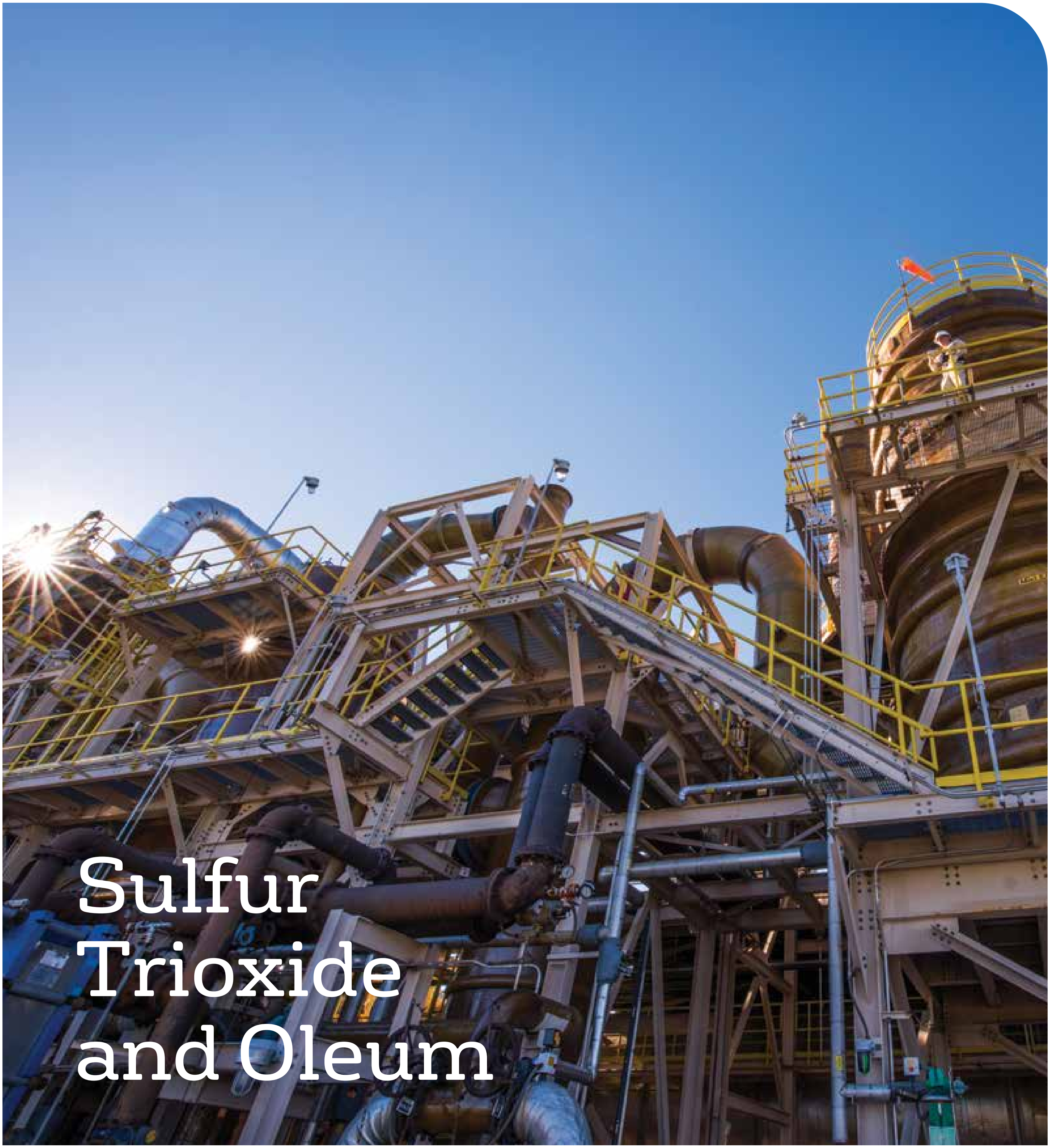


Sulfur Trioxide and Oleum

Properties
Usage
Storage
Handling

Technical Information

TABLE OF CONTENTS

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. Sulfur trioxide and oleum are the strongest inorganic acid produced from sulfur. Some of the industries that find sulfur trioxide and oleum essential include:

- Surfactants
- Soaps/detergents
- Shampoo bases
- Personal care products
- Bromide-based flame-retardants
- Engineering polymers
- Inorganic chemicals (FSA)
- Oil well drilling muds
- Optical brighteners
- Chemical intermediates
- Dyes and pigments
- Nitrocellulose & high explosives production
- Ion exchange resins

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 "Acid Production", page 6). 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, portable tanks and tank trucks. 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.

"In July 2016, Veolia North America finalized an agreement with Chemours (formerly DuPont) to purchase the assets of its Sulfur Products division."

Product Stewardship

Veolia fully endorses American Chemistry 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, 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, 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 Veolia's sulfuric acid products. Veolia personnel may visit sites before making the first shipment.

Regulatory Compliance

Sulfur trioxide (SO_3) and oleums are included in the SARA Extremely Hazardous Substance, CERCLA Hazardous Material, and SARA Toxic Chemical lists. SO_3/oleums are also specifically listed in Appendix A of the Process Safety Management Regulation (29 CFR 1910.119) and are listed as a regulated toxic substance in 40 CFR 68.130 in EPA's Risk Management Plan regulation (40 CFR Part 68) as directed by the Accidental Release Provisions of the Clean Air Act. The storage, handling and use of SO_3/oleums may require compliance with the above regulations, and there may be additional federal, state and local regulations. Be sure to check the specific regulations that affect your location.

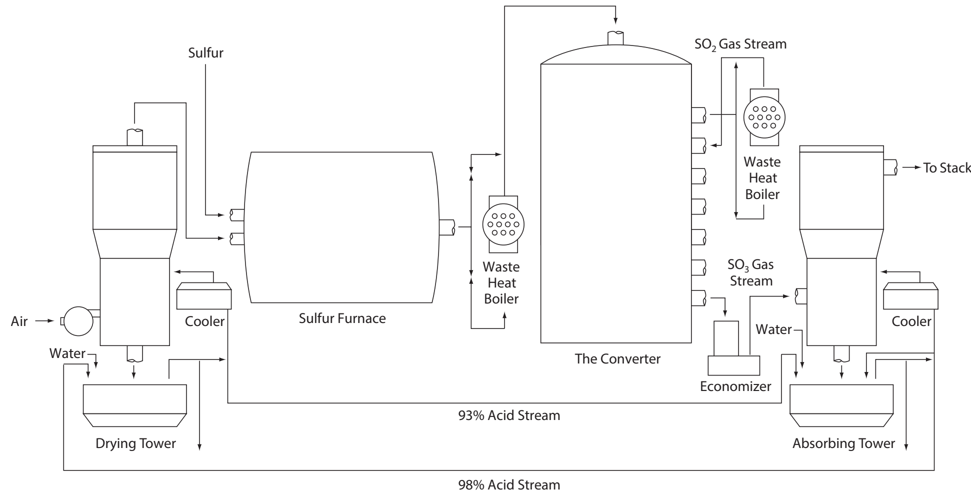


FIGURE 1: Acid Plant

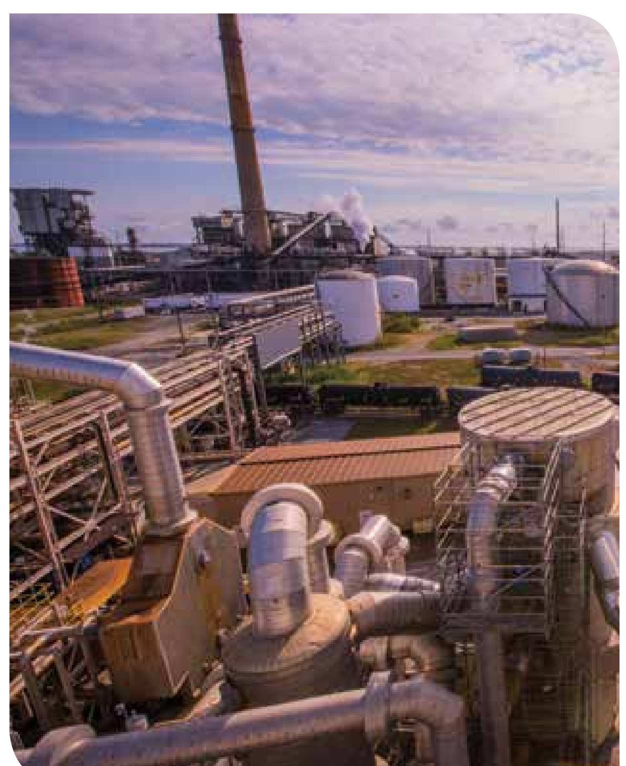
Acid Production Process

Figure 1 above 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.

Chemical and Physical Properties

Sulfur trioxide and oleum have a strong, irritating, acrid odor and are very hygroscopic. They react violently with water, so uncontrolled contact with any aqueous system should be avoided. They are oxidizing agents and may cause ignition by contact with combustible materials.



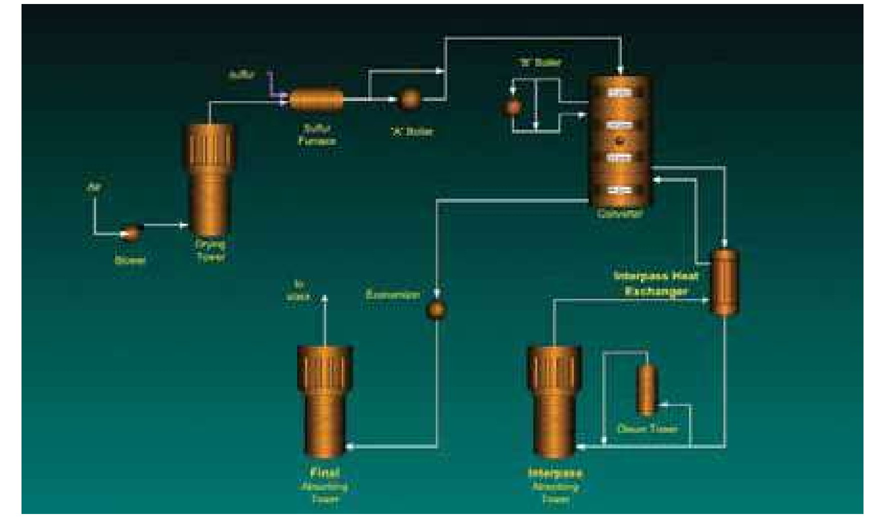


FIGURE 2: SAR Process

Sulfur Trioxide (SO_3)

Sulfur trioxide (SO_3) is normally a clear, colorless, oily liquid that may contain a slight haze and be off-white to light brown in appearance when shipped. As normally handled, SO_3 has a vapor pressure of up to 10 pounds per square inch (psi). SO_3 fumes react with the moisture in the air to produce dense, white clouds of sulfuric acid mist. Table 1 shows the physical and chemical properties of Sulfur Trioxide. Figures 3, 4A, and 5 give the viscosity, vapor pressure, and specific gravity of Sulfur Trioxide, respectively, at different temperatures.

Sulfur trioxide can exist in three forms: gamma, beta and alpha, each having different properties, as shown in Table 2. Gamma is the desirable form and exists when SO_3 is maintained absolutely pure and anhydrous. Beta and alpha are the undesirable forms, because they have higher melting points. Moisture is what promotes the formation of these undesirable forms. Moisture promotes polymerization, allowing the monomer and gamma forms to polymerize to the straight chain beta form. In time, cross-linking of the straight chains results in the formation of the alpha form.

