

## Introduction

This is a follow-up the previous, 'Chlorine in General' article, and will provide more information concerning chlorine gas. In particular, it will try to explain some of the reasons behind the actions specified in the emergency response guides.<sup>1</sup>

## Properties

MW	70.91
CAS	7782-50-5
Boiling point	-34 deg C
Gas density	2.5 (air = 1.00)
Liquid density	1.41 kg/L (20 deg C)
Liquid to vapour	457 times expansion
Vapour pressure	689 kPa (or 6.8 atm)
Solubility	0.73 % (20 deg C)

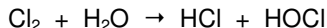
Chlorine is a greenish - yellow gas, which is visible down to 2-3% in air. It has a sharp, suffocating, bleach-like odour, and when compressed, forms a clear, amber liquid.

## Reactions

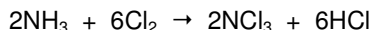
Chlorine is a powerful oxidizer, and will react with many compounds. Some reactions with commonly available substances such as oils, greases, solvents and hydrocarbons can be violent, even explosive. For this reason safety information for chlorine, always carries warnings not to use greases and lubricants (unless designed for chlorine), and to avoid contamination of fittings used in chlorination systems.

Chlorine will immediately react on contact with aluminium, while most other common metals will be corroded in the presence of moisture, or humidity.

Chlorine is slightly soluble in water, in which the solubility is associated with a reaction to form dilute hydrochloric and hypochlorous acid.



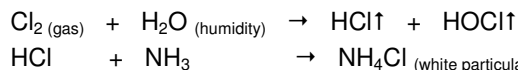
Chlorine also reacts with ammonia to form nitrogen trichloride, an unstable, highly explosive gas.



It is therefore a requirement under the Australian Standards, that chlorine and anhydrous ammonia must be stored at least 10 metres apart.<sup>2</sup>

Dilute ammonia vapours however, are used to detect chlorine leaks in chlorination systems. A 'puff' of ammonia is directed towards the suspected leak, by squeezing a plastic bottle containing dilute ammonia solution. A transient white smoke indicates a leak.

This smoke forms by the following mechanism:



Chlorine reacts with moisture in the air to form hydrogen chloride, which then reacts with ammonia to form ammonium chloride particulates, which is the smoke. The chlorine is sufficiently dilute that it is consumed by excess humidity, and the nitrogen trichloride reaction is avoided.

Chlorine also reacts with caustic soda, to form sodium chloride and sodium hypochlorite.



This reaction is used to manufacture sodium hypochlorite and as a means to neutralize chlorine as a consequence of a major leak.<sup>3</sup>

## Dangerous Goods

**UN** 1017

**Class**

2.3 *toxic gas*

**Sub-Risks**

5.1 *oxidizing agent*

8 *corrosive*



**Hazchem** 2XE

Chlorine is stored and transported as a compressed, liquefied gas, under its own vapour pressure in distinctive yellow cylinders or drums, in the following net quantities:

- Cylinders (33 & 70 kg)
- Drums (920 kg)

It is also stored as a refrigerated liquid at -35 deg C, in a bank of three insulated tanks, each with a capacity of 25 tonnes, in the Kwinana Industrial Area.

The 920 kg drums are commonly found in chlorination systems. They are about 2.1 m in length, and 0.8 m in diameter. The gas and liquid valves are located at one end above each other. It is important to understand that both valves are connected on the inside to an off-take pipe from the top and bottom of the drum respectively (picture).



The ends are also designed to be convex for added strength and safety.

## Toxic and Concentration Effects

Chlorine is so irritating at levels above about 5 ppm that people will not voluntarily remain, unless they are trapped or are unconscious.<sup>4</sup>

Inhalation	
Low concentrations	Tears, runny nose and sneezing
Increasing concentrations	Coughing, choking, laboured breathing and chest pain
High concentrations	Asphyxiant (cramps to larynx muscles, swelling of mucous membranes).
Delayed effects	Accumulation of fluid on the lungs, bronchitis and pneumonia
Continuous (low levels)	Chloracne, corrosion of the teeth.
Skin contact	
High gas concentrations	Causes a burning sensation that eventually results in blistering.
Eye contact	
	May cause permanent damage

**Table: Toxic effects of chlorine**

Conc (ppm)	Effect
0.001 – 0.4	Odour threshold range
1	Australian OH&S Exposure Standard <sup>5</sup> Time Weighted Average (TWA) - Peak Limitation
1-3	Mild mucous membrane irritation
5-15	Moderate irritation upper respiratory tract
10	NIOSH Standard for respirators <sup>6</sup> Immediately Dangerous to Life and Health (IDLH)
30	Immediate chest pain, vomiting, shortness of breath and cough
40-60	Concentration dangerous in 30 minutes. Fluid build-up in the lungs
430	Lethal over 30 minutes
1000	Fatal after a few deep breaths.

