

Evaluation of Loading and Unloading Operations for Sulphuric Acid and Spent Sulphuric Acid Rail Tank Cars

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EXECUTIVE SUMMARY

The Sulphur Institute (TSI) entered in a cooperative agreement with the Office of Research, Development and Technology (RDT) of the US Department of Transportation (DOT), Federal Railroad Administration (FRA) to observe, review, and provide a summary of procedures for loading and unloading sulphuric acid and spent sulphuric acid rail tank cars and identify leading practices and opportunities for information sharing to enhance safety and operations. These observations have led to development of this document with a focus on reducing the number of non-accident releases (NARs) of rail tank cars and providing ideas to improve training, practices and procedures for loading and unloading operations.

The Institute conducted a confidential survey of existing member company locations, including average number of sulphuric acid rail tank cars loaded or unloaded moves per day, at several operating facilities. From this survey, sites were selected and solicited for peer review. Companies were contacted to assess their interest in participating in this study. Copies of loading and unloading procedures were requested and received from these and other interested companies.

This Evaluation of Loading and Unloading Operations for Sulphuric Acid and Spent Sulphuric Acid Rail Tank Cars is an effort to share a variety of leading practices collected and aggregated from several facilities within the United States and Canada. TSI visited three oil refineries, two acid regeneration plants, a liquid tank ocean terminal, a rail tank car to tank truck transloading site, and a metals smelter plant to observe and collect data on possible reasons for NAR occurrences. This data has allowed TSI to identify potential causes, analyze associated trends, and provided an opportunity for industry to share practices and reduce NARs for rail shipments of sulphuric acid and spent sulphuric acid. This summary report provides the sulphuric acid industry multiple examples of loading and unloading practices from which to select those most appropriate for their facility. In addition, this summary report provides general information about properties of sulphuric acid and available references for safe handling.

The focus of this summary report is to address common issues faced when an individual is performing standard loading and unloading procedures through the top fittings arrangements of sulphuric acid rail tank cars. While this study is intended to show industry leading practices, including worker safety procedures, each particular location may require the use of additional, or different, precautions for loading and/or unloading operations to be performed safely, as each site or operating company may have unique attributes that need to be addressed.



1.0 Introduction

1.1 Purpose of the study

The Federal Railroad Administration (FRA) Office of Research, Development and Technology (RDT) designated The Sulphur Institute (TSI), through a federal grant, to work with industry to minimize the occurrences of product releases during rail transportation of sulphuric acid products, namely, sulphuric acid (UN 1830) and spent sulphuric acid (UN 1832). The purpose of this study is to reduce the number of product releases/spillages on rail tank cars (also referred to as "tank cars") as a result of loading and unloading operations at facilities handling sulphuric acid and spent sulphuric acid. In the railroad industry, these product releases are commonly referred to as a non-accident release (NAR). The outcome of this study is to document and report on leading practices to load, transport, and unload sulphuric acid and spent sulphuric acid rail tank cars in as safe and effective manner as possible. To accomplish this, TSI is to identify, document, and share leading practices used for loading and unloading sulphuric acid and spent sulphuric acid rail tank cars. The results of the study can be used by shippers of sulphuric acid products to improve local operations and develop or improve existing training programs for their employees. Through observation of onsite facilities, TSI assessed existing operating practices and identified improvements to sulphuric acid and spent sulphuric acid loading operations.

An additional benefit to the study is identification of protection mechanisms for workers in terms of personal protective equipment (PPE), other safety equipment at loading and unloading racks, and other means of protecting the environment by reducing spills at loading racks.

1.2 Background

The Association of American Railroads (AAR) defines a non-accidental release (NAR) as "the unintentional release of a hazardous material while in transportation, including loading and unloading while in railroad possession, that is not caused by a derailment, collision or other rail related accident." NARs consist of leaks, splashes, and other releases from improperly secured or defective valves, fittings, and tank shells, and also include venting of non-atmospheric gases from safety relief devices. (AAR Website). Similarly, the U.S. Department of Transportation's (USDOT) Hazardous Material Regulation (49 Combined Federal Regulation (CFR) § 171.16) defines an unintentional release as "the escape of a hazardous material from a package on an occasion not anticipated or planned. This includes releases resulting from collision, package failures, human error, criminal activity, negligence, improper packing, or unusual conditions such as the operation of pressure relief devices as a result of over-pressurization, overfill or fire exposure. It does not include releases, such as venting of packages, where allowed, and the operational discharge of contents from packages." (49 CFR § 171.8). Also, 49 CFR § 173.24 (b) requires that each package used for the shipment of hazardous materials shall be designed, constructed, maintained, filled, its contents so limited, and closed, so that under conditions normally incident to transportation ... there will be no identifiable (without the use of instruments) release of hazardous materials to the environment.

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Regardless of definition, under 49 CFR § 171.16, it is a federal law to report the unintentional release of a hazardous material. Many times this results in a federal penalty or other related costs attributed to a railroad service provider's remediation of the problem. It is TSI's desire that industry stakeholders will benefit from the findings in this study, not only to reduce potential penalties, but to protect workers and the environment from incidents related to sulphuric acid products.

1.3 Scope of the study

The project manager of the hazardous materials and tank car projects of the Office of RDT directed TSI that the study encompass six observations of loading operations and six observations of unloading operations for both sulphuric acid and spent sulphuric acid. Since many locations receive sulphuric acid for manufacturing processes and return spent sulphuric acid for regeneration purposes, often using the same rail tank car for backhaul, this study encompasses both products. In all, TSI made nine site visits to industrial facilities observing the required twelve loading and unloading operations. TSI chose to observe operations at several different types of facilities in the supply chain to gain an understanding of the unique challenges operators may face at a given site. These visits included oil refineries, acid regeneration plants, a water terminal, a rail tank car to tank truck transloading site, and a metals smelter plant.

In addition to the mandate for the number of site observations, the FRA directed that TSI accomplish the following tasks. TSI will reference these tasks throughout the report ensuring the terms of the grant agreement are met.

