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AHCl anhydrous hydrogen chloride

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Anhydrous hydrogen chloride, AHCl, is a colorless gas with a sharp, irritating odor. It is readily absorbed in water to form hydrochloric acid. It is very hydroscopic (attracts moisture) and in moist air, forms white fumes which are a mist of hydrochloric acid.

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Because of its low boiling point (-85°C, -121°F) and high vapor pressure (603 psia at 20°C (68°F)) AHCl is shipped as a refrigerated liquid.

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In the U.S., AHCl has a subsidiary label of Class 8 (corrosive). AHCl is shipped as a liquefied, compressed gas in small cylinders containing up to 65 lbs in 600-lb containers, and in tube trailers normally containing up to 21,000 lbs. All persons handling cylinders and tube trailers should be familiar with all applicable regulations and safety procedures for AHCl.

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AHCl will react with oxidizing agents to form chlorine gas. AHCl is nonflammable. However, in the presence of water, AHCl attacks most metals with release of flammable hydrogen gas. Potentially explosive mixtures of air and hydrogen could be formed in confined spaces or closed equipment and lines, and in equipment and lines after opening. Confined spaces should be well ventilated and equipment lines should be purged with inert gas or dry air until explosimeter tests show them to be free of hydrogen

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Mention polymerization considerations? Others?

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AHCl forms a strong acid solution and generates considerable heat when exposed to water. Proper handling procedures must be followed to prevent vigorous boiling, splattering or violent eruption of the diluted solution. To prepare an aqueous solution from AHCl, **ALWAYS ADD VAPOR AHCl TO WATER** while providing agitation and cooling as necessary.

CAUTION: Never add liquid AHCl to water unless specifically addressed by detailed operating procedures. Never add water to AHCl.

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HYDROGEN CHLORIDE, ANHYDROUS (AHCL), REFRIGERATED LIQUID (UN 2186),

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HYDROGEN CHLORIDE, ANHYDROUS (AHCL), REFRIGERATED LIQUID (UN 2186),

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This normally means that there is frostbite potential while handling AHCl. Uninsulated liquid lines will frost from atmospheric moisture. The normal boiling

point for AHCl is -121°F (-85°C). **NOTE:** Protective clothing may become brittle at very low temperatures.

If the pressure in a tank car is allowed to drop to 76.5 psig, the corresponding liquid temperature will drop to -50°F (-45.6°C). This will result in the tank car metal being cooled below its safe low temperature embrittlement limit. AHCl tank cars must be designed for loading at -50°F with material meeting Charpy V-notch test requirements (49CFR 179. 102-17).

NOTE:

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AHCl refrigerated liquid will auto-refrigerate when the pressure of a vessel is reduced. The liquid AHCl temperature can drop down to the freezing point of -174°F (-114.4°C) if vapors are removed at a high rate.

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AHCl

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AHCl

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AHCl is a gas at atmospheric pressure. It is very irritating to the skin, eyes, and mucosal surfaces because of the rapid absorption by body moisture forming hydrochloric acid. It can cause serious burns. High inhalation exposures may cause delayed pulmonary edema with cough, chest discomfort, and difficulty in breathing. Contact with vapor can damage the eyes. Prolonged overexposure can cause dental erosion. Ingestion may cause severe acid burns of the mouth, throat, esophagus, and stomach with burning pain of the mouth, throat, chest, and abdomen. Prolonged over-exposure may cause death.

Exposure Guidelines

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The OSHA PEL and ACGIH TLV exposure limits for AHCl are 5 ppm (or 7 mg/m3 and 7.5 mg/m3, respectively). NIOSH's Immediately Dangerous to Life or Health Concentration (IDLH) limit is 100 ppm.

The odor threshold for AHCl is 1-5 ppm. 5-10 ppm will cause physical discomfort.

The Emergency Response Planning Guideline (ERPG) exposure guidelines for a 1 hour exposure period of hydrogen chloride are:

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SPILL PREVENTION PROGRAM

All sites should have a documented spill prevention and containment program for all hazardous materials. Consideration must be given to the containment of AHCl releases or spills (in the case of making contact with water) to comply with applicable federal, state and local regulations.

