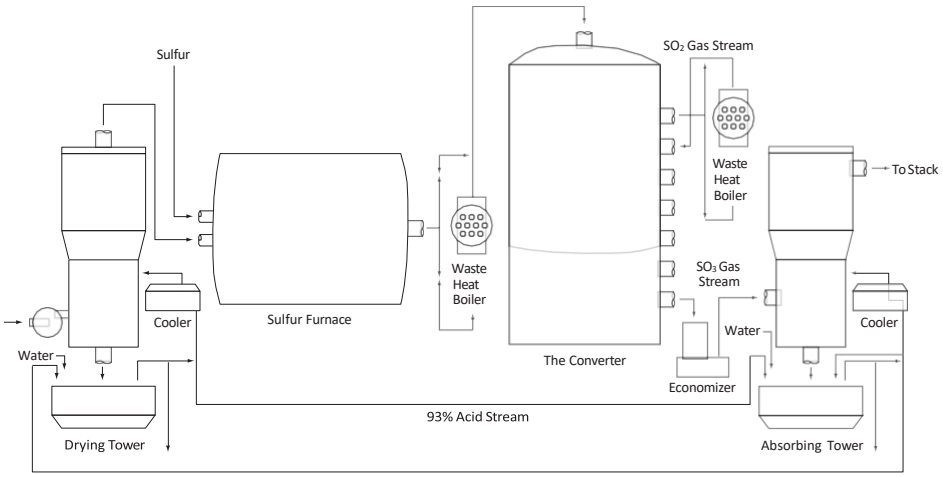


Figure 1

Figure 2. In this process, spent sulfuric acid is combusted in air to produce sulfur dioxide (SO_2). The SO_2 is cooled and cleaned through a series of scrubbers, reheated, and sent to a catalytic converter with more air to make sulfur trioxide (SO_3). The remainder of an SAR plant process is essentially the same as a sulfur-burning sulfuric acid plant.

.

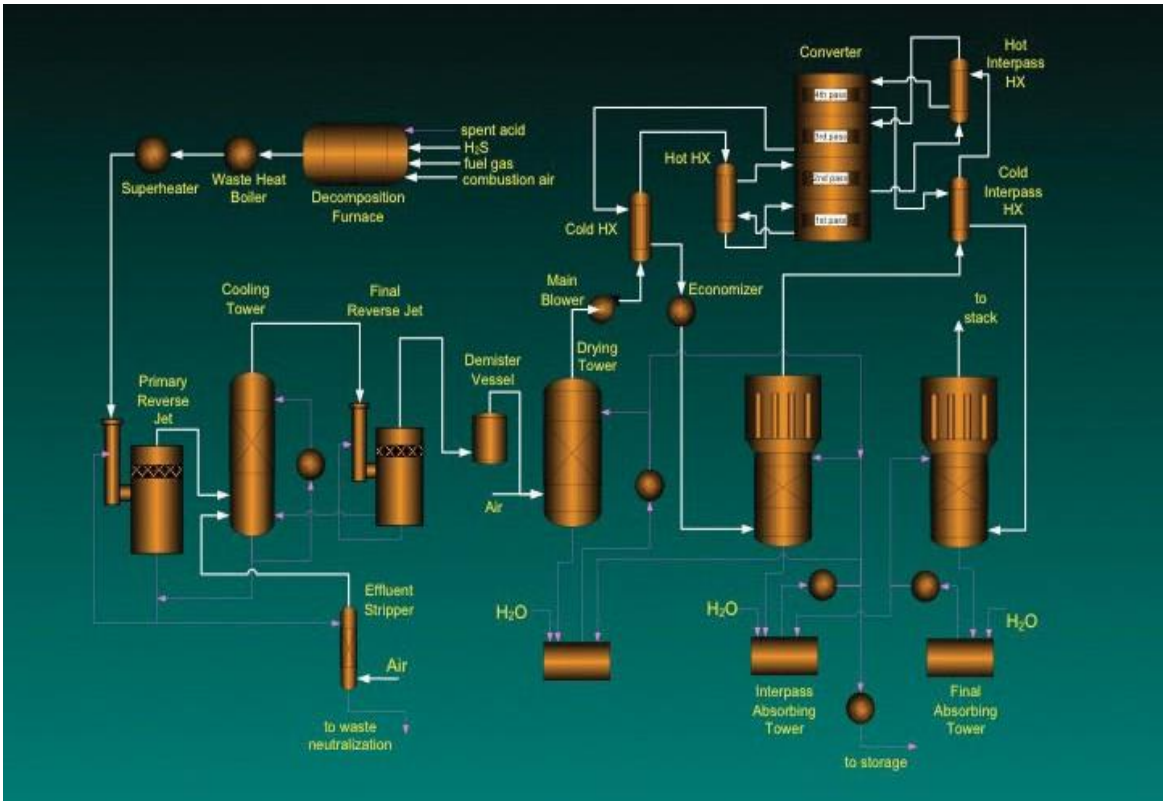


Figure 2

SPENT SULFURIC ACID

Spent sulfuric acid is the nomenclature used to describe strong sulfuric acid that has been "used" in another process, but not chemically reacted. The spent sulfuric acid still has the same safety and health concerns as strong sulfuric acid, plus may have additional concerns from the other components in the spent acid. Spent sulfuric acid can be categorized into two segments - alkylation spent acid and chemical spent acid. Alkylation spent acid is generated by petroleum refineries that have sulfuric acid alkylation processes. The alkylation process converts low octane components into high-octane components, typically for automotive gasoline, using sulfuric acid as a "catalyst". Chemical spent acid comes from two main sources. The chlor-alkali industry uses sulfuric acid to ''dry" the chlorine gas before it is liquefied. Others use sulfuric acid to sulfate/sulfonate organic compounds to produce surfactants for soaps, detergents, pharmaceutical, et cetera.

Alkylation Spent Acid

Alkylation spent sulfuric acid is typically in the 90% sulfuric acid strength range, with ~2-4 % water and ~6-8% organics. It also contains some sulfur dioxide (SO_2). In addition to the corrosivity posed by the sulfuric acid, alkylation spent acid has additional concerns for "flammable/combustible" characteristics and for fume generation (SO,). If the storage vessel is not circulated or agitated, the organics may tend to form a layer on top of the sulfuric acid. Many refineries prefer to do this, as the organic layer then can be "skimmed" and recovered for further processing. The storage tank should also have a scrubber/fume collection system to capture the organic vapors and the SO2. Special care must be taken to "blanket" the storage tank with nitrogen or other inert gases to keep oxygen out.

Chemical Spent Acid

Chemical spent acid from a chlor-alkali operation will contain some quantity of chlorine gas dissolved in the acid, typically in the 100-500 ppm range. Chlorine gas, even at this level, can pose additional health and safety hazards. Appropriate personal protective equipment (PPE) should be used when handling this product, including respiratory protection. Chemical spent acid from sulfation/sulfonation reactions will usually be discolored (brownish to blackish in color) from residual charred reactants. It may also have a distinct SO_2 odor. Respiratory protection may be required when handling this type of spent acid.

PHYSICAL PROPERTIES

Physical properties of spent acid are dependent on the process used to make the spent acid.