Task 1	Improve loading practices at origin
Task 2	Improve unloading practices at destination
Task 3	TSI will collect the following data:
	 Documentation of all non-accident related releases associated with rail transportation of sulphuric and spent sulphuric acid from January 2012 to present.
	2) Documentation of the general arrangement and fitting assemblies of tank cars used in the transportation of sulphuric and spent sulphuric acid.
	 Survey of producers and consumers to determine the type of equipment used to load/unload sulphuric and spent sulphuric acid.
	4) Survey TSI members to develop a gap analysis of written operating procedures and training needs with respect to pre-shipment inspection and securing of tank cars.
Task 4	Development of educational material and guidance
Task 5	Reporting and liaison with FRA and industry. The grantee will maintain close communication with FRA staff during this project in order to make sure that the results meet FRA goals for the project and in order to ensure that stakeholder inputs and concerns are taken into account.

Table 1: FRA Directed Tasks



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1.4 Data collection and analysis

At the onset of the study, TSI worked with member companies to establish a set of protocols for the visit and subsequent observations. The checklist agreed upon, and vetted with TSI's Sulphuric Acid Working Group, is attached at Enclosure 1 to this report. In addition to the observation checklist, TSI interviewed each facility supervisor on the depth and breadth of employee training for operating the sulphuric acid loading and unloading rack. While training varied site to site, TSI found that each site used USDOT and Occupational Safety and Health Administration (OSHA) standards as a baseline for training. In addition to federally mandated training, each site had additional requirements pertaining to that particular operation. On one site visit, TSI had the opportunity to observe USDOT refresher training that was scheduled concurrent to TSI's visit.

In addition to the data collection process and training interviews, TSI collected formal company procedures that support quality or safety management systems. TSI used these procedures to help rationalize common industry norms that will support TSI's findings for the leading practices.

In addition to observations at loading and unloading sites, TSI was asked to analyze non-accident release data for rail tank car shipments of sulphuric acid and spent sulphuric acid. This data was provided by the AAR and substantiated with the Pipeline and Hazardous Material Safety Administration's (PHMSA) online hazardous material incident reporting database.

See <u>https://hazmatonline.phmsa.dot.gov/IncidentReportsSearch/Welcome.aspx</u> for PHMSA data.

The charts below show the five year trend for NARs for sulphuric acid and spent sulphuric acid.



Graph 1: Sulphuric Acid NAR from 2012 – 2016 (Source: Association of American Railroads)





Graph 2: Spent Sulphuric Acid NAR from 2012 – 2016 (Source: Association of American Railroads)

The number of NAR alone do not provide sufficient granularity on how nor why the NAR occurred, therefore, the AAR also applies cause codes to each NAR reported. Likewise, in the PHMSA database a detailed description of the cause of the incident is documented.

The top five cause codes, or reason why the NAR occurred, for sulphuric acid shipments during the period 2012 to 2016 are listed in the table below.

Cause Code	Occurrences from 2012 to 2016			
Frangible disc (rupture disc)	23*			
Liquid line closure cap loose	19			
Torn/missing gasket	9			
Fill hole cover bolts loose	8			
Fill hole cover misaligned5				
* Top cause code for spent sulphuric acid, 9 occurrences				
Table 2: NAR Cause Codes & Occurrences from 2012 – 2016				

(Source: Association of American Railroads)

The NAR data served two purposes for TSI. First, TSI used the NAR information as a discussion point with supervisors as part of the orientation prior to loading and unloading observations. Site supervisors were appreciative of the information provided and some stated they would use the data during the annual review of company procedures. Secondly, during the loading and unloading operations, TSI focused its observations on areas where a high number of NARs occurred. For example, given the number of NARs that were reported due to frangible disc failure, TSI observed the removal, inspection, and replacement

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of the frangible disc and compared the loader's actions with that found in the company's written procedures. There will be more discussion on this in subsequent sections of the study.

2.0 Uses and Characteristics of Sulphuric Acid

2.1 Uses in fertilizer production and manufacturing

Sulfuric acid is an important commodity chemical; a nation's sulfuric acid production is a good indicator of its industrial strength. Sulphur is the major raw material used in the production of sulphuric acid. The other methods of sulphuric acid production include production from smelter gas and iron pyrites. Sulphuric acid finds its applications in a myriad of sectors and industries. Major applications of sulfuric acid include production of fertilizers, industrial chemicals, additives for the pulp and paper industry, rubber vulcanizing applications, and as battery acid in the automotive sector. In the United States over 40 million tons of sulphuric acid is produced annually through sulphur burning at agricultural manufacturing facilities, acid regeneration plants, or smelter gas recovery processes – the latter two which are likely transported by rail tank cars and tank trucks to other manufacturing or refining sites.

2.2 Chemical and physical properties

Sulphuric acid is a colorless to yellow, viscous liquid; it is hazardous and corrosive in nature. The physical properties (Table 3 below) are dependent on acid concentrations, temperature and pressure. It is important to note that different concentrations of sulphuric acid freeze at differing temperatures. Graph 3 below shows the freezing point curves for sulphuric acid which is of importance if stored or transported under very cold conditions.



Graph 3: Freezing points of sulphuric acid



Properties	93% (66° Be')	98%
Strength, %H ₂ SO ₄	93.2 Min	98 Min
Freezing Point, °F	-31	29
Freezing Point, °C	-35	-2
Boiling Point, °F	535	621
Boiling Point, °C	279	327
Specific Gravity, 60°F (15.6°C)	1.835	1.844
Density, Ibs/gal, 60°F (15.6°C)	15.3	15.4
Viscosity, cP, 68°F (20°C)	22	25
Specific Heat, cal/g • °C	0.38	0.35
Appearance	Clear to slightly turbid oily liquid	Clear to slightly turbid oily liquid
Odor	None	None

Table 3: Physical properties of sulphuric acid

2.3 Health hazards

Sulphuric acid is not very volatile and workplace exposures are therefore primarily due to accidental splashes or to processes or actions that generate an acid mist. It is extremely corrosive to all body tissues, causing rapid tissue destruction and serious chemical burns on contact with the skin or eyes. Skin or eye contact requires immediate first aid. Inhalation of sulphuric acid mist or fumes may produce irritation of the nose, throat and respiratory tract. High levels of acid mist are also irritating to the skin and eyes. Chronic inhalation of acid mist may cause pitting and erosion of tooth enamel. Under the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), pictograms are used to communicate these health hazards in the work place (Figure 1). Hazardous materials (HAZMAT) include corrosive material like sulphuric acid. Due to the potential risks and consequences involved with these materials, they are monitored by carriers, the US DOT and emergency personnel while in transit to ensure the safety of the public. HAZMAT placarding helps with these efforts because it allows substances to be quickly identified in case of emergency.