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TSA REGULATIONS

The U.S. Department of Homeland Security's (DHS's) Transportation Security Administration (TSA) establishes regulatory requirements for the security of passengers and freight in various modes of transportation, including freight rail. TSA security regulations for the transportation of certain hazardous materials, including AHCl and other poisonous-inhalation-hazard (PIH) materials, are included in 49 CFR Parts 1520 and 1580. These regulations establish requirements for designating rail security coordinators, incident reporting requirements, TSA inspections and chain of custody and control (*11.3*).

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INSPECTION CHECKLIST

An inspection checklist should be used for all aspects of the unloading operation. It should include all recommendations contained in this pamphlet plus any company procedures or special requirements specific to each facility. The checklist documents that proper unloading and securement procedures have been completed. The checklist should be retained for records retention as per company policy.

The checklist for procedures to be followed after spotting the tank car or cargo tank should at a minimum include the following items:

Verify the tank is loaded with AHCl by careful inspection of the bill of lading (or other shipping documents), any manway tags, the car/vehicle number and commodity marking.

Inspect the running gear, safety appliances, marking (including stenciling), placarding and other pertinent items. The purpose of this portion of the inspection is to identify all defects in the tank before unloading any AHCl

Verify that the tank security has been maintained. (i.e. protective housing sealed with cable, if provided by supplier, or driver assurance)

Remove the cable seal and open the housing cover and inspect the manway fittings for evidence of a leak.

If unloading to a storage tank, verify there is sufficient capacity to receive the AHCl to be transferred.

Verify the angle valve is fully closed before removing the angle valve plug.

Check discharge systems and transfer hoses

Verify that brakes are set, wheels are chocked, derails are in place (for tank cars) and appropriate caution signs are in place.

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It is the responsibility of each unloading site to ensure all applicable regulations and Institute guidance are followed. Quoted below is an excerpt from the Spring/Summer 1991 (Volume 91, Number 1) issue of DOT Hazardous Materials Transportation Safety Newsletter (*11.2.*), which provides guidance on monitoring during transloading/unloading operations.

Railroad Tank Cars: The tank car and all components directly involved in unloading must be under continuous observation, either human or non-human, such as mechanical or electronic. See 174.67(a)(1) and 174.67(i). This requirement would be satisfied by employing the following guidelines, as applicable.

Human Monitoring:

must be performed by the person responsible for unloading;

may be on-site or from a remote location;

(the observer) must have an unobstructed view of the tank car and unloading components; and

(the observer) must have the capability to halt the flow of product immediately.

Non-Human Monitoring:

the equipment used must provide, on-site or at a remote location, surveillance capability at least equal to that of a human observer;

the equipment used must be designed to provide immediate notification of malfunction to a person responsible for unloading OR, if not so designed, the equipment must be checked at least once every hour for proper functioning;

in the event of known equipment malfunction, human observation of the unloading, (see above), must be instituted immediately; and

the person responsible for unloading must have the capability to halt the flow of product immediately.

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Insulation blanket and spray-on foam

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this can be estimated by knowing how many days have elapsed since the tank was shipped. Depending on the time of year, a conservative pressure will be approximately:

Summer: ((Days elapsed since shipment) X (14 psig/day)) + 90 psig

Winter: ((Days elapsed since shipment) X (8 psig/day)) + 90 psig

NOTE: Empty cars will normally contain no liquid heel and will be at a pressure of 60-90 psig. Also, higher pressure rates per day are possible when the car has significant damage to the insulation.

If the tank car sustained damage to the insulation the pressure rise can be significant.

The pressure rise will be dependent on the amount of tank which is exposed. The resultant pressure rise cannot be estimated, but expect a significant pressure rise rate even for small areas of damage.

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If the tank is upright and valves are accessible and operable, install a pressure gauge in the vapor valve of the tank.

If the tank is not upright, or damage to valves prevents their use, install a thermocouple through the insulation jacket (11 gauge steel) and through the 6" of urethane insulation. Ideally the thermocouple end should be in contact with the outer skin to the tank (below liquid level in car).

This temperature measurement can then be converted to a pressure (not valid if tank is empty) using the vapor pressure data in Appendix C. The outer temperature as measured by the thermocouple will likely be a little higher than the core AHCl temperature in the tank. This may result in a pressure that is 5-10% higher than actual.

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Tank pressure is high (about 300 psig) and/or movement is delayed or insulation has major damage or tank is leaking.

