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ANALYSIS OF THE ACCIDENTAL RELEASE OF CHLORINE

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Abstract: Due to its properties, chlorine is one of the highly toxic substances used by humans. This gas attacks the respiratory system, eyes and skin. In higher concentrations, its inhalation leads to death. It is mainly used in water treatment plants where it guarantees a bacteriologically safe water in water supply systems. It is also used as a disinfectant and bleaching agent.
The use, transport and storage of chlorine may pose serious hazard associated with its uncontrolled release from technological installations or tanks. The level of this threat will depend on the run of the release scenario or meteorological conditions. The article presents an analysis of the hazards associated with the uncontrolled release of chlorine. The ranges of zones with dangerous level of gas concentration are presented as a result of its instantaneous and continuous release.
Keywords: chlorine, hazard zones, toxic

1. INTRODUCTION

Human activity and the relentless strive to improve the conditions of human existence involve in many manufacturing processes and installations the use of different substances, some of which pose significant hazards. Chlorine is an example here. It is widely used, and considering its properties it is classed as one of the most toxic substances used by man. The actions aiming to minimize the consequences of a potential chlorine-related failure are thus an essential research issue. Among others, the level of the hazard created by an uncontrolled release of chlorine, or any other toxic substance, depends on the hazardous event scenario, meteorological conditions and the substance physiochemical properties (Brzozowska and Niesyto, 2018, Law et al., 2019, Scenne and Santa Cruz, 2005).
In the first place, chlorine is commonly used in water treatment plants, swimming pools and water supply systems to ensure appropriate bacteriological quality of water. It also finds application as a disinfectant and a bleaching agent. It plays an important part in industry, e.g. in the making of medicines, paints, solvents and plant protection products (Brzozowska and Niesyto, 2018, Majder-Łopatka et al, 2014).
Chlorine is considered as one of the ten most hazardous chemical substances, a release of which may cause serious harm to the human body and death. It causes irritation of the respiratory system, skin and eyes (Khanmohamadi et al., 2018,

Sitarek, 2008). During the first world war it was used as a chemical warfare agent (Govier and Coulson 2018). An accidental release of chlorine is usually due to a failure of the equipment and devices used in process installations or, less frequently, to a human error. A release can also be caused by natural phenomena or illegal actions (Ruj and Chatterjee, 2012, Gowier and Coulson, 2018).

Chlorine-related catastrophes took place e.g. in 2005 in Graniteville (USA), where several dozen tons of the gas were released after a railway collision. The created toxic cloud killed 9 people and about 500 were taken to hospital. More than 5000 were evacuated. The accident also generated considerable costs related to emergency actions. In the same year in China, chlorine was released due to a leak from a road tanker. Twenty-seven people died and 285 were intoxicated. About 10,000 were evacuated. In 2004, a train was derailed in Texas (USA) and 4 people died when 41,000 tons of chlorine were released. Although no one died in 2010 when chlorine was released in a metal recycling plant due to a rupture of a one-ton tank, 23 people had to be taken to hospital (Govier and Coulson 2018, Węsierski and Majder-Łoparka, 2012). In Poland, the most serious chlorine-related accident occurred in Białystok in 1989. Due to rail cracks, 3 tank cars of the train set overturned and one was derailed. Fortunately, the tank cars remained tight and no uncontrollable release of chlorine occurred, which made it possible to avoid casualties (Węsierski and Majder-Łoparka, 2012).

2. CHLORINE PROPERTIES

Chlorine is a member of the halogen family. It is a gas with a green and yellow colour and an unpleasant smell. It is produced on the industrial scale through electrolysis of an aqueous solution of the sodium chloride. This reaction also produces sodium hydroxide and hydrogen. On the laboratory scale, chlorine is obtained by hydrochloric acid oxidation with a strong oxidant, e.g. manganese dioxide or potassium permanganate (Majder-Łopatka et al, 2014).

Chlorine is highly toxic. The mechanism of its impact on the human body has not yet been fully explained. The results of the research conducted so far indicate that the acute toxic effect of gaseous chlorine is probably due to the formation of hydrogen chloride in contact with moisture (of the mucous membrane or skin). If dissolved in water, hydrogen chloride forms hydrochloric acid (Majder-Łopatka et al, 2014).