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Figure 2: Transportation placards for sulphuric acid (left) and spent sulphuric acid (right)



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3.0 Loading and Unloading Operations

3.1 General

3.1.1 Employee training and documentation

The US Hazardous Material Regulation (49 CFR) requires training of all employees handling hazardous material. A HAZMAT employee as defined in 49 CFR §171.8 is a person who has one or more of the following:

- Employed full-time, part time, or temporarily
- Directly affecting hazmat transportation safety
- Self-employed
- A railroad signalman or maintenance-of-way employee
- Loads, unloads or handles HAZMAT
- Designs, manufactures, inspects, marks, tests, or reconditions containers
- <u>Prepares HAZMAT for transportation</u>
- Operates a transport vehicle

It is the responsibility of each HAZMAT employer to ensure that HAZMAT employees are trained and that appropriate records are kept (49CFR§172.704(d)). Documents such as this study may be referenced in developing training, however, many more training requirements are outlined in 49 CFR §172.704, they include:

- General awareness/familiarization training
- Function-specific training
- Safety training
- Security awareness training
- In-depth security training
- Initial and recurrent training

During the course of the site-visits, TSI interviewed supervisors with regard to training within their organization and observed one HAZMAT training session in progress. For employees new to sulphuric acid loading and unloading operations there was commonly a 90 day "probationary" period whereby new employees in training were closely supervised by more experienced employees throughout the loading or unloading operation. Supervisors reiterated that the "probationary" period ended only when new employees were able to demonstrate proficiencies in accordance with company procedures. If not, the new employee continued to train under supervision until they could attain proficiency.



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3.1.2 Equipment for loading and unloading operations

Standard equipment necessary for loading and unloading operations found throughout site visits include:

- Safety shower and eye wash station •
- Fire extinguisher •
- Piping & valve systems used to attach to tank car fittings •
- Loading arms •
- Eductor hose to capture vapors (during spent acid loading) •
- Crescent wrench •
- Pipe wrench •
- Calibrated torque wrench •
- Grounding equipment
- Rail car wheel chocks/blue flags (See AAR Pamphlet 34, Section 1 for use of wheel chocks) •
- Load level detector •
- Sampling equipment, measuring rod •
- DOT approved hazardous material placards (4 per car, both UN1830 and UN1832)





Image 1: Fill or load level detector installed for automatic shut off while loading through fill hole

Image 2: Operator using open-ended wrench to achieve a tool tight condition



Federal regulations (49 CFR § 173.3) requires securement of a rail tank car "to a tool-tight condition." The tool inventories observed during the site visits can achieve a tool tight closure, however, loading rack personnel could also use calibrated torque devices when securing a package for transportation. Using a torque wrench, for example, could eliminate any consequences from overtightening of bolts that result in damage to washers, gaskets, seals, etc. Rail tank car manufacturers, gasket manufacturers, and manufacturers of specialized fittings or valves will normally publish torque tightness values for their products. Loading rack personnel should consult manufacturer representatives to attain specific information.

3.1.3 Tank car fittings and arrangements

It is important to note the service equipment fitted on top of new nonpressure tank cars in sulphuric acid service, ordered built new after June 30, 2010, must meet the requirements of Appendix E, paragraph 9.2.1 (AAR's Manual of Standards Specification for Tanks Cars M-1002 Section 2.2.3.3).



Image 3: Enclosed dome top fittings protection meeting AAR standard for new build

Image 4: Partial top fittings protection

Image 5: No top fittings protection





Image 6: Common fitting arrangements for sulphuric acid tank car

3.1.4 Workplace safety and personal protective equipment (PPE)

Sulphuric acid is extremely corrosive and several precautions should be taken to ensure that the acid does not come in contact with skin and eyes. Skin contact can cause pain, redness, burns, and blistering. Permanent scarring can result. A severe exposure can even cause death. If acid comes in contact with the eyes it can cause severe burns with redness, swelling, pain and blurred vision. Permanent eye damage including blindness can result.

Recommended minimum standard for exposure prevention include:

- Hard hat (ANSI/ISEA Z89.1-2009)
- Face shield (ANSI Z87.1-2003)
- Chemical splash goggles (ANSI Z87.1-2015)
- Acid resistant full body outer garments
- Acid resistant gloves (ANSI/ISEA 105-2000)
- Acid resistant boots (boots should meet ASTM F 2413-11 standard for steel toe caps and made of material, such as neoprene, that stands up to acid)
- Safety shower and eye wash station (ANSI / ISEA Z358.1)





Image 7: Safety shower and eye wash station on ground level



Image 8: Safety shower and eye wash station at transload rack



Image 9: Full hood used as face shield



Image 10: Face shield attached to hardhat



Several loading and unloading sites still use hardhat and face shield, however, a full hood protecting the neck and the side of the face is recommended. On the picture above (right side) observe that in the event of a splash, the side of the neck and neck are vulnerable.







Image 13: Exposed skin above gloves

Image 11: Cuffing Gloves

Image 12: Uncuffed Gloves

Measures such as cuffing gloves (left photo) into protective outerwear should be taken to ensure skin is not exposed to sulphuric acid. Center photo shows uncuffed glove where acid could spill into glove potentially coming into contact with skin. Photo on right shows exposed skin during operations.

3.2 Loading and Unloading Sulphuric Acid Leading Practices

3.2.1 Loading sulphuric acid

3.2.1.1 Loading Sulphuric Acid through Fill Hole Cover (Prior to commencing loading operations, consult guidelines listed in Section 1: Loading and Unloading General Purpose Tank Cars to Association for American Railroads Pamphlet 34 -- Recommended Methods for the Safe Loading and Unloading of Non-Pressure (General Service) and Pressure Tank Cars.) If tank car arrives on site with evidence of an acid spill, thoroughly rinse tank car with water prior to loading operation.