Venting caps used to stop an angle valve or pressure relief system leak
Making a field transfer of AHCl to tank

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AHCl

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AHCl

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, copper, or plastic

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, copper, or plastic

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The heat of solution between water and HCl will heat up the solution. Temperature should be monitored. Absorbing AHCl into water results in a temperature increase because of the heat of solution. (Infinite dilution is 882 btu/lb.). Because of the temperature increase, the final concentration of HCl in the tank will be minimized. Absorbing 5,000 lbs. of AHCl into 35,000 lbs. of water will increase the temperature about 120°F from the starting water temperature. It may be necessary to further dilute the solution with cool water to lower the temperature or use another scrubbing vessel. If adding H_2O to control the temperature excess flow from scrubbing vessel could be diverted over crushed limestone for further neutralization. The diverted flow should be contained. Monitor the pH. Add more limestone if the pH is below 6.0. **Note:** Need local EPA approval for any discharge to the ground.

There will be additional heat of reaction between the HCl solution and any caustic medium (the heat of neutralization is about 1,000 btu/lb). The temperature of the solution should be monitored.

Aqueous HCl is very corrosive and almost all metals are not recommended. Rubber lined equipment, TFE lined equipment, certain plastics or fiberglass materials are recommended.

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The heat of solution between water and HCl will heat up the solution. Temperature should be monitored. Absorbing AHCl into water results in a temperature increase because of the heat of solution. (Infinite dilution is 882 btu/lb.). Because of the temperature increase, the final concentration of HCl in the tank will be minimized. Absorbing 5,000 lbs. of AHCl into 35,000 lbs. of water will increase the temperature about 120°F from the starting water temperature. It may be necessary

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Aqueous HCl is very corrosive and almost all metals are not recommended. Rubber lined equipment, TFE lined equipment, certain plastics or fiberglass materials are recommended.

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as may be needed to lower the pressure or in transloading operations, the options below can be considered. Approximately 2,500-3,000 pounds (as AHCl) is required to be vented for every 25 psig reduction in tank pressure desired.

The preferred method of doing this is to vent/scrub into a limestone pit. This pit could be above or below ground. For scrubbing a full tank car the following size and amount of material is recommended. A cargo tank will require a smaller pit and the process should be sized accordingly. A pit approximately 30 x 50 x 10 feet is required for this operation. The pit needs to be lined with a 30-50 mil liner constructed of neoprene, polypropylene or other compatible material. A distribution/sparger system constructed out of a suitable material (schedule 80 stainless steel, CPVC) needs to be constructed to disperse the HCl at the bottom of the pit. Stainless steel flex hose is used to connect the car's liquid lines to the distribution system. Approximately 75,000 pounds of six inch limestone needs to be used as the first layer and covered with 150,000 pounds of crusher run. Cold water is added to the pit and the scrubbing operation is begun. Water will need to be added to the system to keep the operation cool. An equivalent amount of water will have to be removed for disposal. **NOTE**: Water should be removed from the top of the pool to avoid capturing unreacted material.

CAUTION: Vacuum breaks are required on the flow line, because water will backflow all the way to tank valves if blocked in with HCl fumes in line. Very hydroscopic! Attracts H_2O!

Figure 10.1 provides a schematic example of venting/scrubbing into a limestone pit.

