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RETRACTED ARTICLE: Consequence Analysis of Fire and Release of Mercaptan Spills in Pressure Reducing Station of a Provincial Gas Company

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Abstract

Background: Mercaptans are the highly flammable and malodorous natural gas odorants in the urban gas distribution network and are used to detect gas leakage. Exposure to high concentrations of this substance has deleterious impacts on human health.
Objectives: The purpose of this study was to determine the hazard distance and to examine the consequences of fire and the distribution of Mercaptans spills in its containing station in a specific provincial gas company.
Methods: Modeling scenarios were defined based on the valid existing events and related consequences with respect to the gas pressure reducing station. To determine the safe distances of hazardous areas, applicable data and criteria were used in accordance with total GS SF 253. These criteria include the amount of flammable radiation in the event of Mercaptan fire, the amount of LFL (low flammable level) Mercaptan distribution, and the distribution rate of various concentrations of Mercaptan (0.5, 10 and 100 ppm). Subsequently, modeling was performed using input parameters and via Process hazard analysis software Tools (PHAS) software. Finally, the consequence evaluation of scenario occurrence and hazard distance were identified through the modeling results.
Results: The distribution and pool fire caused by Mercaptan spill from containers were considered as the worst scenario at the respective gas station. Results from the modeling indicated a large distance distribution (3997 m) from the concentration of 0.5 ppm of Mercaptan (concentration of respiratory tract burning threshold) in case of a spill. Furthermore, according to the results of modeling in the event of a fire, the maximum radiation distance is 4.7 kW/m^2 in the 10/D climate class, which extends up to 28 meters.
Conclusions: Given the distribution of Mercaptans at long distances and the proximity of gas pressure reduction stations of the respective gas company to the residential and medical facilities, it is strongly recommended that the location of these barrels be moved away from residential areas.

Keywords: Consequence Analysis, Hazard Distance, Mercaptan Spill, Gas Pressure Reducing Station, PHAST

1. Background

Energy is the foundation of life and a major factor influencing human welfare and well - being. Among the various forms of energy, oil and natural gas have attracted major attention since the 20th century (1). Gas supplied by city gas networks for the use of consumers is a natural, colorless and odorless substance, which in case of leakage and forming explosive compounds with air, can be highly hazardous. When gas transportation lines reach the pressure reduction stations located in the city gas stations (C.G.S.), the gas is odorized by adding certain chemicals called odorants, thus, making the gas leak easily detectable (2). In the odorizing unit, the odorizing substance primarily used to odorize natural gas is Mercaptans, with the general formula of R-SH. Mercaptan has a distinctive putrid smell and a low odor threshold (3). As is highlighted in the AMERICAN SOCIETY OF MECHANICAL ENGINEERS BOILER (ASMEB) 31.8 standard, the amount of odorant should be as low as one fifth of the minimum gas explosion capacity. Concentration of this substance within the city gas is such that it exerts no detrimental impact on humans. Nevertheless, people who are exposed to high concentrations of the substance at the time of injection or displacement as required in their jobs, are inevitably exposed to the harmful safety and health effects. Contact and exposure to Mercaptan triggers nasal irritation, anosmia, nausea, vomiting, diarrhea, respiratory problems, headache, tingling, dizziness, blue spots on the skin, severe lung and kidney damage, loss of alertness, and even in critical situations, coma. The substance is also highly flammable and when the vapors are compounded with air, it quickly reaches the explosive level (2, 3). Refining and purifying the extracted gas in refineries is a crucial step in the gas production process and as a result, gas refineries in Iran have to be continuously operational. These industries often deal with hazardous chemicals and operating units function under high thermal and pressure conditions, such as reactors and storage tanks. Therefore, production, storage, transportation, and use of natural gas as fuel, despite all the advantages, have always resulted in hazards such as explosion and fire (4, 5). Furthermore, the release of chemical substances from the process plants is a significant hazard in process industries, which may endanger the staff and public health within the vicinity of such facilities. A brief review of the history of refinery incidents reveals that gas - related disasters have frequently occurred over the previous decades (6-8). Given the above - mentioned examples, it must be noted that consequence evaluation of hazards such as fire and discharge of substances from the oil and gas reservoirs is a crucial step in order to enhance the level of safety in existing or developing units (9). To determine the fire hazard distance, explosion, and also release of toxic substances, consequence modeling is utilized.

