A Summary of the Dow Chemical Company’s quick method to calculate toxic vapour dispersion

The Dow Chemical Company was a participant in the S2S consortium.

This description supports the software calculation tool also available from S2S. ( CEI_workbook_s2s.xls )

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The Chemical Exposure Index (CEI) provides a simple method of rating the relative acute health hazard potential to people in neighboring plants or communities from possible chemical release incidents. Absolute measures of risk are very difficult to determine, but the CEI system will provide a method of ranking one hazard relative to another. It is **NOT** intended to define a particular design as safe or unsafe.

The CEI is used:

- For conducting an initial Process Hazard Analysis (PHA)
- As a screening tool for further study
- In Emergency Response Planning.
1. To develop a Chemical Exposure Index (CEI), the following items are needed:
   a. An accurate plot plan of the plant and the surrounding area.
   b. A simplified process flow sheet showing containment vessels, major piping and chemical inventories.
   c. Physical and chemical properties of the material being investigated, as well as the AIHA ERPG values.

   Figure 1 is a schematic overview of the CEI calculation. This chart will be helpful as you proceed through this guide.

2. Identify on the process flow sheet any process piping or equipment that could contribute to a significant release of an acutely toxic chemical.

3. Determine the Chemical Exposure Index and the Hazard Distances as explained in the following pages of this guide.

4. Fill out a summary form for CEI
FIGURE 1

PROCEDURE FOR CALCULATION OF CHEMICAL EXPOSURE INDEX (CEI)

1. Define Possible Chemical Release Incidents
2. Determine ERPG-2
3. Determine the Airborne Quantity (AQ) of scenarios
4. Select scenario with largest Airborne Quantity (AQ)
5. Calculate the CEI
6. Calculate the Hazard Distances
7. Complete CEI Summary Sheets
The purpose of scenario selection is to determine which process piping or equipment has the greatest potential for the release of significant quantities of acutely toxic chemicals. Since the CEI now serves as a screening tool for further process hazards analysis, it is important that the calculations be done consistently on a global basis. The scenario selection process for determining airborne release rate has, therefore, been standardized to help achieve this goal.

Evaluating several scenarios will aid in determining the largest potential airborne release. Process conditions such as temperature, pressure and physical state should be considered as well as pipe size since they have a significant impact on airborne release rates.

### Scenario Selection for CEI:

1. **PROCESS PIPES**
   - Rupture of the largest diameter process pipe as follows:
     - For smaller than 2-inch diameter — full bore rupture
     - For 2- to 4-inch diameter — rupture equal to that of 2-inch diameter pipe
     - For greater than 4-inch diameter — rupture area equal to 20% of pipe cross section area

2. **HOSES**
   - Full bore rupture

3. **PRESSURE RELIEF DEVICES RELIEVING DIRECTLY TO THE ATMOSPHERE**
   - Calculated total release rate at set pressure. Refer to pressure relief calculation or contact process engineering. All material released is assumed to be airborne.

4. **VESSELS**
   - Rupture based on largest diameter process pipe attached to the vessel using pipe criteria above.

5. **TANK OVERFLOWS AND SPILLS**

6. **OTHERS**
   - Scenarios can be established based on the plant’s or technology’s experience, they can be the outcome of a review or derived from hazard analysis studies. They can also be based on the experience of another technology if the event could occur in this unit. Contact Process Engineering for special cases that may include reactivity or mixtures.

The treatment of instantaneous and very short duration continuous releases is simplified for the CEI calculation. Release from all scenarios are assumed to continue for at least a five minute duration. If a release is instantaneous or exceeds the total inventory within this duration, the release rate is calculated by dividing the total inventory by five minutes.

*After this evaluation, choose the largest airborne release rate for the CEI calculation*
The American Industrial Hygiene Association (AIHA) has published Emergency Response Planning Guidelines® (ERPG) values which are intended to provide estimates of concentration ranges where one might reasonably anticipate observing adverse effects.

These guidelines are intended to be used as a planning tool for various Process Safety programs to determine priority concerns, to evaluate the adequacy of containment, to identify downwind areas which might need to take action during a release and to develop community emergency response plans. The need for an ERPG is based on the volatility of a chemical, its toxicity, the releasable quantity and the public’s perception of the potential hazard.

