MODELLING OF INDOOR RELEASES OF WATER REACTIVE TOXIC MATERIALS

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This paper presents a case study to demonstrate the modelling of indoor releases of water reactive toxic materials. The materials of concern were phosphorus trichloride and phosphorus oxychloride, both of which are classed as very toxic, but which produce toxic hydrogen chloride gas on reaction with water. To assess the risk from the storage and handling of phosphorus trichloride and oxychloride, it is required to determine the extent and nature of the toxic gas cloud produced. In the far field, this gas cloud will be hydrogen chloride, and thus the source terms are required for the rate of production of hydrogen chloride following a spill of phosphorus trichloride or oxychloride. The methodology used for this modelling is described using phosphorus trichloride as the example.

Keywords: water reactive materials, toxic gas cloud, phosphorus trichloride, phosphorus oxychloride, hydrogen chloride

INTRODUCTION

Where significant quantities of phosphorus trichloride (PCl_3) and phosphorus oxychloride ($POCl_3$) (or other water reactive materials) are stored and processed on a chemical plant, these may qualify the site to come under the UK COMAH Regulations. In the case of 'top-tier' sites, it is thus necessary to model the behaviour of such materials should a major accident occur, whereby the materials are released to the atmosphere.

PCl_3 and $POCl_3$ are classified as very toxic. They are liquids at normal temperature and pressure and if released from storage will form liquid pools on the ground. There boiling points are 75.5°C and 105°C respectively, and whilst there will be some vaporisation from a standing pool, the amount of vapour produced will not result in a large vapour cloud that would move downwind.

However, the materials are highly reactive with water. When they react with water, they give off heat and evolve toxic hydrogen chloride gas. The materials will react with the moisture in the atmosphere and in the worst case with precipitation. In such cases, a HCl cloud will form which may move downwind and have toxic effects at a greater range than the vapour cloud formed by the original spill.

For modelling purposes, it is required to have a 'release rate' of HCl as input to a consequence model. The modelling of the HCl 'release' following the reaction of PCl_3 with the moisture in the atmosphere is very complex and should take into account the relative humidity, temperature, and the size of the bunded area from which HCl will be emitted (or the size of the pool formed), among other parameters.

PCl_3 and $POCl_3$ are stored and handled at the Rhodia Oldbury site and formed a major part of the submission under the COMAH Regulations.

INTENT OF THIS PAPER

This paper is a case study on how PCl_3 and $POCl_3$ were modelled to obtain an estimate of their potential offsite impact should a major accident occur. The modelling described in this paper was for indoor releases of PCl_3 and $POCl_3$. Both materials are processed and stored onsite in process buildings, the materials being highly water reactive and thus the amount of water in the area is kept to a minimum.

The case study described below is for PCl_3 only. The modelling of $POCl_3$ releases used the same methodology.

It was not the intention of the model, and thus this paper, to provide a completely accurate method of modelling HCl releases following the reaction of PCl_3 and $POCl_3$ with water. Rather, it was the intention to produce a best estimate of HCl mass release rate that could be used as input to relevant dispersion models. Work has been carried out recently on a code for modelling spills of water reactive materials[1], and this is a useful reference source.

PHOSPHORUS TRICHLORIDE RELEASE RATES

The major hazardous events considered in this case study are given in Table 1, along with their corresponding mass flow rates and release durations. The mass flow rate from a hole (below the liquid level) is calculated using the Bernoulli equation:

$$m = C_d\, \rho\, A\, (2\, ((P_i - P_a)/\rho + g\, h)))^{1/2} \qquad \text{(Equation 1)}$$

where:
m = mass discharge rate, kg/s
C_d = discharge coefficient (0.61)
ρ = liquid density, kg/m^3
A = hole area, m^2
P_i = pressure at which the liquid is stored, Pa
P_a = ambient pressure, Pa
g = gravitational constant, m/s^2
h = static head of liquid, m

Only liquid releases of PCl_3 are considered in this case study, as these would have the most severe consequences. Vapour releases may also occur and HCl may be produced which would travel downwind, but the concentration of HCl would quickly disperse to below dangerous levels. This is because the pressure is relatively low where vapour is present, e.g. the distillation column is at 5 psig (0.35 barg), and this would soon reduce to atmospheric for a major failure. Hence, the mass flow rate of PCl_3 from the failure would be low. (For other studies, it may be the case that the PCl_3 in the vapour phase may be at high pressure and thus be released at a relatively high rate. Such a case would likely produce significant amounts of HCl as the PCl_3 would also be in the vapour phase following release.)

The liquid releases will form pools on the ground and the vaporisation from the release will be low, as the releases are at temperatures well below the boiling point of PCl_3.

