

A Study on the Determining Role of Timely Emergency Management Based on Bhopal Accident

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The years 2014 and 2016 mark the anniversaries of two notable process accidents: respectively thirty years from the unparalleled Bhopal tragedy and forty years from the Seveso accident. These events shaped developments in process safety worldwide, so that after them risk analysis and legislation got applied more generally focusing on prevention and control of major chemical incidents. Even if completely different in their evolution according to “black swan” scenarios, these events cause us to recall that a more positive stance can and should be taken to emergency response and to improve major hazard awareness. Starting from a systemic view of accident causation, this paper illustrates by a simplified quantitative approach the determining role of organizational deficiencies in the safety procedures for handling abnormal situations and emergencies.

1. Introduction

On December 2nd 1984, one of the world worst accident in the chemical industry occurred in Bhopal, India and even after 30 years, this tragedy is unparalleled in the history of chemical accidents. A massive release of approximately forty tons of Methyl Isocyanate (MIC) stored in a nearly full stainless steel tank in its liquid state was caused by a runaway reaction triggered by water entering the tank and leading to boiling and over pressurization of the tank. A valve designed to prevent tank failure correctly opened and discharged unreacted MIC vapour to the atmosphere. Following the release, maybe as many as 20,000 people died and many more faced long term morbidity with health effect on a half million people (Edwards, 2005). Bhopal is a well-known and thoroughly investigated accident: still many questions are open on the underlying causes and responsibility. Accident analysis by AcciMap can be helpful to define the conditions for safe operation and devise risk management strategies (Rasmussen, 1997), so as to identify factors sensitive to improvement rather than to responsibility allocation. The interacting levels in a top-down causal sequence start from “External” followed by “Organizational factors”, then “Physical processes and actor activities” and “Equipment and surroundings”, at last leading to the bottom level representing the topography of the accident and its “Outcomes”. A simplified analysis is provided in Figure 1, highlighting investigated causal factors related to emergency management, in shaded format. The attitude towards prevention was rather limited in Bhopal: measures not properly implemented in the plant include hazard awareness and evaluation, plant design and structure, processes and machineries, piping material selection, personal training and information, emergency planning & response. Personnel reductions in production and maintenance departments due to financial loss for several years played a key role in the accident. This cutback also affected the training schedules for MIC operations by plant personnel, taking it to a limited number and creating a lack of safety awareness (Shrivastava, 1992). Implementation of the following non-standard procedures, due to poor safety culture, introduced new hazards, while managing to reduce personal exposure hazard after several fugitive MIC leaks from centrifugal pumps: 1. export of MIC into the derivative unit by a N₂ flow excluding the transfer pump; 2. shut-down of MIC refrigeration system, thus raising the MIC storage temperature. 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, defined as “a mind boggling sequence of failures” (e.g. design of MIC tank relief valve, scrubber/ water barrier design and maintenance, etc.).

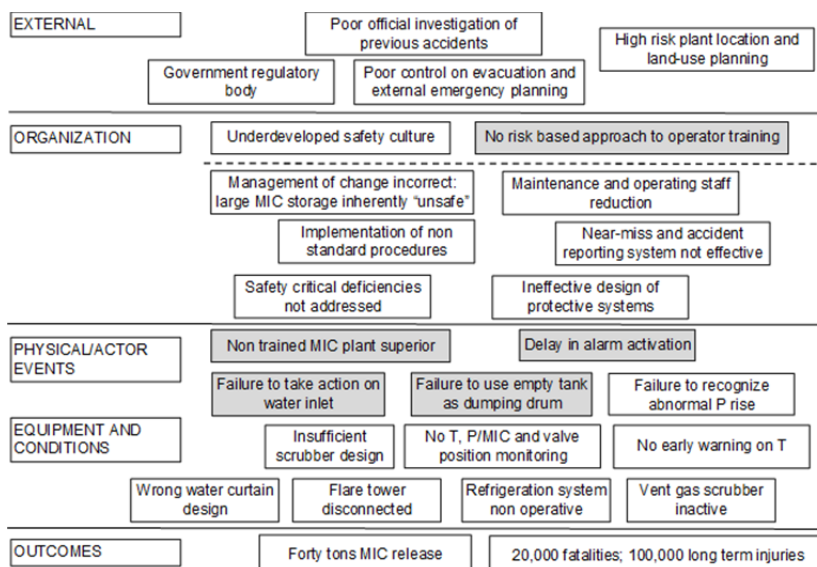


Figure 1: Accident analysis and causal factors with a perspective on emergency management (shaded).