Consequence modeling involves the modeling of materials diffusion into the environment and later modeling the consequences of fire or explosion associated to these materials. Since the equations are complex and their solution is time consuming, the task is usually performed via computer software's. The PHAST process hazard analysis software is one of the most powerful and popular software's introduced by Det Norske Veritas (DNV) for this purpose (10, 11). Among the features of the software are a powerful database of materials and simulation models, the ability to define the composite materials, the adaptability of the results on the map, and the possibility of plotting time - varying charts (12).

Meysami et al. (2013) (10), Ruiz et al. (2012) (13), and Witlox et al. (2009) (14) acknowledged the PHAST software as a useful and reliable tool for modeling and analyzing the consequences of the diffusion of flammable and toxic materials.

Multiple studies have been conducted in Iran in the area of modeling and consequence evaluation of fire, explosion and diffusion of toxic substances diffusion, either exclusively or as part of quantitative risk analysis (QRA), among which the following can be enumerated: Kariznovi et al., (2017) (7) on the cylindrical storage tanks of liquid gas, Mohammadfam and Zarei (2015) (15) on the diffusion of natural gas and hydrogen (15), Parvini et al., (16) and Badri et al., (17) at CNG stations in 2014 and 2011, respectively, Zarei et al. on the hydrogen production units in 2013 (11), and Haghnazarloo on storing toluene in 2015 (18). The review of literature shows that within the limited studies carried out in the field of gas companies, the major focus has been on risk assessment and analysis. In addition, the modeling and evaluation of the consequences of incidents have been less studied by researchers as well. Therefore, the present study aims at identifying and analyzing the possible scenarios of diffusion and combustion caused by Mercaptan spills from storage tanks in pressure reduction stations of a provincial gas company. This is carried out through the investigation of the consequences of possible fire caused by Mercaptan and its diffusion along with determination of hazard distance of these scenarios, using the PHAST software.

2. Methods

2.1. Basis for Computations

This study was conducted at one of the pressure reduction stations of a provincial gas company (C.G.S.) in 2017. The distance between the mercaptan tanks and residential areas was about 700 meters. The maximum number of population is overshadowed in this area is 230 persons.

The odorant substances are usually transported to the city gas stations C.G.S in metal barrels and injected into the gas stream by the odorizer in the last section of the station. In this provincial gas company, the Mercaptan city gas used at the gas reduction stations of CGS is composed of 80% Iso Propyl Mercaptane (IPM), 10% Tertiary Butyl Mercaptane (TBM) and 10% Normal Propyl Mercaptane (NPM), all to be injected into natural gas. The modeling scenarios are defined based on the existing valid incidents and the relevant consequences from the gas pressure reduction station. The documents and software used for computing the consequence analysis and determining hazard distance are defined based on the documents enlisted in the reference standard (Impacted Area, Restricted Area and Fire Zones) (TOTAL GS - EP - SAF - 253 (2012)). Here, the PHAST 7.11 (DNV) software is used to simulate and evaluate the consequences of incidence scenarios.

2.2. Defining the Valid Scenarios and Respective Consequences

Each scenario is defined by the following features:

- Location (one or a set of equipment that feeds leakage). Mercaptan storage barrels comprise the location in this project.

- Source process conditions (normal operating conditions prior to the leakage spot, including component composition, phase, pressure, and temperature): the Mercaptan operating conditions include environment temperature and pressure in this study.
- The amount of leaking material (the amount of material that has the potential to leak): The amount of discharged material equals the volume of the barrels (220 liters).
- Leakage size: sizes of 5, 10, 20, 50, and 100 mm were identified.
- Leakage height: A leakage height of 0.2 meter (equivalent to the approximate height of storage of barrels) was set as the criteria.

