

MODELLING RELEASES OF WATER REACTIVE CHEMICALS

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Water reactive chemicals are commonly used in many manufacturing processes, particularly in the soap and detergent industry. The hazardous nature of these chemicals is recognised in the Approved Supply List where they are generally attributed risk phrases such as R14, 'Reacts violently with water' and R29, 'Contact with water liberates toxic gas'. This paper is principally related to chemicals which liberate toxic gas on contact with water. Pool models typically deal with boiling and/or evaporating liquids. However, few are available to model the behaviour of water reactive pools. There are a number of properties which influence the behaviour of the pool such as: pool diameter, composition and temperature. The detailed interaction of these and other time dependent pool properties requires a 'complex' computer model which, depending on the spill size, may take some time to generate results. Clearly this may be impractical if many release sizes require modelling. This paper details a simplified method for calculating toxic gas evolution rates from releases of water reactive chemicals. This method has been used as the basis for calculating consultation distances around major hazard sites with the results shown to closely match those calculated by the Health and Safety Executive.

KEYWORDS: Water reactive chemicals, dispersion modelling, oleum, sulphur trioxide, phosphorus oxychloride, thionyl chloride, chlorosulphonic acid

INTRODUCTION

A number of chemicals react violently with water liberating toxic gas and/or flammable gases, that can present a major accident hazard. This paper focuses on those water reactive chemicals (WRCs) that liberate toxic gases on contact with water, though the method can be adapted and applied to those that liberate flammable gases.

Where significant quantities of WRCs are stored and processed on a chemical facility, it may be necessary to model the consequences of a spillage in order to determine harm extents. The time dependent complex nature of the pool and its properties makes detailed calculation time consuming and complicated. These detailed methods may be suited to 'one off' calculations, but are considered less suited to calculating consequences from many releases.

Numerous studies have employed a method developed by ERM Risk, based on that described in a monograph published by the IChemE¹. The model has been modified, adapted and refined according to the studies it has been used for. Therefore, it is felt that the model is versatile, robust and consistently constructed to account for case specific detail. The model has been used to replicate results calculated by the UK Health and Safety Executive (HSE) and has been adapted to model other WRCs.

OTHER MODELS FOR WATER REACTIVE CHEMICALS

For releases which are entirely indoors in perfectly 'dry' conditions (i.e. no surface water), the method described by Pettitt et al² can be employed. However, perfectly 'dry' conditions

are unlikely unless special measures are in place as described later. In addition, unlike the model proposed here, this method assumes that the release is for a fixed duration of 1 hour (though it can be adapted for 30 minutes duration since typically, HSE assume that the release has been controlled after 30 minutes). Furthermore, the limited egress of toxic gas from the building is not accounted for. Essentially, the model assumes that a column of air, of specified height above the pool contains some moisture according to the humidity. This column is continually moving, according to the building air change rate, providing a continuous supply of moisture for the WRC to react with. The evaporation rate from the pool is not calculated. Instead it is assumed that sufficient WRC is evaporated to react with the moisture in the column of air above the pool.

A more detailed model for the behaviour of water reactive chemicals is described by Kapias³. This is an extension to the models describing the behaviour of the water reactive materials, oleum and sulphur trioxide^{1,4}.

DESCRIPTION OF THE MODEL

The model developed by ERM can model indoor and outdoor releases of WRC, accounting for toxic gas evolution by wind driven evaporation and reaction with water. Site specific characteristics can be incorporated. For example, the minimum pool depth can be increased according to the ground type, or the forced ventilation in a building can be considered to account for limited egress from the building. A suitable decision process has been derived to determine the minimum pool depth, water thickness, a building's air change rate and wind speed, all of which have an important affect on toxic gas evolution rates which can significantly affect results. The model is versatile and has been used successfully in a number of studies.

EVOLUTION FROM A POOL

Pool Size Calculation

The release is assumed to form a circular pool of uniform depth.