ERPG definitions are as follows:

**ERPG-1** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for one hour without experiencing other than mild transient adverse health effects or perceiving a clearly objectionable odor.

**ERPG-2** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.

**ERPG-3** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.
This section of the CEI guide provides a description of the method to calculate the airborne quantity. The airborne quantity, as used in this guide, refers to the total quantity of material entering the atmosphere over time, directly as vapour or due to liquid flashing or pool evaporation.

CEI scenarios consider materials to be released as liquid or vapour. For example, the contents of a vessel can escape as a liquid through nozzle A, a vapour through nozzle B or “as calculated” through the relief device attached to nozzle C. Complex calculations that consider two-phase flow from ruptures are not included.

Airborne quantity for vapour releases from nozzle (B) or a pressure relief device (C) is the highest total flow rate calculated given the conditions of the vessel when the release occurs.

Liquid releases require a more complex treatment. As a liquid exits a vessel or pipe as a result of a failure, it can simply run out on the ground forming a pool (see Figure A), partially vapourize forming both a pool and a vapour cloud (see Figure B) or flash to such an extent that all the residual liquid exists as small droplets that are carried away with the vapour (see Figure C).

A simple treatment of these events uses the operating conditions of the process to estimate the behavior of the material after the release.
Liquids reaching the ground form a pool that spreads according to the terrain. If the vessel is surrounded by a dike, the liquid usually flows to the walls of the dike and the pool assumes the area within the dike. In all other cases, the pool is assumed to have an area that is predicted by the amount of liquid that enters the pool. Once a pool is formed, the liquid begins to evaporate from the surface. The vapour from the pool will combine with the vapour from the original flash and be dispersed downwind. This incident is treated by taking a “picture” of the release at a moment in time and then assuming it does not change. (See Figure D)

![Figure D](image)

The airborne quantity for a liquid spill is determined by what happens to the liquid as it leaves the tank. If the liquid flashes to a high degree, then the airborne quantity is the discharge rate from the vessel. But if the liquid flash is low enough to allow pool formation, the airborne quantity is the gas flow resulting from the flash plus the airborne quantity that evaporates from the pool surface. Finally, as the tendency of the liquid to flash becomes small, the airborne quantity becomes the rate of evaporation from the pool surface.

Figure 2 provides a simplified flowchart for calculating airborne quantity.
FIGURE 2
FLOWCHART FOR CALCULATING AIRBORNE QUANTITY

Start

Airborne Quantity (AQ) known

No

Type of release

Gas

Calculate AQ (Eqn. 1)

Select scenario with largest AQ then go to CEI calculation (Eqn. 10)

Liquid

Calculate liquid release rate (Step 1, Eqn. 2)

Determine total liquid released (Step 2, Eqn. 3)

Operating temp. less than boiling point

No

Calculate flash (Step 3, Eqns. 4, 5)

Yes

Determine pool size (Step 4, Eqns. 6, 7)

Determine vapor from pool (Step 5, Eqn. 8)

Calculate AQ (Step 6, Eqn. 9)

Yes

Is all material airborne?

No

Yes

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The following equations, based on the sonic gas flow rate equation, are used to estimate the airborne quantity for a gas release.

Airborne Quantity (AQ) = \(4.751 \times 10^{-6} D^2 \frac{P_a \sqrt{MW}}{T + 273}\) \(\text{kg/sec}\) \(\text{ (Equation 1A)}\)

*where*
- \(P_a\) = absolute pressure = \(P_g + 101.35\)
- \(P_g\) = gauge pressure (kPa gauge)
- \(MW\) = molecular weight of the material
- \(T\) = temperature \(^\circ\text{C}\)
- \(D\) = diameter of the hole (millimetres)
The following steps describe a simplified procedure for estimating the airborne quantity for liquid releases.