Veolia offers two grades of SO_3; stabilized and unstabilized. The stabilized grade contains a small quantity of a stabilizer to retard the formation of the less desirable beta and alpha forms. The stabilizer makes it possible to more readily re-melt the SO_3 if it is allowed to solidify. In unstabilized liquid SO_3, moisture and temperatures below the freezing point of beta SO_3 (32.5 C, 90.5 F) favor polymerization to produce asbestos-like crystals that settle out. Two different polymers may be present in these crystals – the metastable beta form referred to above, and the stable alpha form, which melts at 62.3 C (144.1 F). Solid forms of SO_3 rarely have well-defined melting points because it may contain a mixture of the three forms. The theoretical possibility of a sudden increase in vapor pressure accompanying the melting of the higher polymers in such mixtures exists, but SO_3 stabilization and the use of proper techniques in handling reduces this possibility. SO_3 maintained in the liquid state will only consist of the gamma form. SO_3 should be stored at an elevated temperature of 35-41 C (95-105 F) to minimize the formation of the undesirable polymeric forms (alpha and beta) and still be safely below the boiling point of 44.8 C (112 F).

Oleum (Fuming Sulfuric Acid)

Oleum is the term used to describe fuming sulfuric acids. Oleum is produced in various strengths and consists of SO_3 dissolved in 100% Sulfuric Acid (H_2SO_4). Thus, 20% oleum contains 20% SO_3 and 80% H_2SO_4 by weight. More information on oleum product specifications is given in Table 3. Oleum is normally clear to turbid and off-white in appearance. Depending on strength, the vapor pressure is such that SO_3 fumes evolve and combine with moisture in the air to form sulfuric acid mist particles that are visible and can create clouds of dense white fumes. Physical properties of oleum are given in Table 3. Figure 4B gives the vapor pressure of oleum with strengths up to 35% as a function of temperature, whereas Figure 4C does so for 65% oleum. Figure 6 depicts the freezing points of oleums of different strengths.

Table 1
Chemical/Physical Properties of Sulfur Trioxide

Molecular Weight		80.06
Boiling Point (760 mmHg),	°C	44.8
	°F	112.6
Freezing Point (see properties of solid SO_3)		
Density, 38°C (100°F),	g/mL	1.84
	lb/gal	15.4
Viscosity, 38°C (100°F),	cP	1.3
Vapor Pressure, 38°C (100°F),		
	mmHg	517
	psia	10
	kPa	68.9
Heat of Vaporization (at bp),		
	cal/g	130.7
	Btu/lb	235.3
	kJ/kg	546.8
Specific Heat		
Liquid, 38°C (100°F),	cal/g-C	0.77
	Btu/lb-F	0.77
	kJ/kg-K	3.22
Vapor, 100°C (212°F),	cal/g-C	0.19
	Btu/lb-F	0.19
	kJ/kg-K	0.80
Critical Pressure,	atm	81.0
Critical Temperature,	°C	217.8
	°F	424.0

Table 2
Properties of Solid Sulfur Trioxide*

Description		Gamma Form Ice-like	Beta Form Asbestos-like	Alpha Form Asbestos-like
Equilibrium Melting Point				
°C		16.8	32.5	62.3
°F		62.2	90.5	144.1
Heat of Fusion				
kcal/mol		1.8	2.9	6.2
kJ/mol		7.5	12.1	25.9
Heat of Sublimation				
kcal/mol		11.9	13.0	16.3
kJ/mol		49.8	54.4	68.2
Vapor Pressure				
0°C (32°F),	mmHg	45	32	5.8
	kPa	6.0	4.3	0.77
25°C (77°F),	mmHg	433	344	73
	kPa	57.7	45.9	9.7
50°C (122°F),	mmHg	950	950	650
	kPa	127	127	86.7
75°C (167°F),	mmHg	3,000	3,000	3,000
	kPa	400	400	400

* In the solid state, sulfur trioxide can exist in three forms, each having different physical properties. At low temperatures, the polymerization to the higher melting beta and alpha forms is catalyzed by moisture. Care should be exercised to keep this moisture content below 0.3%, expressed as H_2SO_4.

Table 3
Oleum

Strength	Equivalent H_2SO_4	Sp. Gr. 15.6°C (60°F)	Density 15.6°C (60°F) lb/gal	Approximate Freezing Point °C	Approximate Freezing Point °F	Approximate Boiling Point °C	Approximate Boiling Point °F	Viscosity cP (mPa·s) 20°C (68°F)	Sp. Heat cal/g·°C (Btu/lb·°F)
20% Oleum	104.50	1.915	16.0	5	23	142	288	39	0.32
25% Oleum	105.62	1.934	16.1	9	48	131	268	42	0.32
30% Oleum	106.75	1.952	16.3	19	66	121	250	48	0.32
65% Oleum	114.63	1.992	16.6	2	36	58	137	55	0.41

"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."

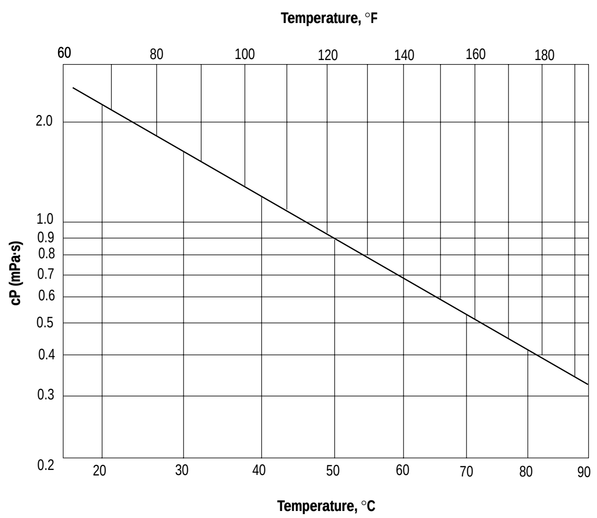


FIGURE 3: Viscosity of Sulfur Trioxide, Liquid

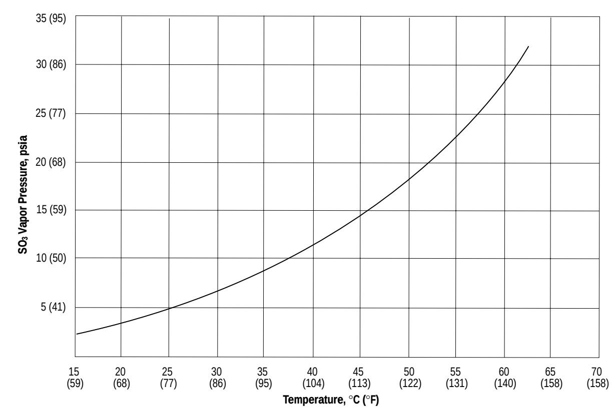
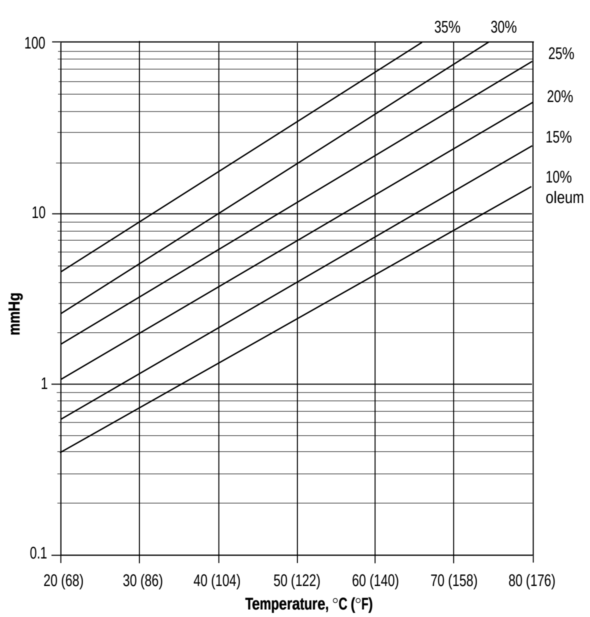
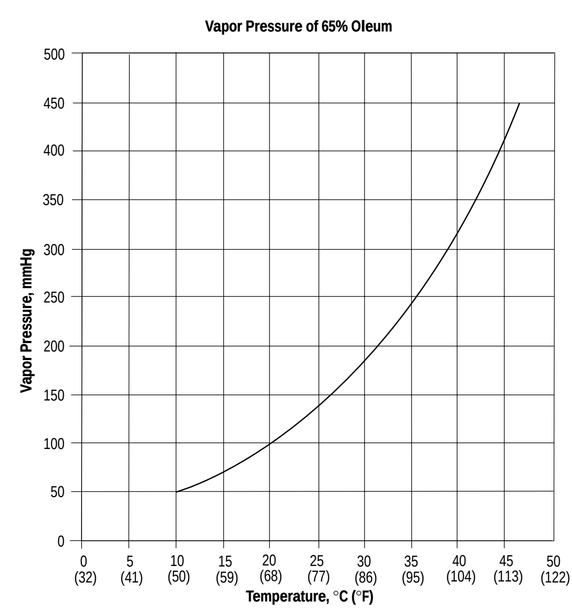


FIGURE 4A: Vapor Pressure of Sulfur Trioxide



Ref: J.C.D. Brand and A.J. Rutherford, *J. Chem. Soc.*, **10**, 3916 (1952).

FIGURE 4B: Vapor Pressure of Oleums



Ref: F.D. Miles, H. Niblock and G.L. Wilson, *Trans. Faraday Soc.*, **36**, (1940) pp. 345–356.