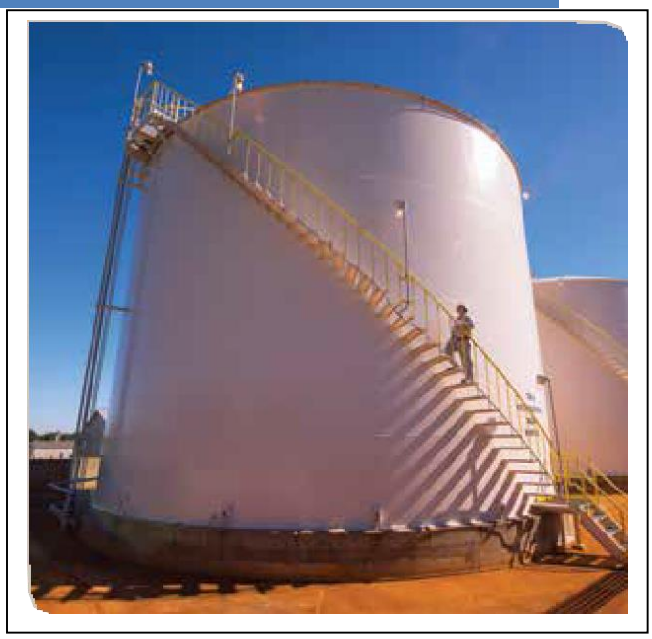
Fresh Sulfuric Acid (H_2SO_4), Molecular Weight (98.08) is a heavy, oily, strong, liquid mineral acid, clear and colorless in pure form. Technical grades may be turbid and off-white in appearance. Grades below 100% have a very low vapor pressure at room temperature. Pure sulfuric acid does not have good "warning" properties. Visually, pure sulfuric acid looks just like water, and it has no odor or fumes. **Figure 1** (on page 6) shows the freezing and boiling points. Figure 2 (on the page following Figure 2) is the thermal properties of sulfuric acid,

Spent Sulfuric Acid is also a heavy, oily, strong liquid mineral acid with many characteristics similar to fresh acid. It can also have some different physical properties, depending on the process used to make the spent acid.

Alkylation spent acid usually is dark colored (purplish to black), and can contain sulfur dioxide (SO_2) and alkylate organics. "Typical" acid analysis is 88-90% H SO2 ~2-4% H2O, and ~6-8% organics. The spent acid can be odorous due to the SO2 and/or organics. Respiratory protection may be required when handling the spent acid. Also, the spent acid may exhibit "flammable/combustible" characteristics, depending on the level of organics in the acid.

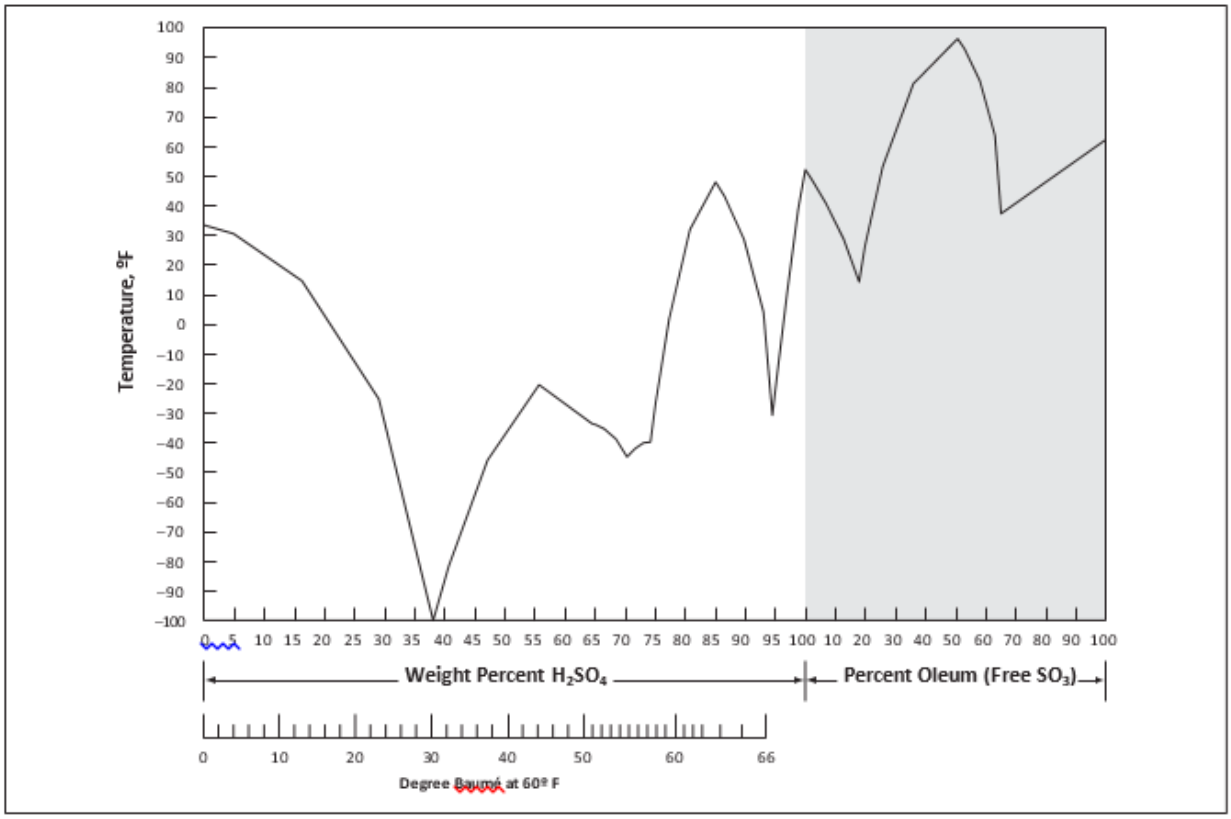
2

Chlorine-drying spent acid is usually turbid and may have a slight green coloration to it. The spent acid will contain some dissolved chlorine (50-500 ppm) and will have a "chlorine" odor. Respiratory protection may be required. The presence of the chlorine may change the corrosion characteristics of the spent acid versus fresh acid. The acid strength for this spent acid is typically in the 70-77% range.

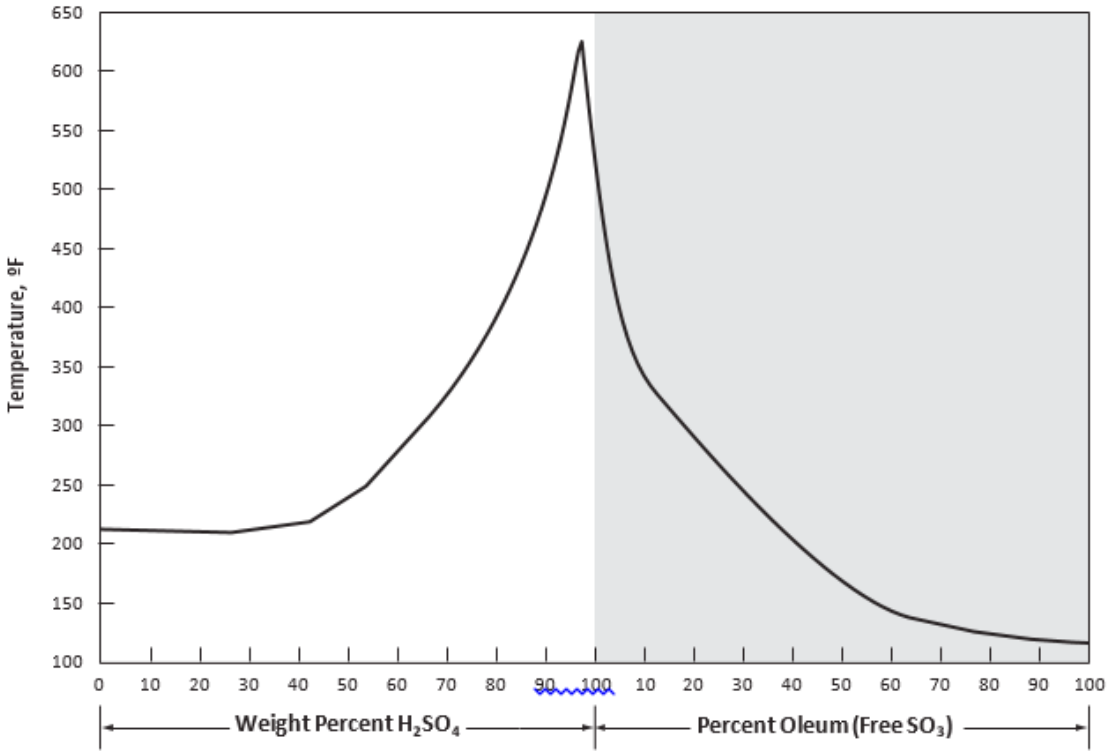


Sulfonation/sulfation spent acid from sulfation/sulfonation reactions is usually discolored (brown to dark black) and has some level of organics, usually not in the flammable/combustible range. The spent acid can also contains levels of SO2 enough to make the product odorous. Additional PPE may be necessary, depending on the SO2 level for the specific spent acid. Acid strength will depend on the sulfonation/sulfation reaction used to produce the spent acid. Physical properties of technical grades of sulfuric acid are found in the Nexpera Sulfuric Acid "Properties, Uses, Storage and Handling" bulletin, available from Nexpera.