**Step 1: Determine the liquid flow rate being released.**

The liquid release rate \( L \) is given by the following equations:

\[
L = 9.44 \times 10^{-7} D^2 \rho_l \sqrt{\frac{1000 P_g}{\rho_l} + 9.8 \Delta h}
\]

(Equation 2A)

Where:

- \( P_g \) = gauge pressure (kPa gauge)  
  *(Note: for a tank open to the atmosphere \( P_g = 0 \))*
- \( \rho_l \) = density of the liquid at operating temperature (kg/m³)
- \( \Delta h \) = height of the liquid above the release point (metres)
- \( D \) = diameter of the hole (millimetres)

**Step 2: Determine the total liquid released.**

The total amount of material contributing to the pool formation must be estimated in order to determine the pool size. If a release is large enough to empty a vessel in less than 15 minutes (including very large releases that occur in less than 5 minutes), the mass of liquid entering the pool is the total inventory of the vessel. For a longer duration continuous release (one lasting more than 15 minutes) the pool is assumed to reach a final size after 15 minutes. In this case, the mass determining the pool size is the release rate times 15 minutes (900 seconds).

The total liquid release \( W_T \) is the tank inventory (the tank is emptied in less than 15 minutes) or given by:

\[
W_T = 900 L
\]

(Equation 3A)

Where:

- \( L \) = liquid flow rate (kg/sec)

Compare the calculated \( W_T \) to the inventory of the system involved in the release. The total liquid assumed to be involved in the release is taken as the smaller of these two values.

\[ W_T = \text{smaller of calculated } W_T \text{ or system inventory} \]

**Step 3: Calculate the fraction flashed.**

Compare the operating temperature of the liquid to its normal boiling point. If the temperature is less than the normal boiling point, the flash fraction is zero. Go to Step 4, Equation 6. If the temperature is greater than the normal boiling point, calculate the fraction flashed \( F_v \).

The fraction of the liquid that will flash \( F_v \) when released is given by:

\[
F_v = \frac{C_P}{H_v} (T_s - T_b)
\]

(Equation 4)
where

\[ \begin{align*}
T_b &= \text{normal boiling point of the liquid} \quad \degree \text{C} \\
T_s &= \text{operating temperature of the liquid} \quad \degree \text{C} \\
C_p &= \text{average heat capacity of the liquid} \quad \text{J/kg}/\degree \text{C} \\
H_v &= \text{heat of vapourization of the liquid} \quad \text{J/kg}
\end{align*} \]

The CEI data table contains the ratio of heat capacities to latent heats of vaporization \( \left( \frac{C_p}{H_v} \right) \) for many chemicals. If a chemical is not listed and the needed information cannot be found, then a value of 0.0044 (SI) may be used for the ratio \( \frac{C_p}{H_v} \).

As flashing occurs, some liquid will be entrained as droplets. Some of the droplets are quite small and travel with the vapour while the larger droplets fall to the ground and collect in a pool. As an approximation, the amount of material staying in the vapour is five times the quantity flashed. Therefore, if 20% of the material flashes, the entire stream becomes airborne and there is no pool formed.

The airborne quantity produced by the flash (AQf) is given by:

\[ \text{AQf} = 5 \cdot (F_v) \cdot (L) \quad \{\text{kg/sec}\} \quad (\text{Equation 5}) \]

where

\( L = \text{liquid flow rate (kg/sec)} \)

If \( F_v \geq 0.2 \) then \( \text{AQf} = L \) and no pool is formed. Proceed to Step 6.

**Step 4: Determine the pool size.**

The total mass of liquid entering the pool (\( W_p \)) is given by:

\[ W_p = W_T \cdot (1 - 5F_v) \quad \{\text{kg}\} \quad (\text{Equation 6}) \]

where

\( W_T = \text{total liquid released (kg)} \)

\( F_v = \text{fraction flashed} \)

Please note that if none of the material flashes,

\[ W_p = W_T \quad \{\text{kg}\} \]

The size of the pool is approximated by assuming a pool depth of one centimeter. If the spill is in a diked area and of sufficient size, then the pool size is equal to the diked area.