In acute poisoning in smaller concentrations, chlorine causes irritation of the mucous membrane of the nose, eyes and throat. In medium concentrations, the patient feels strong pain in the chest, suffers from lacrimation and violent paroxysmal coughing. In higher concentrations, the patient experiences substernal pain and circulatory deficiency leading to pulmonary oedema and death within a few hours. In the case of chronic poisoning, in concentrations from 20 to 50 ppm, strong irritation of mucous membranes of the nose, eyes and the upper respiratory tract occurs. Sneezing, lacrimation, headaches and gastro-intestinal disorders may also occur (Sitarek, 2008).

Chlorine-related hazards to human health will be a combination of the substance concentration and the time of exposure thereto. The chlorine smell upper perceptibility threshold is 14.8 mg/m^3. In most countries, the occupational concentration exposure limit is 1.5 mg/m^3, and the maximum momentary exposure concentration totals 3 mg/m^3. In Poland, the values are 0.7 mg/m^3 and 1.5 mg/m^3, respectively (Sitarek, 2008).

Table 1 presents the effects of chlorine in the conditions of an acute inhalation exposure (Sitarek, 2008, Work Safe BC Publications 2006)

Table 1
Chlorine effects in the conditions of an acute exposure to inhalation by humans

concentration (exposure time)	effects
1000 ppm	death (after a few breaths)
833 ppm	death
40 – 60 ppm (30 – 60 min)	pulmonary oedema
30 ppm	suffocation, cough
15 ppm	eyes, nose and throat irritation
1 ppm	slight irritation of eyes, throat dryness, coughing, difficulties in breathing
0.45 ppm	conjunctival irritation
0.2 ppm	throat dryness, coughing, conjunctival irritation

Source: (Sitarek, 2008, Work Safe BC Publications 2006)

3. FAILURE-RELATED EVENTS

Being chemically aggressive, chlorine creates transport and storage difficulties and poses a serious hazard of its uncontrollable release from technological facilities or tanks.

Unwanted events/failures in buildings where chlorine is stored present a smaller risk because such buildings are usually fitted with appropriate protection systems. Fast detection and prompt information of a hazardous event enable rapid elimination of leaks and significant restriction of the hazard zone. A much more dangerous scenario is the release and spread of chlorine, e.g. due to an accident of a tank car. The hazard level will depend on the amount of the released substance, type of release (continuous or instantaneous), as well as on atmospheric conditions.

The presented scenarios of an accidental release of chlorine take account of events where chlorine tanks are damaged due to a total rupture or a puncture. The analysis is performed using the PHAST v6.7 software.

Table 2 presents the ranges of hazard zones arising due to an instantaneous release of different amounts of liquid chlorine. The results were obtained assuming partly cloudy skies, the wind speed of 1.5 m/s and the air temperature and humidity of 15^{o}C and 60%, respectively.

Table 2
Ranges of zones with a specific concentration of chlorine

mass of released chlorine (ton)	zone range (m)	
	1000 ppm	30 ppm
0.2	109	339
0.5	147	338
1	178	532
20	566	>1000

Fig. 1 presents ranges with chlorine concentration of 100 and 1000 ppm. The results relate to a failure of a 100 l tank. Atmospheric conditions are assumed as identical.

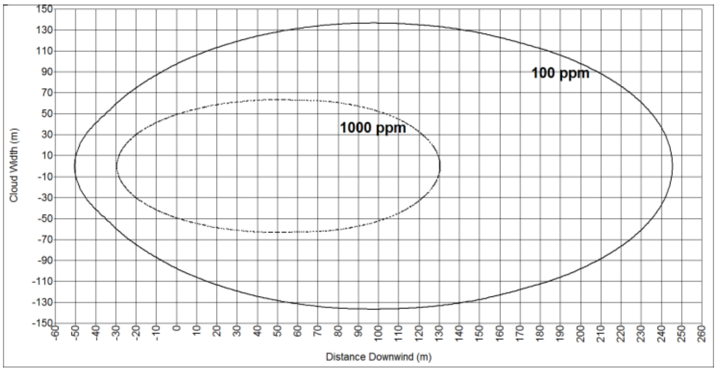

Fig. 1. Hazard zone due to an instantaneous release of chlorine (u_w = 1.5 m/s)

Fig. 2 presents the hazard zones arising at a higher wind speed.

