Safety aspects of chlorine handling in process industry

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The chemical and related industries occupy a key position in the economic life of a nation. The chemical industry supplies a wide spectrum of products which find their way into a wide range of human activity. Until sometime ago, it was considered to be one of the safest industry but the Bhopal disaster has about a dramatic change in the thinking not only in India but all over the world. Safety has quickly become one of the highest priorities in the chemical process industry.

Sudden and uncontrolled loss of containment will give rise to a disastrous condition, magnitude of which will depend on the type of chemical as well as inventory. The main objective of this paper is to highlight the safety aspects of chlorine handling. Hazards associated with chlorine handling are attributed to its chemical reactivity. physicical properties and toxological character. Engineering control of these hazards has been discussed with special emphasis on material of construction for chlorine service.

CHARACTERISTICS OF CHLORINE

Chlorine in commerce is a compressed, liquified gas under pressure, about 1.5 times as heavy as water, packed in steel containers. The liquid chlorine vaporizes under normal atmospheric temperature, the gas, about 2·5 times as heavy as air, has a characteristic penetrating and irritating odour.

Chlorine is a greenish yellow, non explosive and non-flammable gas which is capable of supporting combustion in presence of hydrogen, turpentine, ether and hydrocarbons. Dry chlorine gas does not corrode but it is highly corrosive in presence of moisture due to formation of HCl and HOCl.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

The chlorine gas can be liquified by the application of refrigeration and compression. Liquid chlorine has a high coefficient of thermal expansion. One volume of liquid chlorine when vaporised yields about 460 volumes of gas. It expands about 0 15% in volume for every °F increase in temperature.

The relationship of various physical properties of liquid chlorine with temperature are given in Figure Nos. 1 to 3.

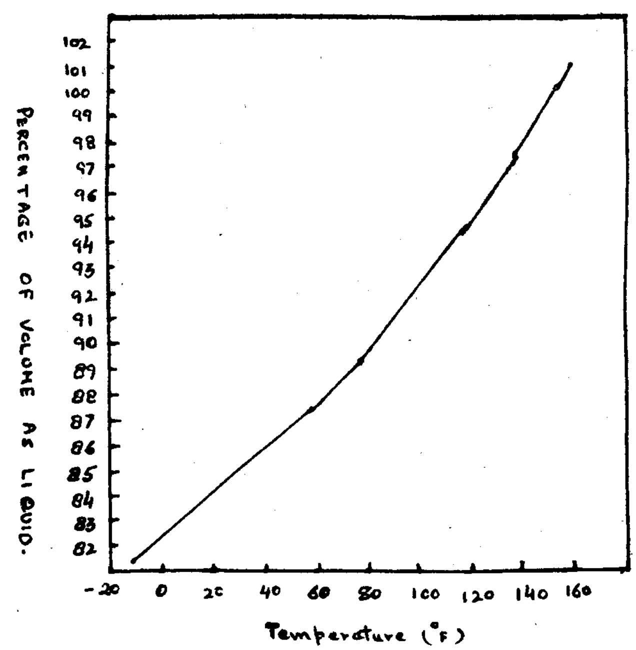

Fig 1 : Volume - Temperature Relation of Liquid Cl_2 Loaded to its Authorised Limit

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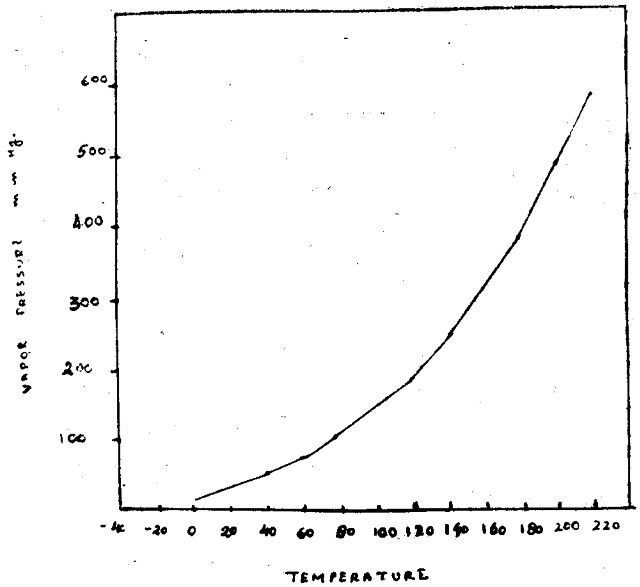