- De-pressure car through vent valve when venting, the operator should be positioned out of the line of flow and ensure no personnel are present in the area to prevent exposure to possible trace amounts of acid spray. When removing plug from vent valve ensure valve is in closed position. Once plug is removed, slowly open the vent valve to release pressure from the car. Inspect plug for corrosion and any thread defects, replace if needed.
- Once car is vented through vent valve, open fill hole cover. Carefully loosen all fill hole cover bolts and swing safety bolts to down position and open cover slowly to allow for any remaining pressure to release. On the fill hole cover, there is usually a safety catch swing bolt. The safety catch swing bolt should be loosened and cover cracked open to ensure car was properly depressured. In the



event it was not, the safety catch swing bolt will prevent the fill hole cover to opening completely and reduces the risk of acid splashing on the operator.

- Visually inspect the tank car interior prior to loading to ensure tank car is free of product of any foreign objects.
- Connect air supply to air supply line and ensure vent valve remains in open position.



- Remove and inspect both sides of the rupture disc prior to each load, replacing if necessary. Sulphate build up in the area of the rupture disc is possible. If sulphate build up is present clean out rupture disc assembly. Replace rupture disc and secure rupture disc assembly. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Remove siphon pipe cap and inspect gasket or o-ring, replace if necessary. Secure pipe cap following gasket or o-ring inspection.
- Bring loading arm into place, lower into rail car low enough to avoid splashing and secure into place.
- Install load level indicator (NOTE: During TSI visits, 3 of the 4 sulphuric acid loading sites used an electronic load level indicator that was connected to the pump system's automatic shut off procedure.)



Image 15: Chain Securing Loading Arm & Load Level Indicator Installed



- Turn on pumps and begin loading, monitoring pumps, making observations for any spills throughout the process.
- Once tank car is loaded, turn off pumps and remove loading arm and secure into spill saddle.



Image 16: Loading arm correctly placed in saddle to prevent spills to the environment

• At this point, it may be prudent to take a sample of the acid from the loaded rail tank car. This allows for quality control of acid production and helps ensure product loaded meets company specifications prior to shipment.



Image 17: Plastic bottle used to retrieve product sample



- Secure fill hole cover ensuring correct placement of gasket and ensuring that eye bolts are tool tight. If using a torque wrench, refer to tank car manufacturer's recommendations on proper torque of fill hole bolts. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Turn on air/nitrogen supply to 25 psi; hold pressure at 25 psi for 10 minutes while checking for any acid leaks from any primary or secondary closures on the tank car. If any leaks are present, depressurize car before any repairs are made to the tank car.
 - NOTE 1: It is imperative that loading operators understand the limits of their repair authorizations. Any repairs necessary outside of their authorization must be made by an Association of American Railroads authorized repair facility (which can include a certified mobile repair team). Regulatory and railroad industry specifications, standards, and requirements are contained in: USDOT Title 49 Code of Federal Regulations, Parts 173 (Subpart B), 174, 179, and 180 (Subpart F); Transport Canada Transportation of Dangerous Goods Regulations (Transport Canada TDG Regulations) and Containers for the Transport of Dangerous Goods by Rail (Standard TP 14877E); and Association of American Railroads Manual of Standards and Recommended Practices (MSRP) Section C-III, Specifications for Tank Cars, Specification M-1002.
 - NOTE 2: During TSI visits, 7 of 9 facilities visited used 25 psi for pressurizing tank cars with a range of 15 to 30 psi for all facilities visited. Also, a 10 minutes hold time once pressure was attained was the average time spent pressurizing cars to ensure a leak free package.
- Close air/nitrogen valves and open air/nitrogen bleed valve from the air/nitrogen supply line ensuring all pressure has vented from rail tank car.
- Close vent valve on car (if chain present leave on car, if no chain, place handle in tool box)
- Remove air/nitrogen supply line hose from vent valve.
- Replace vent valve plug, securing to a tool tight condition.
- Rinse the tank car and all fittings with fresh water. NOTE: 49 CFR 173.24(b)(4) specifically states: "There will be no hazardous material residue adhering to the outside of the package during transport." By rinsing the tank car with fresh water, any sulphuric acid residue on the tank car is removed and reduces the risk of acid exposure to others that may handle the car throughout transportation.
- Affix security seal, and product identification tag
- Affix DOT approved placards to four sides of car
- Complete post-loading checklist paperwork and prepare secured rail tank car for shipment.





Image 18: With Security Seal

Image 19: Without Product Information Tag



Image 20: USDOT Approved Placards

For correct placarding methods see US Department of Transportation Chart 16 at <u>https://www.phmsa.dot.gov/sites/phmsa.dot.gov/files/docs/training/hazma</u> <u>t/18371/usdot-chart-16-10-24-2017.pdf</u>



3.2.1.2 Loading through siphon pipe (Prior to commencing loading operations, consult guidelines listed in Section 1: Loading and Unloading General Purpose Tank Cars to Association for American Railroads Pamphlet 34 -- Recommended Methods for the Safe Loading and Unloading of Non-Pressure (General Service) and Pressure Tank Cars.) If tank car arrives on site with evidence of an acid spill, thoroughly rinse tank car with water prior to loading operation.

- De-pressure car through vent valve when venting, operator is positioned out of the line of flow and ensure no personnel are present in the area to prevent exposure to possible trace amounts of acid spray. When removing plug from vent valve ensure valve is in closed position. Once plug is removed, slowly open the vent valve to release pressure from the car.
- Connect air supply to air supply line and ensure vent valve remains in open position.
- Remove and inspect both sides of the rupture disc prior to each load, replacing if necessary. Sulphate build up in the area of the rupture disc is possible. If sulphate build up is present, clean out rupture disc assembly. Replace rupture disc and secure rupture disc assembly. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Remove siphon pipe cap slowly. Never remove siphon pipe cap before venting the car. Inspect gasket or o-ring, replace if necessary. Some tank car top fittings arrangements are equipped with flange assemblies in lieu of siphon pipe cap. Never remove flange covers before venting the car.