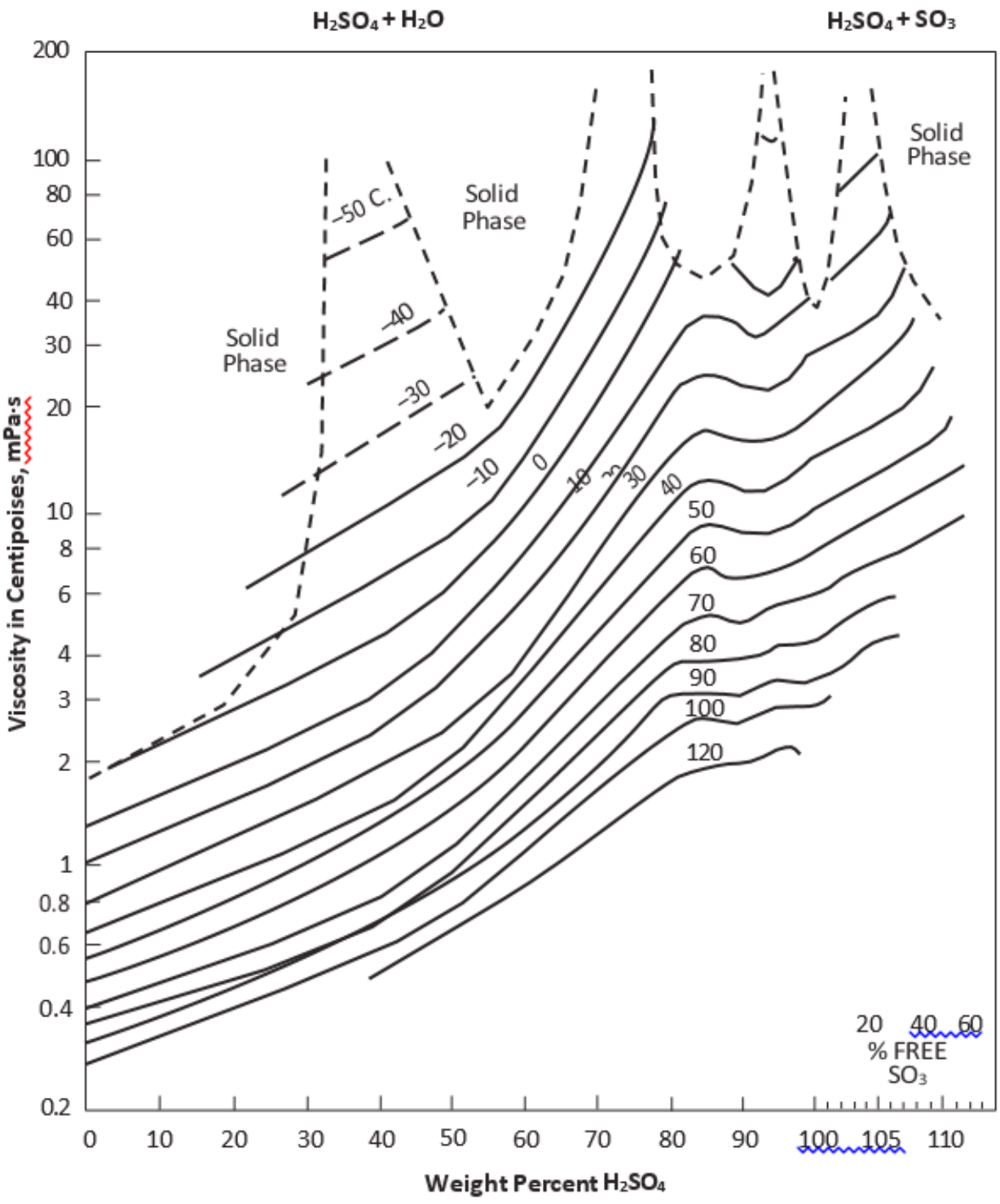
All personnel working with sulfuric acid should be thoroughly familiar with the health and safety precautions, and have the equipment needed to handle this product safely. The Nexpera SDS for sulfuric acid should be reviewed prior to using this product.



Freezing Points of Sulfuric Acid



Boiling Points of Sulfuric Acid


H₂SO₄ + H₂O
H₂SO₄ + SO₃
Viscosity in Centipoises, mPa·s
Weight Percent H₂SO₄
Solid Phase
Solid Phase
Solid Phase
-50 C.
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
120
20 40 60
% FREE SO₃

PERSONAL SAFETY AND FIRST AID

Health Hazards

Concentrated sulfuric acid and spent sulfuric acid are strongly acidic materials that react rapidly with water, evolving considerable heat. They can rapidly dehydrate body tissues and cause severe chemical and thermal burns. Inhalation of fumes or mists may cause nose, throat and delayed lung injury. Contact of aqueous solutions of sulfuric acid with the skin and eyes may cause severe irritation or burns. The more concentrated the solution, the faster the damage will occur.

Spent sulfuric acid can also pose respiratory health hazards, depending on the concentration of SO2 and/or organics in the acid. Spent sulfuric acid, especially spent acids from Alkylation processes, may also exhibit "flammable/combustible" characteristics, and appropriate safety precautions should be used when handling the spent acid (proper grounding, eliminate ignition sources, inert blanketing, etc.).

The U.S. Department of Labor has ruled that an employee's exposure to sulfuric acid mists in any 8-hour work shift of a 40-hour week must not exceed a time-weighted average of 1 mg/m3 (29 CFR 1910.1000 Air Contaminants).

Safety Precautions

Do not get fresh or spent sulfuric acid in eyes, on skin, or on clothing. Use of appropriate personal protective equipment is essential to safely handle fresh and spent sulfuric acid. Eye protection is particularly important when working around sulfuric acids. Avoid breathing vapor or mist. Use with adequate ventilation. For spent sulfuric acid, use respiratory protection if SO_2 or chlorine fumes are detected.

Fresh sulfuric acid by itself is not flammable, but weak sulfuric acid can attack most metals, generating hydrogen gas. Spent sulfuric acid can contain some organics, and as a precaution should be treated as "flammable/combustible". Precautions must be taken to avoid ignition sources near both fresh and spent sulfuric acid.

Personal Protective Equipment

Personal protective equipment must be used to protect a worker whenever contact with acid could occur. However, it should not be considered a substitute for safe working conditions and practices.

Have available and wear as appropriate for exposure conditions when handling containers or operating equipment containing sulfuric acid: chemical splash goggles; full-length face shield/chemical splash goggle combination (face shield alone is inadequate); acid-proof gauntlet gloves, apron, and boots; long-sleeve wool, acrylic, NOMEX' (for spent acid) or polyester clothing; acid-proof suit and hood; and NIOSH/ MSHA-approved respiratory protection. In case of emergency or where there is a strong possibility of considerable exposure, wear a complete acid suit with hood, boots, and gloves. If acid vapor or mist is present and exposure limits may be exceeded, or if handling spent sulfuric acid with SO_2, or chlorine fumes detected, wear permissible respiratory protection.

Proper selection and care of respiratory protective equipment is an essential part of personal protection. Standby respiratory equipment is necessary in areas where sulfuric acid is handled (unloading stations, storage areas, etc.).