The scenarios, principle input data (based on existing valid incidents), and the applicable criteria for determining the safe distances of the hazardous areas are determined in accordance with Total GS SF 253 depicted in Table 1.

2.3. Software Input Parameters for Modeling

The input parameters required for the PHAST software include the specific amount of the Mercaptan, which will leak into the environment, the Mercaptan's thermal and pressure conditions, discharge type, discharge rate and speed, discharge height, discharge coordinates, leakage quality, as well as weather conditions.

The information was next inserted into the software based on the process data used in this study and the available evidence, including the geographic location, weather information, safety data sheet, and physical and chemical specifications.

The weather condition and information used for simulation were as follows:

Environmental temperature:

- 15 °C during the day (annual average) and 0 °C during the night (minimum annual)
- Relative humidity: 70% (annual average), Surface roughness: 1 m
- Sun Radiation: 0.8 kW/m^2 during the day and 0 kW/m^2 during the night
- Maximum wind speed: 10 m/s

All scenarios are designed for simulation for three different wind speeds of 1.5, 5, and 10, taking into account the neutral atmosphere based on the Pasquill F (moderately stable) and D (neutral) climate class. Finally, three different climate classes were selected according to Table 2.

A liquid pool is formed when flammable liquids leak from a storage tank or the pipelines. As the pool is formed, some liquid will evaporate and if the flammable vapors reach the source of spark, the flame can spread to the spilled liquids and create a pool fire (which includes burning the vapors above the liquid pool). If the source of spill is Mercaptan storage containers and there is a nearby source of ignition, fire in the Mercaptan barrel storage area is inevitable. Table 3 displays the consequences of different radiation levels.

Having gathered the pertained data, the diffusion range of various Mercaptan concentrations, as well as different levels of radiation were calculated using the software. The PHAST software measures and displays distances related to the diffusion of various concentrations of Mercaptan and the amount of radiation created by the fire. Next the results are compared with health standards. Finally if hazardous quantities of Mercaptan or harmful levels of radiation are produced, corrective recommendations and measures are needed to prevent or reduce the effects of the incidence are provided.

3. Results

3.1. Modeling Results of Mercaptan Gas Cloud Emission

The parameters examined in this study on Mercaptan diffusion size are due to spills from the storage containers including the leakage size, climate class, and the respective concentration. First, using the PHAST software, the Mercaptan diffusion diagram was plotted at LFL concentration for the leakage sizes of 5, 10, 20, 50, and 100 mm in three climate classes of 1.5/F, 5/D, and 10/D. Results of the calculated distances are presented in Table 4. As an instance, the diffusion diagram for the 10 mm leakage size is shown in Figure 1.

Similarly, the diagrams related to the diffusion of Mercaptan at concentrations of 0.5, 10, and 100 ppm with leakage sizes of 5, 10, 20, 50, and 100 mm in three climate classes of 1.5/F, 5/D and 10/D are plotted using the PHAST software. The calculated distances are presented in Table 4. Figures 2 for instance, depict the diagrams for the diffusion of Mercaptan with a leakage size of 5 at concentrations of 0.5 plotted by PHAST software.

As depicted in Table 4, the low flammable level (LFL) concentration diffusion of Mercaptan gas occurs in 5 mm in its minimum leakage size and the distance of 2 meters. Increasing the amount of leakage raises the gas cloud diffusion distance as well, such that in the leakage size of 100 mm, the maximum distance (32 meters) was obtained.

