Korean J. Chem. Eng., 35(2), 348-354 (2018)
DOI: 10.1007/s11814-017-0288-6

pISSN: 0256-1115
eISSN: 1975-7220

Evaluation of a mitigation system for leakage accidents using mathematical modeling

Kwang Oh Lee, Jae Yeon Park, and Chang Jun Lee†

Department of Safety Engineering, Pukyong National University, 45, Yongso-ro, Nam-gu, Busan 48513, Korea
(*Received 28 July 2017 • accepted 11 October 2017*)

Abstract−Chemical accidents generated during maintenance, repair, and normal operation, such as dispersion, fire, and explosions, can cause massive losses within and outside workplaces. Since a 2012 hydro fluorine leak in Gumi, South Korea, many studies have investigated mitigation systems for reducing accident impact. However, due to potential costs, and lack time and expertise, most companies have hesitated to install mitigation systems without accurate impact evaluations. Therefore, it is essential to analyze mitigation system efficacy under various possible accident scenarios. We considered a mitigation system incorporating a reserve vessel installed next to a storage vessel. When a leakage accident occurs, the chemical in the main vessel is transferred to the reserve vessel by a pump. Simulation results based on Torricellis' theorem indicate that this mitigation system could significantly reduce leakage, and reduce leakage consequences in terms of maximum diffusion distance and hazardous gas concentrations based on consequence analysis.

Keywords: Mitigation System Modelling, Torricelli's theorem, Consequence Analysis

INTRODUCTION

Hazardous material usage has rapidly increased with high-tech industrial development, such as the semiconductor and fine chemicals. Thus, the likelihood of a major chemical accident has also been increasing. Accidental leakage from a vessel is one of the most important causes of catastrophic events, potentially causing hazardous material dispersion, fire, and explosion [1]. Representative examples of accidental material release from vessels include Fixborough, England (1974) [2]; Seveso, Italy toxic gas release (1978) [3]; and Gumi, South Korea accidental release of hydrogen fluoride (HF) (2012). It is essential to develop mitigation systems to reduce material release impact.

Many mitigation systems have been proposed. Water spray or curtain is a common representative system to mitigate a vapor cloud [4-7]. Rana et al. [4] tested two water curtain systems to identify their effectiveness for a liquefied natural gas (LNG) release. McQuaid and Fitzpatrick [5,6] performed an analytical study to investigate the impact of a water spray system for a heavy-gas plume. Moodie [7] tested various water spray barrier configurations to disperse clouds of carbon dioxide released in differing atmospheric conditions.

Suardin et al. [8] also tested fire suppression materials on suppression of LNG pool fires for reducing radiant heat from the pool fire. A set of experiments should be performed to evaluate a given system's efficacy. However, generally when hazardous materials are tested, the experiments represent significant danger and significantly large spaces must be secured for safety. Furthermore, it is rarely possible to perform experiments at the level of academic laboratories.

Computational simulations are popular alternatives to physical experiments. Busini and Rota [9] simulated mitigation barrier effectiveness to interrupt LNG travel using computational fluid dynamics (CFD). Liu and Wei [10] simulated continuous dense gas leakage based on a modified plate model. Swain et al. [11] simulated an accident scenario considering a vehicle parked in a single-car garage with a fuel-line leak based on computational fluid dynamics.

However, most research based on CFD has focused on gas dispersion models, and there have been only few studies evaluating the efficacy or impact of mitigation systems based on computational simulations. However, computational simulations can reduce cost, effort, and time to verify mitigation system performance. The current study proposes a new mitigation system based on a reserve vessel being installed next to the storage vessel and connected with a pipe. If a leakage occurs, the chemical substance in the storage vessel is transferred to the reserve vessel by a pump. Even if a few workplaces already employ this system in South Korea, there is no scientific analysis to identify how much the proposed system contributes to leakage reduction.

Section 2 introduces the proposed mitigation system model. Section 3 applies the model to several case studies, and Section 4 presents a consequence analysis for gas dispersion using ALOHA. Section 5 summarizes the outcomes and concludes the paper.

MODELING A MITIGATION SYSTEM

1. Process Conditions

We propose a mitigation system for a material leakage. To evaluate a material leakage, the following parameter must be previously determined.

- Diameter of the open hole.
- Location of the hole on the vessel.