Site Facilities

The following safety equipment should be easily accessible in all areas where sulfuric acid is handled (unloading stations, storage areas):

Safety Showers - Water should be supplied to the shower by a 2-inch line (minimum pressure 30 psig) through a quick-opening valve that will stay open. 30 gallons per minute (gpm) minimum is the recommended flow.

Both the valve (actuated by a push/pull handle at hip level) and a 0.25-inch weep hole directly above the valve should be located below the frost line and surrounded by crushed rock or gravel to provide drainage. Shower locations should be appropriately identified by colored (usually green) lights and/or signs, and access to showers must not be obstructed in any manner. Safety showers should be tested on a periodic basis and the results recorded.

Water Hydrant and Hose - Some means of flushing spills with large volumes of water under adequate pressure should be provided.

Eyewash Fountain - An eyewash fountain or a hose with a gentle flow of cool tap water is suitable means for flushing the eyes. Eyewash stations are usually part of a safety shower station.

First Aid

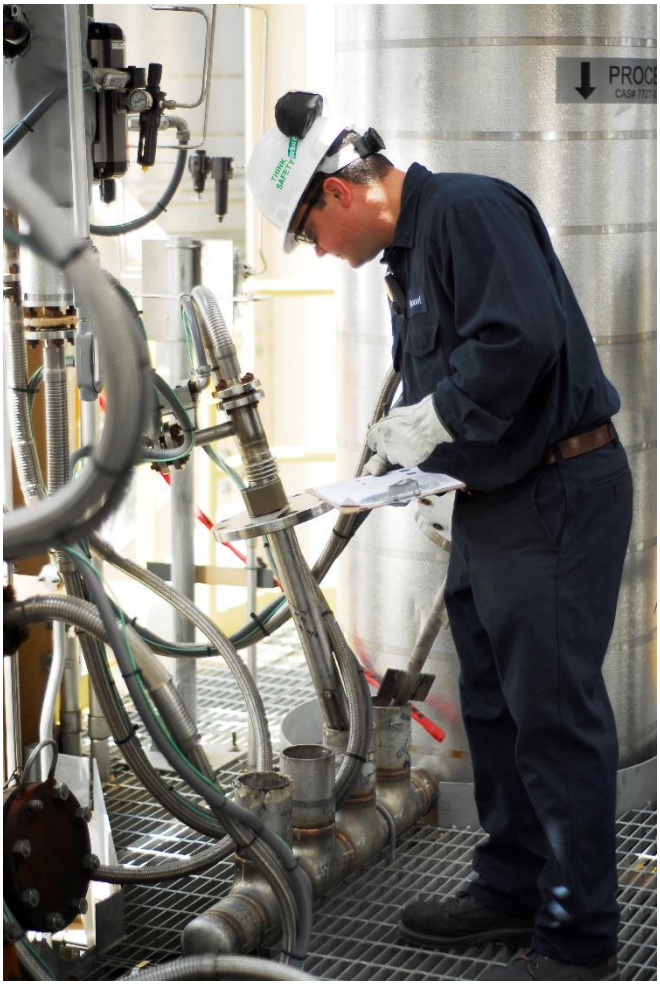
In case of contact: *Immediately* (within seconds) flush the skin or eyes with plenty of water (preferably cold water) for at least 15 minutes while removing all contaminated clothing and shoes - forget modesty! Call a physician. Wash clothing before reuse. Do not "scrape" the acid off the skin - this greatly increases the probability for removing the upper skin layer and exposing the area to infection.

While the patient is being transported to a medical facility, apply compresses of ice water. If medical treatment must be delayed, immerse the affected area in ice water. If immersion is not practical, compresses of ice water can be applied. For more detailed instructions consult the Nexpera Sulfuric Acid First Aid treatment manual, available from Nexpera Technical Service.

Note to Physician: Continued washing of the affected area with cold or ice water will be helpful in removing the last traces of sulfuric acid. Creams or ointments should not be applied before or during the washing phase of the treatment.

If inhaled: Remove patient to fresh air immediately and have patient lie down and remain quiet. Apply artificial respiration if breathing has stopped. Give oxygen if breathing is difficult. Call a physician.

If **swallowed:** Do not induce vomiting. Give large quantities of water. Call a physician. Do not give carbonates. Never give any1hing by mouth to an unconscious person



HANDLING PRECAUTIONS

Spills or Leaks

Spillage of sulfuric acid should be given immediate attention to avoid dangers of body contact, corrosion of equipment, and possible generation of hazardous gases. Comply with Federal, State and local regulations on reporting releases. The CERCLA reportable quantity for sulfuric acid is 1000 pounds (as 100% sulfuric acid). Dilute sulfuric acid has a high rate of corrosion on steel as well as other metals, and spills on external tank surfaces and other equipment must be washed off immediately.

Acid spills should be contained and runoff to sewers avoided. Spills of acid at 100% strength or less should be flooded with large quantities of water, and the resulting solution neutralized with lime, soda ash or other alkali material prior to disposal.

Small spills and leaks are usually diluted with water spray or foam and then neutralized. Sodium bicarbonate or a soda ash-slaked lime mixture can be used for neutralization. Laboratory supply houses also provide packaged kits containing absorbents and neutralizing agents such as J.T. Baker Chemical Company's Neutrasorb' or Ansul's Spill X-A'. Follow label instructions. Wear personal protective equipment to avoid exposure acid-see section on Safety Precautions on page 6.

When neutralizing acid spills (i.e., in neutralization pits, holds of barges, etc.), care must be taken to assure adequate ventilation of fumes or gases such as CO_2, that could cause suffocation.

Hazardous Chemical Reactions

CAUTION

Water or caustic solutions should never be added directly to sulfuric acid (fresh or spent) because of violent reaction and spattering. When diluting, always add the acid to water. Never add water to the acid.

Sulfuric acid is an active acid that reacts with many other compounds. Most of its reactions are well known and have been employed safely for many years. For a compilation of chemical reactions reported to be potentially hazardous, refer to NFPA No. 491 M, "Manual of Hazardous Chemical Reactions."

Sulfuric acid reacts readily with iron and other metals at strengths below 75%, and hydrogen gas is evolved. At higher strengths, sulfuric acid is a strong oxidizing agent and reacts with organic and inorganic reducing materials with considerable heat generation.

Sulfuric acid also reacts with carbonates to generate carbon dioxide gas and with cyanides and sulfides to form poisonous hydrogen cyanide and hydrogen sulfide gases, respectively. Thus, there is not only the danger of a violent eruption that could result in acid burns, but also the possibility of generating explosive or poisonous atmospheres that could present additional hazards. For these reasons, sulfuric acid should be used strictly in accordance with the directions of a qualified chemist or technically trained person.

Fire and Explosion Hazard

Sulfuric acid is nonflammable, but is highly reactive and capable of igniting finely divided combustible materials on contact. It reacts violently with water and organic materials with high evolution of heat. It is extremely hazardous in contact with many materials, particularly carbides, chlorates, fulminates, nitrates, picrates and powdered metals. In higher concentration, ignition may occur on contact with combustible materials such as sawdust and oily rags. Sulfuric acid attacks many metals to release flammable hydrogen gas. Therefore, no open flames, open lights or matches or other ignition sources should be allowed in or around acid containers or lines. Spent sulfuric acid may contain enough organics to give the liquid "combustible" characteristics. Again, no open flames, open lights or matches or other ignition sources should be allowed in or around acid containers or lines.

Fire Fighting

In case of fire, use dry chemical or carbon dioxide extinguishing methods. Water can be used on combustibles burning in the vicinity of sulfuric acid, but care must be exercised not to apply water directly to acid with evolution of heat and violent spattering. Cool tank with water if exposed to fire, but do not get water in tank.

High-pressure water fog or mechanical foam can also be used to keep tank cool if exposed to fire. Do not allow water or water-containing foam to contact spent or fresh sulfuric acid, particularly oleums, in a confined area or tank, because it might cause violent eruptions that could result in structural damage.

