INTERNATIONAL JOURNAL OF
ENERGY AND ENVIRONMENT

Volume 2, Issue 6, 2011 pp.1039-1052
Journal homepage: www.IJEE.IEEFoundation.org

A typical small-scale chlorine leak and dispersion simulation in industrial facilities

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Abstract
The liquefied chlorine release is the most frequent accident in hazardous materials (HAZMAT) releases. A typical small-scale accidental release of chlorine was simulated using a FLUENT code (CFD software). In addition, consequences of continuous and instantaneous release scenarios were investigated here. Case studies showed that, for a continuous release scenario, buildings and eddies would slow down the chlorine dispersion and resulted in a much lower concentration behind the buildings than other zones. As for an instantaneous release scenario, chlorine was trapped in the eddy zones. Inside these zones, the presence of chlorine lasted longer. Further, cause and effect diagram was adopted here to conduct cause-consequence analysis. Also, risk reduction measures and accident prevention strategies resulted from accident causal analysis were proposed for the emergency management and regulatory circles.
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Keywords: Chlorine release; Small-scale dispersion; Computational fluid dynamics; FLUENT code.

1. Introduction

Chlorine is one of many industrial agents that are harmful, yet used extensively in processing and transported in bulk. Chlorine gas is so deadly that it was used as a chemical weapon in the trenches of World War I. Yet chemicals like chlorine are essential to modern life and supplies are needed in every city. Chlorine is used as a key disinfectant for the water supply in cities, and is commonly-used in cleaning and bleaching agents for paper production, and to manufacture plastic products. In these applications, chlorine usually is preserved in a form of liquid in cylinders. The capacity of each cylinder varies from 100, 500 to 1,000 kg. If chlorine in a cylinder was not handled and preserved properly, a valve or bottle in a cylinder was likely to be damaged or corroded, especially in the case of improper operation, a release accident would occur suddenly.

Among HAZMAT releases accidents, a small amount of release, i.e. 1-10 kg / min release, took up 38 percent of the total number of chlorine release accidents [1]. Chlorine is an acute poisoning gas and can be inhaled into human bodies through respiratory systems. Its occupational exposure threshold is 1mg/m3. Even a small amount of chlorine can quickly reach the threshold of acute poisoning and cause casualties [2]. So, in this paper, we applied computational fluids dynamics (CFD) method to study a typical small amount of chlorine release in a factory. Our purpose was to investigate the flow field under continuous and instantaneous leak on this scale which served for the emergency preparedness if accident occurred. Especially, heavier-than-air and obstruction effect by the industrial facilities in each scenario were investigated. We finally conducted accident causal analysis and proposed related risk reduction measures and accident prevention strategy.

The remainder of this paper was organized as follows. In Section 2, we stated the theoretical foundation for heavy gas dispersion problem formally and discussed three categories models before. In Section 3, we introduced an accidental release of chlorine in a small zone, and under credible conditions, the gas cloud would exert toxic effect on a dense population living and working nearby. In Section 4, we conducted an accident causal analysis using fishbone diagram and put forward risk reduction measures accordingly. In Section 5, we concluded the paper and pointed out future research directions.

Similar studies of potential HAZMAT releases concur with this scale of disaster from chlorine leaks. The scenario of a major chlorine leak caused by a terrorist attack on a rail car passing through Washington, D.C. could produce a chlorine cloud covering a 14-mile (23-km) radius that would encompass the White House, the Capitol, and the Supreme Court, endangering nearly 2.5 million people, and killing 100 people per second [3]. A study in the Groningen province of the Netherlands indicated that if an area of about 0.2 square miles (0.5 square km) was exposed to chlorine for 45 minutes it would cause 5,000 deaths and 17,800 other casualties [4]. Chlorine railcar releases in industrial and urban areas and its consequence analysis also used a CFD method similar to this paper to investigate its dispersion process [5, 6].

Also, the effect of obstruction of buildings upon dispersion under flashing releases was studied in detail especially [7]. More research fruits on this focused on the area of street canyon [8-16].

2. A theoretical basis

The density of chlorine is greater than air; the dispersion of chlorine can be classified as heavy gas dispersion. The research on heavy gas dispersion began in the 1960s. After several decades of development, a series of heavy gas dispersion models were proposed. According to the complexity of these models, they can be divided into three categories: empirical model, box-type model and computational fluid dynamics model [17].

The empirical model is the most simplistic one. Based on large-scale field experiments and wind tunnel test data, using certain simplifications and assumptions, concentrations of heavy gas cloud and its main parameters are calculated. A typical experience model is the B&M model proposed in 1983 by Britter and McQuaid. It is mainly applied to long-distance, flat, open space dispersion [18].

The box-type model assumed that heavy gas clouds can form certain shapes by the heavier-than-air effect, and the parameters of clouds (such as concentration, the quality of flux, enthalpy) followed certain distributions (uniform distribution or Gaussian distribution) [19]. For a small amount of chlorine release (1-10 kg / min) from a cylinder, leaked chlorine is insufficient to form a cloud that is the prerequisites for the box-type model (Figure 1). Also obstructions and other external conditions have greater impacts on chlorine release process.

A CFD model is a three-dimensional model. It describes the distribution of various fields by establishing the basic conservation equation (including quality, momentum, and energy components, etc.) under various conditions. Combining with the initial and boundary conditions and the support of the numerical theories and methods, a detailed model, including the flow field, temperature, concentration etc. in the process of dispersion, can be developed for any release scenarios under any terrains and weather conditions [20, 21].

All in all, in the field of numerical simulation of gas diffusion, the most influential model consists of FEM3, FEM3A model [22], ADREA- HF model [23] and W. Jacobsen and B. F. Magnussen 3D diffusion models [24]. The Lagrangian particle models for dense gases (e.g. the QUIC model or Anfossi's model) and the Lagrangian puff models for dense gases (e.g., SCIPUFF) are widely used too. Through the comparison with these models, after decades of development, differential equations in describing gas flow are basically the same. Present research in the numerical simulation has shifted to the choice of turbulence model, initial and boundary conditions, leak source treatment and so on.

This paper adopted a CFD method to study a small-scale dispersion of chlorine in a factory. From the simulation result and accident causal analysis for a typical small-scale dispersion of Chlorine, we can find the risk reduction measures and accident prevention strategies for the daily safety management and emergency response.