Unbunded Effective Pool Radius (UEPR)

The UEPR is calculated from the volume, using Equation 1.

$$r = 6.85V^{0.44537} \quad \text{Equation 1}$$

where

r pool radius (m)
 V volume released (m³)

Equation 1 has been regressed from the formula for a spreading pool⁵, based on a 5 mm minimum depth, which is usually related to smooth concrete surfaces. This leads to the 'worst case' (i.e. maximum radius pool), and is understood to be the method typically employed by HSE to calculate pool radius.

If required, the volume released may be calculated from the liquid density and the mass released.

$$V = \frac{M}{\rho} \quad \text{Equation 2}$$

where

M mass released (kg)
 ρ liquid density (kg/m³)

Effective Bund Radius (EBR)

Spill size may be limited if contained within a bund. Typically, bunds are a rectangular shape, having a certain floor surface area. The effective bund radius is equal to that of a circle whose area is equal to the bund floor surface area.

Actual Effective Pool Radius (AEPR)

Clearly the AEPR cannot be larger than the effective bund radius (EBR). The following applies:

- if UEPR > EBR, then AEPR = EBR;
- if UEPR < EBR, then AEPR = UEPR.

Wind Driven Evaporation

The wind driven release rate is calculated using the Sutton correlation⁶ for evaporation from a free liquid surface in the atmosphere, adapted as described by Grint and Purdy⁷.

$$E_{w,WRC} = 1.684 \times 10^{-6} \left(\frac{mP}{T} \right) U^{0.78} r^{1.89} Sc^{-2/3} \quad \text{Equation 3}$$

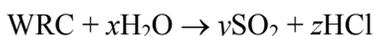
where

$E_{w,WRC}$ wind driven release rate of WRC (kg/s)
 m molecular weight (kg/kmol)
 P vapour pressure of the evaporating WRC (N/m²)
 T temperature of the evaporating WRC (K)
 U wind speed at a height of 10 m (m/s)
 r pool radius (m)
 Sc Schmidt number of the evaporating WRC (no units)

The Schmidt number for sulphur trioxide is 1.1¹.

Note that Equation 3 calculates the wind driven release rate of the evaporating WRC. It is judged that the WRC will completely react with atmospheric moisture according to the general form of chemical reaction detailed below.

The quantity of toxic gas can be calculated from the mass of water and the stoichiometry of the reaction. In general, the chemical reaction is of the form:



where

WRC water reactive chemical
 x number of moles of water required per mole of WRC

- y number of moles of sulphur dioxide produced per mole of WRC
 z number of moles of hydrogen chloride produced per mole of WRC

The stoichiometry is summarised in Table 1.

Note that the reaction of sulphur trioxide with water yields sulphuric acid mist and sulphur trioxide vapour which subsequently reacts with atmospheric moisture. Sulphur trioxide reacts with water according to the equation:



Table 1. Stoichiometric summary for selected water reactive chemicals

| WRC | x | y | z |
|------------------------|---|---|---|
| Chlorosulphonic acid | 1 | 0 | 1 |
| Phosphorus oxychloride | 3 | 0 | 3 |
| Thionyl chloride | 1 | 1 | 2 |

It is judged that the vast majority of the evaporating WRC will react with water to form toxic gas(es). Therefore, for the purpose of modelling wind driven releases, it is assumed that all the WRC evaporated by wind reacts with water and there is sufficient atmospheric moisture to facilitate this. The evolution rates of toxic gases can be calculated:

$$E_{w,HCl} = \frac{36.5z}{m} E_{w,WRC} \quad \text{Equation 4}$$

$$E_{w,SO_2} = \frac{64y}{m} E_{w,WRC} \quad \text{Equation 5}$$

where

$E_{w,HCl}$ evolution rate of $\text{HCl}_{(g)}$ from wind driven release of WRC (kg/s)

E_{w,SO_2} evolution rate of SO_2 from wind driven release of WRC (kg/s)

