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Sulfuric acid (H_2SO_4) safe storage and handling

Scope

This TIP provides basic information for personnel to unload and store bulk concentrated sulfuric acid safely. It is vitally important that any new bulk concentrated sulfuric acid facility design be undertaken with advice from a producer/supplier of sulfuric acid in order to cover all of the unique design parameters. Users of concentrated sulfuric acid are urged to comply with these standards and to review periodically their practices to ensure that they remain in compliance.

Definitions

Tank trucks or railcars deliver 93% and 98% concentrated sulfuric acid liquid to the pulp mill. It is used to maintain the acidity in the chlorine dioxide generator and reacts to form a by-product or leaves the generator as a spent acid effluent. It is also used to control acidity in other areas of the mill. It is used to generate chlorine dioxide when combined with water, sodium chlorate (a powerful oxidant) and sodium chlorate reducing agent. It should not come into contact with sulfide containing streams (*e.g.*, white, black & green liquor) due to hydrogen sulfide gas formation.

Properties of Sulfuric Acid [*1*]

General Information		
Chemical name	Sulfuric Acid	
Synonyms	Sulphuric acid, oil of vitriol, electrolyte acid, battery acid, matting acid, dihydrogen sulfate	
Chemical formula	H_2SO_4	
CAS Number	7664-93-9	
Molecular weight	98.08	
Physical state	Liquid	
Color	Colorless, but impurities may give it a yellow to brown color	
Odor	Odorless	
Solubility in water	100%	
Physical Properties	**93% Concentration**	**98% Concentration**
Density	1.8279 g/ml @ 20°C 15.3 lb/gal @ 60°F	1.8361 @ 20°C 15.4 @ 60°F
Viscosity	22 cP @ 20°C (68°F)	25 cP @ 20°C (68°F)
pH	<0.1	<0.1
Freezing point	-35°C (-31°F)	-2°C (28.4°F)
Boiling point @ 760 mm Hg	279°C (534.2°F)	327°C (620.6°F)
Vapor pressure	0.0016 mm Hg @ 40°C (104°F)	0.02 mm Hg @ 40°C (104°F)

Sulfuric acid is stable but reacts violently with water and organic materials with the evolution of heat. Sulfuric acid chars most organic substances upon contact, which results in the formation of carbon. Very small quantities of organic material will blacken the acid due to the suspended carbon.

Sulfuric acid attacks most common metals. However, for acid at normal ambient temperatures and commercial strengths, carbon steel or certain stainless steels are generally satisfactory if there is no need to enter the tank for inspection on a periodic basis. If periodic entry is expected, consider lining a carbon steel tank with a baked phenolic acid resistant lining. Washing the iron sulfate paste from the tank to facilitate entry and inspection can cause significant corrosion in a carbon steel tank. Plasite 4550 and Duromar 4320 XC are two examples of linings that can be used.

Vigorous reactions occur between sulfuric acid and alkaline solutions, metals, metal powders, carbides chlorates, fulminates, nitrates, picrates, strong oxidizers, reducing, or combustible organic materials. Hazardous gases are evolved on contact with chemicals such as cyanides, sulfides and carbides.

Diluting sulfuric acid with water generates significant heat. Always add acid to water. Never add water to the acid. This is because the reaction between these two materials is extremely exothermic, such that the water will boil immediately on contact with the acid, resulting in a violent reaction.

Safety precautions

Hazards and personal protection

Sulfuric acid is identified by UN number 1830. It is a Class 8 (subsidiary Class 9.2 in Canada), corrosive liquid. It has the CAS registry no. 7664-93-9.

