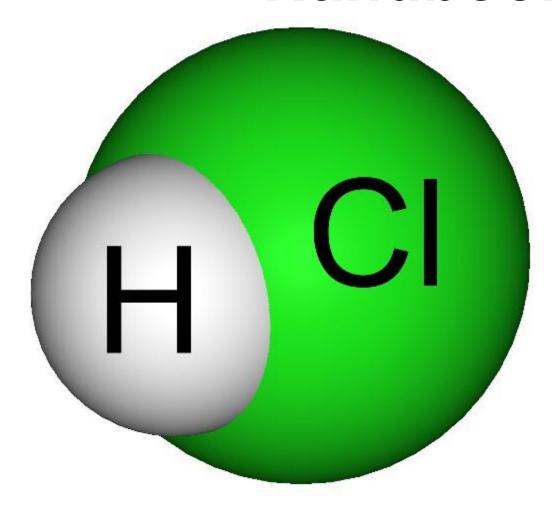
# Hydrochloric Acid Handbook





Dallas-based Occidental Chemical Corporation is a leading North American manufacturer of basic chemicals, vinyls, and performance chemicals directly and through various affiliates (collectively, OxyChem). OxyChem is also North America's largest producer of sodium chlorite.

As a Responsible Care® company, OxyChem's global commitment to safety and the environment goes well beyond compliance. OxyChem's Health, Environment and Safety philosophy is a positive motivational force for our employees, and helps create a strong culture for protecting human health and the environment. Our risk management programs and methods have been, and continue to be, recognized as some of the industry's best.

OxyChem offers an effective combination of industry expertise, experience, online business tools, quality products and exceptional customer service. As a member of the Occidental Petroleum Corporation family, OxyChem represents a rich history of experience, top-notch business acumen, and sound, ethical business practices.

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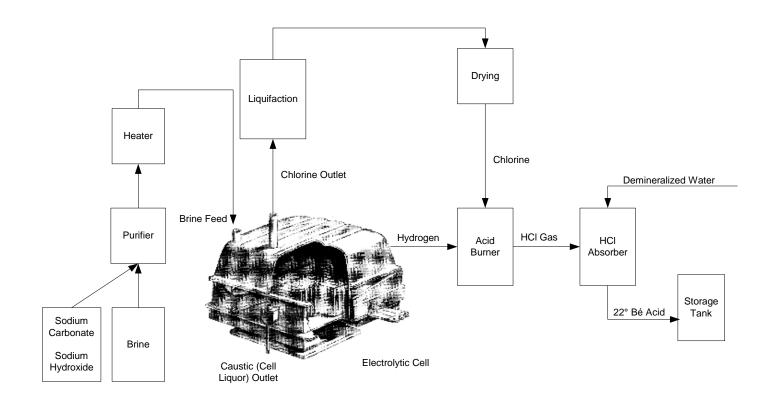
#### **Introduction to Hydrochloric Acid**

#### Manufacturing

Hydrochloric acid, also known as muriatic acid, is an aqueous solution of hydrogen chloride gas. Hydrochloric acid is produced in the United States primarily by four basic methods: the chlorination of organic chemicals, the combination of hydrogen and chlorine, the salt-sulfuric acid production process, and as a co-product in the manufacture of silica. Most hydrochloric acid is produced from the chlorination of organic chemicals with much smaller amounts from the other processes.

OxyChem produces its hydrochloric acid by combining hydrogen and chlorine in "acid burners." The resulting hydrogen chloride gas is then absorbed in demineralized water to yield a high purity hydrochloric acid. OxyChem also markets hydrochloric acid produced by a number of other manufacturers. This material is a co-product from the production of other chemicals.

#### **OxyChem Production of Hydrochloric Acid**



#### **Hydrochloric Acid Uses**

Hydrochloric acid is an important and widely used chemical. The largest end uses for hydrochloric acid are steel pickling, oil well acidizing, food manufacturing, producing calcium chloride, and ore processing.

#### Steel pickling

Hydrochloric acid is used in pickling operations for carbon, alloy, and stainless steels. Steel pickling is the process by which iron oxides and scale are removed from the surface of steel by converting the oxides to soluble compounds. Pickling is required for steel products that undergo further processing such as wire production, coating of sheet and strip, and tin mill products. Hydrochloric acid is used primarily for continuous pickling operations in which hot-rolled strip steel is passed through a countercurrent flow of acid solution.

In addition to steel pickling, hydrochloric acid is used in aluminum etching, metal prefixing for galvanizing and soldering, and metal cleaning.

#### Oil well acidizing

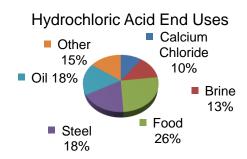
Hydrochloric acid is used both to remove rust, scale, and undesirable carbonate deposits in oil wells to encourage the flow of crude oil or gas to the well. This use is called "stimulation." Acidizing is generally done in carbonate or limestone formations by stimulation. An acid solution is injected into the formation, which dissolves a portion of the rock and creates a large pore structure in the formation, increasing its effective permeability and the flow of oil.

#### Food

The food industry uses hydrochloric acid in the processing of a variety of products. A major use of hydrochloric acid by the food industry is for the production of corn syrups such as high-fructose corn syrup (HFCS). Much of the hydrochloric acid consumed in the HFCS industry is used to regenerate the ion exchange resins that are employed to remove impurities. Hydrochloric acid can also be used to acid-modify cornstarch and to adjust the pH of intermediates, final product, and wastewater. The largest use of HFCS is in the production of soft drinks, which accounts for 70-75% of demand.

#### Other food uses

Hydrochloric acid is also used in other food processing applications including the production of hydrolyzed vegetable protein and soy sauce. It is used in acidulating crushed bones for the manufacture of gelatin and as an acidifier for products such as sauces, vegetable juices and canned goods.



Hydrochloric acid is also consumed in the production of artificial sweeteners and in the production of lysine, choline chloride (both used primarily as animal feed additives) and citric acid.

#### **Production of Calcium Chloride**

Neutralizing hydrochloric acid with limestone (CaCO<sub>3</sub>) produces calcium chloride. The largest use for calcium chloride is highway deicing with production dependent on weather conditions. Other uses include dust control, industrial processing, oil recovery, concrete treatment, and tire ballasting. Calcium chloride is also used in oil recovery products such as drilling muds and work over/completion fluids.

#### **Ore Processing**

Hydrochloric acid is consumed in many mining operations for ore treatment, extraction, separation, purification, and water treatment. Significant quantities are used in the recovery of molybdenum and gold. Hydrochloric acid is used to convert high-grade scheelite concentrate (CaWO<sub>4</sub>) and crude sodium tungstate to tungstic acid, which in turn, can be used to produce tungsten metal and chemicals. Hydrochloric acid is also used in uranium and zirconium processing, solution mining of borate ores, as a pH regulator in the froth flotation of potash ores, and in rare earth extraction from bastnasite.

#### Other

Aqueous hydrochloric acid is used in a variety of miscellaneous applications. These include recovery of semiprecious metals from used catalysts, use as a catalyst in synthesis, use in catalyst regeneration, pH control, regeneration of ion exchange resins used in wastewater treatment and electric utilities, neutralization of alkaline products or waste materials, and in brine acidification for use in the production of chlorine and caustic soda.

Hydrochloric acid is also used in many other production processes for organic chemicals. It can be used in the production of p-phenylenediamine, polycarbonate

resins, bisphenol A, polyvinyl chloride resins, and ethanol (from ethylene).

The pharmaceutical industry consumes hydrochloric acid as a catalyst in synthesis, for pH control, for deionization of water and as a reduction agent (e.g., in the production of ascorbic acid and para-aminobenzoic acid).

Numerous other uses of hydrochloric acid include: the manufacture of dyes and pigments; the removal of sludge and scale from industrial equipment, the deliming, tanning and dyeing of hides by the leather industry, manufacture of permanent wave lotion, the carbonizing of wool, as a bleaching and dyeing assistant in the textile industry, and the purification of sand and clay.

#### **Specifications and Product Grades**

OxyChem produces and markets Technical Grade Hydrochloric Acid in two concentrations: 22° Baumé (35.21% HCl by wt.) and 20° Baumé (31.45% HCl by wt.). Other dilute concentrations of hydrochloric acid may be available upon request

Technical Grade acid meets the testing The requirements of Food Chemicals Codex as well as ASTM Standard E 1146. Material produced and shipped from OxyChem's Wichita plant is Star-K Kosher certified and is certified by NSF under ANSI/NSF Standard 60 Drinking Water Treatment Chemicals. The manufacturing process for Technical Grade Hydrochloric Acid does not incorporate all of the Food measures specified in the and Drua Administration's current Good Manufacturing Practices (cGMP). It is the responsibility of the user to assess their use of Technical Grade Hydrochloric Acid products in food, feed, or pharmaceutical related applications and determine whether appropriate regulatory requirements are being met.

OxyChem's Technical Services Department can provide product information for each grade of hydrochloric acid. Call or write:

Technical Services Department OxyChem 6200 S. Ridge Rd Wichita, KS 67215 Phone: 800-733-1165, option #1

Oxychem tech service@oxy.com

#### Safety & First Aid

Protective Clothing



#### **Hazards**

Hydrochloric Acid is a highly corrosive and hazardous chemical and should be handled with extreme care. Personnel should be properly trained in the handling of hydrochloric acid and should always wear the proper protective equipment when working around hydrochloric acid. All users should read the Safety Data Sheet (SDS) before handling hydrochloric acid.

Hydrochloric acid is very corrosive to the skin and mucous membranes and can cause severe burns to any part of the body. The corneas of the eyes are especially sensitive to hydrochloric acid and exposure to it or its vapors immediately causes severe irritation. If the eyes are not quickly and thoroughly irrigated with water, partial or total visual impairment or blindness can occur.

It is recommended that employees be provided with and required to use acid impervious clothing, gloves, boots, splash proof goggles and other appropriate protective clothing necessary to prevent any possibility of skin contact with hydrogen chloride mists or solutions. Material types which may be considered for this service include nitrile, neoprene, polyvinyl chloride (PVC), butyl rubber, Responder®, Trellchem®, and Tychem®. Face shields should also be provided when there is a chance of splashing liquid hydrochloric acid. Face shields can augment protection provided by splash-proof goggles and safety glasses, but are not intended to replace these safety appliances.

Hydrochloric acid has excellent warning properties. Concentrations of 0.3 parts per million (ppm) can be detected by smell, and concentrations above five parts per million will cause discomfort.

OSHA has established a ceiling value of five parts per million (5 ppm) for hydrochloric acid. This means that an employee's exposure to hydrogen chloride should at no time exceed five parts per million. Effective in 2003, the ACGIH TLV® for hydrogen chloride is a ceiling value of 2 ppm

#### **Respiratory Protection**

OSHA requires that employees using respirators should be properly fitted and trained in their use.

#### There are three main types of respirators:

#### 1. Escape

In areas where the unexpected release of hydrogen chloride vapors may lead to potentially dangerous exposure, appropriate escape respirators should be carried by or be readily accessible to each employee. The most common respirator used for this purpose is the mouthpiece respirator. This respirator contains a single cartridge with a mouthpiece and nose clip. Employees should only use this respirator when escape times are short and airborne concentrations of hydrogen chloride vapors are low.

#### **MOUTHPIECE RESPIRATOR (Escape Only)**



#### 2. Air Purifying Respirators

Air purifying respirators contain cartridges or canisters of absorbent or reactive material to remove harmful gases from breathing air. These respirators are available as either half face or full-face units. For hydrochloric acid service, use a cartridge or canister designed for hydrogen chloride service.

Where vapor concentration exceeds or is likely to exceed 5 ppm, a cartridge or canister respirator should be used. When working in environments where airborne concentrations are irritating to the eyes, full-face piece respirators should be used. Cartridge or canister respirators are strictly air-purifying devices and must never be used in an oxygen deficient atmosphere (less than 19.5% oxygen by volume), in environments immediately dangerous to life or health (IDLH), or areas containing unknown concentrations of hydrochloric acid.

It is important to remember that cartridges and canisters

have a limited service life. Conditions such as humidity, chemical concentrations in the workplace, other chemicals in the workplace, and frequency of use will affect cartridge and canister service life. Therefore, an evaluation of workplace conditions should be made to determine the appropriate cartridge/canister replacement schedule.

#### **FULL FACE AIR PURIFYING RESPIRATOR**



#### 3. Self-contained Breathing Apparatus

Self-contained breathing apparatus (SCBA) can provide respiratory protection in an oxygen-deficient environment and in situations where unknown concentrations of hydrogen chloride vapors are present. The SCBA can also provide protection in emergency situations.

#### **SELF-CONTAINED BREATHING APPARATUS**



The SCBA is an atmosphere-supplying respirator for which the breathing air source is designed to be carried by the user (OSHA definition). A full-face mask is always used with this type of apparatus. OSHA requires that when wearing the SCBA in an IDLH atmosphere (i.e. oxygen deficient or unknown concentrations of hydrogen chloride, as could be expected in an emergency situation), the SCBA be operated in the pressure demand mode and be certified by NIOSH for a minimum service life of 30 minutes. Escape SCBA devices are commonly used with full face pieces or hoods and, depending on the supply of air, are usually rated as 3 to 60 minute units.

OSHA requires that all respirators must be NIOSH approved and shall use breathing gas containers marked in accordance with the NIOSH respirator certification standard, 42 CFR part 84. For further information on regulations pertaining to respirator equipment, see 29 CFR 1910.134 and 30 CFR § 57.5005 For additional information see DHHS (NIOSH) Publication No. 2005-100, NIOSH Respirator Selection Logic 2004 or Publication No. 87-116, NIOSH Guide to Industrial Respiratory Protection.

#### **Safety Precautions**

Water should always be easily accessible whenever hydrochloric acid is stored or used. Safety showers and eye wash fountains should be located in the immediate work area and clearly marked. These units should be tested on a regular basis. Portable or temporary systems are available. Every precaution should be taken to ensure that a suitable system is in place and operational before handling hydrochloric acid. Only trained and properly protected personnel should be allowed to enter areas where hydrochloric acid is present. ANSI Standard 2358.1 contains placement and performance criteria for emergency eyewash and shower equipment.

Before entering tanks or opening pipelines that have contained hydrochloric acid, they should be drained or pumped out and thoroughly flushed with water. Contact with the liquid draining from the equipment should be avoided. Do not enter a confined space (which includes tanks or pits) without following proper entry procedures such as 29 CFR 1910.146.

Good housekeeping practices are important where hydrochloric acid is used. All spills should be contained and immediately recovered or flushed with water into a chemical sewer or a segregated holding basin which is provided for the specific purpose of neutralization. Hydrochloric acid must never be flushed to a sanitary sewer or other outlet which connects to waterways or uncontrolled runoff streams. Contact local and federal authorities for applicable regulations.

See Page 29 of this handbook for specific

recommendations on spills and neutralization.