FIGURE 4C: Vapor Pressure of Oleums

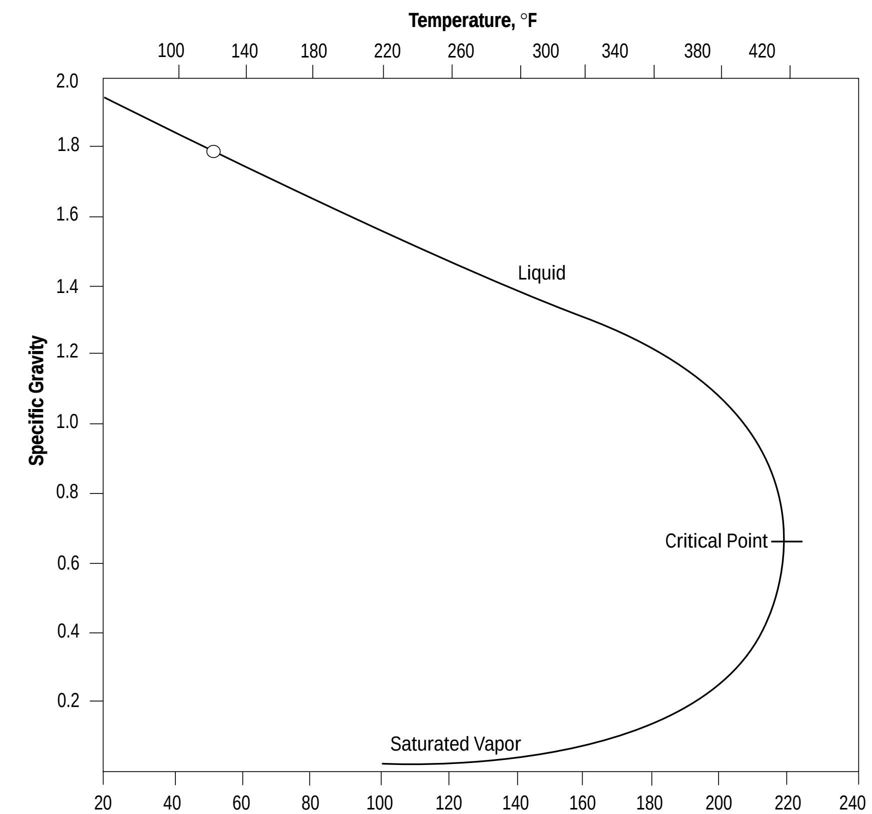


FIGURE 5: Specific Gravity of Sulfur Trioxide

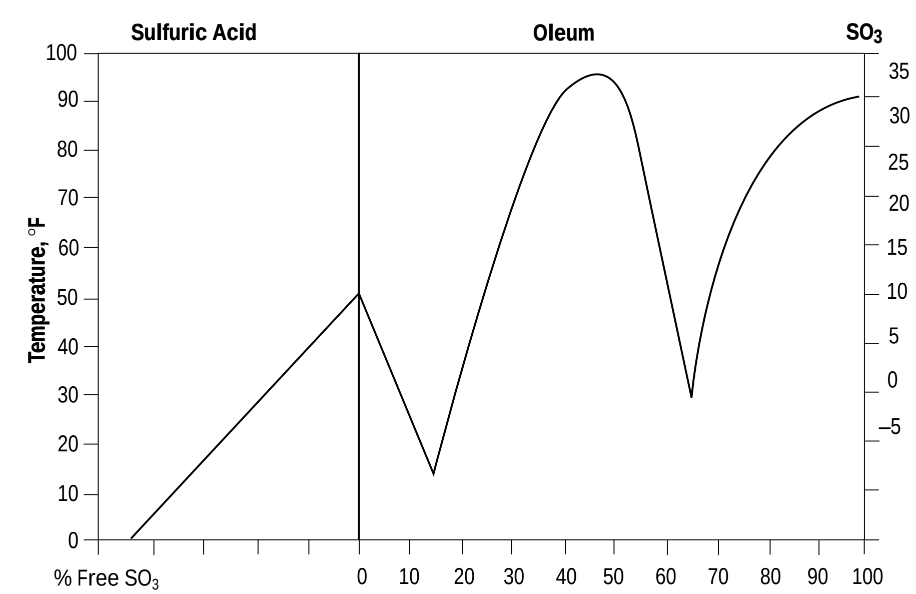


FIGURE 6: Freezing Point Curve, Oleum

SPECIAL PRODUCT TRAINING

Fuming Acids Safety Symposiums

Veolia North America sponsors periodic Fuming Acids Safety Symposiums, which 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 Acids 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 AND FIRST AID

All personnel working with sulfur trioxide (SO_3) and oleum products 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 SO_3 and oleums should be reviewed prior to using this product.

Health Hazards

Sulfur trioxide and oleums are strongly acidic materials that react rapidly with water to form sulfuric acid, evolving considerable heat. It can rapidly dehydrate body tissues and cause severe chemical and thermal burns.

Human health effects of skin exposure to liquid sulfur trioxide and oleums include skin burns, ulcerations, corrosion with pain, or cracking and peeling of skin. Skin exposure to the acid mists may result in severe skin irritation, discomfort or a rash. Eye exposure may result in corneal or conjunctiva ulceration, redness or swelling. Repeated or prolonged exposure to the acid mists may cause eye irritation with discomfort, tearing or blurring of vision. Ingestion of the liquid may cause gastrointestinal tract damage, including severe burns to the mucosal membranes of the mouth and esophagus. Overexposure to mists by inhalation may cause upper respiratory irritation or erosion of dental enamel. Higher inhalation exposures or repeated exposures may lead to temporary lung irritation with cough, discomfort, difficulty in breathing, or shortness of breath. Sometimes modest initial symptoms are followed hours later by severe shortness of breath or rapid loss of consciousness with serious lung tissue damage and pneumonitis, requiring prompt medical attention.

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 and does not apply to sulfur trioxide or oleums. The basis for the IARC classification rests on several epidemiological studies, which have several deficiencies. These studies did not account for exposure to other substances some known to be animal or potential human carcinogens and social influences (smoking or alcohol consumption). In addition, studies included a small number of subjects. Based on the overall weight of evidence from all human and chronic animal studies, no definitive causal relationship between sulfur trioxide/oleum mists exposure and respiratory tract cancer has been shown.

The U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) has not set exposure limits specifically for sulfur trioxide and/or oleums, but they have set limits for sulfuric acid mist exposure. 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 (TWA) of 1 mg/m3 (29 CFR 1910.1000 Air Contaminants). The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a TWA exposure limit of 0.2 mg/m3 as a Thoracic fraction. Veolia's Acceptable Exposure Limit (AEL) is a TWA limit of 0.5 mg/m3 for 8 to 12 hour work shifts. For 15 minutes of exposure, the AEL is a TWA limit of 1.5 mg/m3. Note: where government-imposed occupational exposure limits are lower than the AEL, such limits shall take precedence.

Safety Precautions

Use of appropriate personal protective equipment is essential to safely handle sulfur trioxide and oleum. Do not get sulfur trioxide or oleums in eyes, on skin or on clothing. Do not breathe vapors or mists and use with adequate ventilation. Wash hands thoroughly after handling. Remove contaminated clothing or shoes immediately. Wash clothing before reuse.

Sulfur trioxide and oleums can react violently with water or aqueous solutions. Do not mix water and/or aqueous solutions with sulfur trioxide or oleums in an uncontrolled manner. Only experienced personnel with proper training should add water and aqueous solutions to SO_3/oleums.

"All personnel working with sulfur trioxide and oleum products should be thoroughly familiar with the health and safety precautions."

Personnel Protective Equipment (PPE)

Personnel protective equipment should be used to protect workers whenever contact with 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 personal protective equipment are used when working with sulfuric acid:

- 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 SO_3/oleum 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 sulfur trioxide/oleum 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 SO_3/oleum 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 sulfur trioxide and oleum. 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 required 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 splash goggles and chemical resistant gloves. With Level D clothing, workers may enter a SO_3/oleum area, read gauges or visually inspect equipment.

CLASS C

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

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

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

CLASS B

To provide protection for a high-risk exposure to sulfuric acid, the following Class B PPE is required:

- Head Protection: splash hood and hard hat (limit duration of tasks to avoid oxygen deficiency in hood)
- Eye Protection: chemical splash goggles
- Respiratory: not required for non-fuming sulfuric acid
- Hand Protection: acid-resistant gauntlet length gloves with sleeves over gloves
- Body Protection: acid suit, 1 piece or 2 piece (fabric must pass ASTM testing for SO_3 or oleum)
- Foot Protection: acid-resistant boots with pant legs over boots

With Class B clothing, personnel can make line breaks into a SO_3/oleum system, sample or connect/disconnect hoses from tank cars, tank trucks or portable tanks.

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: resistant, fully-encapsulated suit (Fabric must pass a 45 min breakthrough ASTM F739 chemical permeation test for SO_3 or oleum)
- Foot Protection: acid-resistant boots with pant legs over 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 SO_3/oleum fume (sulfuric acid mist) 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 SO_3/oleum or step into puddles of liquid SO_3/oleum.

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 SO_3/oleum contact with any part of the body. For Level A and B activities, most SO_3/oleum handling sites require that the personnel wash under a safety shower before removing the acid-suits.

Site Facilities

The following safety equipment should be easily accessible in all areas where SO_3/oleum 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.

Speed is of utmost importance when removing exposed personnel from a contaminated area and removing SO_3/oleum/sulfuric acid from the skin and eyes. First aid must be started immediately (within seconds) in all cases of contact with SO_3/oleum/sulfuric acid in any form. All workers and supervisors that could be potentially exposed should be trained in first aid care for SO_3/oleum/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 sulfuric acids 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 SO_3/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 SO_3/oleum 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

HANDLING PRECAUTIONS

Spill Mitigation

All sites handling SO_3/oleum must have equipment and trained personnel available to render spills/leaks non-fuming, neutralize the spill, and 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 sulfuric acid is 1000 pounds (as 100% sulfuric acid) and the reportable quantity for sulfur trioxide is 100 pounds (as 100% sulfur trioxide).

Diluted sulfuric 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 cleanup. 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 application mitigation

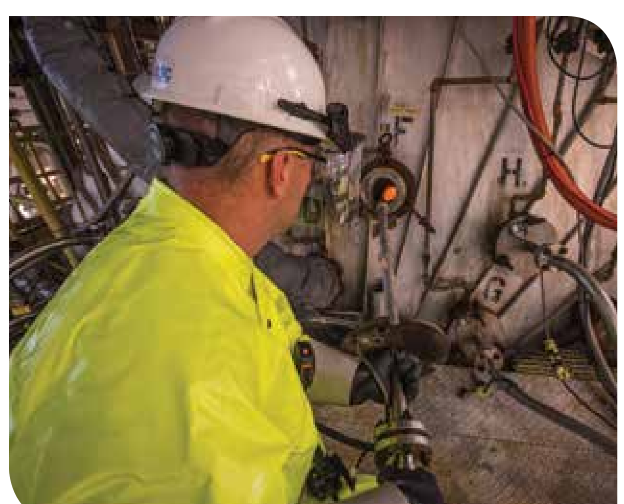
Other techniques that have been used with limited success include freezing the SO_3/oleum with CO_2 fire extinguishers or dry ice, covering the spill with white mineral oil (only successful for oleums <30%), or covering the spill with a fluorocarbon oil/glass bead mixture.

WATER FOG MITIGATION
Water fog is only marginally effective in reducing the fume cloud when sprayed into the cloud. It is a recommended way to cautiously add water to a liquid SO_3 or oleum spill to convert it to non-fuming sulfuric acid solution. The fog should be sprayed about 10 feet downwind of the leak/spill from the upwind side. The fog spray pattern should be verified before spraying on the spill. Streams of water must be avoided because of the violent reaction between SO_3/oleum and water.

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

Water fog mitigation causes a rapid temperature increase which results in a temporary increase in fume evolution. The vapor cloud drifts downwind and continue to heat up as it reacts with moisture in the air. The heat effect causes the cloud to rise and look larger. When the SO_3/oleum is completely reacted with water, the fuming subsides until there are only wisps of vapors, mostly steam, coming from the acidic solution.

FOAM MITIGATION
Foam mitigation is intended primarily for liquid spills and uses commercially available foams to blanket the fumes. It also provides a controlled way to introduce water into the SO_3/oleum to convert it to non-fuming.



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 SO_3/oleum – 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 suppresses fuming by sealing the SO_3/oleum from the moisture in the air. The foam blanket will eventually char and degrade, making it necessary to periodically reapply the foam.

Once the fuming has been reduced, water fog can be gently applied through the foam to react with the remaining SO_3/oleum to convert it to non-fuming.

To successfully apply the foam, follow the foam manufacturer's recommendations - 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.

Hazardous Chemical Reactions

Water or caustic solutions should never be directly added to SO_3/oleums in an uncontrolled fashion, or by untrained personnel, because of the potential for a violent reaction and subsequent spattering. When diluting, SO_3/oleum may be added to strong sulfuric acid while mixing and cooling to remove the heat of dilution.

Sulfur trioxide and oleum are very reactive aids that react with many compounds. Most of these reactions are well known and have been employed safely for years.

Sulfur trioxide and oleum are strong oxidizing agents that react with organic and inorganic reducing materials while rapidly generating heat. SO_3/oleum are powerful dehydrating agents and readily char many organic substances including human tissue. On contact with combustible materials (such as wood shavings, sawdust, cardboard) the heat produced by dehydration may be sufficient to cause a fire.

In addition, when heated, sulfuric acid decomposes to sulfur dioxide and water.

Sulfur trioxide and oleum also react with carbonates to generate carbon dioxide gas. They also react with cyanides and sulfides to form poisonous hydrogen cyanide gas and hydrogen sulfide gas, respectively. Thus, there is not only the danger of violent eruption that could cause acid burns, but also the possibility of generating poisonous or explosive atmospheres which could present additional hazards. For these reasons, SO_3/oleum should be used strictly in accordance with directions prepared by qualified technical personnel.

