Chlorine

Product Outreach Information

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Contents

What is Chlorine?

11th

MOST ABUNDANT NATURAL ELEMENT

11 2 8 1 Na Sodium 22 98976928	17 2 8 7 Cl Chlorine 35.453	**Sodium + Chlorine = Sodium Chloride (Salt)**
Hydrogen + Chlorine = Hydrogen Chloride (or hydrochloric acid with water present)	1 1 H Hydrogen 1.00794	17 2 8 7 Cl Chlorine 35.453

What is Chlorine?

Chlorine is essential to health and society

- 40% of industries use chlorine directly
- Water disinfection
- Water delivery (plastic containers and piping)
- Food production and transportation
  - Insecticide & herbicide manufacture
  - Refrigerant component
- Pharmaceutical production
- Polyurethane foam manufacture
- Paint component

What is Chlorine?

PURIFIED SALT WATER (BRINE) +
ELECTRICITY

Cl_2, H_2 + WEAK ALKALI

1 TON OF **CHLORINE** **PRODUCES** **~1.1 TONS** OF **NaOH** (~1.6 TONS OF KOH)

What is Chlorine?

17

2
8
7

Cl

Chlorine

35.453

Physical Properties of Chlorine

- At atmospheric temperature and pressure it exists as gas
- It is normally compressed and cooled to a liquid for shipping
- Pungent odor, like bleach but much stronger

Liquid

- Amber in color
- About 1.5 times as heavy as water

Gas

- Greenish-yellow color
- About 2.5 times as heavy as air
- Gathers in low, confined spaces

Volume of Liquid Chlorine

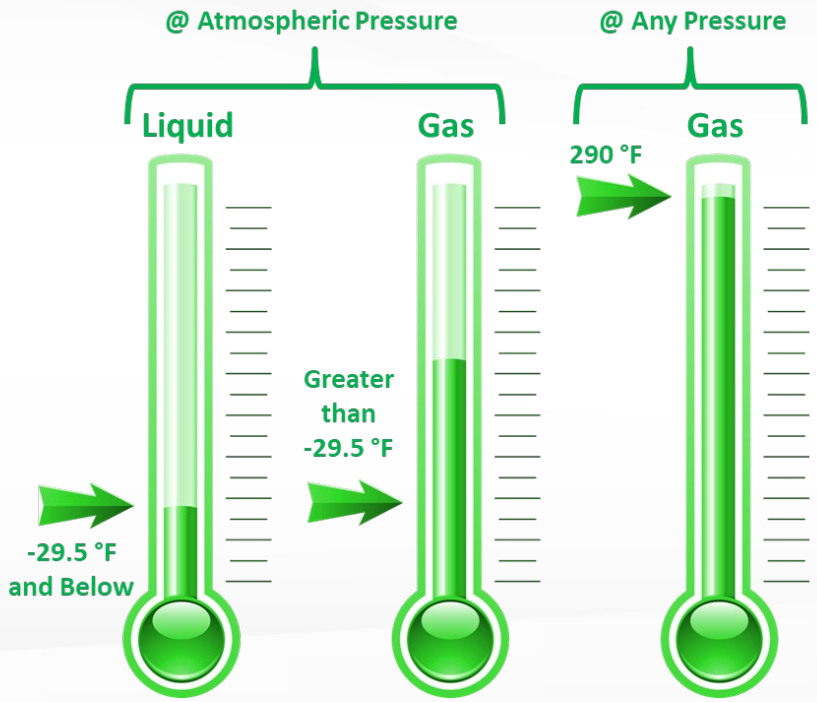
1 volume gas = 1/460 volume liquid

1 volume liquid = 460 volume gas

460 volume gas = 1 volume liquid

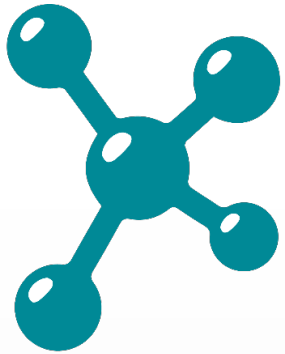
Chlorine Atmospheric Pressure

- Chlorine's boiling point = -29.5 °F (-34 °C)
- Chlorine is liquid below boiling point
- Chlorine is gas above boiling point