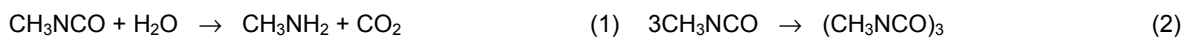
As argued by Kletz (1990) even if the refrigeration, scrubbing and flare systems were not properly designed, if they had been in full working order they would certainly have reduced the size of the discharge and delayed its start, and if the vessel had burst, the loss of life might have been lower. It is evident how accident investigation is like peeling an onion, with subsequent layers of causes and recommendations: outer layers are the immediate technical recommendations, while the inner ones deal with improvement to the management system (Fabiano & Currò, 2012). Bhopal represents an organizational accident characterized by technical and maintenance failures exerting both a determining role and an exacerbating feature. As AcciMap approach evidences, maintenance errors and human failures in emergency management are consequence of upstream organizational factors. Even if Bhopal can be categorized as a "black swan" event considering the unforeseen severity of the toxic release, in the next chapter we will discuss a simple approach to identify emergency actions and intervention time, thus recalling the reminder of Kletz (1990) that "accidents are not due to lack of knowledge, but by failure to use the knowledge we have".

2. A simplified framework to emergency management

A correct management effort should ensure the implementation of emergency actions suitable to stop temperature increase inside the MIC tank in case of contamination, firstly by stopping and removing the cause of contamination and secondly by minimizing the development of the complex series of runaway reactions. The evolving scenario and following evaluations are mainly based on event descriptions and thermodynamic data available from scientific literature (Joseph, 2005; Ball, 2011, Castro et al., 1985), or from standard tables.

2.1 Reference reaction scheme

The simplified approach developed here considers a linear two-step reaction sequence (Palazzi et al., 2015): firstly, isocyanates by hydrolysis react exothermically to the corresponding amine and carbon dioxide; secondly, the most relevant reaction is the condensation of MIC, as the cyclic trimer was the main product found by chemical analysis of the residue in the MIC tank E610 at the plant (D'Silva et al., 1986).



Starting from the functional group method (Perry & Green, 2008), the reaction molar enthalpies are calculated:

$$\Delta H_{\text{hydr}} = \sum v_i \Delta H_{fi} = -2.2970 \cdot 10^4 - 3.937 \cdot 10^5 + 9.002 \cdot 10^4 + 2.860 \cdot 10^5 = -4.065 \cdot 10^4 \text{ J mol}^{-1}$$

$$\Delta H_{\text{tri}} = \sum v_i \Delta H_{fi} = -4.9245 \cdot 10^5 - 3(-9.002 \cdot 10^4) = -2.224 \cdot 10^5 \text{ J mol}^{-1}$$

The total water mass entering the tank is assumed to be equal to 908 kg with a contaminant content of 1% w/w, mainly consisting of Fe compounds (Joseph et al., 2005). In fact, according to Union Carbide data (Chouhan, 2005), in the absence of a catalyzer, the second reaction is rather slow with time to runaway, τ , slowing down from 67 h at $T = 279 \text{ K}$ to 23 h at $T = 293 \text{ K}$. In presence of iron compounds (1-3 % FeCl_3) or sodium compounds (1-3 % NaOCH_3), τ reduces respectively to 60 min and 10 min. Considering carbon steel made pipes and the runaway actual behaviour ($\tau \approx 1 \text{ h}$), it is reasonably assuming that the reaction be catalysed by Fe compounds in water, or by tank corrosion products due to CHCl_3 (MIC impurity) and water.