TABLE 1 MAJOR ACCIDENT HAZARD EVENTS FOR PCL_3

Area	Event No.	Leak Size (mm)	Mass Flow Rate (kg/s)	Duration (s)
Lines to storage or reflux lines	PCl-1	12.5	1.1	890
	PCl-2	25	4.2	240
	PCl-3	50	17	60
Storage	PCl-4	12.5	1.1	3600
	PCl-5	25	4.2	3600
	PCl-6	50	17	3600
	PCl-7	rupture	150,000 kg	n/a
Burn down tank	PCl-8	12.5	1.1	3600
	PCl-9	25	4.2	3600
	PCl-10	50	17	1200
Lines to processes or loading	PCl-11	12.5	2.7	1200
	PCl-12	40	4.4	600
Tanker loading	PCl-13	12.5	2.7	300
	PCl-14	40	4.4	300
Head tank	PCl-15	12.5	0.8	3600
	PCl-16	25	3.0	3600
	PCl-17	50	12	1100
Drum filling	PCl-18	12.5	0.8	300
	PCl-19	25	3.0	300
Tanker	PCl-20	12.5	0.7	3600
	PCl-21	25	2.6	3600
	PCl-22	50	10	1760

DURATION OF EXPOSURE

As PCl_3 and HCl are toxic gases, one of the most important parameters is the time of exposure, in determining the potential toxic dose experienced by people. The magnitude of the hazard will be a function of the action taken (or not taken). These actions relate to the control and mitigation of major hazards in terms of quantifying the consequences. For example, in the case of failure of the loading hose, there is an emergency stop that will shut down the pump. This human interaction is taken into account in the failure events, where applicable.

It is important here to provide reasoning in the choice of durations used. The maximum duration used is 60 minutes. It is assumed that by this time people will have sought shelter, or they would have been overcome by the toxic cloud, although some calculations use a duration of exposure of 30 minutes. Hence, a maximum duration of exposure of 60 minutes tends to the side of conservatism.

For small leaks, although detection would likely be relatively quick in areas where there are HCl detectors (which are very reliable), there may still be a significant inventory left in the system downstream of any isolation valve that could be closed. Therefore, the release duration may still be significant.

The time to detection for larger leaks would be relatively quick, due to the array of detectors, and the fact that the leak would soon be noticed by onsite personnel. The leak may also be recorded by a process upset, e.g. loss of level in a reactor that would result in an alarm and trip of the process.

For leaks in the piping to downstream processes, e.g. $POCl_3$, and the loading area, the pressure would be reduced to the head of the storage tank by stopping the pumps. This would reduce the release rates significantly, in practice, particularly where the leak is at an elevated level above the head in the tank, e.g. at the loading arm. Furthermore, for major leaks in the piping or guillotine ruptures, the pump would not be able to maintain the flow rate, i.e. it would fall off its 'pump curve' and trip. Again, in this case the driving pressure would be the head in the storage tank. In these cases it is assumed that the release rate is the flow rate in the line, which is a reasonable assumption when taking into account pressure drops across control valves, etc.

For releases that can be isolated, this may be achieved by closing relevant isolation valves upstream of the leak. There are no remotely operated valves on the plant downstream of the reactors. If necessary an operator would put on special PPE in order to reach the appropriate isolation valve.

For both the tanker loading and the drum loading, an operator is always present. If there are signs of problems then the operator will shut down the process, e.g. by pushing the emergency stop button. In these cases a duration of 5 minutes is assumed.

CONSEQUENCE MODELLING OF PHOSPHORUS TRICHLORIDE RELEASES

DERIVATION OF HYDROGEN CHLORIDE SOURCE TERMS

For modelling purposes, it is required to have a 'release rate' of HCl as input to a consequence model. PCl_3 reacts with the moisture in the atmosphere or precipitation (in the worst case) to form HCl. This then forms a toxic vapour cloud that will be at dangerous concentration levels in the area of the spill and may still be at dangerous concentrations offsite.

The modelling of the HCl 'release' following the reaction of PCl_3 with the moisture in the atmosphere is very complex and should take into account the relative humidity, temperature, and the size of the bunded area from which HCl will be emitted (or the size of the pool formed), among other parameters.

MASS OF WATER FOR REACTION

One of the major rate determining parameters is the amount of water available for the reaction with PCl_3 to take place to form HCl.

The humidity in the air, in terms of unit mass of water /per unit mass of dry air can be found from a humidity-enthalpy diagram[2]. At atmospheric pressure, 10°C and 70% relative humidity, the humidity is 0.006 kg_{H2O}/kg_{air}. The density of air[3] is 1.2928 kg/m^3, hence the mass of water in 1 m^3 of air is 0.0078 kg.

