A Study Of Occupational Exposure Assessment In Chlorine Liquefaction System


PG Research Scholar, Industrial Safety Engineering, Knowledge Institute of Technology, Salem- 637504.

Address For Correspondence:

ABSTRACT
Chlorine is a yellow-green non-combustible gas with a pungent irritating odor. It is widely used in industries and is one of the most commonly produced chemical substances worldwide. In particular, it is utilized as a reagent in the fabrication of solvents, pesticides, polymers, synthetic rubbers, refrigerants, and plastic, and ash bleach agent in the pulp and paper industry. It is also used as a disinfectant for purifying water. People are exposed to chlorine gas released by industries, either chronically by handling chlorine materials or acutely through exposure to high-concentration chlorine because of accidents or careless handling. Acute & Chronic exposure to chlorine gas tends to cause mostly respiratory symptoms. Chlorine gas is partially soluble in water, and upon inhalation is often deposited on hygroscopic surfaces such as the eyes, nose, pharynx, and nasopharyngeal airways. Acute exposure to chlorine gas may initially cause eye and throat irritation. Such exposures can result in symptoms of acute airway obstruction. The aim of the project is to analyze & assess the occupational exposure of chlorine in liquefaction system with the production stage, consumer end and transportation stage, develop, improve and implementation of the occupational health & safety management system and create a safety culture among the workers.

KEYWORDS: Chlorine occupational exposure OSHA, STEL, PEL, ACGIH standards.

INTRODUCTION
Chlorine [from the Greek word, meaning ‘pale green’] is the chemical element with atomic number 17 and symbol Cl. It is a halogen, found in the periodic table in group 17. Chlorine is a essential chemical and very useful in various applications in our day to day life starting from drinking water chlorination to sanitation, insecticides, pesticide, agriculture, drugs, pharmaceuticals, automobiles, paper, textiles, plastic and many more. On the other hand, Chlorine is very hazardous & toxic because of its properties and it is categorized as hazardous chemical in Schedule – I of ‘The Manufacture, Storage and Import of Hazardous Chemicals Rules 1989’. Chlorine is a toxic by way of respiratory irritant. The gas irritates the mucus membranes and the liquid burns the skin. In fact, chlorine was used as a war gas in 1915. Threshold Limit Value (TLV) of chlorine is 0.5 ppm (8-hour time-weighted average - 40 hour week). As little as 0.2 ppm can be detected as an odor, and 1000 ppm is likely to be fatal after a few deep breaths. Chlorine is a gas because their boiling point is – 340 °C which less than ambient temperature. Due to low boiling point it rapidly volatilizes when released from storage tanks and Tonners to the atmosphere. One volume of liquid chlorine expands to 457 volume units of gas.
Manufacture Of Chlorine:
Chlorine is produced by passing an electric current through a solution of brine (common salt dissolved in water). The chemical term for salt is Sodium Chloride (NaCl).

Essential co-products are caustic soda (Sodium Hydroxide (NaOH)) and Hydrogen (H₂). All three are highly reactive, and technologies have been developed to separate them and keep them apart. Caustic soda is an alkali and widely-used in many industries, including the food industry, textile production, soap and other cleaning agents, water treatment and effluent control.

Hydrogen is a combustible gas used in various processes including the production of hydrogen peroxide and ammonia as well as the removal of sulphur from petroleum derivatives.

Chlorine has been manufactured industrially for more than 100 years. During this time, the industry’s firm commitment to the best safety, health and environmental practices has ensured continuous improvement.

The three technologies of producing chlorine are:
- Diaphragm Cell Process
- Mercury Cell Process
- Membrane Cell Process

1.2 Chlorine Treatment, Drying, Compression & Liquefaction:
The chlorine in the depleted brine is removed by addition of Hydrochloric acid to reduce pH and by applying vacuum. Any further traces of chlorine in the depleted brine are removed by the addition of Sodium Sulphite. After complete dechlorination, the depleted brine is pumped to the saturators. The wet chlorine after getting separated in the anolyte tank is cooled by cooling water.