2.2 Temperature and pressure profile

We assume that water flow into the tank started at 22.00 at $p = 1$ atm and $T_0 = 288$ K, while, as the complete temperature profile is unknown due to instrumentation deficiencies and failures, we consider the following scenario evolution. The condensation started above the normal boiling point of MIC ($T_{eb} = 312.5$ K), so we assume hydrolysis as the relevant reaction during the time span 22.00-23.00 and that condensation reaction be dominating only after 23.00. As hydrolysis reaction proceeds, the temperature increases rather slowly due to the thermal capacity of the liquid phase, while MIC molar fraction in 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 from the liquid to the gaseous phase. We suppose that MIC molar fraction in the gaseous phase increases linearly as time goes on, until reaching a critical value some degree below MIC boiling point, when according to the classical ignition theory, the imbalance of the heat generation by reaction and heat loss yields the thermal runaway onset. Ball (2011) hypothesized thermal runaway occurrence already at $T = 292$ K, due to the onset of a hard thermal oscillation at a subcritical Hopf bifurcation. The current analysis is based on water flow rates and time evolution given by Union Carbide so that, accounting also on the liquid heat capacity, the limiting reactant entering Tank E610 at the calculated flow rate seems not able to induce the thermal runaway at T lower than the critical one. After local time 23.00, as the tank internal pressure increases, water flow rate ends and the gaseous release into the atmosphere takes place with increasing flow rates, so that carbon dioxide and methylamine tend to zero. We assume that after 00.15 the release composition be pure MIC: $y=1$.

2.3 Water and gas flow evaluation

The quantitative evaluation of the reaction enthalpy of MIC hydrolysis is useful to optimize an intervention strategy focused on limiting the temperature inside the tank below a safety threshold. The analysis of the instantaneous water molar balance can be written as (Ball, 2011):

$$dn_w/dt = \dot{n}_{wg} + \dot{n}_{we} \quad (3) \quad \dot{n}_{wg} = -kcV_{react} = -kn_w \quad (4)$$

where: n_w = moles of water in the storage tank at instant t , mol; \dot{n}_{wg} = generation term, mol·s⁻¹

$$\dot{n}_{wi} = \text{molar rate of water, mol} \cdot \text{s}^{-1}$$

$$k_{\infty} = 3.9 \cdot 10^{12} \text{ s}^{-1}$$

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

$$E_a = 6.4 \cdot 10^4 \text{ J mol}^{-1}$$

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 $9.6 \leq k \leq 42.5$ from Eq (4), the resulting order of magnitude of n_w ($0.33 \leq n_w \leq 1.5$) is 1 mol. Being the value of the average water in-flow rate nearly $10 \text{ mol} \cdot \text{s}^{-1}$, the accumulation term in Eq(3) is negligible and water reacts quasi-instantaneously as it enters 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. The instantaneous reaction rate corresponds to the molar in-flow rate of water, representing the limiting reagent. The water in-flow rate can be expressed in a simplified form as:

$$\dot{n}_{wi} = \beta_i (p_e - p_i)^{1/2} \quad (5)$$

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

β_i = coefficient depending on fluid and pipe characteristics, mol·Pa^{-1/2}·s⁻¹.

According to Eq (5), 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), since an overpressure of 98,000 Pa avoids any material incoming. Integration of Eq (5) yields:

$$n_{wi} = \int_0^{t_{end}} \beta_i (p_e - p_i)^{1/2} dt \quad (6)$$

$t_{end} = 4,800$ s is obtained by graphical method, in connection with $p_e = 199,300$ Pa. The gaseous release rate is:

$$\dot{n}_o = \beta_g (p - p_a)^{1/2} \quad (7)$$

being: p_a = atmospheric pressure, 101,300 Pa; p = actual pressure Pa;

β_g = coefficient depending on fluid and pipe characteristics, mol·Pa^{-1/2}·s⁻¹.

Integration of Eq(7), yields:

$$n_o = \int_0^{t_{end}} \beta_g (p - p_a)^{1/2} dt \quad (8)$$

Under these conditions the value for β_l is $0.048 \text{ mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$, the water flow rate entering the tank at $t=3600 \text{ s}$ and the total entered one are respectively $\dot{n}_{wi,3600} \cong 8.2 \text{ mol} \cdot \text{s}^{-1}$; $n_{wi,3600} \cong 4.4 \cdot 10^4 \text{ mol}$. Coeteris paribus, $\beta_g = \beta_l (\rho_g / \rho_w)(M_w / M_g) \cong 0.001 \text{ mol} \cdot \text{Pa}^{-0.5} \cdot \text{s}^{-1}$, however, since the other factors affecting β_g are unknown, we cautiously assume $\beta_g \cong 0.01 \text{ mol} \cdot \text{Pa}^{-1/2} \cdot \text{s}^{-1}$, thus obtaining: $n_{o,3600} \cong 5.5 \cdot 10^3 \text{ mol}$; $\dot{n}_{o,3600} \cong 2.6 \text{ mol} \cdot \text{s}^{-1}$; $n_{o,MIC,3600} \cong 2.3 \cdot 10^3 \text{ mol}$ and $\dot{n}_{o,MIC,3600} \cong 1.2 \text{ mol} \cdot \text{s}^{-1}$.

2.4 Energy balances

The integral energy balance in the first hour of the event course can be written as (Palazzi et al., 2015):

$$\Delta H_L + \Delta H_o + \Delta H_{hyd} + \Delta H_{tri} = Q \quad (9)$$

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

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

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

$Q = \dot{Q} \tau = -KS \Delta T_m \tau \cong -3.1 \cdot 10^8 \text{ J}$ 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(9) the value of the trimerization enthalpy is $\Delta H_{tri} \cong -0.8 \cdot 10^8 \text{ J}$, lower by an order of magnitude when compared to the hydrolysis one. At $t=3600 \text{ s}$, the instantaneous energy balance is:

$$\Delta \dot{H}_L + \Delta \dot{H}_o + \Delta \dot{H}_{hyd} + \Delta \dot{H}_{tri} = \dot{Q} \quad (10)$$

where: $\Delta \dot{H}_{hyd} = \dot{n}_{wi,3600} \Delta \tilde{H}_{hyd} \cong -3.4 \cdot 10^5 \text{ W}$ and $\dot{Q} = -KS \Delta T_{3600} \cong -1.7 \cdot 10^5 \text{ W}$. From the energy balance, we can calculate the instantaneous value of trimerization reaction just after 1 hour: $\Delta \dot{H}_{tri} \cong -3.1 \cdot 10^5 \text{ W}$.

2.5 Kinetics verification

In this section, we provide a simplified verification of the trimerization enthalpy value starting from available data over the time span (23.00-00.30). We firstly estimate the apparent kinetic constant of the trimerization reaction by performing the calculation according to a pseudo first order reaction. Secondly, we apply the obtained kinetic law to estimate ΔH_{tri} over the time span 22.00-23.00, so as to verify the value calculated by the energy balance. From the instantaneous energy balance, at local time 00.30, assuming $y=1$, it follows:

$$\Delta \dot{H}_L + \Delta \dot{H}_o + \Delta \dot{H}_{tri} = \dot{Q} \quad (11)$$

from which: $\Delta \dot{H}_L \cong 1.06 \cdot 10^7 \text{ W}$; $\Delta \dot{H}_o \cong 2.4 \cdot 10^5 \text{ W}$; $\Delta \dot{H}_{tri,9000} \cong -1.2 \cdot 10^7 \text{ W}$.

We assume the validity of Arrhenius law and a pseudo first order reaction, so that it follows:

$$k = k_\infty e^{(-E_{ac}/RT)} = k_\infty e^{(-T_c^*/T)} \quad (12) \quad \dot{n}_{triMIC,g} = kc_{MIC}V = kn_{MIC} \quad (13)$$

$$l_c = E_{ac}/R \quad (14) \quad k = \Delta \dot{H}_t / (n_{MIC} \Delta \tilde{H}) \quad (15)$$

being: E_{ac} =activation energy corresponding to the maximum amount of catalyst, $\text{mol} \cdot \text{s}^{-1}$

$$n_{MIC} = m_L / M_{MIC} \cong 740 \text{ kmol}; \quad \Delta \dot{H}_{triMIC,g} = \dot{n}_{triMIC,g} \Delta \tilde{H}_t = kn_{MIC} \Delta \tilde{H}_t$$

At the end of the first phase: $k_{3600} = k_{305K} \cong 1.9 \cdot 10^{-6} \text{ s}^{-1}$ and at the emergency discharge start:

$k_{9000} = k_{376K} \cong 7.4 \cdot 10^{-5} \text{ s}^{-1}$. From Eq (12), we can easily obtain $T_c^* \cong 5.9 \cdot 10^3 \text{ K}$ and at last the activation energy corresponding to the maximum catalyst amount in the tank, at water flow interruption

$E_{ac} = RT_c^* \cong 4.9 \cdot 10^4 \text{ J} \cdot \text{mol}^{-1}$. The apparent pre-exponential factor is obtained as: $k_\infty = k_{305K} e^{T_c^*/305} \cong 480 \text{ s}^{-1}$.