Image 21: Top fittings with flange assembly as alternative to siphon pipe cap

Note: The vent valve in the open position with air/nitrogen line attached.

• Secure loading arm pipe assembly to pipe fittings or secure flange assembly per company procedures. TSI observed a number of different methods for securing loading arm to the tank car for siphon pipe operations. These included threaded pipe, cam lock devices and bolt and



flange fittings. These design variables should be addressed in company procedures to ensure proper closure during the loading process.

- Once all siphon pipe fittings are secured, turn on pumps and begin loading, monitoring pumps and volume gauges. During siphon loading, loaders will normally preset volume limits to avoid overfilling tank cars.
- When the tank car is filled to the desired volume, turn off pumps.



- Since siphon pipe cap and vent valve have been open, the tank car is vented for inspection of fill hole gasket. Carefully loosen all fill hole cover bolts and swing safety bolts to down position. Open cover slowly to allow for any remaining pressure to release. Inspect fill hole cover gasket.

Disassemble siphon pipe fittings and secure siphon pipe cap or flange cap for transportation.

- At this point, it may be prudent to take a sample of the acid from the loaded tank car. This allows for quality control of acid production and helps ensure product loaded meets company specifications prior to shipment.
- Secure fill hole cover ensuring correct placement of gasket and ensuring that eye bolts are tool tight. If using a torque wrench, refer to tank car manufacturer's recommendations on proper torque of fill hole bolts. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Turn on air/nitrogen supply to 25 psi; hold pressure at 25 psi for 10 minutes while checking for any acid leaks from any primary or secondary closure on the tank car. If any leaks are present, depressurize car before any repairs are made to the tank car.
- Close air/nitrogen valves and open air/nitrogen bleed valve from the air/nitrogen supply line ensuring all pressure has vented from railcar.



- Close vent valve on car (if chain present leave on car, if no chain, place handle in tool box)
- Remove air/nitrogen supply line hose from vent valve.
- Replace vent valve plug, securing to a tool tight condition.
- Rinse tank car and all fittings with fresh water. NOTE: 49 CFR 173.24(b)(4) specifically states: "There will be no hazardous material residue adhering to the outside of the package during transport." By rinsing the tank car with fresh water, any sulphuric acid residue on the tank car is removed and reduces the risk of acid exposure to others that may handle the car throughout transportation.
- Affix security seal, and product identification tag.
- Affix DOT approved placards to four sides of car.
- Complete post-loading checklist paperwork and prepare secured rail tank car for transportation.

3.2.2 Unloading Sulphuric Acid – The unloading of sulphuric acid from tank cars at consumer sites or transloading locations takes on many of the same risks as loading sulphuric acid at production sites, however, there may be additional risks supervisors and personnel at unloading sites may need to consider. Some of these risks include acceptance of tank cars that are owned or leased by different sulphuric acid producers, perhaps with differing top fittings design; operating in a more confined space at unloading facilities; fewer tank cars cycled in and out of a facility resulting in less experienced unloading personnel; and tank car unloading at remote facilities with fewer supervision and emergency response resources. Another factor that needs to be considered and understood is the volume capacity of the sulphuric acid storage tank at the unloading facility. Close coordination between unloading personnel and those responsible for tank storage levels is necessary to ensure a smooth unloading process. Because of these factors, great caution needs to be taken when unloading sulphuric acid tank cars and preparing them for transportation when emptied. Prior to commencing unloading operations, consult guidelines listed in Section 1: Loading and Unloading General Purpose Tank Cars to Association for American Railroads Pamphlet 34 -- Recommended Methods for the Safe Loading and Unloading of Non-Pressure (General Service) and Pressure Tank Cars.) If tank car arrives on site with evidence of an acid spill, thoroughly rinse tank car with water prior to unloading operation. The following steps should be considered when unloading sulphuric tank cars.

- De-pressure tank car through vent valve when venting, be positioned out of the line of flow and ensure no personnel are present in the area to prevent exposure to possible trace amounts of acid spray. When removing plug from vent valve ensure valve is in closed position. Once plug is removed, slowly open the vent valve to release pressure from the car. Inspect plug for corrosion or thread wear and replace if necessary. Note: the operator can also open fill hole cover in manner described in 3.2.1.1 for added assurance that the tank car is relieved of pressure.
- Connect air/nitrogen supply to air/nitrogen supply line and ensure vent valve remains in open position.



- Remove and inspect both sides of the rupture disc prior to each load, replacing if necessary. Sulphate build up in the area of the rupture disc is possible. If sulphate build up is present clean out rupture disc assembly. Replace rupture disc and secure rupture disc assembly. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Remove siphon pipe cap slowly. Never remove siphon pipe cap before venting the car. Inspect gasket or o-ring, replace if necessary. Some tank car top fittings arrangements are equipped with flange assemblies in lieu of siphon pipe cap. Never remove flange covers before venting the car.
- Secure unloading assembly to pipe fittings or secure flange assembly per company procedures. TSI observed a number of different methods for securing loading arm to the tank car for siphon pipe operations. These included threaded pipe, cam lock devices, hammer lock unions, and bolt and flange fittings. These design variables should be addressed in company training and company procedures to ensure a leak proof closure during the unloading process.
- Once all siphon pipe fittings are secured, verify that all valves on the tank car are in the correct position to start unloading acid.
- Turn on nitrogen/air supply. (See Section 4.0 Conclusions for alternate unloading methods)
- When the pressure in the tank car reaches 15-30 psi, open the unloading flow control valve to begin unloading process – acid is now flowing through the piping system into the acid storage tank. Monitor offloading and observe valves and fittings for leaking. Unloading rack operators should make contact with person responsible for storage tanks to ensure product was flowing throughout the system and storage tank volumes were increasing.
- When the tank car is empty, a drop in pressure and the sound of air passing through the discharge pipe will be heard.
- Shut off the nitrogen/air supply line.
- Close any valves in the unloading line.
- Vent all pressure from the tank car through the vent valve.
- Open fill hole cover and inspect tank car to ensure the tank is completely empty.
- Disconnect nitrogen/air supply line.
- Disconnect unloading assembly and place in saddle to prevent any spills to the environment
- Disassemble siphon pipe fittings and secure siphon pipe cap or flange cap for transportation.
- Secure fill hole cover ensuring correct placement of gasket and ensuring that eye bolts are tool tight. If using a calibrated wrench, refer to tank car manufacturer's recommendations on proper torque of fill hole bolts. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Close vent valve on tank car (if chain present leave on car, if no chain, place handle in tool box)
- Replace vent valve plug, securing to a tool tight condition.