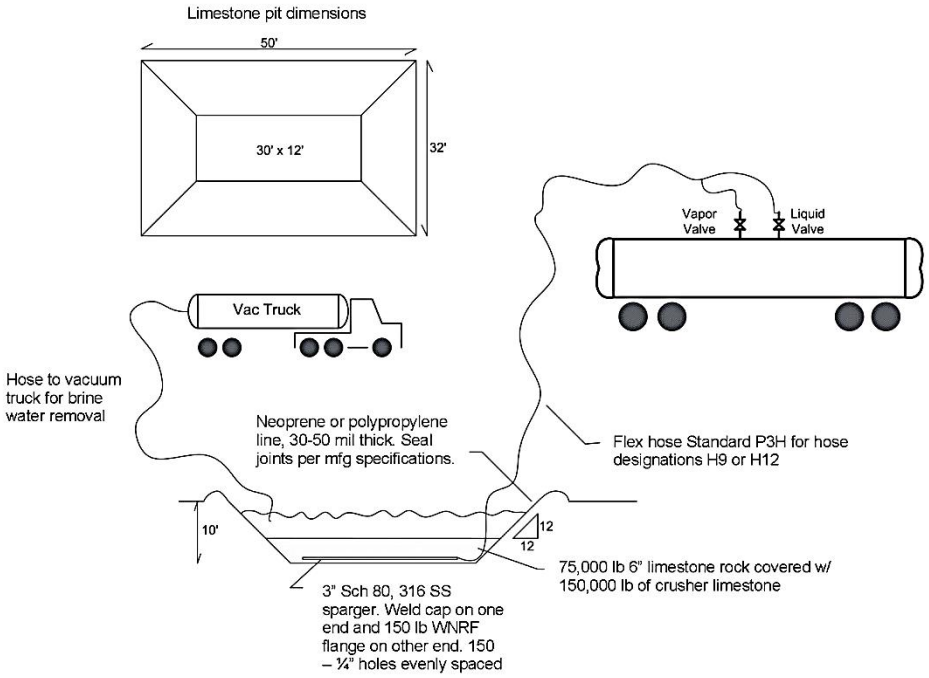

Figure 10.1 Example of Venting/Scrubbing of AHCl into Limestone Pit

An alternative preferred option is the use of rubber-lined equipment (cargo tank, tank cars) that can be used for scrubbing AHCl vapors, if available. A distributor or sparger (plastic or other non-metal) should be placed on the bottom of the equipment. The piping can have small holes drilled in it every few inches to maximize the distribution of AHCl and scrubbing efficiency. The equipment should be full of cold water, allowing enough outage for the AHCl that will be absorbed. For example, a rubber-lined tank truck should contain evolution of fumes from the scrubbing equipment. The heat of solution will heat up the water/HCl in the rubber lined equipment and the temperature should not be allowed to go above 150-175°F, depending on the type of rubber. Absorbing 5M pounds of AHCl into 35M pounds of water will result in a temperature increase of around 120°F, so the initial water temperature must be cold.

CAUTION: Vacuum breaks are required on the flow line. H_2O will back up into and all the way to tank valves if blocked in with HCl fumes in line. Very hydroscopic! Attracts H_2O!

Figure 10.2 provides a schematic example of using a rubber-lined cargo tank or tank car for scrubbing.

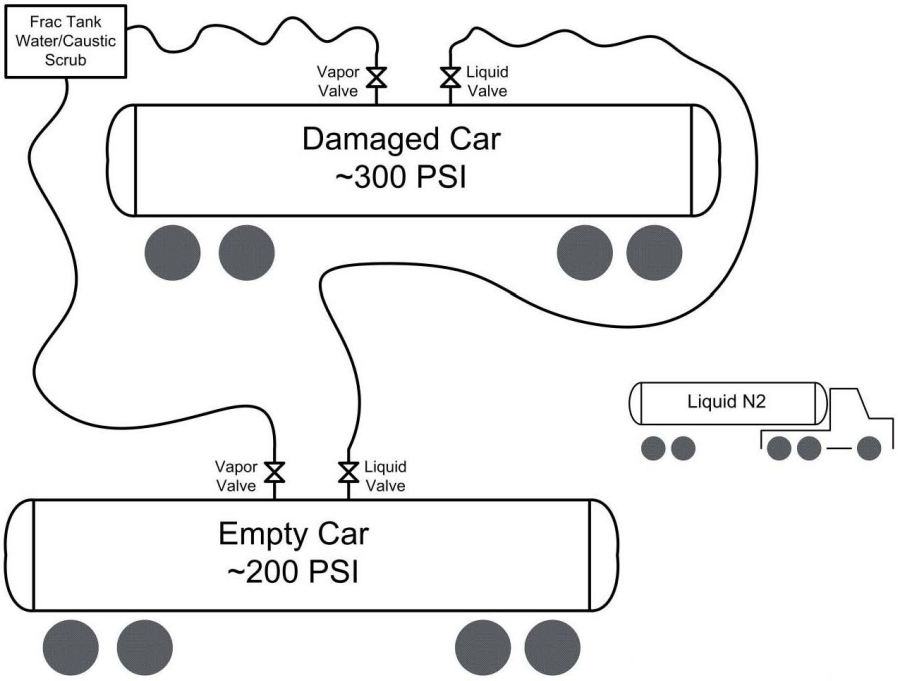

Figure 10.2 Example of Using Rubber-Lined Cargo Tank or Tank Car for Scrubbing AHCl