**Table: Concentration effects**

The odour threshold values are extremely variable for several reasons.<sup>7</sup> The values quoted can depend on whether trained 'sniffers' were used, or whether it was picked up by the most sensitive nose, or by 50% of the noses involved. Values can be also quoted where an odour was 'detected', or where it was 'recognised' as chlorine. Recognition values are always much higher.

## A chlorine release

This variability in odour threshold, presents a problem in the event of a chlorine release, as to how far downwind, to advise people to remain indoors. If people can smell it, they have reason for concern, and will need guidance, even if only as a precaution.

On the other hand, when diluted to threshold levels, chlorine will be consumed by reaction with moisture in the air, and therefore will disappear quickly. This illustrates some of the difficulties confronting those required to provide advice involving prediction, since there is a corresponding loss of accuracy, the further you move from the scene.

However, in those areas downwind in which chlorine concentrations are still high enough to be hazardous, it is possible to provide reasonable estimates of concentration. To do this, the rate of release from a 920 kg drum will be considered.

### Rate of release - pressure / heat dynamics

If sufficient pressure is applied, certain gases, including chlorine can be liquefied at room temperature. And in reverse when the pressure is relieved, these liquefied gases want to revert back to the gas. However, to do so the liquid must absorb sufficient latent heat,<sup>8</sup> either from the liquefied gas itself or from its surroundings.

Liquid chlorine has a boiling point of -34 deg. C, and therefore when stored as a liquefied gas at ambient temperatures, it will be about 50-60 degrees above its boiling point. If it is suddenly opened to the atmosphere, it becomes a super-heated liquid, and as a consequence, it will flash boil, in which the excess heat will provide enough latent heat, to enable 17% of the liquid to be immediately converted into vapour.<sup>9</sup>

The remaining 83% will remain a liquid, but will have cooled down to -34 deg C, or down to its boiling point. This remaining cold liquid chlorine will then boil off, at the rate, at which heat can be drawn into it from the surroundings.

This cooling effect is a critically important factor when considering leakages from any liquefied gas (including LPG and ammonia). This flash-boiling process creates dense cold gas clouds which hug the ground, cause blockages on release outlets due to icing and a contact hazard due to the cold.

### Liquid leak from 920 kg drum

While a liquid leak from a 920 kg drum is far more hazardous than a gas leak from their corresponding outlet valves, they behave quite differently.

With a liquid, the internal pressure will push liquid chlorine out as a thin stream at about 30 kg/min, and as already discussed, it will flash boil into a liquid and vapour fraction. However the liquid fraction on being ejected in this fashion forms a mist and becomes airborne. The end result is a cold mixture of entrained air, chlorine vapour and liquid chlorine droplets.

This cold mass will have a density much greater than air, and will sink to the ground before it begins to disperse downwind. The mist component will quickly evaporate, either as heat is drawn from the surrounding air, or from contact with adjacent surfaces, as heavier droplets fall to the ground.

While the drum should be empty in about 35 minutes, instead the cooling effect eventually predominates, in which a small amount of cold liquid chlorine remains inside the drum.<sup>10</sup> A line of frost will be seen on the outside, and the discharge will become sporadic as the pressure builds up and is released as the chlorine continues to boil off inside the drum ... a process that may take many hours.

If there is large hole, or even a complete rupture, then a much larger quantity may initially be released to the atmosphere, however the liquid fraction is much less likely to form into a mist. Rather, it would tend to remain as pools of liquid chlorine at the release point.

### Chlorine hydrate.

If the leak continues long enough, chlorine may absorb moisture from the atmosphere to form a solid crust of Chlorine Hydrate (Cl·8H<sub>2</sub>O), at the release point. It is a greenish ice-like substance that may form when the temperature is less than 9.6 deg C. It will quickly decompose and disappear with the return to ambient temperature conditions.

### Gas leak from a 920 kg drum

If a leak occurs from the vapour space, drum pressure will drive out the gas. And once again, as the internal pressure falls, so the liquid undergoes the same flash boil - latent heat - evaporation - cooling cycle, to the point where liquid chlorine is cooled to its boiling point.

