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DEVELOPMENT OF A MITIGATION MODEL FOR STORAGE FACILITY TO REDUCE THE CONSEQUENCE OF TOXIC RELEASE

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ABSTRACT

Chlorine is highly toxic and in the event of accidental release has the potential to kill or inflict injury to the people. This kind of release may occur unexpectedly and cause huge loss. Hence proper mitigation methods should be devised. In this study the accidental release of liquid chlorine from the storage tank is considered and a new mitigation model is proposed. The model is proposed using add-on active protective measures with the existing plant facilities. Consequence assessment of accidental release of chlorine from the existing and proposed system has been done. It has been demonstrated that significant consequence reduction of chlorine release is possible through the proposed mitigation system.

Keywords: chlorine, consequence, mitigation, vaporization

NOMENCLATURE

A	Area of the liquid chlorine pool (m^2)
Ap	Cross-sectional area of pipe (m^2)
C	Chlorine concentration (ppm)
C_D	Discharge coefficient (Unit less)
C_p	Heat capacity of chlorine (KJ/KgK)
Di	Diffusivity of air (m^2/S)
d	Depth of pool over the entire area (m)
d_p	Pool diameter (m)
e	Fraction of chlorine entrained (unit less)
F_v	Mass fraction of chlorine flashed (unit less
g	Gravitational constant (m/s^2)
H	Total heat flux in to the pool (kW)

H_v	Heat of vaporization (Kj/mole)
h_{fg}	Latent heat of vaporization (kJ/kg)
h^*	Initial head of liquid from pipe (m)
h_{grd}	Heat transfer coefficient of ground (J/m^{2}s °C)
h_{liq}	Heat transfer coefficient of chlorine (J/m^{2}s °C)
k_g	Mass transfer coefficient (m/s)
K_{liq}	Thermal conductivity of chlorine (J/h m K)
K_{grd}	Thermal conductivity of ground (J/h m K)
L	Heat of vaporization of the liquid (Kj/Kg)
M	Molecular weight of chlorine (Kg/Kg-mole)
m	Discharge rate (Kg/s)
m_p	Mass of the pool (Kg)
$\dot{m}$	Evaporation rate (kg/s.m^2)
m^*_{mass}	Mass transfer evaporation rate (Kg/s)
m^*_{sol}	Evaporation rate (Kg/s)
m^*_{tot}	Net evaporation rate (Kg/s)
P^{sat}	Saturation vapour pressure of chlorine (KPa)
P_1	Upstream pressure in the tank (N/m^2)
P_2	Downstream pressure (N/m^2)
Q_{sol}	Solar radiation (J/m^{2}s)
R_g	Ideal gas constant (KPa m^3/kg)
Sc	Schmidt number (unit less)
T	Initial temperature of the liquid (°K)
T_b	Atmospheric boiling point of the liquid (°K)
T_L	Temperature of the liquid (°K)
t	Duration after spill (sec)
U_{grd}	Overall heat transfer coefficient (KJ/m^{2}s K)
u_w	Wind velocity (m/s)
W	Total mass of cloud (Kg)
$\varnothing$	Liquid resistance (assumed as 1)
α	Thermal diffusivity of ground (m^2/s)
β	Dimensionless parameter
v	Kinematic viscosity of chlorine in air (m^2/S)
ρ	Liquid chlorine density (Kg/m^3)
$\sigma y, \sigma z$	Dispersion coefficients

1.INTRODUCTION

Chlorine is of great industrial importance and it is widely used in making various products. It is inevitable for producing safe drinking water the world over. On the other hand, chlorine, a highly toxic chemical, liquefied and stored at (-) 10 °C and having an expansion ratio of 460 is a matter of great public concern. With the rapid development of modern technology and large-scale industrial projects all kinds of risk potential have become extremely intricate in every industrial activity. A number of illustrations on such situations have been reported [1-4].

It is not surprising that most of the industrial accidents were in process facilities, due to improper storing and handling of hazardous materials. Different techniques and design practices that contribute to mitigation of the results of chlorine release are reported [5]. Modified safety system is proposed for an existing plant and the benefits are reported [6]. Hence an exercise has been taken up to develop a dedicated system for storage facility to reduce the impacts of toxic release.

