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CHLORINE LEAKAGE FROM THE BOTTOM OF A BABY CHLORINE CYLINDER – HUMAN FACTOR AND LESSON LEARNED

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ABSTRACT

Accidental release of chlorine from a baby cylinder, 60 kg capacity occurred in a congested locality of Kolkata in one winter night from a small factory. The chlorine gas dispersed over the nearby area resulting in death of 4 persons and injury to 87 persons. This paper presents the incident, the factor involved and the lesson-learned. What-if analysis was used to identify the possible errors, and to identify the unsafe activities. The necessary safe preventive measures are also discussed.

Keywords: Chlorine, baby cylinder, inhalation, human error, what-if analysis.

INTRODUCTION

Chlorine is a toxic, corrosive gas that can cause severe burns if inhaled or upon skin contact. It is a greenish-yellow nonflammable liquefied compressed gas packed in cylinders under its own vapor pressure. It form fume on contact with moisture in air. The degree of fuming is related to the amount of humidity in the air. It is also an oxidizer and will support the combustion. Products of combustion gases are generally toxic in nature. Chlorine exposure occurs through inhalation or skin or eye contact. Inhalation irritates the mucous membranes of the eyes, nose, throat, and lungs. Prolonged exposure or exposure to high concentrations is fatal, as outlined below (The chlorine Institute, Inc., 2000),

1-3 ppm	mild mucus membrane irritation
5-15 ppm	moderate irritation of upper respiratory tract
30 ppm	immediate chest pain, vomiting, dyspnea, and cough
40-60 ppm	toxic pneumonitis and pulmonary edema
430 ppm	lethal over 30 mins.
1,000 ppm	death within a few minutes

Although inhalation is the primary mode of exposure, direct skin contact with gaseous or liquid chlorine may result in chemical burns as the chlorine reacts with moisture on the skin. In addition, the extremely cold temperatures associated with liquid chlorine and vaporized gas escaping from pressurized containment can cause frostbite. The exposure limits are as follows,

OSHA	: PEL	= 1 ppm
ACGIH	: TWA/TLV	= 0.5 ppm
NIOSH	: IDLH	= 10 ppm

Chlorine is widely used in making large numbers of everyday products. It is used to produce safe drinking water through out the world. It is extensively used in the production of paper, dye stuffs, textiles, petroleum products, medicines, antiseptics, paints, insecticides, plastics and many other consumer products. The potential for leaks and spills of chlorine is present with its use (Gangopadhyay and Das, 2007). MHIDAS database indicated that 96 accidents of chlorine release to atmosphere occurred in the period 1964-1996 (Macro et al., 1998). These resulted in 39 deaths and over 2700 injured. They also showed that the contribution of human errors were 26% of incidents resulting in chlorine release. In general the chlorine leakage from a cylinder occurs due to the operational error, maintenance error; crack or rupture due to miscellaneous causes. In some cases human errors are also responsible for operational and maintenance errors. Fig. 1 shows the generalized fishbone diagram of accident causes that release of chlorine from chlorine cylinder.

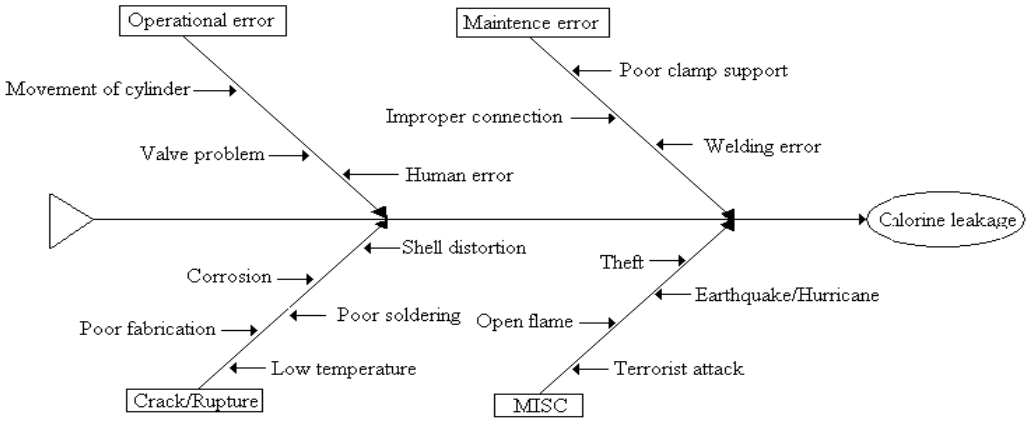

Fig. 1

Human error defined by Chemical Manufacturer's Association (1990) as "any human action that exceeds some limit of acceptability (i.e. an out-of-tolerance action) where the limits of human performance are defined by the system". Fig. 2 shows categorization of human errors (HSE, 2005).