†To whom correspondence should be addressed.
E-mail: changjunlee@pknu.ac.kr

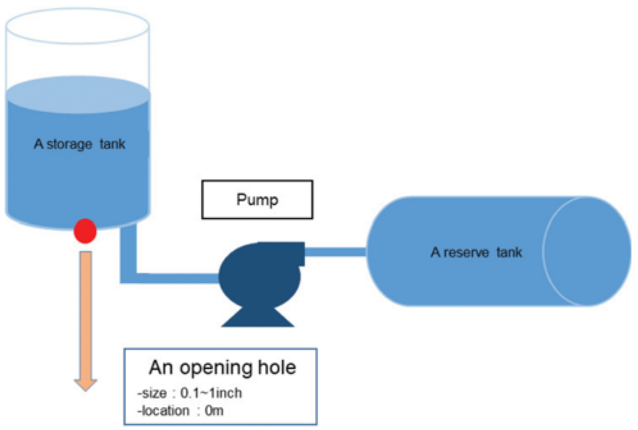

Fig. 1. Proposed a mitigation system. Reserve tank is connected to the storage tank by a pump that directly transfers HF when a leakage occurs.

- Start time of the mitigation system after a leak occurs.
- Atmospheric conditions.
- Vessel operating conditions.
- The properties of a chemical compound.

Three vessel types were considered: vertical cylinder, horizontal cylinder, and sphere. The vessel total storage capacity for each case was 112.64 ton, with only half of the total capacity, i.e., 56.32 ton, stored under normal operating conditions. Nitrogen was assumed as the inert gas in the vessel.

We assumed the mitigation system commenced simultaneously with HF leakage occurrence, i.e., there was no time delay between the leakage and mitigation commencement. In this mitigation system, a pump directly transfers HF from the storage vessel to a reserve vessel, as shown in Fig. 1.

2. Calculating the Leakage Rate at an Opening Hole

Torricelli's theorem was used to evaluate fluid velocity for an open hole under hydraulic pressure. Eq. (1) represents the principle of conservation of energy, fluid potential energy is converted into kinetic energy, where v_1 and h_1 are the velocity and height, respectively, at the top of the fluid; v_2 and h_2 are the velocity and height, respectively, at the open hole; ρ is the fluid density; P_1 and P_2 are the pressures at the top and open hole, respectively; and g is the gravitational acceleration.

Table 1. Vessel parameters, properties, and process conditions

Horizontal cylindrical vessel	Radius	2.275 m
	Length	6.824 m
Vertical cylindrical vessel	Radius	2.275 m
	Height	6.824 m
Spherical vessel	Radius	2.9806 m
Operating	Pressure	5 bar
	Temperature	−3 °C
Atmospheric	Pressure	1 atm
	Temperature	23 °C
van der Waals constants for nitrogen	a	0.1408 m^3 Pa/mol^2
	b	0.00003913 m^3/mol^2

$$\frac{v_1^2}{2}+gh_1+\frac{P_1}{\rho}=\frac{v_2^2}{2}+gh_2+\frac{P_2}{\rho}, \tag{1}$$

As leakage progresses, the inert gas volume increases and its pressure decreases, following a van der Waals' relationship. In Eq. (2), n, V, and T are the total amount (mole), volume, and temperature of the inert gas, respectively; R is the ideal gas constant; and a and b are constant parameters indicating intermolecular forces and molecular size, shown in Table 1. The initial amount of nitrogen can be derived from the process conditions.

$$P_1=\frac{nRT}{V-bn}-a\left(\frac{n}{V}\right)^2 \tag{2}$$

The velocity at the open hole, v_2, can be derived from Eq. (1). If we assume that the fluid velocity at the top, v_1, is the same as the change of a fluid height per a unit time (dh_1/dt), then

$$v_2=\sqrt{2g(h_1-h_2)+\frac{2(P_1+P_2)}{\rho}+\left(\frac{dh_1}{dt}\right)^2}. \tag{3}$$

3. Leakage Flow Rate According to Vessel Shape

To evaluate the leakage amount, we assumed that the value obtained by multiplying the surface area at the top by the height change of a fluid per a unit time is the same with the leakage amount of a fluid at the opening hole for a unit time. This value would be determined by the hydraulic pressure and a pump capacity. Fig. 2 shows a horizontal cylindrical vessel with radius R and width L. The red point indicates an open hole with radius r. In Eq. (4), A is the