Table 1. The Scenarios, Principle Input Data and Applicable Criteria in Determining Hazard Distance

Scenarios	Type	Consequence	Description	Criteria
First scenario	Gas diffusion/ Spray cloud caused by Gas Release/ Biphasic or liquid	Flammability	Leakage size 5, 10, 20, 50 and 100, Leakage height 0.2 m	LFL
Second scenario	A pool fire created in the pond	Thermal radiation	Pond size formed	4.7, 6.3, 9.5, 15.9 kW/m^2

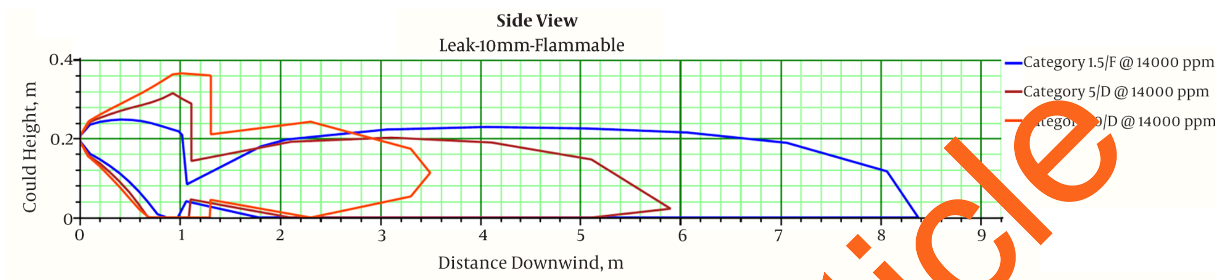

Figure 1. LFL Mercaptan Gas Diffusion Diagram with a 10 mm Leakage Size

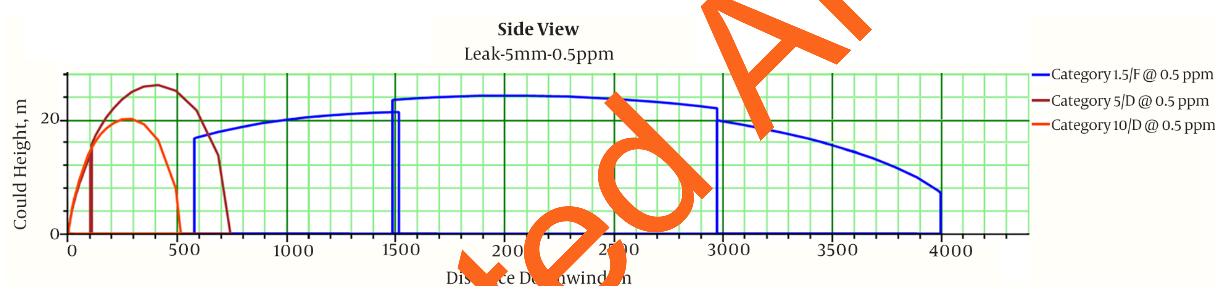

Figure 2. Diagram of Mercaptan Gas Cloud Spread at Concentrations of 0.5 ppm, with a Leakage Size of 5 mm

Table 2. Selected Climate Classes in Consequence Modeling (19)

Climactic condition	D/10	D/5	F/1.5
Pasquill Class	D	D	F
Wind speed (m/s)	10	5	1.5
Temperature (°C)	15	15	0
Sun radiation (kW/m^2)	0.8	0.8	0

Table 3. Impacts of Fire Radiation (19)

Consequences	The Amount of Radiation (kW/m^2)
Sun radiation	0.8
The pain threshold is such that the person is able to escape.	4.7
Second - degree burn and blister after 18 seconds	6.3
Second - degree burn and blister after 9 seconds	9.5
Second - degree burn and blister after 5 seconds	15.9

As the modeling results show, the Mercaptan gas diffusion distance in the D climate class is significantly lower compared to the F climate class. The impact of wind on diffusion is also significant, such that in lower speed, gas diffusion rate increases.

3.2. Results of Fire Modeling

In this section, pool fire was modeled as a major hazard caused by Mercaptan spill in the presence of a source of spark. Figure 3 demonstrates the radiation caused by Mercaptan fire.

The results of analysis and modeling of the fire pool in Table 5 demonstrate that radiation of 4.7 kW/m^2 will cover the distance up to 28 meters and a radiation of 15.9 kW/m^2 travels up to 20 meters distance. Hence in case of a fire, safe distance and appropriate control measures must be taken into account.