Fig. 2 : Vapor - Pressure of Liquid Chlorine

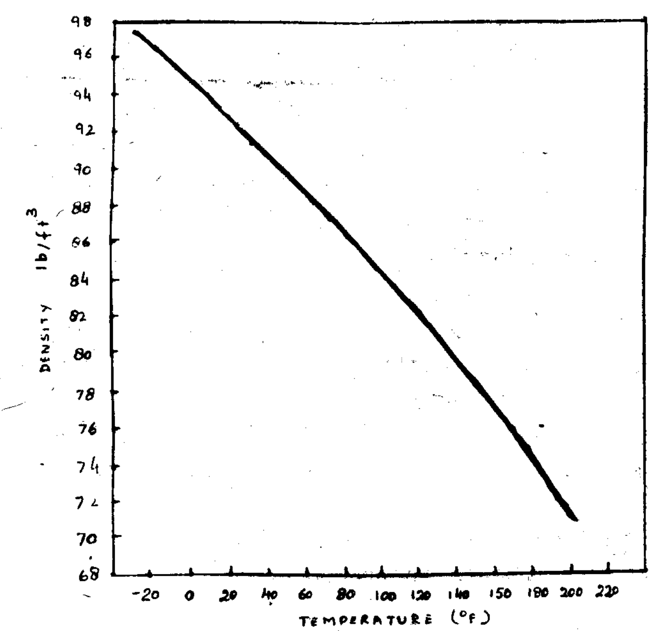


Fig 3 : Density - Temperature Relationship of Cl_2

HANDLING OF CHLORINE

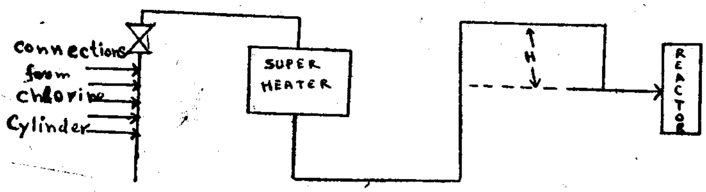
Chlorine in industry is generally transported in tonne containers and cylinders. Cylinders are of seamless/welded construction with a capacity of not more than 100 kgs, while the tonne containers are welded tanks with a capacity of 900-1000 kgs. The valves of cylinder and tonne containers are protected by a hood which should always be kept in place except during evacaution of chlorine. Cylinders or tonne containers, whether empty or full should be stored in a dry, well ventilated area protected from external heat source (such as steam pipes). Fire resistant storage areas are recommended and subsurface area are to be avoided.

Cylinders normally should be emptied in gas phase standing secured in upright position. If it is necessary to empty them in the liquid phase, they should be partially inverted and clamped securely on a reck set at an angle of about 60 degrees to the horizontal.

Tonne containers set in a horizontal position, with the valves in a vertical plane, deliver gas from the upper valve and liquid from the lower valve- When emptied in the liquid phase a vaporizer is used The flow of chlorine gas from any container depends on the internal pressure which in turn depends upon the temperature of liquid chlorine. At low discharge rates when sufficient heat can be obtained from the surrounding air, the pressure in the container normally will remain constant and uniform flow can be maintained. At high discharge rates, however, the temperature and pressure within the container will fall due to the cooling effect of vaporisation and rate of flow will slowly diminish. The discharge rate can be increased by forced circulation of room temperature air around the container. Immersion of chlorine containers in hot water or application of direct heat should not be permitted. More care must be taken when more than one cylinder/tonne containers have to be connected to a manifold to get a higher discharge rate. All cylinders/tonne containers should be at same temperature otherwise chlorine will be transferred from warm to cool container and the cooler container may become completely filled with liquid chlorine. Should this occur and container valve then be closed, hydrostatic pressure may cause bursting.

A flexible connection between the container and piping should be used. Copper tubing suitable for 500 psi service, a clamp and adapter connector should be used. If a union connector is used the threads on the connector must match the valve outlet thread.

The open end of any disconnected line should be plugged to prevent entry of moisture. When chlorine is being absorbed in a liquid, proper precautions must be taken to prevent suck back of the liquid into the container when it becomes empty (due to creation of a partial vacuum). A barometric leg or a vacuum breaking device should be used to avoid accidents due to this tendancy of the system.



$$H = \frac{34}{d}$$

Where

H = Height of barometric leg (in ft.)

d = Density of liquid gm/cc.