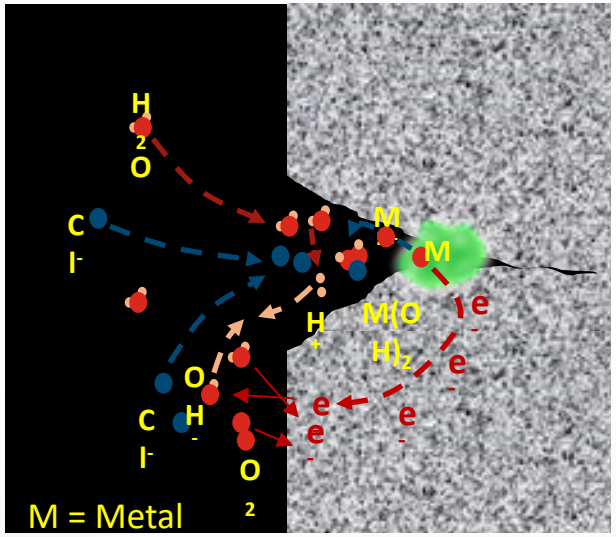


NOTE: Chlorine is always a gas above 290 °F (143 °C)

Chemical Properties of Chlorine



- Corrosive with moisture
- Reactive with organic materials and most metals
- Strong oxidizer
- Can support combustion (under specific conditions)



Chlorine readily combines with most substances. However, reacts violently with:

- Petroleum products
- Solvents
- Hydrogen compounds
- Some organic materials

Violent reactions may lead to potentially dangerous consequences.

Handling Considerations

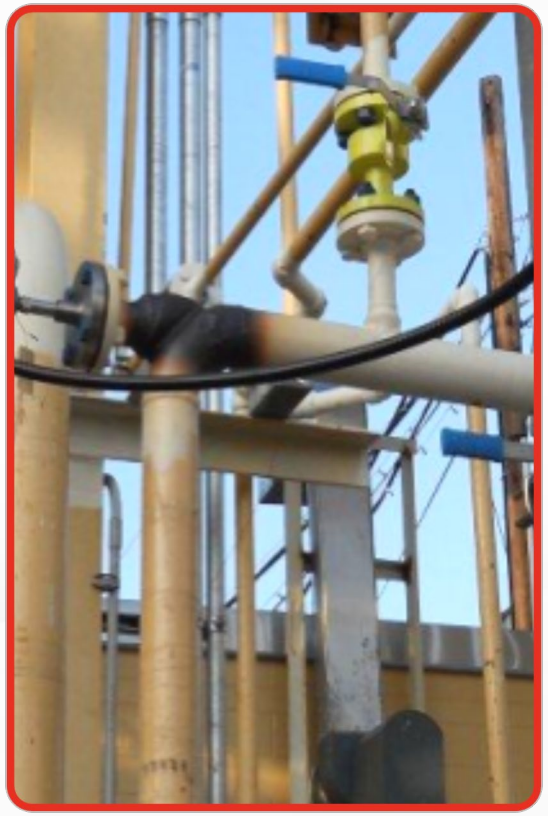
Handling Considerations

Dry chlorine

- Non-corrosive to most metals, including carbon steel (black iron)
- Incompatible metals and chlorine may result in fires

DO NOT USE:

- Titanium
- Aluminum
- Tin



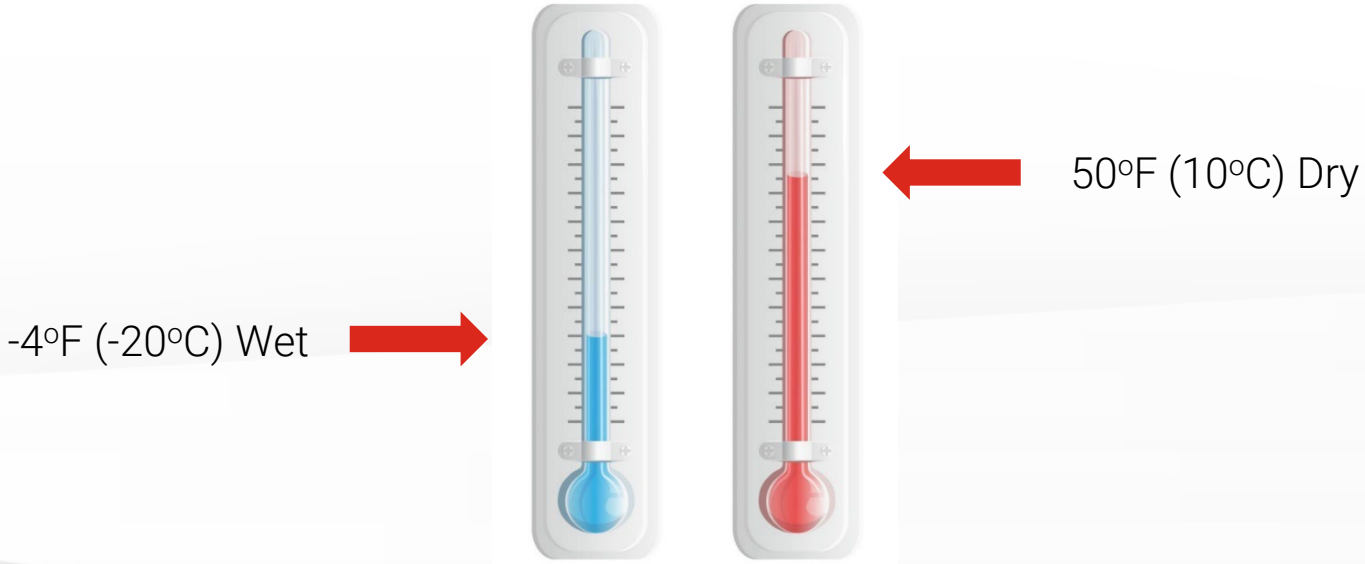
Handling Considerations

Wet chlorine

- When water is not dissolved in the chlorine
- Water exists as a liquid
- Highly corrosive

Temperature Effect on Moisture in Chlorine

Liquid chlorine at 30 ppm water can be considered wet or dry, dependent on temperature

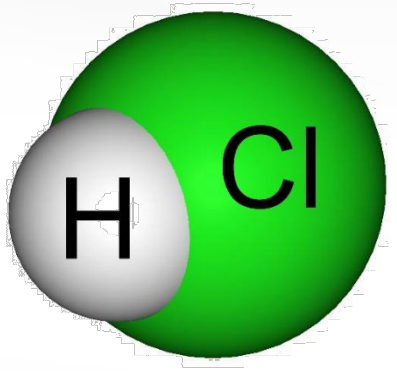


Handling Considerations

Wet chlorine handling

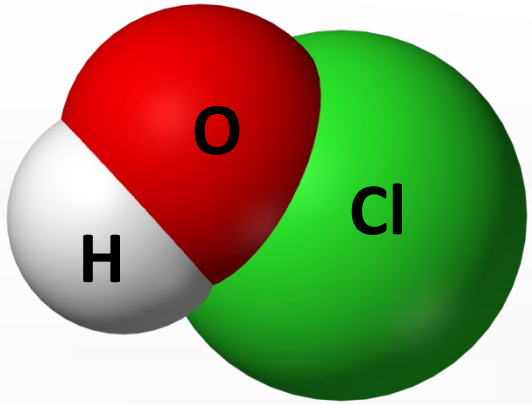
Wet chlorine produces corrosive acids

- Hydrochloric acid
- Hypochlorous acid



Handle with appropriate materials:

- Titanium
- Fully halogenated fluorocarbons (TFE, Kynar)
- FRP (Fiber Reinforced Plastic)



Materials NOT to use

- Carbon Steel
- Monel and Stainless Steel

Handling Chlorine Equipment Safely

- Keep piping, hoses and coupling dry and clean
- Cap and seal ALL unused piping

Handling Considerations

Organic oils and greases

- Chlorine reacts violently with oils, greases, and petroleum products
- Use non-reactive lubricants on chlorine equipment
- Acceptable Oils, Greases, Sealants and Lubricants
  - Krytox®
  - Fluorolube®
- See Chlorine Institute Pamphlet 164 for other acceptable lubricants

Handling Considerations

Specific conditions for chlorine combustion

- Chlorine is not flammable but will support combustion under certain conditions.
- Many materials that burn in oxygen (air) atmosphere will also burn in chlorine atmosphere.
- Chlorine combustion can occur when:
  - Steel is exposed to temperatures as low as 300 F (149 C)
  - In presence of finely divided metals such as powders, shavings, etc.

