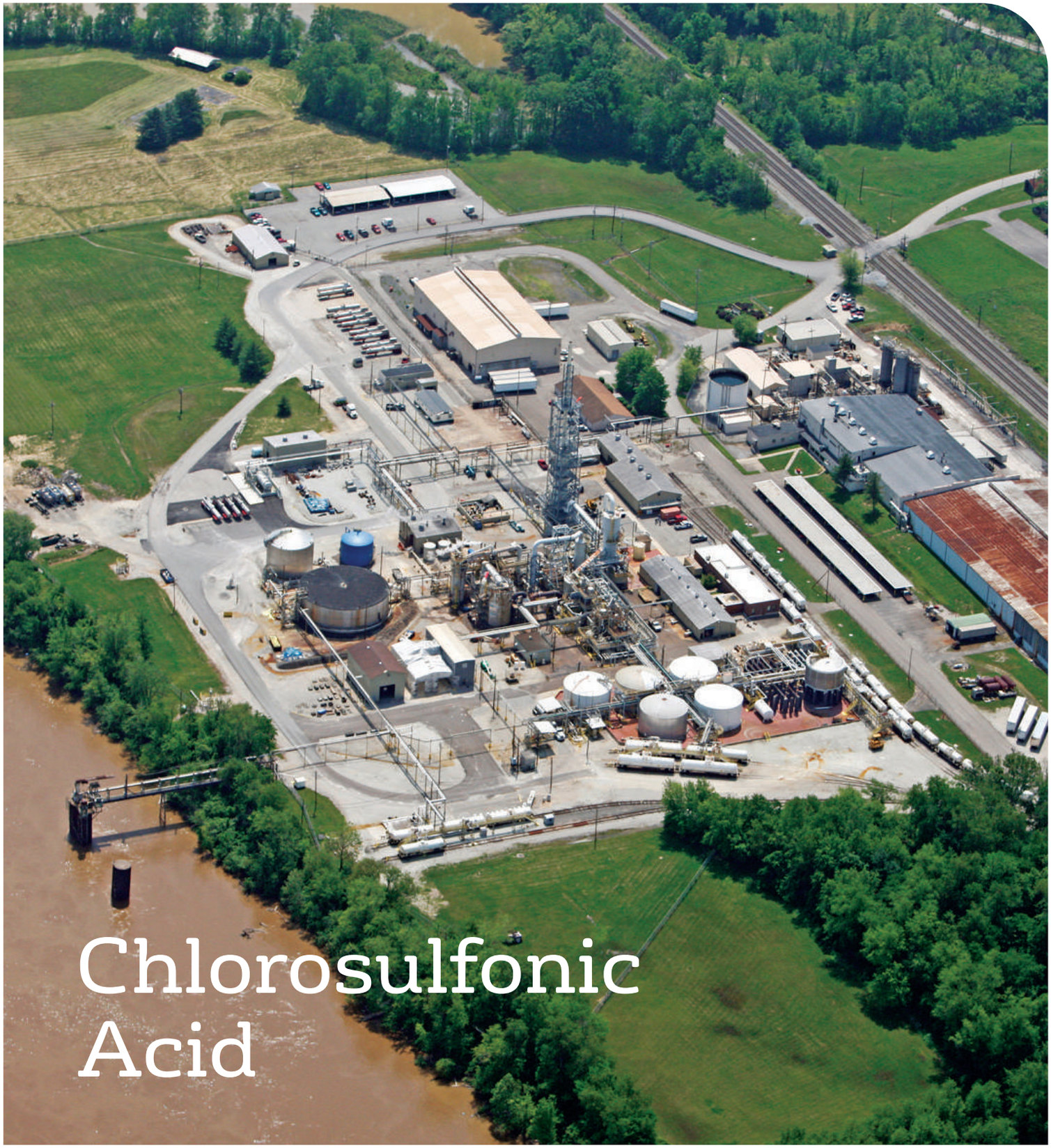

Chlorosulfonic Acid

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VEOLIA

Technical Information

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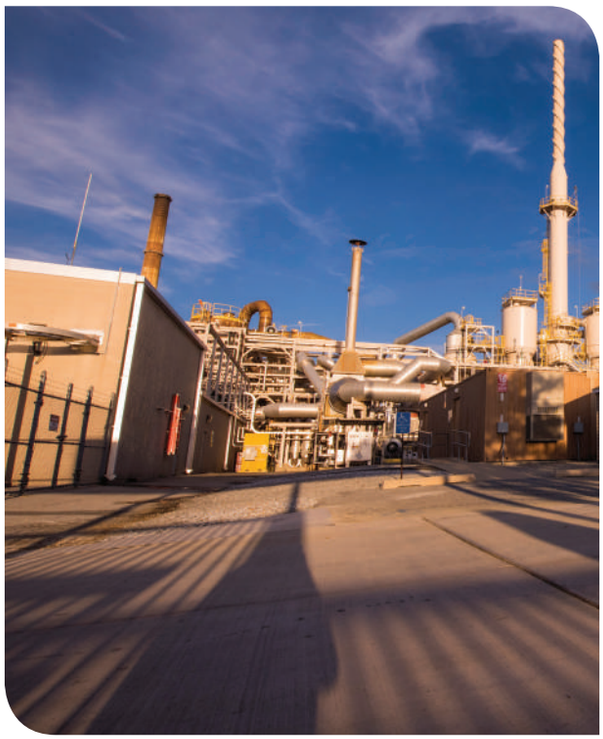


INTRODUCTION

Chlorosulfonic acid ($ClSO_2OH$) is a clear to straw-colored liquid with a pungent odor. It is a highly reactive chemical compound containing equimolar quantities of HCl and SO3 with a molecular weight of 116.52. Its Chemical Abstract name is Chlorosulfuric Acid, with Registry Number (CAS) 7790-94-5. It reacts violently with water evolving heat and large quantities of white fumes of hydrochloric and sulfuric acid. The uses are principally in organic synthesis as a sulfating, sulfonating or chlorosulfonating agent. It is preferred in many applications because it is a strong agent that is less destructive than sulfur trioxide.

Veolia is the global leader in optimized resource management, providing water, waste and energy management solutions that contribute to the sustainable development of communities and industries. Through our complementary business activities, Veolia helps to develop access to resources, preserve available resources and to replenish them. 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 July 2016, Veolia North America finalized an agreement with Chemours (formerly DuPont) to purchase the assets of its Sulfur Products division. 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. Chemours, and previously DuPont, 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 Veolia's ownership, continues to be the benchmark for sulfuric acid plant operations and services.

Veolia owns and operates seven sulfuric acid plants throughout the United States. Some of these plants are sulfur-burning plants that use a contact process (refer to Figure 1: Acid Plant). 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, tank trucks and portable tanks. We partner with highly skilled transportation providers to ensure the product gets to you on time and safely, and we provide them with annual training on the handling and management of sulfuric acid products.

Product Stewardship

Veolia fully endorses American Chemistry Council's (ACC) Responsible Care® Program. We encourage customers to thoroughly review their safety management practices in the handling of sulfuric acid. In support of product stewardship, Veolia 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, personnel 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 Veolia's sulfuric acid products. Veolia personnel may visit sites before making the first shipment.

Acid Production Process

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. Chemically, sulfur trioxide (SO_3) reacts with water (H_2O) to make sulfuric acid (H_2SO_4).

Veolia also produces sulfuric acid using the Spent Acid Regeneration process, as shown in 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. For more information on Spent Acid, refer to Veolia's Spent Sulfuric Acid "Properties, Uses, Storage and Handling" bulletin.

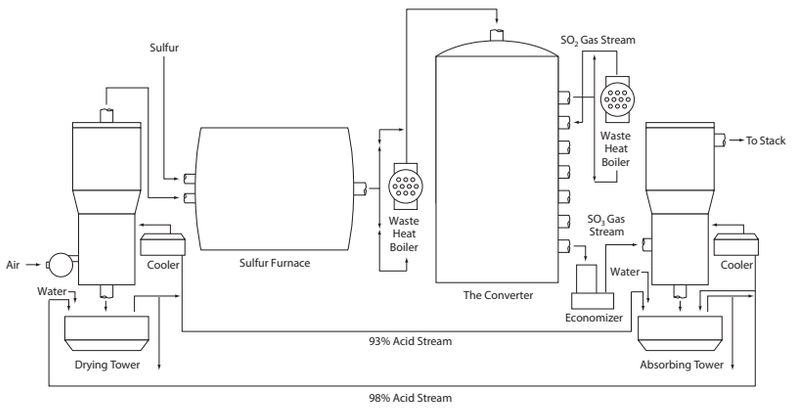


FIGURE 1: Acid Plant

Physical Properties

Chlorosulfonic acid has a strong, irritating, acrid odor and is very hydroscopic. CSA reacts violently with water, so uncontrolled contact with aqueous systems should be avoided.