Hazard Classification Summary for 93% &98% Sulfuric Acid [*1,2*]

Transportation Classifications	
UN Number	1830 (applies to H_2SO_4 concentration > 51%)
DOT/TDG Hazard Class Subsidiary Hazard Class Packing Group	8 9.2 in Canada II
Storage & Use Classifications	
NFPA Ratings Health Flammability Reactivity Special	 3 0 2 ~~W~~
WHMIS Classification	D1A, E
Subject to PSM?	No
Exposure Limits	
OSHA PEL (8-hour TWA) NIOSH REL (8-hour TWA) ACGIH® TLV® (8-hour TWA) OSHA PEL (15 min STEL) ACGIH® TLV® (15 min STEL) NIOSH IDLH	1 mg/m^3 1 mg/m^3 0.2 mg/m^3 n/a 3 mg/m^3 15 mg/m^3
Miscellaneous	
RTECS Number	WS5600000
CAS Number	7664-93-9
ICSC Number	0362
EC Number	231-639-5

Health hazards

Being virtually colorless and odorless, sulfuric acid has no readily apparent warning properties.

Contact with the skin will cause rapid destruction of tissue and severe chemical burning.

Personnel protective equipment

Wear complete protective clothing when working near sulfuric acid.

- Acid resistant coveralls that fit snugly at the neck. Place the jacket sleeves and trouser legs outside to keep acid from running into the gloves and boots. Do not tuck the in the jacket.
- Steel-toed acid resistant boots.
- Acid resistant gloves. The gloves should be loose fitting for ease of removal in case the sulfuric acid does get inside.
- Close-fitting, splash-proof monogoggles at all times. Use a face shield to protect the rest of the face.
- A hard hat for protection against overhead drips or spills.

Safety equipment

Well-marked showers and eye wash fountains should be accessible within 10 seconds (by walking) and, in cold climates, located inside a nearby heated structure. Water lines should be tested frequently and the water supply must be tempered (close to body temperature). Turning on either the shower or the eyewash should trigger an alarm to summon help.

First aid

In case of skin contact by sulfuric acid, activate the shower immediately. Remove all affected clothing while showering. It is extremely important that the water be applied to the affected areas as any delay increases the severity of the resulting injury. Flood the affected areas with water continuously for at least 20 minutes. Obtain medical attention as soon as possible after the shower. Never apply any neutralizing agents, oils or ointments, as these could aggravate the burn. Such treatments, if required, must be applied only under the supervision of qualified Medical Professionals.

For contact involving only the eyes, use the eye wash fountain. Hold the eyelids apart and irrigate eyes and surrounding areas for at least 20 minutes. No matter how minor the incident, obtain medical attention immediately after eye washing.

Fire and explosion hazards

Sulfuric acid will react slowly with steel to produce hydrogen gas, which can form an explosive mixture with air.

Smoking, welding or other sources of ignition should not be allowed near tank cars, tank trucks or storage tanks. If hot work is required in the immediate vicinity of an acid storage tank containing product, vent the tank at the top with a large volume of air (*e.g.*, copus blower), then run an atmospheric explosives test to ensure no hydrogen is present. Keep air blowing while hot work is ongoing as an additional safety step.

Environmental impact and disposal

Neutralize small spills during loading or unloading immediately with soda ash or calcium hydroxide (*i.e.*, lime). See Figure 1 to ascertain the quantity of base to neutralize a sulfuric acid spill (*1,3,4*). All neutralized material should then be washed *via the acid sewer* into an effluent treatment system. Use a very large amount of water when washing down a spill, because adding a small amount to sulfuric acid will cause a violent heat generating reaction.

Contain large spills immediately by diking to keep the sulfuric acid out of drains or water courses. Then take appropriate action to dispose of the spill. Obey all local legislation.