Steel Wool in chlorine

Handling Considerations

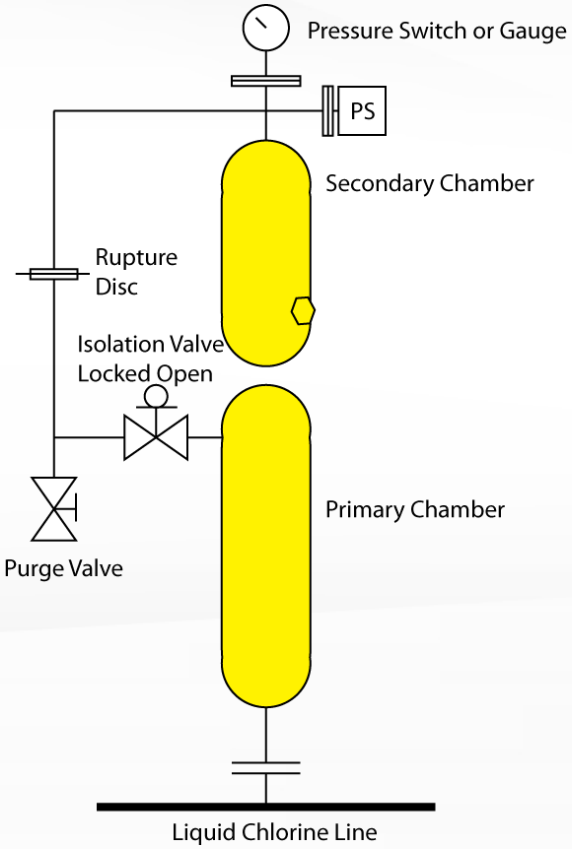
Precautions with chlorine equipment

- Keep away from sources of heat or fire
- Evacuate chlorine from component
- Hot work permitting required for use of welding/cutting torches, etc.

Handling Considerations

Causes of rupture

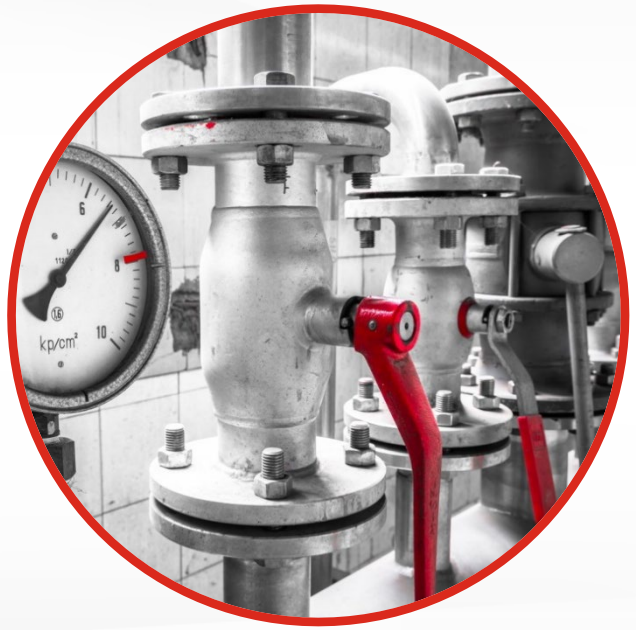
- Liquid chlorine expands as temperature increases
- Pressure build-up due to the thermal expansion of liquid chlorine in a section of piping between two isolation points
- A 5° F temperature rise in a liquid full line can increase pressure >500 psig



Handling Considerations

Runaway reactions can occur due to:

- Improper control of chlorine flows
- Backflow of process reactants into chlorine system
  - Moisture/Liquids from process



Systems Design

Systems Design

Pipe Stabbers

- Stabbers constructed of appropriately rated materials
- Shall be installed so that access to connectors are free of obstructions
- Shall be inspected prior to each use to ensure threads are adequate
- Shall have a defined replacement plan

Threads on a new connector passing the thread inspection

Threads of a worn connector failing the thread inspection

Systems Design

Chlorine Hoses

- Shall be constructed with appropriate materials of construction for use.
- Shall be installed so that hoses are not kinked / stressed when connected or stored after use.
- Shall be inspected prior to each use to ensure no signs of wear or deterioration exists
- Shall be replaced at least every 24 months

Systems Design

Hose / Stabber Connectors

Two or Four-bolt flanged connector

Ammonia ‘knock’ or ‘hammer’ union

Hil-Tap half-turn connector

HiLoSeal Coupling

Systems Design

Valves

- Shall be constructed with appropriate materials of construction for Chlorine use.
- Shall be installed so vents within cavities vent upstream when closed.
- Shall be carefully chosen based on service to be used; isolation vs continued cycling
- Shall have a defined replacement schedule