Many lubricants are attacked by SO_3/oleum. Use only silicone or fluorocarbon based lubricants.

Corrosion Hazards

SO_3/oleum attacks cast iron, brass, bronze and most other non-ferrous metals. Mild steel (carbon steel) and stainless steel are resistant to corrosion, and are recommended for storage systems and piping. Teflon® is the only known resistant plastic material. Rubber, neoprene, polyester, PVC, FRP and other elastomers are readily attacked and unsuitable for this service.

SO_3/oleum rapidly absorb moisture upon contact with the air to form weak sulfuric acid, which can cause severe corrosion to the surrounding equipment metal surfaces, such as tanks, pumps and/or pipelines. A by-product of the corrosive reaction is hydrogen gas, which is highly flammable.

Fire and Explosion Hazards

Sulfur trioxide and oleum are nonflammable. However, they are highly reactive and capable of igniting finely divided combustible materials on contact. They are 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. In addition, sulfur trioxide or oleum may cause spontaneous combustion in contact with organic materials, such as sawdust and oily rags.

When diluted to non-fuming concentrations, the acid attacks many metals to release flammable hydrogen gas. Therefore, no open flames, open lights, matches or other ignition sources should be allowed in or around acid containers or lines.

"In case of fire, evacuate personnel to safe areas. Use extinguishing methods that are appropriate to local circumstances and the environment. "

Fire Fighting

In case of fire, evacuate personnel to safe areas. Use extinguishing methods that are appropriate to local circumstances and the environment. Dry chemical or carbon dioxide extinguishing methods are viable options. 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 to avoid evolution of heat and violent spattering. Cool the acid storage tank with water if exposed to fire, but do not get water in the tank.

Fine mist water fog or mechanical foam can also be used to keep the tank shell cool if exposed to fire. Do not allow water or water-containing foam to contact sulfuric acid in a confined area or tank, because it might cause violent eruptions or pressure increases that could result in structural damage to the confined space or tank.

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.

Design factors to consider include:

1. A tight system that minimizes plant and community exposure potential.
2. Location of storage tank and unloading spot(s) relative to other chemicals and working areas. Plants handling SO_3/oleum should be preferably located away from densely populated areas or major highways.
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 the event of fire, explosion or release of SO_3/oleum fumes.
5. 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.
6. Means of detecting SO_3/oleum leaks while they are still small through the use of video cameras and other remote sensors (smoke detectors, opacity meters, chemical detectors).
7. Suitable scrubbing facilities for venting/evacuating unloading, storage and handling equipment.
8. Provisions should be made to allow de-inventory of SO_3/oleum equipment/storage to other vessels in the event of leaks. This may be accomplished by utilizing empty SO_3/oleum tank cars or trucks.
9. The number of nozzles on the storage tank should be minimized. Bottom nozzles should be avoided.
10. Appropriate, remotely activated automatic valves should be installed to allow isolation of equipment in the event of a leak.
11. Avoid using small diameter piping (less than 1 inch) except for fit-up to instrumentation, because small diameter piping is not mechanically very strong. A small line can break if hit by another object.
12. Adequate lighting and appropriate alarms and interlocks for the system. Redundant alarms should be provided for critical alarms, interlocks and tank level measurements.
13. Piping systems should be sloped and provisions made for clearing the lines. Screwed fitting should not be used except for fit-up to instrumentation. Build to ASME piping standards B31.3 (normal fluid service).
14. Means of isolating the tank car or tank truck with remotely actuated block valves in the event of a hose failure.
15. 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.

Operating and maintenance factors to consider include:

1. Inspection and thickness testing of equipment and piping on a periodic basis using API-570 as the reference guide. Up-to-date isometric piping drawings, with testing points, should be used to correlate test data to equipment in the plant. Particular attention should be paid to high-temperature and high-velocity areas.
2. Internal inspections on SO_3/oleum storage and process vessels should be made periodically. The inspections should be done every six years. 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. Special care should be taken to look for corrosion under insulation, if the tank is insulated. External ultrasonic thickness testing should be done every three years at a minimum. Follow the guidance in NACE SP 029406 for inspection protocol.
3. Regular inspection and periodic replacement of unloading hoses (at least annually).
4. Clearly written unloading, storage and handling instructions, including checklists, to ensure that correct procedures are followed each time to avoid incidents.
5. Materials of construction verification for critical equipment (valves, gaskets, bolts, etc.) whose failure could cause a major release.
6. Regular inspection and/or testing of alarms, interlocks, pressure relief valves and rupture disks.
7. An administrative system that ensures equipment inspections are completed and results are documented (Mechanical Integrity Program).
8. Conducting periodic process hazards reviews, which closely examine procedures, equipment layout, past incidents, etc., and make changes to improve equipment reliability and personnel safety.
9. Labeling of lines and equipment that contain SO_3/oleum.

10. Thorough training and regular retraining of personnel in the important aspects of handling SO_3/oleum. These include:
    - Use of personnel protective equipment (PPE)
    - Hazards resulting from improper handling of SO_3/oleum
    - Prevention and detection of leaks
    - Maintenance procedures, including equipment decontamination
    - Emergency procedures
    - Cleanup procedures
    - First aid and medical treatment procedures
11. Performing a consequence analysis of credible and worst-case incident scenarios, including modeling 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.

Transportation Emergencies

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

(800) 424-9300

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

(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, etc. 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.

WASTE DISPOSAL

Sulfur trioxide and oleums are regulated as RCRA hazardous wastes. Disposal of waste liquid streams containing sulfur trioxide, oleums or sulfuric acids must be accomplished within the regulations and guidelines applicable at the specific location under consideration. Users should check with the appropriate local, state and federal authorities to stay up-to-date on rules in force and changes being considered for the future.

Small quantities of waste acid, sulfur trioxide or oleum may be added slowly to a larger volume of agitated soda-ash solution or slaked-lime slurry. The neutralized solution may be added to excess running water prior to final disposal, but be sure to follow local regulations for disposal.

Larger quantities of acid, sulfur trioxide or oleum 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. Acid, sulfur trioxide and oleum 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 product, 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, sulfur trioxide or oleum 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, sulfur trioxide or oleum 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.

SHIPPING CONTAINERS

Veolia ships sulfur trioxide and oleum in portable tanks, tank trucks, rail cars and barges (20% oleum only). Labeling/placarding on the portable tanks, tank trucks and rail cars of sulfur trioxide and oleums (>30%) bear the DOT CORROSIVE and INHALATION HAZARD placards. Oleum (<30%) shipments must have the DOT Class 8 CORROSIVE placard. All shipments must have the appropriate UN number (SO_3 – 1829, Oleums – 1831). Oleum barges follow appropriate U.S. Coast Guard requirements.

Due to changing governmental regulations, such as those of the Department of Transportation (DOT), U.S. Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA), Food and Drug Administration (FDA) and U.S. Coast Guard, references herein may be superseded. Users should consult and follow all applicable local, state and federal regulations as they pertain to sulfur trioxide and oleums.

Consult with Veolia's Customer Service Center (800) 441-9362 for additional information, or if you have special requests.

"Users should consult and follow all applicable local, state and federal regulations as they pertain to sulfur trioxide and oleums."

Portable Tank

The portable tanks used for sulfur trioxide and oleum service consists of a stainless steel cylindrical tank equipped with electrical tracing and an insulation jacket. The portable tanks are shipped in enclosed trailers equipped with a heating source. The box trailer delivering the portable tanks is heated while the trailer is in transit. The design criteria for the portable tanks is:

- **Specification:** DOT 51
- **Tank Capacity:** 220 gallons
- **Dimensions:** 48" wide by 42" deep by 77" high
- **Tare weight:** 2,530 lbs
- **Gross weight:** 5,000 lbs
- **Shell:** 3/8" 316L S/S, 125psig MAWP, 188 psig test
- **Rupture Disk/Pressure Relief Valve Assembly:** 136/125 psig
- **Heating system:** Chromolox@ electrical temperature control unit, 20 A @ 120 V

Tank Truck

The tank trucks used for sulfur trioxide and oleum all meet DOT HM-181 regulations. The trailers are dedicated to the fuming sulfuric acid service. The trailers are equipped with a glycol heating system and are insulated to maintain the temperatures above the product's freezing point. The SO_3 trailers are also equipped with canned, submerged pumps for unloading. The oleum trailers can also be supplied with these pumps. The design criteria for the tank trailers is:

- **Specification:** DOT-312
- **Capacity:** 3,000 gallons
- **Tank Shell:** 3/8" 316L S/S
- **Tank Head:** 3/8" 316 S/S
- **Net Weight:** Approx. 38,500 lbs
- **Design Pressure:** 100 psig MAWP, 154 psig test pressure
- **Rupture Disk/Relief Valve Assembly:** 120/100 psig
- **Pump:** 440V, 5 hp

Rail Car

The rail cars are designed and built to safely transport SO_3 and oleums. The rail cars are equipped with external heating panels and are insulated. An insulation jacket with electrical tracing (120V) for the fittings in the rail car's dome area is standard on all SO_3 rail cars. The SO_3 and oleum (>30%) rail cars meet the following design criteria:

- **Specifications:** DOT105A300W or DOT105J500W
- **Shell:** ASTM A-516-7- normalized carbon steel
- **Shell Thickness:** 5/8"- 11/16"
- **Design Pressure:** 300 lbs. and 500 lbs
- **Rupture Disk/Relief Valve Assembly:** 225 psig/213 psig
- **Eduction Pipe:** 2" Schedule 80
- **Valves and Fittings:** AAR approved, 2" Jamesbury S/S valves and trim

Barge

The barges are designed and built to safely transport <30% oleums. The barges are equipped with a double-hull to minimize the risk of breaching the containment. They are also equipped with pumps to enable closed-loop pump-unloading. The oleum barges meet the following design criteria:

- Annual "Certificate of Inspection" by the U.S. Coast Guard per 46 CFR 151
- Double-hulled, ASTM A-516-7- normalized steel
- **Shell Thickness:** > 0.5"
- **Pressure Relief:** 3 psig
- **Vacuum:** 1 psig
- **Eduction Pipe:** 6" Schedule 80 carbon steel
- **Valves and Fittings:** Coast Guard Approved, 6" 316 stainless steel valve bodies and trim

UNLOADING AND TRANSFER

For safety reasons, pump unloading is preferred over pressure unloading. If a leak occurs in the hose or associated unloading piping during the unloading process, the leak can be stopped promptly by shutting down the pump. Pump unloading also avoids the large volume of SO_3 laden air/nitrogen that must be vented from the tank truck or rail car at the end of the unloading operation, minimizing the size if the scrubber required. It may be necessary to supply a nominal amount of air/nitrogen for pump priming (external pump) or to avoid creating a vacuum in the transportation vehicle. In this case, the pressure should be the minimum required for effective pump operation. The air/nitrogen supply system must be equipped with the appropriate valving and automatic controls for emergency shutoff of the air/nitrogen and depressurization

All Veolia SO_3 tank trucks are equipped with an onboard-submerged pump so that the trailer contents can be unloaded into the customer's tank with the vapors vented back to the trailer in a closed-loop system. Oleum can also be delivered using similar onboard pumps.

Dry compressed air or nitrogen may be used to unload rail cars, since they are not equipped with onboard pumps. The pressure must not exceed 30 psig. The air/nitrogen must be dry (-40 F dew point). Safeguards must be included to ensure that this pressure cannot be exceeded. The pressure supply valves should be remotely located to protect the operator from potential leaks at fittings when the rail car is pressurized. Remote shut-off and depressurizing valves should be installed on the system for emergency shutdown of the system. Provisions must also be made to scrub the large volume of pressurizing gas that results from blowing the tank empty.