The big difference this time is no liquid escapes, only gas. The initial discharge will be about 4.3 kg/min quickly dropping down to 1.3 kg/min and lasting for about 60 to 90 minutes. At this time most of the chlorine will be remaining in the tank as a cold liquid. The amount and rate of release is a lot less, and so is the downwind hazard.

### Dispersion

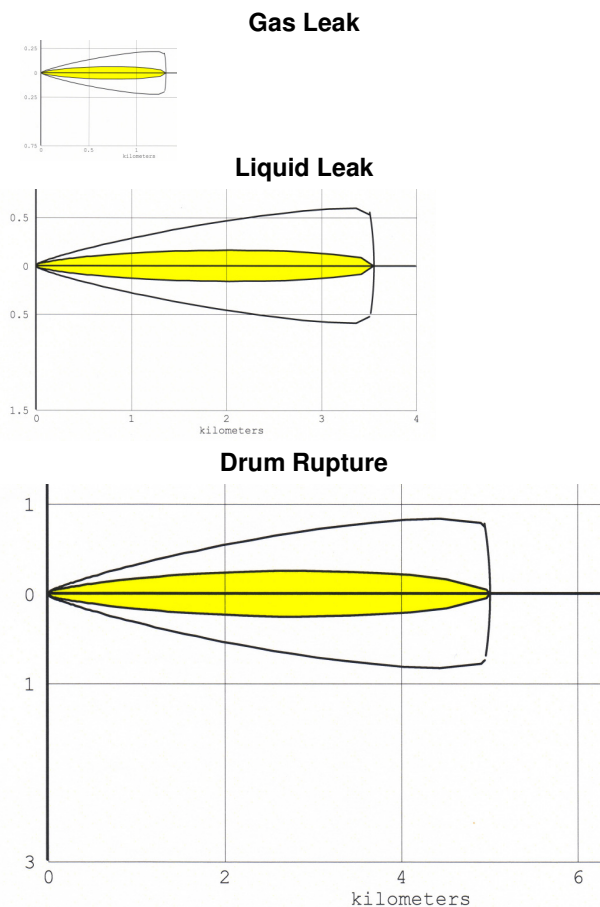
Once escaped, chlorine will move with the wind. And depending on the wind speed, it may have travelled a considerable distance before emergency services arrive on scene (refer following table).

Wind speed km/hr	Distance travelled in kms after	
	10 mins	30 mins
6	1	3
12	2	6
18	3	9
24	4	18

**Table: Wind speed and distance travelled**

Dispersion of any gas is an extremely random process. It is something like clouds of smoke moving along the ground, only it's mostly invisible. As with smoke, near the source it appears as big random puffs jumbled together, and then as they move away, so they open-up and spread out.

While this randomness makes it impossible to precisely determine exact concentrations at any spot downwind at any time, it is possible to provide estimates where concentrations may present an unacceptable hazard. This can be done using tables from the Emergency Response Guidebook (ERG2008), or through a computer model, of which the most commonly available is the Areal Locations of Hazardous Atmospheres (ALOHA) model.<sup>11</sup> ALOHA draws an envelope which can be overlaid on a map; for example, the following are envelopes for chlorine concentrations at or above 0.5 ppm.



Envelope (0.5 ppm)	Distance (kms)
Gas leak	1.3
Liquid leak	3.5
Rupture	5.0

Please note that envelopes can be quite different for different weather conditions, and those provided are for information only, NOT operational use.

In summary, a gas leak will last for about 60-90 mins, in which most chlorine remains in the cylinder as a cold liquid. A liquid leak will last for about 30 mins, in which some chlorine will remain in the cylinder as a cold liquid. With a massive one time release from a complete drum rupture, it will form a single large gas cloud which will last as long as it takes to travel 5 kms, however a lot will remain behind as a cold liquid.

## Heat effects

### Heat and expansion

Liquid chlorine has a high coefficient of expansion with temperature, and industry has to be careful not to over-fill cylinders or drums. With drums:

- On filling at -35 deg C, there is 25% ullage.
- At ambient temperatures, the ullage is 17%.
- At 60 deg C, the ullage is 9%.
- At 90 deg C drums are completely full.

The maximum temperature attainable, is considered to be 60 deg C, when it is standing in the open sun. If ever they reach 90 deg C, it has been found that the concave ends invert rather than burst.<sup>12</sup> If both ends are involved, this provides an additional volume of about 70 L. It also has been found when this happens, a small leak is likely to occur from the educator tube flange or drum threads.