#### First Aid

Eye Contact - The eyes should be immediately flushed with large amounts of water continuously for at least 15 minutes. Get immediate medical attention. It is necessary to hold the eyelids apart while flushing to ensure complete irrigation of the eye. Washing eyes within several seconds is essential to achieve maximum effectiveness. A delay of a few moments or incomplete washing can result in partial or permanent blindness. Never attempt to neutralize hydrochloric acid in the eyes with chemicals. Do not apply oils or ointments unless specifically prescribed by a physician.

**Skin Contact** - Flush the area of contact with large amounts of water. Contaminated clothing should be removed while underneath a safety shower. Get immediate medical attention. Do not attempt to neutralize the acid with alkaline solutions. No oils or ointments should be applied unless specified by a physician.

Inhalation – Remove individual to fresh air and get immediate medical attention. In cases of severe exposure, humidified oxygen should be administered by someone medically trained to administer oxygen. If respiration or pulse has stopped, have a trained person administer Basic Life Support (Cardio-Pulmonary Resuscitation and/or Automatic External Defibrillator) and CALL FOR EMERGENCY SERVICES IMMEDIATELY.

**Ingestion** - Get immediate medical attention. If individual is a fully conscious, give large amount of water. Do not use sodium bicarbonate in an attempt to neutralize the acid. Do not induce vomiting. Never give anything by mouth to an unconscious person.

**Traumatic Shock** - Whenever injured persons are being cared for, the person administering first aid should watch for signs of traumatic shock. Traumatic shock may follow serious injury and is a depressed condition of many body functions due to inadequate blood circulation throughout most of the body. Signs of shock are pale, moist, cool skin, shallow and irregular breathing, and weak pulse.

Beads of perspiration may be noted about the lips, forehead, palms, and armpits. The patient may become nauseated.

To treat shock, keep the patient lying down and as warm and comfortable as possible. Raise the patient's feet eight to twelve inches unless there is head injury, breathing difficulty, or if the patient complains of added pain.

#### Regulatory

The regulations discussed below are specifically applicable to hydrochloric acid. These summaries are not intended to be complete or legal interpretations, nor a thorough summary of all applicable regulations. Rather, these summaries are intended to address regulatory issues that frequently prompt questions from users.

These summaries also do not address any similar state or local regulations, some of which may impose additional or different obligations from those imposed by federal regulations. All users are responsible for a complete review of the applicable regulations pertaining to their own operation.

## Reporting requirements under the Emergency Planning and Community Right-To-Know Act (EPCRA)

Hydrochloric acid is subject to some, but not all of the reporting provisions of EPCRA. Since hydrochloric acid is listed in 40 CFR Part 302.4 as a hazardous substance, it is subject to the emergency release notification requirements under Section 304 of EPCRA. It is also subject to the hazardous chemical storage reporting requirements under Section 312.

Hydrochloric acid (solution) is not listed under 40 CFR Part 355 as an extremely hazardous substance.

Hydrochloric acid (in aerosol form) is listed under 40 CFR Part 372.65 as a reportable substance, and is subject to Toxic Chemical Release Inventory (TRI) Reporting rules found at 40 CFR 370 and 372.

#### **Calculations**

Reportable quantity and threshold quantity limits are based on the pounds of HCl in the solution, not the pounds of product. As an example, the reportable quantity for 22° Bé (35.21%) Hydrochloric acid is 14,200 lbs., or about 1,448 gallons.

#### Spill Reporting

The reportable quantity (RQ) for Hydrochloric Acid is 5,000 pounds (calculated as anhydrous HCl). Any spill or release in excess of the RQ within a 24-hour period must be reported immediately to the following agencies:

Local Emergency Planning Commission (LEPC) State Emergency Response Commission (SERC) National Response Center (800-424-8802)

And any other state or local authority requiring incident notification. Note that some state or local authorities may have a more restrictive reportable quantity.

At a minimum, the following information should be reported:

- Chemical name or identity of the substance involved in the release
- If the release incident is stopped or ongoing
- An indication whether the substance is an extremely hazardous substance
- An estimate of the quantity of the release into the environment
- The time and duration of the release
- Whether the release was into air, water and/or land
- Any known or anticipated acute or chronic health risks associated with the emergency and, where appropriate, advice on medical attention necessary for exposed individuals
- Proper precautions to take as a result of the release, including evacuation (unless such information is readily available to the community emergency coordinator pursuant to the emergency plan)
- The names and phone numbers of the persons to be contacted for further information
- Follow-up written reports must be submitted to the LEPC and SERC "as soon as practicable" following the release.

#### **Hazardous Chemical Storage Reporting**

As required by the rules at 40 CFR Part 370, owners/ operators of facilities storing 10,000 pounds or more per reporting year of hydrochloric acid must report this information to local and state authorities. An initial, one-time notification must be submitted to the LEPC, SERC, and the local fire department within three months after the facility begins to handle hydrochloric acid in excess of the threshold quantity (10,000 pounds).

Following this initial notification, these facilities must also annually submit an Emergency and Hazardous Chemical Inventory Form to the same authorities. Depending on state requirements, facilities will need to use either a Tier I or Tier II Form. The appropriate Tier I/II forms should be obtained from the State Emergency Response Commission.

The forms must be submitted to the LEPC, SERC, and the local fire department by March 1st of each year. Tier I reports must contain the following information:

- An estimate (in ranges) of the maximum amount of hydrochloric acid present at any given time during the reporting year
- An estimate of the average daily amount of the material present during the reporting year
- The general location(s) of the material at the facility.

Tier II reports contain the same information as Tier I reports but also include the following additional information:

A brief description of the manner of storage of the

material

 An indication of whether the owner elects to withhold location information of a specific hazardous chemical from disclosure to the public under Section 324 of EPCRA. For purposes of Tier I and Tier II reporting, hydrochloric acid is classified as an immediate (acute) health hazard.

For more information on EPCRA, see the EPA Fact Sheet, *The Emergency Planning and Community Right-to-Know Act* (EPA 550-F-00-004) or call the EPA EPCRA Hotline at 800-424-9346.

## Section 313 Toxic Chemical Release Inventory Reporting

Hydrochloric acid (in aerosol form) is listed under 40 CFR Part 372.65 as a reportable substance, and is subject to Toxic Chemical Release Inventory (TRI) Reporting rules. In 1996, the EPA modified the listing for hydrochloric acid to include only "acid aerosols including mists, vapors, gas, fog and other airborne forms of any particle size" (61 FR 38600, 7/25/96). Nonaerosol forms of hydrochloric acid are no longer subject to TRI reporting requirements.

The EPA provides a guidance document to assist facilities in determining the sources and amounts of hydrochloric acid aerosols that are to be included in threshold and release determinations under EPCRA section 313. For further information, see the EPA guidance document, EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT - SECTION 313 - Guidance for Reporting Hydrochloric Acid (acid aerosols including mists, vapors, gas, fog, and other airborne forms of any particle size) (EPA-745-B-99-014)

Under Section 313, certain facilities are required to file an annual report on Form R or Form A (available from the EPA) if the facility "uses" 10,000 pounds or more per year or if the facility "manufactures" or "processes" 25,000 pounds or more per year. Questions on TRI reporting may be directed to the EPCRA hotline (800/424-9346).

#### **EPA Risk Management Program**

Facilities that use concentrated HCI (37% HCI, 22.93 B or greater) may also be subject to the requirements of the EPA's Risk Management Program (RMP). These requirements apply only to facilities that manufacture, store, use, or otherwise handle 15,000 lbs. of HCI (40,540 lbs. of a 37% HCI solution) at any single time. Facilities handling HCI at concentrations below 37% are not subject to this rule.

#### **Hazardous Air Pollutants**

Hydrochloric acid is listed in Section 112(b) of the Clean Air Act Amendments of 1990 as a Hazardous Air Pollutant (HAP). Under the Clean Air Act, the EPA is required to develop regulations that apply to major sources of emissions of hazardous air pollutants. A major source is defined as any facility that has the potential to emit 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of HAPs.

National Emission Standards for Hazardous Air Pollutants (NESHAPs) have been established for several source categories using hydrochloric acid. These technology-based standards require the affected users to employ certain control technologies to reduce emissions. Typically, record keeping, reporting, and emission control technologies must be enhanced to meet the requirements of these standards.

NESHAPs potentially affecting hydrochloric acid users include those for:

Pulp and Paper (40 CFR Part 63, Subpart S)
Steel Pickling – HCI Process Facilities
(40 CFR Part 63, Subpart CCC)
Hydrochloric Acid Production (40 CFR Part 63, Subpart NNNNN)

Many state and local agencies also have regulations governing emissions of hydrochloric acid. These agencies should be contacted to determine if state and local regulations affect your operation.

#### **Methods of Handling and Storage**

#### **Storage**

Hydrochloric acid is most commonly stored either in rubber-lined steel storage tanks fiberglass-reinforced plastic storage tanks. rubber-lined steel tanks are usually more expensive to install and are generally used when larger volumes of acid are stored and the chance of tank damage (puncture, tear, etc.) is greater due to external physical stress in a high density work or traffic area. A storage tank should have a concrete containment dike coated with an acid-resistant coating to confine any spilled Storage tanks should be equipped with instrumentation to accurately measure tank inventory and provide notification if the storage tank is approaching an over-filled condition.

#### **Rubber-Lined Steel Tanks**

The rubber-lined steel storage tank should be made of welded steel in accordance with American Petroleum Institute Standard 650. The American Petroleum Institute (API) standard is a recommendation for material, design, fabrication, erection, and testing requirements for above ground, atmospheric storage tanks. Figure 1 shows a vertical, rubber-lined steel storage tank. The steel tanks should be constructed of ASTM-283 Grade C steel or an equivalent material, and they should be lined with a strong, acid-resistant soft rubber. The rubber lining should withstand a maximum temperature of 160°F and the thickness of the rubber should be at least 3/16 inch.

Tanks should be equipped with two 24-inch rubber-lined manways, one at ground level and the other on top of the opposite side of the tank. This provides better air circulation for confined space entry. Filling nozzles should be 3-inch, rubber-lined flanged nozzles. The bottom drain or unloading nozzle should also be a 3-inch rubber-lined flange nozzle. The tank manufacturer should be consulted for a recommendation on proper vent openings and pressure/vacuum relief systems.

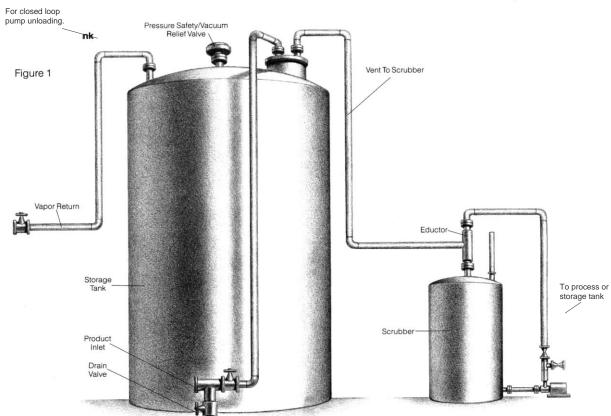


FIGURE 1: Storage Tank and Scrubber

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#### Fiberglass-Reinforced Plastic (FRP) Tanks

A fiberglass-reinforced plastic (FRP) tank is constructed in layers of fiberglass and each layer is mixed with resin. The selection of the resin is extremely important, and the tank manufacturer should specify how each layer will be constructed and specify the correct type of resin for the specific application. Fiberglass tanks are not always designed to withstand pressure or vacuum so proper venting is critical, especially if the product is to be loaded into the tank with air pressure. The tank manufacturer should be consulted for a recommendation on proper vent openings and pressure/vacuum relief systems.

Fiberglass storage tanks should also be equipped with two 24-inch manways, 3-inch flanged nozzles and 3-inch flanged product inlet line. The tank manufacturer should be consulted for a recommendation on proper vent openings and pressure/vacuum relief systems.

### Storage Tank Venting and Hydrochloric Acid Fume Scrubbing

#### **Storage Tank Venting**

To prevent possible tank failure, all hydrochloric acid storage tanks should be vented so that the pressure or vacuum ratings of the tank are not exceeded. Exceeding the design limits of the storage tank could lead to possible failure of the storage tank. A properly designed vent system will maintain the tank at or near atmospheric pressure and within the tank design parameters. A pressure/vacuum relief device should be in place in addition to the tank vent.

Significant increases in pressure occur when storage tanks are being filled. As acid is transferred into the tank and displaces air in the tank, the pressure tends to increase unless the vent system has the capability to relieve the pressure. When liquid is withdrawn from the tank, an equal volume of outside air must enter the tank through a vent system or a partial vacuum will be created inside the tank. This vacuum could cause cracking or collapse of the tank. Smaller changes in pressure occur during static storage conditions due to changes in ambient temperature.

A properly designed vent is especially important when acid is unloaded into the storage tank from a tank car or trailer utilizing air pressure because of the sudden surge of air through the unloading hose and into the storage tank at the end of unloading. The vent system must be designed to handle this air surge condition.

The air flow rate approximates 1350 Standard Cubic Feet per Minute (SCFM) at the completion of a typical unloading operation. This calculation is based upon a 2-

inch unloading hose 25-feet long; maximum pressure in the tank car or trailer of 30 PSIG; unloading into a storage tank 8 ½ feet high; and with a vertical tank vent line not exceeding 3-feet in length.

Vent designs must be based upon a specific system, starting with the pressure/vacuum rating for the tank and incorporating maximum anticipated venting requirements which are dependent upon: liquid flow rates, maximum air flow rates for air unloading, transfer line size, length and configuration, and tank pressure/vacuum rating. As an example, using the parameters of the 1350 SCFM air surge, the following tank design pressures require certain vent line sizing:

- (a) A tank designed for +25-inches Water Column requires a 3-inch diameter vent.
- (b) A tank designed for +10-inches Water Column requires a 4-inch diameter vent.
- (c) A tank designed for +1-inch Water Column requires a 5-inch diameter vent.

The use of a larger diameter unloading line, longer vent line or vent line tied into a scrubber will require an even larger size vent line. The scrubber back-pressure can make a large difference in the pressure in the storage tank during and immediately after unloading. A typical packed column scrubber or re-circulating scrubber exerts very little back-pressure, however venting into the bottom of a vessel below a liquid head may exert a back-pressure above the tank design in routine venting operations.

The potential for over-pressuring FRP and other low-pressure design tanks when using air pressure unloading is especially high. The air surge at the end of unloading will cause a rapid pressure rise in the tank and can exceed the tank design pressure unless the vent system is sized properly. Catastrophic failures of FRP tanks have occurred due to over-pressurization. Professional engineering services should be employed to design and size the vent system.

Facilities are encouraged to frequently inspect scrubber systems for evidence of obstructions and proper operation to minimize back-pressure buildups.

Refer to OxyChem's Technical Data Sheet "Venting Hydrochloric Acid Tanks" and Chlorine Institute Pamphlet 163: *Hydrochloric Acid Storage and Piping Systems* – Appendix H for additional information.