2.FACILITY DESCRIPTION

The storage tank is placed in a cement concrete dyke located in an open asbestos roofed container building as shown in Figure 1. The existing size of the dyke wall is 10m*4m*1m.

A partial pressure of 3Kg/cm^2 and temperatures of -10 ^oC in liquid are maintained in the storage tank. The diameter and length of the horizontal cylindrical dished end tank are 250 mm and 8830mm respectively.

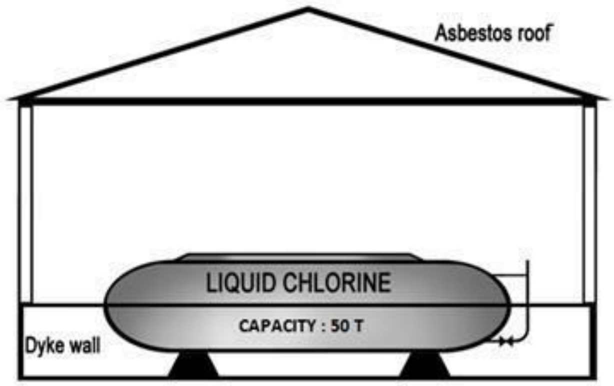

FIGURE. 1 EXISTING CHLORINE STORAGE FACILITY

3.MODIFICATIONS PROPOSED

The proposed new mitigation system for the building of chlorine storage tank is shown in Figure 2. The existing dyke wall should be overlapped with materials having poor-heat transfer properties to reduce the rate of vaporization of chlorine. Poly tetra fluoro ethylene (PTFE) is one such material. It has a thermal conductivity of 0.25w/mK [7] and is suitable for liquid chlorine handling. The existing floor should be provided with a PTFE lining (shown in Fig. 2). Thickness of the lining is assumed as 10mm.

In the event of chlorine leakage the proposed mitigating system starts operating automatically. As soon as the leakage of chlorine is sensed by the sensor, the alarm device beeps and it communicates to the control room immediately. The Immediately Dangerous to Life or Health (IDLH) concentration for chlorine (10ppm) is considered as setting value of the sensor. The chlorine release from the storage tank is considered to be in liquid phase.

In liquid release, about 10% of chlorine spill will vaporize immediately [5].

After flash vaporization, the remaining liquid is spilled on the floor and flows in to the collecting sump. Then it evaporates slowly under ambient pressure and at temperature of -34 ^oC. The blower sucks the chlorine vapour from the collecting sump and is fed to the absorption unit. The response time for the operators for manual arrest of the leak is 10 minute [8]. The roller shutters, blower and related valves will work automatically with different response time with the help of the control panel. The response time for blower to start up operation is considered as two minute after release where as the roller shutter will close 10 minutes after release. The closing of roller shutters makes the storage tank facility a fully closed containment which prevents the wind-flow in to the containment and prevents the spreading of chlorine to the atmosphere.

4. RELEASE SCENARIO

The chlorine discharge is assumed to flow through the 20 mm diameter pipe connected at the dish end of the storage tank for sight glass fitting, which is 280mm from the base of the tank. It is assumed that the pipe gets broken at 50mm away from the tank. The quantity of chlorine considered for the study is 42.0 tones and the corresponding height of the liquid from the base is 1.4 meters. The worst case scenario considered is the incident that may occur at initial stage of transferring liquid chlorine from storage tank to truck container by using compressed air at 10 Kg/cm^2.

Discharge Rate Calculation

The discharge rate is given by [9]

$$m = ApC_D\sqrt{2\rho(P_1 - P_2)} + Ap\, C_D\rho\sqrt{2gh^*} \qquad (1)$$

Where, Ap - $3.14{*}10^{-4}$ m^2, 1,468 Kg/m^3, P_1 - $3{*}10^5$ N/m^2 and $10{*}10^5$ N/m^2, P_2 - $1{*}10^5$ N/m^2, h^* - 1.2m and g - 9.81m/s^2.