For indoor process areas, it is assumed that the water available for reaction is the volume contained within the process building up to a height of 5 m, which is considered conservative, because the reaction will only take place at the boundary layer of the pool. It is also necessary to consider the number of air changes per hour and it is assumed that the mass of water available for reaction is the mass of the assumed volume up to 5 m, multiplied by the number of air changes per hour. For the process building and storage building, it is assumed that there are 12 air changes per hour. These buildings are relatively closed to the atmosphere. (Twelve air changes per hour is the number which is often used for offshore assessments where modules have grating or forced ventilation and thus this is considered conservative here.) For the loading area, this is open on one side, and thus 60 air changes per hour is assumed, i.e. one air change every minute. The mass of water available in the building over one hour is represented by the following equation:

$$m_w = \mathrm{H}\,\rho_\mathrm{a}\,l\,w\,h\,N_{ac} \qquad \text{(Equation 2)}$$

where:
m_w = mass of water available in the building over one hour, kg
H = humidity, $\mathrm{kg_{H2O}/kg_{air}}$
ρ_a = air density, $\mathrm{kg/m^3}$
l = length of building, m
w = width of building, m
h = height of building (up to 5 m), m
N_{ac} = number of air changes per hour

The mass of water available in the buildings over one hour in each area is shown in Table 2.

POOL GROWTH

Another important parameter is the size of the pool formed, i.e. the surface area over which the reaction can taken place. The pool sizes will be restricted by either:

i. the size of the bunded area,
ii. the area of the building,
iii. other restrictions.

It is assumed that the maximum pool size that can be formed would be of 20 m in diameter, i.e. restrictions due to kerbing, etc. The size of the pool will also be determined by the volumetric release rate and the release duration, i.e. the volume released. It is assumed that the average pool height is 10 mm, which takes into account sumps, etc.

As stated above, a maximum duration of one hour is assumed (although the pool will have generally reached its maximum pool size by this time. Taking all the above into consideration, the pool sizes formed are listed below in Table 3.

TABLE 2 MASS OF WATER AVAILABLE IN EACH AREA OVER ONE HOUR

Area	Length (m)	Width (m)	Mass of Water to Height of 5 m (kg)	Number of Air Changes/Hour	Mass of Water Available in 1 hr (kg)
Process area	25	15	14.54	12	174.5
Storage area	25	15	14.54	12	174.5
Loading area	25	15	14.54	60	872.6

TABLE 3 POOL SURFACE AREAS FOR PCL_3 RELEASES

Area	Event No.	Volumetric Release Rate (m^3/s)	Duration (s)	Restricted Area (m^2)	Pool Area (m^2)
Lines to storage or reflux lines	PCl-1	0.00072	890	314	65
	PCl-2	0.00265	240	314	65
	PCl-3	0.01061	60	314	65
Storage	PCl-4	0.00072	3600	73	73
	PCl-5	0.00265	3600	73	73
	PCl-6	0.01061	3600	73	73
	PCl-7	n/a	n/a	73	73
Burn down tank	PCl-8	0.00072	3600	27	27
	PCl-9	0.00265	3600	27	27
	PCl-10	0.01061	1200	27	27
Lines to processes or loading	PCl-11	0.00168	1200	314	202
	PCl-12	0.00280	600	314	167
Tanker loading	PCl-13	0.00168	300	314	50
	PCl-14	0.00280	300	314	84
Head tank	PCl-15	0.00051	3600	314	183
	PCl-16	0.00188	3600	314	314
	PCl-17	0.00750	1100	314	314
Drum filling	PCl-18	0.00051	300	314	15
	PCl-19	0.00188	300	314	56
Tanker	PCl-20	0.00044	3600	314	158
	PCl-21	0.00162	3600	314	314
	PCl-22	0.00650	1760	314	314

For modelling the releases, the fraction of pool area per area of building is used, i.e.:

$$m_r = m_w A_p/A_b \qquad \text{(Equation 3)}$$

where:
m_r = mass of water available for reaction over one hour, kg
A_p = area of pool, m^2
A_b = area of building, m^2

MASS FLOWRATE OF HCL PRODUCED

The mass of HCl produced is that which has been formed by the reaction of the water available. In the equation for the reaction shown below it can be seen that 1 mole of HCl is formed for 1 mole of water reacted.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl \qquad \text{(Equation 4)}$$

Thus, the amount of HCl formed in one hour is:

$$m_{HCl} = m_r\, MW_{HCl}/MW_{H2O} \qquad \text{(Equation 5)}$$

where:
m_{HCl} = mass of HCl produced over one hour, kg
MW_{HCl} = molecular weight of HCl, g/mol
MW_{H2O} = molecular weight of H_2O, g/mol

Thus, the average release rate is this mass divided by the time taken for the release, taken as one hour. The release rates of HCl calculated are shown in Table 4.

