Korean J. Chem. Eng., 35(5), 1225-1230 (2018)
DOI: 10.1007/s11814-018-0013-0

pISSN: 0256-1115
eISSN: 1975-7220

Design of the safety standard at hydrofluoric acid handling facilities for risk reduction

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(*Received 24 August 2017 • accepted 2 February 2018*)

Abstract−Although spill incidents at loading and unloading facilities account for only 4% of the chemical accidents that occurred in Korea during the last four years, the increase is incremental each year. Loading and unloading facilities are equipped with trenches in preparation for mass drainage because transports by vehicle are frequent and physical blocking is difficult when a release accident occurs. Particularly, in the case of a chemical release with a high vapor pressure, the trench is effective to mitigate accidents by reducing the liquid surface to primarily prevent dispersion. This study proposes an improved trench system that can effectively and rapidly withdraw large amounts of chemicals spilled from transport vehicles. Assuming a total volume leakage of a 55% hydrofluoric acid (HFA) solution from a transport vehicle, the study confirmed the risk-reducing effect by comparing using the consequence analysis program (ALOHA) and Probit analysis. The results show that minimizing the time that the released chemicals stay in the trench using control system (pH meter and automatic valve) can reduce the amount of chemicals vaporizing, thereby minimizing the effect distance of the release incident.

Keywords: Trench, Hydrofluoric Acid (HFA), Risk Reduction, Probit Analysis, Consequence Analysis

INTRODUCTION

From 2013 to October 2016, 378 chemical accidents occurred in Korea [1]. Although only 15 of these accidents (4.0%) occurred during loading and unloading, their proportion has increased every year, from 2.3% in 2013 to 6.8% in 2016. Loading and unloading facilities are difficult to physically shield because of the frequent entrance and exit of vehicles. Particularly, when a material with a high vapor pressure leaks, the vapor from the surface of the liquid disperse into the atmosphere more rapidly, which can seriously affect the residents and environment surrounding the workplace. At a business site in Geumsan, Chungcheongbuk-do, two incidents occurred during loading and unloading operations, in which anhydrous hydrofluoric acid (HFA) and an aqueous HFA solution (55%) leaked [2]. In 2014, the leak involving anhydrous HFA (which has a low boiling point) caused serious injuries to nearby residents from the dispersion of HFA vapor. In 2016, a HFA aqueous solution (55%) leaked into a trench as it was being transferred from the tank of a transport vehicle. Some of the solution overflowed out of the trench (the effective capacity of the trench was less than the total amount released) and formed a liquid pool; HFA evaporated from the surface of the pool, affecting the outside of the business site.

The trench is a type of diffusion-preventative equipment for loading or unloading facilities that must allow vehicles to pass without physically blocking loading or unloading areas; the trench is in the form of a pit in the earth and can accommodate the discharged material [3]. In this regard, when a leak occurs, the trench effectively blocks the spread of the liquid material and minimizes the liquid surface area [4]. Thus, it is practically difficult to indefinitely increase the effective capacity with respect to the best design conditions and physical space so that the trench can accommodate the entire amount released from the vehicle. Furthermore, when the trench area is large, a large amount of vapor components evaporate at the surface of liquid, and the chemical may affect a large area (generally, a liquid with a high vapor pressure is more likely to exhibit such a tendency). Therefore, blocking the spread of the liquid and minimizing the surface area of the liquid must both be considered when designing a trench. However, current laws and regulations of Korea only provide just legally required criteria for trenches rather than effective design guidelines [3].

We investigated the detailed criteria for a trench at the site of chemical loading and unloading. A 55% aqueous solution of HFA, which is increasingly used in the semiconductor and electronics industries, was selected, and the accident scenarios assumed that all of the HFA leaked from the tank of the transport vehicle. To analyze the effect of trenches with an optimum design against the legal criteria acceptable, we used an atmospheric dispersion analysis program (ALOHA) to analyze the range of vapor dispersion for each method, and further compared the damaging effects (i.e., death probability) according to the leakage time using Probit analysis.