TABLE 1: Physical Properties of Chlorosulfonic Acid

Molecular Weight	116.52				
Weight, 15.6°C (60°F)	14.6 lb/gal				
Specific Gravity	15.6°C (60°F) 1.75 g/mL				
Freezing Point, °C (°F)	–80 (–112)				
Boiling Point, °C (°F)	151–152 (304–307)				
Specific Heat	0.282 cal/g-°C (BTU/lb-°F)				
Heat of Vaporization	12.8 Kcal/g-mole				
Specific Electrical Conductivity	160–170 µmhos/cm 25°C (77°F) (µmhos/cm = microSiemens)				
Dielectric Constant	60 ± 10 at 15°C (59°F)				
	0°C (32°F)	10°C (50°F)	20°C (68°F)	40°C (104°F)	60°C (140°F)
Viscosity, cP	4.2	3.3	2.6	1.7	1.2
Vapor Pressure, mmHg	0.2	0.4	1.0	3.8	12.9

Uses & Applications

Chlorosulfonic acid is used most widely for sulfating liquid long chain alcohols. The reaction is relatively simple and rapid and goes to completion through the loss of HCI. CSA is a strong agent, but reacts more moderately than sulfur trioxide with good yields and color. Solid alcohols as well as ethoxylated alcohols, ester alcohols and long chain hydroxy amides can be sulfated in halogenated solvents. Sulfation with CSA generally requires close to stoichiometric amounts, thus minimizing purification problems. Long chain fatty acids and aromatic compounds can be sulfonated with CSA, and sulfamation reactions can be carried out with aliphatic and aromatic amines. Specific reactions are improved in some cases by the use of solvents, additives or CSA complexes with other agents such as SO_3, ethers, amides and tertiary amines.

SURFACTANTS

The major commercial use for chlorosulfonic acid is for sulfation or sulfonating operations in the manufacture of a variety of cleaning and wetting agent products.

Usually these materials are of a proprietary nature for use in shampoos and other personal care products or for formulating commercial laundry detergents and wetting agents.

DYES AND PIGMENTS

Chlorosulfonic acid is used as a sulfonating or chlorosulfonating agent to prepare intermediates for the manufacture of numerous dyes and pigments. It also is employed as a solvent or reaction medium for dyestuffs that are difficult to solubilize.

PHARMACEUTICALS

Manufacturers of various medicinals use CSA as a reactant in intermediate steps of synthesis processes. The major categories of these products are sulfonamides (anti-infectives) and benzothiadiazines (diuretics). They are used in both human and veterinary medicine as well as for preparation of animal feed additives.

CHEMICAL BLOWING AGENTS

Products to expand volume and reduce density of rubbers and plastics are made with CSA. These products fall chiefly in the categories of sulfonhydrazides and semi-carbazides.

PESTICIDES

A number of proprietary pesticides utilize CSA as chlorosulfonating or sulfonating agents in the manufacturing process. Ultimately these products find usage for protection of livestock, for weed control and in treatment of vegetable, fruit and other crops.

OTHER USES

The wide range of use of organic sulfates, sulfonates and sulfamates creates many in-process applications for CSA. The following partial listing gives product types and use areas which now or can require CSA in the manufacturing process:

- Plasticizers (from toluene sulfonyl chloride) resins
- Catalysts for polymerization, esterification and other organic reactions
- Alkylation processes
- Hydrogen chloride and carbon monoxide (from formic acid)
- Synthetic tanning agents

SPECIAL PRODUCT TRAINING

Fuming Acids Safety Symposium

Veolia North America sponsors periodic Fuming Acids Safety Symposiums that cover a variety of safety, environmental, facility and regulatory issues for customers, users and handlers of fuming acids. The agenda for the symposium is geared towards operating, safety, maintenance, technical support and emergency response personnel. The symposium usually consists of general session presentations, intermixed with small workshop sessions. The smaller workshop sessions permit longer, more detailed discussions on specific topics. For more details, contact your Veolia technical service or marketing representative.

Fuming Acid Spill Mitigation Workshop

Veolia North America also provides periodic Fuming Acids Spill Mitigation Workshops, held at the Department of Energy's Non-Proliferation Test and Evaluation Complex (NPTEC) in Mercury, Nevada. The workshops were initiated to test the best method for mitigating a fuming sulfuric acid release in controlled conditions. It is the only training available that uses "live" releases of fuming sulfuric acids.

The objectives of the workshops are to:

- Witness firsthand the fumes which result from a fuming sulfuric acid spill/release
- Train responders in the proper mitigation techniques for a fuming sulfuric acid spill/release
- Enhance emergency preparedness for local community hazmat responders

Participants receive training and education on fuming acids, including an understanding of the unique properties and characteristics of fuming acids; techniques on how to control and manage fuming acid safely and, perhaps most importantly, how to avoid any release of fuming acid from primary containment.

The workshops provide 24 hours of hazardous materials training developed specifically for the fuming sulfuric acids (sulfur trioxide, oleum and chlorosulfonic acid). This includes ten hours of classroom training and 14 hours of "hands-on" training. For more details, contact your Veolia technical service or marketing representative.

PERSONAL SAFETY & FIRST AID

All personnel working with chlorosulfonic acid should be thoroughly familiar with the health and safety precautions, and have the equipment needed to handle this product safely. The current Veolia Safety Data Sheets (SDS) for chlorosulfonic acid should be reviewed prior to using this product.

"Use of appropriate personnel protective equipment is essential to safely handle chlorosulfonic acid. "

Health Hazards

Chlorosulfonic acid is a strong acid and powerful desiccant. Skin or eye contact with the liquid acid will cause severe chemical burns. Prolonged skin contact may cause corrosion with pain, ulcerations, blisters or peeling of skin. Prolonged eye contact may cause corrosion, redness or swelling. Ingestion of chlorosulfonic acid will lead to gastrointestinal tract damage. The vapor is also hazardous and is extremely irritating to the skin, eyes, nose and throat. Vapors may cause delayed lung damage and difficulty in breathing. The vapor has such a sharp and penetrating odor that the inhalation of toxic quantities is unlikely unless it is impossible to escape the fumes.

Chlorosulfonic acid reacts violently with water. When exposed to the atmosphere, chlorosulfonic acid fumes release hydrochloric acid fumes and sulfuric acid mist by reacting with moisture in the air. Inhalation of these fumes or mist may cause lung injury.

The OSHA Permissible Exposure Limit (PEL) for hydrogen chloride is 5 ppm (C) /7 mg/m3 (C) in air. The PEL for sulfuric acid is 1 mg/m3 (CFR 29, 1910.1000 Air Contaminants). *

(C) denotes a ceiling limit.

The International Agency for Research on Cancer (IARC) has classified "strong inorganic acid mists containing sulfuric acid" as a Category 1 carcinogen, a substance that is "carcinogenic to humans." This classification is for inorganic acid mists only.

** Due to changing governmental regulations, such as those of the Department of Transportation, Department of Labor, US Environmental Protection Agency, and the Food and Drug Administration, references herein to governmental requirements may be superseded. You should consult and follow the current governmental regulations, such as Hazard Classification, Labeling, Food Use Clearances, Worker Exposure Limitations, and Waste Disposal Procedures for the up-to-date requirements for the product described in this literature.*

Safety Precautions

Use of appropriate personnel protective equipment is essential to safely handle chlorosulfonic acid. All persons handling chlorosulfonic acid should exercise care to prevent contact with skin, eyes or clothing and to prevent breathing of mists or vapors. Use with adequate ventilation and wash hands thoroughly after handling.

Personnel Protective Equipment

Personnel protective equipment (PPE) should be used to protect workers whenever contact with chlorosulfonic acid could be encountered. However, it should not be considered a substitute for safe working conditions and practices. It is the responsibility of the employer to make a PPE assessment per OSHA 29CFR1910.132 requirements.

The following four classes of personnel protective equipment are used when working with chlorosulfonic acid (CSA)

- Class D: For low risk of exposure
- Class C: For moderate risk of exposure
- Class B: For high risk of exposure
- Class A: For maximum risk of exposure, used during an emergency leak/spill situation

The general PPE requirements for Levels A, B, C and D are given to provide guidance in selecting the appropriate level of protection for a given job assignment. Each chlorosulfonic handling site may have its own standards with respect to the specific PPE requirements, especially for the lower risk levels of exposure.

Protective clothing should be made of an acid-resistant material suitable for chlorosulfonic acid exposure, such as treated PVC, butyl rubber or other composite materials. Remember, PPE is only acid-resistant, not acid-proof. Selection of appropriate PPE materials should be based on the following criteria:

- Have a low relative chlorosulfonic acid permeation and long breakthrough times.
- Be composed of materials that have good resistance to tears, rips and chemical degradation.
- Be sufficiently flexible to allow the worker to adequately complete the job at hand.