#### **Hydrochloric Acid Fume Scrubbers**

A fume scrubber should be utilized as part of the storage system to eliminate the release of irritating and corrosive vapors into the workplace and atmosphere, both during unloading operations and during "static" storage conditions. Many localities require the use of a fume scrubber. Figures 1 illustrates the use of a re-circulating fume scrubber in conjunction with a typical storage tank.

The re-circulating scrubber shown in Figure 2 shows how a scrubber is utilized in a trans-loading system used in some acid distribution facilities. This system transfers hydrochloric acid from a tank car directly into a tank trailer. The fume eductor draws the acid vapors from the tank truck, and by recirculating water through the eductor the vapors are absorbed. This system can also absorb vapors from the tank car as it is depressurized. By recirculating the water, the solution will gradually build strength and eventually reach a concentration, which is acceptable for product use.

The re-circulating fume scrubber is typically 50 to 60% efficient. Some states require a certain hydrochloric

acid fume scrubber efficiency for a scrubber to be covered under permit-by-rule, eliminating the need to obtain an air permit. Facilities should check with their respective states for air permitting requirements.

An alternative scrubbing system for acid vapors is the use of a packed column scrubber. Water is fed into the top of a packed column and the gas is fed into the bottom. The acid vapors are removed from the air by scrubbing them with the counter-current flow of water. The air then vents out of the top of the scrubber and the weak acid flows into a permitted disposal system. Scrubber efficiencies of 99% or greater can be achieved with a properly designed packed column scrubber.

Air permitting requirements, the method used to unload or transfer material (pump or air pressure), and the volume of hydrochloric acid throughput are key considerations in the design and selection of a hydrochloric acid fume scrubber.

Professional engineering services should be employed to select and design a hydrochloric acid fume scrubber.

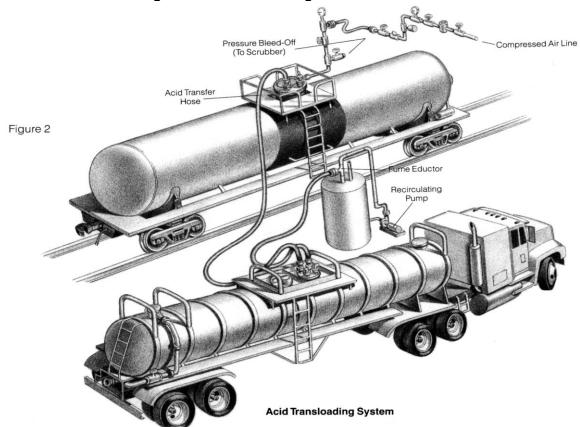


FIGURE 2: Tank Car Unloading to Tank Trailer Utilizing Scrubber

#### **Equipment**

Hydrochloric acid is extremely corrosive to metals including the following: carbon steel, stainless steel, nickel, Monel®¹, bronze, brass, copper, Inconel®¹, and aluminum. These are commonly used industrial materials. Great care should be taken to avoid contact of these materials with hydrochloric acid.

Piping - All piping systems should be well supported. The coldest ambient temperature that may be encountered should be considered in the selection of piping. Lined steel is often used in piping system for hydrochloric acid because it is the most structurally rigid and is less likely to be adversely affected by physical abuse. Lined steel systems also do not require gaskets at flanged connections. The liner itself acts as the gasket mating material. Common lining materials are polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). Pipes are typically carbon steel manufactured to ASTM specifications.

FRP (Fiberglass Reinforced Plastic) piping systems used in hydrochloric acid service are constructed of chemically resistant resins (polyesters and epoxy-based vinyl esters are often used) that are structurally reinforced with glass fibers during the molding process. Consideration should be given to coating FRP piping with an ultraviolet (UV) light resistant barrier. This will extend the life of the piping.

Thermoplastic piping systems used in hydrochloric acid service consist of materials such as polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC), polyvinylidene fluoride (PVDF) and perfluoroalkoxy (PFA). Because of its weaker structure as compared to lined steel and FRP, thermoplastics are typically used for tank vents and other applications where structural strength is not a requirement.

Dual laminate piping may find application in hydrochloric acid service. This consists of a thermoplastic liner overwrapped with an FRP outer pipe. This type of piping system provides excellent internal corrosion protection along with strength and external corrosion resistance.

**Hoses -** Acid resistant hoses can be used to handle hydrochloric acid for both suction and discharge applications. Viton®², natural rubber, neoprene, butyl rubber and Hypalon®² are some of the materials that offer good chemical resistance to hydrochloric acid.

**Pumps** – Composite and lined-steel pumps in hydrochloric acid service are mostly constructed of one of the following:

PVDF (polyvinylidene fluoride) ETFE (ethylene tetrafluoroethylene) FRP (fiberglass reinforced plastic) PFA (perfluoroalkoxy) PP (polypropylene)

Centrifugal pumps are commonly used when pumping hydrochloric acid. Magnetic drive centrifugal pumps have an advantage in that no seal is required which eliminates the possibility of leakage through a seal. A double mechanical seal should be considered if sealed pumps are used. The gland area of the pump should be shielded for personnel protection. Hydrochloric acid transfer or offloading pumps should be equipped with instrumentation to prevent continued operation when the pump is dead-headed or running dry. A minimum flow recycle line will also help to prevent pump damage from dead-heading.

Suction lift is required in order to unload tank cars and tank trailers with top outlets. Self-priming centrifugal pumps are often used for this application. Standard centrifugal pumps will require priming if used in these applications. Diaphragm and other positive displacement pumps do not require priming and may find use in these applications. If a diaphragm pump is used, however, and the diaphragm ruptures, fumes may be worse because of compressed air used to operate the pump.

Valves - Depending upon the type of valve employed, a number of chemically resistant polymers may be suitable for valve lining. Examples are: PFA (perfluoroalkoxy), PTFE (polytetrafluoroethylene), PVDF (polyvinylidene fluoride) and PP (polypropylene). Composite body ball valves have bodies, balls, and handles made of a fiberglass reinforced epoxy resin.

**Gaskets** - Suitable materials for gaskets are Teflon envelope, Hycar®³ rubber, ethylene-propylene rubber, or vinyl materials.

**Pressure Gauges** - Pressure gauges need to be protected by a diaphragm from direct contact with hydrochloric acid.

<sup>&</sup>lt;sup>1</sup>Trademark of International Nickel Company

<sup>&</sup>lt;sup>2</sup>Trademark of E.I. DuPont de Nemours Company

<sup>&</sup>lt;sup>3</sup>Trademark of B.F. Goodrich Chemical Co.

#### **Equipment Sources**

The equipment suppliers listed here are believed to be reliable. This is, however, only a partial listing as space does not permit a listing of every supplier of each type of equipment.

Listing in this section is for information only and should not be considered as a recommendation for one supplier's products over another.

#### **Pumps**

Flowserve Corporation 5215 N. O'Conner Blvd.; Suite 700 Irving, TX 75039 (972) 443-6500 www.flowserve.com

ITT Goulds Pumps, Inc. (FRP\*, Teflon-lined, Ceramic) 240 Fall Street Seneca Falls, NY 13148 (315) 568-2811 www.gouldspumps.com/

March Manufacturing, Inc. (Polypropylene)
1819 Pickwick Avenue
Glenview, IL 60025
(847) 725-0580
www.marchpump.com

Ceco Environmental Solutions (Fybroc) Fybroc Division 700 Emlen Way Telford, PA 18969 (215) 723-8155 800-392-7621 www.cecoenviro.com

Sundyne (Ansimag Inc.) 14845 W. 64<sup>th</sup> Ave. Arvada, CO 80007-7523 (866) SUN-DYNE www.sundyne.com

Pump Solutions Group (Wilden Pump) 22069 Van Buren Street Grand Terrace, CA 92313-5607 (909) 422-1700 www.psgdover.com

#### **Piping**

NOV Fiber Glass Systems 17115 San Pedro Ave Suite 200 San Antonio, TX 78232 (210) 434-5043 www.nov.com

P.E.P 50 Tannery Rd. Branchburg, NJ 08876 (800) 407-3726 www.pep-plastic.com

Crane ChemPharma & Energy (Plastic Lined Steel)
One Quality Way
Marion, NC 28752
(828) 724-4000
www.cranecpe.com/resistoflex

#### **Rubber Hoses**

Birmingham Rubber & Gasket Company Inc. 200 Industrial Drive Birmingham, AL 35211 (205) 942-2541 www.bragusa.com

Goodyear Engineered Products (866) 711-4673 www.goodyear.com

Rubber Belting & Hose Supply Inc. 1850 North Ohio Wichita, KS 67214 (316) 269-1151 www.rbhinc.com

#### **Valves**

Flowserve Corporation 5215 N. O'Conner Blvd. Suite 700 Irving, TX 75039 (972) 443-6500 www.flowserve.com ITT Engineered Valves 33 Centerville Road Lancaster, PA 17603-2064 (717) 509-2200 http://www.engvalves.com

Crane Xomox 4444 Cooper Road Cincinnati, OH 45242 (513) 745-6000 www.xomox.com

Crane Resistoflex (Teflon)
1 Quality Way
Marion, NC 28752
(828) 724-4000
www.resistoflex.com

#### Rubber-Lined Storage Tanks/Rubber Lining <u>Fabricators and Applicators</u>

Gates Rubber Company 1144 15<sup>th</sup> Street Denver, CO 80202 (303) 744-5070 www.gates.com

Kennedy Tank & Manufacturing Company, Inc. 833 E. Sumner Avenue Indianapolis, IN 46227 (317) 787-1311 <a href="https://www.kennedytank.com">www.kennedytank.com</a>

Protective Coatings, Inc. 1602 Birchwood Avenue Fort Wayne, IN 46803 (260) 424-2900 www.proco-fwi.com

#### **Fiberglass-Reinforced Plastic Tanks**

Ershigs, Inc. 742 Marine Drive Bellingham, WA 98225 (360) 733-2620 www.ershigs.com

Heil Process Equipment Company 34250 Mills Road Avon, OH 44011 (440) 327-6051 www.heilprocessequipment.com Composites USA, Inc.
One Peninsula Drive
North East, MD 21901
(410) 287-2700
http://www.compositesusa.com

Indelco Plastics Corp. 32 Flicker Street Memphis, TN 38104-5918 (901) 452-6527 www.plastico-memphis.com

#### **Gas**kets

Garlock Sealing Technologies 1666 Division Street Palmyra, NY 14522 (800) 448-6688 www.garlock.com

O'Brien Corporation 1900 Crystal Industrial Court St Louis, MO 63114 (314) 423-4444 www.obcorp.com

#### Gauges

Siebe Controls Company 33 Commercial Street Foxboro, MA 02035 (508) 543-8750 www.foxboro.com

Meriam Instrument Division Scott & Fetzer Company 875 Bassett Rd. Westlake, OH 44145(800) 817-7849 www.meriam.com

Ashcroft Instrument Corp 681 Grand Boulevard Deer Park, NY 11729 (866) 415-2002 www.ashcroft-gauges.com

Jogler, Inc. 6646 Complex Dr. Baton Rouge, LA 70809 (800) 223-8469 www.jogler.com

#### **Scrubbers**

Schutte and Koerting 2510 Metropolitan Drive Trevose, PA 19053 (215) 639-0900 www.s-k.com

Artisan Industries, Inc. (Custom design only) 44 Camparelli Pkwy Stoughton, MA 02072 (781) 893-6800 www.artisanind.com

Croll-Reynolds Company, Inc. 6 Sample Drive Parsippany , NJ 07054 (908) 232-4200 www.croll.com

Heil Process Equipment Company 34250 Mills Road Avon, OH 44011 (440) 327-6051 www.heilprocessequipment.com

Indelco Plastics Corp 2115 Spicer Cove, Suite 118 Memphis, TN 381134 (800)-486-6456 www.plastico-memphis.com

#### **Acid Resistant Coatings for Concrete**

Coatings Unlimited 1911 Gramblin St. Enumclaw, WA 98022 (425) 251-3268 www.coatingsunltd.com

C&M Restoration 3115 East 12<sup>th</sup> Street Kansas City, MO 64127 (816) 920-5600 www.cmrestore.com

Carboline Company 2150 Schuetz Road St. Louis, MO 63146 (314) 644-1000 www.carboline.com

Tnemec Corporation 2150 Schuetz Road Kansas City, MO 64116 (816) 483-3400 www.tnemec.com

#### Unloading Hydrochloric Acid from Transportation Vehicles

There are two methods used to unload hydrochloric acid from transportation vehicles: compressed air and pump. A well-designed pump unloading system has the following advantages:

- Significantly less vapor is generated, resulting in lower volume to the scrubber
- De-pressuring the trailer or tank car after unloading is eliminated
- Line drainage is reduced by transferring most of the acid in the hose to the pump
- Pump unloading is generally faster

The following instructions for unloading hydrochloric acid tank cars are based on good engineering practices along with many years of industrial experience. These instructions are meant to serve as a general guideline only and may not be appropriate for all unloading circumstances. The operation of valves and equipment which may be present in the customer's system is also not included. If material is being offloaded into a bottom-fill storage tank, an offloading sequence should be followed that prevents back-flow of material from the storage tank to the tank car due to back-pressure exerted by hydrochloric acid in the storage tank.

### Unloading Hydrochloric Acid Tank Cars

#### **Preparations**

The unloading track should be level. Once the car is spotted, set the hand brake and block the wheels. The unloading area should be designed so that any spillage that might occur will be properly contained for recovery or neutralization. The unloading area should be secured to prevent the entry of untrained or unauthorized persons.

Department of Transportation (DOT) regulations [49 CFR 174.67 (a)(2) - (a)(3)] include an outline of steps to be taken and signage to be placed in order to properly spot and secure the tank car and warn that unloading is taking place. Unloading personnel should consult and be familiar with the latest edition of this regulation.

Personnel unloading hydrochloric acid from tank cars must be trained and made responsible for compliance as outlined in 49 CFR 174.67 (a)(1). Unloading personnel should consult and be familiar with the latest edition of this regulation.

Receiving personnel should verify the correct product by paperwork and arrange for a sample to be taken from the tank car where required. The line into which material will be offloaded should be labeled or tagged with the identity of the material being offloaded. Access to top fittings on the tank car should be provided by safe steps, platforms,

or drop-bridges. Guard rails for the protection of personnel must meet OSHA standards. If air padding is used for unloading, the air must be clean and properly regulated. Emergency shut-off equipment is recommended on all product lines.

#### **Precautions**

DOT Regulations for unloading (49 CFR 174.67(i)) require that throughout the entire period of unloading, and while the tank car is connected to an unloading device, the tank car must be attended by the unloader. If it is necessary to discontinue unloading a tank car for any reason, all valves must be tightly closed and unloading connections disconnected. This is intended to assure that the flow of hydrochloric acid from the tank car is carefully controlled and the tank car can quickly be shut off should problems in unloading develop. Letters of clarification from DOT indicate that "attending" the unloading includes having an employee physically present at the unloading site, or electronic monitoring with remote shut-off equipment, or television camera monitoring or by any means where the tank car is monitored and the flow of hydrochloric acid can be stopped if unloading difficulties develop.