Portable Tank

Veolia ships SO_3 both stabilized and unstabilized and oleum in DOT 51 returnable portable tanks. All tanks are constructed under ASME Code. The tanks contain approximately 2,500 net pounds and have a gross weight of 5,000 pounds. Portable tanks are electrically traced, insulated and jacketed to maintain tank temperatures loaded or empty. The tanks are equipped with 1" – 150 lb. flanged connections on both the liquid and vent/vapor connection. Portable tanks have a design pressure of 125 psig and are equipped with a combination rupture disk/relief valve assembly set at 136 and 125 psig respectively.

SHIPPING POLICY
Portable tanks are shipped in Veolia freight trailers that have been specifically designed and equipped to transport and maintain portable tank temperatures.

Only drivers who have been trained and are equipped to safely handle these products in Veolia dedicated trucks make SO_3 and oleum deliveries. These drivers ensure the safe transportation, and monitor the portable tank temperatures (full and empty) during transit.

Use of dedicated trucks and trained personnel provides proper controls and minimizes the potential exposure to the customer and the general public to an incident.

RESTRICTED DELIVERIES
Due to limitations on delivery, equipment and driver availability, pre-scheduling of delivery dates is necessary. The following information is a guide when ordering SO_3 and oleum portable tanks:

- Shipments can normally be delivered on the date requested. Customers will be notified when the order is placed with the Veolia Customer Service Center (CSC), (800) 441-9362 if there is a conflict in scheduling.
- Whenever possible less-than-truckload (LTL) orders are consolidated with other orders to make a full shipment (milk-run).
- Veolia can make emergency LTL shipments if the equipment is available and the customer agrees to pay for the exclusive use of the truck. The Veolia CSC representative receiving the order can supply the approximate cost of such a delivery.
- When a portable tank arrives at a customer location, customers may elect to unload the tank contents into the receiving vessel while the Veolia truck stands-by, and then ship the empty tank back on the same truck. Prior notification must be given by the customer for this to ensure adequate unloading time is allotted at the customer site.

REQUIREMENTS OF PORTABLE TANK CUSTOMER
- A loading dock or a suitable level surface with forklift truck access. If a loading dock is not accessible, the driver will deliver the portable tank to the rear door of the trailer for unloading.
- A forklift truck with the capability to safely handle 5,000 lbs.
- A hot room maintained at 100 F, or a dedicated 120 VAC, 60 Hz, 20 A electrical service equipped with suitable electrical cord, terminating with a Hubbell Twist-Lock plug (female) 125V, 20A, part no. 231-A.

CUSTOMER RECEIPT OF PORTABLE TANK
- Check container for indications of damage or leakage.
- If not being stored in a hot room, plug tank into power source to maintain portable tank temperature.

PRESSURE UNLOADING OF PORTABLE TANK
Wear proper personal protective equipment. Complete body protection (acid suit, acid-resistant gloves and boots, acid hood) should be worn while connecting and disconnecting the unloading hose. Personnel within 25 feet of the portable tank and unloading hose (while they are pressurized) should wear the acid suit, acid-resistant gloves and boots and acid hood. Steps to unload the portable tank are:

1. Verify the level in the receiving vessel to ensure it can hold the amount of SO_3 or oleum to be transferred.
2. Remove outer manhole cover, open hinged inner cover and remove insulating cap to expose the tank fittings.
3. Open tank pressure gauge isolation valve and read tank pressure. Pressure should be 5 psig or less.
4. Verify vapor and liquid valves are closed.
5. Remove blind flange from vapor valve and attach the Teflon®-lined "transfer medium" hose using an approved Teflon® gasket.
6. Remove the blind flange from the liquid valve and attach Teflon®-lined liquid unloading hose using an approved Teflon® gasket.
7. Cautiously open liquid and vapor valves on portable tank.
8. Open all valves to receiving vessel.
9. Start the "transfer medium" (dry air or nitrogen). Maintain minimum pressure needed to transfer SO_3 or oleum (not to exceed 25 psig). Monitor portable tank pressure during the transfer procedure.
10. When the portable tank is empty, as indicated by a drop in portable tank pressure and the sound of air rushing through the unloading line, shut off the "transfer medium" pressure, and continue to let the pressure blow through the tank briefly to clear the unloading line.
11. Close the portable tank liquid and vapor valves, and all valves to the receiving vessel.
12. Verify that the pressure has been relieved on both the unloading hose and the "transfer medium" hose.
13. Disconnect both hoses and replace the blind flanges and gaskets on the portable tank valves.
14. Close pressure gauge isolation valve.
15. Wash down any spillage/drippage on the portable tank with large quantities of water. Replace the insulating cap, close inner cover and secure outer manhole cover.

RELEASE OF EMPTY PORTABLE TANK
Portable tank temperatures must still be maintained even though the tank has been unloaded. Disconnect power cable and remove from hot room only when unit is ready to be picked up by Veolia. An empty tank must not be internally washed out with water or rinsed with sulfuric acid without specific instructions from Veolia. The tank will still contain small amounts of SO_3/oleum residue and vapors, which will react violently with water. If sulfuric acid is added, the quality of the next shipment using that portable tank may be affected. Do not remove, reverse or alter the placards. According to DOT regulation, portable tanks that last contained a hazardous material, and have not been cleaned or purged, must be labeled, placarded and certified as if they were full.

SO_3 Tank Truck

Veolia ships both stabilized and unstabilized liquid SO_3 in fully insulated and jacketed, temperature-controlled tank trucks (see Figure 7) designed to maintain the trailer temperature between 95-105 F, whether full or empty. The trucks have a nominal capacity of 3000 gallons. The amount of SO_3 shipped depends on highway weight limits. The average weight shipped will range from 36,000 to 38,000 net pounds. All Veolia SO_3 trailers are similar in design and construction. Trailers have been engineered and fabricated for safe transportation as well as environmental protection. Trailers are constructed to DOT MC-312 and ASME Code requirements, with 3/8" thick stainless steel shells and heads rated at 100 psig design pressure. All containing welds have been 100% x-rayed. An internally mounted pump is used for unloading, and eliminates the need for bottom outlets or flanges. Liquid and vapor connections used for unloading are located on the top rear of the trailer, inside a domed area protected by a rolling cover. The vapor connection enables pressure to equalize by returning vapors back to the trailer as the storage tank is filled, rather than venting the vapors to a scrubber, then the atmosphere. Drivers who have received specialized training for SO_3, and are familiar with the safe handling of liquid SO_3 operate all Veolia SO_3 trucks. Drivers receive annual refresher training and recertification.

TO RECEIVE AN SO_3 TRAILER, THE CUSTOMER NEEDS:

1. An all-weather serviceable road to the unloading spot. Railroad sidings having open ties and full-height rails are not suitable for tank truck movements.
2. Vertical clearances of at least 13 feet.
3. An open area at the unloading spot sufficient to permit normal maneuvering of the tractor and trailer.
4. A tractor-trailer spotting area with a surface capable of supporting 20,000 pounds per axle, or 79,000 pounds maximum gross weight.
5. Securely anchored, free-draining, overhead intake lines. The receiving couplings should be within 6 feet (1.8 m) of the side of the rear end of the Veolia tank truck spotted in normal unloading position. The customers should provide their own transfer hoses, preferably set up in vertical manner for complete drainage. Hoses should be Teflon®-lined or equivalent. Call Veolia Technical Service for the latest hose recommendation.

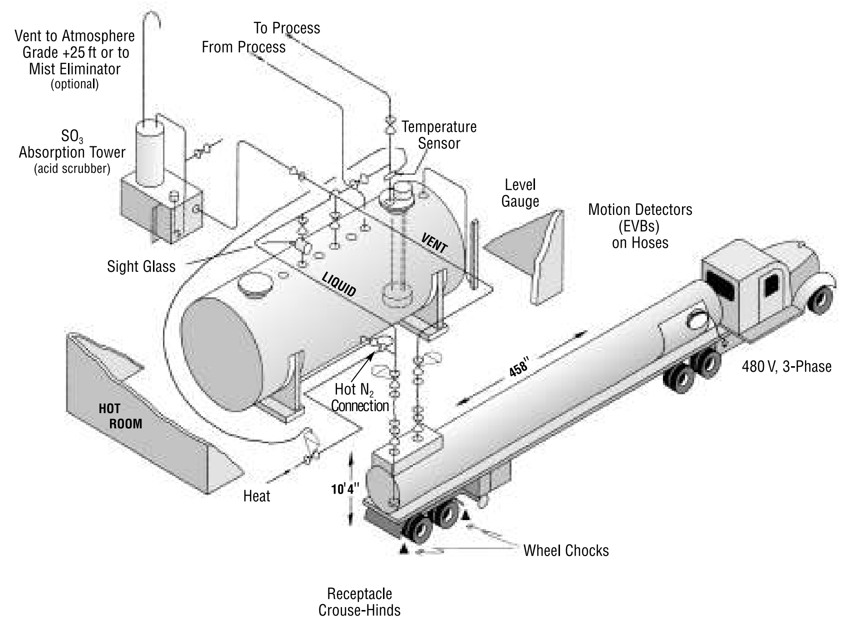


FIGURE 7: Sulfur Trioxide Unloading and Storage Tank Truck Delivery

A 440/480 VAC, 3 phases, 60-hertz power source for the trailer unloading pump. The customer's electrical connection is a Crouse Hinds (female) receptacle, P/N AR-342, rated for 30 amperes. As a safety concern, Veolia recommends providing a disconnect switch or contactor to allow the receptacle to be energized after the connection has been made. A remote shut-off for the power source is also highly recommended to aid emergency response. If the unloading is to be accomplished at night, the unloading spot must be well-lit.

DOT Cargo Tank Hazardous Material Regulations (Section 177.834) state that a cargo tank must be attended by a qualified person at all times when it is being unloaded. A person who attends the unloading must:

1. Be in attendance throughout the entire unloading process.
2. Be awake.
3. Have an unobstructed view of the cargo tank.
4. Be within 25 feet of the cargo tank.

If the attendant must leave during the unloading process, the transfer of liquid SO_3 must stop. The person in attendance may be a Veolia driver, an employee of the customer, or a combination of both.

SO_3 TANK TRUCK CONNECTION SUMMARY:

Liquid Unloading connection:
2" WECO Figure 400 Oil Field Union (Female)

Vapor Unloading connection:
2" WECO Figure 400 Oil Field Union (Female)

Transfer Hoses (Provided by customer):
2" Teflon®-lined, equipped with 2" WECO Figure 400 Oil Field Union (Male). Note: The Speed-Thread nut will be on the hose (Male) end.

Electrical Service:
440/480 VAC

- Power Cord Plug: Crouse Hinds APJ-3485
- Customer Receptacle: Crouse Hinds AR-342
- Power Cord Length (on truck): 75 feet

SO_3 TANK TRUCK PLACEMENT AND UNLOADING
Plant personnel should:

1. Be sure the storage tank has adequate capacity to receive the entire load.
2. Make certain the unloading hoses are labeled specifically for SO_3, with the liquid and vapor connections identified.
3. Ensure that all valves to and from the storage tank and unloading spot are open and line is clear.
4. Ensure that the storage tank vent line to the scrubber system and the trailer is open. The vent lines must be maintained above 95° F at all times to avoid freeze-up and possible blockage.

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

1. Safety shower and eyewash station.
2. Water hydrant or hose for wash down.
3. Spill mitigation (water spray, foam or dry chemical) equipment.

