

# **A critical approach to safety equipment and emergency time evaluation based on actual information from the Bhopal gas tragedy.**

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As amply reported, after Bhopal disaster process safety got a boost worldwide and risk analysis got applied more generally. Even if the concept of inherent safety, strongly promoted by Trevor Kletz, represents one of the main lessons from this tragedy, in the first part of the paper we focus on Bhopal mitigation measures representing the ultimate relevant layer of protection. Starting from a technical analysis of the whole safety equipment of the plant and relevant empirical evidences, we face the short-cut design of critical safety devices suitable to mitigate release effects. The applied method allows a preliminary design and management tool to evaluate the effectiveness of safety systems and the impact on surroundings. In the second part, we develop an empirical-based framework allowing to identify emergency actions and intervention time and demonstrate how the implementation of these safety measures when reaching a critical pressure of 10 psig in Tank 610, even under the condition of protective equipment out of commission, would have surely mitigated such a high profile tragedy. The paper illustrates the determining contribution to this tragedy of such deficiencies in the safety procedures for handling abnormal situations and emergencies by the company.

**Keywords:** Bhopal incident; emergency planning; human factor; runaway reaction; safety equipment design.

## **1. Introduction**

On December 2<sup>nd</sup> 1984, one of the world worst accident of chemical industry occurred in Bhopal, India, and even after 30 years, this tragedy is unparalleled in the history of chemical accidents.

Many key-facts of Bhopal tragedy are well established. The accident was caused by a massive release of approximately forty tons of Methyl Isocyanate (MIC) stored in a nearly full stainless steel tank in its liquid state. The immediate release cause was a runaway reaction triggered by water entered the tank and leading to boiling and over pressurization of the tank. A valve designed to prevent tank failure opened and discharged unreacted MIC vapour to the atmosphere (Sharan et al., 1994). 520,000 persons were exposed to gases, about 8,000 died immediately and 12,000 thereafter (Edwards, 2005) and many more than 100,000 persons faced long term morbidity, with health effect and permanent injuries (Eckerman, 2005). Even if Bhopal is a well-known incident, which have been thoroughly described in the literature (Gustin, 2002), there are questions which are still discussed on this issue by many authors, like if and how this could have been prevented, what were the probable components of gases, what were the effect of these gases and number of casualties and permanent injuries, how the immediate treatment for the survivors could have been more efficient, how socio-economic effects could have been mitigated and what influence this accident had left on the safety policies of the chemical industry in India (Eckerman, 2005). After thirty years there are at least four theories on the immediate cause and who was responsible, including: the accidental entry of water from a washing operation; sabotage by a disgruntled employee; confusion between a hose containing nitrogen and one containing water; gradual entry of water and other contaminants into the tank over many weeks (Macleod, 2014). In any case, the underlying cause of the incident can be attributed to poor management controls of the operating system, including:

- underinvestment in personnel and safety systems;
- not following or maintaining critical emergency safety systems;
- adequacy of equipment and safety regulations;
- bi-annual safety audits instead of annual audits.

The severity of the accident was undoubtedly connected to the fact that operating instrumentation, safety interlock and mitigation systems were not efficient, not properly designed or undersized. Clearly, complexity and consequent causal interaction between its different technical, human and organizational elements represented a source of unpredictable system behaviour (Bouloiz et al., 2013). Risk reduction strategies aiming at reducing frequency or mitigating the magnitude of the impact can be categorized as: 1. engineered active and passive; 2. managerial and procedural; 3) inherent. Among these three classifications, the first and second one are the subject of discussion in this paper, being inherent safety methodology already amply explored (Edwards, 2005) (i.e. by selecting an inherent safer route to produce carbaryl without the intermediate by-product MIC, though at a greater manufacturing cost). Additionally, it must be recognized that adding on or

bolting on safety measures to an existing system is not very effective and that the preferred method would be to design safety into the target. Prevention measures not properly implemented in Bhopal plant include hazard awareness and evaluation, plant design and structure, processes and machineries, personal training and information, emergency planning & response. Change of any original design, installation, or processing operation can also cause any catastrophic consequences, so that management change is recognized as an important part of preventive measures and faulty Management of Change is recognized among the causes of Bhopal tragedy (Joseph et al.,2005). Personnel reductions in production and maintenance department due to financial loss for several years were also an important factor, as this item plays sharply affects both personnel and process safety performances (Fabiano et al., 2008). This cutback also influenced the training schedules on MIC operations for plant personnel, taking it to a limited number and creating a lack of safety awareness (Shrivastava, 1992). Mitigation measures are always needed, whatever the prevention level may be and can be distinguished among in situ prevention measures, aiming at minimizing the immediate consequences of the accident and external protection measures aiming at the emergency management. Dealing with the former issue, examples include the design of MIC storage tank relief valve and water spray system which was unable to adequately mitigate the release. High temperature and pressure instruments were not maintained properly and those were known to be unreliable (Kletz, 2001). Considering the latter issue, there was also a need for proper emergency planning, notification, and response in case of any toxic chemical releases (Joseph et al., 2005). A large number of papers can be found dealing with the topics of MIC dispersion and the determining role of the urbanization and meteorological conditions during the post release evolution (Havens et al., 2012 ). In this context, the absence of land use planning causing the combination of sharp development of densely populated slums without any minimal infrastructure and hygienic supplies and limited capacity to cope with the crisis made the incident worse (Bisarya & Puri, 2005). As previously anticipated, we firstly faced technical protection measures within the plant fence line, providing some qualitative and quantitative understanding on the extent to which different options can handle the demand. Theoretically, it may be appropriate to select one, or to use several devices in combination, considering that a particular solution may have side effects, while several options interact. Referring to Bhopal plant and available design and process data, in the following we discussed the practicability of a single option, utilizing a short-cut design approach. We did not distinguish between passive and active protection, even if this item is important in relation to dependability. There are in the Bhopal plant a number of design problems illustrating also the importance of the cost of the different options, side effects and cost effectiveness. Bhopal

experience described here confirms that a truly holistic, or integrated approach would have resulted in a by far lower profile accident. Therefore, after the critical review of the various protective equipment, the remainder of this paper is focused on the development of a combined integrated approach by short-cut calculating appropriate stack dimensions, flare systems and a water spray curtain.

## **2. Single protective equipment approach**

A complex set of interdependent organizational and technological factors played a critical role in Bhopal incident with several safety systems that should have prevented or minimized the release out of order, or not in full working order (Joseph et al., 2005). As outlined by Casson et al. (2012) the majority of accidents involving runaway reactions are associated with the failure of controls and safe-guards, or with human error and their handling can be performed by venting, containment, venting with containment and reaction inhibition. Theoretically, the primary protection principle can be faced by applying only one of the methodologies outlined as an abstract model in Fig. 1 (C, A or D), by proper design and operating a key protective equipment, suitable to attain the safety target. This is the case of environmental protection when the chemico-physical characteristics of the substances, the emission concentration and mass or flow rate do not represent an immediate hazard for health and safety (e.g. stack or chimneys to disperse atmospheric pollutants; spray barriers to dilute atmospheric release etc.). Dealing with process safety and loss prevention, the correct design implies the adoption of redundant different equipments to attain defence in depth and avoiding that the failure of a single protective equipment could result in an accident. This practical need is also connected to the inherent properties of hazardous materials to be handled, to their concentration and mass flow rate, to available intervention time and, at last, to cost effectiveness of a single apparatus. Table 1 summarizes the technical safety barriers and protective equipments/devices aiming at environmental protection and loss prevention considering release and emissions into the atmosphere. The whole problem can be treated following a unified approach and Bhopal plant layout is considered and modeled on the basis of the data summarized in Table 2. As for MIC operating manual of the Bhopal plant “if a leak develops in a tank that cannot be stopped or isolated, the material in the tank may be pumped to another tank”. Theoretically, in case of emergency procedure, a closed containment tank could be designed, possibly with a reacting liquid. The evaluation of a suitable catch tank is a rather standard problem to be solved that can be faced, as an illustrative example, according a short-cut method summarized in the following. Considering a dumping tank, on the basis of the reference values above mentioned, the design volume

corresponding to the containment of MIC at the vapour phase, for a calculated total  $n_{MIC,g} \cong 237$  kmol, can be easily calculated as  $V = 6200 \text{ m}^3$  at a target design pressure of 2 bar. In case of utilization of a reacting solution to neutralize MIC, cautious reference is made to the following hydrolysis reaction and relevant data by Havens et al., (2012),



by means of a NaOH aqueous solution at 20% w/w.