At $t=8100 \text{ s}$, i.e. at local time 00.15, we can verify the instantaneous energy balance:

$$\Delta \dot{H}_{t,8100} = k_{8100} n_{MIC} \Delta \tilde{H}_t \cong -2.9 \cdot 10^6 \text{ W} \quad \Delta \dot{H}_{u,8100} = \beta \Delta p_{8100}^{1/2} \Delta \tilde{H}_v \cong 1.4 \cdot 10^5 \text{ W}$$

$$\dot{Q}_{8100} = -KS \Delta T_{8100} \cong -5.7 \cdot 10^5 \text{ W}$$

From the energy balance we obtain $\Delta \dot{H}_L \cong 2.2 \cdot 10^6 \text{ W}$ and $(\Delta T/dt)_{8100} = (\Delta \dot{H}_L / m_L \hat{c}_{pl}) \cong 0.025 \text{ Ks}^{-1}$, corresponding to the slope of the curve $T(t)$. As a congruity check, from the calculated kinetic data, a rough estimate of the enthalpy of the trimerization reaction ΔH_{tri} over the period 22.00-23.00 can be performed by the assumed kinetic scheme. Over one hour time span, ΔH_{tri} can be obtained by kinetic law integration:

$$\Delta H_{tri} = \int_0^{3600} \Delta \dot{H}_{tri} dt = \int_0^{3600} k n_{MIC} \Delta \tilde{H}_{tri} dt = k_{\infty} n_{MIC} \Delta \tilde{H}_{tri} \int_0^{3600} e^{-(T^*(t)/T(t))} dt \quad (16)$$

The problem to be solved evidences a singularity, as the activation energy decreases while time proceeds, due to the gradual catalyst accumulation into the tank. We approached the solution starting from the assumption that both the activation energy E_a and T^* be linearly dependent on the catalyst mass and assuming the catalytic dependence relation previously described (Chouhan, 2005).

$$T^* = T_0^* - (T_0 - T_c/4500)t \quad (17) \quad k_o/k_c = \exp[-(T_0 - T_c/293)] \cong 23^{-1} \quad (18)$$

At last, we can estimate the value of the enthalpy variation due to trimerization as: $\Delta H_{tri} \cong -1.2 \cdot 10^8 J$, which results comparable, at least as order of magnitude, with the previously calculated one.