The discharge rate of chlorine from the pressurized tank will vary with time [10]. As the level of the liquid in the tank falls, the hydrostatic head, upstream pressure and, therefore, the rate of release will be reduced. This may lead to an overestimation of total quantity of discharge. To overcome this drawback, calculation of the discharge rate will, at best, take a set of piecewise constant pressure values with each piece as 1-10sec. The values of upstream pressure P_1 and liquid height above release point h^* will vary in each set of discharge rate calculation. Table 1 shows the chlorine discharge in 10 seconds stepwise duration corresponding to the initial upstream pressure of $10{*}10^5$ N/m^2.

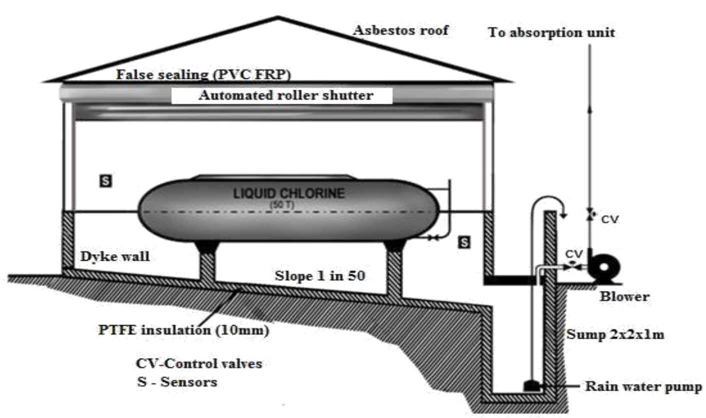

FIGURE. 2 PROPOSED MITIGATION SYSTEMS FOR CHLORINE STORAGE FACILITIES

Evaporation of the liquid pool

Vaporization from a pool is determined using total energy balance on the pool,

$$m_p C_p \frac{dT}{dt} = H - L\dot{m} \qquad (2)$$

Liquid chlorine itself is easily contained if it spills. The greater hazard lies in its vaporization. There are two stages of vaporization to consider, immediate flashing to the atmospheric boiling point and slower continuous vaporization from liquid pool.

Where C_p - 0.9412Kj/Kg, T- 263 °K, T_b - 239 °K and h_{fg} -288 kJ/kg.

Fraction of liquid entrained is given by [12]

TABLE. 1 DISCHARGE OF LIQUID CHLORINE IN 10 SECONDS INCREASE (P_1, 10 $*10^5$N/m^2)

Time (sec)	Pressure P_1 (N/m^2)	Pressure P_2 (N/m^2)	Liquid height h (m)	h* = h-0.28 (m)	Liquid Volume in the tank (m^3)	Vapour Volume in the tank (m^3)	Discharge (m^3)
10	1000000.00	100000	1.4	1.12	28.67	11.99	0.07554
10	993739.33	100000	1.395	1.115	28.59	12.07	0.07529
10	987577.07	100000	1.392	1.112	28.52	12.14	0.07505
10	981510.13	100000	1.388	1.108	28.44	12.22	0.0748
10	975536.52	100000	1.384	1.104	28.37	12.29	0.07456
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10	757106.15	100000	1.208	0.928	24.82	15.84	0.06505
10	754009.20	100000	1.205	0.925	24.76	15.90	0.0649
10	750944.41	100000	1.201	0.921	24.69	15.97	0.06475
10	747911.48	100000	1.199	0.919	24.63	16.03	0.06461
10	744909.46	100000	1.195	0.915	24.56	16.10	0.06446
600							4.17037

The mass fraction of liquid flashed can be represented as [11]

$$F_v = C_p(T - T_b)/h_{fg} \quad (3)$$

The vaporization rate of the pool is controlled by heat transfer from the ground (by conduction), the air (both by conduction and convection), and the sun (radiation). A number of useful references are available for estimating the evaporation rate from liquid pool [13, 14]. The mass transfer evaporation rate is given by [15]

Fraction of liquid entrained is given by [12]

$$e = F_v \ (\text{if } F_v < 0.5) \quad \text{or}$$
$$e = 1 - F_v \ (\text{if } F_v > 0.5) \quad (4)$$

Total mass of cloud, $W = (e + F_v)w_o$ (5)

$$m^*_{mass} = \frac{M k_g A P^{sat}}{R_g T_L} \quad (6)$$

Where M - 70.9 Kg/Kg-mole, P^{sat} - 97.17 KPa, R_g - 8.314 KPa m^3/kg and T_L - 239 °K.