According to Havens et al, (2012), the total reacting mass, including gaseous and liquid MIC, is calculated as  $m_{MIC} = 20,250 \text{ kg}$  with a corresponding mass of solution of  $m_{sol} = 16,000 \text{ kg}$ .

Taking into account heat exchanges, ambient temperature and solution specific heat, the final temperature can be calculated  $T_f \cong 304 \text{ K}$ . At last, the tank volume can be conservatively estimated as  $V = 18000 \text{ m}^3$  at a target design pressure of 2 bar. Having briefly examined the containment option, and based on the abstract model schematized in the already mentioned Fig. 1, we approached the short-cut design of the other risk mitigation measures, i.e.; by forced jet release, by a flaring system and by chemical reacting curtain, respectively in paragraph 2.1, 2.2 and 2.3.

## 2.1 Forced release dispersion into the atmosphere.

The design problem requires essentially determining stack diameter, emission height and location within the plant layout to obtain suitable atmospheric jet dispersion. We considered the approach by Palazzi et al.(2003), based on the laws of air entrainment and momentum conservation and directed to the selection of a conveniently high emission velocity to realize an efficient dilution of the release by enhanced air mixing. The most significant results of the model can be summarized as follows:

the mathematical description of the boundaries of the flammability area, obtained as the locus of the points  $L(x_L, z_L)$  on the jet axis where, varying wind speed, the release concentration reaches the lower flammability limit, C:

$$z_L = 3.8 [(\Delta^2 - x_L^2)/2x_L] \ln[(\Delta + x_L)/(\Delta - x_L)] \quad (1)$$

the behaviour of the gravity centre G ( $x_G, z_G$ ) of the jet:

$$x_G = \alpha/k[\text{Ch}(k z_G / \alpha) - 1] \quad (2)$$

where  $k = 1.2$  is an entrainment constant and  $\alpha$  is the parameter defined by Hoehne (1970) as follows:

$$\alpha = d_0 (\rho_0/\rho_a)^{1/2} (v_0/u). \quad (3)$$

The limiting value of the emission velocity corresponds to the sonic speed at the outlet conditions:

$$v_s = (\gamma_0 R T_0 / M_0)^{1/2} = 299 \text{ m s}^{-1} \quad (4)$$

In case of hydrocarbon releases, the design criteria for safety valves suggested by API (1976) give values of  $v_0$  in the range 100-150  $m s^{-1}$ , then comparable with a half of  $v_s$ , that is:

$$v_0 \cong 0.5 v_s \cong 150 m s^{-1} \quad (5)$$

Assuming that the release be pure MIC at the gaseous phase ( $y=1$ ), the corresponding exit diameter is  $d_0 = 0.17 m$ .

Taking into account the lower flammable limit LFL of the released compound  $C = 0.053 (v/v)$ , the safety distance from possible ignition sources, defined as  $x_i$ , can be related to mass flow rate and velocity of emission, as follows:

$$\chi_i \cong 45 / (C M_0 v_0^{1/2}) = 1.2 m kg^{-0.5} s^{0.5} \quad (6)$$

$$\Delta = \chi_i m_0^{1/2} \cong 2.7 m \quad (7)$$

The scaling factor  $\Delta$  represents the maximum horizontal extent of flammability region and linearly increases with the vent diameter, as follows:

$$\Delta = 1.5 (1/C) (M_a/M_0) (\rho_0/\rho_a)^{1/2} d_0 \quad (8)$$

where  $M_a \cong 29 g mol^{-1}$  is the mean molecular weight of the air and  $\rho_a \cong 1.2 kg m^{-3}$  its density at SATP. According to Eq. (8), it results that, owing to the jet phase dispersion, the extension of the flammability area depends much more on the vent diameter than on the release characteristics. At last, the safe distance to avoid the cloud ignition can be expressed by assuming the most conservative safety coefficient,  $s_i$ , (being:  $1.2 \leq s_i \leq 1.4$ ):

$$x_i = \Delta s_i \cong 3.8 m$$

Dealing with the design problem, the emission height must be calculated under the constraint of ground concentration lower than the admissible level for any meteorological condition. The worst immission condition can be connected to very unstable conditions (e.g. B2 category according to Brookhaven National Laboratory B.N.L.).

In order to obtain the value of the ground concentration reference is made to:

$$c_{max} = 2 \cdot 10^6 \psi_i m_0 / [\pi e u (h + \Delta h)^2] \quad (9)$$

where  $\Delta h$  represents the rise of the plume centerline above the vent:

$$\Delta h = A/u \quad (10)$$

$$A = 1.5 d_0 v_0 (\rho_0/\rho_a)^{1/2} \cong 43 m^2 s^{-1} \quad (11)$$

and  $\psi_i$ ,  $b$ ,  $c$  are parameters depending on atmospheric stability as indicated in Table 4 (Palazzi et al., 2003).

Taking into account Eqs. (9) and (10), from Eq. (7) one can write:

$$c_{max} \cong 5.9 \cdot 10^5 / (h + 21.5)^2 \quad (12)$$

As anticipated, the main requirement for safely discharging is that independently of the atmospheric conditions, the ground level concentration of the toxic material,  $c_{max}$ , be contained into an admissible level,  $c_{adm}$ , so that  $c_{max} \leq c_{adm}$ . Considering the current value of MIC IDLH set by the National Institute for Occupational Safety and Health (NIOSH) ( $c_{adm} = 6.9 \text{ mg m}^{-3}$ ) the resulting limiting height can be calculated as:

$$h_t \cong 271 \text{ m}$$

$$x_{max} = [(h + \Delta h) / (2^{1/2} b)]^{1/c} \cong 1900 \text{ m} \quad (13)$$

Assuming as reference value the IDLH of MIC stated in 1984 ( $c_{adm} = 46 \text{ mg m}^{-3}$ ), one can obtain the corresponding values:

$$h_t \cong 107 \text{ m}$$

$$x_{max} = 769 \text{ m}$$

It must be remarked that according to the design model, the stringent value of the exit velocity,  $v_0$ , ensures a notable and effective dilution effect due to air entrainment and mixing during the jet phase of the release dispersion into the atmosphere (Palazzi et al., 2003). On this basis, the short-cut model here applied did not consider slumping effects of the release due to its density as, by design hypotheses, the release dispersion is dominated by the atmospheric conditions in the plume phase following the sharp initial dilution.

## 2.2 Elevated flare system

These systems are considered as last line of defence and are amply used in process industries like petrochemical, oil and gas industries etc. Flares play an essential role in disposing waste gases in safe and environmentally acceptable way (Schwartz et al., 2006), provided that they are properly designed, operated and maintained. Usually, a flare system consists of gas collection header, knockout drum, proprietary seal, water seal, purge gas supply and a flare stack with gas pilot. The correct design depends upon flow rate, gas composition, gas temperature, gas pressure, utility costs, safety requirements, environmental requirements and social requirements (Ling & Kolmetz, 2007). The Bhopal flare system was originally designed to burn out carbon monoxide excess and only 25% of MIC emission rate, corresponding to a value of  $5 \text{ kg s}^{-1}$  (Chouhan, 2005). The correct design of the flare system should consider the right flow-rate and the gas collection header from the storage tanks to the system. Referring to the design problem, it is essentially a matter of comparing some admissible levels of concentrations and thermal exposures, often fixed by law, with the theoretical ones coming from the emergency release behavior, so that the aforesaid concentrations and exposures be contained into acceptable levels. In locating the flare, the exposure of people and

structures to heat radiation, as well as the toxic effects of emitted pollutants and combustion products must be considered.