SUBJECTS AND METHODS

1. Materials

We selected a 55% aqueous solution of HFA because the frequency of accidents is proportional to its increasing use in the

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semiconductor and electronics industries. The domestic hydrogen fluoride (HF) distribution increased from 39,172 ton in 2010 to 88,366 ton in 2014, and the number of sites handling HF increased from 378 to 472 [5]. Moreover, with 13 leak incidents over the past four years, HF has a relatively high accident frequency among all liquid toxic materials [1]. HF penetrates skin tissue and can cause death; thus, special care should be taken to avoid spreading the detrimental effects of a leak to the surrounding region. However, the high vapor pressure of HFA means that the vapor rapidly disperses into the atmosphere; thus, safety measures are required to minimize dispersion of HFA vapor when preparing for a leak. The high vapor pressure of HFA means that it is a good representative material for managing the effects of atmospheric dispersion. HFA (55%) has the following physical or chemical properties: molecular weight=20.01 g/mol, specific gravity=1.19, boiling point=96 °C, melting point=−36 °C, and vapor pressure=9.1 kPa [6].

2. Equipment

We examined two types of trenches. First, a trench (Case A) with a general structure was installed in minimum compliance with the legal standards and functions [3]. This type of trench can physically block the discharged materials and can fully accommodate the amount of liquid that could be released during loading and unloading (including the area where the transport vehicle is parked) (Fig. 1(a)). Furthermore, the scale is enlarged because the trench must be a sufficient distance from the stop line of the transport vehicle to prevent the splashing effect from overfilling and to secure the space required for emergency control work. Otherwise, the trench path can be deepened or widened to provide a capacity that exceeds the amount released, or a sump can be simultaneously installed to temporarily trap the discharged liquids. Second, a trench (Case B) with a minimized area that processes the discharged amount by automatic control was considered [2]. In Case B, a control system, such as a pH meter or liquid level meter, that is automatically connected to the automatic valve was installed at the bottom of the trench to promptly discharge the materials to a wastewater treatment plant with automatic operation ("opening") of the valve when the set value is exceeded (Fig. 1(b)). This type of trench can accommodate the released amount regardless of the trench size and reduces the surface area by automatically and promptly processing the discharged materials. However, even for Case B, it is necessary to secure a minimum space for splash prevention and control work; thus, the trench should be installed at a certain distance from the stop line of the vehicle.

In this study, the trench size was designed by considering the loading and unloading facilities for a 25,000-L transport tank, which is widely used in Korea. The 25,000-L tanker vehicle has dimensions of 10.5 m×3.7 m (length×width). The minimum control distance (1.5 m) from the stop line of the tanker vehicle to the trench must be considered. Case A has a length (L) of 14.5 m, a width (A) of 6.7 m, and a depth (D) of 0.5 m. The waterway length (B) from the trench to the catchment tank is 1 m, the catchment tank is 4.0 m in both length and width (C), and the depth (H) of the catchment tank is 1.0 m. In contrast, Case B is designed to have no catchment tank because the discharged material is automatically treated. The specifications for Case A and Case B are shown in Table 1.

3. Methods

When chemicals with high vapor pressures are spilled, consid-

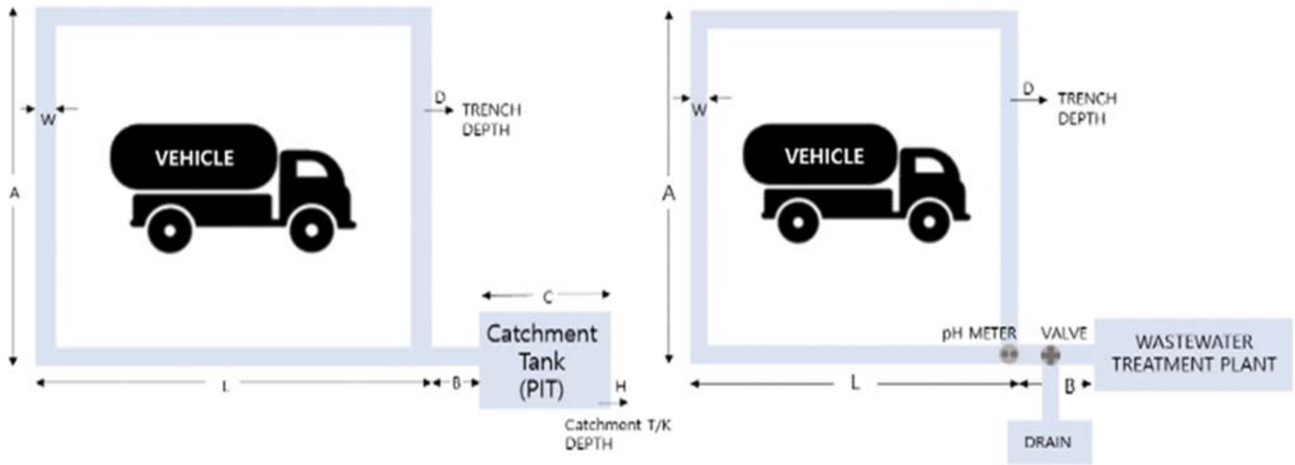

Fig. 1. Installation diagram for trench facilities: (a) Current system, (b) Advanced system.