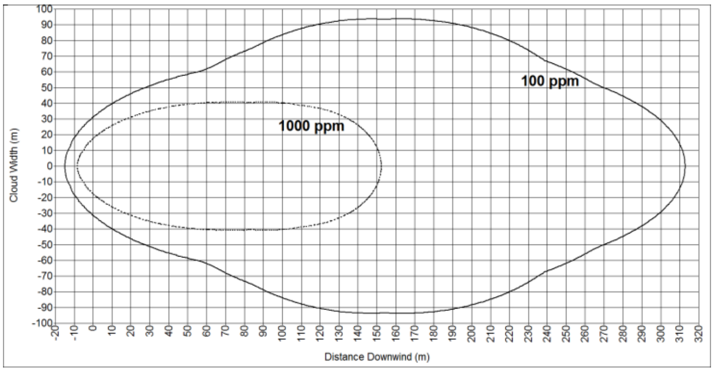

Fig. 2. Hazard zone due to an instantaneous release of chlorine (u_w = 5 m/s)

Analysing the charts, it can be seen that atmospheric conditions (the wind speed in the first place) have an essential impact on the level of hazards created by chlorine. A rise in the wind speed lengthened the range of the zone with a lethal concentration of chlorine by about 45 metres. However, the total surface area affected by the 1000 ppm concentration is smaller. A drop in the air temperature from 15^{o}C to 0^{o}C involves a decrease in the lethal zone range by about 20 metres for either of the two wind speeds under consideration.

If chlorine is released through a puncture (continuous release), time has an essential impact on the hazard level. The zones with specific concentrations of the gas will vary with changes in the chlorine flow rate through the hole. Fig. 3 presents the hazard range due to a release of liquid chlorine from a 100 l tank through a hole with the diameter of 50 mm. The assumed atmospheric conditions are the same. Fig. 3a and Fig. 3b, respectively, illustrate zones with the concentration of 1000 ppm for the time of 5 and 30 seconds from failure.

a) t = 5 s b) t = 30 s

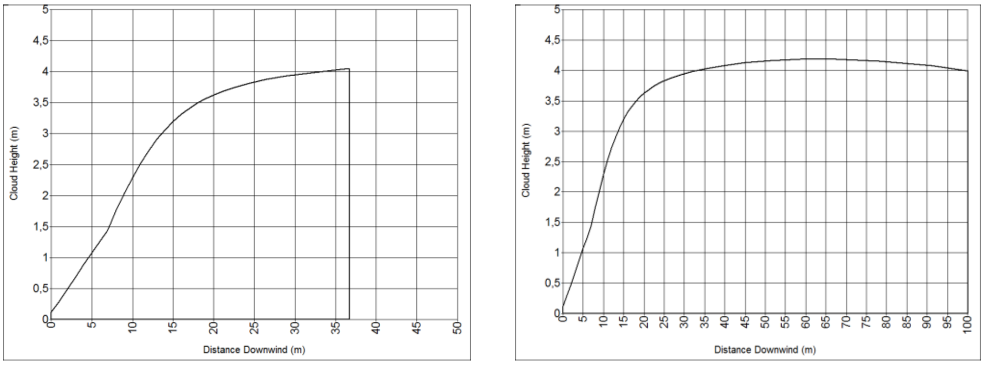

Fig. 3. Hazard zone due to a continuous release of chlorine

After 5 s, the 1000 ppm concentration hazard zone will cover the range of about 36 metres. After another 25 s, it will get longer by about 65 metres. At the critical moment, it will reach the maximum distance at the level of about 270 m, as presented in Fig. 4.