According to the unified approach (Palazzi et al., 2003), the emission height can be calculated as follows:

$$h_s = (\psi_s - \psi_i) m^{1/2} \quad (14)$$

where:

$$\psi_s = (q_m / Q_\infty)^{1/2} \quad (15)$$

$$\psi_i = (n/2) \chi_i \quad (16)$$

$$\text{Being } q_m = \varepsilon Q_c / 4\pi \quad (17)$$

On the basis of Bhopal plant data and considering the intensity of the thermal radiation tolerable for any time  $Q_\infty = 1.6 \text{ kW m}^{-2}$ , following results were obtained:

$$q_m = 315 \text{ kJ kg}^{-1} \quad \psi_s = 13.7 \text{ m kg}^{-0.5} \text{ s}^{0.5} \quad \psi_i = 0.3 \text{ m kg}^{-0.5} \text{ s}^{0.5} \quad h_s \cong 31 \text{ m}$$

It is worth noting that the calculated flare height is practically the same adopted for Bhopal original design ( $h = 33 \text{ m}$ ), even if the flare design was performed by Union Carbide focusing on different technical targets, so that, even if in order, it could have only handled a quarter of the gas that leaked in 1984.

### 2.3 Absorption by chemical reaction

The absorption tower in Bhopal was designed to neutralize a MIC flow rate of  $0.24 \text{ kg s}^{-1}$  at a pressure of 15 psig (Chouhan, 2005). However, in order to be able to deal with the given release, the target design flow rate should be higher by 21 times and proper modification should adequately consider as well the elevated working pressure (180 psig).

Water spray curtain represents a useful technique to overcome industrial hazards as it is very simple and efficient technique and it becomes an attractive tool due to its adaptability to different types of hazards, like gas dispersion, absorption, and fire-attenuation. Water spray curtain effectiveness in controlling the hazardous cloud spreading and its environmental and toxic effects depends upon internal and external parameters of the system. Internal parameters include nozzle type and size, direction, water droplet distribution, width and height, water pressure etc., while external parameters include vapour cloud features, gas properties, wind speed, atmospheric stability etc. (Mannan et al., 2008). The correct selection and design of a water curtain system can be based on a fundamental approach based on the global amount of air entrained by the curtain, where the correlations among the main parameters are expressed by means of theoretical formulae, suitable in scaling problems. The design problem requires selecting the proper absorbing solution and its

concentration, curtain height, length, nozzle spacing etc. on the basis of the different constraints (connected to fluid-dynamics, stoichiometry, health, environment etc.). Referring to the current IDLH limit of 3 ppm (National Institute for Occupational Safety and Health) and considering no recycle of the released compound into the atmosphere, following the approach of Palazzi et al. (2007, 2009), the downwind molar fraction can be expressed as:

$$\omega_{dMIC} = \frac{2\dot{m}_r}{a_c(1-u^*) + a_j[1 + tg\theta_c]} \frac{1 - X_c}{1 + \alpha_c X_c} \quad (18)$$

where:

$\dot{m}_r = 2.25 \text{ kg s}^{-1}$  considering that the spray barriers operates only on gaseous MIC, after flash.

$a_c = 0.5 \text{ A L } \rho_a v_j h = 1,282 \text{ kg s}^{-1}$

$u^* = 0.4$

$a_j = s v_0 / v_j = 125 \text{ kg s}^{-1}$

$$\alpha_c = \frac{1 - \tan \theta_c}{1 + \tan \theta_c} \quad (19)$$

$\tan \theta_c = 0.68$

$$X_c = 1 - \exp\left(-6 \frac{h_c}{\delta} \frac{M_a}{\rho_s v_0} k_G P\right) \quad (20)$$

From Eq. (20) a downwind concentration lower than IDLH concentration of MIC can be calculated, provided that, contrarily to Bhopal situation, the water spray system be designed to absorb relief valve discharge at a high level. In fact, the water pressure of Bhopal deluge system was too weak for the guns to spray high enough to reach the gas and significantly reduce its concentration. To this end, we can notice that the short-cut design refers to a spray curtain having a length  $L = 180 \text{ m}$  a height  $h = 7 \text{ m}$  and a solution flow rate  $s = 40 \text{ kg s}^{-1}$  with a NaOH concentration corresponding to 10% (w/w), operating for 100 min. The results are clearly affected by uncertainties connected to the validity of the adopted hypotheses and of the empirical coefficients the model is based upon.

## 2.4 Considerations on Bhopal critical safety equipment

On the basis of a short-cut analysis presented in the previous paragraphs, the conventional design solution involving “bolt on” safety features evidences the need of multiple layers of protection and connected high overall capital and operating costs. However, the omissions of the prevention measure contributing to the final breakdown, magnitude of the release and fatalities are connected rather than to inadequate undersized design of the single safety equipment, to their unavailability

and to the absence of co-ordination in their use. In addition to the basic error of taking protective equipment out of commission, determining factors are: the absence of proper response procedures on intervention time and actions to be taken in case of deviation of operative parameters exceeding critical values; inadequate planning and training in loss prevention of the personnel and low attention to identification of process anomalies and consequent corrective actions to be implemented. In other words, recalling Kletz, Bhopal shows how accident investigation is like peeling an onion with subsequent layers of causes and recommendations, beneath one layer of causes and recommendations there are other layers: outer layers are the immediate technical recommendations, while the inner ones deal with improvement to the management system (Fabiano & Currò, 2012). Considering the severity of possible MIC runaway reaction and excluding the design of a single equipment for the technical and economic implications previously outlined, a correct and continuous management effort should have also been devoted to ensure the implementation of procedures suitable to stop temperature increase inside the tank, in case of contamination. In the next section, we offer an emergency time evaluation based on experimental findings to evidence that, irrespectively of the incident technical causes, the severity could have been by far lower by developing an internal and external emergency plan including warning signals and consequent appropriate measures.

### **3. A safety approach to intervention time evaluation**

As amply recognized, plant workers and managers had very less hazard potential information of Bhopal plant and this lack of awareness played a very critical role in causing the incident (Shrivastava, 1992). In case of high temperature and pressure alarm on the MIC tank, the correct emergency procedure should firstly foresee stopping and removing the cause of contamination and secondly minimizing the development of the complex series of runaway reactions. The reference scenario and the theoretical approach here developed are mainly based on event descriptions and thermodynamic parameters available in the scientific literature (Joseph, 2005; Ball, 2011, Castro et al., 1985), or from standard tables.