Systems Design

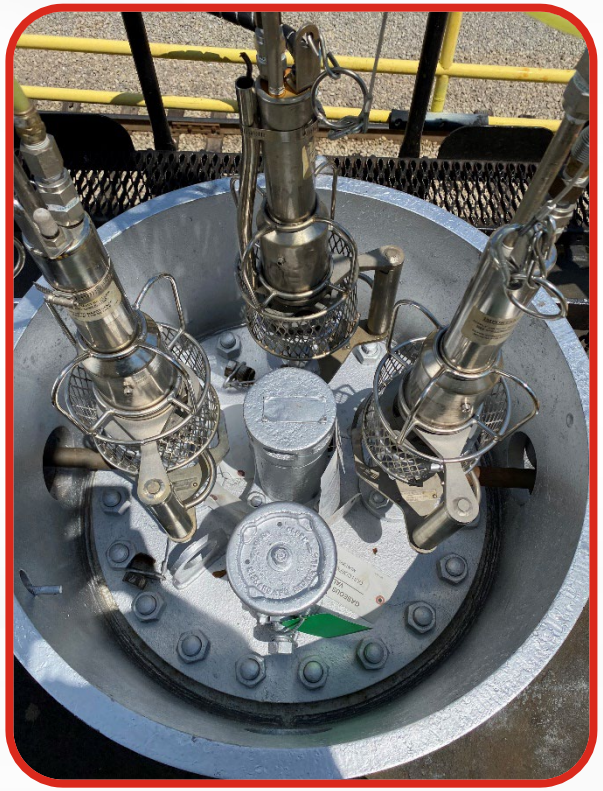
Rail Controls

- Movement Prevention
- Unauthorized tank car movements still occur
- Positive control deterrents are required

Systems Design

Auto Closures

- Shall be carefully chosen based on service to be used – direct mount / inline
- Shall have a defined maintenance schedule to include and meet manufacturers guidance (auto closures)
- Inline units should be bench tested to ensure actuated unit, as well as valve work/seal properly



Systems Design

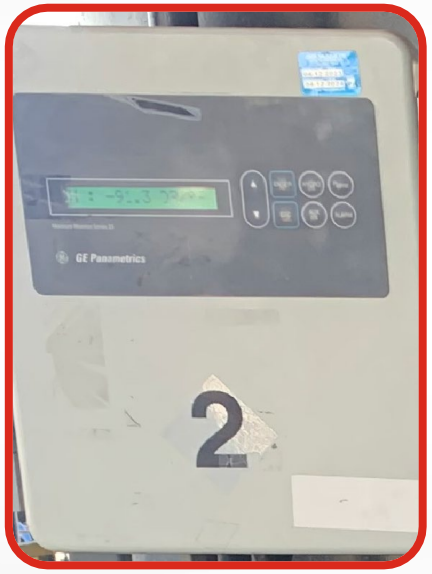
Pressure Transmitters

- Shall be carefully chosen based on service to be used
- Shall have a defined maintenance schedule to ensure units work accurately

Systems Design

Dew Point

- Shall have means to continuous monitor
- Shall have a means to validate accuracy of single installed unit.
- Shall have a defined replacement/calibration schedule
- Shall have a minimum dew point of -40 deg F



Systems Design

Detection Systems

- Shall have means to continuous monitor & detect close to source
  - Connection / end use
- Shall be set to meet permissible exposure limit set by OSHA 1PPM
- Shall have a defined calibration schedule
- Shall operate to notify in the event leak occurs/is present.

Personal Safety

Personal Safety

Acute Chlorine Exposure & Clinical Effects:

0.2 – 0.4 ppm	Odor detection threshold
1 – 3 ppm	Mild mucous membrane irritation, tolerated up to 1 hour
5 – 15 ppm	Moderate irritation of the respiratory tract
25 – 60 ppm	Visibility threshold (dependent on humidity)
30 ppm	Immediate chest pain, vomiting, dyspnea & cough
40 – 60 ppm	Toxic pneumonitis & pulmonary edema
430 ppm	Lethal over 30 minutes
1000 ppm	Fatal within a few minutes

Personal Safety

One Liter Liquid Chlorine => 460 Liters Chlorine Gas:

- In a medium size auditorium 16 ft X 35 ft X 65 ft:
  - One liter liquid Cl_2 is enough to fill room with 430 ppm
  - Two liters liquid Cl_2 is enough to fill room with 1000 ppm
  - Few deep breath's, can't exit room…
- In a typical room 8 ft X 10 ft X 12 ft:
  - It takes only 25 mL of liquid Cl_2 to get 430 ppm
  - It takes only 60 mL of liquid Cl_2 to get 1000 ppm
- Do not mix Bleach and Vinegar to clean bathroom tiles
  - Chlorine Gas !!!

Personal Safety

Acute chlorine gas exposure

- What is the odor threshold for chlorine?
  - As low as 0.25 ppm, varies from person to person
- Exposure to respiratory system is primary concern, followed by eye exposure
- Impact of exposure effects dependent on both chlorine concentration and length of exposure time
- Dosage = chlorine concentration X length of exposure time

Reference: Cl_2 Chlorine Basics

Personal Safety

Acute chlorine gas exposure- what are the hazards of chlorine?