DOT has issued a number of company-specific regulatory exemptions to permit tank cars containing hydrochloric acid to remain standing with unloading connections attached when no product transfer is taking place. Special provisions must be followed to meet the terms of the DOT exemption. These provisions are outlined in the exemptions, and include the designation of an employee responsible for on-site monitoring of the transfer facility. It is the responsibility of each unloading site to ensure all applicable regulations are followed.

Protective equipment, as described in the Safety and First Aid section of this handbook, must be worn while transferring hydrochloric acid from a tank car to a storage tank.

Before starting the unloading operation, it must be verified that the storage tank is adequately vented to a properly sized acid scrubber system and that the tank will hold the entire contents of the tank car. The storage tank must remain vented throughout the unloading operation. If unloading with compressed air, the tank vent and scrubber should be properly sized for the air surge that occurs at the end of product transfer, which is approximately 1350 SCFM (Standard Cubic Feet per Minute) based on 30 psig air pressure. An additional pressure/vacuum relief device with appropriate settings should also be installed on the storage tank.

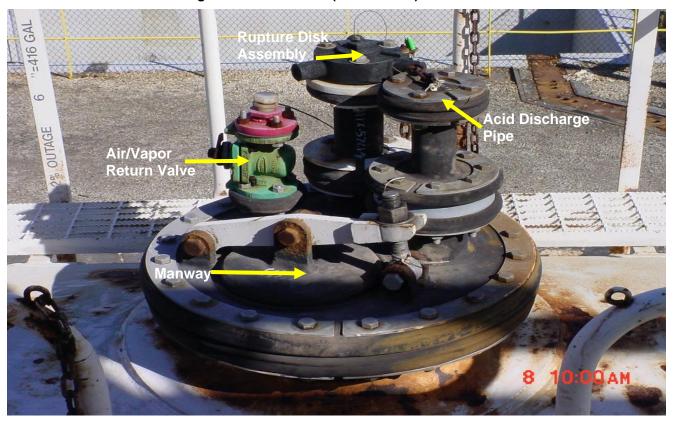
If a tank car sample is required, all pressure must be bled off the tank car through a properly sized acid scrubber system before opening the manway. Well-marked emergency showers and eye wash fountains must be located in the immediate work area and easily accessible in case of accidental exposure. These units should be tested on a regular basis as well as prior to transferring product to ensure correct operation.

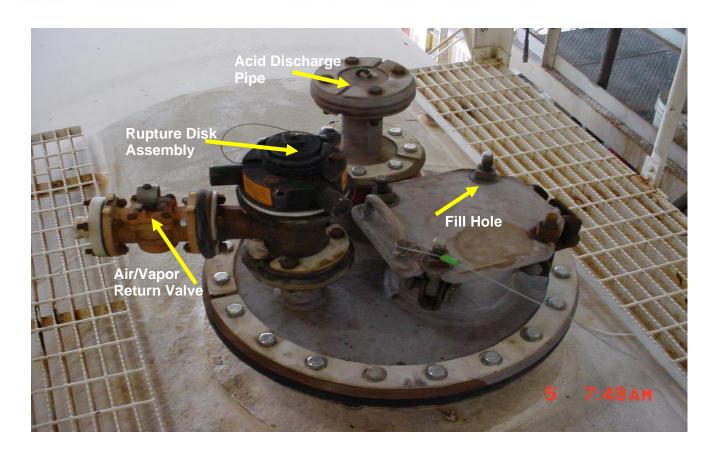
Smoking should not be allowed in or around the unloading area. If the tank car lining should fail, the hydrochloric acid will react with the metal to form flammable hydrogen gas.

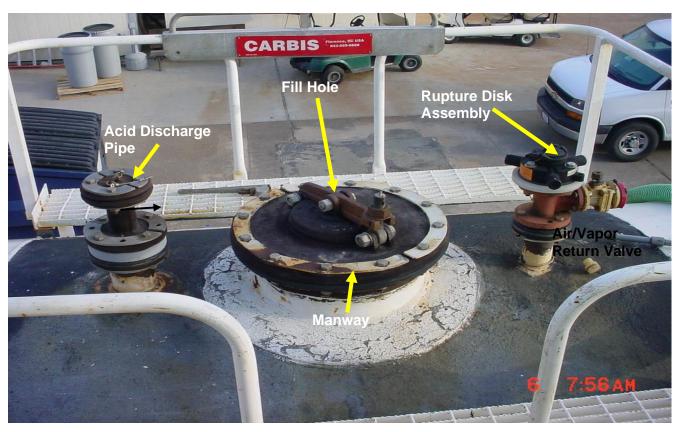
Unloading should take place during daylight hours. If it is necessary to unload after dark, adequate lighting must be provided.

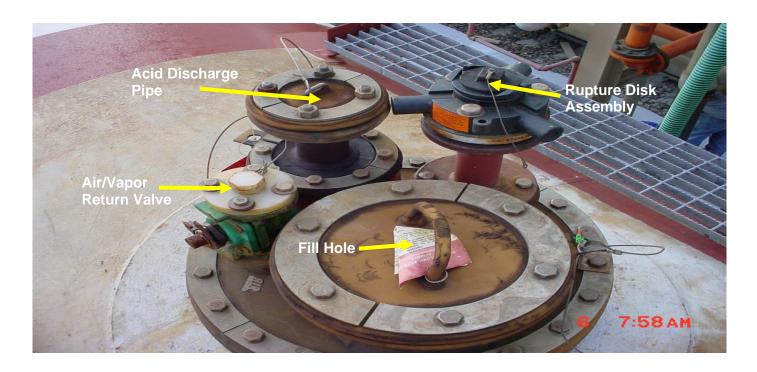
If a tank car must be moved before it is completely unloaded or if it is necessary to discontinue unloading a tank car for any reason, 49 CFR 174.67(j) specifies disconnection and closure operations that must be performed. 49 CFR 174.67(l) and (k) specify disconnecting and closure operations that must be performed after unloading is completed. Unloading personnel should consult and be familiar with the latest edition of this regulation.

FIGURE 3: Tank Car Dome Configurations 263 Series (Photos 1 – 5)









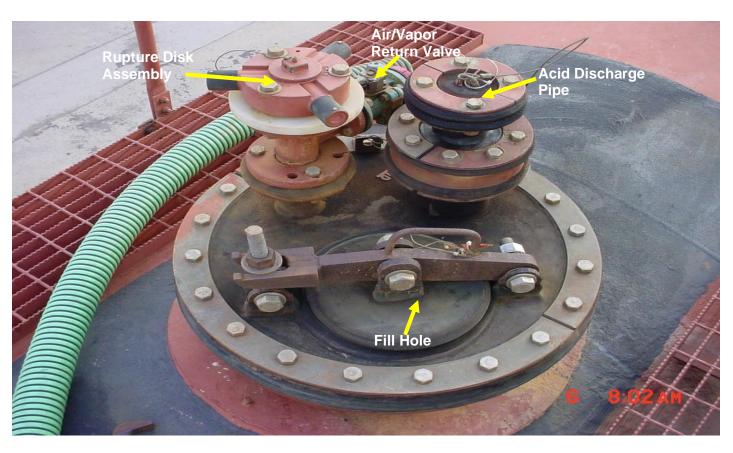
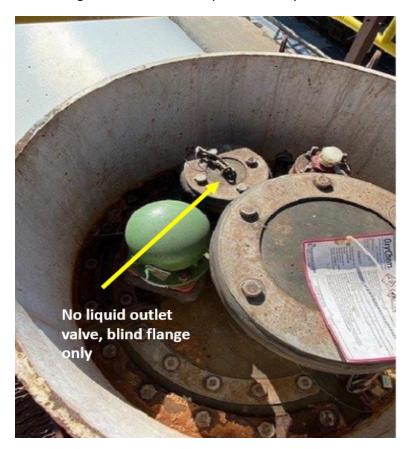
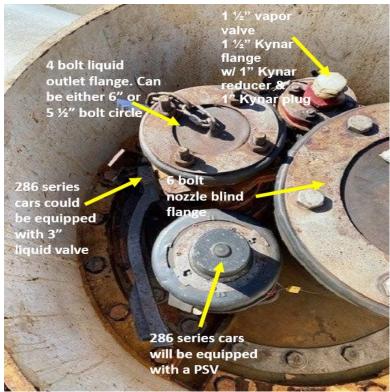


FIGURE 4: Tank Car Dome Configurations 286 Series (Photos 1 – 3)







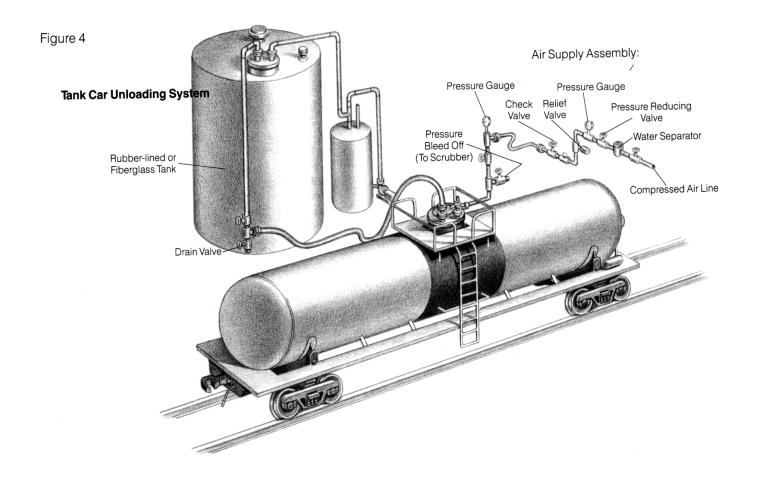
#### **Unloading Procedures for Tank Cars**

All hydrochloric acid tank cars are unloaded from the top. They are unloaded through the acid discharge pipe by using either compressed air or a pump. Most OxyChem tank cars are equipped with one of the five manway configurations shown in the previous photos of Figure 3.

#### **Unloading with Compressed Air**

Before starting the unloading operation, it must be verified that the storage tank will hold the entire contents of the tank car.

The recommended compressed air supply assembly referred to in the following procedures should consist of: a check valve, pressure reducing valve, water separator, shut-off valve, a pressure bleed-off valve connected to a suitable scrubber system and a pressure relief valve set at 30 psig. (See Figure 4).



#### Follow these instructions:

- 1. Start the scrubber system and make sure it is operating properly.
- 2. Verify the manway configuration on the tank car, (refer to manway arrangements Figure 3) and connect the air supply assembly to the one inch valve provided on the tank car. DO NOT REMOVE THE RUPTURE DISC ASSEMBLY. Use of the air valve allows the rupture disc on the incoming tank car to be left undisturbed during the unloading operation. The rupture disc protects against excessive pressure buildup and must not be removed during the unloading operation. An intact rupture disc must also be in place when the empty tank car is returned.
- Cautiously open the air valve on the tank car and bleed pressure from the tank car to a suitable scrubber system.
- 4. Carefully remove the blind flange on the acid discharge pipe. NEVER REMOVE THE BLIND FLANGE ON THE DISCHARGE PIPE UNTIL THE TANK CAR HAS BEEN FULLY VENTED AND DE-PRESSURED. If the blind flange is removed before venting the tank car, acid could be forced up the discharge pipe and spray the person removing the flange.
- Connect the acid unloading line to the tank car and the other end to the storage tank inlet. Rubber-lined or plastic flanges should be used for all connections.
- 6. Close the vent valve to the scrubber.
- 7. Open product inlet valve on storage tank.
- Open valves on the air supply assembly and the tank car air valve; apply air pressure slowly through the air valve until a steady stream of acid is flowing into the tank. The air pressure in the tank car should not be allowed to exceed 30 psig.
- When the tank car is empty there will be a drop in pressure and the sound of air rushing through the discharge pipe. When this occurs, shut off the air inlet valve.
- 10. When the unloading line is blown free of acid, close the inlet valve to the storage tank.

- 11. Slowly open the pressure bleed-off valve on the airline to vent the fumes to the scrubber and allow the pressure in the tank car to be released. This will enable the acid in the tank car dip leg to drain back into the tank car.
- 12. When the pressure gauge on the air line reads zero, close vent valve to the scrubber. Cautiously disconnect the scrubber vent line and the air assembly from the tank car. Replace the plug in the air valve.
- 13. Bleed the pressure and residual acid from the product hose by slowly opening the drain valve between the hose connection and storage tank inlet valve. Disconnect the unloading hose. Contain any residual acid remaining in the hose for proper disposal.
- 14. Disconnect the acid unloading line from the tank car. Replace the blind flange on the acid discharge pipe, and bolt securely in place.

#### **Unloading By Pump**

Before starting the unloading operation, it must be verified that the storage tank will hold the entire contents of the tank car. A self-priming, centrifugal pump proven suitable for hydrochloric acid service must be provided by the customer for this type of unloading. (See Figure 5)

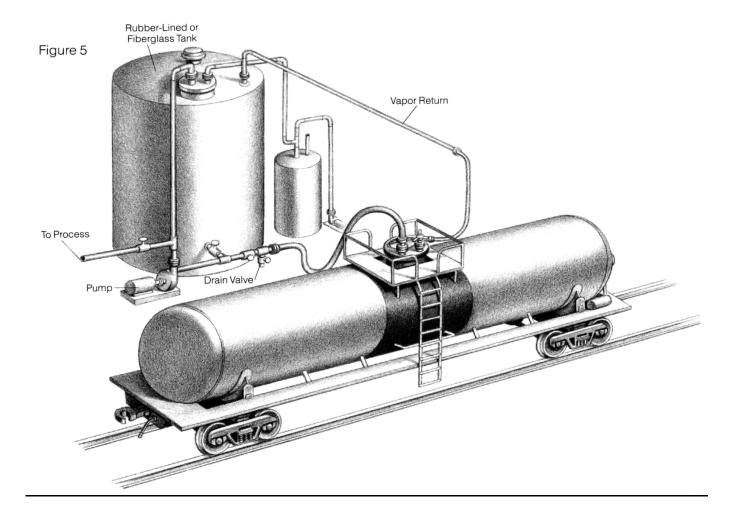
#### Follow these instructions:

- 1.Start the scrubber system and make sure it is operating properly.
- 2. Verify the manway configuration on the tank car, (refer to Figure 3) and connect the vapor return line to the one inch valve provided on the tank car. DO NOT REMOVE THE RUPTURE DISC ASSEMBLY. Use of the air valve allows the rupture disc on the incoming tank car to be left undisturbed during the unloading operation. The rupture disc protects against excessive pressure buildup and must not be removed during the unloading operation. An intact rupture disc must also be in place when the empty tank car is returned.
- 3. Open the air valve and bleed pressure from the tank car to the storage tank, which is vented to a suitable scrubber system. Leave this valve open for make-up air while unloading to avoid pulling a vacuum on the tank car. The dome lid may also need to be opened slightly to allow for sufficient make-up air. Acid vapors will flow from the

storage tank to the tank car during unloading.