The first step consists in the selection of the reference reaction scheme and in the evaluation of the pertinent energetic and mass terms. According to sparse scientific literature, isocyanates by hydrolysis react exothermically to the corresponding amine and carbon dioxide. The most relevant subsequent reaction to be considered is the condensation of MIC: according to chemical analysis of the residue in the MIC tank 610 at the Union carbide plant, the main product was the cyclic trimer (D'Silva et al., 1986). On these bases, we considered a simplified two-step reaction sequence. The

corresponding reaction molar enthalpies were calculated according to the functional group method (Perry & Green, 2008), as detailed in the following.



$$\Delta\tilde{H}_r = \sum \nu_i \Delta\tilde{H}_{f_i} = -2.2970 \cdot 10^4 - 3.937 \cdot 10^5 + 9.002 \cdot 10^4 + 2.860 \cdot 10^5 = -4.065 \cdot 10^4 \text{ J mol}^{-1}$$



$$\Delta\tilde{H}_f = \sum \nu_i \Delta\tilde{H}_{f_i} = -4.9245 \cdot 10^5 - 3 \cdot (-9.002 \cdot 10^4) = -2.224 \cdot 10^5 \text{ J mol}^{-1}$$

According to Joseph et al., (2005), we considered the total water mass entering the tank equal to 908 kg with a contaminant content of 1% w/w, mainly consisting of Fe compounds. In fact, according to Union Carbide data reported by Chouhan, (2005), in the absence of a catalyzer, reaction 2 according to Eq. (22) is rather slow with time to runaway ranging from 23 h at  $T = 293 \text{ K}$ , to 1 h in presence of  $\text{FeCl}_3$  at a concentration of 1-3 % and 10 min in presence of  $\text{NaOCH}_3$  at a concentration of 1-3 %. Experiments reported in literature indicate that the condensation started above the normal boiling point of MIC ( $T_{\text{eb}} = 312.5 \text{ K}$ ), so we assumed that between 22:00 and 23:00 the relevant reaction was only the hydrolysis and that the condensation be dominating only after 23:00. Table 3 summarizes the MIC molar fraction values and the pressure and temperature evolution calculated starting from available data. We assumed that water flow into the tank started at 22:00 at  $p = 101,300 \text{ Pa}$  and  $T_0 = 288 \text{ K}$ , while, being the whole temperature profile unknown due to instrumentation deficiencies and failures, following assumptions are considered. During the time span 22:00-23:00 as hydrolysis reaction proceeds, the temperature increases rather slowly due to the thermal capacity of the liquid phase. It must be remarked that in the considered time span, MIC molar fraction the gaseous phase,  $y$ , does not increase linearly with its partial pressure due to the formation of carbon dioxide and methyl amine and to their transport at the gaseous phase, as the hydrolysis reaction proceeds. Furthermore, the different compounds at the gaseous phase leave the tank as the pressure increases. As working hypothesis, we assumed that MIC molar fraction in the gaseous phase increased linearly as time went on, until reaching a critical value at  $T = 305 \text{ K}$ , i.e. at an average temperature between the underestimating value indicated by Ball (2011) and the overestimating MIC boiling point. At this point, according to the classical ignition theory the imbalance of the heat generation by reaction and heat loss yielded the onset of thermal runaway. It should be noticed that according to the assumption of Ball (2011), thermal runaway occurred already at  $T = 292 \text{ K}$ , due to the onset of a hard thermal oscillation at a subcritical Hopf bifurcation. However, the analysis here performed is based on water flow rates and time evolution provided by Union Carbide, so that taking into account the liquid heat capacity, the limiting reactant entering

Tank 610 at the calculated flow rate seems not able to induce the thermal runaway. Some minutes after 23:00 water flow rate ends, as the tank internal pressure increases, and the gaseous release into the atmosphere takes place with increasing flow rates, so that the concentrations of carbon dioxide and methylamine tend to zero. We assumed that after 00:15 the release composition be pure MIC ( $y=1$ ). As second step, we calculated on the basis of the above mentioned assumptions and available experimental points the approximated pressure and temperature profiles. As shown in Fig. 2, we started from the pressure value detected inside the tank (Chouhan, 2005) and by applying Raoult law we derived the component partial pressure and subsequently the corresponding temperature.

In the third step, we optimized an intervention strategy focused on limiting the temperature inside the tank below a safety threshold, starting from a quantitative evaluation of the reaction enthalpy of MIC hydrolysis. To this purpose, we started from the instantaneous water molar balance, that, according to Ball (2011), can be written as:

$$\frac{dn_w}{dt} = \dot{n}_{wg} + \dot{n}_{wi} \quad (23)$$

where:

$$\dot{n}_{wg} = -kcV_{react} = -kn_w \quad (24)$$

$$k = k_{\infty} \exp\left(\frac{-E_a}{RT}\right) = \text{kinetic constant, s}^{-1}$$

By assuming hydrolysis duration of nearly one hour, the mean reaction rate is

$$\dot{n}_{wg,m} \cong -14 \text{ mol} \cdot \text{s}^{-1}$$

Since  $288 \leq T \leq 305$  and correspondingly  $9.6 \leq k \leq 0.33$ , from Eq. (24), the resulting order of magnitude of  $n_w$  is 1 mol. Being the value of the average water in-flow rate nearly 10 mol, the accumulation term in Eq. (23) is negligible, so that one can write:

$$-\dot{n}_{wg} \cong \dot{n}_{wi} \quad (25)$$

Summarizing, under the adopted assumptions, water reacts quasi-instantaneously as it enters into the storage tank, except during two very short transient periods: at the beginning and at the end, respectively due to the accumulation and to the consumption of nearly one mol. In other words, it follows that the instantaneous reaction rate corresponds to the molar in-flow rate of water, representing the limiting reagent.

Assuming the following expression of molar flow rates:

$$\dot{n} = \beta_l (\Delta p)^{1/2} \quad (26)$$

water in-flow rate can be written as:

$$\dot{n}_{wi} = \beta_l (p_e - p_i)^{1/2} \quad (27)$$

where:

$p_e$  water pressure outside the storage tank [101,300 - 199,300], Pa

$p_i = p_i(t)$  water pressure inside the storage tank, Pa

$\beta_l$  coefficient depending on fluid and pipe characteristics,  $\text{mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$

Eq. (27) shows that the water flow rate decreases to zero as  $p_i$  increases and MIC hydrolysis takes place. The value of  $p_e$  providing the best-fit of the considered energetic balance is the maximum possible (i.e. 199,300 Pa), considering that according to Union Carbide design data an overpressure value of 98,000 Pa avoids any material incoming.

By integrating Eq. (27), we obtained:

$$n_{wi} = \int_0^{t_{\text{end}}} \beta_l (p_e - p_i)^{1/2} dt \quad (28)$$

where  $t_{\text{end}} \cong 4,800$  s, is calculated by graphical method at the conditions  $p_e = 199,300$  Pa.

Under these assumptions, the calculated value for  $\beta_l$  is  $0.048 \text{ mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$ , and by Eq. (28) we obtained the values of the water flow rate entering the tank at  $t = 3600$  s and of the total entered water, respectively as:  $\dot{n}_{wi,3600} \cong 8.2 \text{ mol} \cdot \text{s}^{-1}$  and  $n_{wi,3600} \cong 4.4 \cdot 10^4 \text{ mol}$ .

Analogously, the rate of gaseous release was written as:

$$\dot{n}_o = \beta_g (p - p_a)^{1/2} \quad (29)$$

being:

$p_a$  atmospheric pressure, 101,300 Pa

$\beta_g$  coefficient depending on fluid and pipe characteristics,  $\text{mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$

Under the previously defined conditions, we conservatively assumed  $\beta_g \cong 0.01 \text{ mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$ .

At  $t = 3600$  s, the following values of the gaseous release rate are obtained:

$$n_{o,3600} \cong 5.5 \cdot 10^3 \text{ mol}; \quad \dot{n}_{o,3600} \cong 2.6 \text{ mol} \cdot \text{s}^{-1}; \quad n_{o,MIC,3600} \cong 2.3 \cdot 10^3 \text{ mol} \text{ and } \dot{n}_{o,MIC,3600} \cong 1.2 \text{ mol} \cdot \text{s}^{-1}.$$

The energy balance referred to the first hour of the event (local time 22:00 – 23:00), can be written as follows:

$$\Delta H_L + \Delta H_o + \Delta H_{hyd} + \Delta H_{tri} = Q \quad (30)$$

where:

$$\Delta H_L = m_L \hat{c}_{pL} (T_{3600} - T_0) \cong 1.5 \cdot 10^9 \text{ J} \quad \text{enthalpy variation of the liquid phase}$$

$$\Delta H_o = n_{o,MIC,3600} \Delta \tilde{H}_v \cong 7.1 \cdot 10^7 \text{ J} \quad \text{enthalpy variation of the gas phase}$$

$$\Delta H_{hyd} = n_{wi,3600} \Delta \tilde{H}_{hyd} \cong -1.8 \cdot 10^9 \text{ J} \quad \text{enthalpy of the hydrolysis reaction}$$

$$Q = \dot{Q} \tau = -KS \Delta T_m \tau \cong -3.1 \cdot 10^8 \text{ J} \quad \text{heat exchange between tank and atmosphere.}$$

We omitted the terms that are two or three orders of magnitude lower, i.e., the sensible heat of inflowing water and outflowing gases.