Table 4. Calculated Distances Mercaptan Gas Clouds Using the Software of PHAST (m)

Scenario	The Amount of Leakage (mm)	Climate Condition	Gas Cloud Spread (LFL)	Gas Cloud Spread (0.5 ppm)	Gas Cloud Spread (10 ppm)	Gas Cloud Spread (500 ppm)
Mercaptan diffusion due storage container spill	5	1.5/F	7	3997	772	46
		5/D	3	744	150	20
		10/D	2	516	105	14
	10	1.5/F	8	4401	905	64
		5/D	6	1248	251	32
		10/D	4	902	184	25
	20	1.5/F	13	5526	1024	79
		5/D	10	1415	340	[illegible]
		10/D	7	1215	[illegible]	37
	50	1.5/F	24	6028	[illegible]	102
		5/D	19	2044	[illegible]	71
		10/D	16	1546	[illegible]	62
	100	1.5/F	32	7190	2912	125
		5/D	29	3722	649	91
		10/D	27	[illegible]	534	88

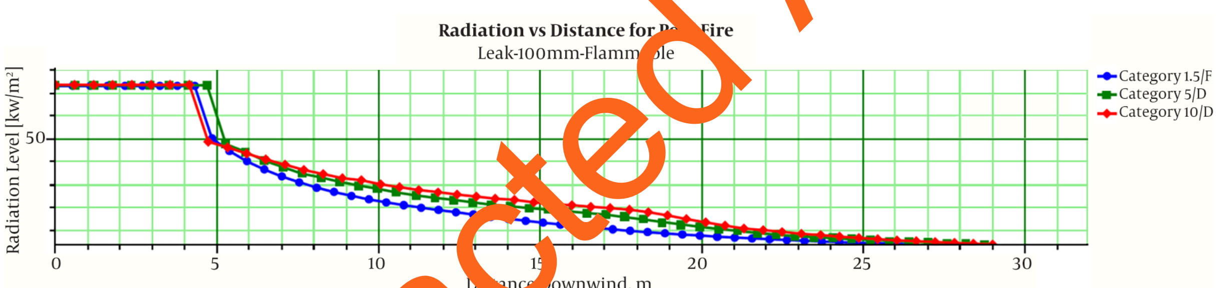

Figure 3. Mercaptan Fire Radiation

Table 5. Results of Pool Fire Radiation Analysis

Scenario	Climate Condition	Pool Fire			
		4.7 kW/m²	6.3 kW/m²	9.5 kW/m²	15.9 kW/m²
Pool fire in Mercaptan containers	1.5/F	25	22	18	13
	5/D	27	25	21	18
	10/D	28	25	22	20

4. Discussion

Given the hazards and conditions studied above, the analysis of incidents caused by fire fountain and explosion were almost impossible to examine.

Based on the data presented in Table 4, if a leakage of 5 mm is produced, the concentration of 0.5 ppm will diffuse to 3997 meters and concentrations of 10 and 500 ppm will be 772 and 42 meters respectively. For a leakage size of 10 mm, the Mercaptan gas cloud diffusion distances at concentrations of 0.5, 10, and 500 ppm, are 4401, 905, and 64 meters, respectively. For the leakage size of 20 mm and the three concentrations of 0.5, 10, and 500 ppm, distances of 5526, 1024 and 79 meters have been identified, respectively. Concentrations of 0.5, 10, and 500 ppm of Mercaptan will produce a leakage size of 50 mm, measuring up to 6028, 1727, and 102 meters. Finally, for the 100 - mm leakage size and concentrations of 0.5, 10, and 500 ppm, the affected distances of gas cloud diffusion are 7190, 2912, and 125 meters, respectively.

As the modeling results by PHAST software in Table 4 indicates, the results of Mercaptan gas cloud diffusion modeling at LFL concentration show that by increasing the stability and decreasing the velocity of airborne layers, the distances where certain concentrations of Mercaptan diffusion increase. Taking leakage size as fixed, the F/1.5 climate class is the worst case in the realm of Mercaptan diffusion. On the other hand, as the leakage size increases, the distance of LFL cloud gas diffusion increases as well.