The wet chlorine is dried in drying tower using concentrated Sulphuric Acid and sent to liquefaction system for liquefaction. Liquid chlorine is sent to storage tanks for further use. Liquid Chlorine received in storage tanks is also filled in Chlorine cylinders (Tonners).

1.3 Liquefaction:
Liquefaction can be accomplished at different pressure and temperature levels, at ambient temperature and high pressure (for example 18 °C and 7-12 bar), at low temperature and low pressure (for example -35 °C and 1 bar) or any other intermediate combination of temperature and pressure.

The chosen liquefaction pressure and temperature influence the choice of cooling media and the safety precautions necessary to operate safely. However, the efficiency of liquefaction is limited because hydrogen is concentrated in the residual gas and its concentration needs to be kept below the explosive limits.

The choice of the cooling medium in a certain stage of the liquefaction depends on the temperature of the chlorine. When the temperature is sufficiently high, water can be used as an indirect cooling medium. When the temperature is relatively low, other cooling media such as HCFCs or HFCs (indirect cooling), ammonia (indirect cooling) or liquid chlorine (direct cooling) are used. The temperature of the chlorine gas in a certain stage depends mainly on the initial temperature and on the pressure increase during compression. A large pressure increase generally enables water cooling, but implies an increased hazard risk. Chlorine temperature has to be kept well below the point where it reacts spontaneously and uncontrollably with iron (approx. 120 °C). Construction materials must be chosen to suit the conditions under which chlorine is being handled:
- Wet or dry
- Gas or liquid
- Temperature
- Pressure

In terms of safety, it is very important to avoid, during compression and liquefaction, any possibility of mixing chlorine with oils or greases which are reactive as regards chlorine.

Table 1.3: shows the possible trade-off between different types of chlorine gas liquefaction, cooling methods applied and safety aspects.

<table>
<thead>
<tr>
<th>Liquefaction system</th>
<th>Cooling medium</th>
<th>Safety aspect</th>
<th>Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>High pressure (7-16 bar) and high temperatures</td>
<td>Water</td>
<td>High precautions</td>
<td>Lowest energy costs but high material costs</td>
</tr>
<tr>
<td>Medium pressure (2-6 bar) and medium temperatures (between -10 and -20 °C)</td>
<td>Water-HCFC/ HFC or ammonia</td>
<td>Moderate precautions</td>
<td>Moderate energy and material costs</td>
</tr>
<tr>
<td>Normal pressure (~1 bar) and low temperatures (below -40 °C) energy and lower material costs</td>
<td>Mainly HCFC/HFC or ammonia</td>
<td>Precautions</td>
<td>Cryogenic storage of liquid chlorine is possible. High</td>
</tr>
</tbody>
</table>
1.4 Chlorine Storage Methods:
In order to be stored and transported economically chlorine has to be liquefied. Liquid chlorine is stored in bullets and generally liquid chlorine is supplied / transported in ton containers (Tonners) and cylinders.

1.4.1 Containers:
There are basically two types of containers used in the supply and consumption of Chlorine.

1.4.2 Cylinders:
Cylinders are small containers with a net carrying capacity in the range of 65 to 100 kgs.
The standard cylinder is cylindrical container of welded steel construction with one end closed and a valve at the other end. A valve protection hood is fitted on the threaded neck ring.

1.4.3 Cylinder details:
Nominal Dia Approximate
➢ Inside 356 mm
➢ Outside 368 mm
➢ Approximate height 988 mm (excluding valve & cap)
➢ Water capacity 84 ltr
➢ Chlorine capacity 100 kg
➢ Design pressure 19.9 kg/cm²
This is the vapour pressure of liquid chlorine in equilibrium with its vapour at 65 °C.

1.4.4 Tonners:
A tonner is welded steel tank with a gross weight of approximately 1500 kgs when filled with 900 kgs of liquid chlorine. It is a cylindrical in shape with conclave dished ends as a safety measure to prevent explosion in case of undue pressure buildups inside, in which contingency the conclave dished ends will bulge out, reducing the pressure inside. On one side of dished end, two valves are located near the centre. Both valves are covered by a protective hood connected to container by means of lugs. The inside ends of the valves are connected to the eduction pipes. The tonners are always kept horizontally. When the two valves are in a vertical alignment, one below the others, gaseous chlorine can be drawn by opening the upper valve. The lower valve will deliver liquid chlorine when opened.