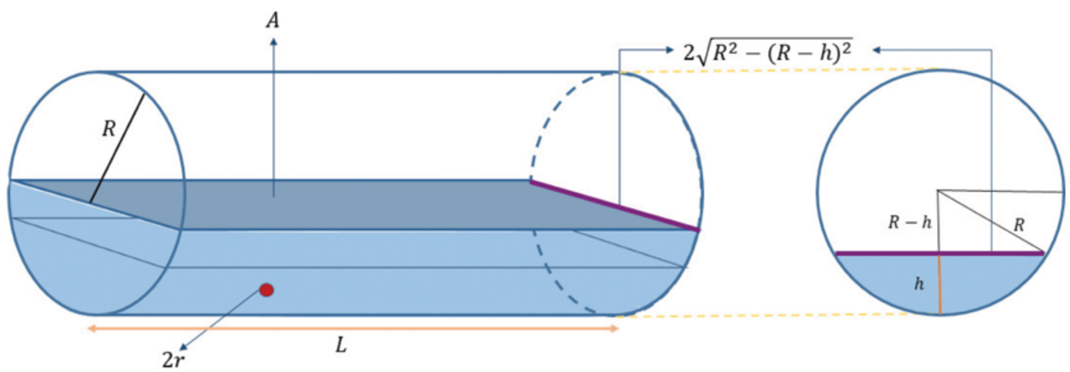

Fig. 2. Horizontal cylindrical vessel: red circle indicates an open hole with radius r; h is the HF level; and A is the surface area at the top of HF.

cross-sectional surface area at the top level, and the volume change per a unit time in the vessel is where K is the pump capacity.

$$A\frac{dh_1}{dt}=2L\sqrt{(R^2-(R-h_1)^2)}\frac{dh_1}{dt}=\pi r^2 v_2+K, \tag{4}$$

Thus, the fluid volume change rate is determined by the hydraulic pressure and pump capacity. Substituting Eq. (3) for v_2, Eq. (5) can be derived.

$$\frac{dh_1}{dt}=\frac{\pi r^2\sqrt{2g(h_1-h_2)+\frac{2(P_1-P_2)}{\rho}+\left(\frac{dh_1}{dt}\right)^2}+K}{2L\sqrt{(R^2-(R-h_1)^2)}}. \tag{5}$$

Fig. 3 shows a vertical cylindrical vessel with radius and height $\bar{R}$ and $\bar{L}$ where A is $\pi\bar{R}^2$.

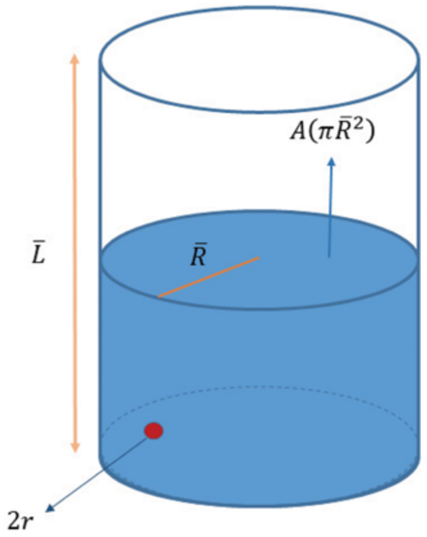

Fig. 3. Vertical cylindrical vessel: red circle indicates an open hole with radius r; h is the HF level; and A is the surface area at the top of HF.

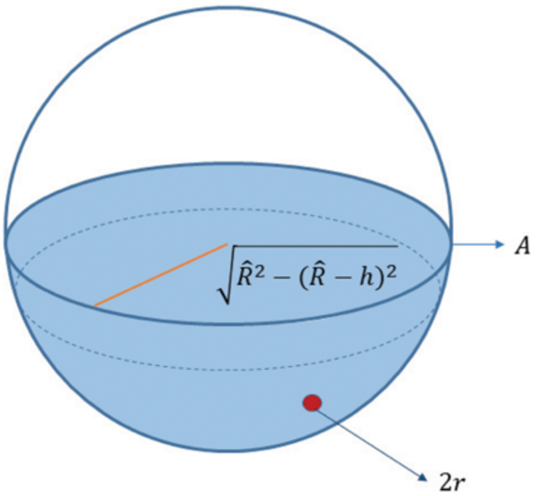

Fig. 4. Spherical vessel: red circle indicates an open hole with radius r, h is the level of HF, and A is the surface area at the top of HF.