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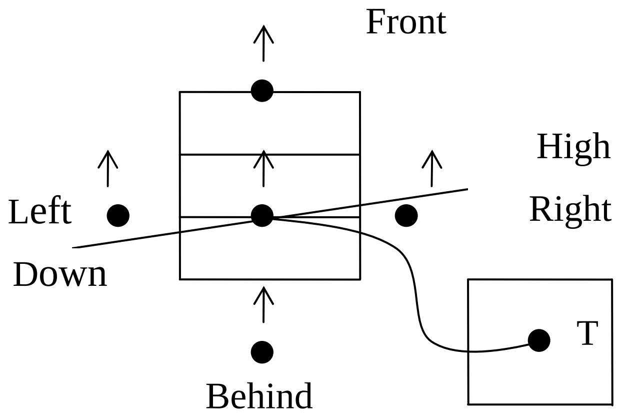

Figure 1. Grid P and its adjacent grids

3. CFD simulation and results

3.1 Case descriptions

In a small scale chlorine release accident, part of the reason is an improper handling of obsolete cylinders. The target factory was reduced as a combination including two plants and a storage building. An obsolete chlorine cylinder was broken due to corrosion which situated between two plants. The release source was red in Figure 2.

In this paper, two scenarios including continuous and instantaneous release were considered respectively. First, 10kg liquefied chlorine was left over in the cylinder. Chlorine release lasted for one hour under westerly wind with speed 1.5 m/s. Second, 10kg liquefied chlorine remained in the cylinder. Release continued for 5 seconds under westerly wind with speed 1.5 m/s. To take the release of the residues in an obsolete cylinder as an example, characteristics of a small-scale dispersion accident were chosen to analyse. Also the relevant factors on diffusion and the accident consequences were considered at the same time.

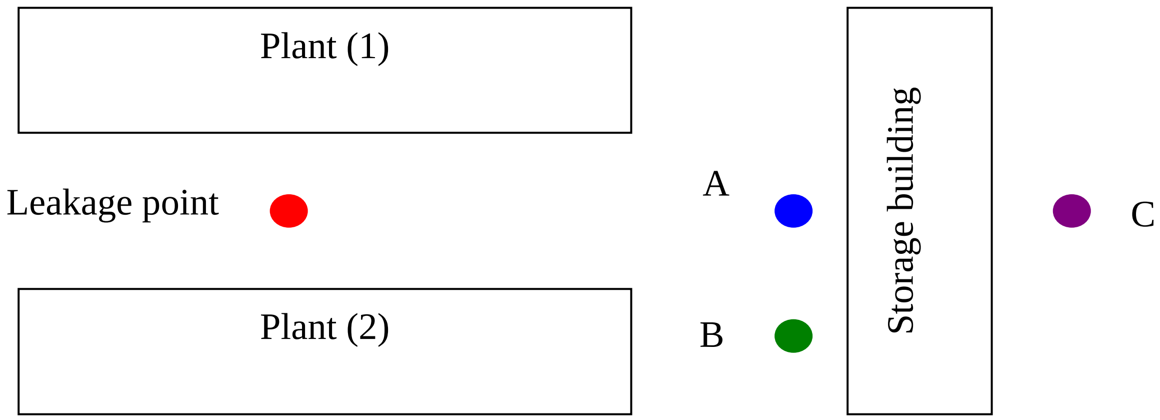

Figure 2. Schematic map of targeted factory

3.2 Wind speed field analysis

A FLUENT code can depict the detailed and complex flow field within the affected zone. Figure 3 shows the velocity vector contour 1m from the ground in the case of wind speed 1.5 m/s.

As a whole, the wind speed became smaller gradually because of the friction of obstacles. From this contour, it can also be observed that the largest wind speed occurred in a narrow passage. When the total influx kept unchanged, the cross-sectional areas of passage shrank gradually resulting in a higher wind speed.

By contrast, the wind speeds far away three buildings were much smaller. So the ventilation conditions in these regions were poor. It can speculate that if release accidents occurred, toxic gases retarding in those regions would dissipate slowly.

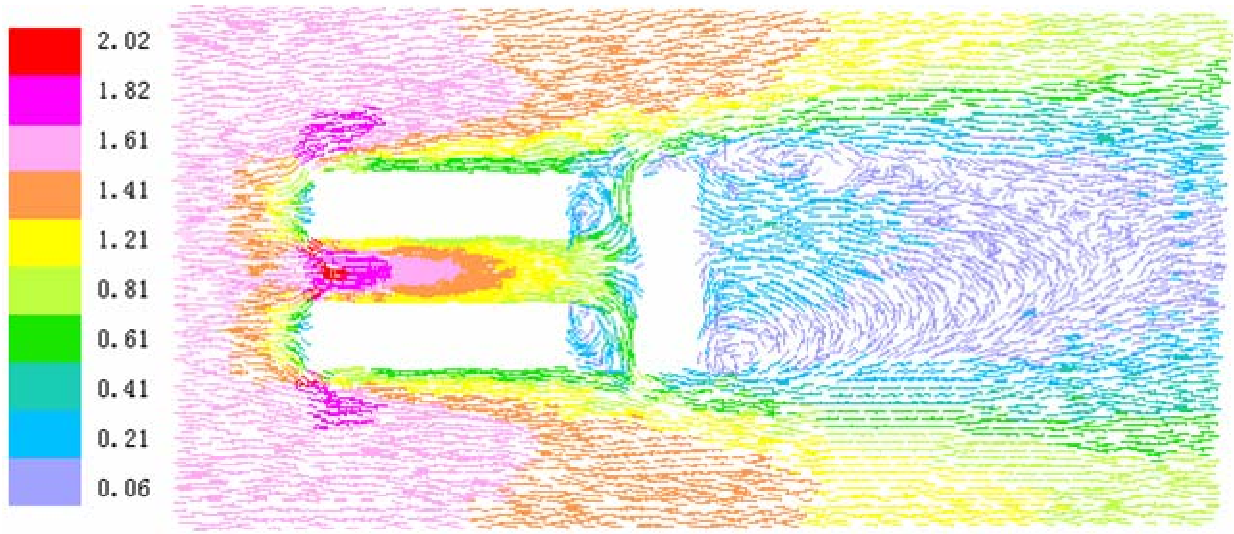

Figure 3. Velocity vector contour 1m from the ground (m/s)

3.3 Continuous release

In this paper, the first accident scenario studied here was a continuous release. A cylinder was placed in the middle of two plants, 10kg residual chlorine leak lasted for one hour, the leak rate was 0.00278kg/m3, the average wind speed was 1.5m /s.