The pool area (\( A_p \)) is given by:

\[ \text{Pool Area} (A_p) = 100 \cdot \frac{W_p}{\rho_l} \quad \{\text{m}^2\} \quad (\text{Equation 7A}) \]

where

\( W_p = \text{total mass entering the pool (kg)} \)

\( \rho_l = \text{density (kg/m}^3\)
If the liquid falls into a diked containment area, then the pool size may be equal to the diked area minus the area taken up by the tank. But, if the spill does not fill the diked area or occurs outside the diked area, use $A_p$.

**Step 5: Determine the airborne quantity evaporated from the pool surface.**

Airborne Quantity evaporated from the pool surface ($AQ_p$) is given by:

$$AQ_p = 9.0 \times 10^{-4} (A_p^{0.95})(MW) \frac{P_v}{T + 273}$$

{kg/sec}

(Equation 8A)

where

- $A_p$ = pool area (m²)
- $MW$ = molecular weight
- $P_v$ = vapour pressure of the liquid at the characteristic pool temperature (kPa)
- $T$ = characteristic pool temperature (°C) (see Conditions 1 and 2)

**Condition 1**

If the liquid is at or above ambient temperature but below its normal boiling point, the characteristic pool temperature is equal to the operating temperature.

**Condition 2**

If the liquid is at or above its normal boiling point, the characteristic pool temperature is the normal boiling point of the liquid. The normal boiling point is the boiling point of the liquid at atmospheric pressure.

**Step 6: Calculate the total airborne quantity.**

The total airborne quantity ($AQ$) is calculated by:

$$AQ = AQ_f + AQ_p$$

{kg/sec}

(Equation 9)

where

- $AQ_f$ = airborne quantity resulting from the flash (kg/sec)
- $AQ_p$ = airborne quantity evaporating from the pool surface (kg/)

If the total Airborne Quantity ($AQ$) is greater than the liquid flow rate ($L$), set $AQ = L$. 
Chemical Exposure Index

All CEI calculations assume a windspeed of 5 m/sec and neutral weather conditions.

The Chemical Exposure Index (CEI) is given by:

\[
\text{CEI} = 655.1 \frac{\text{AQ}}{\text{ERPG-2}}
\]

(Equation 10A)

where

AQ = airborne quantity (kg/sec)
ERPG-2 = value (mg/m³)

If the CEI calculated value is greater than 1000, set CEI = 1000.

Hazard Distance

The Hazard Distance (HD) is the distance to the ERPG-1, -2 or -3 concentration and is derived from the following equation:

\[
\text{HD} = 6551 \frac{\text{AQ}}{\text{ERPG}} \text{ (metres)}
\]

(Equation 11A)

where

AQ = airborne quantity (kg/sec)
ERPG = ERPG-1, ERPG-2 or ERPG-3 (mg/m³)
CHLORINE VAPOUR RELEASE

The 3/4 inch vapour connection on a 1 ton chlorine cylinder stored at ambient temperature (30 °C or 86 °F) has broken.

Needed information:

- Pressure inside the cylinder, $P_g$: 788.1 kPa gauge
- Absolute Pressure, $P_a$: 889.5 kPa
- Molecular Weight, MW: 70.91
- Storage Temperature, $T$: 30 °C
- Diameter of Hole, $D$: 19 mm

Determine Airborne Quantity.

(Equation 1A)

$$AQ = 4.751 \times 10^{-6} \times D^2 \times \frac{MW}{(T+273)}$$

$$AQ = 4.751 \times 10^{-6} \times (19)^2 \times \frac{70.91}{(30+273)}$$

$$AQ = 0.74 \text{ kg/sec}$$

Calculate the CEI.

(Equation 10A)

where ERPG-2 = 9 mg/m³

$$CEI = 655.1 \sqrt{\frac{AQ}{ERPG-2}}$$

$$CEI = 655.1 \sqrt{\frac{0.74}{9.0}}$$

$$CEI = 188$$
Calculate Hazard Distances.