- 4. After the pressure has been bled off, remove the blind flange on the acid discharge pipe. NEVER REMOVE THE BLIND FLANGE ON THE DISCHARGE PIPE UNTIL THE TANK CAR HAS BEEN FULLY VENTED AND DE-PRESSURED. If the blind flange is removed before venting the tank car, acid could be forced up the discharge pipe and spray the person removing the flange.
- 5. Connect one end of the acid unloading line to the acid discharge flange on the tank car and the other end to the pump inlet. Rubber lined or plastic flanges should be used for all connections.
- Open the pump product inlet valve and storage tank inlet valve.
- Next, start the pump and continue pumping until the tank car is empty. High-volume pumps equipped amp-sensing cutoff switches may shut down prematurely due to vortex action within the

- car near the end of unloading. If this occurs, restart pump and if possible, throttle pump to assure complete unloading of the tank car.
- 8. When the tank car is empty, shut off the pump and immediately close the valve at the pump inlet. Close and secure the dome lid if opened.
- 9. Bleed the pressure and residual acid from the product hose by slowly opening the drain valve between the hose connection and storage tank inlet valve. Disconnect the unloading hose. Contain any residual acid remaining in the hose for proper disposal.
- 10. Close the valves on the vapor return line from the storage tank to the tank car and disconnect the vapor return line from the tank car.
- 11. Replace the blind flange on the acid discharge pipe, and bolt the flange securely in place. Also, replace the plug in the air valve assembly.



#### **Preparing Empty Tank Cars for Return**

When returning empty tank cars, the following procedures must be followed:

- If it was not done in previous operations, start the scrubber system and make sure it is operating properly, and de-pressure the tank car through the scrubber.
- 2. Use water to wash off any hydrochloric acid which may have spilled onto the tank car when disconnecting and draining the unloading line. This will prevent damage to the car and possible exposure to railroad personnel who will be handling the car. All wash down water must be drained off to a suitable chemical sewer.
- 3. DOT regulations (49 CFR 173.31(d)(1)) require the persons offering the returned empty tank car to ensure that the tank car is in proper condition and safe for transportation. Specifically, all tank car openings must be properly secured prior to shipment. The person offering the car for shipment must also perform an external visual inspection that includes:
  - (d)(1)(i) the tank shell and heads, except where insulation precludes an inspection, for abrasion, corrosion, cracks, dents, distortions, defects in welds, or any other condition.
  - (d)(1)(ii) the piping, valves, fittings and gaskets for corrosion, damage, or any other condition.
  - (d)(1)(iii) bolts and nuts that may be missing or elements that make the tank car unsafe for transportation.
  - (d)(1)(iv) inspection and tightening of closures and fastenings by the use of a bar, wrench, or suitable tool.
  - (d)(1)(v) securement of protective housings.
  - (d)(1)(vi) the pressure relief device including a careful inspection of the frangible disc in non-closing pressure relief devices. However, if the tank car operates under the DOT-E-11761 exemption, the disc does not have to be inspected unless modifications occur.
  - (d)(1)(viii) tank-head puncture resistance system, coupler vertical restraint system and bottom discontinuity protection.
  - (d)(1)(ix) required tank car markings for legibility.
  - (d)(1)(x) periodic inspection date markings that are within the prescribed intervals.

- 4. Ensure that the tank car has proper placards. They should read "Corrosive".
- Return all cars as promptly as possible. All problems should be discussed with OxyChem Customer Service.

49 CFR 173.31(d)(2) outlines the legal ramifications for failure to perform the requirements specified in 49 CFR 173.31(d)(1).

Personnel offering empty hydrochloric acid tank cars for return should consult and be familiar with the latest edition of this regulation.

#### **Unloading Hydrochloric Acid Tank Trailers**

The following instructions for unloading hydrochloric acid tank trailers are based on good engineering practices along with many years of industrial experience. These instructions are meant to serve as a general guideline only and may not be appropriate for all unloading circumstances. The operation of valves and equipment that may be present in the customer's system is also not included. If material is being offloaded into a bottom-fill storage tank, an offloading sequence should be followed that prevents back-flow of material from the storage tank to the tank trailer due to back-pressure exerted by hydrochloric acid in the storage tank.

#### **Preparations**

The unloading area should be arranged so that any spillage that might occur will be properly contained for recovery or neutralization. The unloading area should be level and secured to prevent entrance by untrained and unauthorized persons.

- 49 CFR 177.834(e) specifies requirements, including setting the handbrake, for preventing motion of the tank trailer during offloading.
- 49 CFR 177.834(2) (3) specify attendance requirements by a qualified person at all times during unloading.
- 49 CFR 177.834(4) specifies what a qualified person is.

Carrier personnel should make certain shipping papers and other required documentation is delivered to responsible receiving personnel before unloading. Carrier personnel should also receive, prior to unloading, signed documentation from receiving personnel that the receiving location is set up to deliver the material to the proper storage tank and that the storage tank will hold the entire contents of the tank trailer. Carrier personnel should also obtain a signed delivery receipt before the

motor carrier leaves the area. Carrier personnel should work with receiving personnel to hook up and begin the unloading process after all procedures have been reviewed.

Receiving personnel should verify the correct product by paperwork and arrange for a tank trailer sample to be taken where required. When a sample is taken, the person collecting the sample must verify that the tank trailer is not pressurized if the sample is taken from the tank trailer dome. Pressure, if present, should be relieved through a properly sized scrubber.

The line into which material will be offloaded should be labeled or tagged with the identity of the material being offloaded. Receiving personnel should point out the proper connection and line into which the product will be offloaded and verify that the storage tank will hold the entire contents of the tank trailer.

Access to top fittings on the tank trailer should be provided by safe steps, platforms, or drop-bridges. Guard rails for the protection of personnel must meet OSHA standards. If air padding (either carrier supplied or supplied by the receiving location) is used for unloading, the air must be clean and properly regulated not to exceed the tank trailer maximum working pressure. Emergency shut-off equipment is recommended on all product lines.

#### **Precautions**

Trained personnel wearing protective equipment are required for safe unloading of hydrochloric acid tank trailers. (Refer to Safety and First Aid section for equipment needed). The unloading operation should be continuously attended and if it should be necessary for the operator to leave, the operation should be shut down.

Before starting the unloading operation, it must be verified that the storage tank is adequately vented to a properly sized acid scrubber system and that the tank will hold the entire contents of the tank trailer. If unloading with compressed air, the tank vent and scrubber should be properly sized for the air surge that occurs at the end of product transfer, which is approximately 1350 SCFM (Standard Cubic Feet per Minute). The storage tank must remain vented throughout the unloading operation. An additional pressure/vacuum relief device with appropriate settings should also be installed on the storage tank.

If a tank trailer sample is required and must be taken from the manway, all pressure must be bled off the tank trailer before opening the manway. For tank trailers with a sample valve, the sample can be taken without bleeding off the pressure. Well-marked emergency showers and eye wash fountains should be located in the immediate work area and easily accessible in case of accidental exposure. These units should be tested on a regular basis as well as prior to offloading to ensure correct operation.

Receiving personnel should point out to carrier personnel the exact location of these units prior to beginning unloading.

Smoking should not be allowed in the unloading area. If the tank trailer lining should fail, the hydrochloric acid will react with the metal to form flammable hydrogen gas.

Unloading should be done during daylight hours. If it is necessary to unload after dark, adequate lighting should be provided.

## Unloading Procedures for Tank Trailers Unloading with Compressed Air

Before starting the unloading operation, it must be verified that the storage tank will hold the entire contents of the tank trailer. (See Figure 6)

Follow these instructions:

- 1. Start the scrubber system and make sure it is operating properly.
- Connect the vapor line from the tank trailer to the fume scrubber. Open bleed valve to de-pressure the tank trailer. Disconnect the vapor line to the scrubber prior to opening manway for sampling. (These steps are not necessary if manway is not to be opened for sampling.)
- Connect the unloading hose to the tank trailer's outlet and the storage tank's inlet. Rubber-lined or plastic flanges should be used for all connections.
- Connect the unloading air hose to the tank trailer's air inlet.
- 5. Open the inlet valve on the storage tank.
- 6. Open the tank trailer's outlet valve.
- 7. Slowly apply air pressure until there is a steady flow of acid into the storage tank. The air pressure in the tank trailer must not be allowed to exceed 30 psig. The person performing the unloading should verify that the scrubber is operating properly and that fumes are not being released to the atmosphere. It should also be verified that the unloading hose and other transfer system components are not leaking hydrochloric acid or HCI fumes.

- 8. When the trailer is empty, shut off compressor or other source of air pressure.
- 9. Allow acid to be blown through the unloading line into the storage tank. If the customer's scrubber system is adequately sized, depressurize the tank trailer through their scrubber system.
- 10. Close the product inlet valve to the storage tank and the tank trailer's outlet valve.
- 11. Bleed the pressure and residual acid from the product hose by slowly opening the drain valve between the hose connection and storage tank inlet valve. Disconnect the unloading hose. Contain any residual acid remaining in the hose for proper disposal.
- 12. Disconnect the unloading hose from the customer's transfer system. If any acid has spilled on the outside of the tank trailer or on the ground, it should be washed off with plenty of water and

drained into an appropriate chemical sewer.

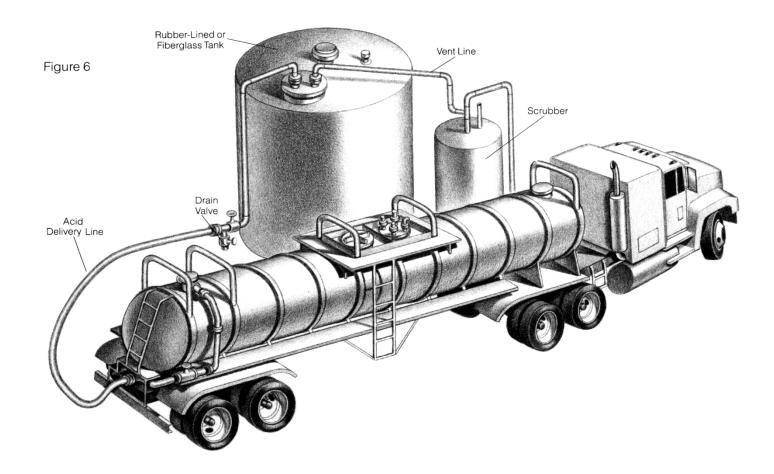
13. Check all valves and connections to make certain they are closed and capped.

#### **Unloading By Pump**

Before starting the unloading operation, it must be verified that the storage tank will hold the entire contents of the tank trailer. A self-priming, centrifugal pump proven suitable for hydrochloric acid service must be provided by the customer for this type of unloading. (See Figure 7)

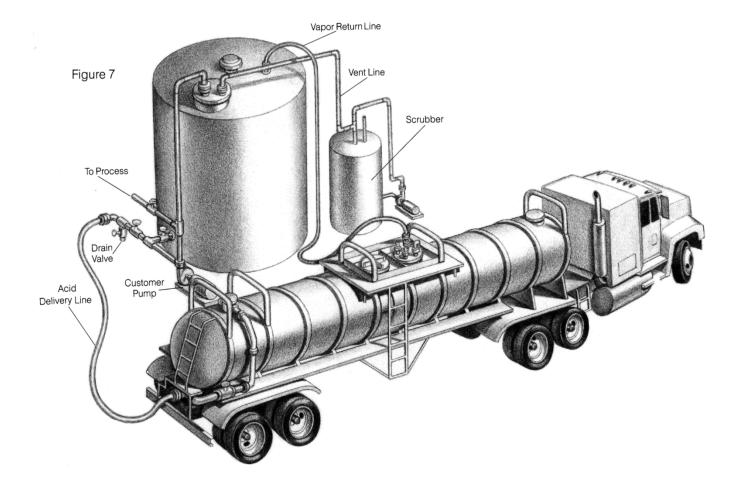
#### Follow these instructions:

- 1. Start the scrubber system and make sure it is operating properly.
- 2. Connect a vent line to the air/vapor return connection on the tank trailer and bleed pressure from the trailer to the scrubber system.



- Disconnect the scrubber line and connect the vapor return line from the storage tank to the tank trailer. This vent must remain open to avoid pulling a vacuum on the tank trailer during unloading. Acid vapors will flow from the storage tank to the tank trailer during unloading.
- 4. Connect one end of the acid unloading hose to the tank trailer's outlet and the other end to the customer's pump inlet. Rubber-lined or plastic flanges should be used for all connections.
- Open the outlet valve on the acid discharge piping on the tank trailer.
- 6. Open the pump product inlet valve.
- 7. Start the pump and continue pumping until the tank trailer is empty. The person performing the unloading should verify that the scrubber is operating properly and that fumes are not being released to the atmosphere. It should also be verified that the unloading hose and other transfer system components are not leaking hydrochloric acid or HCl fumes.

- 8. After the tank trailer has been emptied, shut off the pump and close the pump product inlet valve and the tank trailer product outlet value.
- Bleed the pressure and residual acid from the product hose by slowly opening the drain valve between the hose connection and storage tank inlet valve. Disconnect the unloading hose. Contain any residual acid remaining in the hose for proper disposal.
- Disconnect the unloading hose from the customer's pump inlet and secure the hose on the tank trailer.
- 11. Close the air/vapor returns valve and disconnect the vapor return line.
- 12. Check all valves and connections to make certain they are closed and capped.



#### **Spills & Neutralization**

Containment of a spill or leak is of primary importance. The storage tank should have an impervious containment dike and the entire hydrochloric acid unloading area should be designed to properly contain any spills. All persons working around the spill area should wear the full set of protective equipment as recommended in the Safety and First Aid Section, page 5. Rubber boots are absolutely necessary when working around a spill. Personnel should keep upwind of the spill, and if it is necessary to enter the spill area, a self-contained breathing apparatus should be worn. People who are not involved with the leak or spill should be kept away.

Facilities expecting employees to engage in emergency response must develop an emergency response plan as specified by OSHA in 29 CFR 1910.120(q). Where employees are not expected to assist in handling emergencies, an emergency response plan is not required; however, an emergency action plan in accordance with 29 CFR 1910.38(a) is required.

Courtesy notifications to the National Response Center (NRC), state, and local authorities should be made anytime an appreciable amount of hydrochloric acid is spilled. See spill reporting information on page 10.

The hydrochloric acid can be neutralized with an alkaline material but the reaction between concentrated hydrochloric acid and an alkali gives off heat and can be quite violent. Therefore, the acid should first be diluted by using a water spray and then neutralized. The spray will also reduce the fuming of the hydrochloric acid. Alkaline materials to be used and quantities necessary for neutralization are shown in Table 1. Caution should be taken to ensure the diluted acid remains contained.