PPE should be regularly inspected before each use to confirm it is suitable for use with chlorosulfonic acid. Any acid suit with flaws, rips or tears should be discarded. In addition, gloves should be tested for holes by immersing them in water while applying a small amount of air pressure to detect leaks. PPE must also be washed and decontaminated between uses.

CLASS D
The minimum PPE recommended for Class D is:

- Hard hat
- Steel-toed safety shoes with PVC, neoprene, or composite soles
- Pants and long-sleeved shirt or coveralls made of acid-resistant polyester, acrylic, or wool
- Safety glasses with side shields

In addition, some sites may choose to add coverall chemical goggles and work gloves. With Level D clothing, workers may enter an area where CSA is used, read gauges, or visually inspect equipment.

CLASS C
The minimum PPE recommended for Class C protection is the same as that for Class D, plus the following:

- Coverall splash goggles
- Acid-resistant gauntlet gloves
- Optional, acid-resistant jacket
- Optional, face shield can be added over the goggles if desired, but it is not a replacement for goggles.

With Level C clothing, personnel may operate valves and switch on pumps, etc.

CLASS B
To provide protection for a high-risk exposure to CSA, the following Class B PPE is recommended:

- Head Protection: acid resistant hood and hard hat
- Eye Protection: chemical splash goggles
- Respiratory: NIOSH approved respiratory protection
- Body Protection: acid resistant suit, one or two piece *(fabric must pass ASTM testing for CSA)*
- Hand Protection: acid-resistant gauntlet length gloves with sleeves over gloves and liner gloves recommended
- Foot Protection: acid resistant boots with pant legs over boots

With Class B clothing, personnel can make first breaks into a CSA system, sample, or connect/disconnect hoses from shipping containers.

CLASS A
Class A is the most complete protection and is used in the event of a large leak or spill, or other emergency situation. For Class A the following PPE is required:

- Head Protection: hard hat
- Eye Protection: full face mask
- Respiratory: NIOSH approved respiratory protection
- Body Protection: acid resistant, fully-encapsulated suit
  (fabric must pass a 45 min breakthrough ASTM F739 chemical permeation test for CSA)
- Hand Protection: acid-resistant gauntlet length gloves
- Foot Protection: acid-resistant boots

"Standby or backup personnel provide prompt response to a job situation where something unexpected has occurred."

Class A protection is for extreme conditions, where it is necessary to enter areas having a high CSA fume concentration, or where there is a liquid acid mist spray. Class A suits, like other protective clothing, should be considered a "last-line-of-defense." The limitations of the suits must be recognized. Under no circumstances should personnel enter a situation where they may be sprayed with a stream of liquid CSA or step into puddles of liquid CSA.

Working in Class A or B suits for long periods of time in warm climates may produce heat stress in the wearer. Provisions should be made to provide rest periods and/or use of devices for heat removal, such as ice vests or cooling air.

Standby and backup personnel should be specified for Class A and Class B jobs. Standby or backup personnel provide prompt response to a job situation where something unexpected has occurred.

PPE should not be worn or carried beyond the operating area. Each item should be decontaminated with water and removed according to a written sequential procedure to avoid possible CSA contact with any part of the body. For Level A and B activities, most CSA handling sites require that the personnel wash under a safety shower before removing the acid-suits.

Safety Showers & Eyewash Stations

The following safety equipment should be easily accessible in all areas where chlorosulfonic 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. Per OSHA, 30 gallons per minute (gpm) is the minimum 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

Speed is of utmost importance when removing exposed personnel from a contaminated area and removing CSA from the skin and eyes. First aid must be started immediately (within seconds) in all cases of contact with CSA in any form. All workers and supervisors that could be potentially exposed should be trained in first aid care for CSA/sulfuric acid burns/exposure.

Medical assistance should be promptly obtained for all affected persons. The physician should be informed in detail of the incident. Joint training sessions between the users of chlorosulfonic acid and the neighboring medical emergency response groups (hospital emergency room, paramedics, etc.) should be done annually.

IN CASE OF EYE OR SKIN CONTACT: Immediately (within seconds) flush the affected area with plenty of water (preferably cold water) for at least 15 minutes while removing all contaminated clothing and shoes – forget modesty! Call a physician. Do not "scrape" or "wipe" the acid off the skin – scraping or wiping could greatly increase the probability of removing the upper skin layer, exposing the area to infection, and delays the water flushing.

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 soaked in iced water can be applied. For more detailed instructions consult the Veolia Sulfuric Acid/Oleum/Chlorosulfonic Acid First Aid and Medical Treatment Manual, available from Veolia technical service. Watch for signs of "shock."

Note to Physician: Continued washing of the affected area with cold or ice water will be helpful in removing the last traces of SO3/oleum/sulfuric acid. Creams or ointments should not be applied before or during the washing phase of the treatment.

IF INHALED: Move 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. Immediately give patient large quantities of water. Immediately call a physician. Do not give carbonates. Never give anything by mouth to an unconscious person.

TRAINING

On-site first aid responders should receive hands-on training for CSA burns at least once per year. Off-site support medical personnel (hospital/trauma center doctors and nurses, ambulance attendants and paramedics) should be provided refresher training annually. A primary off-site support facility should be selected.

SUPPLIES

The recommended on-hand supplies for first aid include:

- A clean 5-gal bucket and lid
- Prewashed cloth towels
- A bag of ice or ice machine

“Prevention of spills and releases of chlorosulfonic acid should be carefully considered in the design and operation of facilities handling this acid. ”

HANDLING PRECAUTIONS

Spills and Releases

Chlorosulfonic acid forms dense white clouds of sulfuric acid mist and hydrogen chloride gas when exposed to air.

Prevention of spills and releases of chlorosulfonic acid should be carefully considered in the design and operation of facilities handling this acid. Factors important in spill prevention include facility design, facility monitoring, detailed operating and unloading procedures, and employee training and education. See further discussion of factors to consider in design under Engineering Control of Hazards.

Even with the best efforts aimed at preventing spills, they may still occur, so consideration should be given to possible problem areas such as: vessels, piping, unloading areas, etc. Chlorosulfonic acid spills should be contained to prevent run-off to sewers and waterways. Drainage to sewers should be avoided because the violent reaction with water can result in eruptions or mini explosions. However, containing the release in a dike around the tank may make it difficult, if not impossible, to determine the source of the leak because of excessive fuming. It is best to evaluate the drainage pattern and install diversion dikes that contain the spillage in such a location that the release can be controlled.

Spills Mitigation

All sites handling chlorosulfonic acid must have equipment and trained personnel available to render spills/leaks non-fuming, neutralize the spill, and then provide for the proper disposal of the neutralized acids. Personnel must be familiar in firefighting and handling procedures in order to proceed with cleanup.

Comply with Federal, State, and local regulations on reporting releases. The CERCLA reportable quantity for chlorosulfonic acid is 1000 pounds (as 100% chlorosulfonic acid).

Dilute chlorosulfonic acid has a high rate of corrosion on steel and other metals. Spills on external tank surfaces and other equipment must be washed off immediately.

Use appropriate personal protective equipment during clean-up. Keep people away from the source and upwind of the spill or leak. Evacuate personnel to safe areas. Acid spills should be contained to avoid runoff to sewers.

Two basic mitigation techniques have been successfully used.

- Water fog mitigation
- Foam mitigation

WATER FOG MITIGATION

One recommended spill mitigation method is to use water fog to add water to a liquid CSA spill. The acid is hydrolyzed to a non-fuming acidic solution. It requires about 16 lb of water to react with 100 lb of CSA to make a non-fuming solution of sulfuric acid and hydrochloric acid (~ 1 gallon of water for 3 gallons of CSA).

$$ClSO3H + H2O \rightarrow H2SO4 + HCl + (heat)$$

The non-fuming solution can then be neutralized. Sulfuric acid mist and HCl gas are evolved during the water fog or foam treatment until the chlorosulfonic acid has been sufficiently diluted. Water fog mitigation causes a rapid temperature increase that results in a temporary increase in fume evolution. When the chlorosulfonic acid is completely reacted with water, the fuming subsides until there are only wisps of vapors, mostly steam, coming from the acidic solution.

The fog should be sprayed from the upwind side and allowed to fall on the liquid spill. The fog spray pattern should be verified before spraying on the spill so that a stream of water is not added to the chlorosulfonic acid which can cause a violent, even explosive, reaction.

Caution: Do not spray directly on the point of a leak, because it will increase the corrosion rate and may increase the size of the leak.