Engineering Control of Hazards

Proper design of the storage and handling system from point of delivery to point of consumption is necessary to safeguard against the hazards of sulfuric acid. Factors to consider in design include:

1. Location of storage tank relative to other chemicals and working areas
2. A tight system that minimizes the chances of sulfuric acid leaking and endangering people.
3. Means of confining accidental leaks as well as proper drainage and cleanup of leaks and spills in a manner consistent with plant and regulatory agency requirements.
4. Provision for more than one escape route in event of fire, explosion or release of SO, fumes when handling oleum.
5. Easily accessible safety showers, firefighting and other emergency equipment.
6. Provisions for venting storage and unloading facilities to recovery or abatement facilities, particularly for spent sulfuric acid where so, or chlorine fumes from venting, can exceed allowable limits set by government pollution regulations (29 CFR 1910.1000 Air Contaminates) or safety standards for ground level concentrations.
7. Blanket spent sulfuric acid tanks (Alkylation process) with nitrogen or other inert gas.

Acid should never stand in a line completely sealed between two closed valves such as in gravity-filling operations. Pressure may build between the two valves, resulting in a line rupture or hazardous acid spray when a valve is opened. Relief valves discharging to a safe location should be installed in those line sections where acid could become entrapped between closed valves.

Sulfuric acid storage should be in the open or in a well ventilated area. Tank foundations should be slightly above grade and sloped to facilitate drainage away from the tank. Vertical tanks should be mounted on grillage, not directly on the ground, to minimize potential for external corrosion of the tank bottom.

Any liquid leaks or spills that occur in pipes or equipment where sulfuric acid is handled should be considered acid leaks and treated accordingly.

Indoor storage or heated storage tanks should be provided to prevent acid freezing where severely cold weather conditions exist. Under no conditions should storage tanks have internal steam coils.

All exterior piping that carries acid grades susceptible to freezing should be heat- traced and insulated (99% H_2SO_4 freezes at~ 40°F). Care must be exercised to avoid overheating by use of high-pressure steam as localized hot spots and pressure buildup by liquid expansion or vaporization between two closed valves can occur. **Electric tracing is preferred.**

Storage tanks should be thickness-tested at least every two to three years, or as required by local ordinances. It is recommended that the tanks be cleaned and an internal inspection be made every five years.

Transportation Emergencies

If a shipment of Nexpera sulfuric acid is involved in an accident or emergency anywhere in the continental United States, make a toll-free telephone call to the American Chemical Council's Chemical Transportation Emergency Center ("CHEMTREC") in Washington DC:

(800) 424-9300

The information specialist on duty will ask the name and location of the caller, the name of the shipper, the product, the shipping point and destination; what happened, nature of any injuries, weather conditions, proximity to populated areas, etc. He/she will then give the caller recommendations for controlling the emergency situation until the shipper's specialist can provide help. "CHEMTREC" will immediately advise Nexpera of the emergency and one of our specialists will get in touch with the caller promptly.

WASTE DISPOSAL

Sulfuric acid (fresh and spent) may be an RCRA hazardous waste due to its pH. Disposal of waste-liquid streams containing sulfuric acid must be accomplished within the regulations and guidelines applicable at the specific location under consideration. Users should check with the appropriate local, state or federal authorities to stay up-to-date on rules in force and changes being considered for the future.

Small quantities of waste acid may be added slowly to a larger volume of agitated soda-ash solution or slaked-lime slurry. The neutralized solution is then added to excess running water prior to final disposal.

Larger quantities of sulfuric acid wastes are also best disposed of by neutralization, keeping the pH of the effluent in the range of 6 to 9, as required by many regulatory agencies. Sulfuric acid wastes may be neutralized with waste alkali streams, lime, dolomite, ammonia, caustic soda or soda ash. The choice of neutralizing agent usually depends on the volume of the waste acid, the allowable pH and the cost of the neutralizing agent. Lime is often used and requires the separation of suspended solids by filtration and/or sedimentation in settling ponds before discharge of wastes to water courses. Acid wastes should not be discharged to sewer treatment facilities without neutralization treatment because of:

Corrosive effect on collecting systems

Possible effect on biological treatment systems

Possible interaction with other industrial wastes to produce toxic gases such as H2S, HCN, etc.

Sulfuric acid wastes generally are diluted to concentrations below 15% before neutralization because of the limited solubility of calcium sulfate. The neutralization reaction is highly exothermic so that cooling or further dilution is necessary to remove liberated heat.

When very large volumes of acid wastes are involved, particularly higher-strength acids, recovery may be more economical than neutralization. Many factors must be considered in evaluating the practicality of acid recovery, such as chemical market conditions, geographical location relative to possible uses, possible reuse within the plant, etc. Practical processes for recovery of acid value or of useful products from waste acid streams have been developed and are commercially available.

SHIPPING CONTAINERS

Nexpera ships sulfuric acid (fresh and spent) in tank cars, tank trucks, and barges. The lank cars, tank trucks, and barges bear placards as prescribed by the DOT. The DOT hazard classification: Corrosive Material. Fresh sulfuric acid is placarded with UN 1830. Spent sulfuric acid is placarded UN 1832.

Barges

Nexpera has a number of barges dedicated to sulfuric acid (fresh and spent) service. The barges are all double-walled, with a capacity of 2000-2200 tons and constructed of carbon steel. The barges are multi-compartmented. The unloading pumps in the barges require 480 volt, 3-phase power (to be supplied at the unloading spot). Typical unloading rates from the barge are in the 600-800-gpm range. Adequate unloading pipe size must be used to maintain the liquid fluid velocity at less than 3 feet per second (if the unloading line is made of carbon steel). The unloading line should be drained or blown clean after the unloading. The unloading line should not be left stagnant, liquid-full. Excessive corrosion (hydrogen grooving) can occur in stagnant, liquid-full lines.

For spent acid, the vapors/fumes displaced from the barge during the loading operation should be vented back to the spent acid storage tank, or routed through a scrubber system designed to remove the SO_2, and/or organics. Typically a weak caustic (~10.5 pH caustic solution) packed-column scrubber is used to remove the SO_2, and an activated carbon bed used to remove any organics.

Tank Cars

Nexpera ships sulfuric acid in tank cars of 50- to 100-ton capacities (7,000-14,000 gallons). Spent acid is returned to Nexpera in these same rail cars.

No bottom outlet is allowed on tank cars carrying sulfuric acid. The discharge pipe is located in the dome on the longitudinal centerline of the car and extends into a well in the bottom of the tank. Tank cars have varied dome arrangements and the user should consult the Customer Service Center (800-441-9442) if not familiar with a particular car.

For spent acid, the vapors/fumes displaced from the rail car during the loading operation should be vented back to the spent acid storage tank, or routed through a scrubber system designed to remove the so,and/or organics. Typically a weak caustic (~10.5 pH caustic solution) packed-column scrubber is used to remove the SO, and an activated carbon bed used to remove any organics.

Rail Car Dome Fittings

1. Dome fittings of tank cars may be of different types. All are designed for unloading through the dome acid connections by means of pump or compressed air. The following fittings and connections are usually identified by name and stenciled for identification:
    a. Fill-hole Cover (hinged or secured by center screw
    b. Discharge (or eductor) Pipe (closed with cap, plug, or valve), usually 2" or 3" diameter.

c. Air Connection: A pipe nipple closed with a safety vent, or a separate air connection closed with a cap, valve, or plug cock. When car is equipped with two vents, one is sealed and must not be removed.

d. Safety Vent. A safety device equipped with a frangible disc, designed to relieve abnormal pressure, which may build up in the tank during transit. All cars are equipped with a safety-vent device. Some cars require removal of the safety-vent assembly to make the air connection for unloading. Other cars are equipped with two safety vents, one of which is a seal vent to be removed.

2. Removal and replacement of connections should be made with a proper wrench. After all fittings are secured on the spent acid rail car, the car should be "pressure- tested" to ensure all fitting are leak-tight.