Cleanup and waste disposal must conform to current hazardous waste regulations.

Table 1:	Quantities of Hydrochlor		Alkalis Requi	red to Neu	tralize 100 C	Sallons of	
Acid Actual Concen- Specific Pounds of tration Gravity Acid per		Neutralizing Chemicals CaO Ca(OH) <sub>2</sub> Quicklime Lime		Na₂CO₃ Anhydrous Soda Ash	50% NaOH Liquid Caustic Soda	NaOH Flake Caustic Soda	
Wt.% HCI	Solution	100 Gals.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
0.1	USE 1.000	.837	.644	.852	1.27	1.836	.918
0.2	USE 1.000	1.674	1.28	1.70	2.54	3.672	1.836
0.3	USE 1.000	2.511	1.93	2.52	3.81	5.50	2.75
0.4	USE 1.000	3.35	2.58	3.41	5.08	7.34	3.67
0.5	USE 1.0015	4.19	3.19	4.22	6.35	9.18	4.59
0.6	USE 1.0015	5.02	3.86	5.11	7.62	11.02	5.51
0.7	USE 1.0015	5.86	4.51	5.93	8.89	12.86	6.43
0.8	USE 1.0015	6.70	5.15	6.82	10.16	14.68	7.34
0.9	USE 1.0015	7.53	5.79	7.63	11.43	16.52	8.26
1.0	1.0032	8.37	6.44	8.52	12.7	18.36	9.18
2.0	1.0082	16.83	12.94	17.12	24.6	36.96	18.48
3.0	1.0131	25.41	19.54	25.79	37.0	55.70	27.85
4.0	1.0181	33.99	26.14	34.53	49.3	74.4	37.2
5.0	1.0230	42.73	32.86	43.42	62.0	93.6	46.8
6.0	1.0279	51.47	39.56	52.31	74.6	112.8	56.4
10.0	1.0474	87.41	67.22	88.92	126.8	191.4	95.7
20.0	1.0980	183.3	141	186	267	402	201
25.0	1.1261	234.8	179	237	339	512	256
30.0	1.1526	288.4	221	293	419	632	316
35.0	1.1778	343.8	264	348	498	752	376

#### **Technical Data**

#### **Billing Procedure**

Hydrochloric acid is sold on a net ton basis as 20° Bé or 22° Bé hydrochloric acid. It is normal practice to deliver full tank trailer or tank car quantities.

#### **Dilution of Hydrochloric Acid**

For convenience, Table 3 was prepared for the rapid determination of acid and water quantities used in making some of the more standard solutions. Those values not appearing on the chart can be calculated by using the formulas shown below.

#### 1. To Dilute to a Lower Strength Acid:

A = Acid solution to be adjusted

B = Desired acid solution

Lbs. of water required = (Lbs. A) (%HCl A - HCl B) (%HCl B)

#### **Example:**

1000 gals. of 22° Bé acid is to be diluted to 12% HCl. How much water is needed?

A = 35.21% HCl (from Dilution Table)

B = 12.0% HCI

Lbs. A = gals. of A x specific gravity (from Table 3) x 8.34 = 1000 gallons x 1.1789 x 8.34 = 9832 pounds.

Lbs. of water required = (9832 lbs) (35.21%-12.0%)12.0%

=19,016 lbs. of water required

Gallons of water = <u>lbs. of water</u>

8.34 lbs./gallon

= <u>19,016 lbs.</u> 8.34

= 2280 Gallons

#### 2. To Adjust to a Higher Strength Acid:

A = Acid solution to be adjusted

B = Desired acid solution

C = Stock acid of higher strength

Lbs. of stock solution = (Lbs. A) (%HCI B - %HCI A) (%HCI C - %HCI B)

#### Example:

500 gallons of 7.15% HCl is to be adjusted to 12% HCl by using 20.1 Bé acid. How much 20.1 Bé acid should be used?

A = 7.15% HCI

B = 12% HCI

C = 31.64% HCI (from Dilution Table, Table 3)

Lbs. A = gallons of A x specific gravity (from Table 4, Equivalent Properties)  $\times 8.34$ 

= 500 gallons x 1.0357 x 8.34

= 4319 lbs.

Lbs. C = (4319 lbs.) (12% - 7.15%) (31.64% - 12%) = 1067 lbs. of 20.1 Bé acid

Gallons of C =

Lbs. of C

Specific gravity x 8.34 lbs./gallon

= <u>1067 lbs.</u> (1.1609 x 8.34)

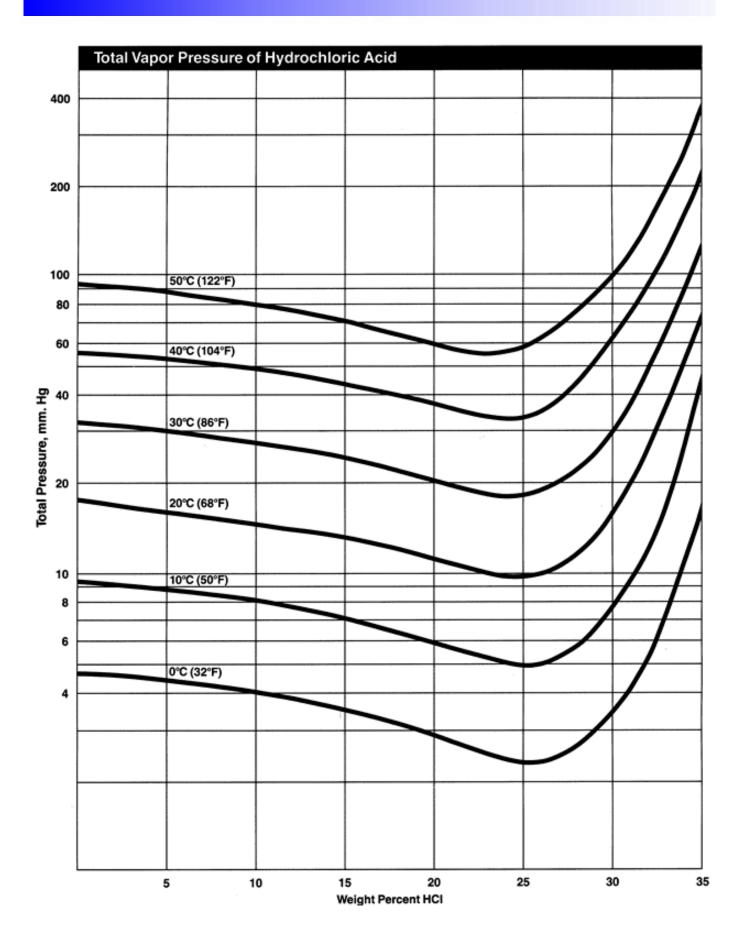
= 110 Gallons of 20.1 Bé Acid

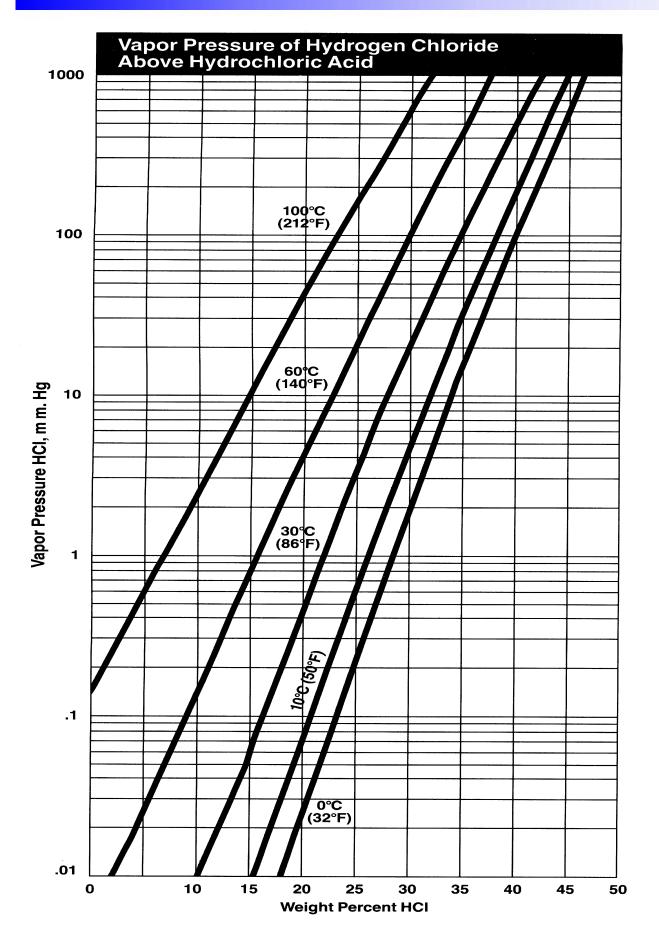
Table 2: Miscellaneous Physical Properties							
_	% HCI						
	<u>5%</u>	<u>10%</u>	<u>20%</u>	<u>30%</u>	<u>40%</u>		
Heat Evolved on Infinite Dilution <sup>a</sup> © 25°C (KCal/Mole HCl)	.57	.90	1.6	2.9	4.3		
Electrical Conductivity <sup>a</sup> (Mho/Cm x 10 <sup>4</sup> )	3948	6302	7615	6620	5152		
Thermal Conductivity <sup>b</sup> @ 90°F     Gm Cal/(sec) (SqCm) (°C/Cm)			1.195	1.110	1.030		
Surface Tension @ 68°Fb     (Dynes/Cm)	72.4	72.2	71.3	69.4	65.9		
a. Kirk – Othmer, Encyclopedia of Chemical Technology     b. Lange's Handbook of Chemistry							

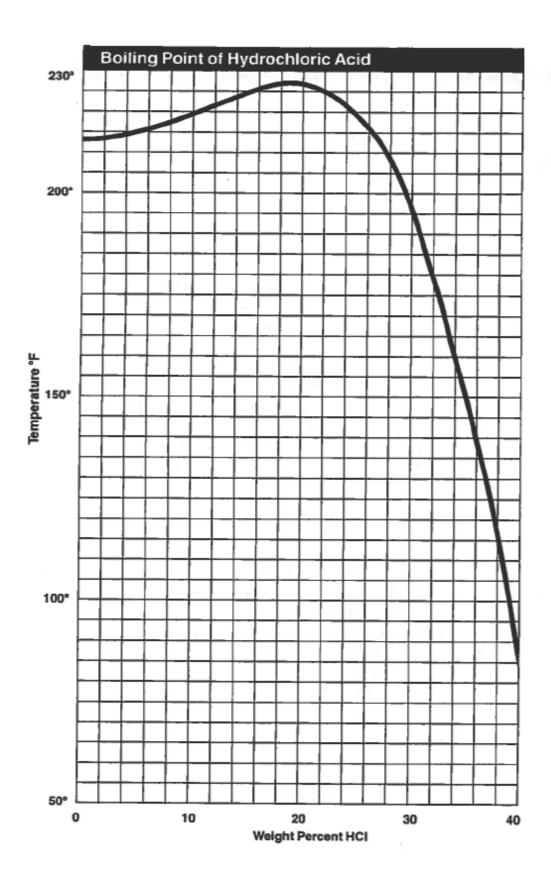
Tabl	Table 3: Dilution Table for Muriatic Acid													
Gallon		and Water to N	Make 10	00 Gallons	Dilute A									
-	Stock	Acid				D	esired S	Strength	of Dil	ute Acid				
	ength	Sp.Gr.		Acid	7 1/2%			Acid		Acid		Acid		Acid
°Bé	%HCI	60/60°F	Acid	Water										
18.0	27.92	1.1417	161	841	244	759	207	674	506	497	690	312	007	2
18.1 18.2	28.09 28.26	1.1426 1.1435	160 159	843 844	242 241	760 762	327 325	676 678	502 499	501 504	686 681	317 322	997 990	3 10
18.3	28.44	1.1444	157	845	239	764	323	681	495	508	676	327	983	17
18.4	28.61	1.1453	156	846	237	765	320	683	492	511	672	331	977	23
18.5	28.78	1.1462	155	847	236	767	318	685	489	515	667	336	970	30
18.6	28.95	1.1471	154	848	234	769	316	687	486	518	662	341	964	36
18.7	29.13	1.1480	153	849	233	770	314	690	482	521	658	345	957	43
18.8	29.30	1.1489	152	850	231	772	312	692	479	525	653	349	951	49
18.9	29.48	1.1498	151	851	230	773	310	694	476	528	648	354	944	57
19.0 19.1	29.65	1.1508 1.1517	150 149	852 853	228 226	775 777	308 306	696 698	473 469	531 534	645 641	358 363	938 931	63 70
19.1	29.83 30.00	1.1517	149	854	225	777 778	306	700	469 466	538	636	363 367	925	70 76
19.2	30.18	1.1535	147	855	223	780	302	702	463	541	632	371	919	82
19.4	30.35	1.1544	146	856	222	781	300	704	460	544	628	375	913	88
19.5	30.53	1.1554	145	857	221	783	298	706	457	547	624	379	907	94
19.6	30.71	1.1563	144	858	219	784	296	708	454	550	620	384	901	100
19.7	30.90	1.1572	143	859	218	785	294	710	451	553	615	388	895	106
19.8	31.08	1.1581	142	860	216	787	292	712	448	556	611	392	889	112
19.9	31.27	1.1590	141	861	215	789	290	714	445	559	607	397	883	119
20.0			140	862 I→	[213→	790]	288	716	442	562	603	401	877	125
20.1 20.2	31.64 31.82	1.1609 1.1619	139 139	863 864	212 210	791 793	286 284	718 720	439 436	565 568	599 595	405 409	871 866	131 136
20.2	32.01	1.1628	138	865	209	793 794	282	720 722	433	571	591	409	860	142
20.4	32.19	1.1637	137	866	208	795	280	724	430	574	587	417	854	148
20.5	32.38	1.1647	136	867	206	797	278	726	428	577	584	421	849	153
20.6	32.56	1.1656	135	868	205	798	277	728	425	580	580	424	843	159
20.7	32.75	1.1666	134	868	204	800	275	729	422	583	576	428	838	164
20.8	32.93	1.1675	133	869	202	801	273	731	419	585	572	432	833	170
20.9	33.12	1.1684	132	870	201	803	271	733	417	588	569	436	827	176
21.0	33.31	1.1694	132	871	200	804	270	735	414	591	565	440	821	182
21.1 21.2	33.50 33.69	1.1703 1.1713	131 130	872 873	198 197	805 806	268 266	737 738	411 409	594 596	561 558	443 447	816 811	187 192
21.2	33.88	1.1713	129	874	196	808	264	730 740	409	599	554	447 451	806	192
21.4	34.07	1.1732	128	875	195	809	263	742	403	602	550	454	801	202
21.5	34.26	1.1741	127	875	193	810	261	744	401	604	547	458	796	207
21.6	34.45	1.1751	127	876	192	812	259	745	398	607	543	462	790	214
21.7	34.64	1.1760	126	877	191	813	258	747	396	609	540	465	786	218
21.8	34.83	1.1770	125	878	190	814	256	749	393	612	537	468	781	223
21.9	35.02	1.1779	124	879	189	815	255	750	391	615	533	472	776	227
22.0	35.21	1.1789	123	879	187	816	253	752	388	617	530	475	771	233
22.1 22.2	35.40	1.1798	123	880	186	818	251	754 755	386	619	527 524	479	766	238
22.2	35.59 35.78	1.1808 1.1817	122 121	881 882	185 184	819 820	250 248	755 757	384 381	622 624	524	482 485	761 757	243 247
22.4	35.76	1.1827	120	883	183	821	247	757 758	379	627	517	489	752	252
22.5	36.16	1.1836	120	883	182	822	245	760	377	629	514	492	748	257
22.6	36.35	1.1846	119	884	181	823	244	761	374	631	511	495	743	262
22.7	36.54	1.1856	118	885	180	824	242	763	372	634	508	498	739	266
22.8	36.73	1.1866	118	885	179	826	241	764	370	636	505	501	734	271
22.9	36.93	1.1875	117	886	177	827	239	766	368	638	502	504	730	275
23.0	37.14	1.1885	116	887	176	828	238	767	365	641	499	508	725	280
23.1	37.36	1.1895	115	888	175	829	236	769	363	643	495	511	720	285
23.2 23.3	37.58	1.1904	115 114	889 880	174	830	235	771 772	360	646 648	492 480	515 518	715	291 285
23.4	37.80 38.03	1.1914 1.1924	113	889 890	173 172	832 833	233 232	772 774	358 356	648 651	489 485	522	711 706	300
20.4	00.00	1.1327	110	000	112	000	202	117	000	001	700	ULL	700	500