DISPERSION MODELLING OF HYDROGEN CHLORIDE

The output of the HCl source term modelling is then used as input to a relevant gas dispersion model. This is not described in this paper.

TABLE 4 HCL SOURCE TERM OUTPUT FOR INPUT TO DISPERSION MODEL

Area	Event No.	Mass of Water for Reaction (kg)	HCl Produced in One Hour (kg)	HCl Release Rate (kg/s)	Duration of Exposure (s)
Lines to storage or reflux lines	PCl-1	30.3	60.9	0.017	3600
	PCl-2	30.3	60.9	0.017	3600
	PCl-3	30.3	60.9	0.017	3600
Storage	PCl-4	34.0	68.4	0.019	3600
	PCl-5	34.0	68.4	0.019	3600
	PCl-6	34.0	68.4	0.019	3600
	PCl-7	34.0	68.4	0.019	3600
Burn down tank	PCl-8	12.6	25.3	0.007	3600
	PCl-9	12.6	25.3	0.007	3600
	PCl-10	12.6	25.3	0.007	3600
Lines to processes or loading	PCl-11	470.1	946.4	0.263	3600
	PCl-12	388.6	782.4	0.217	3600
At loading	PCl-13	116.4	234.3	0.065	3600
	PCl-14	195.5	393.5	0.109	3600
Head tank	PCl-15	85.0	171.1	0.048	3600
	PCl-16	146.2	294.4	0.082	3600
	PCl-17	146.2	294.4	0.082	3600
Drum filling	PCl-18	7.1	14.2	0.004	3600
	PCl-19	26.2	52.8	0.015	3600
Tanker	PCl-20	368.0	740.8	0.206	3600
	PCl-21	731.1	1471.9	0.409	3600
	PCl-22	731.1	1471.9	0.409	3600

DISCUSSION

This case study is a demonstration of how indoor releases of water reactive materials were modelled. What was required in this particular case was input into a gas dispersion model of the rate of HCl formed following the reaction of PCl_3 and $POCl_3$ with the moisture in air.

It is important that the modelling of the released material takes into account the actual physical effects to which it is subjected. For example, in this case, dispersion modelling of a release of PCl_3 would not be representative of the problem. Certainly, the building that PCl_3 is released into would have very toxic vapours of PCl_3 within. However, these would soon disperse to concentration below dangerous levels. Thus, it is vital to model the reaction with water vapour where HCl gas is evolved.

However, modelling of such effects in the past has often tended to overpredict the amount of toxic gas liberated, as Kapias et al. point out[1]. An overprediction of the amount of HCl liberated per unit time in this case would overpredict the consequences of the toxic gas cloud produced. For example, if it was assumed that the continuous release of PCl_3 was all converted into HCl as it was released from containment, then a vast overprediction would occur.

Whilst the modelling described in this case study has made a number of assumptions, it was attempted to provide a more accurate representation of the amount of HCl produced for indoor releases. The rate determining step is actually the amount of water vapour available for reaction rather than the release rate of PCl_3. The model also takes into account the size of the pool produced by the release, i.e. the surface area available for reaction with the moisture in air. In this way, it can be seen that the 'release rate' of HCl for input into a dispersion model is only a fraction of the actual release rate of the PCl_3 originally released to the atmosphere.

Even though this 'release rate' is reduced significantly, the modelling still tends to the side of conservatism, particularly for the smaller release rates of PCl_3. It can be seen that the HCl 'release rate' is the same for say releases from storage, no matter the size of the leak from the storage tank. This is because it is assumed that the bunded area is immediately filled and thus the surface area over which the reaction with moisture in air takes place is always constant. In reality the liquid pool would grow to its limiting size[1] and there would also be the surface area of the liquid as it is released from the hole. This may be significant if there was aerosolisation of the released material, but the release velocity is not sufficient to cause such an effect.

In conclusion, although the model is not a completely accurate representation of the mechanisms involved in releases of water reactive materials, it does provide a more representative picture than if instantaneous conversion to the toxic gas (in this case HCl) is assumed. Such mechanisms are important for the source term effects if dispersion modelling of the toxic gas is to be conducted. If the off-site risk from a facility that stores and processes PCl_3 and $POCl_3$ is to be assessed, then it is important than more realistic modelling techniques are used, otherwise the off-site risk may be grossly overstated. To put it in perspective, the off-site risk from PCl_3 and $POCl_3$ is not significant compared to, say, chlorine, for similar inventories of material.

REFERENCES

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