Figure 4 showed the mass fraction of chlorine contour on the centre vertical plane at 30s and 90s. Figure 5 showed the mass fraction of chlorine contour on the plane 1.5 m from the ground. From Figures 4 and 5, topographic effects can clearly be found.

From Figure 4, chlorine must transit the 4m high storage building and then continued to dissipate along the ground controlled by gravity and turbulence effect. Also, compared to the concentration in the upper space above storage building, the chlorine concentration near the ground was still zero after 30s. Until 60s later, the concentration in the upper space was much higher than that near the ground.

Figure 5 also demonstrated this phenomenon. Vortexes generated in the rear of the plant. These vortexes vanished slowly and the exchange rate with the surrounding fresh air was low that caused the accumulation of chlorine. Therefore, it can be seen from Figure 5 that the chlorine bypassing the obstruction along both sides was bounded by these vortexes. Then the chlorine traveling through both sides of plant was difficult to merge in the middle. So the concentration along the central line was lower than those in the two side wings.

A FLUENT code can also describe the concentration change at any time on any point.

Figures 6 and 7 showed that concentration changes on point A and C. Point A situated in 2m before the storage building. Point C situated in 2m behind the storage building.

The chlorine concentration at point A and C differed greatly. Although the distance between point A and C was only 10 m, chlorine concentration at point A was at least 5 times higher than that of point C because of the obstruction of buildings. In addition, the chlorine concentration on point A was grown faster than point C. The main reason lied in higher wind speed on point A and there were no obstructions. However the wind speed at point C was lower and then vortexes generated that reduced the proliferation speed.

In addition, chlorine concentration reached the maximum value after 20s and then gradually dropped to a constant value at point A. The concentration at point A was overlapped by the initial concentration and the reflected concentration. With the time elapsed, the accumulated chlorine at point A began to bypass the obstacle and concentration gradually dropped to the average value.

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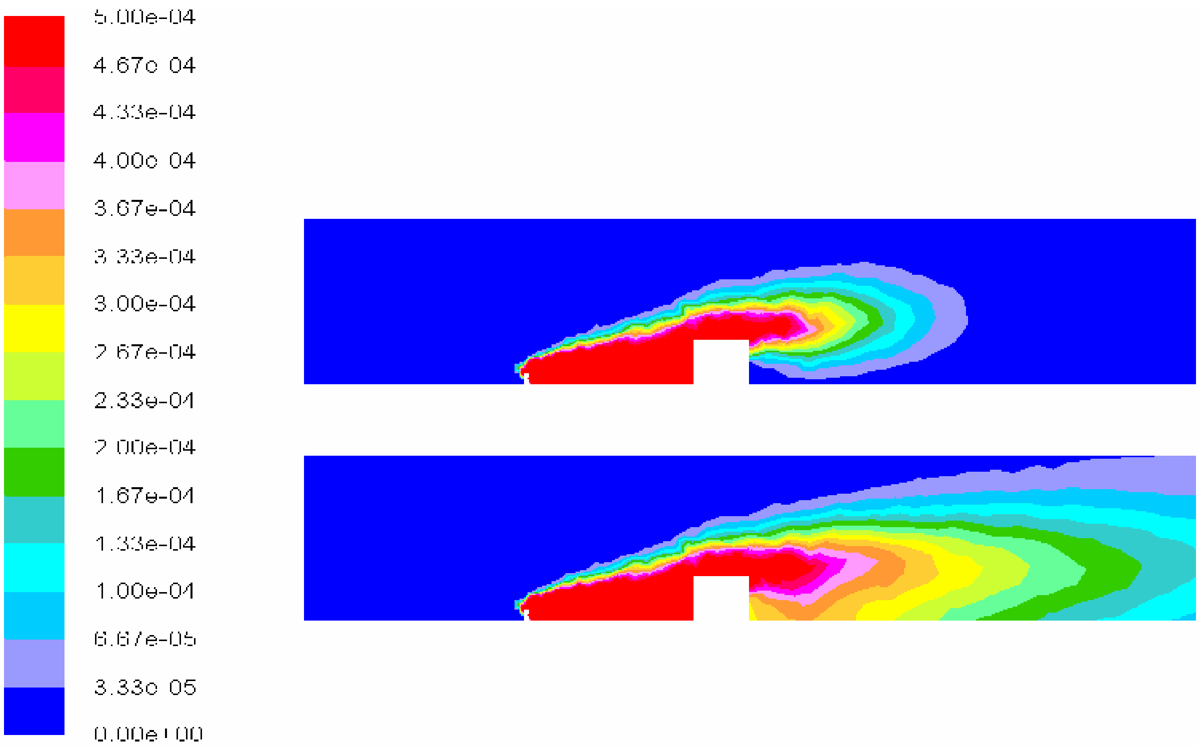

Figure 4. Mass fraction contour of Chlorine on the centre vertical plane at 30s and 90s