$$\frac{dh_1}{dt}=\frac{\pi r^2\sqrt{2g(h_1-h_2)+\frac{2(P_1-P_2)}{\rho}+\left(\frac{dh_1}{dt}\right)^2}+K}{\pi\bar{R}^2}. \tag{6}$$

Fig. 4 shows a spherical vessel with radius $\hat{R}$, and the instantaneous the fluid level change rate is represented by Eq. (6).

$$\frac{dh_1}{dt}=\frac{\pi r^2\sqrt{2g(h_1-h_2)+\frac{2(P_1-P_2)}{\rho}+\left(\frac{dh_1}{dt}\right)^2}+K}{\pi\sqrt{(\hat{R}^2-(\hat{R}-h_1)^2)^2}}. \tag{7}$$

Since the maximum HF storage is only half the total capacity, h<radius for all times for each case. Thus, the situation where h> radius can be excluded.

CASE STUDIES

To verify efficacy, the effect of the mitigation system was compared to the absence. For the case studies open hole diameter=0.1-1.0 inch, with 0.1 inch interval, i.e., ten hole sizes; the height of the opening hole was fixed to 0, the bottom of the vessel; atmospheric

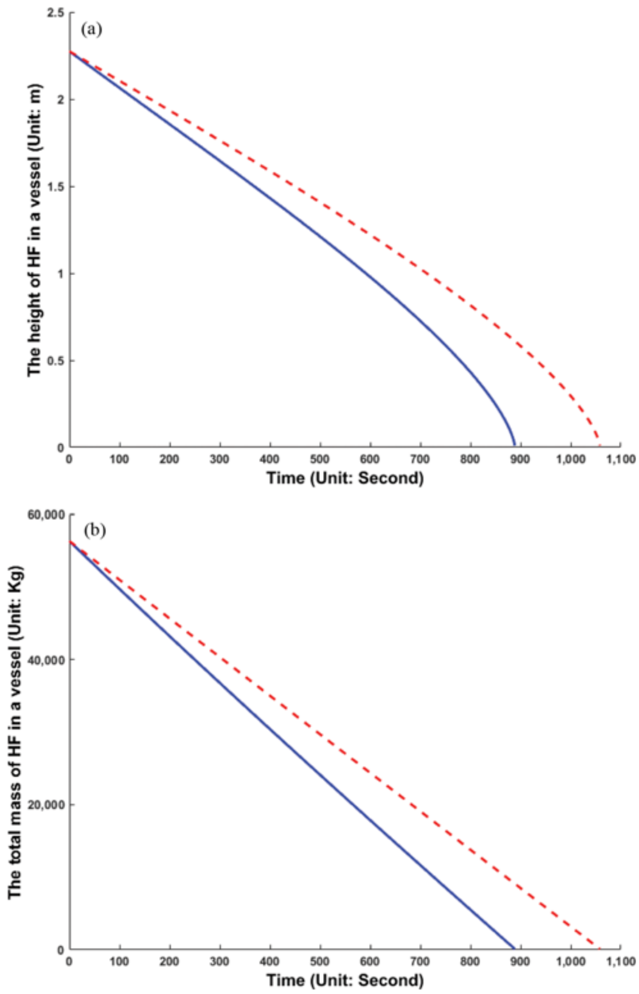

Fig. 5. Changes of (a) height and (b) total mass of HF for a horizontal cylindrical vessel. Blue solid line: hole diameter=1.0 inch; red dashed line: hole diameter=0.3 inch.

Table 2. Total leakage time for horizontal cylindrical vessel

Hole diameter (inch)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Total leakage time (s)	1076	1070	1058	1043	1024	1001	976	949	919	888

Table 3. Final ratio between leakage and reserve vessel volume for horizontal cylindrical tank after leakage accident

Hole diameter (inch)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
HF in reserve vessel (%)	99.6	99.0	97.9	96.5	94.7	92.6	90.3	87.8	85.0	82.2
HF leakage (%)	0.4	1.0	2.1	3.5	5.3	7.4	9.7	12.2	15.0	17.8

condition was 23 °C and 1 atm; total leakage duration was fixed at 10 min, and pump capacity K=185 m^3/h. The problems were solved using ODE45 solver of MATLAB. Vessel properties and processing conditions are summarized in Table 1.