1.4.5 Tonners details:
Inside Dia 760 mm
Shell Thickness 10 mm
Dished end thickness 12mm nominal (9.6 mm min)
Overall length 2085 ± 12 mm
Water capacity 780 ltr
Chlorine capacity 930 kg
Design pressure 19.9 kg/cm²
This is the vapour pressure of liquid chlorine in equilibrium with its vapour at 65°C. The quantity of liquid chlorine to be filled in a container is dependent on its water capacity/ 
Water capacity (l) * Filling ratio (Kg/l)
Water capacity * 1.19

1.5 Chlorine Scrubber:
The Scrubber is provided to take care of normal, emergency & shutdown activities of the plant.
The scrubber capacity is designed & equipped to take care of any sudden chlorine surge for a minimum continuous period at full operating capacity from the plant.
The chlorine gas released from the electrolyser and from the chlorine treatment section during normal and emergency operation is scrubbed with caustic lye of 20% concentration, scrubbing towers be designed in series to ensure no possibility of chlorine emission to the atmosphere.
All the critical equipments of the scrubber are connected to Emergency DG set which supplies power during power failure.
As an additional safety measure, in case of DG set failure also, a provision of caustic head tank through automatic opening of a control valve to draw caustic to the polishing column to be provided.
On-line continuous chlorine sensor with alarm system is installed in the scrubber stack and connected to main control room for continuous monitoring to detect any leak and for taking corrective action.
1.6. Hazard Associated With Chlorine:

1.6.1 Physiological Effects:
- Chlorine is respiratory irritant.
- If exposure / concentration are excess – will cause restlessness, throat irritation, sneezing and salivation.
- In extreme cases, lung tissues may be attacked

<table>
<thead>
<tr>
<th>S.No</th>
<th>Effects</th>
<th>Chlorine concentration by volume, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Least amount required to produce slight symptoms after several hours of exposure</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>Least detectable odour</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>Maximum amount that may be inhaled for 1 hr without serious disturbance</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>Noxiousness impossible to breathe for several minutes</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>Least amount required to cause irritation of throat</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>Least amount required to cause coughing</td>
<td>30.2</td>
</tr>
<tr>
<td>7</td>
<td>Amount dangerous in 30 minutes to 1 hr</td>
<td>40 – 60</td>
</tr>
<tr>
<td>8</td>
<td>Amount likely to be fatal after few deep breaths</td>
<td>1000</td>
</tr>
</tbody>
</table>

1.6.2 Acute Health Effects:
- Liquid Cl\textsubscript{2} in contact with body will result in freeze burn of varying severity.
- Inhaling the gas causes coughing, tears, a running nose and breathing problem.
- If trapped for long period in high concentration, loss of consciousness and possibility of death can result.
- Symptoms are reversible if an exposed person quickly removed from the area and given prompt medical attention.

1.6.3 Chronic Human Health Effects:
- No significant connection between chronic exposure to low concentration of chlorine and adverse health effects.
- No significant effects indicated for work place chlorine level (<1 ppm).

1.6.4 Chlorine on Aquatic Life:
- Chlorine is widely used as disinfectant.
- Elevated chlorine levels can create aesthetic problem.(taste & odour)
- Will affect fishes and other living organism
- If excess amount of chlorine is released, It may harm aquatic plants and animals until it is diluted to a harmless level.

1.6.5 Chlorine on Animals:
- Rabbits exposed to inhalation up to 1.5 ppm displayed no adverse reproductive effects.
- Rabbits and guinea pigs were exposed to 1.7ppm for 9 months showed weight loss & decreased resistance to disease.
- Rats and mice were exposed to 0.4,1.0 or 2.5ppm up to 6 hrs/day and 3-5 days/week for up to 2 years shows no evidence of cancer.
- Monkeys appear to be less sensitive than Rat.
- LC50 is 239 ppm in Rats and 137 ppm in Mice.