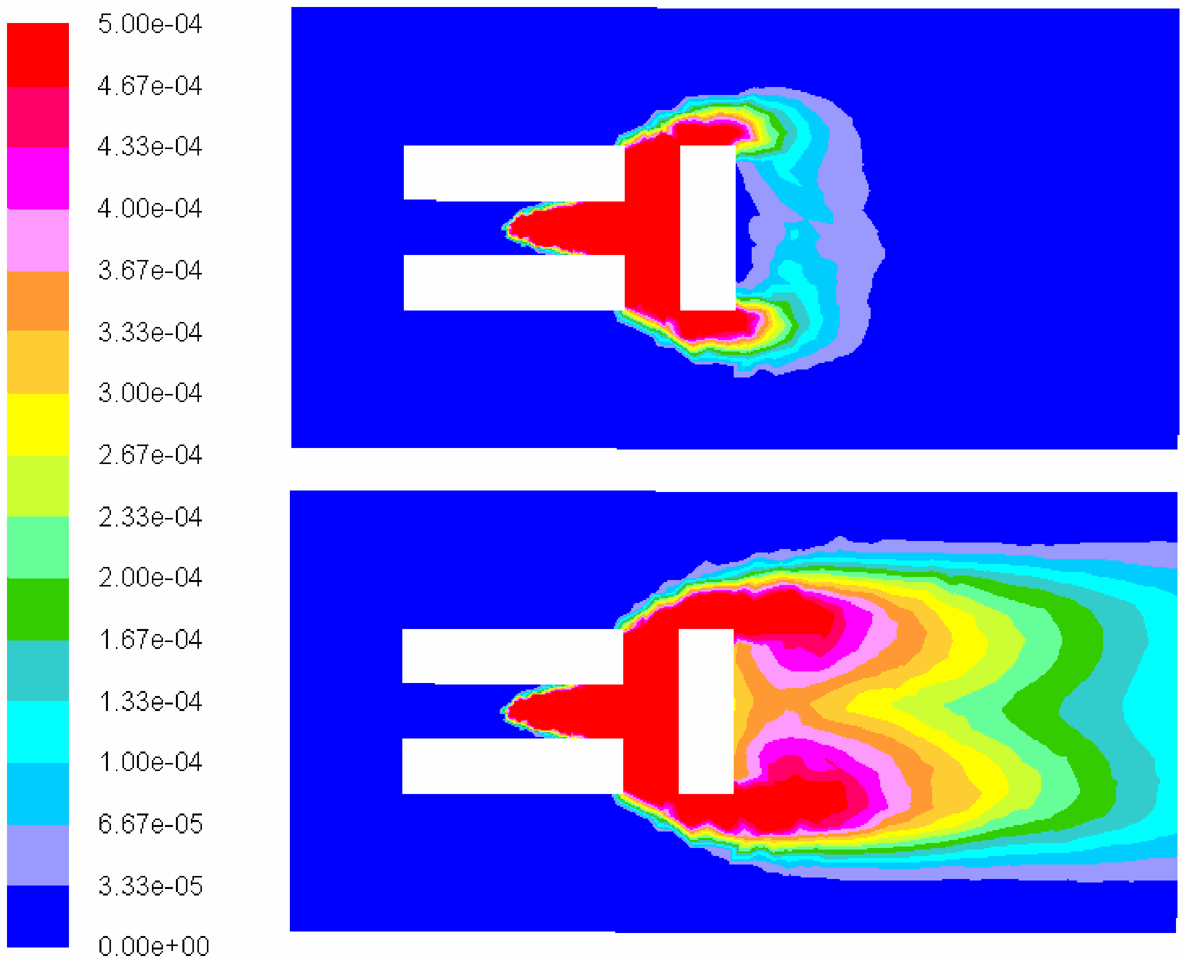

Figure 5. Mass fraction contour of Chlorine on the plane 1.5 m from the ground at 30s and 90s

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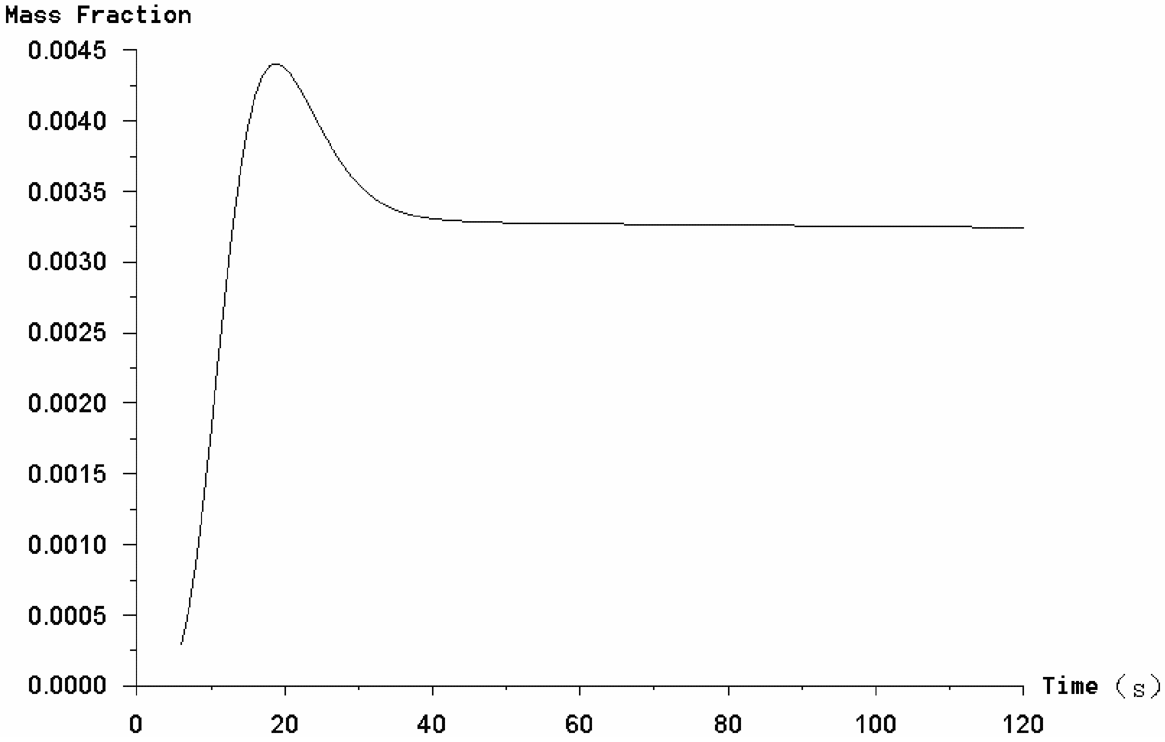