Fig. 5 shows case study outcomes for hole diameter=0.3 and 1 inch. The most important factor is the pump capacity. Thus, the slopes for the changes of a height and a total mass of HF in a vessel can be changed by the capacity of a pump, and these changes look linear since the amount of HF carried by a pump is constant for a unit time.

Table 2 shows the total leakage time and Table 3 the final ratio of leakage and reserve tank storage for the various cases. For the worst scenario (hole diameter=1.0 inch), total leakage time with and without mitigation was 888 and 5,117 s, respectively; and the amount of HF leaked outside the vessel reduced approximately 82% using the mitigation system. Although the mitigation system performance is determined by the pump capacity, mitigation can significantly decrease the leakage, hence reducing the potential dam-

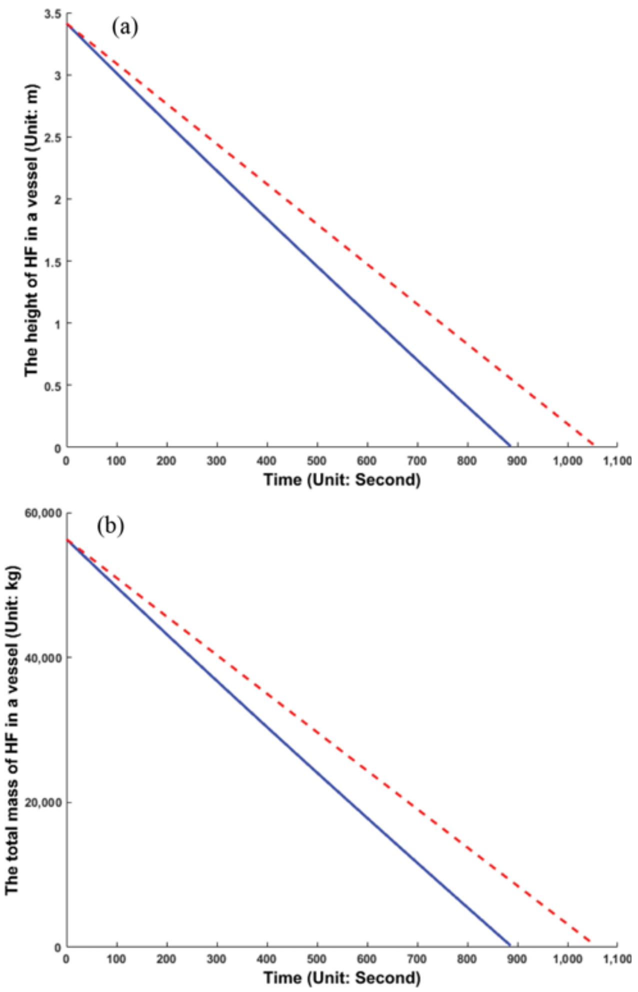

Fig. 6. Changes of (a) height and (b) total mass of HF for a vertical cylindrical vessel. Blue solid line: hole diameter=1.0 inch; red dashed line: hole diameter=0.3 inch.