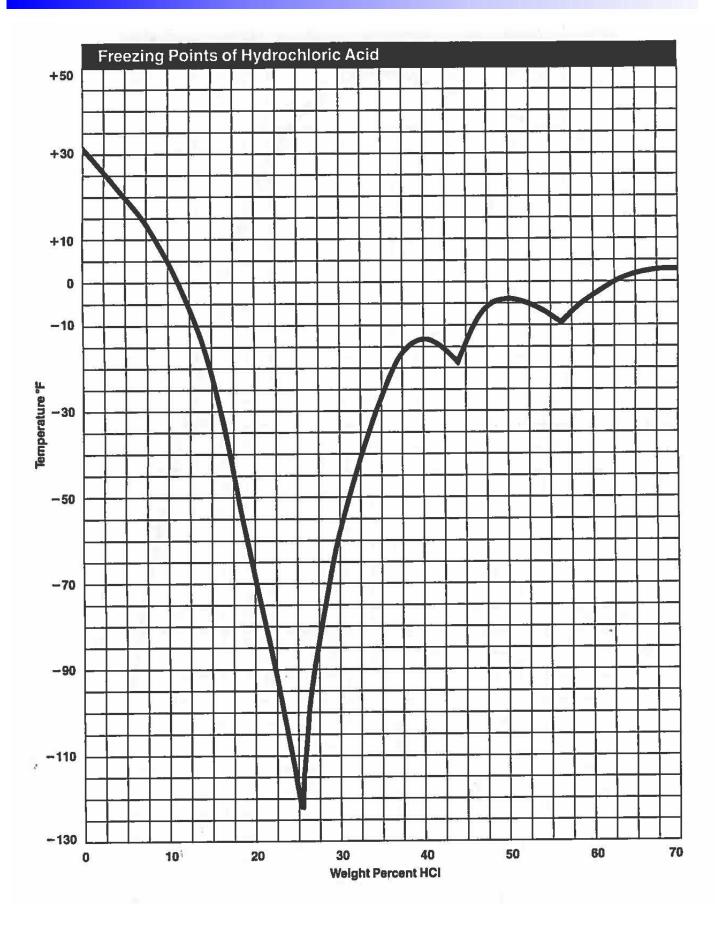
**Example:** To make 1,000 gallons 7 ½% dilute acid from 20 °Bé stock acid, use 213 gallons of stock acid and 790 gallons water (see bracketed figures in 20.0 line above). Although gallons of acid plus gallons of water total more than 1000 gallons, only 1,000 gallons of dilute acid will result when mixed.

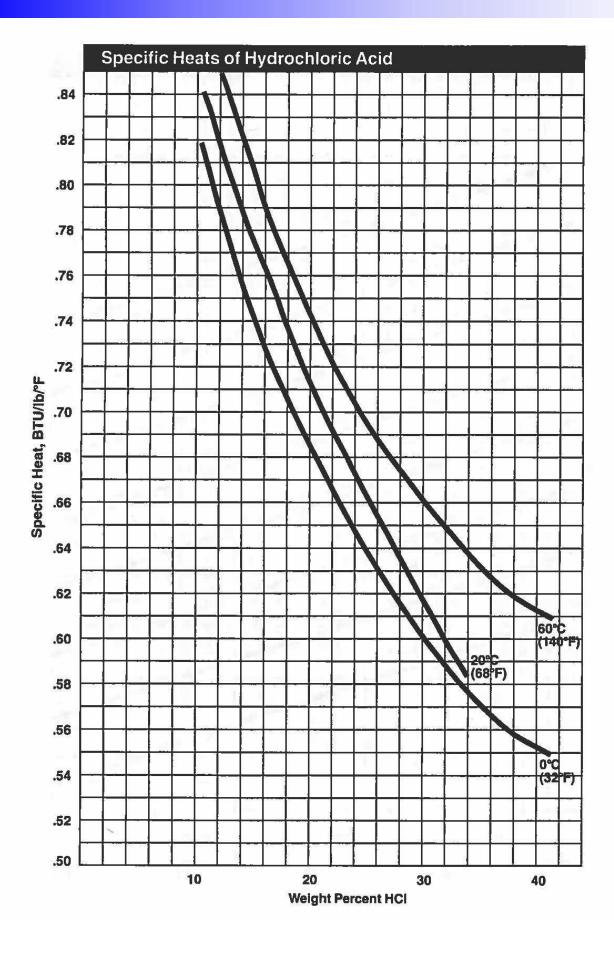
Table 4:	Hydrochlo	oric Acid E	guivalent	Properties				
	Sp. Gr.			Sp. Gr.			Sp. Gr.	
°Bé	60/60°F	% HCI	°Bé	60/60°F	% HCI	°Bé	60/60°F	% HCI
1.00	1.0069	1.40	16.0	1.1240	24.57	20.8	1.1675	32.93
2.00	1.0140	2.82	16.1	1.1248	24.73	20.9	1.1684	33.12
3.00	1.0211	4.25	16.2	1.1256	24.90	21.0	1.1694	33.31
4.00	1.0284	5.69	16.3	1.1265	25.06	21.1	1.1703	33.50
5.00	1.0357	7.15	16.4	1.1274	25.23	21.2	1.1713	33.69
5.25	1.0375	7.52	16.5	1.1283	25.39	21.3	1.1722	33.88
5.50	1.0394	7.89	16.6	1.1292	25.56	21.4	1.1732	34.07
5.75	1.0413	8.26	16.7	1.1301	25.72	21.5	1.1741	34.26
6.00	1.0432	8.64	16.8	1.1310	25.89	21.6	1.1751	34.45
6.25	1.0450	9.02	16.9	1.1319	26.05	21.7	1.1760	34.64
6.50	1.0469	9.40	17.0	1.1328	26.22	21.8	1.1770	34.83
6.75	1.0488	9.78	17.1	1.1336	26.39	21.9	1.1779	35.02
7.00	1.0507	10.17	17.2	1.1345	26.56	22.0	1.1789	35.21
7.25	1.0526	10.55	17.3	1.1354	26.73	22.1	1.1798	35.40
7.50	1.0545	10.94	17.4	1.1363	26.90	22.2	1.1808	35.59
7.75	1.0564	11.32	17.5	1.1372	27.07	22.3	1.1817	35.78
8.00	1.0584	11.71	17.6	1.1381	27.24	22.4	1.1827	35.97
8.25	1.0603	12.09	17.7	1.1390	27.41	22.5	1.1836	36.16
8.50	1.0623	12.48	17.8	1.1399	27.58	22.6	1.1846	36.35
8.75	1.0642	12.87	17.9	1.1408	27.75	22.7	1.1856	36.54
9.00	1.0662	13.26	18.0	1.1417	27.92	22.8	1.1866	36.73
9.25	1.0681	13.65	18.1	1.1426	28.09	22.9	1.1875	36.93
9.50	1.0701	14.04	18.2	1.1435	28.26	23.0	1.1885	37.14
9.75	1.0721	14.43	18.3	1.1444	28.44	23.1	1.1895	37.36
10.00	1.0741	14.83	18.4	1.1453	28.61	23.2	1.1904	37.58
10.25	1.0761	15.22	18.5	1.1462	28.78	23.3	1.1914	37.80
10.50	1.0781	15.62	18.6	1.1471	28.95	23.4	1.1924	38.03
10.75	1.0801	16.01	18.7	1.1480	29.13	23.5	1.1934	38.26
11.00	1.0821	16.41	18.8	1.1489	29.30	23.6	1.1944	38.49
11.25	1.0841	16.81	18.9	1.1498	29.48	23.7	1.1953	38.72
11.50	1.0861	17.21	19.0	1.1508	29.65	23.8	1.1963	38.95
11.75	1.0881	17.61	19.1	1.1517	29.83	23.9	1.1973	39.18
12.00	1.0902	18.01	19.2	1.1526	30.00	24.0	1.1983	39.41
12.25	1.0922	18.41	19.3	1.1535	30.18	24.1	1.1993	39.64
12.50	1.0943	18.82	19.4	1.1544	30.35	24.2	1.2003	39.86
12.75	1.0964	19.22	19.5	1.1554	30.53	24.3	1.2013	40.09
13.00	1.0985	19.63	19.6	1.1563	30.71	24.4	1.2023	40.32
13.25	1.1006	20.04	19.7	1.1572	30.90	24.5	1.2033	40.55
13.50	1.1027	20.45	19.8	1.1572	31.08	24.6	1.2043	40.78
13.75	1.1048	20.86	19.9	1.1590	31.27	24.7	1.2053	41.01
14.00	1.1048	21.27	20.0	1.1600	31.45	24.7	1.2063	41.24
14.25	1.1009	21.68	20.0	1.1609	31.64	24.9	1.2003	41.48
14.50	1.1111	22.09	20.1	1.1619	31.82	25.0	1.2073	41.72
14.75	1.1132	22.50	20.2	1.1628	32.01	25.0	1.2003	41.72
						25.1		
15.00	1.1154	22.92	20.4	1.1637	32.19		1.2103	42.30
15.25	1.1176	23.33	20.5	1.1647	32.38	25.3	1.2114	42.64
15.50	1.1197	23.75	20.6	1.1656	32.56	25.4	1.2124	43.01
15.75	1.1219	24.16	20.7	1.1666	32.75	25.5	1.2134	43.40

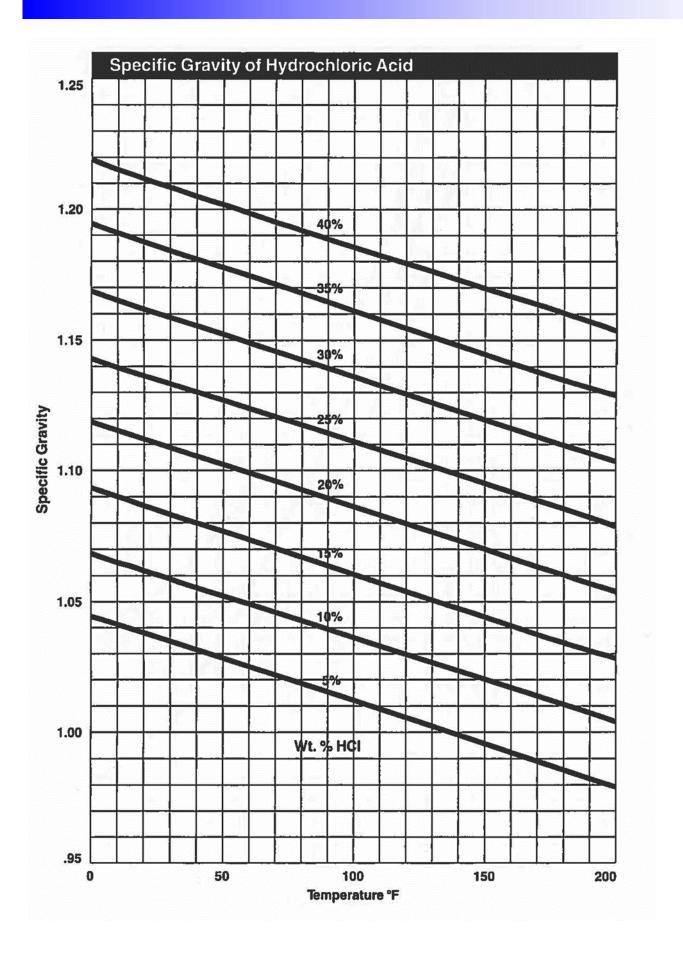


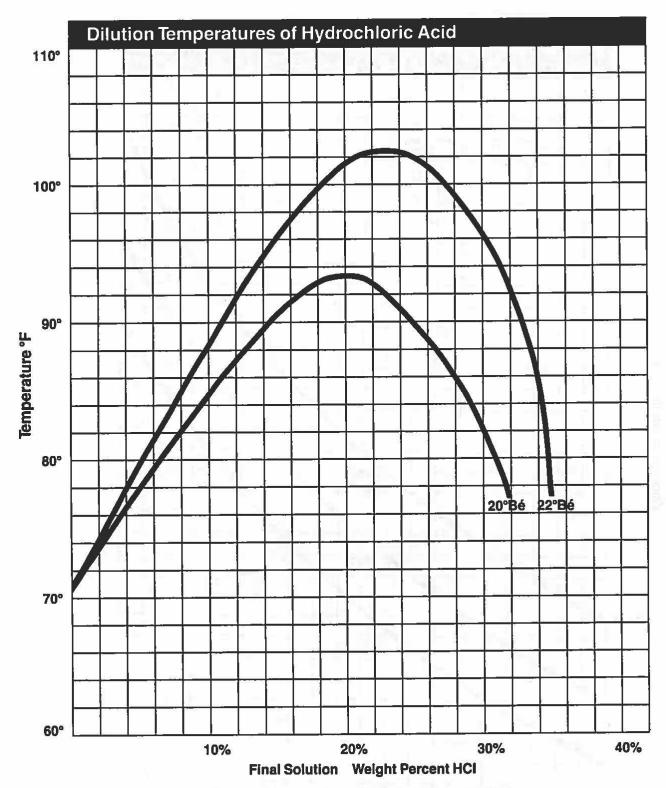




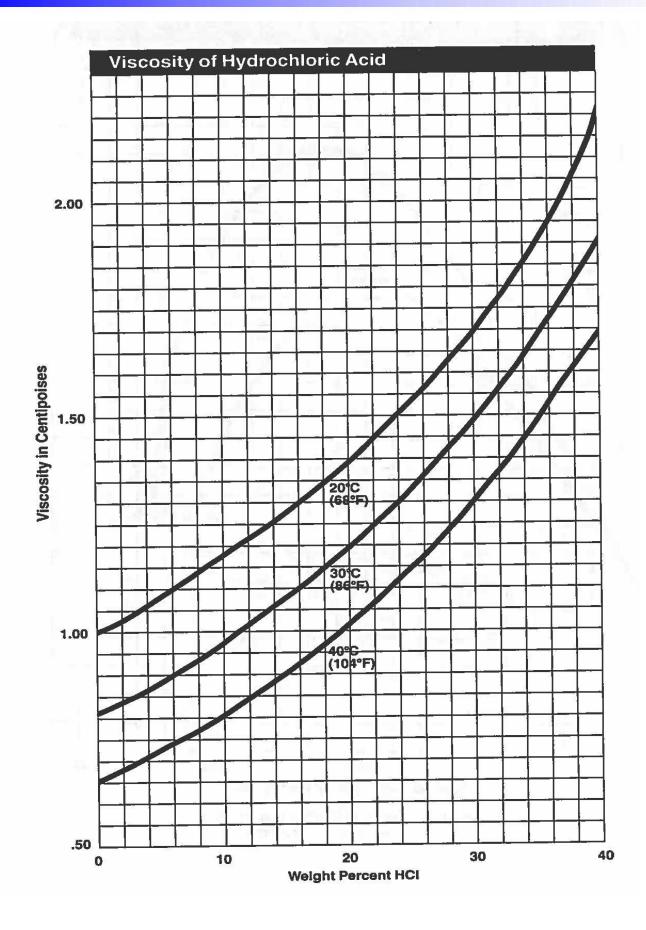








Notes: Temperature of Diluting Water @ 70°F Initial Temperature of Acid @ 77°F



# **Methods of Analysis**

# Sampling

It is imperative that proper sampling procedures be followed because the presence of extremely small quantities of metal will cause discoloration of the hydrochloric acid. Iron is the most common contaminant and hydrochloric acid containing iron will have a yellow color.