1.6.6 Chlorine on Vegetation:
- Plants in the path of Cl\textsubscript{2} release may be damaged.
- Chlorine bleaches leaves
- Stops the plant producing chlorophyll.
- Healthy plant recover over time, although yield and growth rate may be retarded.

1.6.7 Fire & Explosion Hazard:
- It may react to cause fires or explosions upon contact with Turpentine, Ether, Hydrocarbon, Hydrogen, Powdered metals, saw dust, & phosphorous.

1.6.8 Other Hazards:
- Chlorine reacts violently with oils, greases, paints, some solvents, steel wool, oil fillings.
- Dry chlorine reacts violently with titanium.
- Chlorine & Hydrogen can react violently in equivalent mixture.
- Chlorine dissipates more rapidly on a warm, windy day than on cold, calm days.

II. Literature Survey:

This study shows the benefits of developing an adequate emergency response plan (ERP) with safety and industrial hygiene resources to deal with the effects resulting from a chlorine gas leak, in order to lessen or avoid injury to plant personnel and citizens in the neighboring community. (A study by J.M. Tsenga, M.Y. Liub, R.H. Changc, J.L. Sud, C.M. Shua).

Chlorine is a gas, heavier than air, toxic, nonflammable, and an economically available oxidizing agent that provides properties desirable in disinfection usage. (Gerald F. Connell and John J. Fetch)

The increasing and widespread use of liquid chlorine during the last twenty years in water works plants for disinfection and as aid to filtration processes. (H. H. Gerstein).

Humans can come into contact with chlorine gas during short-term, high-level exposures due to traffic or rail accidents, spills, or other disasters (Carl W. White and James G. Martin).

This study analyzes the risk involved in the chlorine industry in North America. (Richard J. Helmeste’ and Colin R. Phillips)

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**Fig. 3.1:** Methodology of the proposed work

The ton container is therefore a distinct and valuable contribution to the art of handling liquefied chlorine gas, and of great use to both maker and user. That contemplating ton container use should carefully figure costs and avail themselves of the experience and counsel of chlorine makers. (Robert T. Baldwin).

This paper deals with the accidental release of chlorine from bonnet of a valve in a bullet installed in a chloro-alkali industry, and the probable causes of the accident and the ensuing sequence of events. Emergency
procedures are also discussed. Finally, in the conclusions reached at some useful recommendations, which has been drawn for industrial facilities handling chlorine (R.K. Gangopadhyaya, S.K. Dasa,*, M. Mukherjee).

This study shows the benefits of developing an adequate emergency response plan (ERP) with safety and industrial hygiene resources to deal with the effects resulting from a chlorine gas leak, in order to lessen or avoid injury to plant personnel and citizens in the neighboring community. Results from systematic planning indicate that properly trained personnel could immediately and effectively handle each level of incidents occurring in the process plants in (Taiwan.J.M. Tsenga, M.Y. Liub, R.H. Change, J.L. Sud, C.M. Shua).

**METHODS AND MATERIAL**

The proposed study is based on the following methodology. Fig 3.1. The methodology concentrates on the tools or techniques used for data collection, data sources and assessment.

The Following methodology has been adopted in preparing this project work:-

- By discussions with the senior officials in the Chlor-Alkali industry.
- Site inspections and interactions with the Safety Managers/ Deputy Managers / officers/ Asst. Managers/ Shift-In charges/ Operators/ Site Engineers and the workers.
- Understanding the safety systems presently being practiced in Chlor-Alkali industry.
- Collection of safety & technical details of the Chlor-Alkali industry.
- Past incidents / accidents happened due to chlorine.
- Reviewing ‘what went wrong analysis report’ and corrective preventive measures taken to avoid reoccurrence of incident/accidents.
- Guide lines from the Bureau of Indian Standards (BIS), National safety council of India training material, internal and external safety audit reports, experienced officials in this field and other applicable statues.
- Referring all literature and case studies available on chlorine safety.

