Anhydrous Hydrogen Chloride

Hydrogen Chloride is a high pressure liquefied gas, toxic and corrosive acid
HCl, Halogen Acid
CAS# 7647-01-0
UN# 1050
Molecular Weight 36.46
Liquefied Gas with Vapor Pressure of 613 psig @ 70°F (21°C)
Gas Density of 0.095 lb/ft^3, (1.522 gm/l) @ 70°F (21°C)
Liquid Density of 52.7 lb/ft^{3,} (0.842 kg/l) @ 70°F (21°C)
Toxic Gas with TLV and PEL of 5 ppm, LC_{50} 3120 ppm, IDLH 50 ppm
Shipping Labels Poison Gas and Corrosive
Boiling Point, 1 atm. -121°F (-85°C)
Freezing Point, 1 atm. -173.6°F (-114.2°C)
Critical Temperature 124.5°F (51.4°C)
Hydrogen Chloride has a vapor density heavier than air. - 1.266
Gas Specific Volume @ 70°F (21°C) - 10.55 ft^3/lb (657 cc/gm)
Autoignition - Not Flammable
Flammability (LFL -UFL) - Not Flammable
Thermal Stability - Hydrogen Chloride is thermally stable
Water Solubility - Hydrogen Chloride is very soluble in water
Odor - Hydrogen Chloride is reported to have a sharp irritating odor
Latent Heat of Vaporization -121°F (-85°C) - 205.5 btu/lb (478 kJ/kg) at Boiling Point

Hydrogen chloride is used in many applications. It has a high vapor pressure and is extremely soluble in water. It is extremely corrosive when hydrolyzed with the moisture in the air to form hydrochloric acid.

Fig. 1: HCl Cylinder Leak

Most Electronic grade HCl in the US was shipped in a insultated refrigerated railcar by Dow Chemcal to the gas supplier for repackaging. These railcars are designed to ICC-105A-600W specification with a design pressure of 600 psig, they had a pressure rating 425-450 psig which less than the HCl vapor pressure at 70°F of 630 psig.[1,2] They filled with cold HCl (-50°F) a saturated vapor pressure of 76 psig. While it has been estimated that it would take 30 days for it to warm to a temperature of 47oF activating the 450 psig pressure releif device, the Dept of Transportation requires these to reach their destination within 10 days to insure that they do not.[2]

The older railcars (89,000 lbs) had a refrigeration coil in the railcar to cool the liquid HCl to -20°F.

Fig. 2: Older HCl Railcar with Cooling Coil

The larger railcars (150,000 lbs) did not have a cooling coil, instead a heat exhanger is mounted on top of the railcar at the gas supplier site to condense and cool the HCl vapor. The liquid returning back to the railcar to keep the liquid cold.

During Katrina (2005) this was not possible at a gas supplier filling facility in New Orleans, LA. Due to flooding electric power was lost for many weeks. This allowed the vapor pressure to build to unsafe levels over many days. The typical pressure relief device has a metal rupture disk that blew at 450 psig into a spring loaded relief valve which reset at 275 psig.

Fig. 3: HCl Railcars In Flood

Periodically workers would row out to the railcars and vent some HCl gas directly into the flood waters to cool the HCl in order to drop the pressure to prevent the pressure relief device from activating and venting the gas into the atmosphere.

Dow Chemical due to safety concerns of transporting the railcars throughout the US announced in 2006 that they would no longer ship railcars. Since they were the only qualified source for most pharmaceutical and semiconductor companies they continued until 2012. Air Products and Linde formed the Anhydrous Hydrogen Chloride a 50-50 Joint Venture Hydrochlor in 2011.

Hydrochlor built a facility immediately outside of Dow's Freeport, Texas, site to process and repackage HCl into a tube trailer with HCl supplied via pipeline. The facility, was commissioned in the second quarter of 2012.

Hydrochlor sold HCl exclusively to the joint venture partners, who continued to market HCl independently. In 2021 it was announced by Dow Chemical (Now DuPont) that the process would be shutdown by Jan 1, 2022.

Niacet a suppleir in Niagra Fall, NY has HCl byproduct, they purcahsed the assetts of Alexander Chemical and are suppling the industry since Jan 1. 2022. They are ona steep learning curve regarding purity, cylinder conditioninig, analysis, stuck/corroded valves, etc.

HCl is supplied in cylinders, ton cylinders and tube trailers.

Fig. 4: HCl "Ton" Y Container

Incidents

Because of its high vapor pressure and corrosivity, HCl has been involved in numerous incidents. The following are significant incidents.

Pressure Relief Device (PRD)

Because of the high vapor pressure, HCl cylinders have a combination pressure relief device, (CG-4) which is a 165°F fuse metal with a metal rupture disk sized for the cylinder pressure rating. In some rare cases the rupture disk might not have sealed properly or is defective exposing the fuse metal to the pressure of HCl. With this high vapor pressure the fuse metal will cold flow until it starts to leak.