From Eq. (30) we calculated the value of the global trimerization enthalpy in the first hour of the event:  $\Delta H_{tri} \cong -0.8 \cdot 10^8 \text{ J}$ . Comparing the attained value with the molar enthalpy of the overall reaction according to Eq. (22),  $\Delta \tilde{H}_f \cong -2.224 \cdot 10^5 \text{ J mol}^{-1}$ , it follows that in the first hour the mole percentage of trimerization gas is negligible ( $< 0.1\%$ ). Additionally, we pointed out that the value of the global trimerization enthalpy in the first hour of the event is lower by an order of magnitude when compared to the hydrolysis reaction value, in accordance with the indications available in the literature (D'Silva et al., 1986). The evaluation of emergency time is faced in the following chapter, starting from the calculation of relevant enthalpy contributions, based on energy balance. In fact, understanding heat balance and correctly assessing thermal phenomena are essential when considering thermal safety and this applies to the industrial scale for both storage units (e.g. Fabiano et al., 2013) and reactors (e.g. Fabiano et al., 2015).

The instantaneous energy balance at  $t = 3600 \text{ s}$  can be written as:

$$\Delta \dot{H}_L + \Delta \dot{H}_o + \Delta \dot{H}_{hyd} + \Delta \dot{H}_{tri} = \dot{Q} \quad (31)$$

being:

$$\Delta \dot{H}_L = m_L \hat{c}_{pL} \left( \frac{dT}{dt} \right) \cong 4.4 \cdot 10^5 \text{ W}$$

$$\Delta \dot{H}_o = \dot{n}_{o,MIC,3600} \Delta \tilde{H}_v \cong 3.7 \cdot 10^4 \text{ W}$$

$$\Delta \dot{H}_{hyd} = \dot{n}_{w,3600} \Delta \tilde{H}_{hyd} \cong 3.4 \cdot 10^5 \text{ W}$$

$$\dot{Q} = -KS \Delta T_{3600} \cong -1.7 \cdot 10^5 \text{ W}$$

At last, from the energy balance described by Eq. (31), we obtained the instantaneous value of trimerization reaction just after one hour:

$$\Delta \dot{H}_{tri} \cong -3.1 \cdot 10^5 \text{ W}$$

#### 4. Discussion

Thinking highly of the role played by human factor, in this chapter, by applying a lessons learned approach, we outline the countermeasures and corrective actions that could have been implemented

to mitigate Bhopal event. The immediate cause elimination avoiding hazard is obviously the water inflow interruption. However, the effectiveness of this emergency response requires the evaluation of the intervention time suitable to induce a thermal excursion decay. It is clear that the earlier a disturbance is detected and recognized as a potentially hazardous precursor, the more effective possible recovery may be realized (De Rademaeker et al., 2014). Given the peculiar hazard of a thermo-reactive storage, additional measures can be implemented in connection with possible delay of water flow interruption. For the sake of simplicity, we discuss this point making reference to the classical ignition of a thermo-reactive system occurring at a steady-state turning point.

To illustrate the key effect of intervention time we started from the instantaneous heat balance, referred at a generic time  $t$ , in the form described by eq. (31). It can be inferred the determining role of the trimerization reaction enthalpy  $\Delta\dot{H}_{tri}$ : as long as its contribution is negligible ( $\Delta\dot{H}_{tri} \cong 0$ ) water stopping allows reaching a safe condition ( $dT/dt < 0$ ). In presence of the trimerization reaction, the different conditions depicted in Fig. 3 can be sorted. At time  $t_1$ ,  $\Delta\dot{H}_L > -\Delta\dot{H}_{hyd}$  so that MIC polymerization reaction mainly contributes to the liquid heating and water inflow interruption is not effective in stopping the runaway behavior; as an indication in Fig. 3, reference is made to  $t_1 = 3600$  s, but, more generally, this condition applies at any time in the interval  $[t_2, 4800$  s]. At time  $t_2$ , the system will be in a pseudo steady-state condition where the second reaction instantaneously provides to the system all the heat power exchanged with the environment, as the reactant depletion (MIC) is rather low and the atmospheric emission has a long duration. Time  $t_3$  represents the critical intervention time that based on actual incident data corresponds to the condition:

$$-\Delta\dot{H}_{hyd}(t_3) = \Delta\dot{H}_L(3600)$$

so that just water flow interruption could theoretically be able to stop runaway behavior.

Given the harmful situation connected to MIC release under runaway conditions, a convenient safety margin must be considered, by introducing a proper safety coefficient  $\eta$ :

$$-\Delta\dot{H}_{hyd}(t_3) = \eta \Delta\dot{H}_L(3600)$$

In this case, the emergency intervention is effective in limiting the release environmental impact by a rather fast reduction of the system temperature. As an illustrative example, considering a safety coefficient  $\eta = 1.2$ , intervention should have been taken nearly at local time 22:50, when the resulting pressure was  $p \cong 154,000$  Pa.

Even if, on the basis of the presented simplified approach, a timely water flow interruption seems capable of avoiding runaway behaviour, additional measures should have considered the utilization

of a refrigeration system (that would have been in action to maintain MIC storage temperature at 277.5 K advised by operating manual), so as to enhance tank fluid refrigeration and consequently reduce emission flow rate and total duration, even under the hypothesis of simple atmospheric dispersion. Additionally, we remarked that a technical measure to be implemented in view of a possible delay in performing the main safety intervention, could consider a further refrigeration effect by means of the extraction of a convenient gaseous stream, possibly utilizing a nitrogen flow. For an effective refrigeration, the overall gaseous emission rate resulting as sum of the release mass flow rate,  $\dot{m}_r$ , and the additional air/nitrogen flow rate,  $\dot{m}_a$ , was calculated as nearly 1 kg s<sup>-1</sup>. This is explained as follows, referring to the intervention time corresponding to the pressure  $p=170,000$  Pa or, in other words, to the time  $t=3600$  s (local time 23:00).

