MODELLING THE DISPERSION OF SPILLS IN BUILDINGS

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Many parts of the chemical industry carry out much of their processing in closed side buildings. This is particularly true where there are large numbers of manual operations and serves to protect raw materials and personnel from the weather. However, this enclosure leads to the accumulation of released chemicals, which can then present flammable or toxic hazards.

Batch chemical manufacturing is characterised by large numbers of different raw materials and intermediateswhich frequently change with seasonal product campaigns or new and different products. Rapid risk ranking techniques are required to assess processes so that the important issues are given appropriate priority.

There are a number of software tools for looking at consequences of loss of containment, but these are primarily targeted at outdoor release and dispersion. Indoor dispersionwithin some of these packages just assumes a source term and good mixing. Evaporation from indoor spills is not commonly addressed.

This paper presents a rapid evaluation technique for assessing the indoor impact of a chemical spill. This can be used to estimate the maximumaccumulated concentration, the speed of concentration build up and hence the time to detection of the chemical spill by monitoring systems or odour. Only molecular weight and an appropriate vapour pressure are required: liquid density can help estimate spill surface area.

INTRODUCTION AND BACKGROUND

The fine and speciality chemicals industry extensively use batch processing often with manual charging. Facilities often have closed sides to protect operators from the weather, but also to protect (what may be at least temporarily open) from ingress of the elements. Although some facilities consistently produce the same product year in year out, others have a turn over of products seasonally, and with the development of new products and processes. These different products and processes bring with them and even larger number of rawmaterials and solvents, all of these need to be risk assessed and techniques applied so that this is carried out as efficiently and effectively as possible.

This model was developed in response to a particular need to evaluate the impact of potential spills of toxic chemicals in a building. The chemicals concerned had very low vapour pressures but very low thresholds of toxicity. Little data was available on the materials.

The type of scenario being examined was during risk assessment where the exact facility to be used had not yet been selected, so exact calculations on the building, its ventilation and the location of a spill were not possible.

Despite the low levels of design information available it is still necessary to be able to estimate the magnitude of hazard so that this can be used in risk assessment. Once this is done it can be ranked against other risks and the an appropriate level of response applied. Such information may also help choose or at least short list an appropriate processing facility. More detailed calculation can be performed at a later stage.

CONCENTRATION FROM RELEASES IN A BUILDING

The concentration in the building and at the vent exit to a building can be estimated from a mass balance. See Figure 1.

Consider a volume V, with a ventilation flowrate Q, and the concentration of the volatile is c. The generic mass balance equation is

$$\text{accumulation} = \text{mass in} + \text{mass generated}$$
$$- \text{mass out} \tag{1}$$

The mass of volatile in the volume is Vc. The evolution rate of volatile into the volume is given by q_v and the flow of volatile out is Qc. We assume no volatile flows in with the ventilation air.

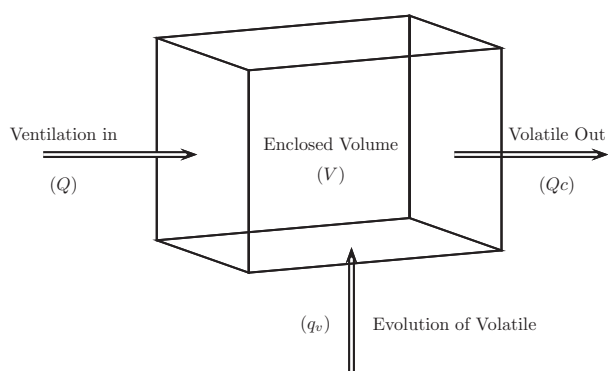Hence the mass balance for this situation can be expressed as

$$\frac{d(Vc)}{dt} = V\frac{dc}{dt}$$
$$= qv - Qc \tag{2}$$

In this particular scenario the evolution of volatile will be evaporation from a spill.