**3.1 Chlorine Safe Standard Work Practices:**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Exposure level (parts per million)</th>
<th>Exposure Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2 to 0.4ppm</td>
<td>Odor Threshold (Varies by individual)</td>
</tr>
<tr>
<td>2</td>
<td>Less than 0.5 ppm</td>
<td>No known Acute or chronic effect</td>
</tr>
<tr>
<td>3</td>
<td>0.5ppm</td>
<td>Maximum allowable concentration over an eight hour period (ACGIH 8-hour time weighted average)</td>
</tr>
<tr>
<td>4</td>
<td>1 ppm</td>
<td>Maximum allowable short term exposure (15 minutes) OSHA ceiling level (PEL) &amp; TLV-STEL</td>
</tr>
<tr>
<td>5</td>
<td>10 ppm or More</td>
<td>Immediately Dangerous to life and Health (IDLH) (as published by NIOSH)</td>
</tr>
</tbody>
</table>

Note: The Immediately Dangerous to Life and Health (IDLH) exposure level is the point at which a person without appropriate respiratory protection could be fatally injured or could suffer irreversible or incapacitating health effects. NIOSH is the National Institute for Occupational Safety Health in the United States.

**3.2 Data Analysis:**

The obtained data are analyzed by using the current versions of Microsoft excel, absolute figures, tables, percentages and statistical tools such as graphs, charts were used.

**3.3 Identifying Areas Of Chlorine Exposures:**

After the data analysis, the areas of chlorine exposure levels are obtained by comparing it individually with the standards. The areas are listed for the purpose of determining the high risks and medium risks level. This research was conducted in various areas of chloro alkali industry in production site on October 2016. Those selected areas were surveyed and noted the exposure levels in day time with working condition. The selected spots are brine de-chlorination, chlorine treatment, drying, compression and liquefaction & storage sections.

Minimum number of readings were measured in each areas and found mean values of each areas. All measured values were recorded. The gas analyzer level meter was used for measure exposure level readings. By using this meter can able to measure the exposure in PPM (parts per million).

It has features of low/medium/high exposure response to measure readings. Taken of minimum and maximum exposures level readings should be comparison with standards like ACGIH/OSHA/NIOSH.
IV. Problem Identification & Statement:

The list of following problems have been identified during the line tracing and questioners while inspecting the chlorine liquefaction section with the help of plant operators, production engineer, safety engineer, etc.:

- In each shift while changing the tonner cylinder, there is an exposure of chlorine to the employees and contract labor has been identified and short out the issues.
- There is an leakage in chlorine liquefier (E506 A) outlet valve to be identified and isolated for a certain period then bypass valve has been opened.
- The frequent liquefier choke & sludge accumulation is seen while opening the dish end of liquefier (E506 A).
- Sludge accumulation is found in the compressor suction inlet line. Revamping of drying tower (Packed column, and in the seal pot having sludge).
- Sludge formation:
  * Nacl formation.
  * Sulphuric acid mist & acid carry over.
  * Fe react with chlorine to form ferric chloride.
  * PVC welding compound react with chlorine to form sludge.(If conditions are favorable).
  * Gasket material due to ageing react with chlorine to form sludge.
  * Due to back migration of OH ions in the electrolyser little amount of caustic forms in anode side and sludge forms while react with sulphate.
- Top of the liquid chlorine storage tank, valve was passing during the filling operation of chlorine to tonner cylinder has been identified and blind flange has been fixed to inlet line of HYPO section.