Evaporation Due to Reaction With Water

It is assumed that all the surface water covered by the pool reacts. Therefore, the mass of water available for reaction is calculated as follows:

$$M_{r,H_2O} = \pi r^2 \rho_{H_2O} h_{H_2O} \quad \text{Equation 6}$$

where

M_{r,H_2O} mass of water available for reaction (kg)

r pool radius (m)

ρ_{H_2O} density of water (kg/m^3)

h_{H_2O} depth of water (m)

The quantity of toxic gas can be calculated from the mass of water and the stoichiometry of the reaction. In general, the chemical reaction is of the form described above.

Assuming that there is complete reaction with water, limited by the quantity of available water (i.e. WRC is in excess), the mass of toxic gas produced from the reaction is calculated:

$$M_{r,HCl} = \frac{36.5z}{18x} M_{r,H_2O} \quad \text{Equation 7}$$

where

$M_{r,HCl}$ mass of HCl produced in the reaction (kg)

It is assumed that the mass of toxic gas produced, as a result of reaction with water, is released over a 3 minute period. Therefore, the release rate is calculated as follows:

$$E_{r,HCl} = \frac{36.5z}{18 \times 180x} M_{r,H_2O} \quad \text{Equation 8}$$

where

$E_{r,HCl}$ HCl evolution rate from the reaction with water (kg/s)

Overall Average Evolution Rate

Evolution of toxic gas is assumed to continue for 30 minutes. In most cases, it is understood that HSE assumes that releases from pools last for 30 minutes, by which time it is assumed that onsite emergency action will have controlled the evaporation from the pool. For many releases, it is judged that the pool will reach its maximum radius within 3 minutes after the start of release. Therefore, after 3 minutes the pool will not contact additional surface water. Evaporation due to reaction with surface water is assumed to continue for 3 minutes (180 s), with wind driven evaporation only, continuing for the remaining 27 minutes. Increasing the time for reaction with water tends to decrease the overall average toxic gas release rate. It has been found that the release rates calculated for a 3 minute reaction time with water are broadly in line with those calculated using other models. However, the reaction time with water can be altered to reflect the characteristics of specific releases.

The overall average toxic gas release rate is calculated using the root mean square relationship:

$$E_{av} = \left\{ \frac{E_{r,T}^2 t_r + E_{w,T}^2 (t - t_r)}{t} \right\}^{1/2} \quad \text{Equation 9}$$

where

E_{av} overall average evolution rate (kg/s)

t_r duration of pool reaction with water (s)

t duration of release from pool (s)

CALCULATION OF EGRESS FROM A BUILDING

For releases in buildings, the toxic gas egress will be limited according to the volume of the building and its air change rate. The release rate from the building is calculated using a mass

balance, accounting for the gas release rate into the building and its egress rate from the building. During the period where toxic gas is released from the source, assuming perfect mixing, the release rate from the building is:

$$m_{out} = m_{in} \left(1 - e^{-\frac{q_{air}t}{V_B}} \right) = m_{in} (1 - e^{-kt}) \quad \text{Equation 10}$$

After the release from the source has ceased, assuming perfect mixing, the release rate from the building is:

$$m_{out} = m_{out,max} e^{-\frac{q_{air}(t-t_{max})}{V_B}} = m_{out,max} e^{-k(t-t_{max})} \quad \text{Equation 11}$$

where

- m_{out} release rate of toxic gas from the building (kg/s)
- m_{in} release rate of toxic gas within the building (kg/s)
- q_{air} building ventilation rate (m³/s)
- V_B building volume (m³)
- k building air change rate per second (s⁻¹)

The release rate from the building can be calculated at appropriate times and entered into a suitable transient release dispersion model.

GUIDANCE ON RELEASE SPECIFIC PROPERTIES

The consequence analysis is dependent on release and site specific properties. For example, the available water thickness, building air change rate and ‘indoor’ wind speed. These properties are not amenable to accurate measurement and are likely to be unique to the particular storage arrangement. However, ERM has developed some guidance, based on literary sources and judgement.