STEADY STATE (MAXIMUM CONCENTRATION)

At steady state accumulation is zero which means (2) can be solved for concentration to give:

$$c_\infty = \frac{qv}{Q} \tag{3}$$

Figure 1. Mass balance on volatile released in an enclosure

TIME VARIANT PREDICTIONS

By rearrangement of (2) we can solve for t

$$t = V \int \frac{dc}{q_v - Qc} \qquad (4)$$

using standard integral

$$\int \frac{dx}{a + bx} = \frac{1}{b} ln(a + bx)$$

leads to

$$t = \frac{-V}{Q} ln(qv - Qc) + const \qquad (5)$$

by the use of the boundary conditions we can solve for the constant.

$$c = 0$$

$$\implies const = \frac{V}{Q} ln(qv)$$

$$t = 0$$

substituting back into (5) gives

$$t = \frac{-V}{Q} ln\left(1 - \frac{Qc}{qv}\right) \qquad (6)$$

solving for concentration as a function of time this gives

$$c = \frac{qv}{Q}\left(1 - exp\left(\frac{-tQ}{V}\right)\right) \qquad (7)$$

This is a comparable expression to that in Leach and Bloomfield [5] which is for the situation where contaminated air enters a room which is also ventilated by fresh air. In the manner of Leach and Broomfield it can be expressed in terms of the steady state concentration

defined in (3).

$$c = c_{\infty}\left(1 - exp\left(\frac{-tQ}{V}\right)\right) \qquad (8)$$

NON-IDEAL MIXING

In practice mixing is often less than perfect, and this is possible even with forced ventilation systems. Back in 1946 Lidwell and Lovelock [7] noted that concentration decay did not necessarily follow the idealised curve, nor was it necessarily uniform throughout a room. Drivas et al. [2] used tracer gas to study actual residence time distributions for laboratories. They used a mixing factor which is the ratio of the theoretical characteristic time for one air change (i.e. volume divided by flowrate) to the experimentally determined effective time.

$$k_{mix} = \frac{V/Q}{t_{exp}} \qquad (9)$$

Esmen [4] points out that the use of such a definition risks violating the mass balance. Esmen proposes an alternative definition where the mixing factor is the portion of the ventilation air which is completely mixed with the room air. Such an approach is in keeping with the short-circuiting concept used by Reinke and Brosseau [11], and is also included in other models [18]. However, Esmen uses the values of the experimentally determined mixing factor and the same mathematical form.

According to Drivas [2] the mixing factor varies between 1/3 and 1/10. Esmen [4] qualifies this as being for small rooms and that for large spaces it may be even smaller. Much of the work has been performed on domestic and office buildings, but without evidence to show that chemical plants with large internal areas are worse mixed than other buildings it is reasonable to assume a similar order of magnitude for mixing factors.

The effect of the mixing factor will be to decrease exit concentrations below the well mixed theory and to increase accumulated concentrations. In practice it may be easiest to assume that some local concentrations will be up to 10 times the steady state concentration for a well mixed space.

Ventilation Rate

Ventilation rate for buildings housing chemical processes is generally assumed to be in the range of 3 to 4 air changes per hour. Actual ventilation rates can vary by an order of magnitude depending on the prevalent weather conditions [13]. Even buildings with forced ventilation systems will have variable airflow rates through the mas fans are not fixed volume devices. Chemical process buildings do vary as to whether they are naturally or force ventilated. For the purposes of this model assuming 3 to 4 air changes per hour will be a reasonable estimate, unless local knowledge has conflicting data.

EVAPORATION FROM SPILL
To form the mass balance we need the to be able to calculate the vapour evolution term. This is the product of the area available for mass transfer and the flux rate.

$$qv = q_v'' A \qquad (10)$$

This model uses an isothermal approach to simplify calculations. Reinke and Brosseau [11] used this approach sucessfully for predicting the behaviour of actual indoor spills.