- Toxic gas: respiratory tract and eye irritant
- Corrosive: chemical burns
- Strong oxidizer: fire hazard & heat-related burns
- Liquid is very cold: frostbite

Reference: Cl_2 Chlorine Basics

Personal Safety

Following acute exposure

- Delayed Symptoms
  - Up to 4 hours
- Normally complete recovery
- Some decreased lung function may occur

Reference: Cl_2 Chlorine Basics

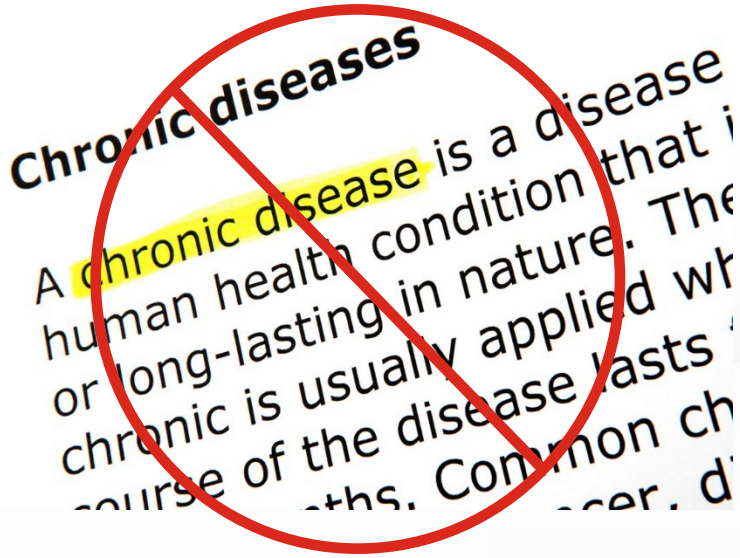
Personal Safety

PPM	EXPOSURE CONTROL
0.5 PPM	ACGIH 8 hr. Time Weighted Average (TWA)
1 PPM	ACGIH Short Term Exposure Limit (STEL)
1 PPM	OSHA Permissible Exposure Limit (PEL) Ceiling Limit (CEIL)
10 PPM	NIOSH Immediately Dangerous to Life and Health (IDLH)

Personal Safety

Chronic (long term exposure)

- No evidence of work-related health dangers



Personal Safety

Treatment for inhalation

- Move person to fresh air
- If difficult breathing, give oxygen
- If unconscious, perform CPR
- Remove contaminated clothing
- Seek advice from medical personnel for further treatment

Personal Protective Equipment

General Recommendations

- Hard Hat
- Protective Footwear
- Safety Glasses
- NIOSH/MSHA Escape Respirators

- PPE noted above is for general everyday use in a Chlorine facility.

Personal Protective Equipment

Line Breaking & Connecting/ Disconnecting

Chlorine:

- Hard Hat
- Footwear Protection
- Neoprene Gloves
- Respiratory Protection
  - Full Face / * SCBA
  - * Based on site specific requirements

- PPE noted above is for Chlorine operations whereas a review/analysis has been performed to determine level of protection required for functional tasks..

Personal Protective Equipment

Unknown or High Concentrations

Chlorine Gas or Liquid:

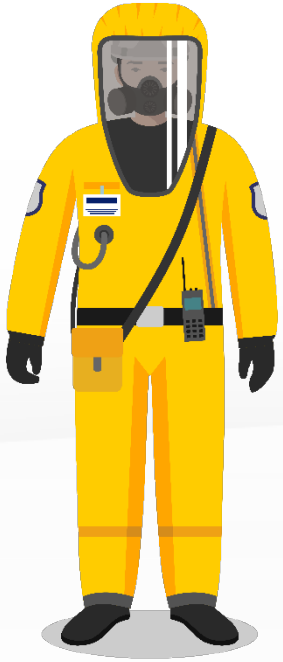
- Hard Hat & Footwear Protection
- Chemical Resistant Suit
  - Level A or Enhanced Level B
- Neoprene Gloves
- SCBA

- PPE to be worn will vary and should be evaluated based on conditions and situations present. Ideally, trained responders will don and execute response required to address materials/conditions.

Personal Protective Equipment

Emergency Situations

- Level A PPE:
- Gas Tight Chemical Suit (One Piece)
- Self-Contained Breathing Apparatus (SCBA)



Personal Protective Equipment

PPE maintenance is critical:

- Have a scheduled inspection program of all components
- Date & track respirators
- Properly store when not in use (sealed containers)

Emergency Preparedness

Emergency Preparedness

Planning for emergencies

- Plan ahead
- Have an up-to-date documented written emergency action/response plan
- TRAIN workers frequently for knowledge & fluency
- ASSESS for adequate PPE copies/stock.