A large skid tank with open top can be partially filled with limestone and water to act as a scrubber/neutralizer. As in Figure 10.1, a distributor or sparger should be placed at the bottom of this tank. The piping can be steel. Because the AHCl will be neutralized very quickly once it is in the tank. The main concern of this operation is temperature generation. The neutralization of the HCl by the limestone will cause additional heat increase compared to water alone. The temperature in this tank should reach the boiling point of water. Multiple tanks will be needed if an entire tank car is going to be scrubbed.

Temperature should be controlled below 175-190°F by removing some of the neutralized solution and replacing with cold water or starting to use a “fresh” skid tank filled with water and limestone.

A vacuum truck filled with lime slurry or calcium hydroxide/water solution. A Teflon lined hose or other piping can be connected to the normal bottom inlet to the vacuum truck tank. As in Figure 10.2, the heat of reaction will gradually heat up the contents in the truck. Because of the temperature limitation on the truck (about 175-195°F), the amount of AHCl that could be absorbed into a 2000

gallon lime slurry would be about 1,125 pounds. Multiple loads will be required to do the scrubbing.

This amount of HCl absorbed would require 875 pounds of lime (as 100% calcium oxide) or 1150 pounds of calcium hydroxide (as 100% Ca (OH) 2). This option has been successfully used in field trials.

An empty AHCl tank car can be used to vent the full, high pressure tank car into, in the event that an empty tank car is readily available. The amount that can be vented into an empty 20,000 gallon car is about 4,000 pounds at an ending pressure of 200 psig in the empty tank car. This would result in a pressure decrease in the event the full tank car is at very high pressures (400 psig) and time is needed until other options can be used. Empty tank cars are unlikely to be available due to the small size of the AHCl tank car fleet.

NOTE: Can get 4,000 lbs. only if empty tank car is at 0 psig.

The resulting neutralized HCl will be in the form of calcium chloride, calcium hydroxide or sodium chloride depending on the caustic source (lime, calcium hydroxide or sodium hydroxide/soda ash). Local regulation should be followed on the proper disposal of the neutralized material.

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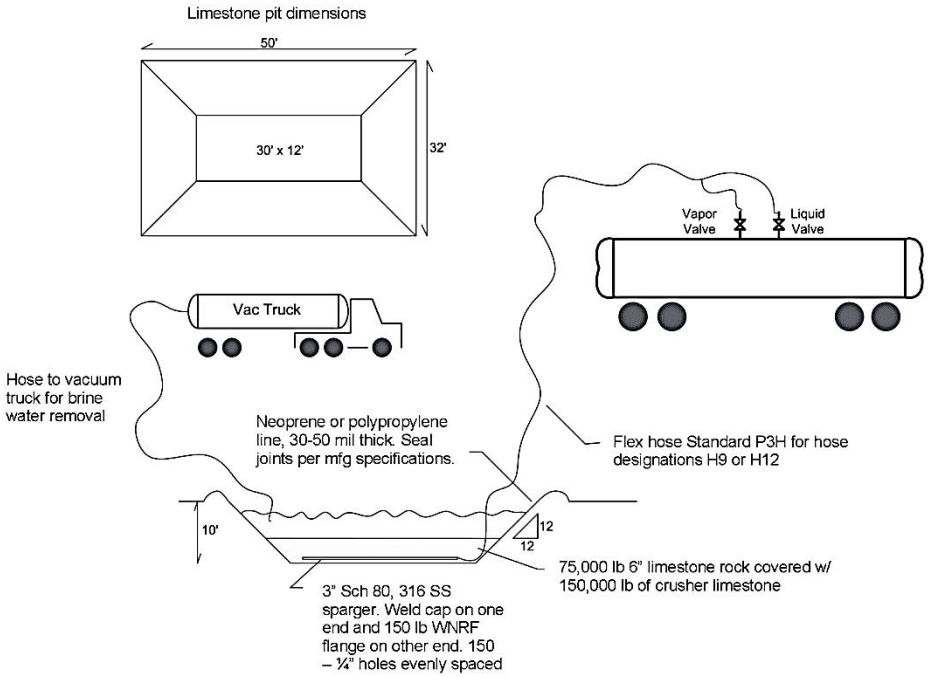