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.
3. Wear the proper personnel protective equipment for the safe unloading of SO_3.
4. Connect the trailer pump power cord to plant 440/480 VAC receptacle.

DISCONNECTING PLANT LINE
When the unloading is complete, the driver will stop the unloading pump and disconnect the power cord. After allowing sufficient time for the lines to drain (usually about 10 minutes) the customer will purge the lines with hot air or nitrogen, if the customer provides such a system. The customer will then close the unloading and vent line valves as the driver closes the valves on the trailer. The customer (with proper PPE) will disconnect the unloading and vent lines from the truck and cap the customer hoses. The customer will wash down any inadvertent drips before the tank truck. The driver will verify all fittings/connections are closed before the dome cover is secured.

Oleum Tank Truck

Oleum shipments are made in DOT MC-312 trailers, which are insulated and jacketed to avoid freezing, similar to the SO_3 trailers. Veolia trailers are equipped with external heat jackets if heat input is needed to prevent freezing. The oleum can be shipped either in trailers with the on-board pump, for closed-loop unloading, or without the pump for pressure-unloading.

OLEUM PUMP UNLOADING
Review the previous section on SO_3 tank truck unloading. The requirements are the same. The advantages of pump unloading versus pressure unloading are: 1) a smaller scrubber is needed and 2) a leak during unloading can be stopped by just shutting down the pump.

OLEUM PRESSURE UNLOADING
Veolia oleum trailers are designed without a bottom outlet valve or connection. A discharge pipe located in the rear of the trailer extends into a sump, and is equipped with a three-way valve on top of the trailer. Either top unloading (platform required) or bumper unloading (ground-level) can be safely accomplished. The position and type of fittings for the oleum receiving line must be reviewed with Veolia prior to the initial delivery.

The pressure can be supplied either by the truck's on-board air compressor, or by the customer. If supplied by the customer, dry air or nitrogen is preferred. The piping arrangement should include a pressure reducing station set at 28 psig (maximum); a pressure relief valve set 5 psig above the regulator setting; a pressure gauge; and a valve capable of quickly releasing the pressure. Provision should be made to automate the pressure release valve so it can be remotely activated in the event of an emergency.

"The oleum can be shipped either in trailers with the on-board pump, for closed-loop unloading, or without the pump for pressure-unloading."

SO_3 Tank Car

Veolia ships SO_3 in 8,000 gallon (60 ton) and 12,600 gallon (90 ton) tank cars. The tank cars are high-pressure design DOT105J300W and DOT105J500W cars, insulated and jacketed, with DOT-approved head shields and rollover protection.

SO_3 cars should not be stored in a frozen condition in order to avoid formation of the unmeltable polymer (alpha). Unload cars promptly upon receipt and monitor car shipments to minimize turnaround time.

No bottom outlet is allowed on SO_3 tank cars. The discharge pipe is located in the dome on the longitudinal centerline of the car and extends to a sump in the bottom of the car.

A typical tank car unloading station is shown in Figure 8. A typical dome valving arrangement is shown in Figure 9.

Deliveries during winter months may require low-pressure steam, and electrical service to warm the car contents before unloading. The SO_3 tank cars are equipped with:

- External steam coils for warming the car contents. The 2 in. standard pipe-thread inlet and outlet to the steam coils are under the middle section of the car.
- Electrical heat tracing to supply heat to lines and fittings at the top of the car during heat-up and unloading.
- Electrical standpipe heater (Chromolox tubular heating element 120V 575W) to enable warming of the unloading standpipe prior to unloading.
- Thermowell for measuring car temperatures during heat-up.

The customer should supply a dedicated electrical service (120V 15A) equipped with a suitable electrical cord of proper length, to connect to the electrical control box located on the exterior of the protective housing. The cord should terminate with a Hubbell Twist-Lock® plug (Female) 125 Volt, 20 A, part number 231-A. A remote means to de-energize the power source and a weather proof storage location for the cord are recommended.

To receive an SO_3 rail car, the unloading station requires an elevated transfer line, which permits free drainage of the line. The transfer line can be of 2 in. Schedule 80 steel pipe with suitable swing connections, or it can be a 2 in. hose lined with Teflon® fluorocarbon resin and covered with stainless steel braid or reinforced rubber (flexibility is necessary to accommodate changes in tank car elevation during unloading, but care must be taken to ensure the hose is not bent beyond the specified "minimum hose bending radius"). The lines should be designed so that they can accommodate the dome fittings regardless of which direction the car is spotted.

The tank car liquid discharge valve and the vent valve are both equipped with a 2 in. flange (150 lb.) The transfer line/hose and vent line/hose must be connected using a 2 in. flange and a Teflon® gasket. It is highly recommended to have automated shut-off valves located on both ends of the transfer lines/hoses. The automated valves should be able to be activated remotely ("panic button" or from DCS) or interlocked to close for:

1. High level in storage tank
2. Inadvertent rail car movement
3. Fume detection in process area
4. Other local safety considerations

See Figure 8.

When the tank car arrives on site, be sure to check its identification number and placarding versus the shipping papers to confirm you have the proper car.

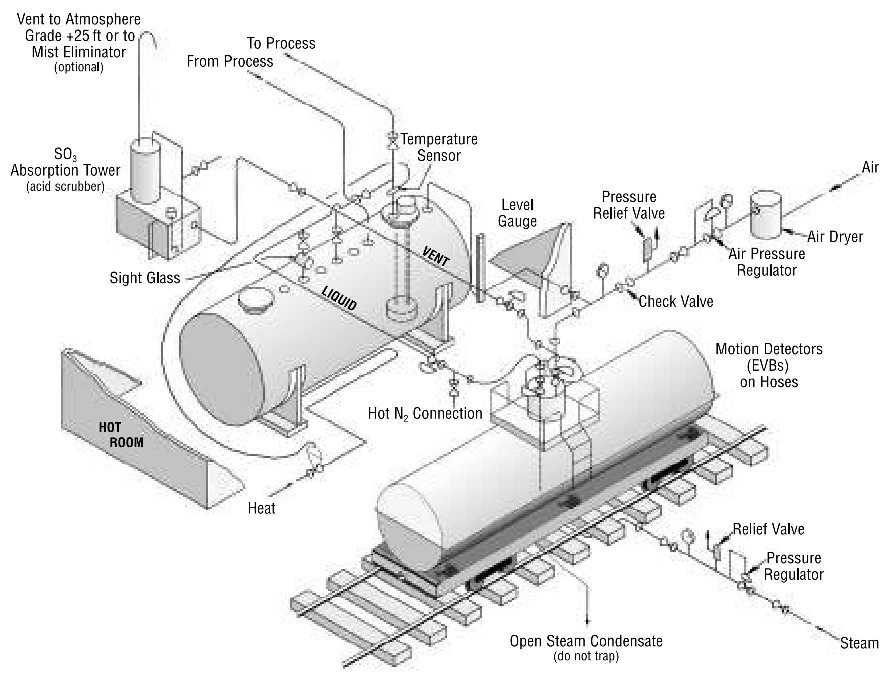


FIGURE 8: Sulfur Trioxide Unloading and Storage Tank Car Delivery Air Unloading

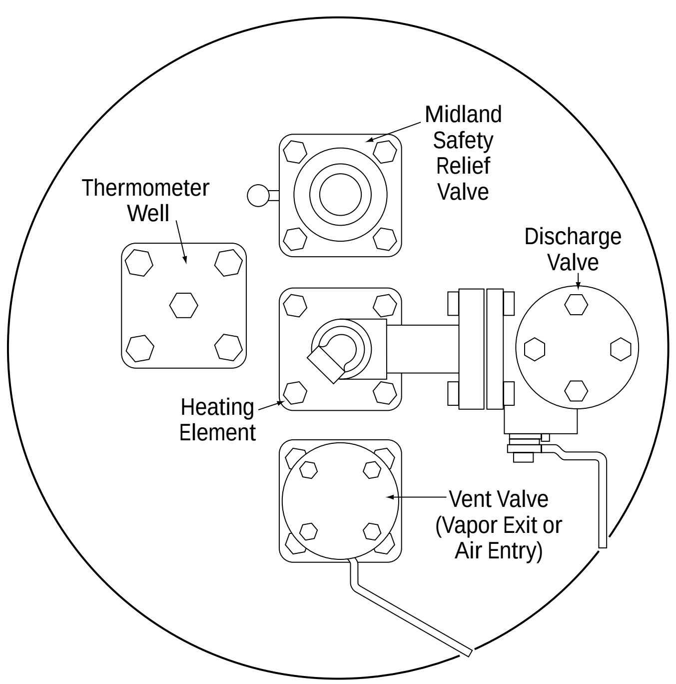


FIGURE 9: Typical SO_3 Dome Arrangement and Fittings

CAR PLACEMENT
Cars should be positioned on the center of the unloading dock's access platform, with hand brakes firmly set. Chocks should be set on both sides of the wheels to prevent accidental 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 the 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 Customer Service Center (1-800-441-9362). You will be advised on the proper procedure for accepting or rejecting the shipment.

PREPARATION FOR UNLOADING
Unloading facilities should be in good repair and all connections, hoses, gaskets, thermocouples, tools and safety equipment should be ready for use. Unloading personnel must be familiar with the properties and hazards of SO_3, the SO_3 rail car equipment and functions, the thawing procedures and the emergency response procedures.

Complete body protection (acid jacket and pants, chemical gloves and boots, chemical hood) should be worn at all times while loading/unloading an SO_3 car. Respiratory protection should be provided while connecting/disconnecting the transfer lines/hoses.

The vapor line must be connected to the tank car vapor valve before the liquid unloading line is connected. The tank car must be relieved of all internal pressure by venting the SO_3 vapors through a properly designed scrubber/demister system.

Connect the liquid unloading line/hose to the car's liquid discharge valve. Liquid and vapor lines, along with the tank car valves (including the pressure relief valve assembly) must be maintained above 35 C (95 F) with heat input.

Take the temperature profile of the tank car. The car temperature should be measured by inserting a calibrated thermocouple (0-50 C or 32-122 F range) into the thermowell. About an 86 in. length (218 cm) is required to reach the thermowell bottom. A 4-point thermocouple designed to measure temperatures at 4 locations enables remote readout of the car temperature during heat-up. The four locations preferable for temperature surveillance are:

- Bottom of car
- 2 feet off bottom
- Middle of car
- Vapor space above liquid level

All four temperature read-out points should be between 35-41 C (95-105 F) before unloading the car. If car temperatures are below this range, it will be necessary to warm the car prior to unloading.

WARMING/THAWING SO_3 CARS
If car temperatures are below the 35-41 C (95-105 F) range, plug electrical service into control box on dome of tank car. A 120V, 15A electrical service is needed. Turn the switch for the proper heat needed, which activates:

1. **Minimum heat** electrical tracing
2. **Maximum heat** electrical tracing
3. **Stand-pipe heater**

The minimum heat electrical tracing and the stand-pipe heater should be in use during the entire heat-up process. The maximum electrical tracing is required for the first four hours only. After the maximum tracing has been on for four hours, shut it off.

Check for standpipe blockage by applying air pressure (25-30 psi) at 30 minutes intervals. In cold weather the standpipe may require up to 8 hours at 35-41 C (95-105 F) to thaw completely.

Oleum Rail Car

Veolia ships oleum in 8,000 gallon (60 ton) and 12,600 gallon (90 ton) tank cars. The tank cars are high-pressure design DOT105J300W, DOT105J400W, DOT105J500W and 112S500W cars. The "J" cars are insulated and jacketed, with DOT-approved head shields and rollover protection. The "S" cars are un-insulated with DOT-approved head shields and rollover protection.

Unload cars promptly upon receipt and monitor car shipments to minimize turnaround time.