Figure 6. Chlorine concentration trend on point A

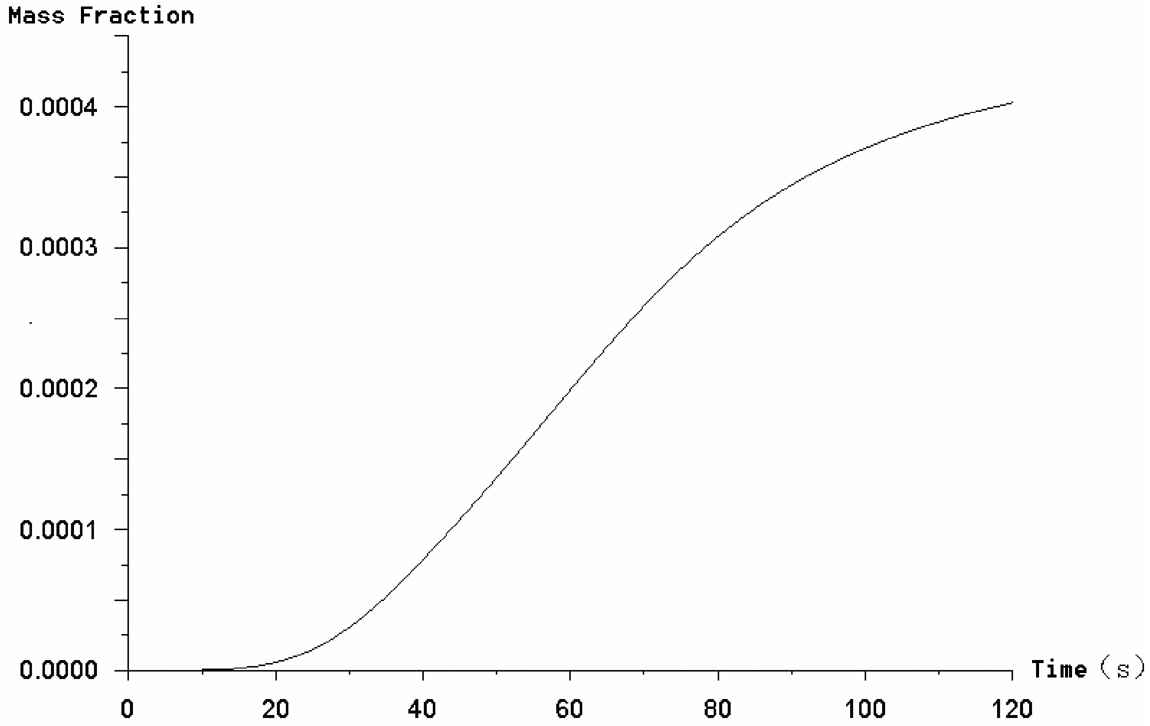

Figure 7. Chlorine concentration trend on point C

3.4 Instantaneous release

In this scenario, 10kg residual chlorine leaked in five seconds and the average release rate was 2kg/s. Figure 8 described the mass fraction contour of chlorine on the plane 1.5m from the ground after 20s and 60s.

Similar to the continuous release scenario, the obstruction clearly took effects when instantaneous release occurred. Chlorine concentrations behind storage building were smaller than that surrounding around the storage building. In addition, simulation results for instantaneous release reflected the binding effect of vortex. It could be seen from Figure 3 that there were vortexes in the rear of the two plants. So, chlorine accumulated in these zones and was difficult to diffuse to other zones. From Figure 8, chlorine concentration in the passage between two plants was zero; however the vortex behind the factory kept the concentration still very high. Then the dispersion was extremely slow in these regions. High concentration chlorine lingered for a longer time.

The effects of vortex can be seen from Figures 9 and 10. Point A situated 2m left the storage building in the centre line down wind. Point B situated 5m away from point A horizontally.

Also it just located in the vortex area. Both of the two points 1.5m from the ground (see Figure 2). Figures 9 and 10 displayed chlorine concentration change over time at points A and B.

From Figures 9 and 10, maximum chlorine concentration at point A was greater than that of point B. But at point A, chlorine dissipated after 40s and then its concentration reduced to zero. While at point B, a small amount of chlorine still remained after 80s. This showed that the vortex had played a significant role on the binding effect of dispersion, which had significantly reduced the diffusion rate of chlorine. If there were staffs in these regions, a longer exposure time would thus cause more damage.