WATER THICKNESS

It should be noted that although it is less likely that surface water will be available for reaction with indoor releases, some consideration of its presence is recommended. For example, surface water may accumulate indoors from process water, condensed steam or be transported inside buildings on the surface of vehicles that have been out in the rain. Judgements must be made as to how much water is likely to be present. Furthermore, WRC can react with the water content of substrates such as concrete.

For releases outdoors, it is assumed that water is available to react with any spillage. Although it is recognised that ‘special’ acid resistant and water repellent tiles may limit the amount of water available for reaction, it is understood that HSE would be unlikely to attribute any credit in their calculations. Therefore, even for indoor releases which are more likely to be in ‘dry’ conditions, it is understood that HSE would still assume a small amount

of water. The scheme summarised in Table 2 may be used as guidance on determining the mean water depth.

Table 2. Guidance on mean water depth

| Description | Recommended mean water depth |
|----------------------------------------------------------------------------------|------------------------------|
| Well sealed building or room featuring locking doors, limited openings (if any). | 0.5 mm |
| Sealed road tanker offloading building with roller shutter door. | 1 mm |
| Building or room with frequently opened doors and/or windows. | 1.5 mm |
| Building or room with process water and/or condensed steam frequently present. | 1.5 mm |
| Outside in 'dry' conditions | 2 mm |
| Outside in 'wet' conditions | 5 mm |

BUILDING AIR CHANGE RATE

When estimating a suitable air change rate for a building, the following characteristics need to be considered.

- Is there forced ventilation?
- If so, what height above the ground are the ventilation intakes?
- Is there a noticeable draft?
- Is the building well sealed (double glazing)?
- Are windows and doors typically closed?
- Is the building occupied much of the day by numerous amounts of people?

For example, 5 and 3 air changes per hour (ACH) have been judged suitable for a sulphur trioxide road tanker offloading building and bulk storage building, respectively. Note that buildings used as laboratories, may have a higher air change rate than for a similarly constructed building used for other purposes. This is largely due to the presence of forced ventilation, in the form of fume cupboards or systems to help prevent flammable and/or toxic atmospheres developing. Laboratories and areas having forced ventilation typically have a minimum air change rate of 12 ACH and could be as high as 40 ACH. For such buildings, it may be that the ventilation intakes are sufficiently elevated that toxic gas is unlikely to enter the building via the forced ventilation system.

WIND SPEED WITHIN BUILDING

The wind driven evaporation from a pool inside a building is determined by the assumed wind speed. Although the inside of a building is somewhat shielded from wind, there will be some air movement which will facilitate evaporation by the 'wind driven' mechanism. In general, an upper bound for operator comfort is considered to be 0.5 m/s. Therefore, in practice lower wind speeds may be experienced. Similarly, wind speeds of 5 m/s or greater,

are generally felt as a draft. Therefore, judgement must be used for specific buildings. The following examples are based on judgements made for different types of building:

- Open-sided storage building, ‘dutch barn’ – 2 m/s.
- Road tanker offloading building with roller shutter door, typically closed – 1.5 m/s.
- Typically unoccupied bulk storage building – 0.25 m/s.

DISPERSION MODELLING

The calculated overall average evolution rate or the time dependent release rates from a building are the principal entries to a suitable gas dispersion model. Gas dispersion models are widely described and are included in consequence modelling software such as BP Cirrus⁸. Therefore, gas dispersion models are not described in detail here.

The toxic gases which may be produced when WRCs contact water are typically denser than air at ambient temperature. However, these toxic gases are typically produced in an exothermic reaction which tends to produce ‘warm’ gases. Therefore, the gases tend to be more buoyant and hence, a neutral, ‘Gaussian’ dispersion model is often judged most suitable.