- Rinse tank car and all fittings with fresh water. NOTE: 49 CFR 173.24(b)(4) specifically states: "There will be no hazardous material residue adhering to the outside of the package during transport." By rinsing the tank car thoroughly with fresh water, you eliminate any sulphuric acid residue on the tank car and reduce acid exposure to others that may handle the car throughout transportation.
- Affix DOT approved placards to four sides of tank car.
- Complete post-unloading checklist paperwork and prepare residue/empty tank car for transportation.

3.3 Loading and unloading spent sulphuric acid leading practices

3.3.1 Loading Spent Sulphuric Acid

In many cases the process of loading spent sulphuric acid comes immediately following the unloading of sulphuric acid, after the tank car is emptied, and in preparation for back haul transportation to a sulphuric acid regeneration facility. Many of these steps are the same or similar to loading of sulphuric acid. Prior to commencing loading operations, consult guidelines listed in Section 1: Loading and Unloading General Purpose Tank Cars to Association for American Railroads Pamphlet 34 -- Recommended Methods for the Safe Loading and Unloading of Non-Pressure (General Service) and Pressure Tank Cars.) If tank car arrives on site with evidence of an acid spill, thoroughly rinse tank car with water prior to loading operation.

- De-pressure tank car through vent valve when venting, be positioned out of the line of flow and ensure no personnel are present in the area to prevent exposure to possible trace amounts of acid spray. When removing plug from vent valve ensure valve is in closed position. Once plug is removed, slowly open the vent valve to release pressure from the car.
- Connect air or nitrogen supply to air/nitrogen supply line and ensure vent valve remains in open position.
- Remove and inspect both sides of the rupture disc prior to each load, replacing if necessary. Sulphate build up in the area of the rupture disc is possible. If sulphate build up is present, clean out rupture disc assembly. Replace rupture disc and secure rupture disc assembly. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Remove siphon pipe cap slowly. *Never remove siphon pipe cap before venting the tank car.* Inspect gasket or o-ring, replace if necessary. Some tank car top fittings arrangements are equipped with flange assemblies in lieu of siphon pipe cap. *Never remove flange covers before venting the tank car.*
- Secure loading arm pipe assembly to pipe fittings or secure flange assembly per company procedures. *TSI observed a number of different methods for securing the loading arm to the tank car for siphon pipe operations. These included threaded pipe, cam lock devices, hammer lock unions, and bolt and flange fittings. These design variables should be addressed in company training and company procedures to ensure proper closure during the loading process.*



• Open fill hole cover and install vent tube. This step is important as many gaseous impurities exist in spent sulphuric acid and by venting these gases to a facility scrubbing unit to prevent exposure of these gases to the environment and to employees.



Image 24: Vent tube located above open fill hole to capture the gases of spent sulphuric acid

- Once all siphon pipe fittings are secured, turn on pumps and begin loading, monitoring pumps and volume gauges. During siphon loading, loaders will normally preset volume limits to avoid overfilling tank cars.
- Disassemble siphon pipe fittings and secure siphon pipe cap or flange cap for transportation.
- Since siphon pipe cap and vent valve have been open, tank car is vented for inspection of fill hole gasket. Carefully loosen all fill hole cover bolts and swing safety bolts to down position. Open cover slowly to allow for any remaining pressure to release. Inspect fill hole cover gasket.
- At this point, it may be prudent to take a sample of the acid from the loaded tank car. This allows for quality control of acid production and helps ensure product loaded meets company specifications prior to shipment.
- Secure fill hole cover ensuring correct placement of gasket and ensuring that eye bolts are tool tight. If using a torque wrench, refer to tank car manufacturer's recommendations on proper torque of fill hole bolts. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Turn on air/nitrogen supply to 25 psi; hold pressure at 25 psi for 10 minutes while checking for any acid leaks from any primary or secondary closure on the tank car. If any leaks are present, depressurize tank car before any repairs are made to the tank car.
- Close air/nitrogen valves and open air/nitrogen bleed valve from the air/nitrogen supply line ensuring all pressure has vented from tank car.



- Close vent valve on car (if chain present leave on tank car, if no chain, place handle in tool box)
- Remove air/nitrogen supply line hose from vent valve.
- Replace vent valve plug, securing to a tool tight condition.
- Rinse tank car and all fittings with fresh water. NOTE: 49 CFR 173.24(b)(4) specifically states: "There will be no hazardous material residue adhering to the outside of the package during transport." By rinsing the tank car with fresh water, any sulphuric acid residue on the tank car is removed and reduces the risk of acid exposure to others that may handle the car throughout transportation.
- Affix security seal, and product identification tag.
- Affix DOT approved placards to four sides of tank car.
- Complete post-loading checklist paperwork and prepare secured tank car for transportation.

3.3.2 Unloading spent sulphuric acid

Prior to commencing unloading operations, consult guidelines listed in Section 1: Loading and Unloading General Purpose Tank Cars to Association for American Railroads Pamphlet 34 -- Recommended Methods for the Safe Loading and Unloading of Non-Pressure (General Service) and Pressure Tank Cars.) If tank car arrives on site with evidence of an acid spill, thoroughly rinse tank car with water prior to unloading operation.