This barometric leg will serve as a vacuum breaking device.

HAZARDS AND ENGINEERING CONTROL OF HAZARDS :

Chlorine is an extremely toxic and irritating gas which reacts explosively with many common materials like acetylene turpentine, ether, ammonia gas, fuel gases, hydrocarbons, hydrogen and finally divided metals. Most combustible materials burn in chlorine as they do in oxygen.

Low concentration of chlorine gas irritates the mucous membranes, the respiratory system and the skin-Large amounts cause irritation of eyes, coughing and labored breathing. If the duration of exposure or concentration is excessive, general excitement of the person affected, accompanied by restlessness, throat irritation, sneezing and copious salivation will result. The symptoms of exposure to high concentration are itching and vomitting followed by difficult breathing may increase to the point where death can occur from suffocation. The physiological effects of various concentration of chlorine gas are shown in table below :

S/n.	Effect	Part chlorine gas per million parts air by volume (ppm)
1	Least detectable odour	3 5
2	Least amount required to cause irritation of throat	15.1
3	Least amount to cause coughing	30 2
4	Least amount required to produce symptoms (of poisoning) after several hours of exposure	1.0
5	Maximum amount thet can be breathed for one hour without serious effect.	4.0
6	Amount dangerous in 1/2 to 1 hour	40 60
7	Amount likely to be fatal after deep breaths.	1000

These hazards can be controlled by proper design, operation and maintenance of the system. Specific emphasis should be given to the materials of construction of the chlorine system. Following points are important for the engineering control of hazards :

a. **Building Design**

Containers and equipments containing chlorine should be preferably located indoors, in a suitable fire resistant building. Standard fire walls may be needed to separate chlorine equipment from flamable materials. There should be atleast two means of exit from each separate room or building where chlorine is stored, handled or used.

b. **Heating and Venting**

If comfort heating is provided (or if the area is otherwise heated to increase chlorine discharge rates) care must be exercised to avoid overheating chlorine containers and equipments.

A suitable ventillation and air circulation system must be provided in the building.

Chlorine gas has a tendency to settle at floor level. The suction of ventillation fans should be located at or near floor level. · Fresh air inlets should be located to provide cross ventilation and to prevent the development of vacuum in the room. Multiple fresh air inlets and fan suctions may be necessary to exhaust air from rome equipment areas.

c. **Material of Construction**

At moderate temperature, neither liquid nor gaseous chlorine attacks most metals. Before any material is chosen it should be valuated under specific conditions of use especially where operating temperatures and pressure exceed normal conditions or where other corrosive chemicals are present. Evaluation should include both physical (mechanical) and chemical (resistancy) limitations. At low pressure, non metallic materials such as ceramics, glass, glass lined steel, hard rubber and some plastics can be employed. For high pressures common metals lined with resistant materials are suitable. Metals recommended at various temperatures for dry as well as wet chlorine are shown in table 1.

TABLE—1

GUIDE TO MATERIALS OF CONSTRUCTION FOR CHLORINE SERVICE TO APPROXIMATE TEMPERATURE LIMIT.

Material	Dry Chlorine	Wet Chlorine	Uses
Carbon Steel	300°F	Unsatisfactory	Pipe fittings, valve vessels & tower.
Stainless steel (304, 316, 317)	600°F	—do—	—do—
High Silicon irons.			
i. Durion	300°F	Unsatisfactory	Pipe fittings, valves, valve parts,
ii. Durichlor	300°C	100°F (with 3% Mo.)	pump parts.
Tantalum	300°F	300°F	Heat transfer equipments, speciality parts, diaphragm orifice.
Titenium	Unsatisfactory	200°F	Pipe fittings, valve parts, heat transfer equipments.
Nickel Molybdenum alloys:			
Hastelloy C	1000°F	100°F	Valves, valve parts, Pumps, pump parts.
Chlorimet 3	1000°F	200°F	—do—
Nickel & Alloys			
Nickel	1000°F	Unsatisfactory	Pipe fittings, valves, vassels, heat transfer equipments.
Monel	800°F	—do—	Vessels and towers packing
Lead	200°F	200°F	gaskets, lining material.
Copper & Alloys	400°F	Unsatisfactory	Pipe fittings, valves, heat transfer equipments.
Glass	200-300°F	200°F	—do— & tower packings.
Ceramics	200°F	200°F	Fume ducts & —do—
Hard rubber	Not usually recommended, unsuitable for liquid.	750°F	Lining material.