*Equation 11A*

For ERPG-2 = 9 mg/m³

\[ HD = 6551 \sqrt{\frac{AQ}{ERPG}} \]

\[ HD = 6551 \sqrt{\frac{0.74}{9}} \]

HD = 1,878 metres

For ERPG-1 = 3 mg/m³

\[ HD = 6551 \sqrt{\frac{0.74}{3}} \]

HD = 3,254 metres

For ERPG-3 = 58 mg/m³

\[ HD = 6551 \sqrt{\frac{0.74}{58}} \]

HD = 740 metres
AMMONIA LIQUID RELEASE

Ammonia is stored in a 12 ft diameter by 72 ft long horizontal vessel under its own vapour pressure at ambient temperature (30 °C or 86 °F). The largest liquid line out of the vessel is 2 inch diameter (50.8 mm).

Needed information:

- Pressure inside vessel, $P_g$ 1064 kPa gauge
- Temperature inside vessel, $T$ 30 °C
- Normal boiling point -33.4 °C
- Liquid density in vessel, $\rho_l$ 594.5 kg/m$^3$
- Ratio $C_p/H_v$ 4.01 E-03
- Height of liquid in tank, $\Delta h$ 3.66 m
- Diameter of hole, $D$ 50.8 mm
- Molecular weight, MW 17.03

Estimate liquid released.

(Equation 2A)

$$L = 9.44 \times 10^{-7} D^2 \rho_l \sqrt{\frac{1000 P_g}{\rho_l} + 9.8 \Delta h}$$

$$L = 9.44 \times 10^{-7} (50.8)^2 (594.5) \sqrt{\frac{1000(1064)}{594.5} + 9.8(3.66)}$$

$$L = 61.9 \text{ kg/sec}$$

Estimate flash fraction.

(Equation 4A)

$$F_v = \frac{C_p}{H_v} (T_v - T_b)$$

$$F_v = 0.00401(30-(-33.4))$$

$$F_v = 0.254$$

Since $F_v > 0.2$ \( AQ = L \)

$$AQ = 61.9 \text{ kg/sec}$$
Calculate CEI.

(Equation 10A)

where ERPG-2 = 139 mg/m³

\[
\text{CEI} = 655.1 \sqrt{\frac{\text{AQ}}{\text{ERPG-2}}}
\]

\[
\text{CEI} = 655.1 \sqrt{\frac{61.9}{139}}
\]

\[
\text{CEI} = 437
\]

Calculate the Hazard Distances.

(Equation 11A)

For ERPG-2 = 139 mg/m³

\[
\text{HD} = 6551 \sqrt{\frac{\text{AQ}}{\text{ERPG}}}
\]

\[
\text{HD} = 6551 \sqrt{\frac{61.9}{139}}
\]

\[
\text{HD} = 4,372 \text{ meters}
\]

For ERPG-1 = 17 mg/m³

\[
\text{HD} = 6551 \sqrt{\frac{61.9}{17}}
\]

\[
\text{HD} = 12,500 \text{ metres}
\]

For ERPG-3 = 696 mg/m³

\[
\text{HD} = 6551 \sqrt{\frac{61.9}{696}}
\]

\[
\text{HD} = 1,953 \text{ metres}
\]
CHLORINE LIQUID RELEASE

Chlorine is stored in a sphere at 5 °C A 2-inch nozzle fails on the bottom of the vessel allowing liquid to escape.

Needed information:

- Pressure inside the cylinder, $P_g$ 332 kPa gauge
- Molecular weight, MW 70.91
- Storage temperature, $T$ 5 °C
- Liquid density, $\rho_l$ 1458 kg/m³
- Height of liquid in the sphere, $\Delta h$ 6 m
- Diameter of hole, $D$ 50.8 mm
- Capacity of sphere 1.134 x 10⁶ kg

Estimate liquid released.

(Equation 2A)

$$L = 9.44 \times 10^{-7} D^2 \rho_l \sqrt{\frac{1000 P_g}{\rho_l}} + 9.8 \Delta h$$

$$L = 9.44 \times 10^{-7} (50.8)^2 (1458) \sqrt{\frac{1000(332)}{1458}} + 9.8 (6)$$

$L = 60.1$ kg/sec

Determine the total liquid released.

For 15 minutes (900 seconds), the total liquid leaving the tank is:

$$W_T = 900(60.1) = 54,090 \text{ kg}$$

The capacity of the tank when full is 1.134 x 10⁶ kg. Since $L_T = 54090$ kg is less than the capacity of the tank.

$$W_T = 54,090 \text{ kg}$$

Calculate the flash fraction.