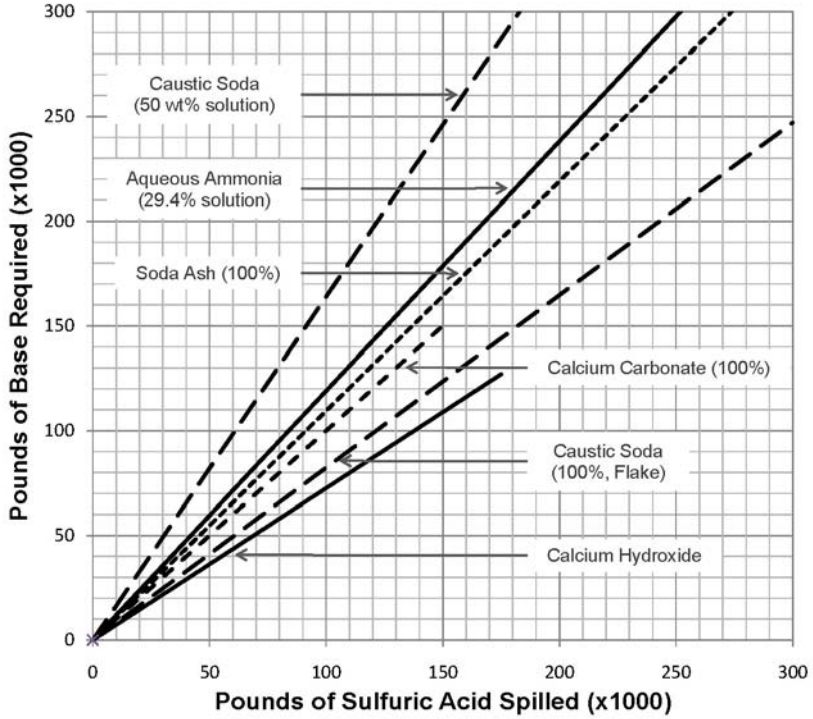


Fig. 1. Amount of base required to neutralize a given sulfuric acid spill (*1,3,4*)

Transportation

Suppliers ship sulfuric acid in top unloading tank cars, as well as top or bottom unloading tank trucks. (The use of bottom unloading concentrated sulfuric acid tank cars is not permitted in the USA or Canada unless special exemptions have been obtained. These exemptions are granted for shipments of "unit trains" only.) A corrosive placard, bearing the UN number 1830, indicates that the tank contains normal, commercial strength sulfuric acid (>51% but less than 100% H_2SO_4). Placards must always be in place even when the tank is empty. Placards must not be removed from tank cars or tank trucks unless these tanks have been thoroughly cleaned and all the acid neutralized.

Tank cars

Suppliers transport sulfuric acid in 100 ton tank cars. Tank cars containing 93% sulfuric acid are not insulated. Tank cars shipping 98% sulfuric acid may or may not be insulated and are equipped with or without heating coils, depending on local climate conditions. Tank cars for 93% and 98% acid are fabricated from carbon steel. These cars are lined with a baked phenolic coating to protect the integrity of the steel tank and preserve the acid quality.

All tank cars can be unloaded from the dome assembly at the top of the car. The dome fittings include a hatch cover with a gasket seal and a safety vent. The safety vent contains a rupture disc, as protection against over pressure; it is set at 165 psig (1240 kPa). Replace any broken or defective rupture discs immediately. In all cases, padding air is fed to the top of the tank. The two or three-inch discharge, or eduction pipe, is always on the centerline of the car and leads to the bottom of the tank.

Carefully release the pressure in the tank car through the air inlet connection before the opening the eduction pipe or the hatch cover.

Tank trucks

Single unit tank trucks are used for shipping all grades of sulfuric acid in capacities ranging up to 45 tons. The trailers are predominantly 316 L stainless steel, or in some instances, carbon steel with a baked phenolic lining. Trailers for 93% are not insulated, while trailers for 98% may have insulation and external heating coils. Product identification placards are located on all four sides of the trailer.

The dome fittings include a latch cover with a gasket seal and a safety vent as protection against overpressure. The safety vent may contain a rupture disc, set to release at 42 psig (390 kPa). (This could vary, depending on the age, design and condition of the trailer.) The air padding is fed to the top of the tank.