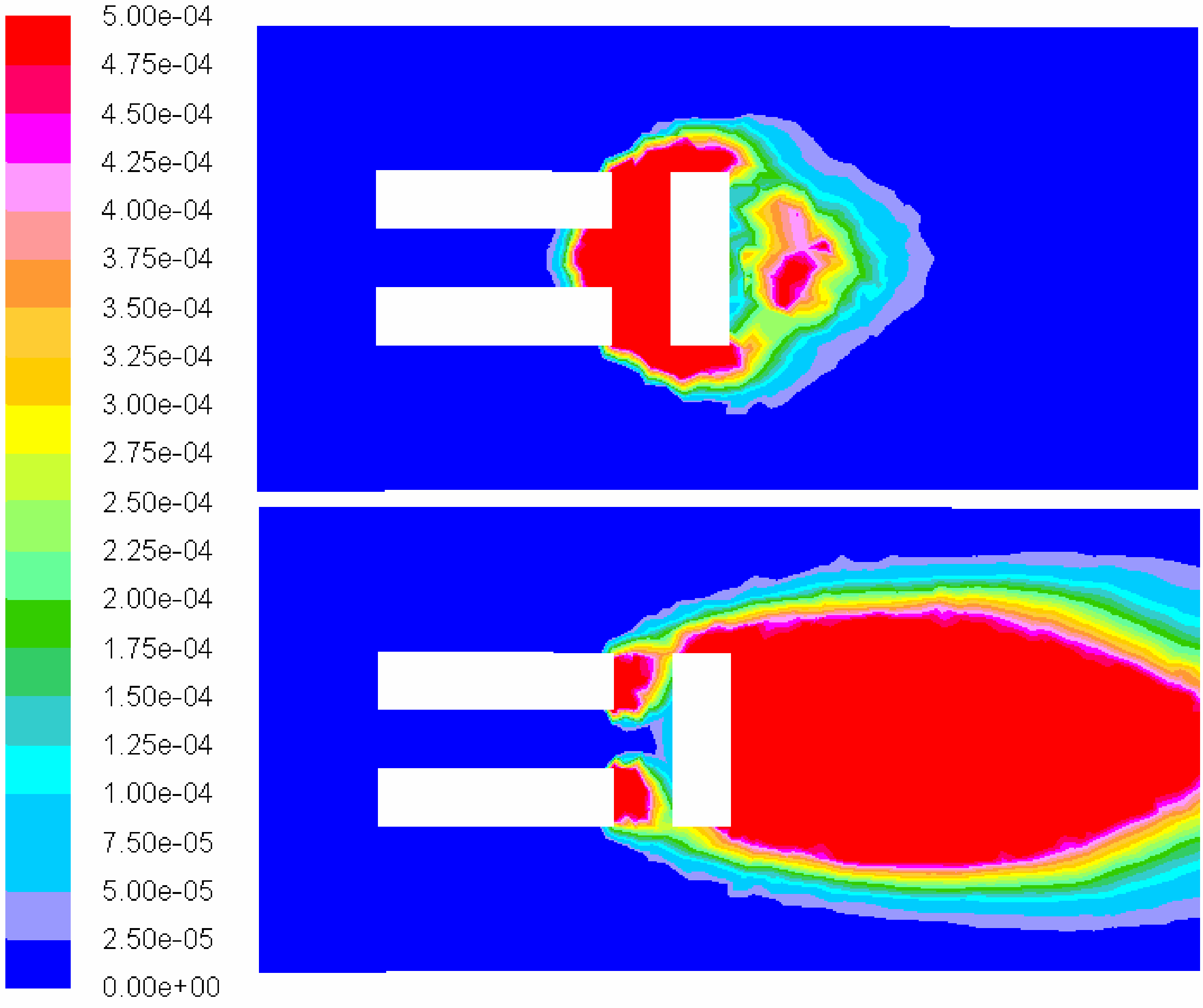

Figure 8. Mass fraction contour of Chlorine on the plane 1.5 m from the ground at 20s and 60s

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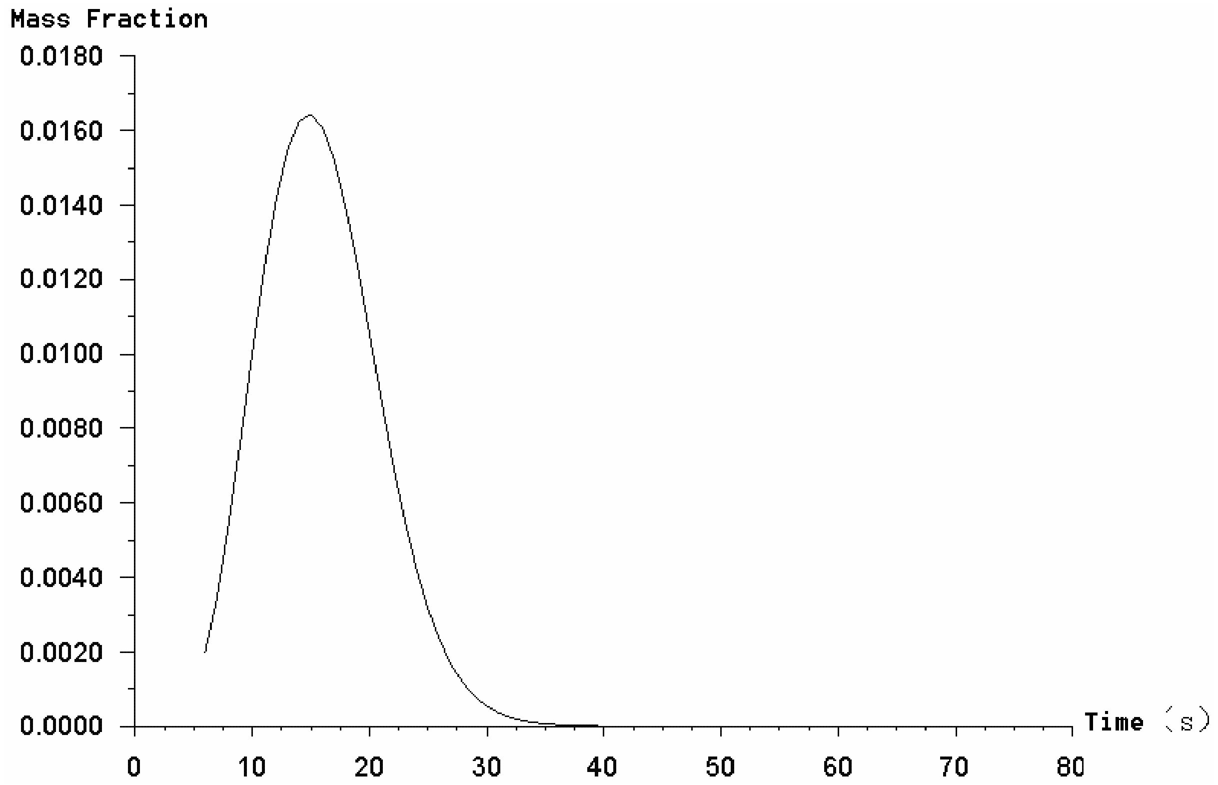