No bottom outlet is allowed on oleum tank cars. The discharge pipe is located in the dome on the longitudinal centerline of the car and extends to a sump in the bottom of the car.

A typical tank car unloading station is shown in Figure 8. A typical dome valving arrangement is shown in Figure 9.

Deliveries during winter months may require low pressure steam, and electrical service to warm the car contents before unloading. The oleum tank cars are equipped with:

- External steam coils for warming the car contents. The 2 in. standard pipe-thread inlet and outlet to the steam coils are under the middle section of the car.
- Thermowell for measuring car temperatures during heat-up.

To receive an oleum rail car, the unloading station requires an elevated transfer line, which permits free drainage of the line. The transfer line can be of 2 in. Schedule 80 steel pipe with suitable swing connections, or it can be a 2 in. hose lined with Teflon® fluorocarbon resin and covered with stainless steel braid or reinforced rubber (flexibility is necessary to accommodate changes in tank car elevation during unloading, but care must be taken to ensure the hose is not bent beyond the specified "minimum hose bending radius"). The lines should be designed so that they can accommodate the dome fittings regardless of which direction the car is spotted.

If car contents are to be warmed or thawed, connect low-pressure steam (5-10 psig, regulated) to external steam coil inlet. Do not install valve or steam trap on the steam coil outlet. Steam should be applied so that the condensate runs out of the coil outlet at 90-105 F. If live steam is emitted from the coil outlet, reduce steam supply to the coils. Warning: Rapid application of steam may cause SO_3 vaporization at the coil surfaces and internal pressure may increase rapidly, overloading the scrubber system.

The internal temperature of the SO_3 in the rail car should be monitored as the car is heated. This can be accomplished using a 4-point thermocouple (top, mid-top, mid-bottom and bottom levels) inserted into the thermowell on the rail car. The car should be heated until all 4 of the temperature readings are within the 95-105 F range.

In freezing weather (below 0 C , 32 F) special precautions must be taken to avoid condensate freezing in steam supply lines and tank car coils. Blow out steam supply line and tank car coils with dry air (100 psig max) if steam supply is shut off, but is not disconnected from the car coil inlet connection. When steam supply is disconnected from the coil inlet connection, condensate will gravity drain thoroughly from the coils. Do not apply caps or valves to the inlet or outlet connections of the steam coils when steaming is complete.

The tank car liquid discharge valve and the vent valve are both equipped with a 2 in. flange (150 lb.) The transfer line/hose and vent line/hose must be connected using a 2 in. flange and a Teflon® gasket. It is highly recommended to have automated shut-off valves located on both ends of the transfer lines/hoses. The automated valves should be able to be activated remotely ("panic button" or from DCS) or interlocked to close for:

5. High level in storage tank
6. Inadvertent rail car movement
7. Fume detection in process area
8. Other local safety considerations

See Figure 8.

When the tank car arrives on site, be sure to check its identification number and placarding versus the shipping papers to confirm you have the proper car.

CAR PLACEMENT
Cars should be positioned on the center of the unloading dock's access platform, with hand brakes firmly set. Chocks should be set on both sides of the wheels to prevent accidental 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 the 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 Customer Service Center (1-800-441-9362). You will be advised on the 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 oleum, the oleum rail car equipment and functions, the thawing procedures and the emergency response procedures.

Complete body protection (acid jacket and pants, chemical gloves and boots, chemical hood) should be worn at all times while loading/unloading an oleum car. Respiratory protection should be provided while connecting/disconnecting the transfer lines/hoses.

The vapor line must be connected to the tank car vapor valve before the liquid unloading line is connected. The tank car must be relieved of all internal pressure by venting the oleum (SO_3) vapors through a properly designed scrubber/demister system.

Connect the liquid unloading line/hose to the car's liquid discharge valve. Liquid and vapor lines, along with the tank car valves (including the pressure relief valve assembly) must be maintained above 35 C (95 F) with heat input.

"Cars should be positioned on the center of the unloading dock's access platform, with hand brakes firmly set. "

WARMING/THAWING OLEUM CARS
Check for standpipe blockage by applying air pressure (25-30 psi) at 30 minutes intervals. In cold weather the standpipe may require up to 8 hours at 35-41 C (95-105 F) to thaw completely.

If car contents are to be warmed or thawed, connect low-pressure steam (5-10 psig, regulated) to external steam coil inlet. Do not install valve or steam trap on the steam coil outlet. Steam should be applied so that the condensate runs out of the coil outlet at 90-105 F. If live steam is emitted from the coil outlet, reduce steam supply to the coils. Warning: Rapid application of steam may cause SO_3 vaporization at the coil surfaces and internal pressure may increase rapidly, overloading the scrubber system.

The internal temperature of the oleum in the rail car should be monitored as the car is heated. This can be accomplished using a 4-point thermocouple (top, mid-top, mid-bottom and bottom levels) inserted into the thermowell on the rail car. The car should be heated until all 4 of the temperature readings are within the 95-105 F range.

In freezing weather (below 0 C, 32 F) special precautions must be taken to avoid condensate freezing in steam supply lines and tank car coils. Blow out steam supply line and tank car coils with dry air (100-psig max) if steam supply is shut off, but is not disconnected from the car coil inlet connection. When steam supply is disconnected from the coil inlet connection, condensate will gravity drain thoroughly from the coils. Do not apply caps or valves to the inlet or outlet connections of the steam coils when steaming is complete.

EQUIPMENT

Materials of Construction

Carbon steel is generally satisfactory for the storage and handling of oleums and sulfur trioxide at temperatures up to 60 C (140 F). The use of carbon steel is velocity sensitive for oleums.

Carbon steel is generally not used for moving parts because of the velocity sensitivity. Austentic stainless steels, such as grades 304, 304L, 316, 316L, and Alloy 20 have been used successfully for valve and pump wetted parts.

Among the plastics, Teflon® PTFE, FEP and PFA are resistant to SO_3 and oleums vapors and liquids up to the maximum temperature of the fluoropolymer material. It should be noted, though, that the higher the temperature, the more permeation of the fluoropolymer can occur. Care must also be taken with any filler material that may be used with the fluoropolymer. Some fillers have proven unsuitable for SO_3 and oleum service.

The selection of construction materials for oleum and SO_3 systems is influenced by factors such as temperature, fluid velocity, aeration and other chemical present (such as in a reactor).

PROHIBITED MATERIALS:
The following is a partial list of materials considered unsatisfactory for SO_3 and oleum service: natural and synthetic rubbers, non-fluorinated polymers, aluminum, copper-based alloys and cast iron.

Storage Tanks

Mild steel is generally considered satisfactory for storage and handling of oleums and SO_3 at normal ambient temperatures. In the absence of moisture, corrosive attack is very slow (0.02 mil/month at 30 C / 86 F). If low iron content is extremely important, or if the tank is located in an environment where it is exposed to external corrosion, 304 stainless steel should be used.

The capacity of the storage tank should be at least 1-½ times the maximum quantity normally ordered to protect against both running out of product and overfilling the tank. A typical storage tank for a tank truck delivery system should be 4000 gallons minimum and for rail car 18,000 gallons minimum.

The high (>30%) strength oleum and SO_3 storage 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 to ½ inch thick, with standard ASME dished heads of the same thickness.

Tank supports should be installed on firm foundations. Floor loading and soil bearing must be considered to provide adequate support. Structural steel supports or concrete saddles are satisfactory. Steel support saddles should be installed against the tank wall and seal-welded to prevent external moisture penetration and subsequent external corrosion.

For high strength (>30%) SO_3 and oleum storage, tanks should be preferably installed above ground in a building (hot room). The building temperature should be maintained in the 35-41 C (95-105 F) range. See Building section.

All nozzles should be installed on the top of the tank. The storage tank will require one 22 inch minimum diameter manhole with cover, one manhole for the submerged pump and openings for the inlet line, vent line, pressure and level sensing devices and temperature thermocouple. The tank should be equipped with a sump (5/8" minimum thickness) sized to accommodate the pump. The tank should be designed with no subsurface nozzles.

Storage tanks should be externally examined visually at least annually for corrosion-induced weaknesses. Acid spills on the tank exterior can be extremely corrosive as acid becomes diluted with atmospheric moisture or rainwater. An ultrasonic thickness test should be done biennially.
An internal visual inspection should be done every six years, based on your individual experience and plant's Mechanical Integrity program. Use NACE SP 029406 as the guidance document for tank inspections.

New storage tanks should be equipped with containment dikes sized at 110% of the tank capacity. 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.

Care must be exercised when filling storage tanks with SO_3 and oleums by use of controlled pumping rates, particularly on the initial fill or on tanks that have been idle for a period of time. A controlled pumping rate over a sufficient time period will allow the vapor space to equilibrate and vent off tank inerts (air, nitrogen) commensurate with the vapor pressure of the oleum/SO_3 being delivered. Unless transfer rates are properly controlled, pressure surges can be experienced that exceed the design pressure of the vessel.

Building

Because of the high freezing temperatures of SO_3 and oleums, locating the storage tanks, lines, valves, pumps, metering devices, vaporizers and associated equipment inside of a building (hot room) eliminates the need for tracing and insulation, and reduces handling difficult. The following factors should be considered when designing hot room facilities:

- Minimum of two exits should be provided for the building in which SO_3 and oleums are stored, handled and used.
- Exit doors should open outward in the direction of travel and should be provided with "panic hardware."
- Hot room temperature must be maintained between 34-41 C (95-105 F).
- Floors should slope towards the drain/sump. The lower portion of the building should be designed to also serve as secondary containment, sized to hold the entire tank contents if a tank failure should occur.
- Sumps in the hot room should be isolated from the plant or public sewer system. The sump should be piped and valved so that spilled SO_3 and oleums can be pumped into another tank or tank truck for emergency temporary storage.
- A video surveillance system aimed at the storage tank should be installed with a display in the control room.

"Storage tanks should be externally examined visually at least annually for corrosion-induced weaknesses."

Vents

The tank should be provided with a 4-to-6 inch diameter vent line to the fume scrubber system. This line vents SO_3 vapors from the SO_3 or oleum storage tank to the scrubber when liquid product is transferred into the tank. It allows dry air to enter the tank through the scrubber when liquid product is pumped out of the tank to the process. The 2 inch vent line from the unloading station can also vent directly to the fume scrubber or storage tank at a point that is always above the liquid level. Proper location of the vent line will allow it to serve as an overflow line should the storage tank be overfilled. The vent pipe must be designed so that the line drains to the scrubber, not the SO_3 or oleum storage tank. The vent line must be heat traced and insulated to keep the temperature above the freezing point of SO_3.

Fume Scrubber/ Demister

Every fuming acid storage system requires some means of controlling sulfuric acid mist to meet environmental requirements. SO_3 vapors coming off an SO_3 or oleum storage system can be readily absorbed in 93-96% sulfuric acid. Thus, an acid tank and packed scrubbing column is usually considered an integral part of an SO_3 or oleum storage system. This scrubbing must be specifically designed for the expected vapor loading, especially if dry air or nitrogen pressure is used to unload the product. The system sees a large pressure surge into the scrubber at the end of the unloading procedure if pressure is used.

A scrubber tank of 500-1,000 gallons (1,900-3,900 liters) capacity with a 12-24 inch diameter packed column makes a satisfactory unit for most installations. If dry air or nitrogen pressure is used for unloading, the system must be large enough to accommodate the high gas volume released at the end of unloading. The scrubber column should be made of Alloy 20 or lined with Teflon®. The packing should be ½"-1" diameter ceramic Raschig® rings or Intalox® saddles. The sulfuric acid scrubber tank should also be made of Alloy 20 or lined with Teflon®

The scrubbing column can be mounted directly on the scrubber tank, which should be equipped with a level gauge, temperature sensor, and a pump for recirculating the acid. A submerged pump mounted on a manhole cover for ready removal makes a suitable installation. An external sealless pump can also be used.