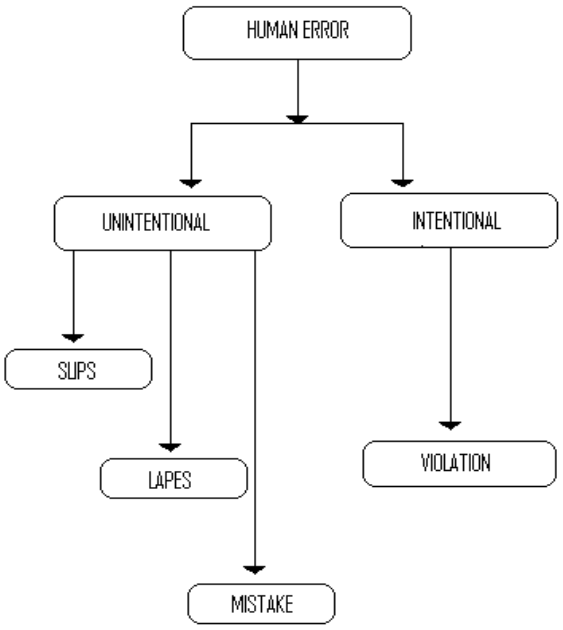

Fig. 2

Some times human attention about various information, perceptions towards safety, capacity for remembering things and logical thinking not work properly as

1. Ignorance – one does not have the necessary/ knowledge for the activity;

2. Pseudo knowledge – one does not have the necessary knowledge for the activities, but believes they have the adequate knowledge;

3. Imprudence – one has the necessary knowledge for the activities but due to faulty thinking has convinced herself or himself that she or he is the exception to the rule.

The important task is to identify and reduce human errors for minimize the accident. Literature review shows that Human Reliability Analysis (HRA), Process Hazard Analysis (PHA) What-if analysis, HAZOP, Checklist, Failure mode and Effect analysis etc. use to predict the errors occurred which resulted an accident. Among them "what-if analysis" one of the useful applicable techniques to find out predictable human error, improve the safety levels and manages the risk successfully. This paper deals with the description of the incident, identification of errors and the lesson learned from the accidental release of chlorine from a baby cylinder.

THE INCIDENT

A small unit manufactured calcium hypochloride solution by passing chlorine into lime solution. The occupier brought a cylinder of chlorine (baby cylinder – 60 kg capacity) from the nearby dealer for the preparation of hypochloride solution. In the night time the cylinder, which was, kept lying in the ideal condition started leaking from its bottom all on a sudden (Anandabazar Patrika, 1990). The worker brought some ice from the nearby shop and kept the cylinder in the ice pot with anticipation that the chlorine leak from the cylinder will stop if the cylinder is cool down by ice. After a few minutes the leak increased instead of stopping.

Chlorine gases profusely spread from the cylinder and dispersed according to the direction of wind affecting the people on its path in the adjacent houses, four people died by the chlorine gas and other person who were sleeping in the nearby areas and on the passage of the dispersion of the gas was also died. The calcium hypo chloride unit was located in a heavily populated area in a metropolitan city, Kolkata and most of the buildings were multistoried, normally shops were in the ground floor and residential accommodation on the first floor onward. As the chlorine gas is heavier (vapor density of 2.48 gm/cc) than air it spreads very little quantities in the first floor level. 87 people were affected need only first aid treatment for the minor injury by inhalation of the chlorine gas.

Nature and extent of damage

1. Within the establishment:
   - Casualties : Nil
   - Material damage : Nil
   - Damage to environment : Could not be ascertained

2. Outside the establishment:
   - Casualties : Killed : 4
     : Injured: 87
   - Material damage : Nil
   - Damage to environment : Could not be ascertained

Incident analysis

The main event was identified as

1. The chlorine cylinder was badly corroded.
2. Chlorine dispersed according to the wind direction and caused the death and injury.
3. No emergency first aid response was there.

Major contributing conditions were also identified:

4. The man engaged in the manufacturing process had no knowledge regarding the hazards of the chlorine.
5. Due to the management and worker's ignorance, the management's reaction was to put the chlorine cylinder on the ice pot and the reaction of the metals of the chlorine cylinder with chlorine and water ultimately increases the diameter of the leaky portion of the cylinder.