3. If leakage at any of the tank car dome fittings occurs and cannot be stopped by tightening the bolts or fittings, shut off air supply. When pressure in the car has been reduced to atmospheric, remove the leaking fitting and apply a new, approved gasket (Viton' B) and/or fitting. Special gaskets are used. II the wrong type is used as a replacement, contents of the tank may be contaminated. **DO NOT USE A RUBBER (NATURAL OR NEOPRENE) HOSE FOR THE ACID CONNECTION.** Nexpera recommends Teflon'-lined transfer hoses for sulfuric acid service

Tank Trucks

Nexpera ships sulfuric acid in tank trucks of capacities up to 20-23 tons (2600-3000 gallons). Spent sulfuric acid is returned to Nexpera in the same trucks. For spent acid, the vapors/fumes displaced from the tank truck during the loading operation should be vented back to the spent acid storage tank, or routed through a scrubber system designed to remove the so,and/or organics. Typically a weak caustic (~10.5 pH caustic solution) packed-column scrubber is used to remove the SO, and an activated carbon bed used to remove any organics.

To receive/ship such a truck, the consignee needs:

1. An all-weather serviceable road to the unloading station. Railroad sidings having open ties and full-height rails are not suitable for tank truck movements.

2. Vertical clearances of at least 11-1/2 feet.

3. An open area at the loading/unloading station sufficient to permit normal maneuverability of the tractor and trailer. Tractor and trailer have maximum overall length of 45 feet, and a maximum width of 8-1/2 feet. The turning radius is 50 feet.

4. A tractor-trailer spotting area having a good surface capable of supporting about 24,000 pounds per axle (80,000-pound maximum gross weight of vehicle). The surface should be slightly pitched so that any liquid spillage will be contained away from the truck and exposed structures. The spotting area should allow the truck and trailer a 4-foot minimum clearance at each end and 2-foot clearance on each side.

5. Securely anchored, free-draining intake lines, the receiving couplings of which are within 6 feet of the rear end of the tank truck trailer spotted in normal unloading position. The carrier usually provides one 15-foot length of unloading hose. If desired, the customer can provide his own unloading hose.

6. To load spent acid into tank trucks, a loading platform must be used.

7. A functioning safety shower and eyewash station meeting OSHA requirements, readily accessible

8. A running water hose to wash down any minor leaks/spills/drips.

If unloading/loading is to be performed at night, the unloading/loading spot should be well lighted so the truck driver will have no difficulty unloading properly and safely, spotting hazards and moving quickly in case of an emergency.

Tank Truck Placement and Unloading

Plant personnel and the driver should jointly inspect and test the following site-safety equipment periodically:

- Safety shower
- Eye wash fountain
- Water hydrant or hose for wash-down

If any equipment is not working properly, it should be fixed as soon as possible. Unloading/loading should not proceed if there is no safety water.

The driver will:

1. Observe DOT regulations spelled out for common carrier shipments in Part 177, Subpart B, Section 177.834
2. Spot the trailer properly and prepare it for unloading/loading
3. Connect the unloading/loading hose to the proper connection on the trailer
4. Open valves on the trailer and unload/load trailer contents to customer's storage tank

The discharge pipe is located in the rear of the truck and is generally accessible from the ground.

EQUIPMENT

Corrosion Hazards

Mild steel is generally satisfactory for storage and handling of the concentrated technical grades of sulfuric acid (93 to 99% H_2SO_4 and spent sulfuric acid at normal atmospheric temperature).

However, more dilute solutions are highly corrosive and special materials of construction are required. The corrosion resistance of materials to sulfuric acid over different concentration and temperature ranges is illustrated in **Figure 3** (on the following page). The supplier should be consulted for materials of construction recommendations based on specific conditions. Unless the process is unique, corrosion data should be readily available to indicate what materials should be selected.

NOTE: For spent acid, corrosion rates should be evaluated on an "organic-free" basis. The corrosion rates of sulfuric acid with most metals is based on the ratio of sulfuric acid to water. The organics are essential "inert" to the corrosion process. To determine the "organic-free basis" (OFB) for corrosion calculations/evaluations, subtract the % organics from the solution and recalculate the % sulfuric acid. Example: The spent acid has a composition of 4% organics, 6% water (H_2O) and 90% sulfuric acid (H_2SO_4). The "organic-free basis" composition would be:

90% H_2SO_4 / (100% - 4% organics) = 93.8% H_2SO_4 (OFB).

Therefore, when looking at corrosion charts for this spent acid, the acid strength to use would be 93.8%, not 90%.

Storage Tanks

Either horizontal or vertical cylindrical storage tanks can be used. Horizontal tanks of 10,000-40,000-gallon capacity should be constructed with standard ASME dished heads of the same thickness. This thickness should include a corrosion allowance of 1/4 inch, which provides a tank life of 15-20 years, depending on acid concentration and handling temperature. Vertical tank thickness depends on size and tank configuration, and addition of up to 1/4 inch corrosion allowance for carbon steel.

Vertical tank designs generally conform to American Petroleum Institute (API) Standards 650 or 620, which provide a rating slightly above atmospheric pressure. Pressure rating must be taken into account in designing the vent system to ensure tank limitations are not exceeded when unloading by air pressure and when storing high vapor-pressure oleums. Vertical tanks should be placed on grillage, not directly on the ground or concrete to minimize potential for external corrosion of the tank bottom.

Welded construction is recommended for tank fabrication per the above applicable codes. At normal service temperatures, stress relieving is not necessary.

The tank should have the following top openings: a 22-inch minimum diameter manhole with cover, a 3-inch vent line, a 2-inch filling line inserted through a 3" nozzle, and a suitable opening for measuring acid content.

An opening of 2 to 3 inches for transferring acid to process can be located either on top or bottom, depending on whether pump or gravity transfer is used.

If transfer is from the bottom, no other outlet is needed. Preferably all discharge piping is located on the side of the tank) with appropriate nozzle insert) and not on the tank bottom (floor). On vertical tanks, a 22-inch (minimum)

diameter side manhole, fabricated with the upper 180 degrees of the inside of the manhole neck lined with 3/16" stainless steel or Alloy 20 to prevent hydrogen grooving, is recommended. A 1/2-inch thick cover should be provided for the manhole. This manhole, located near the tank bottom, will facilitate cleaning.

Other nozzles should project several inches into the top of the tank, particularly the nozzle for the filling line from the tank car or truck. This prevents acid from running down the side of the tank and forming an acid film. Moisture from the air could dilute the film and cause corrosion (dilute sulfuric acid is more corrosive than concentrated acid). It is desirable to avoid acid impinging on tank surfaces and causing erosion.

Extending the fill line below the liquid level near the bottom of the tank minimizes fumes from fuming grade products. A wear plate should be installed below the fill line, on the tank floor. The fill line should be vented to prevent siphoning the contents from elevated tanks either accidentally or in the case of hose rupture during unloading. Four holes (3/8-inch) drilled into the fill line just beneath the top of the tank should provide adequate venting. A wear plate (1/8" thick) should be installed on the tank bottom under the fill line if the line extends to within 2 feet of the tank bottom.

Storage tanks should be placed on supports above the ground. A horizontal tank of 20,000-gallon capacity will normally be grouted in 2 or 4 concrete saddles, each approximately one foot wide. Flashing or mastic can be used between tank and saddle. 11 is recommended to have the repad plates seal-welded to the tank in the area in which the tank sits in the saddles. Structural steel supports are satisfactory and in some cases may be more economical.

Storage tanks should be sandblasted and painted on the outside with a suitable acid-resisting coating system. Regardless of the coating system selected, sandblasting of commercial quality is required, per Steel Structure Painting Council Specifications SP 6-63. A coating system that gives long-term color and gloss retention uses CORLAR' 825 zinc chromate epoxy primer followed by an intermediate coat of CORLAR 823-HB epoxy enamel, followed by a topcoat of IMRON' 326 polyurethane enamel.