### Fire

If involved in fire, chlorine begins to corrode the container as it heats up. Chlorine has no effect, under ambient conditions, however above 250° steel will burn in chlorine.<sup>13</sup>

In a fire, hot spots form on the vapour space, since it is less able to dissipate heat relative to the liquid layer, where heat can be transferred into the bulk of the liquid. It is here that accelerated corrosion will take place, until a hole may form and the chlorine escape. Under these circumstances most chlorine is carried with the up-draught into the air.

## Some final points

### Water sprays

Chlorine is not very soluble in water so water sprays will not knock down chlorine clouds. However it can be used to increase dispersion; direct water across the cloud and directed slightly upwards. It is estimated that if you can double the amount of dispersion at the point of release, you will halve the concentration 100 metres downwind.

### Gas density

While pure chlorine is heavier than air and will sink, things can be quite different as chlorine is increasingly diluted in air. For example, when diluted down to its IDLH value, the theoretical vapour density is 1.000025. While chlorine is at a dangerous concentration, it will move with the air currents. Vapour density has no meaning at this point. It will not sink.

## Major leak within a chlorination plant

If a leak is detected at a major chlorination installation, these installations are designed to shut down both the chlorination and ventilation system. They are also designed to contain the gas volume equivalent of a whole drum.

## Caustic soda scrubbers

Caustic soda scrubbers can be used to neutralize chlorine leaks. Either dispose through a caustic soda scrubber to neutralize, or allow slow release into the atmospheres as directed.<sup>14</sup> The Australian Standard details caustic soda scrubbing systems that can be employed in the event of a leak inside a chlorination plant.<sup>15</sup>

<sup>1</sup> 2008 Emergency Response Guidebook, Guide 124

<sup>2</sup> AS/NZS 2022:2003 Anhydrous ammonia – Storage and handling.

<sup>3</sup> AS/NZS 2927:2001 The storage and handling of liquefied chlorine gas.

<sup>4</sup> Chlorine Manual (The), 6<sup>th</sup> ed., The Chlorine Institute, Inc, American National Standard, February 29, 2000, <http://www.chlorineinstitute.org/> (accessed 15<sup>th</sup> May 2008)

<sup>5</sup> Australian Exposure Standards, <http://hsis.ascc.gov.au/SearchES.aspx> (accessed 15<sup>th</sup> April 2008)

<sup>6</sup> IDLH, <http://www.cdc.gov/niosh/idlh/intridl4.html> (accessed 15<sup>th</sup> April 2008)

<sup>7</sup> Ruth JH, Odor Thresholds & Irritation Levels of Several Chemical Substances: A Review, Am. Ind. Hyg. Assoc. J., 47:A142-A151 (March 1986)

<sup>8</sup> Latent heat of vaporization is the amount of energy required to convert 1 kg of a substance from liquid to gas (or vice-versa) without a change in temperature. Usually expressed as kJ/kg

<sup>9</sup> The latent heat of liquid chlorine is about 13% that of water.

<sup>10</sup> Chlorine Handbook, April 2006, Orica Watercare

<sup>11</sup> ALOHA download, <http://www.epa.gov/OEM/content/cameo/aloha.htm>

<sup>12</sup> Private communication from Orica

<sup>13</sup> Pamphlet 164, Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials, The Chlorine Institute, 2<sup>nd</sup> ed, Aug 2007

<sup>14</sup> The Chlorine Handbook advises the safe limit for atmospheric venting is 200 grams per minute through a 10 metre stack. AS/NZS 2927:2001 require exhaust stacks to be sufficiently tall to permit safe disposal of chlorine vapours.

<sup>15</sup> AS/NZS 2927:2001

Prepared by Leith Higgins, Principal Scientific Officer, FESA

Any comments 08 93239311 or [Leith.Higgins@fesa.wa.gov.au](mailto:Leith.Higgins@fesa.wa.gov.au)

Dec, 2008 © by the Fire & Emergency Services Authority of Western Australia (FESA)

This material is copyright and provided courtesy of FESA and published in the member's only area of the AFAC Knowledge Web. The material is subject to the operation of the *Copyright Act 1968* and its subsequent amendments.

Material may be downloaded, displayed, printed and reproduced in unaltered form only for the sole use of AFAC members or partner organisations. This material may not be used for commercial purposes.

Distribution of material from the member's only area of the Knowledge Website to personnel outside of AFAC members and partner agencies is not permitted unless written authorisation is obtained from the content owner.