3. Discussion

According to the resilience concept, for prevention the approach forces focus on flexible, timely and adequate risk control, both from an organizational and a technical point of view. 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). The elimination of the immediate cause by water inflow interruption within a frame suitable to induce a thermal excursion decay is the simplest action. Referring to the classical ignition of a thermo-reactive system, occurring at a steady-state turning point and applying the instantaneous heat balance by Eq(10) at a generic time t , the determining role of trimerization reaction enthalpy $\Delta \dot{H}_{tri}$ is clearly evidenced. At any time t_1 , in the interval $[t_2, 4800 \text{ s}]$, when $\Delta \dot{H}_L > -\Delta \dot{H}_{hyd}$, MIC polymerization reaction contributes to the liquid heating and water inflow stop is not effective in stopping the runaway behaviour. At time t_2 when $\Delta \dot{H}_L = -\Delta \dot{H}_{hyd}$ the system will be in a pseudo steady-state condition where the second reaction is able to provide the system instantaneously 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 corresponding to the condition: $-\Delta \dot{H}_{hyd}(t_3) = \Delta \dot{H}_L(3600)$ so that water flow interruption could theoretically be able to stop runaway behaviour. Given the hazard connected to MIC release under runaway conditions, a convenient safety margin must be considered, by a proper coefficient: $-\Delta \dot{H}_{hyd}(t_3) = \eta \Delta \dot{H}_L(3600)$, so that the emergency intervention be effective in limiting the release environmental impact by a fast system temperature reduction. Considering a safety coefficient $\eta = 1.3$, intervention should have been taken nearly at local time 22.45, at $p \approx 146,000 \text{ Pa}$. Given the peculiar reactivity hazard, further measures can be foreseen in view of a possible operator's delay in performing the main safety intervention, e.g. a convenient refrigeration system adoption (that would have been in action to maintain MIC storage temperature at 278 K), so as to reduce emission flow rate and overall release duration. A further enhancement of refrigeration effect could have been obtained by the extraction of a convenient gaseous stream from the tank, possibly utilizing a N_2 flow, so as to attain a calculated overall emission rate $\dot{m} = 1 \text{ kg s}^{-1}$. Considering intervention time $t = 3600 \text{ s}$ corresponding to the pressure $p = 170,000 \text{ Pa}$, the enthalpy flow is: $\Delta \dot{H}_{ext} = \eta (\Delta \dot{H}_{L,3600} + \Delta \dot{H}_{i,3600}) \cong 1.2 \cdot 10^5 W$ from which, being $\Delta \dot{H}_{ext} = \dot{n}_{extr} y \Delta \tilde{H}_v$ it follows $\dot{n}_{extr} = 8.4 \text{ mol s}^{-1}$, corresponding to a total molar flow rate leaving the tank of about 11 mol s^{-1} . In case of air dilution, the additional air flow can be estimated as $\dot{m}_a = 0.485 \text{ kg s}^{-1}$ or else $\dot{n}_{ar} \cong 17 \text{ mol s}^{-1}$. In this event, a forced dispersion system addressing environmental protection should ensure an exit velocity $v_0 = 150 \text{ ms}^{-1}$, to enhance jet phase and effective emission height in case of safety mitigation systems unavailability (Palazzi et al., 2015). 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). Even if MIC is a dense gas, the accidental plume can be considered a borderline case between one having a density effect and the passive one: in fact, Union Carbide gas plant was the least affected and the first touchdown occurred at about 500 m from the stack, so that MIC could not have slumped as a totally heavy gas (Sharan and Gopalakrishnan, 1997). Given the purpose of this work and accounting for air entrainment, initial dilution, mixing and heat generation, we consider a passive plume behaviour in the following approximate evaluation on the implementation of a better emergency management. To this end, we assume that the technical procedure previously discussed be enforced at local time 23.00, utilizing only available protective equipment. Assuming that a forced extraction with air from Tank E610 be utilized, by the existing vent line ($d_0 = 0.2 \text{ m}$), according to the approach, the exit velocity would have been $v_0 \approx 13 \text{ ms}^{-1}$ with a

resulting maximum concentration of the simple Gaussian plume below IDLH (20 ppm). In case of forced extraction of the vapour phase from Tank E610, without any diluting agent (air or nitrogen) at a calculated total flow rate of 1 kg s^{-1} the maximum concentration, calculated in analogy with the method by Palazzi et al., (2014), is slightly higher than IDLH and equal to nearly 23 ppm. We underline that the approach relies upon simple gas dispersion without accounting for density and possible condensation effects, so that spreading due to gravitational setting is not accounted for. A more accurate dispersion model should consider these items by advanced tools (e.g. Vairo et al, 2014, 2016). We adopted the Gaussian approach as a first to evidence how the severity of the accident is the result of a chain of events, which could have been broken at many points, by taking adequate organizational measures regarding roles, training, procedures and emergency planning.

4. Conclusions

The failures of prevention measures contributing to the final breakdown, magnitude of the release and fatalities are not connected to inadequate/undersized design of the individual safety equipment, but rather to their unavailability and to the absence of use co-ordination. Key organizational factors are the implementation of non-standard procedures, inadequate planning/training in loss prevention of the personnel and low attention to identification of process anomalies, coupled with the absence of a proper response plan including timely actions in case of critical deviations. The approach to intervention time even if affected by uncertainties connected to hypotheses and empirical coefficients, demonstrates how proper actions taken shortly after the hazardous event can have a significant impact in reducing the response time, consequences and costs.

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