FOAM MITIGATION

Foam mitigation is intended primarily for liquid spills and uses commercially available foams to blanket the fumes. However, its main function is to introduce water (from the foam) in a controlled way into the chlorosulfonic acid to convert it to a non-fuming acidic solution. The use of the Mid-expansion foams, around 50 to 1 ratio, have produced the optimal foam blanket for fume suppression. The foam should be applied in a back and forth sweeping motion until the surface of the spill is covered. Foam generation must be verified before applying to the spill. Do not plunge the foam into the chlorosulfonic acid —a violent reaction will occur. Once the foam blanket is established, it will form a layer of non-fuming sulfuric acid on the surface of the spill/leak. This layer helps suppress fuming by sealing the chlorosulfonic acid from the moisture in the air. The foam blanket degrades rapidly as the hydrogen chloride attacks the foam bubbles, making it necessary to reapply the foam. If desired, water fog can be gently applied through the foam to hasten the hydrolization of the remaining chlorosulfonic acid and form a non-fuming acidic solution. To successfully apply the foam, the correct hose nozzle must be used, and water pressure at the foam aspirator must be at least 120 psig. This may require the use of a booster pump.

NEUTRALIZATION

A commercially available, magnesium oxide based, dry chemical agent can be applied to spills/releases of chlorosulfonic acid to render them non-fuming and at the same time neutralize the acid. This technique is most effective on shallow-depth spills (<1/2 in). (Some examples of dry chemical agents are lime, soda ash, or other alkali material. See the Veolia technical service representative for the latest recommendations on the agent). The dry chemical agent causes a very rapid temperature increase. The thermal rise can carry away small particles (dust) of the dry chemical, temporarily making the "fume" evolution look worse. While the dry chemical is reacting with the chlorosulfonic acid, a water fog spray can be applied to provide better contact between the dry chemical and the acid and to provide some cooling. Once the dry chemical has been completely reacted with the acid spill, the fuming subsides.

OTHER TECHNIQUES

Relatively small spills can be best treated by absorption in expanded clay, diatomaceous earth, dry sand, limestone or other absorbents. Such materials with the absorbed acid can then be removed from the area for controlled dilution with water or neutralization with alkali.

For contained pools of chlorosulfonic acid, as in a diked area, the spill can be covered with white mineral oil or with a fluorocarbon oil/glass bead mixture. The oils seal the top of the acid from atmospheric moisture, stopping the fuming.

Note: All neutralization and disposal of chlorosulfonic acid must in accordance with applicable federal, state or local regulations.

"Do not plunge the foam into the chlorosulfonic acid—a violent reaction will occur. "

Spill Control

Users are urged to determine which of the methods of control is best suited for their plant and equipment. It is important that appropriate equipment be available and suitably located to handle a leak or spill without delay. Personnel should be provided with appropriate personnel protective equipment and instructed in equipment location and operation. It is desirable to incorporate a spill handling procedure into a plant's emergency response plan so that the appropriate regulatory agencies are promptly notified and public relations contacts are properly carried out. It is useful to review spill handling procedures with the local fire department.

Veolia can provide a film video clip showing spill control measures that may be helpful in instructing new users who are not familiar with the handling of chlorosulfonic acid.

Hazardous Chemical Reaction

Water or caustic solutions should never be added uncontrolled to CSA because of violent reaction and spattering.

Chlorosulfonic acid reacts readily with many other compounds. Many of these reactions are well known and have been employed safely for many years.

CSA reacts with organic and inorganic reducing materials with rapid generation of heat. CSA is a powerful dehydrating agent and readily chars many organic substances. On contact with combustible materials such as wood shavings, the heat produced by dehydration may be sufficient to cause fire.

CSA 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 violent eruption that could result in acid burns, but also the possibility of generating explosive or poisonous atmospheres which could present additional hazards. For these reasons, CSA should be used strictly in accordance with the directions prepared by qualified technical personnel.

Many lubricants are attacked by CSA. Use only silicone or fluorocarbon-based lubricants.

“Water or caustic solutions should never be added to CSA because of violent reaction and spattering.”

Corrosion Hazards

The recommended materials of construction are 316ss for ambient temperatures and low velocities. For elevated temperatures or high velocities, Teflon™ lined steel or glass lined steel is recommended. Stainless steel is resistant to corrosive attack in the liquid and vapor areas of equipment as long as moisture is not present. Teflon™ is the only known resistant plastic material. Chemical glass is essentially impervious to CSA.

CSA attacks cast iron, brass, bronze and most other non-ferrous metals. Elastomers such as rubber, neoprene, hypalon, buna-N are all attacked by CSA. Polyethylene, polypropylene, polyester, epoxy, PVC, and CPVC are all readily attacked by CSA and, therefore should never be used in this service.

The corrosion rate of 316ss is 0.2 mil/yr at ambient temperature and static velocity and 6.5 mil/yr at 70 C and 8 fps velocity. 304ss has roughly 1.5 times the corrosion rate of 316ss and can be an economical alternative to 316ss. The corrosion rate of carbon steel is roughly 10 times that of 316ss; therefore, it is moderately resistant to CSA, but there can be appreciable iron pick-up, discoloration of acid, and possible sludge formation over time.

CSA vapors react with moisture in the air to form dense white fumes. Such fumes consisting of HCl and sulfuric acid can cause severe external corrosion damage to metal surfaces such as tanks and pipe lines.

Fire and Explosion Hazard

CSA is nonflammable. It is highly reactive and capable of igniting finely divided combustible materials on contact or may cause spontaneous combustion in contact with such organic materials as sawdust and oily rags. It is extremely hazardous in contact with many materials, particularly carbides, chlorates, common metals, cyanides, fulminates, nitrates, perchlorates, picrates, powdered metals, reducing agents, strong oxidizers, and sulfides.

When diluted to non-fuming concentrations, the hydrochloric acid and sulfuric acids so formed attack many metals to release flammable hydrogen gas. Therefore, open flames, open lights or matches should not be allowed in or around acid containers or lines.

Fire Fighting

In case of fire, evacuate personnel to safe areas. Use extinguishing methods that are appropriate to local circumstances and the environment. For example, dry chemical or carbon dioxide extinguishing methods may be used. Water can be used on combustibles burning in the vicinity of CSA but care must be exercised not to apply water directly to CSA to avoid rapid evolution of heat and violent spattering. Cool tank with water if exposed to fire, but do not get water into 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 CSA in a confined area such as a tank because it may cause violent eruptions that could result in structural failure.

“CSA attacks cast iron, brass, bronze and most other non-ferrous metals. ”

Engineering Control of Hazards

Proper design of storage and handling systems from point of delivery to point of consumption and proper operating and maintenance procedures are essential to safeguard against serious incidents.

DESIGN FACTORS TO CONSIDER INCLUDE:

- A tight system that minimizes plant and community exposure potential.
- Location of storage tank and unloading spot(s) relative to other chemicals and working areas. Plants handling CSA should be preferably located away from densely populated areas or major highways.
- Means of confining accidental leaks, a proper drainage system, and a spill and leak cleanup procedure that is consistent with plant and regulatory agency requirements.
- Provision for more than one escape route in the event of fire, explosion, or accidental release of CSA fumes.
- Readily accessible safety showers, eyewash stations, breathing air supply, evacuation alarms, public address systems, and other emergency equipment such as fire hydrants, fog nozzles, foam equipment, and dry chemical/neutralizing agents.
- Means of detecting CSA leaks while they are still small through the use of video cameras and other remote sensors (smoke detectors, opacity meters, chemical detectors).
- Suitable scrubbing facilities for venting/evacuating unloading, storage, and handling equipment.
- Provisions should be made to allow de-inventory of CSA equipment/storage to other vessels in the event of leaks. This may be accomplished by utilizing spare (empty) CSA tank or empty tank cars or trucks.
- The number of nozzles on the storage tank should be minimized. Bottom nozzles should be avoided. Sufficient corrosion allowance should be allowed to give long term life.
- Appropriate, remotely activated automatic valves should be installed to allow isolation of equipment in the event of a leak.
- Avoid using small diameter piping (less than 1 in), except for fit-up to instrumentation, as small diameter piping is not mechanically very strong. A small line could break if hit by another object.
- Adequate lighting and appropriate alarms and interlocks for the system. Redundant alarms should be provided for critical alarms, interlocks, and tank level measurements.
- Piping systems should be all welded or flanged. Screwed fitting should not be used except for fit-up to instrumentation. Piping should be sloped and provisions made for clearing the lines. Build to ASME piping standards B31.3 (normal fluid service).
- Means of isolating the tank car or tank truck with remotely actuated block valves in the event of a hose failure.
- Depending on site-specific considerations, such as proximity to the community or major highways, consider providing stationary water fog nozzles and/or foam nozzles (manual or remotely activated) to minimize the time required to mitigate a spill and minimize the fume release.
- CSA should never be blocked in a line completely sealed between two closed valves. Thermal expansion of the acid can cause gasket failure or line rupture resulting in a leak. Relief systems discharging to a safe location should be installed in these line sections.