Fig. 5: Fuse Metal That Extruded Until the HCl Leaked

Figs. 6 and 7 : Leaking HCl PRD Fully Activates

Residence, June 5, 1996

In one incident a HCl Cylinder for unknown reasons was partially buried in a residential yard for years. It started to leak at some point corroding the cylinder and valve over time. It was not until the leak got worse that the homeowner called 911.

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Gas prompts evacuation

Cylinder leaked hydrogen chloride in Solebury

By Rachel Dickler and Bill Devlin
Staff Writers

SOLEBURY — A strange gas that was leaking from a cylinder buried in the ground on a Stovers Mill Road property Wednesday was determined to be hydrogen chloride.

Dealing with the problem was a giant headache for emergency workers.

The Bucks County Hazardous Incident Response Team (HIRT) began removing the cylinder, described as about the size of an oxygen tank, from the property about 7 p.m., a little more than eight hours after the property owner reported the leak to the Point Pleasant Fire Department.

However, after the cylinder was placed in a large tank, called a "casket," the light green gas began to leak from the sealed tank. Late Wednesday night, Bucks emergency management officials, joined by crews from the Environmental Protection Agency and state Department of Environmental Protection were still attempting to seal the leak in the casket.

Adam Selaker, deputy chief of HIRT, reached later in the evening, said the hydrogen chloride was neutralized on site.

Earlier in the day, two homes were evacuated by police, after the property owner had called the Point Pleasant Fire Department to report that gas was leaking from a steel tank buried in the ground.

The area around Stovers Mill Road was sealed off by fire police. In addition to Point Pleasant, firefighters from Midway and New Hope were called to the scene to assist if a larger area had to be evacuated.

Solebury Police Chief Richard J. Mangan said the cylinder had been abandoned on the property some time ago. In addition to a residence, the property houses a dentist office.

Solebury Supervisor Timothy Brought, who serves as assistant director of emergency management, said the abandoned cylinder had no connection with the dentist

See GAS on Page A 5

A member of the Bucks County Hazardous Incident Response Team is hosed off Wednesday with a decontaminant after working to remove a cylinder filled with a gas from a Solebury Township property. Officials neutralized the gas later Wednesday night.

(Staff photo by Donald R. Boorse)

Figs 8, 9 and 10: Buried Cylinder Solebury Township, PA

Cylinder Rupture 1969, US

At a gas supplier facility where HCl was filled into trailers and cylinders from a refrigerated railcar. The practice, at the time, was to top off returned HCl cylinders. The operator would put the cylinder on the scale, take its weight, subtract its tare weight, then add enough HCl to end up with 65lbs net.
One day after filling several cylinders, one of the cylinders began to heat up. Upon noticing it, the operator called to his supervisor and they decided to move the cylinder outside and away from the building. Before they got the cylinder outside of the building it ruptured violently, killing both men.

The investigation revealed that the cylinder had gotten backfilled with nearly 20 lbs of propylene, at a customer's site. The difference in densities between propylene and HCl meant that the cylinder was nearly hydrostatically full. The exothermic addition reaction that ensued heated the cylinder and raised the internal pressure to the bursting pressure of the cylinder.

Topping off cylinders was banned throughout the company as a result.

Tube trailer flex line shear, 1985? US

Gas supplier filling HCl cylinders from tube trailer. A shutoff valve failed and the operator was instructed to not startup the system. He proceeded anyway. After he opened the trailer valve the 6,000 psig rated braided stainless steel hose sheared. The plant manager donned an SCBA and attempted to close the system valve by climbing on top of the tubes. He could not reach the valve. He finally climbed down and grabbed the hose and closed the valve.

It is not known if corrosion was the cause of the failure or if the line was overpressurized at some point when liquid HCl was trapped in the line. As a Best Practice many companies will have a time limit on how long a flexible hose can be used.

Tube Trailer Rupture, 1990, US

A returned tube trailer was refilled with HCl. The practice was to weigh the tube trailer to determine the amount of residue. This was assumed to be distributed evenly throughout the 8 tubes. It was then filled with cold HCl from a refrigerated railcar. As the HCl warmed up it expanded and the liquid filled a tube causing it to rupture the next morning. No injuries

Fig. 11: Ruptured Tube Flew Over 800 ft

Fig. 12: Tube Trailer With the Adjacent Tube Dislodged

Investigation determined that a tube was contaminated with cotton oil (1650 lbs) at the user site. It was filled with 2,600 lbs of HCl until it stopped flowing. It ruptured at an estimated pressure of 7000 psig,(due to the BLEVE) rapidly expanding liquefied gas tearing the tube into pieces
The tube was torn into two major pieces. The largest section consisting of ~80% of the tube ripped through the bulk head of ½" steel and landed 837 feet away.
Trailers are now no longer filled with any residue. They must all be emptied before fill