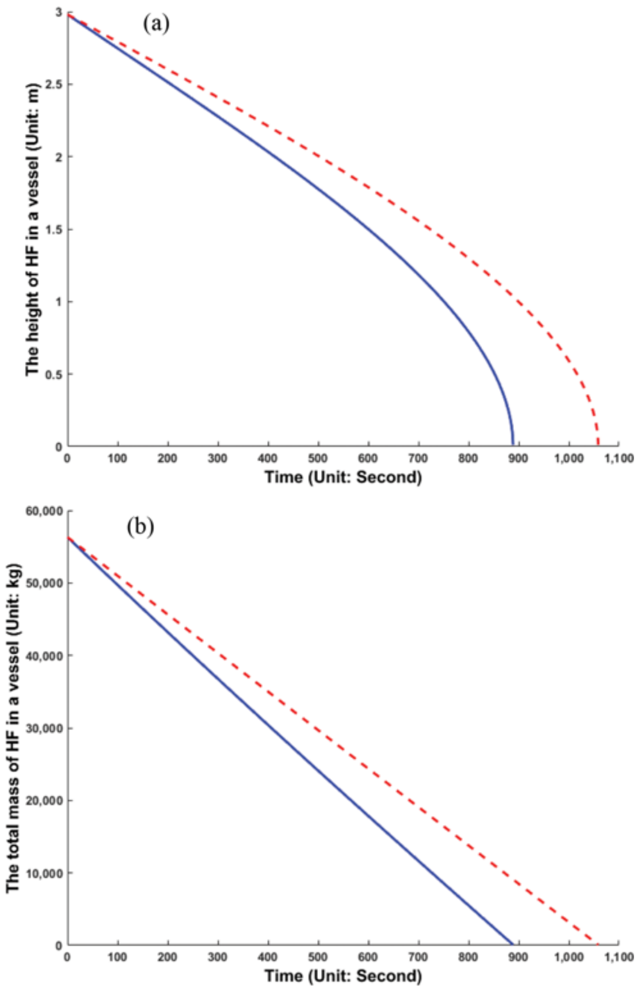

Fig. 7. Changes of (a) height and (b) total mass of HF in a spherical vessel. Blue solid line: hole diameter=1.0 inch; red dashed line: hole diameter=0.3 inch.

Table 4. Final ratios between leakage and reserve vessel volume for vertical cylindrical vessel after leakage accident

Hole diameter (inch)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
HF in reserve vessel (%)	99.3	98.7	97.7	96.2	94.5	92.4	90.1	87.5	84.8	82.0
HF leakage (%)	0.7	1.3	2.3	3.8	5.5	7.6	9.9	12.5	15.2	18.0

Table 5. Final ratios between leakage and reserve vessel volume for spherical vessel after leakage accident

Hole diameter (inch)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
HF in reserve vessel (%)	99.6	99.0	98.0	96.5	94.8	92.7	90.4	87.8	85.1	82.2
HF leakage (%)	0.4	1.0	2.0	3.5	5.2	7.3	9.6	12.2	14.9	17.8

Table 6. Leakage and reserve vessel HF quantities after leakage accident with different pump capacities for hole diameter=2.9205 inch (worst case scenario)

	Pump capacity (m^3/h)		
	185	95	18
Total leakage time (s)	383.9	465.2	568.7
HF mass in reserve vessel (t)	20.0	24.2	29.6
HF mass leaked (t)	36.3	32.1	26.7

age from a leak accident.

Figs. 6 and 7 show the simulation outcomes for the vertical horizontal and spherical vessels, respectively, for hole diameter=0.3 and 1.0 inch, and Tables 4 and 5 show the corresponding final ratio of leakage and reserve tank storage, respectively.

The Technical Guidance for Hazard Analysis [12] defines the worst-case scenario for liquid releases as:

"The maximum quantity of stored material would be released in ten minutes under worst-case weather conditions."

For considering the worst-case scenario, a hole diameter of a horizontal cylindrical vessel should be 2.9205 inch to release all HF in 10 min without a mitigation system. Therefore, three pump capacities (K=18, 95, and 185 m^3/h) were assessed using the horizontal cylindrical with hole diameter 2.9205 inch. Since the pump capacities are constant, the amount of HF transferred into a reserve tank is the same, even if diameters of an opening hole vary. Table 6 shows the simulation outcomes, and an appropriate mitigation pump capacity can be determined by the proposed method.

CONSEQUENCE ANALYSIS

Emergency response planning guidelines (ERPGs) have been widely used to provide a decision tool for emergency response and planning [12]. The American Industrial Hygiene Association specifies ERPGs, where all hazardous chemical materials have three concentration ranges: ERPG-1, ERPG-2, and ERPG-3, corresponding to light, medium, and heavy risk, respectively.

• ERPG-1: The maximum concentration that nearly all individuals could be exposed for up to 1 h without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor.

• ERPG-2: The maximum concentration that nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.