OPERATING AND MAINTENANCE FACTORS TO CONSIDER INCLUDE:

- Inspection and thickness testing of equipment and piping on a periodic basis, at least every two years or as determined by previous inspection history. Up-to-date isometric piping drawings, with testing points, should be used to correlate test data with equipment in the plant. Particular attention should be paid to high temperature and high velocity areas where corrosion would be exacerbated. Special care should be taken to look for corrosion under insulation or flange guards.
- Internal inspections of CSA storage and process vessels should be made periodically. The inspections should be done every 6-12 years based on tank history and thickness testing. Emptying the tanks/ vessels for the inspection can be a difficult job. Consult Veolia technical service for procedures and equipment needs. External walk-around inspections should be done annually. External ultrasonic thickness testing should be done every three years at a minimum.
- Regular inspection and periodic replacement of unloading hoses (annually).
- Clearly written unloading, storage, and handling instructions, including checklists, to ensure that correct procedures are followed each time to avoid incidents.
- Materials of construction verification for critical equipment (valves, gaskets, bolts, etc.) where a failure could cause a major release.
- Regular inspection and/or testing of alarms, interlocks, pressure relief valves, and rupture disks.
- An administrative system that ensures equipment inspections are completed and results are documented (Mechanical Integrity Program).
- Conducting periodic process hazards reviews, which closely examine procedures, equipment layout, past incidents, etc., and make changes to improve equipment reliability and personnel safety.
- Labeling of lines and equipment that contain CSA.
- Thorough training and regular retraining of personnel in the important aspects of handling CSA. These include:
    - Use of personnel protective equipment (PPE)
    - Hazards resulting from improper handling of CSA
    - Prevention and detection of leaks
    - Maintenance procedures, including equipment decontamination
    - Emergency procedures
    - Cleanup procedures
    - First aid and medical treatment procedures
- Performing a consequence analysis of credible and worst-case incident scenarios; model fume release effects on the surrounding community. Some locations may want to complete a quantitative risk assessment (QRA) to help determine the ranking of hazard/risk reduction programs.

WASTE DISPOSAL

CSA is regulated as RCRA hazardous waste. Disposal of waste liquid streams containing chlorosulfonic 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 and changes being considered for the future.

Because of the high pollution potential of chlorosulfonic acid wastes, they must be disposed of properly.

Usually CSA is cautiously diluted (hydrolyzed) by adding the acid to water or ice in an agitated and ventilated corrosion resistant vessel to form sulfuric acid and hydrochloric acid.

$$ClSO_3H + H_2O \rightarrow H_2SO_4 + HCl + (heat)$$

Temperature should be maintained below 50-60 C with additional ice or cooling. The diluted acid can then be neutralized with caustic soda, soda ash or lime solutions.

Chlorosulfonic acid can be hydrolyzed using a sulfuric acid solution (93%) without temperature rise.

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 H_2S, HCN, etc.

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 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.

TRANSPORTATION & UNLOADING

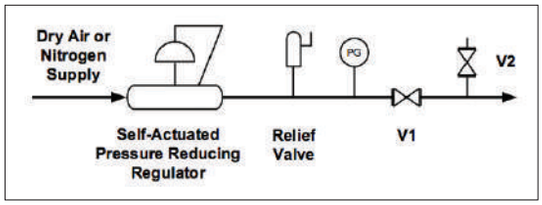
Veolia ships chlorosulfonic acid in

- Portable Tanks, nominal 3,300 lb (DOT – 51 container)
- ISO Tainers, nominal 38,000 lb (DOT – IM 101 container)
- Tank Trucks, nominal 38-40,000 lb, (DOT MC-312 trailers)
- Tank Cars, 60 and 90 ton cars, (DOT 112S340W & DOT 112S500W)

Labeling includes the DOT CORROSIVE and TOXIC INHALATION labels. Tank trucks and tank cars bear the DOT CORROSIVE and TOXIC INHALATION placards. DOT Hazard Classification: CORROSIVE MATERIAL (8) and TOXIC INHALATION (6.1).

Due to changing governmental regulations, such as those of the Department of Transportation, Department of Labor, U.S. Environmental Protection Agency and the Food and Drug Administration, references herein to governmental requirements may be superseded. You should consult and follow the current governmental regulations, such as Hazard Classification, Labeling, Food Use Clearances, Worker Exposure Limitations and Waste Disposal Procedures for the up-to-date requirements for the products described in this literature.

FIGURE 2:
Dry Air or Nitrogen Supply for Pressure Unloading



Unloading and Transfer

For safety reasons, pump unloading is preferred over unloading by air or nitrogen pressure. Pump unloading puts the unloading hose under suction pressure so that any leak can be stopped promptly without the need for venting the container of padding pressure. It may be necessary to supply a nominal amount of air (1-10 psig) for pump priming or to avoid creating a vacuum in the transportation vehicle being unloaded. In this case, the pressure should be the minimum needed for effective pump operation, with appropriate valving and controls for emergency shut off of air supply and depressurizing. When pumping from a tank car or tank truck without padding with air pressure, insure that the vessel is adequately vented to prevent tank collapse. A self-priming pump (1) avoids the hazards attendant to air pressure unloading and (2) provides sufficient discharge pressure for transfer to distant or elevated storage tanks. By proper location of the pump, the lines and valves can be so arranged that the same pump can be used in transferring acid from storage to process.

It is recommended that a remote emergency stop switch be located a safe distance away from the pump so that the pump can be shut down if a leak develops near the pump.

Dry compressed air or nitrogen may also be used to unload containers. If compressed air is used in place of pumping, the air piping arrangement should include a pressure reducing regulator valve set at 28 psig maximum, a safety relief valve set at not over 30 psig, an air pressure gauge and a 2” valve to release air pressure as shown in Figure 2. In the event of a tank or pipeline leak, provision should be made for quick shutdown of air supply and de-pressuring of the trailer including automating valves V1 and V2.

Tank Trucks

Veolia ships chlorosulfonic acid in stainless steel tank trailers of capacities up to 20-23 tons (2600-3000 gallons). However, over-the-road weight restrictions usually limit the amount of CSA to 19-20 tons.

To receive tank trucks, 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 13 feet through the plant and at unloading station.

3) An open area at the unloading station sufficient to permit normal maneuverability for the tractor and trailer.

4) A tractor trailer spotting area having a good, level surface capable of supporting about 20,000 pounds per axle (78,000 lb maximum gross weight of vehicle).

5) The tank trailer may be off-loaded at the rear bumper or from the top of the trailer. If the trailer is off-loaded from the top, the customer supplies the equipment to connect to the trailer (overhead piping, hose, valve, etc)

6) If the trailer is unloaded from the rear bumper, a securely anchored, free-draining, intake line is required. The receiving couplings must be within 12 feet of the rear end of the Veolia tank truck trailer spotted in normal unloading position.

7) A safety shower within 50 feet of the unloading spot and a source of running water at the unloading spot.

If unloading is to be performed at night, the unloading spot should be well lit to allow visibility for egress quickly in case of an emergency.

TANK TRUCK PLACEMENT AND UNLOADING

PLANT PERSONNEL SHOULD:

1) Be sure the storage tank can take the entire delivery.

2) Make certain the unloading hoses are labeled specifically for the product to be received and for the vent (if used) so that the unloader can make proper connections to the trailer.

3) Be sure that all valves to and from the storage tank are open.

4) Be sure the storage tank vent line to scrubber system, to trailer, (or to atmosphere) is open.

Unloader should inspect and test the 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.

The unloader must comply with the applicable DOT regulations for cargo tank unloading, including those specified in 49 CFR 177.834.

It is preferable that the truck pad be arranged so liquid spillage will drain away from the truck and exposed structures. The pad should be of sufficient length to allow the truck and trailer a minimum of a 4-foot clearance at each end and 2-foot clearance on each side. Because of the hazard of backing equipment into roadways and the possible need to move quickly from the unloading spot, drive-through arrangements are preferable. Where a drive-through arrangement is used, a chain, gravity-swing guard gate, or equivalent, should be provided across the truck entrance to the driveway when it is not in use.

Whether unloading by pump or air pressure, the piping should, if possible, be arranged so the acid will drain toward the storage tank when the pump is shut down or when the discharge valve is closed.

Wherever practicable, unloading should be accomplished by pumping. Whether pumping or unloading by air pressure, observe the following procedure.

1) Operate vent valve or air valve to vent the tank using precautions to avoid possible acid spray.

2) Remove blind flange from air inlet line and either connect to plant vent line or leave this line open during pumping.

3) After making certain there is no air pressure, remove blind flange from standpipe and connect unloading line to standpipe.

4) If transfer is by means of air pressure, connect air line to trailer and apply air slowly until there is normal flow of acid into the storage tank.

5) The air pressure must not exceed the safe working pressure of the tank or the relief valve set pressure.

6) A pressure reducing valve should be provided in the air line when higher pressures are possible.

7) When the tank truck is empty, shut off the air and operate the relief valve to vent off the pressure.

8) After pressure has been vented, disconnect the air line.

9) Do not disconnect the acid unloading line until the tank truck is at atmospheric pressure and the tank truck standpipe is drained.