Figure 10.1 Example of Venting/Scrubbing of AHCl into Limestone Pit

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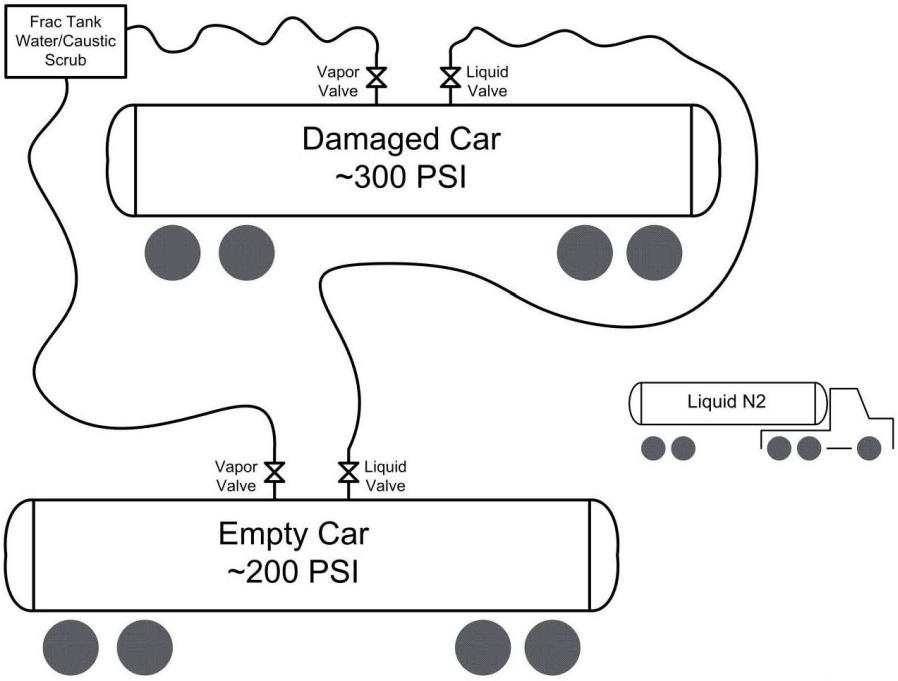

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NOTE: Can get 4,000 lbs. only if empty tank car is at 0 psig.

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Also refer to it as Health, Safety, and Work Plan (HSWP) here (name used further below)?

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This should be considered a last option – (all other options have been eliminated and/or the local authorities are requiring it). An empty AHCl tank will need to be transported to the incident scene. This will take considerable time since the AHCl tank car fleet size is quite small. Time may not permit this operation.

Transfer Technology

Transfer full tank to empty tank using pressure differential; vent the empty tank to a scrubber system as described above.

General Procedure

Loaded tank is at 300 psig (-10°C), empty tank will be controlled at 200 psig (-24°C); therefore, 100 psig differential. The empty tank will initially be at 0 psig and ambient temperature (25°C). Empty tank venting requirements are divided into two parts:

The amount of AHCl flashed to cool down the empty tank from 25°C to -10°C. This is estimated to be between 7,000 lbs. and 10,000 lbs. AHCl. Comment: The amount will be less if the empty tank is already cold. The empty tank can be cooled (if desired) using cold carbon dioxide ($CO_{2)}$ or nitrogen (N_2) gas.

The amount of AHCl flashed to lower the empty tank temperature from -10°C to -24°C. This is estimated to be between 9,000 lbs. and 10,000 lbs.

NOTE: Lower differential pressures will result in less being vented; if a 50 psig differential is used, only 5,000 lbs. will be required to lower

the AHCl liquid temperature to the final conditions. Total Venting = 16,000 lbs. to 20,000 lbs.

The venting could be directed to a portable scrubber or rubber-lined trucks that have distributor piping along the bottom for distributing the AHCl vapor. Rubber-lined equipment can tolerate up to 150° through 175°F. The vapor pressure of a 12.5% HCl solution is 1.3 mm Hg at 175°F. The initial water temperature would need to be between 32°F and 55°F (may want to consider adding ice to water). Three to four empty, rubber-lined trucks would be required to complete this transfer.