Table 1. Comparison of the specifications for Case A and Case B

Type	L: Length (m)	B: Waterway length (m)	A: length (m)	W: Width (m)	D: Depth (m)	Catchment tank		Trench volume (m^3)	Puddle area (m^2)
						C: Length/ Width (m)	H: Depth (m)		
Case A	14.5	1.0	6.7	0.5	0.5	4.0	1.0	26,350	36.7
Case B	14.5	1.0	6.7	0.5	0.5	-	-	10,350	20.7

Table 2. ALOHA modeling input values

Scenario type	Wind speed	Atmospheric stability	Atmospheric temperature	Humidity	Surface roughness	Trench material
Alternative	1.5 m/s	D	25 °C	50%	Urban	Concrete
Worst-case	3.0 m/s	F				

erations other than physical blocking are used to minimize the effect of vapor dispersion. The effect here can be explained by the extent to which the vapor is dispersed and the effect duration at which it reaches an endpoint (or reference value) that can affect a person or the environment. The effect distance of vapor is expressed as a range calculated according to the consequence analysis program, and the effect duration can be calculated as the inverse proportion to the time to process the released amount and the amount that remains on the liquid surface. In this study, assuming a scenario in which the entire amount of HFA leaks from a 25,000-L tanker vehicle, we analyzed the dispersion distance of HFA vapor for each case and produced a design guideline that minimizes the effect of atmospheric dispersion by combining the effect duration [7]. The program used to analyze the effect distance and the weather conditions is described below.

3-1. Consequence Analysis Program and Weather Conditions

Diffusion of liquid toxic materials depends on the amount of evaporating leaked materials, which form a liquid layer (hereinafter referred to as the liquid surface) at the liquid surface. Therefore, we consider the case where the leaked aqueous HFA acid forms a liquid surface on the inside or bottom of the trench and evaporates and disperse as a vapor. The consequence analysis was performed using ALOHA (version 5.4.7), a consequence analysis program developed by the US Environmental Protection Agency [7]. The meteorological conditions required for the analysis and the evaluation conditions of the alternative scenario and worst-case scenario are shown in Table 2. The roughness depends on the trench material (concrete).

3-2. Endpoint (Reference Value)

The endpoint is the point at which the conditions reach the numerical values of toxic concentration, overpressure, and radiant heat that can affect people or the environment. The endpoint can be used as a reference value for incident consequence analysis. The aqueous solution of HFA has a higher risk of toxic substance leakage than fire or explosion; thus, only the toxic concentration reference value is considered [9]. We applied emergency response planning guidelines (ERPG) to define the endpoints: ERPG-1 (2 ppm), ERPG-2 (20 ppm), and ERPG-3 (50 ppm). These guidelines were adopted from the American Industrial Hygiene Association [10].

RESULTS

1. Comparison in Dispersion Distance of HFA Vapor

The predicted dispersion distances of HFA vapor using ALOHA are shown in Table 3, Fig. 2 and Fig. 3. It shows that the range for Case A is 78-505 m and the range for Case B is 60-373 m at the

Table 3. Dispersion distance at each scenario conditions

Level of concern of HF (ERPG)	Dispersion distance					
	Worst-case scenario			Alternative scenario		
	Case A (m)	Case B (m)	Difference value (m)	Case A (m)	Case B (m)	Difference value (m)
ERPG-1 (2 ppm)	505	373	132	251	191	60
ERPG-2 (20 ppm)	138	104	34	75	58	17
ERPG-3 (50 ppm)	78	60	18	44	34	11