10) After disconnecting the acid unloading line, replace blind flanges on standpipe and air line.

If a spill or overflow should occur during a transferring operation, the pump or supply of air should be stopped, valves shut off and spill cleaned up before other actions are taken.

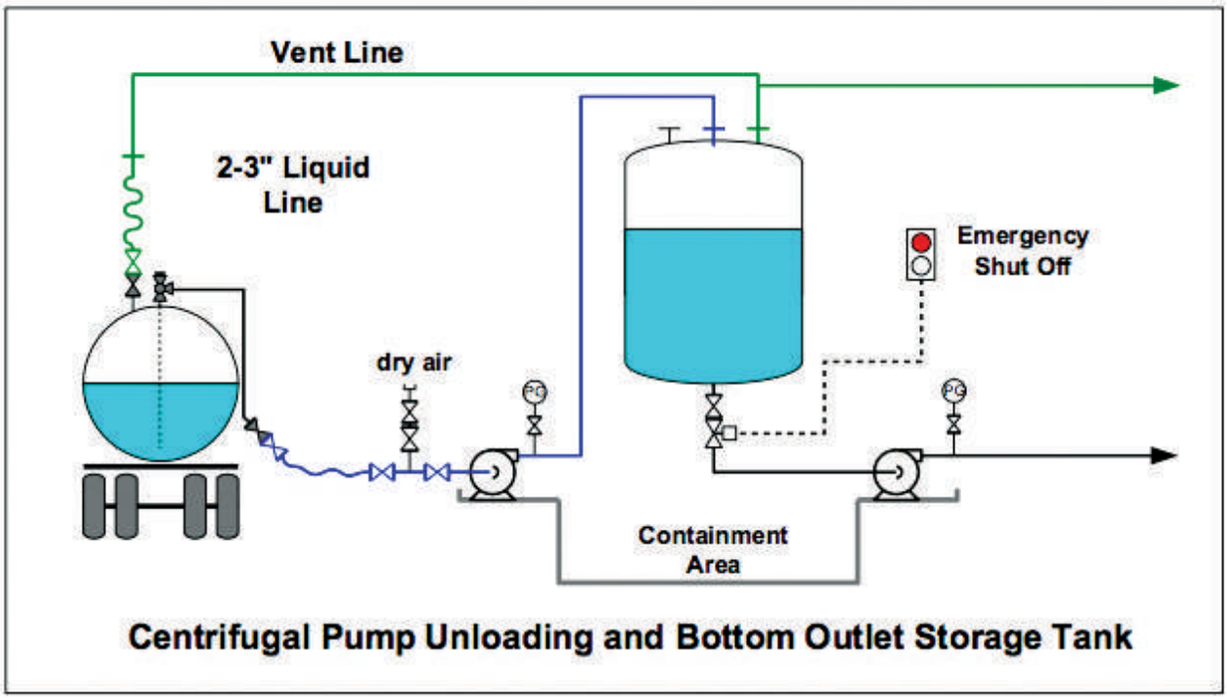
When unloading is completed, the unloader will blow through briefly into the storage tank to clear the line. The tank truck is empty when the pressure on the truck drops off sharply and approaches the storage tank pressure. The unloader will shut off the gas pressure or air compressor and close the valves on the truck. Then the liquid and vapor valves on the storage tank should be closed. Any liquid remaining in the unloading lines should be drained to either the tank or the truck and the lines vented so they can be disconnected. The unloader will disconnect the unloading hoses at the truck, check that the valves are secure and replace the plugs on lines. The unloader will wash down any drippage at the unloading station.

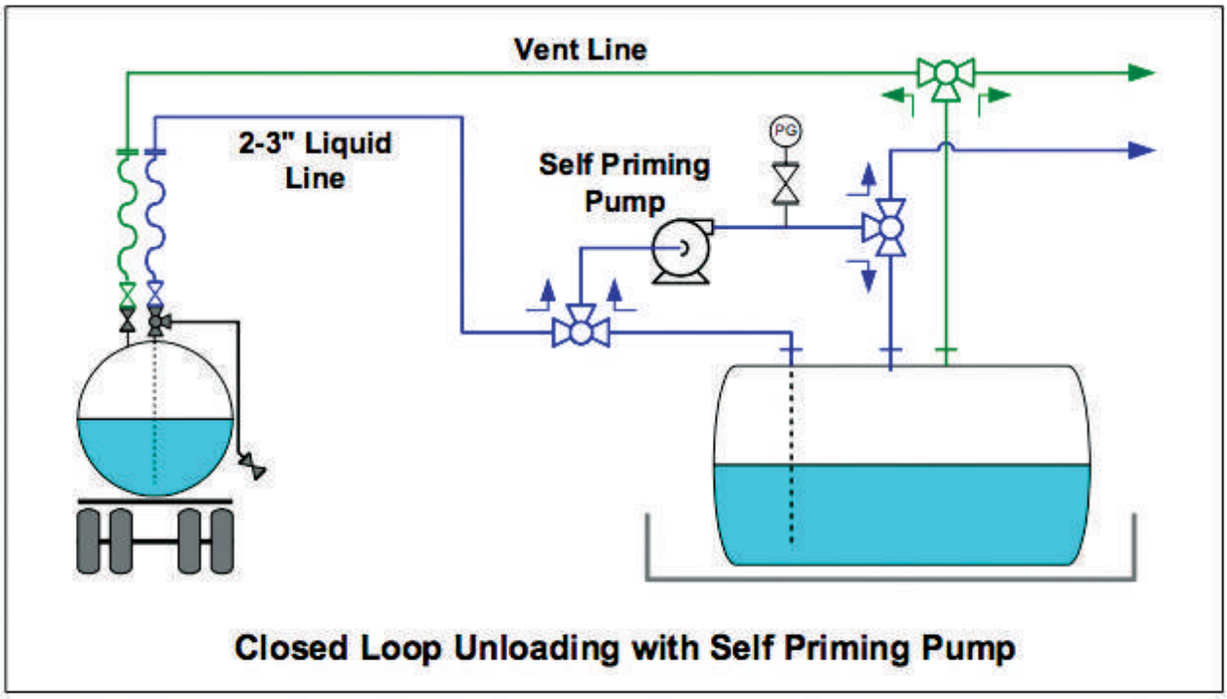
The discharge pipe on the tank truck utilizes a three way valve so that unloading can be over head or located at the rear of the truck. No bottom outlet is allowed on tank trucks carrying chlorosulfonic acid.

Tank truck unloading arrangements are shown in Figure 3.

Air piping arrangement should include a pressure reducing valve set at 28 psig maximum, a safety relief valve set at not over 30 psig, an air pressure gauge and a 2” valve to release air pressure as described in Figure 2. In the event of a tank or pipeline leak, provision should be made for quick shutdown of air supply and de-pressuring of the trailer.

FIGURE 3: Tank Truck Unloading





Tank Cars

Veolia ships chlorosulfonic acid in tank cars of 60 to 90 ton capacities (8000 to 13000 gallons).

No bottom outlet is allowed on tank cars carrying CSA. The discharge pipe is located in the dome on the longitudinal centerline of the car and extends to a well in the bottom of the tank. Tank cars have varied dome arrangements and the user should consult the Veolia Sales and Service Center if he is not familiar with a particular car. A typical tank car dome arrangement is shown in Figure 4.

To receive one of these cars, the unloading station will require an elevated transfer line that permits free drainage of the line. The transfer line can be of 2-inch stainless steel pipe with suitable swing connections, or it can be of 2-inch hose lined with Teflon™ fluorocarbon resin and covered with stainless steel braid or reinforced rubber. Flexibility in the unloading line is necessary to accommodate changes in tank car elevation during unloading. If a hose is used, care must be taken to ensure that the hose is not bent beyond the specified minimum hose bending radius to prevent "kinking" and damaging the hose.

When the tank car arrives, be sure to check its number against the shipping papers to confirm you have the proper car.

"Unloading personnel must be familiar with the properties and hazards of CSA."

CAR PLACEMENT
(Refer to 49 CFR 174.67 for requirements for tank car unloading)

Car should be centered on the unloading dock's access platform with hand brakes firmly set. Wheel chocks should be set on both sides of wheels to prevent movement in either direction. A locked derail and railroad warning flag (blue flag) must be installed per DOT regulations to guard against premature movement of the car. Install safety guard across outside handrail opening.

Visually inspect external appearance of the car for damage that may have occurred in transit. Cars should arrive with a seal on the protective housing to prohibit tampering. Check and inspect the car outlets for leakage. REPORT ANY DAMAGE OR TAMPERING IMMEDIATELY to the Veolia Sales and Service Center. You will be advised on proper procedure for accepting or rejecting the shipment.

PREPARATION FOR UNLOADING
Unloading facilities should be in good repair and all connections, hoses, gaskets, tools and safety equipment should be ready for use.