Corrosion mechanism

In dry chlorine service, carbon steel is most commonly used material of construction for system piping. The iron in carbon steel is reactive with dry chlorine

$$2Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3 \quad (1)$$

The ferric chloride ($FeCl_3$), forms a passive layer on the steel surface, which protects the underlying iron. Ferric chloride is a very hygroscopic salt; it absorbs moisture and water very quickly when exposed to the atmosphere, which accelerates the overall corrosion rate. Carbon steel is corrosion resistance to chlorine as long as high water concentrations or temperatures do not deliquesce the protective layer (The Chlorine Institute, 2000). The corrosion mechanism for chlorine attack on steel is a water-rich phase and also increases with increase in temperature. In both cases, ferric chloride forms; this solution is an electrolyte, a very strong oxidizer, and a strong acid. The water-rich phase not only dissolves the protective layer of ferric chloride, but also forms an acid medium by reaction of chlorine with water (Updyke, 1982, Saroha, 2006). The chlorine-water reaction forms hypochlorous acid (HOCl) and hydrochloric acid (HCl) as,

$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (2)$$

The hypoclorous acid is not very stable and further dissociates according to following equation,

$$2HOCl \rightarrow 2HCl + O_2 \quad (3)$$

The acids and the dissolved ferric chloride form a concentrated solution that is corrosive to steel.

Lessons learned from this incident

1. Understanding of the Hazards and Effects Management Process needs to be implemented.

2. Incident scenarios and appropriate job safety analysis (task risk assessment) should be performed with the involvement of first line supervision. Methods statements should be prepared which clearly define roles, responsibilities and the controls to be applied.

3. Chlorine cylinder supplier's recommended practices for safe handling of the cylinder should be understood, communicated and applied.

4. Cylinder leakage should be addressed to the manufacturer or local task force to tackle this problem immediately and to provide rescue staff with breathing apparatus and resuscitation equipment.

5. The awareness of the hazard of chlorine should be enhanced for all staff.

Human errors

The "What-if" table generated for the human factor analysis shown at Table 1.
After investigation it was observed that the worker was illiterate and he had no knowledge about the hazardous nature of chlorine. The small establishment did not have a telephone for communication. The following human errors are identified,

- Lack of knowledge – awareness of the hazards of chlorine.

- Lack of logical thinking – In any technological situation logical procedures are necessary, but illogical thinking or the behavior lead to accident. Liquid chlorine is leaking from the cylinder if the cylinder was titled to facilitate the leak of chlorine gas, then the amount of chlorine leak is minimum, as the gas release is 15 times less compared to the liquid release from the same size. The worker put the leaked cylinder on the ice pot which increases the leak diameter.

- Mental inefficiency – A situation which does not have the mental capacity to deal with the information that must be processed in the activity. The worker is illiterate and his mental capacity is also very limited to process any information in acute condition.

What-if	Consequences	Recommendations
1.If the chlorine cylinder titled to facilitate the leak of chlorine gas	The amount of chlorine leak is minimum	Ideal solution for initial period of liquid chlorine leakage
2. If the leak cylinder put on the ice-pot	Increases the leak due to corrosive action with water	Educating workers about the hazards of chlorine and also encourage to participate in training and monitoring programs in the work place and set up emergency plan
3. If chlorine gas come out from chlorine cylinder	It may fume while on contact with moist air and create highly corrosive atmosphere	Establish an emergency response plan for responding to leaks and also arrange the proper training for workers
4. If chlorine gas spreads offsite	Severe irritant to the eyes and respiratory system and also burn the skin	Establish an emergency response plan for responding to leaks
5. If the workers are illiterate or if the operating procedure is not properly follow	Accidents may occurred	General chemical and hazardous information should be displayed and provide contact no. for possible help. Proper information and training for proper handling chlorine should give all the workers.
6. If chlorine cylinder become corroded	There is a possibility of leakage	Cylinder should be checked in regular interval of time

Table 1 What-if analysis

Accident prevention and recommendation as preventive measures

Fig. 3 shows the general accident prevention methodology in a fish bone diagram. There is a need for major precautions while working with chlorine, which when mis-handled is a very dangerous gas.