The discharge pipe is usually at the rear of the trailer, at bumper level, although the truck can sometimes be unloaded from the top. The discharge line may lead directly from the bottom of the tank truck or through an eduction pipe to the top of the tanker. On bottom unloading trucks only, the outlet is equipped with an external valve, as well as a remotely activated internal emergency valve as additional safeguards.

Unloading and storage installations

Tank truck sulfuric acid storage and unloading facilities should be located in areas where there is good access and where the trailer can be securely parked (and wheels chocked) on level ground. Tank car unloading sites must be located on sidings that can be locked out to prevent inadvertent movement of the tank car while unloading is in progress. All sulfuric acid storage/unloading stations should be designed and located in areas such that there is no chance that any accidentally released acid will contact incompatible chemicals (*e.g.*, caustic soda, hydrochloric acid, sodium chlorate, sodium bisulfate/sulfite, sodium hypochlorite or sulfide-containing materials).

Sulfuric acid storage tanks can be vertical or horizontal cylindrical vessels. However, many factors should be considered in the design of sulfuric acid storage and handling facilities. At a minimum, tank design for bulk storage of concentrated sulfuric acid should be based upon the American Petroleum Institute (API) standard 650, "Welded Steel Tanks for Oil Storage," (*5*) for vertical tank design, or the American Society of Mechanical Engineers (ASME) Code, Section VIII, Division 1 for horizontal tank design. However, it is highly recommended that the design of any new sulfuric acid storage tank follow the NACE (National Association of Corrosion Engineers) Standard RP0294-94, ("Standard Recommended Practice – Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures" [*6*]). This Standard specifically addresses the unique properties and corrosion caused by sulfuric acid. The NACE. Standard recommends that all sulfuric acid storage tanks be inspected internally at least every five years and externally every two years. The sulfuric acid supplier should also be contacted for additional and more specific design and tank inspection information. Entrance manholes at the top should be a minimum of 24-in. diameter.

Typical Materials of Construction for 93% &98% Sulfuric Acid [*1,3*]

Storage Tanks	Mild steel is suitable for all tanks. Small tanks (<10,000 gallons) are sometimes made from stainless steel or a special HDPE (high density polyethylene) made especially for sulfuric acid service. These materials reduce or eliminate formation of hydrogen gas and iron sulfate.
Piping	Alloy 20 if velocity > 6 ft/s (1.8m/s) Otherwise 316L stainless steel or Kynar® lined pipe recommended Seamless schedule 80 carbon steel pipe can be used if velocity < 3 ft/s (0.9 m/s) but may develop pinhole leaks at localized defects in the steel PVC and CPVC, although corrosion resistant, are not recommended due to risk of mechanical failure.
Flexible Hoses	Teflon® lined hoses with abrasion resistant outer covering.
Gaskets	VITON® B

It is essential to provide proper foundations for sulfuric acid storage tanks. Stable support and foundations must be provided to keep the tank bottom and shell-to-bottom joint dry (See NACE Standard [*6,7*]). The storage tank should be surrounded by a dike, with capacity of not less than 110% of the tank capacity. The dike should also be protected with an acid-resistant protective coating, since sulfuric acid and sulfate salts will rapidly destroy most concrete

materials. Slope the area within the dike toward a sump where a submersible pump can be used to remove any water. Use flange tank connections, since leaks at such connections can sometimes be stopped by tightening the flange bolts. Outlet nozzles can be located on the side or on the bottom of the tank, which facilitates installation of an internal emergency plug valve assembly.

Position all inlet nozzles, both fill inlet and circulation inlet nozzles, as close as possible to the center of the top of the tank. An inlet position too close to the shell can result in serious corrosion of the shell. Inlet pipes should protrude 1-in. (2.54 cm) beyond the shell to eliminate the possibility of localized corrosion. If the flow of acid at an inlet or outlet will exceed 3 ft/s (0.9 m/s), carbon steel is not recommended. Use 316 or alloy 20 for concentrations greater than 93% and alloy 20 if concentrations will be lower than 93%. Due to high flow velocities at the inlet or outlet, it is recommended to build up the area around the nozzle outlet with a ¼-in. (64 mm) reinforcement pad. Alloy 20 spuds can be welded to a carbon steel shell with C22.