In analogy with the previous calculations, we evaluated the enthalpy flow:

$$\Delta\dot{H}_{extr} = \eta (\Delta\dot{H}_{L,3600} + \Delta\dot{H}_{hyd,3600}) \cong 1.2 \cdot 10^5 W$$

from which, being:

$$\Delta\dot{H}_{extr} = \dot{n}_{extr} y \Delta\tilde{H}_v$$

it resulted  $\dot{n}_{extr}=8.4$  mol s<sup>-1</sup>, corresponding to a total molar flow rate leaving the tank of nearly 11 mol s<sup>-1</sup>. In case of air dilution, in order to attain the calculated global mass flow rate  $\dot{m}=1$  kg s<sup>-1</sup>, the additional air flow can be estimated as  $\dot{m}_a=0.485$  kg s<sup>-1</sup>, or else  $\dot{n}_a \cong 17$  mol s<sup>-1</sup>. Again, as previously outlined, a suitable forced dispersion system should ensure environmental protection also in case of safety mitigation systems unavailability. Making reference to the same approach (Palazzi et al., 2002) and to MIC IDLH = 20 ppm envisaged by legislation in 1984, once fixed an exit velocity  $v_0=150$  ms<sup>-1</sup>, so as to enhance jet phase, dilution by air entrainment and effective emission height, the corresponding vent diameter could be calculated as  $d_0=0.058$  m, at a geometrical height of 18 m. Even if MIC is a dense gas, as discussed by Sing and Gosh (1987), under the considered assumptions and to the purpose of this paper, the behavior can be considered as a passive plume, in view of substantial entrainment, initial dilution in the correctly designed jet phase, air mixing and heat generation. As previously detailed by Singh and Gosh (1985), Union Carbide gas plant was the least affected and first touch down occurred at about 500 m from the stack, so that MIC could not have slumped as a totally heavy (Sharan and Gopalakrishnan, 1997). Additionally, Sharan et al., (1995) pointed out that the plume in question can be considered a borderline case between one having a density effect and the one which is passive. It must be remarked that Havens (2012) calculated a 40 ppm (IDLH) concentration contour at the ground at about 410 m downwind the release point, considering the existing plant layout (no engineered “jet

vent” design) under the assumptions of aerosol presence. Other potential sources of uncertainty are related to possible MIC chemical reaction in atmosphere and dry deposition (Sing and Gosh,1987) and to eventual condensation of the vapors on the nuclei of suspended particulate matters that characterized the urban area of Bhopal (Sharan et al., 1994).

As argued by Kletz (1990), even if the refrigeration, scrubbing and flare systems were not properly designed, if they had been in full working order they would certainly have reduced the size of the discharge and delayed its start. Moreover, if the vessel had burst, the loss of life might have been lower, as there would have been less dispersion of the vapour. Starting from these observations, as a concluding remark, we carried out an approximate quantitative evaluation on the results of the implementation of a better emergency management in Bhopal, by assuming that the technical procedure previously discussed be enforced at local time 23:00, utilizing only actual Bhopal protective equipment. Clearly, operating procedures and training in facing abnormal situations are determining issues in preventing high profile consequences and this is particularly true in cases where formalized process safety management principles are not applied and reliable safeguards are not in place (Bird, 1985). Assuming that a forced extraction with air from Tank 610 be utilized, by means of the existing vent line ( $d_0=0.2$  m), according to the presented procedure, the corresponding exit velocity would have been  $v_0 \cong 13 \text{ ms}^{-1}$  with a resulting maximum concentration under the hypothesis of Gaussian plume below IDLH (20 ppm). In case of forced extraction of the vapour phase from Tank 610, without any diluting agent (air or nitrogen) at the previously calculated total flow rate of  $1 \text{ kg s}^{-1}$ , the resulting maximum concentration under the hypothesis of Gaussian plume performed in analogy of the short-cut method detailed in Palazzi et al., (2014), can be calculated as slightly higher than IDLH and equal to nearly 23 ppm. We must underline that, given the purpose of this paper, the approach is based on simple gas dispersion after the jet phase, without accounting for density and possible condensation effects, so that spreading due to gravitational setting is not considered.

## 5. Conclusions

In the first part of this paper, we focused on calculating appropriate stack dimensions, flare systems and a water sprat curtain, based on actual information from the Bhopal incident. Subsequently, starting from empirical evidences, we developed a framework allowing to identify emergency actions and intervention time and demonstrate how the implementation of these safety measures when reaching a critical pressure of 10 psig in Tank 610, even under the condition of protective

equipment out of commission, would have surely mitigated such a high profile tragedy. To the purpose of this study, we adopted the Gaussian approach as a first approximation, to evidence how the severity of the accident is the result of a chain of events which could have been broken at many points, both from an organizational and a technical point of view. As concluding remarks, also on the basis of the results here presented, from one side Bhopal gas tragedy recalls us that accidents are not due to lack of knowledge, but by failure to use the knowledge we have (Kletz, 1990). Even if inherent safety is beyond the aim of this paper, this philosophy represents the only credible way to reduce the risk at acceptable levels (Edards, 2005), instead of costly “add on” reduction measures according to the conventional approach. From the other side, it evidences that Bhopal type accident could have happened in 1984 even in a developed country, as long the management gave only lip service to process and personnel safety and the governments did not ensure compliance with the regulations (Gupta, 2002).

## NOMENCLATURE

$a_c$	mass flow rate of air entrained into the curtain, $\text{kg}\cdot\text{s}^{-1}$
$a_i$	mass flow rate of air entrained by inertial effect at distance $z$ from the nozzles, $\text{kg}\cdot\text{s}^{-1}$
$A$	parameter defined by Eq. (7), $\text{m}^2\cdot\text{s}^{-1}$
$b$	parameter defined in Table 4, -
$c_{adm}$	admissible concentration, $\text{mg m}^{-3}$
$c_{max}$	maximum concentration, $\text{mg m}^{-3}$
$c_{LFL}$	lower flammability limit, v/v
$\hat{c}_{pL}$	specific heat capacity of liquid phase, $\text{J}\cdot\text{kg}\cdot\text{K}^{-1}$
$d_0$	vent diameter, m
$E_a$	activation energy, $\text{mol}\cdot\text{s}^{-1}$
$E_{ac}$	activation energy corresponding to maximal quantity of catalyst, $\text{mol}\cdot\text{s}^{-1}$
$h$	emission height, m
$\Delta h$	plume rise, m
$h_c$	curtain height, m
$\Delta\tilde{H}_{fi}$	standard enthalpy of formation of the $i$ -th component, $\text{J}\cdot\text{mol}^{-1}$
$h_s$	minimum emission height allowing to work everywhere and anytime near the flare, m
$h_t$	minimum emission height required to contain the ground level concentration of the release into admissible levels, m

$k$	kinetic constant, $s^{-1}$
$\Delta\dot{H}_{extr}$	instantaneous enthalpy due to forced extraction, $J \cdot s^{-1}$
$\Delta H_{hyd}$	hydrolysis reaction enthalpy, J
$\Delta\tilde{H}_{hyd}$	standard enthalpy of hydrolysis reaction, $J \cdot mol^{-1}$
$\Delta\dot{H}_{hyd}$	instantaneous hydrolysis enthalpy, $J \cdot s^{-1}$
$\Delta H_L$	liquid phase enthalpy, J
$\Delta\dot{H}_L$	instantaneous liquid phase enthalpy, $J \cdot s^{-1}$
$\Delta H_o$	gas phase enthalpy, J
$\Delta\dot{H}_o$	instantaneous gas phase enthalpy, $J \cdot s^{-1}$
$\Delta\tilde{H}_r$	standard enthalpy of reaction, $J \cdot mol^{-1}$
$\Delta H_{tri}$	trimerization enthalpy, J
$\Delta\dot{H}_{tri}$	instantaneous trimerization enthalpy, $J \cdot s^{-1}$
$\Delta\tilde{H}_v$	enthalpy of vaporization, $J \cdot mol^{-1}$
$K$	heat transfer coefficient, $J \cdot m^2 \cdot K^{-1} \cdot s^{-1}$
$k_G$	overall mass transfer coefficient in gas phase, $kmol \cdot m^{-2} \cdot s^{-1} \cdot atm^{-1}$
$L$	length of the curtain, m
$\dot{m}_a$	additional air/nitrogen flow rate, $kg \cdot s^{-1}$
$m_L$	mass of liquid phase, kg
$m_{MIC}$	MIC reacting mass, kg
$m_{sol}$	mass of solution to neutralize MIC, kg
$m_o$	release mass, kg
$\dot{m}_r$	release mass flow rate, $kg \cdot s^{-1}$
$M_o$	mean molecular weight of the release, $kg \cdot kmol^{-1}$
$M_{MIC}$	MIC molecular weight, $kg \cdot kmol^{-1}$
$\dot{n}_a$	additional air flow rate, $mol \cdot s^{-1}$