Depending on acid strength and facility location, the scrubber column may need to be insulated to prevent freezing. The scrubber column vent should be made of stainless steel, Teflon®-lined pipe or PVC to minimize blockage from iron sulfate build-up. The vent should be set up for periodic inspection/rodding to remove accumulated solids.

The acid strength should be checked regularly and maintained in the 93-96% range. The strength can be checked either by manual sampling or by in-line acid strength analyzers. If the acid strength increases above 96% (as it absorbs SO_3 vapors), the acid must be replaced or diluted (with water or acid addition) to bring it back to the desired range.

A BRINK® oleum vent system may be used in place of or in addition to the acid scrubbing system. A BRINK® (MECS) mist eliminator is a proven unit for removal of sulfuric acid mist from vent gas streams.

Recirculation Line

Where practical, closed loop recirculation lines provide a means of mixing tank contents, better temperature control and minimize line blockages. SO_3 freezes and can build-up near valves and controls that may be difficult to adequately insulate and heat, even in well-designed systems.

The SO_3/oleum delivery lines must also be designed to make them "self-draining", with no low points to trap SO_3 or oleum. If an SO_3 or oleum line should block/freeze, contact Veolia Technical Service for advice.

Piping

Schedule 80 carbon steel pipe with butt-welded fittings is the standard for SO_3 and oleum pipelines. Piping should meet ASME 31.3 standard for normal fluid service. Threaded fittings are not recommended. The pipelines should be self-draining. The lines should drain to the tank truck/ rail car, the storage tank and/or the process vessel. This will prevent the accumulation of liquid SO_3 or oleum at low points minimizing potential freezing and making line clearing easier for any required maintenance work on the lines.

All SO_3 and oleum liquid and vapor lines must be heat traced and insulated to maintain the line temperature between 35-41 C (95-105 F) at all times. Self-limiting electric heat tracing is preferred, with appropriate controls. A redundant heat tracing system (activated only when the primary system fails) should also be installed under the insulation.

Piping should also be designed to minimize potential to trap SO_3 or oleum between closed valves. Over time SO_3 and oleum will heat up (from the heat tracing), expand and possibly rupture the piping and/or valve gaskets.

Valves

Recommended valves for SO_3 and oleum service are made from Alloy 20. Gate valves, full-port ball valves or plug valves with Teflon® stem packing give good performance and require minimum maintenance.

Whenever possible, valves should be mounted in a horizontal position with the stem up. All valves must be heat traced and insulated.

Pumps

Due to the high vapor pressures of SO_3 and oleum (>30%), submerged pumps must be used. The two types that have provided good service are vertical submerged pumps and sealless "canned" pumps. The wetted parts of the pump should be made of 304 or 316 stainless steel. The pumps should be mounted on a tank manhole cover for ready removal for maintenance. Care must be taken when removing the pumps to ensure they are decontaminated, or they will emit fumes as they are pulled from the tank. A portable sleeve with a "maintenance" fume collection hose may be used to capture the fumes and convey them to the scrubber system. If this cannot be accomplished, the system should be designed with an installed spare pump to continue operations until the tank and pump can be emptied and decontaminated.

Gaskets

Solid Teflon® TFE gaskets are recommended for flanged connections. Contact Veolia Technical Service for specific recommendations. Teflon® envelope gaskets are not recommended.

"Whenever possible, valves should be mounted in a horizontal position with the stem up. All valves must be heat traced and insulated."

Instrumentation

The key to reliable and accurate instrumentation is that the measuring devices be kept warm (35-41 C, 95-105 F) and free of frozen SO_3. The wetted parts should be made of 304 or 316 stainless steel or Alloy 20, or lined with Teflon®.

TANK LEVEL MEASUREMENT
A reliable level indication must be part of the storage system. Suitable level indication devices for oleum and SO_3 include:

- Differential Pressure (d/P) cell with purged dip-tube
- RF Admittance (Capacitance) probe
- Ultrasonic Level Sensor (Gap Switch)
- Radar Level Sensor

FLOW MEASUREMENT
Liquid SO_3 and oleum flow can be accurately measured using:

- Magnetic flow meter
- Coriolis meter (true mass flow meter)
- Armored rotameter
- Ultrasonic meters (limited success)

ACID STRENGTH MEASUREMENT
Accurate strength analysis is dependent on the range of expected acid or oleum strength. Due to the unusual physical properties of sulfuric acid and oleum, one meter is not good for all ranges of acid and oleum strengths. It is important that the user understand this to gain the full benefit of the analyzers. Some types that have been successfully used include:

- Conductivity analyzers
- Sonic velocity analyzers
- Refraction index meters
- Density (<97% sulfuric acid)

TEMPERATURE MEASUREMENT
Temperature of oleum and SO_3 can be easily measured using thermowells in the storage tanks and/or piping systems. The thermowells must meet the same pipe code standards as piping systems (butt-weld full penetration welds, x-rayed) to ensure the integrity of the thermowell. Redundant temperature measuring systems should be used to ensure that the oleum and SO_3 stay within the desired temperature range to prevent both boiling and freezing of the product.

Consult Veolia Technical Service for any specific instrumentation application inquiries you have.

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-lined 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 oleum or SO_3 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.

Remote Leak Detection

At present there are no commercially available "chemical sensor" products available to detect SO_3 or oleum releases into the atmosphere. The remote leak detection systems that have varying degrees of success include:

- Video camera for visual observation
- Smoke detectors (in buildings)
- Opacity meters

Each method has shown some promise, but also some weaknesses. Contact Veolia Technical Service for the latest recommendation.

Cleaning Storage Tanks

Over time, SO_3 and oleum tanks may build up a deposit of polymer and/or iron sulfate sludge that can cause pumping or blockage problems. To mitigate this, it is necessary to clean and internally inspect the tanks. There are two basic methods for cleaning SO_3 and oleum storage tanks. They are "acid-dilution" and "vaporization." The method used will depend on:

- Allowable "out-of-service" time for the tank
- Size and condition of scrubber system
- Local regulations

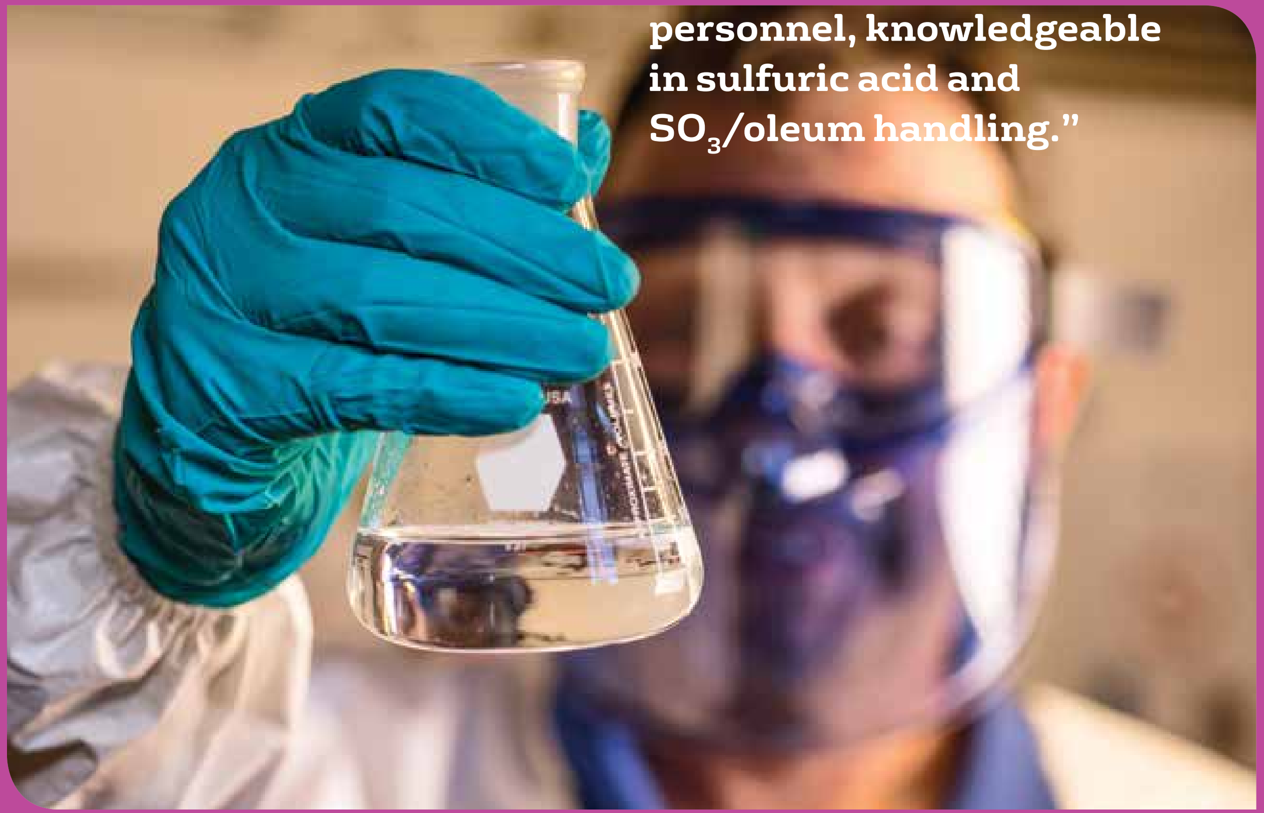
Before starting either method, it is advisable to get a good reading on the amount remaining in the tank. This can be accomplished by using a hard wood stick (oak or maple) to "rod" the tank. The tank must be kept under negative pressure and vented to the scrubber during this step to minimize fuming from the tank.

Acid dilution is the most commonly used method for cleaning oleum storage tanks. It involves slowly adding weaker oleum and non-fuming sulfuric acid to the tank until the entire tank contents become non-fuming (<100% H_2¬SO_4). The amount of SO_3/oleum remaining in the tank must be known (from the "rodding step") to calculate the amount of non-fuming acid required. Tank temperature, pressure and the scrubber discharge vent are observed during this process to ensure the acid is added slowly enough.

Once the entire tank contents are rendered non-fuming, the acid can be pumped out of the tank and either reused or disposed.

Vaporization is most commonly used for SO_3 tanks. The heat input to the tank is increased to above 170 F. This will ensure any remaining SO_3 in the tank, including any SO_3 "ice", is vaporized to the scrubber. It is very important to ensure the scrubber acid strength is maintained in the 93-96% range during the vaporization to absorb all SO_3 vapors. Again, tank temperature, pressure and the scrubber discharge vent are monitored during this procedure, as is the acid scrubber strength. The tank is kept at above 170 F for at least 24 hours to ensure all SO_3 is vaporized. The tank is then cooled down and water can be added to the tank to rinse it before entering the tank. Care must be taken to monitor the tank pressure and temperature, and scrubber discharge vent during this step also to ensure all SO_3 has been vaporized.

Cleaning of SO_3 and oleum tanks presents significant incident potential and the job should be done under the guidance of experienced personnel, knowledgeable in sulfuric acid and SO_3/oleum handling. Anyone cleaning their SO_3 or oleum tanks for the first time should review their proposed procedure with Veolia's Technical Service team prior to starting.



"Cleaning of SO_3 and oleum tanks presents significant incident potential and the job should be done under the guidance of experienced personnel, knowledgeable in sulfuric acid and SO_3/oleum handling."

Resourcing the world

Veolia North America

twitter: @veolia_va
www.veolianorthamerica.com