Figure 9. Chlorine concentration trend on point A

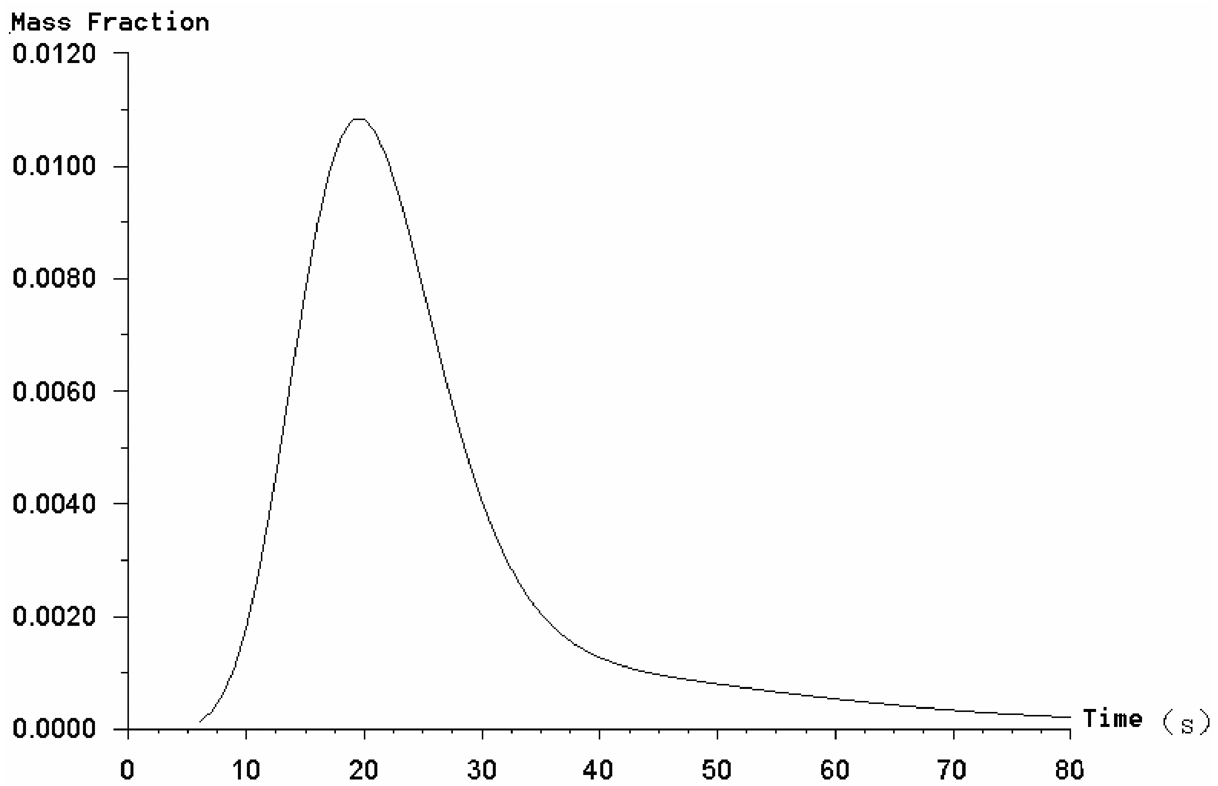

Figure 10. Chlorine concentration trend on point B

4. Discussions

Simulation results showed that, being the existence of plant and wall friction, wind speed gradually decreased along down wind direction, also on the both sides of plants and its rear, vortex appeared.

As for the continuous leak, the concentration contour at two points (A and C) showed the concentration changes originated from the building obstruction and the vortex in front of and behind this building. Chlorine was difficult to entry the region behind the building, which resulted in lower concentration in these regions.

As for the instantaneous leak, by comparing the chlorine concentration changes at two points (A and B) with the same distance away from the leak source, it can be seen that the vortex exerted its binding effects on chlorine dispersion. Being the regional existence of vortexes, chlorine dispersion was very slow. If at this time there is a worker staggering in these regions, a longer exposure time will cause more severe poisoning effect.

4.1 Accident causal analysis

System safety analysis is an important means to identify the hazards and reduce risks. Dozens of accident analysis methods have been produced until now. As much as to complete an accurate analysis, it needs to figure out appropriate methods.

The primary cause of a typical small-scale chlorine dispersion accident in the industrial enterprise is clear. However, the key problem is to identify the potential causes behind these accidents and accordingly propose some preventive measures. The cause-consequence analysis and fishbone diagram was adopted here.

A cause-consequence analysis is used to clarify the causes of an accident and pose a combination of causal relationships using concise text and lines. A fishbone diagram is used to describe the causes and consequences of accidents as the graphical map, which is characterized by analyzing the reasons using the consequences.

From environmental factors, management deficiencies, equipment defects and victims' features, cause-consequence analysis of chlorine release accident was performed and the result was displayed in Figure 11.

4.2 Risk reduction measures

1) Emergency rescue teams

The general headquarters for emergency rescue on the spot should contain the vigilance team, lighting team, dilution team, rescue team and detection team. Each team is in charge of different tasks.

The following task allocation needs to be considered:

• Vigilance team, whose task is to set up the warning line 50 meters away from the factory entrance, and another external warning line would be set 300 meters away from the plant, which is strictly prohibited vehicles into accident locations.

• Rescue team, whose task is to use the medical life-saving equipment such as a ventilator, first aid kit, rescue package, stretchers, etc..

• Dilution team, whose task is to use water jet/spraying gun to dilute the contaminated area. A water jet/spraying gun is preferable equipment that provides not only long range shooting water but spraying form. By changing its functions, a water jet/spraying gun can be used in long-range case and large area case at the same time or to spray fog as a protective shelter for rescue team.

• Lighting team, whose task is to use mobile lighting equipment in the evening.

• Detection team, whose task is to enter the accidental site and conduct reconnaissance, search for trapped persons; to use the toxic gas detectors and other equipment to determine the location of the release of liquefied Chlorine.

2) Absorbent selection

Commonly used absorbents are caustic soda, sodium thiosulfate and sodium. Each absorbent has different characteristics so it the following criteria:

• Alternative absorbent would be not corrosive or otherwise destructive to the items undergoing decontamination.

• The users must read and follow the manufacturer's label directions concerning the recommended disinfectant concentration, contact time and method of application.

• The rescue team members should wear the appropriate gloves, lab coats and eye protectors whenever using chemical disinfectants.

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• It must be determined whether the design of the equipment or its construction materials would have an effect on the decontamination process.

A sodium thiosulfate is a preferred absorbent for Chlorine release accidents. The use of sodium thiosulfate will not hurt the site operators, and greatly reduce the harm to the rescuers. Also the products of sodium thiosulfate reaction with Chlorine will not produce decomposition products - Chlorine, which reduces the environmental pollution caused by decontamination process.