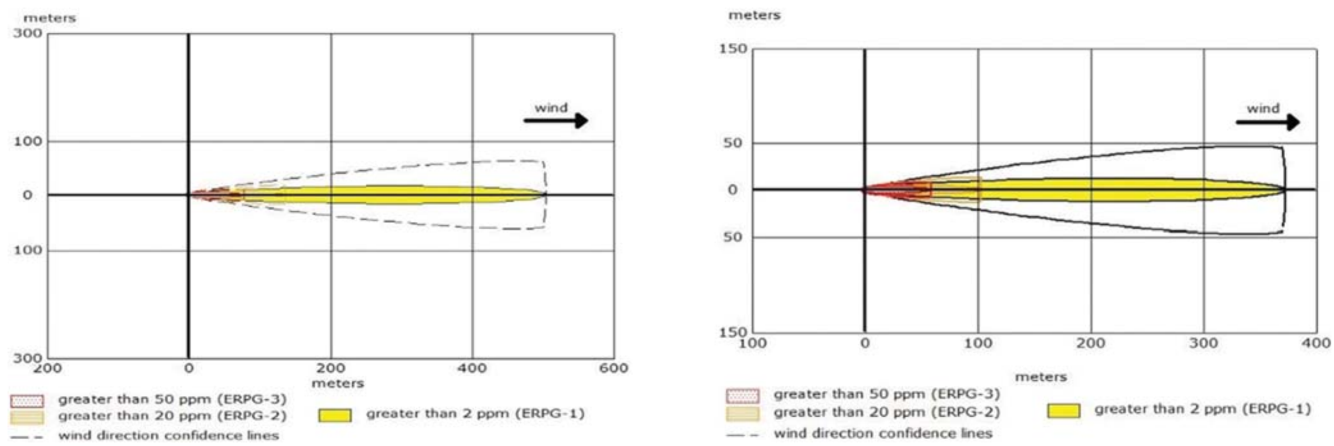

Fig. 2. Plots of the ERPG dispersions at the worst-case scenario: (a) Case A, (b) Case B.

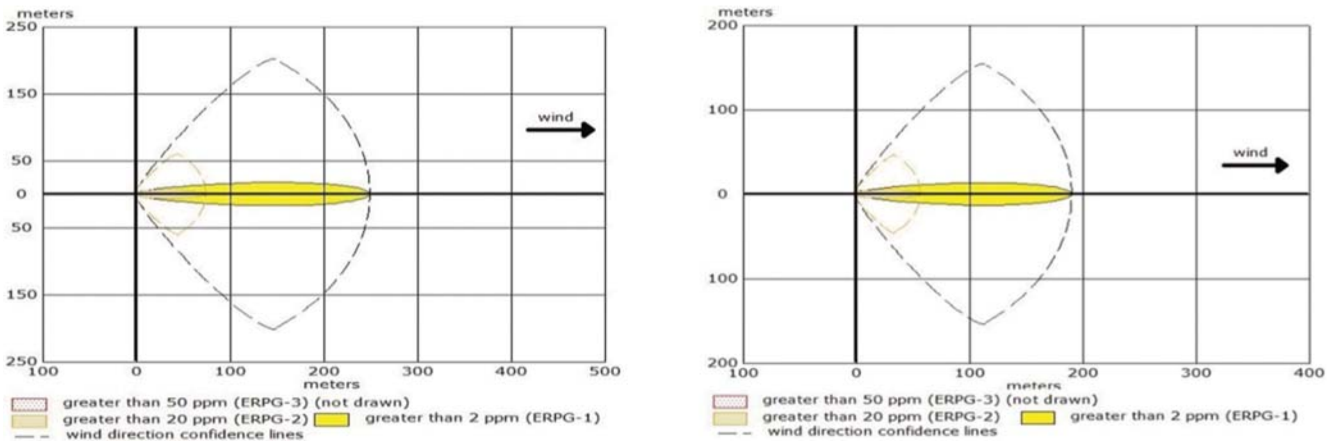

Fig. 3. Plots of the ERPG dispersions at the alternative scenario: (a) Case A, (b) Case B.

worst-case scenario and Case A is 44-251 m and Case B is 34-191 m at the alternative scenario. In addition, the difference value of dispersion distance according to the ERPG concentrations are as follows. At the worst-case scenario, the endpoint of ERPG-1 decreases from 505 m for Case A to 373 m for Case B, the endpoint of ERPG-2 decreases from 138 m to 104 m, and the ERPG-3 endpoint also decreases from 78 m to 60 m. We can know that the tendency of results at the alternative Scenario is similar to that at the worst-case scenario. The difference values between Case A and Case B at the worst-case scenario are 132 m, 34 m and 18 m, respectively, and at the alternative scenario, those are 60 m, 17 m and 11, respectively.