• ERPG-3: The maximum concentration that nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

Table 7. Input parameters for Areal Locations of Hazardous Atmospheres (ALOHA) software

Building type	Single storied building/ Unsheltered surroundings
Chemical	HF
Atmospheric options	1.5 m/s, Partly cloudy, 23 °C, medium humidity, no inversion
Ground roughness	Open country
Puddle diameter	10 m
Mass of HF	36.32 and 56.32 ton
Ground	Default soil, 23 °C
Pasqual stability	B

Since most people would experience serious and irreversible health effect at concentrations above ERPG-2, this concentration is generally adopted for consequence analysis as the endpoint for the emergency response and planning [12].

Consequence analyses were performed using the Area Locations of Hazardous Atmospheres (ALOHA) software developed by the US Environmental Protection Agency and National Oceanic and Atmospheric Administration. Section 3 evaluated total external leakage for the worst scenario (hole diameter=2.9205 inch) for the three considered vessels. Those outcomes and other parameters, as shown in Table 7, were input to the ALOHA software to investigate HF ERPG-2 levels.

Figs. 8 and 9 show the results of consequence analysis for the horizontal cylindrical vessel with and without a mitigation system. Maximum ERPG-2 distances are 805 and 828 m, respectively. Thus, mitigation reduces the ERPG-2 distance approximately 2.7%, even though HF leakage amount can be reduced by approximately 35.5%. The maximum dispersion is mainly determined by the fluid leak velocity, i.e., v_2; hence the mitigation system mainly reduces the total leakage, with no significant change in terms of ERPG-2 distance. However, considering the total leakage, the mitigation system has a critical role in reducing the accident impact for emergency response.

CONCLUSION

We evaluated the efficacy of a proposed mitigation system where

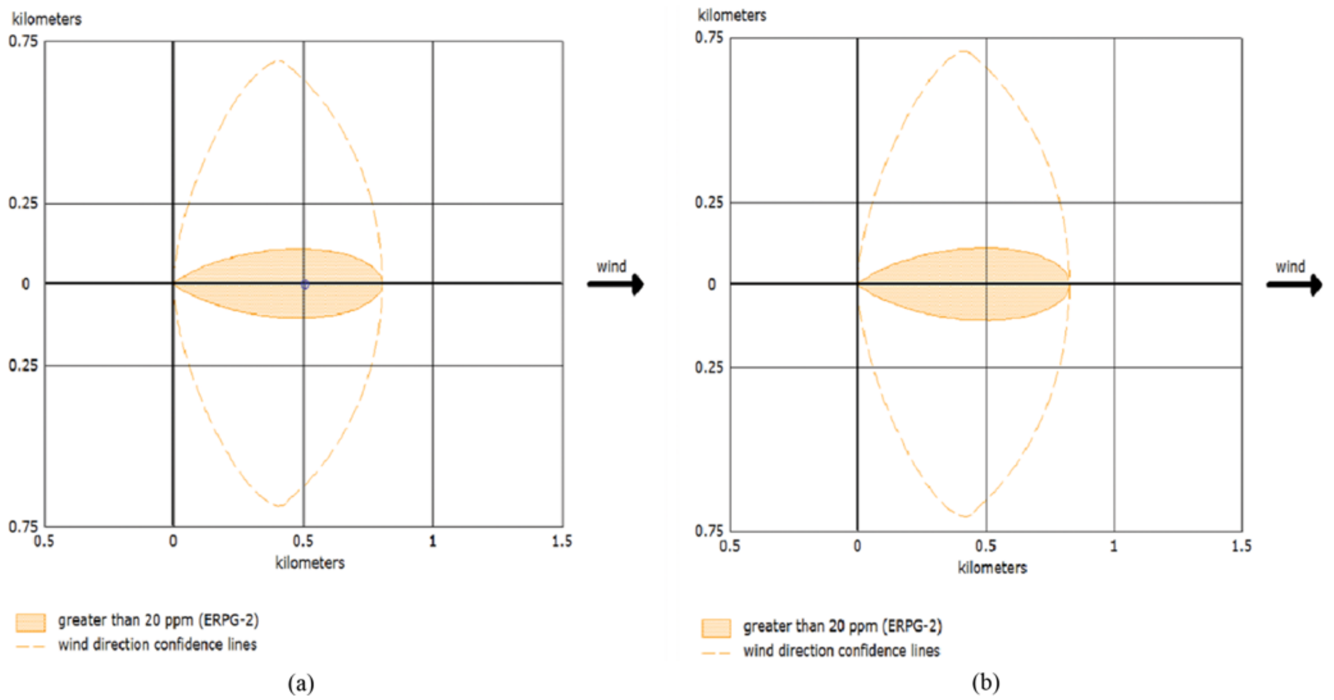

Fig. 8. Consequence analyses for a horizontal cylindrical vessel under worst case scenario (a) with and (b) without proposed mitigation system. Zero point is vessel location, wind direction is along the x axis.