$n_{MIC}$	moles of MIC, mol
$n_o$	moles of gaseous release at instant $t$ , mol
$n_w$	moles of water in the storage tank at instant $t$ , mol
$n_{wi}$	moles of in-flow water at instant $t$ , mol
$\dot{n}_{extr}$	gaseous molar flow rate by forced extraction, $\text{mol}\cdot\text{s}^{-1}$
$\dot{n}_o$	gaseous release rate, $\text{mol}\cdot\text{s}^{-1}$
$\dot{n}_{wg}$	generation term, $\text{mol}\cdot\text{s}^{-1}$
$\dot{n}_{wg,m}$	mean reaction rate, $\text{mol}\cdot\text{s}^{-1}$
$\dot{n}_{wi}$	molar water in-flow rate, $\text{mol}\cdot\text{s}^{-1}$
$p$	pressure, Pa
$p_a$	atmospheric pressure, Pa
$p_e$	water pressure outside the storage tank, Pa
$p_i$	water pressure inside the storage tank, Pa
$Q$	heat exchange between tank and atmosphere, J
$Q_c$	heat of combustion for unit mass of the release, $\text{kJ}\cdot\text{kg}^{-1}$
$Q_\infty$	intensity of thermal radiation tolerable for any time, $\text{kW}\cdot\text{m}^{-2}$
$\dot{Q}$	heat exchange rate between tank and atmosphere, $\text{J}\cdot\text{s}^{-1}$
$R$	ideal gas constant, $\text{J kmol}^{-1}\cdot\text{K}^{-1}$
$S$	tank surface, $\text{m}^2$
$s$	mass flow rate of the sprays, $\text{kg}\cdot\text{s}^{-1}$
$s_i$	safety coefficient for cloud ignition, -
$t$	duration of the event, s
$T$	temperature, K
$T_{eb}$	boiling point, K
$T_f$	final temperature, K
$\Delta T_m$	mean variation of temperature, K
$T_0$	release temperature, K
$u$	wind velocity, $\text{m}\cdot\text{s}^{-1}$
$u^*$	non-dimensional wind velocity, ratio of wind velocity to inversion velocity, -
$u_{crit}$	critical wind velocity, $\text{m}\cdot\text{s}^{-1}$
$v_0$	emission velocity, $\text{m}\cdot\text{s}^{-1}$
$v_j$	liquid velocity in the barrier at the end of the jet phase, $\text{m}\cdot\text{s}^{-1}$

$v_0$	liquid velocity at the nozzle exit, $\text{m}\cdot\text{s}^{-1}$
$v_s$	theoretical velocity of emission, $\text{m}\cdot\text{s}^{-1}$
$V_{\text{reac}}$	reaction volume, $\text{m}^3$
$V$	volume of dumping tank, $\text{m}^3$
$x_i$	safe distance against the risk of ignition, m
$x_{\text{max}}$	downwind distance where the maximum ground level concentration occurs, m
$X_c$	intrinsic absorption efficiency, -
$y$	molar fraction, -

### Greek letters

$\alpha$	parameter defined by eq. ( 3) according to Hoehne (1970)
$\alpha_c$	curtain parameter defined by eq. (19)
$\beta_g$	coefficient depending on fluid (gas phase) and pipe characteristics, $\text{mol}\cdot\text{Pa}^{-1/2}\cdot\text{s}^{-1}$
$\beta_l$	coefficient depending on fluid (liquid phase) and pipe characteristics, $\text{mol}\cdot\text{Pa}^{-1/2}\cdot\text{s}^{-1}$
$\delta$	mean droplet diameter, m
$\Delta$	safety distance from ignition source, m
$\varepsilon$	flame emissivity
$\gamma_0$	coefficient of Poisson at outlet conditions, -
$\eta$	safety coefficient, -
$A$	entrainment constant, -
$\rho_a$	air density at SATP, $\text{kg}\cdot\text{m}^{-3}$
$\rho_0$	release density at SATP, $\text{kg}\cdot\text{m}^{-3}$
$\rho_s$	density of the sprayed solution, $\text{kg}\cdot\text{m}^{-3}$
$\tau$	overall duration of the considered event, s
$\theta$	tilt of the curtain, rad
$\theta_c$	critical tilt of the curtain, rad
$\nu_i$	stoichiometric coefficients, -
$\chi_i$	parameter defined by Eq. (2), $\text{m}\cdot\text{kg}^{-1/2}\cdot\text{s}^{1/2}$
$\chi_s$	parameter defined in Eq. (10), $\text{m}\cdot\text{kg}^{-1/2}\cdot\text{s}^{1/2}$
$\chi_t$	parameter defined by Eq. (4), $\text{m}\cdot\text{kg}^{-1/2}\cdot\text{s}^{1/2}$
$\omega_{\text{dMIC}}$	downwind MIC concentration, ppm (w/w)
$\psi_i$	parameter defined by Eq. (12), $\text{m}\cdot\text{kg}^{-1/2}\cdot\text{s}^{1/2}$

$\psi_s$  parameter defined by Eq. (11),  $m \cdot kg^{-1/2} \cdot s^{1/2}$

$\psi_t$  parameter defined in Table 4, -

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## Tables

Plant/safetyequipment	Main protection action	Additional action	Side effect
Closed tank	C (t)	-	-
Retention basin (liquid release)	C (p)	-	Release evaporation/boiling
Ground flare	A(p/t)	-	Combustion products pollution
Elevated flare	A(p/t)	D	Combustion products pollution
Liquid absorption			
• catch tank	C (t)	A(p/t)	-
• absorption tower and stack	A(p)	D	Formation of reaction products
• spray barrier	A(p)	C(p)	Formation of reaction products
Venting stack	D	-	-
Release into the atmosphere			
• (PSV/rupture disk)			
• process emission			
Refrigerant system	D <sup>1</sup>	-	Depending on refrigerant type and following action <sup>2</sup>

Table 1. Examples of technical safety barriers for emergency protection and mitigation following an accidental release into the atmosphere, at different phases (<sup>1</sup> refrigeration does not mitigate the release but can reduce the flow rate and consequently enhance atmospheric dispersion with lower immission concentrations; <sup>2</sup> possible interaction with the release; in case of following stack, the effective plume elevation reduces; in case of subsequent flare, nitrogen addition could cause flare extinction or interaction with the release, etc.).

Design parameter	Value	Reference
Tank volume	$V = 62.4 \text{ m}^3$	Chouhan
Tank filling ratio	$f = 0.5$	Union Carbide
MIC volume at the liquid phase inside the intermediate storage tank	$V_{\text{MIC,l}} = 31.2 \text{ m}^3$	Havens et al.
MIC density at the liquid phase	$\rho_{\text{MIC,l}} = 940 \text{ kg m}^{-3}$	Havens et al.
MIC mass	$m_{\text{MIC}} = 30.000 \text{ kg}$	
MIC moles	$n_{\text{MIC}} = 526 \text{ kmol}$	
Release rate	$\dot{m}_r = 5 \text{ kg s}^{-1}$	Havens et al.
Release pressure	$p_0 = 180 \text{ psig} = 1.242 \cdot 10^6 \text{ Pa}$	Havens et al.
Release temperature	$T_0 = 473 \text{ K}$	Havens et al.
Residual mass fraction after MIC flash at $p=1 \text{ atm}$ and $T_{\text{nb}}=312 \text{ K}$	$\phi_{\text{MIC,g}} = 0.45$	Havens et al.
MIC admissible concentration	$C_{\text{adm}} = \text{IDLH} = 20 \text{ ppm} = 46 \text{ mg m}^{-3}$ $= 3 \text{ ppm} = 6.9 \text{ mg m}^{-3}$	referred to the year 1984 current value

Table 2. Reference data for the design of protection and mitigation measures.