Unloading personnel must be familiar with the properties and hazards of CSA, the CSA car hardware and functions, and emergency procedures and action.

It is recommended that Class B personal protective equipment be worn to connect and disconnect the tank car (see PPE section). Class C personal protection (jacket, pants, boots, gloves and coverall goggles) should be worn at all other times while attending a CSA car. An acid hood should be on hand for immediate use in case of emergency.

Connect the liquid unloading and vent line/air connection to the proper fittings on tank car.

UNLOADING BY PUMP

Pump unloading is recommended. The pump should be constructed of materials resistant to chlorosulfonic acid. A self-priming centrifugal pump is preferred over the positive displacement type. If the latter is used, it should be provided with an un-valved by-pass from outlet to inlet with properly rated rupture disc of suitable material. Also, car must be vented to prevent a vacuum and to permit air to replace the acid as car is unloaded. All connections to the pump should be made in such a manner as to avoid excessive stresses at the pump. The pump packing should be checked prior to unloading to avoid acid leakage. Where a relief valve is required on a centrifugal pump, it should be arranged to discharge to a safe location or into the suction side of the pump.

Pump unloading operations should be carried out as follows:

1) Verify liquid/load and air/vent valves are closed.

2) Cautiously loosen bolts on air/vent blind flange and move (jiggle) flange before removing bolts. Remove blind flange and connect to plant vent line.

3) Slowly open air/vent valve to vent the tank car. Care is necessary, for the tank car may be under pressure, particularly during hot weather. If this pressure is not relieved gradually, there is danger of acid spray with the escaping air.

4) Cautiously loosen bolts on liquid/load blind flange and move (jiggle) flange before removing bolts. Remove the blind flange from top of acid discharge pipe and make connection to the pump inlet. The pump outlet should be piped to acid storage tank.

5) Start pump. If priming is required, pad car with air pressure to prime pump. Storage tank must be vented while acid is being transferred.

6) Follow car and storage tank levels until the tank car is empty.

7) Shut off the pump.

8) After lines have completely drained, close car valves.

9) Disconnect plant acid line from car discharge pipe fitting. Tightly replace blind flanges on tank car and plant acid line and with wrench.

10) Disconnect plant vent line from car air/vent flange. Tightly replace blind flanges on tank car and plant acid line and with wrench.

11) Hose down any spillage with water.

12) Close dome cover and secure.

Discharge connections must be detached immediately after tank car is unloaded. Unloader must stay with car throughout the unloading operation and until all discharge fittings are disconnected, valves closed and car fittings replaced.

Smoking is strictly forbidden in the vicinity of the rail car. All tools used in connection with unloading must be kept free from oil, dirt, and grit. Never strike tank fittings with tools or other hard objects. Do not use hammer and chisel at any time. Failure to observe these precautions may result in the ignition of hydrogen gas and create an explosion.

UNLOADING THE CAR BY PRESSURE

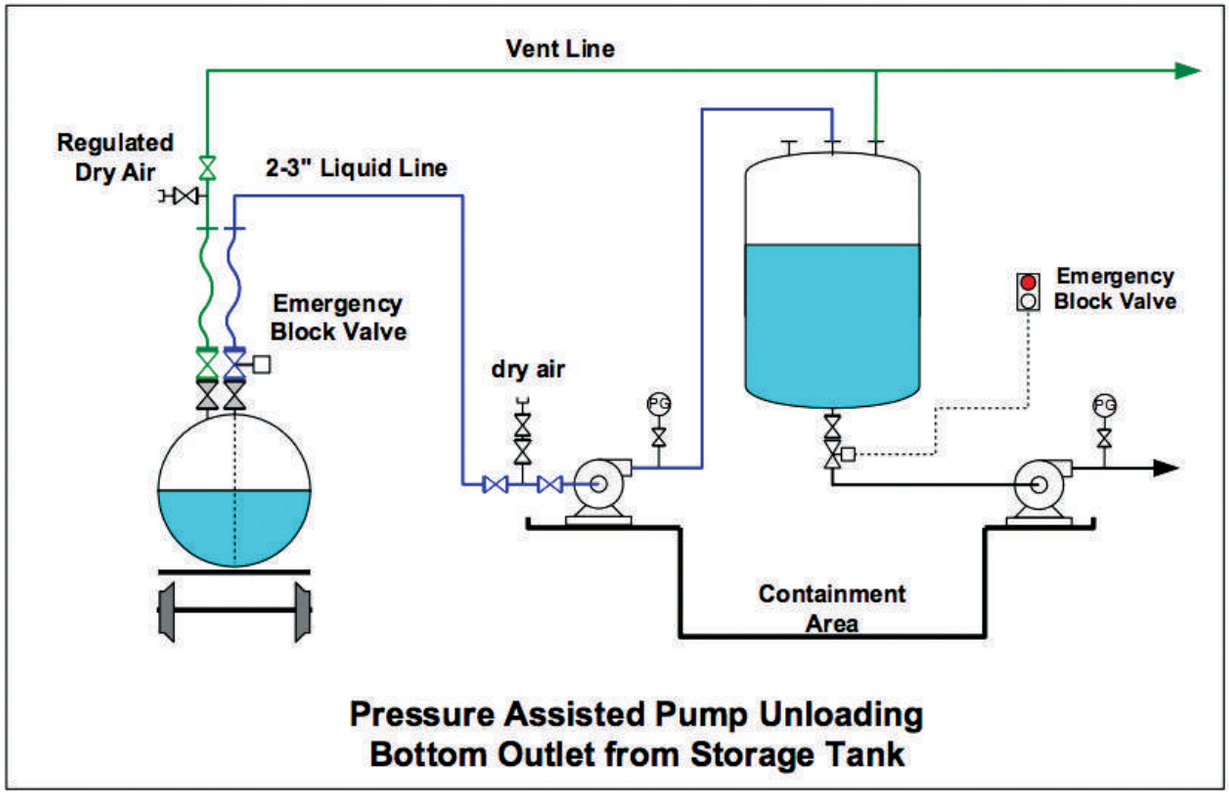
The car may be unloaded using a source of clean, dry air or inert gas at a maximum pressure of 28 psig. The compressed air or nitrogen must be free of oil, moisture and foreign matter.

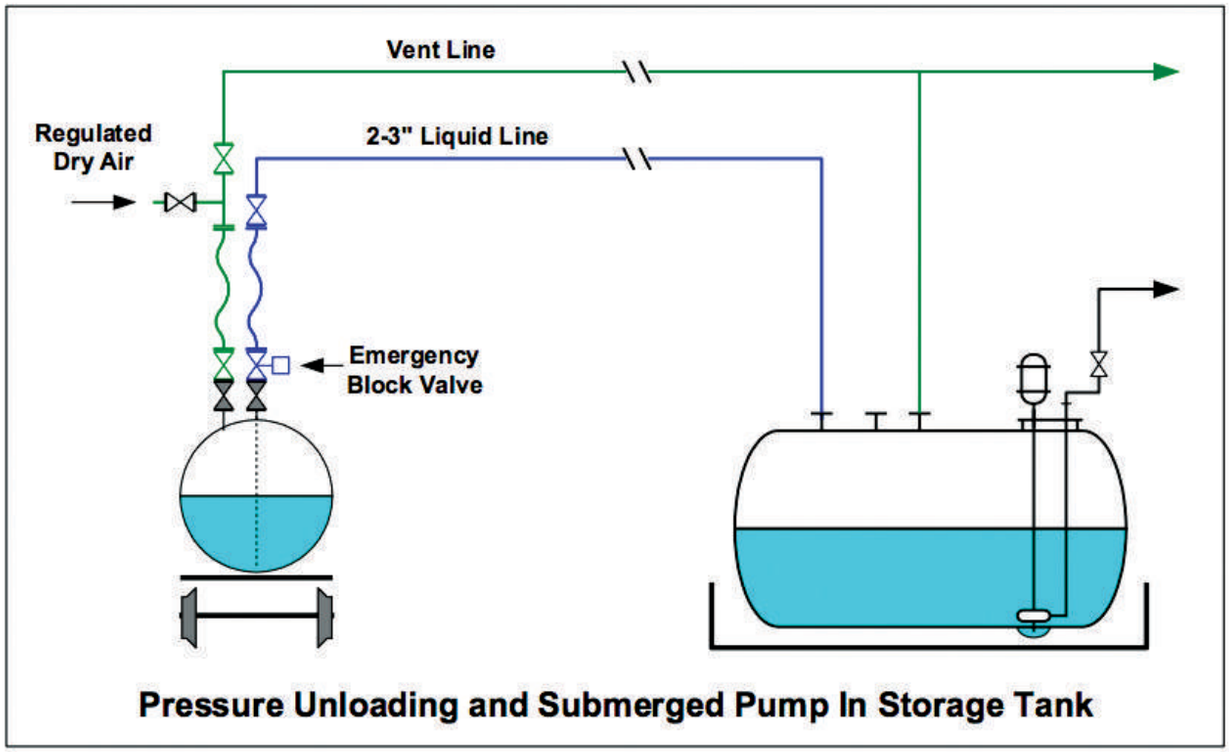
When ready to unload the car to storage, pressurize the car with up to 28 psig and check the car and connections for leaks. Open all liquid line valves from the storage tank to the car and unload car contents to storage tank.