The mass transfer coefficient from the pool is available from the correlation [13]. .

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$$k_g = 4.786 * 10^{-3} u_w^{0.78} d_p^{-0.11} Sc^{-0.67} \qquad (7)$$

Schmidt number is given by

$$Sc = \frac{v}{Di} \qquad (8)$$

Where, v - 4.24 *10^{-6} m^2/S and Di - 7.1*10^{-6} m^2/s.

The evaporation rate due to solar radiation is given by [13]

$$m^*_{sol} = \frac{Q_{sol} M A}{H_v} \qquad (9)$$

Where Q_{sol} - 642 J/m^{2}s [13], H_v - 4.06Kj/mole.

The net evaporation rate is given by [13].

$$m^*_{tot} = m^*_{sol}\left(\frac{1}{1+\beta}\right) + m^*_{mass}\left(\frac{\beta}{1+\beta}\right) \qquad (10)$$

β is a parameter which is function of vapour pressure (dimensionless).The parameter β is given by [13].

$$\beta = \left[\left(3650 \frac{kJ\ Pa}{mol\ K}\right) Sc^{0.67} + \frac{U_{grd} R_g T}{k_g}\right] \frac{R_g T^2}{P^{sat} H_v^2} \qquad (11)$$

The overall heat transfer coefficient of the ground is given by

$$\frac{1}{U_{grad}} = \frac{1}{h_{liq}} + \frac{1}{h_{grd}} \qquad (12)$$

Where h_{liq} is the heat transfer coefficient of liquid chlorine (J/m^{2}s °c) and which is given by

$$h_{liq} = \frac{K_{liq}}{\emptyset d} \qquad (13)$$

where K_{liq} - 540 J/h m K, $\emptyset$ - assumed as 1 [13].

The heat transfer coefficient of ground h_{grd} is given by [13]

$$h_{grd} = \frac{2K_{grd}\left(\frac{t}{\pi\alpha}\right)^{0.5}}{t} \qquad (14)$$

Where K_{grd} (concrete)- 1.13 J/h m K , K_{grd} (PTFE)- 0.25 J/h m K), α(concrete)- 5.65*10^{-7} m^2/s, α(PTFE)- 0.124*10^{-6} m^2/s and t - 600sec.

5. DISPERSION OF CHLORINE

The dispersion calculations provide an estimate of the area affected and the average vapour concentrations expected.
The centerline ground level concentration is [16]

Where h_{liq} is the heat transfer coefficient of liquid chlorine (J/m^{2}s ^{o}c) and which is given by

$$C = \frac{Q}{\pi u \sigma y \sigma z} \quad (15)$$

Where u - assumed as 3.5 m/s and the stability class is F (conservative). The dispersion coefficients are obtained graphically or numerically using the downwind distance and stability category of the atmosphere [17].

6. DOSE-RESPONSE MODEL

The probit variable Y for gas exposure is [18]

$$Y = k_1 + k_2 \ln(tC^n) \quad (16)$$

Where values of k_1, k_2 and n are – 8.29, 0.92 and 2 respectively, and t is the duration of exposure time in minutes. An exposure time of 10 minutes is assumed for the proposed storage facility and an exposure time of 76 minutes (average time for complete evaporation of liquid pool) for existing storage facility.

7. RESULTS AND DISCUSSION

In this research, rupture of pipe for sight glass fitting of a liquid chlorine storage tank is chosen for consequence assessment. The release time of liquid is considered as 10 minute.