- De-pressure tank car through vent valve when venting, be positioned out of the line of flow and ensure no personnel are present in the area to prevent exposure to possible trace amounts of acid spray. When removing plug from vent valve ensure valve is in closed position. Once plug is removed, slowly open the vent valve to release pressure from the tank car.
- Connect air/nitrogen supply to air/nitrogen supply line and ensure vent valve remains in open position.
- Remove and inspect both sides of the rupture disc prior to each load, replacing if necessary. Sulphate build up in the area of the rupture disc is possible. If sulphate build up is present, clean out rupture disc assembly. Replace rupture disc and secure rupture disc assembly. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Remove siphon pipe cap slowly. *Never remove siphon pipe cap before venting the tank car.* Inspect gasket or o-ring, replace if necessary. Some tank car top fittings arrangements are equipped with flange assemblies in lieu of siphon pipe cap. *Never remove flange covers before venting the tank car.*
- Secure loading arm pipe assembly to pipe fittings or secure flange assembly per company
 procedures. TSI observed a number of different methods for securing loading arm to the tank car
 for siphon pipe operations. These included threaded pipe, cam lock devices and bolt and flange
 fittings. These design variables should be addressed in company procedures to ensure a leak
 proof closure during the unloading process.
- Once all siphon pipe fittings are secured, verify that all valves at the tank car are in the correct position to start unloading acid



- Turn on nitrogen/air supply. (See Section 4.0 Conclusions for alternate unloading methods)
- When the pressure on the tank car reaches 15-30 psi open the unloading flow control valve to begin unloading process – acid is now flowing through the piping system into the acid storage tank. Monitor offloading and observe valves and fittings for leaking. TSI observed that unloading rack operators normally made contact with person responsible for storage tanks to ensure product was flowing throughout the system and storage tank volumes were increasing.
- When the tank car is empty, a drop in pressure and the sound of air passing through the discharge pipe will be heard.
- Shut off the nitrogen/air supply line.
- Close any valves in the unloading line.
- Vent all pressure from the tank car through the vent valve.
- Open fill hole cover and inspect tank car to ensure the tank is completely empty.
- Disconnect nitrogen/air supply line.
- Disconnect loading arm and place in loading arm saddle to prevent any spills to the environment
- Disassemble siphon pipe fittings and secure siphon pipe cap or flange cap for transportation.
- Secure fill hole cover ensuring correct placement of gasket and ensuring that eye bolts are tool tight. If using a calibrated wrench, refer to tank car manufacturer's recommendations on proper torque of fill hole bolts. (See 49 CFR 173.31 for gasket and rupture disc inspection criteria.)
- Close vent valve on tank car (if chain present leave on car, if no chain, place handle in tool box)
- Replace vent valve plug, securing to a tool tight condition.
- Rinse car and all fittings with fresh water. NOTE: 49 CFR 173.24(b)(4) specifically states: "There
 will be no hazardous material residue adhering to the outside of the package during transport."
 By rinsing the tank car thoroughly with fresh water, the operator eliminates any sulphuric acid
 residue on the tank car and reduces acid exposure to others that may handle the tank car
 throughout transportation.
- Affix DOT approved placards to four sides of tank car.
- Complete post-unloading checklist paperwork and prepare residue/empty tank car for transportation.



4.0 Conclusions

Over the course of the twelve loading and unloading site visits and subsequent consultation with TSI member company representatives several common themes surfaced as overriding imperatives when loading and unloading sulphuric acid and spent sulphuric acid tank cars. Some of the data that contributed to these themes was collected during the site visit in the form of TSI observations and other data was derived from documented non-accident releases provided by the Association of American Railroads. Themes from the list below fall into three general categories: they may attribute to the safety of individuals loading and unloading sulphuric acid tank cars; they may attribute to the general care and maintenance of the tank car itself, or they may prevent a possible citation from federal inspectors.

- Exposed skin during loading and unloading operations it is critical that loading/unloading personnel are provided with the right personal protective equipment (PPE) to eliminate chemical burns associated with sulphuric acid. While environmental conditions such as extreme heat or extreme cold may factor into PPE decisions, the safety and welfare of the employee should be paramount. To the greatest extent possible all skin should be protected from possible exposure of acid. Consulting with PPE suppliers when selecting equipment for your operation is a good way to help mitigate exposure risks. In addition to the having the right equipment on hand, loading/unloading personnel should be trained and evaluated on proper wear of the PPE.
- Venting of cars the first step during the unloading or loading operations is to vent the tank car
 of any pressure that may have built up during transit. Throughout this study TSI has highlighted
 this as an exposure risk. Company procedures should address this clearly in written instruction
 as well as during safety discussions prior to commencing loading/unloading operations in order
 to mitigate acid exposure to employees to the greatest extent possible.
- Limits of repair if a repair is required for a defect or malfunction on a rail tank car it is imperative that loading operators and supervisors understand the limits of their repair authorizations. Any repairs necessary outside of their authorization must be made by an Association of American Railroads authorized repair facility (which can include a certified mobile repair team). If the repair is made outside the authorized level of repair, the resulting action may damage the tank car further and incur costs to tank car owners/lessees. Federal or state regulatory agencies may also propose citation and monetary fines for unauthorized repairs. Regulatory and railroad industry specifications, standards, and requirements are contained in:
 - USDOT Title 49 Code of Federal Regulations, Parts 173 (Subpart B), 174, 179, and 180 (Subpart F)
 - Transport Canada Transportation of Dangerous Goods Regulations (Transport Canada TDG Regulations) and Containers for the Transport of Dangerous Goods by Rail (Standard TP 14877E)
 - Association of American Railroads Manual of Standards and Recommended Practices (MSRP) Section C-III, Specifications for Tank Cars, Specification M-1002.