Emergency Preparedness

Planning for emergencies

- All departments should be involved in emergency planning
- Conduct scheduled inspections of emergency equipment
  - Shut-down systems and alarms
  - Emergency kits
  - PPE
- Test plan by running periodic drills
  - Have varying drills on different scenarios

Emergency Preparedness

Active training

- Involvement with local agencies and response groups
- Periodic testing

Emergency Preparedness

General smart practices

- Have a solid and up to date Emergency response plan
- Clearly visible wind direction indicators (multiple)
- Well-known evacuation routes
- Store emergency equipment in well-marked, easy-to-reach locations
  - Out of hot zone areas.

Leak Response

Leak Response

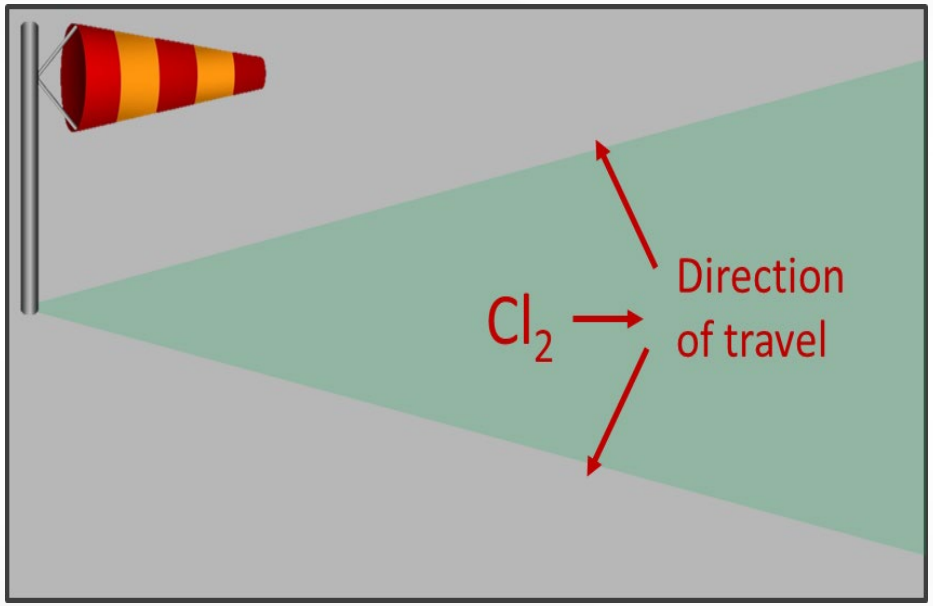
Chlorine leaks/spills

- Typically, first detected by atmospheric monitoring equipment / alarm
- Very strong, pungent odor
- Don escape respirator - Evacuate
- Evacuate area immediately along quickest route
- Once safe, notify management

Leak Response

Evacuating Release Area

- Proceed upwind or crosswind (if possible)
- NEVER proceed downwind



Leak Response

Finding and isolating leaks

- Spray ammonia vapor – NEVER ammonia liquid – to pinpoint
- Turn off valve closest to leak

Leak Response

Leak containment kits

Used by qualified / trained personnel ONLY

- Kit C
  - Rail Cars
  - Barges - Special kits available from supplier

Chlorine Emergency Response
The Chlorine Institute

UNITED STATES

CHEMTREC
Emergency Response Plan Activation
and Technical Assistance
1-800-424-9300

CANADA

Emergency Response
Plan Activation - 1-800-567-745

Technical Assistance (CANUTEC)
1-613-996-6666

Always notify supplier of railcar Immediately.

Chlorine Transportation

Stencils & Markings

Tank Car Construction

- Carbon Steel Rating of 500 or 600 PSIG
- Insulated
- Metal jacketed car
- Top outlet only
- Double shelf couplers