These results can be explained as follows. The surface area of the liquid layer that was formed by leaking in Case B (20.74 m^2) is lower than that in Case A (36.7 m^2); the initial vapor concentration formed from the liquid layer is low, and the effect distance is reduced in proportion to the concentration [11-14]. In particular, it is possible to reduce the effect on residents and workers within the effect range because the distance is reduced by 34 m (24.6%) or 17 m (22.6%) based on ERPG-2, respectively. As a result, the effect distance from a massive spill from a transport vehicle is reduced, reducing the potential risk of an HFA spill incident.

2. Comparison of the Impact Durations

In Case A, the entire amount of HFA flows into the trenches. Then, the plant reports the incident to the Ministry of Environment. The fire department conducts the first response, and the Ministry of Environment measures the concentration around the accident site. The municipality safely removes the controlled materials from the site using a waste vehicle. However, it is very difficult to remove the released materials because it is difficult to access the vicinity of the accident because of the dispersion of HFA vapor. The statistics for chemical accident responses in 2016 indicate that the fire department generally dispatched a team within 10 min after being notified of the incident to start the disaster prevention work. The Ministry of Environment and local governments arrived within approximately 1 h to clear the accident site. After completing the first response, it takes another 2 h for a waste transport vehicle to arrive at the site. It takes approximately 167 min (2 h 47 min) to collect the 25,000-L spill using the 150 L/min feed pump at the maximum feed rate. The transfer time can be calculated by assuming that the effect of the water head is small because of the low depth of the trench and that the maximum transfer rate was applied. Generally, the total required time is 5 h and 47 min.

In Case B, when the entire amount of HFA flows into the trench, the pH meter detects the outflow and promptly operates the automatic valve to transfer the discharged materials to the wastewater treatment plant. Assuming a maximum transfer rate of 150 L/min for the feed pump used to transfer the HFA from the workplace, it takes approximately 167 min (2 h 47 min) to transfer 25,000 L. The feed amount corresponds to the amount in the waste transport vehicle in Case A. The total required removal time is thus 2 h and 47 min.

The removal time in Case A is 5 h 47 min (347 min), and the transfer time (to transfer materials to the wastewater treatment plant) in Case B is 2 h 47 min (167 min). The damage depends on the discharge duration. Probit analysis was conducted as described below to calculate the damage effect from the leakage of toxic materials [15],

$$Pr=A_t+B_t \ln T_L \tag{1}$$

$$T_L=C_t^n t_e \tag{2}$$

where A_t and B_t are constants for specific toxins (ppm) (see Table 4), T_L is the toxic load (ppm·min), C_t is the toxic concentration during exposure (ppm), n is a constant for specific toxins (see Table 4), t_e is the exposure time, and Pr refers to Probit. The concentration was set at 20 ppm, which is the concentration for ERPG-2.

Table 5 shows the conversions from Probits to percentages, and Table 6 outlines the Probit results for Case A and Case B. The probability of death from the Probit equation in Case B is 3.7-

Table 4. Constants from the probit equation for HF

Probit	Hydrogen fluoride		
	A_t (ppm)	B_t (ppm)	n
US Coast Guard (1980)	−25.87	3.354	1.00
World Bank (1988)	−26.3	3.35	1.0

Table 5. Conversion from probits to percentages

Percentage (%)	Probit (n applications below)									
	0	1	2	3	4	5	6	7	8	9
0	-	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.65	7.88	8.09

Table 6. Conversion from probits to percentages

Type	Te (min)	C_t (ppm)	T_L (ppm/min)	Probit (Pr)		Death Percentage (%)	
				US Coast Guard	World Bank	US Coast Guard	World Bank
Case A	347	20	6,940	3.80	3.33	11.6	4.7
Case B	167	20	3,340	1.34	0.88	>1	>1

10.6%, which is lower than that for Case A. Different results were obtained because the leakage duration in Case A is approximately 180 min longer than that of Case B, and the exposure time increases accordingly, resulting in a higher probability of death. In addition to the exposure degree, the system proposed in this study shows a reduced probability of death compared to that provided by the existing trench system, thereby providing the basis for the design of a new trench.

CONCLUSIONS

A trench is a mitigating device to prevent materials from a transport vehicle at loading and unloading facilities from discharging outside of the facility. Although capacity is an important design factor when designing trenches, the possibility of atmospheric diffusion should be considered for materials with high volatility, such as HFA. This study estimated and compared the effect range with respect to the trench installation conditions using ALOHA, which is one of the consequence analysis programs, assuming that the entire amount of HFA (55%) is released from a transport vehicle with a capacity of 25,000 L. The trenches designed according to the current laws and regulations are classified as Case A, and the trenches for automatic treatment of the released materials are classified as Case B. Accordingly, alternative scenario modeling assumptions were applied for further experiments.