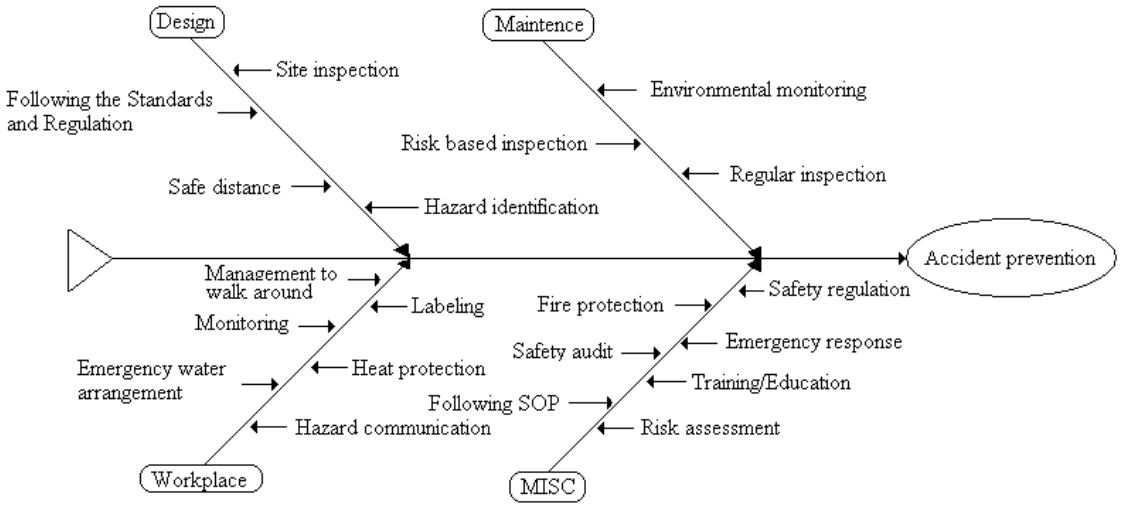

Fig. 3

The following outlines a programme governing the moving, storage, and maintenance procedures to be used for handling chlorine gas. Consult the Safety Engineer/supplier's safety officers for procedures to be followed in an emergency, and the type of first treatment to be rendered to persons exposed to chlorine fumes (Spellman,2003;http://erd.dli.mt.gov/safetyhealth/brochures/chlorinesafety.pdf; http://www.tdi.state.tx.us/pubs/videoresource/t5chlorine.pdf.; Gangopadhyay et al., 2005, Gangopadhyay and Das, 2007).

Some general recommendations set up as per "What – if analysis" for handling chlorine, control human error, administrative control and safety work procedure control were followed.

Handling chlorine

Cylinder movement

The appropriate technique for cylinder movement is the valve cap should be placed and dropping a cylinder or allowing an object to strike the container with extreme force must be prevented. Never expose a cylinder to heat and never lift a cylinder by its hood. Always use clamp support for cylinder movement. Lifting the cylinder by crane, rope sliding chain or magnetic device should not be use. Lifting the cylinder by holding the valve cap or its neck is prohibited.

Cylinder storage

The chlorine cylinder storage area is to be a well ventilated, secured and protected from weather away from heavily traveled areas and emergency exits. Never cylinder stored near salted or other corrosive, combustible or flammable materials. Full or empty cylinder should be marked. To prevent full container from being stored for stored long periods of time use first-in first-out inventory system. Check the cylinders visually at last weekly for any indication of leakage or other problems. Provide leak detectors and high concentration audio visual alarm in storage area. To avoid liquid/water ingress in the cylinder while consuming the chlorine, outlet line from cylinder to consumption point should be provided with 32 ft high barometric leg.

Control human error

i. The workers need proper education and training about the hazards of chlorine.
ii. They must have knowledge about the emergency response plan for responding to leaks or accidents.
iii. Workers must wear appropriate protective clothing and respirators when handling chlorine cylinders or compounds.
iv. Follow the manufacturer's instructions during emergency and display the instructions from the material safety data sheet.
v. Never spray water on leaking containers; it can make the leak worse.
vi. Workers must not eat, drink or use tobacco products during handling chlorine. The hands and face should be washed before eating or drinking.

General control

i. Dragging, rolling or dropping of cylinder should be avoided.
ii. Fusible plug safety device on containers should not be tampered.
iii. Chlorine supplier is to be immediately contacted if any damage is found.
iv. Repair a container or its part like valve should not be done – immediately contact the supplier.
v. Never place a container in hot water, or apply direct heat to increase the flow rate, or for any other reason.
vi. Once the cylinder has been connected to the process, cylinder is to be opened slowly and carefully.
vii. If user experiences any difficulty in operating cylinder valve, disconnect use and contact supplier.
viii. Never perform maintenance work on a system unless the tank valves are closed.

Administrative control

(www.employment.elberta.Ca/documents/WHS/WHS-PUB_ch067.pdf.**)**

i. Train workers on the health hazards from exposure to chlorine and the safe work procedures developed by the employer.
ii. Establish an emergency response plan for responding to leaks and spills of chlorine at the work site.
iii. Prepare escape plans from areas where there might be a chlorine emission. Always remember to move uphill and upwind.
iv. Comply with requirements for handling and storage of hazardous materials.
v. Ensure that the need for ventilation is properly assessed and systems that are installed are properly designed and maintained. Workers also need to be trained on the proper operation and maintenance of these systems.
vi. Provide proper and approved self-contained breathing apparatus in areas where chlorine is stored or used.
vii. The ventilation system in the chlorine storage room should be on and functional when workers are in the room.
viii. Chlorine alarm system should be installed, with an indicator located outside the room.
ix. Clean up chlorine spill, if any, quickly and properly using appropriate protective equipment and clothing.

CONCLUSION

The incident of chlorine leakage from a baby cylinder and the off-site consequences are described. The analysis of the incident has been carried out with respect to human errors and causes due technical faults.

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