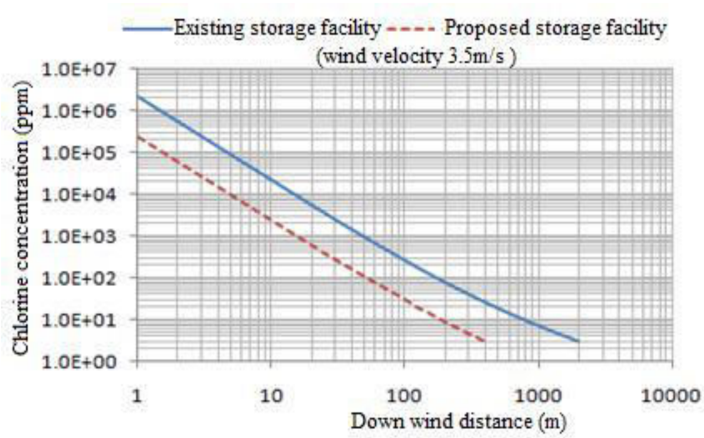

FIGURE. 3 CHLORINE CONCENTRATION WITH DOWN WIND DISTANCE

Total quantity of chlorine released in 10 minute is found to be 2.28m3 (3347 kg) and 4.17m3 (6121.56Kg) corresponding to the initial upstream pressure of 3*105 N/m2 and10*105 N/m2 respectively.
Equation 5 is used to calculate the mass of vapour flashed during release which is found to be 505.35 Kg and 924.35 Kg corresponding to the initial upstream pressure of 3*105 N/m2 and 10* 105 N/m2 respectively.
The worst –case scenario of chlorine released from the tank at upstream pressure of 10*105 N/m2 and

wind velocity of 3.5 m/s is considered for consequence assessment. The net evaporation rate in existing storage facility is found to be 1.152Kg/s where as it is 0.127 Kg/s in proposed storage facility.

Equation 15 is used to determine the chlorine concentration in the vicinity of the tank. The chlorine concentrations from different sources at different distances are calculated and the results are shown in Figure 3.

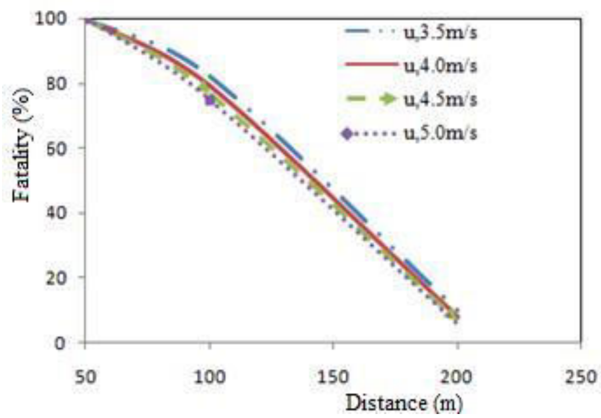

FIGURE.4 THE RELATIONSHIP BETWEEN DISTANCE AND FATALITY FOR EXISTING STORAGE FACILITY

For the existing storage facility, the percentage fatality is 82% at 100 m where as it is 10% at a distance of 200m.

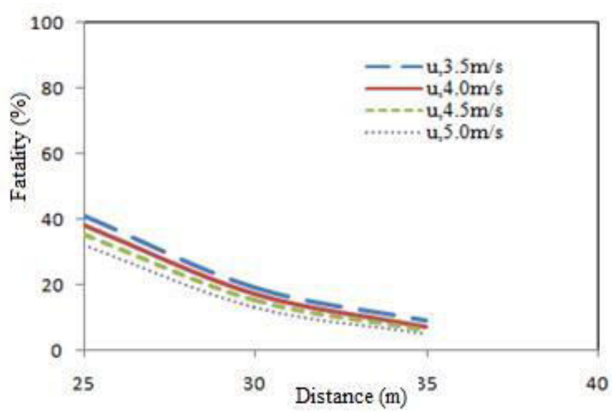

FIGURE. 5 THE RELATIONSHIP BETWEEN DISTANCE AND FATALITY FOR PROPOSED STORAGE FACILITY

For the proposed storage facility, the percentage fatality is 41% at 25 m where as it is 2% at a distance of 45 m. For the existing storage facility the minimum concentration of 3.06 ppm is estimated at a location of 2000 m which is outside the company premises.

8. CONCLUSIONS

This paper proposes a new dedicated mitigation system for chlorine storage facility which aims to reduce the consequences of accidental release of chlorine. The consequence analysis of chlorine release from the existing and proposed storage facility is done and results are compared. Any chlorine release from the existing storage facility warrants off-site emergency response planning whereas chlorine release from the proposed storage facility can be managed by on-site emergency response planning.

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