- The railcar or truck should be sampled from the top through the manway. CAUTION: Railcar may be pressured. Manway should be opened carefully after pressure has been bled off. A glass or plastic sample bottle should be used, and the caps should be plastic. The cap lining should be an acid resistant material. The sample bottle should be thoroughly washed and dried before using.
- The sample should be taken a few inches below the top surface of the acid. The sampling apparatus should be constructed of acid resistant materials. Care should be taken to assure that no metal is accidentally dropped into railcar or truck. A few flakes of rust or a small washer could discolor an entire load of acid.
- 3. If an off-color acid sample is obtained, resample the railcar or truck. Examine sampling equipment for metallic surfaces which could come into contact with the acid.

# **Determination of Total Acidity**

## **Apparatus**

- 1. Burette, 50 ml, Class A.
- 2. lodine flasks, glass-stoppered, 125 ml.
- 3. Analytical balance.
- 4. Pipette, 3 ml.
- 5. Thermometer, centigrade.

## Reagents:

 Phenolphthalein Indicator, alcoholic solution: Dissolve 1 gram of phenolphthalein in 100 ml of ethanol. Satisfactory end points may be determined by titrating to the first trace of pink that persists for 15 seconds of swirling, when titrating a strong acid such as HCI. 2. Sodium Hydroxide, Standard Solution, 0.5 Normal: Standardize against primary standard potassium acid phthalate (KHC<sub>8</sub>H<sub>4</sub>0<sub>4</sub>, abbreviated KHP) which has been dried in a glass container at 120°C for 2 hours. Cool in a desiccator. Weigh out 4.0 grams of KHP to the nearest 0.1 mg, add 50 to 100 ml de-ionized water, and stir gently to dissolve. Add 3 drops phenolphthalein indicator. Titrate with NaOH to a pink end point. Calculate the normality of the NaOH solution as follows:

$$A = B = 0.20423 \times C$$

where:

A = normality of the NaOH solution,

B = grams of KHP used, and

C = milliliters of NaOH solution consumed.

Duplicate determinations which agree within 0.0010 normality units are acceptable for averaging, with a 95% confidence level.

Correct each subsequent titration for differences in temperatures according to the following formula:

$$N = N_s + 0.00014(s-t)$$

where:

N = normality of NaOH solution at temperature t,

 $\begin{aligned} N_s &= \text{normality of NaOH solution at temperature s}, \\ &\quad \text{during standardization,} \end{aligned}$ 

- s = temperature of NaOH solution during standardization, °C, and
- t = temperature of NaOH solution during analysis, °C.

#### Procedure:

- 1. Transfer approximately 30 ml of de-ionized water to a 125 ml glass-stoppered iodine flask, stopper, and weigh to the nearest 0.1 mg.
- Add rapidly a convenient size sample, depending upon the acid strength as given in Table 5, stopper immediately, and reweigh.
- 3. Add 3 to 5 drops of phenolphthalein indicator solution.
- 4. Record the temperature of the 0.5 N NaOH solution, and then titrate the sample to a pink end point.
- 5. Record the titration to the nearest 0.02 ml.

Table 5: Sample Size for Total Acidity		
HCI, percent	Baumé	Sample Size, grams
37	22.9°	1.0 to 2.3
35	21.6°	2.0 to 2.4
33	20.8°	2.2 to 2.6
31	19.8°	2.3 to 2.8
29	18.6°	2.5 to 3.0
27	17.5°	2.7 to 3.2

#### Calculation:

- Record as V the delivered volume at the recorded temperature.
- 2. Calculate the total acidity as percentage of hydrochloric acid as follows:

where:

V = milliliters of NaOH solution required for titration of the sample.

N = temperature corrected normality of the NaOH solution

W = grams of sample used.

## Precision:

Duplicate determinations which agree within 0.15% are acceptable for averaging, with a 95% confidence level. This method should yield equivalent results to ASTM E-224, "Standard Test Methods for Analysis of Hydrochloric Acid."

# **Determination of Gravity**

#### Apparatus:

- Hydrometer, streamline or torpedo design, precision grade, for liquids heavier than water in ranges from 17.5 to 23° Bé, with divisions of 0.1° Bé, and standardized at 60/60° F.
- 2. Thermometer, 30 to 90°F with 0.5 divisions.
- 3. Cylinder, glass, diameter 38 to 40 mm, height 325 to 375 mm.

#### Procedure:

- 1. Rinse a clean hydrometer cylinder with the sample to be tested and add the sample.
- 2. Place the cylinder in a vertical position in a location free of air currents.

- Insert the hydrometer to the level at which it floats.
   As the hydrometer is released, spin it gently. This will center the hydrometer in the cylinder, help dislodge any air bubbles which may be clinging to the hydrometer, and release surface tension distortions of the meniscus.
- 4. Read the hydrometer. The correct reading is that point of the hydrometer scale at which the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and slowly raising the eye until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale.
- 5. Insert the thermometer into the cylinder and stir gently until the thermometer reading stabilizes. Read the temperature of the sample.
- 6. Perform the above procedure fairly rapidly, as HCl has a high vapor pressure, and the sample will become weaker if allowed to sit open for too long a time.

#### Calculation:

1. Correct the reading for differences in temperature according to the following formula:

$$B_{60} = B_t + 0.033(t-60)$$

where:

B<sub>60</sub> = corrected Baumé at 60°F

B<sub>t</sub> = observed Baumé

= temperature of sample during analysis °F

2. To convert a Baumé reading to specific gravity, calculate as follows:

#### Precision:

Duplicate determinations which agree within 0.2° Baumé are acceptable for averaging, with a 95% confidence level. This procedure is equivalent to ASTM E-224.

## **Determination of Iron**

#### **Apparatus:**

- 1. A UV/Vis spectrometer or other suitable instrument with absorbance range from 500 to 525 nm
- 2. 100 ml class A stoppered graduated cylinders
- Analytical balance capable of weighing 0.1 milligrams
- 3. A one-milliliter class A pipette
- 4. A 50-milliliter graduated cylinder
- 7. Absorption cells, 2-cm light path

## Reagents:

- 6 Molar ammonium acetate solution (dissolve 462.5 grams in 1 liter of distilled or de-ionized water).
- 2. Sodium sulfite solution (dissolve 126 grams in 1 liter of distilled or de-ionized water).
- Orthophenanthroline indicator (0.2 grams of 1,10phenanthroline [monohydrate]) is dissolved in 20 mL of reagent grade ethanol and diluted to 100 mL with distilled or de-ionized water.
- Distilled or de-ionized water.
- A standard 1,000 ppm iron solution (either can be a purchased solution or prepared by dissolving 1.0 gram of reagent iron wire in hydrochloric acid and diluting to 1,000 mL with distilled or de-ionized water).

# **Preparation of a Standard Curve:**

- A. Prior to analyzing a sample, a standard curve containing at least five points should be established. The curve should read milligrams of iron in the final 100 mL of solution. The absorbencies of the standards measured at 510 nm should bracket the absorbance of the sample.
- B. A typical iron standard curve for 20° Baumé or 22° Baumé hydrochloric acid would have the following iron concentration:

.010 milligrams

.025 milligrams

.050 milligrams

.075 milligrams

.100 milligrams

#### Procedure:

- Accurately weigh 1.0 to 10.0 grams of the hydrochloric acid sample into a stoppered graduated cylinder.
- 2 Dilute to 20 milliliters with de-ionized or distilled water.
- 3. Add 20 milliliters of the sodium sulfite reagent. Mix the cylinder well.
- 4. Add one milliliter of o-phenanthroline indicator to the cylinder and mix the contents well.
- 5. Add 10 milliliters of ammonium acetate buffer to the cylinder and mix the contents well. [Note: the contents of the cylinder should have a faint acetate smell]. When tested with pH indicator paper, the sample should read neutral or slightly basic. If the odor of sulfur dioxide is present, add additional buffer until the sulfur dioxide odor is gone.
- Dilute the samples to 100 milliliters with distilled or de-ionized water and mix well.
- 7. Prepare a blank containing all the reagents used in the sample at the same time the sample is being prepared.
- 8. Allow the blank and the sample to stand for 15 minutes for full color development.
- Determine the absorbance of the sample at the same wavelength used for the calibration curve, blanking the instrument at zero absorbance with the blank solution.
- 10. Determine from the calibration curve the milligrams of iron.

## **Calculations:**

ppm Fe = mg Fe from Std. Curve X 100 X 10000 Sample weight (grams) X 1000

#### Precision:

This procedure should yield equivalent results to ASTM E-224 under normal conditions but may give different results with heavily contaminated samples.

## **Determination of Color**

#### Apparatus:

- 1. Two Hellige® Nessler Tubes, number 611-T, with caps, number 611-PL.
- 2. Hellige® Color Testing Disc, number 611-10, Range 0-50 APHA.
- 3. Hellige® Aqua Tester.

#### Procedure:

- 1. Swing open the back cover of the Aqua Tester. Remove the right-hand Nessler tube, rinse it with the sample to be tested, and fill it to the mark with the sample. Insert a cap into the tube. Rest the bottom of the tube in the right-hand circular depression in the base of the cover, and then press the tube into the right-hand spring clip.
- Remove the left-hand Nessler tube, rinse it with deionized water, and fill to the mark with de-ionized water. Insert a cap into the tube. Place this tube in the left-hand circular depression and press into the left-hand spring clip. Press caps as close as possible to each other.
- 3. Close the cover and switch on the lamp.
- 4. Make the color comparison by revolving the color disc so that one standard after another is brought into the observation field. The observation fields for the colorimetric comparison are seen as half-fields in the magnifying prism. The right-hand field is produced by the Nessler tube containing the sample. The left-hand field is formed by one of the glass color standards in conjunction with the Nessler tube containing water. It is necessary to compare liquid vs. liquid media. The color fields should be viewed with the eye in line with the center of the magnifying prism. The half-fields should be free of shadow effect, which is caused by off-center of oblique observation. For normal eyesight, the preferred viewing distance is approximately 10 inches. Do not make the mistake of placing the eye close to the apparatus housing. Do not prolong the observation for more than 10 to 15 seconds.

When a color match is obtained with one of the standards, the result is read directly from the figure seen through the circular opening within the light shield. If the color of the sample is intermediate between two glass standards, choose the standard closest to the sample color.

#### **Notes**

- The Aqua Tester should be placed so that the color fields seen through the magnifying prism do not receive direct light from behind the observer. The color comparison is best made in a room that is not too brightly illuminated. The darker the interior of the light shield, the easier the color comparison.
- 2. The position of the filament varies slightly in different lamp bulbs. Therefore, for uniform illumination of the color fields, it is necessary to adjust the bulb before the apparatus is first used. Fill the two Nessler Tubes to the mark with deionized water and insert a cap in each tube. Swing open the back cover of the Aqua Tester, rest the bottoms of the tubes in the circular depressions in the base of the cover, and press the tubes into the spring clips. Close the cover and switch on the lamp. Release the screw near the bulb socket and slide and turn the socket until the two fields are of equal brightness, then tighten the screw. No further adjustment is necessary unless the bulb is replaced.
- 3. To insert a color disc, remove the light shield from the upper platform of the apparatus housing and place the center of the color disc on the ring, with the number plates facing upward. Then replace the cover. As the disc is rotated, the number plates representing the values of the permanent glass color standards will be seen through the circular opening within the light shield.
- 4. This method will not produce the same results as ASTM E-224. The results will be somewhat lower and less accurate.

# **Further Information**

More detailed information on hydrochloric acid or any of its specific applications is available on request through the OxyChem Technical Service Department.

Call or write: Technical Service Department OxyChem 6200 S. Ridge Rd. Wichita, KS 6715

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# References

Annual Book of ASTM Standards, Volume 15.05, American Society for Testing and Materials, 2002

2004 North American Emergency Response Guidebook

Food Chemicals Codex,  $5^{\text{th}}$  Edition, National Academy of Sciences, 1996

EPA Fact Sheet, *The Emergency Planning and Community Right-to-Know Act* (EPA 550-F-00-004)

49 CFR, Code of Federal Regulation Title 49 – Transportation, Hazardous Materials Regulations, U.S. Government Printing Office

2007 TLVs® and BEIs®, Threshold Limit Values for Chemical Substances and Physical Agents, ACGIH®, 2007

NIOSH Respirator Decision Logic, DHHS (NIOSH) Publication No. 87-108, May, 1987

NIOSH Guide to Industrial Respiratory Protection, DHHS (NIOSH) Publication No. 87-116, September, 1987

Hydrochloric Acid Storage and Piping Systems, Pamphlet 163, The Chlorine Institute, 2001

29 CFR§1910.120(q), Code of Federal Regulations Title 29 - Department of Labor, OSHA Regulations on Hazard Communications, U.S Government Printing Office.

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