ESTIMATING POOL SIZE (AREA)
If bunds or curbs are present then pool size will be dictated by these physical constraints. Otherwise as a first approximation assume the pool depth to be 1 cm [3] and use the volume spilt and liquid density to give the surface area. It is reasonably conservative to assume a relative liquid density of 0.7.

FLUX FROM AN EVAPORATING POOL
The model for evaporation from a pool in line with methods from the "*TNO Yellow Book* [17]".

Assume a volatile solvent below boiling point where evaporation only takes place at the liquid surface. The flux can be calculated from the vapour pressure at the liquid surface ($z = 0$), and the mass transfer coefficient.

$$q_v'' = D_v \frac{dc_i}{dz}$$
$$= k_m c_i(z = 0) \qquad (11)$$

By using the perfect gas assumption the concentration can be restated in terms of molecular weight, temperature of the liquid surface and vapour pressure at that temperature.

$$c_i = \mu_i \frac{n}{v}$$
$$= \mu_i \frac{P_v(T_{ps})}{RT_{ps}} \qquad (12)$$

Substituting 12 into 11 gives:

$$q_v'' \approx \frac{k_m \mu_i P_v(T_{ps})}{RT_{ps}} \qquad (13)$$

Strictly the driving force should be the difference between the saturation vapour pressure of the volatile and the ambient vapour pressure. If the ambient vapour pressure is sufficiently low then this term can be ignored.

VAPOUR PRESSURE
Although for many compounds detailed correlations exist for vapour pressure and other physical properties data the materials of real interest for this methodology often have scant data, and are likely to only have a single data point for vapour pressure, such as appears on the safety data sheet, at 15 or 20°C. For some of the scenarios of concern this would be adequate. The model ignores much of the heat transfer and cooling effects associated with pool evaporation, so not having a correlation is not an issue in this case.

MASS TRANSFER COEFFICIENT
A commonly [6, 11, 14, 15] used mass transfer coefficient for pool evaporation is the Mackay and Matsugu [8] definition

$$k_m = \frac{C_{m\&m} u_{w,10}^{0.78}}{(2r_p)^{0.11} Sc^{0.67}} \qquad (14)$$

The constant is quoted as 0.004786. This definition is from the "Yellow book" [17] where the units are different to the original reference. Calculation from the original reference suggests that the value should actually be 0.00482, although the original reference makes use of a wind speed at 1 m height and the "Yellow book" uses 10 m height. Given the other assumptions of the model the associated errors will be low.

Sparks et al. [14] also use a mass transfer coefficient for indoor environments (for coating materials) which is a similar order of magnitude to the Mackay and Matsugu mass transfer coefficient. Reinke and Brosseau [11] also looked at a flat plate mass transfer coefficient and one derived from penetration theory.

The Mackay and Matsugu mass transfer coefficent was determined outdoors where winds may be more unidirectional thanmight be expect outdoors, but it was derived for evaporating pools, and also some of the data used was for very low wind speeds. Reinke and Brosseau [11] used it sucessfully for predicting the results of spills in a laboratory.

SCHMIDT NUMBER
The Schmidt number is given by

$$Sc = \frac{v_v}{D_v} \qquad (15)$$

The "Yellow book" [17] points out that in general for gases and vapours a figure of 0.8 should be conservative. This conclusion is supported by the data presented in Sparks et al. [14] for several species.

If using this approximation is not acceptable the diffusivity will needed. References such as Cussler [1] or Thibodeaux [16] contain tables of diffusivities in air for a number of species, although many of those of particular interest are not listed. The diffusivity of the species in air can be calculated by methods such as those contained in Poling et al. [10] (there are even online tools to perform the calculations).