Odor threshold for Mercaptan has been reported at a concentration of 0.001 ppm. The TLV - TWA exposure limit for Mercaptan is 0.5 ppm, which in some cases is the threshold of respiratory tract burning. Furthermore, the reported PEL - TWA by OSHA is 10 ppm and the concentration of 500 ppm is identified as the IDLH benchmark.

As depicted in Table 4, a 500 ppm Mercaptan concentration diffuses up to 125 meters distance. Due to the harmful effects of Mercaptan on human health in such a concentration, the area must be evacuated to a radius of 125 meters from the leakage site and merely experienced, trained, and equipped people with respiratory and relief equipment be present in the area.

Concentrations of 10 ppm diffuse up to 2912 meters, while concentrations of 0.5 reach up to 7190 meters. Although the effect of Mercaptan is not significant at these concentrations, it is important to note that if these amounts reach the urban areas, they will have temporary harmful effects on the citizens and also legal issues.

In an effort to model the consequences of natural gas leakage from reservoirs, Siong [illegible]o et al., (2014), announced the size of the leakage diameter as a major factor in expanding the range affected by the explosion, eruptive, and abrupt fire (1). In another study by Mortazavi et al., with the aim of examining chlorine gas leakage from its reservoirs, the atmospheric stability rise was identified as a factor for increasing the affected range (20) and both studies are consistent with the results of the present study.

According to the modeling results in Table 5, in the case of a fire in the Mercaptan storage container and the radiation chart of pool fire in Figure 3, the maximum radiation distance belongs to 4.7 kw/m^2 in the 10/D climate class, which extends up to 28 meters.

Maximum radiation distances of 6.3, 9.5, and 15.9 relate to radiations of 25, 22, and 20 meters respectively. Therefore, appropriate measures should be taken in case of a fire. Due to the more intense effects of radiations of 9.5 and 15.9, the area must be wholly evacuated to 22 meters from fire and in case there is a need to approach the fire, fireproof clothing must be used.

The impact of weather conditions on the amount radiation is of vital importance as well, since radiation in the climate class D covers more distances compared to class F.

The study by Kariznovi et al., (2017) (7) as well as a research by Dormohammadi et al., (2014) (6) showed that the weather condition has an impact on the severity of eruptive and abrupt fire (6, 7), which is consistent with the results of this study.

Shahedi Aliabadi et al., (2016) (21) conducted a study with an aim of evaluating and consequence modeling of methane gas storage fire at a gas refinery, using the PHAST software. As the results of the consequence modeling of the study depicted, fire - induced thermal radiation is the principle consequence of the incidence and weather condition and leakage size in the distance are influenced by radiation (21), findings which were in line with the present study.

Most studies in this field relate to LPG, oil or hydrogen gas tanks, or compressed natural gas stations (CNG) and chemical leakage modeling is highly dependent on the nature of the matter, weather conditions and the process conditions. Therefore, comparing the results of the study or studies different from the present research in terms of the above mentioned factors will render inaccurate estimates.

4.1. Conclusion

In this study, Mercaptan spill of storage barrels were introduced as a hazard zone. Due to the diffusion at long distances and the proximity of pressure reduction stations of this city gas company to residential and therapeutic areas, it is vital to prevent any leakage and spill of Mercaptan barrels. It is also strongly recommended that the location of these barrels be transported to the places away from residential areas and a safe storehouse be allocated to keep Mercaptan barrels (either empty of full). When needed, barrels will be shipped to the injection area. Such a place is inevitably in need of Mercaptan diffusion modeling studies.

Furthermore, an area of at least 28 meters radius must be evacuated in case of fire and individuals at the site must use respiratory equipment.

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Footnotes

Authors' Contribution: Leila Jodakinia and Seyed Hojat Mousavi kordmiri were involved in the development of the study design and protocol, data interpretation and manuscript drafting and guarantor. Sharzad kesmati and Sogand Sakari and Seyed Hamid Reza Mousavi contributed to the development of the study protocol, data analysis, and manuscript drafting.

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