The following tables show the direct effects in humans of controlled exposure to chlorine in Brine Dechlorination, Chlorine Treatment, Drying, Compression and Liquefaction

<table>
<thead>
<tr>
<th>Concentration (exposure in ppm)</th>
<th>Number exposed</th>
<th>Effect (cases observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.027 ppm [0.081 mg/m3]</td>
<td>7</td>
<td>Tickling of nose</td>
</tr>
<tr>
<td>0.058 ppm [0.174 mg/m3]</td>
<td>3</td>
<td>Tickling in throat</td>
</tr>
<tr>
<td>0.06-0.2 ppm [0.18-0.6 mg/m3]</td>
<td>1</td>
<td>Itching in the nose</td>
</tr>
<tr>
<td>0.09 ppm [0.27 mg/m3]</td>
<td>6</td>
<td>Tickling and stinging in the nose (4), cough (1), dryness in throat (1)</td>
</tr>
<tr>
<td>0.2 ppm [0.6 mg/m3]</td>
<td>11</td>
<td>Slight tickling in the nose and throat (7), cough (1), sensations in the ocular conjunctiva (3)</td>
</tr>
<tr>
<td>0.3 ppm [0.9 mg/m3]</td>
<td>3</td>
<td>Stinging in the throat</td>
</tr>
<tr>
<td>0.36 ppm [1.08 mg/m3]</td>
<td>1</td>
<td>Sensation of choking</td>
</tr>
<tr>
<td>0.45 ppm [1.35 mg/m3]</td>
<td>7</td>
<td>Burning of conjunctiva, pain after 15 min</td>
</tr>
<tr>
<td>0.5 ppm [1.5 mg/m3]</td>
<td>5</td>
<td>Cough, stinging</td>
</tr>
<tr>
<td>1.0 ppm [3 mg/m3]</td>
<td>3</td>
<td>Headache, Cough, stinging</td>
</tr>
<tr>
<td>1.0 ppm [3.0 mg/m3]</td>
<td>10</td>
<td>Tickling and stinging in the nose (6), scratchiness and dryness in the throat (4), dull sensation in the teeth and a slight metallic taste (1), headache and pressure, burning of ocular conjunctiva/ outer skin, coughing, constriction of breathing (1)</td>
</tr>
</tbody>
</table>

RESULT AND DISCUSSION

The following recommendations, control measures and suggestions will help to reduce the chlorine exposure problem in that specified area,

Root Cause Analysis:-
For Nacl Carry over:
It appears that BMF (Brink mist Filter) is not functioning properly, as seen in the last shutdown present status, modification, suggestions are given below.

1. Brink Mist Filter:

<table>
<thead>
<tr>
<th>Present condition</th>
<th>Suggestion</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Filter Diagram" /></td>
<td><img src="image" alt="Suggestion Diagram" /></td>
</tr>
</tbody>
</table>

2. Dechlorination vacuum tower and Exchanger:
   Present Condition:
   - E-161 A/B Dechlorination vacuum tower cooler is directly connected with chlorine gas header through Vacuum pump. This exchanger is not working properly and Exchanger 161 A no condensate drain.
   - E-161 B condensate flooding occurs this is also one of the reasons for carryover of Nacl.
   Suggestions:
   - E-161 A/B cooler to be de-scaled properly & lined up
   - The organization of work could limit the duration and intensity of exposure by keeping the number of workers in exposure areas to a minimum and task rotation.
   - Having appropriate work schedules with adequate rest periods.
   - Isolation of the unit with proper engineering controls and administrative controls.
   - Use wear appropriate PPE’s like double cartridges mask and chemical canister mask while handling of tonners and separate track for handling crane operations.
   - Conduct health medical checkup program in six months once or yearly once as per the standard.
   - Conduct pulmonary function tests (PFT) in regular interval of time.

Conclusion:
By the occupational exposure assessment study, a set of resources that may help us understand how chlorine exposure conditions may constrain or facilitate safety work are identified. The areas of chlorine exposure in the liquefaction section are finally identified. All the areas are measured individually by the safety engineer on that time of exposure, by using the gas analyzer level meter obtained values are then compared it with the standards mentioned in the OSHA/ ACIGH/NIOSH.

The areas of limited chlorine exposure in the liquefaction section are finally identified and here with provided some control measures and recommendations to reduce the chlorine exposure level in the particular area in chloro alkali industries.

REFERENCES
11. Chlorine – a medical dictionary, Bibliography and annotated research guide to internet references by icon health publications.
13. Alkali Manufactures’ Association of India.