Thibodeaux [16] suggests that Graham's law can be used to relate diffusivity of a known species to an unknown species based on the ratio of the square of molecular weights

$$\frac{D_{A1}}{D_{A2}} = \sqrt{\frac{\mu_2}{\mu_1}} \qquad (16)$$

This result is used by Matthiessen [9] who then combines it with another relationship for Thibodeaux relating mass transfer coefficient to diffusivity.

$$\frac{K}{K_{ref}} = \left(\frac{D}{D_{ref}}\right)^{2/3} \qquad (17)$$

Combining (16) with (17) leads to

$$K = K_{ref}\left(\frac{\mu_{ref}}{\mu}\right)^{1/3} \qquad (18)$$

Hence, a mass transfer coefficient for a species can be calculated from a known mass transfer coefficient for another species provided that molecular masses of the two components are known. The mass transfer coefficient according to (14) is weakly dependent on the pool radius, so further uncertainty may be added if it is not applied to a similarly sized spill, although in the context of this model this may be unimportant.

WIND SPEED

According to Rothschild [12] wind speed can be approximated by ventilation air flowrate divided by the end cross sectional area of the building.

$$u = \frac{Q}{WH}k_{vent} \qquad (19)$$

This wind speed can then be modified by a ventilation factor. Rothschild suggests using a factor of 0.5 for areas of poor ventilation (for example corners), and 2 for areas of good ventilation (near to ventilation inlets or outlets) and otherwise 1. See Figure 2 for an illustration. It should be noted that areas with poor ventilation will also have a correspondingly lower mixing factor.
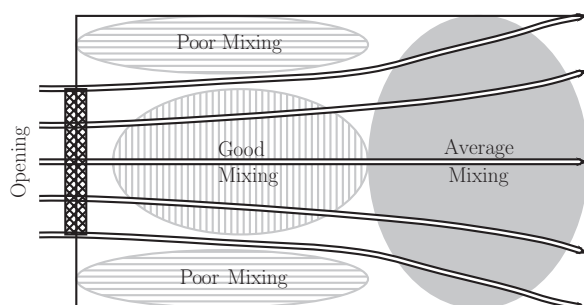

Figure 2. Ventilation factor in a building

Actual wind speeds may be have a distribution stretching to almost zero, although the form of this distribution is unknown. Assuming a ventilation factor of one will suffice to provide an appropriate order of magnitude estimate.

CONCLUSIONS

A model has been presented to estimate concentrations in a building following a spill. An idea of the likely magnitude of events will be needed. For the material itself the model only requires molecular weight and an appropriate vapour pressure. Some simple data on the size of the building is also required to estimate another parameter.

The model can also estimate the time take for concentration to rise.

NOMENCLATURE

A	area of spill	[m^2]
ci	concentration of component i	[kg/m^3]
$C_{m\&m}$	Mackay and Matsugu mass transfer constant (0.004786)	[m$^{0.33}$/s$^{0.22}$]
D_v	vapour diffusion coefficient in air	[m^2/s]
H	building height	[m]
k_m	mass transfer coefficient	[m/s]
k_{mix}	mixing factor (dimensionless)	[−]
k_{vent}	ventilation factor	[−]
n	amount of substance	[mole]
P_v	saturation vapour pressure at surface temperature	[Pa]
Q	Volumetric flowrate	[m^3/s]
q_v	liquid evaporation rate	[kg/s]
q''_v	vapourisation mass flux	[kg/m^{2}s]
R	Universal gas constant	[J/(mol K)]
r_p	Pool radius	[m]
Sc	Schmidt number (dimensionless)	[−]
t_{exp}	experimental characteristic time for 1 air change	[s]
T_{ps}	temperature at pool surface	[K]
$u_{w,10}$	wind speed at standard 10 m height	[m/s]
V	volume of building or room	[m^3]
v	volume	[m^3]
W	building width	[m]
z	distance in vertical direction	[m]

GREEK SYMBOLS

μ	molecular weight of component i	[kg/mole]
u	kinematic viscosity	[m^2/s]

SUBSCRIPTS

ref	reference material

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