Local time	Time sequence [s]	Overpressure $\Delta p$		P [Pa]	MIC Molar fraction y	$p^0$ [Pa]	T [K]
		[psig]	[Pa]				
22:00	0	0	0	101,300	0.37	37,085	288
22:20	1,200	2	13,800	115,100	0.40	43,738	293
23:00	3,600	10	69,000	170,300	0.46	68,120	305
0:15	8,100	30	207,000	308,300	1	308,300	345
n.a.	n.a.	55	380,000	481,300	1	481,300	360
0:30	9,000	180	621,000	722,300	1	722,300	376

Table 3. Experimental and calculated values utilized in developing Bhopal evolution scenario.

Stability	a	b	c	$\psi = b/a$
very	0.215	0.215	0.91	1.00
unstable	0.137	0.125	0.86	0.91
neutral	0.070	0.048	0.76	0.69
stable	0.042	0.008	0.71	0.19

Table 4. Power law forms:  $\sigma_y = a x^c$  and  $\sigma_z = b x^c$  ( $\sigma$  and  $x$  in km), (from Palazzi et al., 2003).

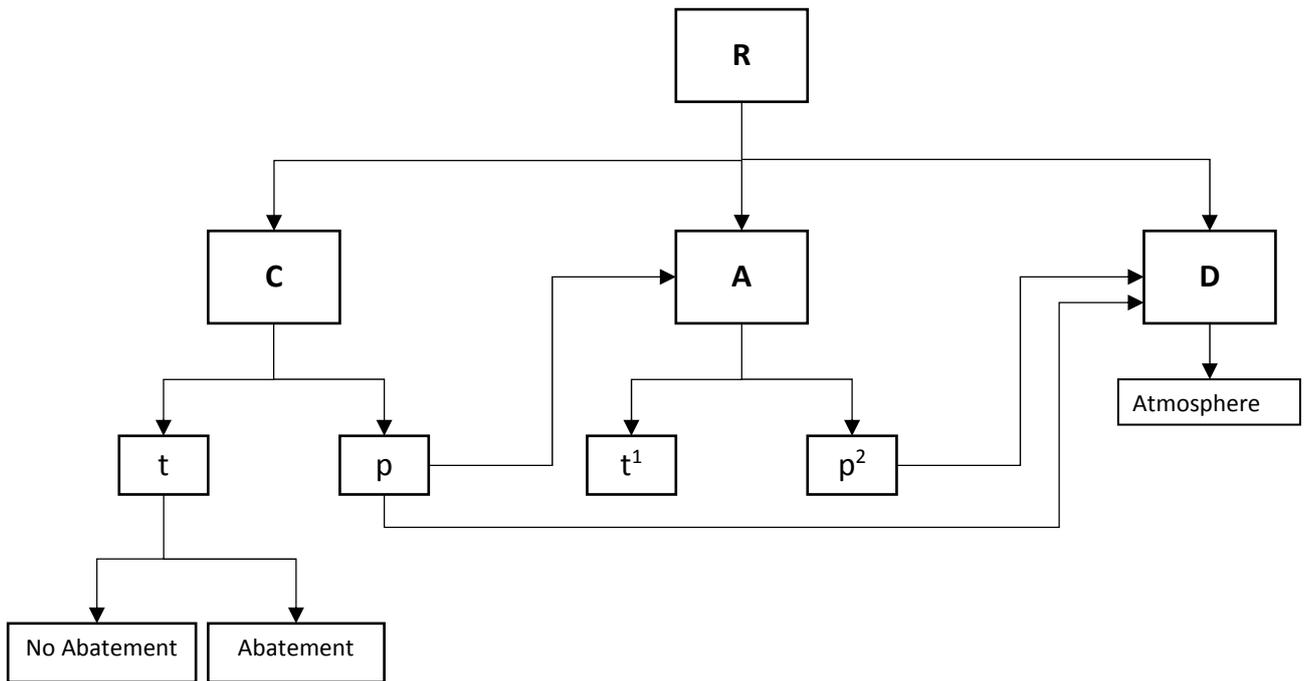


Figure 1. Engineered “add on” measures addressed to environmental protection and risk mitigation, considering gas/vapour releases into the atmosphere (R= Release; C= Containment; A= Abatement; D= Atmospheric dispersion; t= total; p= partial; <sup>1</sup> combustion; <sup>2</sup> gas/liquid absorption or chemical reaction).

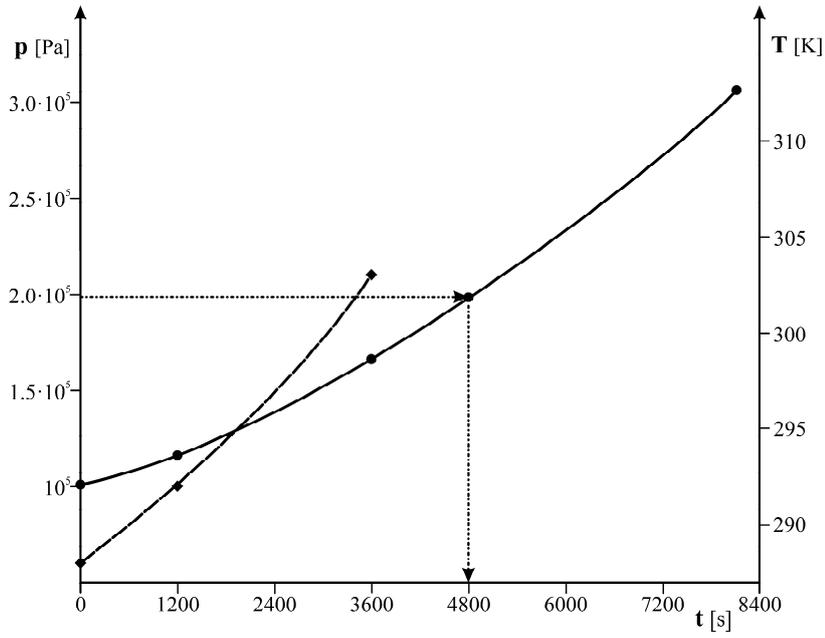


Figure 2. Temperature (- - -) and pressure (—) profiles assumptions on the basis of available experimental points.

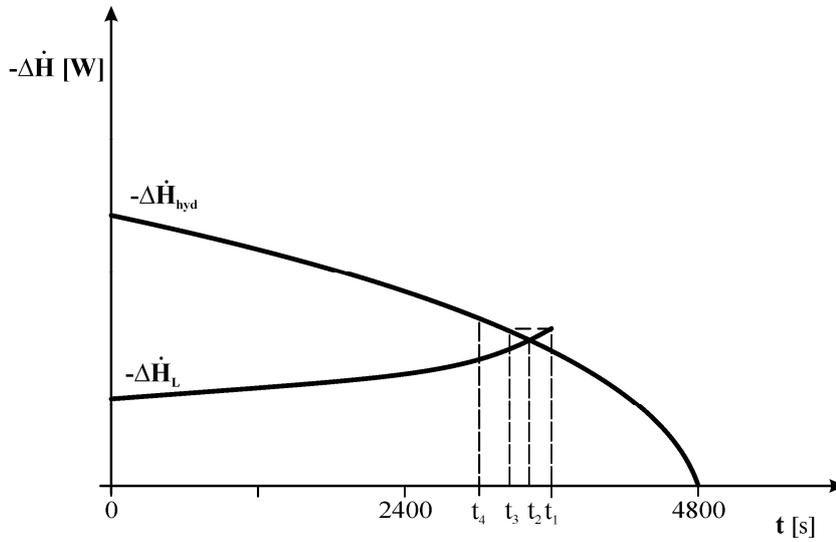


Figure 3. Evaluation of effective intervention time based on the instantaneous heat balance described by Eq. (31).