Spent sulfuric acid tanks should also be blanketed with inert gas, such as nitrogen or argon. This is due to the "combustible characteristics" which may be present in the spent acids, particularly if it is generated in an Alkylation process.

Storage tanks should be examined periodically (every 2-3 years or more frequently if needed) for corrosion-induced weaknesses. Thickness measurements should be taken every three years (minimum) until a corrosion rate is established for the particular tank and operating conditions, then follow API 653 guidelines for further testing. The use of an ultrasonic thickness tester or similar device facilitates inspection. The entire system should be examined visually annually for external signs of failure. Acid spills on the tank exterior can be particularly corrosive as acid becomes diluted with atmospheric moisture or rain water, so the use of acid-resistant paint is important. The tanks should be cleaned and internally inspected every five years.

Tanks may need to be diked where release of contents due to broken connections or tank rupture may endanger other facilities. Local authorities may require diking to prevent acid from getting into water ways. Dikes may be of either the impounding or diversion type. Diversion-type dikes are preferred for fuming acids to contain the acid away from the tank to an area where it can be diluted to non-fuming concentration and disposed. This permits better access to repair the leak.

Vents/Scrubbers/Absorbers

Fresh sulfuric acid storage tanks must always have an open vent for normal breathing and to prevent dangerous pressure build-up due to hydrogen. Hydrogen gas may be produced from the action of acid on the steel tank and cause an increase in pressure.

Proper venting of storage tanks is essential to dissipate any hydrogen evolved. Potential sources of ignition (such as sparks and flames) should be excluded from the vicinity of the storage tank to minimize the fire or explosion hazard from hydrogen generation.

The vent line must be constructed of acid-resistant material. Polyvinyl chloride (PVC or CPVC) pipe is recommended for sulfuric acid for vent lines only. Iron sulfate can build up in the vent line over a period of time. Periodic documented inspection of the vent line for blockage may prevent tank collapse during acid transfer.

The vent line should be flush with the inner surface at the highest point of the tank to get rid of any hydrogen evolved. This vent can be equipped with a gooseneck bend or point straight up and be protected with a cover to prevent entrance of rainwater.

If the tank is located indoors, the vent line should extend

outside the building. Installation of an air dryer is optional. An air dryer may be desirable when there is high humidity and a low turnover rate of the tank contents.

For spent sulfuric acids, the vent line should tie into a fume scrubber using a caustic solution to prevent the escape of SO_2 or chlorine vapors into the atmosphere. Activated carbon absorption may also be used after the scrubber to absorb any organic vapors that may be present in the spent acid.

Piping

All pipe lines should be installed so they drain toward the storage tank, or toward the point of consumption forever possible. This will prevent the accumulation of acid in low points, thereby eliminating possible safety hazards when repairs are necessary.

The line from the unloading/loading point to storage should be equipped with a valve so the acid flow may be stopped at any time. The unloading/loading line can be 2-inch pipe if the distance is short between the unloading spot and storage; otherwise a 3-inch line is recommended. The size of the transfer line from storage to process depends on the required flow, but normally a 1-1/2 to 3-inch-diameter line will be sufficient. Schedule 80 steel pipe is recommended. Steel is velocity-sensitive. Piping should be designed for fluid flow between 1-3 feet per second (fps). Al low fluid velocities, hydrogen-grooving failure may occur, while at fluid velocities above about 3 fps, erosion-corrosion will cause failure. Consider upgrading the piping to stainless steel, Alloy 20 or Teflon•-lined pipe if flow velocities are outside the 1-3 feet per second range.

The overflow line (larger in size than acid-inlet line to tank) should drain to containment or approved waste-treatment facilities.

There are two recognized types of fittings for acid-handling lines: welded flanges and pipe bends with a suitable type of gasket and socket-weld fittings. Welded flanges make a much better and more permanent installation and is **HIGHLY** recommended. ***Screwed piping is strongly discouraged.***

Where flanges are used, standard 150 lb.-flange fittings are recommended. Flange guards should be used ONLY on flanged joints where there is significant exposure risk to personnel in a high traffic area. Some newer types of rigid PVC (Type I, Grade 1) or PVDV (Type IV, Grade 1) plastic piping may be more economical. However, they are only recommended for vent lines, not liquid lines due to low mechanical strength and brittleness. Continuous support should be provided for plastic pipe along its entire length.

For severe conditions, steel pipe lined with TEFLON© FEP fluorocarbon resin should be considered. Teflon'-lined hoses are recommended for strong (>77%) sulfuric acid service for the flexible connection required for unloading tank cars. Hoses must not be flexed beyond the manufacturer's recommended bend radius. Hoses should be inspected for deterioration before each use and tested annually to ensure that they are satisfactory.

A swing connection using swivel joints such as OPW© or Chiksan©, with gaskets of TEFLON©, can also be used.

70-99% H_2SO_4 (Organic-free Basis) Fluid Flow Velocity Limitations Feet per Second (FPS)	
Carbon (mild) steel, Schedule 80	1-3 fps
304 Stainless Steel, Schedule 40	0-6 fps
316 Stainless Steel, Schedule 40	0-8 fps
Alloy 20, Schedule 40	0-20 fps
Teflon'-lined pipe	0-50 fps

Pumps

Selection of the proper type of pump for handling sulfuric acid will depend upon the specific requirements of an installation. A sealless centrifugal pump is usually recommended for handling acids of strength from 60' Be to 20% oleum (77% - 105% H,SO_4), including spent acids.

When a submerged pump is used, it should be mounted in a manhole so the entire pump assembly may be easily removed.

To ensure protection of the top bearing from acid, vertical submerged pumps should be constructed

with the top bearing above the packing gland and external to the tank.

In general, horizontal pumps should be self-priming with 50% excess head, and volume characteristics to compensate for the relatively high viscosity of the acid that may be encountered at low temperatures. Special alloys have been developed by pump manufacturers for sulfuric acid handling.

Valves

Experience has shown that for lowest overall cost and minimum maintenance, Alloy 20 or "Durco"' T-line valves with a Teflon© liner or equivalent will give the best performance. Plug valves or full-port ball valves are recommended. Valves should be purchased with a stainless steel guard as a safety feature to protect the operator against acid leaking through the packing.

Whenever possible, valves should be mounted in a horizontal pipe with the stem up.

Gaskets and Packing

Viton B (for H2SO4 <100%) or expanded PTFE are recommended for flange gaskets.

Valve packing should be of TEFLON© fluorocarbon resin; pump packing should be of braided TEFLON©. Alternatively, on pumps, an outside mechanical seal or a double mechanical seal can be used. Sealless pumps are recommended.

Consult manufacturers for specific grades and style numbers.

Measuring Storage

Storage-tank calibration can be obtained from the supplier, calculated from internal measurements, or determined by filling the tank with known weights of water.

Liquid level can be measured by a wide variety of level measurement devices, including bubblers, differential pressure, sonar, radar or electrical conductance, etc.

Operators can also physically check acid depth with a stainless steel or polyvinyl chloride rod or other manual device. Care should be taken not to touch any overhead electrical wires with the measuring rod. Acid contact with skin or clothing during manual measurement can be avoided by proper use of prescribed protective equipment.

Respiratory protection may be required with spent acid storage tanks.

Spill or Leak Prevention and Control

In design of a storage facility, all steps should be taken to minimize the possibility of a major spill or leak. Consideration should be given in design to such items as alarms, interlocks, remote operated valves, relief devices and emergency shutdown buttons. It is important to select proper materials of construction and to include a corrosion allowance. Thickness testing of vessels and piping on a regular basis may indicate potential problems before a major spill or leak occurs.

Written procedures for unloading and transferring acid to process should prescribe a proper procedure and assign responsibility. Thorough training of operating and maintenance personnel is essential to minimize personnel error.