Needed information:

- Normal boiling point temperature $= -34$ °C
- Heat of vaporization $= 275,030$ J/kg
- Heat capacity of liquid (at average temperature) $= 943.8$ J/kg°C

A technically correct solution for evaluating the flash fraction requires the heat capacity ($C_p$) to be evaluated at the average temperature (storage and boiling point) and the heat of vapourization at the boiling point. For example:

$$C_p (@ -15 \text{ °C}) = 943.8 \text{ J/kg°C}$$

and

$$H_v (BP) = 285,457 \text{ J/kg}$$
(Equation 4A)

\[ F_v = \frac{C_p}{H_v}(T_b - T_a) \]

\[ F_v = \frac{943.8}{285,457} \left( 5 - (-34.0) \right) \]

\[ F_v = 0.129 \]

Calculate vapour source strength from the flash.

\[ A_{Q_f} = 5(F_v)(L) = 5(0.129)(60.1) \text{ kg/sec} \]

Calculate the total liquid entering the pool.

\[ W_p = W_T (1 - 5F_v) = 54,090(1 - (5)(0.129)) = 19,202 \text{ kg} \]

Liquid density of chlorine at its boiling point = 1,562 kg/m³

(Equation 7A)

\[ A_p = 100 \frac{W_p}{\rho_l} \]

\[ A_p = 100 \frac{19202}{1562} \]

\[ A_p = 1,229 \text{ m}^2 \]
Calculate the vapour flow rate from the pool.

Since chlorine is boiling in the pool, \( P_v = 101.3 \text{ kPa} \) Molecular weight of chlorine = 70.91

\[(\text{Equation 8A})\]

\[
AQ_p = 9.0 \times 10^{-4} \left( \frac{A_p^{0.95}}{T+273} \right) (\text{MW}) \frac{P_v}{T}
\]

\[
AQ_p = 9.0 \times 10^{-4} \left( \frac{1229^{0.95}}{(-34.0)+273} \right) \frac{70.91(101.3)}{(-34.0)+273}
\]

\[
AQ_p = 23.3 \text{ kg/sec}
\]

Calculate source strength of release.

\[(\text{Equation 9A})\]

\[
AQ = AQ_f + AQ_p
\]

\[
AQ = 38.8 + 23.3
\]

\[
AQ = 62.1 \text{ kg/sec}
\]

Compare to the liquid release: 62.1 kg/sec is greater than 60.1 kg/sec

\[
AQ = 60.1 \text{ kg/sec}
\]

Calculate the CEI.

\[(\text{Equation 10A})\]

where ERPG-2 = 9 mg/m³

\[
\text{CEI} = 655.1 \sqrt{\frac{AQ}{\text{ERPG-2}}}
\]

\[
\text{CEI} = 655.1 \sqrt{\frac{60.1}{9}}
\]

\[
\text{CEI} = 1,963
\]

This is greater than 1000; thus

\[
\text{CEI} = 1,000
\]
Calculate the Hazard Distances.

*(Equation 11A)*

*For ERPG-2 = 9 mg/m³*

\[
\text{HD} = 6551 \sqrt[ \frac{\text{AQ}}{\text{ERPG}} ]
\]

\[
\text{HD} = 6551 \sqrt[ \frac{60.1}{9} ]
\]

\[
\text{HD}=16,929\text{metres}
\]

HD is greater than 10,000 metres, thus

\[
\text{HD}=10,000\text{metres}
\]

*For ERPG-1 = 3 mg/m³*

\[
\text{HD} = 6551 \sqrt[ \frac{60.1}{3} ]
\]

\[
\text{HD}=29,321\text{metres}
\]

HD is greater than 10,000 metres, thus

\[
\text{HD}=10,000\text{metres}
\]

*For ERPG-3 = 58 mg/m³*

\[
\text{HD} = 6551 \sqrt[ \frac{60.1}{58} ]
\]

\[
\text{HD}=6,668\text{metres}
\]