Case A has a trench capacity of 26,350 L and a puddle area of 36.7 m^2 when the total volume is discharged from a 25,000 L transport vehicle. In Case B, when the total amount is released from the transport vehicle, an automatic valve is automatically operated by a pH meter that senses the discharge, and the released materials can withdraw into the wastewater treatment plant; the puddle area is 20.7 m^2. The ALOHA evaluation indicates that the effect distances in Case B are reduced by 18-132 (23.1-26.1%) at the worst-case scenario and 11-60 m (22.7-23.9%) at the alternative scenario compared to the ERPG concentration in Case A. The effect distance from the evaporated vapor components from the liquid surface can be reduced as the surface area of the liquid in the trench is reduced. These results confirm that the proposed system, whereby the effect distance by dispersion was reduced, could be applied as a trench installation standard.

The removal time for Case A was 5 h and 47 min (347 min), and the transfer time to the wastewater treatment plant in Case B was 2 h and 47 min (167 min). The discharge duration in Case B was reduced by 3 h (180 min). As a result, the probability of death (calculated from the Probit equation) is 3.7-10.6% lower for Case B than Case A; thus, Case B can be used as a design standard for reducing the risk of trenches. The results further show that minimizing the time that the released chemicals stay in the trench by control system (pH meter and automatic valve) can reduce the amount vaporizing of chemicals, thereby minimizing the effect distance of release incident.

To obtain reliability, a real test has to be conducted. However, a real test with chemicals is highly dangerous and difficult, considering toxicity. The pilot-scale test is necessary in the future as an alternative.

ACKNOWLEDGEMENTS

This paper was supported by the Chemical Process Safety System Laboratory in Chonnam National University and the Material and

Equipment Safety Laboratory in Chungbuk National University.

TABLE OF NOMENCLATURE

A	: length
A_t	: constant for a toxin
B	: waterway length
B_t	: constant for a toxin
C	: catchment tank length
C_t	: concentration
D	: depth
H	: catchment tank depth
L	: length
n	: constant for a toxin
Pr	: Probits
t_e	: exposure time
T_L	: toxic load
W	: width

REFERENCES

1. KOREA NICS, Chemical Safety Clearing-house, csc.me.go.kr (2016).
2. C. H. Shin, S. J. Lee and J. H. Park, *Crisisonomy*, **13**, 85 (2017).
3. KOREA ME, Chemicals Control Act, Ministry of Environment, me.go.kr (2016).
4. UK HSE, Storage of flammable liquids in tanks, Health and Safety Executive, www.hse.gov.uk/pubns/books/hsg176.htm (2015).
5. KOREA ME, Environmental White Paper, Ministry of Environment, me.go.kr (2016).
6. CAMEO CHEMICALS, cameochemicals.noaa.gov (2017).
7. United States Environmental Protection Agency, Risk Management Program Guidance for Offsite Consequence Analysis (2013).
8. C. H. Shin, B. C. Ma and J. H. Park, *Crisisonomy*, **12**, 1 (2016).
9. KOREA NICS, Guidelines for Evaluating End Point of Chemical Accidents, nics.me.go.kr (2015).
10. American Industrial Hygiene Association (AIHA), AIHA Guideline Foundation, ERPG/WEEL Handbook (2015).
11. Center for Process Safety of the American Institute of Chemical Engineers (AIChE), Guidelines for Use of Vapor Cloud Dispersion Models, 2nd Ed. New York, *AIChE J.* (1996).
12. Y.-k. Jung, B. Kim, H. Heo, B. Yoo, C. Sin, Y. Yoon, J. Yoon and B. Ma, *J. Korean Soc. Safety*, **32**(2), 52 (2017).
13. Y.-k. Jung, H. Heo, B. Yoo, Y. Yoon, J. Yoon and B. Ma, *J. Korean Inst. Gas*, **20**(2), 49 (2016).
14. D. A. Crowl and J. Louvar, *Chemical Process Safety* (3rd Ed.) (2011).
15. Centre for Chemical Process Safety, Guidelines for Chemical Process Quantitative Risk Analysis, 2nd Ed. (1999).