The HSE has published a series of reports on the toxicology of materials in relation to major hazards. These reports are primarily directed at establishing toxicity values for land use planning in the vicinity of industrial facilities. Toxicological data are reviewed to derive a measure referred to as the Dangerous Toxic Load (DTL).

The DTL is associated with a level of impact which is designated the Specified Level Of Toxicity (SLOT) where the SLOT would “...*cause severe distress to almost everyone, many [would] require medical treatment, some [would] be seriously injured and highly vulnerable people might be killed.*” Therefore, to judge the extent of impact to persons from airborne toxic releases, the distance to the SLOT concentration is calculated.

Depending upon the properties of the material, the relationship between concentration and DTL can be linear or non linear:

$$DTL = c^n t \quad \text{Equation 12}$$

where

- c concentration (ppm)
 n concentration exponent (no units)
 t exposure duration (minutes)

The downwind distance at which a person outdoors would receive a dangerous toxic load is calculated. Selected dangerous toxic loads are detailed in Table 3.

The reaction of sulphur trioxide and oleum with water yields sulphuric acid mist. Similarly chlorosulphonic acid yields hydrogen chloride gas. However, other chemicals, for example phosphorus oxychloride and thionyl chloride, can produce more than one toxic component. These substances require further dispersion modelling techniques as follows.

Phosphorus Oxychloride

There is evidence to suggest that, although phosphorus oxychloride (POCl₃) reacts violently with water, a significant proportion may remain unreacted³. Phosphorus oxychloride has the

risk phrase R26, 'Very toxic by inhalation'. The reaction of POCl_3 with water produces hydrogen chloride gas ($\text{HCl}_{(g)}$) (risk phrase R23, 'Toxic by inhalation'). Therefore, it is judged that POCl_3 is 'more toxic' than the toxic gas produced when it reacts with water. However, it is judged that the majority of the POCl_3 will react with atmospheric moisture, on account of its affinity to reaction with water.

Table 3. Selected dangerous toxic loads⁹

| Substance | Dangerous toxic load (ppm ⁿ minute) | Concentration exponent 'n' |
|------------------------|---------------------------------------------------|-------------------------------|
| Hydrogen chloride | 23,700 | 1 |
| Sulphur dioxide | 4.655×10^6 | 2 |
| Sulphuric acid mist | 13,000 | 2 |
| Phosphorus oxychloride | 2,880 | 1 |

Thionyl Chloride

On contact with water, $\text{HCl}_{(g)}$ and $\text{SO}_{2(g)}$ are produced. The release rates of $\text{HCl}_{(g)}$ and $\text{SO}_{2(g)}$ can be calculated. The two components have different dangerous doses, therefore, to calculate a cumulative dose, the release rates are 'standardised'.

In general, at a certain downwind distance, the concentration is proportional to the release rate. That is, double the release rate will produce double the concentration at a particular distance downwind. For example, if a concentration of 100 ppm is calculated at a distance 400 m from the source for 1 kg/s release rate, then a 2 kg/s release will result in a 200 ppm concentration, at that same downwind distance.

The dangerous toxic loads (DTL) for $\text{HCl}_{(g)}$ and SO_2 are 23,700 ppm.minute and 4.655×10^6 ppm².minute, respectively. The corresponding 30 minute SLOT concentrations for $\text{HCl}_{(g)}$ and SO_2 are 790 ppm and 394 ppm, respectively. Therefore, the following two cases yield approximately the same downwind dispersion distance:

1. a release rate of 1 kg/s of SO_2 , modelled to an end point corresponding to a concentration of 394 ppm; and
2. a release rate of 2 kg/s ($790/394 \times 1$ kg/s) of SO_2 , modelled to an end point corresponding to a concentration of 790 ppm.

Therefore, as guidance a release rate of SO_2 can be scaled up (by multiplying by 2) such that its toxic load characteristics can be summed with those of $\text{HCl}_{(g)}$.

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