- **Rinsing tank cars thoroughly** by rinsing the tank car thoroughly with fresh water following loading or unloading, the loader/unloader eliminates any sulphuric acid residue on the tank car and reduces acid exposure to others that may handle the tank car throughout transportation. In addition to mitigating acid exposures to others, rinsing the tank car thoroughly extends the life of the exterior coating that protects the steel tank car shell from corrosion. Federal or state regulatory agencies may also propose a citation and monetary fine for residue on the outside of the tank car. It is also imperative to contain and treat rinse water so that acid contaminated water is not discharged into sewer or other waste water systems.
- Rupture disc and gasket inspection and placement the NAR data reviewed by TSI suggests
 that some loading/unloading operators may not have adequate training for inspecting gaskets or
 placement of gaskets. Gaskets not properly aligned prior to securing a package for transportation
 can rip or otherwise damage a gasket which can result in a product release. Not only is this incur
 a cost to replace the gasket, it also exposes the loader/unloader receiving the tank to acid as a
 result of the leak. In addition, federal or state regulatory agencies may also propose a citation
 and monetary fine for a NAR. In addition to initial and sustained training, consultation with gasket
 suppliers may help to ensure proper torque values are applied on securement bolts and proper
 materials are used for acid service.
- Differing loading and unloading methods during TSI site observations, there were many differing loading and unloading methods from facility to facility while a closed system may mitigate operator exposure to acid, wearing the proper PPE also mitigates exposure to the open fill hole cover loading method. It is important to recognize the loading and unloading risks associated with any operation. It is equally important to understand that tank car top fittings and loading/unloading facilities work together as a system. When considering a change in supplier, the consuming facility must understand that tank car top fittings may be different and improvements or changes to the loading and unloading equipment may require upgrading. There is also associated training that should be completed when loading/unloading a tank car with differing top fittings.
- **Pump unloading** while the majority of unloading sites TSI visited have equipment designed for unloading tank cars using air pressure, for safety reasons, pump unloading is preferred over pressure unloading for sulphuric acid tank cars. Pump unloading puts the unloading hose under suction so that any leak can be stopped promptly without the need for venting the tank car of the padding pressure. It may be necessary to supply a nominal amount of pressure (1-10 psig) for pump priming or to avoid creating a vacuum in the tank car being unloaded. In this case, the pressure should be the minimum needed for effective pump operation, with appropriate valving and controls for emergency shut-off of air supply and depressurizing. When pumping from the tank car without priming/padding pressure, ensure that the vessel is adequately vented to prevent collapse.



5.0 References

- 1. *Manual of Standards and Recommended Practices Specification for Tank Cars (M-1002),* Association of American Railroads, November 2014
- 2. Pamphlet 34, Recommended Methods for the Safe Loading and Unloading (General Service) of Non-Pressure and Pressure Tank Cars, Association of American Railroads, Bureau of Explosives, January 2013
- 3. 49 Combined Federal Regulation, Transportation (Hazardous Materials Regulation), US Department of Transportation, Pipeline and Hazardous Material Safety Administration, March 2018

Frequently referenced paragraphs from 49 CFR

- a. 49 CFR § 171.8 Definitions and abbreviations
- b. 49 CFR § 171.16 Detailed hazardous material incident reporting
- c. 49 CFR § 172.704 Training requirements
- d. 49 CFR § 173.3 Packaging and exemptions
- e. 49 CFR § 173.24 General requirements for packagings and packages
- f. 49 CFR § 173.31 Use of tank cars
- 4. *Emergency Response Guidebook*, US Department of Transportation, Pipeline and Hazardous Material Safety Administration, 2016
- 5. Sulphur, Sulphur Dioxide and Sulphuric Acid, The British Sulphur Corporation, 1984



6.0 Enclosures

- $1-Loading \ and \ unloading \ check \ lists \ used \ for \ data \ collection \ study$
- 2 Emergency response information



Enclosure 1

Sulphuric Acid Facility Evaluation Checklist - Loading

Category	Yes	No	Comments
Facility Name			
Location			
Type Facility			
Photos Allowed			
Guests Allowed			
Storage Capacity			
Average Loads/Day			
PPE Outerwear			
PPE Head/Face			
PPE Boots			
Compressor (s)			
Pump (s)			
Hose Material(s)			
Valve(s)			
Type(s)/Location(s) of Valve(s)			
Disc / PRV Condition			
Grounding Method			
Check Volume/Weight			
Load Limit Calculation			
Inspect for Leaks			
General Car Condition			
Pre-Load inspection			
Venting Tank Car			
Inspect Dome Gasket			
Inspect Tank Interior			
Loading Arm			
Calculate Loading Time			
Sample / Frequency			



Safety Vent Disc		
Placards (1830 / 1832)		
Pneumatic Closure		
Torque Wrench Closure		
Water Rinse Top of Car		
Additional Observations		

Sulphuric Acid Facility Evaluation Checklist - Unloading

Category	Yes	No	Comments
Facility Name			
Location			
Type Facility			
Photos Allowed			
Guests Allowed			
Storage Capacity			
Average Loads/Day			
PPE Outerwear			
PPE Head/Face			
PPE Boots			
Compressor (s)			
Pump (s)			
Hose Material(s)			
Valve(s)			
Type(s)/Location(s) of Valve(s)			
Disc / PRV Condition			
Grounding Method			
Check Volume/Weight			
Load Limit Calculation			
Inspect for Leaks			
General Car Condition			
Pre-Load inspection			
Venting Tank Car			



1	1	1	1
Inspect Dome Gasket			
Inspect Tank Interior			
Loading Arm			
Usual Unloading Time			
Sample / Frequency			
Safety Vent			
Placards (1830 / 1832)			
Pneumatic Closure			
Torque Wrench Closure			
Water Rinse Top of Car			
Additional Observations			



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Enclosure 2 – Emergency Response Information

It is important to understand the responsibilities of each interested party when shipping hazardous materials, especially during an emergency where a hazardous material release may have occurred. As stated in Section 2.0 of this study, sulphuric acid has unique chemical and physical properties that need to be clearly understood by all stakeholders in the event of a unintended release from a rail tank car. Incident response and incident management following a hazardous material release includes representatives from shippers, carriers, first responders, local and possibly federal government emergency management services, and third party remediation services. Each stakeholder listed above has unique responsibilities during an emergency response. To help with the understanding of these responsibilities, information sharing and conduct of emergency response training or exercises are a good venue to help preclude confusion or mishandling of the product during the emergency causing further risk to responders and the public. There are differences in how emergency response is conducted from state to state as well as differences at the federal level in the United States and Canada. Please refer to the current edition of USDOT Emergency Response Guide or contact local emergency management agencies for further information.



Figure 3: Excerpt on sulphuric acid and spent sulphuric acid from 2016 Edition of Emergency Response Guidebook (ERG); retrieved from:

https://www.phmsa.dot.gov/sites/phmsa.dot.gov/files/docs/ERG2016.pdf