d. **Piping System**

Chlorine piping arrangements should be as simple as possible having a minimum number of screwed or flanged joints and a minimum number of loops and traps. Chlorine pipes should be above ground so that leaks can be readily located, repaired and inspection facilitated. Pipes should be well supported, sloped to allow for drainage and set at an elevation that leaves adequate clearance. Shut off valves at each end of a line, valves at intermediate points in a long line provide a means of isolating serious leaks. Liquid chlorine lines that are isolated may require expansion chambers to avoid excessive hydrostatic pressure. Liquid chlorine should never be trapped between two shut off valves unless the line is protected by a suitable expansion chamber.

e. **Process Control**

In a chlorine handling plant, main emphasis should be given on automation to avoid accidents and for smooth running of the plant. Automatic shut-off system should be provided in case of equipment/power failure otherwise it may result in accident. In automation main emphasis should be given on the air compressor system. The air compressor system must deliver a reliable supply of cool, clean and dry (dew point-40°C) air in sufficient volume and at a suitable pressure for the service required.

Some of the likely causes of chlorine leakages are :

1. Failure of equipment/power.
2. Malfunctioning of equipment/operator.
3. Defective valves and glands of gas containers and pipelines.
4. Abnormal change in process variables
5. Leakage through joints.
6. Improper handling/storage of chlorine cylinders/containers.

Following precautions/measures should be taken at the time of leakage :

1. If a tonner is leaking in such a position that Cl2 is escaping as a liquid, the tonner should be turned so that chlorine gas escapes. The quantity of gas escaping from a gas leak is 1/15th amount that escapes from a liquid leak from same size hole.
2. Water should never be sprayed on a chlorine leakage as it will only make the leak worse.
3. The severity of a Cl2 leak may be lessened by reducing the pressure on a leaking container. This may be done by absorbing chlorine gas from container in a solution of caustic soda, soda ash or hydrated lime slurry. Caustic lye (3-5% is recommended as it absorbs chlorine more readily. If hydrated lime is used the slurry must be continuously agitated for chlorine absorption. The proportions of alkali and water recommended for this purpose are given in table 2.

SAFTY - CASE STUDY

In West Coast Paper Mills Ltd., Dandeli, the amount of chlorine used varies between 12-18 tonnes per day, Despite the chlorine usage of such a high order there has been no major accident for the past several years. It is all due to the initiative taken by the Management. Proper safety arrangements are made to ensure the safety of the persons working in this process. An

TABLE—2

Cl_2 container capacity	100% Caustic Soda		100% Soda Ash		100% Hydrated lime	
	Kg	Water (Lit)	Kg.	Water (Lit)	Kg.	Water (Lit)
100 kg	125	400	300	1,000	125	1,250
900 kg	1125	3,600	2700	9,000	1125	11,250

independent safety departmen; has been set-up and safety arrangements provided are regularly checked up by the cancerned personnel. These safety arrangements are discussed regularly in a weekly meeting of the safety committee comprising of managers, safety officer, depart mental heads, process engineers and operators.

Analysis of minor accidents have revealed that those could have been avoided by taking proper care. In one case of such minor accidents; the leakage started due to the improper fixing of clamp used for connecting the chlorine container with the main header. The valve of the containers was opened without fixing the clamp properly. This resulted in the chlorine leakage from the connecting point of container to main header.

In anothrr case, a minor accident took place while detecting the chlorine leakage. The air pipe of the gas mask used by the operator got disconneted. Such an accident could have been avoided by proper checking of the gas mask before using them.

CONCLUSION

The need to design aud build safe chemical plant has been accepted as a healthy practice in the present day context and this has led to an enormous increase in ths proportion of design time devoted to safety studies, the figure being as high as 30 percent. Despite this, little or no time is allocated to this subject of safety both in under-graduate and post graduate curriculum with the result that the engineer, learn the aspects only on job. The purpose of this article is to present before the practicing and student chemical engineers, the interesting and important principles, theories, applications and techiques with particular emphasis on the hazards, design and operation as regards the safety in chemical plant.

Safety studies have to be very thorough and it is necessary to read relavent codes to understand all features relating to the safe design practice. Process availablity go hand in hand with safety. An important safe guard with respect to equipment and piping design is to ensure that operating limits and mechanical restrictions are clearly established at the time of design of plant. Design of a chemical plant calls for much concrted work by a team of engineers from various disciplines who are well versed in safe practices in their respecsive fields.

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