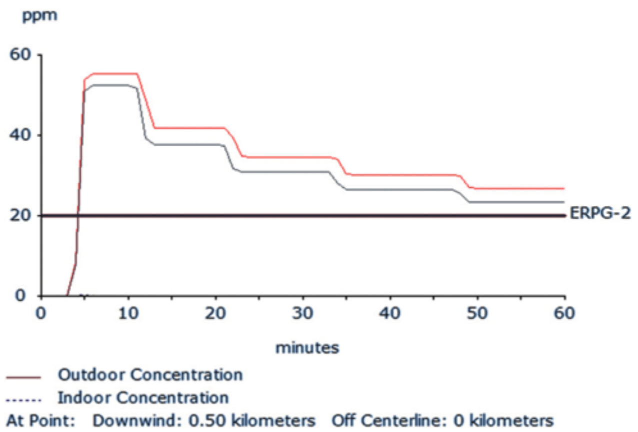

Fig. 9. Concentration evaluation with and without the proposed mitigation system. Measuring point was 500 m from the storage vessel. Blue and red line: with and without mitigation, respectively.

a reserve vessel is connected to a storage vessel, and the liquid (HF in this case) is transferred by pump when a leak accident occurs. Although some workplaces have installed this type of a mitigation system, no evaluation of mitigation impact has been previously attempted. Therefore, the mitigation systems have been installed without prior knowledge about the probable performance and efficacy. Consequence analysis without these details can provide ambiguous outcomes for emergency response planning.

Mathematical differential equations based on fluid dynamics were derived and simulated using MATLAB. Several case studies identified that the proposed mitigation system would have significant impact on reducing the scale of an accident. Even if it is assumed that HF is stored with only half of the total capacity in case studies, this model can be applied for various capacities.

The current study provides guidelines to determine the pump capacity appropriate for various workplace situations, and will contribute to reducing cost, effort, and time to develop a suitable mitigation system.

ACKNOWLEDGEMENT

This study received substantial support from the Geo-Advanced Innovative Action (GAIA) Project (2016-000530003) of the Korea Environmental Industry & Technology Institute (KEITI).

REFERENCES

1. H. Meysami, T. Ebadi, H. Zohdirad and M. Minepur, *J. Loss. Prevent. Proc.*, **26**, 1407 (2013).
2. R. J. Parker, *The Flixborough Disaster. Report of the Court of Inquiry*, Her Majesty's Stationary Office, London (1975).
3. M. J. Assael and K. E. Kakosimos, *Fires, explosions, and toxic gas dispersions: effects calculation and risk analysis*, CRC Press, Taylor and Francis Group, New York, U.S.A. (2010).
4. M. A. Rana, Y. Guo and M. S. Mannan, *J. Loss. Prevent. Proc.*, **23**, 77 (2010).
5. J. McQuaid and R. D. Fitzpatrick, *North Western branch paper*, Inst. Chem. E. (1981).
6. J. McQuaid and R. D. Fitzpatrick, *J. Occup. Accid.*, **5**, 121 (1983).
7. K. Moodie, *Process Saf. Prog.*, **4**, 234 (1985).
8. J. A. Suardin, R. Qi, B. R. Cormier, M. Rana and Y. Zhang, *J. Loss.*

Prevent. Proc., **24**, 63 (2011).
9. V. Busini and R. Rota, *J. Loss. Prevent. Proc.*, **29**, 13 (2014).
10. D. Liu and J. Wei, *J. Loss. Prevent. Proc.*, **48**, 14 (2017).
11. M. R. Swain, J. Shriber and M. N. Swain, *Energy Fuels*, **12**, 1 (1998).
12. US Environment Protection Agency, Federal Emergency Management Agency, and US Department of Transportation, *Technical guidance for hazard analysis - emergency planning for extremely hazardous substances*, U.S.A. (1987).