User Site, Tube Cracked, 1990, US

Three tube trailer at user, site cotton delinting suddenly developed a crack 18” exterior and 4 ft interior, releasing the HCl. No injuires and minor damage. Moisture causing interior corrosion appeared to be the root cause.. There were not further incidet=nts like this

Transportation, Tube Trailer PRD Leak, May 12, 2014, US

Leaking PRD noted by a driver on Route 85. ER team packed tube with dry ice to cool

Decision to cold coil transfer into an “empty” trailer. Empty trailer from Texas drove 20 hours to act as a reservoir for cascading the HCl. Dry ice on the tube surface was used to enhance the transfer.

Fig. 13: Leaking Tube Trailer

Emergency Response

To isolate a small leak the following device was designed, tested and patented for HCl tube trailers. It provides the ER team with a system to quickly isolate a leak and convey it to a scrubber where it can be neutralized while it is being transported to another location or plans are prepared to transfer it in place into another trailer

Chemically Speaking LLC

(12) **United States Patent**
Martrich et al.

(10) **Patent No.: US 7,448,402 B2**
(45) **Date of Patent: Nov. 11, 2008**

(54) **LEAK CONTAINMENT APPARATUS FOR REACTIVE GASES**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 23 days.

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F16J 13/02 (2006.01)
F17C 13/06 (2006.01)

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(58) **Field of Classification Search** 137/312, 137/377, 382, 15.11; 220/724, 725, 728, 220/323, 324, 326; 73/49.2, 49.3, 46
See application file for complete search history.

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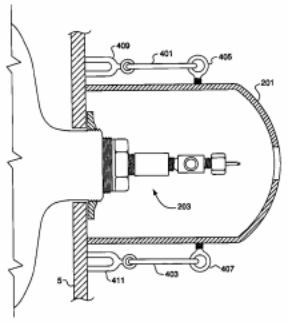
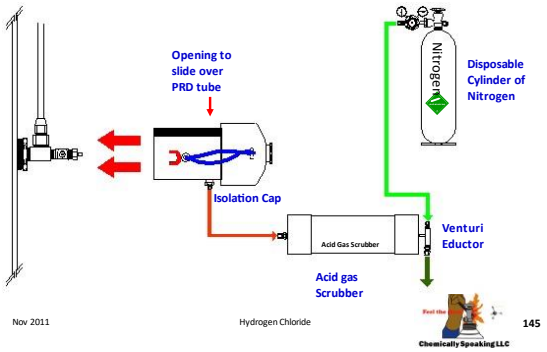
(57) **ABSTRACT**

Fluid storage and leak containment comprising (a) a fluid storage vessel comprising at least one vessel having an interior, an exterior, and an outlet opening between the interior and the exterior; (b) a fluid flow fitting sealably connected to the outlet opening and adjacent the exterior of the at least one vessel, wherein the fluid flow fitting is adapted for withdrawing reactive gas from the interior of the vessel; and (c) a containment enclosure having an interior, an exterior, an open end, and an extraction port adapted for the withdrawal of gas from the interior of the containment enclosure, wherein the open end is adapted to fit over and around the fluid flow fitting such that the containment enclosure surrounds the fluid flow fitting and is adapted to collect any reactive gas leaking from the fluid flow fitting.

22 Claims, 7 Drawing Sheets

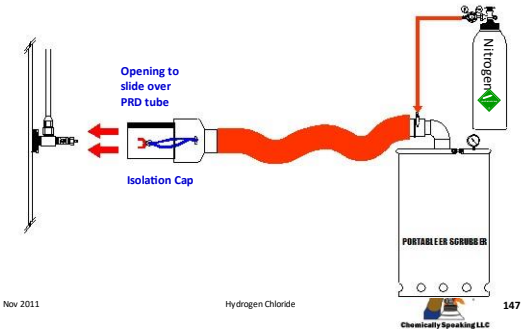


Setup for small leak <50 cc/min



Nov 2011 Hydrogen Chloride 145

Setup for large leak >50 cc/min



Nov 2011 Hydrogen Chloride 147

Sigri ERCV Flange Seizure

The Sigri ERCV breech closure has proven to be sensitive to HCl corrosion of the threads which causes it to seize and gall shut. At least 3 Sigri ERCV's have been cut apart due to HCl leakage. Making it impossible to open even with plates welded to the door for mechanical leverage.

Fig. 5: Plate Welded Onto Door In Attempt to Open ERCV

Repeated attempts to open the door failed so the ERCV, has to be cut open using a torch or a saw.

Eugene Ngai

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