Stencils & Markings

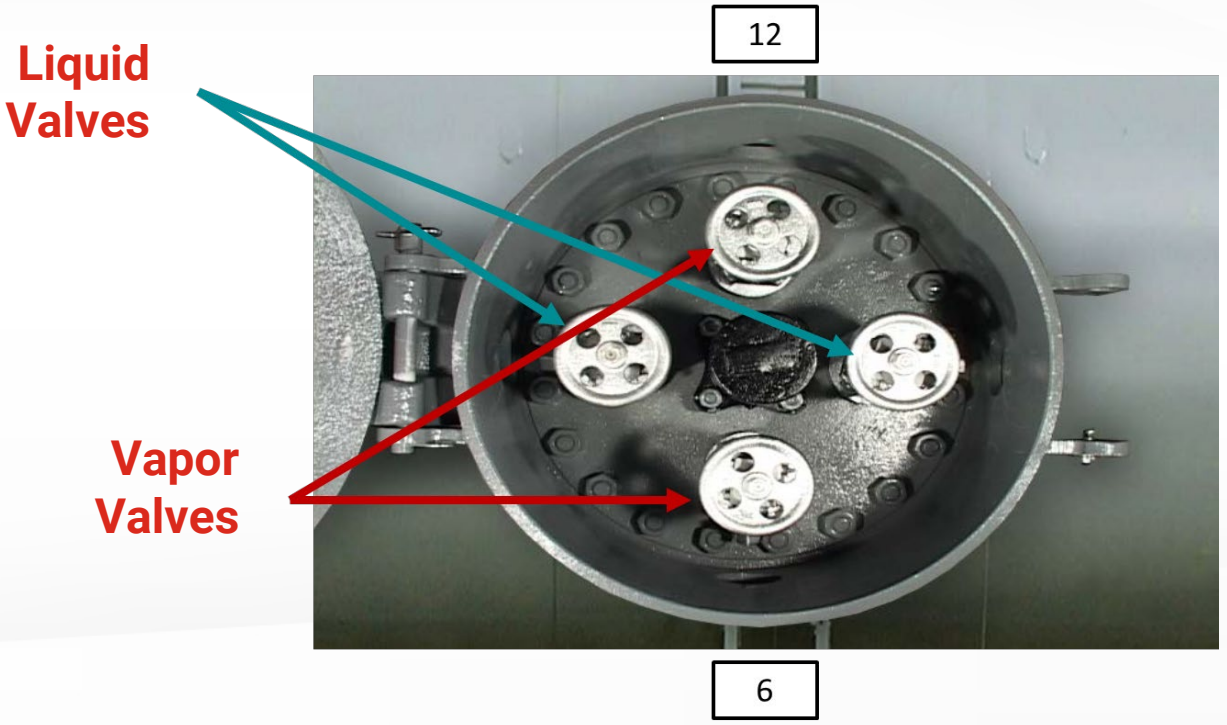
Loaded tank car

- 80% Liquid Full
- Loaded pressures 60-100 PSIG
  - May increase dependent upon ambient temperatures during transport and or storage
  - Will vary and may increase dependent upon ambient temps and duration exposed to excessively high temps.

Residue tank car

- Residue = 3000 +/- Pounds Mix Vapor & Liquid
- Depressure tank car
  - Always ensure departing pressures are less than 150psig.

Valve Arrangement –Tank Car



Procedure & Detailed Inspection is Critical

- Improper tank car preparation can result in leakage events
- Leakage evidence might not be observed during pre-release inspection
- Inadequate inspection or poor procedural diligence can place others at risk
  - Carrier
  - Community
  - Receiving personnel

Tank Car Information

Returned to Olin with Leak Residues

Possible Causes

- Angle valve left slightly open
- Angle valve plug not tool tight
- Pressure relief device activation
- Leaking pipe stabber connector (during unloading)
- Tattle tale valve on pressure relief device not closed

Tank Car Information

Typical Root Causes & Next Steps

- Improperly-trained staff
- Inadequate procedures
- Lack of robust checklist
- Lack of pre-departure leak check
  - Remember, you are the shipper of record!

Review your Process Safety Management Program for:

- Adequate detail – procedures & checklists
- Adequate knowledge
- Adequacy of testing program
  - Re-train personnel – either procedures are too generic or personnel don't understand the risks & consequences

For Further Information

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http://www.chlorineinstitute.org

References

Useful References

Pamphlet № 1 – Chlorine Basics	*Pamphlet № 5 – Bulk Storage of Chlorine*
Pamphlet № 6 – Piping Systems for Chlorine	*Pamphlet № 57 – Emergency Shut off Systems*
Pamphlet № 60 – Chlorine Pipelines	*Pamphlet № 65 – Personal Protective Equipment*
Pamphlet № 66 – Handling Chlorine Tank Cars	*Pamphlet № 72 – Atmospheric Monitoring*
Pamphlet № 89 – Chlorine Scrubbing Systems	*Pamphlet № 164 – Reactivity and Compatibility of Chlorine and NaOH with various materials.*

These publications are provided through The Chlorine Institute.
To obtain any C.I. publication, please call (703)894-4140 or visit www.chlorineinstitute.org

Web Sites – Key Resources

- **Olin Chlor Alkali Products and Vinyls**
  http://www.olinchloralkali.com

- **The Chlorine Institute**
  http://www.chlorineinstitute.org