Design the tank overflow system to prevent acid from being expelled from the vent, as this will protect the vessel from undue stress. Direct any overflow from the tank to a safe area within 18 inches (46 cm) of ground level, and within the containment dike.

As bulk storage tanks are built for atmospheric pressures, they have common goose-neck type atmospheric vents to protect the vessel from excess pressure or vacuum. In humid environments, ingress of atmospheric moisture could cause excessive corrosion to the inside of the sulfuric acid storage tanks. The head-spaces of such tanks can be flushed with a slight flow of a dry inert gas, such as nitrogen to displace the moist air. Installation of desiccant pots to the vent can also be considered. However, this practice is not recommended, as desiccant systems must be scrupulously maintained and isolated from rainfall. Wet desiccants could cause blockage of the tank vent, which could cause the tank to rupture or implode when acid is being pumped into or out of the tank.

Seamless schedule 80 carbon steel pipe – butt welded construction -- is often used for concentrated sulfuric acid lines, but will sometimes develop pinhole leaks at localized defects in the steel. For that reason, use 316-L Stainless Steel piping -- butt welded construction -- to handle concentrated sulfuric acid or Kynar lined pipe. If the velocity will exceed 6 ft/s (1.8 m/s), use alloy 20 in place of 316-L pipe. Design the system to allow for expansion and contraction of the pipe. Slope the piping system to allow for complete drainage.

Provide a reliable means of determining the liquid content in the sulfuric acid storage tanks. Several types of level indicators are available. Contact the supplier for further assistance. It is highly recommended that the tank be equipped with a separate high level alarm to prevent overfilling.

Unloading

Compressed air or nitrogen are often used to unload sulfuric acid from transport vessels. The padding gas line should include a shut-off valve and a pressure reducing valve set from 25 to 28 psig (274 to 294 kPa), in addition to a safety relief valve set at 30 psig (308 kPa). It is desirable to have an emergency closing valve on the tank car unloading arm.

Important note: With compressed gas unloading systems, it is extremely important that a “quick release valve” be installed between the tanker and the primary air supply shut-off valve. This is required to vent padding gas from the tank car or trailer to a safe place when unloading is complete. Such a system can also be used to quickly relieve the gas pressure in the delivery vessel, should a leak occur in the hose or piping used to deliver the product from the delivery container to the storage tank or process. Failure to include such a vent system *has* resulted in significant releases of sulfuric acid at certain locations. Many chemical suppliers are now recommending that mechanical pumps (instead of compressed gas padding) be use to off-load their products from the delivery containers to the customer. Mechanical pumping minimizes the amount of product released because of “stored energy” (*i.e.*, leakage and spray resulting from trapped, compressed gas) in an unloading system.

All flexible unloading lines should be fully supported to prevent stress on the hose caused by the high density of sulfuric acid. Follow manufacturers’ recommendations for materials, inspection, testing, maintenance and

replacement of all hoses. If quick connect fittings are used, they should be a dry disconnect style that seals from each end when separated.

Even small amounts of moisture and contaminants can result in damage to equipment and deterioration of acid quality. Exposure of baked phenolic lining to both sulfuric acid and to wet air or to water can cause severe damage to these linings. Plant air used for off-loading sulfuric acid must be very dry (less than -40°C (-40°F) dew poin)t and free from entrained moisture, oil and particulate matter. The tank cars should be kept closed to minimize exposure of the acid and tank car linings to contaminants and to wet air.

Unloading installation should include a purge/drain capability.

Contact the sulfuric acid supplier prior to the design of an installation for storage, handling and unloading concentrated sulfuric acid.

Keywords

Sulfuric acid, Safety, Transport, Unloading, Storage, Environments

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Additional information

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