However, spills or leaks may occur regardless of preventive measures. All storage and process areas should have facilities for quick clean-up in case of a spill or leak. Consideration should be given to likely problem areas and where the spill will drain. Drainage pattern and methods of containment should be considered. In the case of fuming acids, it is desirable to divert the spillage to a containment area away from the tank. Combating a fume release may require the use of specialized equipment such as foam generators and fog nozzles. Personnel should be trained in handling a spill emergency, and such emergency actions should be incorporated into a plant emergency response plan.

A contaminated area should be immediately zoned off to avoid anyone being exposed to the acid spray or stream, and valves closed to stop leakage. The contaminated area should be flushed with water and neutralized.

If water is not available, the contaminated area should be covered with sand, ashes or gravel and acidity neutralized with soda ash or lime.

If the acid spill or leak is of sufficient quantity to

contaminate the plant sewer system, soda ash or other alkaline material should be added to neutralize the acidity. Sulfuric acid spills, leaks, or draining must not come in contact with any sulfide wastes, such as in sewers, because of the danger of evolving hydrogen sulfide gas. Similarly, other hazardous reactions may occur, depending on sewer contents. Local authorities should be consulted for spill-reporting requirements.

Cleaning Storage Tanks

Over a period of years, steel sulfuric acid storage tanks tend to build up a deposit of iron sulfate sludge, which can cause line blockage. It is recommended that storage tanks be cleaned and inspected at five-year intervals before sludge causes line blockage. Sludge that has accumulated over many years can become similar to clay and be extremely difficult to remove.

Any material removed from a storage tank for the purpose of disposal must be handled within RCRA regulations. Before attempting a tank cleaning, become thoroughly familiar with all pertinent Federal, State and local regulations, and the permits that may be required, so all cleaning operations are within compliance.

In preparation for tank inspection and cleaning, the acid level should be run as low as possible by postponing deliveries and transferring to process.

Spent sulfuric acid tanks have the additional hazard of a potential organic layer in the tank. The tank should be blanketed with an inert gas (nitrogen and/or argon) until the tank can be completely flushed of the organics. The tank should be tested for "combustibles" before cleaning the tank. If organics persist after the inert gas "flush", fresh acids should be added to the spent acid tank to "rinse" the tank to remove the organics. This step may have to be repeated several times to eliminate the organics from the tank prior to cleaning.

PROCEDURE

1. Be sure the tank has an inert gas blanket. Using proper safety equipment, including breathing protection, inspect the inside of the tank through the top manhole cover for the amount of sludge. Determine the amounts of acid and sludge by probing with a wooden pole or steel rod. Sampling and analysis of sludge for heavy metals may be required to determine the correct disposal method

2. Choose a sludge disposal method. Contractors who specialize in acid-tank cleaning are generally available. Some contractors can neutralize RCRA waste on site and are knowledgeable in pertinent regulations. RCRA includes the Elementary Neutralization Exemption (ENE), which is a federal provision covered in Section 264.1. This allows neutralization in a "tank," "container," "transport vehicle," or "vessel" without a permit if the waste is considered hazardous only because it is corrosive. States have the option of not accepting this exemption as they administer RCRA. Make certain the ENE applies in the location where cleaning takes place. Make certain that neutralization is performed in a container that meets the specific definition of "tank," "transport vehicle," etc.-a pond, ditch or impoundment is not allowed. Other contractors may remove the RCRA waste by vacuum truck for transport to approved waste treatment facilities.

3. Disconnect or isolate all lines into and out of the tank to avoid getting wash water into them. The tank should be prepared for vessel entry in accordance with local plant procedure.

4. To remove sludge, flush the tank with large quantities of water. A large hose with ample pressure, such as a fire hose, can be used.

   Wash out any acid and sludge as rapidly as possible. Dislodge sludge with an air stick made of a section of steel pipe and attached to a low-pressure air supply. Move the location of the air stick frequently to avoid undue corrosion at the point where air

impinges on the tank wall. Once slurried, the sludge can be removed by vacuum or "mud" pumps to an approved RCRA container for transport or neutralization.

It is important that the tank be washed and drained as quickly as possible to prevent tank damage by contact with the diluted residual acid.

Weak acid is very corrosive. To minimize corrosion, a commercial corrosion inhibitor can be added to the acid and sludge before dilution.

If sludge remains after the first wash, the procedure may need to be repeated.

5. After inspection and testing, if the tank is to be reused without repairs, it should be refilled immediately with strong acid to minimize corrosion.

SAFETY PRECAUTIONS

1. During the tank-cleaning operation, personnel should_ be protected against acid contact or inhalation. Use appropriate safety equipment, such as acid-resistant hood, suit, and gloves sealed to the acid jacket sleeve, boots sealed to the acid pant legs, and respiratory protection.
2. The tank should not be entered until it is clean and has been checked to determine that there is adequate oxygen and no combustibles/flammables present. There are hazards from sludge containing strong acid and presence of hydrogen due to the action of dilute acid on steel of the tank. Spent acid tanks may also have SO_2, chlorine and/or organic fumes present. Use appropriate respiratory protection.
3. Smoking, welding and sparks must not be permitted in or around the tank until it has been filled with water and neutralized because of the potential explosion hazard of the hydrogen. An explosivity meter should be used to test for concentration of combustible gases prior to performing welding, grinding or drilling work in sulfuric acid storage areas.
4. Before entering any tank, special provisions must be taken to ensure safety of the individuals involved. Be sure to follow all your plant procedures for "Confined Space Entry."

   Tank entry requires careful planning to outline precisely what tank preparations must be made, what is to be done inside and how it will be accomplished, hazards involved, safety equipment needed, and a plan developed for handling emergencies. Follow all appropriate plant procedures.

Pipeline Repairs

The following procedures are recommended to maintenance personnel for safely repairing sulfuric acid pipelines. Repair of pipes carrying spent sulfuric acid concentrations requires additional preparation to minimize fuming.

PROCEDURE

1. Obtain release of the line and supplementary equipment from the Operating Department.
2. Check line and equipment for possible inter-connections.
3. Check safety shower.
4. Provide ample source of water to wash tools and repair equipment as necessary.

   Unless release of carbon dioxide gas is objectionable, solutions of soda ash or other carbonate can be used for washing tools. Such solutions should be checked for acidity during prolonged or heavy use, and then replaced as necessary.
5. Smoking should not be allowed in the area where repairs are being performed
6. Wear personal protective equipment (see recommendations on page 6).
7. Close, tag and lock out the supply valve, and transfer pump. Drain all lines where possible. Provide positive isolation for the equipment to be repaired.
8. Provide for standby assistance.
9. Open all valves at the exit end of the line and allow acid to drain to containment or waste treatment.
10. Physically disconnect the line from the source of acid supply, preferably at a point adjacent to and

immediately following the closed supply valve. Appropriate precautions should be taken when breaking flanges to ensure that no acid is sprayed. Assume that all lines are under pressure and wear a full acid suit accordingly.

11. Blow line clean with dry air or nitrogen. Do not flush with water unless absolutely necessary - weak sulfuric acid will greatly accelerate the corrosion rate in the piping.
12. If the pipe has been flushed with water, dry thoroughly by blowing with dry air or nitrogen. (The air should be as free as is practical of oil, excess moisture, and foreign matter).
13. Immediately before welding, use an explosion meter to check the atmosphere inside the line for absence of explosive gases. Continue to blow nitrogen through the line while welding or cutting. Check lines at frequent intervals for buildup of explosive gases.
14. Use a gas shielded arc to give a slag-free weld with good fit-up and full (but not excessive) penetration.
15. Test weld for tightness (for example, using air pressure inside and soapsuds outside).
16. Reconnect the pipeline at the source of supply, leaving the supply valve closed and all valves at the exit end of the line open.
17. When operations are ready to resume, open the supply valve and flush acid through the line before closing the exit end of the line. This is to ensure removal of all moisture from the line.
18. Return line and equipment to Operating Department.

Next Level Expertise in Industrial Chemistry

Nexpera

www.nexpera.com

Revised 2/12/2025