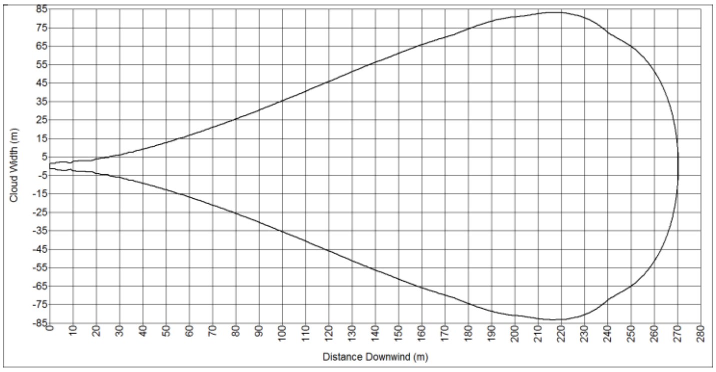

Fig. 4. Hazard zone due to a continuous release of chlorine

Apart from the duration and atmospheric conditions of the release, the location of the emission source is another essential factor that has an impact on the spread of the cloud with a specific concentration of chlorine. Fig. 5a and Fig. 5b present results of an example analysis of a chlorine release through a 50 mm hole using the same assumptions as previously but taking account of the chlorine emission source elevation of 5 m.

a) t = 5 s b) t = 30 s

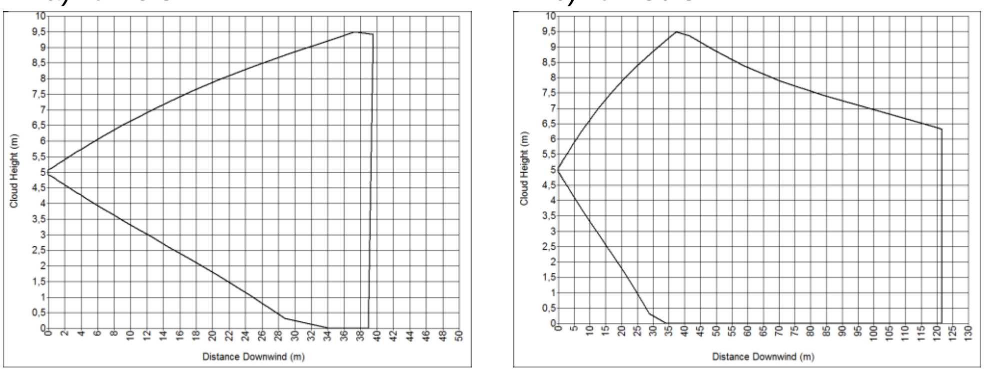

Fig. 5. Hazard zone due to a continuous release of chlorine (source elevation = 5 m)

If the chlorine emission source is located at the height of 5 m, the hazard zone will cover the distance of about 40 and 123 metres for the time from failure of 5 and 30 s, respectively.

4. CONCLUSIONS

The hazards presented by the use and transport of chlorine should by no means be underestimated. Both the results of the presented analyses and the consequences of past failures prove unequivocally that even small amounts of chlorine can pose a serious hazard to humans and the environment. Failures related to an uncontrollable release of chlorine also generate considerable costs of emergency actions, e.g. evacuation of residents from endangered areas.

If considerable amounts of chlorine are released, for example due to railway accidents, the hazard zone for humans due to the effect of the concentration of 30 ppm, i.e. one that causes breathing problems and coughing, can spread over the distance of more than 1000 m. The zone with a concentration causing death after a few breaths will have the range of about 570 metres. This will have far more dangerous consequences if the chlorine cloud spreads over a densely populated area.

The course of failures related to a chlorine release is affected by many factors. They include, for example, the way in which the substance is released (continuously or instantaneously), the time and atmospheric conditions. After an instant release of 100 litres of chlorine, the range of the hazard zone with a concentration lethal to humans will total about 100 metres. If the wind speed gets higher, it will be lengthened by about 45 metres downwind. However, the total surface area affected by the toxic cloud will be smaller. The hazard zone range also decreases with a drop in ambient temperature. In the case of a continuous release through a hole with the diameter of 50 mm, the maximum hazard zone range will total 270 m, but it will cover a much smaller surface area compared to the case where the release is instantaneous.

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