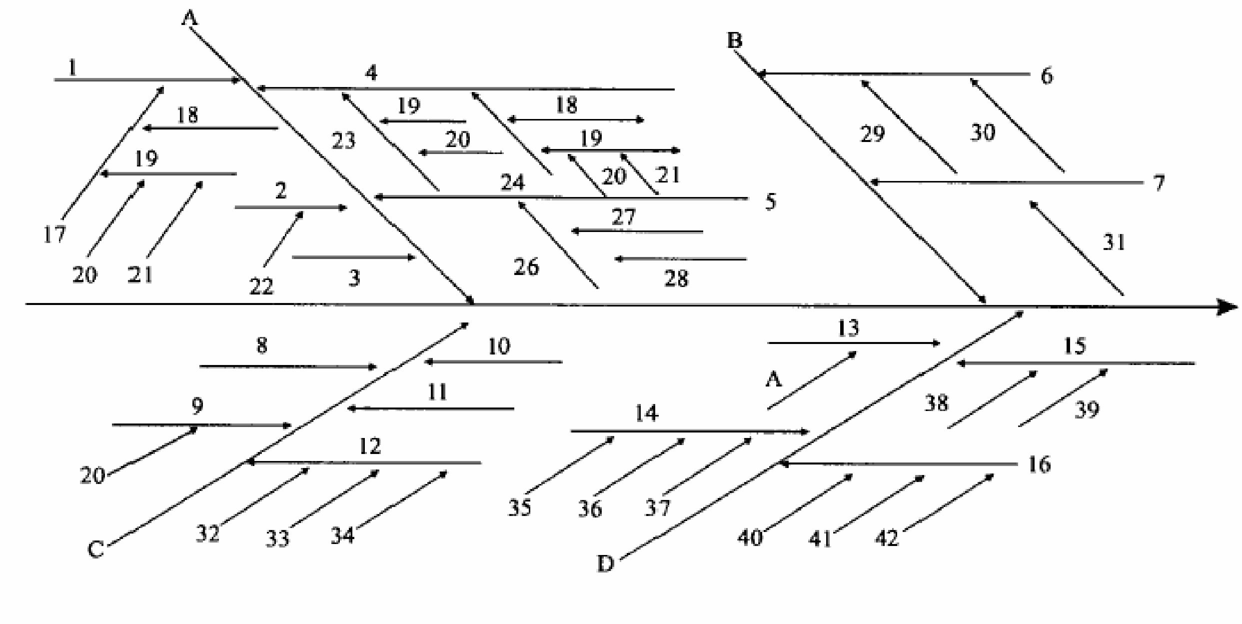

Figure 11. The cause-consequence analysis of the Chlorine leakage accident

<u>Notes:</u>

A. Equipment defects;
B. Victims' features;
C. Environmental factors;
D. Management deficiencies;
1. Plugging failure;
2. Incomplete safety accessory;
3. Extended storage;
4. Leakage channels;
5. Inadequate bearing capacities;
6. Unknown to the dangerous environment;
7. No effective protections;
8. Temperature variations;
9. No exclusive treasury;
10. Wind;
11. Chemical plant located in residential areas;
12. Inadequate accident emergency rescue conditions;
13. Warning sign is unavailable;
14. Lack of the management measures of major hazards installations;
15. Not strict security systems;
16. Restrictions on the system are not implemented;
17. Valves failure;
18. Long time open storage;
19. No maintenance;
20. Dereliction of leaders;
21. Dereliction of mechanics;
22. Theft;
23. Seal failure;
24. Outlet valve damage;
25. Stem rust;
26. Pressure increase;
27. Temperature change;
28. Residual Chlorine;
29. No warning sign;
30. Lack of awareness of the dangers;
31. Lack of protection knowledge;
32. No Chlorine-free pool;
33. Lack of fire service facilities;
34. No reserve limes for emergency rescue;
35. Lack of security checks of the cylinder;
36. Lack of safety assessment of cylinder;
37. The cylinder is not identified as a major hazardous installation;
38. Lack of management system of the use of hazardous chemicals;
39. Lack of emergency plans for hazardous chemical accidents;
40. Personal responsibility is not clear;
41. Lack of hazardous chemical registration to authorities;
42. No report to the authorities about the use of the liquid Chlorine.

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4.3 Accident prevention strategy

Considering diversities of accident causes, the accident prevention and control strategies can not only emphasize technical measures but also take all related aspects into account. As the management factor in the accident is vital, this paper will be mainly focused the accident prevention measures on management aspects.

4.3.1 To improve equipment reliability

(1) In accordance with relevant requirements, it needs to cyclically conduct strict inspections and periodic maintenances.
(2) A strict maintenance regulation will be customized to strengthen preventive maintenances and eliminate potential hazards.
(3) According to the hazardous chemical management requirements, cylinders or storage tanks should be placed in a specific storage building and its architecture should be consistent with the requirement for fire protection.

4.3.2 To establish strict safety management system

(1) Regulatory circle must strictly enforce the hazardous chemical production and storage approval process.
(2) Regulatory circle must juristically execute requirement of hazardous chemicals registration procedure. The quantity, use and daily management of hazardous chemicals should be registered to local authorities initiatively.
(3) Staff must identify major hazardous installations in the plant and carry out safety assessment according to legal requirements.
(4) Any plants must establish and improve the responsibility system of work safety and to clarify the respective responsibilities to any leaders at all levels and working staff.
(5) Any plants must strengthen safety education and vocational and technical training. Special operation workers also must adhere to certificate requirements.

4.3.3 To reduce the accident severity

(1) The staff must set up obvious warning signs in the hazardous chemical storage site.
(2) Near the site to hazardous chemicals storage, any plants must prepare emergency facilities and protective equipment and life-saving equipment.
(3) Regulatory circle will publicize knowledge of hazardous chemicals and simple self-rescue methods when workers are exposed to hazardous chemicals.
(4) Any plants must send the scrapped Chlorine cylinder / tank to a qualified unit for destructive processing and avoid the troubles left.

4.3.4 To improve the management of local government

In order to avoid accidents, the government must strengthen its administration using legal means to induce the company and other officers to strictly enforce the relevant laws, regulations, and other systems.

5. Conclusion and future researches

First, chlorine was an acute poisoning gas. Its occupational exposure threshold was 1mg/m3, i.e. 7.7 × 10-7 in mass fraction. 0.5 ~ 1 hour inhalation ceiling dose that caused serious illness was 0.000014 ~ 0.000021 in volume fraction, i.e. 3.5 × 10-5 ~ 5.2 × 10-5 in mass fraction. As for two scenarios studied here, even if the Chlorine leak rate or amount was very low, the chlorine dispersion still could reach 100 meters down wind and caused damage to humans that were far beyond the boundary of the factory. When an accident occurred, if the staff in and around factory were not timely evacuated, these staff will be poisoned and resulted in casualties.
Second, from the simulation results, it can be seen that in the case where obstacles exist, chlorine did not diffuse homogeneously down wind. The barrier would exert great impact on the dispersion of chlorine. The most obvious phenomenon was that vortex was formed on both sides of building or its rear, the existence of chlorine vortex would cumber dispersion and binding effect can reduce the diffusion speed of chlorine and increase accident consequences.

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Third, cause-consequence analysis of chlorine release accident was applied and the result showed that the accident consequences were greatly influenced by at least four aspects including environmental factors, management deficiencies, equipment defects and victims.
Fourth, the accident scenarios have been simplified by artificial adjustment, but have not been validated by experimental data. The future task would be the reappearance of the real accident scenarios, and the accuracy of the simulation can be further authenticated using measured data. On the other hand, the chlorine dispersion range and impact from barriers on the dispersion can provide the basis for the emergency rescue, and to optimize the design of the plant structure that can reduce the consequences of toxic hazards.

Acknowledgements
The authors appreciate the support of the Key Technologies R&D Project of 11th 5-Year Plan National Science and Technology (No. 2006BAK08B01, 200603746006).

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