Check storage tank level before, during and after unloading. When the car is empty as indicated by blow-through of air and increased gassing at fume scrubber tower vent, shut off air supply and liquid and vent valves at the tank car and slowly vent off air pressure in tank car to fume scrubber at a rate (45-60 minutes) which will not cause excessive gassing at fume scrubber tower vent.

Close all liquid and vent valves and disconnect car.

FIGURE 4: Tank Car Unloading





Transportation Emergencies

If a shipment of Veolia chlorosulfonic 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 (ACC's) Chemical Transportation Emergency Center ("CHEMTREC") in Washington DC:

1-800-424-9300

If outside of the U.S. make a telephone call to CHEMTREC via the following number:

1-703-527-3887

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, and such other questions as may be necessary to define the extent of the emergency situation. He/she will then give the caller recommendations for controlling the emergency situation until the shipper's specialist can relay help. CHEMTREC will immediately advise Veolia of the emergency, and one of our specialists will get in touch with the caller promptly.

EQUIPMENT

Storage Tanks

Chlorosulfonic acid should be stored away from nitrates, carbides, chlorates, metallic powders, and organic materials. Contact with combustible materials may cause fire. Because of the low freezing point of chlorosulfonic acid, heated storage is neither necessary nor desirable.

The capacity of the storage tank should be at least 1-1/2 times the maximum quantity normally ordered to protect against both running out of product and overfilling the tank. It is best to install the largest economical storage system. A larger installation permits future expansion, less precise scheduling of shipments and larger inventories when desired. Recommended minimum sizes are 4000 gallon (15 m3) for tank-truck deliveries and 15000 gallon (57 m3) for tank car deliveries.

Normally, only horizontal storage tanks are used. The material of construction may be glass-lined steel, stainless steel, clad stainless steel, or mild steel, depending on the period of acid storage and acid quality requirements. Where stainless steel or carbon steel tanks are used, the tanks should be designed as a pressure vessel, 50 psi minimum, per ASME codes and API 510 code. The tank should be a horizontal cylindrical tank, welded construction, 3/8–1/2 in thick, with standard ASME dished heads of the same thickness.

The corrosion resistance of mild steel is satisfactory, but there will be iron pick-up, discoloration of acid and possible sludge formation over time. If color and iron pick-up are critical, the storage tank should be glass lined. The use of stainless steels, such as 316L or 304L, results in only a very slight iron pick-up over extended periods of time.

“Store CSA away from nitrates, carbides, chlorates, metallic powders and organic materials. ”

The tank should be equipped with a bottom sump (5/8 inch minimum thickness) to permit pumping the tank substantially dry. The tank should be designed with no subsurface nozzles.

Tank supports should be installed on firm foundations. Floor loading and soil bearing must be considered to provide an adequate support. Structural steel supports or concrete saddles are satisfactory.

Storage tanks should be externally examined visually at least annually for corrosion-induced weaknesses. Ultrasonic thickness testing should be done biennially. An internal visual inspection should be done every 6-12 years, based on your individual experience and plant’s Mechanical Integrity program.

New storage tanks should be equipped with containment dikes sized at 110% of the tank capacity. Dikes may be earthen or concrete of either the impounding or diversion type. Diversion-type dikes are preferred for fuming acids to contain the acid away from the tank where it can be diluted to non-fuming concentration and disposed, but still allow access to the tank during emergencies. The geometry of the dike should be made to minimize surface area of any potential spill (and thus minimize the fume cloud). Diking for existing tanks should be considered per local regulations and your Process Hazard Analysis (PHA) report.

Pipe Lines

Schedule 40 316L stainless steel with welded flanged connections or Teflon™ lined steel is preferred. In some cases, schedule 80 mild steel may be applicable. Threaded connections are not recommended. All pipe lines should be sloped to permit complete draining to the unloading station, the storage tank and the point of consumption. This will prevent the accumulation of CSA at low points. thereby avoiding potential leaks if repairs are necessary.

Unloading Hoses

Unloading hoses are a critical component of the unloading system. Every care must be taken to ensure that the correct hoses are used and that they are well-maintained. Seamless, helical corrugated, unpigmented virgin Teflon™ PTFE lined hoses with stainless steel overbraiding and stainless steel end fittings are recommended. DO NOT USE polyethylene- or rubber-lined hoses. DO NOT USE quick-connect fittings, such as Camlock® (only flanged or hammer-lock fittings are appropriate). The hose vendor should supply verification that the hose meets the requirements for CSA service. The hose should be tested and certified before it is put in service. The actual installation date of the hose should be stenciled/stamped on the hose. Support of the hose must be addressed so that the manufacturer's minimum bending radius is not exceeded so that hose is not kinked.

Gaskets and Packing

Gaskets should be made of Teflon™ fluorocarbon resin. For piping systems Garlock's Gylon™ 3500 (fawn, PTFE with silica) or Gylon™3504 (blue, PTFE with glass microspheres) may be used. Virgin Teflon™ PTFE gaskets are acceptable as long as the "cold flow" characteristics are understood and addressed.

For fragile or lightly loaded flange assemblies such as glass lined equipment, Teflon™ envelope gaskets or Goretex GR gasket material (expanded PTFE) may be used.

For pressure applications Flexitalic, spiral wound gaskets made of 316ss or 304ss with Teflon™ filler may be used.

Valve packing should be of Teflon™ fluorocarbon resin; pump packing should be of braided white Teflon™ PTFE yarn, lattice braid, Teflon™ impregnated throughout and chemical resistant lubricant.

Consult manufacturers for specific grades and style numbers.

Dow Corning High Vacuum grease or a fluorocarbon oil can be used to lubricate pumps and valves.

Valves

Experience has shown that Alloy 20 valves or Durco T-line (Teflon™ lined plug valve by the Duriron Co, Inc) valves give good performance and require minimum maintenance.

Flanged valves are preferred. Valves should be purchased with a stainless steel guard to protect the operator against acid leaking through the packing. The stem packing should be Teflon™ PTFE fluorocarbon resin. Whenever possible, valves should be mounted in a horizontal position with the stem up.

Pumps

Stainless-steel submersible centrifugal pumps mounted internally or externally are recommended for pumping from storage tank to process. Vertical submerged pumps mounted on a manhole cover for ready removal give good service. The impeller, shaft and submerged discharge line should be of 316 or 304 stainless steel. Intermediate bearing must be lubricated with fluid from the pump discharge.

A sealless magnetic drive self-priming pump is recommended for unloading. Where equipment layout permits, it may be possible to use the unloading pump for transfer from storage to process.

Vent System

The vent system must be designed to prevent damage to the tank via over-pressurization or pulling vacuum inadvertently. It should be inspected periodically to assure that it is open. Glass or Teflon™ lined steel pipe systems have proved effective in this service. The system should be designed so that it can control discharge of fumes. Chlorosulfonic acid will fume vigorously when the shipping vessel is finally emptied and air or nitrogen pressure pushes vapors through the storage tank vent. Vapors are also displaced continuously during unloading by the liquid entering the tank. The vent from the tank should pass to a fume-abatement system, which must be designed to meet environmental requirements. The system will generally comprise a humidifying tower and a demister, together with neutralizing facilities for the effluent from both units.

Level Measurement

A reliable level indicator must be a part of storage tank auxiliaries. Veolia recommends separate, redundant level systems. Suitable level devices include differential pressure (bubbler), float, radar, conductance and magnetic type level gauges. Overflowing the tank can present a significant potential for an environmental incident and must be avoided.

Cleaning Storage Tanks

Over a period of years CSA tanks may build up a deposit of iron sulfate sludge which can cause pumping or blockage problems. It is then necessary to clean the tank and to inspect it internally. Frequency of cleaning will depend on each particular storage system. Cleaning is simplified by draining as much of the CSA as possible from the tank so as to have a minimum heel.

A concentrated sulfuric acid wash procedure is used to rid the tank of fuming acid followed by a water wash procedure. Several acid washes may be required prior to the water wash.

Cleaning of CSA tanks presents a significant pollution potential and the job should be done under the guidance of experienced personnel who are knowledgeable in CSA handling. Careful attention must be paid to all steps of the clean-out procedure to avoid the release of large volumes of H_2SO_4 mist and HCl fumes. Anyone cleaning a CSA tank for the first time should review his proposed procedure with the manufacturer's product specialist. For Veolia CSA, the product specialist may be reached by calling the Veolia Sales and Service Center.

Resourcing the world

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