The use of pressure gauges on both full and empty tanks and block and bleed assemblies to allow bleeding pressure before break into AHCl line is required. The vent valve on the empty tank should be a globe valve so that the pressure in the empty car can be controlled between 80 psig (minimum) to some pressure below that of the full car.

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If neutralizing into a compatible high pH solution, remember the chemical change taking place and the location of the reaction.

If scrubbing into water, remember that the water is becoming acidic.

Remember that a significant temperature rise will occur in the neutralizing or scrubbing solution.

Insure adequate neutralizing/scrubbing medium is available. Insure adequate neutralizing chemical is available in the neutralizing solution, if used.

Consider sampling the neutralizing/scrubbing solution to determine the pH.

Take into account the ambient temperature conditions in the transloading and neutralization/scrubbing processes.

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A total of at least 20 valves, 5 hoses, 3 check valves and several manifolds will be needed

Transloading will be a slow and labor intensive proces

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Information is available on emergency response kits that can be used on AHCl tank cars, including the Chlorine Institute Kit “C” (or C-Kit) and the Midland Emergency Response Kit (ERK). Information and guidance on the C-Kit can be found in instruction booklet and corresponding video, which are available through CI (*11.1*). Information and guidance on the Midland ERK, which has a maximum

design pressure of 500 psig, can be obtained through Midland Manufacturing at 847-677-0333 or http://www.opwglobal.com/midland.

Capping kits may not be able to contain leaks at a pressure of 250 psig and above. The kit's primary value is to divert the leak to a scrubber (or just away from the dome area) until the car can be emptied. Current designs do not provide any gasket support, so at higher pressure the gaskets are forced away from the cap. Section 10.4 provides additional background on scrubbing options and temperature rise.

Capping kit guidelines:

Do not attempt to cap a car above 250 psig or one with a significant leak below 250 psig. Experience has shown capping a car at pressures above 250 psig is very difficult.

Use the cap to divert the leak to a scrubbing source until the car can be neutralized/scrubbed.

Avoid moving a car that has been capped. Only consider this if the car is liquid-free, the leak has stopped and the distance to a handling/producing or other chemical site is very small. A one-time movement approval (OTMA) must be obtained from FRA, or a temporary certificate from Transport Canada, prior to moving a tank car that has been leaking.

If capping of the pressure relief device is required, pressure monitoring is also required, and the tank car should be emptied (by transloading or to the process). The time in which a pressure relief device is capped must be minimized, because pressure will rise as AHCl warms. Capping the relief device eliminates the design overpressure protection.

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Any tank in the fire will have some amount of insulation missing. Temporary insulation must be added as soon as safely possible.

1. Inject foam into the shell space between the tank and the insulation jacket. (Drill holes in the jacket as required).

2. Infrared scans can identify voids in insulation.

The relief valve may be leaking due to cycling

1. Pressure MUST be considered before capping

2. Insulation issues must be addressed before capping.

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65 *Personal Protective Equipment for Chlor-Alkali Chemicals*, ed. 6; Pamphlet 65; The Chlorine Institute: Arlington, VA, **2015**.

98 *Recommended Practices for Handling Hydrochloric Acid in Tank Cars*, ed. 4; Pamphlet 98; The Chlorine Institute: Arlington, VA, **2013**.

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99	*Hydrogen Chloride, Anhydrous (Non-Refrigerated) – Use, Handling and Transportation of Cylinders and Tube Trailers*, ed. 3; Pamphlet 99; The Chlorine Institute: Arlington, VA, **2008.**
150	*Recommended Practices for Handling Hydrochloric Acid in Cargo Tanks*, ed. 3; Pamphlet 150; The Chlorine Institute: Arlington, VA, **2014**.
160	*Estimating the Area Affected by a Hydrogen Chloride Release,* ed. 1; Pamphlet 160; The Chlorine Institute: Arlington, VA, **1999.**
IB/C	*Instruction Booklet: Chlorine Institute Emergency Kit "C" for Chlorine Tank Cars and Tank Trucks*, ed. 10; Pamphlet IB/C; The Chlorine Institute: Arlington, VA, **2014**.
C-DVD	*Emergency Kit "C" for Chlorine Tank Cars and Tank Trucks*: C-DVD; The Chlorine Institute: Arlington, VA, **2014**.

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